APPENDIX

Publications and conference abstracts reporting progress of this study 1992-1995.

1. RETALLACK, G.J, VEEVERS, J.J. & **MORANTE, R.**, Global coal gap between Permian-Triassic extinction and Middle Triassic recovery of peat-forming plants. Geological Society of America Bulletin (in press).

2. MORANTE, R., 1995. Permian to Early Triassic isotopic records of carbon and strontium in Australian sedimentary basins. In Brock, G.A., (Editor) Abstracts and Programme of the First Australian Conodont Symposium (AUSCOS-1) and the Boucot Symposium, Macquarie University, Sydney New South Wales, p.60.

3. MORANTE, R., 1994. Carbon isotope stratigraphy of the Permian-Triassic in Australian marine and nonmarine sedimentary basins. Final meeting of IGCP Project 293 "Geochemical event markers in the Phanerozoic" University of Erlangen, 1994. Erlanger Geologische Abhandlungen, 122, 43.

4. MORANTE, R., VEEVERS, J. J., ANDREW, A. S. & HAMILTON, P. J., 1994, Determination of the Permian-Triassic boundary in Australia from carbon isotope stratigraphy. APEA Journal, 34, 330-336.

5. MORANTE, R., 1994, Determining the carbon isotope chemostratigraphy across the Permian/Triassic boundary in Australia. In Lanphere, M.A., Dalrymple, G. B. & Turpin, B. D., (Editors) Abstracts of the Eighth International Conference on Geochronology, Cosmochronology and Isotope Geology, U.S. Geological Survey Circular 1107, 225.

6. MORANTE, R. & HERBERT, C., 1994, Carbon isotopes & sequence stratigraphy about the Permian-Triassic boundary in the Sydney Basin. Twenty-eighth Newcastle Symposium on Advances in the study of the Sydney Basin. 102-109.

7. MORANTE, R., 1994, Determining the Permian/Triassic boundary in Australia using carbon isotope chemostratigraphy. Australasian Palaeontological Convention Abstracts, Macquarie University,42.

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9. MORANTE, R., 1993, The Permian/Triassic Extinction: A function of greenhouse overshoot? First International Symposium on Applied Isotope Geochemistry (AIG-1), Institut for energiteknikk IFE/KR/E-93/007. Norway, 2pp.

10. MORANTE, R, 1993, Determining the Permian/Triassic boundary in Australia through C-isotope chemostratigraphy. In Flood, P. G. & Aitchison, J. C. (eds) New England Orogen, eastern Australia, University of New England. 293-298.

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ABSTRACTS & PROGRAMME

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Macquarie University Centre for Ecostratigraphy and Palaeobiology
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Macquarie University, Sydney, July 1995

PERMIAN TO EARLY TRIASSIC ISOTOPIC RECORDS OF CARBON AND STRONTIUM IN AUSTRALIAN SEDIMENTARY BASINS.

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In siliciclastic sediments from marine and non-marine Australian sedimentary basins the Permian/Triassic boundary is marked by a negative isochronous excursion in the $\delta^{13}C$ values of organic carbon that correlates with the negative $\delta^{13}C$ excursion detected in marine carbonate sections at the Permian/Triassic boundary around the world. The magnitude of the negative $\delta^{13}C$ excursion (6-10‰) in organic matter from Australian marine and nonmarine sedimentary basins implies a flux of carbon from ^{13}carbon depleted reservoirs to the relatively ^{13}carbon enriched oxidised reservoirs of up to 33 000 GT equivalent organic matter (Gruszczynski et al., 1989) via a carbon dioxide pathway. The change in Gondwanan vegetation from cool moist temperate *Glossopteris* dominated Permian floras to those dominated by *Dicroidium* (Lele, 1976) occupying a warmer dry environment in the Early Triassic (Dickins, 1993) is associated with this $\delta^{13}C$ excursion of up to 10‰ (Xu and Yan, 1993; Morante et al., 1994).

The $^{87}Sr/^{86}Sr$ seawater curve undergoes a dramatic decrease during the Guadalupian stage followed by a rise during the latest Permian Ochoan Stage through the Early Triassic (Denison et al., 1994) which is recognisable in non-luminescent brachiopods from the Bowen and Canning Basins.

The $^{87}Sr/^{86}Sr$ minimum about the Ochoan/Guadalupian boundary and negative $\delta^{13}C$ excursion about the Permian/Triassic boundary provide two global datums in Late Permian sediments that may assist in correlation of Australian biostratigraphic scales to the international geological timescale.

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Lele, K.M., 1976. Paleoclimatic implications of Gondwana flora. **Geophytology,** 6: 207-229.

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CARBON ISOTOPE STRATIGRAPHY OF THE PERMIAN-TRIASSIC IN AUSTRALIAN MARINE AND NONMARINE SEDIMENTARY BASINS

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A change to more negative $\delta^{13}C$ values occurs at the palaeontologically determined Permian/Triassic boundary (P/Tr) in marine sediments in China, Austria and the margins of Paleotethys. In siliciclastic Gondwanan sediments from sections in three Australian marine (Bonaparte, Carnarvon and Canning) and four nonmarine (Bowen, Sydney, Perth and Cooper) basins $\delta^{13}C$ values measured on total organic carbon change by -4 to -10‰ coinciding with the extinction of the *Glossopteris* flora and cessation of coal deposition in Eastern Australia.

In Australian sections interpreted as lacking a significant hiatus, the change in $\delta^{13}C_{org}$ values is gradual suggesting an extended time interval for $\delta^{13}C$ value changes about the P/Tr. In all Australian sections the change in $\delta^{13}C_{org}$ values occurs within or near the base of the *Protohaploxypinus microcorpus* palynology zone. That zone is therefore concluded to straddle the P/Tr in Australia. The *P. microcorpus* zone marks the beginning of the *Falcisporites* Superzone that represents a significant turnover of palynomorph species in Australian sediments implying a major floral extinction about the P/Tr.

The similarity of the sense and magnitude of the change in $\delta^{13}C$ values in nonmarine Australian basins is comparable $\delta^{13}C$ to that preserved in marine basins so therefore it is interpreted that equilibration of the $\delta^{13}C$ of marine and nonmarine carbon reservoirs occurred via atmospheric CO_2. The change in $\delta^{13}C$ values (assuming global isochroneity) may thus be used as a correlation tool having the potential to calibrate biostratigraphical and lithostratigraphical schemes across sedimentary environments.

The magnitude of the change in $\delta^{13}C$ values suggests a large transfer of ^{12}C-enriched carbon from reduced (buried organic matter, clathrate CH_4, mantle carbon) to oxidised global reservoirs. This may have led to enhanced CO_2 greenhouse conditions that contributed to the Permian-Triassic mass extinction. The end Permian extinction of photosynthesisers such as *Glossopteris* that preferentially fixed ^{12}C and had high potential for preservation (high lignin, deciduous and coal forming) may explain the persistence of relatively low $\delta^{13}C$ values until the Middle to Late Triassic.

DETERMINATION OF THE PERMIAN-TRIASSIC BOUNDARY IN AUSTRALIA FROM CARBON ISOTOPE STRATIGRAPHY

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ABSTRACT

Significant excursions in the carbon isotope composition of organic matter from sedimentary sections across the Permian/Triassic boundary are documented from the Bonaparte, Canning, Carnarvon, Perth, and Bowen Basins. The analysed sections represent a wide range of depositional environments from marine to non-marine, among which precise time correlation is uncertain. The sense and magnitude of the isotopic excursions are comparable to those found elsewhere around the world from marine carbonates at this time. Early Triassic sediments consistently bear carbon more depleted in the carbon-13 isotope than do latest Permian sediments. The isotope excursion provides an isochronous global datum in the sedimentary record at the palaeontologically determined Permian/Triassic boundary. This carbon isotope chemostratigraphic scheme has application for:

1. **correlation between different depositional environments, at scales ranging from intra-basinal to global;**
2. **comparison of sedimentation rates; and**
3. **recognition of lacunas in the sedimentary record.**

INTRODUCTION

Isotope chemostratigraphy is based on the sedimentary record of changes in the isotope ratio of certain elements with time. Elements that are useful for isotope chemostratigraphy include carbon from carbonates (C_{carb}), carbon from organic sources (C_{org}), sulphur, oxygen and strontium. Because of the nature of the geochemical cycles of most of these elements, their potential as correlation tools is usually restricted to marine sediment. The isotopic composition of these elements in the oceanic reservoir is generally homogeneous because their residence times are greater than the mixing times for the oceanic water mass. This is not the case for the bulk terrestrial reservoir for these elements except carbon because of the existence of substantial sub-reservoirs between which mixing cannot occur or because local environmental factors affect isotopic compositions on a time scale less than that for mixing between the sub-reservoirs. For the oceanic and continental reservoirs of carbon, however, there is an interactive link through atmospheric carbon dioxide

The two stable isotopes of carbon, ^{13}C and ^{12}C, are distributed differently between organic and inorganic compounds because of the preferential partitioning of ^{12}C into reduced carbon compounds during photosynthesis. A change in the $^{13}C/^{12}C$ ratio of organic carbon reflects a change in the $^{13}C/^{12}C$ of atmospheric carbon dioxide at the time of photosynthetic reduction by plants and in turn reflects a change in the carbon flux rates between reservoirs. Such reservoirs include those relatively enriched in ^{12}C, for example the organisms of the biosphere, organic matter in sediment, clathrate methane and mantle carbon; and those relatively depleted in ^{12}C, for example carbonate carbon, atmospheric CO_2, and CO_2 dissolved in the oceans. The $^{13}C/^{12}C$ excursion observed at the Permian/Triassic boundary reflects an increased flux of carbon from the ^{12}C enriched to the ^{12}C depleted reservoirs. Correlation between marine and non-marine environments of deposition using carbon isotope chemostratigraphy has been demonstrated for the Paleocene/Eocene boundary (Koch et al, 1992). Here an isotope excursion for oxidised carbon reservoirs has been correlated between marine carbonates, paleosol carbonates and mammalian tooth enamel. This is an unusual example because local environmental and diagenetic effects commonly overprint the primary record. However, it does demonstrate that a link between marine and non-marine carbon reservoirs existed in the past. Organic carbon profiles in Australian basins indicate a similar link between the marine and non-marine records in reduced carbon at the Permian/Triassic boundary (Morante, 1993a, Morante, 1993b).

