

Anoxic Evolution of Deep-water Sapropels S5 and S7

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Late-Middle Pleistocene sapropels S5 and S7 are among the most strongly developed eastern Mediterranean Sea sapropels. Their formation is the outcome of atmospheric-oceanic coupling in which a buoyant surface water layer slowed down thermohaline overturning circulation, creating oxygen depleted deep-water conditions below a shallow redoxcline. Here we utilize the combined strengths of Fe isotope and Fe speciation studies to define redox progression during S5 and S7 deposition in core ODP 967 (2550 mbsl), located south of Cyprus.

Classic geochemical proxies (RSTE, Fe/Al, U/Mo) and Fe speciation studies indicate similar development in both sapropels: progressive increase to maximum anoxic reducing conditions in the upper sapropel followed by rapid collapse at termination. The Fe/Al vs $\delta^{56}\text{Fe}$ crossplots follow the inverse trends characteristic of the shelf to basin shuttle [1], with bulk $\delta^{56}\text{Fe}$ values as low as -0.72% . The $\delta^{56}\text{Fe}$ depletion in the sapropels correlates with an increase in the pyrite fraction, implying that the light Fe isotopic signature primarily resides in authigenic pyrite. On the other hand, pyrite-bearing anoxic sediments underlying the sapropel display typical marine $\delta^{56}\text{Fe}$ values compatible with diagenetic reduction in the absence of a benthic Fe shuttle [2].

Fe_{py} vs Fe_{HR} plots [3] show that the onset of the Fe shuttle in the sapropel occurs in ferruginous conditions, which then develop toward euxinic conditions at the sapropel peak. The occurrence of ferruginous conditions reflects the significant presence (in addition to pyrite) of Fe(III) oxide minerals (Fe_{ox}) in the sapropel, despite the fact that such minerals will be metastable in reduced Fe(II) waters. Their presence could reflect rapid Fe(III) oxide shuttling into the benthic basin, which did not allow sufficient time for their reduction to Fe(II). Alternatively, Fe(II) could be sequestered into the sapropel, but then undergo later oxidation. The anoxic development sequence in sapropels S5 and S7 is relevant to organic carbon-rich shales formed in deep geological time.

[1] Severmann *et al* (2008) *Geology* **36**, 487-490. [2] Matthews *et al* (2017) *Chem. Geol.* **475**, 24-39. [3] Poulton & Canfield (2011) *Elements* **7**, 107-112.