Geochemical records of the end-Triassic Crisis preserved in a deep marine section of the Budva Basin, Dinarides, Montenegro.

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Abstract

The end-Triassic extinction event (~201.5 Ma) is one of the five major mass extinction events in Earth’s history, however, considerable discussion continues on the exact causes and timing of the event. This is because, whilst certain geochemical data on T-J sections appears to be largely comparable globally, with for example a significant (up to 6‰) negative carbon-isotope ($\delta^{13}$C) excursion at the extinction horizon, more often than not other geochemical variations are neither uniform nor fully consistent between sections. Critical to this discussion is that the majority of the studied sections containing the end-Triassic extinction event are limited to shallow marine or terrestrial sections, which are prone to discontinuities and hiatuses. In this study, we present carbon isotopes ($\delta^{13}$C$_{\text{carb}}$), total organic carbon (TOC), major and trace, mercury (Hg) and highly siderophile elements (HSE), osmium-isotope compositions and paleomagnetic data of a relatively less studied deep-marine T-J succession in the Budva Basin, Čanj, Montenegro. At Čanj, deep-marine Triassic limestones are abruptly interrupted by a ~6 cm finely laminated clay layer, before transitioning to more argillaceous Jurassic red beds. The clay layer is interpreted to represent the end-Triassic extinction interval and is characterized by a negative carbon isotope excursion, relative heavy rare earth element (HREE) enrichment, Hg increase, HSE enrichment and a sharp shift to unradiogenic osmium-isotopic ratios. This establishes the Čanj section as a unique and well-preserved outcrop that exquisitely encapsulates the end-Triassic extinction in the Tethyan marine realm. The distinct geochemical markers recorded at Čanj are consistent with the Central Atlantic Magmatic Province as the main driver behind the end-Triassic extinction.
1. Introduction

The Late Triassic featured one of the five major mass extinction events of the Phanerozoic Eon.

Predating the end of the Triassic by ~140 ky, the onset of the End-Triassic extinction (ETE) event (~ 201.5 Ma; Schoene et al., 2010; Blackburn et al., 2013; Wotzlaw et al, 2014) marked the demise of close to 50% of known genera in both the marine and continental realms (see e.g., Raup and Sepkoski, 1982; Bambach, 2006; Kiessling et al., 2007). The event coincided with an acute carbon-cycle perturbation, as indicated by a large (up to 6‰) negative carbon-isotope ($\delta^{13}$C) excursion (e.g., Pálfy et al., 2001; Ward et al., 2001; Hesselbo et al., 2002; Whiteside et al., 2010; Lindström et al., 2017, 2021) in both marine and terrestrial sedimentary records, as well as stomatal index and pedogenic carbonate evidence for a rise in atmospheric CO$_2$ (McElwain et al., 1999; Schaller et al., 2011; Steinthorsdottir et al., 2011). Stratigraphic records of the extinction are also marked by mercury (Hg; Thibodeau et al., 2016; Percival et al., 2017; Lindström et al., 2019; Kovács et al., 2020; Yager et al., 2021) and highly siderophile element (HSE) enrichments (e.g., Ir, Ru, Rh, Pt, Pd; Olsen et al., 2002a, b; Whiteside et al., 2021), as well as a shift towards a relatively unradiogenic $^{187}$Os/$^{188}$Os$_i$ composition of seawater (Cohen and Coe, 2002; Kuroda et al., 2010).

The ETE was contemporaneous with the early onset of volcanism associated with the Central Atlantic Magmatic Province (CAMP), based on radioisotopic dating of volcanic ash layers just above the extinction horizon, CAMP igneous units themselves, and the documentation of CAMP lavas interbedded with sedimentary records of the event (e.g., Schoene et al., 2010; Marzoli et al., 2011; Blackburn et al., 2013; Wotzlaw et al., 2014; Davies et al., 2017). Consequently, increased emissions of CO$_2$ and other gases such as SO$_2$ (Bacon et al., 2013; Steinthorsdottir et al., 2018) from CAMP volcanic outpouring and/or sill intrusions are widely implicated as the main trigger of the extinction (e.g., Wignall, 2001; Deenen et al., 2010; Davies et al., 2017; Heimdal et al.,...
The Hg and platinum-group element (PGE: Ru, Rh, Pd, Os, Ir, Pt) enrichments and shifts towards more unradiogenic osmium-isotope seawater compositions have been explained as a further consequence of, and proxy for, this volcanism (e.g., Kuroda et al., 2010; Thibodeau et al., 2016; Percival et al., 2017; Lindström et al., 2019; Whiteside et al., 2021). Alternative hypotheses have been proposed, such as methane hydrate release as an alternative source of the carbon emissions (Beerling and Berner, 2002), and a meteorite impact event as a source of the HSE enrichment (Olsen et al., 2002a,b; de Graaff et al., 2017), which is similar, though an order of magnitude lower, to the well-documented HSE enrichment associated with the Cretaceous-Paleogene (K-Pg) boundary mass extinction (Alvarez et al., 1980, Smit and Hertogen, 1980; Goderis et al., 2013, 2021). However, the mounting evidence for CAMP volcanism over methane hydrate release from other sources (see e.g., Heimdal et al., 2018, 2019; Lindström et al., 2019; Whiteside et al., 2021) and the lack of additional supportive evidence for an impact event such as impact spherules, Ni-rich spinel crystals, shocked quartz or an impact structure of a correct age (see e.g., Tanner et al., 2004, 2008), leaves CAMP volcanism as the more widely accepted cause.

The emplacement of the CAMP initiated the break-up of Gondwana and Pangaea, ultimately forming one of the largest continental flood-basalt provinces on Earth, exceeding 7 million km$^2$ in aerial extent (Marzoli et al., 1999). The earliest known CAMP magmas formed intrusive bodies in Africa and South America at ~201.635 ± 0.029 Ma, roughly 100 kyr prior to the ETE (Davies et al., 2017). The oldest dated extrusives of the main CAMP volcanic activity yields 201.566 ± 0.031 Ma (North Mountain Basalt; Blackburn et al., 2013). This earliest known pulse of extrusive magmatism is thought to have been coeval with the geologically abrupt negative carbon-isotope excursion (named the Initial, or Marshi carbon-isotope excursion: ICIE; Hesselbo et al., 2002; Lindström et al., 2017) and a dramatic turnover in marine fauna (Ward et al., 2001;
Hori et al., 2007; Deenen et al., 2010; Ruhl et al., 2011). Additional intrusive sills from the Amazonas Basin (Brazil) have also been dated to that time and could have resulted in the generation of non-magmatic gases via the heating of volatile-rich lithologies (Davies et al., 2017; Heimdal et al., 2018). The initial onset of volcanism in Morocco was rapidly (within a few kyr) followed by a series of magmatic pulses recorded by lavas in both NE North America and Morocco (Deenen et al., 2010), with eruptions also documented in SW Europe. Whilst the exact sequence of environmental and biospheric perturbations remains debated, with, for example, a carbon-isotope excursion preceding the ICIE (termed the pre-cursor CIE; Ruhl and Kürschner, 2011) suggesting that a global carbon cycle disturbance preceded the onset of CAMP, the main CAMP eruptions broadly coincided with a calcification crisis in calcareous nannofossils (van de Schootbrugge et al., 2007), extinction of numerous faunal groups, including the conodonts, and the development of widespread marine anoxia (Wignall and Bond, 2008; Kasprak et al., 2015; Jost et al., 2017a). Furthermore, long-lasting disturbances to the global environment continued long after the onset of major CAMP volcanism, with evidence for a further carbon-cycle perturbation (recorded as the Main CIE), oceanic acidification, marine faunas dominated by bio-siliceous taxa, and at least localized marine anoxia recorded from several locations (e.g., Hesselbo et al., 2002; van de Schootbrugge et al., 2007; Greene et al., 2012; Richoz et al., 2012; Kasprak et al., 2015; Thibodeau et al., 2016; Jost et al., 2017a,b), before the first occurrence of Jurassic ammonites ~100–200 kyr after the onset of the extinction marking the start of the Jurassic (201.36 Ma; Schoene et al., 2010; Wotzlaw et al, 2014). U-Pb geochronology indicates that CAMP emplacement continued for at least 600 kyr after its onset (see Marzoli et al., 2018; and references therein), broadly similar to the durations of other well dated LIPs (e.g., Siberian and Deccan Traps; Burgess et al., 2017; Schoene et al., 2019; Sprain et al., 2019). However, $^{40}\text{Ar}/^{39}\text{Ar}$ ages suggest a
considerably longer duration for the CAMP, with some basalts dated as being up to 10 My younger than the oldest erupted products (Jourdan et al., 2009; Marzoli et al., 2011), and potentially suggesting that (minor) CAMP volcanism continued until long after faunal recovery took place in the Jurassic. With a clear synchronicity between the extinction and CAMP eruptions, but possible disconnect between the continued outpouring of CAMP and faunal recovery, it is apparent that questions remain regarding the exact mechanisms behind the extinction, and the respective roles of magmatic degassing, thermogenic emissions, and/or other processes such as methane clathrate destabilization or a possible impact event.