The Late Permian is of particular interest for a carbon isotope investigation as it marks the time of the most extensive extinction event during the Phanerozoic. During this event there must have been marked changes in the carbon fluxes between the oxidised and reduced global reservoirs of carbon. The Permian/Triassic boundary in marine sediments in Eurasia is characterised by a dramatic reduction in $^{13}C/^{12}C$ in carbonate sediments (Holser and Magaritz, 1987). This may reflect oxidation of vast amounts of stored ^{12}C-enriched reduced carbon that altered the $^{13}C/^{12}C$ of carbon incorporated into the living organic matter and carbonate precipitating at the time. This is shown by the $^{13}C/^{12}C$ profiles at Chinese

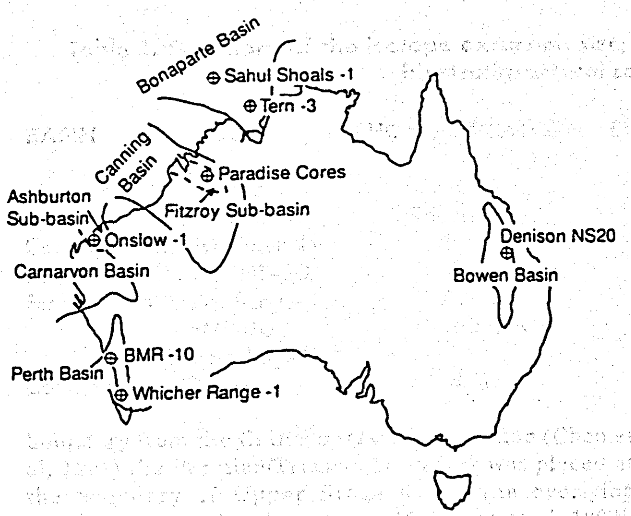

Figure 1. Location map of Australian basins and coreholes studied.

stratotype sections, where a negative $^{13}C/^{12}C$ isotopic excursion occurs across the palaeontologically determined Permian/Triassic boundary (Baud et al, 1989, Chen et al, 1991; Dao-Yi and Zheng, 1993). Similar negative excursions are detected in Permian/Triassic sections in Austria (Holser et al, 1989; Magaritz et al, 1992) and Tethys (Baud et al, 1989). A C_{org} isotope excursion to more negative values paralleling the well documented C_{carb} isotope excursion at the Permian/Triassic boundary was reported in Magaritz et al, (1992). The significant negative excursion of the C-isotope record at the Permian/Triassic boundary may therefore provide a globally correlable time horizon independent of traditional biostratigraphical correlation in both carbonate and organic rich facies. Data presented herein document progress in demonstrating the existence of this geochemical marker through isotopic analysis of organic carbon in Australian sedimentary basins of Permian/Triassic age.

METHODS

All samples used in this study were fine grained pelitic whole rocks, where possible obtained from drill cores or side wall cores. Ditch cuttings were used only if no sidewall core or conventional core was available. Sampling based on drill holes has the advantages of avoiding effects due to weathering and enabling accurate stratigraphic positioning of samples with respect to one another within any single section. Samples analysed were from drill depths of 15 m to about 4 000 m. For this study, biostratigraphy based on available palynology supplemented by new determinations by R.J. Helby were used to calibrate the isotope profiles.

The organic carbon in the samples was prepared for analysis largely following the technique reported in Magaritz et al, (1992). Crushed cleaned samples of one to two grams were treated with hydrochloric acid heated to 80° C for three hours to eliminate carbonate. The acid-treated samples and cupric oxide were placed in 6 mm quartz tubes, which were evacuated and sealed before furnace combustion at 800° C for five hours. The measured ratio of $^{13}C/^{12}C$ in the CO_2 evolved in combustion was determined on a Finnigan MAT 252 mass spectrometer. The measured ratios of $^{13}C/^{12}C$ are reported in the standard format of $\delta^{13}C$ relative to a standard carbonate (PDB), this being the difference in isotope ratio between the sample and standard and expressed in parts permil (‰). The standard deviation of the $\delta^{13}C$ determinations on 23 repeat analyses of an anthracite laboratory standard was 0.1 ‰. The combustion yield of CO_2 enabled the Total Organic Carbon (TOC per cent) to be determined.

RESULTS

The most detailed studies conducted so far are from sections in the Bonaparte and Canning Basins, northwestern Australia, and the Bowen Basin of eastern Australia (Fig. 1). Some of these data have been discussed in more detail elsewhere (Morante, 1993a; Morante, 1993b; Morante et al, 1993). Additional data are presented for sections in the Carnarvon and Perth Basins, Western Australia (Fig. 1). In all sections traversing the Permian/Triassic boundary, the profiles of $\delta^{13}C$ against depth show a pronounced depletion in $\delta^{13}C$ values from the latest Permian to the earliest Triassic. This is in the same sense as $\delta^{13}C$ profiles determined on C_{org} in a marine section in Austria (Magaritz et al, 1992) and on C_{carb} in the same and other marine sections in Eurasia straddling the Permian/Triassic boundary (Baud et al, 1989; Holser and Magaritz, 1987; Chen et al, 1991). The magnitude of the $\delta^{13}C$ isotope excursion (-4 to -8.5 ‰) in the Australian sections is comparable to those detected elsewhere (-3 to -10 ‰) and indicates that the $\delta^{13}C$ isotope shift to more ^{13}C-depleted values is a primary isochronous feature of global extent. There is no direct correspondence for any section between TOC and $\delta^{13}C$ values implying that the $\delta^{13}C$ excursion is unrelated to alteration effects. The TOC of individual samples is commonly higher in Permian sediment (around 0.5 to 12 per cent) than in Triassic sediment (around 0.1 to 2 per cent). Changes in $\delta^{13}C$, the interpreted environments of deposition and the degree of palynological definition of the biostratigraphy are shown in Table 1.

Palynological definition of the Permian/Triassic boundary in Australia depends on recognition of the *Protohaploxypinus microcorpus* zone. Traditionally the boundary was placed at the contact of the 'Permian' coal measures and overlying 'Triassic' Narrabeen and Rewan Groups in Eastern Australia (David, 1950). Subsequently, on the basis of correlation of palynomorph assemblages from Australia with those of Pakistan (Balme, 1970) the boundary was placed at the top of the *P. microcorpus* zone (Balme, 1970; Helby et al, 1987). More recently, on the basis of C-isotope data from the Canning Basin showing a negative excursion correlatable with that occurring at the palaeontologically determined Permian/Triassic

Table 1. **Summary of the isotope excursion size, interpreted environment of deposition, and degree of biostratigraphical control on sections studied.**

BASIN	WELL	$\delta^{13}C$ ‰ EXCURSION	ENVIRONMENT OF DEPOSITION	PALYNOLOGICAL CONTROL
Bonaparte	Tern–3	-8 ‰	Marine	Good
	Sahul Shoals–1	Triassic only	Marine	Spot
Canning	Paradise Coreholes	-8.5 ‰	Marginal marine	Good
Bowen	Denison NS–20	-6 ‰	Fluvial	Good
Perth	Whicher Range–1	-5.5 ‰	Fluvial	Spot
	BMR–10 (Beagle Ridge)	Triassic only	Marine	Good
Carnarvon	Onslow–1	-4 ‰	Marine	Spot

boundary from the Chinese stratotype section (Chen et al, 1991) the Permian/Triassic boundary was placed at the boundary of Upper Stage 5 and the overlying *P. microcorpus* palynology zones (Morante et al, 1993). The position of the Permian/Triassic boundary in Australia as indicated by the carbon isotope excursion lies at or just above the base of the *P. microcorpus* zone and follows the disappearance of the *Glossopteris* flora at the top of Stage 5.Reworked C_{org} is probably responsible for displacing the shift upwards.The boundary is here systematically located at a point in the isotope depth profile where $\delta^{13}C$ values are consistently less than -26‰, and at the beginning of the negative excursion in all profiles (Figs 2-5).This boundary lies at or within a few metres of the base of the *P. microcorpus* zone.

Bonaparte Basin

Tern–3 was drilled in 1982 in NT/P28 to investigate the prospectivity of a salt diapir. It penetrated a marine section through the Early Triassic Mount Goodwin Formation and the underlying Late Permian Hyland Bay Formation. Palynological control is excellent, with 75 m of the *Weylandites* and 44 m of the *P. microcorpus* zone indicating continuous or near continuous sedimentation across the Permian/Triassic boundary. The Hyland Bay Formation was deposited in a shelf-deltaic environment and the overlying Mount Goodwin Formation in an unspecified shallow marine environment (Gunn and Ly, 1989). In the C-isotope profile (Fig. 2) a group of six of the Hyland Bay Formation samples representing the *Weylandites* zone (Helby, 1983) have similar $\delta^{13}C$ values at about -24‰, a seventh sample has a more ^{13}C-enriched composition at -22.1‰. In the overlying 35m there is a marked decrease of about 8‰ in $\delta^{13}C$ within the *P. microcorpus* zone. Five of a set of six samples in the upper part of the *P. microcorpus* zone and the lower part of the *Lunatisporites pellucidus* zone have similar $\delta^{13}C$ values about an average of -32.2‰. The sixth sample has an even lower value at -34.5‰. Higher in the profile, $\delta^{13}C$ increases to an average value of about -29‰ for a set of six samples in the *L. pellucidus* zone. The excursion in $\delta^{13}C$ values (Figure 2) is correlated to that occurring at the Permian/Triassic boundary in Eurasian sections. The isotope excursion is about -8 ‰ and occurs gradually over a 35m sediment column that begins in the *P. microcorpus* palynology zone, (Helby 1983).The Tern Sandstone Member was originally regarded as lying 50 metres below the top of the sandy claystone Hyland Bay Formation (Helby, 1983). Here, the Tern sandstone is regarded as the top of the Hyland Bay Formation. We pick the Permian/Triassic boundary at the beginning of the negative isotope excursion near a formation boundary and the boundary between *P. microcorpus* and *Weylandites* palynology zones. Based upon the isotope profile the *Weylandites* zone is Late Permian in age.

Sahul Shoals–1 drilled in 1969-70 to investigate an anticlinal feature in NT/P15 provides one of the most complete Triassic sections on the Australian northwestern margin (Jones and Nicoll, 1985). This 1955 m thick

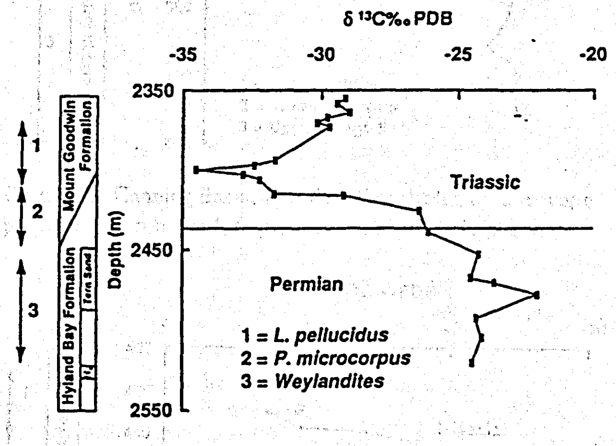

Figure 2. Bonaparte Basin; Tern–3 $\delta^{13}C$ isotope profile, formations, (H4 is the H4 limestone member), and palynology zones.

Triassic section is interpreted as predominantly marine. A preliminary study of six samples ranging in age from Scythian to Norian (Jones and Nicoll, 1985) yielded $\delta^{13}C$ values between -24 and -28 ‰ (Table 2), a range more positive than in the other Early Triassic sections. Partial oxidation of buried organic carbon tends to produce more positive $\delta^{13}C$ values, and may be the case with the more positive $\delta^{13}C$ value of -24.2‰ in the sample at 2 769.8m.

