

Water weirdness of nanophase manganese oxides: Rapidly reversible surface-mediated redox transformation triggered by water sorption at room temperature

NANCY BIRKNER AND ALEXANDRA NAVROTSKY*

University of California, Peter A. Rock Thermochemistry Laboratory and NEAT ORU, One Shields Avenue, Davis, CA 95616 (*anavrotsky@ucdavis.edu)

Variable manganese oxidation state (Mn^{2+} , Mn^{3+} , Mn^{4+}) lends complexity to mineral phase behavior and physical and chemical properties. The thermodynamic stability of manganese oxide nanoparticles helps determine the robustness of such oxides and their behavior in soils and larger scale geochemical cycles, as well as in applications in catalysis (1), renewable energy and environmental remediation. The structure and energetics of nanoparticle surfaces are influenced by the phase present and its oxidation state and by the extent of surface hydration. Thus, dry surfaces are structurally and thermodynamically distinct from hydrated surfaces (2, 3). We have shown (4) that the position, in temperature - oxygen fugacity space, of oxidation - reduction (redox) equilibria among Mn_3O_4 (hausmannite), Mn_2O_3 (bixbyite) and MnO_2 (pyrolusite) are shifted at the nanoscale due to differences in surface energy. These differences depend on whether such surfaces are wet or dry.

Recently, we examined (5) the role of water chemisorption on dry nanoparticle Mn_2O_3 and found thermodynamically controlled rapidly reversible mineral phase transformation as confirmed by calorimetry, X-ray diffraction, and manganese average oxidation state titrations. Surface reduction of bixbyite (Mn_2O_3) to hausmannite (Mn_3O_4) occurs in nanoparticles arising from differences in surface energies of the two phases under conditions where no such reactions are seen or expected according to bulk thermodynamics. Measured water adsorption enthalpy (endothermic shift) confirms reduction reaction coupled with water adsorption. The driving force for reduction becomes less unfavorable for nanoparticles, with a significantly greater effect for hydrated particles. Thus, both size diminution and hydration favor hausmannite over bixbyite.

[1] Birkner *et al* (2013) *Proc Natl Acad Sci USA* **110** (22) 8801-8806 [2] Navrotsky (2009) *Int J Quant Chem* **109** (12) 2648-2657 [3] Navrotsky *et al* (2010) *Science* **330** 199-201 [4] Birkner & Navrotsky (2012) *Am Mineral* **97** 1291-1298 [5] Birkner & Navrotsky (2014) *Proc Natl Acad Sci USA*, under review.