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An integrated biomarker, isotopic and palaeoenvironmental study through the Late Permian event at Lusitaniadalen, Spitsbergen

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ABSTRACT

The largest extinction of the Phanerozoic occurred near the Permian/Triassic (P/Tr) boundary some 252 Ma ago. Several scenarios and drivers have been proposed for this event. Here we report for the first time an integrated study comprising sedimentological data, biomarker distributions/abundances and selected stable carbon and hydrogen isotopes along with bulk isotopes ($\delta^{34}S_{pyrite}$, $\delta^{13}C_{carb}$, $\delta^{13}C_{org}$) for a Late Permian section from Lusitaniadalen, Spitsbergen, Norway. Sedimentological and geochemical data support a marine transgression and collapse of the marine ecosystem in the Late Permian. Strong evidence for waxing and waning of photic zone euxinia throughout the Late Permian is provided by *Chlorobiaceae*-derived biomarkers (including $\delta^{13}C$ data) and $\delta^{34}S_{pyrite}$, implying multiple phases of H_2S outgassing and potentially several pulses of extinction. A rapid decrease in abundance of various land-plant biomarkers prior to the marine collapse event indicates a dramatic decline of land-plants during the Late Permian and/or increasing distance from palaeoshoreline as a consequence of sea level rise. Changes in δD of selected biomarkers also suggest a change in source of organic matter (OM) or sea level rise. We also found biomarker and isotopic evidence for a phytoplanktonic bloom triggered by eutrophication as a consequence of the marine collapse. Compound specific isotope analyses (CSIA) of algal and land-plant-derived biomarkers, as well as $\delta^{13}C$ of carbonate and bulk OM provide strong evidence for synchronous changes in $\delta^{13}C$ of marine and atmospheric CO_2, attributed to a ^{13}C-depleted source. The source could be associated with isotopically depleted methane released from the melting of gas clathrates and/or from respired OM, due to collapse of the marine ecosystem.

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1. Introduction

The extinction marking the Permian/Triassic (P/Tr) transition (ca. 252 Ma) was the most catastrophic of all the Phanerozoic mass extinctions (Erwin, 1994). Several scenarios for this biotic crisis have been proposed. Currently, most researchers accept that the extinction event(s) occurred during an episode of global warming, possibly triggered by CO_2 emissions from the Siberian volcanic eruptions and enhanced by methane release from the decomposition of gas hydrates (Benton and Twitchett, 2003; Twitchett, 2007). Probably due to a subsequent reduction in circulation, the oceans became oxygen deficient and in many places euxinic (Wignall and Twitchett, 1996; Kidder and Worsley, 2004; Grice et al., 2005a; Hays et al., 2007).

Associated with the biotic crisis is a sharp negative excursion in the stable carbon isotopic composition of marine carbonate ($\delta^{13}C_{carb}$) and OM ($\delta^{13}C_{org}$), generally attributed to the release of ^{13}C-depleted methane (Retallack et al., 2007). Although many sections show significant variation in $\delta^{13}C_{carb}$ and $\delta^{13}C_{org}$, these can also be attributed to input from diagenetically altered carbonate or changes in OM type (Scholle, 1995; Foster et al., 1997).

Globally, $\delta^{34}S$ of sulfide minerals also shows an isotopic shift near the P/Tr boundary, attributed to perturbations in the marine sulfur cycle and thus the redox-state of marine waters (Kajiwara et al., 1994; Grice et al., 2005a; Fenton et al., 2007; Holser et al., 1989). Isotope analysis of carbonate-associated sulfate ($\delta^{34}S_{CAS}$) at localities in China (Riccardi et al., 2006), Italy (Newton et al., 2004) and Iran (Korte et al., 2004) also infer the development of euxinic conditions.

Evidence for the development of photic zone euxinia (PZE), where H_2S occurs in the photic zone, is the presence of biomarkers derived from *Chlorobiaceae* (Green sulfur bacteria, GSB) (Summons and Powell, 1987; Grice et al., 1996, 1997). GSB are strict anaerobes and

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use a distinct assemblage of light-harvesting pigments. These include bacteriochlorophylls *c*, *d*, and *e* (**I**) and carotenoids isorenieratene (**II**) and/or chlorobactene (**III**) used to fix CO_2, using H_2S as an electron donor for photosynthesis. Biomarkers derived from GSB precursors have been reported in P/Tr sequences from both the Palaeotethys (Grice et al., 2005a,b) and Panthalassa Oceans (Hays et al., 2007).

