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Biomarker and Isotopic Trends from a Permian-Triassic Sedimentary Section at Kap Stosch, Greenland

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Abstract

Here we report a geochemical study of a composite sedimentary section that captures the Permian-Triassic (PT) transition at Kap Stosch, East Greenland. The samples were from the

original paleontological collection of early PT researchers Teichert and Kummel. The sedimentary rocks, which include samples from four proximal outcrop localities, were deposited during the Late Permian and Early Triassic at the margin of the Boreal Sea with a depositional hiatus and erosional event of unknown duration. Bulk geochemical measurements for most of the samples show good correlation between S2 and TOC % which, combined with low Tmax values, indicate that the organic matter that formed contemporaneously with sediment deposition is of relatively low thermal maturity. Significant changes occur up through the PT transition that include a pronounced switch in the $\delta^{13}C$ of TOC from high values near -24‰ to lower values averaging -32‰ VPDB that is matched by a significant increase in the hydrogen index of the kerogen. The Permian samples containing ^{13}C-enriched organic matter also have low Rock-Eval hydrogen indices and anomalous pyrograms indicating that the kerogen is heterogeneous in terms of source and maturity. Microscopic analysis of the kerogen concentrates confirmed this; samples from the Permian section contained an abundance of black, angular fragments of woody tissue in addition to gymnosperm pollen and spinose acritarchs of the *Vittatina*-Association of Balme (1979). In contrast, black woody tissue was rare in samples from the Early Triassic section with well-preserved gymnosperm and lycopod pollen and spores of the *Protohaploxypinus* and *Taeniaesporites* associations. In respect to the biomarker ratios, there is a predominance of values for Permian samples indicating moderate thermal maturity with the 20S/(20S+20R) ratios of the C_{27} steranes, the C_{31} homohopane 22S/(22S+22R) ratio, as well as the Ts/(Ts+Tm) ratio all being higher than those for Triassic sediments. The marked switch in maturity indicators across the PT transition suggests an unconformity consistent with palynological observations for this section. The pristane/phytane ratios are low, and the homohopane indices high, indicating anoxic conditions prevailed throughout deposition of the sediments. Additionally, markers of photic zone euxinia (i.e. isorenieratane, crocetane and 2,3,6-aryl isoprenoids) were present in all samples and all show a maximum abundance in sediments closest to the PT transition. The C_{33} *n*-alkylcyclohexane, a potential event marker for the onset of the biotic crisis in the Late Permian, was identified in sedimentary rocks at, and immediately following, the paleontological PT transition. Despite the distinct change in lithology across the PT transition, the redox and Chlorobi-derived biomarkers indicate that photic zone euxinic conditions prevailed throughout the deposition of the Kap Stosch sedimentary sequence.

Key Words:

1 Introduction

1.1 Boreal Sea at the Permian-Triassic Boundary

The sedimentary section exposed at Kap Stosch was deposited at the margin of the nascent Boreal Sea, an epicontinental basin forming in the northwest of Pangea in the late in the Permian Period. Sedimentary rocks deposited beneath this sea and a connecting basin further inland, the Zechstein Sea, can be found throughout East Greenland (Figure 1). Sediments from the latter have been studied for presence of biomarkers in a wide range of European sections (Bechtel and Püttmann, 1992; Grice et al., 1996b, 1997; Pancost et al., 2002).

Previous studies of an expanded sedimentary succession of 40 meters in Jameson Land in East Greenland (Twitchett et al., 2001; Wignall and Twitchett, 2002) report paleontological and sedimentological results for the Permian-Triassic (PT) marine ecosystem collapse. The authors provide details of conformable shale contacts within this section that appear to capture the complete PT transition. Framboidal pyrites just beneath the boundary and other observations indicate deposition under anoxic conditions. Evidence for increasing but intermittent oxic conditions was seen beginning in the Triassic period, but the return to oxic conditions was much more gradual than the sudden onset of anoxia. The documentation of anoxia in this region during the Late Permian period has been supported by other studies using different methodologies. For example, one study of a section in East Greenland focused on the size and stable sulfur isotopic composition of framboidal pyrites in the Ravnefjeld Formation (Nielsen and Shen, 2004). The presence of smaller pyrites within a limited range was considered indicative of the presence of sulfidic deep water during the late Permian period. The large fractionation in $\delta^{34}S$ of pyrite led the authors to conclude that these values may represent different forms of sulfur cycling beneath a sulfidic water column.

Additionally, several studies have focused on the biogeochemistry of the Late Permian Kupferschiefer succession of the Lower Rhine Basin, Germany. These sediments, deposited

at the southern margin of the Zechstein Sea, display molecular evidence for microorganisms that thrive in euxinic environments. Initially Grice and co-workers (1996b) identified both saturated and aromatic carotenoid-derived hydrocarbons and were able to link these compounds to the green sulfur bacteria (Chlorobi) by virtue of their low $\delta^{13}C$ values. In a second study (Grice et al., 1996a), the authors identified Me *i*-Bu maleimide, specific to the bacteriochlorophyll *c, d, (e)* of the Chlorobi as well as the less specific Me *n*-Pr and both were enriched in ^{13}C relative to other maleimides. A follow-up study of different samples from the Kupferschiefer deposit of the Lower Rhine Basin also documented the presence of Me *i*-Bu in maleimides in both the free bitumens and in oxidized porphyrin fractions (Pancost et al., 2002).

A study of the polycyclic aromatic hydrocarbons from just below the PT boundary in the Schuchert Dal section in Jameson Land found high abundances of dibenzofuran (DBF), dibenzothiophene (DBT) and biphenyl (Fenton et al., 2007). These authors attributed their observations to terrestrial organic matter input that decreases synchronously with the marine collapse and onset of euxinic conditions. They also measured the $\delta^{34}S$ values for pyrite and found a positive excursion concurrent with the increase of DBF and DBT. Together, these two observations were considered by the authors to be indicative of a trend in the redox state toward the onset of anoxic conditions at the PT boundary in the studied interval. Deep-water anoxia in the Zechstein Sea during the Late Permian period could be the result of the restricted nature in the basin. However, the evidence for photic zone euxinia presented in these studies above indicates that the basin must have been stratified in the shallow waters, similar to the modern-day Black Sea, at least intermittently.

PAH distributions for the Kap Stotsch section have been reported in an earlier study comparing PT sections worldwide (Nabbefeld et al., 2010a). The key observations were detection of enhanced concentrations of putative combustion-derived PAH including pyrene, fluoranthene and benzo [*a*] anthracene in Late Permian samples from the section and a major spike in DBT abundances at the Kap Stotsch PT transition.

1.2 Kap Stosch, Greenland

The Kap Stosch region in East Greenland was first studied as an outcrop of a PT boundary section in the 1920s and samples from the section described here were collected in 1967 (Teichert and Kummel, 1972, 1976). These studies are the most complete of this section to date. The sampling of Teichert and Kummel was focused on two discrete areas spanning a range of about 15 km. The first area is southwest of Kap Stosch and includes outcrops between rivers designated as 0 and 1. The second area is southeast of Kap Stosch between the rivers designated as 6 and 14. (See Figure 1.) Permian units in these locations include those previously referred to as "*Productus* limestone" and "*Martinia* shale," that have been grouped together as the Late Permian Foldvik Creek Formation (Birkelund et al., 1974); the uppermost Permian rocks are identified by the occurrence of the ammonoid *Cyclolobus* (Teichert and Kummel, (1976). The Triassic sedimentary rocks include *Glyptophiceras* beds as well as broken and re-worked fragments of Permian bryozoans and brachiopods – "mixed faunas" as identified by the authors – and are correlated by the Triassic fossil, *Otoceras woodwardi boreale* (Teichert and Kummel, (1976). In addition, Teichert and Kummel report coalified wood fragments and glassy coal stringers from the Lower Triassic in the river 1 locality. In a palynological analysis of the Kap Stosch section, Balme (1979) assigned all palynofloras from the Permian to the *Vittatina*-Association, characterized by low species diversity, the eponymous, non-saccate gymnosperm pollen, and absent plant spores. The areas to the southwest and southeast have two distinct plant microfossil associations, assigned to the *Protohaploxypinus*-Association, and the younger *Taeniaesporites*-Association, indicating Triassic terrestrial communities from two periods migrated through the area. Spinose acritarchs are common in the Triassic palynofloras, in the latter association they accounted for up to 95% of the total microfossil suite (Balme 1979). Also occurring in, and described from the *Taeniasporites*-Association, are cyst-shaped bodies of *Tympanicysta stoschiana*, considered as either algal remains, and assigned to *Reduviasporonites chalastus* (Foster et al., 2002), or remains of fungi that contributed to the devastation of vegetation at the close of the Permian (Sephton et al., 2009; Visscher et al., 2011). These fossils occur widely around the world in PT transition sections. Relative to the exposures in Jameson Land, the different lithologies in Kap Stosch likely correspond to the Permian Martinia Limestone and Schuchert Dal Formation and the Triassic Wordie Creek Formation discussed by Wignall and Twitchett (2002).

In their 1976 paper, Teichert and Kummel report that in the first area (Localities 0 and 1, Figure 1), the exact placement of the PT boundary is difficult to determine because the likely transition interval is obscured due to solifluction. In the second area (Localities 6.75 and 13.75, Figure 1) the PT transition is more clearly exposed and defined by a thin basal Triassic conglomerate. Where it is exposed, the difference in lithology across the transition is drastic and abrupt, changing from the dark colored shale and siltstone facies of the Permian rocks to the medium greyish brown arkosic sandstone of the Triassic rocks. According to Teichert and Kummel (1972), the Permian sediments were deposited in a moderately shallow shelf setting. Across the boundary, the Triassic sedimentary rocks were deposited after some local uplift in a shallower marine environment, and the Permian-age fossils of the "mixed faunas" in the Early Triassic rocks are interpreted as the result of redeposition from local land areas (Teichert and Kummel, 1976). Based on this fossil evidence, the work by Teichert and Kummel demonstrated that the Triassic is unconformable on the Permian, and that in the Kap Stosch area, there is a non-depositional interval potentially equivalent to the Changhsingian Stage. However, Balme (1979) concludes that the palynological evidence does not indicate extensive reworking of fine clastic material from Permian types in the Triassic, although this certainly does not preclude the mixing of the larger fossils of the "mixed faunas" which would not be degraded to the same extent during weathering and deposition.

Samples from four river outcrop localities were selected and have been arranged in relative stratigraphic order, using faunal data from Teichert and Kummel (1976) and sample information presented by Balme (1979) to derive a composite stratigraphic section (Figure 1). As the PT transition is obscured in these localities, the boundary has therefore been assigned to a level between the lithologic sections that are established as Permian and Triassic in age, and the composite section can be used to examine large-scale changes that occurred on either side of the transition (Teichert and Kummel, 1972). Given the historic nature of the samples, and the recent organic geochemical findings from other, nearby, East Greenland sections (Fenton et al., 2007; Looy et al., 2001; Sephton et al., 2005; Twitchett et al., 2001; Visscher et al., 2004), Kap Stosch is a potentially valuable PT boundary section both to interpret environmental information from biomarker data and to explore the nature

of the proposed unconformity by comparing it with other sections worldwide.

2 Methods

Outcrop samples from Kap Stosch were prepared at Geoscience Australia where bulk geochemical analyses, including Rock-Eval pyrolysis (Rock-Eval II Instrument) and $\delta^{13}C_{org}$ measurements (Themo-Finnigan Mat 252 instrument equipped with dual inlet system) were performed as described earlier (Strauss et al., 1992). Because of the low TOC of many samples, kerogen enrichment was conducted using treatment with HCl and HF. No heavy liquid separations were attempted, however. These partially 'enriched' samples were then subjected to a further round of Rock-Eval pyrolysis and TOC analysis using a Rock-Eval VI instrument.

For palynological examination (Wood et al., 1996), samples were cleaned of any obvious contamination and crushed to pea size fragments. These were digested using HCl and HF to remove carbonate and siliceous minerals. After neutralization, the residue was processed through a zinc bromide SG 2.0 heavy liquid separation to recover the organics. A representative slide of kerogen material was produced with this residue. A portion was sieved through 20 and 10 micron woven sieve cloths and slides were then made of the filtered material. Oxidation was performed on remaining sieved residue using hot HNO_3 followed by neutralization with 5% KOH and re-filtering. Further slides were produced with the oxidised material.

The remaining powdered whole rock samples were analyzed for lipid biomarkers at the Massachusetts Institute of Technology. Because of their limited size, samples were extracted manually from the powdered rock fraction using a 9:1 dichloromethane (DCM) to methanol (MeOH) solution and ultra-sonicated in a VWR Aquasonic 150HT. This process was repeated three times, and the extracts pooled, filtered and then treated with activated copper to remove elemental sulfur. This total lipid extract was separated chromatographically on a silica gel column (~1.5ml dead volume) into three fractions yielding the saturated hydrocarbons, aromatic hydrocarbons and polar compounds by eluting with solvents of increasing polarity (hexane, 4:1 DCM:hexane, and 4:1 DCM:MeOH, respectively). The

saturated and aromatic fractions were weighed and re-suspended in hexane with either d4-ααα-ethylcholestane (20R) or D_{14} p-terphenyl added, respectively, as internal standards.

Both the saturated and aromatic fractions were analyzed by gas chromatography coupled to mass spectrometry with a HP 6890 GC attached to an Agilent 5973 mass selective detector (MSD). Saturated hydrocarbons were analyzed in the full scan mode while aromatics were run in selected ion monitoring (SIM) mode. The saturated fraction was also analyzed using gas chromatography, again using a HP 6890 GC, coupled to an AutoSpec Ultima. The GC was fitted with a DB-1 fused silica capillary column (60 m; 0.25 mm I.D.; 0.25 μm film thickness; J&W Scientific) and He was used as carrier gas. The GC temperature program was: 60 °C (2 min) to 150 °C at 10 °C min^{-1}, to 315 °C (held 24 min) at 3 °C min^{-1}. The AutoSpec source was operated in electron ionization (EI, 70 eV) mode at 250 °C, with 8 kV accelerating voltage for multiple reaction monitoring (MRM) function where two groups of precursor-product transitions were monitored with a cycle time of ca. 1.5 seconds, the first for cheilanthanes and short-chain steranes and the second for C_{26}-C_{30} steranes and C_{27}-C_{35} triterpanes. The GC-MS-MS data were quantified using the D4 internal standard without taking into account potential differences in response factors. The hydrocarbons were identified by their mass spectra (on the GC-MSD) and comparing their retention times to a synthetic reference oil (AGSO Standard Oil). Aryl isoprenoids in the aromatic fraction were identified by direct comparison of relative retention times with the same compounds present in the aromatic fraction of a sample of Barney Creek Formation (Brocks et al., 2005). The distributions of other aromatic compounds, including PAH, have been reported earlier (Nabbefeld et al., 2010a).

