Triple Oxygen and Hydrogen isotope analysis of gypsum hydration water from the evaporites of the Messinian Salinity Crisis

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During the Messinian Salinity Crisis (MSC; 5.97-5.33 Ma), a combination of climatic and geodynamic factors resulted in the deposition of over one million cubic kilometers of evaporitic minerals in the Mediterranean basin [1]. Attempts to determine the origin and composition of the brines from which the Primary Lower Gypsum (5.97-5.60 Ma), Halite (5.6-5.55 Ma), and Upper Gypsum (5.55-5.33 Ma) units precipitated have met with conflicting results, and their onshore-offshore correlation remain poorly constrained. Here we analyze the triple oxygen (17O/16O, 18O/16O) and hydrogen (2H/1H) isotope ratios of the gypsum hydration water and halite fluid inclusions from both onshore and deep basin deposits to obtain the $\delta^{18}O$, δD , ^{17}O -excess, and dexcess of the mother fluids from which they formed. We combine >400 oxygen and hydrogen isotopic measurements together with 87Sr/86Sr, salinity deduced from fluid inclusion melting temperatures, trace element data and other isotopic measurements to reconstruct the hydrological changes in the Mediterranean basin during the three main MSC stages.

Modeling of the ¹⁷O-excess and d-excess parameters demonstrate that all Primary Lower Gypsum deposits are formed via the evolution of source fluids through a multibasin environment with variable connectivity of the Mediterranean to the Atlantic. The deep basin "Upper Evaporites" from DSDP/ODP sites 107, 372, 374, and 654 are characterized by values that deviate from those of the onshore Upper Evaporites, suggesting that different hydrologic conditions characterized the deep basins during evaporite formation. Importantly, the oxygen and hydrogen isotopic results from site 374 are consistent with the hydration of anhydrite from non-evaporated seawater. This indicates post-depositional isotopic alteration and is in agreement with proposed on-going bacterial sulfate reduction, potentially mediating subsurface dolomite precipitation.