Critical to this discussion is that most of the studied sections containing the ETE event are limited to shallow marine or terrestrial sections, which are prone to discontinuities and hiatuses (see e.g., Lindström et al., 2019 for an overview), with comparatively few examples of well-studied deep-marine T-J records, with those that do exist being limited to Panthalassic Ocean sections (see e.g., Hori et al., 2007; Fujisaki et al., 2018). In Čanj, Montenegro, a relatively less studied continuous deep-marine section of the T-J boundary exists; first described by Goričan (1994), the Čanj section has since that time only been further investigated by Črne et al. (2011) (Fig. 1A and B). These studies presented stable-isotope records and radiolarian data, which support a Triassic–Jurassic age and preservation of a relatively complete ETE horizon. In this study, we present carbon isotopes ($\delta^{13}C_{\text{carb}}$), total organic carbon (TOC), major and trace elements, with a special focus on mercury (Hg), highly siderophile elements (HSE), osmium-isotope compositions and paleomagnetic data of the Čanj section. Through this approach we aim to provide a detailed geochemical record from a deep-marine succession in the Tethyan realm, and present new insights into the causes of the ETE.
2. Geological setting

The Čanj section is located in coastal Montenegro near the village of Čanj (42° 9' 40.04” N, 18° 59’ 29.85” E; Fig. 2). It is part of the Budva tectonic zone of the External Dinarides (Petković, 1956; Goričan, 1994), which encompasses several south-west verging thrust units spanning from Budva to Herceg Novi (Goričan, 1994). The Budva Zone separates the Dalmatian Zone (Aubouin, 1960) in the southwest from the High Karst Zone (Kossmat, 1924) in the northeast. The Budva Zone is generally subdivided into a lower and upper tectonic unit (Goričan, 1994), with the Čanj section representing part of the lower unit. The subdivision in tectonic units corresponds approximately to the Mesozoic paleogeography, with sediments deposited in the lower Budva Zone tectonic unit thought to be more distal with respect to the upper tectonic unit (Goričan, 1994).

Paleogeographically, the Budva Zone records a narrow area of deposition, commonly referred to as the Budva Basin, located between two carbonate platforms, the Adriatic Carbonate Platform in the west and the Dinaric Carbonate Platform in the east (D’Argenio et al., 1971). This intra-platform deep-marine basin was formed by the rifting and separation of Adria from Africa during the Middle and Late Triassic, separating the Adriatic and Dinaric Carbonate Platforms (Čadjenović et al., 2008; Schmid et al., 2020). The basement rock of the Budva Basin consists of volcanic rocks of Middle Triassic age (Fig. 2). The oldest sediments deposited on the volcanic basement are Upper Triassic limestones, which consist of thin beds of pelagic limestone with intercalated chert nodules and infrequent (thin) chert or clay layers (Fig. 2; Goričan, 1994; Črne et al., 2011; Đaković et al., 2018; van Unen et al., 2019). The Triassic succession is conformably overlain by near-continuous Lower Jurassic red radiolarites, limestones and shales and Middle Jurassic to Upper Cretaceous thinly bedded pelagic micritic limestone and radiolarite lithologies (Fig. 2; Goričan, 1994; Črne et al., 2011). The entire stratigraphic succession contains carbonate gravity-flow deposits and
turbidites (Črne et al., 2011). Sedimentation stopped with lower Eocene flysch (Fig. 2; Schmid et al., 2020), which provides a time constraint regarding the age of thrusting of the High Karst unit over the Budva Zone (Schmid et al., 2020).

3. The Čanj section

The Čanj section exposes at least 20 m of the Upper Triassic Halobia limestone Formation, which consists of thin beds of pelagic carbonates with intercalated chert nodules and chert layers (varying from a few cm to upwards of 15 cm), alternated with shales and/or marls (Fig. 1A). This part of the section is characterized by a near-continuous repetition of grey, fine-grained, and fossiliferous limestone beds (Črne et al., 2011) of ~1 – 20 cm thickness followed by a marl or shale bed, or a combination of both (varying between 0.1 ~ 2 cm in thickness) (Fig. 1A; Appendix A). The Halobia limestone formation is interrupted at Čanj by two slump intervals. The first slump occurs ~ 9 m below the top of the Halobia limestone and has a varying thickness of approximately 1.65 m at its maximum. It contains clasts of reworked material originating from the beds below. Underlying limestone beds terminate laterally due to incision of the slump. The second, approximately 1 m thick, slump occurs ~ 4.5 m below the top of the formation. This slump is less brecciated and instead has an internal structure of undulating layers with chert nodules, which are not laterally continuous. These slumps are the only gravity-flow deposits observed in the Halobia limestone formation at the Čanj section, marking the top of the last slump as the start of a continuous sedimentary succession until well into the Jurassic.

The Halobia limestone is overlain by the Lower Jurassic Passée Jaspeuse Formation (Črne et al., 2011), which consists of red siliceous limestones, radiolarian cherts, sandstones, siltstones, shales, marls, and clays well over 30 m in thickness (Fig. 1A; Goričan, 1994). The boundary
between the Halobia limestone and the Passée Jaspeuse is marked by a clay layer of varying thickness, which can be subdivided into 2 distinct clay beds (Fig. 1B). At the base, a bed of grey to red, platy shale of ~ 3 cm, which is slightly undulating with thin laminae of less than 0.1 mm and no visible grains. This bed is overlain by a ~3.5 cm, dark brown to grey black clay. No distinct bedding or laminae are visible and calcite grains, likely secondary in origin, have been observed. Above this clay layer, the basal strata of the Passée Jaspeuse remain relatively argillaceous for tens of centimeters before carbonate-rich lithologies reappear. A switch from Triassic to Jurassic radiolarian fauna somewhere between ~ 90 cm below the clay layer to ~ 40 cm above it (near the top of the carbonate-depleted layers), together with documentation of the ICIE correlative with the clay layer itself (Črne et al., 2011), supports placement of the Triassic–Jurassic boundary slightly above the clay layer interval.

4. Methods and materials

4.1. Sample selection and preparation

The Čanj section was visited and sampled in May 2019. The entire Čanj section was logged from ~ -6.5 m to + 21.8 m (0 m marking the base of the clay layer); at the millimeter scale with continuous sampling every few centimeters (Appendix A). Further sample selection and geochemical analyses were carried out at the Analytical, Environmental and Geo-Chemistry (AMGC) laboratory at the Vrije Universiteit Brussel (Brussels, Belgium; VUB), except for HSE and Re-Os isotopic analyses, which were done at the University of Tokyo at Komaba and the Japan Agency for Marine-Earth Science and technology (JAMSTEC) in Japan, respectively. Eighty samples were selected for carbon-isotope analysis, to construct a continuous curve across the ETE interval, spanning strata from just above the last slump of the Halobia limestone at around -4 m
and up to the highest sampled carbonate layer of the Passée Jaspeuse at +21m. Further sample selection for total organic carbon (TOC) contents (n=40), major and trace element analyses (n = 40), with S being done separately (n = 36), Hg contents (n = 40) and HSE and osmium-isotopic analyses (n = 21) focused around the clay layer to resolve potential variations in the concentrations and isotope ratios of these elements across the extinction horizon (see Appendix B and III). Sampling for paleomagnetic analyses (n = 24) was done on site using a modified STIHL drill with diamond tipped Hoffmann drill bits. Sample locations were chosen based on the expected occurrences of magnetic reversal intervals using the sedimentation rate estimates in the Halobia limestone and the Passée Jaspeuse (Črne et al., 2011; de Graaff et al., 2017) and magnetostratigraphy data of the T-J interval (Korte et al., 2019).

For carbon-isotope analyses, samples were powdered using a hand-held drill on fresh surfaces and collected in clean glass vials. For major and trace elements, including TOC contents, Hg and HSE concentrations, and osmium isotope analysis, approximately 5 cm$^3$ of sample was crushed to a homogenous powder using an agate mortar and pestle, followed by sieving until a ~<125 µm grain size was achieved. Larger rock samples were cut using a diamond board table saw beforehand and were subsequently washed with ultrapure 18.2 MΩ cm water in an ultrasonic bath before crushing. Samples that required sawing were not selected for HSE or $^{187}$Os/$^{188}$Os analyses, to avoid possible contamination.