Table 2. Isotope and TOC values determined from Sahul Shoals-1, Onslow-1 and BMR-10 (Beagle Ridge) samples.

WELL	DEPTH m	$\delta^{13}C$‰	TOC%
Sahul Shoals-1	1883.9	-27.9	0.3
	2769.8	-24.2	0.4
	3005.6	-26.6	1.1
	3005.9	-26.5	0.8
	3268.9	-27.2	0.4
	3272.9	-27.0	0.2
Onslow-1	1906.82	-27.0	0.8
	2023.6	-26.8	0.7
	2168.5	-22.7	5.6
BMR-10 (Beagle Ridge)	681.2	-34.4	0.5
	735.9	-34.4	0.4
	780	-32.9	0.3
	978.3	-33.3	2.2

Canning Basin

Six coreholes from Paradise Station were drilled in 1971 to assess the economic prospects of Permian coal seams within the Fitzroy Sub-basin. The cores provide good stratigraphic coverage of the lower Blina Shale and upper Liveringa Group formations. Corehole-4 of the series traverses the Permian/Triassic boundary in sediment deposited in a marginal marine environment determined on the basis of the presence of acritarchs and microplankton in palynology preparations (Helby, 1975). The biostratigraphic zonation of this section is excellent. Determination of the depth of the lowermost Blina Shale/uppermost Liveringa Group boundary is uncertain in this section but based on description of the basal transgressive sandstone of this formation (Gorter, 1978) it is placed at a depth of 251 m (Fig. 3). Between depths 251 to 257 m in a composite section, and within sediments approximately at the Liveringa Group/ Blina Shale formation boundary, a shift in $\delta^{13}C$ values from around -24.5 ‰ to -33 ‰ occurs (Fig. 3). This abrupt negative $\delta^{13}C$ excursion occurs in sediments straddling a single sample of *P. microcorpus* zone age at 254 m determined by Helby. The sharp change in $\delta^{13}C$ values in comparison to that in the Tern-3 well is consistent with an interpretation of either a very condensed section or lacuna within the Upper Stage 5, or *P. microcorpus* zone or both at the Permian/Triassic boundary.

Bowen Basin

The Denison NS-20 corehole, drilled in 1978 in the Denison Trough and commissioned by the Queensland Geological Survey, penetrated the non-marine Early Triassic Rewan Group and the underlying Rangal Coal Measures (Foster, 1982). The palynology zones are well defined in this section (Fig. 4) and include a 22 m thick *P. microcorpus* zone (Foster, 1982). The $\delta^{13}C_{org}$ profile (Fig. 4) changes about -6‰ occurring gradually over a 10 m interval within the *P. microcorpus* zone, from a start within metres of the boundary between the Coal Measures and the overlying Rewan Group at 447 m. The start of the excursion at 447 m is interpreted as indicating the P/Tr boundary. The *P. Crenulata* zone is correspondingly Permian.

Carnarvon Basin

The Onslow-1 well drilled in the Ashburton Sub-Basin (Hocking et al, 1985; Hocking, 1990), penetrated the marine Locker Shale and the deltaic Chinty Formation. Palynology analyses for this section indicate an Upper Stage 5c age for a sample at depth 2 166.2 m,(Backhouse, pers. comm., 1993). Samples from 2 023.6m and 1 906.82 m are from the *Tigrisporites playfordii* zone stratotype section in the Early Triassic (Dolby and Balme, 1976). Palynological determinations on two samples from depths of 2 051.3 m and 2 090.7 m indicate the *Kraeuselisporites saeptatus* zone age (Dolby and Balme, 1976). The *K. saeptatus* zone is thought to be equivalent, at least in part, to the *L. pellucidus* and *Protohaploxypinus*

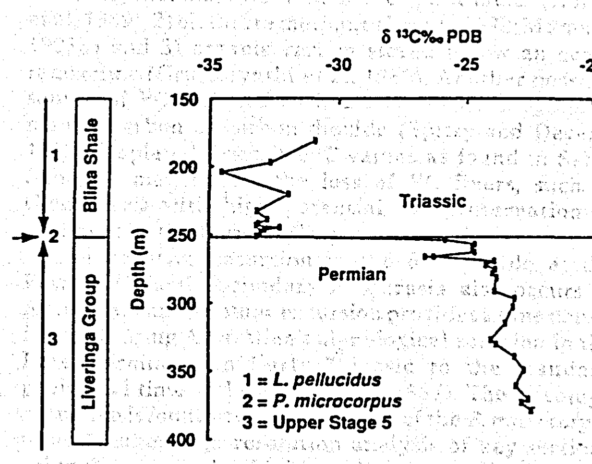

Figure 3. Canning Basin, Paradise Coreholes $\delta^{13}C$ isotope profile of Corehole-4, formations and palynology zones.

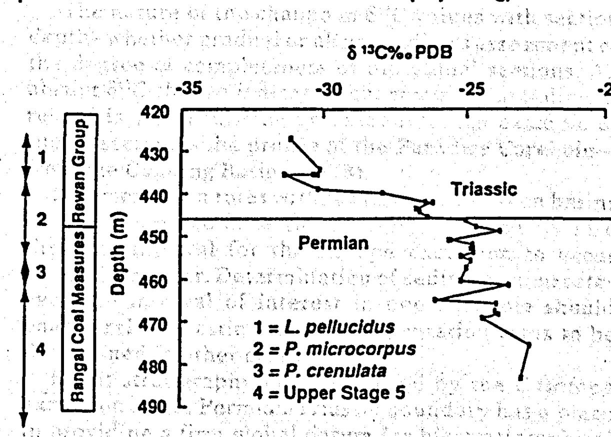

Figure 4. Bowen Basin, Denison NS-20 $\delta^{13}C$ isotope profile, formations and palynology zones.

samoilovichii zones of eastern Australia (Helby et al, 1987). Warris (Fig. 6, 1993) indicates the lower part of the Locker Shale in the Carnarvon Basin to extends into the *P. microcorpus* zone. Two samples from the Locker Shale, with $\delta^{13}C_{org}$ values around -27 ‰ (Table 2) are in the *T. playfordii* zone and one from the Chinty Formation, -22.7 ‰ at 2 168.5 m is Upper Stage 5c. These data document a $\delta^{13}C_{org}$ excursion of -4 ‰ between the uppermost Chinty Formation and the lower 73 m of the Locker Shale. This $\delta^{13}C$ excursion is in the same sense as the excursion in the Canning and Bonaparte Basins and demonstrates potential for $\delta^{13}C_{org}$ analyses to identify the Permian/Triassic boundary and distinguish Late Permian from Early Triassic sediments in the Carnarvon Basin. Detailed sampling of this section would be required to make a firm determination.

Northern Perth Basin

BMR-10 (Beagle Ridge) was drilled in 1959 to investigate the narrow sub-surface Beagle Ridge. The well penetrated an important section of the Early Triassic Kockatea Shale (Balme, 1969). The Kockatea Shale contains a shelly fauna assigned to the Otoceratan division of the Early Triassic (Dickins and McTavish, 1963; Balme, 1969; McTavish and Dickins, 1974). Four samples from the Kockatea Shale, all within the ref-erence stratotype section of the *K. saeptatus* zone (Dolby and Balme, 1976) have $\delta^{13}C$ values ranging from -34.4 ‰. to -32.9 ‰ (Table 2). These values are appropriately negative for the Early Triassic, as found in the Early Triassic of Tern–3 in the Bonaparte Basin.

Southern Perth Basin

The results from Whicher Range–1 well (Table 2), drilled by Union Oil in 1968 in the Bunbury Trough, are too few to indicate the P/Tr boundary, but they are presented in Figure 5 as an example of the potential of the method even where sampling is meagre.Five samples spanning the fluvial Lesueur Sandstone and Sabina Sandstone type section (Cockbain 1990) (3 samples) and uppermost Sue Coal Measures (2 samples) have a change in $\delta^{13}C$ of -5.5‰. Samples in the Late Permian Sue Coal Measures from 4 014.8 m and 3 946 m show $\delta^{13}C$ values typical of those found for Permian organic carbon in Western Australia at around -23 to -24 ‰. At a depth of 3 737.76 m an isotope value of -25‰ has been determined from a sample described as showing affinity to the *P. microcorpus* zone (Backhouse, pers. comm., 1993). At 3 583.84m and 3 490 m, within the *K. saeptatus* zone typical Triassic like values of -27.1‰ and -28.6‰ have been determined. Based upon available isotope and palynology data,the P/Tr boundary lies somewhere between depths of 3 737.76 m and 3 583.8 m about the boundary between the Sabina Sandstone and Lesueur Sandstone within the *P. microcorpus* zone.

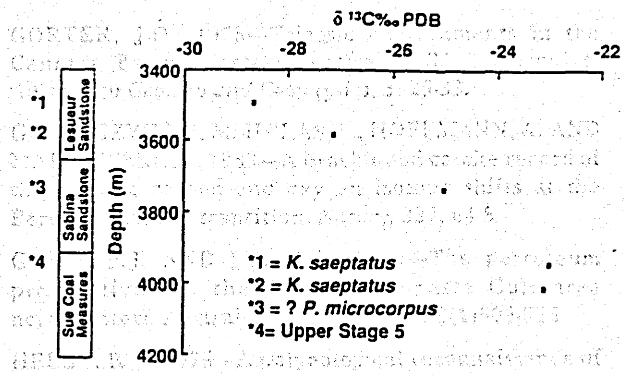

Figure 5. Perth Basin, Whicher Range-1 $\delta^{13}C$ isotope profile formations and palynology zones.

DISCUSSION AND CONCLUSIONS

Sources of ^{12}C-enriched carbon that caused the negative excursion in the $\delta^{13}C$ profile at the Permian/Triassic boundary include; oxidation of 1) organic facies (Holser et al, 1989), 2) clathrate methane (Erwin, 1993; Morante, 1993b) and 3) organic carbon stored below an ocean redoxcline (Gruszczynski et al, 1989). Another possible source of ^{12}C-enriched carbon is volcanic eruption of mantle carbon as carbon dioxide (Spitzy and Degens, 1985). Depleted Triassic $\delta^{13}C$ values as found in Sahul Shoals–1 may reflect the loss of ^{12}C fixers, such as *Glossopteris* with high potential for preservation in sediment at the Permian/Triassic extinction.

The negative excursion in the $\delta^{13}C$ profile at the Permian/Triassic boundary in Eurasia also occurs in Australia. This C-isotope excursion provides a time datum for calibrating Australian palynological zonation in the Late Permian and Early Triassic to the standard geological time scale (Helby et al, 1987). The C-isotope excursion is found at or near the base of the *P. microcorpus* zone. Further high resolution analysis of key sections using C-isotopes should determine the precise location of the Permian/Triassic isotope excursion with respect to palynology zones.

The nature of the change in $\delta^{13}C$ values with section depth– whether gradual or abrupt– allows assessment of the degree of completeness of individual sections. An abrupt $\delta^{13}C$ change indicates that some of the sediment record is either missing or condensed. An example of such a section is the profile of the Paradise Corehole–4 from the Canning Basin (Fig. 3).

