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Significance of carbon, nitrogen and their isotopic changes in a Permian-Triassic non-marine boundary section at Carlton Heights (Karoo Basin), South Africa

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ABSTRACT

We performed analyses of C_{org}, N_{org}, $\delta^{13}C_{org}$, and $\delta^{15}N_{org}$ from the non-marine Permian-Triassic boundary section at Carlton Heights in the Karoo Basin, South Africa. The Carlton Heights section is thus far unique in the Karoo in containing the Permian-Triassic palynological boundary between the Upper Permian *Klausipollenites schaubergeri* Zone and the Lower Triassic *Kraeuselisporites-Lunatisporites* Zone, separated by a 1-m thick "fungal event" zone, marked by abundant fungal cell remains (*Reduviasporonites*) and woody debris. The C_{org} values obtained are very low (below 0.05%), but reach a maximum of 0.1% in the middle of the fungal event zone. N_{org} varies little from 0.02%, except in the middle and top of the fungal event, where it rises to 0.04%. C/N ratios are extremely low throughout the section (less than 3), reaching a maximum of 2.49 during the fungal event, co-incident with the peaks in N_{org} and C_{org}. The very low C/N ratios resemble those found in modern burned soils with low bacteria/fungi ratios, and the lack of variation suggests no change in the organic matter source. $\delta^{15}N_{org}$ values vary between 2.46‰ and 4.25‰, showing no significant changes in the fungal event zone. The $\delta^{13}C_{org}$ values are all below −25‰, and reach a low of −27.41‰ in the fungal event zone. This negative shift in $\delta^{13}C_{org}$ is an example of the global negative shift in $\delta^{13}C$ found associated with the end-Permian extinctions and fungal event.

1. Introduction

The Permian-Triassic boundary section at Carlton Heights, in the Northern Cape, South Africa (GPS: 31°13.03′S, 24°56.96′E) is one of the most thoroughly studied non-marine sections in South Africa (e.g., Schwindt et al., 2003; Steiner et al., 2003; Retallack et al., 2003; Ward et al., 2005; Tabor et al., 2007; Gastaldo and Rolerson, 2008) (Fig. 1a and b). In latest Permian time (~252 million years ago), Carlton Heights lay at about 70°S latitude in the center of Gondwanaland (Zharkov and Chumakov, 2001). The lower part of the section shows uppermost Permian medium-to fine-grained sandstones alternating with siltstones and mudstones of the Balfour Formation, deposited by a high sinuosity meandering stream-floodplain complex in a semi-arid climate (Smith, 1987; Katemaunzanga and Gunter, 2009). These beds are abruptly overlain by lowermost Triassic medium-to coarse-grained sandstones of the Katberg Sandstone Formation, deposited by swiftly flowing, low sinuosity, braided, ephemeral streams (Stavrakis, 1979) (Fig. 1c). The change in sedimentation has been attributed to the catastrophic loss of land vegetation during the end-Permian extinction event, causing increased run-off and physical erosion rates (Retallack and Krull, 1999; Sephton et al., 2005; Smith and Botha-Brink, 2014). Such changes in erosion rates are detectable and widespread in both non-marine and marine Permian-Triassic boundary sections (e.g., Visscher et al., 1996). In the Karooo basin, late Permian paleosols have root traces comparable to those of open shrub land and riparian woodland, whereas early Triassic paleosols have root traces and profile forms like soils of open woodland (Retallack, 2001). This is a significant paleoenvironmental change, but not as dramatic a change as would be expected from the devastating extinctions of vertebrate genera (Retallack et al., 2003).

This study concentrates on the changes that take place in the uppermost Permian Palingkloof Member of the Balfour Formation, which consists of about 20 m of laminated to massive maroon mudstones, with thin sandstones at its base, overlain by about 10 m of green fine-grained sandstones interbedded with green and red siltstones and mudstones (Fig. 1c). Retallack et al. (2003) placed the Permian-Triassic boundary

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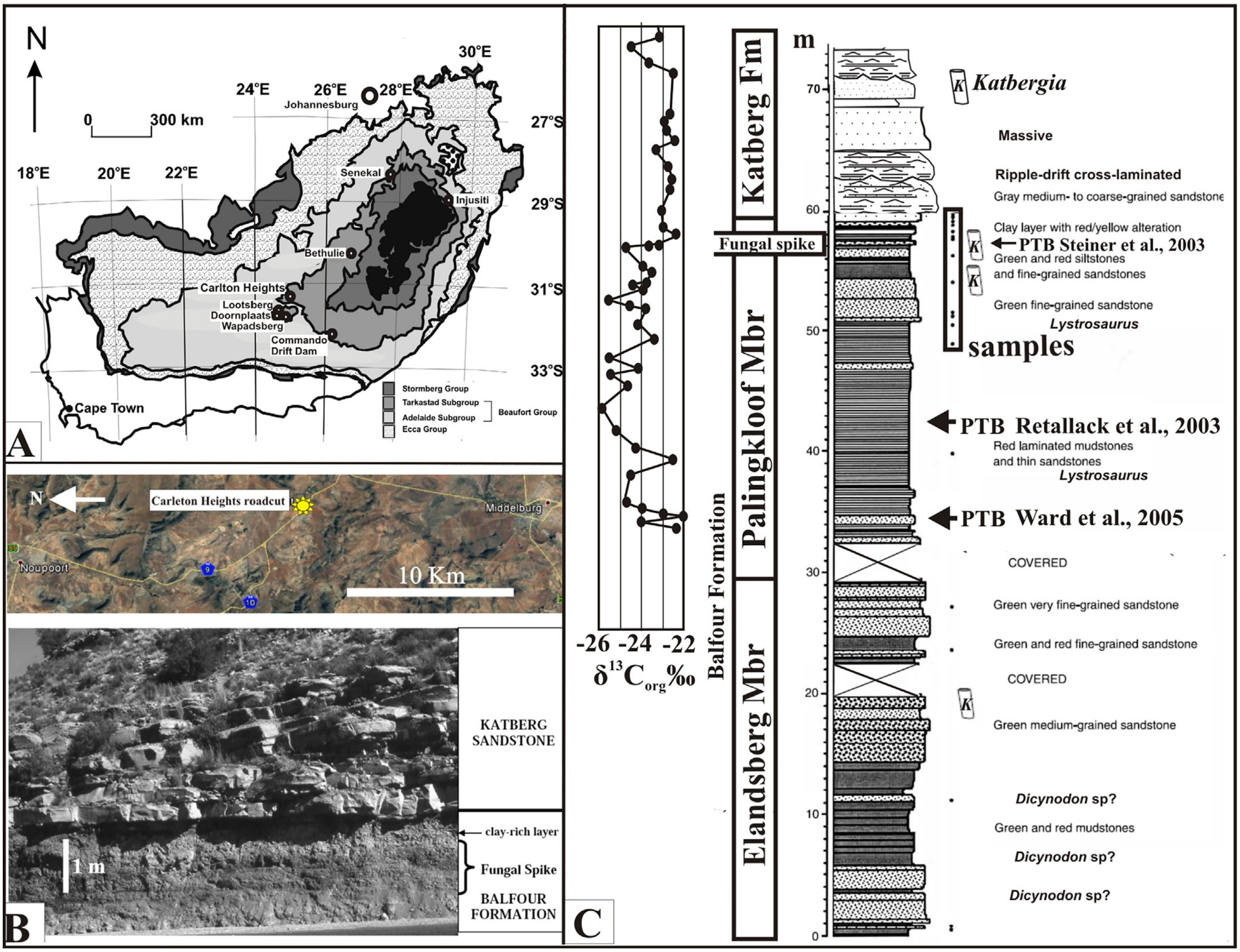

