

Sulphur isotope partitioning during formation of pyrite and incorporation of sulphur into organic matter in eastern Mediterranean sapropels

H. F. Passier

Paleomagnetic Laboratory, Utrecht University, NL-3584 CD
Utrecht, The Netherlands

M. E. Böttcher

Department of Biogeochemistry, Max-Planck-Institute for Marine
Microbiology, D-28359 Bremen, Germany

G. J. de Lange

Institute of Paleoenvironments and Paleoclimate, Utrecht
University, NL-3508 Utrecht, The Netherlands

The Neogene sedimentary record of the eastern Mediterranean is characterized by the occurrence of organic-rich layers. The formation of these 'sapropels' is thought to have been initiated by palaeoclimatic-related increased productivity in the surface waters and/or enhanced preservation of organic matter (OM) due to oxygen-depletion in stagnant bottomwaters. The sapropels contain high contents of inorganic reduced sulphur species (mainly pyrite) derived from the microbial dissimilatory sulphate reduction (Passier *et al.*, 1998). Under conditions of high abundant dissolved reduced or intermediate sulphur species, OM can be sulphidized leading to a reduction of the lability and thus an enhancement of the overall preservation of OM (e.g. Sinninghe Damsté and de Leeuw, 1990). Here, we present the contents and sulphur isotopic signatures of pyrite and sulphur in OM. A model for organic sulphur formation and the timing with respect to pyrite formation is proposed.

Methods

Three sapropels were investigated: S1 (boxcore UM26), ODP-Leg 160-967C and 160-969E. The ages of the sapropels are 5 to 9 kyr, 1.808 Ma, and 2.943 Ma, respectively (Passier *et al.*, 1998). The Cr(II) reduction method was used to extract the pyrite fraction from the sediments and the total organic sulphur content was measured on the residue by combustion isotope ratio monitoring mass spectrometry (C-irmMS; Böttcher *et al.*, 1998). Humic substances were isolated from the OM by the extraction with 0.1 M NaOH/0.1 M Na₂P₂O₇, and the humic and fulvic acid fractions were further separated by the acidification with HCl. Sulphur isotope ratios (³⁴S/³²S) were analysed on the

fractions by C-irmMS (Böttcher *et al.*, 1998) and are given relative to the V-CDT standard.

Results and discussion

The predominant sulphur compound in the sapropels is pyrite which formed from the reaction of Fe with sulphide. Within the sapropels, pyrite mainly occurs as framboids, but below the sapropels, pyrite is mostly present as euhedral crystals (Passier *et al.*, 1998). The pyrites have an extremely light sulphur isotopic signature between -33.1 and -49.6‰ (FIG.1; Passier *et al.*, 1998). This implies that fractionations of at least 54 to 70‰ occurred relative to present Mediterranean seawater sulphate (+20.6‰). This observed high sulphur isotope fractionation indicates that sulphate reduction took place in an open system (with respect to sulphate), where exchange with seawater readily occurred, so that sulphate supply via diffusion or advection was large relative to the sulphate reduction rates. However, it can not be related to microbial sulphate reduction alone, but indicates that reoxidation of hydrogen sulphide with further disproportionation reactions of intermediate sulphur species (elemental sulphur, thiosulphate), which have been found to further increase the fractionation between hydrogen sulphide and sulphate (Canfield and Thamdrup, 1994; Smock *et al.*, 1997), took place in an environment with abundant dissolved hydrogen sulphide.