Sedimentation rates within a basin or between basins may be compared in sections lacking a lacuna because the time interval for the isotope excursion to occur should be similar. Determination of sedimentation rates over the interval of interest in one borehole should enable relative estimates of sedimentation rates to be determined in other cores.

Event stratigraphy as represented by the C-isotope excursion at the Permian/Triassic boundary has a place in providing a firm global datum for biostratigraphical correlation schemes, and as such, isotope stratigraphy provides a powerful and useful addition to the range of correlation tools available to the petroleum industry.

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Supported by an ARC Special Investigator Award to John Veevers and a Macquarie University Postgraduate Award to Ric Morante. Analyses were conducted at the Centre for Isotope Studies (CIS). We thank Robin Helby for palynological determinations. Robin Helby and Peter Price provided core samples from Inland Exploration N.L.. John Backhouse provided core samples from WAGS collections and supplementary palynological determinations. SANTOS Petroleum provided samples for Tern-3. Bowen Basin samples were obtained from the GSQ. Roger Summons provided samples from BMR-10 (Beagle Ridge) and Sahul Shoals-1 from AGSO collections. Andrew Todd (CIS) and Andrew Bryce (CSIRO) assisted with sample analysis.

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APEA

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Edited by M.A. LANPHERE, G.B. DALRYMPLE, and B.D. TURRIN

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DETERMINING THE CARBON ISOTOPE CHEMOSTRATIGRAPHY ACROSS THE PERMIAN/TRIASSIC BOUNDARY IN AUSTRALIA

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A negative $\delta^{13}C$ excursion at the palaeontologically determined Permian/Triassic boundary (P/Tr) in marine sediment has been well established. A similar $\delta^{13}C$ excursion to more negative values occurs in organic carbon in pelitic whole rock samples from conventional or sidewall cores from seven Australian sedimentary basins. The $\delta^{13}C$ excursion in marine and nonmarine sediment occurs within or near the base of the *Protohaploxypinus microcorpus* palynology zone. This zone is therefore interpreted as straddling the P/Tr. The size of the $\delta^{13}C$ excursion, interpreted environment of deposition at the boundary and degree of biostratigraphic control based upon palynology in each basin is summarised in the table below.

Basin	$\delta^{13}C$ ‰ excursion	Depositional environment	Palynological control
Bonaparte	-8	Marine	Good
Carnarvon	-4	Marine	Spot
Canning	-8.5	Marginal marine	Good
Bowen	-6	Fluvial	Good
Sydney	-6	Fluvial	Good
Perth	-5.5	Fluvial	Spot
Cooper	-6	Fluvial	Spot

The $\delta^{13}C$ excursion in marine and nonmarine sediment alike is interpreted as reflecting a shift of up to -10‰ in the $\delta^{13}C$ of atmospheric CO_2 that masked expected variations in enclosed basins. The possible global extent of this $\delta^{13}C$ excursion at the P/Tr may provide a correlation tool enabling calibration of biostratigraphy schemes world wide at the P/Tr across a range of sedimentary environments. The shape of the negative $\delta^{13}C$ excursion varies from sharp to gradual. A sharp $\delta^{13}C$ excursion indicates a lacuna, a condensed section, or a rapid change to more negative $\delta^{13}C$ values in the Triassic. A gradual shift in $\delta^{13}C$ indicates either a real, prolonged continuous $\delta^{13}C$ excursion or a mixture of Permian and Triassic values. The $\delta^{13}C$ excursion is explained by a flux of ^{12}C enriched carbon as CO_2 from the reduced to the oxidised global reservoir. Possible sources of ^{12}C enrichment suggested include, a) oxidation of organic facies and clathrate methane and b) volcanic eruption of mantle carbon as carbon dioxide. Depleted $\delta^{13}C$ values until at least the Middle to Late Triassic may reflect the loss of ^{12}C fixers having high preservation potential at the Permian/Triassic extinction. A large transfer of carbon from the reduced to the oxidised global reservoir and release of methane may have produced greenhouse conditions that contributed to the Permian/Triassic extinction.

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CARBON ISOTOPES & SEQUENCE STRATIGRAPHY ABOUT THE PERMIAN-TRIASSIC BOUNDARY IN THE SYDNEY BASIN

R. MORANTE & C. HERBERT
School of Earth Sciences, Macquarie University

INTRODUCTION

The largest extinction event of the Phanerozoic occurred at the end of the Permian when it is estimated that over 90% of marine species and about 70% of land vertebrates became extinct (Erwin 1994). This was accompanied by a postulated sea-level fall of the order of 300 m (Holser and Magaritz 1987). During this event there must have been marked changes in carbon flux between the oxidised and reduced global reservoirs of carbon. This is reflected at the Permian/Triassic (P/Tr) boundary in marine sediments in Eurasia by a dramatic reduction in the ratio of $^{13}C/^{12}C$ in carbonate sediments (Holser and Magaritz 1987). The oxidation of vast amounts of stored ^{12}C-enriched reduced carbon led to the alteration of the ratio of $^{13}C/^{12}C$ in living organisms and precipitated carbonate rocks, which is shown by $^{13}C/^{12}C$ profiles of the Chinese stratotype section, where a $\delta^{13}C$-excursion to more negative values occurs across the palaeontologically determined P/Tr boundary (Baud et al. 1989, Chen et al. 1991, Dao-Yi & Zheng 1993). The negative $\delta^{13}C$-excursion, generally reported in *marine* intervals for inorganic carbon (C_{carb}), has also been found in organic carbon (C_{org}) in Austria (Magaritz et al. 1992). Our investigations into C-isotope stratigraphy in the Sydney Basin reveal similar $\delta^{13}C$-excursions in *non-marine* organic carbon. This suggests that the negative excursion of the C-isotope record at the P/Tr boundary may provide a globally correlatable time horizon independent of traditional biostratigraphical correlation in carbonate and organic-rich siliciclastic facies in both marine and non-marine environments.

Traditionally the P/Tr boundary in the Sydney Basin was placed at the contact of the "Permian" coal measures and overlying "Triassic" Narrabeen Group (David 1950). Subsequently, on the basis of palynomorph correlation between Australia and Pakistan, the

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boundary was placed at the *top* of the *P. microcorpus* zone (Balme 1970, Helby et al. 1987) well above the base of the Narrabeen Group in the transition from the Dooralong Shale to the Munmorah Conglomerate in the north, and in the lower part of the Scarborough Sandstone in the south. The position of the P/Tr boundary in Australia, as indicated by the carbon-isotope excursion correlated with the Chinese stratotype (Chen et al. 1991), lies close to or at the base of the *P. microcorpus* zone and is closely linked with the disappearance of the *Glossopteris* flora at the top of Stage 5.

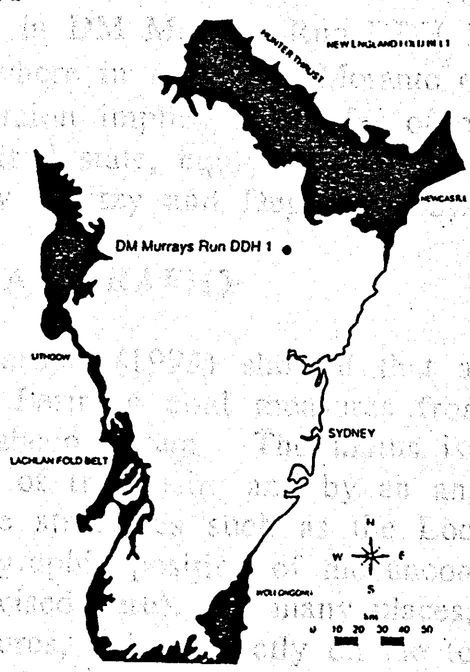

Figure 1. Location of DM Murrays Run DDH 1 in the Sydney Basin.

METHODS

Samples of organic carbon were obtained from shales in the fully-cored borehole DM Murrays Run DDH 1 (Fig. 1). Borehole sampling avoids surface weathering effects and enables accurate stratigraphic positioning of samples. DM Murrays Run DDH 1 was chosen for detailed study because it penetrates the earliest Triassic section identified in the Sydney Basin to date. Biostratigraphy was based on existing palynology supplemented with new determinations by R. J. Helby.

Preparation of the organic carbon for analysis largely followed the methods of Magaritz et al. (1992). Crushed cleaned shale samples of 1-2 grams were treated with heated hydrochloric acid at 80° C for 3 hours to react carbonate. The acid-treated samples and cupric oxide were placed in 6 mm quartz tubes, that were evacuated and sealed before furnace combustion at 800°C for 5 hours. The measured ratio of $^{13}C/^{12}C$ in the CO_2 produced by combustion of the organic carbon was determined on a Finnigan MAT 252 mass spectrometer. The measured ratios of $^{13}C/^{12}C$ were reported in the standard format of $\delta^{13}C$ relative to a standard carbonate (PDB) expressed in parts permil (‰). The standard deviation of the $\delta^{13}C$ determinations on 45 repeat analyses of an anthracite laboratory standard was 0.13 ‰. The combustion yield of CO_2 enabled the total organic carbon (TOC%) to be determined.

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ISOTOPE RESULTS

In DM Murrays Run DDH 1 the profile of $\delta^{13}C$ against depth shows a negative excursion in $\delta^{13}C$ values from about -24 $^{o}/_{oo}$ at depths greater than 780 m to values predominantly less than -26 $^{o}/_{oo}$ and as low as -29.6 $^{o}/_{oo}$ at depths less than 742.7 m (Fig. 2). This $\delta^{13}C$-excursion is in the same sense as $\delta^{13}C$ profiles determined on C_{org} in a marine section in Austria straddling the P/Tr boundary (Magaritz et al. 1992). The magnitude of the $\delta^{13}C$-excursion (as much as -5 $^{o}/_{oo}$) in DM Murrays Run DDH 1 is comparable to excursions detected elsewhere in Australia (Morante et al. 1994). A -5 $^{o}/_{oo}$ $\delta^{13}C$-excursion implies a transfer of carbon, from the reduced to the oxidised state, equivalent to 4 times the global biomass of carbon today (Spitzy and Degens 1985).

STRATIGRAPHY

Herbert (1993) showed that a significant hiatus separated the Late Permian coal measures from the overlying coal-barren Narrabeen Group. The hiatus is represented by a disconformity over most of the basin, and by an angular unconformity over locally active structures such as the Lochinvar Anticline (note that the stratigraphic position of the unconformity in DM Murrays Run DDH 1 is revised here). In many places, a palaeosol overlies the coal measures, either directly on the top coal or, as in DM Murrays Run DDH 1, on the topmost carbonaceous siliciclastic sediments (Fig. 3).

The Late Permian coal measures were deposited during a large-scale regression as relative sea-level fell from a mid-Permian highstand (Herbert 1980, 1994a in prep). In the Newcastle Coal Measures this is reflected by the up-sequence dominance of thick fluvial conglomerates deposited in the Lake Macquarie Syncline to the east of the Lochinvar Anticline (Herbert 1994b in prep). In contrast, immediately to the west of the anticline, the coal measures in DM Murrays Run DDH 1 are dominated by finer-grained siliciclastic sediments, coal and oil shale.

