

WATER CONTENT AND DEHYDRATION BEHAVIOR OF Mg-SULFATE HYDRATES. S. J. Chipera, D. T. Vaniman, and J. W. Carey, Earth and Environmental Sciences, Los Alamos National Laboratory, MS D469, Los Alamos, NM 87545 (chipera@lanl.gov)

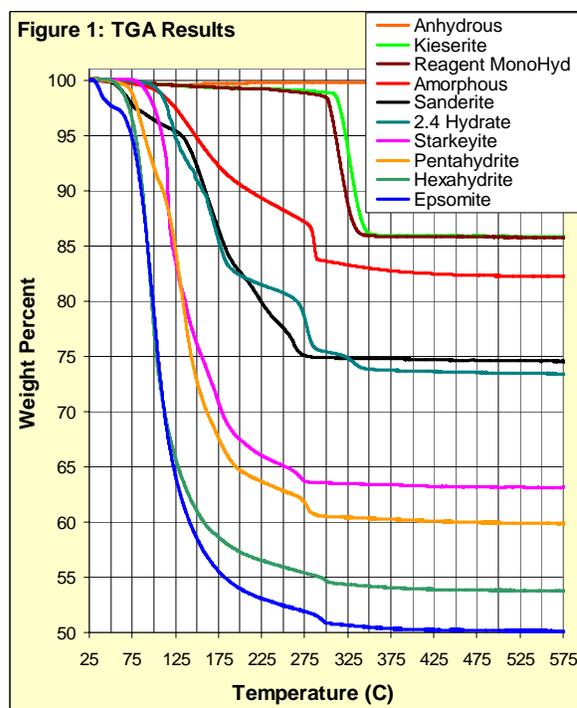
Introduction: Recent studies have been undertaken to characterize stability relationships between the various MgSO_4 hydrates [1,2,3]. These studies have found, however, that the MgSO_4 hydrate system is extremely complicated, with numerous unexpected results. In addition to the known 1, 2, 4, 5, 6, and 7 hydrates found in nature, numerous MgSO_4 hydrates have been synthesized including several phases in these studies which have not been previously described. Thermogravimetric analyses were conducted on the various MgSO_4 hydrates to characterize water content and thermal evolution in an attempt to gain a better understanding of the relationships between these phases.

Methods: Thermogravimetric analyses (TGA) were conducted using a DuPont 951 thermogravimetric analyzer operated with Omnitherm Corporation hardware and software. Typically, ~15 mg samples were analyzed from ambient temperature to 600°C at 10°C/min, using 50cc/min dry N_2 as a purge gas.

Results: TGA is a powerful method that measures both the amount of water and dehydration behavior in hydrous phases. Figure 1 shows the TGA results for various MgSO_4 hydrates plotted as sample weight vs. temperature upon heating. A trend is seen in the data with water release occurring earliest in the most hydrated phases (e.g. epsomite) and later in the least hydrated phases (mono-hydrates) where the water is more tightly bound in the crystal structure.

The more hydrous phases (epsomite-7 H_2O , hexahydrate-6 H_2O , pentahydrate-5 H_2O , starkeyite-4 H_2O) have similar dehydration patterns, where water is evolved in a rather continuous fashion with temperature. Epsomite shows an initial weight loss that corresponds to loss of the single non-octahedrally bound water to form hexahydrate. The intermediate hydrates (2.4-hydrate and sanderite-2 H_2O) have distinctive weight loss curves with several inflections, which are normally indicative of multiple structural sites containing water. However, available data suggest that these hydrates are reacting to form monohydrates which then dehydrate to anhydrous MgSO_4 .

Water content in the amorphous phases can be quite variable, with water contents from 2 to 0.6 H_2O per MgSO_4 . Their weight loss patterns resemble those of the hydrated crystalline phases (epsomite, hexahydrate, starkeyite) that they are made from, even though



they do not retain the crystal structure or water content. The reagent monohydrate and kieserite-1 H_2O both show gradual weight loss until the single distinct weight-loss event occurring at about 300 to 325°C.

Of interest in the TGA data, water content in the Mg-sulfate system is not always integral (e.g., 2, 3, 4, 5, 6, 7). Also of interest is the final distinct weight-loss event that occurs at approximately 280-300°C in the more hydrated phases. The exact cause for this event is uncertain. Ultra-pure MgSO_4 was used to ensure that it was not due to a minor gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) impurity. The amount of water evolving during this event is also variable as can be seen by comparing the weight-loss patterns of the amorphous phase with the hexahydrate from which it was made. It appears to represent a final terminus of water evolution from either the starting product or from the final dehydration of an intermediate reaction product that formed during the heating/dehydration.

References: [1] Chipera, S.J. and Vaniman, D.T., (2006) *Geochimica Cosmochimica Acta*, in press. [2] Chou I.-M. and Seal R. R. II (2003) *Astrobiology* 3, 619-630. [3] Vaniman, D. T. et al. (2004) *Nature* 431, 663-665.