

## $\delta^{13}\text{C}_{\text{org}}$ chemostratigraphy of the Permian–Triassic boundary in the Maitai Group, New Zealand: evidence for high-latitude methane release

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**Abstract** Carbon isotopic studies from marine organic matter of the Permian–Triassic Maitai Group, New Zealand, reveal a significant  $\delta^{13}\text{C}_{\text{org}}$  shift toward more negative values within the Little Ben Sandstone Formation. These isotopic data chemostratigraphically define the previously debated position of the Permian–Triassic boundary in the Maitai Group. The Permian–Triassic record of the Maitai Group is also important because of its high paleolatitudinal setting and the deposition at intermediate depths in the ocean (c. 400 m) within a volcanic arc-related basin. Marine Permian–Triassic strata deposited at water depths deeper than shelf areas are rare. High latitude Permian–Triassic boundary sections document a significantly larger isotopic offset across the boundary compared with lower latitude settings.

Carbon isotopic values decrease rapidly by an average of 7‰ from homogeneous values ( $\bar{x}$  –25‰) in the Tramway and lower Little Ben Sandstone Formation to highly fluctuating and very depleted values ( $\bar{x}$  –32‰) within the Little Ben Sandstone Formation. The lowermost Big Ben and Tramway Formations are considered to be Permian in age, based on their homogeneous and comparably heavier carbon isotopic values and supported by fossil atomo-desmatinid bivalves. Based on the distinct  $\delta^{13}\text{C}_{\text{org}}$  excursion toward negative values and the concurrent onset of strong isotopic fluctuations, the Permian–Triassic boundary is placed in the lower half of the Little Ben Sandstone Formation.

Very depleted  $\delta^{13}\text{C}$  values in the Little Ben Sandstone Formation of –38‰ indicate a contribution from isotopically light methane. A possible methane source is clathrates, released by large submarine slides or warming-induced melting of permafrost. The Little Ben Sandstone Formation has been interpreted as a massive event deposit from a submarine slide (Landis 1980). This hypothesised methane release could have been in part responsible for the larger Permian–Triassic isotopic shift in high latitudes compared with low latitudes because large volumes of clathrates are trapped in continental shelves and high-latitude permafrost.

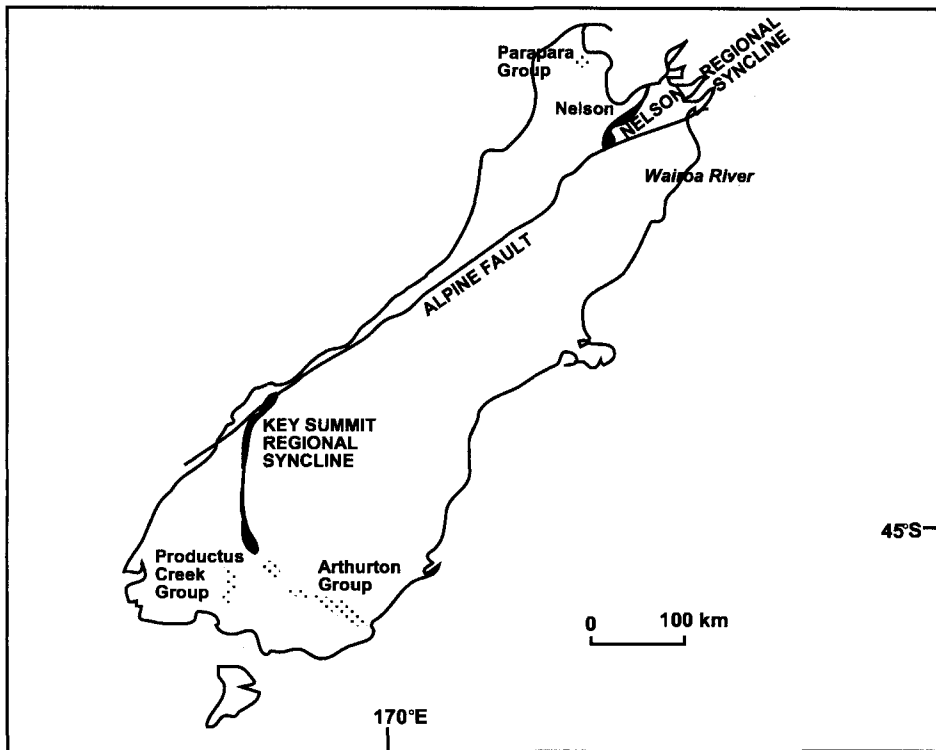
**Keywords** Permian–Triassic boundary; Maitai Group; stable carbon isotopes; methane

### INTRODUCTION

Marine and terrestrial life experienced the most severe crisis in Earth's history during the Permian–Triassic extinction, now dated at  $251.4 \pm 0.3$  Ma (Bowring et al. 1998). An estimated 93–95% of all marine species (Raup 1979) and c. 70% of all vertebrate families (King 1991; Maxwell 1992) did not survive this largest of all extinction events. This important event in geologic history, which was crucial for the structure and composition of post-Paleozoic marine communities, could not be identified previously in the Paleozoic–Mesozoic Maitai terrane of New Zealand.

There has been a long history of debate on the placement of the Permian–Triassic boundary in the Maitai Group of New Zealand. In the 1940s the “Maitai problem” was regarded as the single-most important problem in New Zealand geology (Harrington 1983). Earlier accounts regarded the Maitai Group as entirely Permian in age and placed the Permian–Triassic boundary between the Maitai Group and the overlying Murihiku Supergroup (Waterhouse 1967, 1973b, 1987; Johnston & Stevens 1978; Landis 1980; Pillai et al. 1991; Kimbrough et al. 1992). The Permian–Triassic boundary is now thought to occur within the Maitai Group, between the Tramway and Greville Formations (Dickins & Campbell 1992; Owen 1991, 1992). An exact position of the Permian–Triassic boundary within this sequence has been hampered by poor fossil preservation, by the occurrence of endemic species or long-ranging benthic forms, and by the lack of good biostratigraphic age control (Pillai et al. 1991; Dickins & Campbell 1992; Campbell 1996).

Stable carbon isotope stratigraphy can be used for determination of the Permian–Triassic boundary because of the distinct, worldwide negative  $\delta^{13}\text{C}$  excursion. This excursion has been found in marine limestones (Holser & Magaritz 1987; Baud et al. 1989), marine organic carbon (Magaritz et al. 1992; Wang et al. 1994; Krull 1998; Isozaki 1997), terrestrial organic carbon (Morante 1996; Krull 1998; Retallack & Krull 1999), terrestrial tooth apatite (Thackeray



**Fig. 1** Regional location map for the Maitai Group, South Island, New Zealand, showing the distribution of the Permian-Triassic Maitai Group (black) and correlative strata (dotted). Maitai outcrops occur in the Nelson Regional Syncline and, offset by 480 km along the Alpine Fault, in the Key Summit Regional Syncline (modified from Landis 1980; Owen 1991).

et al. 1990), and pedogenic carbonate (MacLeod et al. 1997). In this study, we present for the first time detailed chemostratigraphic data from the Permian-Triassic  $\delta^{13}\text{C}_{\text{org}}$  marine record in New Zealand, showing a distinct  $\delta^{13}\text{C}$  excursion toward more negative values within the Little Ben Sandstone Formation. Based on this negative carbon isotopic excursion, the boundary can now be placed shortly above the formational contact between the Tramway and Little Ben Sandstone Formations of the Maitai Group.

