

**SULFATE MINERAL PHASE EQUILIBRIA AS A FUNCTION OF RELATIVE HUMIDITY. INTERMEDIATE COMPOSITIONS IN THE (Mg, Fe, Zn)SO<sub>4</sub> - H<sub>2</sub>O SYSTEM AT 1 ATM.** J. L. Anderson<sup>1</sup> and R. C. Peterson<sup>1</sup>, <sup>1</sup>Department of Geological Sciences and Geological Engineering, Queen's University, Kingston ON K7L 3N6, Canada. anderson@geoladm.geol.queensu.ca.

**Introduction:** The presence of magnesium sulfate on Mars has been reported from OMEGA spectral imager data and MER data<sup>[1]</sup>. Vapor pressure and temperature conditions on the surface of Mars suggest polyhydrated Mg-sulfates may exist in Martian soils. Phase stability-relationships among the various Mg-sulfate hydrates are surprisingly complicated, may include metastable phases and can vary with reaction pathway and metal substitution.

Recent laboratory experiments to characterize the polyhydrated Mg-sulfates have included: the systematic study of distinct Raman spectral patterns for each of the Mg-sulfates<sup>[2]</sup>, X-ray diffraction analysis of phase transitions at controlled relative humidity<sup>[3]</sup> and water-vapor pressure and temperature controlled equilibrium studies<sup>[4]</sup>. These studies have contributed greatly to our understanding of the complicated reaction pathways and phase stabilities among the possible Mg-sulfate minerals on Mars. The present study was undertaken to examine the effect of metal substitution on the hydration and dehydration pathways of hydrous metal sulfates.

On Earth occurrences of hydrous metal-sulfate minerals are rarely composed of species with end-member chemical compositions and generally reflect the chemistry of the solutions and metal-sulfide minerals from which they were derived. Epsomite group minerals are intolerant of significant Fe-substitution and solutions with <0.005 mol% Fe or Cu precipitate crystals with the goslarite structure whereas solutions of >0.01 mol% Fe or Cu, yielded coexisting epsomite and melanterite group phases<sup>[5]</sup>. Furthermore, the recently discovered and characterized mineral alpersite (Mg,Cu)SO<sub>4</sub>·7H<sub>2</sub>O<sup>[6]</sup> has the melanterite group mineral structure and contains no Fe. The focus of this study is to explore the effect of metal substitution on the hydration/dehydration behaviour and fields of stability of some of the hydrous metal-sulfate minerals.

**Experimental Procedure:** Several compositions of orthorhombic epsomite group minerals, M<sup>2+</sup>SO<sub>4</sub>·7H<sub>2</sub>O (M<sup>2+</sup> = Mg, Zn) and monoclinic melanterite group minerals, M<sup>2+</sup>SO<sub>4</sub>·7H<sub>2</sub>O (M<sup>2+</sup> = Fe, Mg, Zn) were synthesized. Samples were placed in a glove-box humidity chambers of different relative humidities and hydration and dehydration experiments were conducted for up to one year at 1 atm and a temperature of 23 ± 3°C. Samples were sub-sampled periodically for phase identification by X-ray diffraction analysis.

**Results:** The results of these experiments are presented in the constructed equilibrium phase diagrams of (Fe, Mg, Zn)-substituted hydrous sulfate minerals and illustrate the change in hydration-dehydration pathways due to metal substitution. Results include stable equilibrium phases and non-equilibrium intermediate phases which may or may not have fields of stability outside the conditions employed in this study. Epsomite group minerals dehydrate to stable hexahydrate and kieserite group minerals with rozenite group minerals occurring as an intermediate phase and minerals of the melanterite group are stable as rozenite and kieserite group minerals with hexahydrate group minerals occurring as an intermediate phase. The fields of stability of hydrous sulfate minerals were observed to extend to lower relative-humidity with increasing Mg-substitution.

Of particular interest was the metastable phase of boyleite ZnSO<sub>4</sub>·4H<sub>2</sub>O (isostructural with starkeyite MgSO<sub>4</sub>·4H<sub>2</sub>O) that was observed as a single phase in the dehydration of goslarite ZnSO<sub>4</sub>·7H<sub>2</sub>O (isostructural with epsomite MgSO<sub>4</sub>·7H<sub>2</sub>O) prior to dehydration to gunningite ZnSO<sub>4</sub>·H<sub>2</sub>O (isostructural with epsomite kieserite MgSO<sub>4</sub>·H<sub>2</sub>O). Equilibrium stability conditions for this mineral are currently unknown. Results of phase equilibria experiments, as they relate to the ZnSO<sub>4</sub>-H<sub>2</sub>O system, will be presented and compared with the results of an experiment designed to investigate possible dehydration pathways in the ZnSO<sub>4</sub>-H<sub>2</sub>O system.

The careful characterization of mineral phases present in at the Martian surface requires a detailed understanding of the often complicated hydrous sulfate mineral phase relationships. Experimental studies designed to observe and characterize the hydration and dehydration behaviour of the hydrous metal sulfates with respect to relative humidity, temperature and chemical compositions are essential to our understanding of these complicated mineral relationships.

**References:** [1] Yen A.S. et al. (2005) *Nature*, 436, 49-54. [2] Wang A. et al. (2006) *Geochimica et Cosmochimica Acta* 70, 6118-6135. [3] Vaniman D.T. et al. (2004) *Nature* 431,663-665. [4] Chipera S.J. and Vaniman D.T. (2007) *Geochimica*, 71, 241-250. [5] Anderson J.L. et al. (2005) *Min. Mag.* 69, 257-269. [6] Peterson R.C. et al. (2006) *Am. Mineral.* 91, 261-269.