Another Permian–Triassic biomarker of significance is the C_{33} *n*-alkylcyclohexane (*n*-heptacosylcyclohexane, C_{33}-*n*-ACH, **IV**), reported in East Greenland and Western Australia and attributed to a distinctive community of phytoplankton that bloomed during ecosystem collapse and continued to bloom well into the Lower Triassic (Grice et al., 2005b). In East Greenland, Fenton et al. (2007) reported a high relative abundance of dibenzothiophene (DBT, **V**), dibenzofuran (DBF, **VI**) and biphenyl (BP, **VII**) prior to the marine ecosystem collapse. These compounds disappeared shortly after the collapse, coinciding with a shift in $\delta^{34}S$ of pyrite and with the disappearance of low diversity arborescent cordiaite–conifer–pteridosperm vegetation. Sephton et al. (2005) identified a similar set of aromatic components (but lacking BP, **VII**) in a shallow-marine P/Tr section from northern Italy, and related them to a polysaccharide source of land-plants. Such components have also been reported in outcrop samples from Meishan, South China (Wang and Visscher, 2007).

Stable carbon isotopic compositions of biomarkers measured by CSIA is a complementary tool for establishing biogeochemical changes across the P/Tr boundary (Grice et al., 2005a) and can be used to verify the possibility of synchronous disturbance in atmospheric and marine CO_2 (Fenton et al., 2007). δD values of biomarkers provide additional insights into their sources and thermal maturity (Schimmelmann et al., 2006), and can also be used as a proxy for changes occurring in the ancient water cycle, including palaeotemperature and palaeosalinity (Andersen et al., 2001; Sauer et al., 2001; Dawson et al., 2004).

In the present study, we provide for the first time a more diverse approach than what is presently in the literature. This includes a detailed biomarker data set (focusing especially on GSB derived biomarkers, DBT (**V**), DBF (**VI**), BP (**VII**), C_{33}-*n*-ACH, **IV**) and the stable carbon and hydrogen isotopes of selected biomarkers, as well as bulk stable isotopes ($\delta^{34}S_{pyrite}$, $\delta^{13}C_{carb}$, $\delta^{13}C_{org}$), across a Late Permian section from Lusitaniadalen, Spitsbergen, Norway. This section was chosen because the strata are thermally immature (Mørk et al., 1999) and the sequence is similar to a previously studied section in East Greenland (Twitchett et al., 2001; Fenton et al., 2007). Our aim was to better understand the palaeoenvironmental changes that occurred around the collapse of the marine and terrestrial ecosystems using a combination of geological, sedimentological, palaeontological, isotopic and biomarker studies.

1.1. Geological setting

The studied section crops out in Lusitaniadalen, Spitsbergen (78° 17′ 54.8″N, 016° 43′ 59.3″E), and comprises three main lithofacies (Fig. 1, Table 1). The lower part of the measured section is composed of well-bioturbated fine-medium, greenish, glauconite-rich sandstones. Within these sandstones, chert nodules and more laterally persistent chert bands are frequently encountered, except in the uppermost 1.5 m. The fossil fauna includes locally abundant *Lingula* and occasional articulate brachiopods. Ichnodiversity is high and includes *Zoophycos*, large *Thalassinoides* (up to 33 mm in diameter), *Arenicolites*, *Skolithos* and *Palaeophycus*. The middle part of the measured section comprises 8 m of laminated, dark grey mudstones, with occasional very thin, parallel- or ripple-laminated, pyritic siltstone-fine sandstone beds (up to 5 cm thick) and, in the lower 3 m, 13–14 cm thick tabular carbonate-rich concretions. These concretionary beds yield fragments of marine fish, but there is no evidence of a benthic fauna and the rocks are laminated and unbioturbated. The water depth was much greater than that represented by the underlying sandstones, indicating sea level rise, and the mudstones were deposited under anoxic conditions. The upper 6 m of the measured section comprise lighter grey siltstones with interbedded fine sandstones, each 2–15 cm thick. The sharp-based, erosive, parallel-laminated or ripple cross-laminated sandstones are interpreted as tempestites and indicate shallower conditions relative to the underlying dark mudstones. There is a return of limited bioturbation (ichnofabric indices of ii2–3), including mm-diameter *Planolites* and small (2–6 mm diameter), shallow-penetrating *Skolithos*, *Arenicolites* and *Diplocraterion*, indicating colonisation by small deposit- and suspension-feeders and better oxygenation of the substrate and bottom waters.