### GEOLOGICAL SETTING

The Permian-Triassic Maitai Group is exposed along a narrow fold and thrust belt extending through the South Island of New Zealand from eastern Nelson, to western Southland, to south Otago (Fig. 1). It is composed of a thick sequence of volcanic arc-derived, weakly metamorphosed marine sediments which are in contact with the well-dated Dun Mountain Ophiolite Belt (Coombs et al. 1976; Kimbrough et al. 1992). Together they constitute the fault-bounded Dun Mountain-Maitai Terrane (Bishop et al. 1985).

The Maitai Group consists of 16 formations of which 3 formations (Tramway, Little Ben Sandstone, and Greville) bracket the Permian-Triassic boundary. Stratigraphy and isotopic data of these units will be discussed in greater detail.

### LOCALITY AND METHODS

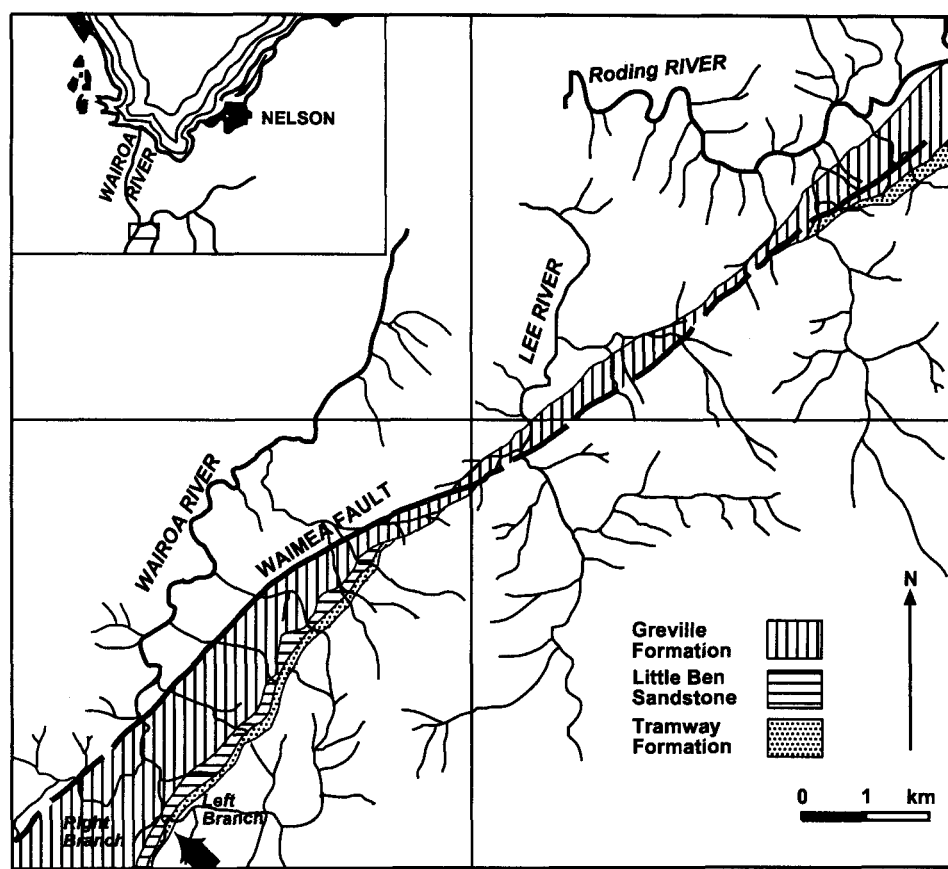
Strata of the Maitai Group are exposed in the Nelson Regional Syncline as steeply dipping beds, situated along the Left Branch of the Wairoa River (Landis 1980). Here, a complete and detailed section of the Tramway, Little Ben Sandstone, and Greville Formations was sampled for carbon isotopic analysis and petrographic studies (Fig. 2).

In preparation for isotopic analysis, samples were powdered and 1 g of sample was treated for 30 min with 100 ml hot (80–90°C), 0.5 M HCl to remove all carbonates and other acid-soluble minerals. Acid-insoluble residues were washed until neutral (pH 6–7) and oven-dried for at least 12 h. Approximately 0.1 g of the dried residue was accurately weighed (to fourth decimal place) and loaded into 9 mm quartz tubes with 1 g CuO and 2 inch (50 mm) silver wire each. The tubes were evacuated, sealed, and combusted at 860°C for 6 h and then slowly cooled to 25°C over 20 h.  $\text{CO}_2$  was collected by cryogenic distillation and analysed for  $\delta^{13}\text{C}$  at the Nuclide Associates 6-60 mass spectrometer in the Institute of Geological & Nuclear Sciences, Lower Hutt, New Zealand. Analytical precision was judged on the basis of 11 replicates of a graphite standard (NBS-21) analysed over a period of several months ( $\bar{x}$  -27.99‰,  $\pm$ SD 0.12‰). Replicates of this standard never differed by more than 0.3‰. The individual mass spectrometry errors are <0.1‰. Total organic carbon (TOC) content was determined by measuring the volume (micromol) of  $\text{CO}_2$  and converting it to total amount of carbon (Boutton 1991). Standard error for TOC determination was  $\leq 0.01$ . Isotope results are reported in the conventional notation as per mil deviation from the PDB standard with analytical error of 0.1‰.

### DIAGENESIS AND THERMAL ALTERATION

The Permian-Triassic Maitai sequence in the Nelson area has been affected by low-grade metamorphism during a Mesozoic folding event that formed the Nelson Regional Syncline (Landis 1980). Abundant authigenic mineral phases include epidote, actinolite, pumpellyite, chlorite, and lawsonite, indicating that metamorphic conditions were at, or below, greenschist facies (Landis 1980).

**Fig. 2** Locality map for the outcrop area of the lower Maitai Group along the Left Branch of the Wairoa River (arrow), showing steeply dipping strata of the Tramway, Little Ben Sandstone, and Greville Formations (modified from Waterhouse 1959).



Stable carbon isotopes of organic matter are robust with respect to post-burial fractionation processes during burial diagenesis (Hayes et al. 1983). At thermal conditions at or below greenschist facies, diagenetic alteration of organic carbon isotopes is negligible (Hoefs & Fry 1976; Deines 1980; Redding et al. 1980; Peters et al. 1981; Hayes et al. 1983; Strauss et al. 1992).

