Negative δ^{13}C excursion and anoxia at the Permo-Triassic boundary in the Tethys Sea

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The Permian–Triassic (P–T) sections in Spiti valley, Himalaya represent sedimentary deposits of a shallow sea and show a sharp negative transition of δ^{13}C in total organic matter, kerogen fraction and carbonate phase. This excursion occurs across the upper part of the Permian shale culminating in a ferruginous band, which marks the peak of anoxicity after a period of generally low-oxygenated condition in the basin, as inferred on the basis of trace element analysis. Presence of carbon isotopic shift along with anoxia is similar to that observed in many P–T sections over the globe and suggests that Permo-Triassic transitional records of the Neo-Tethys are preserved in the ferruginous band of the Spiti valley sections.

THE Permian–Triassic (P–T) transition represents a time of remarkable changes in the Phanerozoic when nearly 90% of shelly marine genera were wiped out[1]. It is characterized by diverse isotopic and chemical markers interpreted variously to indicate catastrophic events such as extra-terrestrial impacts[2–6], marine regression[7], climate change[8,9], oceanic anoxia[10], overturning of the sea[11] and volcanism[12]. A sudden excursion of δ^{13}C of kerogen and organic material has been observed in a few sections across the boundary[13,14]. Recently, Musashi *et al.*[15] confirmed this excursion in the sedimentary organic matter and inorganic carbonates collected across P–T boundary sections of south-western Japan, indicating that it may be a global phenomenon representing an important event horizon.

Permian and Triassic sediments in the extra-peninsular India were deposited in the western periphery of Neo-Tethys, a confined body of water separated from Palaeo-Tethys. These sediments are exposed along Guryul ravine (Kashmir), Lahaul valley and Spiti valley of northwest Himalaya. In the Spiti valley, a thin (1–10 cm) ferruginous band separates the Permian shale from the Triassic limestone[2,16]. In spite of significant advances in chemostratigraphy, inter-basinal correlation among the Phanerozoic sequences is difficult to establish due to problems associated with doubtful faunal record, presence of hiatus in sedimentary deposition, variable sampling resolution, absence of facies control, etc. Well-preserved shale–carbonate sequence straddling the Permian and Triassic in Spiti Himalaya, provides an opportunity to establish the geochemical changes across the P–T boundary (PTB) within a broad global chemostratigraphic framework. In addition, since these sediments formed in a sea, the δ^{13}C of organic matter should reflect the variation of surface-water productivity and dissolved CO_2 concentration across the P–T transition and may serve as global marker.

With this view, we have analysed the carbon isotope ratio of organic matter and marine carbonates across the PTB in shale and limestone sequences from Attargoo, Guling and Lalung sections of the Spiti valley.

The P–T sections, exposed along the Spiti river and its tributaries, the Pin and Lingti rivers are shown in Figure 1. Excellent exposures occur near the villages Attargoo, Guling and Lalung. A reddish ferruginous band separates the upper Permian shale (Gungri Formation of Kuling Group) from the lower Triassic limestone (Mikin Formation of Lilang Group) and provides a regional scale marker. According to Srikantia and Bhargava[16], the Gungri Formation comprises mostly black, calcareous, silty shale bearing phosphatic, cherty and calcareous nodules along with thin limestone and coquina lenses. Rocks of Gungri Formation are believed to be shelf sediments deposited under restricted oceanic circulation. The Mikin Formation comprises dark-grey to grey, locally cherty dolomite and shale lenses repeated in cycles of carbonate–shale units. Sediments of Mikin Formation were deposited under sub-tidal to bathyal environment. Detailed bio-stratigraphy of these sections has been described by Srikantia and Bhargava[16] and summarized by Shukla *et al.*[17]. Briefly, the shale bed contains fossil *Productus* of late Permian age, whereas overlying limestone contains fossils of *Otoceras* genera along with conodonts belonging to earliest Triassic age (Figure 2). For example, Bhatt *et al.*[18] have shown that many Griesbachian conodonts,

Figure 1. Geological map of Spiti Basin of western Himalaya showing Permian–Triassic sections at Attargoo, Guling and Lalung (after Hayden[24]).

