

NEW PROXIES FOR PALEOSALINITY BASED ON STABLE HYDROGEN ISOTOPIC COMPOSITION OF ALGAL BIOMARKERS

Marcel van der MEER¹, Marianne BAAS¹, Irene RIJPS¹, Gianluca MARINO², Eelco ROHLING³, Jaap SINNINGHE DAMSTÉ¹ and Stefan SCHOUTEN¹

1. Royal Netherlands Institute for Sea Research, Marine Biogeochemistry and Toxicology, P.O. box 59,1790 AB Den Burg (Texel), The Netherlands
2. Department of Earth Sciences - Geochemistry, Faculty of Geosciences, Utrecht University, P.O. Box 80.021, 3508 TA Utrecht, The Netherlands
3. School of Ocean and Earth Science, Southampton University, National Oceanography Centre, Southampton SO14 3ZH, United Kingdom

Testing climate models for future climate change critically depend on our ability to quantitatively reconstruct past climate. Paleosalinity is the single most important oceanographic parameter which currently can still not be accurately quantified from sedimentary records. To date, the most promising tool to estimate paleosalinity variations combines reconstructions of paleotemperature and foraminiferal $\delta^{18}\text{O}$. Foraminiferal $\delta^{18}\text{O}$ varies as a function of temperature and ambient seawater $\delta^{18}\text{O}$ which is directly coupled to seawater salinity. The close relation between the stable hydrogen isotope ^2H (deuterium, D) and $\delta^{18}\text{O}$ in precipitation and seawater (so-called meteoric water line) enables an alternative approach to deconvolve palaeosalinity. Deuterium is incorporated into marine organic matter during photosynthesis and can be extracted from seafloor sediments (e.g. Krishnamurthy et al., 2000). Thus, δD analyses on marine organic matter could provide an alternative proxy for seawater palaeosalinity. Recently, we found a strong correlation between salinity and the hydrogen isotopic fractionation of C_{37} alkenones versus water in cultures of *Emiliana huxleyi* and *Gephyrocapsa oceanica*, although growth rate also had some impact (Schouten et al., 2006). This suggest that δD of alkenones can be used to reconstruct past salinities if growth rate and δD_{water} can be constrained.

We applied this newly developed proxy in a core covering the last 3000 yrs of the Black Sea. Approximately 2700 yrs ago *E. huxleyi* invaded the Black Sea, illustrated by the deposition of a coccolith ooze from this time on. Because *E. huxleyi* has never been observed at salinities below 11 practical salinity units (PSU), a salinity increase to above 11 PSU has been suggested for that time period (Hay, 1988). Our results show that the δD values of alkenones gradually decreased over the last 3000 yrs suggesting a decrease in salinity and, therefore, a higher than present day salinity 2700 yrs ago. This makes it likely that the invasion of the Black Sea by *E. huxleyi* is not caused by an increase in salinity. We also analyzed the hydrogen isotopic composition of C_{37} alkenones in the S5 sapropel from an Aegean Sea core. Sapropels are thought to be formed after a massive freshwater flooding of

the Eastern Mediterranean from the African continent. Our results show that simultaneous with sapropel deposition and prior to the development of photic zone euxinia there was a large decrease in salinity of up to 6 PSU (Fig.1), in good agreement with modeling results. These results show that δD of alkenones is a promising new tool for reconstructing past salinities and another tool for reconstructing paleo-environments using alkenones in addition to the widely applied U^{K}_{37} palaeothermometer.

We are currently examining the hydrogen isotopic fractionation patterns of other algae known to produce specific biomarkers, i.e. long-chain diols from *Proboscia* diatoms and dinosterol from dinoflagellates. The results will reveal if, besides alkenones, other algal biomarkers can also be used to trace past fluctuations in salinity.