To ensure that our isotopic data are not the result of contamination or thermally driven loss of hydrocarbons during diagenesis, we cross-plotted total organic carbon content against  $\delta^{13}\text{C}$  values for each formation (Fig. 3). No significant statistical correlation was recognised between the amount of TOC and carbon isotopic composition. From these data, we conclude that our  $\delta^{13}\text{C}_{\text{org}}$  values can be interpreted as an original isotopic signature and that no significant thermal alteration has affected this signature (Wang et al. 1994).

## FORMATIONS AND AGE DETERMINATION

### Tramway Formation

The Tramway Formation consists of bedded, quartzofeldspathic and lithic, greenish grey sandstone, commonly interbedded with dark-grey siltstone and carbonaceous claystone (Fig. 4). Fragments of disintegrated, prismatic, calcitic shells of atomodesmatinid bivalves, and trace fossils,

are common. Graded bedding, sole markings, and flame structures are abundant in the thinly bedded lower part of the Tramway Formation. In the upper, thickly bedded part there are large (up to 10 mm) pyrite euhedra and complete *Atomodesma* valves (Landis 1980). Based on evidence from bryozoans and atomodesmatinid bivalves, a Late Permian (Tatarian) age has been suggested for the Tramway Formation (Waterhouse 1976, 1987; Stratford 1990).

### Little Ben Sandstone

Little Ben Sandstone comprises massive to thinly bedded green volcanogenic sandstone, siltstone, and mudstone, as well as local conglomerate units and has only rare (redeposited?) atomodesmatinids (Fig. 4) (Waterhouse 1964; Landis 1980). Its basal contact with the Tramway Formation is gradational, as dark grey claystone grades into bedded green sandstone of the Little Ben Sandstone Formation. This formation is largely devoid of fossils, and its poorly fossiliferous nature has been used as a criterion for its stratigraphic definition (Waterhouse 1964; Landis 1980). The Little Ben Sandstone Formation has a much higher basaltic-andesitic, volcanogenic, siliciclastic component compared to the quartz-rich Tramway Formation (Landis 1980). Dominance of poorly sorted sediment and only modest occurrence of grading and lamination, load casts, flame structures, and rip-up clasts suggest rapid mass emplacement (Landis 1980). Only plant scraps without biostratigraphic

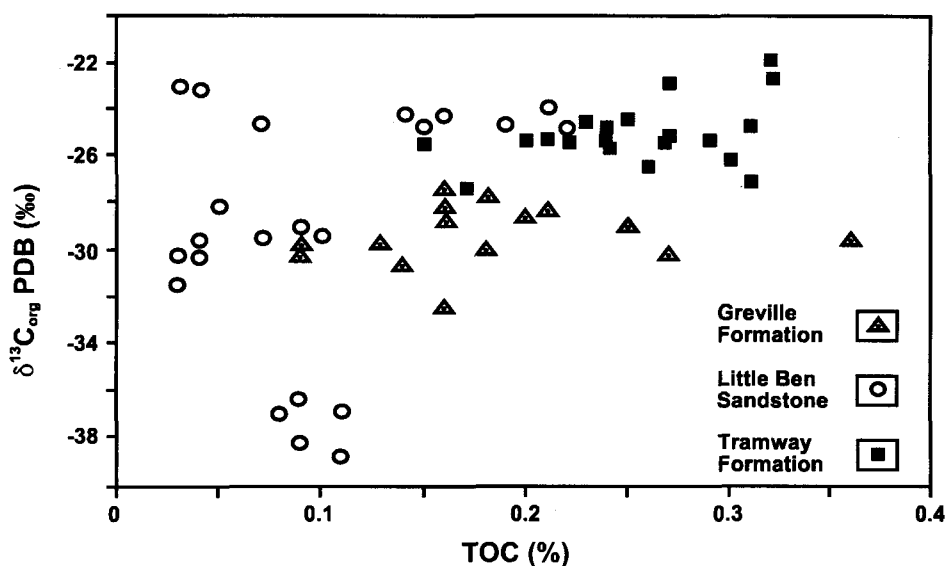


Fig. 3 Cross-plot of  $\delta^{13}\text{C}_{\text{org}}$  and TOC contents shows no significant correlation between isotopic signature and total organic carbon content. Correlation coefficient  $R^2$  Tramway Formation  $R^2 = 0.16$ ; Little Ben Sandstone  $R^2 = 0.06$ ; Greville Formation  $R^2 = 0.02$ ; all formations combined  $R^2 = 0.2$ .

significance, and fragments of (redeposited?) bivalves, have been found in the Little Ben Sandstone Formation; thus, the age of this formation is uncertain (Landis 1980).

#### Greville Formation

The Greville Formation consists of green and grey, laminated siltstone, sandstone, and claystone (Fig. 4). Its lower contact with the Little Ben Sandstone is not exposed in the section we studied but has been reported as gradational and is placed at the transition from thick, bedded sandstone to laminated clay and sandstone sequences (Owen 1991, 1992). The age of the Greville Formation is debated because of its low fossil content and preservation. The ammonoid *Durvilleoceras woodmani* has been found at several localities in the Greville Formation (Waterhouse 1973a), but its age is still controversial. Waterhouse (1973a, 1979, 1987) claimed a Late Permian age for *D. woodmani*, and later suggested a middle Triassic (Anisian) age (Waterhouse 1993). Based on the similarity of *D. woodmani* to Early Triassic Flemingitidae, Furnish et al. (1976) suggested a mid-Early Triassic (Dienerian–Smithian) age. Johnston & Stevens (1978) described two ammonoids (?*Episagicer* aff. *noetlingi* and *Durvilleoceras woodmani*) from the Greville Formation and considered them Early Triassic. A Griesbachian (earliest Triassic) age is suggested, based on another ammonoid (collected by B. Runnegar) from Greville Formation that is comparable with *Hypophiceras* sp. (Owen 1991). Campbell (1996) also attributes an Induan (Dienerian) age to the Maitai Greville Formation, based on the ammonoid fauna including *Durvilleoceras*, *Episagicer*, and an undescribed xenodiscid. Thus, a range from earliest to late Early Triassic is considered most likely (Owen 1991, 1992).

