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# Fe isotope and Fe speciation study of water column redox dynamics during Eastern Mediterranean sapropel events S5 and S7

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Sapropels S5 and S7 formed in the semi-enclosed Eastern Mediterranean Sea during peak interglacial periods MIS5e and MIS7a, respectively. This study investigates the dynamics of water column redox change during their formation, through Fe isotope and Fe speciation studies of cores taken at 2550 m depth at site ODP-967 south of Cyprus. Both sapropels show an inverse correlation between $\delta^{56}$Fe and $Fe_T$/Al, with slopes mostly matching that found for the Black Sea, pointing to a benthic shelf to basin shuttle of Fe and subsequent precipitation of Fe sulphides in highly euxinic bottom waters. An exception to these Black Sea-type trends occurs during the later, peak stages of S7, where the negative $\delta^{56}$Fe - $Fe_T$/Al slope shallows. Fe speciation studies reveal that the dominant highly reactive Fe phase ($Fe_{HR}$) in the sapropels is pyrite, with Fe (oxyhydr)oxides forming the second major mineral component. $Fe_{HR}/Fe_T$ plots show increased strengthening of anoxic water conditions during the transformation from pre-sapropel sediment into the sapropel. Nevertheless, despite the evidence for highly euxinic conditions from both Fe isotopes and high Mo concentrations in the sapropels, $Fe_{py}/Fe_{HR}$ ratios remain below values commonly used to identify water column euxinia. This apparent contradiction is ascribed to the sedimentary preservation of a high flux of crystalline Fe (oxyhydr)oxide minerals to the basin, which resulted in a relatively low degree of sulphidation, despite the presence of euxinic bottom waters. Thus, the operationally defined ferruginous/euxinic boundary for Eastern Mediterranean Sea sapropels is better placed at $Fe_{py}/Fe_{HR}$ = 0.6, which is somewhat below the usually ascribed lower limit of 0.7. Consistent with the significant presence of crystalline Fe (oxyhydr)oxides, the change in the $\delta^{56}$Fe - $Fe_T$/Al slope during peak S7 is ascribed to an enhanced monsoon-driven flux of detrital Fe(III) oxides from the River Nile into the Eastern Mediterranean basin. The euxinic water column conditions that developed in sapropels S5 and S7 are interpreted to reflect the positive balance between dissolved sulphide formation and rates of reductive dissolution of Fe (oxyhydr)oxide minerals. Both of these parameters in turn depend on the extent to which water overturn times are reduced during sapropel formation. Water overturn rate is therefore considered to define the strength of euxinic water column conditions during these periods of organic carbon-rich sedimentation.

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