Organic geochemistry of a high-latitude Lower Cretaceous lacustrine sediment sample from the Koonwarra Fossil Beds, South Gippsland, Victoria, Australia

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Abstract

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The Koonwarra Fossil Beds are widely recognized for their high-fidelity preservation of freshwater/terrestrial vertebrate and invertebrate fossils. A preliminary investigation suggests that organic biomarkers are also exceptionally well preserved and could contribute significantly to understanding the ecology of this ancient lake system. Solvent-extractable organic matter was collected from a single feldspathic siltstone/mudstone sample and analyzed using gas chromatography-mass spectrometry (GC-MS). The distribution of n-alkanes suggests a significant input of terrestrial plant material into the lake. The very low ratio of eukaryotic steranes to bacterial hopanes may reflect the decomposition of abundant plant material in the lake. Polycyclic aromatic hydrocarbons may record wildfire activity in the surrounding watershed.

Keywords

Koonwarra fossil beds, Cretaceous, paleolimnology, biomarkers.

Introduction

The Lower Cretaceous Koonwarra Fossil Beds in South Gippsland, Victoria, Australia (fig. 1), were discovered during road works in 1961 (Jell and Duncan, 1986). They are thought to be a freshwater lacustrine deposit of Barremian-Aptian age based on plant and animal fossils, palynology, and fission track dating (Douglas, 1969, 1974; Dettmann, 1986; Drinnan and Chambers, 1986; Jell and Duncan, 1986). Paleogeographic reconstructions place southern Australia well within the Antarctic Circle at this time, and the $\delta^{18}O$ values of early diagenetic carbonate concretions imply mean annual temperatures of ~5°C, despite a generally warm Cretaceous climate (Embleton and McElhinny, 1982; Rich et al., 1988).

The Koonwarra Fossil Beds are known for high-fidelity preservation of freshwater/terrestrial fossils, including several fish groups, insects, crustaceans, bird feathers and a freshwater xiphosuran (e.g. Riek, 1970; Riek and Gill, 1971; Jell and Duncan, 1986; Vickers-Rich, 1991; Krzemiński et al., 2015). Waldman (1971) interpreted varves and multiple horizons of fish fossils to be the result of winter ice covering a shallow lake and causing anoxia, mass fish kills, and the settling of clay from suspension (which would have further prevented the decomposition of covered carcasses). Warmer conditions during the spring might also be expected to cause decomposition and re-floatation of fish carcasses in a shallow-water environment (Wilson, 1977). Alternatively, Elder and Smith (1988) proposed a stratified lake model, wherein fish carcasses sunk to deep, cold waters, where scavenging and decomposition were inhibited by oxygen depletion. The formation of the fish beds could also be related to toxic summer algal blooms, as suggested by McGrew (1975) for the Eocene Green River Formation.

In this brief report, we present the results of a preliminary study of the organic geochemistry of a sediment sample collected from the Koonwarra Fossil Beds in early 2013. The sample analysed here was collected from the fossil fish beds; approximately 5 m from the bottom of the unit. It is a feldspathic siltstone/mudstone laminated on a mm-cm scale. Fish fossils are abundant in this zone (fig. 2). Our results reveal a well-preserved biomarker record in the Koonwarra deposit and suggest that further geochemical investigation is likely to yield significant insights into Cretaceous paleolimnology and the exceptional taphonomy at Koonwarra. These data also suggest that terrigenous organic matter, deriving both from higher plants and perhaps soil bacteria, was an important supplement to aquatic primary production as a trophic resource for lake consumers.

