

The Paleocene-Eocene boundary in a flysch sequence from Goriška Brda (Western Slovenia): Oxygen and carbon stable isotope variations

Paleocensko-eocenska meja v flišu Goriških Brd (zahodna Slovenija): variabilnost izotopske sestave kisika in ogljika

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Abstract

Stable ($\delta^{13}\text{C}_{\text{carb.}}$, $\delta^{13}\text{C}_{\text{org.}}$, $\delta^{18}\text{O}$) isotopic records were studied to elucidate the problem of the Paleocene/Eocene (P/E) boundary in a flysch sequence at Nozno in Goriška Brda, W. Slovenia. A remarkable disturbance in organic carbon as well as in carbonate C and O isotopic records and associated Ir anomalies provide strong evidence that something unusual happened at the time of the Paleocene-Eocene transition. The diverse character of the negative excursion of $\delta^{13}\text{C}$ of carbonate and sedimentary organic carbon indicates a significant perturbation in the global carbon cycle and climatic changes, most probably controlled by a combination of volcanic activity and fluctuations in bioproductivity. The corresponding $\delta^{18}\text{O}$ variability may be related to global warming due to a higher greenhouse effect and/or diagenetic alteration.

Kratka vsebina

Z namenom, da razjasnimo problematiko paleocensko-eocenske meje v flišu Goriških Brd, smo raziskali potek krivulj $\delta^{13}\text{C}_{\text{carb.}}$, $\delta^{13}\text{C}_{\text{org.}}$ in $\delta^{18}\text{O}$ v mejni flišni sekvenci na območju Nozna. Izrazite motnje v izotopskem zapisu vseh treh parametrov, ki sovpadajo z Ir anomalijami kažejo, da je prišlo na prehodu iz paleocena v eocen do nenavadnih dogodkov. Večkratna negativna anomalija za karbonatni ogljik in ogljik iz sedimentirane organske snovi najverjetneje odraža globalne spremembe v ogljikovem ciklusu in klimatske spremembe. Te so najverjetneje posledica vulkanske dejavnosti in kolebanja v bioprodukciji. Variabilnost parametra $\delta^{18}\text{O}$ pa je lahko povezana z globalno otoplitvijo, zaradi povečanega vpliva efekta tople grede, deloma pa tudi z diagenetskimi spremembami.

Introduction

The transition from Paleocene to Eocene was a time of global climatic, oceanographic and biotic changes resulting in one of the

largest calcareous deep benthic foraminiferal extinction events in the last 100 million years (Kennett & Stott, 1991; Pak & Miller, 1992; Charisi & Schmitz, 1995; Schmitz et al., 1996). This signi-

ficant short-term event, which is placed in the latest Paleocene between 57.5 and 58 m.y. (Corfield, 1994), coincides with distinct negative $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ anomalies, recorded in several marine and terrestrial sections all over the world (Corfield, 1994; Canudo et al., 1995; Bralower et al., 1995; Koch et al., 1995; Charisi & Schmitz, 1995; Lu et al., 1996), as well as in geochemical changes (Schmitz, 1996; Thompson & Schmitz, 1996; Schmitz et al., 1997). Furthermore, Ir anomalies have also been recorded (Schmitz, 1996; Dolenc et al. 1998; Dolenc et al., 2000). A pronounced negative (^{13}C and ^{18}O) excursion indicates major changes in the structure of the deep water circulation system and biological productivity, and is probably related to a transient climatic anomaly also named »The Late Paleocene Thermal Maximum« (Zachos et al., 1993). It remains unclear what triggered such a sudden temperature rise

near the Paleocene/Eocene (P/E) transition. However, several authors proposed that an increase in atmospheric pCO_2 due to the addition of isotopically light CO_2 from seafloor volcanic activity and/or terrestrial sources (Roberts et al., 1984; Owen & Rea, 1985; Rea et al., 1990; Thomas, 1991), together with outgassing of marine CO_2 due to reduced surface water productivity, would account for the temperature rise from the late Paleocene into the early Eocene (Corfield, 1994).

