Department of Geography and Environmental Engineering

The Johns Hopkins University

G.W.C. Whiting School of Engineering

Fax: (410) 516-899

October 14, 2005

The Graduate Board
Wyman Park Building, Suite G-1
Homewood Campus
The Johns Hopkins University

Ladies and Gentlemen:

We have read the dissertation of Ms. Yun Wang entitled "*Electron Transfer and Coordination Reactions between $Mn^{III,IV}O_2$(Birnessite), $Mn^{III}OOH$(Manganite) and Oxygen-Donor Aliphatic Compounds*", submitted as partial requirement for the degree of Doctor of Philosophy in the Department of Geography and Environmental Engineering of the G.W.C. Whiting School of Engineering.

Ms. Wang's research was motivated by the recognition that manganese (hydr)oxides are among the most reactive oxidants found in soils and sediments. Using capillary electrophoresis, Ms. Wang was able to monitor the progress of reductive dissolution reactions in unprecedented detail, most notably by identifying and quantifying organic oxidation products. Ms. Wang carefully documented how the identity and placement of functional groups within the molecular structure of aliphatic organic compounds affect rates of reaction with MnO_2(birnessite) and MnOOH(manganite). Ms. Wang was able to show that the autocatalytic reaction of MnO_2(birnessite) with citric acid is caused by a positive feedback step involving Mn(II)-citrate complexes reacting with the surface. Ms. Wang's research adds to our understanding of ligand-assisted dissolution reactions. Ms. Wang was able to demonstrate that methylenediphosphonic acid, phosphonoformic acid, phosphonoacetic acid, and iminodimethylenephosphonic acid are capable of solubilizing (hydr)oxide-bound Mn(III).

Portions of this thesis are worthy of publication in leading environmental chemistry, interfacial chemistry, and geochemistry journals. We recommend that this thesis be accepted in partial fulfillment of the requirement of the Ph.D. degree.

Respectfully Submitted,

Alan T. Stone, Professor
Department of Geography and
Environmental Engineering

Charles R. O'Melia, Professor
Department of Geography and
Environmental Engineering

Kenneth D. Karlin, Professor

Justine P. Roth, Assistant Professor

313 Ames Hall, Baltimore, Maryland, 21218-2686, USA
(410) 516-7092