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Causes of Permian/Triassic Mass Extinction at the Velebit Mt., Croatia: Geochemical and Isotopical Insights

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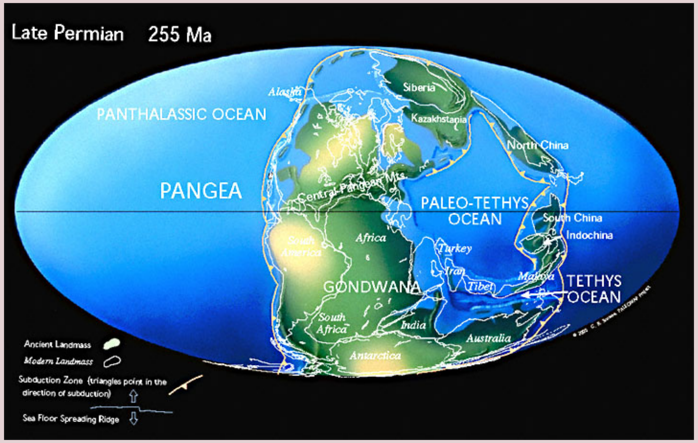
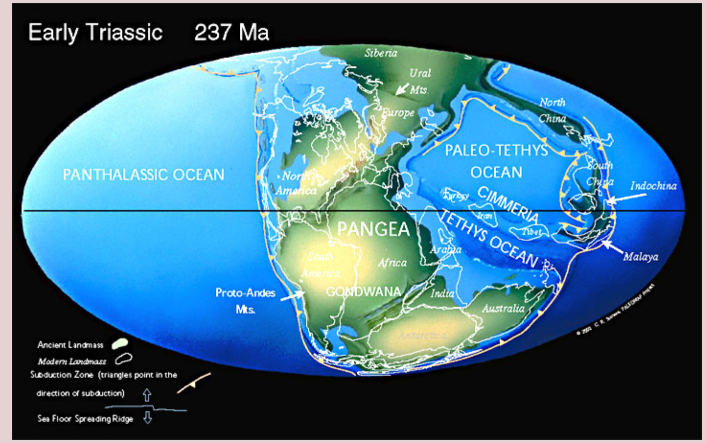
Permian-Triassic Boundary





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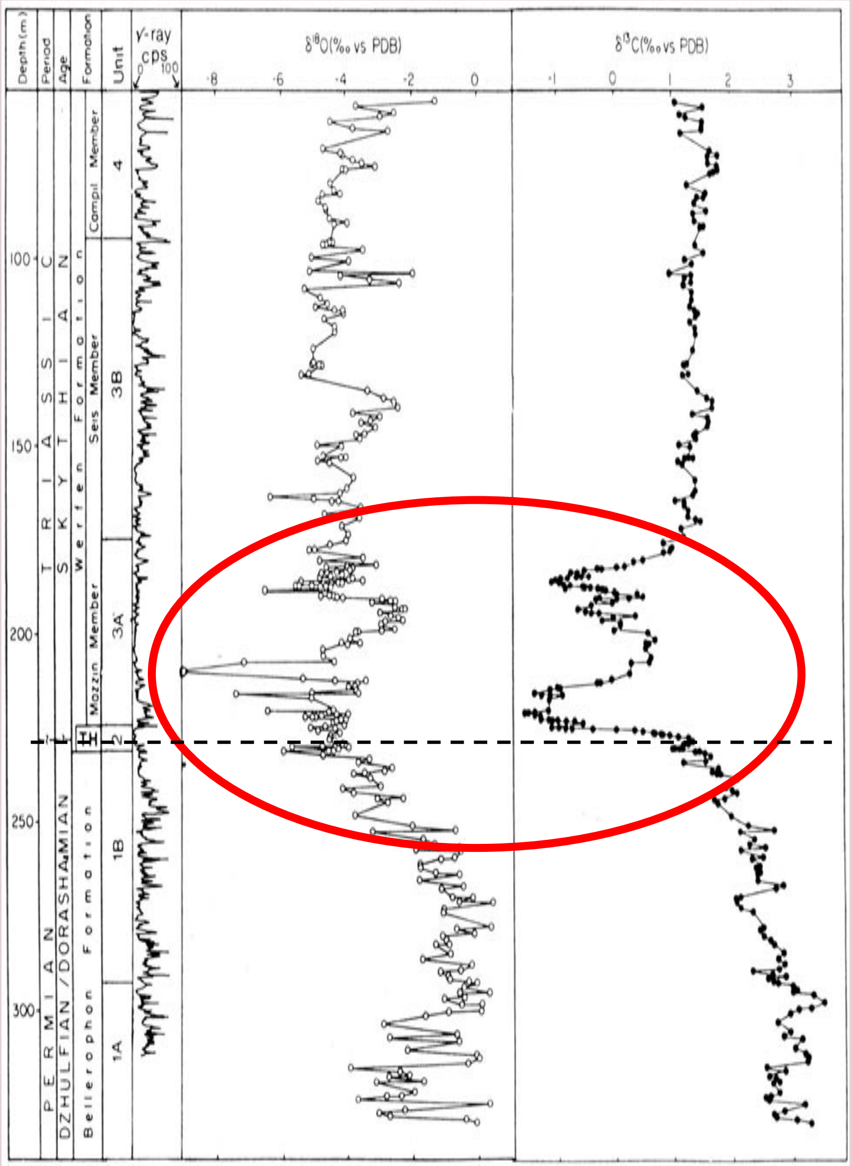
- Possible explanations for P/Tr mass extinction:
  - extra-terrestrial causes (bolide impact, supernova explosion);
  - massive flood basalt and pyroclastic volcanism;
  - environmental changes;
  - ocean stratification with high CO_2 concentrations in deep waters;
  - ocean anoxia;
  - destabilization of methane gas hydrates;
  - synergistic combination of these events.

