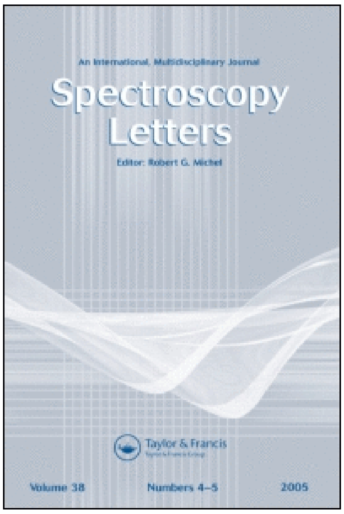

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An EPR Study on the Chemical form of Mn^{2+} in the Chinese Loess Samples

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AN EPR STUDY ON THE CHEMICAL FORM OF Mn^{2+} IN THE CHINESE LOESS SAMPLES

Key words: EPR spectroscopy; Mn^{2+} ; calcite; loess

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ABSTRACT

Electron paramagnetic resonance (EPR) spectroscopy in combination with thermal methods were used to identify and characterize Mn^{2+} in the Chinese loess that is a multimineral system. EPR spectra of the loess samples from the classic loess-paleosol section in central China show the presence of trace amounts of Mn^{2+}; whereas paleosol samples present no Mn^{2+} EPR signal. The spectral changes upon step heating from room temperature to 1000 °C suggest that this EPR signal in the loess arises from Mn substituted into $CaCO_3$. This study provides a direct evidence that the loess-paleosol profiles were formed under the changing redox conditions caused by a past climatic change.

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INTRODUCTION

Electron paramagnetic resonance (EPR) spectroscopy is an analytical tool for identification and characterization of paramagnetic cations such as: Mn^{2+}, Fe^{3+} and V^{4+} in natural systems, and is often used to investigate their behavior during the weathering and pedogenesis (10, 13). In addition to its high sensitivity, needed for investigating elements which are highly diluted in natural systems, EPR gives a detailed description of the cation surroundings, including site geometry and ligand-cation bond covalency. The presence of Mn^{2+} in soils provides information about Mn^{2+}/Mn^{4+} redox equilibrium and thus constrains climatic features during the formation and evolution of soils and sediments.

In northern China nearly half a million square kilometers are covered by loess sediments. Typically they consist of an alternation of loess layers which deposited in cold and arid climatic conditions and paleosol beds which are indicative of warm and humid climate (4). For the past decade or so, the classic loess section, Luochuan, has been a focal point of research into climatic reconstruction (5, 6). The town of Luochuan (35° 45'N, 109° 25' E) is located 190 km north-northeast of Xian, in an area where the average elevation is 1000m. The studied section is situated near the Potou hamlet on the slope of a gully running to the Heimugou stream. The upper part of the section was sampled at 20 cm intervals for the EPR study from the land surface downward through the early Holocene (S0) paleosol, the L1 loess (last glaciation), and the S1 (last-interglacial) paleosol. The S0 paleosol has a dark color, an elevated proportion of organic matter, and is incompletely decalcified. The L1 loess is a light colored calcareous loess, and the S1 paleosol is a typical polygenetic cinnamon soil with a reddish-brown color, and has been completely decalcified (5). These units correlate, respectively, with marine oxygen isotope stages (MIS)1, 2 - 4, and 5 (7, 12).

In a previous study we reported that variations in Mn^{2+} EPR intensity recorded in the loess section, correlate closely with the magnetic susceptibility record and can be used as an index of changing summer monsoon strength (1). Extending this work, we have investigated the chemical form of Mn^{2+} in the loess samples, for understanding the nature of this new proxy climate index by an experimental approach that combines EPR spectroscopy with thermal methods.

EXPERIMENTAL DETAILS

Electron paramagnetic resonance spectra were recorded at RT on a Bruker ER 200D-SRC spectrometer at X-band frequency with 100 kHz magnetic field modulation. The spectrometer settings were 0.4 mT modulation amplitude, 9.766 GHz frequency, and 20 mW microwave power. The g-values were calculated by the relation $h\nu = g\beta B$, where h is Planck's constant; ν is the resonance frequency; g is the electronic "factor"; B is the field at which resonance occurs; and β is the Bohr magneton. A constant amount (100 mg) of each sample was placed in a pure silica tube for a quantitative comparison between the samples. For the thermal experiments, samples were heated incrementally for 1 hr in 100 °C steps between room temperature (RT) and 1000 °C in an oven.

