Isotopic approaches to unravel evaporation history and paleo-atmospheric humidity on Earth and Mars

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Water of crystallization in gypsum can be used as paleo-environmental proxy to study large scale climatic variabilities in arid areas [1]. This is because changes in the isotopic composition of water of crystallization are due to isotopic variations in the mother brine from which the mineral precipitated, and the brine isotopic composition is linked to evaporation processes and humidity [2]. This is particularly important when the salts are the only traces left of the original water, i.e. in modern arid areas or on Mars, where sediments and the geomorphology of the planet hint at the presence of ancient flowing, liquid water. This study aims to prove that the $\delta D/\delta^{18}O$ values of the water of crystallization extracted from successive precipitates or even different growth zones of natural gypsum ($CaSO_4{\cdot}H_2O$) can reconstruct the evaporation history and paleo-humidity of the source water basin. The method was tested in a laboratory experiment that evaporated $CaSO_4$ brines under controlled temperature and humidity conditions. The brine was left to evaporate for five days at two different humidities (45 and 75 RH%); subsequently, brines and precipitated gypsum were sampled at 24 hour intervals. In this way we simulated zoned growth of gypsum. The samples were then analyzed for oxygen and hydrogen isotopic composition. Brines were analysed with a Los Gatos Research Liquid Water Isotopic Analyzer DLT-100 at the Division of Geological and Planetary Sciences, California Institute of Technology, while gypsum was analysed using a Thermo Scientific TC/EA with modified column [3], coupled to a MAT 253 Thermo Finnigan mass spectrometer at JPL. A mass-balance salinity model was also developed, to take into account the salt effects on the activity of the brine. Encouraging preliminary results not only largely agree with theoretical models of brine isotopic evolution but also validate our novel hypothesis that changes in mineral composition can reveal details of paleo-environmental conditions.

[1] Gonfiantini and Sofer (1963), *Science* **200**, 644-646. [2] Sofer and Gat (1975), *Earth and Planetary Science Letters* **26**, 179-186. [3] Rohrssen, Brunner, Mielke and Coleman (2008), *Analytical Chemistry* **80**, 7084-7089.