

# Geochemical and organic carbon isotope studies across the continental Permo–Triassic boundary of Raniganj Basin, eastern India

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## Abstract

Organic carbon isotope and geochemical changes across a continental interior Permo–Triassic boundary section from the Raniganj Basin, India, indicate a  $\sim 9\%$  drop in organic carbon  $\delta^{13}\text{C}$  in the Early Triassic and synchronicity of this event throughout the Pangea. The study demands a common causative mechanism for the perturbation of the global carbon reservoir and not a combination of multiple causes. A global sea-level fall and oxidation of marine gas hydrates possibly increased the  $^{12}\text{CO}_2$  input in the ocean–atmosphere system which caused a climatic shift from humid to warm semi-arid type and consequent extinction of land plants. Simultaneous increase in erosion from near-barren lands, change in the erosional base level and provenance deposited the boundary sandstone with positive europium anomaly and debris flow type matrix rich conglomerate. No extraterrestrial source, therefore, is needed to explain this Eu anomaly. The response of the terrestrial plant community to this perturbation of the carbon reservoir was, however, sluggish and the  $\delta^{13}\text{C}$  drop took place slowly, being maximal in the Early Triassic only.

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## 1. Introduction

The Permo–Triassic (P/T) extinction event was the most catastrophic one in the entire Phanerozoic as about 57% and 95% extinction of marine fossils took place at family and species levels, respectively (Erwin, 1994). On land the events were no less dramatic, manifested by the extinction of

the Permian megafloora (e.g. *Glossopteris*; Retallack, 1999), the global disappearance of coal (Retallack et al., 1996) and changeover to a new reptilian fauna (MacLeod et al., 2000). A rapid negative excursion of  $\delta^{13}\text{C}$  of maximum up to  $\sim 10\%$  has invariably been found to be associated with the marine P/T sections and is now used as a global correlation tool (Holser et al., 1991; Grossman, 1994; Bowring et al., 1998). Until at present a large number of mechanisms have been proposed to explain the events across the P/T boundary, namely oceanic anoxia (Isozaki, 1997) or overturn of deep oceanic  $\text{CO}_2$  (Knoll et al.,

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1996), the environmental greenhouse effect (Retallack, 1999), volcanism (Renne et al., 1995), large scale release of methane gas hydrates (Morante, 1996; de Wit et al., 2002) and impact (Bhandari et al., 1992; Retallack et al., 1998). Many of these models were advanced to explain the negative carbon isotope excursion, observed in the marine records, which can accommodate a large input of  $^{12}\text{C}$  into the ocean. However, for providing a unifying global model it is equally important to know about the events on land. Compared to the marine ones very little high resolution work has been done in terrestrial P/T sections and most of it has been reported from coal bearing sections in Australia, Antarctica and South Africa (Retallack and Krull, 1999; Krull and Retallack, 2000). The Pangean reconstruction during P/T time shows that India was in the Southern Hemisphere sandwiched between Australia and Africa (Fig. 1). Excepting the Tethyan (marine) P/T sequence of Spiti (Bhandari et al., 1992), no high resolution data

are available from peninsular India which could be an important input to any of the models mentioned above. De Wit et al. (2002) have provided  $\delta^{13}\text{C}$  variation across the Permo–Triassic boundary from number of Indian basins. Their materials mainly derive from bore hole samples without much control on either lithology or facies and have large sampling intervals (more than several metres).

Furthermore, in view of the close connection between geochemical changes in the oceans and extinction events in the earth history, as observed in case of the Cretaceous–Tertiary (C/T) event (Asaro et al., 1982; Kyte et al., 1985), it is worthwhile to ask if any such changes took place across the P/T. In particular, the oxygen poor condition, developed in the P/T ocean (Wignall and Twitchett, 1996), can be investigated by the use of redox sensitive elements like U, V, Co, Mo and a rare earth element (REE) like Ce (Sarkar et al., 1993; Wang et al., 1986; Holser, 1997a,b). Bhandari et

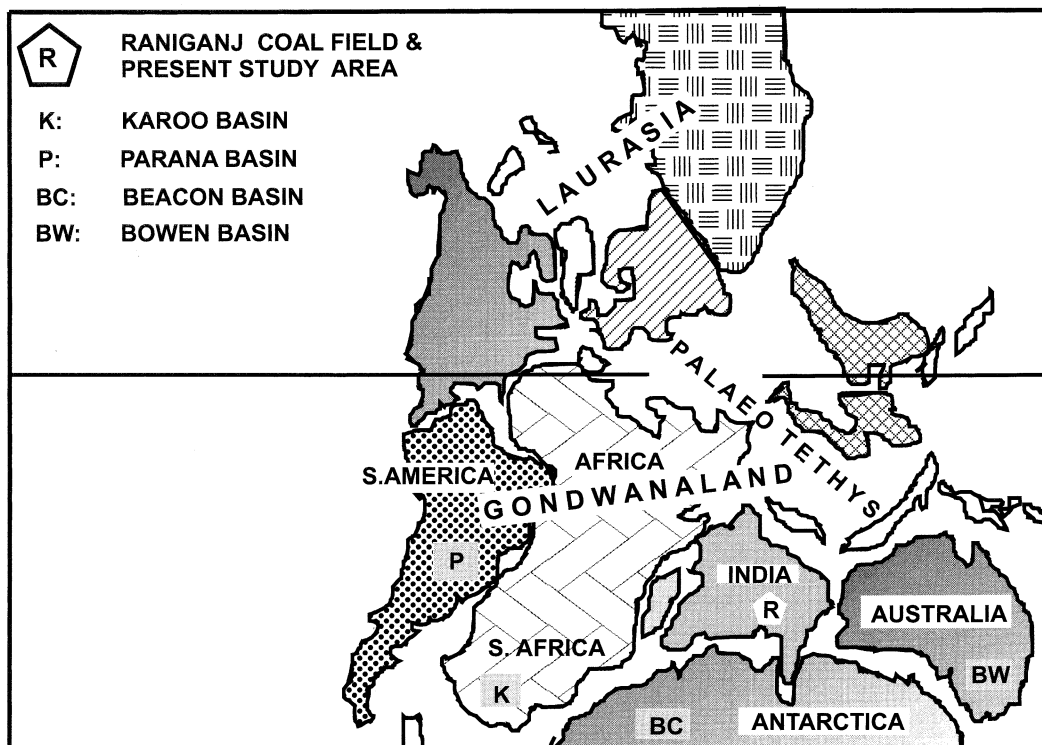


Fig. 1. Pangea during the Permo–Triassic boundary with the location of the Raniganj Basin; also shown are other continental Gondwana basins preserving the boundary.

al. (1992) reported a positive europium (Eu) anomaly (unlikely to be found in terrestrial rocks) in the boundary samples of the marine Spiti section and inferred a possible impact of eucritic meteorite (like Moore County) at the P/T boundary. Negative  $\delta^{13}\text{C}$  spikes, recorded at extinction boundaries, has often been explained by a global collapse of the primary productivity or ecosystem due to a bolide impact or shock heating of marine gas hydrates (Bowring et al., 1998 and references therein). Such an inference, however, requires further high resolution search from other P/T sections both marine and continental. Here we report high resolution organic carbon isotope and geochemical data (including REEs) across a continental P/T section from the Raniganj Basin, the coal mining heartland of eastern India and discuss their implications to the P/T events.

