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Changes in biomarker abundances and sulfur isotopes of pyrite across the Permian–Triassic (P/Tr) Schuchert Dal section (East Greenland)

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Abstract

In this study, we report on biomarker abundances through parts of the Permian/Triassic boundary (PTB) of Schuchert Dal (East Greenland) that contains rich marine faunal records and excellent terrestrial palynological records. Biomarker abundances and sulfur isotopes are used to correlate the series of events (including changes in element cycling and associated redox conditions of the ocean) surrounding the collapse of the marine and terrestrial ecosystems through this record of a major crisis of life on Earth during a mass extinction episode. The Upper Schuchert Dal Formation contains a low diversity palynological assemblage, ascribed to arborescent cordiaite–conifer–pteridosperm vegetation. Samples from this pre-collapse interval are characterised by high abundances of dibenzofuran (DBF), dibenzothiophene (DBT) and biphenyl. Since these compounds have similar base structures, and show comparable abundance curves, it is plausible that they probably derive from a common source. We propose that phenolic compounds of lignin of the woody plants present during this period could be the source for DBF, DBT and biphenyl. The redox conditions during this period of time also support the formation of DBF and DBT. Just above the extinction interval, there is a dramatic decrease in the abundances of DBF and DBT which occurs at the same time as a sudden change in the stable sulfur isotopic composition ($\delta^{34}S$) of pyrite, indicating a change in redox conditions from oxic to anoxic/euxinic conditions. $\delta^{34}S$ values leading up to the extinction are highly depleted in the heavy sulfur isotope (about −40‰ vs. VCDT), whilst shortly after the extinction interval much more positive isotope values are observed (about −25‰). An inferred change in the biogeochemical sulfur cycle is supported by facies evidence from similar neighbouring sections. It is suggested that two processes are operating closely here; 1) Changes in redox conditions and 2) extinction and/or transgression accounting for the absence of woody material.

Keywords: biomarkers; Permian; Triassic; extinction; Greenland; stable isotopes

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1. Introduction

The most pronounced mass extinction in Earth's history occurred in the Late Permian prior to the PTB. The cause of the extinction is still strongly debated. Volcanism, global warming, methane release from the melting of gas hydrates, global anoxia, oceanic overturn of stagnant deep ocean waters, and presence of toxic hydrogen sulfide in the surface waters of the oceans (Knoll et al., 1996; Wignall and Twitchett, 1996; Krull and Retallack, 2000; Grice et al., 2005a; Kump et al., 2005) are some of the (possibly linked) mechanisms that are commonly invoked, but the precise process(es) that caused this crisis still remain(s) enigmatic. It has been suggested that the extinction was caused by a series of changes in the environment with several mechanisms (internal and external) contributing to the biological crisis (Erwin, 1994; Racki and Wignall, 2005; Ward et al., 2005). Scientists continue to use a variety of techniques to study PTB sections from around the world in order to ascertain a greater understanding of this mass extinction.

Fossil data are commonly used when studying PTB sections to identify extinction periods and major changes in the environment. Abundances of biomarkers; components derived from natural products in algae, bacteria, higher plants and heterotrophs can also be used to provide important palaeoenvironmental information on PTB extinction (Sephton et al., 2002; Grice et al., 2005a,b). Along with stable carbon isotopic compositions of biomarkers measured by compound specific isotope analyses (CSIA) it is possible to carry out a comparative isotopic study of both carbonates and sedimentary organic matter (kerogen) which was the primary method for looking at changes across the PTB and other boundaries, with CSIA of biomarkers a more recent and complimentary method. These complimentary approaches can be used to substantiate the notion of synchronous disturbance in oceanic and atmospheric chemistry from the isotopic changes that occur near to the PTB. In addition, palynological and fossil data can be used in conjunction with biomarkers to establish changes in the palaeoenvironment (Grice et al., 2005b).

Here we report biomarker abundances through a part of the PTB Schuchert Dal section that contains a rich marine faunal record and an excellent terrestrial palynomorph record (Looy et al., 2001; Twitchett et al., 2001). For the first time in this section, the biomarker abundances and sulfur isotopes of pyrite have been used to correlate the series of events (including changes in redox conditions) surrounding the collapse of the marine and terrestrial ecosystems through this major crisis interval.

