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Gypsum speleothems record the triple oxygen ($\delta^{17}O$ and $\delta^{18}O$) and hydrogen ($\delta^{2}H$) isotopic composition of cave dripwater: potential paleoenvironmental implications

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Gypsum ($CaSO_4 \cdot 2H_2O$) speleothems (i.e. stalactites, stalagmites, etc.) in caves form frequently through dissolution of the gypsum host-rock by seepage water and subsequent secondary mineral re-precipitation from gypsum-saturated solutions [1]. Gypsum takes its structurally-bound hydration water (GHW) from the liquid; the isotopic composition ($\delta^{17}O$, $\delta^{18}O$ and $\delta^{2}H$) of GHW reflects that of cave dripwater at the time of mineral crystallization, with insignificant effect of temperature on the liquid-GHW isotope fractionation factors [2]; therefore, GHW may be used to reconstruct the isotopic composition of paleo-dripwater in caves. Here we investigate the triple oxygen and hydrogen isotopic composition of GHW in speleothems from circum-Mediterranean gypsum caves, including the gypsum karsts of Emilia Romagna (NE Italy), Sorbas (SE Spain), Sicily and Mesaoria (Cyprus), all of them hosted in gypsum of Messinian age (ca. 5.5 Ma). The climatic settings of the studied caves range from semiarid (i.e. Sorbas and Mesaoria, <300 $mm \cdot yr^{-1}$) to relatively wet (i.e. Emilia Romagna and Sicily >600 $mm \cdot yr^{-1}$).

Our results reveal that most gypsum speleothems in these caves precipitated from unevaporated solutions (e.g. d-excess >8‰ and $^{17}O_{excess}$ >10 per meg), with isotopic compositions similar to those of local meteoric/seepage waters and close to the local meteoric water lines (LMWL) of each region. Gypsum crystallization in absence of evaporation can be explained by the mechanism known as Ostwald ripening [3], a solution-mediated recrystallization under constant temperature by which older crystals (i.e. Messinian gypsum) dissolve to feed new crystals (i.e. gypsum speleothems). Only GHW in speleothems from the Sorbas caves show evidence for solution evaporation prior mineral precipitation. Gypsum speleothems in several caves of Emilia Romagna crystallized from unevaporated waters with significantly different triple oxygen and hydrogen isotopic compositions (e.g. Ca´ Castellina cave: $\delta^{18}O$=-8.3±0.3‰, $\delta^{2}H$=-55.2±1.7‰, $^{17}O_{excess}$=33±9 per meg; Abisso Bentini cave: $\delta^{18}O$=-10.6±0.3‰, $\delta^{2}H$=-73.4±1.8‰, $^{17}O_{excess}$=47±13 per meg). In

absence of chronological data, this can be interpreted as (1) gypsum speleothems formed in different climatic periods or (2) do at present from waters that seepage into the epikarst during different times of the year. Either way, gypsum records the mean isotopic composition of seepage water under distinct environmental conditions in this region.

The $\delta^{18}O$ and $^{17}O_{excess}$ values across the entire dataset are negatively correlated, unlike $\delta^{18}O$ and d-excess values that are, positively correlated for $\delta^{18}O$<-6‰ and negatively correlated for $\delta^{18}O$>-6‰. We suggest that the different behaviors of $^{17}O_{excess}$ and d-excess derive from their distinct sensitivities to environmental parameters (i.e. RH and temperature) during formation of water vapor at the moisture source of rain and local effects during rainfall events in each area. We conclude that gypsum speleothems of known ages may be useful as archives for triple oxygen and hydrogen isotope reconstructions of paleo-rainfall.

[1] Gázquez et al. 2017. Chemical Geology, v. 452, p. 34–46; [2] Gázquez et al. 2017. Geochimica et Cosmochimica Acta, v. 198, p. 259–270; [3] Kahlweit, 1975. Advances in Colloid and Interface Science, v. 5, p. 1–35.