



# Stable hydrogen isotopic composition of hydrocarbons in torbanites (Late Carboniferous to Late Permian) deposited under various climatic conditions

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## Abstract

We measured the stable hydrogen isotopic composition ( $\delta D$ ) of selected aliphatic compounds in torbanites from Scotland and Australia, covering the Late Carboniferous to the Late Permian. The torbanites contain organic matter predominantly from a single algal source, *Botryococcus braunii*, and are of similar thermal maturity. The  $\delta D$  values of *n*-alkanes in the extracts appear to reflect the depositional palaeoclimate of each torbanite, in response to the typical  $\delta D$  values of meteoric waters. The  $\delta D$  values of *n*-alkanes in torbanites deposited at high latitude under glacial conditions are depleted in deuterium by up to 70‰ relative to *n*-alkanes in a torbanite deposited at low latitude under a tropical climate regime. Torbanites deposited in mid-latitude regions under cool-temperature conditions contain *n*-alkanes with  $\delta D$  values between those of *n*-alkanes in tropical and glacial sediments. A saw-toothed profile of  $\delta D$  values obtained for the *n*-alkanes in the Australian torbanites is attributed to a dual-source system, perhaps a predominant *B. braunii* input with a second minor contribution from land plants. Pristane and phytane from two Australian torbanites are significantly depleted in deuterium relative to *n*-alkanes in the same samples and a significant difference between the  $\delta D$  values of pristane and phytane is suggested to be caused by different sources for the two isoprenoids, or isotope effects associated with their derivation from a common phytol precursor. The offset between the  $\delta D$  of values of *n*-alkanes and isoprenoids is similar to that found in modern biological samples, indicating that their indigenous  $\delta D$  signatures may have been preserved for at least 260–280 million years.

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## 1. Introduction

Hydrogen has the largest mass difference between its two stable isotopes ( $^1H$  and  $^2H/D$ ) and, therefore, the largest natural variation in stable isotope ratios. This makes the measurement of stable hydrogen isotope ratios an attractive technique for geological applications. However, accurate measurement of  $\delta D$  values of organic matter in geological samples poses an analytical

challenge, considering the low natural abundance of deuterium ( $D$ , 0.0155%). In comparison, the natural abundance of  $^{13}C$  in carbon is approximately two orders of magnitude greater. The capability of measuring the  $\delta D$  values of individual compounds in complex mixtures is a recent development (e.g. Burgoyne and Hayes, 1998; Hilkert et al., 1999). The tool for hydrogen compound specific isotope analysis (CSIA) is a gas chromatograph-isotope ratio mass spectrometer (GC-irMS), whereby a GC is linked to an irMS via a pyrolysis reactor interface.

This new technique has been used in biological pathway studies (e.g. Sessions et al., 1999; Grice et al.,

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2003) and in the reconstruction of palaeoenvironments (e.g. Xie et al., 2000; Sauer et al., 2001; Anderson et al., 2001; Li et al., 2001). Sessions et al. (1999) studied the fractionation of hydrogen isotopes in lipid biosynthesis by different organisms. Compound-specific  $\delta D$  values of lipid biomarkers from peat deposits (Xie et al., 2000) and sediments (Sauer et al., 2001) have been used as a proxy for palaeoenvironmental and palaeoclimatic conditions. Andersen et al. (2001) reported  $\delta D$  values of individual *n*-alkanes and isoprenoids as evidence of large and rapid climate variability during the Messinian salinity crisis. Li et al. (2001) assessed the usefulness of hydrogen CSIA in petroleum correlation studies and palaeoenvironmental reconstructions using a number of crude oil samples from the Western Canada sedimentary basin. More recently, Yang and Huang (2003) demonstrated the preservation potential of lipid  $\delta D$  values in Miocene lacustrine sediments and plant fossils at Clarkia, northern Idaho, USA. The Clarkia sediments they studied comprise the oldest reported samples (15–20 million years) where original  $\delta D$  values appear to have been preserved. There is concern that diagenetic effects over extended periods of geological time can result in significant hydrogen isotope exchange between organic hydrogen and the surrounding environment (e.g. Alexander et al., 1984; Leif and Simoneit, 2000; Schimmelmann et al., 1999, 2001; Sessions, 2001; Dawson et al., 2003; Sessions et al., 2003). Thus, it is of interest to know the degree to which hydrogen CSIA can be used for palaeoenvironmental studies, especially when applied to older sedimentary organic matter.