3 Results and Discussion

3.1 Microscopy

Microscopic examination of the enriched kerogens and palynological preparations revealed significant compositional differences in the preserved OM types from the different localities (Table 1). Samples from Locality 0 contained abundant and equi-dimensional fragments of black woody tissue as well as some cuticle, very sparse fragments of gymnosperm pollen, foram tests and spinose acritarchs of *Michrystridium* spp. The identified palynomorphs conformed to the *Vittatina*-Association described by Balme (1979). The other Permian samples, from Locality 13.75, contained a much higher content of organic remains with only a few percent of finely comminuted black woody material. The identifiable palynomorphs, mostly gymnosperm pollen grains with rare foram linings, also conformed to the *Vittatina*-Association but were much more poorly preserved with the bulk of specimens being heavily corroded. Samples from the Triassic Locality 1 were well preserved with abundant organic remains. Gymnosperm pollen dominated, including *Lunatisporites*, various lycopsid spores and lycopsid tetrads as described by Looy and co-workers (Looy et al., 2001). *Tympanicysta stoschiana* and resin-like bodies were present in sample 19990449. Compared to the above samples, preservation was poor in those from Locality 7.5. There were degraded taeniate disaccate pollen, lycopsid spores identifiable as *Densoisporites nejburgii* and some spinose acritarchs. Well preserved *Ephedripites* spp. and occasional resin-like bodies were noted in several samples. Likely reworked *Vittatina* and *Michrystridium* spp were observed rarely and *Tympanicysta stoschiana* (syn. *Reduviasporonites stoschianus*) and resin-like bodies were present in sample 19990455. Finely pulverised black woody material comprised only a few percent of the organic material in the Triassic samples. In summary, the age constraints of Balme (1979) were well supported by the identifiable floral elements, the degree of fossil preservation varied from one locality to another as did the colour of the organic matter. Palynomorphs from the Triassic, especially those from Locality 1, were often pale yellow-orange and there was a significant contribution of black to dark brown woody tissue to the OM present in the samples from Locality 0.

3.2 Bulk Geochemical Data

Rock-Eval analysis was conducted on both whole rock powders and kerogen-enriched samples formed by demineralization using strong hydrochloric and hydrofluoric acids. This resulted in a ~ 10-fold increase in TOC but the samples still contained considerable undigested mineral matter. The total organic carbon (TOC) contents of the whole rock samples vary from 0.2-8.0 wt% for samples from the latest Permian period and others having a more constant value of ~0.3 wt% from the Triassic period (Table 2). The S2 peak in the Rock-Eval pyrograms (Espitalie et al., 1985) provides a measure of the hydrocarbons produced during kerogen pyrolysis of non volatile organic matter (OM) over a range from 300° to 550° C and, for the mostly low TOC whole rock data, we see generally low S2 and low HI values indicating that caution should be exercised in their interpretation. This is because, firstly, the peaks are small and, secondly, there may be a mineral matrix effects obscuring informative trends in the data. Demineralization and re-analysis confirms this and the data now cluster into two distinct types, one with low S2 and (23-54 mg HC/g TOC) HI values that dominate the base of the section and others with higher S2 (90-436 mg HC/g TOC) and HI values that predominate in the Triassic (Fig. 2a-d). A distinct shoulder on the S2 peak in the most of the Locality 0 sample pyrograms (data not shown) suggests that the OM in these samples is heterogeneous in terms of its hydrocarbon potential consistent with the analysis of the recovered kerogens and palynofloras from these samples. (See Balme 1979 and Table 1). The most likely scenario to explain the present data is that the OM in samples from Locality 0 comprises two end-member types one of which produces little hydrocarbon on pyrolysis and another that, gram-for-gram, produces more. In the case of these samples, one should be cautious in interpretation of both Tmax and bulk $\delta^{13}C_{org}$ values.

The Rock-Eval data and subsequent evaluation of biomarker maturity parameters of the whole rock powders show no evidence for the samples being affected by post-depositional hydrocarbon migration. High contents of free bitumen (seen as S1 in Rock-Eval data) and good correlation between S2 and TOC% for the demineralised samples (Fig. 2 a and b) indicate that the OM from Kap Stosch is of moderate to low thermal maturity and, for samples other than Locality 0, dominated by hydrocarbon-prone kerogen. This also suggests that there is minimal oil migration in this locality and that the biomarkers should be primarily autochthonous.

The average $\delta^{13}C$ of organic carbon ($\delta^{13}C_{org}$) in the Kap Stosch samples is -24.7‰ for the Permian rocks and -31.2‰ in the Triassic rocks and follow a general trend of decreasing ^{13}C-enrichment up to the PT transition, where the minimum values are recorded, before a gradual increase toward the top of the section. The most ^{13}C-enriched samples are those from river locality 0 and that are also distinguished by their low HI values. Overall, the data show a similar pattern of values to that reported for the Jameson Land section to the south (Twitchett et al., 2001) and, despite the very coarse sampling here, appear to mirror the trend seen in $\delta^{13}C_{org}$ from the type section at Meishan (Cao et al., 2009). However, caution is required to interpret these trends in sections with mixed marine and terrestrial organic inputs. For example, Foster et al. (1997) suggested that fluctuations in the isotopic compositions of sedimentary organic material in Western Australia PT sections of the Perth and Bonaparte Basins were indicative of shifts in the nature of the primary inputs and this was supported by microscopic analyses of the kerogen macerals. In their 1997 study, Foster and colleagues observed that Triassic samples with low $\delta^{13}C$ values (~-30‰) showed a predominance of pale-colored acritarchs and other forms of immature marine organic matter while samples with high $\delta^{13}C$ values (~-24‰) were dominated by terrestrial inputs such as fragments of vitrinitic wood and coal. This pattern was also documented in a PT boundary section (Hovea-3 well) from the Perth Basin, Western Australia from $\delta^{13}C_{org}$ and compound specific isotope data of selected biomarkers (Foster et al., 1997; Grice et al., 2005a; Grice et al., 2007). An important inference we can make from the significant maturity difference between Permian and Triassic organic matter in the Perth and Bonaparte basins is that the isotopic differences reflect not only the contrast in biological origin but also a potentually significant difference in age.

The distinctive character of the Kap Stotsch Locality 0 samples is evident from cross plots of $\delta^{13}C$ versus HI values, and samples coded for the age of the rocks, samples from either side of the PT transition form distinct clusters with the exception of a single sample (Fig. 2c). The disparate behaviours of $\delta^{13}C_{org}$ and HI data for the Kap Stosch Locality 0 samples compared to the others, as well as microscopic analysis of the kerogen concentrates, are similar to observations made in PT sections in the Perth and Bonaparte basins, Australia

(Foster et al., 1997). These Locality 0 samples have $\delta^{13}C_{org}$ values typical of Permian coals despite their predominantly marine character, as attested by the marine macrofossil and biomarker (see below) contents. Accordingly, we cannot confidently interpret the bulk isotopic compositions of OM in these samples as being diagnostic for contemporaneous marine organic matter. On the other hand $\delta^{13}C_{org}$ values from the other localities more likely reflect the authigenic nature of the kerogens and, despite their mixed marine and non-marine compositions, roughly track the isotopic composition of co-eval marine inorganic carbon (Cao et al., 2009) that, in appropriate continental shelf settings (Cao et al., 2010), reflect perturbations in the carbon cycle related to the extinction event.

3.2 Biomarkers

3.2.1 Biomarkers Influenced by Maturity and Lithology

The 20S/(20S+20R) ratio of the C_{27} sterane and the 22S/(22S+22R) ratio of the C_{31} homohopane are commonly used in concert to evaluate thermal maturity of sedimentary OM. When controlled by maturity alone, the hopane isomerization reaches a stable endpoint (~60%) before peak hydrocarbon generation, while the sterane isomerization reaches a stable endpoint (~55%) at a higher maturity and closer to the end of peak generation (Peters et al., 2005). Below the assigned boundary at Kap Stosch, the values for these proxies are significantly higher than those in the transition and above the boundary. It is difficult to rationalize how Triassic sedimentary rocks, which show evidence of sediment input from the "mixed faunas," would show significantly lower maturity proxies than the Permian sedimentary rocks if they were only separated by tens of metres in burial depth as suggested by their present day stratigraphic separation (Fig. 1). Based on inspection of the kerogen slides (Table 1), the Permian sediments include an admixture or more mature and re-worked organic. Additionally, they saw somewhat deeper maximum burial depths and the present-day maturity differences reflect the existence of a significant unconformity. Another potential complication is that the measured biomarker maturity relationships for these biomarkers are responding to changes in facies and lithology, a situation that has been observed previously (Cao et al., 2009; Moldowan et al., 1986; ten Haven et al., 1986). A cross-plot of these two parameters (Fig. 2e) shows a distinct correlation, with the grouping of the samples reflecting different sections measured from the PT transition.

The ratios of C_{30} βα hopane (moretane) to C_{30} αβ hopane (hopane) and C_{27} 17α-trisnorhopane (Tm) to C_{27} 18α-trisnorhopane (Ts) reflect more complex isomerizations and reactions than those described above. These ratios are generally shown to increase with burial depth and thermal maturity, however, they can also be significantly affected by changes in facies and organic matter inputs (Moldowan et al., 1986). Distinct changes in the Ts/(Ts+Tm) ratio and moretane/hopane ratio across the transition that were observed in the Kap Stosch section are similar, though not as significant as the pattern in C_{27} sterane and C_{31} homohopane isomerization (Figs 4 and 5). When one examines the cross-plot of moretane/hopane ratio versus Ts/(Ts+Tm) ratio coded to indicate the localities of the samples (Fig. 2f), the anti-correlation between these proxies in this section is evident with the lithologic change across the transition also being a factor in the grouping of samples. However, there is also a clustering of samples according to section in the cross-plot that reflects additional facies and lithological controls in these triterpane ratios (Peters et al., 2005). These correlations are not as clear-cut as in the S/(S+R) ratios, but the two-stage pattern across the transition that was measured in all of these proxies is consistent with the idea that lithology and organic matter sources are influencing these proxies in this relatively low-maturity section.

The rearrangement of sterenes to diasterenes in sediments has been shown to be catalyzed by the Lewis acid character of clays (Rubinstein et al., 1975). Thus, the ultimate complement of the resultant steranes and their rearranged counterparts, where the latter are more thermodynamically stable, is a function of both thermal maturity and lithology (Peters et al., 2005). In the Kap Stosch section, like the biomarker ratios discussed above, the values for both the C_{27} and C_{29} diasterane/sterane ratio are distinctly different on either side of the PT transition, with higher values in the Late Permian giving way to lower values in the Triassic (Fig. 4 and Table 3). In a cross-plot of C_{29} diasterane/sterane versus C_{27} diasterane/sterane (Fig. 2h), this is evident by the fact that the Permian and Triassic samples fall on a common trend line and with the Permian showing overall higher values. However, we also note that the values for C_{27} dia./reg. are consistently a little higher than their C_{29} counterparts suggesting subtle source and lithological influences as well.

3.2.2 Biomarkers for Depositional Environment

The C_{30} sterane index, the ratio of C_{30} steranes (24-*n*-propylcholestanes) to total steranes, identifies marine input to sedimentary rocks. A C_{30} sterane index greater than 4% is generally considered indicative of significant contributions from marine pelagophyte algae and therefore a marine depositional environment (Peters et al., 2005). Although the macrofossils identified in Kap Stosch samples are from marine organisms (Teichert and Kummel, 1972, 1976), the values for this proxy are low, with the average value being ~2.5% and with values in the Triassic generally lower than those in the Permian. The highest C_{30} values measured were in samples from the latest Permian rocks where they reach a maximum of 7.5% (Figure 3a) in samples from the most distant locality, River 13.75. The patterns in this proxy values agree with the paleontological observations of Balme, Tiechert & Kummel for Kap Stotsch being a predominantly marine sedimentary section with variable inputs of both Permian and Triassic palynofloras. However, the C_{27}/C_{29} sterane ratio (Fig. 2d) which is typically >1 in marine-dominated samples is enigmatic in PT sections where C_{27} steranes are commonly subordinate to C_{29} steranes (Cao et al., 2009). However, since none of the biomarker or floral indices are absolute, the existing data do not enable us to specify either the relative importance of either or whether or not there are secular changes in the contents of marine and terrestrial organic matter.

The ratios of C_{26}/C_{25} tricyclic terpanes and $C_{31}22R/C_{30}$hopanes are additional proxies that are commonly used to infer depositional environment (e.g. Peters et al., 2005). Marine rocks generally have a low (<1.2) C_{26}/C_{25} tricyclic ratio and higher (>0.2) C_{31}/C_{30}hopane ratio. The Kap Stosch samples are ambiguous in their values for these proxies as well. Overall, the tricyclic ratio for these samples is consistent with marine deposition with values that range from 0.30 to 1.03, with an average of 0.49 in the Permian samples and 0.70 in the Triassic samples. In contrast, the $C_{31}22R/C_{30}$hopane ratio has values ranging from 0.14 to 0.33, with an average of 0.18 in the Permian rocks and 0.25 in the Triassic rocks (Figure 2g). Although all localities have samples within and outside the values usually considered indicative of a marine environment, the general pattern supports primarily marine deposition.

3.2.3 Redox-sensitive Biomarkers

Pristane and phytane in sedimentary rocks derive primarily from the diagenesis of the phytol side chain of chlorophylls (Brooks et al., 1969). A pristane/phytane ratio (Pr/Ph) of <1 is commonly held to indicate deposition under typically marine anoxic conditions, and a >1 ratio is indicative of oxic deposition (Didyk et al., 1978). However, a value of <0.8 for anoxic environments and >2.0 for oxic may be considered more conservative. In Permian Kap Stosch sediments, the average Pr/Ph value was 0.78, and the highest value measured in the section was 1.24. Lower values were measured in the Triassic rocks, where the Pr/Ph average is 0.59 (Figure 3b). Although there were some Pr/Ph ratios >1, the overall range of low values indicates that anoxic conditions prevailed in sediments, and in the water column during OM transport, throughout the deposition of the Kap Stosch section.

Further understanding of redox conditions during deposition can be achieved by measuring the homohopane index. Values of C_{35} relative to C_{34} hopanes greater than 0.6 have been interpreted as indicative of deposition under anoxic bottom water (Peters and Moldowan, 1991). In the Kap Stosch samples, the homohopane index is relatively high with an average of 0.72 in the Permian rocks and an average of 0.69 in the Triassic rocks (Figure 3c). There are many fluctuations in this proxy they are relatively small and, like the Pr/Ph values do not reveal any major differences in water column redox in any part of the section.

Aryl isoprenoids with a 2,3,6-trimethyl substitution pattern were detected in nearly all of the samples studied. In many samples close to the identified PT transition, the isorenieratane precursor can also be identified, albeit low in abundance (Fig. 6). The absolute abundance of total aryl isoprenoids reported relative to the total organic content of the samples varies markedly through the Kap Stosch section. The highest values are in the Permian rocks where the average is 0.16mg/g TOC and the highest value is 0.55mg/g TOC. In the Triassic rocks the values are lower with an average of 0.06mg/g TOC and a high value of 0.11mg/g TOC (Fig. 3d). In significant concentrations, such as those measured in Kap Stosch, the presence of these compounds in sedimentary rocks is indicative of photic zone euxinia in the source-rock depositional environment (Summons and Powell, 1986). This evidence supports previous biomarker and lithological evidence that indicate the presence of PZE in this region at the end-Permian period (Grice et al., 1997; Pancost et al., 2002).