## 2. Geology and sampling

Continental Permian and Triassic rocks are exposed in many coal basins in India, e.g. the Bokaro coalfield, Son–Mahanadi Basin. The best sections are, however, preserved in the Raniganj Basin, West Bengal. The basin is an intra-cratonic one where the Permian rocks of the Damuda Group unconformably lie over older Precambrian basement commencing with the Early Permian glacial tillite beds of the Talchir Formation often correlated with the Dwyka and Buckeye tillites of South Africa and Antarctica, respectively (Krishnan, 1982). The Talchir Formation is conformably overlain by sandstones of the Barakar and Ironstone shale formations. In Raniganj Basin the maximum thickness of the Talchir, Barakar and Ironstone shale formations are ~300, 650 and 350 m, respectively (Krishnan, 1982). The topmost unit of the Damuda Group is represented by the Raniganj Formation which in turn lies below the Panchet Formation. The contact between the Raniganj Formation of Late Permian age and the Early Triassic Panchet Formation is either gradational or characterised by local unconformity. In particular, the Banspetali section in Raniganj Basin, exposing the latest Raniganj and earliest Panchet rocks, has recently been sug-

gested as the type continental P/T section of India (Ghosh, 1994). The earliest map of the Raniganj Basin in general and the Banspetali area in particular was prepared by Gee (1932). We have remapped the area (Fig. 2) for critically examining the lithological and faunal changes across the P/T boundary and sampling for geochemical and isotopic studies.

The Banspetali area is located about 160 km WNW of Calcutta (23°37'N, 86°54'E). The uppermost Permian and earliest Triassic rocks are exposed along a stream (nala) section flowing northward almost perpendicular to the E–W striking beds. The sedimentaries occur within the Precambrian basement, composed of granite gneiss, amphibolite and metaquartzites. The basin boundaries are faulted where both the Raniganj and Panchet rocks abut against the basement in the southern part. Evidences of syn- and post-sedimentation faulting are also numerous (Fig. 2). The Permian rocks of the Raniganj Formation include an alternating sequence of sandstone, shale and coal. The white/gray sandstones are plagioclase rich and fine to medium grained. The shales are dark, rich in carbonaceous material. The Panchet sandstones are, on the contrary, rich in unaltered pink coloured potash feldspar easily identifiable in hand specimens. The Panchet shales are gray to olive green coloured, much different from Raniganj ones. In the upper part both Panchet sandstone and shale become reddish indicating the presence of ferruginous cements possibly due to severe oxidising conditions. The topmost litho-unit in the area is red coloured highly immature, poorly sorted, pebbly sandstone and conglomerate of the Supra-Panchet Formation of possible Late Triassic age.

The litho–biostratigraphy across the P/T boundary of the Banspetali section is shown in Fig. 3. The P/T boundary is recognised in the field by the last Permian coal seam (30 cm thick) occurring within dark shale. The coal seam acts as a marker horizon to identify the terminal Raniganj sedimentation and can be traced in another nala section at Tentulrakh, ~3 km east of Banspetali. In the present study area at least 400 m of Raniganj Formation are present below the terminal Permian coal seam but a considerable part of it

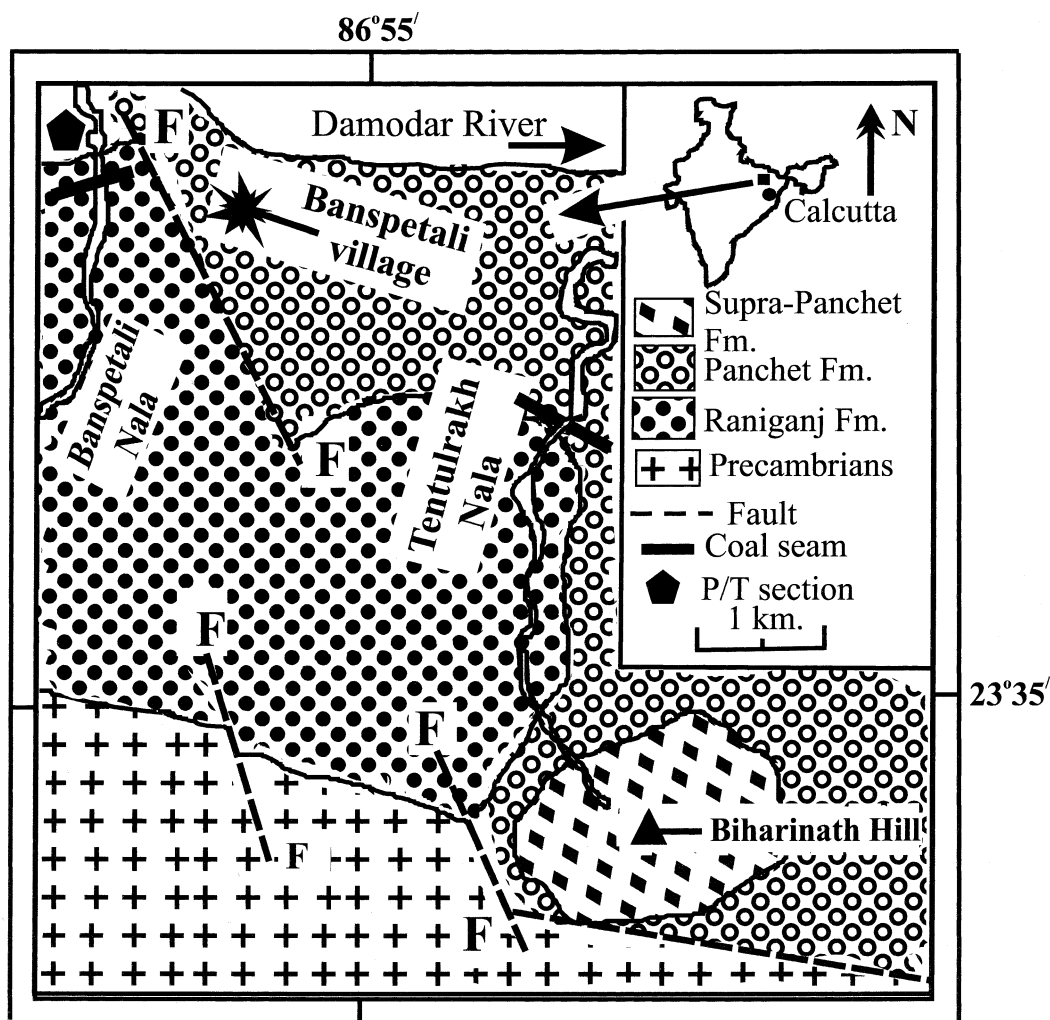


Fig. 2. Geological map of part of the Raniganj Basin around the Banspetali area showing the sampling location of the P/T section.