#### RESULTS

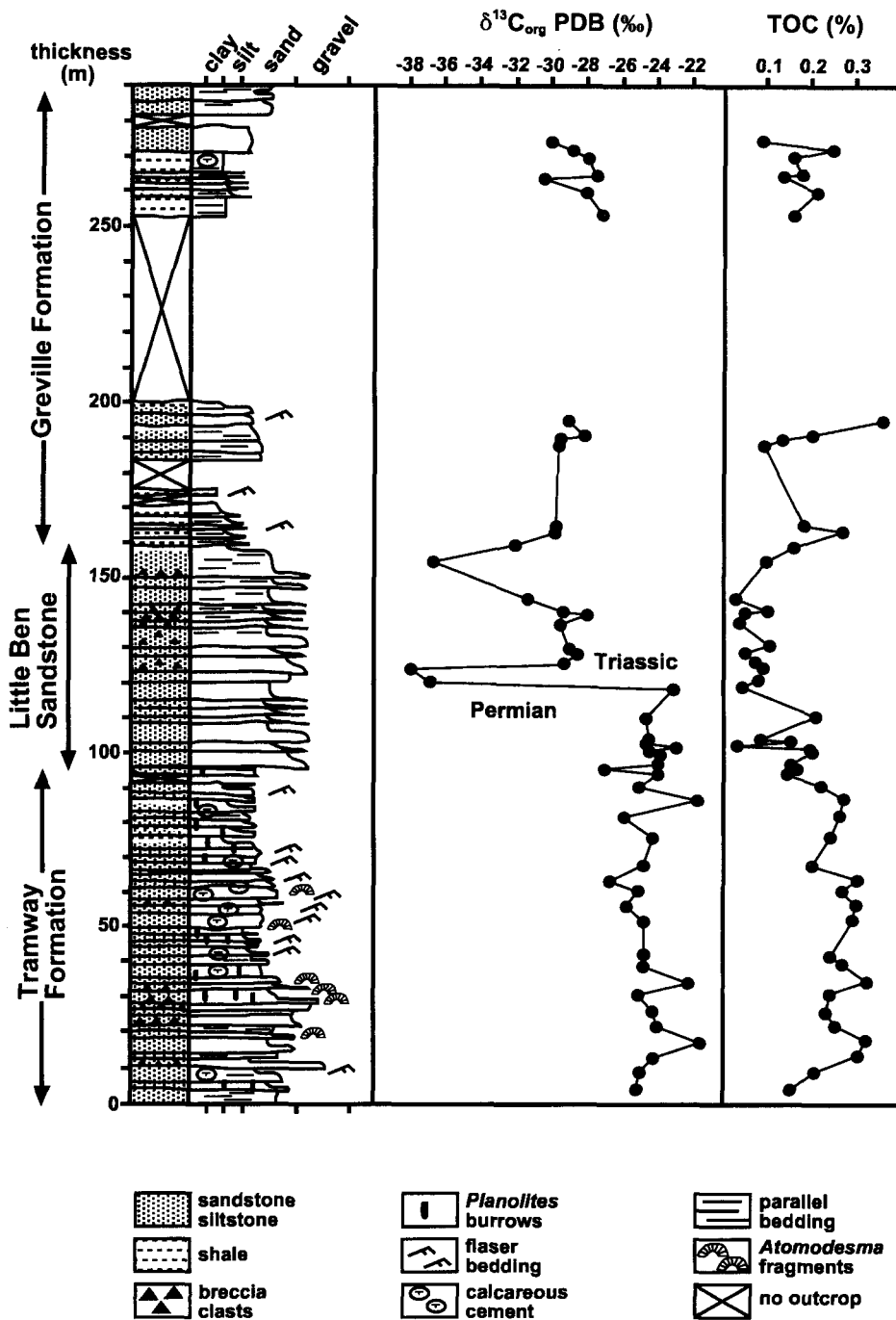
Stable carbon isotopic values and total organic carbon content of the Tramway, Little Ben Sandstone, and Greville Formations are shown in Fig. 4 and reported in Table 1.

Carbon isotopic values of the Tramway Formation average  $-24.94\text{‰}$  ( $\pm\text{SD } 1.3$ ) with average total organic carbon (TOC) contents of 0.25%. The contact between the Little Ben Sandstone and Tramway Formation is gradational. The lower part of the Little Ben Sandstone Formation (116–150 m) does not show significantly different  $\delta^{13}\text{C}$  ( $\bar{x} -24.1\text{‰}$ ,  $\pm\text{SD } 0.6$ ) and TOC ( $\bar{x} 0.13\%$ ) values compared to those of the Tramway Formation (Fig. 4). The upper part of the Little Ben Sandstone is characterised by an abrupt 8‰ shift toward more  $^{13}\text{C}$ -depleted values ( $\bar{x} -32.1\text{‰}$ ), high isotopic variability ( $\pm\text{SD } 4.0$ ), and low TOC contents ( $\bar{x} 0.07\%$ ). The contact between the Little Ben Sandstone and the overlying Greville Formation is also gradational. Compared with the Little Ben Sandstone,  $\delta^{13}\text{C}$  values of the Greville Formation have less isotopic deviation and average  $-29\text{‰}$  ( $\pm\text{SD } 1.3$ ), 3‰ less  $^{13}\text{C}$ -depleted than those of the Little Ben Sandstone. TOC contents of Greville Formation are comparably higher and average 0.18%.

#### INTERPRETATION

The Permian–Triassic boundary in the type section in China at Meishan has been dated at  $251.4 \pm 0.3$  Ma (Bowring et al. 1998). A carbon isotopic excursion towards lower values is closely associated with the dated boundary event. The distinct  $\delta^{13}\text{C}_{\text{org}}$  excursion within the Little Ben Sandstone from  $\delta^{13}\text{C}_{\text{org}}$  values typical for recent marine organisms and marine sedimentary rocks (Fig. 5) toward strongly  $^{13}\text{C}$ -depleted values is similar to the isotopic record of other Permian–Triassic boundary sections. This distinct negative carbon isotopic excursion has been used as a chemostratigraphic marker to identify the Permian–Triassic boundary in marine and terrestrial environments elsewhere (e.g., Holser et al. (Austria) 1989; Xu & Yan (China) 1993; Kajiwara et al. (Japan) 1994; Wang et al. (Canada) 1994; Morante (Australia) 1996; Krull (Antarctica) 1998; Bowring et al. (China) 1998; Wignall et al. (West Spitzbergen) 1998). However, similar negative  $\delta^{13}\text{C}$  excursions have been reported during the Late Permian at the Capitan–Wuchaipingian boundary (Erwin 1994; Grotzinger & Knoll

**Fig. 4** Stratigraphic section of the Lower Maitai Group showing  $\delta^{13}\text{C}_{\text{org}}$  values and TOC contents for the Tramway, Little Ben Sandstone, and Greville Formations. A distinct excursion toward  $^{13}\text{C}$ -depleted and highly fluctuating  $\delta^{13}\text{C}_{\text{org}}$  values occurs at or above the contact between the Tramway Formation and Little Ben Sandstone, which marks the Permian–Triassic. Isotopic values return toward less  $^{13}\text{C}$ -depleted values in the Greville Formation.