Materials and Methods

Geochemical analyses were performed in the Astrobiogeochemistry Laboratory (abcLab) at the Jet Propulsion Laboratory. A sample without visible macrofossils was powdered using an alumina grinding dish in a model 8530 Shatterbox (SPEX Sample Prep). A ~0.5 g aliquot was
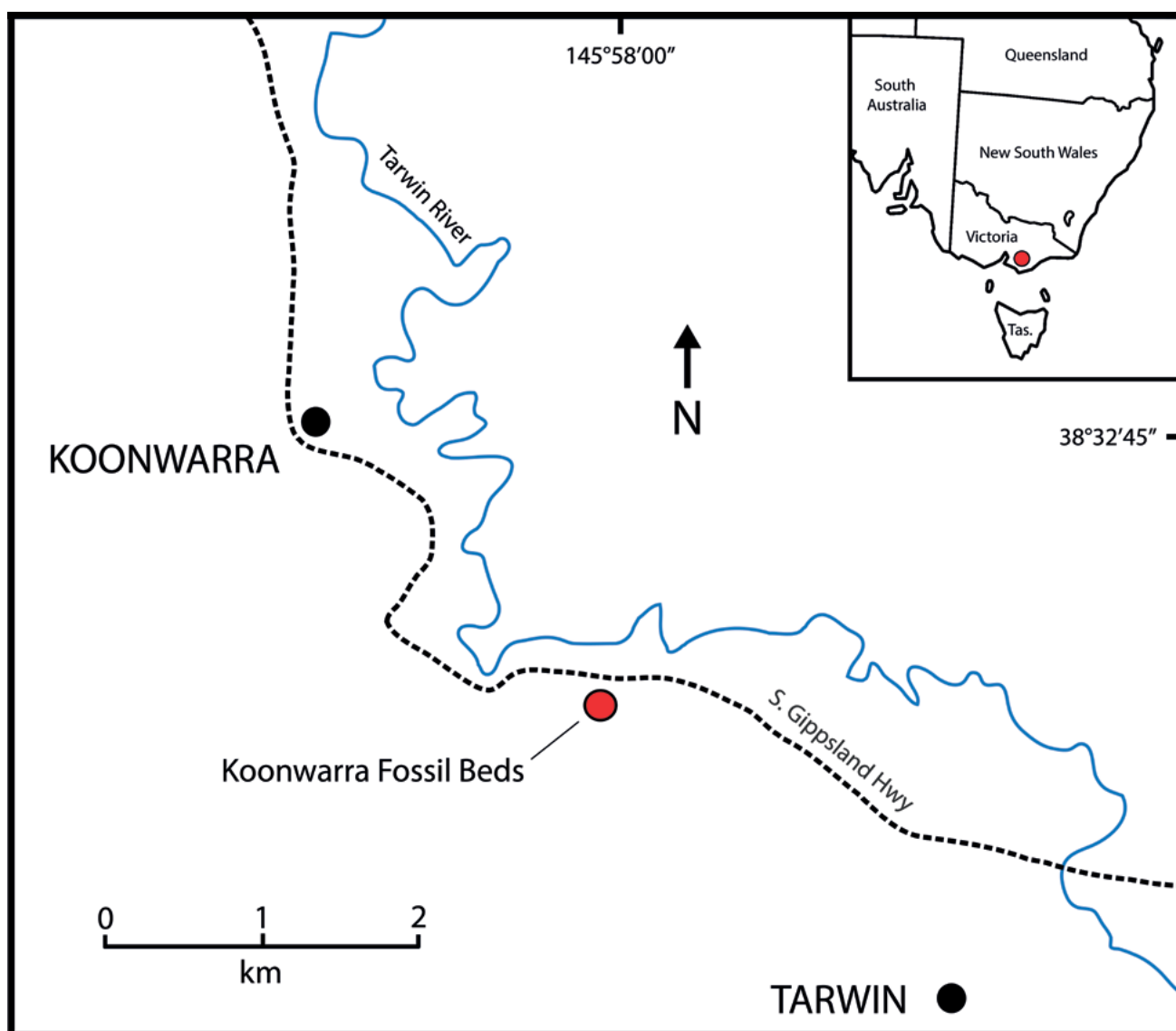
Figure 1: Location of the Lower Cretaceous Koonwarra Fossil Beds in South Gippsland, Victoria, Australia

decarbonated with excess 1N HCl, washed to neutrality with ultrapure (<18 MΩ) deionized water, and dried at 50°C for 48 hours. For determination of total organic carbon (TOC), approximately 30 mg of dried sample was weighed in a tin capsule and combusted at 980°C in a Costech 4010 elemental analyzer. The resulting CO_2 was chemically dried and transferred via He carrier flow to a Delta V Plus (Thermo) isotope ratio mass spectrometer. The mass of organic C was determined by comparison of the area of the mass 44 chromatogram of the sample with the regression of a series of acetanilide standards of known C content ($r^2 = 0.999$).