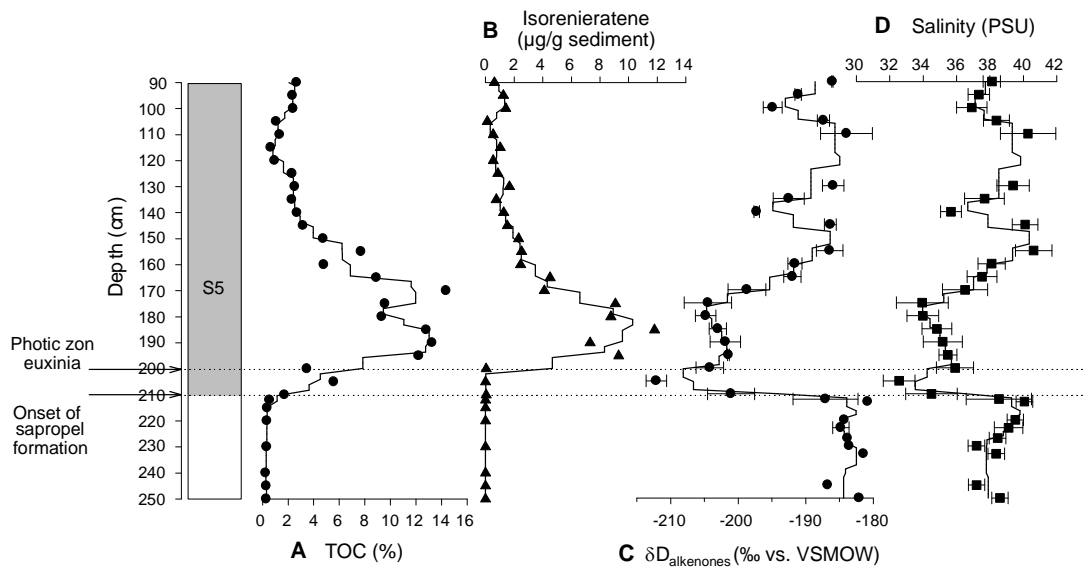


Figure 1. Stratigraphic record of sapropel S5 of (A) TOC in %, (B) isorenieratene in $\mu\text{g/g}$ sediment, (C) $\delta D_{\text{alkenones}}$ in ‰ vs. VSMOW and (D) estimated salinities in PSU.

REFERENCES

- Hay, B.J. (1988) Sediment accumulation in the central western Black Sea over the past 5100 years. *Paleoceanography* **3** 491-508.
- Krishnamurthy, R.V., Meyers, P.A. and Lovan, N.A. (2000) Isotopic evidence of sea-surface freshening, enhanced productivity, and improved organic matter preservation during sapropel deposition in the Tyrrhenian Sea. *Geology* **28** 263-266.
- Schouten, S., Ossebaar, J., Schreiber, K., Kienhuis, M.V.M., Langer, G., Benthien, A. and Bijma, J. (2006) The effect of temperature, salinity and growth rate on the stable hydrogen isotopic composition of long chain alkenones produced by *Emiliania huxleyi* and *Gephyrocapsa oceanica*. *Biogeosciences* **3** 113-119.

NOVEL "ISOHOPANES" AND THEIR USE AS SOURCE MARKERS

Hans Peter NYTOFT

Geological Survey of Denmark and Greenland (GEUS)

Several early eluting hopanes having 33 or more carbon atoms have been detected in coal extracts. Their mass spectra are virtually indistinguishable from those of isomeric regular $17\alpha,21\beta$ -hopanes. 17α -diahopanes which also elute earlier than the regular hopanes have slightly different mass spectra. Furthermore, these compounds are abundant in low maturity coals almost devoid of C_{29} - C_{32} diahopanes. Such hopanes were previously observed in coals (Monthieux and Landais, 1989), but they were not identified.

The mass spectral data suggest a non-rearranged structure and their short retention times indicate a multiple branched side chain. A number of such hopanes were synthesized from isoadiantone, and it was shown that the major unidentified C_{33} - C_{35} compounds coeluted with synthetic hopanes (22S + 22R) having a terminal methyl branch in the side chain (31-methyl-bishomohopanes, 32-methyl-trishomohopanes and 33-methyl-tetrakishomohopanes). Such hopanes could be named "isohopanes". Two minor C_{34} hopanes were tentatively identified as 31-methyl-trishomohopanes and it could be shown that C_{33} - C_{35} 29-methylhopanes are absent in geological samples. In addition to 33-methyl-tetrakishomohopanes, several minor, early eluting C_{35} hopanes were detected (482 → 191) but none of these were identified due to the lack of standards. C_{33} isohopanes isomerize slightly slower at C-22 than regular C_{33} hopanes. The equilibrium 22S/(22S + 22R) ratio for isohopanes is around 0.60.