Recently, crocetane was the subject of a study that examined its potential as a marker for photic zone euxinia in certain samples of high thermal maturity where it may have been derived from the carotenoids of Chlorobi (Maslen et al., 2009). However, this same study reported that no crocetane was identified in sections from the PT boundary described in any studies by Grice et al. (2005a; 1996b), although low quantities were identified in a Triassic age shale (Greenwood and Summons, 2003). Although there was no measurement of $\delta^{13}C$ of this compound, the detection of crocetane in the Kap Stosch samples is a significant observation. In Maslen et al. (2009), the crocetane was found in samples that were the most thermally mature and would be likely to have the least amount of the precursor carotenoids remaining. However in Kap Stosch, the crocetane was identified in many of the same sedimentary rocks with the highest quantities of aryl isoprenoids and isorenieratane. In these samples, large initial quantities of carotenoids present from high TOC potentially allowed for significant crocetane to be produced diagenetically while still leaving a significant surplus of the precursor carotenoids. We also note that an abundance of ^{13}C-enriched, Chlorobi-derived organic matter in the samples from Locality 0 further complicates the interpretation of the bulk $\delta^{13}C$ signal in this part of the section.

The combination of factors described by the C_{30} sterane index, the ratio of C_{26}/C_{25} tricyclic terpane relative to $C_{31}22R/C_{30}$hopane, the pristane/phytane ratio, and the homohopane index all indicate that the Kap Stosch samples were primarily deposited beneath an anoxic marine water column. These rocks were deposited at the margin of a small inland sea, and it is not surprising that many of these proxies show that the region was subject to fluctuations in source inputs, consistent with the findings to the south in Jameson Land (Wignall and Twitchett, 2002), which show the presence of framboidal pyrites in the earliest Triassic rocks, interbedded with dysaerobic taxa like *Claraia*. Even with the increased terrestrial input, the presence of the aryl isoprenoids and isorenieratane (and potentially the crocetane as well) indicate that in this marine environment, euxinia extended to within the photic zone.

3.2.4 Microbial Community Biomarkers

The ratio of total hopanes to total steranes is a general proxy that should approximate the relative proportions of biomass derived from bacteria versus eukaryotes. Within the Kap Stosch section, the values are within typical ranges for the Phanerozoic (0.5 to 2) (Cao et al.

2009). There is a wide range of values for the hopane/sterane ratio in the uppermost Permian rocks, between 0.31 and 6.35, with an average value of 1.92. The average value is slightly lower in the lowermost Triassic rocks (1.44) but there is a smaller range of values with a low of 0.63 and a high of 3.47 (Fig. 3e). Although the values are higher in the Permian rocks, the hopane/sterane ratio throughout the section indicates a water column with relatively high input from bacterial biomass.

The ratio of 2-methylhopanes to C_{30} hopane, the 2-methylhopane index (2-MHI) has been proposed as a proxy for the proportion of organic matter derived from cyanobacteria (Knoll et al., 2007; Summons et al., 1999). The values of the 2-MHI range from 1% to 11% in this section, with a slightly higher average in the uppermost Permian rocks (~4%) than in the lowermost Triassic rocks (~3%) (Fig. 3f). The pattern of 2-MHI shows fluctuations in tandem with the total aryl isoprenoids with major peaks in the oldest samples in the section and at the end of the Permian, but this pattern is not as clear in the Triassic. These values are not especially high for samples of Phanerozic age. The composite nature of the Kap Stosch section and relatively low sampling density do not lend support for, or against, connections between carbon cycle perturbation, nutrient limitation (N and Fe) and cyanobacterial abundances as have been proposed for Mesozoic anoxic events (Kuypers et al., 2004). Still, the moderately high hopane/sterane ratios, together with a 2-MHI that peak in tandem with Chlorobi-derived biomarkers, suggests that bacterial inputs were significant at the locality of Kap Stosch at the end of the Permian.

3.2.5 A PT Event Proxy?

Although the origin of the C_{33} *n*-alkylcyclohexane (C_{33} *n*-ACH) signal is presently unknown, empirical data suggests a correlation between enhanced abundances and the main Late Permian extinction event regardless of thermal maturity. Based on 83 Da selected ion chromatograms, homologous series of *n*-alkylcyclohexanes are often observed in sedimentary rocks and kerogen pyrolysates (Fowler et al., 1986; Largeau et al., 1986) but it is only in those that span the PT boundary that the relative abundance of C_{33} *n*-ACH is reported to be highly elevated compared to adjacent members of the series (Fig 7). Locations where this C_{33} *n*-ACH signal has been identified include the Perth Basin (McIldowie and Alexander, 2005) and the Schuchert Dal section of East Greenland (Grice et al., 2005b)

where it was found to appear in the sediments at the onset of the marine ecosystem collapse. A similar observation has been made more recently in a section from Spitsbergen (Nabbefeld et al., 2010b). It is not surprising that in the Kap Stosch section, the C_{33} *n*-ACH first appears in the uppermost Permian sample and is seen in roughly one-third of the samples, ending in the earliest Triassic interval. The values of C_{33} *n*-ACH relative to *n*-C_{34} peak just above the transition and decrease shortly thereafter (Fig. 7). We also note that lower homologues bear a strong odd over even carbon number preference peaking in the range of C_{17}-C_{19} as does the same series of compounds that are prevalent in Ordovician sediments (Fowler et al., 1986; Hoffmann et al., 1987).

3.2.6 Biomarkers and Maturity Indicators: Comparisons to Other PT Sections

Values of biomarkers for redox conditions, microbial community and thermal maturity, three groups that best represent the extractable OM component from Kap Stosch, may be compared to those from the GSSP in Meishan, China (See Cao et al., 2009), the Peace River Basin, Canada (Hays et al., 2007) and the Perth Basin, Australia (Grice et al., 2005a; Grice et al., 2007) to address the issue of a depositional hiatus. Values for these biomarker ratios are closest to those reported in the Greisbachian from paleogeographically close Peace River section from the eastern edge of the Panthalassic Ocean, and in the Greisbachian of the Perth Basin, whereas biomarker ratios in the Meishan section, from within the eastern Paleotethys Ocean, are distinct. However, the Peace River section samples only a small number of Permian rocks and there is an apparent depositional hiatus in the Perth Basin so, any attempt to understand the depositional hiatus in the Kap Stosch section we only have the biomarker patterns from Meishan for comparison. In Meishan (Cao et al., 2009), there is a convergence of low homohopane index, minor aryl isoprenoids and low hopane/sterane ratio and 2-methylhopane index in the Wuchiapingian and lower Changhsingian rocks that are distinct from the exceptionally high and dramatically fluctuating values of these proxies in the overlying sediments. If the later part of the Changhsingian stage was ignored (or removed as it appears to be in Kap Stosch) the patterns for these proxies at Meishan would resemble those in Kap Stosch. This may be purely fortuitous and, yet, is consistent with the paleontological (Tiechert and Kummel, 1976) and palynological (Balme, 1979) indicators suggesting that a major portion of the Changhsingian has been lost in the Kap Stosch section.

With regard to the 20S/(20S+20R) ratio of the C_{27} sterane and the 22S/(22S+22R) ratio of the C_{31} homohopane maturity indicators, the Meishan section is of uniform maturity at the cusp of the oil maturity window throughout the c. 200m of section analysed by Cao et al. (2009). At Kap Stotsch, these parameters increase significantly down the sampled section, which was measured to embrace c. 180 m of sediment accumulation, and indicate a transition from very immature to mature with samples grouping roughly according to their location (Figs. 2e, 4 and 5). In regard to kerogen colour, samples from Locality 0 are dominated by dark brown to black OM with an admixture of lighter material evident in one of them. Kerogens in the rest of the samples from the 'transitional' and Triassic localities are predominantly pale yellow to orange and clearly immature apart from some finely pulverised black particles. This is consistent with the overall trends in kerogen hydrogen index and also indicative of a significant loss of Permian section.

3.3 Qualifying Factors

Although the Kap Stosch samples studied here capture a PT transition from the Boreal Sea, aspects of the sample set prevent it from being an ideal or representative section. Primarily, Kap Stosch is an outcrop section, with significant erosion, to the extent that the boundary itself is physically obscured in most places. Samples from outcrop are not as ideal for biomarker studies as core samples, because of the potential for contamination in the former. However with careful selection of biomarkers for interpretation (e.g. those which are derived from known sources and not present in vegetation) as was done here, the risk of signal contamination from modern input can largely be avoided. Also, the disconformity between the Permian and Triassic rocks makes this section appropriate only for identification of large-scale differences between the Permian and Triassic rocks. The rates of change of paleoenvironmental biomarker parameters before and across the PT transition is unknown as the key end-Permian interval appears lost from the record. Rapid fluctuations that occurred at the boundary itself, as observed in the Meishan section may not have been captured in the sampling. Finally, in regards to the samples selected here for analysis from the Kap Stosch section, the values of some biomarker ratios seem to show an outcrop effect, particularly in regard to the two samples from the late Permian Locality 13.75 which are

distinctly different from the late Permian samples from Locality 0. Although this effect is not seen in all the biomarker ratios and is far less evident in the Triassic localities, the differences in some biomarkers from locality 13.75 raise the possibility that these two samples may have been stratigraphically mis-assigned.

4 Conclusions

Palynological (Balme, 1979) and macrofossil (Teichert and Kummel, 1972, 1976) data from epicontinental Late Permian through Early Triassic samples from Kap Stosch, Greenland, identify input from both marine and terrestrial sources to these generally low-maturity sedimentary rocks. Biomarker evidence can also be used to provide a general understanding of the Kap Stosch depositional environment. Biomarker ratios indicate that the samples were deposited in a marine setting with mixed marine and terrestrial OM inputs throughout, but under a water column that was anoxic during the period(s) of deposition. The identification of the 2,3,6-aryl isoprenoids, crocetane and isorenieratane indicates that photic zone euxinia was present leading up to, and continuing through, the PT boundary.

Throughout Kap Stosch, the bulk geochemical parameters and biomarker ratios are in general agreement with other studies that have been performed on samples from east Greenland and boundary sections worldwide, including the Greisbachian in Peace River basin, Canada, the Perth Basin, Australia and Meishan, China, although a depositional hiatus and subsequent erosion has removed the key interval linking these. Large fluctuations in bulk geochemical and biomarker proxies reflect a dynamic carbon cycle and euxinic oceanic conditions before and through the PT transition, as they do at other locations where the fossil and other geochemical data record the largest extinction event of the geological record.

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7 Legends to Table and Figures

Table 1. Descriptions of kerogen and palynological preparations made from the Kap Stotsch samples. Samples are ordered according to the sampling localities of Teichert and Kummel (1976, 1979). Abundances of black/dark brown woody fragments could not be quantitatively determined and, hence, are visual estimates.

Table 2. Bulk geochemical parameters measured from the Kap Stosch section. In this composite section, ordered according to the relative stratigraphic position measured relative to their position above and below the boundary assigned by Teichert and Kummel (1976). For the lithology column, gr=greenish, g=grey, pg=pale grey, dg=dark grey, b=black, arg=argillaceous, sand=sandstone, silt=silty. The * in the Tmax column indicates samples with a shoulder peak in the S2 trace, though lower in intensity.

Table 3. A stratigraphically-ordered summary of biomarker abundances and ratio measurements for the compounds discussed in the text.

Figure 1. Locality map for the Kap Stosch, Greenland Permian-Triassic transition section. (a) Global reconstruction for the Late Permian, with the paleolocation of this depositional section identified. This map is modified from the "Late Permian" map on the Scotese Paleomap Project website (www.scotese.com/newpage5.htm). (b) Map of modern Greenland with Kap Stosch (top) and Jameson Land (bottom) localities noted. (c) Map detail for Kap Stosch showing localities sampled for this study. (b) and (c) modified from Teichert and Kummel 1972. (d) Litholog of sampled sections from Kap Stosch. Shown are the four localities measured, with sampled sediment layers noted. Modified from Balme, 1979.

Figure 2. Cross-plots that compare different geochemical characteristics in the Permian and Triassic samples. The four symbols (diamonds, circles, triangles and squares) represent samples from the four different localities from this composite section (Rivers 0, 13.75, 6.75 and 1, respectively). (a) TOC versus Rock-Eval S2 for whole rock samples; (b) TOC versus Rock-Eval S2 for the enriched kerogens; (c) The Hydrogen Index plotted relative to $\delta^{13}C$ of

total organic carbon. (d) The Hydrogen Index plotted relative to the C_{27}/C_{29} sterane ratio, a proxy for marine versus terrestrial OM inputs; (e) The ratio of 22S/(22S+22R) of the C_{31} homohopane plotted relative to the ratio of 20S/(20S+20R) of the C_{27} sterane; (f) The ratio of C_{30} $\beta\alpha/\alpha\beta$ hopane plotted relative to Ts/(Ts+Tm); (g) The ratio of C_{26} to C_{25} tricyclics plotted relative to the ratio of C_{31} to C_{30} hopane and (h) The ratio of diasterane/sterane content of C_{29} steranes plotted relative to the ratio of diasterane/sterane content of C_{27} steranes;

Figure 3. Stratigraphic patterns of biomarkers indicative of depositional environment, redox conditions and microbial community from the Kap Stosch section. The four symbols (diamonds, circles, triangles and squares) represent samples from the four different localities from this composite section (Rivers 0, 13.75, 6.75 and 1, respectively). (a) C_{30} sterane index = 24 *n*-propylcholestane/total sterane. (b) Pristane/phytane ratio. (c) Homohopane index = total C_{35} hopane (22S + 22R isomers)/total C_{34} homohopanes x100. (d) 2,3,6 Aryl isoprenoids abundance normalized relative to total organic carbon contents. (e) Hopane/sterane ratio, measured including all identified hopane and steranes in the section. (f) 2-Methylhopane index = 2-methylhopane / (2-methylhopane + C_{30} hopane) x100. Compounds compared in (a), (c), (e) and (f) were measured in GC-MS MRM mode; (b) pristane/phytane ratio measured from total ion current of full scan GC-MS data; aryl isoprenoids in (d) were measured in GC-MS SIM mode. Error bars for biomarker ratios are less than 3% of the measured values, and are contained within the points. All data are plotted relative to height above or below the boundary placement as in Balme (1979).

Figure 4. GC-MS MRM chromatograms from three selected saturated hydrocarbon fractions from Kap Stosch showing relative abundances of C_{27}-C_{30} steranes and diasteranes. The column on the left is typical of samples the Late Permian; the middle column is from a sample close to the assigned boundary; and the column on the right is from a typical Early Triassic sample.

Figure 5. GC-MS MRM chromatograms from three selected saturated hydrocarbon fractions from Kap Stosch showing relative abundances of C_{27}-C_{31} hopanes and C_{31} methyl-hopanes.

The column on the left is typical of samples the Late Permian; the middle column is from a sample close to the assigned boundary; and the column on the right is from a typical Early Triassic sample.