similar to those found in the Salt Range section of Pakistan (considered the type area), occur in the *Ophiceras* zone, about 50 cm above the ferruginous band and the *Otoceras* bed contains early Triassic conodonts like *Hindeodus typicalis*, *N. carinata*, etc. Regarding the Permian part, a recent study by Wignall (pers. commun.) has shown that the ammonoid *Cyclolobus walkeri*, occurring in the beds underlying the ferruginous layer probably continues up to Changxingian age rather than being confined in Dzulfian, as thought earlier[16]. The presence of Changxingian fossils in the sediments below the ferruginous band suggests that the uppermost Permian is present in these sections and the Spiti valley sequences may have continuous record extending from the late Permian to the early Triassic[17].

The ferruginous band, sandwiched between Permian and Triassic sediments, was earlier interpreted as an indicator of sub-aerial exposure or submarine break[16] indicating a hiatus in sedimentation. To establish the continuity of the section at the boundary, it is worthwhile to compare its $\delta^{13}C$ profile with other sections believed to be complete. We have, therefore, carried out $\delta^{13}C$ analysis of organic material, kerogen and carbonates in these sediments and will discuss these results in relation to chemo-stratigraphy and anoxia.

Samples were collected with a few centimetres resolution using the ferruginous bed as a lithographic marker (Table 1). Nine samples from Attargoo, seven from Guling and fourteen from Lalung sections were collected across the ferruginous band. The shale samples do not have significant carbonate for analysis. Carbon isotopic ratios of the carbonate phase from the limestone samples were determined by reacting the powdered whole rock samples with 100% H_3PO_4 at 25°C, purifying the evolved CO_2 gas in an on-line extraction system and analysing it by a GEO 20–20 mass spectrometer. The results are expressed in standard δ notation (w.r.t. PDB standard), where $\delta^{13}C = (R_{sample}/R_{standard}-1) \times 1000$ and R refers to $^{13}C/^{12}C$ ratio. The overall analytical precision was ± 0.1‰ for $\delta^{13}C$, as determined by using a laboratory standard carbonate (Z-Carrara).

