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Manganese carbonate formation from amorphous and nanocrystalline precursors: Thermodynamics and geochemical relevance

A.V. RADHA[1] AND ALEXANDRA NAVROTSKY[1,*]

[1]Peter A. Rock Thermochemistry Laboratory and NEAT ORU (Nanomaterials in the Environment, Agriculture, and Technology, Organized Research Unit), University of California Davis, One Shields Avenue, Davis, California 95616, U.S.A.

ABSTRACT

The thermodynamic stabilities of different manganese carbonate phases at ambient conditions were determined by acid solution and water adsorption calorimetry. Amorphous manganese carbonate precursor provides a low energy pathway for $MnCO_3$ crystallization analogous to that observed in (Ca-Mg-Fe)CO_3 systems where crystallization enthalpies appear to be controlled by cation size (become less exothermic with increase in ionic radius). The surface energy of nanophase $MnCO_3$ (0.64 ± 0.08 J/m^2 for hydrous and 0.94 ± 0.12 J/m^2 for anhydrous surface) is lower than that of nano-calcite and $MnCO_3$ binds surface water less strongly (-65.3 ± 3 kJ/mol) than calcite (-96.26 ± 0.96 kJ/mol). This probably reflects the greater basicity of CaO compared to MnO. Substantial particle size driven shifts in the $MnCO_3$-manganese oxide Eh-pH and oxygen fugacity-CO_2 fugacity diagrams were calculated using the measured surface energies. These shifts expand the stability field of hausmannite, Mn_3O_4, in both aqueous and anhydrous environments. The particle size driven (caused by differences in surface energy) shifts in oxidation potential (Eh, oxygen fugacity) and pH of phase boundaries could affect stability, a electrochemical and catalytic properties and hence influence geochemical and technological processes. Manganese oxides (mainly hausmannite) dominate at the nanoscale in aerated environments, while manganese carbonate is favored in coarse-grained materials and reducing environments. In supercritical CO_2, the expansion of the $MnCO_3$ stability field leads to significant reduction of the Mn_3O_4 stability field.

Keywords: $MnCO_3$ (rhodochrosite) formation, crystallization enthalpy, surface energy, Eh/pE-pH diagram, CO_2 sequestration