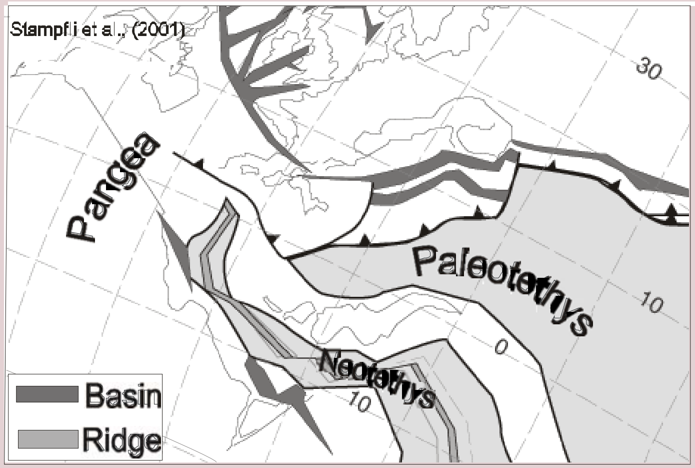
Major geochemical changes at the PTB

- Worldwide negative shift of $\delta^{13}C$ for inorganic and organic carbon.
- Less pronounced $\delta^{18}O$ isotopic shift.
- Changes in $\delta^{15}N$ isotopes.
- Sulfur, $\delta^{34}S$, isotope variations.
- Variations in strontium isotopes ($^{87}Sr/^{86}Sr$).
- Changes in concentration of redox sensitive elements.
- Ce and Eu anomaly.
- Changes in abundance and carbon isotope composition of biomarker hydrocarbons.



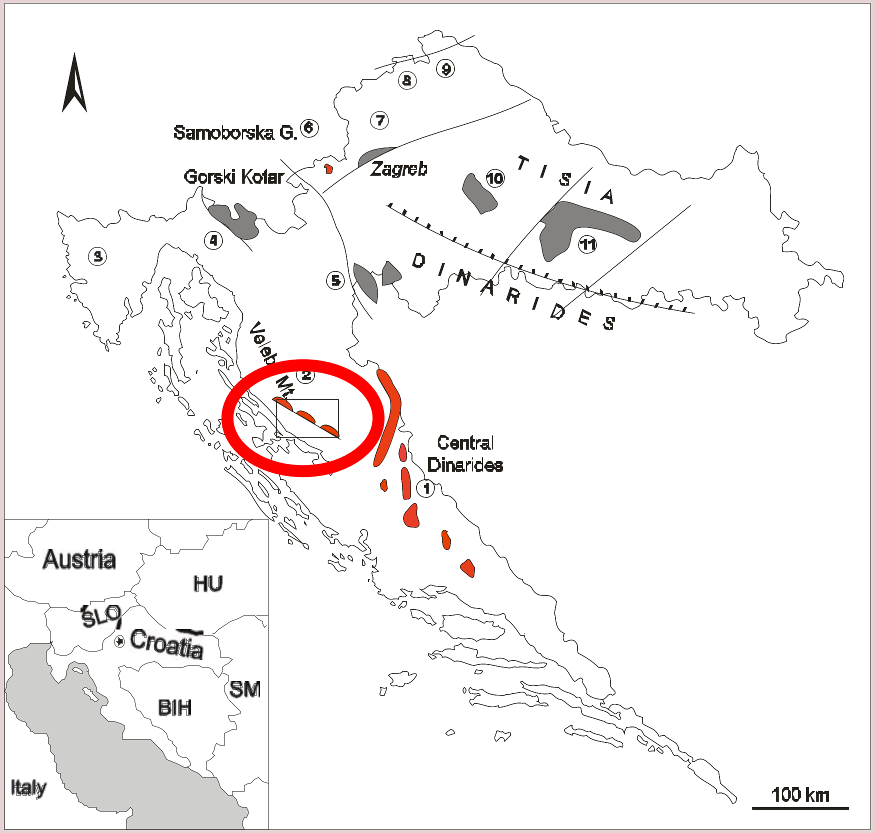
Holser et al. (1989)

Paleogeographic reconstruction and location

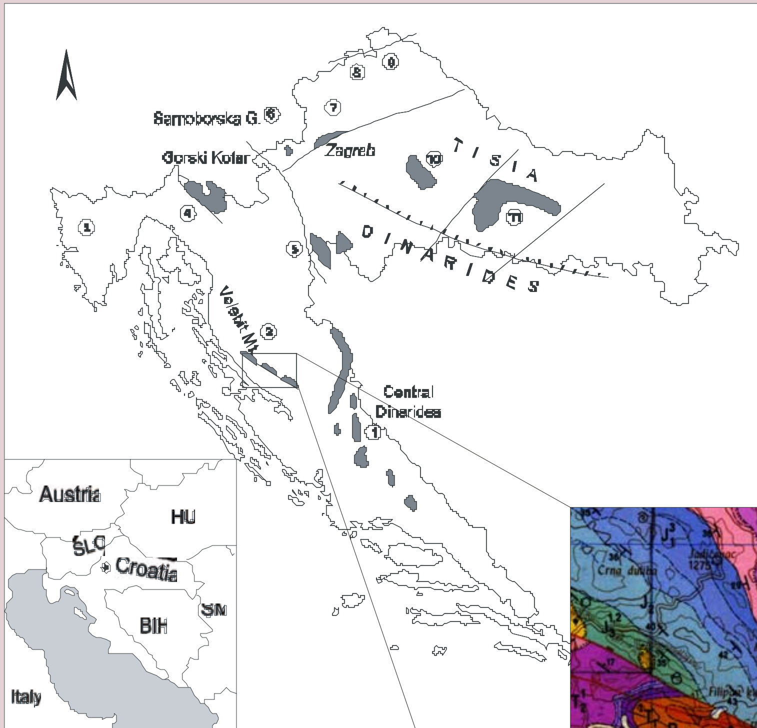


Paleogeographic reconstruction for the latest Permian (after Stampfli et al., 2001).

