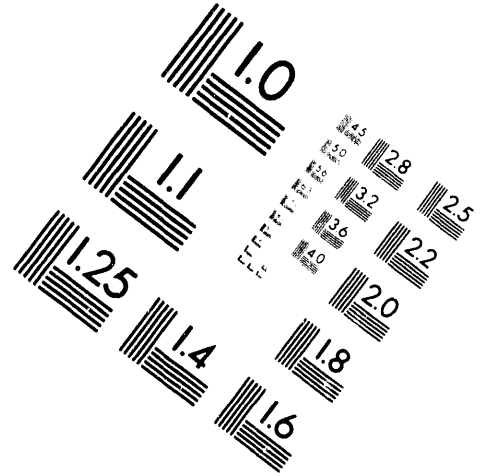
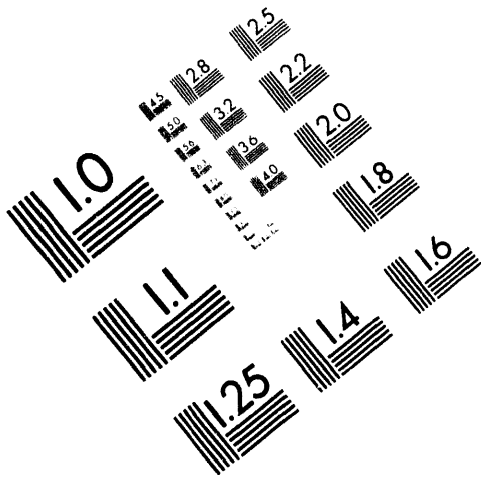




AIM

Association for Information and Image Management

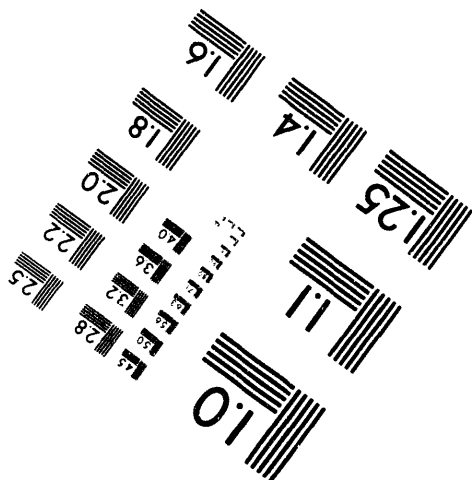
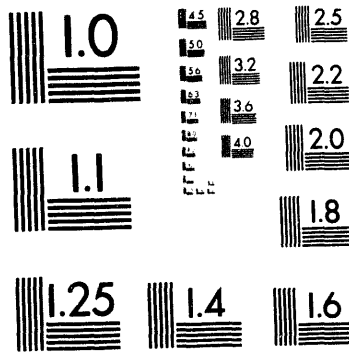
1100 Wayne Avenue, Suite 1100
Silver Spring, Maryland 20910
301/587-8202



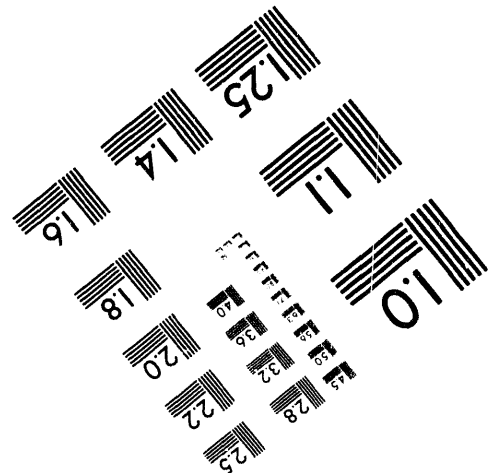
Centimeter



Inches



MANUFACTURED TO AIM STANDARDS
BY APPLIED IMAGE, INC.



1 of 1

July 11, 1994

The Structure of New Synthetic
Manganese Oxide Octahedral
Molecular Sieves

S. R. Wasserman^a, K. A. Carrado^a,
S. E. Yuchs^a, Y. F. Shen^b, H. Cao^b,
S. L. Suib^b

^aChemistry Division, Argonne National Laboratory, Argonne, IL
60439 USA

^bDepartment of Chemistry, U-60, University of Connecticut,
Storrs, CT 06269 USA

Manganese K-edge X-ray absorption spectra are used to examine the average oxidation state and local structure of new synthetic manganese oxide photocatalysts, including the materials known as octahedral molecular sieves. The structures of these materials are compared to the natural minerals cryptomelane and todorokite.