Fig. 1. a: Location of Carlton Heights in South Africa; b: Location of Carlton Heights road-cut section between Middelburg and Noupoort, and view of section (from Steiner et al., 2003); and c: palynological P-T boundary section at Carlton Heights with $\delta^{13}C_{org}$ (Steiner et al., 2003; Ward et al., 2005). Locations of *Katbergia* trace fossils are from Gastaldo and Rolerson (2008).

just below a distinctive claystone breccia at about 42 m in the Carlton Heights section, 18 m below the base of the Katberg Sandstone (Fig. 1c). Such lithological placement of biostratigraphic boundaries is unwise, however, even if the sediment is considered unique, given the variability and repetitive nature of fluvial sediments (MacLeod et al., 2000). Ward et al. (2005) placed the P-T boundary where *Dicynodon* is replaced by their *Lystosaurus* sp. C at about 35 m in the section, 24 m below the base of the Katberg Sandstone Formation (Fig. 1c). This placement of the P-T boundary lies just above a change in magnetic polarity from reversed to normal (De Kock and Kirschvink, 2004). Ward et al's (2005) *Lystrosaurus* species C appears just below the "fungal spike" at Lootsberg (Lucas, 2010) and may be equivalent to *Lystrosaurus curvatus*, considered to be the least derived of the *Lystrosaurus* species, morphologically closest to the rest of the Permian dicynodonts (Botha and Smith, 2007).

Between the P-T boundary based on lithology and vertebrate fauna, and the lowermost Katberg Sandstone, there is a transitional zone about 10 m thick showing evidence of increasing aridity (Smith and Botha-Brink, 2014), which contains more than twenty paleosols of protosol, calcisol and gleysol types (Retallack et al., 2003), representing what were low-lying alluvial areas, with seasonally fluctuating (but locally high) water tables in an arid to semi-arid climate (Mack and James, 1994). Though it is difficult to estimate the rate of formation of such soils, the transformation of protosols to gleysols may take up to 10,000 years (Reintam and Moora, 1998). The large number of paleosols in the 30 m-thick Palingkloof Member sediment package indicates that the sediments may have taken thousands of years to accumulate. Estimates of accumulation rates of up to 50 cm/kyr (Steiner et al., 2003) would make the duration of the 30-m thick unit about 60,000 years. These protosols and gleysols contain the probable callianasid arthropod trace fossil, *Katbergia*, which ranges from the Elandsberg member of the Balfour Formation into the Katberg Sandstone (Gastaldo and Rolerson, 2008), suggesting no major paleoenvironmental changes in the overbank facies from Permian to Triassic (Fig. 1c).

The palynological Permian-Triassic boundary, is at 56 m in the outcrop, only about 3 m below the base of the Katberg Sandstone. At that level, the latest Permian *Klausipollenites schaubergeri* pollen/spore assemblage disappears, and is replaced by a 1-m thick section of siltstones and fine sandstones containing only increased woody fragments and the abundant remains of fungi (*Reduviasporonites*) (Steiner et al., 2003). This "fungal event" layer is overlain by 0.5 m of siltstones with an early Triassic *Kraeuselisporites-Lunatisporites* pollen/spore assemblage of lycopods (clubmosses, quillworts and spike mosses), and two gymnosperm pollen types, just prior to the main sedimentological change to the braided stream deposits of the lowermost Katberg Sandstone Formation (Steiner et al., 2003) (Fig. 2).

The "fungal event", (or fungal spike), is found worldwide in both marine and terrestrial P-T boundary sections . The fungal event is

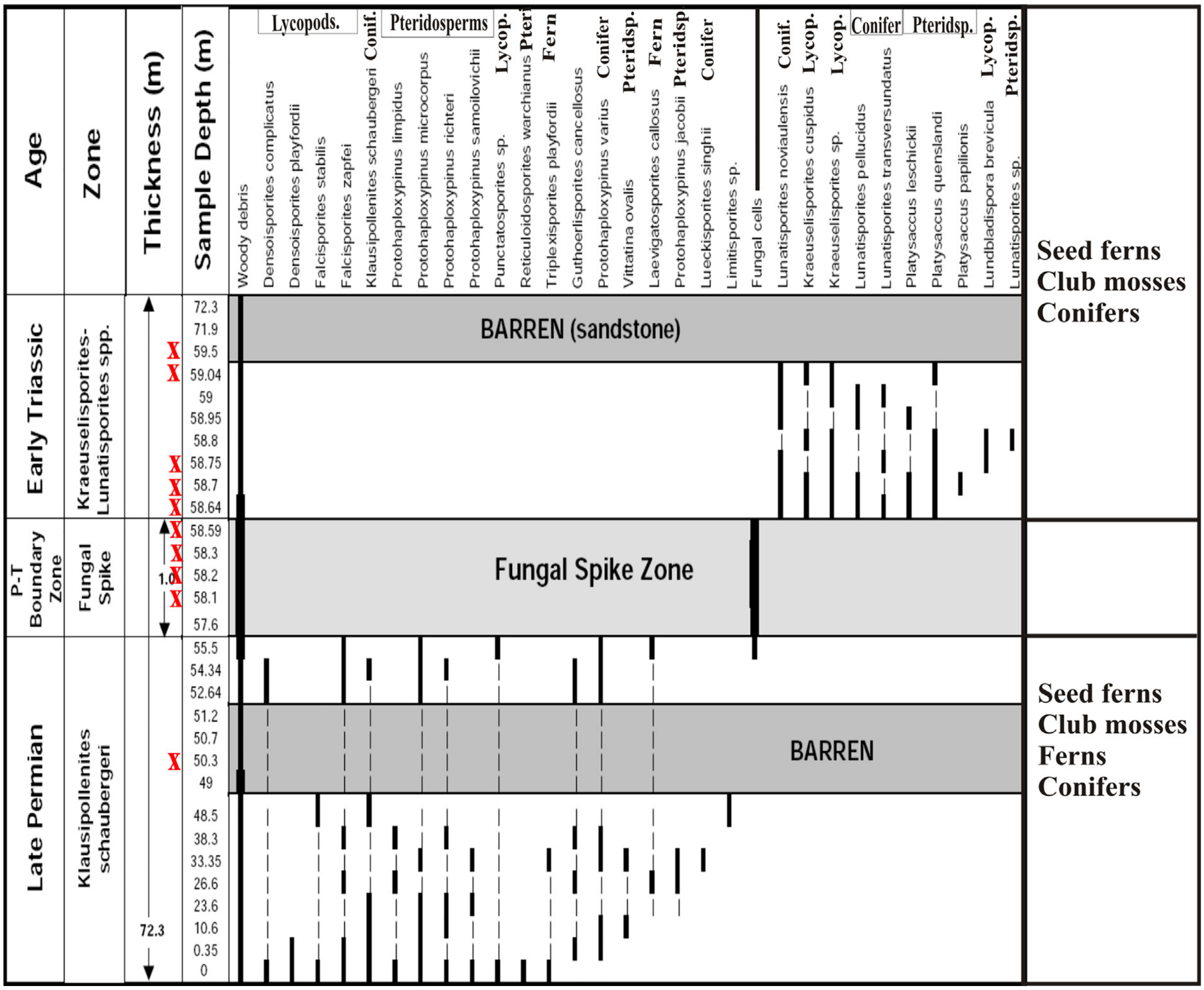

Fig. 2. Palynology of P-T boundary section at Carlton Heights (from Steiner et al., 2003): x's mark samples analyzed here.