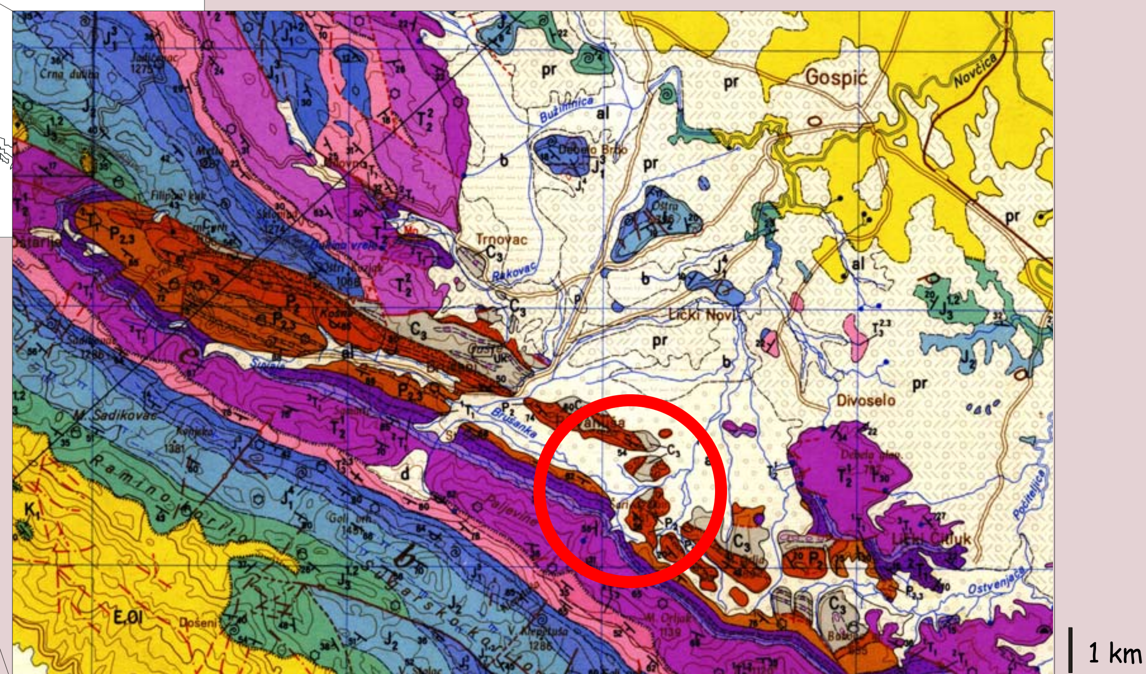
Schematic map of the Paleozoic areas in Croatia with position of the study area...



Geological map of the studied location

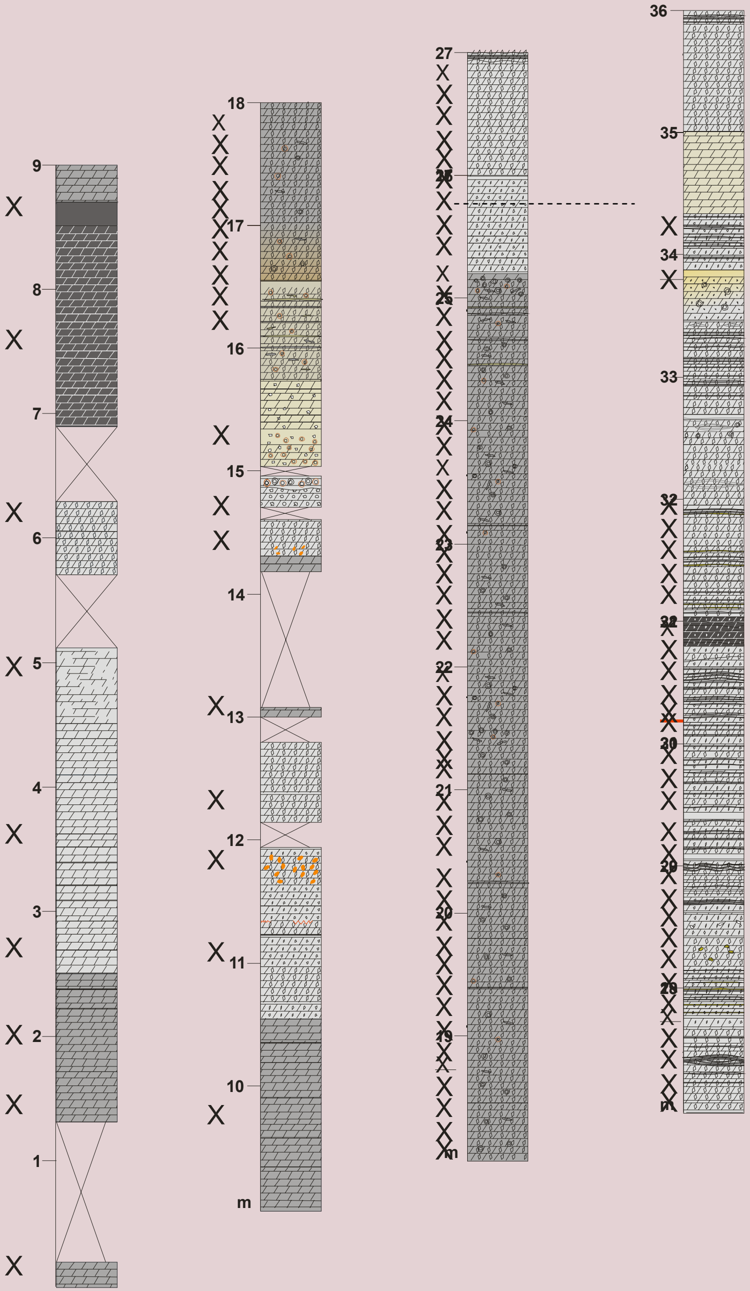


Studied P/Tr section is situated ~8 km SW from Gospić.



Sokač et al. (1974)