The total organic carbon (TOC) was recovered from these samples after dissolving/treating the carbonates with 20% HCl for 24 h. Dried residue (containing organic matter and detrital) was loaded in a 10 cm long quartz break seal tube along with CuO (wire form) and Ag strip. The quartz tube was evacuated, sealed and combusted at 700°C for 6 h. Evolved CO_2 was purified and analysed. Residual samples from the Attargoo section were further treated with HF to remove the silicates and the kerogen fraction was extracted for analysis. To check the reproducibility of measurements, UCLA glucose standard was analysed along with each set of samples. The reproducibility of $\delta^{13}C$ for the organic matter and kerogen samples is about 0.15‰. The TOC content was determined in a separate aliquot by a CHN analyser (FISONS model NA
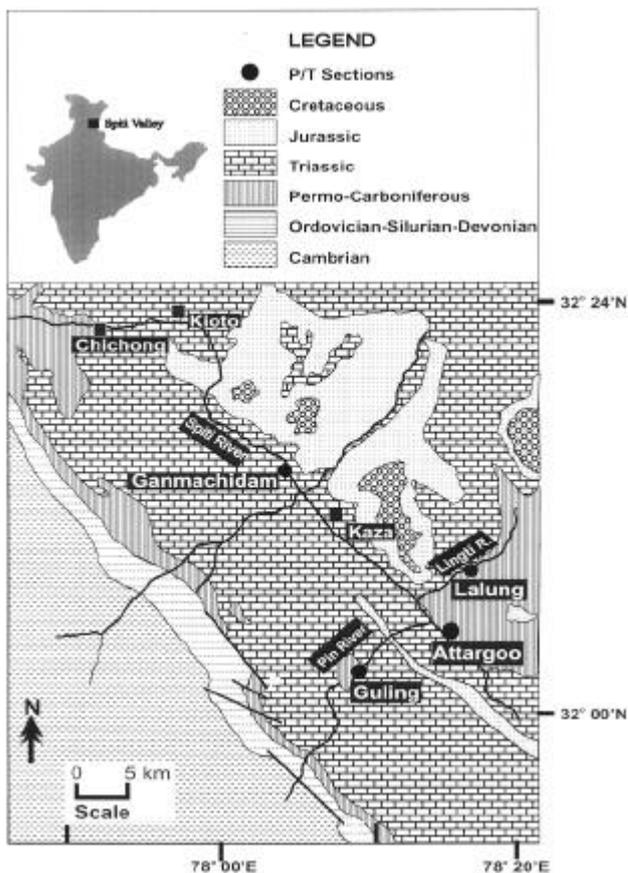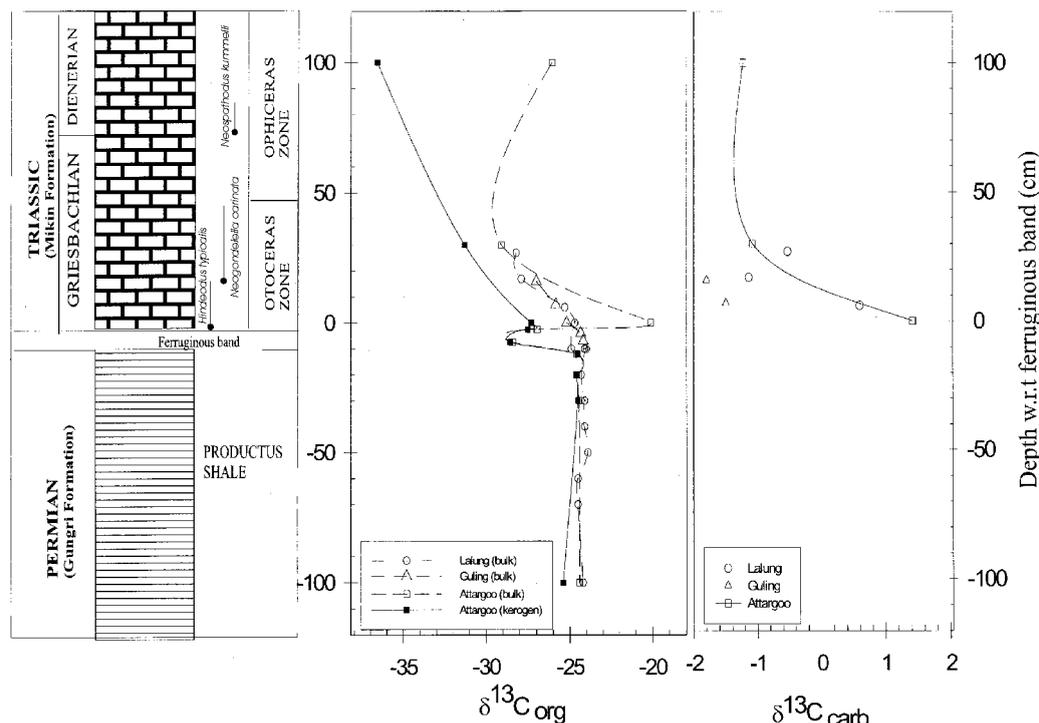
Figure 2. General litho-stratigraphy and bio-stratigraphy of P–T sections of the Spiti valley. Also shown is the variation in $\delta^{13}C_{org}$ and $\delta^{13}C_{carb}$ (w.r.t. PDB) across the ferruginous band from the three sections, i.e. Attargoo, Guling and Lalung.

1500). The measurement of H/C and N/C ratios along with the kerogen content of many samples was carried out by following the procedure of Wedeking et al.[19], using a ELEMENTER-VARIO EL III C–H–N–O–S analyser at IICT, Hyderabad.