interpreted globally as an interval of decreased terrestrial biomass, with large amounts of decaying vegetation associated with the P-T crisis and boundary (Eshet et al., 1995; Visscher et al., 1996; Rampino and Eshet, 2018). Although there has been some dispute as to whether the “fungi” (*Reduviasporonites*) that makes up the fungal event are really fungi (Foster et al., 2002; Hochuli, 2016), recent biogeochemical work supports a fungal affinity and, more specifically, with the living fungus, *Rhizoctonia*, which is often an opportunistic facultative pathogen (Sephton et al., 2009; Visscher et al., 2011; Rampino and Eshet, 2018), whereas the non-fungal affinity is based on morphology (Spina et al., 2015). Even if accepted as fungi, *Reduviasporonites* is not confined to the end Permian, and should be expected at any level where plant remains are being degraded (Hochuli, 2016). But the *Reduviasporonites* level at Carlton Heights marks the sharp palynological change from late Permian to early Triassic plants which, though possibly the result of ecological control, nevertheless marks a major and irreversible change in floras (Anderson, 1977).

At Lootsbergpass, about 80 km SSW of Carlton Heights, *Glossopteris* and a Permian palynoflora occur just below the base of the Katberg Sandstone, with the junction of the *Dicynodont* and *Lystrosaurus* assemblage zones about 10 m below the floral change (Ward et al., 2005). Here there is some dispute, possibly due to taking the boundary at the top of the equivalent of the green sandstones of the Elandsberg member at 15–30 m in the Carlton Heights section, where the *Glossopteris* flora also occurs (Gastaldo et al., 2015). Both Carlton Heights and Lootsbergpass sections thus show the disappearance of the Late Permian *Dicynodon* vertebrate assemblage prior to the floral extinction. There remains the possibility, however, that the actual vertebrate zone boundary lies above the last occurrence of *Dicynodon* in the section because of the Signor-Lipps effect, whereby neither the first nor the last organism in a given taxon will be recorded as a fossil (Signor and Lipps, 1982). An accepted procedure now it to define boundaries on the first appearance datum (FAD) of a fossil taxon; in this case the first appearance of *Lystrosaurus curvatus* (Botha and Smith, 2007).

We do not wish to comment further on the exact position of the vertebrate Permo-Triassic boundary (however defined) at Carleton Heights because equating supposedly distinctive lithological units in very variable continental sediments, even in relatively small area, can lead to misleading correlations and wrong placement of biostratigraphic horizons (Gastaldo et al., 2015). Even the plant record across the Permo-Triassic boundary is poor and dominated by dispersed, fragmentary material in lenticular horizons which are not necessarily the same age, even when assumed to be so (Gastaldo et al., 2005; Ward et al., 2005). But, we do consider the common and easily transportable plant spores to give the most exact continental biostratigraphic resolution, reflecting major biome changes through time across large continents (Stephenson, 2016).

This paper reports on the analyses of the carbon and nitrogen content of organic material (C_{org} and N_{org}) and their $\delta^{13}C_{org}$ and $\delta^{15}N_{org}$ isotopic values from sediments across the proposed P-T boundary based on palynology and the fungal event in the Carlton Heights section, and discusses the significance of these analyses for paleoenvironmental changes at this horizon.

2. Methods

The available samples used for palynology in Steiner et al. (2003) were analyzed here for organic carbon and nitrogen, and their isotopes. Whole-rock powdered samples were acidified with 10% HCl to remove the acid-soluble components. To determine concentration and isotopic ratios, the remaining insoluble residues were weighed into tin capsules and measured using a Costech Elemental Analyzer ECS 4010 paired to a Thermo Delta V + Isotope Ratio Mass Spectrometer at the Environmental Analytical Facility of the University of Massachusetts Boston. Carbon and nitrogen were quantified separately, with a CO_2 trap used for nitrogen. Organic carbon and nitrogen concentrations were calibrated against 5-point calibration curves of the Costech Acetanilide standard. Replicate analyses of check standards for organic carbon and nitrogen concentrations were within 2 and 5 percent error of certified values respectively.

Isotope standards NBS-19, IA-R022, and NIST 8542 were used to calibrate the measured $\delta^{13}C_{org}$ values, and the isotope compositions are expressed in per mil notation relative to Vienna Pee Dee belemnite (VPDB). Isotope standards USGS 40, USGS 41a, and IVA Urea were used to calibrate the measured $\delta^{15}N_{org}$ values, and the isotope compositions are expressed in per mil notation relative to Air. Precision, based on replicate measurements of standards, was determined to be less than 0.2‰ for $\delta^{13}C_{org}$ and less than 0.3‰ for $\delta^{15}N_{org}$.

3. Results

The C_{org} values obtained are very low (below 0.05%), but reaching a maximum of 0.1% in the middle of the fungal event zone. N_{org} varies little from 0.02%, except in the middle and top of the fungal event, where it rises to 0.04%. C/N ratios are extremely low throughout the section (less than 3), reaching a maximum of 2.49 during the fungal event, coincident with the peaks in N_{org} and C_{org} (Fig. 3; Table 1). $\delta^{13}C_{org}$ values are all below −25‰, and reach a low of −27.41‰ in the fungal event zone (Fig. 3). $\delta^{15}N_{org}$ values vary between 2.46 and 4.25‰, showing no significant changes in the fungal event zone (Fig. 3).

3.1. Interpretation

The C_{org} and N_{org} content and isotope ratios most likely come from the wood fragments rather than the pollen and spores, which are volumetrically insignificant. The very low C/N ratios of less than 3 are only found in modern burned soils with low bacteria/fungi ratios (Palese et al., 2004), although decaying wood can also contain 2–3 fold higher N_{org} concentrations with lower C_{org} contents compared with their undecayed counterparts (Ometto et al., 2006). The very low C_{org} values in the very fine-grained sandstones and siltstones of the fungal event zone suggest suspension settling (at low velocities of less than 0.01 m/sec^{-1}) of only the smaller wood particles being transported from elsewhere with the very fine sand.

At Carlton Heights, the rapid and short-lived fungal event likely represents an interval of increased terrestrial devastation with enough decaying wood debris to support a proliferation of fungi (Steiner et al., 2003). The peaks in C_{org} and N_{org} concentrations through the fungal event zone, without a major change to C/N ratios, are likely reflecting the increase in woody debris abundance based on palynological analyses without a change in organic matter source (Fig. 3). Besides the fungal event zone itself, lithological evidence points to drastic vegetation loss at Carlton Heights with the change to the Katberg Sandstone occurring about 50 cm above the fungal event zone (Ward et al., 2000; Steiner et al., 2003). Furthermore, the decrease in palynomorph diversity following the lower barren zone (50–62 m), but below the fungal event zone, could represent an initial pulse of environmental stress at Carlton Heights (Fig. 2), but preservation bias cannot be ruled out (Steiner et al., 2003). At other locations, terrestrial devastation at the P-T boundary is associated with wildfires (Grice et al., 2007; Shen et al., 2011), soil acidification (Sephton et al., 2015) and inferred acid rain (Maruoka et al., 2003).