4.2. Carbon-isotope composition analysis

Carbon-isotope ratios of bulk carbonate material ($\delta^{13}$C$_{carb}$) were determined on a Nu Instruments Nu Perspective isotope-ratio mass spectrometer (IRMS) coupled to a gas preparation (GasPrep) automated gas bench at the VUB. Between 1–10 mg of homogenized powder
(depending on carbonate content) was weighed into a glass vial, which was then sealed and flushed with helium gas, before addition of phosphoric acid to liberate the carbonate-bound CO$_2$ over a few hours. Data calibration, and, if necessary, machine drift correction, was carried out using multiple aliquots of Carrara marble ($\delta^{13}$C = +3.41 ‰) on a daily basis for each individual batch, while international reference material IAEA 603 ($\delta^{13}$C = +2.46 ‰) was also used to assess analytical precision. Measured results for IAEA 603 had an average of 2.49 ‰, consistent with the certified value. Measurement uncertainty on these standards was ± 0.07 ‰ (1σ, n = 30) for Carrara marble and ± 0.05 ‰ (1σ, n = 25) for IAEA 603.

4.3. Total organic carbon analysis

For each sample, between 2–3 grams of homogenized sample powder were decarbonated using 10% HCl following the method outlined in Percival et al. (2022). The organic carbon content of the treated samples was determined on a Nu Instruments Horizon 2 isotope-ratio mass spectrometer (IRMS) coupled to a Eurovector elemental analyzer EuroEA3000 at the VUB. These measurements were then converted to bulk TOC contents by accounting for the mass lost during decarbonation. Data accuracy and reproducibility were monitored through analysis of international standards IVA33802151 (organic-rich sediment) and IVA33802153 (organic-poor soil), yielding 9.06 ± 0.11 (1σ, n = 4) and 1.57 ± 0.03 (1σ, n = 3) respectively.

4.4. Major and trace element composition analysis

Approximately 100 mg (± 0.1 mg) of homogenized sample powder was weighed into in trace metal-clean 15 ml polytetrafluoroethylene (PTFE) beakers. A mixture of 3 ml 14 M HNO$_3$ and 1 ml 29 M HF was added to the PTFE beakers, after which these were left to react for 4 days
at 120˚C. The samples were subsequently dried down, re-dissolved in 2 ml of 14 M HNO₃ and left to react for another 3 days at 90˚C until the liquid was completely clear of any residue and 3 ml of ultrapure 18.2 MΩ cm water was added. Exclusively high-purity trace metal grade acids were used in the procedure. After adequate dilution (by factor 2500 to 5000) and addition of indium as an internal standard, selected major and trace element concentrations were determined using the Thermo Scientific Element 2 high-resolution inductively coupled plasma-mass spectrometer (ICP-MS) housed at the AMGC research unit at the VUB. Both the low and medium resolution modes of the instrument were used for one or more monitored isotopes of the element of interest, and mathematical corrections were applied for isobaric interferences where necessary (as commonly applied for the rare earth elements (REE), see e.g., de Graaff et al., 2022). Elemental concentrations were determined versus an external calibration curve prepared from single element standard solutions. Reference basalt BE-N of the Centre de Recherches Pétrographiques et Géochimiques, basalt BIR-1 of the United States Geological Survey, and limestone CCB-1 of Liège Université were digested and analyzed as secondary standards using the same procedure as the samples. All reported values were consistent with the certified standard data. A fraction of randomly selected samples was digested twice to test sample heterogeneity, after which the results were compared and averaged. The average bias between reference values and experimentally obtained values for international reference values was typically 5 to 10%. Based on the repeated analysis of the reference materials and a subset of samples, the external reproducibility for the elements measured is better than 10% relative standard deviation (RSD) depending on the concentration level.

4.5. Sulphur content analysis
Sulfur concentrations of 36 samples across the Čanj T-J boundary were measured using micro-X-ray fluorescence (µXRF). Besides semi-quantitative high-resolution element mapping, this non-destructive technique also allows quantitative spot analysis to determine major and trace element concentrations (de Winter and Claeys, 2016; Kaskes et al., 2021), with the determination of low concentrations of S (< 0.1 wt%) proven to be successful (Gulick et al., 2019). We used an M4 Tornado benchtop µXRF surface scanner (Bruker nano GmbH, Berlin, Germany) equipped with a Rh tube as X-ray source and two XFlash 430 Silicon Drift detectors, available at VUB (de Winter and Claeys, 2016). Homogenized powders were measured under near vacuum conditions (20 mbar), without the use of an X-ray source filter, and using repeated spot analysis (n = 10) per powder with a spot size of 200 μm and an integration time of 120 s per spot (following Vellekoop et al., 2022). This integration time was selected to allow the Time of Stable Reproducibility and Time of Stable Accuracy to be reached, which allows the concentration of a range of elements to be quantified (de Winter et al. 2017). A range of certified geological reference materials (n = 18) was measured under the same conditions to perform a matrix-matched multi-standard calibration to correct the pre-determined S-data based on the Fundamental Parameters Method. Limit of detection of S was determined to be in the order of 50 ppm based on repeated spot analysis (n = 10) of certified carbonate reference material BCS CRM393 (Bureau of Analyzed Samples Ltd., Middlesbrough, UK).

4.6. Mercury concentration analysis

Mercury (Hg) concentrations were determined on an Advanced Mercury Analyzer (AMA) 254.7 at the VUB, broadly following the method outlined in Liu et al. (2021). Approximately 100 mg of homogenized bulk-rock powder was analyzed for clay-rich samples, whilst ~250 mg was
used for measurements of carbonate-rich samples. Mercury was volatilized from the untreated rock powder at 750 °C, and collected in an amalgamator containing a gold trap, before being analyzed by atomic absorption spectrometry. Blank measurements on the AMA were better than 0.05 ng. Each sample was analyzed at least twice, with measurement reproducibility typically better than 5%, and the mean concentration was taken. Measurement accuracy was confirmed through analysis of multiple aliquots of the international reference materials SRM MESS-3 (89.87 ± 0.6 ppb, 1σ, n = 3) and JP-1 (5.23 ± 0.29 ppb, 1σ, n = 9), consistent with certified values (SRM MESS-3 = 91 ppb Hg) and JP-1 = 5.3 ppb Hg).

4.7. Highly siderophile element concentrations and Re-Os isotopic analysis

Highly siderophile element (HSE: Os, Ir, Ru, Pt, Pd, and Re) concentrations and osmium-isotope compositions were determined by isotope dilution mass spectrometry (ID-MS). Sample digestion was done with quartz glass tube (ø = 14 mm, L = 290 mm) digestion using inverse aqua regia on powdered samples (~0.1–0.5 g) and subsequent complete desilicification in 38% HF on the residual solids (used only for Ir, Ru, Pt, Pd and Re). Chemical purification of osmium was performed using standard microdistillation into HBr using Cr\(^{VI}\)O\(_3\)-H\(_2\)SO\(_4\), following solvent extraction with CCl\(_4\) (Birck et al., 1997; Cohen and Waters, 1996). The detailed methods for sample digestion, chemical purification and mass spectrometry are based on those reported in Ishikawa et al. (2014), following adaptions presented by Sato et al. (2021).

The concentrations for Ir, Ru, Pt, Pd, and Re were measured using a Thermo Element XR ICP-MS at the University of Tokyo at Komaba. For sample introduction, a combination of a 100 µL/min PFA self-aspirating nebulizer and dual cyclonic/Scott double-pass spray chamber was used during all measurements, and the oxide level (based on the HfO/Hf) was set to ~1%. Sample and
standard solutions were interspersed throughout the analytical sessions to monitor and correct for
instrumental fractionation. The average total procedural blanks for the analysed elements were
0.20 ± 0.05 pg Ir, 0.17 ± 0.08 pg Ru, 8.1 ± 4.0 pg Pt, 14.6 ± 3.6 pg Pd, and 0.39 ± 0.09 pg Re (n=3,
1SD). All analyses were blank corrected to account for the variable background contribution for
each sample, depending on their HSE concentrations (0.096–12% for Ir, 0.27–7.5% for Ru, 0.22–
19% for Pt, 0.45–27% for Pd, and 0.038–26% for Re). The reported uncertainties on each sample
were calculated by error propagation of the ICP-MS measurement uncertainty (2 SE) and the blank
correction.