The present study was initiated to determine whether there were any systematic changes in the stable isotope composition of carbonate carbon and oxygen and organic carbon during the P/E boundary transition related to the global events considered. For these purpose the carbonate and sedimentary organic carbon isotopic composition were measured in a flysch sequence from Goriška Brda (Nozno section) in Western Slovenia, in the hope that such a study would provide

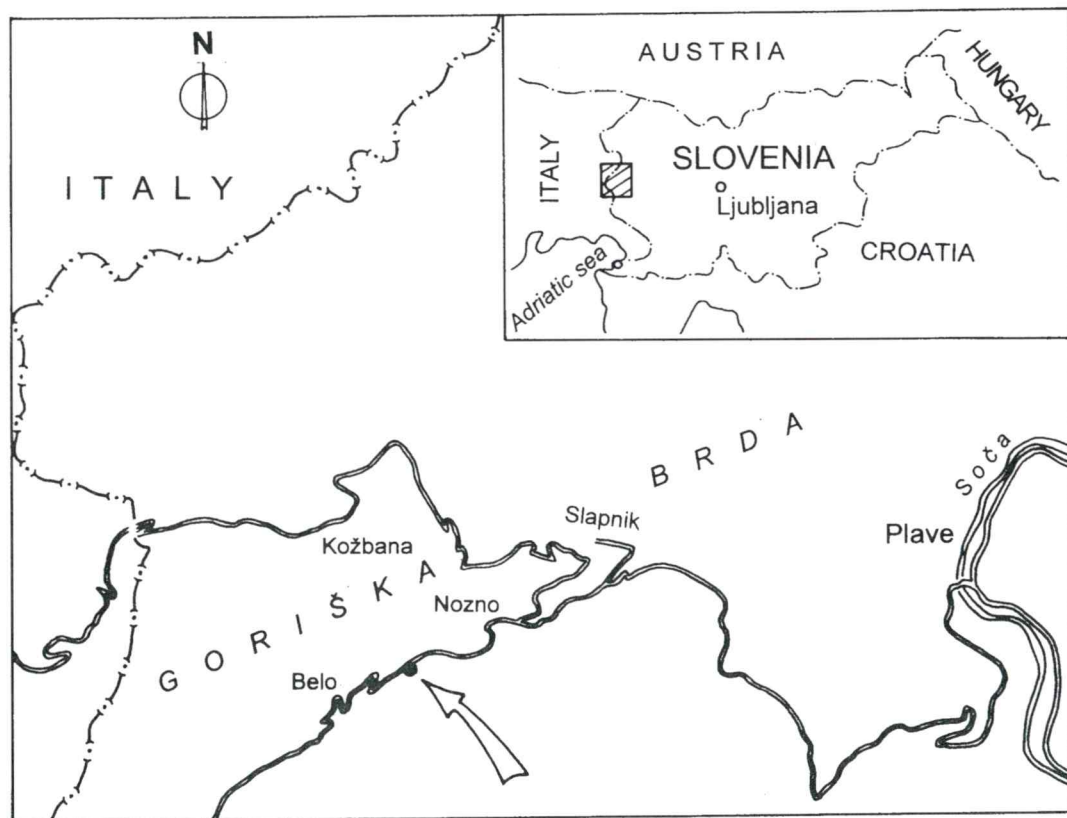


Fig. 1. Map showing location of studied region in Goriška Brda.

further information necessary to elucidate the cause of the isotopic anomalies across the P/E transition.

Geological setting and biostratigraphy

On the Dinaric carbonate platform of the western Tethys sea, flysch sedimentation started in the Paleocene and continued up to the Middle Eocene (Buser & Pavšič, 1978). A well exposed, non-tectonized P/E sedimentary boundary sequence was found only in Goriška Brda (W. Slovenia, Fig. 1). The lower part of the studied section represents 30 m thick unit of the uppermost Paleocene biozone NP9, mostly composed of clayey marls alternating with sandstones. The Upper Paleocene age of these beds is indicated by calcareous nannoplankton assemblages (Pavšič & Dolenc, 1995). This sedimentary sequence is overlain by a 3 m thick limestone breccia unit followed by an up to 11.8 m thick succession of sandstones containing only re-deposited alveolinids and discocyclinids from older Paleocene beds. The first Eocene plankton

species *Rhomboaster bramlettei*, indicating the biozone NP 10, was found in the upper part of the first marl layer overlaying the sandstone. It is followed by a 4 m thick normal flysch sequence predominantly composed of marls and sandstones. Based on the lithology and micropaleontological investigations, the P/E boundary is placed arbitrarily at the base of the limestone breccia unit (Pavšič, 1997).

