

Triple oxygen isotopes of gypsum hydration water

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Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) typically forms in evaporitic environments. The stable isotope composition of gypsum hydration water (GHW) forms in equilibrium with ambient water. Respective isotope fractionation factors ($^{17}\alpha_{\text{eq}}$, $^{18}\alpha_{\text{eq}}$) are temperature independent [1]. GHW can be preserved over millions of years, making gypsum a powerful paleoenvironmental proxy for evaporitic water bodies [2].

Recent gypsum was sampled from a series of 11 ponds with increasing salinities located in the Salar de Llamara within the Atacama Desert in Chile. Extracted GHW was converted to O_2 using CoF_3 and analysed by dual-inlet IRMS. Reproducibility of $^{17}\text{O}_{\text{excess}} = \delta^{17}\text{O} - 0.528 \cdot \delta^{18}\text{O}$ was ± 8 per meg, similar to the precision of pure water samples.

GHW data plot on a parallel curve to the pond water samples in triple oxygen isotope space. The offset is due to equilibrium isotope fractionation. Respective fractionation factors ($^{17}\alpha_{\text{eq}}$, θ) have been determined experimentally. Stratification of the ponds is apparent from variable oxygen isotopic compositions of gypsum sampled at the water line vs. gypsum sampled from the bottom of the ponds. Groundwater recharge from below results in more depleted bottom waters in the low salinity ponds, while isotopic exchange with atmospheric vapor becomes more important for surface waters of highly saline ponds. The individual ponds are close to a steady state with more or less constant in and outflow.

Understanding the triple isotope systematics of evaporitic water bodies such as those investigated here is crucial to interpret GHW and other chemical sediments. Isotope fractionation theory is well established for the classic isotope systems $\delta^{18}\text{O}$ and δD and is now extended for $\delta^{17}\text{O}$ [3, 4]. The novel $^{17}\text{O}_{\text{excess}}$ parameter is far less sensitive to temperature and salinity than the classic d_{excess} parameter, making $^{17}\text{O}_{\text{excess}}$ a simpler proxy that is mostly sensitive to relative humidity [4]. Our results on GHW demonstrate that evaporation systematics of $^{17}\text{O}_{\text{excess}}$ are in principle recorded in gypsum and may become a useful proxy for paleo-humidity.

[1] Gonfiantini and Fontes (1963) *Nature* **200**, 644-646. [2] Evans et al. (2015) *Earth Planet. Sci. Lett.* **430**, 499-510. [3] Surma et al. (2016) this conference, [4] Surma et al. (2015) *Geophys. Res. Lett.* **42**, 8456-8462.