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Sequencing events across the Permian–Triassic boundary, Guryul Ravine (Kashmir, India)

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Abstract

The Permian–Triassic boundary (PTB) section at Guryul Ravine (Kashmir, India) comprises a >100-m-thick, apparently conformable succession of mixed siliciclastic–carbonate sediments deposited in a deep-shelf or ramp setting. This section, although long important in debates concerning placement of the PTB, has not previously been the focus of an integrated chemostratigraphic study. In the present study, samples from a 20-m-thick interval straddling the PTB were analyzed for major- and trace-element concentrations, TOC-TIC, REEs, and organic $\delta^{13}C-\delta^{15}N$ to investigate contemporaneous environmental changes. The Guryul Ravine section exhibits a sequence of discrete events that provide potentially important information about the character and cause(s) of the PTB. Two transient negative C-isotopic excursions within the upper *changxingensis* zone predate the Late Permian event horizon (LPEH, i.e., the global mass extinction event) by ~200–400 kyr and are associated with the onset of a major eustatic rise and with secondary extinction peaks. These excursions may record minor environmental disturbances prior to the main end-Permian crisis, supporting an intrinsic mechanism such as volcanism and climate change rather than an extrinsic mechanism such as a bolide impact. The onset of a large (~-4.0 to -4.5‰), sustained negative C-isotope shift marks the LPEH, which is located at the Zewan–Khunamuh formation contact ~260 cm below the biostratigraphically defined PTB. The Guryul Ravine section exhibits a stepwise extinction pattern, with the largest peak between the LPEH and PTB and a secondary peak just above the PTB, a pattern similar to that observed in the Meishan D GSSP.

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1. Introduction

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The Permo-Triassic section at Guryul Ravine, near Srinagar in Indian Kashmir (Fig. 1), has long figured in

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Fig. 1. Location maps for (A) Srinigar, Kashmir (star) and (B) Guryul Ravine (dashed line). Modified from Kapoor (1996). (C) Generalized Late Permian–Early Triassic stratigraphy of Kashmir. Modified from Baud et al. (1996) with absolute ages from Gradstein et al. (2004) and litho-unit age revisions per Shen et al. (2006).

debates regarding the placement of the Permian-Triassic boundary (PTB) (see Erwin, 1993, for a review). It was a candidate for the Permian-Triassic Global Stratotype Section and Point (GSSP) prior to the selection of Meishan D in Zhejiang Province, China (Kapoor, 1996; Yin et al., 2001). At Guryul Ravine, the Lopingian (Upper Permian) Zewan Formation is overlain by the Lower Triassic Khunamuh Formation in a >100-m-thick, apparently conformable marine succession. The basal few meters of the Khunamuh Formation (Unit E1, the "Claraia beds") contain faunal elements that were considered to be indicative of both a Late Permian and an Early Triassic age (Teichert et al., 1970; Brookfield et al., 2003). Recent formal designation of the base of the Hindeodus parvus zone as the erathem boundary (Jin et al., 2000; Yin et al., 2001) places this "transition interval" entirely within the Upper Permian (Baud, 2001; Shen et al., 2006). The first specimens of H. parvus are found near the base of Unit E2, a level also marked by the appearance of six species of Lower Triassic ammonoids belonging to the genera Otoceras, Lytophiceras, and Glyptophiceras (Fig. 1; Nakazawa et al., 1970, 1975; Nakazawa and Kapoor, 1981; Nakazawa, 1993; Kapoor, 1996; Orchard and Krystyn, 1998; Shen et al., 2006). The conodont biostratigraphy of the section has been worked out in detail (Murata, 1981; Matsuda, 1981, 1982, 1983, 1984; Wignall et al., 1996; Kozur, 2003; Korte and Kozur, 2005): (1) Unit D corresponds to the Late Permian changxingensis zone; (2) Unit E1 to the latest Permian latidentatus-meishanensis zone; (3) Unit E2 to the Early Triassic *parvus* and *isarcica* zones; and (4) Unit E3 to the carinata, kummeli, and lowermost dieneri zones.

The Permo-Triassic section at Guryul Ravine was deposited in an outer-shelf or deep-ramp setting. Although sedimentation rates were only moderate $(\sim 10-20 \text{ m Myr}^{-1})$, the section contains a complex record of the interplay of eustatic, chemical oceanographic, and biotic factors that warranted the present chemostratigraphic study. The sample suites used in this analysis were collected for earlier studies by Mike Brookfield in 1984 (Gupta and Brookfield, 1986; Brookfield et al., 2003) and Aymon Baud in 1987 (Baud and Magaritz, 1988; Baud et al., 1996). Although the number of available samples was relatively small (n=19), further sampling is impossible at the present time owing to unstable political conditions in Kashmir. To supplement an existing carbonate $\delta^{13}C - \delta^{18}O$ record (Baud et al., 1996), we generated major- and trace-element, TOC-TIC, and REE concentrations along with organic $\delta^{13}C - \delta^{15}N$ and magnetic susceptibility (MS) data. The stratigraphic range of the present study is a 20-m-thick interval in Units D through E3 that straddles the biostratigraphically defined PTB. Sample density is greatest (~10 m⁻¹) within a 1-m interval at the Zewan-Khunamuh formation contact, which is characterized by an abrupt change in lithology and is considered to be a major sequence boundary (Shen et al., 2006) as well as the local manifestation of the global Late Permian event horizon (LPEH). This study was intended to investigate (1) relationships between multiple chemostratigraphic proxies, and (2) the relative sequence of boundary-related events recorded at Guryul Ravine, with the goal of generating new insights regarding the character and origin of the PTB.

2. Geologic background

The study locale was located on the northern margin of Gondwana during the late Paleozoic, hence along the southern side of the Neotethys Ocean at a paleolatitude of $\sim 35^{\circ}$ S (see Algeo et al., 2007-this volume, their fig. 2B). Rifting of the Kashmir margin of Gondwana led to rapid thermal subsidence during the Late Permian and Early Triassic (Bhat, 1982; Gaetani and Garzanti, 1991; Stampfli et al., 1991; Brookfield, 1993; Baud et al., 1996). In northern India, the break-up unconformity and subsidence phase is marked by the slow, widespread transgression of Upper Permian marine deposits (Kapoor, 1992; Garzanti et al., 1998). To the north of Guryul Ravine in the Zanskar-Spiti Himalaya, a lithologic transition to black shales with phosphatic nodules (the Kuling shales) occurred already during the Late Permian (Gaetani et al., 1990; Gaetani and Garzanti, 1991; Bagati, 1991; Garzanti et al., 1998), reflecting the anoxic conditions associated with deeper-water environments at that time. At Guryul Ravine, this transition is slightly younger in age and corresponds to the Zewan-Khunamuh formation contact (Fig. 1).