Materials and methods

The boundary profile in the flysch succession was systematically sampled in order to determine all the details of the P/E stable isotope anomalies. The relative stratigraphic position of the samples and isotopic results are presented in Fig. 2. Geochemical analyses were carried out at the Activation Laboratories, Ontario. The isotopic measurements were performed at the Jožef Stefan Institute, Ljubljana, Slovenia. Whole rock samples for $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ analyses of carbonate were prepared by overnight digestion in > 100 % phosphoric acid at 50 °C.

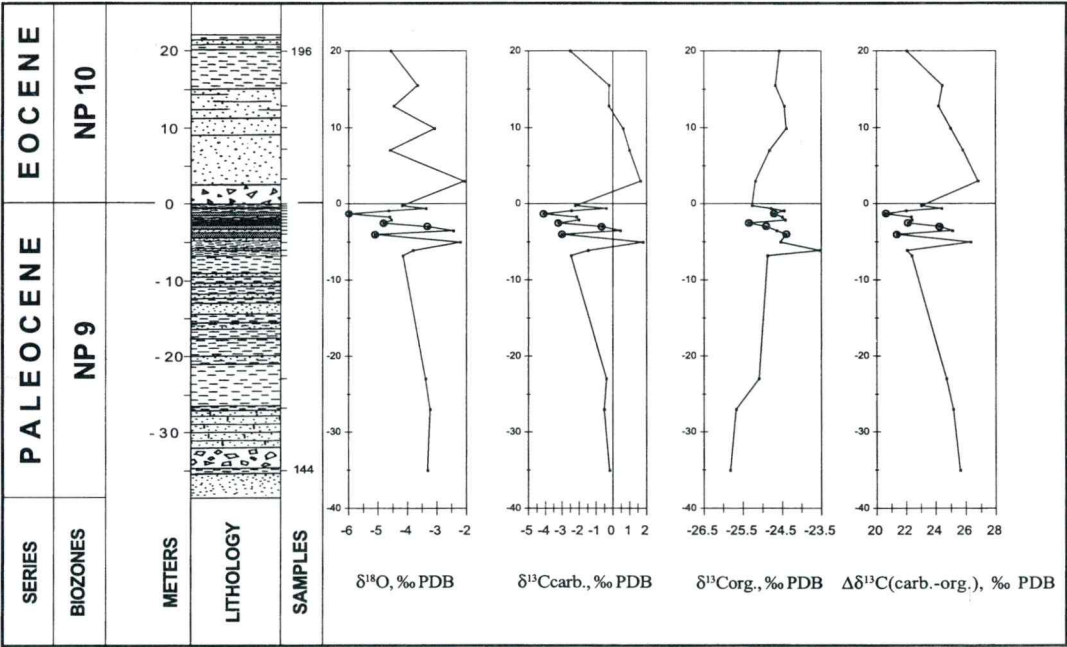


Fig. 2. Stable isotope composition of carbonates ($\delta^{13}\text{O}$, $\delta^{13}\text{C}_{\text{carb.}}$), organic carbon ($\delta^{13}\text{C}_{\text{org.}}$) and isotope fractionation between carbonate and organic carbon ($\Delta\delta^{13}\text{C}_{\text{carb.-org.}}$) across the Paleocene-Eocene boundary at Nozno in Goriška Brda, W. Slovenia (○ Ir anomaly).

CO₂ released during acid treatment was cryogenically cleaned and analyzed using on a Varian MAT-250 mass spectrometer. Organic carbon isotope ratios were determined in the carbonate-free residues in an Europa 20-20 Stable Isotope Analyser (Europa Scientific LTD.) with an ANCA-NT preparation module for on-line combustion of bulk solid samples and chromatographic separation of the gases. All $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values are expressed in standard permil (‰) notation relative to the PDB standard. The analytical precision, based on multiple analysis of internal laboratory standards, was $\pm 0.01\text{‰}$ for $\delta^{13}\text{C}_{\text{carb.}}$ and $\delta^{13}\text{C}_{\text{org.}}$ and $\pm 0.09\text{‰}$ for $\delta^{18}\text{O}$. Overall analytical reproducibility of the isotope data was better than (0.1‰ for $\delta^{13}\text{C}_{\text{carb.}}$, $\delta^{13}\text{C}_{\text{org.}}$, and for $\delta^{18}\text{O}$).