2. Studied section

The Schuchert Dal section, located in East Greenland, comprises a well-preserved (thermally immature) PTB section with rocks containing both marine and terrestrial fossils. The sedimentary rocks are predominately fine-grained siliciclastic mud- and siltstones deposited in a shallow marine basin. Approximately 40 m of sedimentary rock is exposed in the section, spanning the contact between the Schuchert Dal Formation and the overlying Wordie Creek Formation (Twitchett et al., 2001), although only samples from the lower 20 m were analysed in this study. The PTB is defined at the basal Triassic Global Stratotype Section Point (GSSP) Meishan, South China, by the first occurrence of the index fossil *Hindeous parvus* (Yin et al., 2001). In the Schuchert Dal section, the first unequivocal specimens of this conodont species occur 23.5 m above the base of the Wordie Creek Formation, although unidentifiable fragments of *Hindeodus* sp. are encountered a few metres lower (Twitchett et al., 2001).

The Late Permian marine extinction event occurs below the first appearance of *H. parvus*, and is recognised in the Schuchert Dal section by the disappearance of Permian macro- and microfossils, a change from bioturbated to non-bioturbated siltstones, and by changes in the acritarch record preserved in the rocks of the uppermost Schuchert Dal Formation (Looy et al., 2001; Twitchett et al., 2001). This marine ecosystem collapse took place over some 0.5 m of section (Fig. 1). Immediately following this extinction interval a negative carbon isotope excursion in marine carbonate ($\delta^{13}C_{carb}$) and bulk organic matter ($\delta^{13}C_{org}$) is recorded (Twitchett et al., 2001). Associated with the marine extinctions are dramatic changes in the terrestrial plant community, shown by the abrupt changes in abundances and types of spores and pollen (Looy et al., 2001).

Although fossils of fish are common throughout the extinction–recovery interval, benthic invertebrate macrofossils do not reappear until 14 m above the base of the Wordie Creek Formation in this section, with the appearance of the bivalve *Claraia*. Despite some possible Permian records (Yin et al., 1996), and notwithstanding the fact that ancestral forms must have existed prior to the extinction event, *Claraia* is generally regarded as an Early Triassic fossil marker. The benthic ecosystem in the mudstones of the Wordie Creek Formation remains impoverished, and dominated by *Claraia*, throughout the section. Above 23.5 m, however, thin bioclastic limestone gutter casts preserve a more diverse fauna, including gastropods and echinoderms, which may have been transported from slightly shallower settings or