The uppermost 5 m of the Zewan Formation (Unit D, Beds 43-45) consist of bioturbated, fine- to mediumgrained, well-sorted, argillaceous sandy limestones or calcareous shaly quartz sandstones, with minor shaly interbeds (Fig. 2A; Brookfield et al., 2003). Many of the coarser-grained beds exhibit grading from parallel lamination to hummocky cross-lamination typical of deposits of waning storms (e.g., Aigner, 1985). Unidirectional slumping in parts of the section suggests sediment deposition in a slope setting, with softsediment deformation possibly triggered by storm waves or earthquakes (e.g., McLaughlin and Brett, 2004). The uppermost bed of the Zewan Formation (D46-1) comprises three layers (Fig. 2A; Brookfield et al., 2003). Layer D46-1A, ~8 cm thick, consists of bioturbated, irregularly cross-laminated, sandy, ostracod-bearing bioclastic limestone (grainstone). Layer D46-1B, \sim 15 cm thick, consists of parallel-laminated, well-sorted, fine-grained, micaceous, calcareous quartz sandstone with no identifiable fossils. Layer D46-1C, ~ 15 cm thick, consists of irregular bioclastic lenses with large-scale cross-bedding and a hummocky top smoothed by calcisiltite, typical of storm deposits (e.g., Brett and Algeo, 2001). It has three distinct sublayers: the lower (1C-x) is a fine-grained, moderately sorted, cross-bedded packstone/grainstone containing productid brachiopods, green algae, and serpulids; the middle (1C-y) is similar except for the presence of intraformational clasts of pale brown fossiliferous packstone in a brownish, phosphatic microspar matrix; and the upper (1C-z) is a thin, fine-grained, poorly sorted, sandy wackestone passing upward into a calcisiltite. Layer D46-1C has features suggestive of a composite shell bed formed by shell accumulation and reworking, including

intraformational rip-up clasts and complex internal erosion surfaces.

The overlying Khunamuh Formation exhibits a pronounced change in lithology (Fig. 2A; Kapoor, 1996; Brookfield et al., 2003). The basal ~ 16 m consists of interbedded dark calcareous shales and argillaceous limestones (Unit E), overlain by >50 m of cleaner limestones (Unit F). Unit E1 is a 2.5-m-thick transitional unit dominated by silty gray calcareous mudstones with subordinate thin interbeds of fine-grained quartz siltstones and fossiliferous limestones. It is mostly laminated or micro-cross-bedded with no signs of bioturbation. Unit E1 contains rare fossils, mostly brachiopods (especially Strophomenida) and bivalves as small, probably stunted forms (Shimizu, 1981; cf. Twitchett, 2007-this volume). The lack of sorting, good preservation, and angularity of the shells and shell fragments suggest a parauthochthonous origin, with genesis of the more carbonate-rich horizons through winnowing (Brookfield et al., 2003). Upsection within Unit E, sediments become darker, less quartz-rich, and more argillaceous, limestone beds become thinner and less common, and the fauna changes from a relatively shallow-water assemblage composed of brachiopods and bivalves to one dominated by deep-water ammonoids. These changes reflect a substantial increase in relative water depth during the latest Permian and earliest Triassic (events 6 and 7 of Baud et al., 1996).

3. Methods

Samples were visually inspected and any veins and weathered surfaces were removed prior to grinding in a tungsten ball mill to a fine powder. Whole-rock powdered samples were placed in aluminum holders and scanned by X-ray diffraction (XRD) using a Siemens D-500 automated powder diffractometer at the University of Cincinnati. Samples were scanned from 2° to 32° 2 Θ at 0.2° min⁻¹ using CuK α radiation and a graphite monochromator. For clay fraction distilled water after particle separation by ultrasonic disaggregation. The <2- μ m size fraction was recovered by ultracentrifugation and used to make oriented slides by standard smear techniques.

Major- and trace-element concentrations were determined on whole-rock samples using a wavelengthdispersive Rigaku 3040 X-ray fluorescence (XRF) spectrometer at the University of Cincinnati. Results were calibrated using both USGS and internal standards (analyzed by XRAL Incorporated using XRF and INAA). Analytical precision based on replicate analyses



Fig. 2. (A) Stratigraphy of study section, modified from Baud et al. (1996) and Brookfield et al. (2003). (B) Model mineralogic composition, calculated per Eqs. (1), (2) and (3) of text. (C) Magnetic susceptibility (MS) in kg m⁻³ (bottom) and SI units (top). (D) Total organic carbon (TOC), total nitrogen (TN), and total phosphorus (TP). (E) Total sulfur (TS) and total iron (TFe). (F) Zr and average REE concentrations; the latter is in units of log ppm, calculated as $\Sigma(\log [X]_i)/14$ where *i*=La to Lu; see Fig. 5 for definition of shale*. Concentrations in D–F given on a carbonate-free basis. (G) Ce/ Ce*, where Ce* is calculated as (La+Pr)/2. (H) Eu/Eu*, where Eu* is calculated as (Sm+Gd)/2. (J) δ^{13} C and δ^{15} N of organic matter; note anomalous δ^{15} N value (solid square). (K) Carbonate δ^{13} C and δ^{18} O (Baud et al., 1996). C1, C2=Late Permian C-isotopic excursions (see Fig. 8); LPEH = Late Permian event horizon; PTB = Permian–Triassic boundary. Note vertical scale changes: the middle part of the section is shown at 30× the resolution of the upper and lower parts. All data original to this study except A and K.

Table 1

Summary of acquisition parameters, mean estimates of precision (% RSD, relative standard deviation), and detection limits from DRC-ICP-MS analyses

Ar plasma gas	18 L min ⁻¹		Detection limit (ppt)
RF Power	1200 W	La	1.17
Torch	Quartz with 2 mm i.d. injector	Ce	1.25
Nebulizer	Concentric nebulizer (Meinhardt TQ-3O-A3)	Pr	0.42
Ar nebulizer gas	1.0 mL min ⁻¹	Nd	0.94
Spray chamber	Quartz cyclonic	Sm	1.05
Reaction gas	NH ₃ ; 0.8 mL min ⁻¹	Eu	1.67
Cones	Nickel	Gd	1.08
Monitored	% RSD	Tb	1.62
isotopes			
⁸⁹ Y (yield monitor only)	_	Dy	1.48
¹¹⁵ In (internal standard only)	_	Ho	0.97
¹³⁵ Ba	1.14	Er	1.21
¹³⁷ Ba	1.14	Tm	1.13
¹³⁸ Ba	1.12	Yb	1.54
¹³⁹ La	1.22	Lu	1.68
¹⁴⁰ Ce	1.76		
¹⁴² Ce	1.99		
¹⁴¹ Pr	1.87		
¹⁴³ Nd	1.05		
¹⁴⁶ Nd	1.11		
¹⁴⁸ Sm	1.88		
¹⁴⁹ Sm	1.44		
¹⁵¹ Eu	1.25		
¹⁵³ Eu	1.66		
¹⁵⁷ Gd	1.37		
¹⁵⁸ Gd	1.55		
¹⁵⁹ Tb	2.12		
¹⁶¹ Dy	3.11		
¹⁶³ Dy	1.97		
¹⁶⁴ Dy	1.52		
¹⁶⁵ Ho	2.44		
¹⁶⁶ Er	1.04		
¹⁶⁷ Er	1.16		
¹⁶⁹ Tm	1.18		
¹⁷² Yb	1.11		
¹⁷³ Yb	1.58		
¹⁷⁴ Yb	1.76		
¹⁷⁵ Lu	1.22		