Using petrographic and trace element abundance data (unpublished), we evaluated known diagenetic effects that may affect the oxygen and carbon isotopic composition in our studied samples and concluded that the $\delta^{13}\text{C}$ values reported here are predominantly primary. The oxygen isotopic composition of the whole rock samples is lower than those recorded from most coeval marine sections worldwide, most probably indicating diagenetic alteration. However, the low negative correlation ($r = -0.46$) between $\delta^{13}\text{C}_{\text{carb.}}$ and $\delta^{13}\text{C}_{\text{org.}}$ ($r = -0.46$) indicates that the carbon isotopic composition of the whole rock was partially modified by the oxidation of organic matter. Although the post-depositional processes more or less altered the original oxygen and carbon isotopic composition, we believe that the primary paleoceanographic signals were not completely overprinted. This assumption is supported by similar trends of $\delta^{13}\text{C}_{\text{carb.}}$ and $\delta^{18}\text{O}$ values in whole rock and foraminiferal samples of P/E boundary sections from Egypt (Charisi & Schmitz, 1995; Schmitz et al., 1996) and Spain (Lu et al., 1996).

Results and discussion

The short term event recorded in the P/E boundary flysch sequence of the Goriška Brda section is characterized by complex characters of isotopic anomalies which

roughly span the interval between 0 and -5 m. There are four distinct isotopic ($\delta^{13}\text{C}_{\text{carb.}}$, $\delta^{13}\text{C}_{\text{org.}}$ and $\delta^{18}\text{O}$) minima at -0.25, -1.3, -2.5 and -4 m which demonstrate a clear perturbation in both $\delta^{13}\text{C}_{\text{carb.}}$ and $\delta^{18}\text{O}$ records of the whole rock samples, as well as in $\delta^{13}\text{C}$ of organic carbon (Fig. 2). The Ir anomalies (Dolenc et al., 2000) at -4 m (0.1 ppb), -2.5 m (2.3 ppb) and -1.3 m (0.6 ppb) are coincidental with isotopic anomalies, while that at -2.95 m (0.3 ppb) appears after the first negative $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ shift. The possible link between isotopic and Ir anomalies is not yet well understood. The possibility of an impact triggering a P/E biotic crisis and isotopic and Ir anomalies is too speculative. No clear impact signatures have been found in the studied section or in any other P/E section worldwide. A significant decrease of $\delta^{13}\text{C}_{\text{carb.}}$ from +1.80 to -4.87 (and a negative $\delta^{18}\text{O}$ shift from -2.2 to -6.0 (in the whole rock samples is most probably related to a rapid short-term carbon and oxygen isotope excursion associated with the benthic extinction event which occurred close to the NP9/NP10 and P6a/P6b zone boundaries, within the latest Paleocene, as documented on a global scale (Bralower et al., 1995; Lu et al., 1996).

The corresponding organic carbon $\delta^{13}\text{C}_{\text{org.}}$ isotope curve is slightly different with respect to those of $\delta^{13}\text{C}_{\text{carb.}}$ and $\delta^{18}\text{O}$, showing a gradual increase in $\delta^{18}\text{C}$ values from -25.82 to -24.13 ‰, starting in the upper part of the late Paleocene and lasting through the lower part of the early Eocene. Superimposed on this long term trend is a short-term perturbation of $\delta^{13}\text{C}_{\text{org.}}$ values coinciding with the negative shift in $\delta^{13}\text{C}_{\text{carb.}}$ and $\delta^{18}\text{O}$, thus indicating some changes in bioproductivity. The $\delta^{13}\text{C}_{\text{org.}}$ curve also exhibits four isotopic minima. The first one at -5 m appears before the first negative $\delta^{13}\text{C}_{\text{carb.}}$ and $\delta^{18}\text{O}$ excursion, while the last three are coeval with those of $\delta^{13}\text{C}_{\text{carb.}}$ and $\delta^{18}\text{O}$. Hollander et al., (1993) have shown that a decrease in $\delta^{13}\text{C}_{\text{org.}}$ and a subsequent increase in $\Delta\delta^{13}\text{C}_{\text{carb.-org.}}$ where-in dissolved CO₂ was enriched in ^{13}C because of reduced plankton production, while increasing $\delta^{13}\text{C}_{\text{org.}}$ and decreasing $\Delta\delta^{13}\text{C}_{\text{carb.-org.}}$ values are consistent with increased oceanic productivity. The diverse