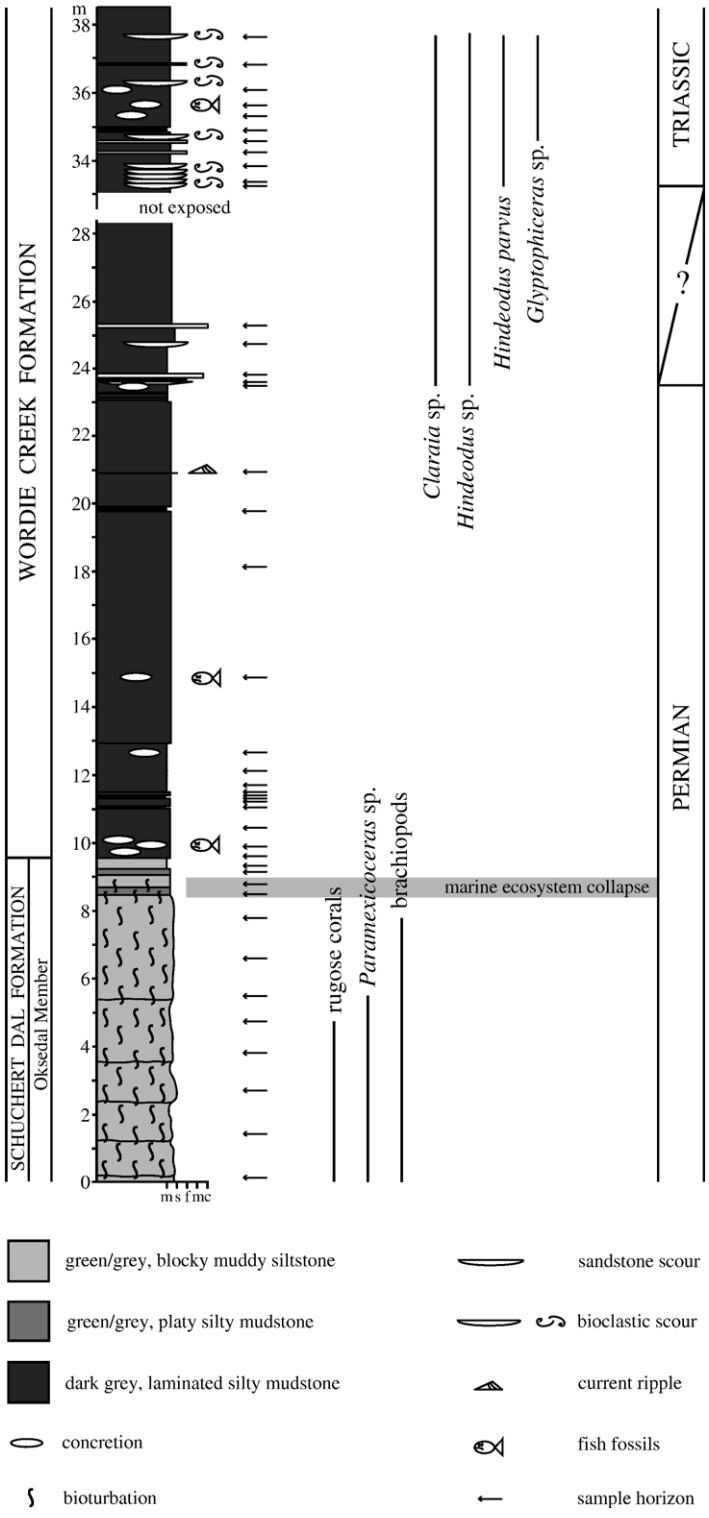


Fig. 1. Summary stratigraphy for the Schuchert Dal section (East Greenland), showing sedimentology, ranges of selected fossil taxa and sampling horizons. The first appearance datum of *Hindeodus parvus* defines the base of the Triassic, but problems with preservation mean that it is possible that *H. parvus* may be present lower down in the section (indicated by the question mark). The interval of marine ecosystem collapse corresponds to the decline and disappearance of trace fossils, Permian microfossils and acritarchs (see Twitchett et al., 2001 for details).

winnowed from the surrounding mudstones (Twitchett et al., 2001).

3. Analytical methods

3.1. Separation

Table 1 lists the 15 samples that were analysed in the present study for biomarker abundances in detail. $\delta^{34}S$ of pyrite for selected samples were also measured.

Between 30 g and 110 g of each sample was ground to a fine powder then extracted several times using an Accelerated Solvent Extractor (ASE) with a mixture of dichloromethane (DCM) and methanol (9:1).

The extractable organic matter was dried and weighed. The extract was transferred to a column of activated (120 °C, overnight) silica gel pre-eluted with *n*-pentane and then fractionated using silica gel liquid chromatography. An aliphatic fraction was eluted with *n*-pentane, the aromatic fraction with a solution of DCM in *n*-pentane (30%) and the polar fraction with equal parts of DCM and methanol. A perdeuterated internal standard was added to the aliphatic and aromatic samples for quantitation purposes.

3.2. GC–MS analysis

GC–MS analysis was carried out on an HP 5973 MSD attached to an HP 6890 gas chromatograph. The column used was a WCOT fused silica capillary column (60 m×0.25 mm i.d.) with a 0.25 μm 5% phenyl–methyl–silicon stationary phase (DB-5). The GC oven was programmed from 40 °C to 325 °C at 3 °C/min with an initial and final hold time of 1 and 40 min, respectively. Samples were dissolved in *n*-hexane and injected on-column by an HP 6890 auto-sampler. The carrier gas used was helium at a linear velocity of 1 mL/min.

Table 1
$\delta^{13}C$ ‰ of organic and inorganic carbon, $\delta^{34}S$ ‰ of pyrite and content of TRIS for East Greenland samples analysed in the present study