The negative $\delta^{13}C$-excursion commences about 50 m below the coal measures/Narrabeen Group boundary (Fig. 2), but accelerates in the last 6 m within thinly interbedded/laminated dark grey siltstone/claystone which can be considered as part of a high-frequency depositional sequence deposited during a single cycle of base-level change (Fig. 3). The interval commences above an erosional surface (sb at 758 m, Fig. 2) indicating a base-level fall. During the following base-level rise, about 14 m of upward-fining fluvial sandstone (lowstand systems tract) was deposited above the sequence boundary. This sandstone was overlain by interbedded fine-grained sandstone and shale above a transgressive surface (ts, Fig. 3), indicating a deepening lacustrine/estuarine margin featuring shrinkage cracks, the sphenopterid fern *Neomariopteris*, and reed-like *Phyllotheca* (transgressive systems tract, Fig. 3). Maximum transgression, when the rate of base-level rise was fastest, is represented by the more shaley dark grey part of the section (mfs, Fig. 3). Above this surface, and as the rate of base-level rise slowed to a highstand and began to fall, the shale coarsens and becomes more silty (highstand systems tract) with shrinkage cracks and plant remains (*Glossopteris* leaf), indicating shallowing conditions. A 30-cm-thick palaeosol cap indicates subaerial exposure with base-level fall to complete the cycle. This last Permian base-level fall recorded in the basin probably coincides with the major 2nd-order, end-Permian sea-level fall (SB at P/Tr, fig. 2, 3).

In DM Murrays Run DDH 1, the Narrabeen Group rests with a sharp, erosional, disconformity on the palaeosol capping the coal measures. The basal Dooralong Shale grades up to the Munmorah Conglomerate in three coarsening-up parasequence sets (M1-3, Fig. 2). These are interpreted as having been deposited in estuarine coastal plain to alluvial plain environments in the highstand systems tract of a 3rd-order depositional sequence as the rate of rising relative sea-level slowed to a highstand and began to fall.

DISCUSSION

The most rapid part of the negative $\delta^{13}C$-excursion takes place in the top part of a 21-m-thick sedimentary cycle at the top of the coal measures in the 3rd-order Belmont Sequence (sb to SB, Fig. 3). This cycle is considered comparable in magnitude to, at least, a high-frequency, 5th-order sequence with a duration of the order of tens of thousands of years. A *Glossopteris* leaf identified by G. J. Retallack (pers comm. 1993) occurs in the upper part of the $\delta^{13}C$-excursion, less than 1.5 m below the coal measures/Narrabeen Group sequence boundary, indicating that end-Permian *Glossopteris* extinction was either gradual or not completed until well into the $\delta^{13}C$-excursion. The steepest slope of the negative $\delta^{13}C$-excursion commences at a maximum flooding surface and is erosively truncated at the lowest value of -29 $^{o}/_{oo}$ at the coal measures/Narrabeen Group sequence boundary (mfs to SB, fig. 3). As the interval from the maximum flooding surface (mfs) to the sequence boundary (SB) in figure 3 is equivalent to about half the high-frequency sequence the duration of the steep part of the excursion could be equivalent to half the sequence duration (i.e.,

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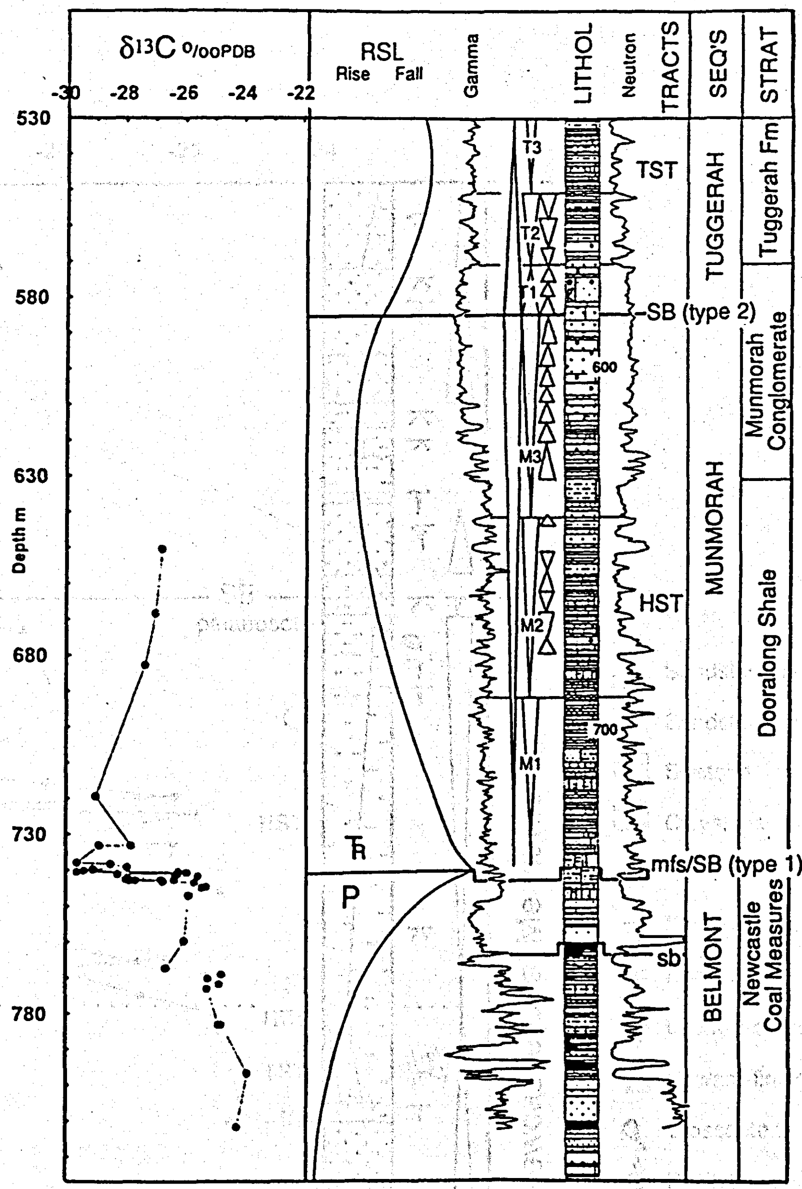

Figure 2. Carbon-isotope data compared with a sequence stratigraphic analysis of 3rd-order sequences in the Late Permian Newcastle Coal Measures and the Early Triassic lower Narrabeen Group (Dooralong Shale to Tuggerah Formation) in DM Murrays Run DDH 1. A number of more positive C-isotope values were obtained from Triassic shales identified as palaeosols by G. J. Retallack. Because the carbon may have been partially degraded these results are not shown. The lower part of the Belmont Sequence (Herbert 1994a in prep.) is not defined here. Bends in P/Tr boundary allow for cable stretch, causing the gamma and neutron logs to be almost 4 m deeper than the graphic log. RSL=relative sea-level, SB= 3rd-order sequence boundary, mfs=maximum flooding surface, LST=lowstand systems tract, TST=transgressive systems tract, HST=highstand systems tract, sb=high frequency sequence boundary. Triangles at right indicate upward-coarsening parasequences and upward-fining fluvial/estuarine sandstones; triangles in middle indicate progradational and retrogradational trends for parasequence sets (M1-3, T1-3); triangles at left indicate trends for systems tracts.

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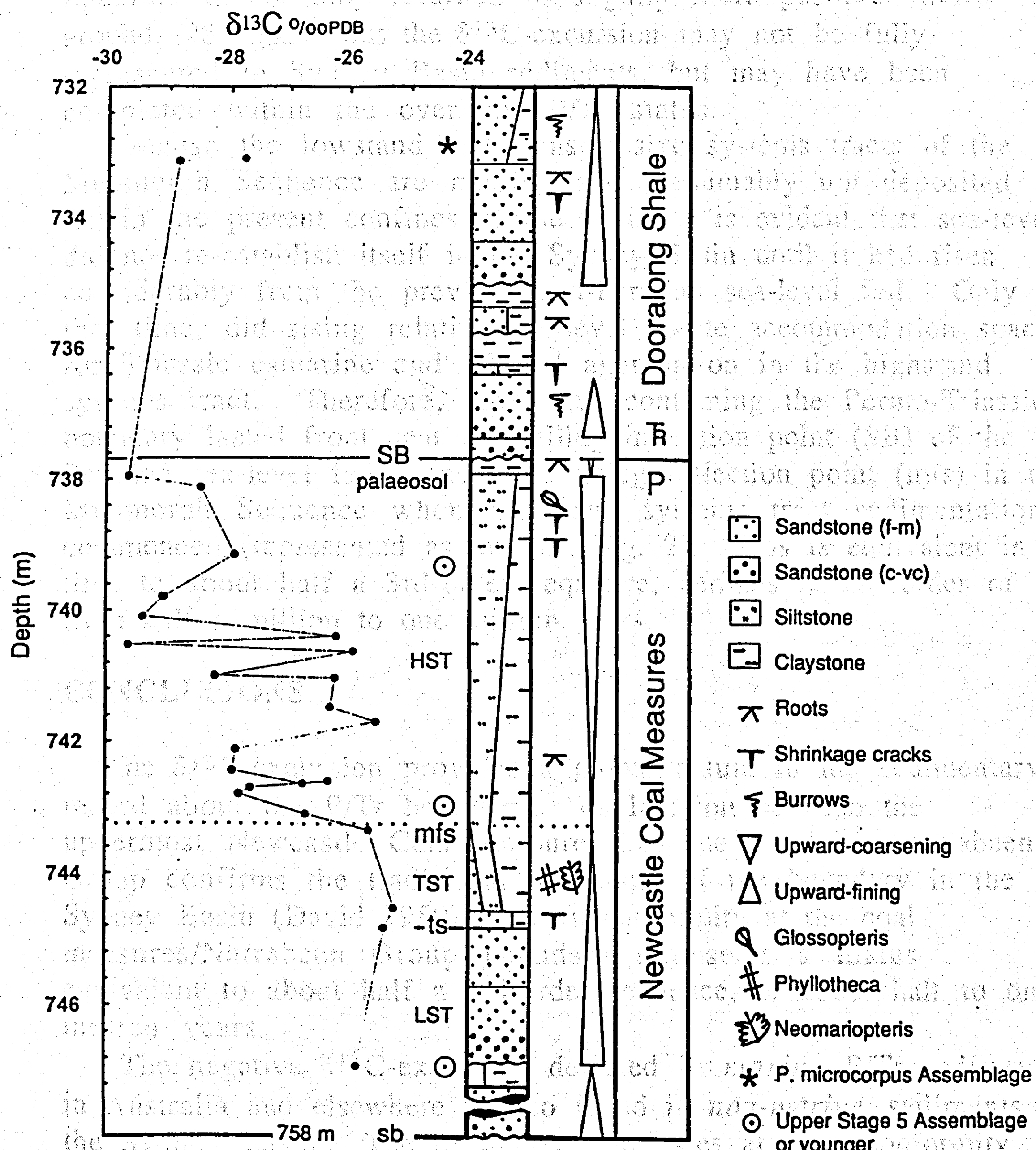

Figure 3. Detailed plot of the upper, steepest part of the negative $\delta^{13}C$-excursion with a high-frequency (5th-order?) sequence at the top part of the 3rd-order Belmont Sequence, Newcastle Coal Measures. sb= high frequency sequence boundary at 758 m (below base of diagram-see Fig. 1), ts=transgressive surface. Other abbreviations as for Fig. 2.

many thousands to tens of thousands of years). This implies that the $\delta^{13}C$-excursion was not geologically instantaneous. In our opinion, this is also an incomplete swing as Morante et al. (1994) obtained values as low as -34 ‰ in Western Australian marine intervals before they returned to slightly more positive values around -28 ‰. Thus the $\delta^{13}C$-excursion may not be fully represented in Sydney Basin sediments, but may have been completed within the overlying P/Tr hiatus.

