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

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Eastern Mediterranean sapropels are organic carbon-rich sediments. Their formation occurred during sub-oxic to anoxic water column conditions related to global climatic forcing events. Processes proposed to account for their formation and for the preservation of organic matter include: (1) higher export productivity, which created anoxicity through the consumption of oxygen and (2) physical disruption (slowdown) of the normal thermohaline water overturn system (Fig. 1), leading to bottom water stagnation. The slowing down of water overturning circulation in Eastern Mediterranean Sea (EMS) is related to freshening of the sea surface layer during enhanced Milankovitch precession cycle insolation-driven riverine discharge, mainly that of the River Nile, and to increased rainfall over the EMS. Sapropels S5 and S7 formed in the semi-enclosed EMS during peak interglacial periods MIS5e and MIS7a, respectively. This study investigates the redox dynamics of the water column during their formation, through Fe isotope and Fe speciation studies of cores taken at site ODP-967 in the Levantine Basin (Fig. 1).

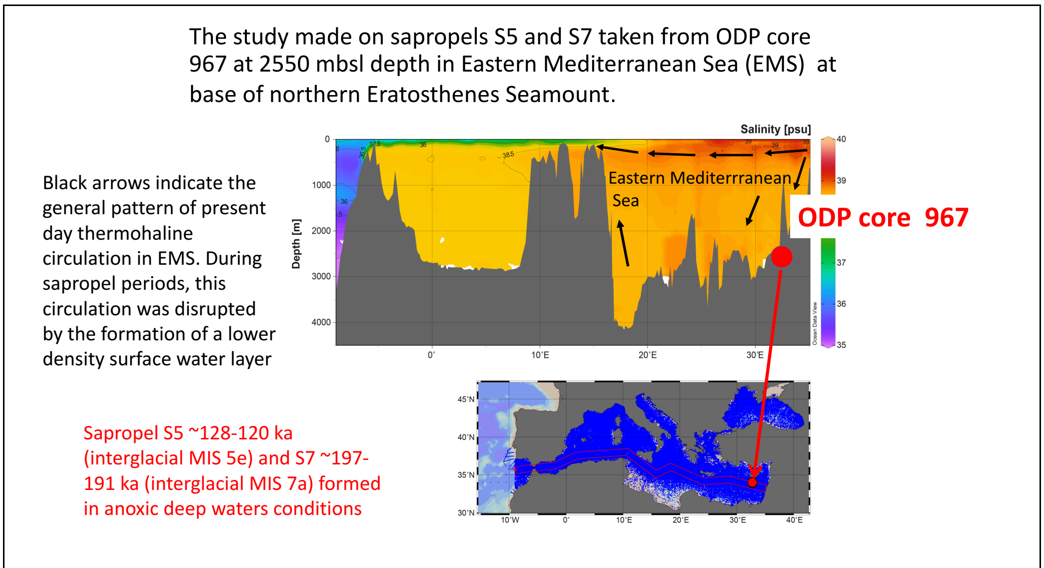

Figure 1. Oceanographic setting of the S5 and S7 sapropels studied in this work. Images generated by Ocean Data View (https://odv.awi.de).

Both sapropels show an inverse correlation between $\delta^{56}Fe$ and Fe_T/Al, (Fe_T = total Fe) 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 EMS bottom waters (Fig. 2). 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 trend (main grey arrow in Fig. 2) changes in slope to more positive $\delta^{56}Fe$ values (small grey arrow in Fig. 2).

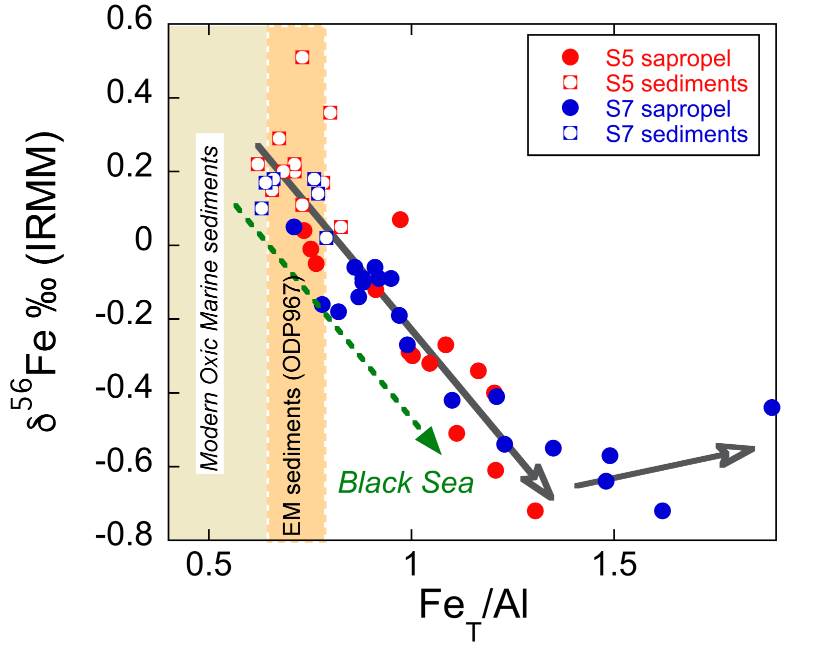

Figure 2. Benthic Iron shuttle plot after Severmann et al (2008) showing inverse trend of δ^{56}Fe vs. Fe_T/Al for Sapropels S5 and S7. The source data for this diagram and its full discussion are given in Benkovitz et al. (2020).

Fe speciation chemical studies described by Benkovitz et al. (2020) show that the dominant highly reactive Fe (Fe_{HR}) phase in the sapropels is pyrite (Fe_{py}), with Fe (oxyhydr)oxides forming the second major mineral phase. However, although Fe isotopes (Fig. 2) and high Mo concentrations in the sapropels point to euxinic water conditions, their Fe_{py}/Fe_{HR} ratios are below values generally accepted to identify water column euxinia. This apparent contradiction is attributed to the sedimentary preservation of a high River Nile input of crystalline Fe (oxyhydr)oxide minerals into the EMS basin, which resulted in a relatively low degree of sulphidation, despite the presence of sulphidic bottom waters. Thus, the operationally defined ferruginous/euxinic boundary for EMS sapropels is better placed at $Fe_{py}/Fe_{HR} = 0.6$, which is somewhat below the usually ascribed lower limit of 0.7 (Poulton and Canfield, 2011). The marked change in the δ^{56}Fe - Fe_T/Al slope during peak S7 (Fig. 2) is attributed to an enhanced monsoon-driven flux of detrital Fe(III) oxides from the River Nile into the EMS basin. Overall, the euxinic water column conditions defined sapropels S5 and S7 are inferred to reflect the positive balance between the rates of dissolved sulphide formation and the rates of reductive dissolution of Fe (oxyhydr)oxides.

Modeling of sulphide formation in an euxinic water column by Helz and Vorlicek (2019) shows that the sulphate to sulphide reduction progress increases with water depth, and positively depends on organic productivity, but is an inverse function of water column overturn rate (τ). U-Mo isotope studies on sapropel S5 show an up to ten-fold decline in deep EMS overturning circulation during MIS5e ($\tau = 1030^{+920}/_{-520}$ yr; Andersen et al, 2018). The similar slopes of the benthic shuttle plots (main trend in Fig. 2) and similar Fe speciation characteristics also suggest comparable euxinic conditions in the EMS during S5 and S7. Thus, it can be argued that both water column overturn slowdown and increased export organic productivity drove the formation of euxinic waters during S5 and S7.

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