Sample	Height (m)	$\delta^{13}C$ (‰) organic	$\delta^{13}C$ (‰) carbonate	$\delta^{34}S$ (‰) pyrite	TRIS (wt.%)
Z1275	0.1	−22.4	−3.7		
Z1277	2.75	−22.6	−3.4		
Z1278	3.8	−23.4	−3.7	−40.7	0.5
Z1300	5.5	−23.5	−4.5		
Z1281	7.8	−22.9	−3.8	−38.4	0.2
Z1299	8.6		−3.9		
Z1298	9.35	−22.3	−3.2		
Z1285	9.6		−4.2		
Z1286	9.85		−5.1	−41.9	0.5
Z1288	11.08		−5.3	−20.7	2.6
Z1294	11.7	−32.1	−8.8		
Z1301	12.1	−32.6	−4.3		
Z1295	12.68	−30.2	−10.9		
Z1296	14.9	−32.4	−9.8		
Z1302	18.15	−28.1	−11.0	−31.2	0.1
Z1328	36.8			−14.4	0.6
Z1329	37.6			−23.2	0.5

3.3. Sulfur isotopes

Total reduced inorganic sulfur (assumed to represent pyrite) was extracted from ground sediment using the hot, acidic chromium(II)chloride distillation method (Fossing and Jorgensen, 1989). The evolved hydrogen sulfide was trapped as ZnS and quantified *via* spectrophotometry (Cline, 1969). For stable isotope measurements, ZnS was converted to Ag_2S by the reaction with $AgNO_3$ solution. $^{34}S/^{32}S$ measurements of pyrite were carried out by means of combustion-isotope ratio mass spectrometry using a Thermo Finnigan Delta Plus isotope ratio mass spectrometer coupled to a EuroVector elemental analyser via a Thermo Finnigan Conflo II split interface. The $^{34}S/^{32}S$ ratios were calculated by the integration of *m*/*z* 64 and 66 ion currents of SO_2 in the delta-notation versus the international VCDT standard. International reference materials (NBS 127, IAEA-S-1, IAEA-S-3) were used to calibrate the mass spectrometer. Reproducibility based on standards was better than ±0.5 ‰.

4. Results and discussion

4.1. Changes in abundance of biomarkers and stable isotope fractionation

Previous palynological studies on the Schuchert Dal section have highlighted a series of major changes in the terrestrial plant taxa through the latest Permian and earliest Triassic, reflected in the distribution of spores and pollen (Looy et al., 2001; Twitchett et al., 2001). Throughout the same period of time, significant changes are observed in the type and abundance of biomarkers present.

The upper Schuchert Dal Formation contains a low diversity palynological assemblage indicative of an arborescent cordiaite–conifer–pteridosperm vegetation (Looy et al., 2001). Samples from this pre-collapse interval are characterised by high abundances of dibenzofuran (DBF), dibenzothiophene (DBT) and biphenyl that peak around the marine collapse (Fig. 2). The origin of these biomarkers is not well established. Previous studies have suggested that DBF may have originated from dehydrated polysaccharides (Pastorova et al., 1994) or by the oxidative coupling of phenols (Born et al., 1989). Whilst others have proposed that