Because the lowstand and transgressive systems tracts of the Munmorah Sequence are missing and presumably not deposited within the present confines of the basin, it is evident that sea-level did not re-establish itself in the Sydney Basin until it had risen considerably from the previous end-Permian sea-level fall. Only at that time, did rising relative sea-level create accommodation space for Triassic estuarine and alluvial aggradation in the highstand systems tract. Therefore, the hiatus containing the Permo-Triassic boundary lasted from near the falling inflection point (SB) of the last Permian sea-level fall to near the rising inflection point (mfs) in the Munmorah Sequence when highstand systems tract sedimentation commenced (represented as mfs/SB, Fig. 2). This is equivalent in time to about half a 3rd-order sequence, perhaps in the order of from half a million to one million years.

CONCLUSIONS

The $\delta^{13}C$-excursion provides a global datum in the sedimentary record about the P/Tr boundary. Its location between the uppermost Newcastle Coal Measures and the overlying Narrabeen Group confirms the traditional placement of the boundary in the Sydney Basin (David 1950). The unconformity at the coal measures/Narrabeen Group boundary represents a hiatus equivalent to about half a 3rd-order sequence, or about half to one million years.

The negative $\delta^{13}C$-excursion detected in *marine* P/Tr sediments in Australia and elsewhere is also found in *non-marine* sediments of the Sydney Basin. The excursion culminates at an unconformity (sequence boundary) 1.5 m above the topmost sample identified as Upper Stage 5 or younger, and 5 m below the lowest sample containing palynomorphs from the *P. microcorpus* zone. This indicates that the P/Tr boundary is associated with major changes in both lithology and flora detected in eastern Australian sedimentary basins. The last *Glossopteris* specimen found in DM Murrays Run DDH 1 occurs less than 1.5 m below the coal measures/Narrabeen

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Group unconformity suggesting the *Glossopteris* flora survived until the latest Permian in the Sydney Basin.

The negative $\delta^{13}C$-excursion began gradually over a 50 m interval representing many tens to several hundreds of thousands of years, and accelerated in the uppermost 6 m of the Late Permian coal measures representing a period of tens of thousands of years.

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AUSTRALASIAN PALAEONTOLOGICAL CONVENTION - 94

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ASSOCIATION OF AUSTRALIAN PALAEONTOLOGISTS

Macquarie University, Sydney, February 1994

DETERMINING THE PERMIAN/TRIASSIC BOUNDARY IN AUSTRALIA USING CARBON ISOTOPE CHEMOSTRATIGRAPHY

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A negative $\delta^{13}C$ excursion is detected at the palaeontologically determined Permian/Triassic boundary (P/Tr) in marine sediment in China (Chen at al., 1991: Gruszczynski et al., 1990; Dao-Yi, X. & Zheng, Y., 1993), Spitzbergen (Gruszczynski et al., 1989), Austria (Magaritz et al., 1992) and the northern margin of Paleotethys (Baud et al., 1989). A similar $\delta^{13}C$ excursion to more negative values occurs in seven Australian sedimentary basins in marine and nonmarine sediment within, or near the base of, the *Protohaploxypinus microcorpus* palynology zone. This zone is accordingly interpreted as straddling the P/Tr. The $\delta^{13}C$ excursion in marine and nonmarine sediment alike is interpreted as reflecting the overwhelming shift of up to -10‰ in the $\delta^{13}C$ of atmospheric CO_2 that masked any expected variation in enclosed basins. The shape of the $\delta^{13}C$ excursion to more negative values varies from sharp to gradual. A sharp $\delta^{13}C$ excursion indicates a lacuna, a condensed section, or a rapid change to more negative $\delta^{13}C$ values in the Triassic. A gradual shift in $\delta^{13}C$ indicates either a real, prolonged continuous $\delta^{13}C$ excursion or a mixture of Permian and Triassic values. The $\delta^{13}C$ shift is explained by a flux of ^{12}C enriched carbon as CO_2 from the reduced to the oxidised global reservoir. Possible sources of ^{12}C enrichment include, a) oxidation of organic facies and clathrate methane (Erwin, 1993) and b) volcanic eruption of mantle carbon as carbon dioxide. Depleted Triassic $\delta^{13}C$ values may reflect the loss of ^{12}C fixers having high preservation potential at the Permian/Triassic extinction.

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CARBON - ISOTOPE CHEMOSTRATIGRAPHY ACROSS THE PERMIAN/TRIASSIC BOUNDARY IN AUSTRALIA

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Summary - The well documented negative $\delta^{13}C$ excursion found at the Permian/Triassic boundary (P/Tr) in China and Eurasia has been located within or at the base of the *Protohaploxypinus microcorpus* palynological zone in seven Australian marine and nonmarine basins.

INTRODUCTION

A negative $\delta^{13}C$ excursion at the palaeontologically determined P/Tr in marine sediment is well established from sections in China and Eurasia. In Australia this $\delta^{13}C$ excursion has been found in organic carbon in pelitic rocks from cores. Organic carbon values are about 28 ‰ more negative than comparable values from carbonate carbon but this constant difference enables profiles from organic carbon and carbonate carbon to be directly compared.

RESULTS AND DISCUSSION

In Australian sections the $\delta^{13}C$ excursion in marine and nonmarine sediments occurs within or near the base of the *P. microcorpus* palynological zone which is therefore interpreted as straddling the P/Tr. The size of the $\delta^{13}C$ excursion, the interpreted environment of deposition and degree of palynological control for studied Australian basins is summarised in Table 1.

Table 1. Summarised interpreted environment of deposition and degree of palynological control for several Australian basins.

Basin	$\delta^{13}C$ ‰ excursion	Depositional environment	Palynological control
Bonaparte	-8	Marine	Good
Carnarvon	-4	Marine	Spot
Canning	-8.5	Marginal marine	Good
Bowen	-6	Fluvial	Good
Cooper	-6	Fluvial	Spot
Sydney	-6	Fluvial	Good
Perth	-5.5	Fluvial	Spot

The $\delta^{13}C$ excursion in marine and nonmarine sediments alike is interpreted as reflecting a shift of up to -10‰ in the $\delta^{13}C$ of atmospheric CO_2. The shift is large enough to mask any secondary effects. The global extent of the $\delta^{13}C$ excursion in P/Tr sediments provides a correlation tool enabling calibration of biostratigraphy schemes world wide across a range of sedimentary environments.

The $\delta^{13}C$ excursion is explained by a flux of carbon enriched in ^{12}C as CO_2 from the reduced to the oxidised global reservoir. Possible sources of ^{12}C enrichment include a) oxidation of organic facies and clathrate methane and b) volcanic eruption of mantle carbon as carbon dioxide. Depleted $\delta^{13}C$ values continued until at least the Late Triassic. The coincidence of the beginning of the palynological *Falcisporites* Superzone and the extinction of the *Glossopteris* flora with the $\delta^{13}C$ excursion in Australia suggests a major floral extinction event parallel with the dramatic P/Tr faunal extinction. A large transfer of carbon from the reduced to the oxidised global reservoir and the release of methane at the end Permian may have produced greenhouse conditions that contributed to the P/Tr mass extinction.

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The C-isotope perturbation at the Permian/Triassic boundary: Evidence of a greenhouse overshoot?

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The faunal and floral extinction in the transition from the Permian to the Triassic is one of the major events in Phanerozoic Earth history. The extinction is manifested by an apparent isochronous shift in the $\delta^{13}C$ values of organic carbon from marine and nonmarine sections which mirrors that which has been detected in numerous carbonate sections around the world. This C-isotope shift offers a unique tool whereby it may be possible to calibrate biostratigraphic schemes based on both marine and nonmarine oganisms worldwide at the P/Tr and suggests C-isotope chemostratigraphy may thus be a useful correlation tool on the inter and intrabasinal scale across the world. Studies of organic carbon in whole-rock fine-grained sediments from Australian marine and nonmarine sedimentary basins have yielded $\delta^{13}C$ shifts of between 6-8 permil consistently within or close to the *Protohaploxypinus microcorpus* palynology zone. This isotope study was carried out on samples obtained from fully cored boreholes drilled to acertain stratigraphy and conventionally cored intervals from petroleum exploration wells. Basins studied, their interpreted paleoenvironment around the Permian/Triassic boundary, palynological control on the section and the size of the detected $\delta^{13}C$ shift are shown in the table below.

SECTION	PALEO-ENVIRONMENT	PALYNOLOGICAL CONTROL	$\delta^{13}C_{PDB}$ SHIFT Permian to Triassic
Bonaparte Gulf Basin	Marine	Good	-24 to -32
Canning Basin	Marginal marine	Good	-24 to -32
Cooper Basin	Lacustrine	Moderate	-24 to -30
Bowen Basin	Fluvial/Lacustrine	Good	-24 to -30
Sydney Basin	Fluvial/Lacustrine	Moderate	-24 to -29

The nature of the isotope shifts at the Permian/Triassic boundary can be characterised as either gradual which is interpreted as indicating complete and representative section or sudden which is interpreted as representing incomplete or condensed section. The suddeness of the shift in the C-isotope profile of the Canning Basin section suggests it to be a disconformity or condensed section at the boundary.

The similarity in the isotope profiles suggests the role of atmospheric carbon dioxide is pivotal in the the equilibration of C-isotopes across a range of sedimentary environments. The shape of the C-isotope profile through the Late Permian and Early Triassic in the interpreted complete sections supports a model of palaeoclimate which suggests greenhouse warming as a major contributing cause to the extinction event at the Permian/Triassic boundary.

The Late Permian in Gondwana was characterised by glacial conditions with extensive *Glossopteris* forests and coal forming basins in a high relative sea-level environment.The abrupt transition to a warmer low sea-level stand in the earliest Triassic is enigmatic but may be explained by the following scenario.

1. Subduction rates might have declined globally as a result of the assembly of the Pangean supercontinent. This slowing may have been due primarily to slower rates of subduction as less dense continental crust subducted upon closure of oceanic basins. A lowered, gravitationally induced, momentum on the less dense continental crust subducting may have slowed the rate of subduction and hence reduced spreading rates at the mid oceanic ridge. This would have produced an overall increase in the depth of the ocean basins as the mid ocean ridge profile contracted due to increased cooling and density of the ocean floor more proximal to the ridge. A decrease in the total length of continental shelf would have occurred with continent amalgamation.