Also, unlike the paleosols of coal measures which were partially or entirely waterlogged as they sank below thick peats and were isolated from the atmosphere, the abundant latest Permian-earliest Triassic paleosols of calcareous red beds are massive and hackly from the activity of roots and burrows, and have a horizon of calcareous nodules below surface rooted horizons formed over substantial periods of time (millennia) in full contact with the atmosphere and biosphere (Retallack, 2001). In the Carlton Heights section, $\delta^{13}C$ and $\delta^{18}O$ values

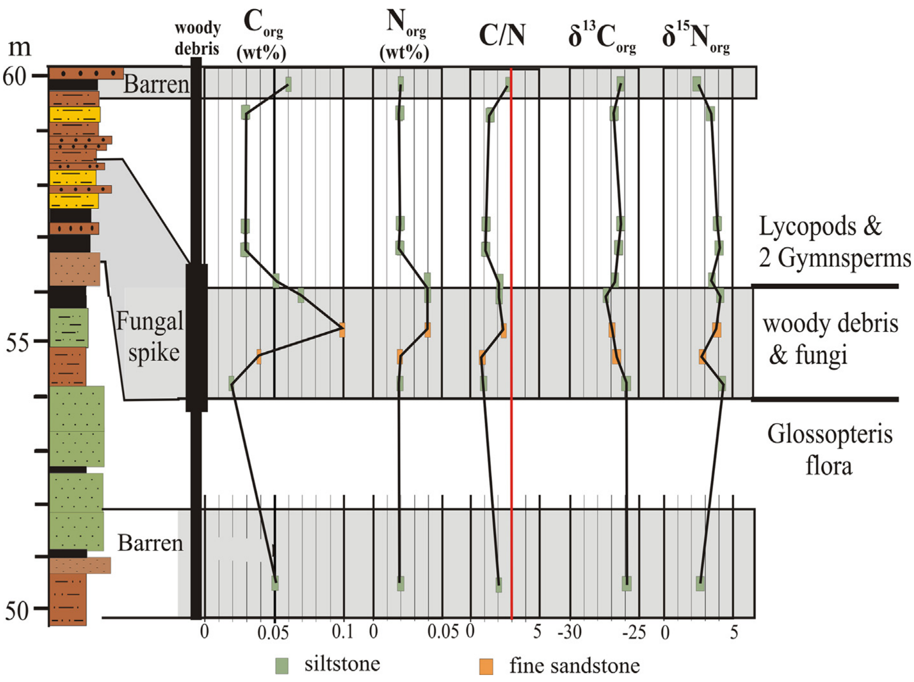

Fig. 3. Plots of C_{org}, N_{org}, C/N, $\delta^{13}C_{org}$ and $\delta^{15}N_{org}$ in the Carlton Heights Permian-Triassic palynological boundary section.

Table 1
Analyses.

Sample	10	9	8	7	6	5	4	3	2	1
Location	+ 59.5 m	+ 59.04 m	+ 58.75 m	+ 58.7 m	+ 58.64 m	+ 58.59 m	+ 58.3 m	+ 58.2 m	+ 58.1 m	+ 50.3 m
N_{org} (wt %)	0.02	0.02	0.02	0.02	0.02	0.04	0.04	0.04	0.02	0.03
C_{org} (wt %)	0.06	0.03	0.03	0.03	0.05	0.07	0.10	0.04	0.02	0.05
$\delta^{13}C_{org}$ (‰ VPDB)	− 26.40	− 26.76	− 26.25	− 26.31	− 26.83	− 27.41	− 26.96	− 26.61	− 25.82	− 25.99
$\delta^{15}N_{org}$ (‰ AIR)	2.46	3.53	3.89	4.05	3.60	4.08	3.95	2.86	4.25	2.87
C_{org}/N_{org}	2.80	1.48	1.26	1.03	2.09	2.03	2.49	0.94	0.95	1.96

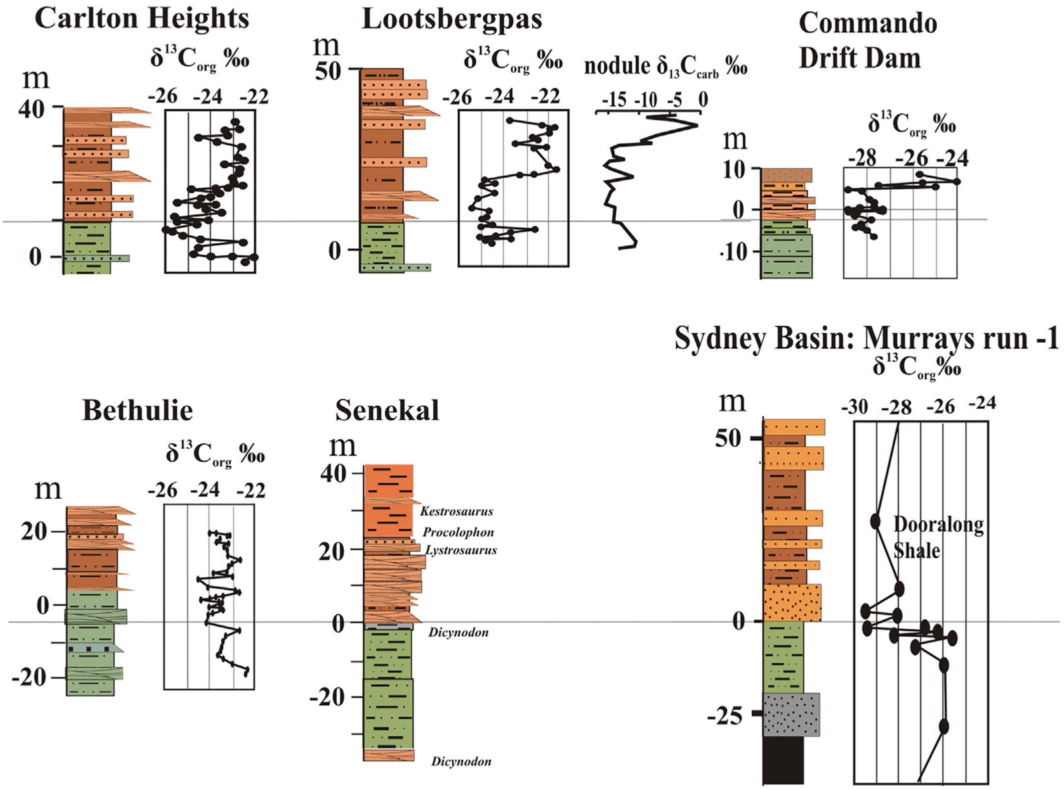

Fig. 4. Detailed $\delta^{13}C_{org}$ trends across non-marine Permian-Triassic boundary sections in Karoo Basin: Carlton Heights and Lootsberg sections (Ward et al., 2005); Commando Drift Dam (Coney et al., 2007); Bethulie (Ward et al., 2005); Senekal (Maruoka et al., 2003); and Australia Sydney Basin- Murrays Run - 1 (Morante, 1996).

from paleosol carbonate nodules composed of micrite are taken to reflect atmospheric carbon dioxide as they formed in well-drained, open system soils, in contrast to the recrystallized nodules which formed in phreatic closed environments (Tabor et al., 2007). Below 37–46 m in the Carlton Heights section, micrite nodule $\delta^{13}C_{nod}$ values range from − 16.9 to − 21.9‰, whereas the $\delta^{18}O_{nod}$ values range from − 2.1 to − 18.2‰. The $\delta^{13}C_{nod}$ values at 49 m and 62 m, rise to − 5.1‰, while the $\delta^{18}O_{nod}$ values remain average at − 11‰. The two values of $\delta^{13}C_{nod}$ at 49 m and 62 m are around 20‰ higher than the $\delta^{13}C_{org}$ values, which is in keeping with the C3 plant Calvin pathway of most land plants, which biochemically discriminates against ^{13}C to produce a $\delta^{13}C_{org}$ shift of about − 20‰ (O'Leary, 1988). Above 71 m in the section, in the Katberg Sandstone, the $\delta^{13}C_{nod}$ values drop again to − 12‰, as do the $\delta^{18}O_{nod}$ values to − 15‰ (Tabor et al., 2007).