Results of the carbon isotope analysis and TOC content are given in Table 1. The Permian shales are poor in carbonates and have TOC content ranging between 0.77 and 2.12%. However, samples from the layer above the ferruginous band are limestones having carbon concentration ranging between 8 and 12%. The bulk organic carbon was measured in all the three sections. In addition, six samples from the Attargoo section and four samples from the Lalung section were measured for kerogen content along with H/C and N/C ratios in kerogen fraction. The kerogen content is slightly less or nearly equal to TOC as expected for well-preserved samples. The H/C ratios are greater than 0.3 and similar in most of the samples. Previous analyses[20] of kerogen and $\delta^{13}C$ have shown that H/C > 0.3 indicates that no significant alteration has taken place. Additionally, the N/C ratios are remarkably uniform at 0.022, reinforcing our assumption that only one type of organic carbon source is involved. Since the value of 0.022 is within the range expected for marine kerogens of Proterozoic and Phanerozoic age[21], any terrestrial contribution can be ruled out. In particular, the ferruginous band also has the same N/C value (0.022), suggesting its derivation from marine organic matter and ruling out the presence of any sub-aerial soil-produced component as inferred previously[16].

Comparison of kerogen and the bulk TOC data helps us to detect possible alteration in $\delta^{13}C$ due to secondary contamination or thermal metamorphism[21]. Our results (Table 1, Figure 2) show similar trend in $\delta^{13}C$ variation of the kerogen fraction and bulk TOC from the Attargoo section, although the magnitudes of the $\delta^{13}C$ excursion for the two are different. The $\delta^{13}C$ values of the TOC for the two carbonate-rich samples (AT-8 and AT-9) are higher than those of the kerogen fraction. The $\delta^{13}C$ (–20‰) seems to be particularly high for AT-1 TOC, indicating significant contribution of labile ^{13}C in the bulk fraction, probably due to thermal metamorphism, and should not be considered for further discussion. The $\delta^{13}C$ of the TOC from the Lalung section changes from –24.0‰ in the late Permian to –28.2‰ in the early Triassic. The $\delta^{13}C$ of the TOC from the Attargoo and Guling sections varies between –24.5 and –29.1‰, and –24.2 and –27‰ respectively (Figure 2). The average $\delta^{13}C$ values of the latest Permian are fairly uniform at about –24.2‰, –24.5‰ and –24.2‰ for Lalung, Attargoo and Guling sections respectively, in contrast to the low values (–28.2‰, –29.1‰ and –27‰) for the early Triassic. An abrupt decrease in $\delta^{13}C$ occurs at about 7 to 12 cm below the red ferruginous band in all the three sections. Above the ferruginous band, the $\delta^{13}C$ values continue to decline up-section.

Table 1. Total organic carbon (TOC), kerogen, H/C and N/C along with δ^{13}C of TOC, kerogen and carbonate from three Permo–Triassic sections of Spiti valley, Himalaya

Sample	Type	Depth (cm)	TOC (%)	Kerogen (%)	H/C	N/C	$\delta^{13}C_{OM}$ (‰)	$\delta^{13}C_{Ker}$ (‰)	$\delta^{13}C_{carb}$ (‰)
Attargoo section									
AT-9	Limestone	+100.0	–	–	–	–	–26.1	–36.6	–1.23
AT-8	Limestone	+30.0	–	0.95	0.654	0.024	–29.1	–31.3	–1.08
AT-1	F band*	0.0	–	0.72	0.478	0.023	–20.1	–27.3	1.42
AT-3	Shale	–2.5	–	0.58	0.448	0.022	–27.0	–27.5	–
AT-4	Shale	–7.5	0.99	0.90	0.413	0.021	–28.4	–28.5	–
AT-5	Shale	–12.0	–	–	–	–	–24.5	–24.5	–
AT-6	Shale	–20.0	1.91	–	–	–	–24.6	–24.6	–
AT-7	Shale	–30.0	1.65	0.95	0.451	0.023	–24.4	–24.5	–
AT-10	Shale	–100.0	1.46	0.77	0.428	0.022	–24.4	–25.4	–
Guling section									
GL-21	Limestone	+16.0	–		–	–	–27.0	–	–1.71
GL-20	Limestone	–	–		–	–	–25.8	–	–1.50
GL-19A1	F band*	0.0	–		–	–	–23.1	–	–
GL-19B	F band*	0.0	–		–	–	–25.2	–	–
GL-18	Shale	–	–		–	–	–24.3	–	–
GL-17	Shale	–7.0	0.77		–	–	–24.2	–	–
Lalung section									
LL-14	Limestone	+30.0	–	–	–	–	–28.2	–	–
LL-13	Limestone	+17.0	–	0.50	0.776	0.023	–27.8	–	–1.14
LL-12	Limestone	+10.0	–	–	–	–	–25.3	–	0.60
LL-11B2	F band*	0.0	–	0.67	0.476	0.022	–24.7	–	–
LL-10A	Shale	–10.0	0.98	0.69	0.410	0.021	–24.0	–	–
LL-10B	Shale	–10.0	1.02	–	–	–	–24.1	–	–
LL-9	Shale	–20.0	1.76	0.98	0.392	0.022	–24.3	–	–
LL-8A	Shale	–30.0	2.02	–	–	–	–24.1	–	–
LL-8B	Shale	–30.0	–	–	–	–	–24.1	–	–
LL-7	Shale	–40.0	–	–	–	–	–24.1	–	–
LL-6	Shale	–50.0	1.45	–	–	–	–23.9	–	–
LL-5	Shale	–60.0	–	–	–	–	–24.5	–	–
LL-4	Shale	–70.0	2.12	–	–	–	–24.5	–	–
LL-1	Shale	–100.0	2.03	–	–	–	–24.2	–	–

