

REPLY

RESIDUAL MANGANESE (II) SPECIATION IN MONTMORILLONITE

McBride (1995) has called attention to the possibility that the residual Mn(II) species in untreated SWy-1 montmorillonite, investigated spectroscopically by Gehring *et al* (1993), could be Mn^{2+} in the structure of calcite, a known impurity associated with the clay mineral. In support of his proposal, McBride (1995) notes that the EPR spectrum for Mn(II) originates primarily from the $>2 \mu m$ fraction of the SWy-1 sample and that the EPR lineshape is similar to that observed for Mn^{2+} substituted in the calcite structure, both at room temperature and after heating at $700^\circ C$.

Gehring *et al* (1993) concluded on the basis of variable-temperature EPR spectroscopy that residual Mn(II) in untreated SWy-1 montmorillonite could be either an isomorphically-substituted species or an adsorbed species. They rejected the former possibility because of the known ready exchangeability of Mn(II) in SWy-1 montmorillonite and instead proposed that residual Mn(II) is a partially-solvated, adsorbed species in the montmorillonite interlayers. This hypothesis was consistent with the observed persistence of the Mn(II) EPR spectrum after heating at $600^\circ C$ and with the drastic changes in the spectrum occurring along with the dehydroxylation of montmorillonite at 600° – $700^\circ C$ and with its decomposition at $800^\circ C$.

The EPR spectrum of Mn(II) after heating at $700^\circ C$ is indeed similar in SWy-1 montmorillonite (Gehring *et al* 1993, Figure 6) and calcite (McBride 1995, Figure 1), giving credence to the proposal of McBride (1995). However, the temperature effect on the signal intensity for the SWy-1 sample was to reduce it by about 90% (Gehring *et al* 1993), whereas little or no reduction of signal intensity occurred for the calcite sample (McBride 1995). The proposal that the drastic change in Mn(II) spectral lineshape observed by Gehring *et al* (1993) after heating at $800^\circ C$ is simply the result of calcite conversion to CaO (McBride 1995) is also not consistent with the evident persistence of the EPR signal in calcite heated at $900^\circ C$ (Figure 1). Gehring *et al.* (1993, Figure 5), by contrast, observed disappearance of the signal already after heating at $800^\circ C$, coincident with the decomposition of the clay mineral at this temperature.

In our view, the assignment of the Mn(II) EPR signal in SWy-1 montmorillonite remains problematic, requiring further experimental investigation. We thank Professor McBride for contributing to the discussion of this point with his most helpful insights.

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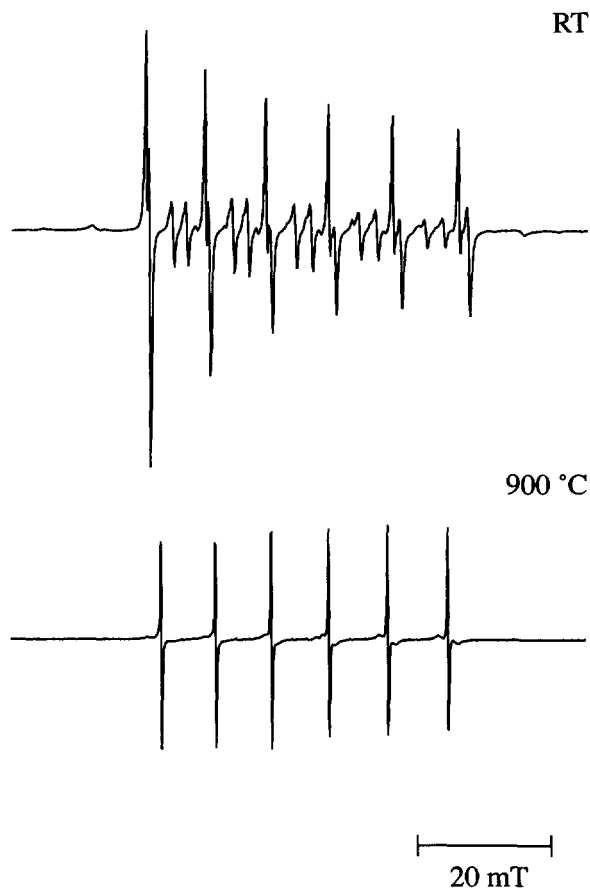


Figure 1. Room temperature EPR spectra of $CaCO_3$ powder, untreated and after heating at $900^\circ C$ for 5 hours.

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Swiss Federal Institute for Forest, Snow and Landscape Research
CH-8903 Birmensdorf, Switzerland

A. U. GEHRING

Division of Ecosystem Sciences
University of California
Berkeley, California 94720-3110

GARRISON SPOSITO

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