Processes underlying barite formation in the Mediterranean: a record of marine microbial activity during sapropel deposition

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Mediterranean sapropels represent an exceptional example of productivity fluctuations reconstructed from Ba proxies. They have been cyclically deposited in the Mediterranean by the combination of climatically induced increases in primary productivity and changes in bottom-water oxygenation. The main driver behind the deposition of sapropels was the monsoon-related freshwater inputs into the eastern Mediterranean in response to periodic northward shifts of the intertropical convergence zone (ITCZ) that resulted in increasing nutrient supply and subsequently enhanced productivity and Ba accumulation. In general, increasing Ba content in marine sediments has been interpreted as a direct indicator of marine primary productivity. However, the diverse processes involved in barite precipitation are still poorly investigated. For instance, types of productivity and modes of nutrient delivery to the photic zone have been poorly explored in terms of spatial variability across the Mediterranean during sapropel deposition, which is crucial for Ba proxies interpretation. Recent insights from experimental work, as well as observations from microenvironments of intense organic matter mineralization in the ocean water column have demonstrated the role of bacteria and extracellular polymeric substances (EPS) production in barite precipitation. Both bacterial cells and EPS provide charged surfaces that bind metals inducing mineralization, therefore, playing an essential role in promoting locally high concentrations of Ba leading to barite formation. This occurs through P-rich amorphous precursor phases, being phosphate groups in EPS, and bacterial cells the main sites for binding Ba. The ubiquitous presence of bacteria in aquatic systems, and in particular in the mesopelagic zone at depths of intense organic matter mineralization, and their inherent ability to biomineralize, make them extremely important agents in the Ba biogeochemical cycle. Thus, reconstruction and interpretations of past productivity and its potential spatial variations as well as fluctuations over time need to consider this microbial paleoperspective. In fact, in the modern Mediterranean, some significant differences in types of productivity and bacterial production exist, which could have also been important in the past, resulting in regional changes in barite production. Assessing the nature of barite-related processes is therefore crucial for the correct interpretations of primary productivity variations during sapropel deposition. In fact, the strong link between organo-mineralization and microbial processes in the past still requires further investigation to determine factors controlling barite accumulation rates in the Mediterranean sapropels.