was better than $\pm 2\%$ for major and minor elements and $\pm 5\%$ for trace-elements, and detection limits were ~ 5 ppm for most trace-elements. C and S elemental concentrations were measured using an Eltra 2000 C–S analyzer, also at the University of Cincinnati. Data quality was monitored via multiple analyses of USGS SDO-1 standard, yielding an analytical precision (2σ) of $\pm 2.5\%$ of reported values for C and $\pm 5\%$ for S. An aliquot of each sample was digested in 2N HCl at 50 °C for 12 h to dissolve carbonate minerals, and the residue

was analyzed for total organic carbon (TOC) and nonacid-volatile sulfur (NAVS); total inorganic carbon (TIC) and acid-volatile sulfur (AVS) were obtained by difference. Elemental C and N compositions were analyzed using a Costech 5010 elemental analyzer at the University of Kentucky. Average standard deviations were 0.52% and 0.08% for C and N of an acetanilide standard, respectively, and <0.01% for both C and N of unknowns. Analytical results for elemental C by the two methods employed generally differed by less than 5%.

The bulk mineralogy of the study section is dominated by quartz, clay minerals (illite with subordinate chlorite), and calcite, as determined by the XRD analysis. Geochemical concentration data were used to estimate the fractions of these minerals in each sample as follows:

$$Calcite (\%) = TIC_{meas} \times 100/12$$
(1)

Clay minerals (%) =
$$Al_{meas} \times 100/\kappa_1$$
 (2)

Quartz (%) = SiO_{2(meas)} – (Al_{meas}/27 ×
$$\kappa_2$$

× 60.1). (3)

Eq. (1) is a standard formula for calculating the amount of calcium carbonate in a sample from the measured concentration of total inorganic carbon (TIC). Eqs. (2) and (3) are formulas for calculating model amounts of clay minerals and quartz in a sample based on measured Al and SiO₂ concentrations. The coefficients 12, 27, and 60.1 represent the molar weights in grams of C, Al, and SiO₂, respectively, and the constants κ_1 and κ_2 represent the average concentration of Al and the average molar Si:Al ratio of the clay mineral assemblage, respectively. Values of 12.5 for κ_1 and 2.0 for κ_2 were found to minimize variance ($\sigma = 5.2\%$) about a mean sum of 100% for the samples as a group. Illite typically contains 13-15% Al and has a molar Si: Al ratio of 2.0 (dictated by its TOT structure), whereas chlorite typically contains 9-13% Al and has a molar Si:Al ratio of 1.0-2.0 (depending on the degree of substitution for Al in its octahedral layers; Grim, 1968). Thus, the κ_1 and κ_2 values obtained in this manner are consistent with a clay fraction dominated by illite with subordinate chlorite. Where deviating from unity, the three-component sum for each sample was normalized to 100% for display purposes (Fig. 2B).

Carbonate $\delta^{13}C - \delta^{18}O$ data were previously generated and reported by Baud et al. (1996). Organic carbon $\delta^{13}C$ and $\delta^{15}N$ analyses were performed at the University of Kentucky. Ground sample powders were



Fig. 3. XRD diffractograms for selected whole-rock (A) and clay fraction samples (B). Sample D43 is located stratigraphically below the Late Permian event horizon (LPEH), samples D46-1a and D46-1c(Z) are between the LPEH and PTB, and sample E2-56 is above the PTB. A large 3.34-Å quartz peak is present in all samples shown. Abbreviations: calc = calcite, chl = chlorite, il = illite, plag = plagioclase, qtz = quartz.

weighed into silver boats and acidified *in situ* using 6% H₂SO₃. Average standard deviations were 0.09‰ and 0.05‰ for the δ^{13} C of USGS-24 and δ^{15} N of IAEA-N1, respectively, and 0.2‰ and 0.4‰ for the δ^{13} C and δ^{15} N of unknowns, respectively. Isotopic results are reported relative to V-PDB (δ^{13} C) and air (δ^{15} N).

Rare earth elements were quantified by Dynamic Reaction Cell Inductively Coupled Plasma Mass Spectrometry (PerkinElmer DRCII ICP-MS) at Arkansas State University. Fifty milligrams of powdered sample were completely dissolved by acid digestion (Murray and Leinen, 1993). Samples were digested under clean-room conditions using Savillex digestion bombs and a digestion block with a combination of concentrated ultrapure HF and HNO₃ acids. Samples were repetitively dried down after digestion using aliquots of HNO₃ to remove any residual HF before analysis. Finally, H_2O_2 (30%) was added to ensure complete oxidation of refractory material. Yttrium was added as an internal spike to quantitatively monitor yield throughout digestion and analysis (>95%). Subsamples (three splits per sample) were diluted within range of the calibration standards (1–200 ppb). Concentrations were measured by external calibration with internal standardization (monitored mass 115In). The DRCII was operated in peak jumping mode with



Fig. 4. Correlation coefficients between elemental concentrations and model mineralogies (Fig. 2B), arranged by lithology. The 5% and 1% confidence intervals for 18 degrees of freedom are shown at top.

reaction cell gas (NH₃) set to 0.8 mL min⁻¹. NH₃ reaction cell gas removed potential isobaric oxide-REE interferents, such as BaO on Eu, from the sample stream (Feldman et al., 1999; Kishi et al., 2004). Most of the REEs are free of isobaric interferences; however, we monitored multiple isotopes as an additional check of isobaric interference (Hodge et al., 1998). REEO+/REE+ ratios measured by the DRC II are consistently below 0.2%. Precision, as determined from triplicate analyses of samples beginning with the original sample weighing, is generally < 2% for the REEs. We used SDO-1 to assess precision with this reference standard processed in the same way that samples were processed. Leastsquare regression was applied with goodness of fit (r^2) greater than 0.999 for all analytes. Measurement conditions, detection limits, and precision data (relative standard deviation from repeated measurement of SDO-1, % RSD) for each element are given in Table 1. Calibration standards and SDO-1 were analyzed after every six samples.

Magnetic susceptibility (MS) measurements were performed using a high-sensitivity susceptibility bridge at Louisiana State University. The susceptibility bridge was calibrated using standard salts for which values are reported in Swartzendruber (1992) and the Handbook of Physics and Chemistry (2004), and it was crosscalibrated against a KLY-3S Kappa Bridge. Reported MS values represent the mean of three measurements in units of m³ kg⁻¹; SI units, calculated using an assumed sample density of 2700 kg m⁻³, are also given to facilitate comparisons with MS data from other studies.