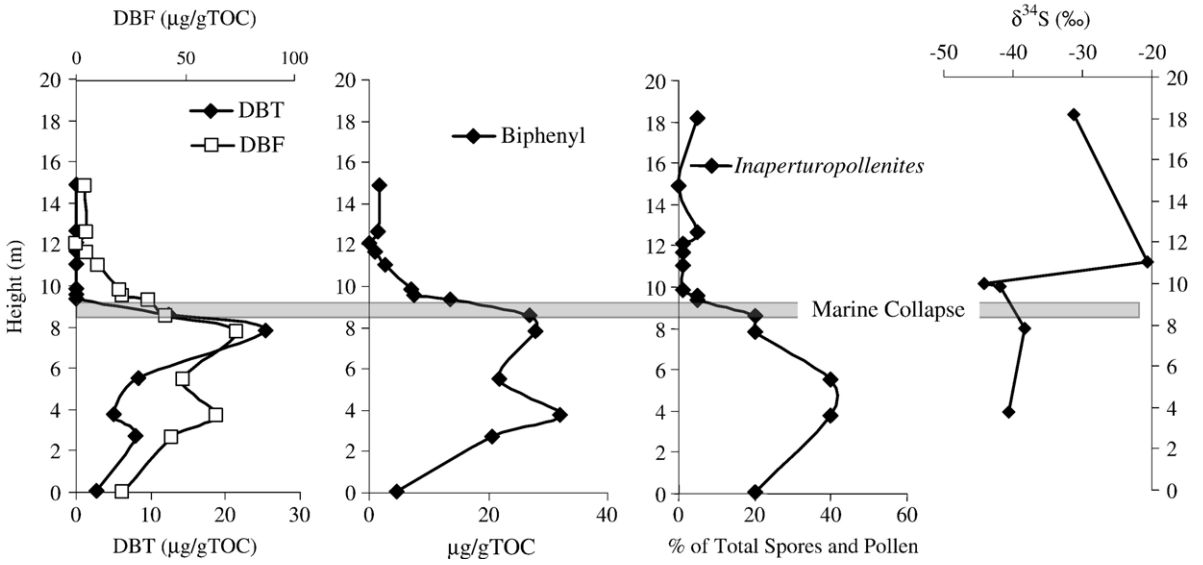


Fig. 2. A comparison of the δ^{34}S (‰) of pyrite, and the abundances of DBT, DBF, Biphenyl and *Inaperturopollenites* through the lower 20 m of the Schuchert Dal section. The pollen *Inaperturopollenites* is attributed to arborescent cordiaites, which formed an open woodland vegetation with other gymnosperms.

alkydibenzofurans could be associated with lichens (Radke et al., 2000). DBT has been associated with phenolic coupling (Trolio, 1999), biphenyls reacting with sulfur, pyrite and/or hydrogen sulfide (White et al., 1988) and diagenetic products from labile organic sulfur compounds (Rospondek et al., 1994).

Since DBF, DBT and biphenyl have similar base structures, and similar abundance curves, it is plausible that they probably derive from a common source. It has been proposed that lignin derived from the woody plants present during this period could be the source for DBF, DBT and biphenyl. Lignin is a co-polymer comprised of phenyl–propenyl alcohols (Odier and Artaud, 1992) and it is plausible that these phenolic compounds could be the precursors for DBF, DBT and biphenyl.

The environmental change recorded through the marine ecosystem collapse of the Schuchert Dal section is a changeover from well oxygenated bottom waters into fluctuating low oxygen (dysoxic to possibly euxinic) conditions; as inferred from the sedimentology and palaeontology, and, additionally, supported by the palynofacies (Twitchett et al., 2001). The redox conditions during this period of time would also favour the formation of DBF and DBT from phenolic compounds.

Just above the extinction interval, there is a dramatic decrease in the abundances of DBF and DBT which occurs at the same time as a sudden change in the stable sulfur isotopic composition (δ^{34}S) of pyrite (Fig. 2), indicating a change in sulfur cycling and associated redox conditions. δ^{34}S values of pyrite up to the extinction show a trend from Permian light isotope data towards heavier post-event isotope values, similar to the general variations observed for Australia (Perth Basin, Grice et al., 2005a) and southern China (Shangsi; Riccardi et al., 2006). This trend seems also to reflect the variations in the isotopic composition of seawater sulfate (Claypool et al., 1980; Cortecci et al., 1981; Kajiwara et al., 1994; Korte et al., 2004; Newton et al., 2004) and implies a perturbation in the sulfur cycle and a relative increase in the fraction of sulfur buried as pyrite (Kajiwara et al., 1994; Grice et al., 2005a).

Amounts of total reduced inorganic sulfur (TRIS) in the sedimentary rocks (Table 1) indicate significant sulfate limitation in PTB sediments (see Grice et al., 2005a,b). A comparison of these results for reduced sulfur with the seawater sulfate trend derived from carbonates (Kajiwara et al., 1994; Korte et al., 2004; Newton et al., 2004) indicate an overall fractionation in δ^{34}S of about 55±7‰ (pre-extinction) and about 43±14‰ (post-event). The post-event data can be explained by experimentally observed fractionation upon single-step sulfate reduction by pure cultures (Kaplan and Rittenberg, 1964). The Permian results, on the other hand, seem to exceed this range and require contributions from the oxidative part of the sulfur cycle, e.g. the activity of bacteria capable of disproportionating sulfur intermediates (Canfield, 1998; Cypionka et al., 1998; Habicht and Canfield, 2001). This is possible under conditions of an established chemocline in a euxinic water column such as the modern Black Sea (Canfield and Thamdrup, 1996, 1998), or at the chemocline of surface sediments below oxic bottom