The  $\delta D$  values of organic compounds preserved in sediments are of interest to organic geochemists and palaeoclimatologists because they can reflect the isotopic composition of water that existed in ancient environments. The transport of water and the energy exchanged as it is converted from one physical state to another are important factors in weather and climate, so hydrogen isotopic fractionations are thought to be related to a wide variety of naturally-occurring processes in the hydrological cycle. Waters that have gone through the hydrological cycle are defined as 'meteoric' waters. The isotopic values of meteoric waters vary with temperature, altitude, latitude, proximity to the ocean and other factors (Dansgaard, 1964; Kehew, 2001). Photosynthetic organisms utilize water as a main hydrogen source and the deuterium concentration in the source water is reflected in the deuterium composition of the organism (e.g. Sessions et al., 1999). The remains of organisms ultimately become incorporated into sediments and contribute to the organic matter in petroleum.

Torbanites are organic matter-rich sediments with high petroleum potential, containing high amounts of organic carbon (TOC contents generally between 30 and 70%; e.g. Boreham et al., 1994). The organic-matter is largely derived from the Chlorophyte *Botryococcus*

*braunii* (*B. braunii*; Hutton et al., 1980; Largeau et al., 1984; Derenne et al., 1988; Gatellier et al., 1993; Boreham et al., 1994; Audino et al., 2001; Grice et al., 2001). *B. braunii* is a colonial unicellular organism that can flourish in most climates, including temperate, tropical and arctic zones and has been reported to occur strictly in fresh and brackish waters (Tyson, 1995).

To elucidate the potential of hydrogen CSIA for palaeoenvironmental studies, and to investigate further the preservation potential of lipid  $\delta D$  values in older sedimentary organic matter, the stable hydrogen isotopic compositions of hydrocarbons (individual *n*-alkanes and acyclic isoprenoids) from a selection of torbanites with similar biological inputs and of similar thermal maturity, from different palaeogeographical locations and deposited under various climatic conditions, have been investigated.

## 2. Experimental

### 2.1. Sample description and geological setting

Five torbanites from Australia and Scotland covering the Late Carboniferous to the Late Permian were analysed (Table 1). These were deposited in inland lakes under a variety of climate regimes including glacial, cool-temperate and tropical. The torbanite from Torbane Hill, Scotland (Fig. 1d) was deposited during the Late Carboniferous when Laurasia (the ancient super-continent in the northern hemisphere) was located at low latitude (Fig. 1a). Climate conditions in Scotland (Fig. 1a and d) were tropical with extensive plant growth. Two torbanites from the southern hemisphere (Temi, Eastern Australia; Fig. 1e) were deposited during the Early Permian under glacial conditions. Gondwana (the ancient super-continent in the southern hemisphere) was located at high latitude (Fig. 1b) as a result of a southward migration that began during the Early Carboniferous (White, 1993). At the Carboniferous–Permian boundary it is believed that a vast sheet of ice covered almost half of the Australian continent (Frakes, 1979; White, 1993). The Gondwana ice sheet receded towards the Middle Permian as the climate became warmer, and there was a rapid rise in sea level during the Late Permian as the ice sheet melted (White, 1993). During the Late Permian Gondwana was located at lower latitude (Fig. 1c) and experienced a cool-temperate climate, when two other torbanites from the southern hemisphere (Newnes, Eastern Australia; Fig. 1e) were deposited.

The torbanite from Scotland is from the Lower Carboniferous coal measures found at Boghead on the Torbane Hill estate, close to Bathgate (Fig. 1d; Beveridge et al., 1991). The torbanites from Temi came from what is commonly called the Murrurundi deposit located due north of Murrurundi in the Liverpool Ranges

Table 1  
Torbanites used in this study

Sample #	Location	Age	Climate
3733	Newnes, Australia	Late Permian	Cool–Temperate
3736	Newnes, Australia	Late Permian	Cool–Temperate
3740	Temi, Australia	Early Permian	Glacial
3742	Temi, Australia	Early Permian	Glacial
3755	Torbane Hill, Scotland	Late Carboniferous	Tropical