Figure 6. GC-MS selected ion chromatograms of m/z 134 from an aromatic hydrocarbon fraction from Kap Stosch compared to a sample from the Barney Creek Formation, Australia, published in Brocks et al. 2005. In the Kap Stosch sample, aryl isoprenoids from C_{18} to C_{24} have been identified, as well as the intact C_{40} carotenoid skeleton of isorenieratane. In the Barney Creek Formation sample, squares indicate the 2,3,6 aryl isoprenoid series, triangles indicate the 2,3,4 aryl isoprenoid series, c=chlorobactane, o=okenane, i=isorenieratane, r=renieratane, and p=renierapurpurane.

Figure 7. C_{33} *n*-alkylcyclohexane from the Kap Stosch section. (a) The ratio of C_{33} *n*-alkylcyclohexane to C_{34} *n*-alkanes. The four symbols (diamonds, circles, triangles and squares) represent samples from the four different localities from this composite section (Rivers 0, 13.75, 6.75 and 1, respectively). Samples plotted relative to height above or below the boundary placement as in Balme (1979). All compounds were measured by GC-MS in full-scan mode. (b) GC-MS selected ion chromatogram of m/z 83 from a saturated hydrocarbon fraction. Elevated abundance of the C_{33} *n*-alkylcyclohexane is typical of sediments deposited near to the paleontological PT transition.

Figure(s)

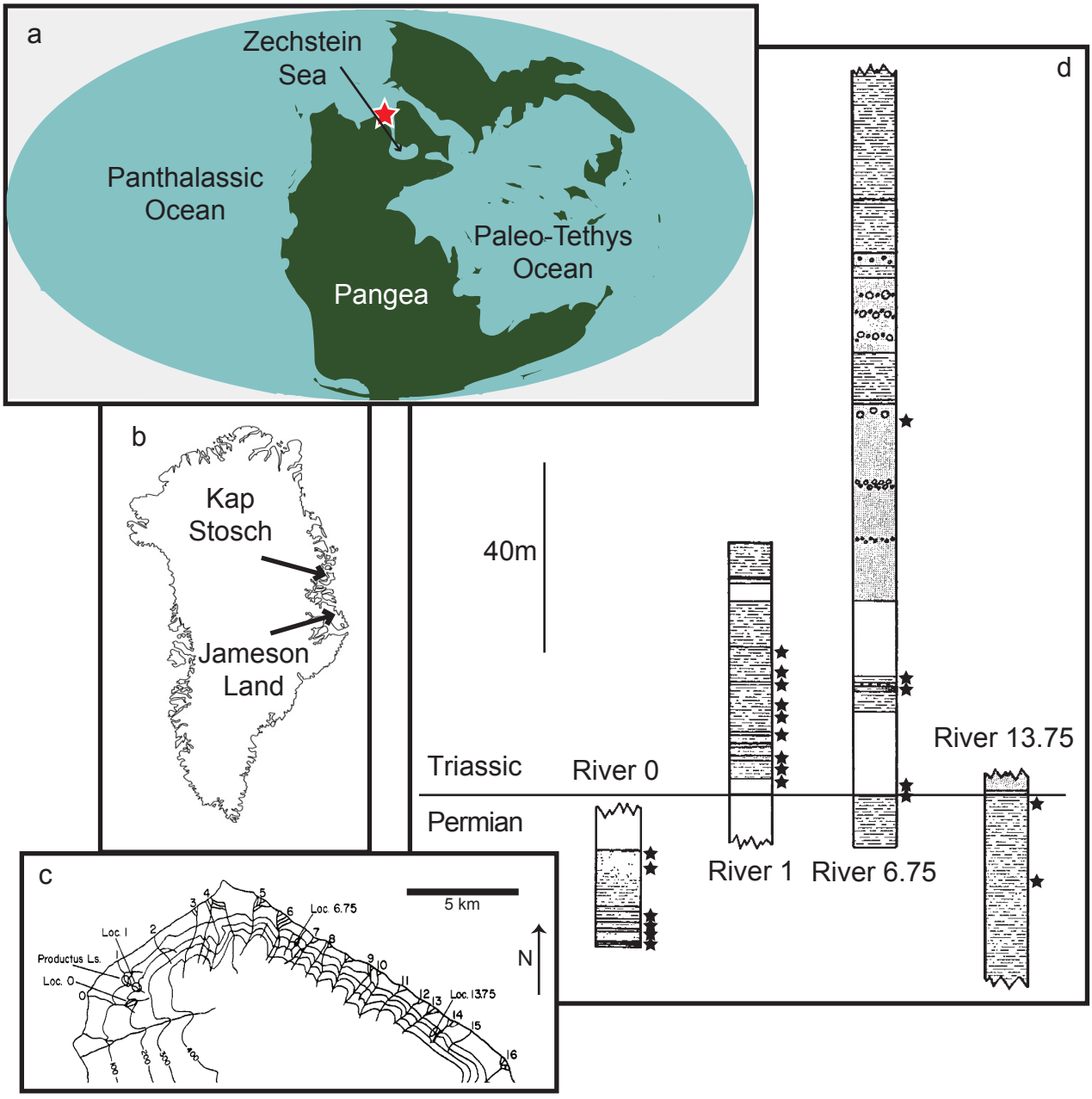
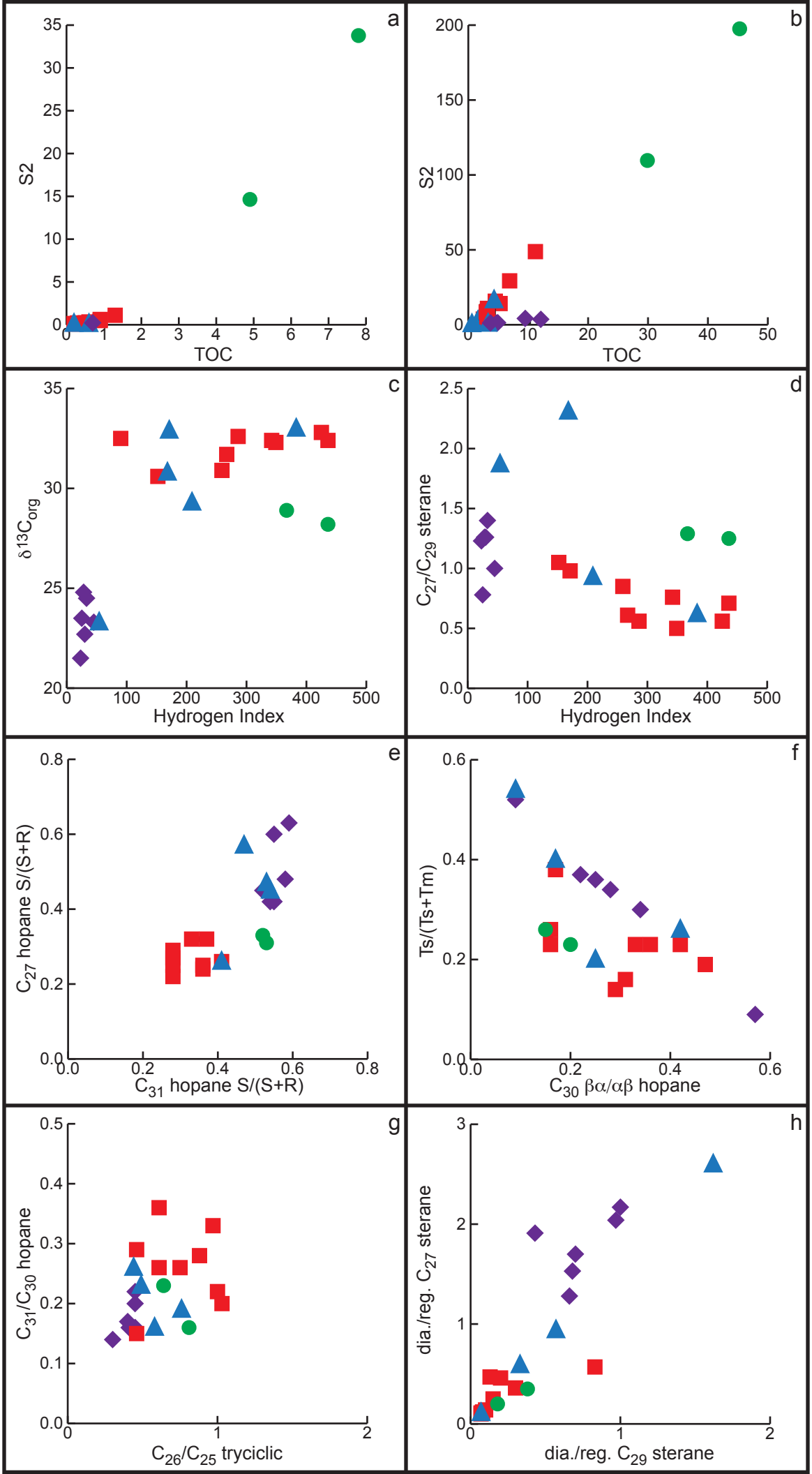


Figure 1


a
S2
TOC
b
S2
TOC
c
δ13Corg
Hydrogen Index
d
C27/C29 sterane
Hydrogen Index
e
C27 hopane S/(S+R)
C31 hopane S/(S+R)
f
Ts/(Ts+Tm)
C30 βα/αβ hopane
g
C31/C30 hopane
C26/C25 tryciclic
h
dia./reg. C27 sterane
dia./reg. C29 sterane

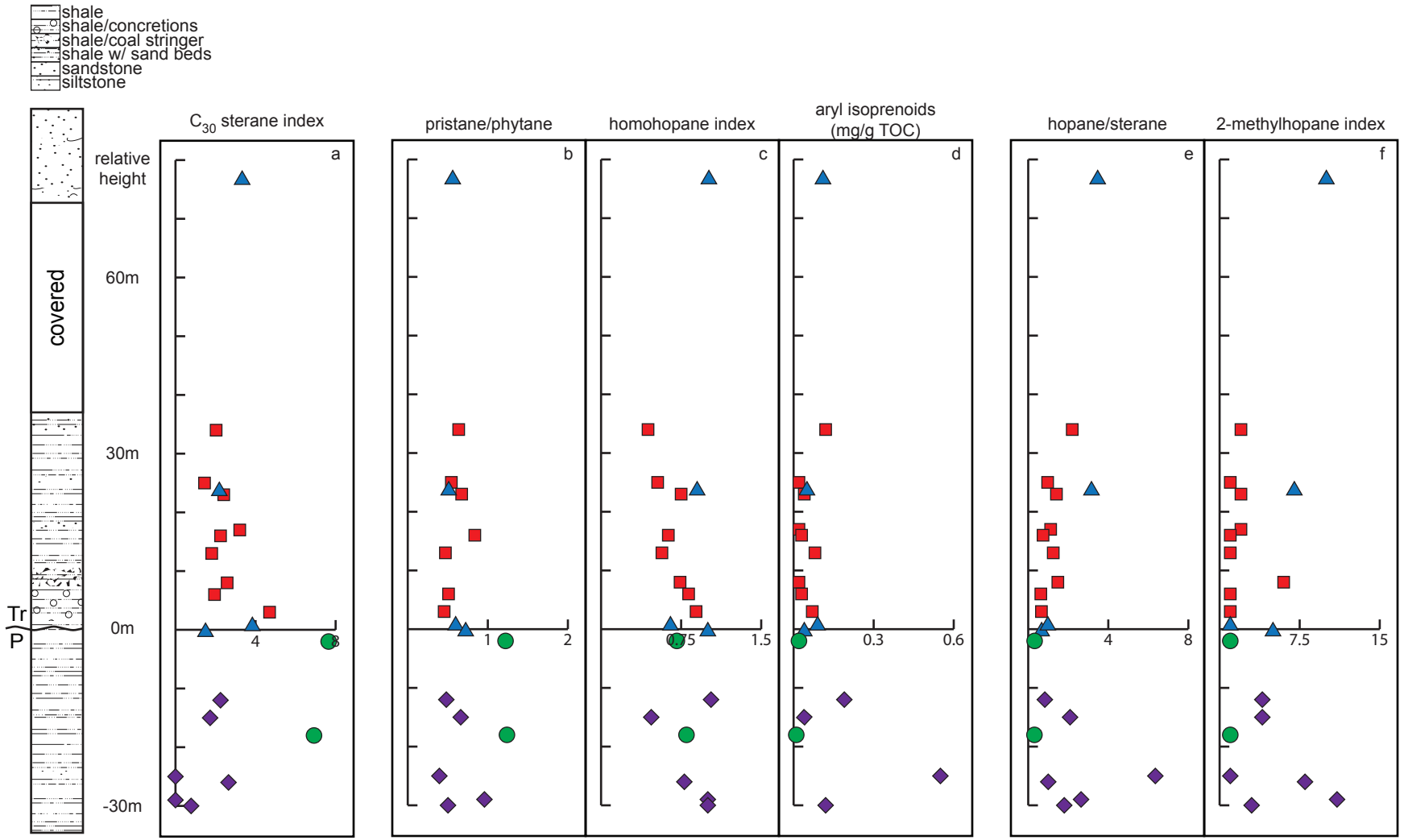

shale
shale/concretions
shale/coal stringer
shale w/ sand beds
sandstone
siltstone
covered
relative height
60m
30m
0m
-30m
Tr
P
C30 sterane index
a
pristane/phytane
b
homohopane index
c
aryl isoprenoids (mg/g TOC)
d
hopane/sterane
e
2-methylhopane index
f
4
8
1
2
0.75
1.5
0.3
0.6
4
8
7.5
15

