



Timing and intensity of anoxic-sulphidic redox conditions in Eastern Mediterranean Sapropels S1 and S5 deduced from metal isotopes and trace and major element variations.

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Redox is a critical control of organic carbon-rich sedimentation, especially for Eastern Mediterranean (EM) sapropels where deepwater stagnation is related to increase freshwater discharge into the EM Sea. We apply the metal isotope systems of Fe and Mo together with redox-sulphide sensitive trace elements (RTSE) to the determination of paleoredox conditions during the formation of Holocene S1 and Last Interglacial S5 EM sapropels (ODP core 967D; 2550m depth).

RTSE are asymmetrically distributed in S1 sapropel, with peak enrichments occurring in its lower part. Negative correlations between $\delta^{57}\text{Fe}$ and Fe/Al and S wt% in the lower sapropel are consistent with the benthic Fe shuttle model for anoxic-sulphidic basins¹. Correspondingly, Mo/U systematics are consistent with open marine conditions, with sulphidic conditions in the lower sapropel compared to sub-oxic conditions in the upper sapropel and enclosing sediments². The Mo paleoredox model for highly sulphidic euxinic marine systems envisages sediments acquiring Mo isotope signatures of sea water ($\delta^{98/95}\text{Mo} = 2.3$ permil) due to quantitative Mo scavenging³. However, in keeping with several recent studies of organic carbon-rich sediments, S1 profile shows 'atypical' light $\delta^{98/95}\text{Mo}$ values, which progressively decrease from sub-oxic values of *ca* 0 permil in the underlying sediment to negative values of -0.9 permil in the lower sapropel, before gradually rising through the sapropel to values of 0 to 0.4 permil in the post-sapropel sediment. The lightest Mo isotopes occur with indicators of peak sapropel conditions - high Fe/Al, Ba/Al, Mo/Al and S. A combination of source effects and isotopic fractionation between sea water molybdate and particle reactive thiomolybdate species in mildly sulphidic conditions can account for such isotopically light values. The proxy methods thus reflect anoxic early S1 redox conditions in mildly sulphidic bottom water, followed by a progressive waning and weakening to sub-oxic diagenetic conditions.

Initial Sapropel S5 data are in marked contrast to the S1 data. RTSE and major elements show stronger enrichments than for S1, and a trend toward peak values in the upper sapropel section. Correspondingly, $\delta^{98/95}\text{Mo}$ values, which reflect sub-oxic to anoxic conditions in the sediments, show a rise to near-seawater values (1.9 to 2.2 permil) in the upper sapropel, indicative of strong euxinic conditions. Mo/U ratios show seawater values at the S5 peak, suggesting these elements are sequestered from sulphidic bottom waters. Thus, peak redox (anoxic-sulphidic) conditions in S5 characterize the later stages and suggest a progressive redox build-up.

The multiproxy use of RTSE, major elements and Fe and Mo isotopes has the potential to reveal the strength and timing of the anoxic-sulphidic conditions during sapropel evolution. Transient drops toward background sediment proxy levels within the sapropel record hiatuses, as exemplified by the hiatus recording of the 8.2 ka event in S1 previously recognised in other studies.

¹Severmann et al. (2008) *Geology* 36, 487-90. ²Algeo and Tribollivard (2009) *Chemical Geology* 68, 211-225.

³Arnold et al. (2004) *Science* 304, 87-90; Neubert et al. (2008) *Geology* 35, 775-778.