1995). The biostratigraphic record of the Tramway Formation does not allow for resolution of the Permian to stage level, and therefore the possibility exists that the earlier excursion in our section could correspond to a Late (Capitanian–Wuchiapingian) but not latest Permian isotopic event. This possibility is considered unlikely, though, for the following reasons. First, the Capitanian–Wuchiapingian negative isotopic event is closely preceded by a distinct positive isotopic excursion of 4% or more within the late Tatarian (Grotzinger & Knoll 1995). Isotopic values enriched in  $^{13}\text{C}$  could not be detected in the Little Ben Sandstone or Tramway Formation. Second, as reported in other Permian–Triassic boundary sections, it is common to not have only

one isotopic “spike” but several (Baud et al. 1989; Oberhänsli et al. 1989; Chen et al. 1991; Xu & Yan 1993). Furthermore, it is unlikely that the interval between the two distinct isotopic excursions in the mass-emplaced Little Ben Sandstone corresponds to 10 m.y., the amount of time required if both the Capitanian–Wuchiapingian and Permian–Triassic isotopic events were recorded. Therefore, we interpret the first negative  $\delta^{13}\text{C}$  excursion in the Little Ben Sandstone as the chemostratigraphic marker for the Permian–Triassic boundary. This placement suggests a Late Permian age for the lower Little Ben Sandstone and an Early Triassic age for the upper Little Ben Sandstone. Remarkable in this upper part of the formation are the extremely negative

**Table 1** Stable carbon isotopic values and total organic carbon content for the Tramway (W3–W22), Little Ben Sandstone (R21677/1–W31), and Greville Formations (W32–W45) of the Permian–Triassic Maitai Group, New Zealand. Sample numbers with the + symbol indicate duplicates.

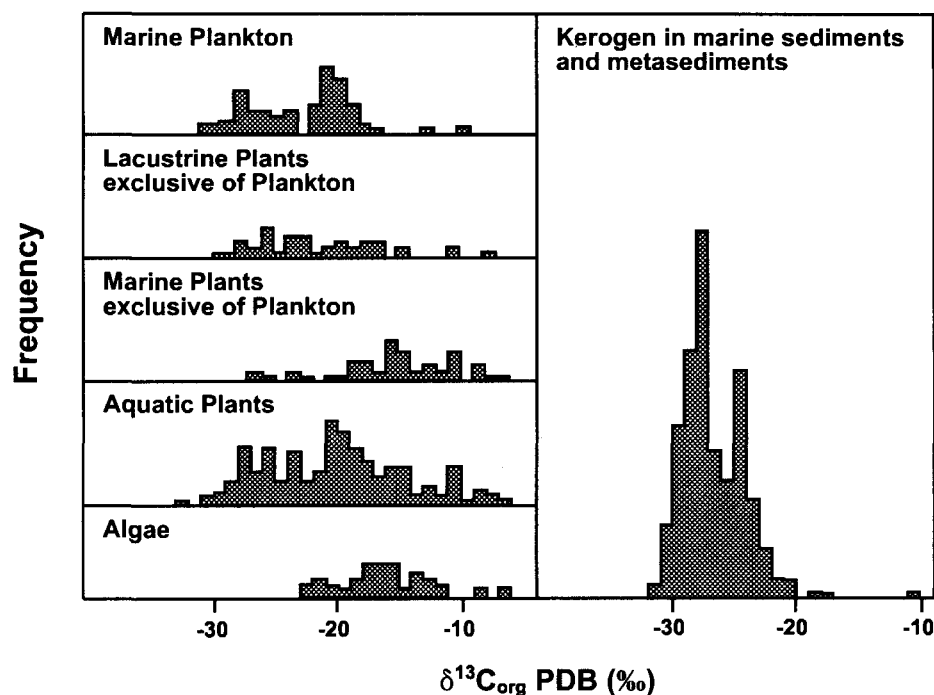
Sample no.	Meter level	$\delta^{13}\text{C}_{\text{org}}$ (‰)	TOC content (%)
W3	3.52	-25.37	0.15
W4	8.35	-25.30	0.20
W5	12.47	-24.49	0.31
W6	17.65	-21.78	0.32
W7	21.30	-24.30	0.32
W8	25.50	-24.50	0.25
W9	30.20	-25.40	0.23
W10	33.40	-22.48	0.24
W11	38.40	-25.00	0.27
W12	41.10	-25.10	0.24
W13	51.20	-25.10	0.29
W14	55.50	-26.00	0.30
W15	60.00	-25.30	0.27
W16	63.00	-26.90	0.31
W17	67.30	-25.10	0.21
W17+	67.30	-24.89	0.21
W18	77.60	-24.61	0.24
W19	81.20	-26.20	0.26
W19+	81.20	-25.43	0.26
W20	86.30	-22.80	0.27
W21	89.70	-25.30	0.22
R21677/10	95.20	-24.20	0.14
W22	95.30	-27.30	0.17
R24677/1	97.00	-24.20	0.16
R21677/2	99.30	-23.80	0.21
R21677/9	100.50	-24.50	0.19
R21677/3	101.70	-23.00	0.03
R21677/5	102.90	-24.70	0.15
R21677/4	104.00	-24.60	0.07
R21677/6	110.90	-24.70	0.22
R21677/7	120.30	-23.20	0.04
W23	119.60	37.00	0.08
W24	123.50	-38.20	0.09
W24+	123.50	-36.40	0.09
W25	126.10	-29.50	0.07
W26	127.60	-28.66	0.05
W26+	127.60	-28.15	0.05
R21677/8	129.13	-29.00	0.09
W27	130.00	-30.30	0.04
W28	136.00	-29.60	0.04
W2	138.70	-28.20	0.05
W29	139.30	-29.40	0.10
W30	143.10	-31.49	0.03
W30+	143.10	-30.26	0.03
W31	154.20	-36.90	0.11
W31+	154.20	-38.73	0.11
W32	158.40	-32.30	0.16
W32+	158.40	-28.62	0.16
W33	162.70	-30.02	0.27
W34	164.60	-29.90	0.18
W35	187.60	-29.71	0.09
W36	189.00	-29.68	0.13
W37	190.50	-28.40	0.20
W38	194.40	-29.30	0.36
W39	253.30	-27.30	0.16
W40	256.10	-28.17	0.21
W41	263.30	-30.50	0.14
W42	264.50	-27.55	0.18
W43	269.20	-28.04	0.16
W44	271.50	-28.82	0.25
W45	273.80	-30.00	0.09

$\delta^{13}\text{C}$  values of organic matter as well as its high isotopic variability and low TOC content. These chemostratigraphic features are comparable with other Early Triassic sediments of high paleolatitudinal settings. By comparison, Permian–Triassic boundary sections in lower paleolatitudes show less pronounced isotopic shifts in organic matter (Baud et al. 1989; Holser et al. 1989) (Fig. 6). Stable carbon isotopic values as negative as  $-37\text{‰}$  are rare in modern and ancient marine sediments.  $\delta^{13}\text{C}$  values in this range are usually associated with carbon derived from isotopically light methane sources (Hayes et al. 1987; Freeman et al. 1990; Hayes 1994). The trend toward more  $^{13}\text{C}$ -depleted values in high compared to lower paleolatitudes may suggest release from methane sources in high latitudes.