The section between ~ 50 and 60 m in the Carlton Heights section thus shows a typical relationship between $\delta^{13}C_{nod}$ and $\delta^{13}C_{org}$ and shows little variation (Fig. 3). The values above and below the fungal event zone, however, show much lower $\delta^{13}C_{nod}$ and $\delta^{13}C_{org}$ values, which indicates removal of $\delta^{13}C$ from the system. The low values for $\delta^{13}C_{nod}$ may be due to crystallization of calcite in semi-closed systems independent of the atmosphere, in reducing swamp conditions, as may the carbonate nodule microspar value of − 15.5‰ at 62 m in lowermost Katberg Sandstone (Tabor et al., 2007).

The $\delta^{13}C_{org}$ values at the Carlton Heights P-T boundary section contains relatively subdued variation with a transient decrease from around − 26‰ to − 27.5‰ in the fungal event zone before increasing back to around − 26.5‰. A similar ~ 1–2‰ negative excursion around the fungal event zone is recorded at this section in Ward et al. (2005), but in our study we can constrain the $\delta^{13}C_{org}$ event to the 1-m thick fungal event zone itself. Ward et al. (2005) recorded a larger $\delta^{13}C_{org}$ negative excursion of around 4‰, (from − 22 to − 26‰) between 33 and 40 m at their biostratigraphic boundary between *Dicynodon* and *Lystrosaurus* zones (Fig. 4). The negative excursion is interrupted by a reversal to − 23‰ at about 35 m in the section (Ward et al., 2005). The complexities shown by Ward et al. (2005) indicate the necessity of fine-scale sampling to determine significant fluctuations. The similar sections at Lootsbergpas, 80 km to the SSW, and Bethulie, ~ 300 km to the NE shows a very comparable $\delta^{13}C_{org}$ pattern, but with a more condensed section, and most seem to correlate with the change from greenish to reddish sediments in most sections and the last occurrence of *Lystrosaurus* in the Senekal section (Fig. 4). *Lystrosaurus* is interpreted as a burrower (Retallack et al., 2003) and, like modern vertebrate burrowers was presumably adapted to low oxygen and high carbon dioxide in its burrows (Shams et al., 2005). It would be interesting to

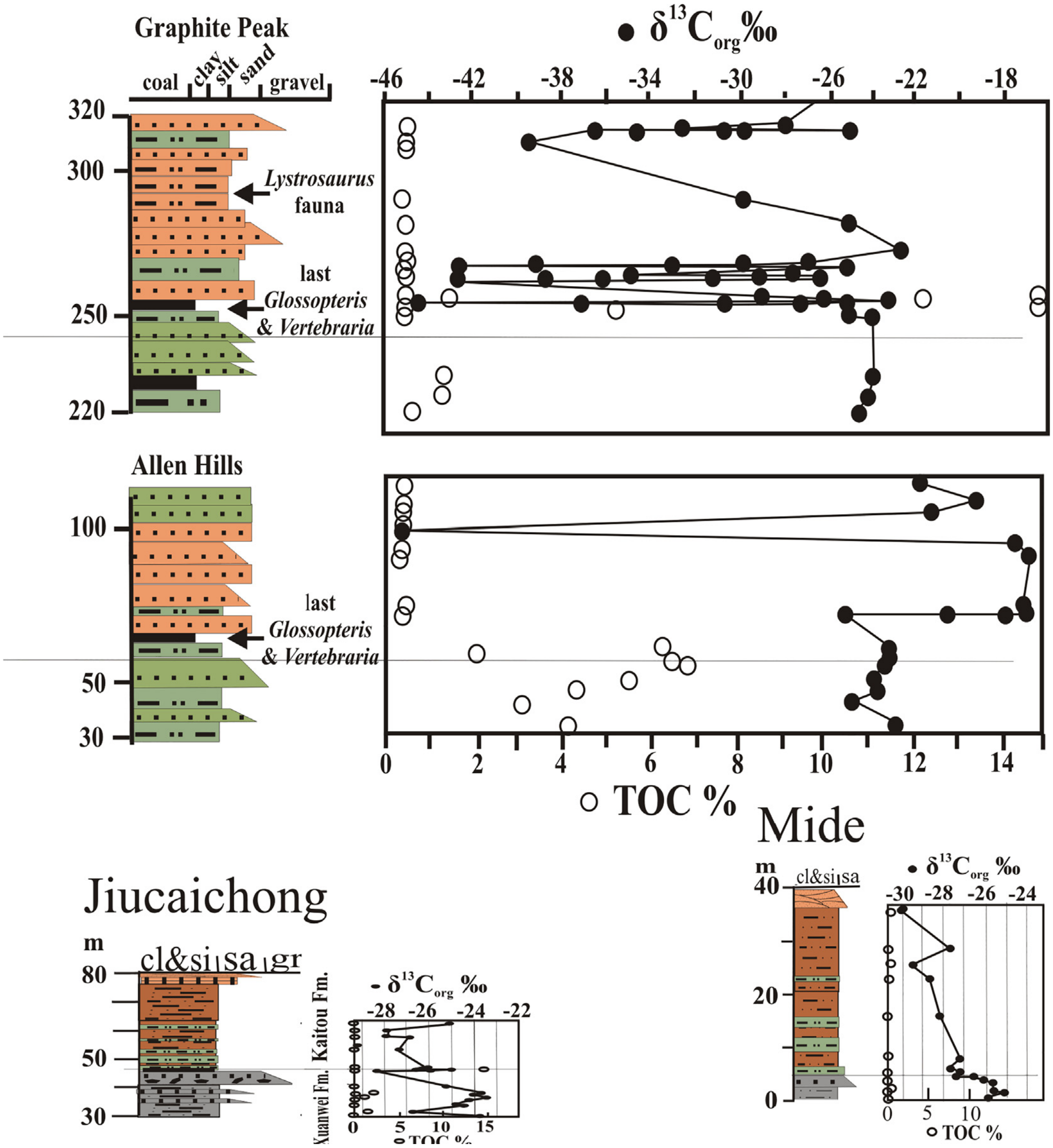

Fig. 5. Detailed $\delta^{13}C_{org}$ trends across non-marine and marine Permian-Triassic boundary sections in Antarctica – Graphite Peak and Allen Hills sections (Krull and Retallack, 2000); and China – Jiucaichong and Mide sections (Cui et al., 2015).

see if the larger $\delta^{13}C_{org}$ negative excursion at the *Dicynodon/Lystrosaurus* boundary is due to methane oxidation and consequent loss of oxygen and increase in carbon dioxide.