4. Results

4.1. Mineralogic and chemostratigraphic patterns

The main mineral phases in the study section are quartz and illite with smaller quantities of chlorite and plagioclase; calcite is locally abundant, especially in Bed D46 (Fig. 3). The clay fraction consists largely of illite with subordinate amounts of chlorite and quartz. The pattern of stratigraphic variation in the dominant mineral phases estimated from Eqs. (1), (2) and (3) (Fig. 2B) is entirely consistent with field descriptions of the study section (Baud et al., 1996; Brookfield et al., 2003; Wignall et al., 2005). Beds D43–D45 consist of argillaceous quartz siltstones or sandstones, Bed D46 of sandy limestone and calcareous quartz sandstone, and Units E1 and E2 of silty shales with local interbeds of sandy limestone (e.g., Beds E1-47y, E1-48x, E2-60).

Magnetic susceptibility (MS) values vary in the range of 0.5 to 4.0×10^{-7} kg m⁻³ with no well-defined stratigraphic trend (Fig. 2C). There is a positive correlation between MS and carbonate-rich horizons such as beds D46-1Cy, D46-1A, and E1-48x. This pattern is unusual because calcite is a diamagnetic phase that typically yields weak negative susceptibility when placed in a magnetic field (Ellwood et al., 2000). However, the calcite-rich horizons at Guryul Ravine are fossil concentrations produced by winnowing (Brook-field et al., 2003), hence they are likely to contain paramagnetic heavy minerals that may contribute to a higher MS signal (Ellwood et al., 2000). The presence of



Fig. 5. REE plot showing degree of enrichment relative to average shale (shale*), calculated as $[REE/Al]_{sample}/[REE/Al]_{shale}*$, where $Al_{shale}*=8.95\%$. Sholkovitz (1990) demonstrated that HF digestion techniques commonly fail to liberate 20–60% of MREEs and HREEs, a problem that afflicts many older datasets, whereas fusion techniques generally result in quantitative yields for all REEs. For this reason, we used Sholkovitz et al.'s (1999) estimates of average REE abundances in shales (B, upper line; values in ppm) in preference to the NASC (Gromet et al., 1984). Because this normalization procedure resulted in an alternating high–low abundance pattern for MREEs and HREEs for samples of the present study (A; only three examples shown), we modeled correction factors (B, middle line) to yield new estimates of average REE abundances in shales (B, lower line; values in ppm), which were then used for normalization of the study samples (C). Values of sample/shale* >1 indicate REE enrichment relative to average shale, whereas values <1 indicate REE depletion.

heavy minerals in the carbonate-rich horizons is supported by elemental correlations (Fig. 4) and REE concentration data (Fig. 5).

Total organic carbon (TOC), total nitrogen (TN), and total phosphorus (TP) concentrations are low (mostly <1%) throughout the section (Fig. 2D). TP exhibits significant positive covariation with TOC in Units D and E1 (r=+0.60, $p(\alpha)$ <0.05; Fig. 4), suggesting a dominantly organic source. Molar C_{org}:N ratios are low (5:1 to 10:1), suggesting a dominantly marine provenance for the organic matter, and molar C_{org}:P ratios are low (1:1 to 3:1), suggesting strong diagenetic retention of organic P within the sediment. Total sulfur (TS) concentrations, although low (<0.25%), covary positively with TOC in Units D and E1 (r=+0.60, $p(\alpha)$ < 0.05; Fig. 4), consistent with a pyrite host phase precipitated via bacterial sulfate reduction (Wignall et al., 2005). Fe is present in relatively large amounts (4.8± 2.5%) through most of the section (Fig. 2E). It exhibits positive covariation with both TP (r=+0.62; $p(\alpha)$ < 0.01) and TS (r=+0.43, $p(\alpha)$ <0.05; Fig. 4), suggesting that the availability of detrital Fe may have controlled the retention of remineralized organic P through Fe redox cycling within the sediment (Algeo and Ingall, in press) as well as pyrite formation (e.g., in reducing sedimentary microenvironments).

Zr and the REEs (rare earth elements, i.e., the 14member lanthanide series) exhibit pronounced stratigraphic variation in their concentrations, both having strong peaks in Bed D46 (Fig. 2F). The Zr peak is about five times the background concentrations, whereas the REE peak is three orders of magnitude greater than



Fig. 6. (A) Ce/Ce* and (B) Eu/Eu* versus clay fraction. Ce/Ce* ratios are independent of lithology, as shown by lack of significant covariation with the clay (r=-0.08), quartz (r=+0.34), and carbonate fractions (r=-0.03; $p(\alpha)>0.05$). Eu/Eu* ratios are lithology dependent, with positive anomalies associated with the clay fraction (r=+0.82; $p(\alpha)<$ 0.01). This difference is significant because it suggests that Ce/Ce* ratios may have been controlled by environmental factors, i.e., watercolumn redox conditions (see text for discussion). Mineralogic fractions calculated per Eqs. (1), (2) and (3) of text.

background levels (note log scale). The REEs covary strongly with Zr (r=+0.77 to +0.89, $p(\alpha)$ <0.01) as well as with Y and Sc (Fig. 4), suggesting a common host phase, perhaps heavy minerals (e.g., Hoskin and Ireland, 2000; Bouch et al., 2002). The REEs exhibit three different distribution patterns (Fig. 5): (1) moderately to strongly REE-enriched samples with a flat to weakly HREE-depleted distribution, typified by samples from Bed D46 (group 1); (2) moderately REE-depleted samples exhibiting strong HREE depletion, typified by samples from Bed D45 and Unit E1 (group 2); and (3) strongly REE-depleted samples exhibiting MREE enrichment, typified by the remaining samples (group 3). Some groups 1 and 2 samples are characterized by a positive Ce anomaly (Ce/Ce*) but no Eu anomaly (Eu/

Eu*), whereas most group 3 samples are characterized by a positive Eu anomaly but no Ce anomaly. Stratigraphically, positive Ce anomalies are associated with Beds D46-1, E1-47, and E1-50 to E2-53, which exhibit maximum Ce/Ce* ratios of 1.90, 1.37, and 1.44, respectively (Fig. 2G). No relationship to sample lithology is apparent (Fig. 6A), which may indicate that Ce/Ce* ratios represent a hydrogenous (seawater) signal. Stratigraphically, positive Eu anomalies are found in most samples above the Late Permian event horizon (LPEH) but in only one below it (Fig. 2H), hence mainly in the comparatively shaly Khunamuh Formation. Eu/Eu* exhibits a strong relationship with the clay fraction (Fig. 6B; r=+0.82, $p(\alpha) < 0.01$) and with elements such as K. Ti, and Ba that are hosted by the clay fraction (r = +0.74 to +0.85, $p(\alpha) < 0.01$; cf. Fig. 4), from which it can be inferred that Eu/Eu* values reflect clay-mineral provenance rather than a hydrogenous signal (cf. Bhandari et al., 1992).