Lithostratigraphic units

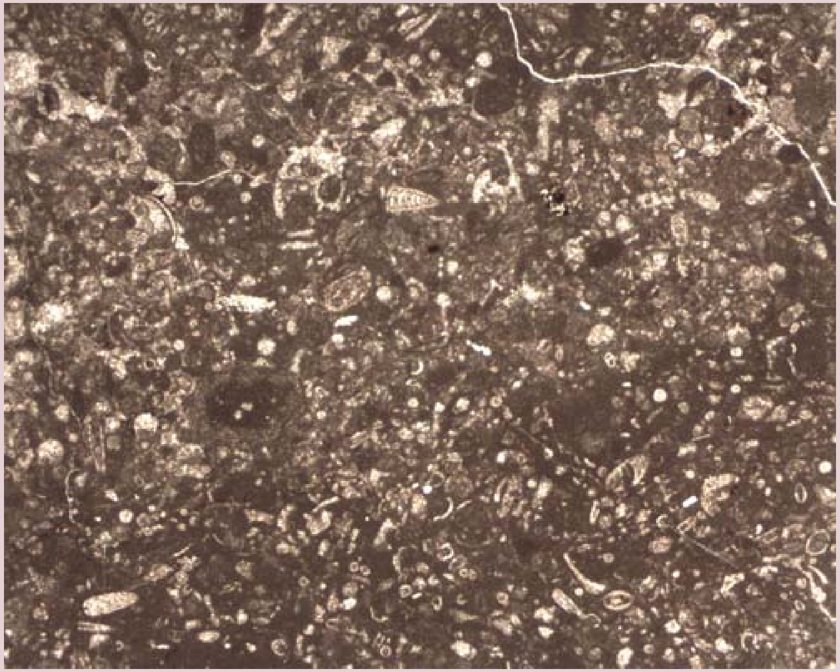


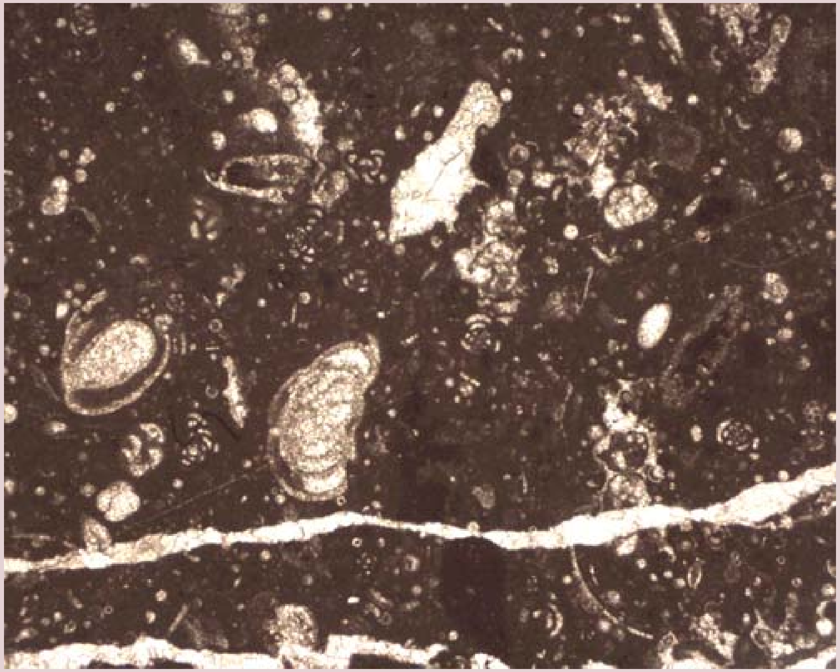
Permian/Triassic boundary in the Velebit Mt. area (**Rizvanuša section**) is located within a thick succession of early- and late-diagenetic dolomites, divided into two informal lithostratigraphic units: *Transitional Dolomite* and *Sandy Dolomite*.

Lithostratigraphic units (continued)

Transitional Dolomites are well-bedded, light- to dark-grey early-diagenetic dolomites, practically without any non-carbonate content.

Lithostratigraphic units (continued)



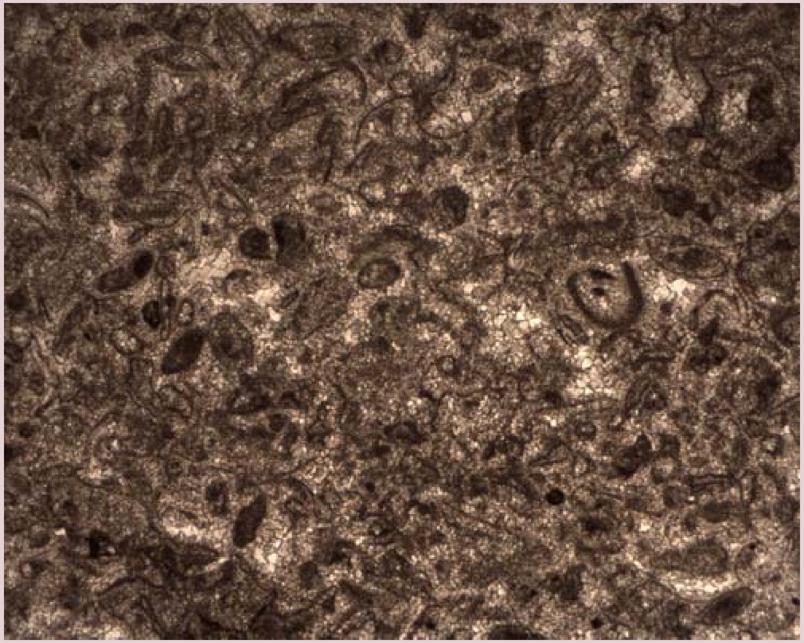


They are characterized by relatively rich fossil assemblage of organisms, some of them indicating stressed environments (*Solenoporaceae*, *Permocalculus*, *Earlandia*, *Ammodiscus*, *Glomospira*, *Pachyphloia*, *Geinitzina*, *Globivalvulina*, *Permodiscus*, *Staffella, Hemigordius*, Lagenidae...).

Lithostratigraphic units (continued)

