

Palaeoceanographic and diagenetic aspects of sapropel formation in the eastern Mediterranean

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Distinct darkgreen organic-rich intervals (sapropels) occur in eastern Mediterranean sediments at an astronomically determined cyclicity. Their occurrence is related to relatively humid climatic periods, resulting in enhanced organic fluxes arriving at the seafloor, whereas the intervening, arid periods are characterized by the deposition of rather high dust fluxes. The 'humid period' occurred from 10.4 to 5.5 kyr simultaneous with the sustained wet period in the circum Mediterranean area and was followed by a rapid increase in aridity (Ti/Al) coinciding with a peak of high Mn-oxide content. This peak occurs in response to an abrupt re-ventilation event, and is confirmed by micropaleontological and organic geochemical proxies. Following the ventilation event, oxygen has continued to progressively move downward into the sediment oxidizing e.g. organic C. In addition, the dissolution of some species of aragonitic pteropods, corresponds to the interval of sapropel oxidation. From the organic geochemical data it is clear that although siliceous microfossils have entirely disappeared, their 'signature' is still there. Clearly, marine biomarkers are enriched in the remaining S1 interval, whereas these are completely removed upon oxidation. Proper recognition of initial versus secondary signals is therefore vital in the interpretation of sedimentary proxies.

Foraminiferal shell heterogeneity and selective diagenesis revealed: LA-ICP-OES as a powerful new tool

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Dissolution in undersaturated and recrystallisation in supersaturated burial conditions alter foraminiferal shell chemistry. We need to understand, recognize and quantify these diagenetic artefacts in order to utilize planktonic foraminifera as a valuable archive of paleoclimatic information.

Ultrastructural changes in foraminiferal shell morphology that accompany diagenesis were examined with the SEM, in samples representing a variety of burial conditions and ages (recent to Miocene). Geochemical changes resulting from *in situ* dissolution were investigated in detail in samples from core tops spanning a depth range across the lysocline and compared with those observed in laboratory dissolution experiments. It is shown that ultrastructural breakdown and the progressive removal of the microgranular, subrhombic and euhedral crystal layers is accompanied by the preferential removal of Mg-rich calcite phases. This progressive destruction of ultrastructural features biases bulk foraminiferal shell chemistry towards lower Mg/Ca and Sr/Ca values.

A newly developed LA-ICP-OES method is used to confirm the magnitude of shell Mg heterogeneity within single specimens. It also illustrates that foraminifera secrete calcite with a significantly higher Mg/Ca and Sr/Ca content than what we measure, i.e. that current cleaning methods induce a dissolution artefact. LA-ICP-OES provides a powerful new method with which to study geochemical heterogeneity within foraminiferal shells on the ultrastructural scale and a means of identifying diagenetic and contaminant phases.