has been down faulted along the southern contact with the Precambrian basement (Fig. 2). Coal seams completely disappear in the overlying Panchet rocks. According to Ghosh (1994), the top-most bed of Raniganj is represented by a 5.5-m-thick single sandstone bed overlying the last coal seam (Plate I). However, lithologically this sandstone is more akin to the Panchet sandstones containing pink potash feldspar. The sandstone is overlain by a 9-m-thick matrix-supported conglomerate (Plate II), the upper 4 m of which is not well exposed. The conglomerate is polymictic

with pebbles of quartz, feldspar and basement rock fragments set in sandy and clayey matrix. There is a lack of any grading and the large angular floating clasts with poor sorting of this unit are much like debris flow products (Postma et al., 1988; Sohn, 2000). The sandstone is convolute laminated. Both the sandstone and conglomerate are laterally persistent and indicate large scale instability of the basin and related syn-sedimentary deformation. The conglomerate is succeeded by gray to olive green shale-siltstone of the Panchet Formation (Plate III). Floristically the Raniganj is

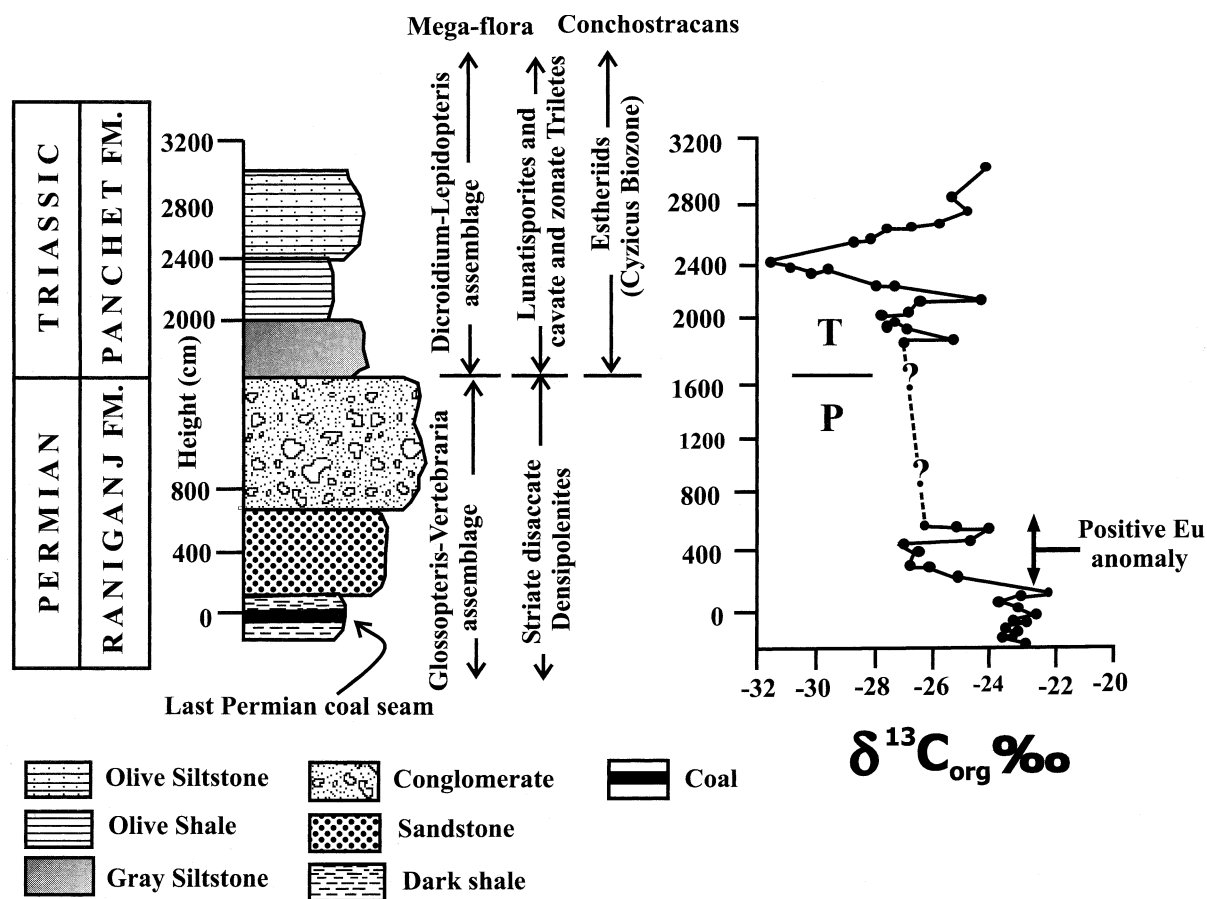


Fig. 3. Litho- and biostratigraphy across the P/T section along with the  $\delta^{13}\text{C}_{\text{org}}$  profile; note large  $\delta^{13}\text{C}_{\text{org}}$  drop in Early Triassic.

characterised by the *Glossopteris-Vertebraria* megafloral assemblage while the Panchet contains the *Dicroidium-Lepidopteris* assemblage. Palynomorph studies indicate a striate-disaccate *Densipollenites* rich microfloral assemblage in terminal Raniganj while the beginning of Panchet is marked by the appearance of *Lunatisporites* and cavate and zonate triletes, *Densipollenites*, *Lundbladispora* assemblage of Early Triassic age (Tiwari and Tripathi, 1992; Ghosh, 1994). The onset of the Panchet is also marked by the widespread occurrence of the fossil conchostracans generally known as estheriids belonging to the *Cyzicus* biozone. The typical assemblage comprises forms like *Cyzicus bengalensis* Tasch, *C. mangaliensis* Tasch, *Cornia panchetella* Tasch, indicating a typical Early Triassic age. Ghosh (1994) has identified

at least three estheriid biozones within the Panchet Formation mostly occurring in fine grained clastics. Specific morphological features of the estheriids along with sedimentary structures like mud cracks, root burrows indicate a shallow freshwater, desiccated high salinity environment for the estheriid bearing rocks of the Panchet. Together, the lithology and biota across the Raniganj-Panchet boundary indicate pronounced climatic and tectonic change from a humid coal bearing regime to warm semi-arid climatic regime. Under the microscope the typical Raniganj sandstones occurring below the last coal seam display a well rounded, low matrix, matured texture. The sandstones of Raniganj above the coal seam and Panchet exhibit an angular, high matrix, immature texture. A well-preserved vertically oriented





Plate I. Late Permian boundary sandstone from the Banspetali area, Raniganj Basin. The last coal seam occurs just below this layer within the underlying dark shale of the Raniganj Formation.



