A UNIFYING BIOGEOCHEMICAL MECHANISM FOR SHALLOW GYPSUM VS. DEEP DOLOMITE FORMATION DURING THE MESSINIAN SALINITY CRISIS

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Abstract

The Messinian Salinity Crisis (MSC) is an event ~ 5.9 Ma ago that resulted in deposition of 0.3 -3 km thick evaporites at the Mediterranean seafloor (1-3). Controversy existed on the formation mode,but recently a consensus was reached on several aspects (3).The latter has also clarified remaining issues, such as for the observed shallow gypsum versus deep dolostone deposits (3-5).A recently proposed scenario for the Lower Gypsum units of the MSC infers that primary gypsum only formed in silled marginal basins while dolostones are found at deeper settings. We agree but reject the suggested coincidental presence of similar sills for all marginal basins. Alternatively, we present here a unifying mechanism in which gypsum formation occurs at all shallow water depths but its preservation is mostly limited to shallow sedimentary settings.

Keywords: Messinian, Evaporites

The onset of the Messinian Salinity Crisis is marked by the deposition of gypsum-sapropel alternations (Lower Gypsum unit). Increasing evidence has recently been put forward to show that this gypsum precipitation only occurred at marginal settings, while non-evaporitic rocks have been reported from deeper settings (5-7). The difference in sedimentary environment between marginal and deep Mediterranean settings is only tentatively explained by physical properties like tectonic restriction and/or sea level lowering, for which there is no solid evidence. The chemical processes of gypsum formation during the Messinian salinity crisis, however, are poorly understood and commonly neglected. These may, however, explain that different MSC deposits formed in shallow versus deep environments without the necessity of exceptional physical boundary conditions. For this we have to consider the following processes that are important:

a. Water column stratification due to continuing (but episodic?) inflow of oceanic water and enhanced evaporation thus enhanced salinity of Mediterranean water

b. Organic Matter (OM) debris fluxes settling into the deep waters and being decomposed through oxygen and sulphate

c. Gypsum precipitation is controlled by the product of Ca^{2+} and SO_4^{2-} concentrations

Gypsum precipitation in evaporating seawater takes place at 3-7 times concentrated seawater (8 and refs therein); seawater is always largely oversaturated relative to dolomite but its formation is thought to be inhibited by the presence of dissolved sulphate (9). Thus the conditions for formation of gypsum exclude those for the formation of dolomite and vice versa. Another process that links the saturation states of gypsum and dolomite is that of OM degradation by sulphate reduction. In stagnant deep water oxygen is rapidly depleted through OM degradation, then sulphate becomes the main oxidant for OM mineralization, thus reducing the deep-water sulphate content. In the latter process also considerable amounts of dissolved carbonate are formed. Implicitly this means that low-sulphate conditions (as anticipated for the MSC deep waters), i.e. unfavorable conditions for gypsum formation, always coincide with anoxic, i.e. oxygen-free conditions, although there is no direct relationship between the two. the Messinian Mediterranean would have been characterized by a reasonably well-mixed upper water mass (‘shallow waters’), and a strongly stratified lower ‘deep-water mass’. The MSC stratification with deep concentrated brines, is very stable, and can only be replaced by an even higher salinity water mass. As a result, continued evaporation and water replacement leads to (episodically) enhanced Ca and SO4 concentrations in the shallow waters, thus potentially to gypsum precipitation. Decreasing sulphate and concomitantly increasing dissolved carbonate in the deep waters limit gypsum preservation and permit dolomite formation to occur. Ultimately, it is the balance between OM-fluxes (primary productivity) and sulphate supply to the deep-water (ventilation, settling gypsum fluxes) that determine the environmental deep-water conditions, thus formation rate of dolomite. On the basis of this unifying mechanism, we have shown that gypsum precipitation in shallow water depths and dolomite formation in deep water settings during the early phase of the MSC in the Mediterranean is not incompatible. As a consequence one would expect a bath tub rim of gypsum at all shallow depths but gyupsum appears mainly at silled marginal basins. However, a thick package of heavy gypsum on top of more liquid mud in a marginal/slope setting is highly unstable, thus any physical disturbance such as tectonic activity or sealevel change, would easily lead to downslope transport of such marginal gypsum deposits. The absence of gypsum and the presence of erosional unconformities at the sill-less Mediterranean passive margins concord to such removal mechanism. In addition, large-scale resedimentation of gypsum has also been found for deep Messinian settings in the Northern Apennines and Sicily. Only at those marginal settings that were silled, the marginal gypsum deposits have been preserved (3-7,10).

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