The chemical form of Mn(II) and V(IV) in mineral phases as determined by EPR spectroscopy

A.U. Gehring *Swiss Federal Institute for Forest, Snow and Landscape Research, WSL/ETH, CH-8903 Birmensdorf, Switzerland*
P.M. Schosseler *Laboratory for Physical Chemistry, Swiss Federal Institute of Technology, ETH, CH-8092 Zürich, Switzerland*
J. Luster *Swiss Federal Institute for Forest, Snow and Landscape Research, WSL/ETH, CH-8903 Birmensdorf, Switzerland*

Electron paramagnetic resonance (EPR) spectroscopy is an analytical tool for the identification of paramagnetic cations associated with minerals. The assignment of an EPR signal obtained from a natural system, such as soils, to a specific mineral phase or a specific chemical form is often ambiguous because an EPR signal reflects the ligand field of a paramagnetic center that can occur in different mineral phases and chemical forms, and secondly EPR signals of different cations can be superimposed. An experimental approach that combines EPR spectroscopy with thermoanalytical methods was developed in order to assign paramagnetic cations unambiguously to a specific chemical form or to specific mineral phases in multimineral systems (Gehring and Karthein 1990; Gehring *et al*, 1993*a*). This approach is based on the assumption that different chemical forms or different mineral phases in a multimineral system differ in thermal stability.

The purpose of this research was to apply this methodological approach to determine the chemical form of Mn(II) and V(IV) in a vermiculite sample (VTX-1) from Texas obtained from the Source Clay Depository of the Clay Minerals Society. Apart from vermiculite, magnesite was found in the sample by X-ray diffraction (XRD). Details of the EPR experiments are described elsewhere (Gehring and Karthein, 1990). The EPR spectrum of the untreated sample exhibited two groups of resonances around $g = 4.3$ and $g = 2$, respectively (Fig.1). The low-field resonance at $g = 4.3$ is characteristic for Fe(III) structure-bound in phyllosilicates (cf. Meads and Malden, 1975) and therefore can be assigned to the vermiculite. The spectrum around $g = 2$ showed a superposition of an eight-line and a six-line hyperfine-split (HFS) signal (Fig.2), that can be attributed to V(IV) and Mn(II), respectively. The Mn(II) signal is characterized by a g-value of 2.002 ± 0.001, and a hyperfine coupling constant $A = 9.44 \pm 0.03$mT. The HFS feature of the V(IV) spectrum contained both parallel and perpendicular components. For the parallel component, $g_{||} = 1.941 \pm 0.001$, $A_{||} = 18.11 \pm 0.07$mT, and for the perpendicular component $g_{\perp} = 1.985 \pm 0.001$, $A_{\perp} = 7.05 \pm 0.02$mT were obtained. These parameters are in excellent agreement with McBride (1990). The Mn(II) and V(IV) could be associated with vermiculite and/or magnesite, either structure-bound, as adsorbate or as cluster. The latter possibility can be excluded because clusters would lead to broad signals without HFS.

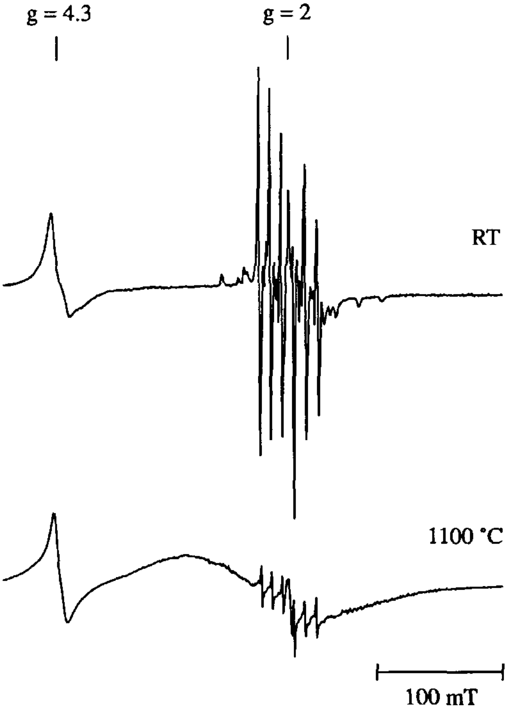

FIG. 1. Wide-range EPR spectra of the untreated sample (VTX-1) at RT and after stepwise heating to 1100°C.