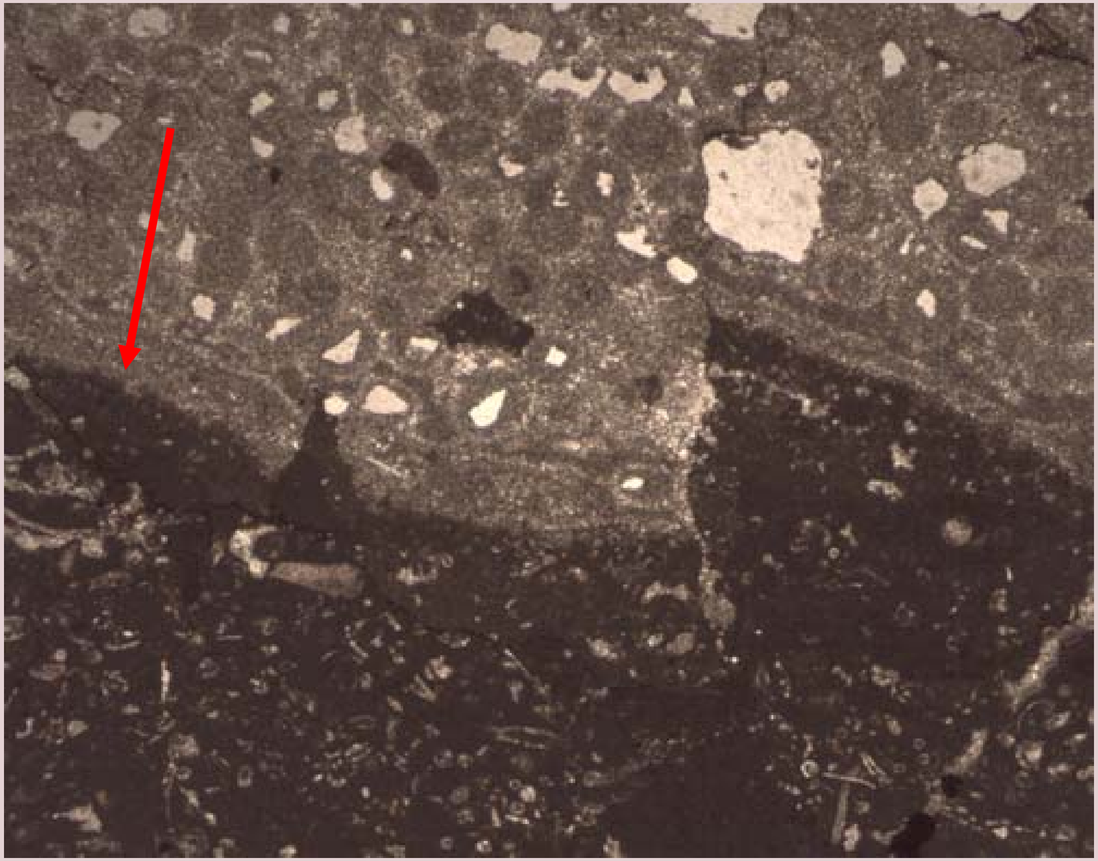
Sandy Dolomites are characterized by variable bedding (from laminated and thin-bedded to massive beds), yellowish to brownish colour, common quartz grains and mica flakes.

Microfacies

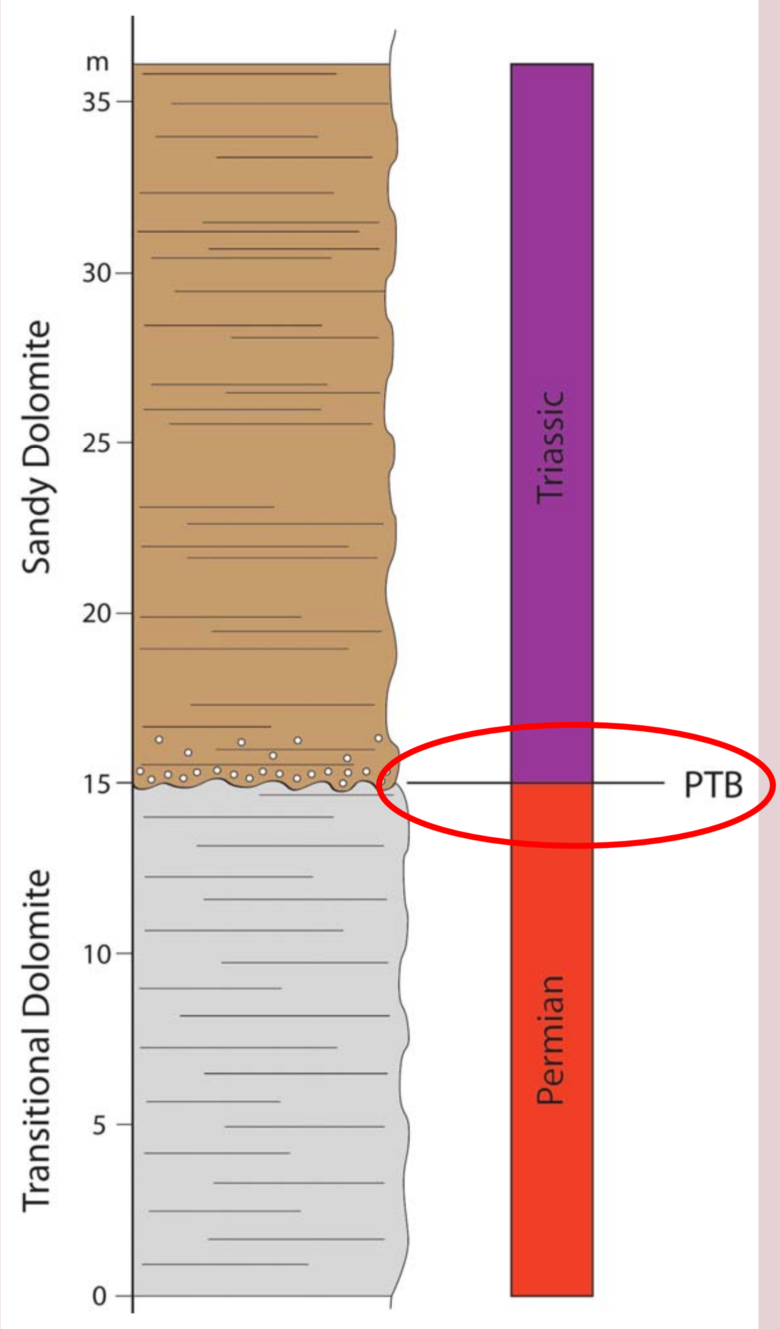


Within *Sandy Dolomites* fossil remains are very rare, as they contain only infrequent layers with probable microbial laminites and mollusc bioclasts.

Lithostratigraphic units (continued)



The boundary between two lithofacies units is sharp, erosional (up to several cm deep erosional features filled with clayey material, ooids, intraclasts and lithoclasts), indicating probable temporary emergence.



Traditionally, this boundary was considered as the Permian/Triassic Boundary (PTB).

Sampling

Initial sampling at the Rizvanuša section was performed in order to cover transition between two lithological units in detail.

After obtaining preliminary data on the approximate position of PTB, samples were taken at 20 cm interval, and close to the boundary at each few cm.