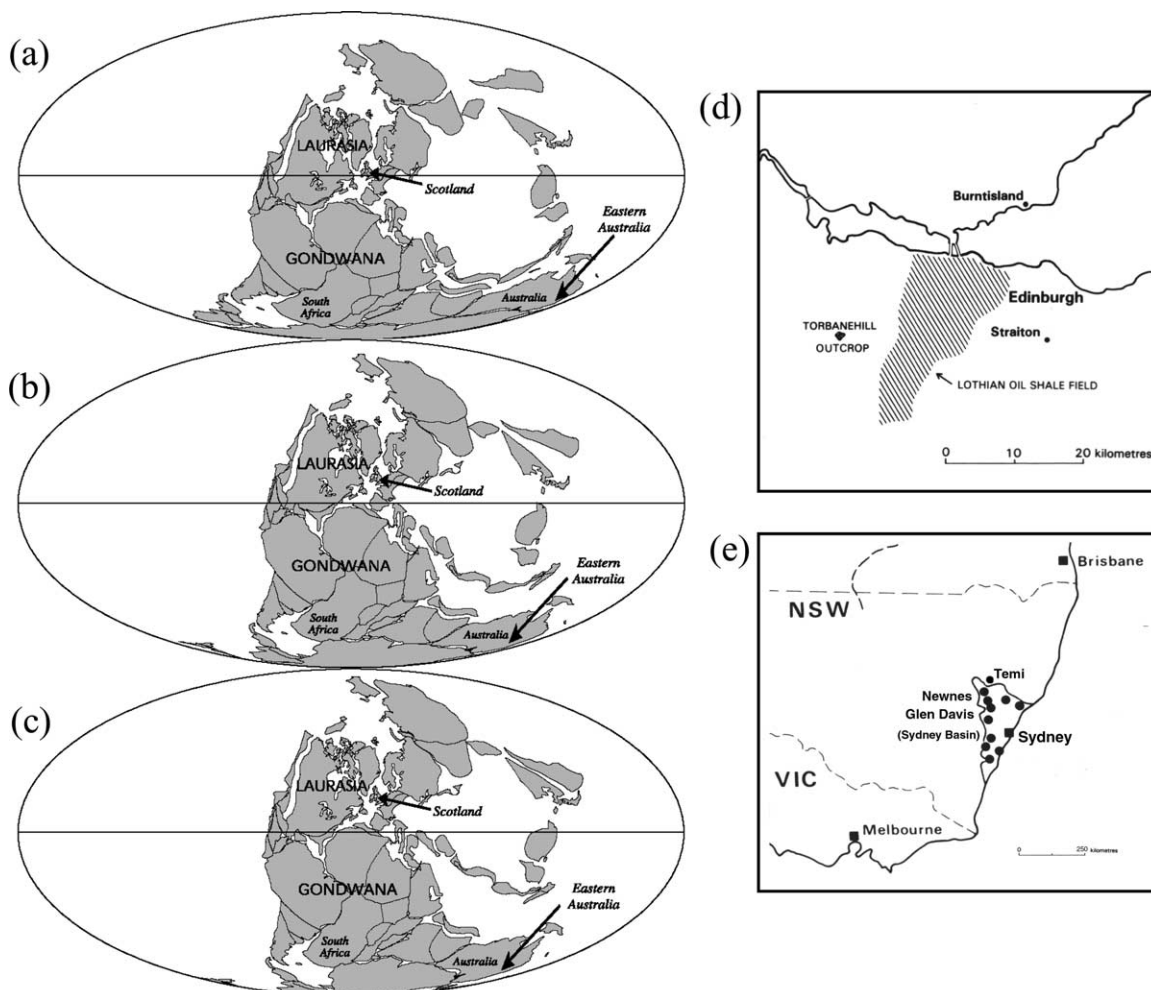


Fig. 1. Palaeogeographical world maps (Scotese, 1997): (a) Late Carboniferous, 310 Ma.; (b) Early Permian, 280 Ma.; and (c) Late Permian, 260 Ma., and present day maps showing the location of torbanite deposits in (d) Scotland (Beveridge et al., 1999), and (e) Eastern Australia (Hutton et al., 1980).

on the northern margin of the Sydney Basin (Fig. 1e). The deposit occurs in the Temi Formation which, in the Temi area, is approximately 30 m thick and comprises mostly sandstone, shale, conglomerate, carbonaceous

shale and coal. The Newnes torbanites come from the contiguous Newnes-Glen Davis deposit located on the western margin of the Sydney Basin, 40 km north of Lithgow (Fig. 1e). The sample occurs in a seam

associated with bituminous coal and shale, approximately 60 m below the top of the Illawarra coal measures.

## 2.2. Sample preparation

The samples were extracted according to the procedures outlined by Boreham et al. (1994). The aliphatic hydrocarbons were isolated using a standard procedure described by Audino et al. (2001). The *n*-alkanes were separated from branched and cyclic hydrocarbons using molecular sieves as described by Audino et al. (2001).

