

## Eastern Mediterranean sapropel formation and preservation; Diagenesis versus palaeoceanography

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Organic-rich intervals (sapropels) occur in eastern Mediterranean sediments at an astronomically determined cyclicity, related to relatively humid climatic periods. The intervening, arid periods are characterized by organic-lean sediments, and the deposition of rather high dust fluxes indicated by Ti/Al. The last of such 'humid periods' occurred from 10.4 to 5.7 kyr ago, simultaneous with the sustained wet period in the circum Mediterranean area. At the end of this humid period, the rapid increase in aridity (indicated by Ti/Al) coincides with a peak of high Mn-oxide content. This peak in all 30 studied cores occurs in response to a relatively abrupt re-ventilation event, and is confirmed by several other proxies. From the comparison of organic C and Ba/Al it is clear, that in the sediments of all cores, the upper part of the youngest sapropel, S1, has been removed. Following the ventilation event, at 5.7 kyr, oxygen has continued to progressively move downward into the sediment oxidizing e.g. organic C. In line with these observations, microfossil assemblages indicate environmental changes occurring at the lower- and upper S1 boundary of the initial S1 sapropel. From the organic geochemical data it becomes clear that although siliceous microfossils have entirely disappeared even from the unoxidized S1-interval, their 'signature' is still there (e.g. diatoms, represented by loliolide. Other marine biomarkers are dinosterol (*dinoflagelates*), and U<sup>K</sup><sub>37</sub> (*E. huxleyi*), whereas B-sitosterol is considered to be a terrestrial biomarker. Clearly, it is in particular the marine biomarkers that are enriched in the remaining organic-rich S1 interval, whereas these are completely removed upon oxidation. The occurrence of such a removal mechanism seriously affects the traditional interpretation based on palaeoproxies, and, therefore, is of vital importance for the interpretation of proxies and our understanding of palaeo conditions. Using all of these proxies, permit a more reliable reconstruction of initial sediment composition, hence of initial palaeo-oceanographic conditions.

## Interpreting the Ca isotope record from marine biogenic carbonates

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It has been proposed that shifts in the concentration of Ca<sup>2+</sup> in seawater can be reconstructed from the calcium isotopic composition ( $\delta^{44/42}\text{Ca}$ ) of sedimentary calcium carbonate, giving information on past weathering fluxes of Ca<sup>2+</sup> to the oceans and atmospheric concentrations of CO<sub>2</sub>. The 18 million year record presented here of the  $\delta^{44/42}\text{Ca}$  of planktonic foraminiferans from ODP site 925, in the Atlantic, on the Ceara Rise, provides an opportunity to critically analyze Ca isotope based reconstructions of the Ca cycle.

$\delta^{44/42}\text{Ca}$  in this record averages  $+0.37 \pm 0.05$  and ranges from  $+0.21$  ‰ to  $+0.52$  ‰. This falls within error of previously published Neogene records based on foraminiferans, but is not similar to the record based on bulk carbonates which has values that are as much as 0.25 ‰ lower, especially further back in time. Fairly recent bulk carbonates and planktonic foraminiferans (i.e. from core tops), on the other hand, differ only by  $0.06 \pm 0.06$  ‰ (n=5). The cause of the greater difference in the isotopic composition of the two materials further back in time remains an open question.

Modeling the global Ca cycle from downcore variations in  $\delta^{44/42}\text{Ca}$  by assuming fixed values for the isotopic composition of weathering inputs ( $\delta^{44/42}\text{Ca}_w$ ) and for isotope fractionation associated with the production of carbonate sediments ( $\Delta_{\text{sed}}$ ), as has been commonly done in the past, results in unrealistically large variations in the mass of Ca<sup>2+</sup> in the ocean during the Neogene. This suggests that  $\delta^{44/42}\text{Ca}_w$  and  $\Delta_{\text{sed}}$  instead fluctuate over time. Indeed, variations of  $\pm 0.1$  ‰ in the isotopic composition of weathering inputs or in the degree of isotopic fractionation during the formation of calcareous sediments could entirely account for the observed variations in  $\delta^{44/42}\text{Ca}$ . Ca isotope fractionation during weathering processes, such as has been recently documented, could easily result in variations in  $\delta^{44/42}\text{Ca}_w$  of a few tenths of permil associated with climate change. Likewise the differing degree of isotope fractionation associated with aragonite versus calcite formation could drive shifts in  $\Delta_{\text{sed}}$  of several tenths of permil with shifts in the relative output of calcite and aragonite from the ocean. Until variations in  $\delta^{44/42}\text{Ca}_w$  and  $\Delta_{\text{sed}}$  over time are better constrained, modeling the mass of Ca<sup>2+</sup> in the oceans from Ca isotope curves should be approached cautiously.