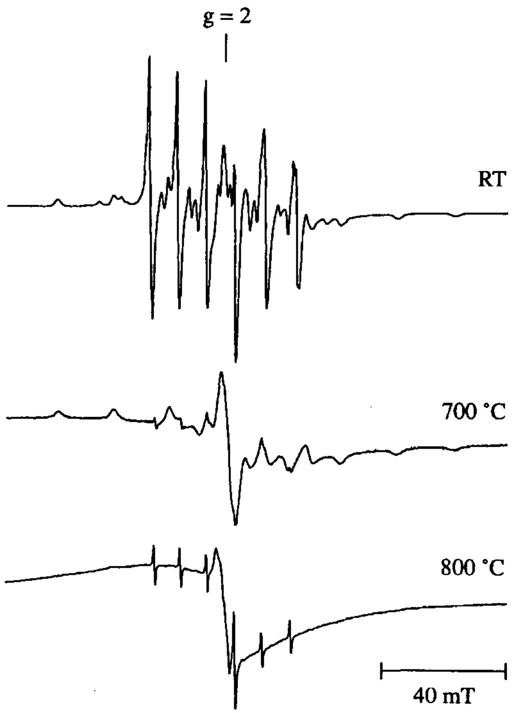

FIG. 2. Narrow range EPR spectra of the untreated sample (VTX-1) at RT and after stepwise heating to 700 and 800°C.

The Mn(II) signal vanished after treatment of the sample with H_2O_2 and therefore it is very likely that this cation is surface adsorbed. Considering the XRD data, Mn(II) can occur as adsorbate either at the vermiculite and/or at the magnesite. Upon heating the untreated sample, the Mn(II) signal was stable up to 575°C. Further heating led to a decrease in intensity and at 625°C a spectral change was observed. The new HFS signal with $g = 2.002 \pm 0.001$ and $A = 8.70 \pm 0.02$mT was stable up to 1100°C (Fig. 1). The high thermal stability of the adsorbed Mn(II) clearly indicates that it is protected from oxidation and thus rules out adsorption by magnesite. A similar spectral behaviour with temperature was observed for exchangeable Mn(II) entrapped in interlayers of single-layer-hydrate montmorillonite (Gehring *et al.*, 1993*b*; Kawano and Tomita, 1991). Therefore it can be postulated that Mn(II) associated with the vermiculite is also coordinated in interlayers.

The eight-line V(IV) HFS signal was stable up to 700°C; that means it has a higher thermal stability than the Mn(II) signal obtained from the untreated sample (Fig. 2). At higher temperatures, where the vermiculite is known to dehydroxylate (Douglas, 1989), the HFS V(IV) signal disappeared and a new signal at $g \approx 2$ was found, which became less intense upon heating to 1100°C. A similar spectral change was observed for structural V(IV) in kaolinite during transformation into metakaolinite and was explained by a coordinational change of the V(IV) during dehydroxylation (Gehring *et al.*, 1993*c*). Therefore, the thermal behaviour of the EPR signal suggests that V(IV) is structure-bound in the vermiculite.

In addition, during the dehydroxylation of the vermiculite a broad signal around $g = 2$ was generated (Fig. 2). This signal was stable up to 1100°C (Fig. 1) and can be attributed to the formation of ferric oxides (Gehring and Karthein, 1990).

In conclusion, the experimental approach, that combines EPR spectroscopy with thermal treatment, can be used to distinguish between different chemical forms of metal ions in a mineral sample without chemical pre-treatment. The assignment to a specific chemical form is based on the thermal behaviour of the EPR signals.

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