Chapter 10

Chemostratigraphy across the Triassic–Jurassic boundary

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Abstract

The Triassic–Jurassic transition (~201.5 Ma) is marked by one of the biggest mass extinctions in Earth history. This was accompanied by significant perturbations in ocean and atmosphere geochemistry, including the global carbon cycle, as expressed by major fluctuations in carbon isotope ratios. Central Atlantic

Magmatic Province (CAMP) volcanism triggered environmental changes and played a key role in this biotic crisis. Stratigraphic and chronological studies link the end-Triassic mass extinction with the early phases of CAMP volcanism, and notable mercury enrichments in geographically distributed marine and continental sediments are shown to have onset coincident with the extrusive emplacement of CAMP. Sulphuric acid induced atmospheric aerosol clouds from subaerial CAMP volcanism may explain brief, relatively cool seawater temperatures in the mid-palaeolatitude pan-European seaway, across the T–J transition. Concomitant CAMP induced carbon degassing may explain the overall, long-term shift towards much warmer conditions. The effect of CAMP volcanism on seawater $^{87}Sr/^{86}Sr$ values might have comefrom other factors, such as associated elevated continental weathering.

Reconstructions of changes in ocean–atmosphere geochemistry and associated (causative) effects on palaeoclimatic, palaeoenvironmental and palaeoceanographic conditions on local, regional and global scales are, however, not fully constrained. For example, the evolution of the global carbon cycle across the T–J transition is still debated because changes in magnitude and rate-of-change in $\delta^{13}C$ – coincident with the end-Triassic mass extinction interval – differ between substrates (organics *vs* calcite) and depositional environments. Thus, fluxes of carbon release at this time and their mechanistic links to the emplacement of CAMP are still poorly understood.

Keywords: T–J boundary; Chemostratigraphy; Carbon isotopes; Oxygen isotopes; Hg enrichments; $^{87}Sr/^{86}Sr$, Redox sensitive elements

10.1. Introduction

The base of the Jurassic System, and therewith the Triassic–Jurassic (T–J) boundary (201.36 Ma, Wotzlaw et al., 2014), is defined in the Global Stratotype Section and Point (GSSP) at Kuhjoch (Karwendel Mountains, Northern Calcareous Alps, Tyrol, Austria) (Hillebrandt et al., 2013). The T–J boundary transition at Kuhjoch, and at coeval successions in the same area (see Hillebrandt et al., 2013, for overview) as well as elsewhere on the globe (see Hesselbo et al., 2007 for overview) are sedimentologically, palaeontologically and chemostratigraphically well studied (Fig. 1). It was recognised already decades ago that one of the most severe mass extinctions in Earth's history, affecting both the marine and continental biota, occurred at this time (e.g., Newell, 1967; Raup & Sepkoski, 1982; Hallam & Wignall, 1997; McElwain et al., 1999, 2007). The biotic crisis occurred in the latest Triassic (end-Triassic mass extinction) and is radio-isotopically dated at 201.564±0.15 Ma (Blackburn et al., 2013; Davies et al., 2017). Several hypotheses have been suggested

inrelation to triggering of this biotic crisis, including extraterrestrial impact (Olsen et al., 1987, 2002; Morante & Hallam, 1996), extensive volcanism in the Central Atlantic Magmatic Province (CAMP) (e.g., Marzoli et al., 1999; Whiteside et al., 2010; Schoene et al., 2010; Blackburn et al., 2013; Davies et al., 2017; Percival et al., 2017), climate change (McElwain et al., 1999; van de Schootbrugge et al., 2009; Ruhl et al., 2011), increased photic zone anoxia/euxinia leading to enhanced ocean stratification (Richoz et al., 2012; Jaraula et al., 2013; Kasprak et al., 2015) or ocean acidification (Hautmann et al., 2008; Hönisch et al., 2012; Greene et al., 2012).