Stable carbon isotopic values return from highly  $^{13}\text{C}$ -depleted values in the Little Ben Sandstone to less  $^{13}\text{C}$ -depleted values in the Greville Formation. Compared with pre-boundary isotopic values in the Tramway Formation,  $\delta^{13}\text{C}$  values in the Greville Formation are on average 4‰ lower. These comparably low isotopic values in the Greville Formation are similar to those of Early Triassic intervals of Permian–Triassic boundary sections elsewhere. These  $^{13}\text{C}$ -depleted values have been documented in some sections lasting throughout the Scythian (Baud et al. 1989; Holser et al. 1989; Magaritz 1989).

The cause of this global  $\delta^{13}\text{C}$  shift across the Permian–Triassic boundary is still not resolved. Traditional interpretations argue for increased erosion and oxidation of previously buried organic carbon from coal and marine shale deposits during the Late Permian regression (Holser & Magaritz 1987; Oberhänsli et al. 1989). It is not certain though, whether this scenario could explain a 4‰ shift in the whole ocean as 6500–8400 Gt of organic carbon would have been required to produce such a shift (Erwin 1993)—an amount that exceeds the total reservoir of oil, gas, and coal (total of 5000 Gt; Erwin 1993). Other interpretations include large input of mantle-derived  $\text{CO}_2$  from the eruption of the Siberian traps (Erwin 1993, 1994; Renne et al. 1995). Given the isotopic value of volcanic  $\text{CO}_2$  ( $-5\text{‰}$ ; Erwin 1993), the  $\text{CO}_2$  released from the Siberian traps could not have contributed significantly to the isotopic excursion (Gruszczynski et al. 1989; Erwin 1993). Wang et al. (1994) proposed a collapse of surface-water primary productivity, analogous to the “Strangelove” ocean of the Cretaceous–Tertiary (K/T) boundary (Hsü & McKenzie 1990; Kump 1991). This scenario assumes that due to the decline of photosynthetic activity in the surface ocean, less  $^{12}\text{C}$  is photosynthetically fixed and buried. As a result, the  $\delta^{13}\text{C}$  surface to deep-ocean gradient would be reduced or even reversed when respiration dominated over photosynthesis. Wignall et al. (1995) and Wignall & Twitchett (1996) argued that such a productivity collapse and negative  $\delta^{13}\text{C}$  excursion could be explained with the spread of highly toxic, anoxic waters onto shelf environments. D’Hondt (1995) challenged these arguments, reasoning that oceanic phytoplankton would recover much quicker than anticipated in these scenarios. Knoll et al. (1996) suggested that overturn of anoxic deep oceans released isotopically light deep-oceanic  $\text{CO}_2$ , resulting in noxious hypercapnia and widespread marine extinction. Isozaki (1997) opposed this argument, reasoning that the superanoxia event and accompanied  $\delta^{13}\text{C}$  excursion must have been the result of a massive net import of organic carbon from sources other than the ocean. Thus

**Fig. 5** Carbon isotopic composition of photosynthetically fixed carbon from modern systems (algae, aquatic plants, marine plants exclusive of plankton, lacustrine plants exclusive of plankton, marine plankton) and from the geologic record (kerogen in marine sediments and metasediments) (modified from Deines 1980).



far, other interpretations such as meteorite impact (Retallack et al. 1998) and methane release (Erwin 1993, 1994; Bowring et al. 1998) were lacking supporting data.

## DISCUSSION

### Depositional environment

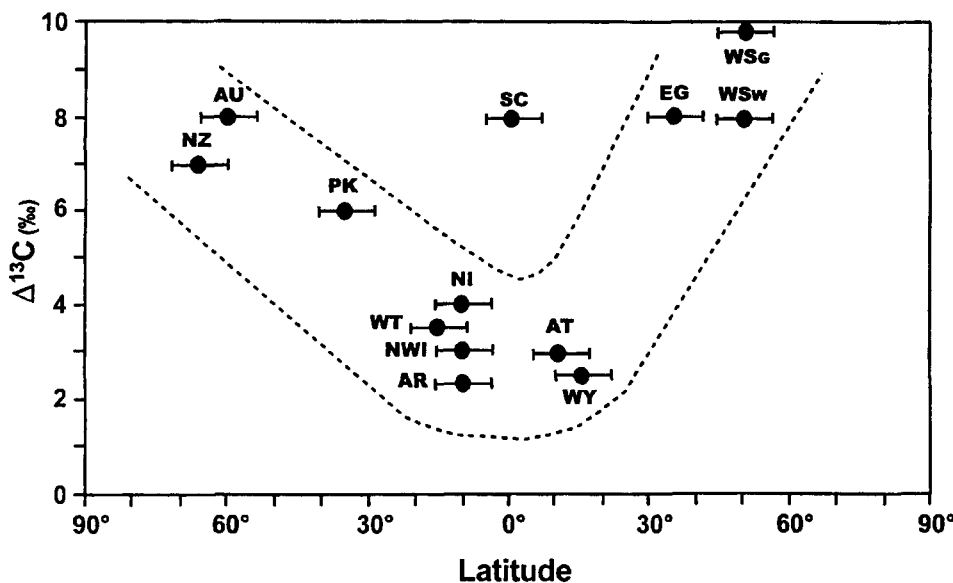
Most records of Permian–Triassic boundary sections are from shallow-water shelf sediments off the coast of Pangea. Deposits exceeding depths of 200 m are rare in the geologic record due to subduction of most pelagic sediments older than the Jurassic. Exceptions are rare and deep-marine sections have been reported from Canada (Wang et al. 1994) and southwest Japan (Kajiwara et al. 1994; Isozaki 1997). Marine sediments of the Permian–Triassic Maitai formations have been deposited as turbidite and submarine fan deposits in mid–upper fan and slope environments in a volcanic-arc related basin (Landis 1980; Owen 1991, 1992). The preservation of probably latest Permian marine sediments deposited on continental slope environments (water depths >400 m) contributes essential data for the carbon isotopic record across the Permian–Triassic boundary. The finding of carbon isotopic excursion not only in shallow but also in marine environments of moderate depths opposes the theory that carbon isotopic excursion can be explained with a collapse of paleo-productivity as suggested by Wang et al. (1994). In this scenario, only the surface waters should record an isotopic excursion, analogous to the Strangelove ocean proposed by Hsü & McKenzie (1990). An isotopic shift toward  $^{13}\text{C}$ -depleted values in the whole ocean, possibly for millions of years (Holser & Magaritz 1987), cannot be explained by surface water, primary productivity collapse alone.