character of the $\Delta\delta^{13}\text{C}_{\text{carb.-org.}}$ and $\delta^{13}\text{C}_{\text{org.}}$ anomalies in the boundary sequence could be related to the fluctuations of primary productivity which would tend to destabilize the global climate and possibly caused significant perturbations in atmospheric CO_2 .

The short term disturbances in $\delta^{13}\text{C}_{\text{carb.}}$ and $\delta^{13}\text{C}_{\text{org.}}$ records in the topmost part of the biozone NP9 can be explained by perturbations in atmospheric pCO_2 levels and/or climatic changes, most probably controlled by a combination of increased sea-floor spreading, volcanic activity (Owen & Rea, 1985; Sloan et al., 1992; Dickens et al., 1995) and fluctuating bioproductivity. The corresponding $\delta^{18}\text{O}$ variability may be related to global warming due to the higher level of greenhouse gases in the atmosphere and/or diagenetic alteration.

Conclusions

The transition from Paleocene to Eocene is characterized by a complex character of isotopic anomalies which demonstrate that something unusual happened at the P/E boundary. Their origin is unclear, but a combination of increased volcanic activity and fluctuating bioproductivity seems to be responsible for a sudden increase of atmospheric pCO_2 , temperature rise and biotic crisis. However, the discovery of an Ir anomaly which is associated with perturbations in isotopic ($\Delta\delta^{13}\text{C}_{\text{carb.}}$, $\delta^{13}\text{C}_{\text{org.}}$ and $\delta^{18}\text{O}$) records may also suggest a link between volcanic processes and/or the highly speculative possibility of extraterrestrial dust contamination. However, our results are inconclusive and further more detailed and complex geochemical studies are required to resolve this problem.

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References

- Bralower, T. J., Zachos, J. C., Thomas, E., Parrow, M., Paul, C. K., Kelly, D. C., Premoli Silva, J., Sliter, W. V., & Lohman, K. C. 1995: Late Paleocene to Eocene paleoceanography of the equatorial Pacific Ocean: Stable isotopes recorded at Ocean Drilling Program Site 865, Allison Guyot. - *Paleoceanography*, 10, 841-865.
- Buser, S. & Pavšič, J. 1978: Pomikanje zgornjekrednega in paleocena bazena v zahodni Sloveniji. - 9. jugoslovanski geološki kongres, 74-81, Sarajevo.
- Canudo, J. I., Keller, G., Molina, E. & Ortiz, N. 1995: Planctic foraminiferal turnover and $\delta^{13}\text{C}$ isotopes across the Paleocene-Eocene transition at Caravaca and Zumaya, Spain. - *Palaeogeography, Palaeoclimatology, Palaeoecology*, 114, 75-100.
- Charisi, S. D. & Schmitz, B. 1995: Stable ($\delta^{13}\text{C}$, $\delta^{18}\text{O}$) and strontium ($^{87}\text{Sr}/^{86}\text{Sr}$) isotopes through the Paleocene et Gebel Aweina, eastern Tethyan region. - *Palaeogeography, Palaeoclimatology, Palaeoecology*, 116, 103-129.
- Corfield, R. M. 1994: Palaeocene oceans and climate: An isotopic perspective. - *Earth Science Reviews*, 37, 225-252.
- Dickens, G. R., O'Neil, J. R., Rea, D. K. & Owen, R. M. 1995: Dissociation of oceanic methane hydrate as a cause of the carbon isotope excursion at the end of the Paleocene. - *Paleoceanography*, 90, 965-971.
- Dolenec, T., Pavšič, J. & Lojen, S. 1998: Stable isotopes, Ir anomaly and other elemental markers near the Paleocene-Eocene transition: evidence from the western Tethys. - *Mineralogical Magazine*, 62A, 399-400.
- Dolenec, T., Pavšič, J. & Lojen, S. 2000: Ir anomaly and other elemental markers near the Paleocene-Eocene boundary in a flysch sequence from the western Tethys (Slovenia). (submitted, Terra Nova).
- Hollander, D. J., McKenzie, J. A. & Kenneth, J. H. 1993: Carbon isotope evidence for unusual plankton blooms and fluctuations of surface water CO_2 in »Strangelove Ocean« after terminal Cretaceous event. - *Palaeogeography, Palaeoclimatology, Palaeoecology*, 104, 229-237.
- Kennett, J. P. & Stott, L. D. 1991: Abrupt deep-sea warming, palaeoceanographic changes and benthic extinctions at the end of the Paleocene. - *Nature*, 353, 225-229.
- Koch, P. L., Zachos, J. G. & Dettman, D. L. 1995: Stable isotope stratigraphy and paleoclimatology of the Paleogene Bighorn Basin (Wyoming, USA). - *Palaeogeography, Palaeoclimatology, Palaeoecology*, 115, 61-89.
- Lu, G., Keller, G., Adatte, T., Ortiz, N. & Molina, E. 1996: Long-term (10^5) or short-term (10^3) $\delta^{13}\text{C}$ excursion near the Paleocene-Eocene transition: evidence from the Tethys. - *Terra Nova*, 8, 347-355.
- Owen, R. M. & Rea, D. K. 1985: Sea-floor hydrothermal activity links climate to tectonics: the Eocene carbon dioxide greenhouse. - *Science*, 227, 166-169.
- Pak, D. K. & Miller, R. G. 1992: Paleocene to Eocene benthic foraminiferal isotopes