Osmium concentrations and isotopic compositions were measured by negative thermal
ionisation mass spectrometry (N-TIMS, Thermo Triton Plus) at JAMSTEC, Japan. The average
total procedural Os blank was 0.12 ± 0.02 pg with a \(^{187}\text{Os}/^{188}\text{Os}\) ratio of 0.159 ± 0.008 (n=3, 1SD).
Blank corrections were applied for all analyses, although the blank contributions to the measured
Os concentrations and \(^{187}\text{Os}/^{188}\text{Os}\) ratios were almost negligible for all samples and less than 4%
and 3%, respectively. The uncertainties of \(^{187}\text{Re}/^{188}\text{Os}\) and \(^{187}\text{Os}/^{188}\text{Os}\) were calculated by error
propagation of the blank uncertainties. The reproducibility for basaltic reference material BIR-1a
yielded 0.4% RSD for \(^{187}\text{Os}/^{188}\text{Os}\), 8.6% RSD for Os, 8.0% RSD for Ir, 4.0% RSD for Ru, 3.8%
RSD for Pt, 2.7% RSD for Pd, and 1.2% RSD for Re (~0.5 g powdered samples; Goderis et al.,
2021), consistent with data for larger sample amounts (~1–2 g; Ishikawa et al., 2014). The
measured \(^{187}\text{Os}/^{188}\text{Os}\) ratios were corrected for post-depositional decay of rhenium to osmium by
utilising the established concentrations of rhenium and osmium in the samples, together with their
estimated age (201.3 Ma) to give the initial isotopic composition of the sediment at the time of
deposition (\(^{187}\text{Os}/^{188}\text{Os}_i\)), following standard protocols (Cohen et al., 1999).
Paleomagnetic analyses were carried out on 24 samples (two specimens per sample) at the Geophysical Centre of the Royal Meteorological Institute of Belgium (Dourbes, Belgium). The cylindrical standard-sized palaeomagnetic samples were subjected to stepwise alternating field (AF) demagnetization in steps from 0 to 70 mT. The remaining remanent magnetization was measured after each step. To do so, an upgraded three-axis, model 760, 2G Enterprises, cryogenic magnetometer with DC SQUIDS and sample access of 7.6 cm was used. The magnetometer is equipped with a Cryomech 4K, model PT405, pulse tube cryorefrigerator; an inline three-axial alternating field demagnetizer and automatic sample handling system.

A subset of 6 samples from different stratigraphic intervals were selected for magnetic property analyses with a magnetic property measurement system (MPMS3) from QuantumDesign. For each sample field cooled and zero-field cooled hysteresis loops were acquired within a field range of ±5 T at following temperatures 20, 50 and 300 K. In addition, field-cooled direct current susceptibility warming curves were measured to reveal characteristic low temperature transitions such as Verwey and Morin to support the interpretation of the magnetic mineralogy.

5. Results

5.1. Carbon-isotope compositions

Our δ^{13}C_{carb} results are consistent with those of Črne et al. (2011). Values are typically between 1–2 ‰ in the Halobia limestone formation, with the lowest δ^{13}C_{carb} ratios occurring as part of a minor fall in values below the base of the clay layer, between -1.7 and -2.6 m (Fig. 3). A significantly more pronounced negative excursion is recorded across the Halobia limestone–Passée Jaspeuse boundary, with values falling to -1.18 ‰ just below the base of the clay layer and
remaining at ~1 ‰ within that level (Fig. 3). Three clay-layer samples record considerably lower \( \delta^{13}C_{\text{carb}} \) ratios (< -4 ‰), but it should be noted that those intervals featured a very low carbonate content; thus, these low values may reflect poor analytical precision (Appendix B). The \( \delta^{13}C_{\text{carb}} \) ratios return to pre-excursion ratios around 25 cm above the base of the clay layer, before a second, smaller, negative excursion of around 0.5 ‰ occurs approximately 75 cm higher up in the succession. Following this second shift, there is a gradual decline of ~0.5 ‰ in \( \delta^{13}C_{\text{carb}} \) until 5–6 m above the base of the clay layer, which is succeeded by a slight rise of ~0.5 ‰ in values across the next 7 meters. The upper 7 meters of the studied strata record two additional transient negative excursions in \( \delta^{13}C_{\text{carb}} \), of between 2 and 3 ‰ in magnitude (Fig. 3).

5.2. Total organic carbonate contents

Sedimentary TOC contents are presented in Appendix C and are shown to be very low throughout the boundary interval of the section. The Halobia limestones are marked by TOC contents of <0.1 wt% on average, with just two thin argillaceous horizons 88 cm and 145 cm below the base of the clay layer reaching slightly higher organic content levels (0.13 wt% and 0.16 wt%, respectively). There is a slight increase in TOC within the four clay layer samples, reaching a maximum of 0.29 wt% 2 cm above its base. Above the clay layer, Passée Jaspeuse samples return to very low TOC contents (<0.1 wt%), similar to the Halobia limestones.

5.3. Major and trace element abundances

Major and trace element compositions are presented in Appendix C. Notable major element oxide variations are shown by differences in MgO, Al₂O₃ and TiO₂ contents of samples from the Halobia limestones, Passée Jaspeuse and the clay layer, with the latter featuring clearly elevated
MgO, Al₂O₃ and TiO₂ levels (up to 9.96, 14.9 and 0.77 wt%, respectively) compared to an average of 1.17 wt%, 3.07 wt%, and 0.11 wt% for the Halobia limestones and 2.08 wt%, 8.63 wt%, 0.39 wt% for the Passée Jaspeuse. These variations follow the dominant lithological changes between both formations and the clay layer. Moreover, they highlight the presence of more clay rich layers in the Halobia limestone at the -265, -247.5, -182 and -145.5 cm sample heights (Appendix C). This is further substantiated with these intervals being relatively enriched in Th (up to 13.8 ppm compared to 2.21 ppm average in calcareous/siliceous samples), an element typically associated with clay content in sediments (e.g., Plank, 2014). Micro-X-ray fluorescence analyses reveal that sulfur concentrations are consistently low (<300 ppm; Appendix D) across the entire interval, with the Triassic Halobia limestone Formation yielding slightly higher values (~100-200 ppm; Appendix D) compared to the Jurassic Passée Jaspeuse Formation, for which all but one sample have sulphur concentrations below the limit of detection (50 ppm for S; Appendix D).

The Halobia limestones display considerable variability in absolute trace element content between the samples, yet show generally consistent chondrite normalized trace element patterns (Fig. 4). The latter show an overall trend of relative light rare earth element (LREE) enrichment compared to the heavy rare earth elements (HREE; Fig. 4). Relative to CI-chondritic values (Sun and McDonough, 1989), La is observed to be up to 100 times chondrite compared to <1 times chondrite for Lu, and the limestones are characterized by a distinct negative Ce anomaly. A similar trend is observed for the Passée Jaspeuse, although with higher LREE contents (up to ~270 times chondrite for La) overall, and less variation in absolute concentrations between the samples (Fig. 4; Appendix C). All element concentrations surpass 4 times chondrite in the Passée Jaspeuse samples (Fig. 4), and no pronounced Ce anomalies are documented. By contrast, the clay layers show a distinctly different trend with relative enrichment in both LREE and HREE (Fig. 4).
5.4. Mercury concentrations

Mercury concentrations in Halobia limestone samples are generally very low (median of 0.38 ppb, with most below 0.1 ppb), likely due to the carbonate-rich lithology. For almost all limestone samples, a Hg content below the reliable detection limit of 0.05 ng (i.e., sub-blank level) was measured from 250 mg of analyzed material, indicating a negligible mercury concentration. By contrast, Hg contents in the argillaceous samples range from 0.58–28.5 ppb (Fig. 5). There is a sharp spike in Hg concentrations spanning 20–30 cm across the Halobia limestone–Passée Jaspeuse boundary, beginning just below the clay layer in the uppermost Halobia strata, and continuing 10 cm above the base of the Passée Jaspeuse (Fig. 5). This excursion is recorded by two samples from the clay layer, which have Hg contents of up to 117 ppb. Further up the Passée Jaspeuse stratigraphy, Hg levels return to relatively low values, reaching a maximum of 7.02 ppb, 91 cm above the base of the clay layer (Fig. 5). When normalizing the Hg concentrations to Al$_2$O$_3$ it is noted that the enrichments persist (Fig. 5), even elucidating a peak before the clay layer, suggesting a lack of correlation between Hg enrichment and clay content (Fig. 5).