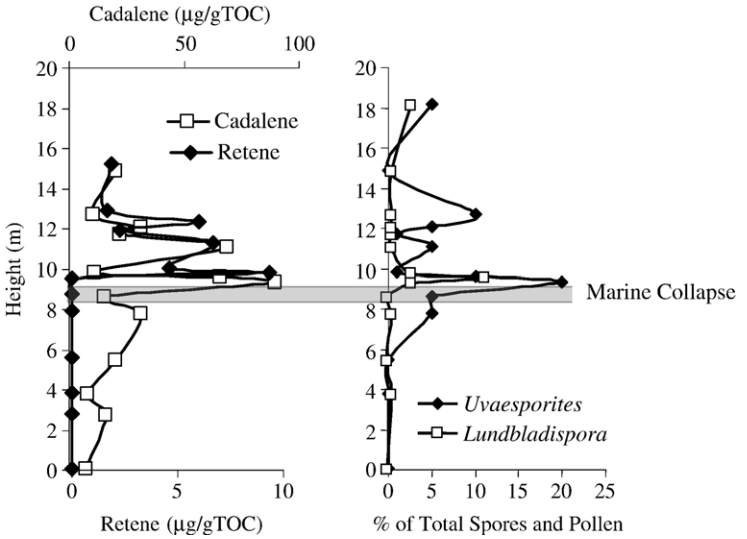


Fig. 3. The abundances of the higher plant biomarkers retene and cadalene and the abundance of *Lundbladispora* and *Uvaesporites* pollen, which are attributed to herbaceous lycopsids (Looy et al., 2001).

waters (Canfield and Thamdrup, 1996). Kajiwara and Kaiho, (1992) used a comparable range of isotope values to differentiate between anoxic and oxic conditions, which are consistent with the sedimentological and palynological observations of the present study.

The redox change inferred in the present study for the PTB sediments is supported by facies evidence from the same and neighbouring sections (Wignall and Twitchett, 2002). Oxic conditions in the upper Schuchert Dal Formation would favour the formation of DBF *via* the oxidative coupling of phenols. Oxic conditions or at least only temporarily sulfidic bottom waters, as observed in the modern upwelling region off Namibia (Emeis et al., 2004), would also allow the reoxidation of hydrogen sulfide to take place, meaning that greater quantities of sulfur intermediates would be available to react with organic matter to form compounds such as DBT. It has previously been reported that concentration of hydrogen sulfide is thought to be a limiting factor in the formation of thiophenes in sediments (Katsumata and Shimoyama, 2001).

A sudden decline in abundance and diversity of several typical end Permian pollen taxa, just below the base of the Wordie Creek Formation, is direct evidence for the ecosystem collapse (Looy et al., 2001; Twitchett et al., 2001). Over a very short stratigraphic section, which probably equates to a very short duration of time (Twitchett et al., 2001), assemblages dominated by gymnospermous pollen are replaced with spore-dominated ones. These latter assemblages represent the earliest phase of repopulation; the vegetation most likely consisted of ferns, lycopsids and seedferns of small stature (Looy et al., 2001). This lycopsid-dominated interval in the basal Wordie Creek Formation is characterised by high abundances of the biomarkers retene and cadalene (Fig. 3). These biomarkers are aromatic hydrocarbons which are generally derived from land plants (Simoneit, 1977). These results indicate that the herbaceous plants present, represented by spore taxa such as *Uvaesporites* and *Lundbladispora,* are a likely source of retene and cadalene.

Higher up in the Wordie Creek Formation, the lycopsid signal declines. Pollen from shrubby seedferns and cycads becomes more dominant, and several end-Permian gymnosperms apparently re-appear (Looy et al., 2001). Samples from these levels in the lower Wordie Creek Formation contain a high abundance of plant waxes as well as pristane and phytane (Fig. 4). These data indicate that plants comprising these post-extinction gymnosperm shrublands (*Ephedripites*), could be a dominant source for these biomarkers, although other sources such as phytoplankton cannot be excluded, especially since pristane and phytane are also abundant in samples where acritarchs are significantly abundant (Grice et al., 2005a).