Organic carbon δ^{13} C ranges from -23.6% to -27.9%, and organic δ^{15} N values from -2.0% to +4.5% (Fig. 2J). Although the $\delta^{13}C_{org}$ values are consistent with both marine and terrestrial sources of organic matter, the δ^{15} N values favor a predominantly marine provenance (White, 2001), as inferred above from molar Corg: N ratios. Whereas organic δ^{15} N values exhibit no overall stratigraphic trend, organic carbon δ^{13} C values exhibit a trend toward more ¹³C-depleted values upsection that is similar to the trend observed in the carbonate δ^{13} C record (Fig. 2K; Baud et al., 1996). The first negative excursion in both the organic carbon and carbonate δ^{13} C records (C1) is found in Bed D45, ~6 m below the PTB and ~ 3.3 m below the Zewan-Khunamuh formation contact. However, both C-isotopic records "recover" to near their Upper Permian baseline values before the onset of a large, sustained negative shift at the formation contact, which represents the global LPEH. Covariation between organic carbon and carbonate δ^{13} C values is significant (r=+0.84; p(α)< 0.01), and the mean difference between paired measurements is 25.2‰ (Fig. 7). Carbonate δ^{18} O values exhibit only limited variation within the study section, ranging from about -9.8% to -11.6% (Fig. 2K), values consistent with diagenetic recrystallization at moderate burial temperatures (e.g., Algeo et al., 1992).

Elemental and isotopic abundances exhibit pronounced relationships to the principal host mineral phases of the study section, as determined from correlation coefficients (Fig. 4; $p(\alpha) < 0.01$ for all *r* values cited below). Some of these relationships are expected, such as correlations of K and Ti with illite (r=+0.97 and +0.92, respectively) and Ca and Sr



Fig. 7. Covariation between $\delta^{13}C_{org}$ and $\delta^{13}C_{carb}$. Shown in the upper left are the regression line equation, the correlation coefficient, and the mean difference between paired $\delta^{13}C_{org} - \delta^{13}C_{carb}$ analyses for this dataset.

with carbonate (r=+0.99 and +0.94, respectively). The strength of these correlations serves to validate the results of the model mineralogic calculations of Eqs. (1), (2) and (3) (Fig. 2B). Other relationships are less intuitive and, hence, provide insights regarding the characteristics of the study section. The REEs and Zr exhibit strong relationships to quartz (r = +0.66 to +0.78 and +0.62, respectively), implying an association between coarser siliciclastics and REE-bearing heavy minerals (cf. Stummeyer et al., 2002). The lack of significant correlations between the REEs and TP suggests little association of the former with phosphatic minerals of detrital or authigenic provenance. It is more likely that the REEs are hosted by heavy minerals such as zircon, sphene, or allanite (cf. Hoskin and Ireland, 2000; Bouch et al., 2002; Yang et al., 2002). TOC and TN exhibit strong relationships to illite (r=+0.66 and +0.91, respectively), suggesting that organic matter accumulated mainly in the shalier beds. The exceptionally strong association of TN with illite may indicate that remineralized organic N was preferentially taken up by clay-mineral phases. TP and Fe exhibit somewhat weaker relationships to illite (r=+0.48 and +0.51,respectively), which is consistent with an organic P source and with subsequent complexation of remineralized P with clay-bound Fe-oxyhydroxides. Some trace metals (e.g., V, Ni, Cu, Ge, and Cr) are associated with illite also. The low total concentrations of these metals make it likely that they are mainly of detrital provenance, rather than a hydrogenous fraction taken up by sedimentary organic matter under reducing conditions.

4.2. Correlation with other PTB sections

Many Permian-Triassic boundary sections exhibit a shift in their C-isotope records of -3 to -8% between the LPEH and the earliest Triassic parvus zone (Fig. 8; Baud et al., 1989, 1996; Atudorei, 1999; Jin et al., 2000; Krull and Retallack, 2000; Twitchett et al., 2001; Krull et al., 2004; Richoz, 2004; Algeo et al., 2007-this volume; Horacek et al., 2007-this volume). At Guryul Ravine, a large, sustained negative shift in both the organic carbon and carbonate δ^{13} C records (C3) commences at the Zewan-Khunamuh formation contact (=LPEH). This shift, which reaches a minimum in the lower *isarcica* zone ~ 5 m above the LPEH and ~ 3 m above the PTB, is correlative with the main C-isotopic shift observed in other PTB sections globally. The gradualness of this shift is an indication of the stratigraphic completeness of the PTB interval at Guryul Ravine; sections exhibiting an abrupt shift at the boundary are either incomplete or highly condensed (e.g., Wang et al., 1994; Jin et al., 2000; Cao et al., 2002; Krystyn et al., 2003). The size of the shifts in carbonate δ^{13} C (from +1% to -3.5% V-PDB) and organic carbon δ^{13} C (from -24‰ to -28‰ V-PDB) are similar (δ^{13} C ~ -4.0 to -4.5‰). Below the C3 shift are two transient negative C-isotopic excursions within Beds D45 and D46: C1 in the $\delta^{13} \hat{C}_{carb}$ record and C1–C2 in the $\delta^{13}C_{org}$ record (Fig. 8). However, both the organic carbon and carbonate δ^{13} C curves "recover" to near their Upper Permian baseline values before the onset of the sustained C3 shift. The fact that the carbonate δ^{13} C record shows a single shift where the organic carbon δ^{13} C record shows two may reflect the longer response time of the carbonate C-isotope system, which is modulated by the residence time of dissolved inorganic carbon (DIC) in seawater (~83 kyr; Berner and Berner, 1987).

The C-isotope records for Guryul Ravine exhibit similarities and differences with records from PTB sections in southern China and northern Italy (Fig. 8; Payne et al., 2004; Horacek et al., 2007-this volume). In all three sections, the negative shift across the PTB commenced at the LPEH and terminated at a δ^{13} C minimum in the Lower Triassic *isarcica* zone. Above the *isarcica* minimum (IM), all three sections exhibit a trend toward more ¹³C-enriched values that is terminated by an early Dienerian minimum (DM). Although the three C-isotope records are readily correlatable, there are some important interregional differences. First, the absolute δ^{13} C minimum coincides with the DM in the Guryul Ravine and southern China sections but with the IM in northern Italy; in the latter section, there is a



Fig. 8. C-isotope stratigraphy and correlation of the study section with PTB sections in South China (Payne et al., 2004, their fig. 2, Dajiang section) and northern Italy (Horacek et al., this volume, their fig. 2; shown here is a composite of the Pufels-Bulla and L'Om Picol/Uomo sections, spliced as indicated in the mid-Dienerian). LPEH = Late Permian event horizon; PTB = Permian–Triassic boundary; IM = *isarcica* minimum in δ^{13} C; DM = basal Dienerian minimum in δ^{13} C; C1–C3=start of negative C-isotope excursions in the Upper Permian (C3=LPEH). For Guryul Ravine, carbonate δ^{13} C data (open symbols) are from Baud et al. (1996) and organic carbon δ^{13} C data (solid symbols) from this study. Lower-right inset: correlation of the study section with the Nhi Tao, Vietnam PTB section (Algeo et al., this volume). No detailed conodont work has been undertaken at Nhi Tao; the biozones shown are based on MS correlation to Meishan D.

strong trend within the Lower Triassic toward more ¹³C-enriched values, and the DM is more than 4‰ enriched in ¹³C compared with the IM. Second, although the overall pattern of C-isotopic variation is fairly similar in the Guryul Ravine and southern China sections, δ^{13} C values in the former are consistently about 2‰ lighter than those in the latter. The significance of these observations is that, while there is clearly a global component to Lower Triassic C-isotope records, a strong regional signal also exists that may carry important information from which contemporaneous controls on global C-cycle dynamics may be decipher-

able. More high-resolution C-isotope records similar to those shown will be needed to work out the details of such controls.