Like regular hopanes, the the isohopanes extend beyond C_{35} . In addition, hexacyclic hopanes having 35 or more carbon atoms have been noted (480 → 191, 494 → 191 etc.). Their mass spectra (from HPLC-purified fractions) show that the extra ring is not fused to the rest of the hopane skeleton. The hexacyclic C_{35} hopanes were tentatively identified as 29-cyclopentylhopanes. Hopanoids having a multiple branched or cyclic side-chain are probably formed from hopanoids bonded to the kerogen matrix by carbon-carbon bonds.

The ratio between C_{33} and C_{34} isohopanes and regular hopanes with the same number of carbon atoms (isohopane ratios) has been measured for a large number of crude oils, source rocks and coals from all parts of the world (immature samples with $\beta\beta$ -hopanes were not included). The C_{33} and C_{34} isohopane ratios of marine crude oils and source rocks are low (0.02-0.09, 0.10-0.22), higher in lacustrine oils (0.07-0.11, 0.19-0.36) and especially high in

most coals (0.04-0.83, 0.19-1.71). Because coals generally have high isohopane ratios, this should also be the case for oils from coaly sources. North Sea crude oils generated from Middle Jurassic coals (Petersen et al., 2000) have higher isohopane ratios than marine oils and source rocks from the same area. An oil from a coaly source (Taranaki, NZ) had the highest isohopane ratios (0.31 and 0.39) of all the oils investigated so far. These observations suggest, that the isohopanes could be useful as source markers and petroleum correlation tools.

