

**KINETICS OF HYDROGEN ISOTOPE EXCHANGE IN GYPSUM: TERRESTRIAL AND PLANETARY APPLICATIONS.** A. K. Thompson and J. P. Greenwood, Dept. of Earth & Environmental Sciences, Wesleyan University, Middletown, CT 06459, USA (akthompson@wesleyan.edu).

**Introduction:** The evaluation of D/H in hydrated minerals has multiple applications, ranging from georeferencing [1] to paleoclimatology [2]. However, minerals fractionate at unique rates, the speed of which can constrain the utility of these methods. Equilibration rates on the order of  $10^8$  years might still reflect ancient environmental factors, but faster rates (on the order of years) yield only contemporary results. The understanding of such sensitivity has critical applications to the mitigation and quantification of terrestrial contamination of planetary samples and the feasibility of future sample return missions.

The discovery of gypsum on Mars [3,4] and in Martian meteorites [5,6] has prompted a recent surge of geochemical research because of its link to water. The rate at which water fractionates stable isotopes will determine the feasibility of using this mineral to look at ancient environmental and aqueous factors. As such, this research hopes to examine the utility of both in situ and sample return analyses of D/H in both terrestrial and extraterrestrial gypsum minerals.

Another goal of this research is to determine the provenance of gypsum found in Martian meteorites. Hydrogen isotope composition of gypsum in the olivine-phyric shergottite Roberts Massif 04262 has a  $\delta D$  of -21‰ [6]. This is indicative of equilibration with atmospheric water vapor at temperate latitudes, such as Houston [6]. We hope to determine how a Martian meteorite can have gypsum that last equilibrated with Houston water.

**Materials and Methods:** Two types of gypsum, alabaster ( $\delta D = -93‰$ ) and selenite ( $\delta D = -122‰$ ), were ground in an agate mortar. Two types of water were also used in these experiments ( $\delta D = -64‰$  and  $+44‰$ ).

Two types of experiments were run: gypsum exchange with water in solution and gypsum exchange with water vapor. Each experiment was contained in an individual serum vial, sealed with a septum and crimped cap. Experiments in solution directly mixed 100 mg of gypsum with 1.5 ml of water. Experiments evaluating vapor exchange also used 1.5 ml of water, but kept the gypsum separated and dry in a smaller borosilicate vial. Due to the high relative humidity within the serum vial, the smaller vial was loosely-capped to help keep condensation from dripping into the gypsum. All experiments were conducted in triplicate in an incubator at 24°C.

Experiments are being run for 4 lengths of time: ~14, 30, 60-100, and 180 days. The gypsum in solution was collected via filtration, and left to dry in a covered petri dish for 2-3 days. In an attempt to minimize the amount of adsorbed water on the grains, the vapor exchange samples were left in a desiccator with their caps removed for a minimum of 2 days.

$\delta D$  values for water and gypsum of each experiment were measured using the Thermo Delta<sup>Plus</sup> XP continuous flow mass spectrometer with TC/EA at Yale University's ESCSIS using established methods [7].

**Results:** Experimental results are shown in Figure 1 and described below.

**Solution.** All of the samples in solution display a trend towards less negative  $\delta D$ , which is consistent with equilibration to the less negative waters. After approximately 100 days, the percent exchange of these experiments ranges from 10-17%.

The presence of large crystals in the recovered gypsum suggests that recrystallization is occurring. However, analysis of the mass of gypsum after filtering suggests that anywhere from 20-70% of the sample dissolved into solution and never recrystallized.

**Vapor Exchange.** Trends for these experiments are either non-existent or very subtle in the less negative direction. An important note is that, despite the protective cap, several of the gypsum samples were observed to either be wet or to have condensation within the borosilicate vial. Wetting of the sample likely affected the results, making it difficult to assign an accurate percent of exchange to these experiments.

**Discussion and Conclusions:** The experiments in solution appear to be the most successful and consistent, allowing the rough extrapolation of 1.5-3 years for complete exchange of the hydrogen isotopes of gypsum.

One unexpected observation is that the gypsum recrystallizing from solution is not fully equilibrating with the D/H of the water. If the recrystallized gypsum was in equilibrium with water, it should be 15‰ lighter than the coexisting water [8]. The implication of this situation is that the original water is remaining bound to a hydrated gypsum solution complex despite dissolution.

Further evaluation of the vapor exchange experiments suggests that they did not actually exchange with a fractionated vapor, but instead with a liquid. Using the equations of [9], the fractionation