Further insights can be gained from comparison of the Guryul Ravine C-isotopic records with the carbonate δ^{13} C record from Nhi Tao, Vietnam (Fig. 8, inset; Algeo et al., 2007-this volume). Both sections appear to exhibit two transient negative C-isotope excursions (C1–C2) below the LPEH, within the upper part of the Late Permian *changxingensis* zone (n.b., only part of C1 was sampled in the Nhi Tao section; cf. Hansen, in press, his fig. 2). This observation is important because it demonstrates that (1) there were multiple perturbations to the global carbon cycle prior to the LPEH, the horizon that represents the major end-Permian disturbance and biotic crisis, and (2) these perturbations were not sustained but, rather, followed by recovery of the global carbon cycle toward pre-existing Upper Permian conditions before the major disturbance at the LPEH. The correlation framework shown in Fig. 8 confirms that the Guryul Ravine section is relatively condensed above the basal Triassic parvus zone and/or that the Nhi Tao section is relatively expanded through this same interval. This is significant because it demonstrates clearly the extraordinary level of chemostratigraphic detail yielded by the Nhi Tao section: the multiple submeter-scale $\delta^{13}C$ cycles observed here are either not present or have not yet been resolved at Guryul Ravine and other PTB sections.

The MS records of PTB sections commonly exhibit a sharp increase in MS values at or just above the LPEH (e.g., Hansen et al., 2000; Algeo et al., 2007-this volume; Ellwood, unpubl. data). The Guryul Ravine MS record is unusual in this regard (Fig. 2C). First, the majority of samples yield MS values $> 1 \times 10^{-7}$ kg m⁻³, considerably higher than typical for other PTB sections. Second, although there is an increase in MS values above the LPEH, it is largely limited to Bed D46-1C and, hence, is transient in nature. The cause of the anomalous character of the Guryul Ravine MS record is not certain but might be related to the lithologic heterogeneity of the section and/or to concentrations of heavy minerals in some beds. The latter inference would imply that winnowing, leading to concentration of heavy minerals with high MS values, was strongest in Bed D46-1 and Unit E1, which is the stratigraphic interval associated with evidence of a major eustatic rise (see Section 5.2).

5. Discussion

5.1. Environmental conditions

Oceanic deep-waters are considered to have been widely oxygen-depleted during the Late Permian and Early Triassic (Wignall and Twitchett, 1996; Isozaki, 1997; Hotinski et al., 2001; Zhang et al., 2001; Wignall and Twitchett, 2002), and some contemporaneous shallow-marine environments may have experienced at least transiently anoxic conditions (Wignall and Hallam, 1992; Woods et al., 1999; Wignall and Twitchett, 2002; Algeo et al., 2007-this volume). PTB or Early Triassic marine anoxia has been inferred for several sections from the northern Gondwanan margin. In the Spiti valley, located in Himachal Pradesh ~ 500 km east of Kashmir, Shukla et al. (2002) inferred anoxia at the PTB on the basis of a small increase in U concentrations (from ~4 to ~8 ppm) and a positive Ce anomaly (~1.3), but these anomalies may be too small and the number of samples analyzed too few to make any reliable inferences. At Guryul Ravine, Early Triassic benthic anoxia was inferred on the basis of a change from non-laminated, pyrite-poor mudstones to laminated shales rich in fine pyrite framboids of probable syngenetic origin ~1 m above the base of the Khunamuh Formation (Wignall et al., 2005).

Interpretation of paleoredox conditions in the Guryul Ravine section requires careful parsing of the geochemical data generated in this study. Total organic carbon and total sulfur concentrations are uniformly low throughout the section (<0.6% and <0.25%, respectively; Fig. 2D-E), as are the concentrations of redoxsensitive trace-elements such as Mo (<1 ppm), U (<3 ppm), V (122±52 ppm), Zn (39±20 ppm), and Cr $(100\pm 56 \text{ ppm})$. The latter values are consistent with a predominantly detrital provenance for these traceelements (Taylor and McLennan, 1985). However, the low concentrations of all of the above elements may reflect a combination of low initial TOC content owing to facies character (e.g., in the coarser-grained Unit D beds) and loss of organic carbon and Corg-hosted trace metals through catagenetic reactions. Although specific information regarding the maximum burial depth and temperature of the study section is not available, much of the Tethyan sedimentary succession in Kashmir has experienced greenschist facies metamorphism (Herren, 1987; Dèzes, 1999).

Ce/Ce* ratios have the potential to yield paleoredox information regardless of the thermal maturity of the sediments if the REEs are hosted mainly by the finegrained siliciclastic rather than the organic fraction of the sediment. This is true for Guryul Ravine (Fig. 6B, see Section 4.1) where, furthermore, Ce/Ce* ratios are independent of lithology and, hence, likely to represent a hydrogenous (seawater) signal (Fig. 6A). Positive Ce anomalies are indicative of watermass anoxia owing to enhanced scavenging of aqueous Ce(III) under reducing conditions (Sholkovitz et al., 1994; Kato et al., 2002), although negative Ce anomalies can be encountered in suboxic settings in which aqueous Ce(III) has been depleted (Kakuwa and Matsumoto, 2006). At Guryul Ravine, positive Ce/Ce* ratios in Beds D46-1 (1.90), E1-47 (1.37), and E1-50 to E2-53 (1.44) may record several episodes of anoxia, the first being the most intense (Fig. 2G). The first two Ce/Ce* peaks, which straddle the LPEH, are separated by only 30 cm and



Fig. 9. Sequence stratigraphic interpretation of the Guryul Ravine PTB section. A major eustatic event was initiated at the base of Bed D46: an initial regression (1) prior to transgression was inferred by Brookfield et al. (2003), although the present study favors transgression alone (2). The eustatic event resulted in strong winnowing in Bed D46 and Unit E1, and deepening led to sedimentation starvation and stratigraphic condensation of the overlying units. The most rapid phase of deepening occurred prior to the Permian–Triassic boundary (PTB), hence during an interval of ~200–400 kyr (based on the timescale of Gradstein et al., 2004; cf. Kozur, 2003; Bachmann and Kozur, 2004). C1, C2, and C3 represent negative C-isotope excursions (Fig. 8); the largest (C3) was coincident with the Late Permian event horizon (LPEH). The main extinction event at Guryul Ravine is in the middle of Unit E1 (Ext-1), although secondary events are found at the base of Unit E2 (Ext-2) and, possibly, the tops of Beds D44 and D45 (ext?) (Shen et al., 2006).

thus might represent pulses of a single anoxic event associated with the end-Permian biotic crisis. The third Ce/Ce* peak straddles the PTB, ~ 2.6 m higher in the section, and, hence, probably represents a separate event. This observation is potentially significant because the Guryul Ravine section is characterized by a secondary extinction event at this level (Fig. 9; see Section 5.2; Shen et al., 2006).