The $\delta^{13}C_{org}$ variations in South Africa are much less than equivalent Gondwanan non-marine P-T boundary sections in higher paleolatitudes, such as in Australia, where they reach as low as −30‰ in the Sydney Basin and nearby basins (Morante, 1996; Thomas et al., 2004; Van de Wetering et al., 2013) (Fig. 4); in Antarctica, where they reach as low as −46‰ (Krull and Retallack, 2000) (Fig. 5); and in marine sections in the Nelson region of New Zealand, where $\delta^{13}C_{org}$ reaches as low as −38‰ at the same stratigraphic level (Krull et al., 2000) (Fig. 6). Comparable patterns are seen in non-marine sections in southwest China at Jiucaichong and Mide, where the ranges of $\delta^{13}C_{org}$ are somewhat more negative in these lower latitude and more coastal sites (Fig. 5) (Cui et al., 2015). A pronounced negative shift in $\delta^{13}C_{org}$ just below the paleontological PTr boundary is seen in all sections, is thus a world wide phenomenon, and can not be due to changes in the isotopic character of local sources like a change in vegetation (Korte et al., 2010). The negativity of this shift, however, seems to decrease from the Permo-Triassic south pole to the equator for reason yet to be investigated.

Even if the fungal remains are present at a high enough abundance to influence the $\delta^{13}C_{org}$ signature over the woody debris, they are unlikely to be the cause of the decreasing $\delta^{13}C_{org}$ trend through the fungal event zone. Fungi are ^{13}C enriched compared to their food source (Kohzu et al., 1999), and this fractionation agrees with the coeval measurements of the fungal remains and land-plant material from a P-T boundary section in Italy (Sephton et al., 2009). Therefore, if anything, the fungal remains likely subdued the $\delta^{13}C_{org}$ depletion event in the fungal event zone.

Compared to $\delta^{13}C_{org}$ values, $\delta^{15}N_{org}$ values show little systematic variation through the fungal event zone, and the values are very similar to samples prior to and subsequent to this zone. This suggests little variation in nitrogen cycling during the measured time interval. The $\delta^{15}N$ values of wood can be diagenetically overprinted, while $\delta^{13}C$ values are more resistant (Gröcke, 2002), and so diagenesis cannot be ruled out for the lack of $\delta^{15}N_{org}$ variation across the fungal event zone.

For the $\delta^{13}C_{org}$, the values of the terrestrial organic matter were likely controlled by atmospheric $\delta^{13}C$ (e.g., Cui et al., 2015), as the relatively constant C/N ratios of terrestrial organic matter at Carlton Heights suggests that the source of the organic matter did not change across the palynological boundary. The decrease of ~1–2‰ in $\delta^{13}C_{org}$

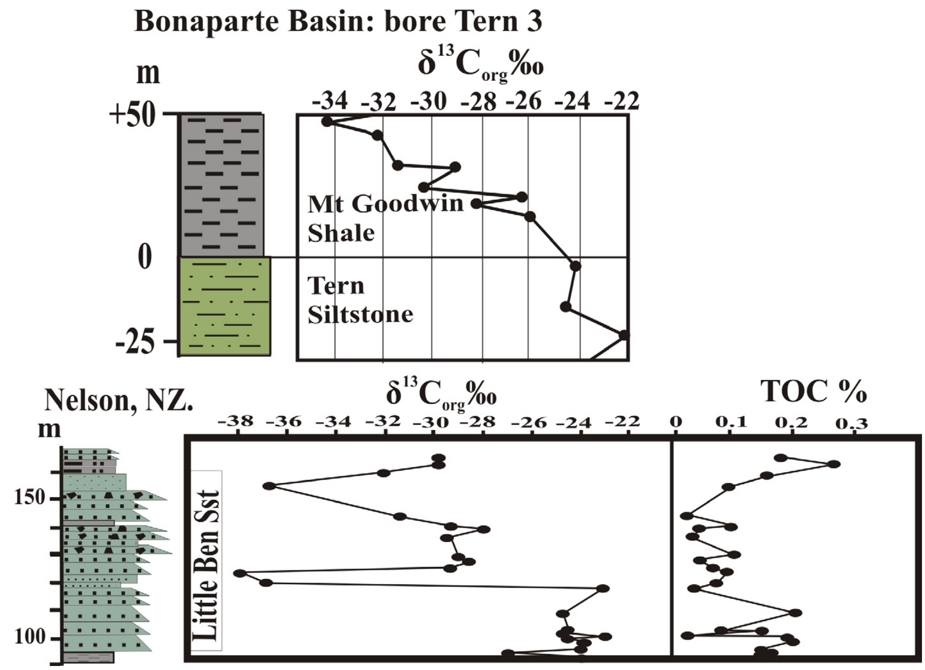

Fig. 6. Detailed $\delta^{13}C_{org}$ trends across marine Permian-Triassic boundary sections in the Bowen basin, northern Australia (Morante, 1996) and Nelson, New Zealand (Krull et al., 2000).

values recorded during the fungal event can be correlated with a global negative shift in $\delta^{13}C_{org}$ in marine and non-marine sections (e.g., Korte et al., 2010). One potential cause of the global fungal proliferation on rotting vegetation is forest-kill by acid rain associated with the eruption of the Siberian Traps (e.g., Visscher et al., 1996; Rampino and Eshet, 2018). In modern forest soils, ratios of bacteria to fungi drop precipitately to less than one below pH 4 (Matthies et al., 1997). And some Permian lakes had negative pH's (Benison, 2013). At Senekal, in the northern Karooo basin (Fig. 1A), dark lake mudstones immediately below the erosional contact with the Katberg Sandstones show a sudden marked negative shift in $\delta^{34}S$, caused by high sulphide accumulation induced by acid rain (Maruoka et al., 2003).

Another effect of the massive volcanism is the release of isotopically light CO_2 and/or CH_4 gases into the atmosphere, which could explain the negative shift in $\delta^{13}C_{org}$ recorded in globally distributed terrestrial and marine sections (e.g., Korte et al., 2010; Svensen et al., 2009). The Carlton Heights data adds to the growing global database of the end-Permian fungal event associated with decreasing $\delta^{13}C_{org}$ values in marine and non-marine sections (Visscher et al., 1996; Cui et al., 2015; Rampino and Eshet, 2018).

4. Conclusions

The Carlton Heights section is thus far unique in the Karoo in containing the Permian-Triassic palynological boundary between the Upper Permian *Klausipollenites schaubergeri* Zone and the Lower Triassic *Kraeuselisporites-Lunatisporites* Zone, separated by the 1-m thick “fungal event” zone, marked by abundant fungal cell remains (*Reduviasporonites*) and woody debris. The C_{org} and N_{org} values obtained are very low but reach a maximum in the fungal event zone. C/N ratios are extremely low (less than 3) throughout the section with little variation suggesting no change in organic matter source across the fungal event. The low values resemble those found in modern burned soils with low bacteria/fungi ratios. $\delta^{15}N_{org}$ values vary between 2.46‰ and 4.25‰, showing no significant changes within the fungal event zone. The $\delta^{13}C_{org}$ values show a ~2‰ negative shift in the fungal event zone and reach a low of −27.41‰. This shift in $\delta^{13}C_{org}$ may correlate with the global shift in $\delta^{13}C$ seen in P-T boundary sections worldwide.

The successive extinction of vertebrates and plants seen in the South African section mirror the inferred two-fold extinction in the marine realm, separated by thousands of years (Song et al., 2013). The first phase of extinction is attributed to a slow injection of carbon into the atmosphere, and ocean when pH remained stable. During the second extinction pulse, however, a rapid and large injection of carbon caused an abrupt acidification event that drove the preferential loss of heavily calcified marine biota and land plants (Clarkson et al., 2015).

