

Oxidation of added Mn(II) in soils as observed by the Cr Oxidation Test and Mn K α XANES spectroscopy

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Soil manganese oxides control the behavior of many contaminant metals through sorption and, in some cases, oxidation. The ability of a soil to oxidize added Cr(III)Cl₃, the Standard Net Cr Oxidation Test (COT), has been used as a tool to assess soil Mn surface reactivity (1). Synchrotron-based Mn K α XANES spectroscopy allows determination of Mn oxidation state on field-moist soil samples. It avoids drying-induced changes in soil redox status (2), although x-ray beam-induced reduction (3) needs to be minimized. While the COT measures only surface reactions, Mn K α XANES measures the average oxidation state of the near-surface region. For a better understanding of the behavior of soil Mn(III)/Mn(IV) oxides and their ability to regenerate, we used both tools in an investigation on the oxidation of added Mn(II). We hypothesized that, over time, increases in Mn oxidation state would mirror the increases in surface reactivity as measured by the COT. The soils studied had a wide range in total Mn (0.04 to 1.75%), COT (0.03 to 4.9 mmol Cr(VI) kg⁻¹ soil), pH (4.6 to 7.2) and organic carbon (3 to 27%). Addition of Mn(II)SO₄ resulted in both an immediate decrease in the COT (as the added Mn (II) blocked reaction sites for Cr oxidation) and the presence of a Mn(II) peak in the XANES spectra. Over a 50-hour period, the COT increased linearly to higher than original and the XANES spectra shifted to nearly the original proportion of Mn(III)/Mn(IV). The rate of change in both measurements were similar but the final location of the Mn K α absorption edge (higher with a higher proportion of Mn(IV):Mn(III) in the oxide) was often lower than original. The COT measured the overall capacity for oxidation while Mn K α XANES spectroscopy measured average oxidation state. Surface reactivity, as measured by the oxidation of added Cr(III), was greatly enhanced by prior addition and oxidation of Mn(II), likely through the increase in Mn oxide surface area.

[1] Bartlett & James (1993) *Adv. Agron.* **50**, 151-208. [2] Ross *et al.* (2001) *Soil Sci. Soc. Am. J.* **65**, 744-752. [3] Ross *et al.* (2001) *Soil Sci. Soc. Am. J.* **65**, 736-743.

New insight into the phase diagram, structure and viscosity of iron at core conditions

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By combining diamond-anvil-cell measurements, and calculations of the iron melting curve, with sound speed measurements made in shockwave experiments, we present a new understanding of the phase diagram, structure and viscosity of iron up to the inner-outer-core boundary (IOCB) of the Earth near 330 GPa (~5000K). Based on the experimental evidence, drawn from diamond-anvil and shockwave measurements, we conclude that the outer core must be that of a viscous structured liquid. The inner core is likely a plastic solid textured by local structures, or clusters, readily distorted in the direction of the magnetic field, as an explanation for the observed seismic anisotropy of the Earth's inner core.