## 2.3. Gas chromatography–mass spectrometry (GC–MS)

GC–MS analysis was performed using a Hewlett-Packard (HP) 5973 MSD interfaced with a HP 6890 gas chromatograph. For routine analysis, the capillary column and the GC and MS conditions were identical to those described by Audino et al. (2001). Samples were dissolved in hexane and injected on-column by a HP 6890 auto-sampler.

## 2.4. Gas chromatography–isotope ratio mass spectrometry (GC–irMS)

Compound-specific hydrogen-isotope analyses were performed on a Micromass IsoPrime isotope mass spectrometer interfaced with a HP 6890 GC, fitted with the same capillary column as described above for GC–MS analysis. The GC oven was programmed from 35 to 310 °C at 3 °C/min with initial and final hold times of 7 and 15 min, respectively. Samples were dissolved in pentane and injected (split/splitless injector) by a HP 6890 auto-sampler using pulsed-splitless mode with the same injection conditions as described by Audino et al. (2001).

Some difficulties associated with the measurement of stable hydrogen isotopic compositions are (i) the production of  $H_3^+$  ( $m/z$  3) in the ion source (along with the desired  $H_2^+$  and  $HD^+$ ) as a by product of ion-molecule collisions, resulting in isobaric interference at  $m/z$  3 ( $HD^+$ ) and (ii) the presence of helium (He,  $m/z$  4), influencing the  $m/z$  3 signal as a result of the  $HD^+$  peak eluting on the shoulder of the large He peak (from the constant flow of carrier gas). To overcome these problems, (i) a  $H_3^+$  correction is made to  $m/z$  3 ion currents (Sessions et al., 1999) and (ii) the use of ion optics separates  $HD^+$  from He, ensuring only a small portion of the helium tail is sampled (Prosser and Scrimgeour, 1995).

The  $\delta D$  values were calculated by integration of the masses 2 and 3 ion currents of the  $H_2$  peaks produced by pyrolysis of the chromatographically-separated compounds using a chromium catalyst at 1050 °C (A. Phillips, personal communication). Contributions from  $H_3^+$  produced in the ion source are corrected for by performing mass 3 measurements at two different pressures of the  $H_2$  reference gas to determine the ‘ $H_3^+$

factor’, which is then added into the data processing software (H2UTILS, Micromass) where the correction is made automatically. Over a two-week period, the  $H_3^+$  factor was typically between 12 and 14 ppm/nA, averaging 13.4 ppm/nA, with a standard deviation of 0.5 ppm/nA. Isotopic compositions are reported relative to that of reference gas pulses produced by allowing hydrogen of known D/H content into the mass spectrometer. The D/H content of the  $H_2$  reference gas was determined daily using organic standards to monitor drift in the  $\delta D$  value as the pressure of the gas in the cylinder decreased. For samples, average values of at least three analyses and standard deviations are reported. An internal standard (squalane) with a predetermined  $\delta D$  value of  $-167\text{‰}$  was added to samples to monitor accuracy and precision of  $\delta D$  measurements. Over the measurements, the  $\delta D$  value of the internal standard averaged  $-166\text{‰}$  with a standard deviation of 3‰. Isotopic compositions of sample components are given in the delta notation relative to Vienna Standard Mean Ocean Water (VSMOW).

## 3. Results and discussion

### 3.1. Characteristics and prior analysis of the torbanites

Comprehensive geochemical analyses of the torbanites used in this study, including biomarker studies, have been carried out previously by Boreham et al. (1994), Audino et al. (2001) and Grice et al. (2001). In summary, the saturated hydrocarbons comprise the common regular isoprenoids, pristane (Pr) and phytane (Ph), *n*-alkanes ranging from *n*-C<sub>14</sub> to around *n*-C<sub>30</sub>, a high relative abundance of hopanes maximising at the C<sub>30</sub>  $\alpha\beta$  hopane, and other less ubiquitous hydrocarbons (e.g. drimanes).

The torbanites used have high TOC contents (52–59%, Table 2). The sediments do not differ significantly in maturity, with C<sub>31</sub>-homohopane 22S/(22S + 22R) ratios ranging between 0.37 and 0.55 (Table 2) and T<sub>max</sub> values from Rock-Eval pyrolysis between 446 and 460 °C (Table 2). They contain fairly immature type I organic matter based on hydrogen and oxygen indices (HI, OI, Table 2) from Rock-Eval pyrolysis. Previous studies of organic matter with large contributions from *B. braunii* have shown it to be enriched in <sup>13</sup>C relative to organic matter from phytoplankton (e.g. Boreham et al., 1994; Grice et al., 2001). Measurement of the  $\delta^{13}C$  values of individual *n*-alkanes (predominantly from *B. braunii*) in some Australian torbanites revealed a ‘saw-toothed’ profile in the higher molecular weight range (*n*-C<sub>20</sub> to *n*-C<sub>30</sub>), the <sup>13</sup>C-enriched even *n*-alkanes being consistent with a contribution predominantly from *B. braunii*, the relatively <sup>13</sup>C-depleted, odd *n*-alkanes being attributed to a contribution from land plants (Boreham et al., 1994; Grice et al., 2001). The  $\delta^{13}C$  values of

