ORGANIC GEOCHEMISTRY OF PLIOCENE SAPROPELS FROM ODP SITES 964 AND 967, EASTERN MEDITERRANEAN BASIN

S.C. George[1], H. Xu[1,2], S.C. Löhr[1], M.J. Kennedy[1]

[1]Macquarie University, Sydney, New South Wales, Australia. [2]China University of Geosciences (Beijing), China.

Sapropels are fine-grained, organic carbon-rich sediments that are cyclically interbedded with organic-lean marls. They are a conspicuous feature of the sedimentary record of the Mediterranean Basin) and have been extensively studied to assess the relative importance of climatic, oceanographic as well as continental influences on the formation of organic-rich mudstones (Rohling *et al.*, 2015). Deposition of Pliocene sapropels under periodically anoxic to sulphidic conditions is demonstrated by preserved sediment lamination, the absence of benthic fauna and/or the dominance of low-oxygen adapted species (Löhr and Kennedy, 2015), abundant framboidal pyrite, and the presence of isorenieretane or its derivatives (Passier *et al.*, 1999), biomarkers characteristic of anoxygenic photosynthetic green sulphur bacteria.

Here we examine the organic geochemistry of three sapropels: 284A from 80.2 m in ODP Site 964, and 280C and 284C from 79.5 m and 80.4 m in ODP Site 967. Four microfacies (MF) are distinguished on the basis of bulk composition, microfabric, organic matter distribution and morphology, and the degree of biological reworking. A key motivation for the organic geochemical analyses was to test the relative magnitude of diatom input to the various microfacies. Sapropel 284C has a TOC of 8-10%, and is composed of MF1, with a high bulk carbonate content (>40%) and a uniform to weakly laminated microfabric. The bulk of the organic carbon is present as organoclay aggregates. Sapropel 284A has a TOC of 11%, and is composed of MF3, with a low carbonate content uniform and a weakly laminated microfabric. Sapropel 280C has a TOC of 8-15% and is composed of MF2, with a low carbonate content and a strongly laminated microfabric, and its reworked equivalent MF4A. MF2 consists of discrete organic and inorganic mineral laminae, suggestive of episodic mass-sedimentation of phytoplankton mats, which is common for diatoms that are prone to mass-sedimentation. Based on an analogy with Quaternary Mediterranean sapropels (Kemp *et al.*, 1999), in which laminated and carbonate-poor samples are diatom-rich, we predicted that sapropels 284A and 280C would contain more diatom biomarkers relative to the carbonate-rich sapropel 284C.

Highly branched isoprenoids (HBIs) are widely used biomarkers for rhizosolenid diatom input. Saturated C_{25} HBI and small amounts of C_{25} HBI dienes and trienes are present in sapropel 284C, but not in the other two sapropels that we hypothesised to be dominated by mat-forming diatoms (MF2 and 3) (Fig. 1). Additionally, a series of unknown compounds that may be related to the HBIs were detected only in sapropel 284C. These results show that, in addition to the calcareous plankton input evident from SEM and geochemical analyses, diatoms contributed to MF1. There are several possible explanations for the absence of diatom biomarkers in the other sapropels. Only five out of > 200 diatom genera are known to produce HBIs (*Haslea, Pleurosigma, Rhizosolenia*, *Navicula*, *Berkleya*), and not all species within these genera produce these characteristic lipids (Brown *et al.*, 2014). Many hundreds of species of diatoms have not had their lipid geochemistry determined, so possibly a diatom species that does not produce HBIs may have contributed to these sapropels. Another possibility is that the precursor C_{25} HBI alkenes were quantitatively sulphurised during early diagenesis, and are thus present but unanalysed in the polar fraction. This possibility was tested by Raney nickel

desulphurisation of the polar fractions. This resulted in a large unresolved complex mixture for all three samples, but no HBIs. However, the de-sulphurised polars of the three sapropels do contain 2α-methylhopanes, which are indicative of a pelagic cyanobacteria contribution to the sapropels. Significant organic matter input by colonial, pelagic cyanobacteria (e.g. *Trichodesmium*) is also supported by the distinct lamination in MF2, light $\delta^{15}N$ values and rather heavy $\delta^{13}C_{org}$ values.

Acknowledgements

We thank IODP ANZIC for special post-cruise analytical funding. Huiyuan Xu was the recipient of PhD scholarship from Macquarie University and China Scholarship Council.

References

Brown, T.A., Belt, S.T., Cabedo-Sanz, P., 2014. Identification of a novel di-unsaturated C_{25} highly branched isoprenoid in the marine tube-dwelling diatom *Berkeleya rutilans*. *Env. Chem. Lett.* **12**, 455–460.

Kemp, A.E.S., Pearce, R.B., Koizumi, I., Pike, J. and Rance, S.J., 1999. The role of mat-forming diatoms in the formation of Mediterranean sapropels. *Nature* **398**, 57–61.