The T–J transition was accompanied by major changes of ocean and atmosphere geochemistry, to which the Triassic–Jurassic biotic crisis is likely associated (e.g. Hallam & Wignall, 1997; Pálfy et al., 2001; Cohen & Coe, 2002, 2007; Hesselbo et al., 2002; Pálfy, 2003; Tanner et al., 2004; McElwain & Punyasena, 2007; Hautmann et al., 2008; Kiessling et al., 2009; Kiessling, 2009; Schaller et al., 2012; Bottini et. al., 2016). Strontium isotope data suggest temporary discontinuation of the long-term decrease of the marine $^{87}Sr/^{86}Sr$ curve around the T–J transition (Veizer et al., 1999). A first indication for a negative carbon isotope excursion at the T–J boundary was reported from the Kendelbach section in the Northern Calcareous Alps (Austria; Fig. 1), but the authors regarded this as likely diagenetically induced (Hallam & Goodfellow, 1990). McRoberts et al. (1997) showed subsequently a negative $\delta^{13}C$ peak on bulk rock carbonates originating from the Lorüns section of the Northern Calcareous Alps; however, this was based on only a single sample with a light value. McElwain et al. (1999) observed two very light $\delta^{13}C$ values in organic material from bulk rocks of the terrestrial Astartekløft succession in Greenland (Fig. 1), where two light carbon isotope data-points occur over 20 m in a low resolution, and biostratigraphically poorly constrained, dataset. Combined, these results were suggestive of a potential global carbon cycle perturbation at the Triassic–Jurassic transition and they presented a starting point for scientists, including the working group from IGCP project 458 (see Hesselbo et al., 2007), to evaluate the evolution of the global carbon cycle at this time.

Here we review and evaluate temporal fluctuations of isotope ratios and elements in geomaterials across the T–J boundary, enabling to develop a comprehensive chemostratigraphy which can be applied for both transcontinental stratigraphic correlation, and understanding the processes causing environmental and climatic perturbations at this important time in Earth history, which ultimately led to biotic change and mass extinction.

10.2 The end-Triassic mass extinction and potential causes

The end-Triassic biotic crisis is one of the big five mass extinction events in Earth history (Raup & Sepkoski, 1982). Triassic ammonoids, scleractinian corals and conodonts became extinct in the oceans (e.g., Guex et al., 2004; Alroy, 2010) and major turnover in megaflora, sporomorphs and early Mesozoic vertebrates occurred on land (e.g., Benton, 1995; McElwain et al., 1999; 2009; van de Schootbrugge et al., 2009). The patterns of this event and the causes of the mass extinction are controversial and different extinction scenarios have been suggested.

An early hypothesis for what might have caused the end-Triassic mass extinction is a potential impact of a celestial body. Such an event was proposed for the end-Cretaceous mass extinction after finding an iridium peak in the event beds at Stevns Klint (Denmark) and Gubbio (Italy) reaching highest values of 3 ng/g at the latter locality (Alvarez et al., 1980). The evidence of an impact event as the cause for the biotic crisis is based on the fact that iridium is rare in crustal rocks (<0.1 ng/g, but relatively enriched in certain typesmeteorites (>1 μg/g) (Ehmann et al., 1970; Crocket & Teruta, 1977; Crocket et al., 1979). An enrichment of Ir was also identified in the Grenzmergel of the T–J boundary section at Kendelbach (Austria) and St. Audries Bay (U.K.) (Orth et al., 1990; McLaren & Goodfellow, 1990), but with much lower concentrations compared to that of the K–T boundaries, and such small enrichment can be explained by volcanic activity only (McCartney et al., 1990). A clear spike of Ir with maximum values of 0.285 ng/g was identified by Olsen et al. (2002) in a white clay layer between typical Triassic and the first typical Hettangian pollen and spore assemblages in the Jacksonwald syncline section of the Newark Basin. Even this Ir peak is much smaller compared to that of the Cretaceous–Paleogene boundary, but it is higher than the typical crustal concentration. No clear evidence of other indicators for an extraterrestrial impact, such as impact glass (microtektites, tektites), Ni-rich spinels, micro-spherules, or micro-diamonds, have been found so far at the T–J boundary (e.g. Tanner et al., 2004). Reports of quartz with planar deformation features from the Grenzmergel at the Kendelbach section in Austria (Badjukov et al., 1987) are probably not impact indicators (Hallam & Wignall, 1997), but rather metamorphic features (Mossman et al., 1998). Furthermore, the Manicouagan impact crater of Quebec, with ~ 100 km diameter one of the largest impacts known in the Phanerozoic (*Grieve*, 1998) and originally favoured by Olsen et al. (1987) to be responsible for the end-Triassic mass extinction, is more than 10 million years older in age (Hodych & Dunning, 1992). Other Triassic craters (for review see Tanner et al., 2004), such as the 80-km Puchezh–Katunki structure in Russia (Ivanov, 1992), did not fit either with the end-Triassic mass extinction, or the stratigraphic background of these structures is too poor to correlate (Pálfy, 2004; Tanner et al., 2004). In addition, the $^{187}Os/^{188}Os$

decrease that was used to identify an impact (Sato et al., 2013), took place already in the Late Triassic Norian Stage, therefore predating the T–J boundary.