5.5. Highly siderophile element concentrations

Concentrations of Os, Ir, Ru, Pt, Pd and Re are low for most samples from the Čanj section (Fig. 6; Appendix C). The exception is enrichment of HSEs in the main clay layer, where Os, Ir, Ru, Pt, Pd and Re contents reach up to 3.33 ppb, 0.41 ppb, 0.12 ppb, 7.6 ppb, 6.3 ppb and 2.1 ppb, respectively, in the most enriched interval (+ 1.5 cm) compared to a section average of 0.43 ppb Os, 0.073 ppb Ir, 0.035 ppb Ru, 1.2 ppb Pt, 1.2 ppb Pd and 0.15 ppb Re (Fig. 6). Overall, the Passée Jaspeuse has a higher Ir, Ru and Pd content compared to the Halobia limestones, with values only slightly above average. When normalizing the HSE concentrations to Th it is noted
that for most elements the enrichments disappear, suggesting a relation between HSE and clay content (Fig. 6).

5.6. Osmium-isotope compositions

Age-corrected whole rock $^{187}\text{Os}/^{188}\text{Os}_i$ (201.3 Ma) ratios for the Čanj section show an overarching gradual trend towards lower, more unradiogenic, values up section: from ~ 0.72 to 0.26. $^{187}\text{Os}/^{188}\text{Os}_i$ values decrease from 0.72 to 0.52 across the Halobia limestone strata, with a further decline up section in the Passée Jaspeuse from 0.50 to 0.26 (Fig. 6; Appendix C). Notable exceptions to this general trend include a minor shift to the most radiogenic values of 0.758 and 0.735, at -1.86 and -1.35 m, respectively, and a more pronounced shift from 0.481 to 0.254 within the clay layer, which records the most unradiogenic $^{187}\text{Os}/^{188}\text{Os}_i$ compositions within the section (Fig. 6). This sharp shift correlates with the overall enrichment in HSEs in the clay layer as described in the previous section; however, there is no correlation between the overarching decline in $^{187}\text{Os}/^{188}\text{Os}_i$ values up section and HSE contents (Fig. 6).

5.7. Paleomagnetic results

Results indicated unstable remanence directions during alternating field demagnetization for most of the samples. In general, about 50 to 80 % of the natural remanent magnetization is left at demagnetizing fields of 70 mT. Only a few samples could be demagnetized almost completely, which indicate the presence of high-coercivity minerals. A primary magnetization component could not be determined. The intensity of the natural remanent magnetization varies between 0.34 and $9.1 \times 10^{-7}$ Am$^2$/kg, which is rather low.
Magnetic property analyses indicate intermediate to high coercive forces ranging from 12 to 116 mT. Four of the six samples analyzed show a magnetization change peaking at 116 to 119 K. These values coincide with the so-called Verwey transition observed in 1.5 mm large magnetite single crystals (Özdemir and Dunlop, 1999). Thus, magnetic mineralogy of the Čanj section consists of multidomain magnetite and single domain hematite and paramagnetic minerals of variable contributions. Significant exchange bias fields, that would induce a shift of the hysteresis loop at low temperatures, and which may occur in oxidized magnetite core-shell nanoparticles (Phan et al., 2016) possibly during weathering or diagenesis, are not observed.

The magnetic property analyses conducted confirm the presence of high-coercivity minerals such as hematite and the absence of nanometer-sized magnetic minerals. The heterogeneity of the magnetic mineralogy and the rather low concentration of potential remanence carries did not favor the acquisition of a stable primary depositional remanent magnetization. A magnetostratigraphic record of the Triassic–Jurassic interval is likely not preserved at Čanj. Therefore, no further effort was undertaken to further investigate the Čanj section for paleomagnetic analyses.

6. Discussion

6.1. Čanj and the global T-J boundary record

We interpret the abrupt negative $\delta^{13}$C_carb excursion recorded at the Čanj section, correlative with the clay layer and turnover in radiolarian fauna, as being stratigraphically equivalent to the ICIE that marks the End Triassic extinction (ETE) horizon globally, as also concluded by Črne et al. (2011). This interpretation is supported by the existence of similar abrupt changes from calcareous to argillaceous lithologies correlative with this CIE at a number of other, more shallow
marine NW Tethyan sites, for example at Kuhjoch (Eiberg Basin, Austria; Ruhl et al., 2009), and Val Adrara (Lombardy Basin, Italy; e.g., Bachan et al., 2012) (Fig. 7). Whilst some of these shifts have been interpreted as resulting from lithological changes and/or diagenetic alteration, a similar secondary origin for the recorded negative excursion at Čanj is deemed unlikely. Firstly, the base of the δ^{13}C_{carb} shift takes place in the uppermost 20 cm of the Halobia limestone, and is thus not associated with any change in lithology, suggesting that it records a genuine variation in the isotopic composition of seawater. Secondly, a similar negative shift in the isotopic composition of bulk organic matter (δ^{13}C_{org}) has been documented at the same level as the δ^{13}C_{carb} shift at Čanj (Črne et al., 2011). Finally, the interpretation of these shifts as documenting a global carbon-cycle perturbation during the T-J faunal turnover is consistent with the worldwide record of this environmental disturbance (see Korte et al., 2018).

By contrast, the radiolarian T-J boundary in Japanese Panthalassic records (Katsuyama and Kurusu) has been interpreted as being stratigraphically correlative with the Main CIE (Fujisaki et al., 2018; Du et al., 2020; or Spelae CIE; Lindström et al., 2020). Thus, it could be argued that the δ^{13}C_{carb} shift at Čanj also records this later excursion, or that it comprises a combination of the Initial and Main CIEs due to the condensed nature of the clay layer. However, if the Čanj shift were indeed equivalent to the Main CIE, it would be expected that a sharp excursion in the uppermost Halobia limestones would mark the Initial CIE, which is not the case. Furthermore, the only other Tethyan site featuring radiolarian biostratigraphic information (albeit poorly constrained) at Csővár (Hungary), shows a δ^{13}C_{carb} shift interpreted as the Initial CIE between the highest known Triassic radiolaria and lowest Jurassic fauna (Pálfy et al., 2007). Thus, our interpretation of the Initial CIE at Čanj is consistent with this Tethyan record, as well as previously
studied eastern Panthalassic sites at New York Canyon (Nevada, USA), and the Queen Charlotte Islands (British Columbia, Canada) (see Orchard et al., 2007; Williford et al., 2007).

Thus, a stratigraphic correlation between the Main CIE and T-J radiolarian turnover in Japan appears to be the exception, rather than the rule. Moreover, the T-J radiolarian turnover in Japan also stratigraphically correlates with the last appearance of conodonts, which is documented around the ICIE level at almost all other sites. Consequently, either radiolarian and conodont turnover in the Tethyan and Panthalassic realms were asynchronous (see Du et al., 2020), or the faunal extinctions were coeval in these two ocean basins, and the isotopic shifts correlative with radiolarian turnover/conodont extinction at Katsuyama and Kurusu are in fact equivalent to the ICIE, as at Kuhjoch and Csővár. Given these uncertainties in global stratigraphic correlations, we favor correlation between Čanj and the more proximal Tethyan sites such as Csővár and Kuhjoč: i.e., that the $\delta^{13}\text{C}_{\text{carb}}$ shift associated with the lithological change and T-J faunal turnover marks the ICIE in the Budva Basin (Fig. 7).

Assuming that the negative $\delta^{13}\text{C}$ excursion associated with the Čanj clay layer is indeed the ICIE, it might indicate that the lower magnitude isotopic shifts 2 m below and 1 m above are equivalent to the Precursor and Main CIEs, respectively (Ruhl and Kürschner, 2011). However, the low magnitude of these excursions and lack of further stratigraphic information means that these interpretations remain speculative. As noted above, it is also possible that the Main CIE is also encompassed (together with the Initial excursion) in the $\delta^{13}\text{C}_{\text{carb}}$ shift around the clay layer. Additionally, the two negative excursions documented at the top of the studied Čanj section (Fig. 3; Fig. 7), likely of Sinemurian age (see Goričan, 1994; Črne et al., 2011), may be equivalent to the isotopic shifts reported in lower Sinemurian strata elsewhere (e.g., van de Schootbrugge et al., 2005; Bartolini et al., 2012) (Fig. 7). However, proving these hypotheses is hindered by the limited
biostratigraphic information and lack of magnetostratigraphic constraints at Čanj. Consequently, the remainder of the manuscript focuses primarily on the ETE interval recorded by the clay layer and the strata immediately above and below, which can be more reliably correlated with the stratigraphy at other sites.

