
ROLE OF TRIVALENT Mn IN OXIDATION OF ORGANIC MATTER

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INTRODUCTION

Manganese(II) and Mn(IV) have received the most attention in aquatic chemistry¹ until recently, where solid Mn(III) oxides and soluble Mn(III) complexes have been shown to be environmentally significant oxidants²⁻⁵. Solid Mn(III,IV) (hydr) oxide minerals are powerful oxidants in soils and geochemical environments because of the vacant orbitals of sigma symmetry that impart significant surface reactivity⁶. Manganese(III) solid phases would be expected to be more kinetically reactive than Mn(IV) minerals, however, no detailed studies have been conducted. This study was undertaken to test the hypothesis that the lability of Mn(III) predicted by frontier molecular orbital theory in solution affects the reductive dissolution kinetics of naturally occurring solid Mn(III,IV) (hydr) oxide minerals by comparing several phases with varying levels of structural Mn(III) in their reactivity with catechol, a model organic ligand of soil organic matter⁷.

MATERIALS AND METHODS

Reactivity studies of solid Mn(III,IV) (hydr) oxide minerals with catechol were followed *in situ* using electron paramagnetic resonance (EPR) spectroscopy and diffuse reflectance spectroscopy (DRS). Micromolar concentrations of Mn(III)-pyrophosphate complexes were measured in the UV region at 210 and 260 nm and mM concentrations at 480 nm as described previously³. Initial rates of pyrophosphate-extractable Mn(III) from solid phase Mn minerals were used as an operationally defined measure of available Mn(III).

RESULTS

No correlation existed between the initial reductive dissolution rates of solid Mn(III,IV) (hydr) oxides by catechol and surface area or thermodynamic driving force. In contrast, the reductive dissolution rates were linearly related to initial rates of pyrophosphate-extractable Mn(III), defined as available Mn(III) (Figure 1). The positions of the Mn(III) ligand field bands, which explained the different levels of availability. Therefore, the role of Mn(III) in different coordination environments merits special attention in abiotic cycling of soil organic matter and Mn.

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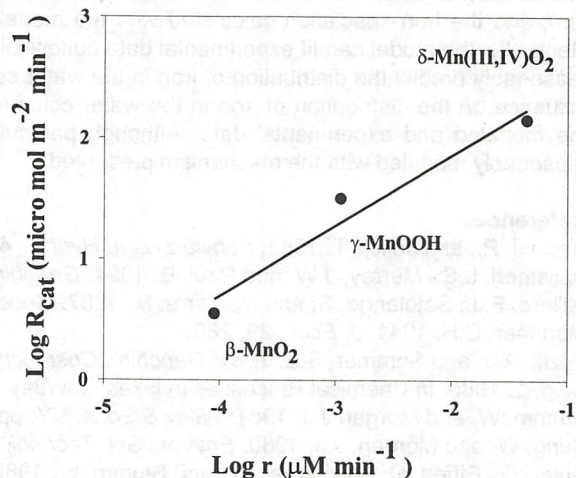


Figure 1. Relationship between the initial rate of Mn(III) extraction by pyrophosphate (r) and the reductive dissolution rate by catechol (R).