We analysed samples around the transition between the lower, glauconitic bioturbated sandstones and the overlying dark grey, laminated mudstones (Fig. 1, Table 1). This interval records the last horizon with Permian shelly fossils (16.22 m above base of section) and the last occurrence of abundant, high diversity and large-sized trace fossils (at 16.85 m). Following the methodology of Twitchett et al. (2001), we equate the cessation of prolific bioturbation to ‘marine ecosystem collapse’, with the last occurrence of the abundant Permian trace fossil assemblage being the local ‘extinction horizon’. The disappearance of chert nodules and bands also occurs in our study interval (Fig. 1). Elsewhere, disappearance of cherty facies in the Changhsingian is interpreted to reflect the collapse of the biogenic silica factory (Beauchamp and Baud, 2002).

Collapse of the Late Permian marine ecosystem here occurs within a marine transgression, as at other sections worldwide. We recognise the base of this transgression to be the flooding surface at the base of the lowest dark grey, thinly bedded, pyritic siltstone at 16.32 m. The last occurrence of abundant Permian body fossils is just below this level. During this transgressive interval, laminated, pyrite-rich, siltstones and fine sandstones alternate with well-bioturbated, dark green, less pyritic sandstones that become thinner up section (Fig. 1).

Mørk et al. (1999) documented the P–Tr strata of Lusitaniadalen during their re-definition of the P–Tr stratigraphy of central and eastern Svalbard. According to their revised stratigraphic framework, our studied section spans the uppermost Kapp Starostin and lowermost Vikinghøgda Formations. Mørk et al. (1999) defined the base of the Vikinghøgda Formation at a ‘weathering surface’ within the upper two metres of the cherty, bioturbated sandstones, rather than at the obvious lithofacies break between the sandstones and mudstones. This ‘weathering surface’ is interpreted by Mørk et al. (1999) to represent a major erosional and transgressive surface, and yet in Lusitaniadalen they note that ‘there is no erosion, but a yellow-weathering bed occurs at the boundary’ (Mørk et al., 1999). We did not find evidence in the field for this yellow-weathering bed in Lusitaniadalen at the position suggested by Mørk et al. (1999). The position of the base of the Vikinghøgda Formation, as re-defined by Mørk et al. (1999), is thus unclear (Fig. 1). The precise position of the local P/Tr boundary is also unclear in this section. The conodont *Hindeodus parvus*, which defines the base of the Triassic (Yin et al., 2001) has not been recorded from Lusitaniadalen or neighbouring sections in central Spitsbergen (Mørk et al., 1999; Hounslow et al., 2008). Using limited and patchy palynological, ammonoid, conodont and magnetostratigraphic evidence, Mørk et al. (1999) correlated the P/Tr boundary with the base of their re-defined Vikinghøgda Formation. More recently, using magnetostratigraphy and ammonoid biostratigraphy from South China and the entire Boreal region, Hounslow et al. (2008) place the P/Tr boundary just prior to a short-duration reverse polarity interval (their local ‘Vh2.r’ magnetozone) that occurs above our sampled section, some 12 m above the base of the Deltadalen Member (Hounslow et al., 2008). This magnetostratigraphic P/Tr boundary definition is consistent with evidence from other marine and terrestrial sections worldwide (Taylor et al., 2009), occurs above the local extinction horizon (Twitchett et al., 2001), and means that the samples analysed in our study are all latest Permian (Late Changhsingian) in age (Fig. 1).

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