Thirty grams of the powdered sample were extracted for 48 hours using a soxhlet apparatus in a DCM:methanol (9:1 v:v) mixture. The extraction yielded 0.57 mg of total lipid extract that was subsequently separated into saturate, aromatic, and polar fractions using small column chromatography (Bastow et al., 2007). The three fractions were eluted using n-hexane, n-hexane:DCM (7:3 v:v), and DCM:methanol (1:1 v:v), respectively. Saturate and aromatic fractions were analyzed via gas chromatography-mass spectrometry (GC-MS) using a Trace GC Ultra (Thermo) connected to an ISQ Series quadrupole MS (Thermo).

Results

The TOC value of the sample is 0.4% and the yield of extractable lipids is 0.02 mg per gram of sample or 4.75 mg per gram TOC. The saturate fraction total ion chromatogram (fig. 3) has a small, unresolved complex mixture (C_{15}–C_{23})

Figure 2: An uncommon example of disarticulation of a fish carcass, collected during an excavation of the Koonwarra Fossil Beds led by Tom Rich in 2013. This specimen was collected approximately 5 m from the bottom of the unit (defined here as the first > 20 cm thick unit of green siltstone/mudstone; the underlying rocks are predominantly cross-bedded, fluviatile arkosic sandstone).

above the baseline suggesting that biodegradation of the fossil organic matter has been minimal. The m/z 85 mass chromatogram reveals a stepwise increase in the abundance of short-chained n-alkanes (C_{15}–C_{22}) with increasing molecular weight likely associated with aquatic sources such as algae. The longer chained n-alkanes (C_{23}–C_{31}) that are indicative of terrestrial higher-plant input (Bourbonniere and Meyers, 1996) show a clear odd-over-even carbon number predominance (OEP = 1.48 where 1.0 means no predominance) (Scalan and Smith, 1970). The OEP preserves a distribution characteristic of terrestrial plant epicuticular waxes and indicates that thermal alteration of the sample that would have diminished the uneven distribution has been minimal (Peters et al., 2005).

A measure of the relative contributions of terrestrial and aquatic organic matter sources is the terrestrial/aquatic ratio (TAR; Bourbonniere and Meyers, 1996) calculated using n-alkane peak areas:

TAR = (C_{15} + C_{17} + C_{19}) / (C_{27} + C_{29} + C_{31}).

Although the ratio is most useful when comparing changes in organic matter sources along a stratigraphic series of samples, the value we determined (TAR = 4.7) indicates a significant higher-plant contribution to the total carbon flux to the sediment. This is supported by the ratio of the regular isoprenoids pristane (Pr) and phytane (Ph) that are usually understood to have derived from the phytol tail of the chlorophyll molecule (Brooks et al., 1969). The ratio is influenced by the source organic matter as well as by the redox state of the environment of deposition. The value for Pr/Ph for this sample of 3.1 is diagnostic of a predominantly terrestrial organic matter source deposited under oxic conditions (Peters et al., 2005).