4.2. Global comparison

The presence of DBF in PTB samples has previously been identified (Sephton et al., 2005), and it was proposed that the furan compounds were derived from polysaccharides in land plants and the rapid burial of soil-eroded material resulted in the preservation of the furan structures (Sephton et al., 2005). A large increase

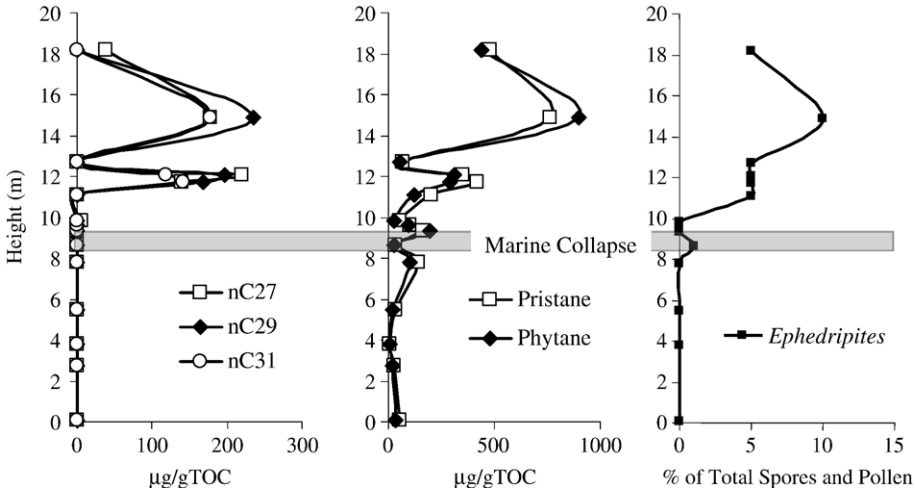


Fig. 4. The abundance of plant waxes, pristane (Pr), phytane (Ph) and the palynomorph *Ephedripites* pollen (Looy et al., 2001).

in the abundance of DBFs and total organic carbon content was observed during the extinction event in a section in northern Italy and was inferred to be the consequence of destruction of land vegetation and enhanced soil erosion (Sephton et al., 2005), although such erosive events are rather short-lived. Given that the DBT and DBF are high in samples spanning a significant interval of time, it is suggested that an increase terrestrial organic matter to the marine setting was a dominating factor and was not associated with enhanced soil erosion. Although peak abundance in the Schuchert Dal section occurs during the collapse interval, DBF increases prior to the extinction event (Fig. 2) when there is no palynological evidence of disturbance to the terrestrial flora, and prior to any changes in the marine ecosystem. In addition, the extinction–soil erosion scenario of Sephton et al. (2005) does not account for the high abundance of DBT and biphenyl also observed.

The trends in biomarker distribution and redox conditions of the depositional environment are not unique to the Schuchert Dal section; similar trends have also been observed in the Hovea-3 PTB section from Western Australia (Nabbefeld and Grice, unpublished results). Just like the Schuchert Dal section, high abundances of DBF and DBT were present in the Hovea section deposited under oxic conditions leading up to the extinction whilst minimal amounts were observed in samples deposited under euxinic conditions in the period after the commencement of the extinction. The interval of the Hovea-3 section that was deposited under oxic conditions, like the Schuchert Dal section is also dominated by woody material and charcoal as evident from the palynology described by Thomas et al. (2004). It is suggested that two processes are probably operating here to account for the changes in palynofacies and biomarker distribution: 1) a change in redox conditions, and 2) extinction and/or marine transgression accounting for the disappearance of preserved woody material.

When comparing the covariation of pyrite sulfur with organic matter contents in PTB section sediments from Greenland with results from southern China and Western Australia (Fig. 5), the Greenland results are at the low-sulfur and organic matter end of the range and are similar to those shown for the Meishan section. A comparison of the different PTB pyrite and carbonate-bound sulfur isotope records found at different locations worldwide (Kajiwara et al., 1994; Korte et al., 2004; Newton et al., 2004; Grice et al., 2005a; Riccardi et al.,