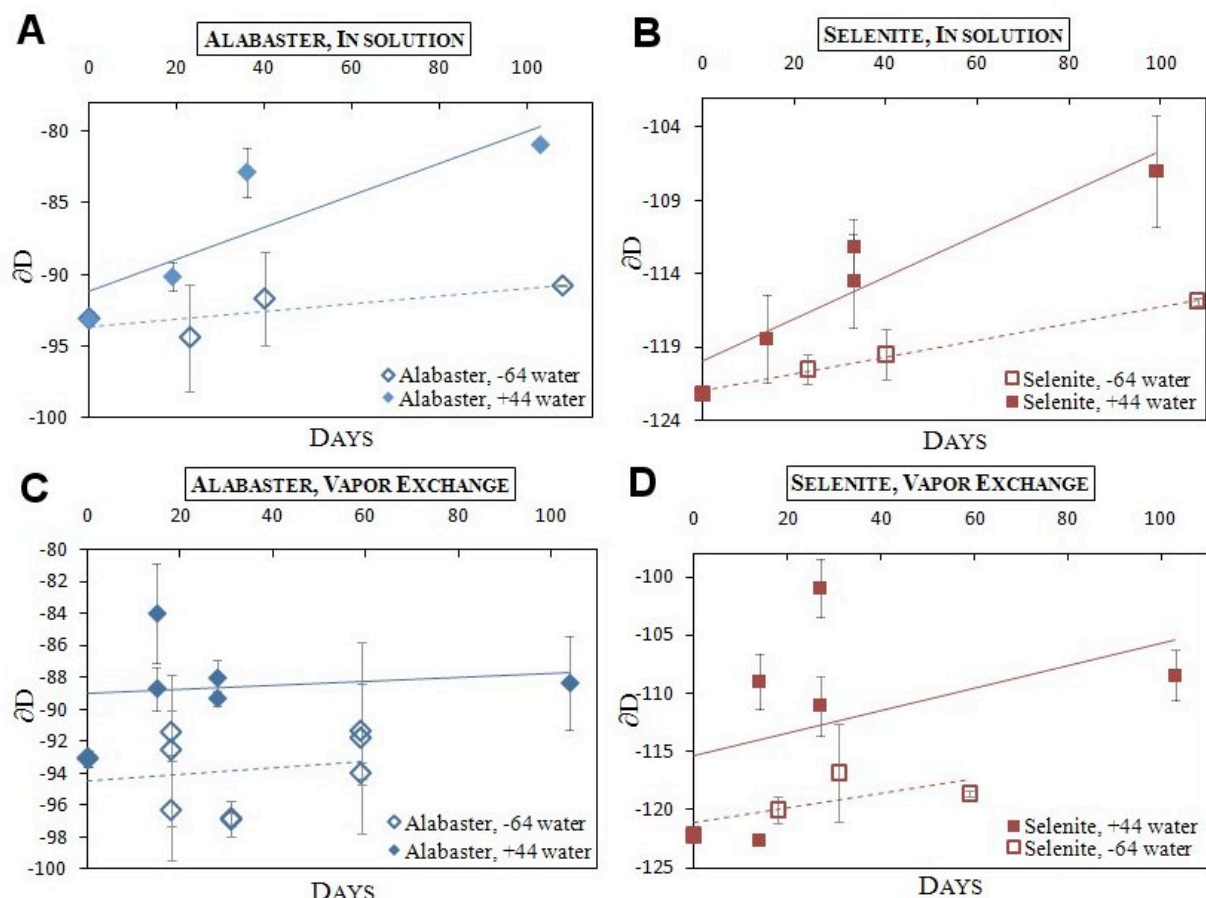
factor of water as it changes from liquid to vapor at 24°C should be -73.9%, meaning that the gypsum should have exchanged with vapors in the range of -30% and -138%. Equilibration to these values is not supported by the data. Instead, it appears that these samples are similar in equilibration to the samples in solution. Two possible reasons for this deviation are that water was either adsorbed onto the grain surface or that the vapor re-condensed within the borosilicate vial and interacted with the gypsum as a liquid.

More data will be available in the spring after the remaining vials in each experimental series are processed. Future research will also include experiments at higher temperatures and with lower relative humidities.

In regards to Martian in situ and sample return analyses for gypsum, this research would suggest that

only contemporary D/H values can be measured. This research further suggests that the  $\delta D$  value measured in RBT 04262 is consistent with gypsum that crystallized in Houston and not on Mars, as it did not have enough time to undergo extensive hydrogen isotope exchange during its residence in Houston.

**References:** [1] Craig, H. (1961) *Science*, 133, 1702-1703. [2] Sofer, Z. (1978) *GCA*, 42, 1141-1149. [3] Langevin, Y. et al. (2005) *Science*, 307, 1584-1586. [4] Gendrin, A. et al. (2005) *Science*, 307, 1587-1591. [5] Gooding, J. L. (1986) *GCA*, 50, 2215-2223. [6] Greenwood, J. P. et al. (2009) *LPSC 40*, Abstract #2528. [7] Sharp, Z. D. et al. (2001) *Chem. Geol.*, 178, 197-210. [8] Fontes, J. C. and Gonfiantini, R. (1967) *Acad. Sci. Comptes Rendus*, 265, 4-6. [9] Horita, J. and D. J. Wesolowski (1994) *GCA*, 58, 3425-3437.



**Figure 1:** Graphs of individual experiment results. Lines are a linear best fit and error bars are the individual standard deviations. (A) Alabaster experiments in solution. (B) Selenite experiments in solution. (C) Alabaster experiments using vapor exchange. (D) Selenite experiments using vapor exchange. Closed symbols and solid trendlines represent experiments using +44‰ water; open symbols and dashed trendlines represent experiments using -64‰ water.