Hopanes are pentacyclic triterpenoids that are derived predominantly from cell wall lipids of prokaryotes (Ourisson et al., 1979). Steranes derive from lipids found only in eukaryotes including microbial photoautotrophs and metazoans (Chapman and Schopf, 1983). A sterane/hopane ratio of 0.03 was calculated using the summed peak areas of 17α-hopane isomers and C_{27}, C_{28}, and C_{29} sterane isomers (fig. 4). Low sterane/hopane ratios are typically indicative of either a dominantly terrigenous organic matter source or biodegradation of organic matter (Tissot and Welte, 1984; Peters et al., 2005). The small contribution of unresolved complex mixture to the saturate fraction indicates that post-
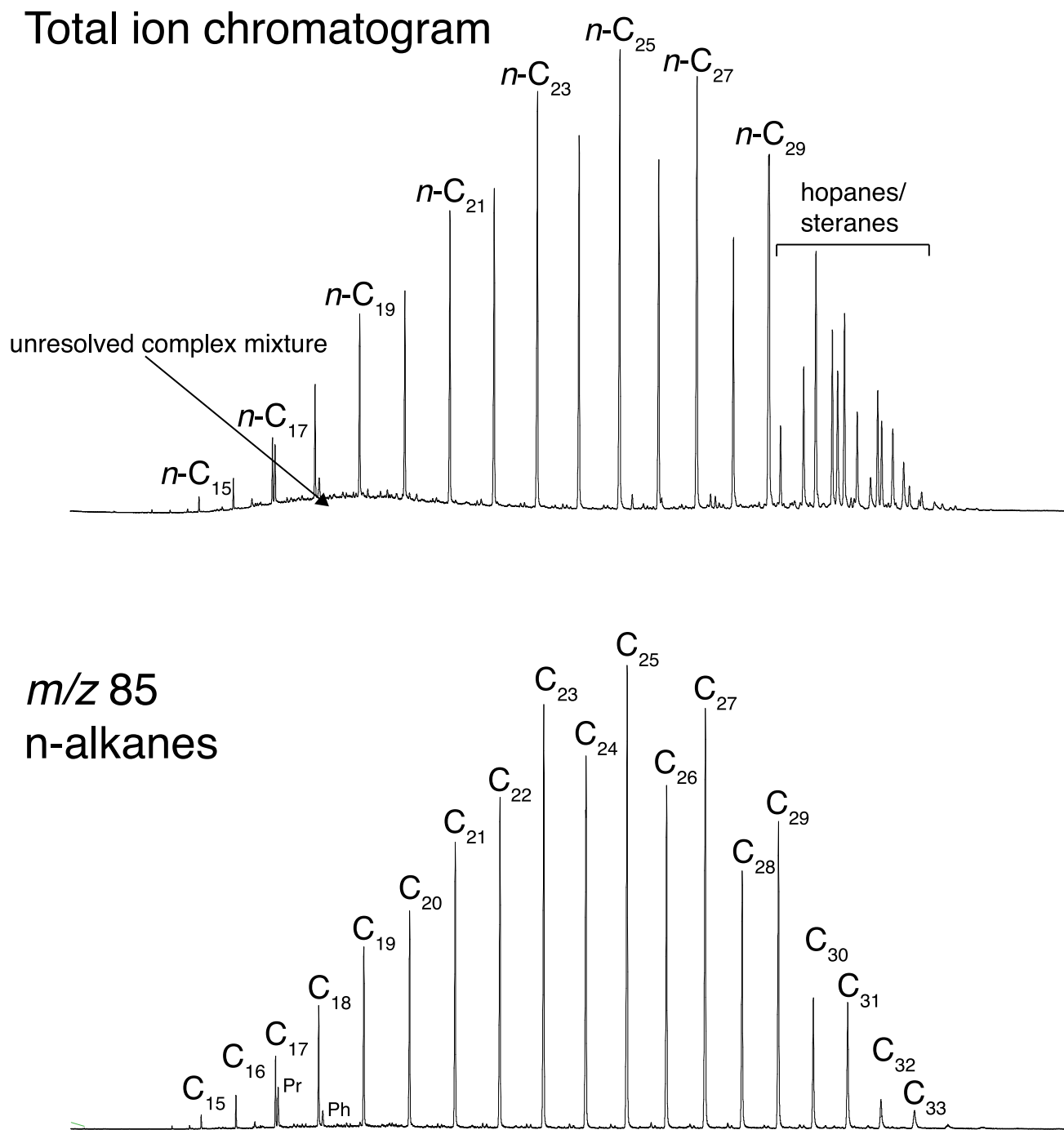
Total ion chromatogram

