



Coupled measurement of $\delta^{18}\text{O}/\delta\text{D}$ in gypsum hydration water and salinity of fluid inclusions in gypsum: A novel tool for reconstructing parent water chemistry and depositional environment

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The measurement of oxygen and hydrogen isotopes in gypsum hydration water ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) is a powerful tool to determine the isotopic composition of the parent fluid from which gypsum precipitated. To be useful, however, the hydration water must retain its original isotope signal and not have undergone postdepositional exchange. We developed a novel method to ascertain whether hydration waters have secondarily exchanged by coupling oxygen and hydrogen isotopes of gypsum hydration water with the salinities of fluid inclusions. Salinity is obtained through microthermometric analysis of the same gypsum crystals measured for hydration water by freezing the sample and then measuring the melting point of the fluid inclusions.

We apply the method to Messinian gypsum deposits of Cycle 6 within the Yesares Member, Río de Aguas section, Sorbas Basin (SE Spain). After correction of oxygen and hydrogen isotopes of gypsum hydration water for fractionation factors, the estimated range of the mother water is -1.8‰ to 2.8‰ for $\delta^{18}\text{O}$ and -12.5‰ to 16.3‰ for δD . In the same samples, estimated salinity of primary fluid inclusions range from 18 to 51ppt. Salinity is highly correlated with $\delta^{18}\text{O}$ and δD , yielding an r^2 of 0.88 and 0.87, respectively. The intercepts of the regression equations (i.e., at zero salinity) define the isotope composition of the freshwater endmember, and average $-4.4 \pm 1.3\text{‰}$ for $\delta^{18}\text{O}$ and $-28.9 \pm 8.7\text{‰}$ for δD . These values are within error of the average isotope composition of precipitation and groundwater data from the local region of Almería today (-4.3‰ and -22.2‰ for $\delta^{18}\text{O}$ and δD , respectively). This agreement provides strong evidence that the gypsum hydration water has retained its isotope composition and has not undergone postdepositional exchange. Furthermore, the isotope and salinity values indicate a significant contribution of meteoric water during gypsum deposition. This observation contrasts with sulfur and oxygen isotopes in sulfate ($21.9 > \delta^{34}\text{S} > 23.3\text{‰}$; $11.3 > \delta^{18}\text{O}_{\text{SO}_4} > 14.5\text{‰}$) and strontium isotopes ($0.708942 > {}^{87}\text{Sr}/{}^{86}\text{Sr} > 0.708971$) that are similar to those measured in other Messinian evaporites of the Mediterranean. We suggest sulfate and strontium isotopes are relatively insensitive to freshwater influence because of the high concentrations of sulfate and strontium in seawater.

The cyclic alternation of gypsum and marl in the Yesares Member has been interpreted as reflecting changing climate related to Earth's precession cycle, but to date direct evidence linking depositional environment and orbital forcing has been lacking. We demonstrate that the $\delta^{18}\text{O}$, δD and salinity of the parent brine increased from low values at the base of the cycle to a maximum in the massive gypsum palisade, and decreased again to lower values in the supercones at the top of the cycle. This pattern is consistent with precession-driven changes in climate with wetter conditions during precession minima (insolation maxima) associated with the interbedded marls and drier climate during gypsum precipitation with the driest conditions during the precession maxima (insolation minima) associated with gypsum palisade formation.