

HIGH ABUNDANCE OF XANTHONES AND DIBENZOFURANS IN A LATE PERMIAN SEDIMENT

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The Tesero Oolite Horizon is thought to have been deposited almost synchronously throughout the southern Alps. In northern Italy, the Tesero Horizon is immediately underlain by a marl that may also show some synchronicity within the area and contains a dramatic shift in carbon isotope ratios that reflects the end Permian mass extinction. In the Vincentian Alps, the marl is thermally immature and contains abundant terrestrially-sourced oxygen containing aromatic compounds such as xanthenes, dibenzofurans and dibenzodioxine in the solvent extractable organic matter (EOM). Alkyl naphthalenes are also abundant with a C₄ alkyl naphthalene being the most abundant compound in the gas chromatogram. Other compounds identified include *n*-alkanes (C₁₃ to C₃₂), phenanthrene and alkylated homologues, fluoranthene and pyrene. The EOM is approximately 1.1 mg/g of sediment and approximate concentrations for selected compounds are 1,2,5,6/1,2,3,5-tetramethylnaphthalene 4000 µg/g EOM, xanthone 2400 µg/g EOM, dibenzofuran 1140 µg/g EOM and dibenzodioxine 410 µg/g EOM.

The naphthalenes display an immature distribution. The methylnaphthalenes (MN) are present in approximately equal amounts. Dimethylnaphthalenes (DMN) are dominated by the 1,6- and 1,2- isomers and the trimethylnaphthalenes (TMN) are dominated by the 1,2,6- and 1,2,5- isomers, the 1,2,7-DMN isomer is absent which is expected since the precursor is thought to be derived from angiosperms which did not appear until the Cretaceous period. A peak due to a tetramethylnaphthalene (TeMN) is the most abundant component in the solvent extract; this component has been identified as 1,2,5,6-TeMN and/or 1,2,3,5-TeMN. Pentamethylnaphthalenes were also present but at a much lower relative abundance compared to the other naphthalenes, the only pentamethylnaphthalene compound positively identified was cadalene (4-isopropyl-1,6-dimethylnaphthalene). Precursors for alkylated naphthalenes are thought to be sesquiterpenoids and triterpenoids, which are derived from land plants and microbes. Both 1,2,5-TMN and 1,2,5,6-TeMN can be derived from pentacyclic triterpenoids *via* cleavage of the C ring. Precursors for the alkyl naphthalenes appear to be absent in these sediments. One possible reason for this omission could be that under acidic conditions aromatisation can occur more rapidly resulting in a loss of the higher plant triterpenoid skeletons. In this context it is interesting to consider that at the end of the Permian, large-scale volcanic emissions were occurring during the emplacement of the Siberia Traps. This episode of flood basalt eruption may have caused widespread acidification and the destabilisation of terrestrial ecosystems causing high erosion levels resulting in deposition of land derived material in marine environments.

The distributions of the hopane and sterane hydrocarbons confirm that this sediment is thermally immature. The hopane hydrocarbons are dominated by Tm (17 α (H)-22,29,30-trisnorhopane) and C₂₉, C₃₀ and C₃₁ hopanes (both $\beta\alpha$ and $\alpha\beta$ epimers), extended hopanes are not present which is usual for terrestrially derived material. Sterane hydrocarbons are dominated by the C₂₉ $\alpha\alpha\alpha$ 20R isomer which is the biological configuration, again indicating that the sediment is thermally immature.

Abundant dibenzofurans have been identified before in late Permian sediments and are thought to be derived from polysaccharides although other sources can not be ruled out (Sephton et al., 1999). Xanthone precursors are produced by higher plants where they act as pigments; functionalised xanthenes are also found in fungi, lichens and ferns. The presence of xanthenes in crude oils has recently been reported (Oldenburg et al., 2002). However, the high abundance of the dibenzofurans, xanthenes and dibenzo[1,4]dioxine is very unusual. Dibenzofurans are known only to occur within a specific thermal window, above 250 °C they are destroyed. Future work will investigate whether end Permian xanthenes were transformed to other products such as xanthenes and dibenzofurans.

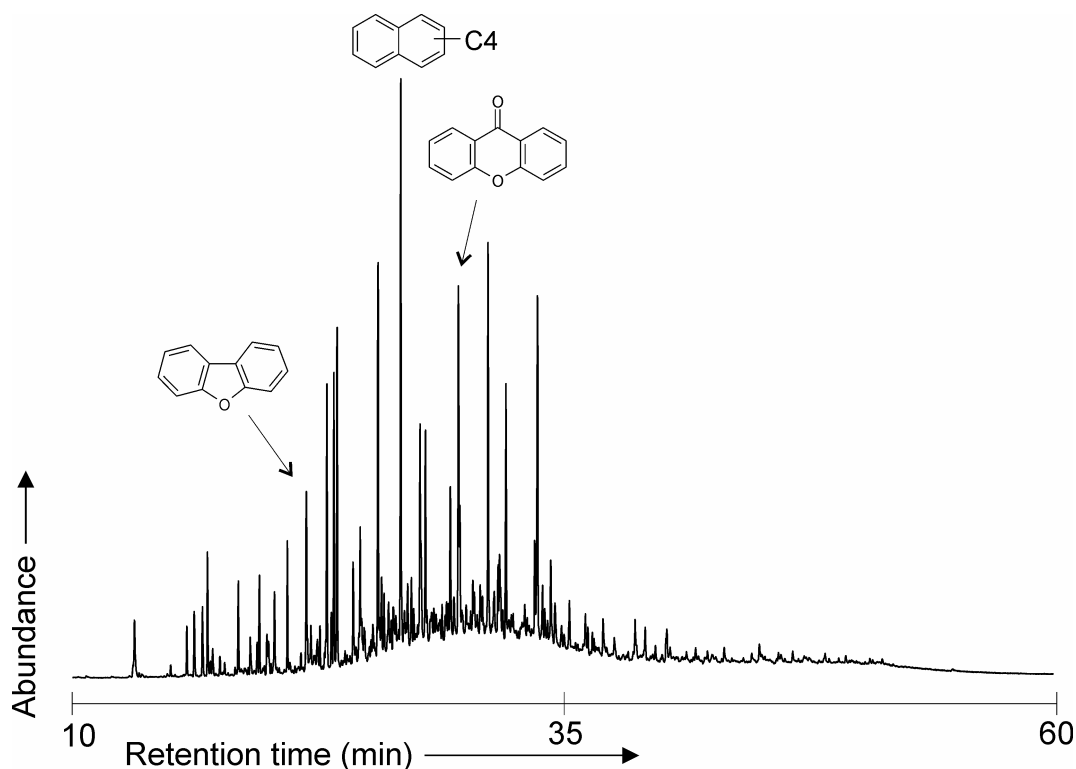


Figure 1. Total ion chromatogram for a solvent extract from a late Permian sediment

REFERENCES

- Oldenburg, T.B.P., Wilkes, H., Horsfield, B., van Duin, A.C.T., Stoddart, D., Wilhelms, A., 2002. Xanthenes – novel aromatic oxygen-containing compounds in crude oils. *Organic Geochemistry* 33, 595-609.
- Sephton, M.A., Looy, C.V., Veefkind, R.J., Visscher, H., Brinkhuis, H., de Leeuw J.W., 1999. Cyclic diaryl ethers in a late Permian sediment. *Organic Geochemistry* 30, 267-273.