Plate II. Matrix supported polymictic conglomerate at the P/T boundary.



Plate III. Earliest Triassic gray siltstone.

stem of *Schizoneura* has been found to be preserved in a normally graded (into mud) coarse siltstone just above the last coal seam indicating rapid sedimentation under a turbidity flow. It seems that the influx of finer clastics into the basin suddenly increased towards the terminal Ranniganj (Permian) reaching its peak just at the boundary when a regional debris flow produced a matrix supported conglomerate. A similarly thick laterally persistent conglomerate at the P/T boundary has also been found at several sections in Australia and is interpreted as the evidence of rapid sedimentation rather than a time gap (Retallack, 1999). The increased sediment input must be a result of the change in the local base level either due to the upliftment of basement Precambrian rocks or a global marine regression (Holser and Magaritz, 1987). Alternatively, an enhanced erosion of the river banks due to the extinction of Permian megaflores might be the cause of this increased sediment input, a mechanism suggested by Ward et al. (2000) for the P/T boundary event in Karoo Basin. Following Ghosh (1994), we place the P/T boundary in Banspetali section at the

junction between the conglomerate and the overlying gray siltstone yielding definitive Early Triassic flora. The sampling for isotopic and geochemical studies of both sandstone and shale/siltstone units have been made over 30 m of the exposed sections (excepting the conglomerate unit) spanning the P/T boundary.

### 3. Methods

For organic carbon isotope the relatively fresh unweathered samples were analysed. The powdered sample was repeatedly treated with 6 N HCl both at room temperature and at 60°C and washed to remove all carbonate phase. The samples were freeze-dried and combusted at 1000°C in a Carlo Erba EA-1108 unit connected online to a Finnigan MAT delta-S mass spectrometer. The purified CO<sub>2</sub> was measured for its  $\delta^{13}\text{C}$  composition with an average analytical precision of  $\pm 0.1\%$ . All the carbon isotope data are reported against the Pee Dee Belemnite (PDB) standard. The trace and REEs were determined by instru-

mental neutron activation analysis. About 50 mg of each powdered ( $<200$ -mesh) sample was irradiated at the F-ring irradiation site (nominal thermal neutron flux:  $1.5 \times 10^{12} \text{ cm}^{-2} \text{ s}^{-1}$ ) of the TRI-GA-II reactor at the Institute for Atomic Energy, Rikkyo University, Japan. The  $\gamma$ -rays emitted by the samples were measured by highly pure Ge-detectors. Elemental abundance values were obtained by comparing the  $\gamma$ -ray intensities of the samples with those of reference standard rocks such as JB-1 (basalt) and JG-1 (granodiorite) supplied by the Geological Survey of Japan. The Allende meteorite reference sample prepared by the Smithsonian Institute, Washington, USA, was simultaneously irradiated. For the calculation the literature values provided by Jarosewich et al. (1987) and Ando et al. (1989) were used for JB-1, JG-1 and Allende, respectively.

#### 4. Results and discussion

The  $\delta^{13}\text{C}$  data are plotted against depth in Fig. 3. We have not been able to analyse any sample from the conglomerate horizon as these samples are extremely weathered due to high matrix content. Although minor fluctuations occur, the  $\delta^{13}\text{C}$  value remains more or less constant at an average  $-25\text{‰}$  level during the Late Permian and earliest Triassic immediately following the boundary. A significant drop in  $\delta^{13}\text{C}$  value is observed at  $\sim 800$  cm above the P/T boundary which slowly returns to the pre-depletion level in the overlying sediments. The average drop in  $\delta^{13}\text{C}$  is  $\sim 6\text{‰}$  while the maximum depletion between the pre- and post-boundary level is more than  $9\text{‰}$ . The highest drop is observed at the base of the olive siltstone of the Panchet Formation. A similarly large depletion in organic carbon  $\delta^{13}\text{C}$  has been observed from several coal bearing Permo–Triassic sections of Australia and South Africa (Faure et al., 1995; Morante, 1996; Retallack, 1999). Large  $\delta^{13}\text{C}$  depletion ( $\sim 10\text{‰}$ ) at the P/T boundary has also been reported in the reptilian tusks from Karoo Basin, South Africa (MacLeod et al., 2000). Our data along with the Australian and African ones indicate the synchronicity in carbon isotope pattern throughout the Pangea and sug-

gest that the change in the carbon reservoir (as observed in the marine realm) indeed affected the continental domain as well. Such a remarkable similarity in carbon isotope pattern from widely different geographical localities also indicates this to be a genuine climatic signal and not an artifact of mixing of various plant components (Foster et al., 1999). This is further supported by the fact that the  $\delta^{13}\text{C}$  gradually goes back to the pre-boundary level in the later part of Triassic even though the *Glossopteris* dominated Permian flora became completely extinct at the P/T boundary. Hansen et al. (2000), on the basis of magnetic susceptibility stratigraphy of both Permian and Triassic segments, have proposed a sedimentation rate (for the shale/siltstone part only) of  $\sim 165$  cm/100 kyr for this section. This is similar to the rate obtained from study of the absolute chronology of Permian authigenic illites (Dutta and Suttner, 1986). If true, the drop in  $\delta^{13}\text{C}$  and its recovery during an interval of 900 cm indicate that the event took place over a period of  $>0.5$  Ma. This is indeed a large time interval and supports the observation of Retallack (1999) that the P/T event (at least the instability in the continental carbon reservoir) was gradual rather than abrupt. The gradational change in  $\delta^{13}\text{C}$  in the Banspetali section also indicates a rather complete stratigraphic record and not a disconformity. The abrupt changes found in some continental records (Morante et al., 1994; Morante, 1996) are possibly due to the incompleteness of the record. The high resolution U–Pb geochronology from the Meishan section of China, however, indicated a catastrophic change in the marine carbon reservoir (Bowring et al., 1998). It is possible that the response of the continental biosphere was sluggish compared to the marine system.