Pyrite formation within the organic-rich layers has been Fe-limited during sapropel deposition, and organic material competed with reactive Fe for reduced sulphur species. Marine OM contains assimilated sulphur, present in labile fractions of organic tissues with an isotopic composition slightly below seawater sulphate. The isotopic composition of

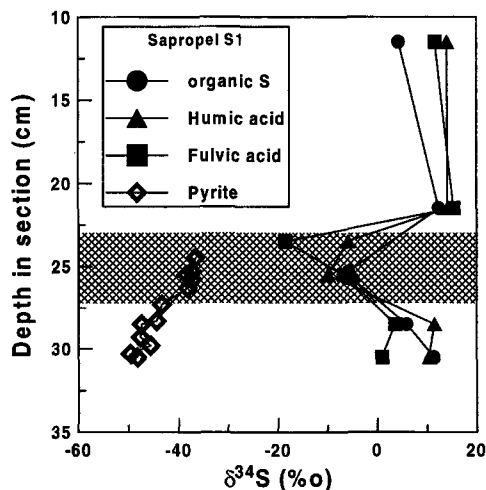


FIG. 1. Downcore variation of the sulphur isotopic compositions of pyrite, humic and fulvic acids and the total organic sulphur. Shaded area: sapropel with maximal 2.3% dwt. TOC.

the humic and fulvic acid fractions as well as the total organic sulphur above the sapropels are only slightly depleted in ^{34}S compared to biosynthetic sulphur (FIG.1), indicating only minor diagenetic addition of sulphur. In the sapropels (FIG.1 and 2), however, the organic sulphur contents are enriched and the sulphur isotope signals are significantly shifted to lighter values (S1: down to -7‰ ; 967: down to -26‰ ; 969: down to -30‰), indicating the addition of diagenetic sulphur to the organic material. In the sediment, the uptake of diagenetic sulphur into organic matter is assumed to take place via reactions of sulphide and/or polysulphides with reactive sites on organic molecules (e.g. Sinninghe Damsté and de Leeuw, 1990). Our data indicate that sulphur incorporation into OM was most effective during the highest sedimentation of organic matter and probably severest Fe limitation. Based on a binary isotope mixing model using biosynthetic and diagenetic organic sulphur as the end-members it is calculated that in the sapropels the diagenetic sulphur

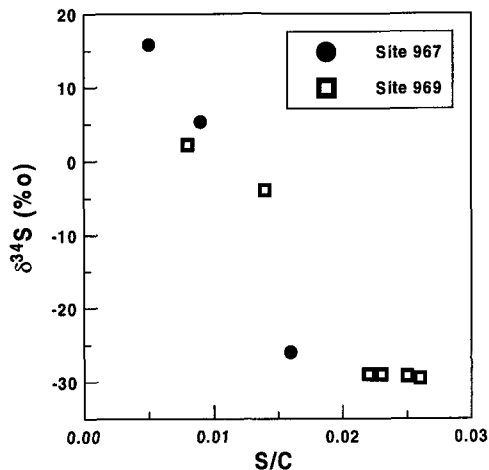


FIG. 2. Isotopic composition of organic sulphur versus organic S/C ratio.

contributes by 40% (S1), 72% (967) and 78% (969) to the total organic sulphur. This fraction is decreased in the non-sapropel sediments to 19% (S1), 13% (967) and 32% (969).

This study was supported by the Netherlands Organisation for Scientific Research (NWO/GOA, #750.00.620-7290), Mast-2 Palaeoflux (#MAS2-CT93-0051), Mast-3 SAP (#MAS3-CT97-1122), the Italian Consiglio Nazionale della Ricerche and the German ODP-SPP (DFG).

References

- Böttcher, M.E., Brumsack, H.-J. and de Lange, G.J. (1998) *ODP Sci. Res.*, **160**, (in press.)
- Canfield, D.E. and Thamdrup, B. (1994) *Science*, **266**, 19–75.
- Sinninghe Damsté, J.S. and de Leeuw, J.W. (1990) *Org. Geochem.*, **16**, 1077–101.
- Passier, H.F., Middelburg, J.J., de Lange, G.J. and Böttcher, M.E. (1998) *Mar. Geol.*, in press.
- Smock, A.M., Böttcher, M.E. and Cypionka, H. (1997) *Biospectrum*, **3**, 112.