Figure 3

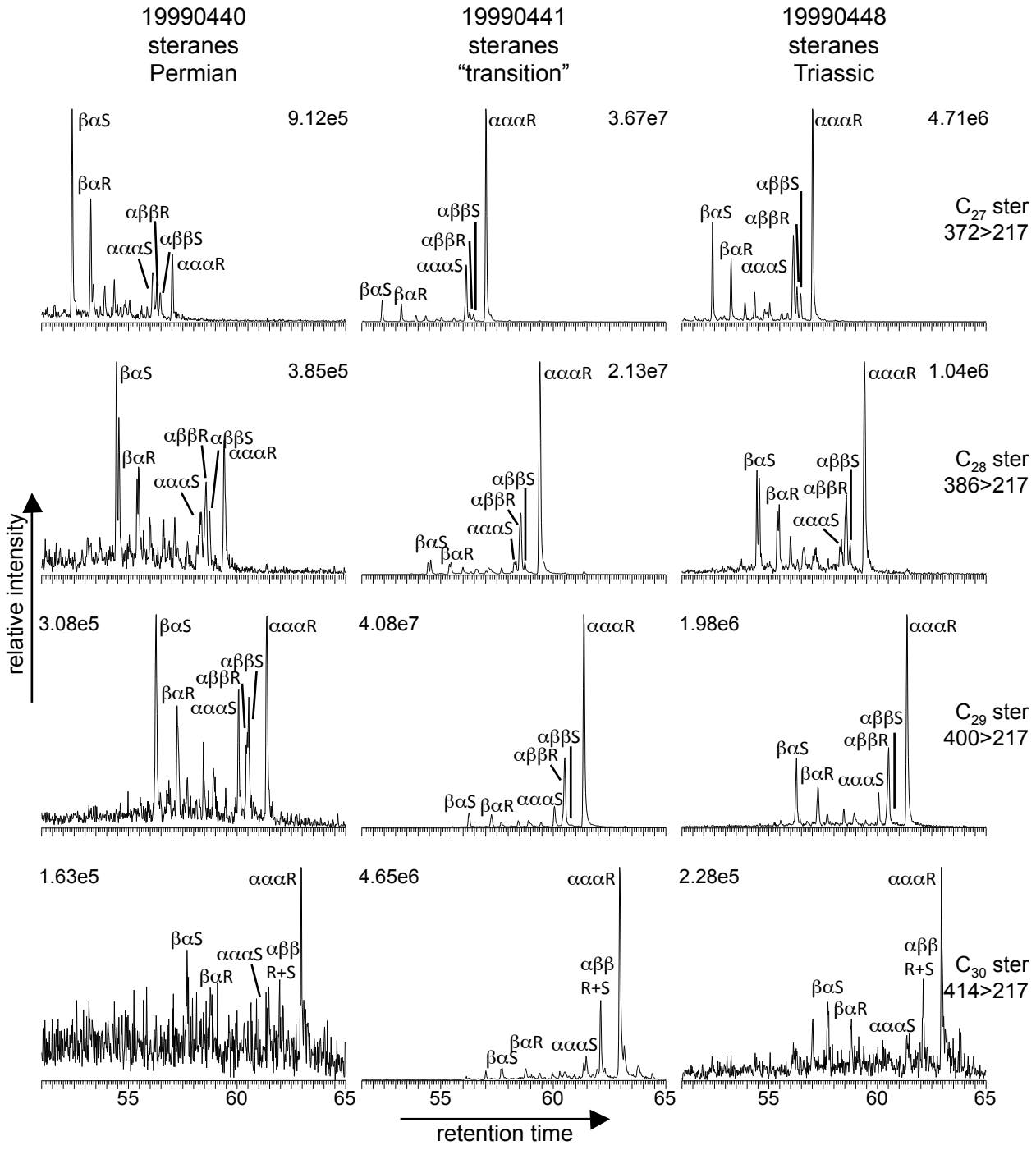

19990440
steranes
Permian
19990441
steranes
"transition"
19990448
steranes
Triassic
βαS
βαR
αββR
αααS
αββS
αααR
9.12e5
3.67e7
4.71e6
C27 ster
372>217
3.85e5
2.13e7
1.04e6
C28 ster
386>217
3.08e5
4.08e7
1.98e6
C29 ster
400>217
1.63e5
4.65e6
2.28e5
αββ
R+S
C30 ster
414>217
relative intensity
55
60
65
retention time

Figure 4

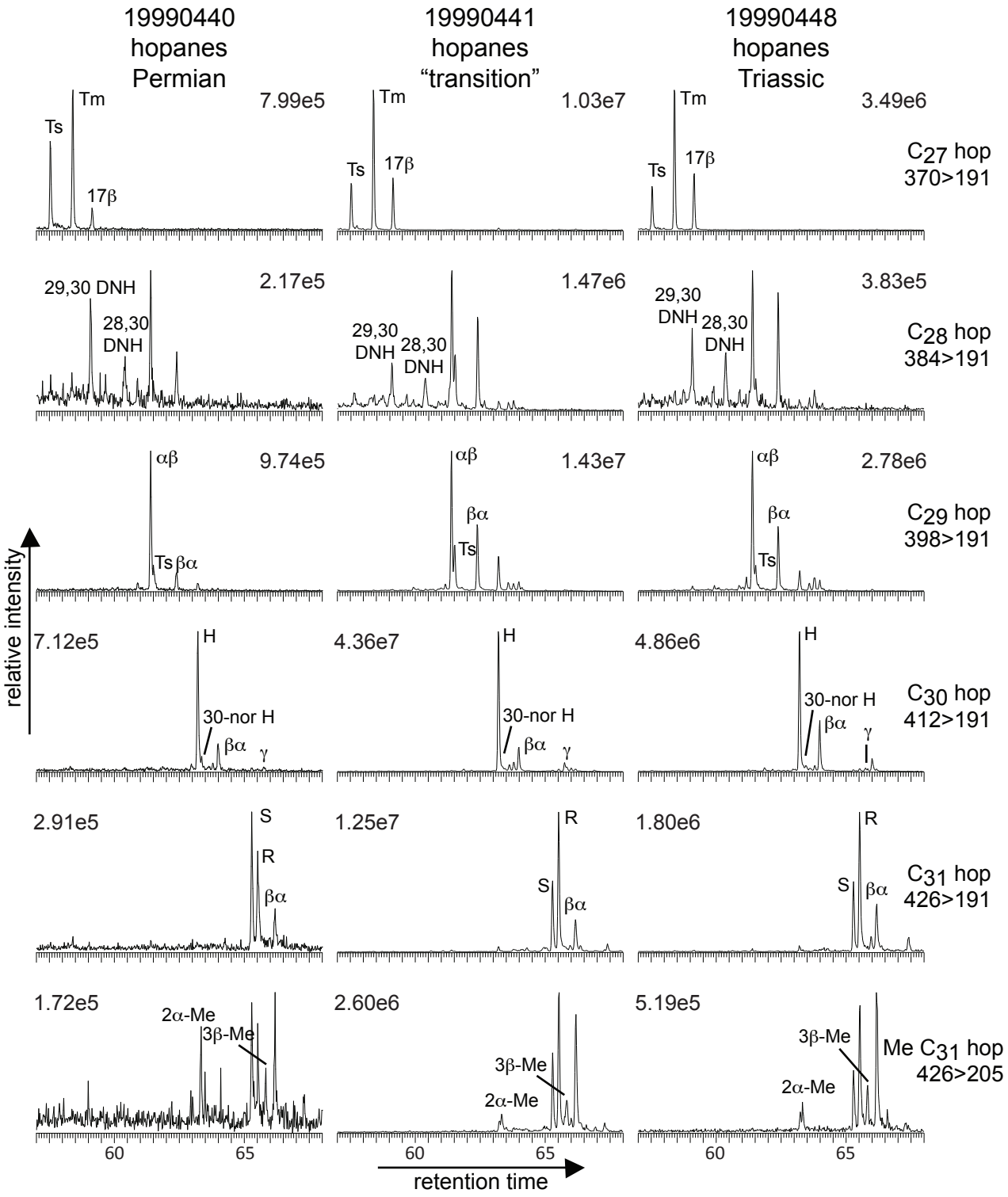

19990440
hopanes
Permian
19990441
hopanes
"transition"
19990448
hopanes
Triassic
7.99e5
1.03e7
3.49e6
Ts
Tm
17β
C27 hop
370>191
2.17e5
1.47e6
3.83e5
29,30 DNH
28,30 DNH
C28 hop
384>191
9.74e5
1.43e7
2.78e6
αβ
βα
Ts
C29 hop
398>191
relative intensity
7.12e5
4.36e7
4.86e6
H
30-nor H
γ
C30 hop
412>191
2.91e5
1.25e7
1.80e6
S
R
C31 hop
426>191
1.72e5
2.60e6
5.19e5
2α-Me
3β-Me
Me C31 hop
426>205
60
65
retention time

Figure 5

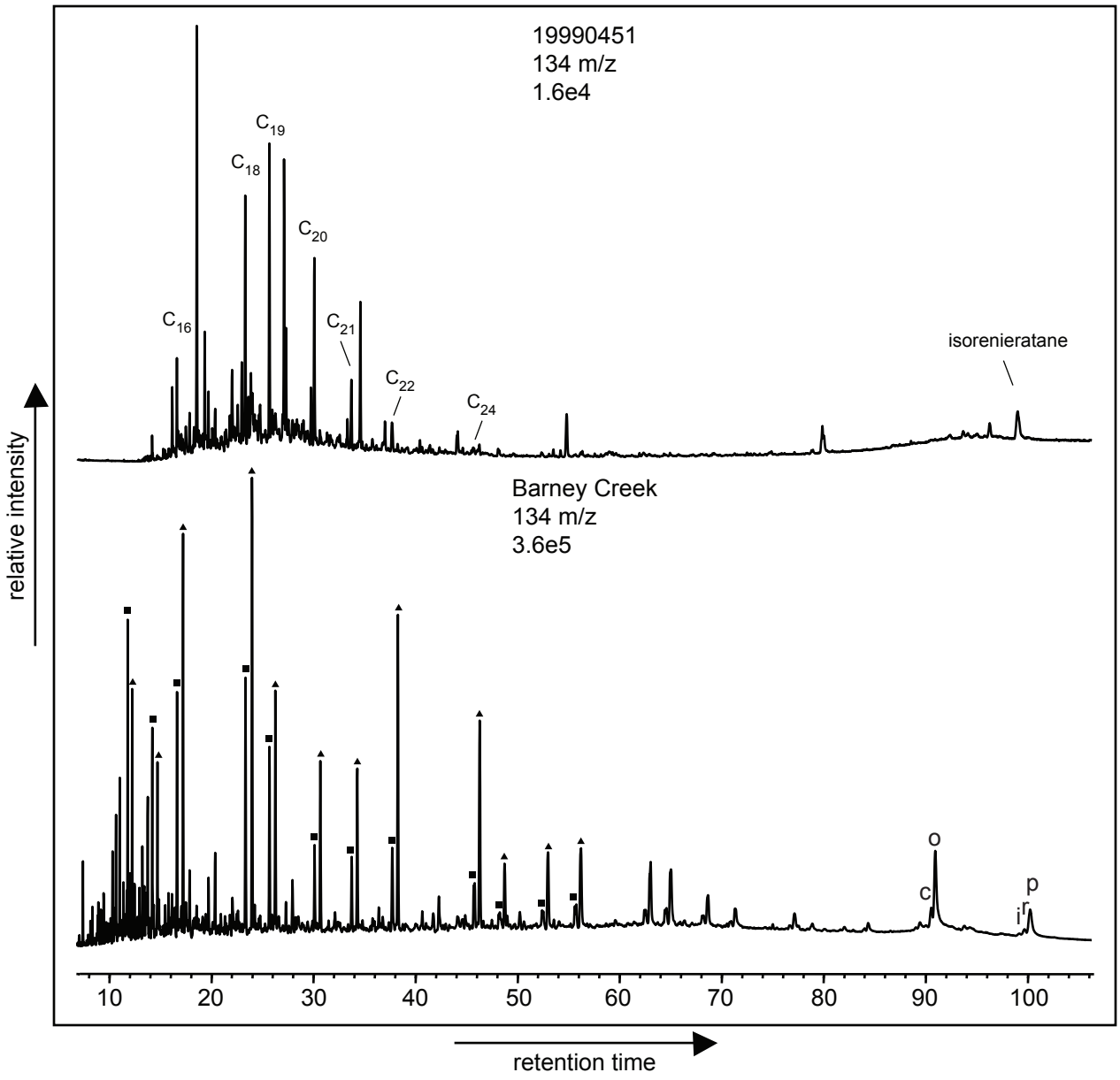

19990451
134 m/z
1.6e4
C16
C18
C19
C20
C21
C22
C24
isorenieratane
Barney Creek
134 m/z
3.6e5
o
c
p
r
i
relative intensity
10
20
30
40
50
60
70
80
90
100
retention time

Figure 6

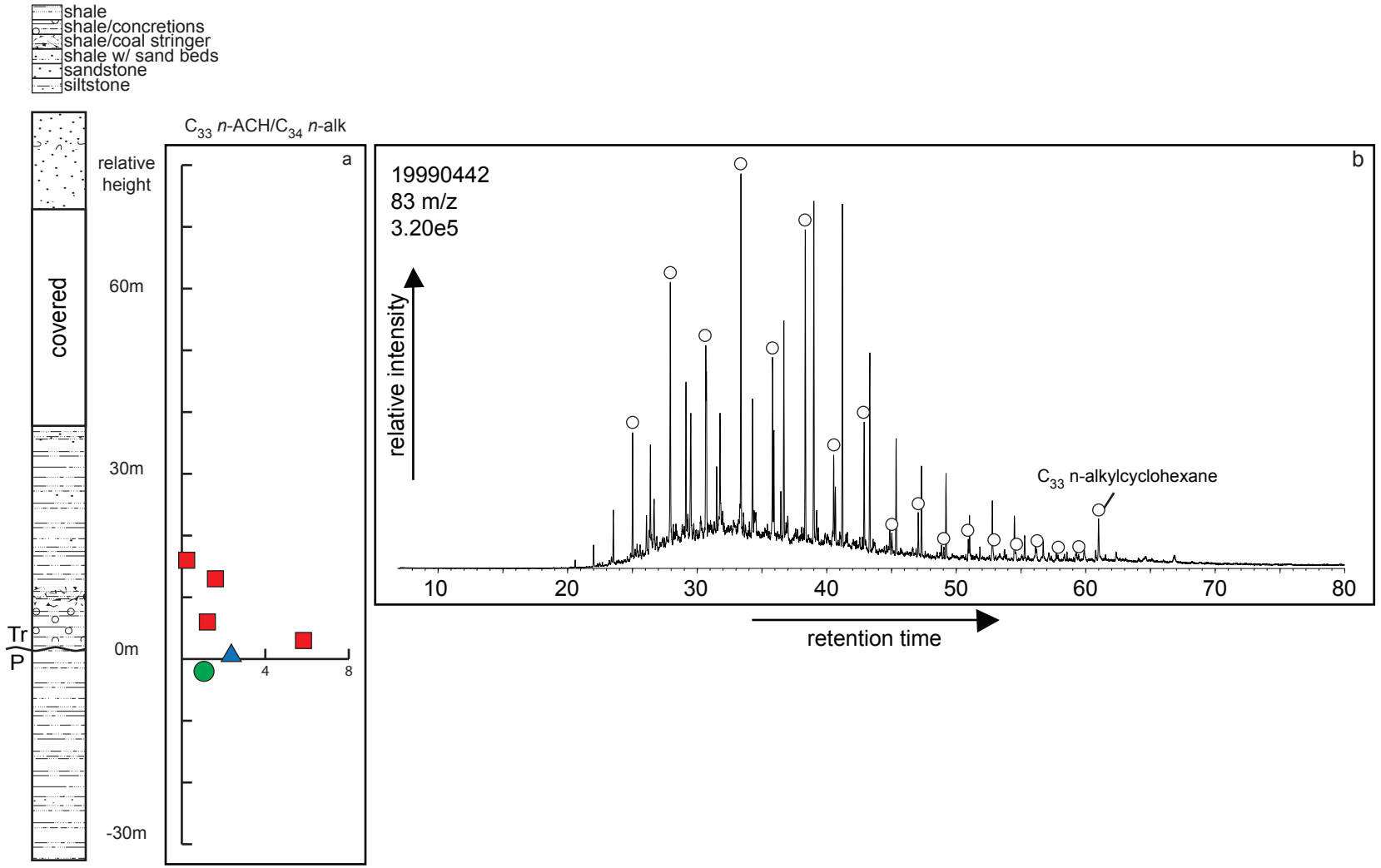

shale
shale/concretions
shale/coal stringer
shale w/ sand beds
sandstone
siltstone
covered
relative height
60m
30m
0m
-30m
Tr
P
C33 n-ACH/C34 n-alk
a
4
8
19990442
83 m/z
3.20e5
b
relative intensity
C33 n-alkylcyclohexane
10
20
30
40
50
60
70
80
retention time