De Wit et al. (2002) reported a  $\delta^{13}\text{C}_{\text{org}}$  profile across several Indian P/T boundary sections including the Raniganj Basin. Large oscillations in  $\delta^{13}\text{C}$  have been observed where the gradual negative trend in the Upper Permian and a similar positive recovery in the Lower Triassic, separated by up to three large negative  $^{13}\text{C}$  spikes, have been observed. The average  $\delta^{13}\text{C}$  value ( $\sim -24\text{‰}$ ) is similar to that obtained in the present study ( $\sim -25\text{‰}$ ), however, the Banspe-



tali section records only one large negative drop in the earliest Triassic. We observe some smaller oscillations (Fig. 3) but the positive swings have never been as large as reported by de Wit et al. (2002). This is indeed surprising as the sampling/analyses resolution is much higher in the present case compared to that reported by these authors. Since all of their samples come from bore holes, it is not possible to know exactly what lithological and facies attributes these isotope maxima and minima have. Our  $\delta^{13}\text{C}$  profile is more akin to those from Australian basins like Sydney, Bowen or Bonaparte or even some of the continuous marine P/T boundary sections.

It is, however, difficult to explain the causative mechanism of the  $\delta^{13}\text{C}$  drop. Absence of (or weak) iridium anomaly (Bhandari et al., 1992; Retallack et al., 1998) and gradual change in continental carbon isotope profiles do not favour the impact hypothesis. Since the  $\delta^{13}\text{C}$  depletion is found both in marine and continental sediments, a mechanism involving the global perturbation of the carbon reservoir must be invoked. Isozaki (1997) provided some geological evidence of super-anoxia in the global ocean at and across the P/T boundary and hence the increased oxidation of marine organic matter cannot explain the depletion. An alternative mechanism of oxidation of continental organic matter, due to collapse of the terrestrial ecosystem and global tectonic uplift, has been proposed by Faure et al. (1995). A slightly different mechanism has been proposed by Ward et al. (2000) where the collapse of the terrestrial biosphere and the consequent increased erosion enhanced the terrestrial negative carbon input into the ocean. An increasingly popular model of oxidation of methane hydrates due to the global sea-level fall has also been forwarded (Morante, 1996; de Wit et al., 2002). Choosing a candidate from any of these models is difficult, although it is tempting to speculate that the 9-m-thick matrix supported conglomerate found just before the boundary in Banspetali (along with the similar ones observed elsewhere) was indeed the result of massive debris flow caused due to the fall in sea-level and the consequent change in base level of erosion (and oxidation of gas hydrates?). The sudden increase in matrix content

(composed of very fine sand sized quartz grains and clay) in the laterally persistent 5.5 m-thick convolute laminated sandstone and the presence of turbidite preserving a vertical plant stem near the P/T transition also indicate a change in the erosional pattern in the source and fluid dynamics. This is, however, not to undermine the local basinal tectonics (evidenced by basin boundary faults) which could have acted together with the sea-level fall (Holser and Magaritz, 1987) to bring the lithological changes across the boundary. The coupled ocean–atmosphere model calculation of de Wit et al. (2002) indicates that the release of  $^{12}\text{CO}_2$  could be episodic as indicated by multiple negative  $\delta^{13}\text{C}$  excursions. At Banspetali too at least two such (smaller) excursions are observed before the final large one at the earliest Triassic. Interestingly, the first excursion also coincides with a major geochemical (REE) anomaly (Fig. 3) as discussed below.

Ward et al. (2000), on the basis of facies and fluvial architecture analyses of Karoo Basin, provided strong evidence of the dramatic changeover in river morphology from meandering to braided systems across the P/T boundary. The changeover was the consequence of basin wide landscape destabilisation and increased erosion of both soil and river banks due to terrestrial plant die-off during this transition. The increase in sediment yield characteristically takes place in the earliest Triassic similar to the one found in the Raniganj Basin. It would be interesting to see if such a river morphology induced facies change is also preserved across the Indian P/T boundary and really forms a global phenomenon. Nevertheless, the matrix rich boundary conglomerate and abruptly overlying olive siltstone–shale package (Fig. 3) indicate that it could well be the product of a rapid flash flood, as proposed by Ward et al. (2000), followed by a quick deceleration of energy. A rapid increase in marine  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio (Faure et al., 1995; Morante, 1996) at the P/T boundary also indicates a dramatic increase in the continental input due to the enhanced erosion of the rivers.

Geochemically, both the Raniganj and Panchet shale/siltstone formations have a higher Fe content (4–7%) compared to the boundary sandstone

(2–3.5%); so are U (maximum 8 ppm against 1 ppm), Ni, Co, and Cr which are relatively more concentrated in organic rich finer clastics of possible over bank origin. The U concentration in the Panchet rocks is less (2–5 ppm) compared to that of Raniganj (6–8 ppm) and is consistent with a more oxidising climatic condition during the Early Triassic. The Na concentration in the sandstone is higher than that in the shale/siltstone due to the potash and alkali feldspar rich modal mineralogy. The chondrite normalised REE patterns of coal and dark shale of Raniganj, the sandstone near the boundary and gray shale, olive shale/siltstone of the Panchet Formation are shown in Fig. 4. The  $\Sigma$ REE of the coal/shale/siltstone of either Raniganj or Panchet is much higher (203 to 348 ppm) compared to the boundary sandstone (59–124 ppm) which is consistent with the fact that the

clays preferentially concentrate about 1.5 times more REE than sandstones (Henderson, 1984; Wang et al., 1986). It is interesting to note that the REE composition of the P/T boundary sandstone is near-chondritic. The most notable feature in Fig. 4 is the presence of a positive europium anomaly ( $\text{Eu}/\text{Eu}^*$ , i.e. the ratio of the measured  $\text{Eu}_N$  value to the interpolated Eu value between neighbouring  $\text{Sm}_N$  and  $\text{Gd}_N$ ) in all the samples of the boundary sandstone (1.2–1.59) compared to either Raniganj shale (0.33–0.35) or Panchet shale/siltstone (0.04 to 0.63) which exhibit normal negative europium anomalies. A similarly positive europium anomaly has earlier been reported in a limonitic layer at the P/T boundary from the marine carbonate sequence of Spiti Himalayas (Bhandari et al., 1992). The Banspetali section is the second location where the positive europium