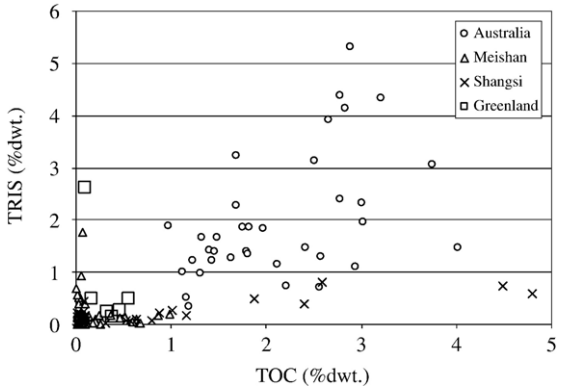


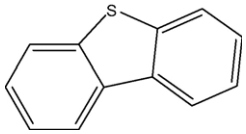
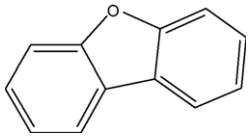
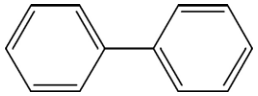
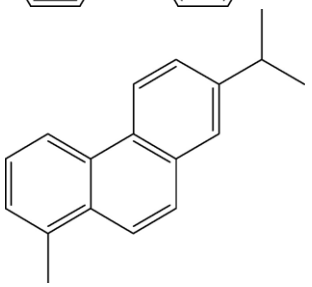
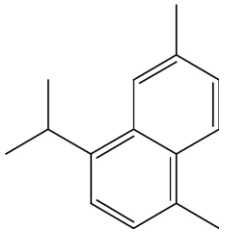
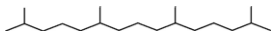
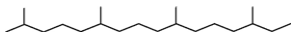
Fig. 5. Covariation of organic carbon and pyrite sulfur (TRIS) in different PTB intervals. Australia contents (% dry weight) in different PTB intervals. Australia: (Grice et al., 2005a) Shangsi and Meishan (Riccardi et al., 2006).

2006) generally reflect perturbations in the sulfur cycle and also are superimposed by regional effects.

5. Conclusions

Biomarker abundances and sulfur isotopes of iron sulfide minerals have been reported through a part of the PTB Schuchert Dal section that contains a rich marine faunal record and an excellent terrestrial palynomorph record. The upper Schuchert Dal Formation, leading up to the collapse of the marine ecosystem, was dominated by a high abundance of DBF, DBT, biphenyl and palynomorphs ascribed to an arborescent cordiaite–conifer–pteridosperm terrestrial vegetation (Table 2). Considering DBF, DBT and biphenyl have similar base structures, and similar abundance curves, it is plausible that they derive from a common source. This source is most likely to be lignin originating from the woody plants abundantly present during this period. The stable sulfur isotopic composition of pyrite throughout this same period indicates reactions in the oxic part of the sulfur cycle took place, probably leading to an enhanced abundance of sulfur intermediates, supporting evidence from facies and fossil analysis. The availability of oxygen and sulfur during this time could have favoured the formation of DBF and DBT from a lignin source. Just above the

Table 2
Summary of the hydrocarbon components and their structures and assigned origins with associated palynomorphs in Schuchert Dal section (East Greenland)

Biomarker	Structure	Origin assigned (this study)
Dibenzothiophene		Lignin in arborescent cordiaite–conifer–pteridosperm vegetation. E.g. *Inaperturopollenites*
Dibenzofuran		Lignin in arborescent cordiaite–conifer–pteridosperm vegetation. E.g. *Inaperturopollenites*
Biphenyl		Lignin in arborescent cordiaite–conifer–pteridosperm vegetation. E.g. *Inaperturopollenites*
Retene		Herbaceous plants E.g. *Uvaesporites* and *Lundbladispora*
Cadalene		Herbaceous plants E.g. *Uvaesporites* and *Lundbladispora*
Pristane		Gymnosperm shrubs E.g. *Ephedripites*
Phytane		Gymnosperm shrubs E.g. *Ephedripites*

extinction interval, there is a dramatic decrease in the abundances of DBF and DBT which coincides with a change of redox conditions and an absence of woody material. This trend is not unique to the Schuchert Dal Section, similar trends have also been observed in the Hovea-3 PTB section from Western Australia. Sulfur isotopic data changes along with green sulfur bacterial derived biomarker abundances have been shown to support the presence of toxic H_2S in the zone of light penetration during the PTB in Western Australia and South China (Grice et al., 2005a).

Following the decline of the cordiaite–conifer–pteridosperm vegetation, lycopsids became more prominent. This lycopsid-dominated interval in the basal Wordie Creek Formation is characterised by high abundances of the biomarkers retene and cadalene. These results indicate that the herbaceous plants present, represented by spore taxa such as *Uvaesporites* and *Lundbladispora,* are a likely source of retene and cadalene. Higher up in the Wordie Creek Formation, the lycopsid signal declines and shrubby seedferns, cycads and gymnosperms become more dominant. These plants could be a dominant source for the biomarkers pristane, phytane and plant waxes, which are profuse throughout this interval.

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