Figure 7

Table(s)

Balme 1979 - Locality data	AGSO Sample Number	Kerogen slide (un sieved)	Kerogen colour/visual strew mount: and slide	Palynomorph yield	Spore/pollen preservation	Palynological Prep- 10 or 20 micron sieving: +/- oxidation	Balme 1979 Palynofloral Association
0-2	19990435	Black/dark brown angular equi-dimensional and rarer lath-like woody tissue- includes some trachieds.Very fine organic material as dominant, discreete particles 2X2 microns; some cuticle, rare foram linings; rare spinose acritarchs	dark grey/ fine material: admixture of mature dark and lighter pollen of the same genus (only in this sample)	low	poor	gymnosperm pollen (Lunatisporites, *Vittatina* spp) in +20 fraction; foram linings and spinose acritarchs (*Michrystridium* spp.), not common but indicative of salinity	*Vittatina*-Association
0-3	19990436	Black woody tissue, some cuticle; very sparse fragments of gymnosperm pollen, spinose acritarchs *Michrystridium* spp.	as above	very low	poor	*Vittatina* spp.	as above
0-6	19990437	as above	as above	barren of recognisable palynomorphs	barren of recognisable palynomorphs	barren	
0-7	19990438	as above	as above	very low	poor	*Michrystridium* spp., taeniate gymnosperm pollen, *Lueckisporites* sp.	
0-9A	19990439	as above	as above	low	poor		
0-9B	19990440	as above	as above	low	poor	black angular tissue abundant in +20 slide, spinose acritarch V*eryhachium* sp present. *Vittatina* sp., ? *Lueckisporites* sp.	
1-1	19990441	DISTINCT COLOUR CHANGE: abundant tissue, and some very well preserved pollen grains: very little woody tissue	organics pale yellow/orange (thermally immature), abundant, sheet-like tissue, some with internal cell wall structure - affinity unknown ?Alga?	moderate	good to excellent	gymnosperm pollen, incl: *Lunatisporites noviaulensis*;lycopod spores common; *Tympanicysta stoschiana*	
1-2	19990442	as above - with some finer comminuted material	as above	moderate	fair to excellent	*Lunatisporites* common, lycopod spores, including abnormal tetrad forms	
1-3	19990443	much less large tissue much more comminuted material: ? Higher energy environment of deposition	as above	abundant	good to excellent	Resin body (very rare) assemblage as above	
1-8B	19990444	as per 1-1- but sheet-like organic matter slightly deeper colour - marginally more mature? Less well preserved, with fine communited material		high	fair to good	same assemblage as above, gymnosperm pollen and lycopod spores, including abnormal tetrads	
1-9A	19990445	much less large tissue much more comminuted material: ? Higher energy environment of deposition		moderate	fair- moderate	gymnosperm pollen dominated, including *Lunatisporites*; lycopod spores	*Taeniaesporites*-Association
1-9C	19990446	CHANGE IN KEROGEN- fewer large tissue fragments, pale yellow, f comminuted discrete organc matter including black woody tissue.		low	moderate	as above	*Taeniaesporites*-Association
1-10	19990447	as above		moderate	moderate	same assemblage as above, gymnosperm pollen and lycopod spores, including abnormal tetrads	*Taeniaesporites*-Association
1-11A	19990448	as above		moderate	poor to good	abnormal tetrad lycopod spores - as described by Looy et al. (2001)	*Taeniaesporites-Association*
1-11B	19990449	CHANGE IN KEROGEN finely comminuted organic matter including angular woody tissue; largest fraction pollen and cuticle fragments		moderate	fair to excellent	gymnosperm pollen and lycopod spores (incl tetrads); *Tympanicysta stoschiana;* resin-like bodies;	*Taeniaesporites*-Association
750-1	19990450	Black/dark brown angular equi-dimensional and rarer lath-like woody tissue- includes some trachieds.Very fine organic material as dominant, discrete particles		barren of recognisable palynomorphs	barren of recognisable palynomorphs		
750-2	19990451	CHANGE IN KEROGEN, sheet-like tissue,light brown/yellow, few black angular woody frags small/comminuted		low	fair	Lycopod spores in tetrad form ?*D. nejburgii* (as per Looy), some spinose acritarchs. Well preserved *Ephedripites* spp, some resin -ike bodies noted.	
750-4	19990452	no kerogen slide		moderate	fair to poor	Gymnosperm pollen, incl: Lunatisporites noviaulensis;lycopod spores common; Tympanicysta stoschiana	
750-6	19990453	some elongate laths of woody tissue present, gymnosperm pollen evident in kerogen slide				predominantly gymnosperm pollen, taeniate, disaccate; *Ephedripites* spp. common; well preserved. *Vittatina* rare (reworked?), rare *Michrystridium* spp. (spinose acritarchs); lycopod tetrads, and dyads (as per Looy)	*Taeniaesporites-Association*
750-8	19990454	Trace fine black angular fragments (woody tissue), brown trachedial material; megaspore fragments, taeniate gymnosperm pollen, *Ephedripites*		moderate	fair to excellent	Lycopod spores, dyad forms (as per Looy). Detached gymnosperm taeniate pollen corporae common	*Taeniaesporites-Association*
750-8(1)	19990455	no kerogen slide		low	fair to excellent	gymnosperm pollen, megaspore ?*Otynisporites eotriassicus;* rare lycopod spores; *Tympanicysta stoschiana*	
1375-1A	19990456	Abundant organic matter, angular black woody low %, very sparse recognisable spores/pollen; foram lining		low	poor	Gymnosperm pollen common in +20 fraction, *Vittatina spp.* present	*Vittatina*-Association
1375-1B	19990457	Abundant organic matter, black woody material finely comminuted		low	poor	Gymnosperm pollen common in +20 fraction, Rare *Vittatina*	*Vittatina*- Association

Table(s)

					RockEval 2 analysis of Rock Powder							RockEval 6 analysis of Kerogen Concentrate						
Sample Number	**Relative Stratigraphic Position**	**River Locality**	**Lithology**	**$\delta^{13}C$ (‰ VPDB)**	**TMAX (°C)**	**S1 (mg/g)**	**S2 (mg/g)**	**S3 (mg/g)**	**HI (mg/g TOC)**	**OI (mg/g TOC)**	**TOC (wt%)**	**TMAX (°C)**	**S1 (mg/g)**	**S2 (mg/g)**	**S3 (mg/g)**	**HI (mg/g TOC)**	**OI (mg/g TOC)**	**TOC (wt%)**
19990454	77	6.75	gr-g arg sand	-29.3	480±20	0.03	0.12	0	57	0	0.2	422	2.83	3.98	0.44	209	23	1.9
19990449	34	1	pg shale	-30.6	430±20	0	0.16	0.15	46	43	0.4	421	1.8	3.79	1.1	152	44	2.5
19990448	25	1	g shale	-31.7	430±20	0.01	0.12	0.11	28	26	0.4	430	2.07	14.17	2.05	267	39	5.3
19990453	24	6.75	gr arg sand	-30.8	480±20	0.02	0.14	0	61	0	0.2	417	2.05	2.68	1.03	168	64	1.6
19990447	23	1	g sand	-30.9	430±10	0.04	0.2	0.2	65	65	0.3	424	4.46	8.3	1.24	259	39	3.2
19990452	22	6.75	gr-g shale	-32.5	>480	0	0.08	0	53	0	0.2	413	0.53	0.54	0.61	90	102	0.6
19990446	17	1	g shale	-32.9	430±10	0	0.15	0.17	33	38	0.5	419	1.33	5.29	2.74	171	88	3.1
19990445	16	1	dg shale	-32.6	432	0.01	0.23	0.12	43	23	0.5	423	2	8.59	1.47	286	49	3
19990444	13	1	pg limestone	-32.3	431	0.02	0.49	0.23	58	27	0.9	426	1.95	15.72	2.52	349	56	4.5
19990443	8	1	pg shale	-32.4	430±20	0.08	0.21	0.04	68	13	0.3	429	3.63	10.93	0.9	342	28	3.2
19990442	6	1	pg shale	-32.8	430	0.05	0.62	0.2	71	23	0.9	430	3.34	29.31	2.79	425	40	6.9
19990441	3	1	pg shale	-32.4	431	0.07	1.11	0.37	84	28	1.3	427	4.54	48.82	4.74	436	42	11.2
19990451	1	6.75	g shale	-33	430	0.03	0.33	0.42	53	68	0.6	426	2.46	16.49	1.94	383	45	4.3
19990450	0	6.75	g shale	-23.3	430±20	0.01	0.1	0.19	42	79	0.2	396*	1.01	1.83	1.03	54	30	3.4
19990457	-2	13.75	b shale	-28.9	431	0.56	14.64	2.1	296	43	4.9	429	7.55	109.65	12.55	367	42	29.9
19990440	-12	0	dg shale	-21.5	430±20	0.02	0.17	0.24	44	62	0.4	362	1.33	1.08	1.55	23	33	4.7
19990439	-15	0	dg shale	-24.8	430±20	0.02	0.19	0.32	46	78	0.4	419*	0.63	1.36	3.09	28	63	4.9
19990456	-18	13.75	b shale	-28.2	425	1.74	33.78	3.54	434	46	7.8	426	12.91	197.55	25.63	436	57	45.3
19990438	-25	0	dg shale	-23.5	430±20	0	0.13	0.15	23	27	0.6	364	1.37	0.83	0.9	25	27	3.3
19990437	-26	0	dg silt shale	-23.3	>415	0.02	0.13	0.32	72	178	0.2	415*	4.94	4.24	2.57	45	27	9.5
19990436	-29	0	dg silt shale	-22.7	430±20	0.01	0.11	0.22	18	36	0.6	412*	2.96	3.63	3.56	30	29	12.1
19990435	-30	0	dg silt shale	-24.5	430±20	0.04	0.22	0.38	32	56	0.7	414*	1.14	1.23	1.14	33	31	3.7

Table 2

Table(s)

Sample Number	Relative Stratigraphic Position	River Locality	C_{30} SI	Pr/Ph	C_{35}/C_{34} hopane	AI (mg/g TOC)	Hopane/ Sterane	2-MHI	C_{26}/C_{25} tricyclic	C_{31}/C_{30} hopane	C_{30} hopane βα/αβ	Ts/ (Ts+Tm)	C_{27} S/(S+R)	C_{31} S/(S+R)	C_{27} dia./reg.	C_{29} dia./reg.	C_{27}/C_{29} sterane	C_{33} ratio
19990454	77	6.75	3.33	0.56	1.01	0.11	3.47	0.1	0.44	0.26	0.17	0.4	0.45	0.54	0.59	0.33	0.93	ND
19990449	34	1	2.03	0.64	0.44	0.12	2.2	0.02	0.46	0.15	0.47	0.19	0.32	0.37	0.47	0.13	1.05	ND
19990448	25	1	1.45	0.54	0.53	0.02	0.97	0.01	0.75	0.26	0.33	0.23	0.32	0.33	0.36	0.3	0.61	ND
19990453	24	6.75	2.19	0.51	0.9	0.05	3.16	0.07	0.49	0.23	0.42	0.26	0.47	0.53	0.94	0.57	2.31	ND
19990447	23	1	2.41	0.67	0.75	0.04	1.41	0.02	0.46	0.29	0.42	0.23	0.29	0.28	0.46	0.2	0.85	ND
19990452	22	6.75	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
19990446	17	1	3.21	ND	ND	0.02	1.12	0.02	0.61	0.36	0.36	0.23	0.25	0.28	0.57	0.83	0.98	ND
19990445	16	1	2.25	0.84	0.63	0.03	0.74	0.01	0.88	0.28	0.31	0.16	0.22	0.28	0.11	0.07	0.56	0.23
19990444	13	1	1.81	0.47	0.57	0.08	1.25	0.01	0.97	0.33	0.29	0.14	0.27	0.28	0.14	0.1	0.50	1.61
19990443	8	1	2.58	ND	0.74	0.02	1.48	0.06	0.61	0.26	0.17	0.38	0.26	0.41	0.25	0.15	0.76	ND
19990442	6	1	1.95	0.51	0.82	0.03	0.63	0.01	1	0.22	0.16	0.23	0.25	0.36	0.1	0.07	0.56	1.22
19990441	3	1	4.7	0.45	0.89	0.07	0.66	0.01	1.03	0.2	0.16	0.26	0.24	0.36	0.12	0.08	0.71	5.83
19990451	1	6.75	3.84	0.6	0.65	0.09	0.98	0.01	0.76	0.19	0.25	0.2	0.26	0.41	0.11	0.07	0.62	2.37
19990450	0	6.75	1.5	0.72	1	0.04	0.67	0.05	0.58	0.16	0.09	0.54	0.57	0.47	2.6	1.62	1.87	ND
19990457	-2	13.75	7.65	1.22	0.71	0.02	0.32	0.01	0.64	0.23	0.2	0.23	0.31	0.53	0.35	0.38	1.29	1.06
19990440	-12	0	2.25	0.48	1.03	0.19	0.83	0.04	0.45	0.22	0.22	0.37	0.45	0.52	1.7	0.7	1.23	ND
19990439	-15	0	1.73	0.66	0.47	0.04	2.09	0.04	0.4	0.17	0.34	0.3	0.6	0.55	2.04	0.97	1.26	ND
19990456	-18	13.75	6.92	1.24	0.8	0.01	0.31	0.01	0.81	0.16	0.15	0.26	0.33	0.52	0.2	0.18	1.25	ND
19990438	-25	0	0	0.4	ND	0.55	6.35	0.01	0.3	0.14	0.57	0.09	0.42	0.55	1.91	0.43	0.78	ND
19990437	-26	0	2.65	ND	0.78	ND	1	0.08	0.45	0.16	0.09	0.52	0.48	0.58	1.53	0.68	1.00	ND
19990436	-29	0	0	0.96	1	ND	2.64	0.11	0.45	0.2	0.25	0.36	0.63	0.59	1.28	0.66	1.26	ND
19990435	-30	0	0.78	0.5	1	0.12	1.8	0.03	0.41	0.16	0.28	0.34	0.42	0.54	2.17	1	1.40	ND

Table 3

*Response to Reviewers

Reviewer #1: Review of Manuscript Number OG-1262
This manuscript is about a geochemical study of a composite sedimentary section that captures the Permian- Triassic transition at Kap Stosch, Greenland. The data is interesting and is worth publishing, however, the paper requires a major improvement in scientific idea and the data requires some further interpretation. My comments are listed below:

1. The major aim of this paper seems to "search for hydrocarbon biomarkers that would be informative about paleoenvironmental redox conditions during the Late Permian period and especially for compounds diagnostic for photic zone euxinia". Unfortunately, this section is congenitally deficient for organic geochemical study (especially to boundary strata), just like that discussed in section 3.3 (Qualifying factors). In this condition, I suggest that the authors pay more attention to the characteristics of this composite section and extent of the unconformity. For example, is it possible to assess the extent of the important unconformity by using the distinct change in biomarker maturity indices between the Permian and Triassic sediments?