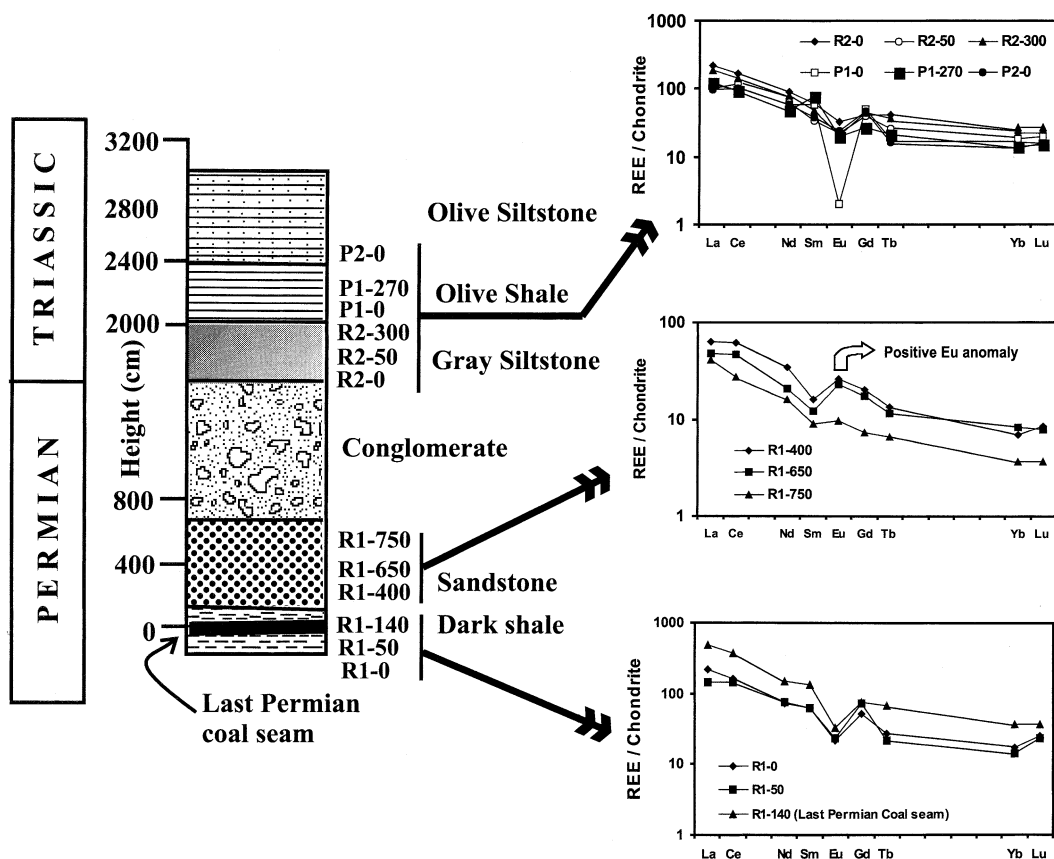


Fig. 4. Chondrite normalised REE patterns of sediments across the P/T boundary; note positive Eu anomaly in all the samples of boundary sandstones.

anomaly has been observed. Compilation of sediment REE data shows that the positive europium anomaly in the post-Archaean rocks is very rare due to the more evolved nature of the crust generating the sediments (Taylor and McLennan, 1985). The only exceptions are sedimentary barite (where  $\text{Eu}^{2+}$  substitutes  $\text{Ba}^{2+}$ ) and some iron formations and sulfides (via interaction of hydrothermal sulfides with felsic volcanic rocks; Cullers and Graf, 1984). In the present case neither any correlation is observed between  $\text{Eu}/\text{Eu}^*$  and the Ba content of these rocks nor any evidence of hydrothermal activity in this clastic sandstone. Therefore, none of these mechanisms can explain the positive Eu anomaly. Change in redox condition, causing change in the  $\text{Eu}^{2+}/\text{Eu}^{3+}$  ratio (Henderson, 1984), is not responsible either as we do not find any correlation between the  $(\text{Ce}/\text{La})_N$  ratio (Ce being redox sensitive) and  $\text{Eu}/\text{Eu}^*$ . Positive Eu anomalies in carbonate rich river sediments have also been reported where the  $\text{Eu}^{2+}$  replacement of  $\text{Sr}^{2+}$  in carbonate minerals has been held responsible for such an effect (Leleuyer et al., 1999). However, the boundary sandstone does not contain carbonate either in framework or in matrix/cement. Bhandari et al. (1992) indicated the possibility of the impact of an eucritic meteorite at the P/T boundary of Spiti which exhibits positive europium anomaly. However, the europium anomaly at Spiti is confined within an only thin ( $\sim 5\text{-cm}$ ) limonitic layer at the boundary whereas at Banspetali all three samples from the bottom, top and middle of the 5.5 m-thick sandstone exhibit the anomaly. In no case such a thick sandstone bed can be the product of an instantaneous deposition as is required for a meteorite impact. Therefore, we consider that the positive  $\text{Eu}/\text{Eu}^*$  anomaly is not produced due to any syn-sedimentary or extraterrestrial process rather that it reflects the REE geochemistry of the provenance rock from which the sandstone minerals are generated.

Lithologically the sandstone is composed of pink potash feldspar and quartz with high matrix content. Although both plagioclase and potash feldspars concentrate more Eu relative to other minerals, even the post-Archaean arkosic rocks are characterised by a typically negative Eu

anomaly only (Taylor and McLennan, 1985). This is consistent with their derivation from negative anomaly bearing typically upper continental potash rich granitic rocks. Hence the boundary sandstone must have had a very specific lithological provenance which gave rise to this anomaly. The Precambrian rocks with positive Eu anomaly are tonalite–trondhjemite gneiss (TTG), granodiorite and quartz diorite. The TTG are mostly confined to the Archaean and their positive anomaly arises not because of feldspar accumulation but is due to hornblende–melt equilibria (Cullers and Graf, 1984). The basement rocks of the eastern Indian coal basin including the Banspetali belong to the Chotanagpur Gneissic Complex (CGC) which has been dated as Middle to Late Proterozoic (Majumder, 1996; Roy et al., 2002). Also, the hornblende content in the sandstone, as an accessory mineral, is extremely low and hence there cannot be any TTG source responsible for this anomaly. Diorite–granodiorites, produced by partial melting of amphibolite or eclogite, often display a positive Eu anomaly (Cullers and Graf, 1984). Although not present within the mapped area of the Banspetali region, in general the CGC has a vast tract of diorite–granodiorite rocks some showing rapakivi like textures of an alkali feldspar core rimmed by plagioclases (Majumder, 1996). It is possible that some of these areas were acting as the provenance of the boundary sandstone. Either basement uplift or sea-level fall and change in the erosion pattern might have induced a switch over in provenance from Eu depleted to Eu rich rocks near the boundary. Only a detail REE analysis of the various components of the CGC can identify the exact source of the positive Eu anomaly in these rocks. In any case the positive Eu anomaly in the Banspetali P/T section is caused by a terrestrial process only and there is no need to invoke an extraterrestrial one. A note of caution, however, must be added at this point. Together, the near-chondritic REE composition and the positive Eu anomaly demands that further search must be made to locate and identify impact components, if any, in this sandstone.