RESULTS AND DISCUSSION

The EPR spectra of the loess samples (Fig.1) show a six-line hyperfine pattern

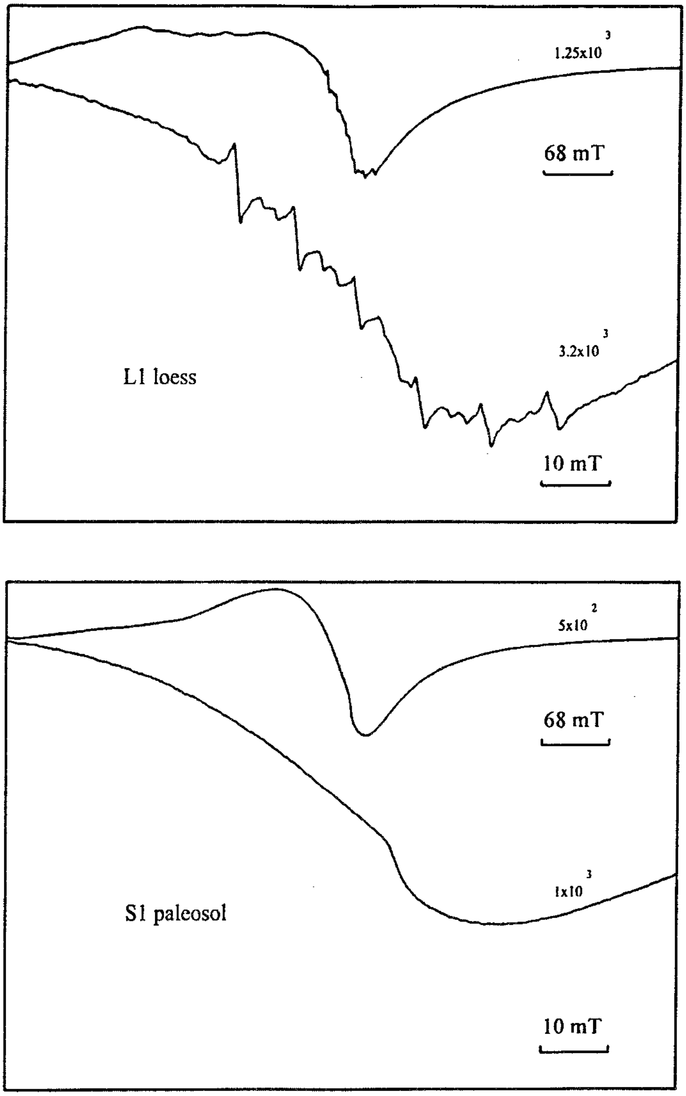

Figure 1. Wide-range EPR spectra of a typical loess (a) and plaeosol (b) samples recorded at room temperature (RT).

characteristic for Mn^{2+} at a g value of 2; whereas, paleosol samples show no Mn^{2+} EPR signal. Moreover, a broad background signal due to Fe Oxide species is found in all loess and paleosol samples.

The Mn^{2+} spectra of the loess samples consisted of six dominant lines separated by five weaker doublets, and 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...-5/2) is split into a doublet. The forbidden resonances (Δm_s= 2) appear as doublets between the main resonances (8). The Mn^{2+} signal of the samples were characterized by: g = 2.0053, and HFS of A = 9.35 mT (Fig. 1).

Upon step heating to 600 °C the signal intensity and spectral parameter remained constant (Fig. 2). The insensitivity of this signal to thermal dehydration suggests that this Mn^{2+} was not hydrated at room temperature, because the loss of hydration water would most likely have changed the ligand field of the Mn^{2+} (9).

Between 600° and 800°C, however, a drastic spectral change was observed (Fig. 2). The newly formed spectrum was isotropic, with A = 8.80 mT and a constant line width of 0.41mT for all the HFS components. The main spectrum consists of 6 hyperfine lines devoid of fine structure, indicative of Mn^{2+} in sites of cubic symmetry, which would be expected for cubic lattice (8). Upon heating to 1000°C, the isotopic HFS signals disappeared (Fig. 2).