and assemblages: Implications for deep water circulation. - *Paleoceanography*, 7, 405 - 422.

Pavšič, J. 1997: Nannoplankton from the Paleocene/Eocene boundary in Goriška Brda. - *Razprave 4. raz. SAZU*, 18, 83-95.

Pavšič, J. & Dolenec, T. 1995: Floristic and isotopic changes at the Paleocene-Eocene boundary in Slovenia. - *Jour. Nann. Research*, 17/2, 79.

Rea, D. K., Zachos, J. C., Owen, R. M. & Gingerich, P. D. 1990: Global change at the Paleocene-Eocene boundary: climatic and evolutionary consequences of tectonic events. - *Palaeogeography, Palaeoclimatology, Palaeoecology*, 79, 117 - 128.

Roberts, D. G., Morton, A. C. & Backman, J. 1984: Late Paleocene-Eocene volcanic events in the northern North Atlantic Ocean. - *Init. Rep. DSDP*, 81, 913-923.

Schmitz, B. 1996: The Latest Paleocene extinction event in the Middle East, Northern Spain and Italy. In: *Early Paleogene Stage Boundaries, International meeting and field conference in Zaragoza, Spain. Abstract and Field Trip Guides*, pp. 46.

Schmitz, B., Speyer, R. P. & Aubry, M. P. 1996: Latest Paleocene benthic extinction

event on the southern Tethyan shelf (Egypt): Foraminiferal stable isotopic ($\delta^{13}\text{C}$, $\delta^{18}\text{O}$) records. - *Geology*, 24, 347 - 350.

Schmitz, B., Charisi, S. D., Thompson, E. I. & Speijer, R. P. 1997: Barium, SiO_2 (excess), and P_2O_5 as proxies of biological productivity in the Middle East during the Palaeocene and the Latest Palaeocene benthic extinction event. - *Terra Nova*, 9, 95 - 99.

Sloan, L. C., Walker, J. C. G., Moore, T. C., Rea, D. K. & Zachos, J. C. 1992: Methane in the early Eocene atmosphere. *Nature*, 375, 320 - 322.

Thomas, E. 1991: The latest Paleocene mass extinction of deep sea benthic foraminifera: Results of global climate change. - *Geol. Soc. Am., Abstr. Programs*, 23: A 141.

Thompson, E. & Schmitz, B. 1996: Barium and the Late Paleocene $\delta^{13}\text{C}$ Maximum. In: *Early Paleogene Stage Boundaries, International meeting and field conference in Zaragoza, Spain. Abstract and Field Trip Guides*, pp. 46.

Zachos, J. C., Lockman, K. C., Walker, J. C. G. & Wise, S. W. 1993: Abrupt climate change and transient climates during the Paleogene: A marine perspective. *Jour. Geol.*, 100, 191 - 213.