We have refocused the introduction and clarified the purpose of the study. We have addressed the change in biomarker ratios across the boundary and the extent of the unconformity using not just maturity indices but also evidence from kerogen color. Comparisons with patterns in Meishan, which show really major fluctuations that are not seen in the KS section, might also be useful.

2. The bulk geochemical indices such as rock-eval HI value may conflict with the immature character based on most of biomarker maturity proxies. For example, C29St 20/(20S+20R), C30Hop 22S/(22S+22R), as well as the higher concentration of 17<beta>(H)-C27 trinorhopane all indicate that the Triassic OMs are typically immature, while the HI values of these samples are extremely low. This means that the Triassic anoxic marine OMs are strongly hydrogen-poor? If so, what is the genesis? Are the OMs predominated by vitrinites or inertinites? If not, is it possible that the samples were contaminated by immature organic matters during weathering and/or long-term (more than 40 years) store? So, OM types should be discussed in detail with both rock-eval data and biomarker data.

The rock-eval analysis was conducted as a screening technique. The hydrogen-poor character of the bulk kerogen at Locality 0 suggests some older re-worked Permian OM in these samples. The situation is analogous to what we observed and reported earlier in our studies of the P-T transition in the Perth and Bonaparte Basins of Western Australia and we have added text to make this connection. We have also added a table that summarises the appearances of the kerogen and the indentifiable palynomorphs in the same samples analysed for biomarkers.

There is no evidence of contamination for these samples which were curated in a paleontological collection. Weathering in the outcrop, however, would have added a layer of complexity as is inevitably the case in any study of outcrop samples. We have added text to make this clear.

3. The data of carbon isotope of OMs are very important for this study, since no carbon isotope of carbonates were obtained.
We made no attempt to measure the 13C of inorganic carbon. There was no little or carbonate present in the clastic-dominated samples and even if there was it would be very difficult to exclude diagenetic effects or confounding influence. Elsewhere, we have comprehensively discussed by the carbon isotope analysis of bulk organic carbon cannot inform about contemporaneous dissolved inorganic carbon in marine waters. The 13Corg of bulk kerogens in Triassic samples but, with so much terrestrial OM in the form of pollens and spores, even those data are equivocal.

The carbon isotope variation pattern around the Permian-Triassic transition is similar to other section worldwide. However, the authors try to relate this this change to organic input (Line 235-238). This interpretation should not be established because they give no suitable evidence for major terrigenous input into the Triassic sediments (in fact, C27 sterane is even more abundant than C29 sterane (Fig. 4), indicating a very limited terrigenous OM input). What is important is that there is no genesis mechanism for that the terrigenous input can cause a strong ?organic carbon isotope excursion (7‰). I suggest that the carbon isotope change here should also be mainly caused by the global change in marine and atmosphere carbon source. In addition, the carbon isotope analysis method is not given in section "2 Methods".

4. about the samples
1) 2 samples were collected from the two covered locations? (see Fig.1)
2) According to the lithological column (Fig.7), at least 3~4 sandstone samples are collected, are samples ideal for biomarker study? Are the biomarkers the migrated hydrocarbons?

1) The placement of these samples was not clear on the figure and we have been repositioned in a revised figure.
2) Though the majority of samples were collected from shale, some samples were designated as sandstone by T&K.This refers to grain size and is independent of organic matter contents. Our Rock-Eval data, showing correlation between S2 and TOC, confirms that the samples are appropriate for geochemical analysis. Futher, the low-maturity of these samples and the lack of evidence for any oil migration suggests that there is no concern about migration of hydrocarbons.

5. about the figures
Fig.2: No Pristane/Phytane data for the third sample of the Triassic sediments? If so, the coordinate axis should be confined to the range of 0~2?
Fig. 3: the quality needs to be improved.
Fig. 4: ?<beta><beta>S is not detected in teh 400-217 mass chromatograms of sample 1999441 and 1999448, does it coelute with ?<beta><beta>R, just like sample 1999440? In addition, diasterane <beta>?S and <beta>?R are very probably mislabeled on the three 414-217 mass chromatograms, please check the retention time.
Fig. 6: UCM should be interpretated; why is sample 19990451 placed here while not the one 19990442? 3 major peaks on the m/z134 mass chromatogram are not identified? Are they contaminations? In addition, I am afraid of that the retention time of the arylisoprenoid hydrocarbons are correctly labeled?
Fig.7e: 4 groups of samples are combined into 2 groups, why?

We have addressed most of these points by making many changes to the figures, and adding new figures. In response to the comment on figure 6 – the UCM is common in sedimentary bitumens, particularly in aromatic fractions, and therefore we do not believe that it needs further interpretation. 19990451 was selected since it featured a prominent isorenieratane peak, and the major peaks are not identified since they are not the focus of this figure. Finally, we have included a published aryl isoprenoid chromatogram for comparison of aryl isoprenoid retention times.

6. about the lithology
1) Line 219-221: What is the lithological evidence for depositional environment? "There may have been an increase in terrestrial input to the sediments in the Triassic period" seems to be unconvincing.

2) Line 410-415: How to show rock-type or lithology? The authors are engaged to relate the difference in biomarker proxies to lithology and/or OMs source, but, what is the difference? In fact, there is no anti-correlation occurred as respect of each group of data. It is must be noticed that 20S/(S+R) ratio is, at immature stage, more closely related to maturation, while Ts/Tm and moretane/hopane are related to both maturity and sedimentary facies.

1) The lithological evidence for depositional environment is entirely drawn from that provided by the original Tiechert and Kummel papers on Kap Stosch, but we have reworked the introduction to further clarify their assessment.
2) We have produced a new figure (3d) that shows a cross-plot of moretane/hopane and its anti-correlation to the Ts/(Ts+Tm) ratio and suggesting, based on grouping of samples according to locality, that it is related, largely to lithology.

7. Line 257-258: the C26/C25 tricycles—C31/C30 hopanes plot can be used to identify the marine OMs from the lacustrine OMs (predominantly derived from algae), but incapable of identifying terrigenous OMs (such as coal measure strata, usually with high C31/C30 hopane ratio).

We have clarified the wording of this section.

8. Line 393-395: The kerogen concentration may be of lower quality, as evidenced by very low TOC content (Table 1)? So, the kerogen Tmax values are not ideal for maturity assessment. It is a pity that this study does not give the data of kerogen elemental composition which is one of the most important indices (H/C and O/C atomic ratio) for OM type and maturity assessment.

We did not have the capability to measure kerogen elemental compositions. Instead, we addrsss this issue with the detailed descriptions of the slides of enriched kerogens and the sieved palynomorphs.

9. Line 420-423: "Wang' Hopane Anomaly" could never be 'discounted' by Cao' suggestion, because that no diagenesis mechanisms have been found for the marine OMs to generate such a 'Hopane Anomaly'. One should consider Wang' detailed genesis mechanisms about the hopane anomaly. In this paper, the higher moretane/hopane is not an 'anomaly' for the Stosch section, but just a common character of hopane distribution in immature sediments.

We have removed references to the "Wang hopane anomaly" and clarified the wording of the moretane ratio section.

10. The conclusion is not concise and to the point:
1) Line 446-449: are not the conclusion based on this study.
2) Line 455-456: in fact, no data or figure showing a correlation between the biomarker and TOC value in this study, how to get such a conclusion? If the Chlorobi-derived biomarkers' concentration is related to TOC value, does it mean that these bacteria are the main contributor to the TOC?

We have rewritten this section to address these concerns and to clarify the conclusions of the study.

11. Decimal problems, etc:
Line 185: "0.2-8 wt%" should be "0.2-8.0 wt%"
Line 198: "-25%" should be "-25.0‰"
Table 1: TOC should be to 1.d.p. or 2.d.p.?

Line 202: where is the Table 4.1?
Line 294: "0.6mg/gTOC" should be "0.06mg/gTOC"?
Line 329-330: "Phanerozoic (0.5 to 2)", Please give the reference to the data.
Line 404: "increase" should be "decrease".

We have made the suggested changes.

12. A data table should be added to show the sample's lithological character and values of molecular proxies, etc.

We have added a Table 3 to include this data.

In summary, this paper is not ready for publication as it now stands, due to the problems noted above.

Thank you very much for your constructive comments.

Reviewer #2: This article by Hays et al. "Biomarker and Isotopic Trends from a Permian-Triassic Sedimentary Section at Kap Stosch, Greenland" presents bulk and molecular geochemical data obtained on a synthetic section of the Permian-Triassic transition in East Greenland. From the molecular data, the authors mainly conclude that in this location, the environment persistently remained under photic zone euxinia, despite a general change from marine influenced during the Permian to more terrestrially-influenced during the Triassic. This study has a potentially large interest, as it brings additional information to the knowledge of paleoenvironmental conditions during the end Permian extinction event, which is one of the major events of Earth history. The geochemical data are generally of good quality. Despite this, the manuscript currently suffers from numerous shortcomings and imprecision described in the following, in particular from a geological point of view. It also appears relatively poorly written, with numerous approximate expressions, and needs reorganization. Finally, the paper length appears not appropriate: it is currently either too long or too short. In conclusion I consider that despite the interest of this study, this paper is not suitable for publication in its present form. I however warmly encourage the authors to resubmit the paper after modification.

Major comments

1 - Analytical strategy and broad interest of the study. On the one hand, I admit that the discovery of biomarkers for photic zone anoxia (PZA) marked an important step because this corresponds to very peculiar environmental conditions. These last years an abundant literature has been published stating the discovery of PZA biomarkers in a wide range of environments of all ages. It however is important to notice that PZA can be reached in very shallow environments, and in this case it is absolutely not spectacular! On another hand, the Permian-Triassic transition was one of the most important events of Earth's history, and there has been growing evidence for widespread oceanic anoxia during this event. Two options are therefore possible: focussing on the redox state of the sediment/water column or try to collect as much information as possible from a biomarker study. Currently the paper balances between these two options without really choosing one. It seems that the authors chose to concentrate only on a few selected biomarkers, some aimed at determining redox conditions, but also a few source-specific compounds, without any clear explanation of this choice. If the aim of this study (only) is to look for redox state and PZA indicators, as seems to indicate the last sentence of the introduction, this manuscript could be shortened and more focussed. If the aim of this study is to go into detailed paleoenvironmental characterisation, **the results (including the bulk geochemical data) should be described and discussed with more detail.**

We believe that both an understanding of the redox state and the gathering of information available by biomarkers not likely to be affected by contamination are both important, and have rewritten the introduction in order to refocus the aim of the study. In addition we have removed some sections that were not as relevant to the point of the paper.

2 - Geological description and stratigraphy of the studied material. The material available to the authors has been collected a long time ago, the relevant geological literature is quite dated and poorly accessible (I couldn't get access to a copy of Teichert and Kummel, 1972 or 76 within allocated time for the review) and the stratigraphy has not been recently re-considered (though recent data from Jameson Land - Wignall and Twitchett, 2002- indicate that the stratigraphy may need revision). For these reasons, geological information in this paper should be detailed and precise, so that the reader can be fully able to understand the qualities and drawbacks of the presented data. Currently however, I am sorry to say that the geological information is imprecise and restricted to the minimum.

- Four outcrops were used, but only 3 lithological logs are shown.
- No legend is given for the lithological patterns used in Fig. 1.
- The text indicates that the lithology comprises "homogeneous shale, silty shale and siltstone facies". From the legend of Fig 7e, it however appears that some samples come "from predominantly sandstone rocks" (L. 657). Moreover, what is "homogeneous"? The colour, the texture? Information about the colour of the rock, presence of bioturbation or lamination should also be given. These data often reflect the oxygenation degree of the environment.
- Coal stringers and concretions appear on the synthetic lithological log of figures 2 and 7 but are not mentioned in the text.
- L 132-134 is mentioned the fact that the Triassic sediments were deposited in conditions generally shallower than the Permian sediments. Which are the arguments for this bathymetric interpretation? Moreover, what was the overall water depth: 50m, 200 m, more? The implication of having PZA will vary according to the water depth.

From the given information, we can only suspect that the stratigraphy used is this study is the one proposed by Teichert and Kummel (1972, 1976). Apart from the location of the Permian-Triassic boundary on fig. 1, no stratigraphic information is available. What exactly is the stratigraphic range of the covered interval? The location of the samples on a stratigraphic scale is needed. Which are the stratigraphic elements which allowed correlation of the 4 outcrops used? From the study of Wignall and Twitchett (2002) in Jameson Land, it can be supposed that the stratigraphy in Kap Stoch area and the presence of a Late Permian hiatus - but also possibly the correlation between the 4 oucrops - may also need revision (see later). L 125-126 is indicated that "The Permian-Triassic transition in the second area (Localities 6.75 and 13.75, Figure 1) is more clearly exposed …", but on Fig. 1 it appears that in locality 6.75, the limit is "covered" and in locality 13.75, it is in the middle of disturbances. This is not exactly what we can call "clear exposure".

The authors are conscient of some of these drawbacks and indicate that their results should be considered with caution (part 3.3). However, I think more caution/discussion is needed than exposed in the small and awkward part 3.3.

The lithological evidence for depositional environment is entirely provided by the original Tiechert and Kummel papers on Kap Stosch, but we have thoroughly reworked the introduction to further clarify the lithology and address these points.
We have changed figure 1 to include all four lithologs based on a figure from Balme 1979, but there was no accompanying legend, so we felt it would be improper to create one
More information on lithology has been added.
Coal stringers are addressed in the text.
Information about water depth and stratigraphic information available from Teichert and Kummel has been added.
Figure 1 has been reformatted and the samples in "covered" sections have been more accurately repositioned.

3 - analytical methods and data/results presentation. More details are needed in the methods section, in particular concerning bulk analyses.
- Samples were collected in 1967. Under which conditions have they been stored prior to analysis ?
- Which temperature programme was used for RE pyrolysis? Which instruments were used?
- How were the "kerogen concentrates" prepared? From the TOC content (average value 7.6%), there are still abundant minerals in this material (one can estimate more than 80 %) and it cannot been reasonably called a "kerogen concentrate".
- How were <delta>13Corg measurements performed? On which material was it analysed and with which type of machine?

- Why choosing not to analyse the aromatic fractions in full scan mode and using only SIM? Because of contaminations?
- I did not find which molecules are monitored by the ions 125, 244, and 287.
- Figures 2, 3, and 7 need a legend for the symbols used, so that the reader can identify the section from which the samples originate (also see comment below).
- Similarly, it would be interesting to indicate the section on table 1.

We included a reference (Strauss et al., 1992) that fully describes the analytical methods used for bulk analysis at Geoscience Australia over many years.
Aromatic fractions are typically and most easily identified using SIM, so we used that method here. GC-MS in scan mode also works but, for low abundance PAH, SIM is more sensitive. There was no intention to obscure contamination.
At MIT, SIM methods for aromatic fractions are made for general lab use and typically include ions (91, 105, 119 etc) that are used to identify compounds (eg for alkyl benzenes) not analyzed by every individual, however, 244 is used to identify the standard for quantification – D14 p-terphenyl.
The symbols used are addressed in the figure captions and the sections have been added to table 1 and table 2.