Though beyond, the scope of this local study, we really need a comprehensive critical review of the abundant available **detailed** stratigraphy, paleobiological and geochemical changes across the Permo-Triassic boundary in both northern and southern hemispheres to adequately evaluate the causes of the mass extinctions. This has yet to be done.

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References

Anderson, J.M., 1977. The biostratigraphy of the Permian and Triassic. Part 3. A review of Gondwana Permian palynology with particular reference to the northern Karroo Basin of South Africa. Mem. Bot. Surv. S. Afr. 41, 1–133.

Benison, K.C., 2013. Acid saline fluid inclusions: examples from modern and Permian extreme lake systems. Geofluids 13, 579–593. http://dx.doi.org/10.1111/gfl.12053.

Botha, J., Smith, R.M.H., 2007. *Lystrosaurus* species composition across the permo–triassic boundary in the Karoo Basin of South Africa. Lethaia 40, 125–137.

Coney, L., Reimold, U., Hancox, J., Mader, D., Koeberl, C., McDonald, I., Struck, U., Vajda, V., Kamo, S., 2007. Geochemical and mineralogical investigation of the permian-triassic boundary in the continental realm of the southern Karoo Basin, South Africa. Palaeoworld 16, 67–104.

Clarkson, M.O., Kasemann, S.A., Wood, R.A., Lenton, T.M., Daines, S.J., Richoz, S., Ohnemueller, F., Meixner, A., Poulton, S.W., Tipper, E.T., 2015. Ocean acidification and the Permo-Triassic mass extinction. Science 348, 229–232. http://dx.doi.org/10.1126/science.aaa0193.

Cui, Y., Bercovici, A., Yu, Jianxin, Kump, L.R., Freeman, K.H., Su, Shangguo, Vajda, V., 2015. Carbon cycle perturbation expressed in terrestrial Permian–Triassic boundary sections in South China. Global Planet. Change 148, 272–285.

De Kock, M.O., Kirschvink, J.L., 2004. Paleomagnetic constraints on the Permian-Triassic boundary in terrestrial strata of the Karoo Supergroup, South Africa: implications for causes of the end-Permian extinction event. Gondwana Res. 7, 175–183.

Eshet, Y., Rampino, M.R., Visscher, H., 1995. Fungal event and palynological record of ecological crisis and recovery across the Permian-Triassic boundary. Geology 23, 967–970.

Foster, C.B., Stephenson, M.H., Marshall, C., Logan, G.A., Greenwood, P., 2002. Revision of *Reduviasporonites* Wilson 1962: description, illustrations, comparison and biological affinities. Palynology 26, 35–58.

Gastaldo, R.A., Rolerson, M.W., 2008. *Katbergia* gen. nov., a new trace fossil from Upper Permian and Lower Triassic rocks of the Karoo basin: implications for palaeoenvironmental conditions at the P-Tr extinction event. Palaeontology 51, 215–229.

Gastaldo, R.A., Adendorff, R., Bamford, M., Labandeira, C.C., Neveling, J., Sims, H., 2005. Taphonomic trends of macrofloral assemblages across the Permian-Triassic boundary, Karoo Basin, South Africa. Palaios 20, 479–497. http://dx.doi.org/10.2110/palo.2004.P04–62.

Gastaldo, R.A., Kamo, S.L., Neveling, J., Geissman, J.W., Bamford, M., Looy, C.V., 2015. Is the vertebrate-defined Permian-Triassic boundary in the Karoo Basin, South Africa, the terrestrial expression of the end-Permian marine event? Geology 43, 939–942. http://dx.doi.org/10.1130/G37040.1.

Grice, K., Nabbefeld, B., Maslen, E., 2007. Source and significance of selected polycyclic aromatic hydrocarbons in sediments (Hovea-3 well, Perth Basin, Western Australia) spanning the Permian-Triassic boundary. Org. Geochem. 38, 1798–1803.

Gröcke, Darren R., 2002. The carbon isotope composition of ancient CO2 based on higher-plant organic matter. Philos. Trans. R. Soc. Lond. A : Math. Phys. Eng. Sci. 360 (1793), 633–658.

Hochuli, P.A., 2016. Interpretation of “fungal spikes” in Permian-Triassic boundary sections. Global Planet. Change 144, 48–50.

Katemaunzanga, D., Gunter, C.J., 2009. Lithostratigraphy, sedimentology, and provenance of the Balfour Formation (beaufort group) in the fort beaufort-alice area, eastern Cape province, South Africa. Acta Geol. Sin. 83, 902–916.

Kohzu, A., Yoshioka, T., Ando, T., Takahashi, M., Koba, K., Wada, E., 1999. Natural 13C and 15N abundance of field-collected fungi and their ecological implications. New Phytol. 144, 323–330.

Korte, C., Pande, P., Kalia, P., Kozur, H.W., Joachimski, M.M., Oberhänsli, H., 2010. Massive volcanism at the Permian–Triassic boundary and its impact on the isotopic composition of the ocean and atmosphere. J. Asian Earth Sci. 7, 293–311.

Krull, E.S., Retallack, G.J., 2000. δ^{13}C depth profiles from paleosols across the Permian-Triassic boundary: evidence for methane release. Geol. Soc. Am. Bull. 112, 1459–1472.

Krull, E.S., Retallack, G.J., Campbell, H.J., Lyon, G.L., 2000. δ13Corg chemostratigraphy of the Permian-Triassic boundary in the Maitai Group. New Zealand: evidence for high-latitudinal methane release. N. Z. J. Geol. Geophys. 43, 21–32.

Lucas, S.G., 2010. The Triassic Timescale Based on Nonmarine Tetrapod Biostratigraphy and Biochronology. Geol. Soc. Lond.Spec. Publ., vol. 334, 447–500.

Mack, G.H., James, W.C., 1994. Paleoclimate and global distribution of paleosols. J. Geol. 102, 36–372.

MacLeod, K.G., Smith, R., Koch, P., Ward, P.D., 2000. Timing of mammal-like reptile extinctions across the Permian-Triassic boundary in South Africa, South Africa. Geology 28, 227–230.

Maruoka, T., Koeberl, C., Hancox, P.J., Reimold, W.U., 2003. Sulfur geochemistry across a terrestrial Permian-Triassic boundary section in the Karoo Basin, South Africa. Earth Planet Sci. Lett. 306, 101–117.

Matthies, C., Erhard, H.-P., Drake, H.L., 1997. Effects of pH on the comparative culturability of fungi and bacteria from acidic and less acidic forest soils. J. Basic Biol. 37, 335–343. http://dx.doi.org/10.1002/jobm.3620370506.

Morante, R., 1996. Permian and early Triassic isotopic records of carbon and strontium in Australia and a scenario of events about the Permian-Triassic boundary. Hist. Biol. 11, 289–310.

O'Leary, M.H., 1988. Carbon isotopes in photosynthesis. Bioscience 38, 328–336.

Ometto, J.P., Ehleringer, J.R., Domingues, T.F., Berry, J.A., Ishida, F.Y., Mazzi, E., Higuchi, N., Flanagan, L.B., Nardoto, G.B., Martinelli, L.A., 2006. In: The Stable Carbon and Nitrogen Isotopic Composition of Vegetation in Tropical Forests of the Amazon Basin, Brazil. Nitrogen Cycling in the Americas: Natural and Anthropogenic Influences and Controls. Springer Netherlands, pp. 251–274.