Figure 3: Saturate fraction total ion chromatogram and *m/z* 85 mass chromatogram showing distribution and relative abundances of *n*-alkanes and isoprenoids pristane and phytane.
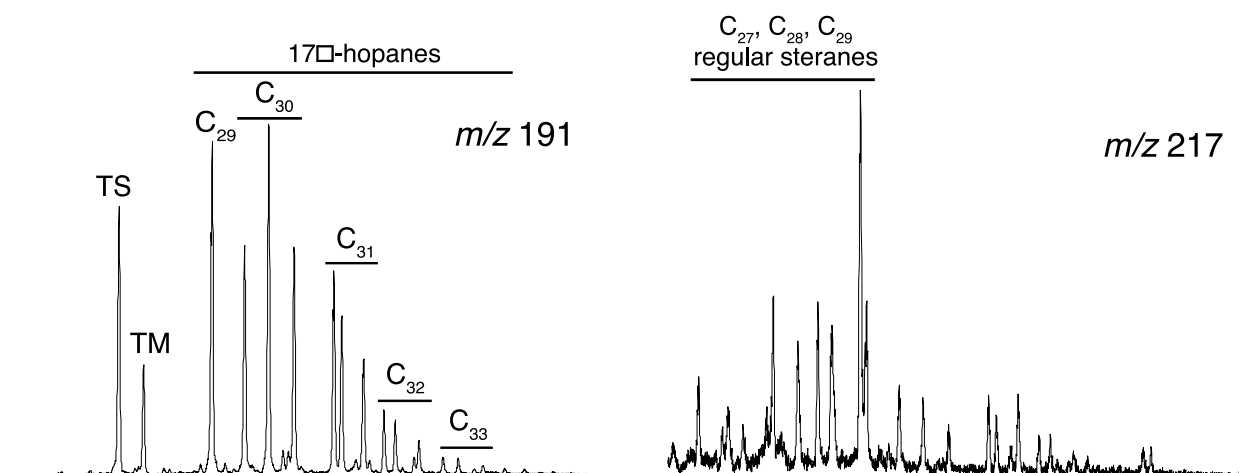
Figure 4: Partial *m/z* 191 and 217 mass chromatograms used in calculation of sterane/hopane ratio. A ratio of 0.03 indicates that a very significant proportion of overall biomass in the lake was derived from bacteria.
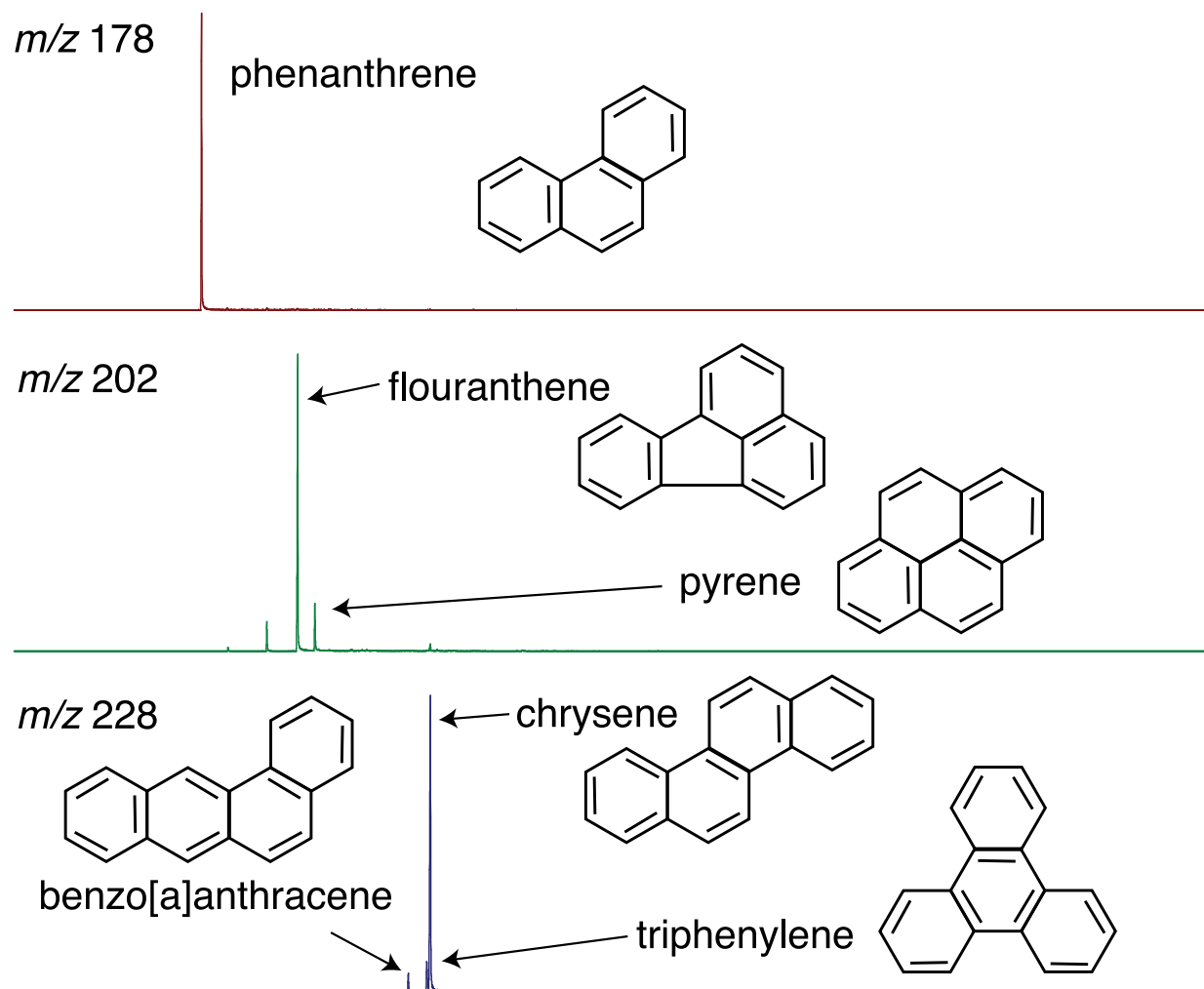