2. The fall in sea-level that should have occurred with deepening of the world's ocean basins was masked by transfer of water from continental reservoirs to the world's ocean and ocean thermal expansion. Warming was accomplished by an increase in flux of carbon as carbon dioxide to the atmosphere. The source of that carbon was oxidation of ^{13}C depleted carbon from continental margin and shelf sediments whenever sea-level fell. A cycle may have been established throughout the latest Permian whereby minor tectonically induced sea-level falls were followed by greenhouse induced sea-level rises. The rise in atmospheric CO_2 levels may be marked on the organic carbon $\delta^{13}C$ isotope profiles by a change from values of around -22 permil PDB in the earliest Late Permian to values of around -24 permil PDB in the latest Late Permian in both marine and terrestrial sections. The similarity of marine and nonmarine C-isotope profiles in this period is probably related to the increase in the flux of carbon to the atmosphere and provides evidence for an enhanced greenhouse effect in the latest Permian.

3. Approaching the P/Tr, transfer of water from terrestrial reserviors such lakes and melting ice sheets may have climaxed. Thermal expansion of the world's ocean may not have been able to keep pace with the tectonically induced deepening. Sea-level would have fallen exposing continental margin and shelf stores of ^{13}C depleted carbon to enhanced erosion and oxidation.

The latest Late Permian was marked by the decline in the Gondwanan wide *Glossopteris* forests which were characterised by high levels of lignin with high carbon preservation potential. Furthermore the great inland Gondwanan lakes and ice sheets disappeared. The world's latitudinal thermal gradient was reduced. Clear evidence of continental ice is lacking in high latitude Latest Permian southern Gondwana. With the consequent reduction in thermohaline circulation of the ocean and its nutrient recycling ability which might be expected to occur with decreased latitudinal thermal gradient, ocean surface productivity may have declined. Continental shelves already reduced in area by the assembly of Pangea would have been subaerially exposed to further reduce ocean productivity while enhancing carbon-rich sediment erosion and oxidation. An increase in the organic load from the terrestrial environment to the continental shelves might have led to dysaerobic, low dissolved oxygen, conditions resulting in the deposition of ^{34}S-depleted sulfides produced by bacterial breakdown of sulfates and extensive shelf faunal extinctions. Reef formation on shelf areas was suppressed during the Early Triassic. A warmer enviroment extending to the polar regions may have led to the release of potentially huge volumes of ^{13}C-depleted methane stored in clathrates in tundra environments and polar continental shelves. The frequency of red bed deposits may have increased because organic productivity was at levels too low to prevent oxidation of the iron in sediments. Overall a situation may have developed throughout the latest Permian whereby positive feedback increased the levels of ^{13}C-depleted carbon that was oxidised in the environment while suppressing carbon storage. This carbon dioxide and associated methane from hydrates created a greenhouse world.

The greenhouse environment may have contributed to a loss of carbon sinks (coal forming environments, carbonate reefs, ocean surface productivity) and enhanced exposure of stored carbon to chemical weathering and oxidation (carbonate reef weathering, erosion of carbon rich sediments, breakdown of methane clathrates). Biodiversity declined in the earliest Triassic environment which was probably much changed from the earlier Late Permian.

These events may be marked on the organic carbon isotope profiles in the transition from the latest Permian to earliest Triassic by a gradual shift over some 300 000 - 600 000 years to C-isotope values of -29 to -32 permil. ^{13}C depleted values were maintained in organic carbon stored in sediments with minor fluctuation until the latest Middle to Early Triassic when there appears to be a return to heavier values around -24 permil. This time may be marked in the sediment record by:

1. Renewed coal deposition and preservation associated with the evolution and proliferation of the gymnosperms

2. Reef formation resumption

3. Decline in red bed deposition, and

4. Biodiversity recovery.

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Determining the Permian/Triassic boundary in Australia through C-isotope chemostratigraphy

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Determinations of the Permian/Triassic (P/Tr) boundary in Gondwanaland, including Australia, by paleontological means is imprecise because the Gondwana facies is almost wholly nonmarine. The distinctive shape of the $\delta^{13}C$ profile at the P/Tr boundary in marine sediments elsewhere provides a means of determining the P/Tr boundary in Australia by C-isotope chemostratigraphy. The P/Tr boundary in marine sediments in the Chinese stratotype is characterized by a negative step in the $\delta^{13}C$(PDB) values in carbonate from about +3 permil in the Permian to +1 permil in the Triassic.

Known marine transitions across the P/Tr boundary in Australia are restricted to the northwest. In the Paradise Station region of the northern Canning Basin, core-holes penetrate a section (Blina Shale, Hardman and Condren Formations), that straddle the P/Tr boundary. The $\delta^{13}C$ profile is offset from about -32 to -23 permil between drill depths of 246 and 281 m. This offset occurs between the palynomorph zones Upper Stage 5 and *Protohaploxypinus reticulatus*, within the lower third of the Hardman Formation. The overlying Blina Shale, dated paleontologically as earliest Triassic, lies 150 m above the P/Tr boundary determined by the $\delta^{13}C$ values.

The P/Tr boundary determined by $\delta^{13}C$ is correlated in Eastern Australia by palynomorphs, (assumed to be isochronous), to the boundary of Upper Stage 5 and *P. microcorpus* zones. This zonal boundary, equivalent to that between the coal measures and the Rewan and Narrabeen Groups, returns the P/Tr boundary to its traditional position before intercontinental palynomorph correlation placed the boundary about 200 m above the base of the coal measures/Rewan and Narrabeen Groups.

Key words: Permian/Triassic boundary, isotope chemostratigraphy, south-eastern Paleo-Tethys, Canning Basin, Australia.

INTRODUCTION

The Permian/Triassic (P/Tr) boundary in marine sediments is characterised by a negative step in the $\delta^{13}C$ values of carbon in carbonates (Holser & Magaritz 1987), as exemplified in the Chinese stratotype (Fig.1a) where the carbon-isotope profile shifts from general values around +3 permil below the boundary to +1 permil above. The step drawn between the arrowed data points corresponds within decimetres to the P/Tr boundary in the Chinese stratotype through the Changxing Formation and Qinglong Formation. Claoue-Long *et al.* (1991) determined by the U-Pb method, using the SHRIMP ion-microprobe, the age of zircons from a 5 cm thick bentonite layer 31cm above the boundary as 251.2 + 3.2 Ma. In a second example from the south-central Paleo-Tethys margin Salt Range, Pakistan, (Fig.1b) the $\delta^{13}C$ step is found toward the top of the Chhidru Formation, 9 m below the paleontologically determined P/Tr boundary.

The $\delta^{13}C$ profile reflects the C-isotope composition of uniformly-mixed seawater, so the step marks a synchronous event at the P/Tr boundary. Another indicator of seawater C-isotope composition is provided by carbon in organic carbon (Corg) in marine sediments. The $\delta^{13}C$ profile of Corg is displaced by about -27 permil from that of Ccarbonate (John Hayes, pers. comm.1992) due to differential isotope fractionation.

Known marine transitions across the P/Tr boundary in Australia are restricted to the northwest. In the Paradise Station region of the northern Canning Basin (Fig. 2), core holes P6, P5, P4, and P3 penetrate the Blina Shale and the Hardman and Condren Formations of the Liveringa Group (Fig. 1c). This analysis is the first $\delta^{13}C$ investigation of the P/Tr boundary in Australia and the south-east margin of Paleo-Tethys. Shales from the top 200 m of the section and shaley partings below were sampled from the intervals marked on Fig.1c. Upper Stage 5, *Protohaploxypinus reticulatus* and *Lunatisporites pellucidus* palynological zones occur in the section (Helby 1975). The boundaries between the zones on either side of the single sample of the *Protohaploxypinus reticulatus* Zone have been arbitrarily selected at halfway between limiting samples from adjacent zones (Fig.1c).

METHOD

From crushed whole-rock shale samples, 500 mg was acidified with 100 ml of 6 M hydrochloric acid heated to 90° C for a minimum of 3 hours to remove carbonate. Samples with obvious carbonate were treated twice. Treated residue (30-90 mg) was loaded into 6 mm diameter quartz tubing with one gram of cupric oxide wire. The tubes were evacuated, sealed, and heated to 850° C for a period of 5 hours to ensure complete conversion of organic carbon to CO_2. The CO_2 was cryogenically separated from impurities produced in the oxidation process on a vacuum line prior to analysis on a Finnigan MAT 252 mass spectrometer at the the Centre for Isotope Studies, CSIRO Division of Exploration Geoscience Laboratories, North Ryde. Every twelfth sample analysed was a control. Results of all analyses were equated to the standard Pee Dee Belemnite (PDB) value for $\delta^{13}C$.

RESULTS

The $\delta^{13}C$ profile of the Paradise section between depths of 246 m and 281 m shows an offset of about 9 permil (from -32 permil to -23 permil).

DISCUSSION

Determination of the P/Tr boundary in Gondwanaland (including Australia) by paleontological means is imprecise because the Gondwana facies is almost wholly nonmarine. The distinctive $\delta^{13}C$ profile at the P/Tr boundary marked by a significant step-down in values, provides a means of determining the boundary independent of paleontology. In the Paradise section, Western Australia, the P/Tr boundary is located within the 35 m interval spanning the offset in the $\delta^{13}C$ profile and correlated with the Upper Stage 5 Zone/*P. reticulatus* Zone boundary (Fig. 1c). Samples below the offset at depths of 281.64 m and 291.69 m contain diverse spinose acritarchs (SA) and marine body fossils. Samples above the offset also contain evidence of a marine environment of deposition; abundant microplankton (Helby 1975). Whilst samples from the Lower Hardman and Condren Formations show no direct evidence of marine influence (Helby 1975) their $\delta^{13}C$-isotopic value is similar to the samples analysed from depths of 281 m and 291 m. This could indicate a marine influence existed lower in the section. The magnitude of the $\delta^{13}C_{org}$ offset in the Paradise section is comparable to that recorded from $\delta^{13}C_{carbonate}$ profiles in the southern Alps,(11 permil, Magaritz *et al.* 1988) and West Spitzbergen, (10 permil Gruszczynski *et al.* 1989).

Balme (1969 pp. 99) questioned the traditional position of the P/Tr boundary in Eastern Australia: "Palynological studies suggest that certain of the strata referred ... to the Lower Triassic are more appropriately assigned to the Upper Permian. These include the lower units of the Narrabeen Group in the Sydney Basin and part of the Ross Sandstone in the Tasmania Basin" Foster (1982 pp. 165) asserted that " Locally there is no correspondence between the P/Tr boundary and the Coal measures/Rewan Formation boundary". The present study supports the traditional placement of the Permian/Triassic boundary at the uppermost coal measures/ Rewan and Narabeen Groups boundary some 200 m below the position espoused by Balme (1969). Thus the Permian/Triassic boundary coincides with the initiation of the Early Triassic-Middle Triassic coal gap (Veevers, Conaghan & Shaw in prep.).