Methods

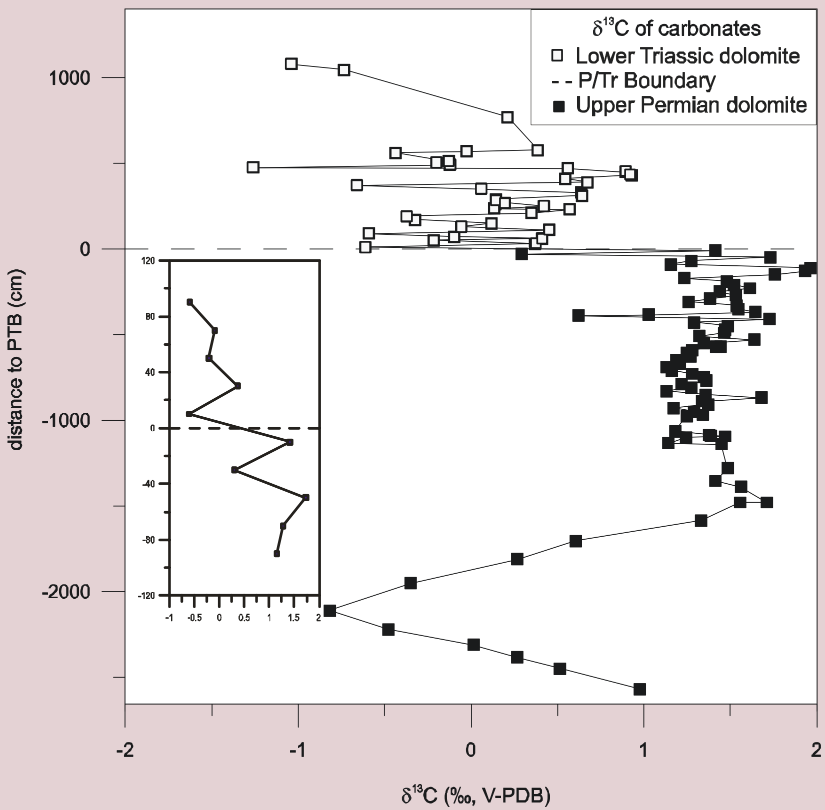
- C and O isotopes of carbonates: samples were analysed by Thermo Finnigan Gas Bench II connected to a Thermo Finnigan Delta Plus XL isotope ratio mass spectometer. The reaction temperature for dolomite was 90°C.

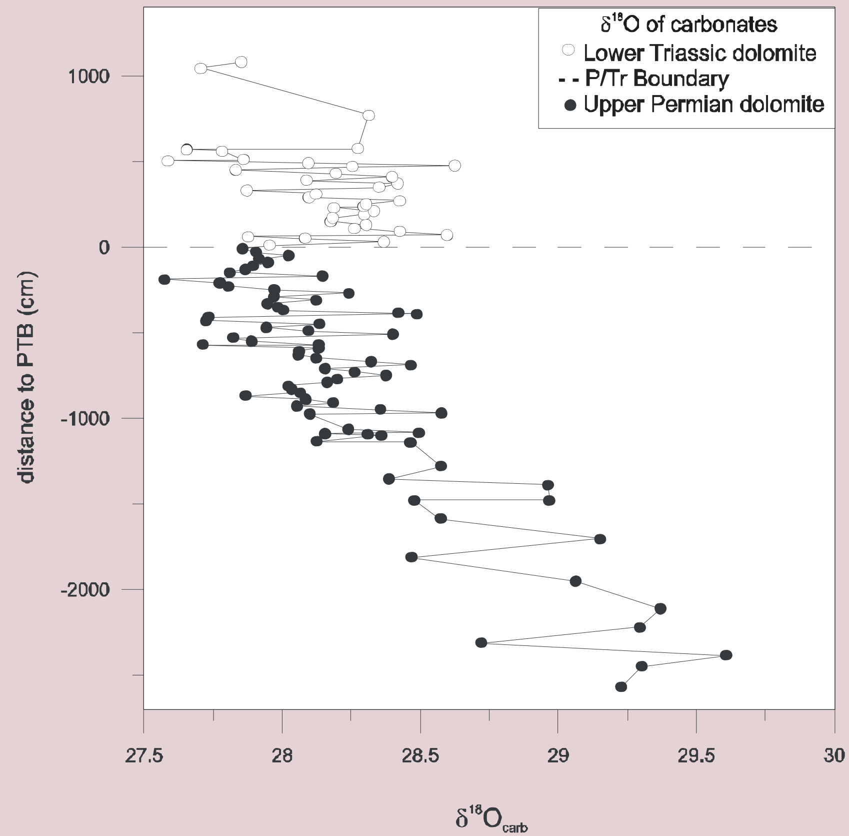
- Kerogen was isolated by HF–HCl treatment, and $\delta^{13}C_{ker}$ and $\delta^{15}N_{ker}$ values were determined using the Elemental Analyser connected to an Isotope Ratio Mass Spectometer (EA–IRMS).

- Chemical characterization of the saturated hydrocarbons was performed by an Agilent Technologies GC HP 6890 coupled to a HP 5973 quadrupole mass selective detector.

- Major, minor, trace and rare earth elements (REE) analyses were made by ICP–MS.