*F band refers to ferruginous band at the PTB.

A negative shift in $\delta^{13}C_{carb}$ is also observed from the end phase of Permian (ferruginous band) to early Triassic (Figure 2). Due to lack of measurable carbonates in the uppermost Permian shale, the entire $\delta^{13}C_{carb}$ profile could not be documented. The maximum decrease was found in the Attargoo section, amounting to about 2.6‰.

The present study thus shows a decrease of 2.6‰ in δ^{13}C of inorganic carbonate and 3.2 to 4.6‰ in organic matter between samples below and above the ferruginous band. The organic matter at 12 to 100 cm below the band has average δ^{13}C value of –24.3‰, whereas the samples above have an average δ^{13}C value of –28.1‰, corresponding to a decrease of 3.8‰. The inorganic carbonate also shows a shift (1.7 to 2.6‰) across the band in Lalung and Attargoo sections. A common shift in both the organic (3.8‰) and inorganic carbon (2.6‰) isotopic ratio can occur only if the sea water composition itself suffered a change.

It is of interest to note that across the ferruginous band Th/U decreased from about 10 to 2 and Ce/La increased from 0.8 to 1.5 (ref. 17), indicating that the material in the band was deposited in an anoxic environment. Therefore, the carbon isotope shift coincides with the establishment of anoxia in this basin.

There are three other studies of PTB sections that have shown similar changes in the carbon isotope ratio δ^{13}C was measured in kerogen separated from sediments of Williston lake in British Columbia and obtained sudden shift from latest Permian values of -29 ± 1‰ to a minimum of –32.6‰, 2 m above the PTB. A large shift of –4‰ in the carbonate phase was observed in the Global PTB Stratotype section at Meishan in China[4]. However, organic carbon was not analysed in that section. Simultaneous analysis of organic and inorganic carbon in the PTB sediments was recently carried out by Musashi *et al.*[15] from southwest Japan, which showed a shift of 2‰

in the organic and 2.6‰ in the inorganic phase. These studies, along with the present study, indicate that there was a large decrease in the $^{13}C/^{12}C$ ratio of the two major carbon reservoirs (i.e. organic and inorganic) of the oceans during the PTB transition. Decrease of carbon isotope ratio by such a large magnitude cannot be ascribed to changes in the ocean biology, because it constitutes only a minor component and cannot make a significant change in the inorganic carbon reservoir. Isozaki[22] proposed a ^{13}C-depleted source like methane hydrates, which can cause such depletion if it is converted suddenly to soluble carbon species in the ocean. The mechanism for releasing carbon from such gas hydrates has to be a catastrophic one, for example, an extraterrestrial impact suddenly exploding the gas hydrate reservoir in the ocean bottom[6]. Interestingly, the same mechanism can also cause the proposed anoxia found by Shukla et al.[17] in this section and by others elsewhere[10]. The impact hypothesis is also supported by the short time scale of the negative excursion in $\delta^{13}C$ across the PTB, estimated to be about 165 ky (ref. 4). Signature of an impact at the PTB in the Spiti valley was first discussed by Bhandari et al.[2] based on the similarity of REE and trace element (Ir) composition of samples from the Lalung section with the composition of eucritic meteorites[23], and is supported by the work of Becker et al.[5] and Retallack et al.[3].