Keywords: XAS, manganese oxide, catalysts

For further correspondence:

Stephen R. Wasserman
Chemistry Division, Building 200
Argonne National Laboratory
9700 S. Cass Ave.
Argonne, IL 60439
USA
708-252-9288 (FAX)
WASSERMAN@ANLCHM.CHM.ANL.GOV

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

The submitted manuscript has been authorized by a contractor of the U. S. Government under contract No. W-31-109-ENG-38. Accordingly, the U. S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or allow others to do so, for U. S. Government purposes.

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED *STB*

The manganese dioxide minerals hollandite and todorokite have one dimensional tunnel structures [1]. These materials contain MnO_6 octahedra which share edges and vertices. In hollandite the tunnels have two octahedra on each side (2×2). Todorokite is a homologue of hollandite, in which the tunnels have expanded to a 3×3 structure. The X-ray absorption spectra of these and other natural manganese dioxide (MnO_2) minerals have been discussed in detail previously [1-3].

Recently octahedral molecular sieves (OMS) based on manganese oxides have been synthesized [4-5]. Two forms of these materials, OMS1 and OMS2, mirror the structures of todorokite and hollandite, respectively. In addition, a new amorphous MnO_2 compound (A- MnO_2) with high photocatalytic activity has been reported [6]. In this paper we describe the use of X-ray absorption spectroscopy to examine the oxidation state and local structure for manganese in these new synthetic materials and compare these compounds with natural analogues.

Experimental

Transmission and fluorescence manganese K edge spectra were acquired at NSLS on beamline X23A2 using a Si(311) double crystal monochromator, standard ion chambers, and a Lytle fluorescence detector equipped with a three absorption length chromium filter. The energy calibration was maintained by simultaneously monitoring the maximum at 6539 in the derivative of the spectrum of a manganese mesh. The precision of the energy calibration is 0.3 eV. The octahedral molecular sieves were synthesized by methods previously described [4-6]. The natural cryptomelane (India) and todorokite (Charco Redondo, Cuba and N'Chwaning Mine, China) samples were obtained from the Smithsonian Institution. Data reduction was performed using a Mathematica® package for XAS analysis developed at Argonne National Laboratory.

Discussion

The near edge and unfiltered EXAFS data (not shown) for OMS2 and cryptomelane, a natural hollandite which contains potassium cations (K^+) within the 2 x 2 tunnel, are virtually

identical. These results demonstrate that the manganese in the synthetic and natural materials possess the same average oxidation state and local structure. The XANES spectra for three of the compounds with 3 x 3 tunnel structures, as well as A-MnO₂, also appear in Figure 1. The absorption edges for each of these compounds occur at lower energies than those of the 2 x 2 materials. OMS1 and MgOMS, two versions of the 3 x 3 compounds for which the magnesium template was introduced at different stages in the synthesis, exhibit lower average oxidation states than natural todorokite. Table 1 lists the fitting parameters for the first coordination shell as well as our estimates for the position of the edge for each of these samples. Except for possibly OMS1, all values are within the error of EXAFS. The edge energies correlate well with the manganese valency that is deduced from elemental analyses.

The near-edge and EXAFS spectra for A-MnO₂ indicate that the valence and local structure within this material are similar to those in natural todorokites. However, the spectra for A-MnO₂ are also similar to birnessite, a

layered manganese oxide. This fact is consistent with the weak X-ray powder diffraction pattern of A-MnO₂ [6].

Acknowledgments

We would like to thank Jeffrey Post for providing the natural todorokite and cryptomelane samples. This work was supported by the Office of Chemical Sciences, Basic Energy Sciences, U. S. Department of Energy under contract W-31-109-ENG-38.

References

- [1] A. Manceau and J. M. Combes, *Phys. Chem. Minerals*, 15 (1988) 283.
- [2] A. Manceau et al., *Am. Mineral.*, 77 (1992) 1133.
- [3] A. Manceau et al., *Am. Mineral.*, 77 (1992) 1144
- [4] Y. F. Shen et al., *Science* 260 (1993), 511.
- [5] R. N. De Guzman et al., *Chem. Mater* 5 (1993), 1395.
- [6] H. Cao and S. L. Suib, *J. Am. Chem. Soc.*, in press.