Whatever may be the cause, the positive Eu anomaly preceded the carbon cycle perturbation ( $\delta^{13}\text{C}$  depletion) by a relatively long period of

time unless both the sandstone and conglomerate represent instantaneous event beds of impact origin. The anomaly also occurs immediately after the last very thin ( $\sim 30$  cm) Late Permian coal seam, coinciding with the first minor negative  $\delta^{13}\text{C}$  excursion, meaning the changes in sedimentation pattern and floral extinction were almost coeval. Oxygen isotope ( $\delta^{18}\text{O}$ ) analyses of early authigenic clays in sandstones across the Raniganj/Panchet boundary showed a large increase from 6.6‰ to 10.4‰ and have been interpreted as a climatic changeover from a humid to warm semi-arid type (Dutta and Suttner, 1986). An overall increase in the abundance of smectite, chlorite, and pink potash feldspar (Basu, 1976; Potter, 1978), specific dry-regime sedimentary structures (mentioned above) and the complete disappearance of coal in Panchet compared to kaolinite and the coal-measure rich Raniganj Formation support such an interpretation. As mentioned above, the extreme ferrugination in the matrix and clays in some of the sandstone and shale of the Panchet Formation also indicates an increased aridity. We envisage that towards Late Permian time large scale release of  $^{12}\text{C}$  enriched  $\text{CO}_2$  from oxidation of gas hydrates (via sea-level fall) possibly introduced a climatic change across the P/T boundary causing extinction of land plants. The ensuing base level readjustment along with increased erosion from near-barren lands and change in provenance deposited the boundary sandstone with positive Eu anomaly followed by a debris flow type matrix rich conglomerate. The response of the terrestrial plant community to this perturbation of the carbon reservoir was, however, sluggish and manifested by a  $\sim 9\%$   $\delta^{13}\text{C}$  drop much later in the Early Triassic only.

## 5. Conclusions

Lithological, biotic, organic carbon isotope and geochemical studies indicate pronounced climatic and/or tectonic change across a continental Permian–Triassic boundary section from the Banspetali area, Raniganj Basin, India. The large drop of maximum up to  $\sim 9\%$  in organic carbon  $\delta^{13}\text{C}$  in the Early Triassic is similar to those observed

from Australian and African P/T sections and indicates synchronicity of this event throughout the Pangaea. The  $\delta^{13}\text{C}$  depletion at the P/T boundary in both the oceanic and continental domains indicate common causative mechanisms of the perturbation of the global carbon reservoir and not a combination of multiple causes. A positive europium anomaly, observed in the boundary sandstone, can be explained by the change in sediment provenance without invoking the contribution from any extraterrestrial source. The sandstone occurs immediately after the last Permian coal seam which indicates that the changes in sedimentation pattern and floral extinction were almost coeval. The observed geological changes favour models of release of  $^{12}\text{C}$  enriched methane hydrates due to the global end-Permian regression (via sea-level fall) which introduced a climatic change (humid to warm semi-arid) across the P/T boundary causing extinction of land plants. The ensuing base level readjustment of the rivers along with increased erosion from near-barren lands and change in provenance deposited boundary sandstone with positive Eu anomaly followed by a debris flow type matrix rich conglomerate. The response of the terrestrial plant community to this perturbation of the carbon reservoir was, however, sluggish (at Banspetali the event is spread over  $> 0.5$  Ma) compared to the marine ones and the  $\sim 9\%$   $\delta^{13}\text{C}$  drop took place much later in the Early Triassic only. Any future modelling of the perturbation of the carbon reservoir at the P/T boundary must take this aspect into account.