Palese, A.M., Giovannini, G., Lucchesi, S., Dumontet, S., Perucci, P., 2004. Effect of fire on soil C, N and microbial biomass. Agronomie 24, 47–53.

Rampino, M.R., Eshet, Y., 2018. The fungal and acritarch events as time markers for the latest Permian mass extinction: an update. Geosci. Front. 147–154.

Reintam, L., Moora, T., 1998. Development of pedogenesis on aqueous deposits within the Holocene in West Estonia. Proc. Est. Acad. Sci. Geol. 47 108ñ129.

Retallack, G.J., 2001. Soils of the Past, second ed. Blackwell, Oxford, pp. 600.

Retallack, G.J., Krull, E.S., 1999. Landscape ecological shift at the Permian-Triassic boundary in Antarctica. Aust. J. Earth Sci. 46, 785–812.

Retallack, G.J., Smith, R.M., Ward, P.D., 2003. Vertebrate extinction across permian–-triassic boundary in Karoo Basin, South Africa. Geol. Soc. Am. Bull. 115, 1133–1152.

Schwindt, D.M., Rampino, M.R., Steiner, M.B., Esbet, Y., 2003. Stratigraphy, paleomagnetic results, and preliminary palynology across the Permian-Triassic (P-Tr) boundary at Carlton Heights, southern Karoo Basin (South Africa). In: Koeberl, C., Martínez-Ruiz, F.C. (Eds.), Impact Markers in the Stratigraphic Record. Springer, Berlin, pp. 293–314.

Sephton, M.A., Looy, C.V., Brinkhuis, H., Wignall, P.B., de Leeuw, J.W., Visscher, H., 2005. Catastrophic soil erosion during the end-Permian biotic crisis. Geology 33, 941–944. http://dx.doi.org/10.1130/G21784.1.

Sephton, M.A., Visscher, H., Looy, C.V., Verchosvsky, A.B., Watson, J.S., 2009. Chemical constitution of a Permian-Triassic disaster species. Geology 37, 875–878. http://dx.doi.org/10.1130/G30096A.1.

Sephton, M.A., Jiao, D., Engel, M.H., Looy, C.V., Visscher, H., 2015. Terrestrial acidification during the end-Permian biosphere crisis? Geology 43 (2), 159–162.

Shams, I., Avivi, A., Nevo, E., 2005. Oxygen and carbon dioxide fluctuations in burrows of subterranean blind mole rats indicate tolerance to hypoxic–hypercapnic stresses. Comp. Biochem. Physiol. A142, 376–382. http://dx.doi.org/10.1016/j.cbpa.2005.09.003.

Shen, W., Sun, Y., Lin, Y., Liu, D., Chai, P., 2011. Evidence for wildfire in the Meishan section and implications for Permian–Triassic events. Geochem. Cosmochim. Acta 75 (7), 1992–2006.

Signor III, P.W., Lipps, J.H., 1982. Sampling Bias, Gradual Extinction Patterns, and Catastrophes in the Fossil Record, vol. 190. Geological Society of America Special Publication, pp. 291–296.

Smith, R.M.H., 1987. Morphology and depositional history of exhumed Permian point-bars in the southwestern Karoo, South Africa. J. Sediment. Petrol. 57, 19–29.

Smith, R.M.H., Botha-Brink, J., 2014. Anatomy of a mass extinction: sedimentological and taphonomic evidence for drought-induced die-offs at the Permo-Triassic boundary in the main Karoo Basin, South Africa. Palaeogeogr. Palaeoclimatol. Palaeoecol. 396, 99–118.

Song, H., Wignall, P.B., Tong, J., Yin, H., 2013. Two pulses of extinction during the Permian–Triassic crisis. Nat. Nat. Geosci. 6, 52–56. http://dx.doi.org/10.1038/ngeo1649.

Spina, A., Cirilli, S., Utting, J., Jansonius, J., 2015. Palynology of the permian and triassic of the tesero and Bulla sections (western dolomites, Italy) and consideration about the enigmatic species *Reduviasporonites chalastus*. Rev. Palaeobot. Palynol. 218, 3–14.

Stavrakis, N., 1979. Sedimentology of the Katberg Sandstone in the Eastern Cape Province. Unpub. M.Sc.. Department of Geology, Rhodes University, Grahamstown, pp. 125.

Steiner, M.B., Eshet, Y., Rampino, M.R., Schwindt, D.M., 2003. Fungal abundance event and the permian-triassic boundary in the Karoo supergroup (South Africa). Palaeogeogr. Palaeoclimatol. Palaeoecol. 194, 405–414.

Stephenson, M.H., 2016. Permian palynostratigraphy: a global overview. Geol. Soc. Lond.Spec. Publ. 450. http://dx.doi.org/10.1144/SP450.2.

Svensen, H., Planke, S., Polozov, A.G., Schmidbauer, N., Corfu, F., Podladchikov, Y.Y., Jamtveit, B., 2009. Siberian gas venting and the end-Permian environmental crisis. Earth Planet Sci. Lett. 277, 490–500.

Tabor, N.J., Montañez, I.P., Steiner, M.B., Schwindt, D., 2007. δ^{13}C values of carbonate nodules across the Permian-Triassic boundary in the Karoo Supergroup (South Africa) reflect a stinking sulfurous swamp, not atmospheric CO_2. Palaeogeogr. Palaeoclimatol. Palaeoecol. 252, 370–381.

Thomas, B.M., Willink, R.J., Grice, K., Twitchett, R.J., Purcell, R.R., Archbold, N.W., George, A.D., Tye, S., Alexander, R., Foster, C.B., Barber, C.J., 2004. Unique marine Permian-Triassic boundary section from Western Australia. Aust. J. Earth Sci. 51, 423–430.

Van de Wetering, N., Esterle, J., Baublys, K., 2013. Decoupling δ^{13}C response to palaeoflora cycles and climatic variation in coal: a case study from the Late Permian Bowen Basin, Queensland, Australia. Palaeogeogr. Palaeoclimatol. Palaeoecol. 252, 370–381.

Visscher, H., Brinkhuis, H., Dilcher, D.L., Elsik, W.C., Eshet, Y., Looy, C.V., Rampino, M.R., Traverse, A., 1996. The terminal Paleozoic fungal event: evidence of terrestrial ecosystem destabilization and collapse. Proc. Natl. Acad. Sci. Unit. States Am. 93, 2155–2158.

Visscher, H., Sephton, M., Looy, C., 2011. Fungal virulence at the time of the end-Permian biosphere crisis? Geology 39 (9), 883–886. http://dx.doi.org/10.1130/G32178.1.

Ward, P.D., Montgomery, D.R., Smith, R., 2000. Altered river morphology in South Africa related to the Permian-Triassic extinction. Science 289 (5485), 1740–1743.

Ward, P.D., Botha, J., Buick, R., Dekock, M.O., Erwin, D.H., Garri Son, G., Kirschvink, J., Smith, R.H.M., 2005. Abrupt and gradual extinction among Late Permian land vertebrates in the Karoo Basin, South Africa. Science 307, 709–714.

Zharkov, M.A., Chumakov, N.M., 2001. Paleogeography and sedimentation settings during permian–triassic reorganizations in biosphere. Stratigr. Geol. Correl. 9, 340–363.