6.2. Implications of the CIE at Čanj

At Čanj, the ICIE occurs at the same stratigraphic level as enrichments in HREEs, Hg, and HSEs, as well as a sharp shift to unradiogenic $^{187}\text{Os}/^{188}\text{Os}$ values (Fig. 4, 5, 6). Črne et al. (2011) interpreted the CIE at Čanj to reflect a global carbon-cycle disturbance that caused either accelerated carbonate dissolution, resulting in shoaling of the calcium compensation depth, or a biocalcification crisis that reduced carbonate input (e.g., a shift from tropical to microbally mediated mud-mound factory). Either of these processes could have been amplified in this region by increased tectonic subsidence, relative sea-level rise and/or a possible gap at the lithological boundary resulting in a relatively low magnitude of the CIE compared to other sites (Črne et al., 2011). Črne et al. (2011) suggested that either scenario causing the CIE can be explained with increased CO$_2$, SO$_2$, and CH$_4$ fluxes due to CAMP volcanism (Črne et al., 2011; see also Greene et al., 2012; Lindström et al., 2021); however, Črne et al. (2011) did not document specific geochemical markers at Čanj that could have directly linked the CIE to CAMP volcanism. The next step is thus to geochemically discern what happened around the ICIE at Čanj.

6.3. Origin of the highly siderophile element enrichment

Specific HSE concentrations can be an indication of either an extraterrestrial signature, (see e.g., Alvarez et al., 1980, Smit and Hertogen, 1980; Goderis et al., 2021), changes in redox states (Wang
et al., 1993), and/or volcanic activity (e.g., Whiteside et al., 2021). The enrichment of all reported HSEs in the extinction interval is apparent. However, when normalizing the HSE content to Th, an element associated with clay dilution, the HSE enrichments mostly disappear, the small peaks of Os/Th, Ir/Th, Pt/Th and Pd/Th that remain present are solely because of the scale used (Fig. 6). These observations suggest the HSE enrichments are closely related to the clay fraction in a given stratum and thus likely reflect terrestrial weathering as the source for HSE enrichment at Čanj. Figure 8 compares the Ir and Pt trends of Čanj and elsewhere in the NW Tethys (Kuhjoch) to that of sections in North America (Partridge Island) and the Panthalassic Ocean (Kurusu). What stands out is that the Ir and Pt enrichments are distinctly inconsistent in both pattern and level of concentrations. These inconsistencies are exemplified by the existence of multiple Ir peaks in the Partridge Island section, which contrasts with other sections either featuring general enrichment (Kuhjoch) or very small enrichments (Kurusu) (Fig. 8). The palynologically determined T-J interval at Partridge Island correlates with the second Ir peak, and, while this is the largest Ir peak, it is not at the same level as the ICIE in that locality (Fig. 8). For Kuhjoch, the comparison with Čanj is more straightforward as the initial enrichment in Ir is synchronous with the ICIE (Tanner et al., 2016), while for Kurusu only a small (~70 ppt) Ir anomaly exists (Hori et al., 2007). Čanj appears to contain the largest Ir enrichment recorded, with only the Partridge Island section matching the Ir enrichment (of up to 450 ppt), whilst lacking a similar peak in Pt content. The exact correlation between these peaks is difficult, as the use of HSEs for correlation remains tentative at best, with so far, no reliable correlation between specific HSE anomalies (see Whiteside et al., 2021 for further details). However, these data do show that Ir and HSE enrichment occur globally for the ETE. With the Čanj section likely indicating a terrigenous derived HSE enrichment, the question that remains is whether this is the case globally. For example, a global
HSE enrichment is observed for the K-Pg boundary, although unlike the ETE the HSE enrichment at the K-Pg is present globally (e.g., Goderis et al., 2013).

Specific HSE ratios can be employed to distinguish between terrigenous or extra-terrestrial sources for these elements. In Figure 9 the Pd and Pt ratio over Ir is presented: for non-fractionated chondrites these ratios should be lower than for fractioned values in mantle material (see e.g., Tegner et al., 2020), whilst the composition of iron meteorites encompasses a large range of compositions (Fig. 9). The observed element ratios of the Čanj section highlight the fractionated nature of the PGEs and, for the majority, the data overlaps with known compositions of CAMP volcanism. This is exemplified when comparing the CI-chondrite normalized HSE content of the Čanj section, where one can observe a strongly comparable normalized signature of all units when compared to CAMP, with notably the clay interval overlapping with CAMP compositions (Fig. 9C). Furthermore, when comparing the Pd/Ir and Pt/Ir ratios of Čanj to that of other T-J sections (Fig. 9B) it becomes apparent that ratios are comparable between sections, regardless of geographic location and absolute enrichment. In contrast, the Pd/Ir and Pt/Ir ratios of K-Pg boundaries overlap in composition with chondritic values, and do not plot close to compositions observed for coeval Deccan volcanism, suggesting that a chondritic origin of HSE enrichment should be observable over a terrigenous source in these elemental ratios, if a large impact occurred coevally with a LIP. This strongly argues that HSE enrichment at Čanj, and globally, are derived from the CAMP. Whilst the Pd/Ir and Pt/Ir ratios of iron meteorites encompass a large range in composition, overlapping in composition with all reported data sets (Fig. 9B), iron meteorites tend to have subchondritic HSE values, which greatly differs from the compositions observed at Čanj (Fig. 9C). Furthermore, Tegner et al. (2020) noted that iron meteorites are also known to be relatively enriched in rhodium, resulting in low Pt/Rh values (Ryan et al., 1990; Hoashi et al.,...
1993; Pateav and Jakobsen, 2004) and that samples from the T-J boundary present Pt/Rh values that are higher than known iron meteorites, further arguing against the HSEs at Čanj being derived from such a source.

Lastly, there appears to be a relation between the paleogeographic location of the T-J sections and HSE enrichment, with the sections that were closer to CAMP (i.e., Partridge Island and NW Tethys sections; Fig 7, 8) showing more absolute Ir enrichment than that of Panthalassic sections. Consequently, this might indicate that the magnitude of HSE deposition is related to CAMP proximity. Whether this indicates the means of deposition to be HSE-rich aerosols as a consequence of volcanic outgassing (Tanner et al., 2008; Tegner et al., 2020; Whiteside et al., 2021), proximal ash fall, and/or CAMP rock weathering (e.g., Tanner et al., 2008), remains to be determined, though the earlier observation that HSE enrichment is related to the clay fraction, implicates weathering of juvenile CAMP basalts as the main cause behind HSEs entering the system. Nonetheless, this apparent correlation of Čanj with both other T-J sections and CAMP, and the incongruity with both chondritic and iron meteorites (in contrast to the distinct correlation of K-Pg sections with chondritic values rather than Deccan Trap basalts) clearly favors a CAMP origin of the HSE compositions observed at Čanj, and thus that the HSE influx at the T-J boundary is terrestrially, rather than extra-terrestrially, derived.

6.4. A further examination of the terrestrial signal

With the HSE signal strongly implying a terrigenous origin of the element enrichment at the Čanj section, it becomes imperative to determine whether this is consistent with other geochemical markers. Despite being lithologically diverse, both the Halobia limestone and Passée Jaspeuse Fm. show trace element patterns typical of sedimentary lithologies, with LREE being relative enriched
when compared to the HREEs, and an overall flat lying MREE to HREE pattern (Fig. 4). Such a
trace element pattern is the common result of the upper continental crustal input of REEs
dominating the signal (Piper, 1974; McLennan, 2001). The observed difference between the two
formations, with the Passée Jaspeuse being overall more enriched in trace element content, is likely
caused by dilution by carbonate in the Halobia limestones compared to the more argillaceous
Passée Jaspeuse. Notably, however, the Halobia limestones show distinct Ce depletion in most
samples relative to neighboring trace elements (Fig. 4). Such a shift in Ce content may suggest that
the Halobia limestones were deposited in well-oxygenated seawater, as cerium can undergo
oxidation in seawater from soluble Ce(III) to the highly insoluble quadrivalent state (Piper, 1974;
Bellanca et al., 1997). Its subsequent fixation in particulate matter, including organics, is thought
to be responsible for distinctive depletion of Ce (Bellanca et al., 1997). In contrast, under reducing
conditions, Ce remains in its soluble Ce(III) state; therefore, marine sediments precipitated in
reducing environments will not show a relative Ce depletion (Piper, 1974; Bellanca et al., 1997).
Following this assertion, as both the boundary clay layer and the Passée Jaspeuse do not indicate
a Ce depletion, their Ce content might suggest that they were deposited under more oxygen-
depleted conditions.

