The biogeochemical sulfur cycle during the formation of the Mediterranean Salt Giant

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Sulfur is a key element to understand ocean biogeochemical processes. Since decades, numerous studies have explained sulfur isotopic variations recorded in the geological record as reflecting changes in continental sulfur inputs, biogeochemical recycling of sulfur and the relative proportion of oxidized (gypsum) vs reduced (e.g. pyrite) sulfur burial fluxes. Geochemical and petrographic studies have showed that these processes were active during the formation of the Mediterranean Salt Giant (MSG), a giant salt deposit formed at the end of the Messinian period (5.9-5.33 Ma) following the restriction of hydrological exchanges between the Mediterranean Sea and the Atlantic Ocean. To date, the biogeochemical sulfur cycle during the formation of the MSG has been investigated by analyzing the sulfur and oxygen isotope composition (δ34S and δ18O, respectively) of the sulfate ion in gypsum accumulated in the deep and marginal Mediterranean basins. In the uppermost gypsum layers (Upper Gypsum unit), significantly higher δ18O isotopic ratios (averaging at 12,7‰) than Messinian marine values suggest implications of microbial sulfate reduction activity followed by complete re-oxidation of sulfide back to sulfate in evaporated marine waters. Nevertheless, these different microbial processes can overprint each other δ34S and δ18O isotopic signatures and could have been provoked by various type of microbial metabolisms, involving different hydrological and environmental conditions. Here we present for the first time a multiple sulfur isotope (δ34S, Δ33S, Δ36S) investigation of samples from the well-known sections of Vena del Gesso (Apennines) and Pollenzo (Piedmont basin) in order to identify and understand how microbial mechanisms were coupled during the MSG formation. We designed a simple steady-state, three-box model representing the analysed S-bearing fractions (SO42-, S0, FeS2) and the different hydrological and biogeochemical S fluxes involved in marginal basin S-cycling. This system of 18 equations allows us to explain the strong isotopic variations we measured (-40.2 to 25.4% in δ34S, -0.001 to 0.160‰ in Δ33S and -1.79 to 0.001‰ in Δ36S‰) as produced by a huge variability in sulfate reduction activity reflecting fluctuations in the availability of organic matter. Moreover, our results, with relatively high λ33net (0.513 to 0.516) suggest than more than 90% of the hydrogen sulfide produced was re-oxidized by disproportionation reactions. Large, cyclic fluctuations of the Mediterranean hydrological cycle, and the presence of easily accessible S-compounds with a variety of oxidation states, makes the MSG a key system to understand the
dynamics of the S biogeochemical cycle in the geological past.