

Geochemical evidence of the post-depositional oxidation of the most recent E. Mediterranean sapropel

J. Thomson
N.C. Higgs
T.R.S. Wilson
I.W. Croudace

Institute of Oceanographic Sciences, Deacon Laboratory, Brook Road, Wormley, Surrey GU8 5UB, UK.

Department of Geology, The University, Highfield, Southampton SO9 5NH, UK.

Sediments are defined as sapropels when their C_{org} content is $>2\%$, or as sapropelic sediments when C_{org} is $0.5\text{--}2\%$. These are high C_{org} values for sediments, particularly for deep-sea sediments. Nonetheless, many sapropels are found in cores from the Eastern Mediterranean basin, where they are prominent as dark-coloured units interbedded with the lighter-coloured sediments laid down in oxic conditions. These sapropel units usually, though not invariably, have sharp bottoms and tops. The colour transitions are usually taken to mark the beginning and end of sapropel-forming conditions, respectively, because most workers believe that sapropels form under an anoxic water column which prevents bioturbation by benthic organisms. De Lange and co-workers (De Lange *et al.* 1988; Pruyers *et al.* 1991,1993), however, have pointed out that the sharp upper surfaces now observed are likely to be the result of post-depositional oxidation which ensues when re-ventilated bottom waters can oxidise the upper reaches of an originally thicker sapropel unit. The thickness observed for a particular sapropel unit in a core will therefore be only some residual fraction of its original thickness. This is highly significant for sedimentological, micropalaeontological or stable isotopic investigations which seek to reconstruct the palaeoenvironmental conditions responsible for sapropel formation from the sediment record.

This presentation concerns an investigation of the most recent E. Mediterranean sapropel, S1, which should be the most amenable to detailed investigation of the oxidation process. One core studied contains a 'representative' 6 cm thickness of S1. Another two cores, however, were collected on the same interface multicorer deployment, and although collected simultaneously within 0.5 m of each other on the sea floor, one contains a 2 cm thick S1 unit while the other contains no evidence of S1. A preliminary account of the investigation of these three cores (Higgs *et al.* 1994) stresses the

importance of the interpretation of the concentration/depth profiles of the elements Mn and Fe (as ratios to Al). In the two cores which contain sapropels, the Mn concentration/depth profiles exhibit two peaks, with the lower peak immediately above the uppermost high C_{org} value in the sapropels, and the upper peak at 15 cm. Both cores have a peak in the Fe concentration/depth profiles which starts at 15 cm and is at a maximum immediately above the uppermost high C_{org} value of the sapropel unit. A progressive oxidation front process was modelled for these cores which operated for 5 ky following cessation of sapropel formation, during which time a further 15 cm of sediments were accumulated. In the model, C_{org} -rich sediment was oxidised and constant upwards Mn^{2+} and Fe^{2+} fluxes were precipitated by downwards-diffusing oxygen. This model replicated the observed shapes of the Fe and lower Mn peaks closely, and suggested the removal of 5-6 cm of sapropel C_{org} . On this explanation, the upper Mn peak represents the bottom water reventilation event at the end of sapropel formation, when the oxidation front was initiated. Such an amount of oxidation was also sufficient for complete oxidation of the sapropel inferred to have been present initially in the third core which now has similar Mn and Fe profile shapes to the other two cores but contains no evidence of any sapropel. Radiocarbon dating has subsequently demonstrated that the sediments hosting the upper Mn peak in this core is 1 ky younger than those of the other two cores, consistent with loss of 2 cm from the top of the sapropel in that core relative to its neighbour.

In many circumstances biogenic barite can be used as a palaeoproductivity indicator, and indeed Ba is normally found to be enriched in sapropels (Calvert, 1983). Barite can redissolve if it encounters strongly reducing conditions where sulphate levels fall markedly below sea water values, and van Os *et al.* (1991) have presented

convincing evidence that Ba diagenesis has occurred around older sapropel units. The Ba profiles observed in and above the S1 sapropel unit in this work, however, are quite unlike those for any other element analysed, although they are similar to those of other published S1 Ba profiles (Pruysers *et al.* 1991). This common S1 Ba profile shape is in the form of a Gaussian wave, with values increasing from low detrital values just below the sapropel and decreasing back to similar values at 15 cm. The highest values of the Gaussian wave are therefore found coincident with the present high C_{org} values of the remaining sapropel and in the zone immediately above where oxidation is inferred to have occurred. This high Ba in excess of detrital values is derived from barite particles 1–3 μm in size, and is not associated with Mn or Fe oxyhydroxides. The Gaussian-shaped Ba profiles are interpreted as the best proxy indicators now available of the C_{org} profiles in the original S1 sapropel, and can be used to estimate the thicknesses of the original units before oxidation. For the three cores with present S1 thicknesses of 0, 2 and 6 cm, the Ba profiles suggest original S1 lengths of 5.5, 7.8 and 10.8 cm, respectively, while alternative estimates based on the distances between the upper Mn peak and the base (or inferred base) of the sapropels are 6, 8.5 and 11 cm.

Modern sapropels are often seen as good analogues for black shales, on the basis that both are enriched in C_{org} , S and many associated trace elements. A surprising finding from the compositional data of the S1 units studied is that the maximum concentrations of most trace elements are not now found in the residual sapropels at all, but rather have been relocated

by diagenesis so that they are now located above or below the remaining C_{org} -rich unit. The elements I and Se exhibit very large and sharp peak values immediately above and below the inferred limit of oxygen penetration, respectively, in both cores with sapropels, and the presence of both peaks is proposed as a good indicator of an active oxidation front (Higgs *et al.* 1994). Above S1 many elements are associated with Fe oxyhydroxide (As, P and V) or Mn oxyhydroxide (Co, Ni, Cu, and Mo), while several elements (Cd, Mo, Sb, V and U) have high or peak values below the sapropel at different depths.

Acknowledgements

We gratefully acknowledge access to the facilities of the NERC ICP-MS Unit and Radiocarbon Laboratory (allocation 522/0193). This work was supported by the European Union Marine Science and Technology programme, contract numbers 900022C and MAS2-CT93-0051.

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