Correlation between Eastern Australia and West Australian palynological zones can be made on the basis of Upper Stage 5, *P. microcorpus*, and *L. pellucidus* Zones (Fig. 1c,1d), assuming these zones are not diachronous. The $\delta^{13}C$ chemostratigraphy profile of the Paradise section divides these zones into those giving a $\delta^{13}C$ profile centred around -23 permil in Upper Stage 5, and -32 permil in *P. reticulatus* Zone, equivalent to the *P. microcorpus* Zone in Eastern Australia, (Foster 1982).

CONCLUSIONS

Extrapolating from the Chinese stratotype, the P/Tr boundary, as interpreted from the isochronous $\delta^{13}C$ offset, is located within the Hardman Formation of the Liveringa Group in the Canning Basin. This is 150 m below the Blina Shale, dated paleontologically as earliest Triassic. The revised boundary in Western Australia is interpreted to be between the Upper Stage 5 Zone and *P. reticulatus* Zone. Additional sampling in the 35 m interval in which the $\delta^{13}C$ offset occurs will further constrain the boundary position. The revised position of the boundary correlates with the *Playfordiaspora crenulata* Zone (Fig.1d) which straddles the boundary between the uppermost coal measures and Rewan Group, (and coeval Narrabeen Group), in Eastern Australia, Foster (1982) . Corroborative evidence for this placement of the P/Tr boundary comes from the Salt Range, Pakistan where the *P. crenulata* Zone assemblage coincides with the uppermost Chhidru Formation (Balme 1970; Foster 1982). Coincidentally the position of $\delta^{13}C$ step, isochronous with the Permian/Triassic boundary in the Chinese stratotype, is located 9 m below the top of the Chhidru Formation, depicted in Fig. 1b as wholly Permian. This requires a shift down section of the Permian/Triassic boundary in that section to coincide with the step.

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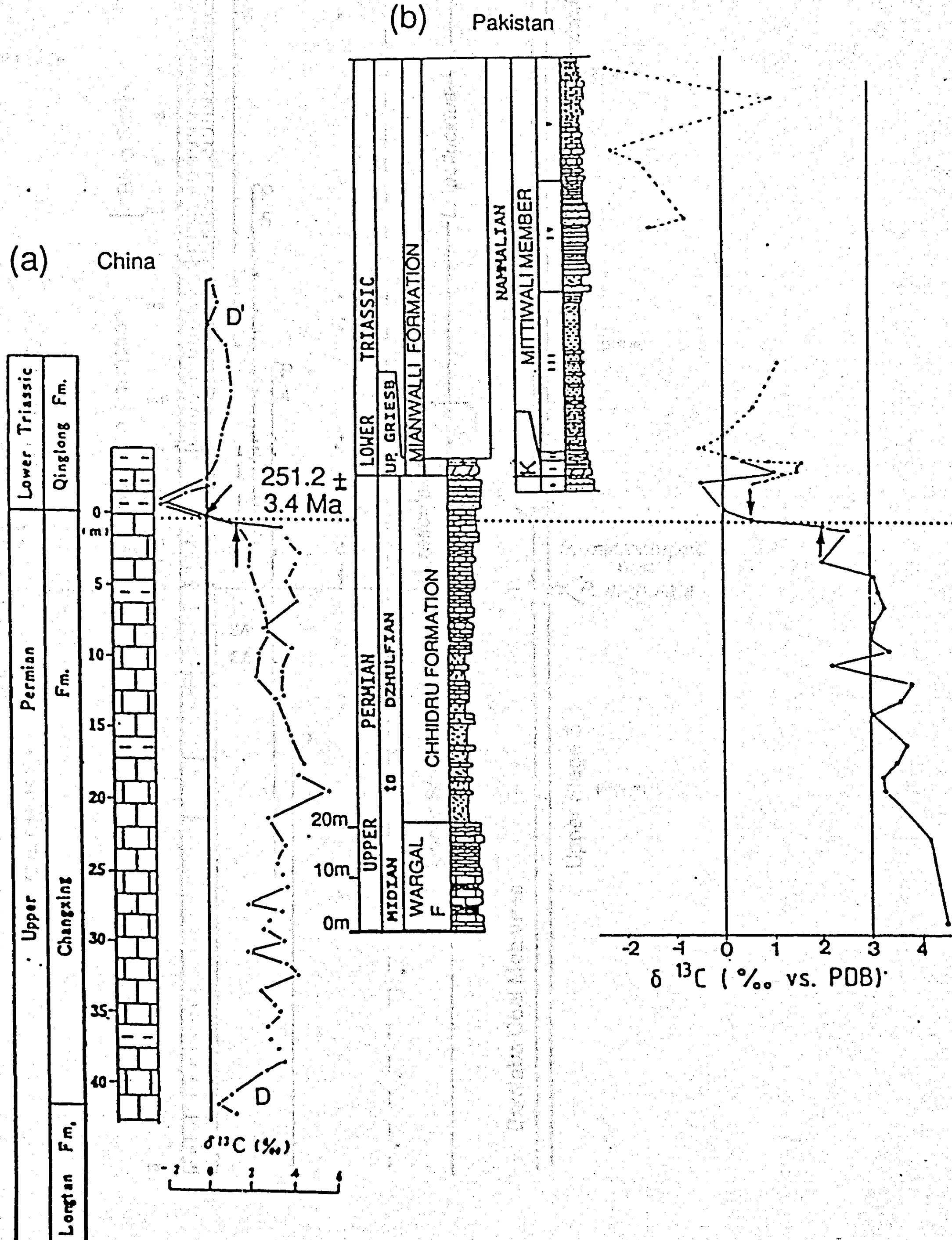
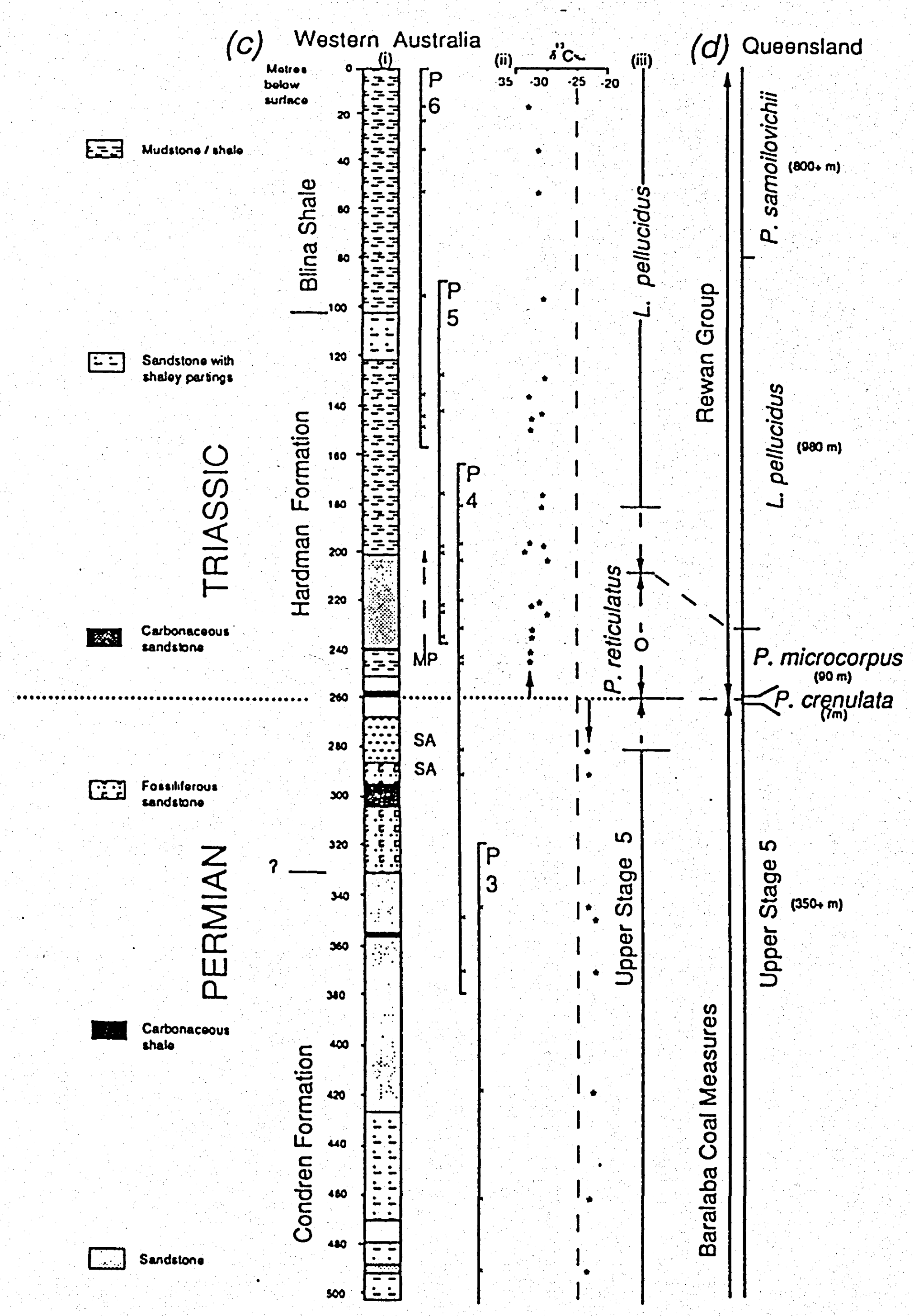


Fig. 1 Stratigaphical columns and $\delta^{13}C$ profile (a-c) correlated by palynomorphs to (d).

(a) $\delta^{13}C$ profiles at Meishan sections D and D', Changxing, Zhejiang, Peoples Republic of China (Chen *et al.* 1991). Arrows indicate values on either side of the step. The age of the clay after the boundary of the Qinglong Formation is from Claoue-Long *et al.* (1991).

(b) $\delta^{13}C$ profile at Nammal Gorge, Salt Range Pakistanfig.11 p. 662 (Baud *et al.*1989). Arrows indicate samples limiting the step. K is the Kathwai Formation.



(c) (i) Profiles of the Paradise core-holes, located in Fig. 2. Composite stratigraphic column of Paradise core-holes P6, P5, P4, P3 with sample locations (<). (ii) δ^{13}C profile of 30 analyses. Arrows indicate the values that border the offset about the -25 permil line. (iii) Palynological zones from Helby (1975). *P. reticulatus* Zone known from one sample only shown as an open circle. Full lines and open circle indicate known ranges, broken lines are interpolated ranges.

(d) Bowen Basin, Queensland Rewan Group/Baralaba Coal Measures related to palynological zones (Foster 1982, fig. 7 p.176).The broken line is aligned with the δ^{13}C-isotope step (dotted line) through the correlation of *P. microcorpus* / Upper Stage 5 in Queensland = *P. reticulatus*/Upper Stage 5 in Western Australia Foster (1982, fig. 4 p. 170).