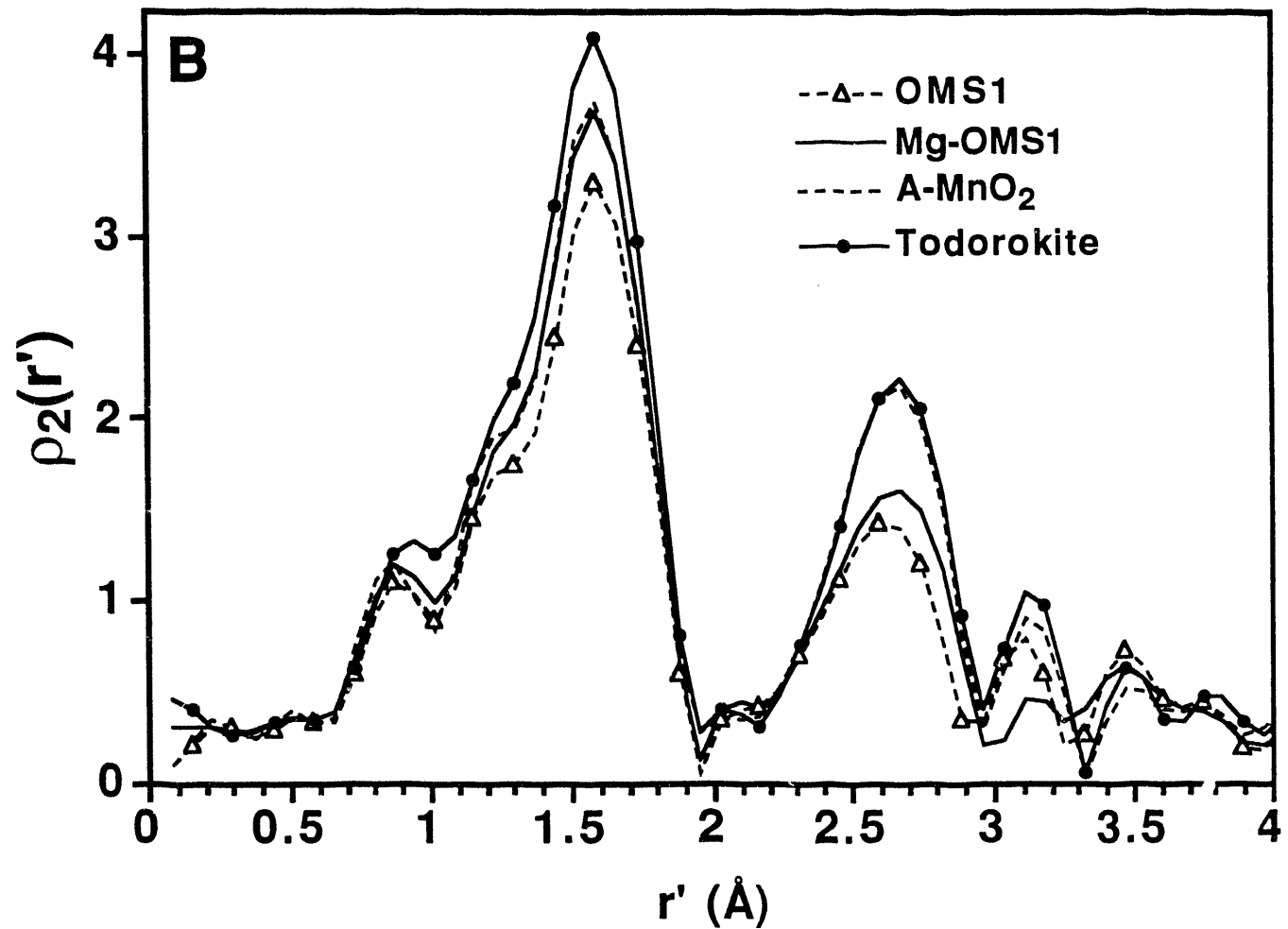
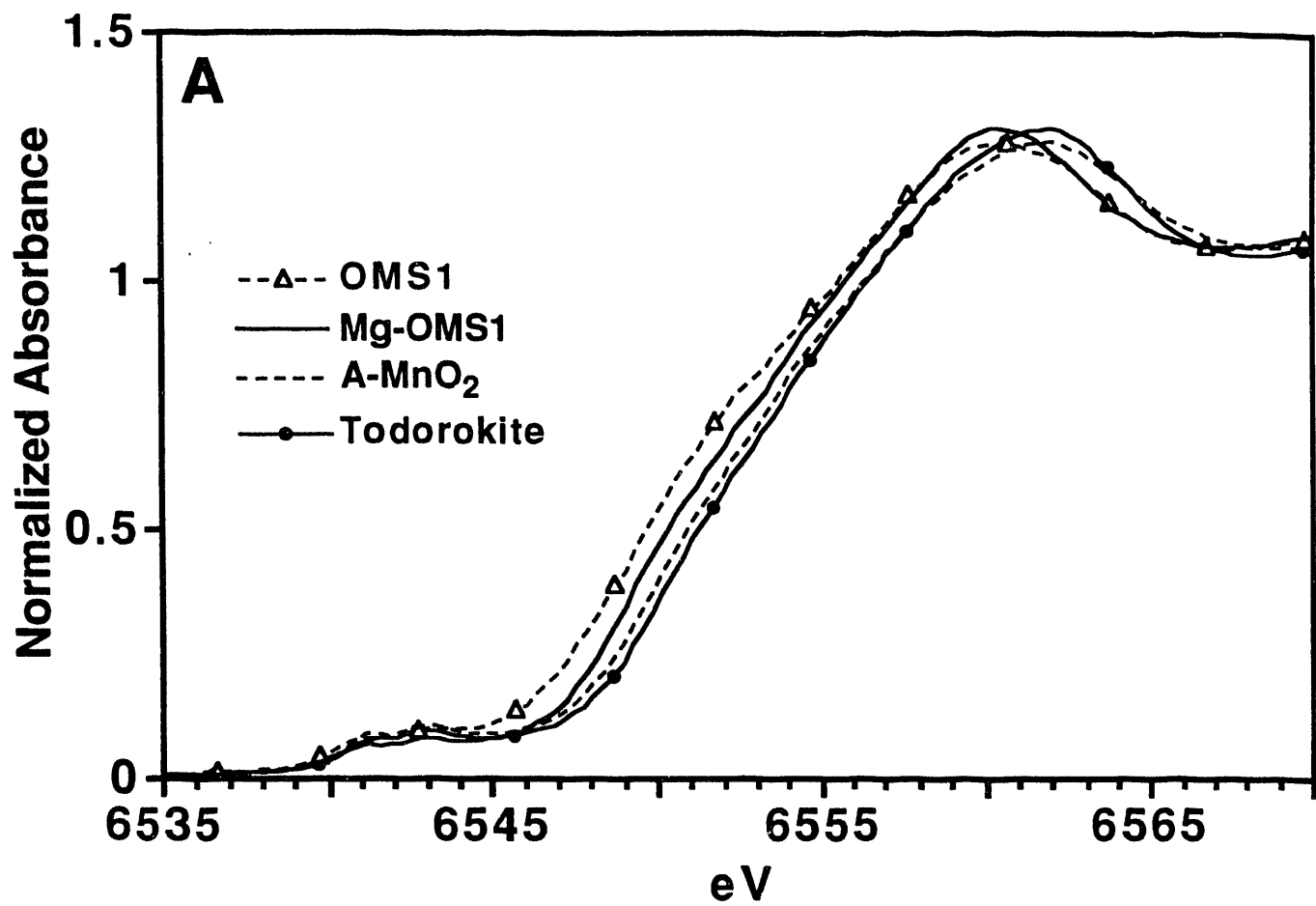
Figure Captions

