

ALGAENAN AND BIOPOLYMER STRUCTURES IN ORGANISMS AND KEROGENS STUDIED USING STEPWISE PYROLYSIS

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Introduction

Pyrolysis–gas chromatography–mass spectrometry (py–GC–MS) has been widely used to characterize the insoluble organic matter (kerogen) in source rocks. A less commonly used variant is to carry out the pyrolysis on a single sample that is firstly heated at low temperatures and the products analysed by GC or GC–MS, after which the remaining residue is reinserted into the pyrolysis chamber which is then heated at a higher temperature and the process repeated in a stepwise fashion at increasing temperatures so that each stage generates a new set of pyrolyzates. Low-temperature steps remove material that is normally volatile or solvent extractable. Successively higher temperature steps degrade the kerogen into constituents depending on bond type or strength. Thus, more details about the macromolecules can be provided by stepwise pyrolysis compared to pyrolysis at a single temperature (e.g., Curie point pyrolysis).

Recently, new instrumentation has been established in our laboratory which consist of a micro-furnace Single-Shot pyrolyzer (PY-3030D, Frontier Laboratories) and an Agilent 7890B-5977A GC–MS. The pyrolyzer is directly interfaced to the GC injector with a deactivated needle. The micro-pyrolysis unit consists of a sampler, a quartz pyrolysis tube that can be preheated to the pyrolysis temperature, and an interface connecting the deactivated needle and quartz tube that can be set at temperature higher than the GC injector (e.g., 310 °C). This system makes stepwise pyrolysis more readily accessible.

With this instrumentation, we carried out sequential stepwise pyrolysis at 50 °C intervals from 310 °C to 660 °C to study the composition of kerogen from the immature Eocene Huadian oil shale in NE China (Zhang et al., 2016). Pyrolysis at 310 °C and 360 °C yielded very small amounts of *n*-alkanes with similar distributions to the extractable hydrocarbons which we presume were occluded within the kerogen. At 410 °C, *n*-alkene/*n*-alkane doublets were observed indicating the commencement of kerogen breakdown. However, at 460 °C the pyrolyzate also contained a series of *n*-alkan-2-ones and novel long-chain C₃₀–C₃₇ mid-chain ketones showing no odd over even predominance. The C₃₅ ketone was the most abundant and the major isomer for each chain-length was the alkan- ω 24-one. We hypothesized that these products were the result of pyrolysis of microalgal algaenan preserved in the kerogen, most likely derived from microalgae closely related to eustigmatophytes even though the chain length range was greater than previously observed in these microalgae (Gelin et al., 1999) and the position of the carbonyl group was unusual.

In a more recent study (Zhang and Volkman, 2017) we showed that distributions of *n*-alkan-2-ones and mid-chain ketones are indeed produced from stepwise pyrolysis of dried biomass of

the marine eustigmatophyte *Nannochloropsis oculata*. In the 460 °C pyrogram, C₁₅–C₁₉ *n*-alkan-2-ones with a strong predominance of C₁₇, together with C₂₉–C₃₃ mid-chain ketones dominated by the symmetrical ketone C₃₁ *n*-alkan-16-one were detected. Small amounts of the mono-unsaturated C_{31:1} mid-chain ketone and *n*-alkene/*n*-alkane doublets were also present indicating that the algaenan structure is mainly composed of inter-linked C₃₂ *n*-alkan-1,17-diols. In contrast, the free plus bound lipids were dominated by the C₃₂ *n*-alkan-1,15-diol.

In contrast, stepwise pyrolysis of the Eocene Maoming oil shale from SE China yielded quite different results. Extractable biomarkers clearly show a strong contribution of biomarkers indicative of the B Race of the green alga *Botryococcus*. At 460 °C the pyrogram was dominated by large amounts of a presumed C₁₅ isoprenoid ketone, prist-1-ene and various long-chain branched alkenes. At 510 °C the pyrogram shows a much larger abundance of alkene/alkane doublets due to more extensive cleavage of algaenan from *Botryococcus* and other microalgae. Mid-chain ketones were not detected implying that eustigmatophytes were not significant contributors to the organic matter in these sediments. However, *n*-alkan-2-ones were detected indicating additional sources which may include cutans from plants.

Conclusions

The early work by Horsfield (1989), Ishiwatari et al. (1993) and Christiansen et al. (1995) demonstrated the potential advantages of stepwise py–GC–MS for the analysis of kerogens and coals. Our work with new instrumentation shows that it can provide structural information on kerogen in immature rocks and is particularly well suited for the analysis of algaenan contributions. Moreover, it can be used to study algaenan and other biopolymers such as proteins in dried microalgal biomass without any need for time-consuming preparation of the macromolecules. The availability of new instrumentation should facilitate adoption of this technique and enhance our understanding of the preservation of biomacromolecules in sediments and as a fast screening tool for unusual lipids in geochemically relevant organisms.

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