Furthermore, findings of organic-rich sediments in the Tramway, Little Ben Sandstone, and Greville Formations

question the worldwide oceanic anoxia event as proposed by Kajiwara et al. (1994), Knoll et al. (1996), and Isozaki (1997). These authors argue for a global marine “super-anoxia” event based on isotopic values of  $\delta^{13}\text{C}$  and  $\delta^{34}\text{S}$  in conjunction with occurrences of organic-rich, deep-marine chert deposits associated with the Permian–Triassic boundary in southwest Japan. Geologic evidence for such a major anoxia event should be ubiquitous in boundary sections of similar depositional environment. Therefore, other marine settings below the photic zone should expose a similar organic-rich interval in association with the isotopic excursion. In the intermediate to deep marine Permian–Triassic interval of the Maitai Group, organic-rich shales occur throughout the Tramway and Greville Formations and are also found in few places in the Little Ben Sandstone (Fig. 4) (Landis 1980; Owen 1991, 1992). However, no distinct increase in the occurrence of organic-rich shales or increase in TOC content, respectively, could be found in association with the carbon isotopic excursion within the Little Ben Sandstone. On the contrary, TOC contents decrease from the Tramway Formation to the Little Ben Sandstone (Fig. 3). This decrease in TOC has been observed in other boundary sections as well (e.g., Oberhänsli et al. 1989; Morante 1996). Thus, the occurrence of a widespread “super-anoxia” event is not supported by the sedimentologic record from our section in New Zealand. Consequently, the TOC-rich interval associated with the isotopic excursion in the Japanese Permian–Triassic section might be a local, basin-related feature and not a global event.

### Highly depleted $\delta^{13}\text{C}$ values: modern clathrate deposits

Anomalously depleted  $\delta^{13}\text{C}$  values of organic matter (–35‰ and lower) have been associated with the presence of isotopically light methane (Schidlowski 1987). Today, the largest methane reservoirs are in clathrate deposits.



**Fig. 6** Latitude versus carbon isotopic offset ( $\Delta^{13}\text{C}$ ) across the Permian–Triassic boundary in marine environments. Permian–Triassic  $\delta^{13}\text{C}$  boundary excursions are commonly larger in high compared to low latitudes. An exception is South China, located at equatorial paleolatitudes and showing large isotopic excursions. Paleolatitudes from Erwin (1993) and Scotese (1994). Abbreviations: AR = Armenia (Baud et al. 1989), AT = Austria (Holser et al. 1989), AU = Australia (Gortner et al. 1995; Morante 1996), EG = East Greenland (Oberhänsli et al. 1989), NI = North Iran (Baud et al. 1989), NWI = Northwest Iran (Holser & Magaritz 1987), NZ = New Zealand (this paper), PK = Pakistan (Baud et al. 1989), SC = South China (Chen et al. 1991; Xu & Zheng 1993), WS<sub>G</sub> = West Spitzbergen (Gruszczynski et al. 1989), WS<sub>W</sub> = West Spitzbergen (Wignall et al. 1998), WY = West Yugoslavia (Baud et al. 1989).

Clathrates (methane hydrates) are crystalline, ice-like solids formed of water and methane gas. They form under specific pressure-temperature conditions in regions of permafrost (offshore and onshore) and beneath the sea in outer continental margins, where water depths exceed 300–500 m (Kvenvolden 1988a, b; Booth et al. 1998; Haq 1998). Today, clathrates are common in high-latitude regions where permafrost is ubiquitous, such as areas of the Siberian platform, northern Russia, in the North American Arctic, and in the western Ross Sea of Antarctica. In mid and low latitudes, methane clathrates occur mostly in outer continental margins such as in the western Central American trench, the Gulf of Mexico, the Nankai Trough off Japan, and the Timor Trough off Australia (Kvenvolden 1988b).

#### Highly depleted $\delta^{13}\text{C}$ values: ancient clathrates

Global isotopic excursions toward  $^{13}\text{C}$ -depleted values, other than the Permian–Triassic boundary, have been associated previously with destabilisation of clathrate deposits and submarine slides. Paull et al. (1996), Rothwell et al. (1998), and Nisbet & Piper (1998) document large-scale submarine slides and associated isotopic excursions toward  $^{13}\text{C}$ -depleted values in late Quaternary sediments, which they interpret as catastrophic methane release after slope failure. These slumps may have been triggered by lowering of hydrostatic pressure due to sea-level low-stand during glacial maxima, resulting in destabilisation of methane clathrates. As hydrostatic pressure decreases to a critical level, clathrates start to dissociate at the base of the gas-hydrate stability zone. Hydrate cements are removed from pore space, which is subsequently filled with gas bubbles and water. This replacement dramatically decreases the confining pressure and weakens the sediment, creating a basal layer of weakness (Dickens et al. 1995; Haq 1998). At this point, a submarine slide and associated methane release may be initiated along this layer of weakness by a small earthquake,

sudden sediment input, or large storms (Nisbet & Piper 1998). Estimates of methane release from individual submarine slides are in the order of 1 Gt, but particularly large slides as the Storegga slide 30 000–50 000 yr ago could have released 5 Gt or more of methane (Nisbet & Piper 1998).

Although the above-mentioned volume of methane is not enough to produce an immediate global isotopic excursion, it would add a substantial amount of greenhouse gases ( $\text{CH}_4$  and  $\text{CO}_2$ ) to the atmosphere, possibly resulting in warmer global temperatures. This global warming could have initiated a positive feedback cycle due to warming of ocean temperatures, causing further destabilisation and release of clathrates. Following this scenario, several “clathrate-burps” could have provided the volume of isotopically depleted methane carbon to the atmosphere ( $>1 \times 10^{18}$  g carbon; Dickens et al. 1995) to produce a shift in the global isotopic signature. This mechanism has been proposed for the late Pleistocene (20 000 yr ago) after emplacement of a megaturbidite and associated methane release (Rothwell et al. 1998).

Climatic warming associated with the release of gas hydrates has been suggested as the cause of global negative  $\delta^{13}\text{C}$  shifts during the latest Paleocene (Dickens et al. 1995, 1997; Bains et al. 1999), early Eocene (Sloan et al. 1992), and mid Cretaceous (Jahren 1998). During the Paleogene, increased slump frequency has been documented during four periods, at the Cretaceous–Tertiary boundary, the Paleocene–Eocene boundary, the top of the lower Eocene, and in the middle Eocene (Mountain & Tucholke 1985; Mountain 1987). These slump events have been suggested to be possibly triggered by gas-hydrate destabilisation during sea-level low-stand (Haq 1998). Therefore, sedimentological and isotopic features indicating possible slump-related gas hydrate releases have been documented in the geologic record previously.



Based on sedimentary structures, petrography, chemistry, and tectonic setting, the depositional environment of the Little Ben Sandstone Formation has been interpreted as mass-emplaced submarine slide deposits and coalescing submarine fans (Landis 1980). The lithology of the formation is characterised by strongly indurated, greenish, volcanogenic sandstone and siltstone and interbedded mudstone (Landis 1980). These sediments were mostly derived from the basaltic-andesitic Alabaster Group, an early–middle Permian volcanic sequence which flanks the western margin of the New Zealand Geosyncline (Landis 1980). Evidence for increased concentrations of methane during the deposition of the Little Ben Sandstone is provided by very  $^{13}\text{C}$ -depleted ( $-37\text{‰}$ ) isotopic values in association with mass-emplaced submarine slide deposits (Fig. 4). Such recurrent destabilisation of shelf deposits could have resulted in a critical decrease in lithostatic pressure and degeneration of the gas-hydrate stability zone.