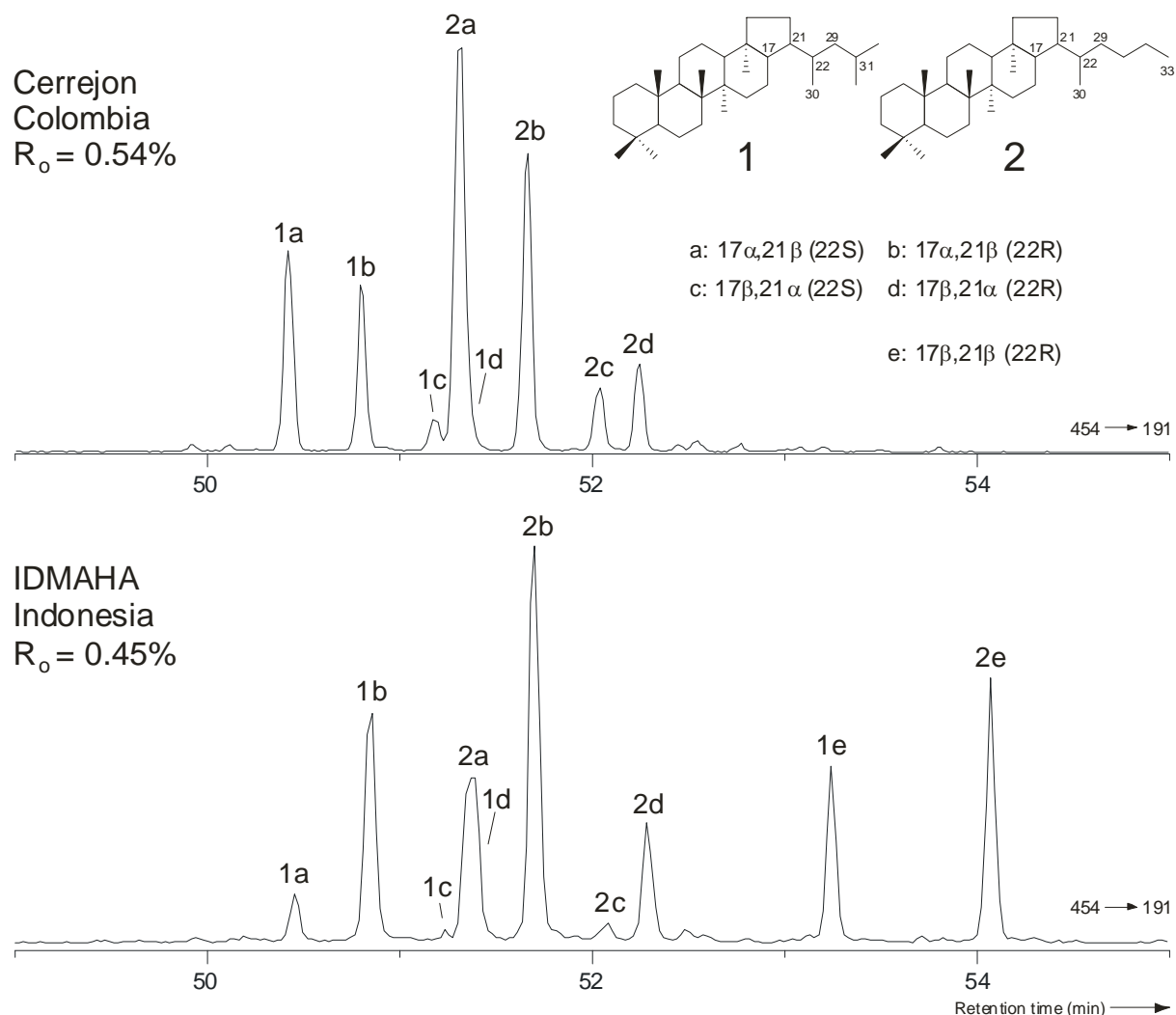


Figure 1. 454 → 191 transition showing C_{33} hopanes in two low rank coals. Note that 31-methyl-bishomohopanes (C_{33} isohopanes) and regular C_{33} hopanes have a similar distribution of stereoisomers. C_{33} isohopane ratio: $(1a + 1b)/(2a + 2b)$. The peak area of 2a is corrected for coeluting 1d assuming identical 1c/1d and 2c/2d ratios.

REFERENCES

- Monthioux, M., Landais, P. (1989) Natural and artificial maturation of coal: Hopanoid stereochemistry. *Chemical Geology*, **75**, 209-226.
- Petersen, H.I., Andsbjerg, J., Bojesen-Koefoed, J.A., Nytoft, H.P., 2000. Coal-generated oil: source rock evaluation and petroleum geochemistry of the Lulita oilfield, Danish North Sea. *Journal of Petroleum Geology* **23**, 55-90.

TREIBS' SCHEME RE-EVALUATED WITH NITROGEN AND CARBON ISOTOPIC COMPOSITIONS OF SEDIMENTARY PORPHYRINS

N. OHKOUCHI¹, Y. KASHIYAMA^{1,2}, Y. CHIKARAISHI¹, N.O. OGAWA¹ and H. KITAZATO¹

1. Institute for Research on Earth Evolution, Japan Agency for Marine-Earth Science and Technology.

2. Department of Earth and Planetary Science, University of Tokyo.

Metallo-alkyl-porphyrins, tetrapyrrole structures of chloropigments and hemes are long preserved in the sediments and sedimentary rock. Over 70 years ago, Alfred Treibs observed deoxyphylloerythroetioporphyrin (DPEP) and related compounds in petroleum, oil shales, and coals and proposed the sedimentary porphyrins to be derived from chlorophylls or hemes. It is still one of the logical grounds that the petroleum originates from maturation of sedimentary organic matter rather than produced through inorganic processes. Treibs also proposed a transformation pathway for the conversion of chlorophyll to DPEP with a series of biological and chemical reactions. Later, based on the distribution of various chlorin/porphyrin species in the sediments and their carbon isotopic composition, several studies confirmed the Treibs' scheme with some modification (Baker and Louda, 1986; Keely et al., 1990; Hayes et al., 1990; Callot and Ocampo, 2000).