Table 2  
Bulk geochemical parameters of the torbanites

Sample #	TOC (%) <sup>a</sup>	$T_{\max}$ (°C) <sup>a</sup>	HI <sup>a</sup>	OI <sup>a</sup>	$C_{31}\alpha\beta 22S / (C_{31}\alpha\beta 22S + C_{21}\alpha\beta 22R)$
3733	59	460	974	51	0.39
3736	59	460	997	10	0.39
3740	52	446	1150	8	0.39 <sup>b</sup>
3742	56	446	1145	6	0.37 <sup>b</sup>
3755	52	455	1174	4	0.55 <sup>b</sup>

TOC, total organic carbon; HI, hydrogen index; OI, oxygen index.

<sup>a</sup> Determined by Boreham et al. (1994).

<sup>b</sup> Determined by Audino et al. (2001).

*n*-alkanes in these samples (see Audino et al., 2001; Grice et al., 2001) obviously reveal no apparent relationship with palaeolatitude/ palaeotemperature.

### 3.2. Stable hydrogen isotopic composition of hydrocarbons

The stable hydrogen isotopic composition ( $\delta D$ ) of individual *n*-alkanes was measured in the five torbanites. The  $\delta D$  values of two acyclic isoprenoids (Pr and Ph) were measured in two Australian (Temi) torbanites. A larger number of samples was available; however only a few of these contained enough organic material for  $\delta D$  analysis. Standard deviations for at least three replicate analyses are mostly within 5‰, and at the worst, 10 to 15‰ for a few *n*-alkanes from torbanite #3740.

#### 3.2.1. *n*-Alkanes

The  $\delta D$  values of individual *n*-alkanes are plotted in Fig. 2. The error bars indicate the standard deviation for at least three replicate measurements. Where error bars are not visible, the error is smaller than the size of the symbol. The *n*-alkanes from the Scottish torbanite (Torbane Hill, #3755) have  $\delta D$  values between  $-140$ ‰ and  $-160$ ‰ (Fig. 2). The *n*-alkanes from two Eastern Australian torbanites (Newnes, #3733 and #3736) have values between  $-150$ ‰ and  $-200$ ‰ (Fig. 2). Those from two other Eastern Australian samples (Temi, #3740 and #3742) have values between  $-180$ ‰ and  $-230$ ‰ (Fig. 2);  $\delta D$  measurements of *n*-alkanes from the two Newnes torbanites were limited to three to five compounds due to the low relative abundance of many of the compounds in these samples.