The main clay layer, when compared to the other lithologies, shows a REE pattern
markedly different to that expected for a typical sedimentary rock (Fig. 4; e.g., McLennan et al.,
2001), presenting a distinct V-shaped pattern, with relative LREE and HREE enrichment
compared to the middle REEs. HREE enrichment is not typically associated with crustal material
(e.g. Rudnick and Fountain, 1995, Rudnick and Gao, 2003), and therefore implies the involvement
of lithologies with a relative HREE enrichment, such as mantle derived material that exhibits
higher Lu/La ratios linked to the decreasing incompatibility from La to Lu (e.g. Salter and Stracke,
Interestingly, a similar V-shaped trace element pattern has been observed in a limestone layer just below the ICIE level in the Kendlbachgraben section (Austria) (Pálfy and Zajzon, 2012). At that site, the paired LREE and HREE enrichment was interpreted to reflect a sedimentary component for the former, and a magmatic component, likely derived from CAMP, for the latter (Pálfy and Zajzon, 2012). To further investigate this assertion, we have plotted different CAMP section compositions in Figure 4. CAMP volcanics from N America and SW Europe, paleogeographically the most proximal part of the LIP to Čanj, have trace element patterns documenting relative HREE enrichment (Marzoli et al., 2011; Callegaro et al., 2014), which is consistent with the clay layer signature and that of the Kendlbachgraben section. CAMP volcanics from NW Africa, which were paleogeographically further from Čanj, exhibit much more variation in their trace element patterns and are overall less enriched in HREE content (Callegaro et al., 2017). This observation is corroborated by the HSE normalized trace element patterns of the Čanj clay interval being largely consistent with Moroccan CAMP lavas (Fig. 9C). In contrast, marine K-Pg sites show trace element patterns that lack a relative HREE enrichment (see e.g., Ebihara and Miura, 1996; Shrivastava et al., 2013; Loroch et al., 2016; Sial et al., 2018). This shows a strong contrast between the trace element enrichments of the extinction horizon at Čanj to that of K-Pg sections. As such, these observations support a genetic link of HREE enrichment at the ETE interval in relation to CAMP proximity and mark geochemical changes related to sedimentary influx and not just a change in facies.

To further emphasize this point, we note that the Hg enrichment observed at Čanj is stratigraphically correlative with the ICIE, consistent with peaks observed in both terrestrial and marine records of the ETE globally (Thibodeau et al., 2016; Percival et al., 2017; Lindström et al., 2019; Kovács et al., 2020). Mercury is typically deposited in sediments bound to organic material
but can also be associated with sulfides or clays (Shen et al., 2020). Given the paucity of organic matter (typically <0.1 wt%) and sulfides (<0.1 wt%) at Čanj, it is likely that Hg is primarily bound to clays in this record. However, some argillaceous intervals do feature slightly higher organic contents (although still very low: typically, <0.2 wt%). In this context, the record of the Hg peak in the main clay layer might suggest that it results from the lithological change to more argillaceous and marginally more organic-rich sediments. However, only two of the four samples in the clay layer record the distinct Hg peak, despite all four featuring a similar Al₂O₃ content, and nor are those two Hg-rich levels marked by notably elevated TOC (indeed, the highest TOC sample has a relatively low mercury concentration; Appendix B). Moreover, there are no comparable Hg enrichments in any other argillaceous levels studied here, suggesting an exceptional input of mercury to the Budva Basin during the extinction event. Given that this mercury peak is stratigraphically correlative with those from other sites, which have been linked to CAMP activity, and that volcanism is a major natural source of mercury to the surface environment (Grasby et al., 2019; Percival et al., 2021), it also suggests that the Čanj input was part of the same LIP-related global Hg-cycle perturbation documented as occurring during the extinction. Interestingly, several other T-J records show further mercury enrichment above the ICIE (e.g., Percival et al., 2017; Kovács et al., 2020; Yager et al., 2021), potentially reflecting continued CAMP activity. Whilst Hg contents in Passée Jaspeuse sediments are slightly higher than in the underlying Halobia limestones, there is no clear peak above the extinction interval at Čanj. In contrast, two low magnitude peaks (albeit each consisting of only one data point) below the main clay layer may support previous hypotheses of pre-extinction perturbations to the global Hg cycle (Lindström et al., 2019).
6.5. Osmium isotope record of the Čanj section

The geochemical evidence presented above supports the involvement of CAMP over an other (extra-)terrestrial influx. To further test this hypothesis, the $^{187}\text{Os}/^{188}\text{Os}$ values of the Čanj section were examined. Due to the relatively short residence time of Os in seawater (~ 10 ky; Peucker-Ehrenbrink and Ravizza, 2000), trends in sedimentary $^{187}\text{Os}/^{188}\text{Os}_i$ record rapid changes in osmium fluxes to the global ocean where sudden shifts to unradiogenic values might indicate juvenile flood basalt weathering, submarine volcanism, and/or impact events ($^{187}\text{Os}/^{188}\text{Os} = \sim 0.13$; Allégre et al., 1999) and shifts to radiogenic values might indicate enhanced terrestrial weathering of continental crust (average modern-day riverine runoff $^{187}\text{Os}/^{188}\text{Os} = \sim 1.4$; Peucker-Ehrenbrink and Jahn, 2001; see also Sato et al., 2013; Goderis et al., 2021).

The $^{187}\text{Os}/^{188}\text{Os}_i$ values at Čanj display an overall gradual decrease upsection, suggesting a rising input of unradiogenic osmium to the global ocean during the T-J interval, with a transient shift to an even more unradiogenic composition at the extinction interval (Fig. 6). The majority of this shift appears to initiate just below the clay layer, with the Halobia limestone featuring relatively stable $^{187}\text{Os}/^{188}\text{Os}_i$ values between 0.76 and 0.61 up to -0.33 m, above which it shifts to more unradiogenic values with a distinct sharp shift to the most unradiogenic composition in the main clay layer (Fig. 6). Notably, above the transient shift in $^{187}\text{Os}/^{188}\text{Os}_i$ values associated with the clay layer, the gradual decrease resumes, with no return towards more radiogenic compositions observed in the remainder of our sampling interval. This trend highlights that a gradual increase in the flux of more unradiogenic osmium to seawater began prior to the ICIE, but with a sharp transient increase in this influx during the extinction interval. This pattern is largely consistent with that of St. Audrie’s Bay, which records a very similar overall decreasing $^{187}\text{Os}/^{188}\text{Os}_i$ trend (Cohen and Coe, 2002; Fig. 10). There, the $^{187}\text{Os}/^{188}\text{Os}_i$ trend was interpreted to reflect the
continued influx of unradiogenic Os from CAMP volcanism (Cohen and Coe, 2002). However, Cohen and Coe (2002) did not sample the stratigraphic interval marked by the ICIE (as determined by Hesselbo et al., 2002), precluding direct comparison of the seawater $^{187}\text{Os}/^{188}\text{Os}$ records at the extinction horizon between St. Audrie’s Bay and Čanj. Nonetheless, the data suggest comparable behavior of the $^{187}\text{Os}/^{188}\text{Os}$ values in sections of the NW Tethys and Northern Europe (Fig. 10).

Interestingly, whilst the Panthalassic Kurusu section records a similar decline in $^{187}\text{Os}/^{188}\text{Os}$ values, this shift is shown as taking place during the Late Norian to middle Rhaetian interval, with a sharp return to more radiogenic compositions during the latest Rhaetian, and no significant unradiogenic shift at the radiolarian defined Rhaetian – Hettangian boundary (Kuroda et al., 2010; Fig. 10). Although this pattern is similarly interpreted as the initial gradual input of unradiogenic Os, likely through weathering of CAMP basalts, and followed by the increased radiogenic Os input from enhanced continental weathering outweighing the unradiogenic Os input during the late Rhaetian (Kuroda et al., 2010), the timing contrasts with data from Čanj and St. Audrie’s Bay. It should be noted that there is currently no evidence for CAMP magmatism as early in the Rhaetian as implied by the Kurusu section, although the geological record of the LIP is limited by relatively poor preservation of the igneous units. If all three sections do indeed record CAMP basalt weathering, the differences between Tethyan and Panthalassic sections might indicate an apparent difference in Os isotopic behavior between the Čanj and St. Audrie’s Bay on the one hand, and the Kurusu section on the other hand, potentially highlighting a different response to the mechanism behind the extinction in the Panthalassic Ocean when compared to the Tethys Ocean and Northwestern Europe. However, this conclusion would demand that the global ocean was heterogeneous with respect to osmium during the Triassic-Jurassic interval, in contrast to today. This assessment highlights the complexity of the events surrounding the T-J boundary, with the
general trends appearing to be comparable globally, with HSE, REE, Hg and unradiogenic Os enrichment, however, with a magnitude of enrichment that is neither uniform nor consistent (Fig. 8 and 10).

