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Redox-driven Ba isotope resetting in marine sediments: insights from Pliocene Mediterranean sapropels and implications for paleoenvironmental reconstructions

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Barium isotopes in sedimentary records show potential for reconstructing past ocean circulation and productivity changes, as the isotopic composition of sedimentary excess Ba is suggested to reflect that of the upper water column during biogenic barite formation. This approach critically assumes that once barite forms in the water column, its Ba isotope signature remains unchanged during subsequent transport and burial processes. While this assumption has been validated for sediments formed in oxic water columns, their validity in anoxic (particularly euxinic) environments remains uncertain. In such settings, depressed sulfate concentrations and enhanced dissolved Ba inventories may facilitate barite dissolution-recrystallization processes, potentially modifying original isotopic signatures. Consequently, it remains unclear whether the isotopic composition of excess Ba in sediments deposited under anoxic conditions is modified during sedimentation and diagenesis processes, and what information it ultimately records.

To investigate these uncertainties, we analyzed Ba isotopes in Pliocene sapropel sequences from the eastern Mediterranean, which are organic-rich deposits formed under persistent anoxia. These sapropels are characterized by progressive enrichment in Ba/Al ratios, predominantly associated with biogenic barite, reflecting an increase in primary productivity. However, the Ba isotope composition remains remarkably homogeneous ($\delta^{138/134}$Ba = -0.15‰ to -0.02‰), displaying no correlation with variations in productivity. Neither post-depositional diagenetic remobilization nor changes in the marine Ba isotope reservoir explain this isotopic uniformity. Instead, our findings suggest that continuous ion-exchange reactions between barite and deep seawater during particle settling effectively overprinted primary isotopic signatures, indicating sapropel Ba isotopes predominantly record deep water mass composition rather than surface processes. These findings carry crucial implications for interpreting Ba isotopes in black shales, which share key geochemical characteristics with Mediterranean sapropels. Our results emphasize that Ba isotope signatures in reducing environments may reflect complex water column processes rather than direct productivity signals. Successful application of this proxy in black shale studies therefore requires multiproxy validation to distinguish between surface productivity effects and deep-water Ba-S cycle dynamics—a critical consideration for reconstructing ancient ocean biogeochemistry.