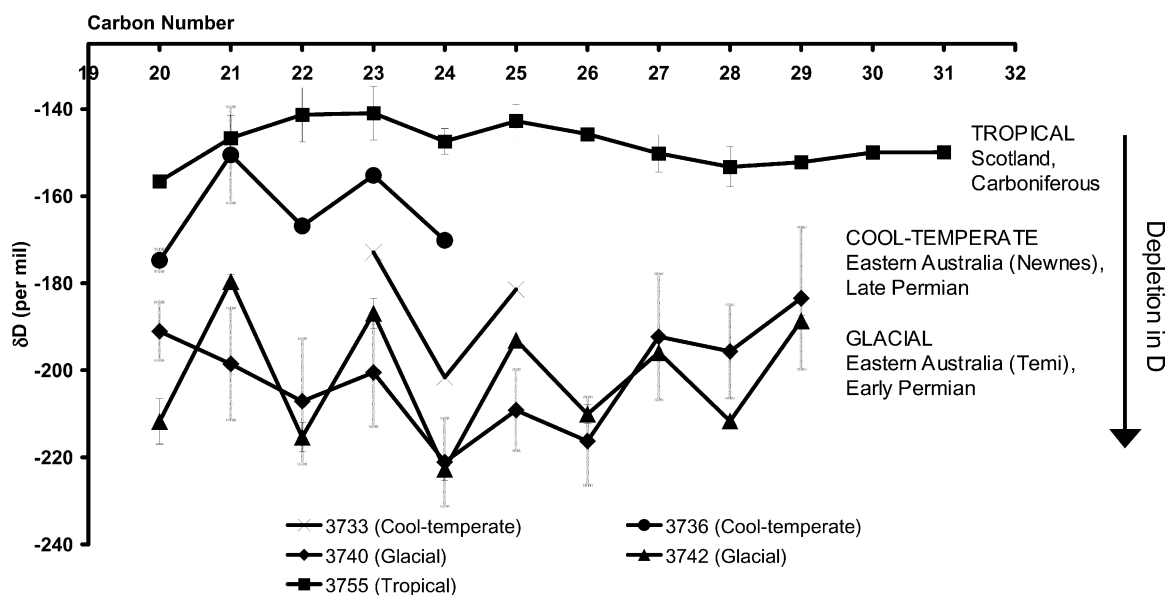


Fig. 2. Stable hydrogen isotopic composition of individual *n*-alkanes in five torbanites (Late Carboniferous–Late Permian) from various palaeogeographical locations deposited under various climatic conditions.

The  $\delta D$  values of *n*-alkanes appear to correlate with the palaeolatitude/ palaeoclimate at the time of deposition. The *n*-alkanes in two torbanites deposited under glacial conditions (#3740 and #3742, Fig. 2) are significantly depleted in D (ca. 40 to 70‰) relative to those in a torbanite deposited under tropical conditions (#3755, Fig. 2). The *n*-alkanes in samples deposited under cool to temperate conditions (#3733 and #3736, Fig. 2) have  $\delta D$  values that generally fall between those for the *n*-alkanes from tropical and glacial samples. The difference in  $\delta D$  values of the *n*-alkanes from samples deposited under different climate regimes is consistent with the variation in the  $\delta D$  value of precipitation at different latitudes, which contributes to meteoric waters used by photosynthetic organisms. Studies of the isotopic effects associated with precipitation have been carried out previously by Craig (1961) and Dansgaard (1964). In summary, when evaporated water condenses in clouds and produces raindrops, isotopic depletion of the cloud takes place through concentration of the heavy stable isotopes in the liquid phase. The heavier isotopic species of water (e.g. HDO) condense preferentially because their saturation vapour pressures are lower than that of the lighter isotopic species (e.g. H<sub>2</sub>O). As clouds move towards the pole, the ‘rain out’ of heavy isotopes causes the cloud to become ‘isotopically lighter’ with increasing latitude. Furthermore, the cooler ambient temperatures at higher latitudes result in less evaporation of seawater, so the water vapour in the cloud is not recharged. Consequently, precipitation in regions of high latitude (e.g. polar, glacial regions) is depleted in the heavy stable isotopes relative to precipitation in areas of low latitude (equatorial, tropical regions). Areas of the plot shown in Fig. 2 have been assigned a depositional climate based on the  $\delta D$  composition of the *n*-alkanes in the various sediments.

The  $\delta D$  composition of precipitation can also vary with elevation (altitude effect), and distance from the ocean (“continentality”). With increasing altitude, meteoric precipitation becomes progressively depleted in heavy isotopes (Criss, 1999 and references therein), although the reason for this behaviour is not well understood. With increasing distance from the ocean, meteoric precipitation also becomes progressively depleted in heavy isotopes as a result of ‘raining out’ (see above), although this effect is highly variable (Criss, 1999 and references therein). Typically, the isotopic composition of meteoric precipitation is principally correlated with temperature (Criss, 1999) and therefore latitude, particularly in this case given the large differences in the palaeolatitude of deposition of each torbanite.

Since the torbanites were deposited under a freshwater setting, it is also important to consider the effect of surface evaporation of the lake water when interpreting the differences seen in the  $\delta D$  values of the *n*-alkanes

in torbanites deposited at different palaeolatitudes. The  $\delta D$  values of lake waters predictably indicate their meteoric parentage (Criss, 1999), but surface evaporation is an important process which affects all surface waters, especially shallow lakes. Of course, such effects are most pronounced in windy, hot, or arid areas (Criss, 1999). It has been shown that the water vapour formed due to evaporation is depleted in the heavy isotopes D and <sup>18</sup>O (Craig and Gordon, 1965; Hoefs, 1987), resulting in a relative enrichment of these species in the liquid phase. This occurs as a result of the vapour pressure of HDO being slightly lower than that of H<sub>2</sub>O, leading to the lighter isotopic species evaporating preferentially. Although the  $\delta D$  composition of the water in the lake will be affected by evaporation to some extent, we believe meteoric precipitation is the dominant process in determining the isotopic composition of the lake water in this case, considering the significant difference in the depositional latitude of each torbanite. However, the fact that the  $\delta D$  values of *n*-alkanes from the two samples deposited under cool-temperate conditions are spread over a wider range in comparison to, for example, the  $\delta D$  values of *n*-alkanes from the two samples deposited under glacial conditions, is possibly a result of an evaporation effect, where the  $\delta D$  values of *n*-alkanes from torbanite #3736 (–150 to –175‰) are indicative of a more evaporative environment in comparison to the values of *n*-alkanes from torbanite #3733 (–170 to –200‰).