In summary, our results show that the PTB sections of the Spiti valley, Himalaya have the characteristic sharp negative excursion in $\delta^{13}C$ noted both in organic and inorganic carbon as observed in other continuous PTB sections of the globe. This result coupled with the evidence of anoxia favours the impact hypothesis.

1. Erwin, D. H., *The Great Paleozoic Crisis*, Columbia University Press, New York, 1993, p. 327.
2. Bhandari, N., Shukla, P. N. and Azmi, R. J., *Geophys. Res. Lett.*, 1992, **19**, 1531–1534.
3. Retallack, G. J., Seyedolali, A., Krull, E. S., Holser, W. T., Ambers, C. P. and Kyte, F. T., *Geology*, 1998, **26**, 979–982.
4. Bowring, S. A., Erwin, D. H., Jin, Y. G., Martin, M. W., Davidek, K. and Wang, W., *Science*, 1998, **280**, 1039–1045.
5. Becker, L., Poreda, R. J., Hunt, A. G., Bunch, T. E. and Rampino, M., *ibid*, 2001, **291**, 1530–1533.
6. Kaiho, K. *et al.*, *Geology*, 2001, **29**, 815–818.
7. Erwin, D. H., *Nature*, 1994, **367**, 231–235.
8. Retallack, G. J., *Science*, 1995, **267**, 77–80.
9. Eshet, Y., Rampino, M. R. and Visscher, H., *Geology*, 1995, **23**, 967–970.
10. Wignall, P. B. and Twitchett, R., *Science*, 1996, **272**, 1155–1158.
11. Knoll, A. H., Bambach, R. K., Canfield, D. E. and Grotzinger, J. P., *ibid*, 1996, **273**, 452–457.
12. Renne, P. R., Zichao, Z., Richards, M. R., Black, M. T. and Basu, A. R., *ibid*, 1995, **269**, 1413–1416.
13. Wang, K., Geldsetzer, H. H. and Krouse, H. R., *Geology*, 1994, **22**, 580–584.
14. Magaritz, M., Krishnamurthy, R. V. and Holser, W. T., *Am. J. Sci.*, 1992, **292**, 727–739.
15. Musashi, M., Isozaki, Y., Koike, T. and Kreulen, R., *Earth Planet. Sci. Lett.*, 2001, **191**, 9–20.
16. Srikantia, S. V. and Bhargava, O. N., *Geology of Himachal Pradesh*, Geological Society of India, Bangalore, 1998, p. 416.
17. Shukla, A. D., Bhandari N. and Shukla P. N., *Geol. Soc. Am. Spec. Pap.*, 2002, **356**, 445–454.
18. Bhatt, D. K., Joshi, V. K. and Arora, R. K., *J. Geol. Soc. India*, 1999, **54**, 153–167.
19. Wedeking, K. W., Hayes, J. M. and Matzigkeit, U., in *Earth's Earliest Biosphere – Its Origin and Evolution* (ed. Schopf, R. W.), Princeton University Press, Princeton, 1983, pp. 428–442.
20. Hayes, J. M., Kaplan, I. R. and Wedeking, K. W., *ibid*, pp. 291–301.
21. Strauss, H., Des Marais, D. J., Hays, J. H. and Summons, R. E., in *The Proterozoic Biosphere* (eds Schopf, J. W. and Klein, C.), Cambridge University Press, Cambridge, UK, 1992, pp. 117–128.
22. Isozaki, Y., *Science*, 1997, **276**, 235–238.
23. Bhandari, N., *Proc. Indian Acad. Sci.* (*Earth Planet. Sci.*), 1998, **107**, 251–263.
24. Hayden, H. H., *Mem. Geol. Soc. India*, 1904, **36**, 1–121.