The complex character of the end-Permian mass extinction makes it likely that multiple factors contributed to biotic stress in the marine ecosystem. However, the association of this extinction event with evidence of anoxia suggests a possibly important role for the latter in the biotic kill-off. At Guryul Ravine, this association is evidenced in the relationship between positive Ce anomalies and extinction events. The evidence for this association is strong also in sections from southern China and Vietnam (Grice et al., 2005; Xie et al., 2005; Algeo et al., 2007-this volume). Wignall and Newton (2003) inferred diachronous onset of anoxia ranging from the PTB to the late Griesbachian in sections from northern India, Tibet, and western Canada, on the basis of which they discounted the importance of anoxia as a causal factor in the end-Permian mass extinction. There is, however, an important distinction to be drawn between long-term anoxia as reflected in general facies character (as documented by Wignall and Newton, 2003) and short-term anoxic events that may be effective at causing mass die-offs while leaving only a subtle geochemical signature in the sediment. Influx of anoxic, sulfidic waters into shallow-marine areas may have been induced by upwelling (e.g., Kajiwara et al., 1994; Algeo et al., 2007-this volume), possibly in conjunction with upward migration of the oceanic chemocline (Kump et al., 2005).

5.2. Sequence and event stratigraphy

Many PTB sections contain a well-defined Late Permian event horizon (LPEH) characterized by collapse of the contemporaneous marine ecosystem and the appearance of diagnostic sedimentologic features (e.g., microbial framestones and inorganic carbonate precipitates such as synsedimentary seafloor cements and ooids) (Grotzinger and Knoll, 1995; Baud et al., 1997; Sano and Nakashima, 1997; Lehrmann, 1999; Jin et al., 2000; Ezaki et al., 2003; Lehrmann et al., 2003; Baud et al., 2005; Algeo et al., 2007-this volume). Such features, although generally best developed at the LPEH, sometimes appear or recur at higher stratigraphic levels within the Lower Triassic (e.g., Woods et al., 1999). The Guryul Ravine section is atypical in that the biotic crisis was not confined to a single horizon, and the sedimentologic features diagnostic of the LPEH are lacking. In this section, the biotic crisis appears to have begun as early as Beds D44 and D45 and continued through Bed E2-52 (Shen et al., 2006, their fig. 14), an interval of ~ 8 m representing $\sim 0.5-1.0$ Myr (based on the timescale of Gradstein et al., 2004). The level equivalent to the LPEH elsewhere is thought to be located at the Zewan-Khunamuh formation contact based on biostratigraphic correlations and the onset of a sustained negative C-isotope shift (C3; Fig. 8). However, the main extinction event (Ext-1) is located in the middle of Unit E1, about 1.0-1.5 m above this level, and a secondary extinction event (Ext-2) is present within Bed E2-52, just above the PTB (Fig. 9). The latter horizon may be correlative with a secondary extinction event in Bed 28 of the Meishan D GSSP (Jin et al., 2000; Xie et al., 2005). The apparent stepwise character of the extinction pattern at Guryul Ravine may reflect faciesrelated local extinctions, although the Signor-Lipps effect cannot be ruled out (Rampino and Adler, 1998).

The character of the facies change marking the Zewan-Khunamuh formation (Unit D-Unit E1) contact and its relationship to sea-level changes warrant discussion. Storm winnowing of the Guryul Ravine seafloor produced most of the thin carbonate shell beds present in Units D, E1, and (increasingly rarely) E2 (Brookfield et al., 2003). The most prominent winnowed shell bed is D46-1, which consists of amalgamated, roughly graded, hummocky cross-bedded shell layers that exhibit poor sorting and only limited abrasion and rounding of bioclasts. Within this bed, the biota changes upsection from a moderately diverse brachiopod-dominated assemblage to a low-diversity mollusc-dominated assemblage. Brookfield et al. (2003) interpreted Bed D46-1 as a "lagoonal" or inner-shelf deposit, which would imply substantial shallowing (sea-level regression; curve 1, Fig. 9). However, the lack of reworking of individual shell layers observed in this bed is typical of storm deposits in an outer-shelf or deep-ramp setting (Aigner, 1985; Saito, 1989; Nummedal, 1991; Brett, 1995), and the absence of a mud matrix can result from winnowing during sea-level rise (Kidwell, 1989; Kidwell and Bosence, 1991; Banerjee and Kidwell, 1991; Kidwell, 1993). High concentrations of Zr, REEs, Y, and Sc (Fig. 2F) may reflect a large heavy mineral fraction, providing further evidence of winnowing (e.g., Hoskin and Ireland, 2000; Bouch et al., 2002; Yang et al., 2002). Transgression may be supported by C-isotope data also: Beds D45 and D46 yield strongly ¹³C-depleted values, consistent with the influence of ¹³C-depleted deep-watermasses (Fig. 2J–K). Thus, the available evidence appears to favor a large sea-level rise commencing around the base of Bed D46-1 (curve 2, Fig. 9), marking this horizon as a major sequence boundary (cf. Shen et al., 2006).

Earlier studies inferred a major eustatic fall at the PTB (Newell, 1967; Holser and Magaritz, 1987; Hallam, 1992; Erwin, 1993), but more recent research favors a eustatic rise commencing at or close to the LPEH and continuing into the Early Triassic (Wignall and Hallam, 1992, 1993; Hallam and Wignall, 1999). This suggests that that the sea-level rise beginning in the uppermost Permian at Guryul Ravine is mostly of eustatic origin (Fig. 9), although possibly reinforced by a tectonic component associated with rifting and thermal subsidence of the northern Gondwanan margin (Stampfli et al., 1991; Brookfield, 1993). The cause of the abrupt eustatic rise is unknown but might be linked to climatic warming, which would have led to thermal expansion of the global ocean by as much as ~ 20 m (Kidder and Worsley, 2004) and melting of any extant ice caps and mountain glaciers. Strong climatic warming following the LPEH is supported by rapid invasion of the southern mesothermal temperate zone (the transitional area between the Paleoequatorial and Gondwanan faunal provinces to which the Guryul Ravine section belongs) by tropical/subtropical Tethyan faunal elements (Wignall and Newton, 2003; Shen et al., 2006). Simultaneous warming of high northern paleolatitudes has been inferred also (Beauchamp, 1994; Beauchamp and Baud, 2002).

One significant feature of the Guryul Ravine section is that the Late Permian sea-level event appears to have commenced during deposition of Bed D46-1 and, thus, predated the LPEH (Fig. 9). Provided that the onset of this event was due to climatic rather than tectonic factors, this implies that the process responsible for the sea-level rise was triggered not by the end-Permian disturbance that produced the LPEH but, rather, by earlier, smaller disturbances. These earlier disturbances may have been recorded in the organic carbon and carbonate C-isotopic records of the study section as excursions C1 and C2 (Figs. 8 and 9). The \sim 3.3 m interval between the first such excursion (C1) and the LPEH represents $\sim 200-400$ kyr (based on the timescale of Gradstein et al., 2004), an interval the duration of which renders a tectonic driver unlikely but that is consistent with eustatic forcing by catastrophic atmospheric warming, e.g., due to buildup of atmospheric CO_2 from massive volcanic eruptions or oxidation of seafloor or bog methane (Campbell et al., 1992; Krull and Retallack, 2000; Hansen, in press).