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## References

- Ando, A., Kamioka, H., Terashima, S., 1989. 1988 values for GSJ rock reference samples, 'Igneous rock series'. *Geochem. J.* 23, 143–148.
- Asaro, F., Alvarez, L.W., Alvarez, W., Michel, H.V., 1982. Geochemical anomalies near the Eocene–Oligocene and Permian–Triassic boundaries. *Geol. Soc. Am. Spec. Pap.* 190, 517–528.
- Basu, A., 1976. Petrology of the Holocene sand derived from plutonic source rocks: implications to paleoclimatic interpretations. *J. Sediment. Petrol.* 46, 694–709.
- Bhandari, N., Shukla, P.N., Azmi, R.Z., 1992. Positive europium anomaly at the Permo–Triassic boundary, Spiti, India. *Geophys. Res. Lett.* 19, 1531–1534.
- Bowring, S.A., Erwin, D.H., Jin, Y.G., Martin, M.W., Davidek, K., Wang, W., 1998. U/Pb zircon geochronology and tempo of the end-Permian mass extinction. *Science* 280, 1039–1045.
- Cullers, R.L., Graf, J.L., 1984. Rare earth elements in igneous rocks of the continental crust: intermediate and silicic rocks—ore petrogenesis. In: Henderson, P. (Ed.), *Rare Earth Element Geochemistry*. Elsevier, pp. 275–316.
- de Wit, M.J., Ghosh, S.C., Joy, G., de Villiers, S., Rakotosolof, N., Alexander, J., Tripathi, A., Looy, C., 2002. Multiple Organic Carbon Isotope Reversals across the Permo–Triassic Boundary of Terrestrial Gondwana Sequences: Clues to Extinction Patterns and Delayed Ecosystem recovery. *J. Geol.* 110, 227–240.
- Dutta, P.K., Suttner, L.J., 1986. Alluvial sandstone composition and paleoclimate. II Authigenic mineralogy. *J. Sediment. Petrol.* 56, 346–358.
- Erwin, D.H., 1994. The Permo–Triassic extinction. *Nature* 367, 231–236.
- Faure, K., de Witt, M.J., Willis, J.P., 1995. Late Permian global coal hiatus linked to C-13 depleted CO<sub>2</sub> flux into the atmosphere during the final consolidation of Pangea. *Geology* 2, 507–510.
- Foster, C.B., Logan, G.A., Summons, R.E., 1999. The Permian–Triassic boundary in Australia: Organic carbon isotope anomalies relate to organofacies, not a biogeochemical 'event'. Ninth Annual V.M. Goldschmidt conference. Lunar and Planetary Institute Contribution 971, pp. 87–88.
- Gee, E.R., 1932. The Geology and Coal Resources of Raniganj Coalfield. Record Geological Survey of India, 61.
- Ghosh, S.C., 1994. Study of Permo–Triassic boundary in Gondwana sequence of Raniganj Basin, India. Ninth International Gondwana Symposium, vol. 1, pp. 179–193.
- Grossman, E.L., 1994. The carbon and oxygen isotope record during the evolution of Pangea: Carboniferous to Triassic. *Geol. Soc. Am. Spec. Pap.* 288, pp. 207–228.
- Hansen, H.J., Lojen, S., Toft, P., Dolenec, T., Jinnan, T., Michaelsen, P., Sarkar, A., 2000. Magnetic susceptibility and organic carbon isotopes of sediments across some marine and terrestrial Permo–Triassic boundaries. In: Yin, H., Dickens, J.M., Shi, J.R., Tong, J. (Eds.), *Permian–Triassic Evolution of Teyhys and Western Circum-Pacific*. Elsevier, pp. 271–289.
- Henderson, P. (Ed.), 1984. *Rare Earth Element Geochemistry*. Elsevier, 510 pp.
- Holser, W.T., Magaritz, M., 1987. Events near the Permian–Triassic boundary. *Mod. Geol.* 11, 155–180.
- Holser, W.T., Schonlaub, H.-P., Boeckelman, K., Magaritz, M., Orth, C., 1991. The Permian–Triassic of the Gartfunkel-1 core (Carnic Alps, Austria): synthesis and conclusions. *Abh. geol. Bundesanst. Wien* 45, 213–232.
- Holser, W.T., 1997a. Geochemical events documented in inorganic carbon isotopes. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 132, 173–182.
- Holser, W.T., 1997b. Evaluation of the application of rare earth elements to paleoceanography. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 132, 309–323.
- Isizaki, Y., 1997. Permo–Triassic boundary super-anoxia and stratified superocean: records from lost deep sea. *Science* 276, 235–238.
- Jarosewich, E., Clarke, R.S. Jr., Barrows, J.N., 1987. The Alende meteorite reference sample. *Smithsonian Contributions in Earth Science* 27, pp.1–12.
- Knoll, A.H., Bambach, R.K., Canfield, D.E., Grotzinger, J.P., 1996. Comparative earth history and late Permian mass extinction. *Science* 273, 452–457.
- Krishnan, M.S., 1982. *Geology of India and Burma*, 6th ed. CBS Publ., 536 pp.
- Krull, E.S., Retallack, G.J., 2000. <sup>13</sup>C depth profiles from paleosols across the Permian–Triassic boundary: Evidence for methane release. *Bull. Geol. Soc. Am.* 112, 1459–1472.
- Kyte, F.T., Smit, J., Wasson, J.T., 1985. Siderophile interelement variations in the Cretaceous–Tertiary boundary sediments from Caravaca, Spain. *Earth Planet. Sci. Lett.* 73, 183–195.
- Leleuyer, L., Probst, J.L., Depetris, P. et al., 1999. Rare earth element speciation in river sediments. *Journal of Conference Abstracts, Symposium on Aqueous Geochemistry*, vol. 4, p. 1.
- MacLeod, K.G., Smith, R.M.H., Koch, P.L., Ward, P.D., 2000. Timing of mammal-like reptile extinctions across the Permian–Triassic boundary in South Africa. *Geology* 28, 227–230.
- Majumder, S.K., 1996. Precambrian geology of peninsular India. *Indian Miner.* 50, 139–174.
- Morante, R., Veevers, J.J., Andrew, A.S., Hamilton, P.J., 1994. Determining the Permian–Triassic boundary in Australia using C-isotope chemostratigraphy. *Aust. Pet. Explor. Assoc. J.* 34, 330–336.
- Morante, R., 1996. Permian and early Triassic isotopic records of carbon and strontium in Australia and a scenario of events about the Permian–Triassic boundary. *Hist. Biol.* 11, 289–310.



- Postma, G., Nemec, W., Kleinspehn, K.L., 1988. Large floating clasts in turbidites: a mechanism for their emplacement. *Sediment. Geol.* 58, 47–61.
- Potter, P.E., 1978. Significance and origin of big rivers. *J. Geol.* 86, 13–33.
- Renne, P.R., Zichao, J., Richards, M.A., Black, M.T., Basu, A.R., 1995. Synchrony and casual relations between Permian–Triassic boundaries and Siberian flood volcanism. *Science* 269, 1413–1416.
- Retallack, G.J., Veevers, J.J., Morante, R., 1996. Global early Triassic coal gap between Late Permian extinction and Middle Triassic recovery of peat-forming plants. *Bull. Geol. Soc. Am.* 108, 195–207.
- Retallack, G.J., Seyodolali, A., Krull, E.S., Holser, W.T., Ambers, C.P., Kyte, F.T., 1998. Search for evidence of impact at the Permian–Triassic boundary in Antarctica and Australia. *Geology* 26, 979–982.
- Retallack, G.J., 1999. Postapocalyptic greenhouse palaeoclimate revealed by earliest Triassic paleosols in the Sydney basin, Australia. *Geol. Soc. Am. Bull.* 111, 52–70.
- Retallack, G.J., Krull, E.S., 1999. Landscape ecological shift at the Permian–Triassic boundary in Antarctica. *Aust. J. Earth Sci.* 46, 786–812.
- Roy, A., Sarkar, A., Jeyakumar, S., Ebihara, M., 2002. Mid-Proterozoic plume related thermal event in eastern Indian craton evidence from trace elements, REE geochemistry and Sr–Nd isotope systematics of mafic–ultramafic intrusives from Dalma volcanic belt. *Gondwana Res.* 5, 133–146.
- Sarkar, A., Bhattacharya, S.K., Sarin, M.M., 1993. Geochemical evidence for anoxic deep water in the Arabian Sea during the last glaciation. *Geochim. Cosmochim. Acta* 57, 1009–1016.
- Sohn, W.K., 2000. Depositional process of submarine debris flow in the Miocene fan deltas, Pohans basin, SE Korea with special reference to flow transformation. *J. Sediment. Res.* 70, 491–503.
- Taylor, S.R., McLennan, S.M., 1985. *The Continental Crust: Its Composition and Evolution*. Blackwell, Oxford, 312 pp.
- Tiwari, R.S., Tripathi, A., 1992. Marker assemblage zone of pore and spollen species through Gondwana Paleozoic and Mesozoic sequence in India. *Paleobotanist* 40, 194–236.
- Wang, Y.L., Liu, Y.G., Schmitt, R.A., 1986. Rare earth geochemistry of South Atlantic deep sea sediments: Ce anomaly change at ~54 Ma. *Geochim. Cosmochim. Acta* 50, 1337–1355.
- Ward, P.D., Montgomery, D.R., Smith, R., 2000. Altered river morphology in South Africa related to the Permian–Triassic extinction. *Science* 289, 1740–1743.
- Wignall, P.B., Twitchett, R.J., 1996. Oceanic anoxia and the end-Permian mass extinction. *Science* 272, 1155–1158.