Löhr, S.C., Kennedy, M.J., 2015. Micro-trace fossils reveal pervasive reworking of Pliocene sapropels by low-oxygen-adapted benthic meiofauna. *Nature Comms.* **6**, 1–8.

Passier, H.F., Bosch, H.J., Nijenhuis, I.A., Lourens, L.J., Böttcher, M.E., Leenders, A., *et al.*, 1999. Sulphidic Mediterranean surface waters during Pliocene sapropel formation. *Nature* **397**, 146–149.

Rohling, E.J., Marino, G., Grant, K.M., 2015. Mediterranean climate and oceanography, and the periodic development of anoxic events (sapropels). *Earth-Sci Rev.* **143(C)**, 62–97.

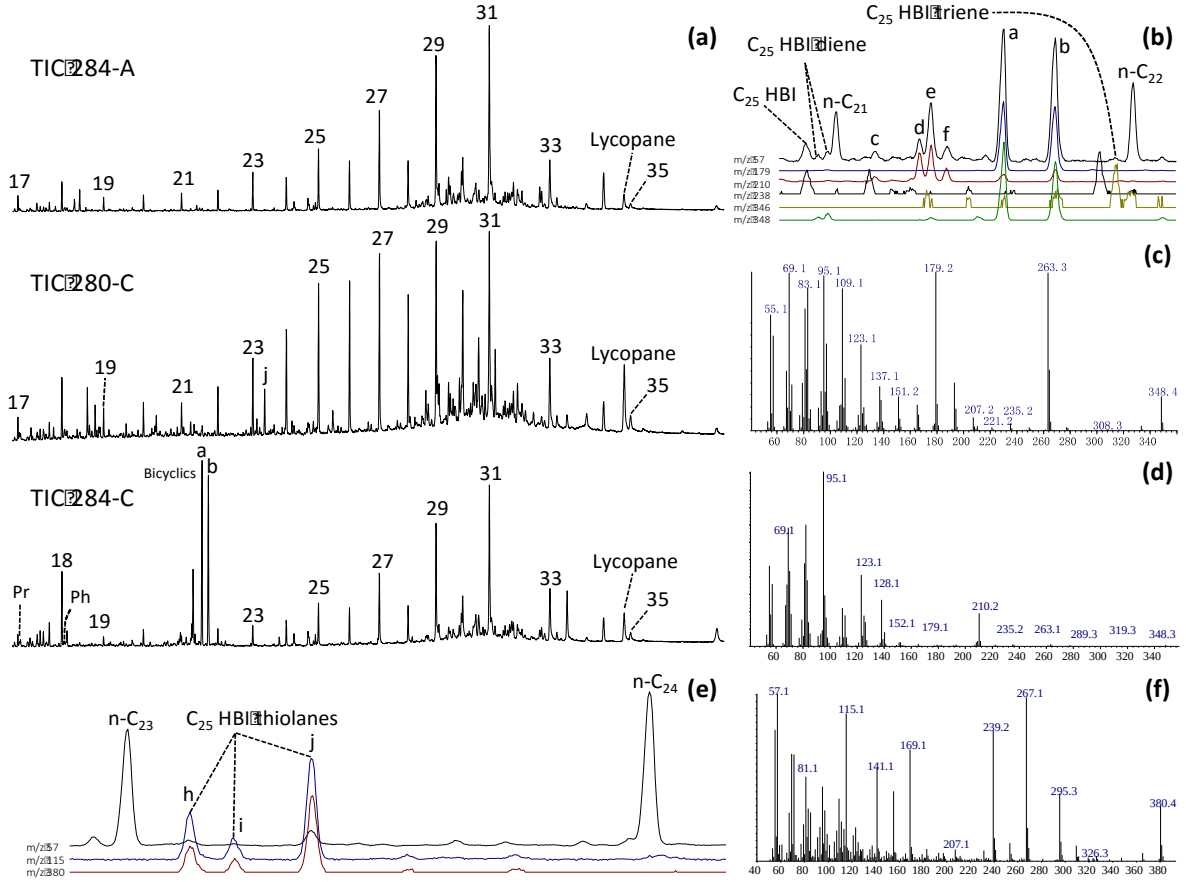

Figure 1 *(a) Total ion chromatograms of the aliphatic fractions of sapropels 284A, 280C, and 284C. (b) Partial mass chromatograms (m/z 57, 179, 210, 238, 346, 348) of sapropel 284C, showing the distribution of C_{25} HBI, C_{25} HBI-dienes, C_{25} HBI-triene and C_{25} HBI bicyclic compounds a and b relative to n-alkanes. (c) Mass spectra of compound a. (d) Mass spectra of compound d. (e) Partial mass chromatograms (m/z 57, 115, 380) of 280-C showing the distribution of C_{25} HBI thiolanes relative to n-alkanes. (f) Mass spectra of thiolane peak j.*