5.3. C-cycle dynamics

The cause(s) of the globally observed C-isotopic shift across the PTB (Baud et al., 1989; Magaritz and Holser, 1991; Atudorei, 1999; Hansen et al., 2000; Jin et al., 2000; Krull and Retallack, 2000; Twitchett et al., 2001; Sephton et al., 2002; de Wit et al., 2002; Pavne et al., 2004; Richoz, 2004; Hansen, in press) and of subsequent large excursions throughout the Lower Triassic (Payne et al., 2004; Korte et al., 2005) have been widely speculated upon. Possible mechanisms include: (1) biomass destruction (Erwin, 1994); (2) decreased primary productivity in surface waters and reduced export of OM to deep-waters (e.g., "Strangelove oceans," Kump, 1991); (3) changes in the fraction of sedimentary carbon buried as organic carbon (Broecker and Peacock, 1999; Payne et al., 2004); (4) release and oxidation of methane from seafloor clathrates or bogs (Krull and Retallack, 2000; de Wit et al., 2002); (5) upwelling of deep-ocean waters (Wignall and Twitchett, 1996; Isozaki, 1997); (6) oceanic eruption (Ryskin, 2003); (7) erosion of organic matter from continental-shelf sediments following eustatic regression (Holser and Magaritz, 1987; Baud et al., 1989; Retallack et al., 1996) or from soils following terrestrial deforestation (Sephton et al., 2005); and (8) volcanic CO₂ emissions (Campbell et al., 1992; Renne et al., 1995; Hansen, in press) (see reviews in Berner, 2002; Corsetti et al., 2005).

Several observations of the present study may assist in understanding controls on the Permo-Triassic global carbon cycle. First, interregional differences are evident in both the absolute values and intraformational trends displayed by Lower Triassic $\delta^{13}C_{carb}$ values (Fig. 8; see Section 4.2). Guryul Ravine is systematically depleted by $\sim 3-4\%$ relative to the sections in southern China, a difference that may reflect greater influence of ¹³Cdepleted deep-watermasses at the former locale. A diagenetic effect is possible, although it would require complete oxidation and uptake of $\sim 1.5-2.0$ wt.% TOC by secondary carbonate precipitates to effect this shift. Whereas both the Guryul Ravine and southern China sections exhibit relatively constant $\delta^{13}C_{carb}$ values through much of the Griesbachian followed by an absolute minimum in the early Dienerian, the sections in northern Italy exhibit an absolute minimum in the early Griesbachian *isarcica* zone followed by a pronounced shift toward more positive values upsection into the Dienerian (Fig. 8). Although various explanations are possible, the most likely may be local variation in watermass chemistry within the semi-restricted Muschelkalk Sea of the Germanic Basin (Korte et al., 2005).

Second, paired organic carbon and carbonate $\delta^{13}C$ analyses exhibit a nearly constant difference ($\delta^{13}C_{carb-org}$) of $\sim 25\%$ at Guryul Ravine (Fig. 7), suggesting that these records have indeed recorded perturbations to the global carbon cycle rather than purely local influences. The magnitude of this offset is less than that reported for eastern Greenland (~20%; Twitchett et al., 2001) but greater than those reported for southern China ($\sim 28\%$); Krull et al., 2004) and northern Italy (~30%; Sephton et al., 2002; n.b., based on alkenone δ^{13} C, which may be depleted several per mille relative to bulk organic δ^{13} C). This range of δ^{13} C_{carb-org} values appears to be too large to be entirely due to regional variation in the diagenesis of organic matter, which can alter the δ^{13} Corg values within a given succession (Freeman, 2001; Freeman and Pagani, 2005). If at least partly due to primary environmental controls, variation in $\delta^{13}C_{carb-org}$ may reflect interregional differences in primary productivity rates and photosynthetic fractionation factors (ε). For example, the smaller $\delta^{13}C_{carb-org}$ values observed at Guryul Ravine and in eastern Greenland might reflect enhanced upwelling and primary productivity rates at higher paleolatitudes (\sim 35–40°S and \sim 35–40°N, respectively) relative to the tropical ($\sim 10-15^{\circ}N$) Chinese and Italian sections (see Algeo et al., 2007-this volume, their fig. 2).

Third, the Guryul Ravine section exhibits evidence of two negative C-isotopic excursions within the upper changxingensis zone but below the LPEH (Fig. 8), and one or more such excursions are known from a number of other PTB sections (Magaritz et al., 1988; Jin et al., 2000; Krull et al., 2004; Algeo et al., 2007-this volume). At Guryul Ravine, these excursions appear to be associated with the onset of both a major eustatic rise and the Late Permian marine biotic crisis (Fig. 9). If these relationships are correct, they have important implications for causal scenarios for the PTB. In particular, they suggest that the PTB crisis did not begin at the LPEH but, rather, that smaller events of similar character initiated biotic and environmental change ~ 200 to 400 kyr earlier, i.e., that whatever process was responsible for the LPEH was already operating but at lesser intensity. This is consistent with a volcanic trigger, in which early eruptions preceding the main eruptive phase resulted in some degree of climate change and upwelling intensity, but it is clearly inconsistent with a bolide model.

6. Conclusions

The Guryul Ravine Permian-Triassic boundary section is atypical in that events that are elsewhere compressed into a narrow stratigraphic interval around the Late Permian event horizon (LPEH) are distributed through a thicker interval in this section. This situation allows recognition of a sequence of discrete events that provide potentially important information about the character and cause(s) of the PTB. Two negative Cisotopic excursions are observed within the upper changxingensis zone but below the LPEH, the first one predating the LPEH by an estimated $\sim 200-400$ kyr. These excursions are associated with the onset of a major eustatic rise that continues into the Early Triassic and with minor extinctions that preceded the main biotic crisis. Their significance is as a possible record of the onset of environmental disturbances prior to the main end-Permian event, supporting an intrinsic mechanism such as volcanism and climate change rather than an extrinsic mechanism such as a bolide impact. The horizon at Guryul Ravine that is equivalent to the LPEH elsewhere, as determined from biostratigraphic and C-isotopic constraints, is within an interval of rapid eustatic rise characterized by a change from heavy mineral-rich calcareous quartz sandstones of the uppermost Zewan Formation (Unit D) to silty organic-rich shales of the lowermost Khunamuh Formation (Unit E). The PTB, as defined by the first occurrence of Hindeodus parvus, is located ~ 260 cm higher in the section, at the Unit E1–E2 contact. The Guryul Ravine section exhibits a stepwise extinction pattern, with the largest peak in the middle of Unit E1 and a secondary peak at the base of Unit E2, a pattern similar to that observed in the Meishan D GSSP.

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