Figure 5: Partial *m/z* 178, 202 and 228 mass chromatograms showing the distribution of common polycyclic aromatic hydrocarbons (PAH) in the aromatic fraction.

depositional biodegradation was probably not significant. Possible sources of the abundant hopanes include soil bacteria from the surrounding watershed and the aquatic bacterial heterotrophs responsible for the decomposition of terrestrial plant matter.

The aromatic organic fraction contains a range of polycyclic aromatic hydrocarbons (PAH). PAHs in sediments may derive from incomplete combustion of wood and plant matter (Blumer and Youngblood, 1975) or from diagenesis of organic precursors (Jiang et al., 1998). Figure 5 shows three mass/charge-specific chromatograms that illustrate the presence of potentially combustion-related PAHs phenanthrene, fluoranthene, pyrene, and benzo[a]anthracene, chrysene, and triphenylene. Venkatesan and Dahl (1989) observed high concentrations of these and other pyrosynthetic PAHs at a variety of Cretaceous/Tertiary boundary sites that they interpreted as evidence of extensive wildfires. Similar distributions of PAHs at the Permian/Triassic boundary also suggest that wildfires were unusually common at the time of the end-Permian extinction (Nabbefeld et al., 2010).

Conclusions

The Koonwarra beds provide fossil evidence of a complex, high latitude lacustrine ecosystem. Organic geochemical evidence suggests that supplementation of aquatic trophic resources by terrigenous organic matter in the form of soil bacteria and plant tissues washed into the lake may have played an important role in sustaining that ecosystem. This supplementation may have been particularly significant given the impact of the high annual variability of solar insolation on aquatic primary production at high latitudes. The presence of combustion-related PAHs indicates an atmospheric pO_2 capable of sustaining combustion and confirms the presence of forested land cover and soils in the vicinity of the lake.

In addition to illuminating the environmental context of the extensive fossil record at Koonwarra, the sample also clearly indicates that the state of organic matter preservation in the unit is highly conducive to further integration of paleontological and geochemical evidence in assembling a comprehensive understanding of an exceptionally well-preserved ecosystem. Further work is likely to yield insights into redox conditions and other environmental factors that led to the high-fidelity preservation of fossils.

Acknowledgements

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