It cannot be completely excluded that the hydrogen isotopic signature has been altered to some extent by diagenetic transformation in the subsurface, even considering the notion that these sediments are relatively immature (based on homohopane distributions and *T*<sub>max</sub> values, Section 3.1). It has been shown that hydrogen exchange between organic matter and water occurs during hydrous pyrolysis (Schimmelmann et al., 1999; Leif and Simoneit, 2000) and, consequently, the  $\delta D$  values of *n*-alkanes in the samples might have been affected by hydrogen exchange reactions between organic matter and formation water during maturation. However, there is evidence to suggest that hydrogen exchange processes have not altered the indigenous isotopic signatures to a large extent (see below).

A feature of the results is a ‘saw-toothed’ profile of  $\delta D$  values for the *n*-alkanes in the Australian torbanites (#3733, #3736, #3740 and #3742, Fig. 2). This type of profile has previously been observed for the  $\delta^{13}C$  values of C<sub>20</sub>–C<sub>30</sub> *n*-alkanes in these samples (Section 3.1), with approximately a 3–5‰ shift between odd and even carbon-numbered *n*-alkanes; however, the odd-even carbon number trend is opposite to that seen with the  $\delta D$  values (the even carbon numbered *n*-alkanes are enriched in <sup>13</sup>C relative to the odd ones). The saw-toothed profile of  $\delta^{13}C$  values can be explained by a dual source system, with contributions from both *B. braunii*

and land plants (Boreham et al., 1994; Grice et al., 2001). The same explanation can be applied to the profile of  $\delta D$  values, where even-carbon-numbered *n*-alkanes are ascribed a predominant *B. braunii* source, while D-enriched odd-carbon-numbered *n*-alkanes are probably related to a land plant input. The land plant contribution causes a relative enrichment in D due to isotopic effects during evaporation of water from leaf surfaces and by transpiration in the plants (Estep and Hoering, 1980 and references therein Grice et al., 2003). Further evidence for a land plant contribution to higher molecular weight odd *n*-alkanes is apparent in the GC-MS total ion chromatograms (TICs) for the saturate fractions of the Australian sediment extracts, where there is an odd/even distribution (odd predominance) of *n*-alkanes in the higher molecular weight region (e.g. Fig. 3). It is likely that hydrogen exchange processes brought about by maturation have only affected to a limited extent (if at all) the  $\delta D$  values of odd *n*-alkanes in the Australian samples, since predominant odd *n*-alkanes in the  $C_{25}$ – $C_{35}$  range can be considered as preserved genuine biological lipids and, according to Schimmelmann et al. (1999), hydrogen exchange reactions between organic matter and formation waters might affect essentially hydrocarbons generated during maturation.

### 3.2.2. Acyclic isoprenoids

The  $\delta D$  values of selected acyclic isoprenoids (specifically, pristane and phytane) from the branched and cyclic fractions of two Australian samples (Temi, Early Permian) were measured. Pristane (Pr) and phytane (Ph) from torbanite #3740 have  $\delta D$  values of  $-283 \pm 2\text{‰}$  and  $-259 \pm 2\text{‰}$ , respectively. Pr and Ph from sample #3742 have values of  $-277 \pm 2\text{‰}$  and  $-268 \pm 3\text{‰}$ , respectively.

Pr and Ph in the Temi torbanites (#3740 and # 3742) are strongly depleted in D (ca. 60 to 80‰) compared to the respective *n*-alkanes. The offset between the  $\delta D$  values of isoprenoids and *n*-alkanes is similar to that seen in modern biological samples, indicating that an apparent biological signal has been preserved for at least 260 to 280 million years, assuming that biosynthetic processes have always produced isoprenoid and *n*-alkyl lipids with different values of  $\delta D$  (e.g. Hoering, 1977; Estep and Hoering, 1980; Session et al., 1999; Sessions, 2001). Significant diagenetic effects would more likely result in a more homogeneous distribution of values (e.g. Hoering, 1977). Unfortunately, the  $\delta D$  values of Pr and Ph in the other torbanites could not be measured due to their low relative abundance, so we cannot be certain that a biological signal exists for these samples. However, because the torbanites appear to have had a similar thermal history (based on various maturity parameters, Section 3.1), we suggest it is likely that indigenous signals are also preserved in these samples. This lends credence to the interpretation given for the observed differences between  $\delta D$  values of *n*-alkanes present in the various torbanites (Section 3.2.1).