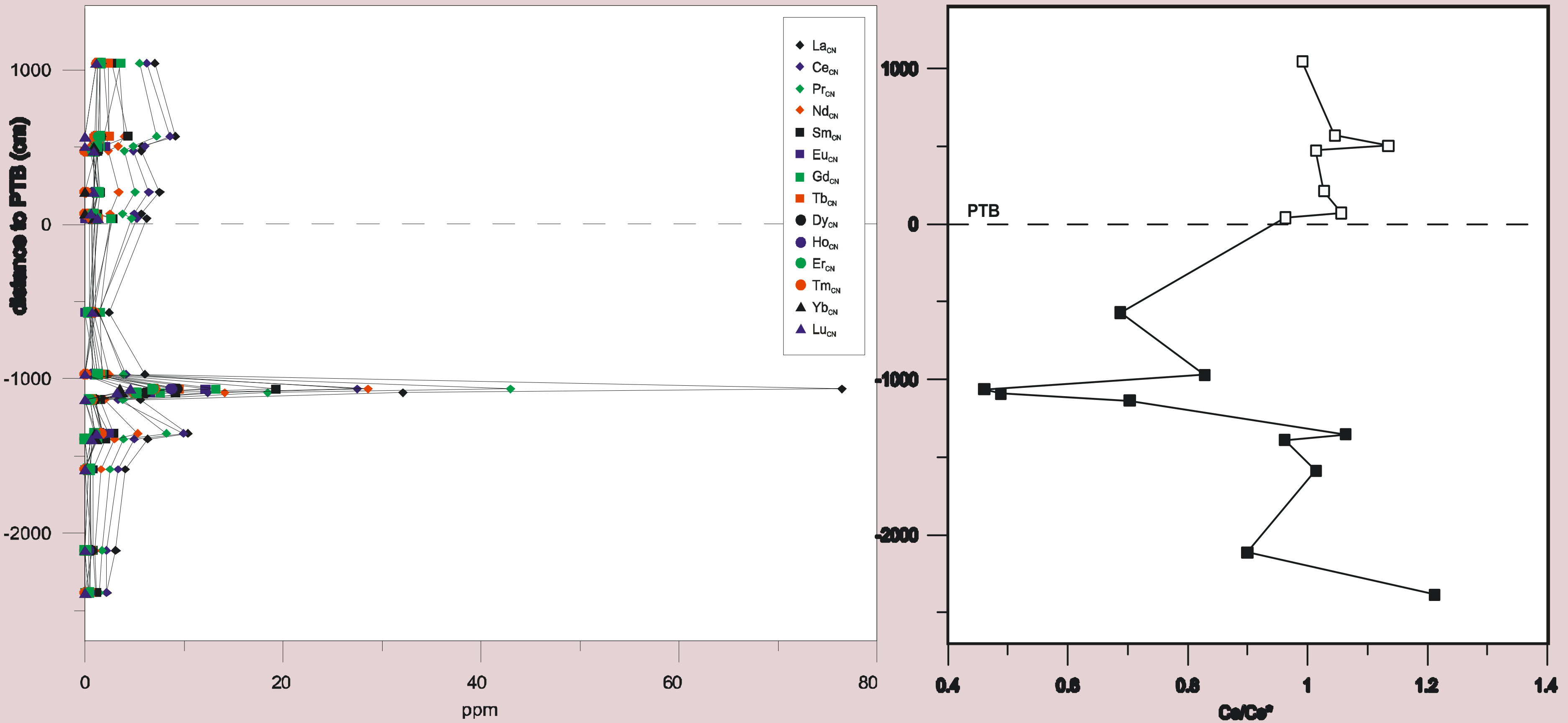
$\delta^{13}C$ and $\delta^{18}O$ of carbonates





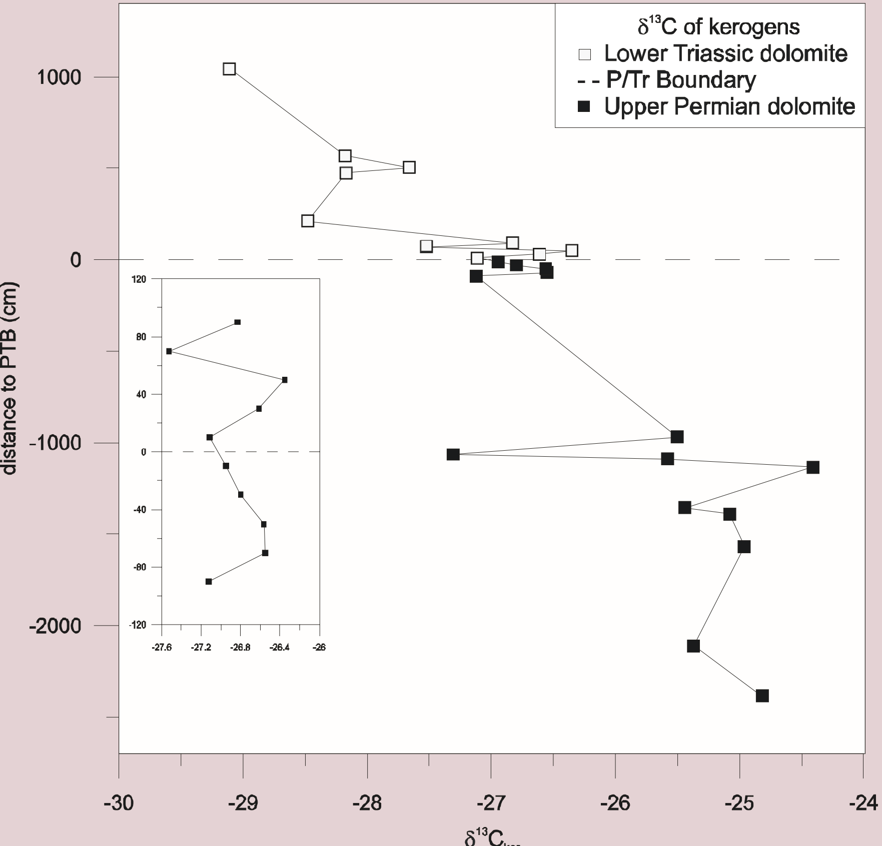
- Gradual impoverishment in biota towards the PTB is associated with a negative excursion of the $\delta^{13}C$ values of carbonates by up to 3‰.
- The $\delta^{18}O$ of carbonates show a constant decrease towards the boundary.

