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Constraining the origin of the Messinian gypsum deposits using coupled measurement of $\delta^{18}O/\delta$D in gypsum hydration water and salinity of fluid inclusions

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We used oxygen and hydrogen isotopes of gypsum hydration water (GHW) coupled with salinity deduced from ice melting temperatures of primary fluid inclusions in the same samples (in tandem with $^{87}Sr/^{86}Sr$, $\delta^{34}S$ and other isotopic measurements) to determine the composition of the mother fluids that formed the gypsum deposits of the Messinian Salinity Crisis from shallow and intermediate-depth basins. Using this method, we constrain the origin of the Messinian Primary Lower Gypsum (PLG) of the Sorbas basin (Betic foreland) and both the Upper Gypsum (UG) and the Lower Gypsum of the Sicilian basin. We then compare these results to measurements made on UG recovered from the deep Ionian and Balearic basins drilled during DSDP Leg 42A.

The evolution of GHW $\delta^{18}O/\delta$D vs. salinity is controlled by mixing processes between fresh and seawater, coupled with the degree of evaporation. Evaporation and subsequent precipitation of gypsum from fluids dominated by freshwater will result in a depressed $^{87}Sr/^{86}Sr$ values and different trajectory in $\delta^{18}O/\delta$D vs. salinity space compared to fluids dominated by seawater. The slopes of these regression equations help to define the end-members from which the fluid originated.

For example, salinity estimates from PLG cycle 6 in the Sorbas basin range from 18 to 51ppt, and after correction for fractionation factors, estimated $\delta^{18}O$ and δD values of the mother water are low (-2.6 < $\delta^{18}O$ < 2.7‰ ; -16.2 < δD < 15.8‰). The intercepts of the regression equations (i.e. at zero salinity) are within error of the average isotope composition of the modern precipitation and groundwater in this region of SE Spain. This indicates there was a significant contribution of meteoric water during gypsum deposition, while $^{87}Sr/^{86}Sr$ (0.708942 < $^{87}Sr/^{86}Sr$ < 0.708971) indicate the ions originated from the dissolution of previously marine evaporites. Gypsum from cycle 2 displays similar mother water values (-2.4 < $\delta^{18}O$ < 2.4‰ ; -13.2 < δD < 17.0‰) to cycle 6, but salinities of fluid inclusions are higher averaging $\sim$100ppt. In contrast to cycle 6, the intercepts of the regression equations of cycle 2 display more positive $\delta^{18}O/\delta$D values. While the estimated range in $\delta^{18}O$ and δD of the mother water and salinities fall below those expected from the evaporation of seawater alone, the slope of the regression equation is similar to that of seawater evaporation. This implies that there is a change up-section from a dominantly marine environment in cycle 2 to a greater influence of meteoric water in cycle 6.

The UG from the Sicilian basin display greater $\delta^{18}O/\delta$D values (2.9 < $\delta^{18}O$ < 6.0‰ ; 16.6 < δD < 38.3‰) compared to the PLG of Sorbas, with average salinities of $\sim$90ppt. The intercept of the regression equations are similar to those of Sorbas cycle 6, indicating the mother fluid was composed of a large percentage of meteoric water that subsequently underwent intense evaporation. This observation concurs with the low values of $^{87}Sr/^{86}Sr$ from the same UG samples (0.708745 < $^{87}Sr/^{86}Sr$ < 0.708810) that have been interpreted previously to reflect a substantial dilution of Mediterranean surface water during this period, and with brackish to fresh-water fauna described from the associated marl of the UG in other studies. Ongoing analyses will test if this pattern of intense evaporation of a predominately meteoric mother fluid is reflected in the isotopic composition of the UG deposited in the deep Ionian and Balearic basins.