Although field and isotopic evidence from our study site in New Zealand can account only for a localised effect of a proposed clathrate release, stable carbon isotopic studies from other high-latitude areas show similar depleted values.

#### High-latitude settings and clathrate deposits

During the Permian–Triassic boundary, the Maitai Group was situated at high latitudes between 50 and 60°S (Waterhouse 1973b). Comparison of carbon isotopic data from high versus low latitude settings shows a significant difference in magnitude of the isotopic excursion (Fig. 6). Results from high-latitude marine settings in the Northern Hemisphere in West Spitzbergen (Gruszczynski et al. 1989; Wignall et al. 1998) and Greenland (Oberhänsli et al. 1989) and in the Southern Hemisphere in Australia (Morante et al. 1994; Gorter et al. 1995; Morante 1996) and in New Zealand (this paper) document isotopic excursions of up to 9‰. Comparable sections in low and mid latitudes in the Austrian Alps, the Dolomites, Transcaucasia, and Iran show smaller isotopic excursions on the order of 3‰ (Baud et al. 1989; Holser et al. 1987, 1989; Magaritz et al. 1992; Wang et al. 1994). A notable exception are equatorial Permian–Triassic sections in South China, where Chen et al. (1991) and Xu & Yan (1993) report over 8‰ excursions shortly above the paleontologically defined Permian–Triassic boundary (Fig. 6). During the latest Permian and earliest Triassic, South China was an isolated terrane in the eastern Tethys, and its paleolatitude position is much less constrained compared to other localities (Erwin 1993). Permian–Triassic boundary sections in South China occur in shallow epicontinental marine facies and even include lagoonal and supratidal facies (Erwin 1993). Close proximity to land may also explain this anomaly because terrestrial boundary sections generally show a greater isotopic shift across the boundary compared with marine sections (Morante 1996; Krull et al. 1998). Thus, in addition to the paleolatitude uncertainty, the large isotopic offset in boundary sections from South China could have been caused by a change of facies. Therefore, reliable paleolatitude comparison of  $\delta^{13}\text{C}$  values can only be achieved if the compared sites are of similar depositional setting. In this study, we compared only open marine sections offshore from Pangea. In these settings, carbon isotopic excursions across the Permian–Triassic boundary are more pronounced in high latitudes compared to lower latitudes (Fig. 6). Our preferred

interpretation for the greater isotopic offset and more depleted values in higher paleolatitude settings is the primary release of isotopically light carbon from high-latitude clathrate deposits.

During the Late Permian and Early Triassic, marine clathrate deposits along continental margins and associated trenches were likely concentrated at high-latitude settings due to increasingly warm temperatures in low and mid latitudes (Crowley 1994). In the terrestrial environment, abundant coal deposits in northern and southern high latitudes of Pangea (Australia, Antarctica, India, Siberia, North China) attest to the existence of cool-temperate peatlands, possibly with continuous permafrost (Erwin 1993). Cool boreal paleoclimate might be also indicated by mid-Permian dropstones and striated pebbles in northern Angara (Stanley 1984, 1988). Conaghan et al. (1994) proposed latest Permian permafrost-bearing stringbogs in the Sydney basin, Australia, and Krull (1999) suggested evidence for the occurrence of permafrost-bearing *palsa mires* in Southern Victoria Land, Antarctica. Thus, conditions in high-latitude terrestrial environments were especially favourable for the formation of clathrate deposits due to the possibility of abundant permafrost.

In contrast, the Early Triassic is widely accepted as having been ice free (Erwin 1993, 1994), significantly limiting areas of clathrate storage and accumulation. The marine regression during the Changxingian Stage would have substantially lowered hydrostatic pressure in shelf environments and could have promoted clathrate destabilisation and methane release. Additional greenhouse gases such as  $\text{CO}_2$  and  $\text{H}_2\text{O}$  from the eruption of the Siberian traps during the latest Changxingian Stage ( $250 \pm 0.2$  Ma) may have furthered paleoclimatic warming (Erwin 1994; Renne et al. 1995; Bowring et al. 1998). In response to this warming trend, permafrost in the polar regions could have become increasingly unstable, resulting in additional release of methane and  $\text{CO}_2$ , adding to further greenhouse warming (Krull 1998; Retallack & Krull 1999). Other hypotheses for global warming include methane destabilisation from meteorite impact (Bowring et al. 1998). Methane release from even a small bolide impact in permafrost-bearing high-latitude peatlands could create wider consequences than the impact alone (Retallack et al. 1998).

The latitudinal difference in isotopic values can be explained by the rapid oxidation of methane by methanotrophic bacteria at the site of primary release in high latitudes. Oxidation of methane from shelf clathrates within the water column and from permafrost in the soil environment is expected to be rapid enough to consume much of the methane before it can reach the atmosphere (Kvenvolden pers. com.). This *in situ* oxidation of methane by methanotrophic bacteria (Freeman et al. 1990; Hayes 1994) allows for incorporation of the very negative isotopic signature of methane in the bacterial organic matter and thus preservation of the isotopic signal at the site of primary methane release. Therefore, rather than methane, the oxidation product  $\text{CO}_2$  is the main carrier of the  $^{13}\text{C}$ -depleted isotopic signature away from the site of primary methane release. In areas away from the primary methane source (i.e., in low latitudes), isotopic values in carbonate carbon and organic matter would be expected to be less negative because the isotopic signal would be recorded indirectly from the atmosphere after mixing of the isotopically light methane-derived  $\text{CO}_2$  with isotopically heavier atmospheric  $\text{CO}_2$ .

Thus, methane release from permafrost clathrates in high latitudes could explain both the global carbon isotopic shift and the more negative carbon isotopic signatures in high latitudes. Furthermore, methane is a highly effective greenhouse gas (by a factor of 50–60 by weight compared to CO<sub>2</sub>; Nisbet 1989), and strong positive feedback mechanisms could have amplified subsequent methane release, resulting in global warming and ice-free conditions in the Early Triassic.

## SYNTHESIS

Stable carbon isotopic data from high-latitude, intermediate to deep marine sediments from the Permian–Triassic Maitai strata show a pronounced isotopic shift toward more depleted values within the Little Ben Sandstone. The previously unidentified Permian–Triassic boundary in the Maitai Group can now be placed at or above the formational contact between the Late Permian Tramway Formation and the Early Triassic Little Ben Sandstone. The very low  $\delta^{13}\text{C}$  values of organic matter in the Little Ben Sandstone suggest contribution from methane carbon, possibly released from extensive methane clathrate deposits in high latitudes. This trend of very  $^{13}\text{C}$ -depleted values in high-latitude settings can be found on a global scale. A significant difference in magnitude of the Permian–Triassic isotopic shift in high compared to low latitudes, together with very negative isotopic values, suggests the release of methane from both shelf and permafrost clathrates, resulting in global warming and greenhouse conditions of the Early Triassic.

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