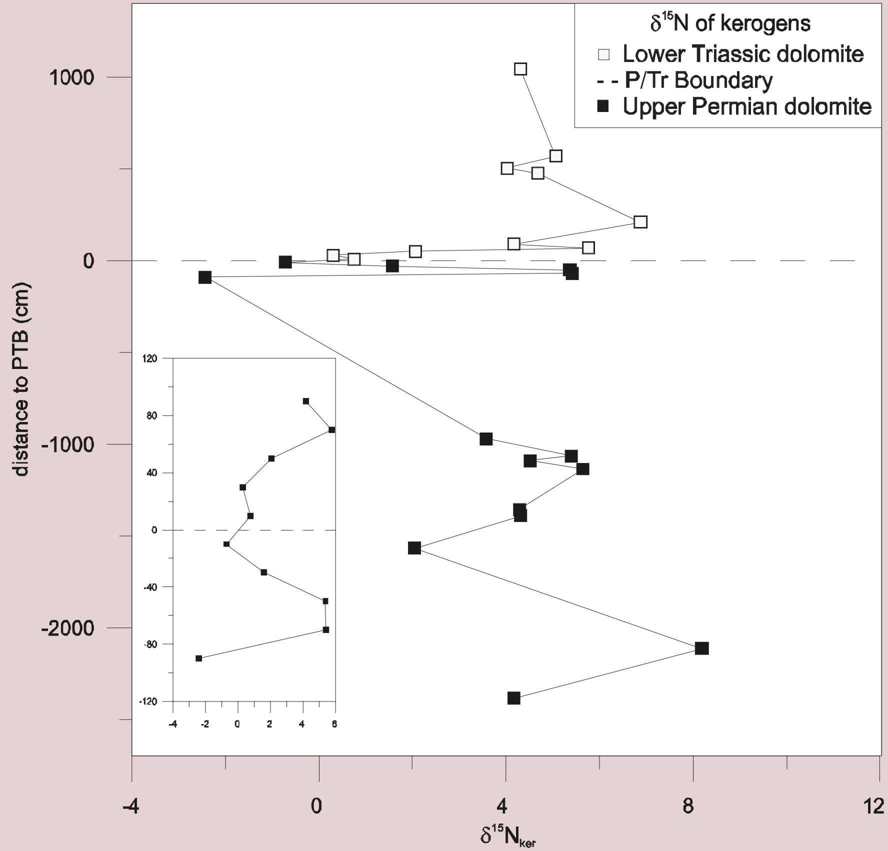
REE abundances and Ce anomaly



- REE abundances
  - P: 3.7 to 82.4 ppm (average 19.8 ppm);
  - Tr: 8.7 to 15.4 ppm (average 10.3 ppm).
- Negative Ce anomaly (1.1 to 0.5) – coincides with an abrupt increase in REE.

$\delta^{13}C$ and $\delta^{15}N$ for kerogens





- Negative excursion of $\delta^{13}C_{\mathbf{ker}}$ by up to 5‰ (P: -27.3 to -24.4‰, Tr: -29.1 to -26.4‰).
- The $\delta^{15}N_{\mathbf{ker}}$ between -2.4 and +8.2 ‰ – mixed contribution of ^{15}N-rich marine (~7‰) and ^{15}N-depleted terrestrial (~0 ‰) organic materials or cyanobacteria (-2 to +4 ‰).

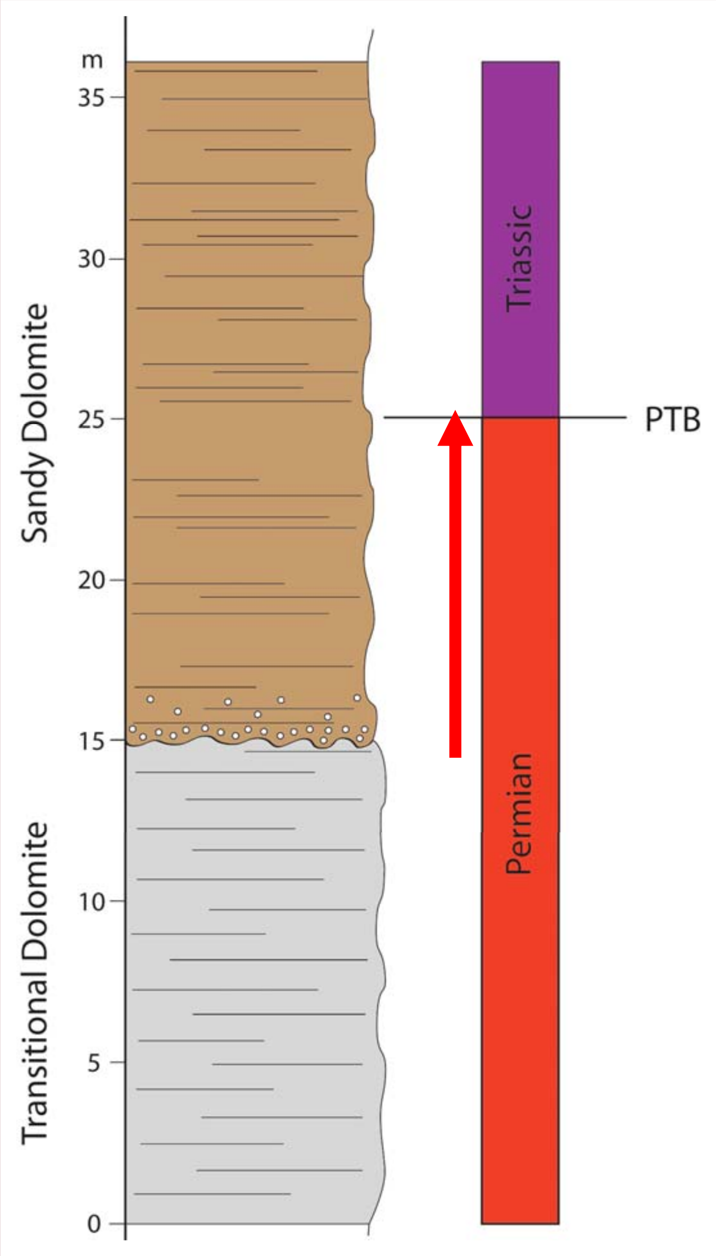
Organic geochemical analyses

Variations in the distribution of *n*-alkanes (C_{13} to C_{34}), acyclic isoprenoids (C_{21} to C_{28}), hopanes and steranes indicate input of bacterial and algal biomass.

The occurrence of odd long-chain *n*-alkanes (maximizing at C_{26}) and C_{39} steranes in all samples indicate a contribution of continental material.

The first results of compound specific C isotope analyses of alkanes indicate a ^{13}C depletion towards the boundary, supporting the lowering of primary productivity.

Conclusions



Within the Rizvanuša section the Permian–Triassic Boundary is located approximately 10 m above the lithostratigraphic boundary (between the *Transitional* and *Sandy Dolomites*), which was traditionally considered as the P/Tr boundary.

Environmental stress – cause of the extinction

- Isotope and geochemical data were crucial in positioning the boundary:
  - Synchronized drop in $\Delta^{13}C_{carb-ker}$ by 2‰ indicates lower productivity.
  - Distribution of $\delta^{15}N_{ker}$ shows dominantly marine conditions in the Late Permian, increase of terrestrial input near the PTB, and domination of cyanobacterial mats in the Early Triassic.
  - Change of concentration of Rare Earth Elements, as well as negative Cerium anomaly are the consequence of changes in lithology, and preceeded the catastrophic event at the boundary.
  - Constant decrease of $\delta^{18}O_{carb}$ indicates marine conditions with gradually increased input of terrigenous material.

- Paleontological data confirm the existence of two phases of environmental stress: the first one coinciding with lithological changes, and the second one indicating the global extinction event at the P/Tr boundary.

THANK YOU

FOR YOUR ATTENTION!