We have recently developed a method for isolating/purifying the sedimentary porphyrins for determining both nitrogen and carbon isotopic compositions of these porphyrins (Kashiyama et al., 2007). We applied the method and determined both carbon and nitrogen isotopic compositions of various porphyrins from Cretaceous black shales deposited in the west Tethys associated with Oceanic Anoxic Events and Miocene black shales distributed in north Japan. These isotopic compositions exhibited unexpectedly wide range of distribution. For example, in the Miocene black shales, both carbon and nitrogen isotopic compositions of C₃₂ DPEP are substantially different between nickel- and vanadyl-chelated C₃₂ DPEPs (Fig. 1a and 1b, respectively). Furthermore, in the Cretaceous black shales, the isotopic compositions of C₃₂ DPEP are also substantially different between nickel- and copper-chelated C₃₂ DPEPs. Together with the distinct distribution of chemical species among Ni(II), V=O(II), and Cu(II) porphyrins in these sediments, the metal insertion process may occur in the early stage (rather than the latest stage) of the transformation pathway (Ohkouchi et al., 2005) at least some portion of the porphyrins, which discriminates the source chloropigments.

In the Cretaceous black shales, we observed abundant Ni C₃₂ etioporphyrin (Fig. 1c) that is substantially enriched in ¹⁵N relative to other porphyrins including Ni C₃₂ DPEP. It

suggests that the C₃₂ etioporphyrin to be derived mainly from hemes rather than chloropigments. In the presentation, we will further discuss the source and transformation pathways of chlorophylls to porphyrins based on dual isotopic compositions.

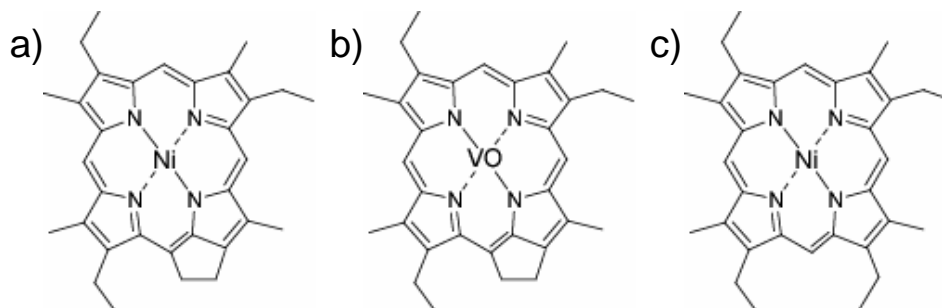


Figure 1. Chemical structures of a) Ni and b) VO-chelated C₃₂ DPEPs and c) Ni C₃₂ etioporphyrin

REFERENCES

- Baker, E. W., Louda, J. W., 1986. Porphyrins in the geological record. In Johns, R. B. (Ed.) *Biological Markers in the Sedimentary Record*. Elsevier, Oxford. pp. 125-225.
- Callot, H. J., Ocampo, R., 2000. Geochemistry of porphyrins. In Kadish, K. M., Smith, K. M., Guilard, R. (Eds.) *The Porphyrin Handbook: Volume 1*. Academic Press, Burlington. pp.349-398.
- Hayes, J. M., Freeman, K. H., Popp, B. N., Hoham, C. H., 1990. Compound-specific isotopic analyses: A novel tool for reconstruction of ancient biogeochemical processes. *Organic Geochemistry*, 16, 1115-1128.
- Kashiyama, Y., Kitazato, H., Ohkouchi, N., 2007. An improved method for isolation and purification of sedimentary porphyrins by high-performance liquid chromatography for compound-specific isotopic analysis. *Journal of Chromatography A*, 1138, 73-83.
- Keely, B. J., Prowse, W. G., Maxwell, J. R., 1990. The Treibs hypothesis: An evaluation based on structural studies. *Energy & Fuels*, 4, 628-634.
- Ohkouchi, N., Nakajima, Y., Okada, H., Kitazato, H., 2005. Copper-chelated bacteriochlorophyll *e* homologues in sediment from an anoxic lake (Lake Abashiri, Japan). *Organic Geochemistry*, 36, 1576-1580.