Fig. 1. (A) Normalized XANES spectra and (B) Radial Structure Functions for OMS1, Mg-OMS1, A-MnO₂, and Todorokite (N'Chwaning Mine, China).

Table I. Parameters for the First Coordination Shell in the Fluorescence XAFS Spectra of Manganese Oxides^a

Sample	n	r (Å)	$\Delta\sigma^2 \times 10^4$	ΔE (EXAFS)	ΔE (XANES)
OMS2	6.0	1.88	0	0	0
Cryptomelane (India)	6.0	1.88	-2	.4	.1
OMS1	4.8	1.89	0	-1.3	-1.8
Mg-OMS1	5.3	1.89	1	-1.5	-1.3
A-MnO ₂	5.4	1.88	1	-.8	-.6
Todorokite (China)	6.0	1.88	2	-.5	-.4
Todorokite (Cuba)	5.6	1.88	3	-.6	-.5

^aThe errors in coordination numbers (n) and radial distance (r) are $\pm 20\%$ of n and ± 0.01 Å respectively. The values for n, r, $\Delta\sigma^2$ and ΔE are referenced to OMS2 (n=6, r= 1.88 Å, $\Delta\sigma^2 = 0$, $\Delta E = 0$). ΔE (XANES) was determined at 0.5 absorbance. Windows for Fourier transforms of $k^2\chi(k)$: forward-2.1 to 13.0 Å⁻¹, inverse-1.00 to 1.95 Å.



DATE

FILMED

9 / 14 / 94

END