4 - The origin of the organic matter, and a change from marine to more continentally-influenced is repeated several times in the text. No clear information however supports these assertions:
- the biomarker content does not particularly document the continental source (higher plant biomarkers?)
- The authors refer to a palynological study but the information is confused: apart from an increase of Gymnosperm pollens (L. 253-254) the authors also indicate the presence of algal remains (L 231) and high abundance of spinose acritarchs (L. 227-229) in Triassic samples. The two latter are not very good arguments for a more terrestrial origin of the organic matter during the Triassic.

The portion of the introduction that includes information from Teichert and Kummel 1972 and 1976 as well as the palynological study by Balme in 1979 was expanded to include much more information about this change in organic matter across the boundary. Co-author Foster has re-examined the kerogens and paly slides and provided new descriptions that now appear as Table 1. These new data are the prime evidence for the statements now made in the text.

5- Finally, and in particular if the authors choose to describe the full range of biomarkers, I recommend to reorganise the manuscript and more rigorously separate results from their interpretation. The discussion on the maturity of the organic matter should also appear prior to the discussion on paleoenvironmental indicators.

We acknowledge that some people prefer results to be separated from discussion. However, in this study, with multiple interwoven elements, it is difficult. We have made a significant rearrangement of the material and believe we have addressed the primary criticism. Maturity is discussed prior to paleoenvironmental indicators.

We have made every effort to incorporate these constructive comments into the manuscript.
The few instances where changes were not made are addressed in specific notes below.

More specific comments and suggestion in the following:
In all the text: the formulas "youngest Permian" and "oldest Triassic" are confusing and give the impression that the authors do not know the stratigraphic succession. The correct stratigraphic terms are: "Late Permian/Early Triassic" for an age and "Upper Permian/Lower Triassic" for

lithological units.
L. 23-25: "Analyses of hydrocarbons…terrestrially-influenced inputs". This sentence can be removed as the same information is given a few lines below.
L 26-27: the maturity parameter given by the Rock Eval is the Tmax value, not the TOC-S2 correlation.
L41 and rest of the text: use Chlorobiaceans or Chlorobiaceae and not "Chlorobi".
** Chlorobi *refers to the Phylum of which all Chlorobiaceae are members and which exclusively includes Chlorobiaceae.*
L. 39 and 367-374: what is the interest of discussing the C28/C29 sterane ratio? The global age of the samples is known and the values are consistent with this age.
L. 57: "Permian-Triassic (PT) transition"
Figure 1: the location of the Zechstein sea on the paleogeographic map is incorrect (but notice that the map does not clearly show the Zechstein sea !). Please give exact reference for the source map (website address, "publication date").
L. 50: The Zechstein deposits have been studied a long time before Grice et al. 1996, 1997 and Pancost et al. 2002 !
L. 74 and following: the detailed history of maleimides identification in Kupferschiefer deposits can be shortened.
L. 93 "toward more anoxic conditions": Anoxia is the absence of oxygen. There is no gradation in the fact of being anoxic and therefore, conditions cannot be more (or less) anoxic. Conditions can be more reducing; anoxia can be more developed geographically or in the water column.
L.98 "in some prior studies": add references
L. 99 and following: "These findings suggest that Kap Stosch is an appropriate site to search for hydrocarbon biomarkers…": from the poor geological control, it does not appear that this location is such an appropriate site.
L. 137-139 : How important in the Late Permian lag ? Is it sure that this lag is similar on the 4 studied outcrops? In the case of Jameson Land basin, Wignall and Twitchett (2002) showed that the supposedly Late Permian sedimentary lag as a matter of fact is due to incised valleys.
L. 173 and following: indicate what MRM stands for. Isn't the sentence rather "two groups of precursor-products transitions, the first for steranes and the second for cheilantanes and hopanes …", as would be expected from monitoring ions m/z 217 and 191, respectively?
Part 3.1: I am surprised by the poor consideration given to the bulk geochemical data. They are generally full of information. Why neglecting them? I took the time to plot the data from table 1 and obtained very interesting features: the two samples that are at the origin of the variability in TOC values during the Permian (L.185) are also responsible of the "high magnitude fluctuations" in <delta>13Corg values (L. 201). Interestingly, their <delta>13Corg values are intermediate between those of Permian and those of Triassic age. These samples are also characterised by HI values that significantly differ from HI values of other Permian samples but are similar to Triassic samples. This is also visible by plotting the S2 vs TOC of "kerogen concentrates": it clearly appears that these two samples are more similar to Triassic samples than to Permian ones. Finally it appears that these two very samples belong to the same outcrop (locality 13.75), where the lithological log indicates sediment perturbation at the Permian-Triassic boundary. Two possible alternatives exist to the scheme used by the authors:
- this outcrop contains a very peculiar type of OM compared to the other outcrops and the two samples should therefore be considered with caution,
- the age determination of these two samples is wrong and they should be placed closer to (or even within ?) the Triassic.

If these two samples are moved - or removed -, the story gets a little different! This is the reason why stratigraphy and correlation of the 4 outcrops is so important!
***The two samples from locality 13.75 were identified as late Permian based on the stratigraphy produced by Teichert and Kummel.*
We have significantly expanded the discussion of bulk data and explained how the kerogen descriptions are helpful in its interpretation.

In general it appears that Permian organic matter (OM) is type III to IV, while Triassic OM is type II but HI values progressively decrease upwards. This change in OM type might reflect changes in the source of the OM but in this case it appears that type II OM (the more marine) is present in the Triassic where the authors continuously indicate that the OM is more continentally influenced. Conversely this change might reflect different preservation degree.
Some "kerogen" Tmax values (<370°C) are anomalously low. Is there an explanation?
L 191 From the low "kerogen" Tmax values (420°C if we remove the two lowest values) the OM is immature. The use of "modest thermal maturity" might be confusing.
L 192 "biomarkers are primarily authigenic": the authors probably mean "autochthonous".
L. 193 "shoulder peaks near the maximum pyrolysis temperature (Tmax)". Where is this shoulder located? Toward lower or higher temperatures?
L 212 and following "An important inference we can make…": the sentence is not clear.
L 217-219 "…similar to patterns seen in other sections worldwide (Cao et al., 2009; Grice et al., 2005a) but opposite in direction". I probably missed something since I have the impression that the pattern here observed is in the same direction as the one observed worldwide. The two cited reference do not exactly represent "worldwide" studies. Reviews are available: Corsetti et al. (2005) C.R. Palevol. 4, 473-486 or Korte & Kozur (2010) J. Asian Earth Sci. 39, 215-235.
L. 245 "these organisms": which ones? No specific organism is named in the previous sentences.
L 249-251: here again it appears that maximum values of the C30 sterane index correspond to the two samples from loc. 13.75. If we remove these two points, the Permian values are not that different from Triassic ones.
L 251-252: how can the lithology indicate the origin of the organic matter?
L. 256 and following, and figure 3: from these data, is concluded that "the Permian samples have a more marine character than the Triassic samples". This is not so clear from Fig. 3: purple Permian samples have low C26/C25 tricyclic ratio indicating marine context, but also low C3122R/C30hopane rather indicating non marine conditions. Conversely for the red triassic samples where the higher C26/C25 tricyclic ratio would indicate less marine conditions but higher C3122R/C30hopane rather indicate more marine conditions. I agree with the fact that this is ambiguous. As a matter of fact the Triassic samples plot the closest to the usually accepted marine field. I am surprised to see on figure 3 that samples from an outcrop tend to group together (this is particularly visible for the blue triagles that should stratigraphically group with the red squares), would there be an "outcrop effect"?
Pr/Ph ratio: the figure 2 does not allow to see strong differences between the samples. The scale should be changed.
L. 290: "figure 2" instead of "figure 6".
L. 294: there is a problem with the average value during the Triassic. 0.06 ? In general, I have the impression that these concentrations of aryl isoprenoids are very high.
L. 296: "photic" instead of "phone".
L 297 "This evidence supports previous biomarker and lithological evidence that indicate the presence of PZE in the Boreal Sea region at the end-Permian period (Grice et al., 1997; Pancost et

al., 2002)": The Zechstein sea is not exactly the Boreal Sea. Conditions for weak ventilation were more favourable in the Zechstein sea. Biomarker information from the Boreal sea in Nabbefeld et al. (2010) Earth and Planetary Science Letters 291, 84-96. Pyrite framboids also indicate water column euxinia in Jameson Land [Nielsen et al. (2010) Earth and Planetary Science Letters 291, 32-38; Bond & Wignall (2010) GSA Bulletin 122(7/8), 1265-1279.]
L 303 and following: this paragraph is poorly consistent. How could high TOC values explain more diagenetic breakdown? Diagenetic breakdown could be as efficient everywhere, so that where aryl isoprenoids are abundant, crocetane also is abundant. This would however imply that crocetane is not derived from thermal breakdown but from another breakdown mechanism. Could it be clay-catalysed (as for instance for certain hopanoids or steroids)? Alternatively, crocetane could derive from methanothrophic bacteria present in the water column as those observed in the Black Sea. Currently it is PMI more than crocetane which is observed in the water column of the black sea (Wakeham et al. (2007) Organic Geochemistry 38, 2070-2097), but PMI is not observed in Paleozoic sediments. The presence of 3<beta>-methylhopanes, as visible on fig. 5, is also consistent with the presence of methanothrophic bacteria. Notice that Greenwood and Summons (2003) Organic Geochemistry 34, 1211-1222 identified crocetane in Permian-Triassic samples from Perth Basin.
L 316: this paragraph is not really useful.
L 331: why looking for a "regular" pattern?
L. 336: "high" instead of "higher".
L. 343 "these indices fluctuate inversely in the Triassic": it is not that obvious.
L. 355 "Although…": cut the sentence.
L. 367 and the following: this paragraph does not seem useful. As indicated by the authors the C28/C29 sterane ratio may be "useful for constraining ages for samples of unknown origin". Here the age is known.
L. 369 "This ratio increases throughout the Cenozoic as the organisms that produce the C28 sterols, the Cenozoic phytoplankton assemblages of diatoms, coccolithophores and dinoflagellates, rise in their relative importance in the phototrophic community (Knoll et al., 2007).": Knoll et al. (2007) indicate that the C28/C29 ratio principally increased in relation to the development of diatoms alone and not of their assemblage with coccolithophores and dinoflagellates.
L. 376 and following: this paragraph is not useful.
Part 3.2.5: This part generally is poorly organised. All data should be first described and then discussed, as it finally appears that the main control on all molecular maturity indicators is lithology. Why not using the <alpha><beta><beta>/(<alpha><beta><beta>+<alpha><alpha><alpha>) and dia/(dia+reg) sterane ratios? From figure 4 it also seems that these ratios are different in the Permian and the Triassic (or at the transition).
L. 387: add reference for maturity indicators.
L. 391: which type of "older, reworked material"? How was this material detected? Is it abundant?
L. 394: Was HF used for preparing the "kerogen concentrates"? If clays are still present, matrix effect might still exist.
HF was used to remove clays but, still, there was a major component of heavy minerals.We did not attempt further enrichment with density separations prior to RE. However ZnBr was used to enrich the kerogen prior to microscopy. We have clarified this in the methods section.
L. 395 and following "Instead, the measured pattern suggests that at Kap Stosch, these biomarkers are responding to changes in facies and lithology as well as maturity…": this is not consistent with the previous sentences indicating the Tmax values (and therefore maturity) are not significantly different. Such a different maturity on a 50m-thick interval is not likely.
"… a situation that has been observed previously in sections from other time periods (Cao et al., 2009; Moldowan et al., 1986; ten Haven et al., 1986).": And so? Do these papers give explanations?

Without reading the following lines, it appears likely that facies/lithology is the major reason and the increased isomerization could be clay-catalysed.
L. 399: even if a hiatus exists - see previous comments- it probably did not represent an important thickness of sediment that might explain maturity differences.
L. 403. remove "during".
L 405: vertical variations of the C30 moretane/hopane and Ts/(Ts+Tm) ratios should be shown.
The expression "two stage change" is confusing.
L. 411 "the anti-correlation between these proxies and lithology in these…" and following phrase. The ratios are anti-correlated (as in Cao et al., 2009), however lithology is not anti-correlated with anything. Rephrase.
L. 423-424: the link between the different isomerization of C29 and C30 hopanes compared to C31 hopane and the different sources of organic matter should be more explained.
Section 3.3 is very awkward. The intention of the authors can be acknowledged, but several potential problems can be overcome:
- Stratigraphy. In case no element firmly justifies the sample order used by the authors, alternative curves corresponding to different sample orders can be shown.
- Outcrop samples. Numerous people work on outcrop samples, and outcrop erosion is a good process allowing to have relatively fresh material. The problem rather is surface oxidation (weathering) and contamination. Oxidation can somehow be estimated based on some biomarker ratios. What about contamination? Is the outcrop a cliff or is it covered by vegetation? What type of contamination is possible on this outcrop? What about contamination after collection, during handling and storage? I am not sure biomarkers selection is the solution to contamination problems. Ignoring some compounds can lead to wrong conclusions, on another hand, bacteria and associated hopanes are ubiquitous...
The last sentence of section 3.3 must be removed. Of course this work is a case study and anyone knows that global issues are not resolved by studying one location!
Conclusion: it is strange to begin the conclusion with palynological data while these data are not clearly exposed in the text.
L. 455-456: the correlation of TOC values with aryl isoprenoids abundance is not that obvious.
The last sentence of the conclusion should be re-written.

Legends to tables and figure:
L 597: remove "Measurements were made at Geoscience Australia", this type of information should appear in the methods section.
L 603: see previous comment on the reference of the map.
L 605: I do not believe a reference is needed for Greenland map.
L607: name of the formations should appear on the figure and not in the title.
Why is the log of locality 0 not shown? The log was not given by Teichert and Kummel ?
There is a slight inconsistency between figs 1 and 2-7 in the location of samples: I suppose locality 0 (exclusively Permian) corresponds to purple diamonds. Locality 13.75 with two Permian samples is green circles. Locality 6.75 with one Permian sample and the highest Triassic sample must be blue triangles. I see 5 samples on the log, but only 4 blue triangles. Locality 1, red squares. According to fig. 1, there should be 2 samples of Permian age however all samples are of Triassic age on fig. 2 and 7.
L. 608: "…the rock was exclusively shale (Modified from Teichert and Kummel, 1976)."
L. 614: C30 sterane index = 24 n-propylcholestane / total sterane.
L. 616 and following : Homohopane index = C35 hopane (22S + 22R isomers) / total C34 homohopanes. (d) 2,3,6 Aryl isoprenoids abundance normalized relative to total organic carbon

contents.
L 619: 2-Methylhopane index = 2-methylhopane /(2-methylhopane + C30 hopane)°—100.
L 621 "The four different symbols (diamonds, squares, triangles and circles) represent samples from the four different localities from this composite section": this information can appear directly in the figure with a cartoon giving the name of the outcrops (there is space available between 40m and 90m). Alternatively the name of corresponding section must be given in the legend.
L. 632: "selected". Also indicate that diasteranes are visible on the traces.
L. 641: "selected"
L. 644: "… chromatogram of m/z 134 from an aromatic…". Similarly for m/z 83 L. 646.
What is the use of showing the TIC chromatogram of a saturated fraction as it is not discussed in the text?
All n-alkylcyclohexanes should be identified on figure 6.
L. 650: remove the "." after "section".