An origin for the 6-line EPR signal can be suggested, as spectrum features presented in Figures 1 and 2 are substantially the same as that for Mn^{2+} substituted in the structural sites of calcite (9), which commonly occurs in the loess samples (6). Similar spectra have been observed in soils known to contain calcite (9, 11). The

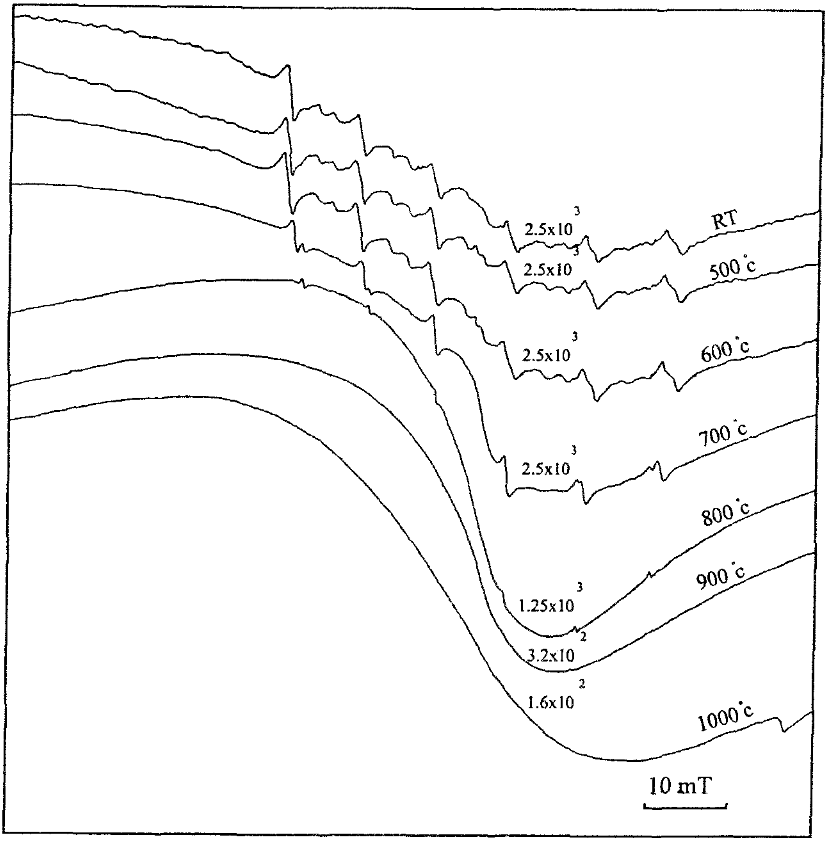

Figure 2. Narrow-range EPR spectra of loess sample recorded at RT after stepwise heating to 500°, 600°, 700°, 800°, 900° and 1000 °C.

marked change in the Mn^{2+} spectrum after heating the loess sample to 700°C can be attributed to thermal decomposition of $CaCO_3$ to CaO near this temperature.

Manganese oxidation-reduction is a common chemical reaction taking place in a soil profile usually caused by climatic change. The decrease of Mn^{2+} EPR intensity from loess to the paleosol samples means that oxidation could prevail during the pedogenesis of loess. Carbonate eluviation and illuviation is believed to be one of the major pedogenic processes involved in the formation of the paleosol (2, 6). The manganese is dissolved from its carbonates by weathering solutions as Mn^{2+}, and remains in this form as long as the solution is slightly acid and not too oxidizing. If the solution becomes more oxidizing, say by prolonged exposure to air so that any organic material is oxidized, the manganese precipitates as one of the oxide minerals. This general sequence of events can be observed wherever manganese deposits are forming at the present time. In fact, the most common amorphous pedofeatures seen in the Luochuan section are segregations of colloidal Fe-Mn oxides/hydroxides (6).

CONCLUSION

The EPR studies suggest that Mn^{2+} ions are associated with carbonate in the Chinese loess samples, and provides a direct evidence that the loess-paleosol profiles were formed under the changing redox conditions caused by a past climatic change. This work confirms that the EPR record of the loess-paleosol sequence is primarily a record of pedogenesis, represents a valuable tool for paleoclimatic reconstruction, and it also demonstrates that the EPR monitoring of soils offers some insight into the nature and distribution of the carbonate in soil profile.

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