The spike of more unradiogenic Os composition in the Čanj clay layer correlates with the extinction horizon and ICIE, which was coeval with the onset of CAMP eruptions (Deenen et al., 2010; Ruhl et al., 2011; Blackburn et al., 2013). As such this unradiogenic shift likely marks the main onset of CAMP. Whilst this shift was not previously detected at St. Audrie’s Bay or Kurusu, the relatively low-resolution dataset at the former site and uncertain stratigraphic position of the ICIE at the latter means that this sharp decline in \(^{187}\text{Os}/^{188}\text{Os}\) values could nonetheless be present at both. Further studies of sites where the ICIE and extinction horizon are stratigraphically well constrained are needed in order to confirm whether the unradiogenic Os isotope shift recorded in the Čanj clay layer is preserved globally. As it might represent a convincing stratigraphic correlation to the onset of CAMP.

This caveat notwithstanding, the overall Os curve at Čanj is consistent with the timing of known CAMP magmatism, with the initial onset predating the ETE by at least 100 kyr (Deenen et al., 2010; Davies et al., 2017; Heimdal et al., 2020), expressed as a small gradual shift to unradiogenic values, while the first known major eruptions coincided with the ETE (Deenen et al., 2010; Ruhl et al., 2011; Blackburn et al., 2013). The continuation of CAMP basalt outpourings for at least 600 kyr after the extinction event (Marzoli et al., 1999; Blackburn et al., 2013; Marzoli et al., 2018) is also consistent with the gradual unradiogenic Os shift observed. Hypothetically, the gradual decline in \(^{187}\text{Os}/^{188}\text{Os}\) values could have resulted from a fall in continental weathering rates and associated runoff of radiogenic Os. However, such a decrease in continental weathering is unlikely at a time of elevated atmospheric CO\(_2\) and associated climate warming (McElwain et
leaving increased input of mantle osmium from weathering of CAMP basalts as the most likely cause. Consequently, we interpret that the sharp shift in $^{187}$Os/$^{188}$Os values at the ETE horizon, as well as the more prolonged shift to a more unradiogenic osmium-isotope composition of seawater observed in the global T-J record, resulted from CAMP weathering. These observations agree with the HSE, REE and Hg data presented in this study and not only argues for the CAMP as the most likely culprit behind the extinction event, but also establishes the Čanj section as one of the best continuous deep marine T-J sections on the planet.

7. CONCLUSION

At Čanj, Montenegro, a well preserved and continuous T-J section was studied where deep-marine Triassic carbonates of the Halobia limestone Formation are abruptly interrupted by a ~6 cm finely laminated clay layer, before transitioning to the argillaceous Jurassic red beds of the Passée Jaspeuse. Within this clay layer a negative carbon isotope excursion, relative HREE enrichment, Hg increase, HSE enrichment and sharp shift to unradiogenic Os ratios are recorded. It is interpreted that this sudden change in lithology marks the end-Triassic extinction event. The observed geochemical variations along the Čanj section are consistent with the Central Atlantic Magmatic Province as the main driver behind the end-Triassic extinction. This marks the Čanj section as a rare T-J section that exquisitely encapsulates the geochemical record of the end Triassic extinction interval in the Tethyan deep sea, especially when compared to the overall inconsistent global record.

Declaration of competing interest
The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data Availability

All data used are listed in the references and appendices.
Supplementary data

Supplementary data to this article can be found online at: XXXXXXXX
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**Figure Captions**

Figure 1 (A) The Čanj section, Montenegro. (B) Zoomed in view of the Čanj clay layers.

Figure 2. Geological map of the area surrounding the Čanj section. Based on the Institute for Geological and Geophysical Research 1 : 100000 Geological Map of former Yugoslavia (Osnovna Geološka Karta SFRJ), Budva, K34-62, 1969 and Bar, K34-64, 1976 from the Federal Geological Institute, Belgrade. ALB = Albania, BIH = Bosnia and Herzegovina, GRC = Greece, MKD = Republic of North Macedonia, MNE = Montenegro, SRB = Serbia, XKX = Kosovo.
Figure 3. Lithological log (this study), radiolarian biostratigraphy showing the last occurrence of Triassic radiolarian and first occurrence of Jurassic radiolarian (Črne et al., 2011), and δ\(^{13}\)C\(_{\text{carb}}\) trends (Črne et al., 2011; this study) for the Čanj section (Budva Basin, Montenegro). Pale red shading indicates the stratigraphic extent of the negative δ\(^{13}\)C\(_{\text{carb}}\) excursion inferred to be equivalent to the Initial CIE. Bold dark blue line indicates the moving five-point average for the new δ\(^{13}\)C\(_{\text{carb}}\) dataset. Question mark indicates that the exact position of the Hettangian–Sinemurian boundary is unknown.

Figure 4. CI-chondrite–normalized trace-element concentrations, with normalization values from Sun and McDonough (1989). CAMP compositions for NW Europe and NW Africa from Callegaro et al. (2014, 2017) respectively, N America data is from Marzoli et al. (2011). CAMP = Central Atlantic Magmatic Province.

Figure 5. δ\(^{13}\)C\(_{\text{carb}}\), Hg, Al\(_2\)O\(_3\), and Hg/Al\(_2\)O\(_3\) trends from Čanj. Pale brown shading indicates clay-rich layers analyzed for Hg concentrations.

Figure 6. Selected highly siderophile element variations for the Čanj section. Shown in black is absolute element concentrations. In red is the selected element normalized to Th\(^*10^{-3}\) as normalizing to Th in pbb would effectively remove all peaks. \(^{187}\)Os/\(^{188}\)Os\(_{\text{ig}}\) is age corrected to 201.3 Ma.

Figure 7. Stratigraphic correlation of Čanj with other T-J records from the NW Tethys and Panthalassia, based on ammonite, conodont, and radiolarian biostratigraphy, and δ\(^{13}\)C
chemostratigraphy. The palaeogeographic location of each site is indicated; the map is adapted from Greene et al. (2012). Čanj biostratigraphy is from Črne et al. (2011); log and δ¹³C data are from this study. All Kuhjoch data are from Ruhl et al. (2009). All Val Adrara data are from Bachan et al. (2012). All Csővár data are from Pálfy et al. (2007). Note that constraints on the stratigraphic extent of radiolarian biozones (and, therefore, the radiolarian T-J turnover) are limited at Csővár. Kennecott Point biostratigraphy is from Ward et al. (2001, 2004); all other information from Williford et al. (2007). Katsuyama biostratigraphy from Carter and Hori (2005); all other information from Fujisaki et al. (2018). Kurusu biostratigraphy is from Hori et al. (2007); lithological information from Du et al. (2020); δ¹³C data are from Kuroda et al. (2010).


Figure 9. Pd/Ir vs Pt/Ir diagram adapted from Tegner et al. (2020) for the Čanj section. (A) Čanj section subdivided per formation, including the clay layer. Shown for comparison are CI (Fischer-Gödde et al., 2010) and ordinary chondrites (McDonald et al., 2001), CAMP volcanism from Morocco and Iron meteorites (Tegner et al., 2020). (B) Čanj section (shown as dark-grey field) compared to sediments from sections containing the end-Triassic extinction event in the Fundy Basin, Canada (Tanner and Kyte, 2005), Kurusu, Japan (Hori et al., 2007), Sidi Rahal, Morocco (Whiteside et al., 2021) and Exeter, USA (Whiteside et al., 2021). Fields for the K-Pg impact layer, Deccan Trap volcanism and Iron meteorites are from Tegner et al. (2020) and references therein.
(C) CI chondrite normalized HSE pattern for Čanj and selected other compositions. CI chondrite normalization value from Palme et al. (2014).

Figure 10. $^{187}\text{Os}/^{188}\text{Os}_i$ site comparison. St Audrie’s Bay data from Cohen and Coe (2002) and Hesselbo et al. (2002), Kuhjoch data from Ruhl et al. (2009) and Tanner et al. (2016). Čanj data from this study. Kurusu data from Kuroda et al. (2010). Katsuyama data from Fujisaki et al. (2018). Error bars (2se) are smaller than line thickness (see Appendix C)