There is a significant difference between the  $\delta D$  values of Pr and Ph of the Temi torbanites, Ph being enriched in D by ca. 24‰ relative to Pr. Li et al. (2001) reported that Ph is mostly enriched in D relative to Pr and suggested this to be consistent with either different origins of Pr and Ph or different isotope effects for their derivation from a common phytol precursor. Further evidence for different origins of Pr and Ph in the Temi torbanites is apparent from the  $\delta^{13}C$  values, where Ph is ca. 2 to 3‰ depleted in  $^{13}C$  relative to Pr (Grice et al., 2001).

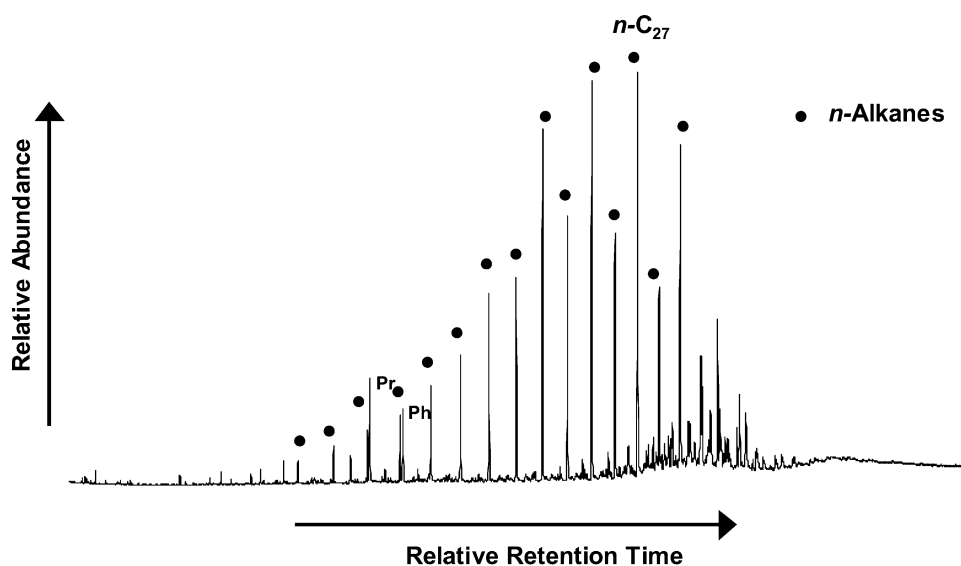


Fig. 3. GC-MS total ion chromatogram of the saturate fraction of torbanite #3740.

#### 4. Conclusions

1. The  $\delta D$  values of *n*-alkanes in the torbanites analysed appear to reflect the depositional palaeo-latitude/palaeoclimate of the sediments, attributed to the  $\delta D$  composition of meteoric waters in the environment where they were deposited.
2. A saw-toothed profile of  $\delta D$  values for the *n*-alkanes in the Australian torbanites is attributed to a dual source system with a predominant *B. braunii* input and a land plant input to the odd carbon number components.
3. A depletion of deuterium in two acyclic isoprenoids (Pr and Ph) relative to the *n*-alkanes in two Australian torbanites is similar to the offset seen in modern biological samples, indicating that an apparent biological signal has been preserved for at least 260 to 280 million years.
4. A significant difference between the  $\delta D$  values of Pr and Ph in the Temi torbanites is suggested to be caused by either different sources for the two isoprenoids, or isotope effects associated with their derivation from a common phytol precursor. Additional evidence for different origins of Pr and Ph is apparent from the  $\delta^{13}C$  values of these compounds.

The fact that the stable hydrogen isotopic compositions of individual hydrocarbons in ancient immature sediments appear to reflect the isotopic composition of meteoric waters and source organic matter after at least 260 to 280 million years, indicates that the preservation potential of lipid  $\delta D$  values is greater than previously thought. This is further evidence that measurement of  $\delta D$  values of individual compounds in sedimentary organic matter can be useful for palaeoenvironmental reconstruction.

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Associate Editor — Philippe Schaeffer

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