A more popular scenario for the cause of the end-Triassic biotic crisis is enhanced volcanism. It is well documented that the supercontinent Pangaea – dominating the late Paleozoic and Triassic palaeogeography for at least 100 million years – began to break-up around the T–J transition substantiated by extensive volcanism in the CAMP, indicating the opening of the Central Atlantic Ocean (Marzoli et al., 1999; Schlische et al., 2003). This province had an extent of about 1.1×10^7 km^2 spanning over North and South America, northeast Africa, and southwest Europe (Fig. 1; e.g., Merle et al., 2014; Pálfy & Kocsis, 2014). The CAMP represents one of the most prominent igneous provinces (LIPs) in Earth history (Wignall, 2001; Blackburn et al., 2013). CAMP comprises about two and a half million cubic kilometres basaltic lava, including continental flood basalts that flowed into the large rift basins, and mafic dykes and sills intruded into sediments (McHone, 2003; Saunders, 2005; Davies et al., 2017). Some CAMP basalt flows, volcanic ashes (Schoene et al., 2010; Blackburn et al., 2013; see also Tanner et al., 2004) or sills (Davies et al., 2017) have been directly related to the end-Triassic mass extinction. It has been suggested that the CAMP activity documented by seismites occurring worldwide and by mafic rocks in Morocco, started already before the end-Triassic biotic event (Dal Corso et al., 2014; Lindström et al., 2015).

In any case, vast amounts of CO_2 were exhaled by the CAMP volcanism and, in addition, more CO_2 was generated by thermal metamorphism of organic-rich sediments (McElwain et al., 2005; Svensen et al., 2007; Korte et al., 2009). This CO_2 injection has been suggested to be responsible for an abrupt global warming (e.g., Blackburn et al., 2013). At T–J boundary sections of the Western Carpathians, an abrupt cessation of carbonate deposition of the Fatra Formation led to the ‘boundary shale’ facies of the Kopienec Formation, with an increase of riverine influx delivering siliciclastic material. This sudden shift has been taken to indicate a sudden climate change at the erosional T–J boundary (Michalík et al., 2007), potentially induced by an enhanced hydrological cycle upon rising temperatures. On the other hand, strong short-term fluctuations and a general eustatic sea level fall has been suggested for North American and European successions, and it has been suggested that this was caused by glacial eustasy, thus by climate cooling brought about by sulphur degassing in an early stage of the CAMP (Guex et al., 2004, 2012; Schoene et al., 2010). However, the finding of photic zone anoxia/euxinia resulting from enhanced ocean stratification (Kasprak et al., 2015), as well as the marine biodiversity drop (van de Schootbrugge et al., 2009), have rather been attributed to warming global climates.

10.3. Well investigated Triassic–Jurassic boundary successions

Geochemical and chemostratigraphic studies of marine and continental Tr–J boundary successions, including some previously proposed Global Stratotype Sections and Points (GSSPs) for the base of the Jurassic, have been conducted in recent years. Here, we present a synoptic stratigraphic framework and discuss some of the outstanding problems (see Fig. 1).

10.3.1. Alpine sections including the GSSP Kuhjoch succession (Austria)

The Triassic–Jurassic transition has been extensively studied in marine shelf settings, such as the Eiberg Basin (Austria), along the passive margin of the northwestern Tethys Ocean. Triassic–Jurassic boundary successions in the Northern Calcareous Alps (NCA) are stratigraphically expanded and highly fossiliferous and mainly found in the Eiberg Basin, a Rhaetian intraplatform depression, which extends for over 200 km from the Salzkammergut in the east to the Lahnewiesgraben valley (Bavaria) in the west (Hillebrandt et al., 2013). The intraplatform Eiberg Basin was bordered to the southeast by a broad Rhaetian carbonate platform (Dachstein platform), locally with fringing reefs and, further southeast, an outer shelf (Hallstatt Basin), transitional to the Tethys Ocean (Hillebrandt et al., 2013). Another partly terrigeneous-influenced carbonate platform, represented by the Oberrhaet Limestone, existed to the north. Intraplatform depressions within the Oberrhaet Limestone, are also marked by sedimentary successions across the T–J transition, similar to those in the Eiberg Basin.

The Rhaetian Kössen Formation spread over the Hauptdolomit, with subtidal mixed limestone and clay bearing bioclastic rocks. The sedimentary facies of the Rhaetian Kössen Formation changed around the middle to late Rhaetian boundary (base of *marshi* Zone), with the onset of a basinal facies (Eiberg Member), following on the shallow water sequences of the Hochalm Member (Golebiowski, 1989). The subsiding Eiberg Basin reached 150-200m water depth in Late Rhaetian (Golebiowski 1989; Krystyn et al., 2005; Mette et al., 2012; Hillebrandt et al., 2013, and references therein). Marine conditions therefore prevailed across the Triassic–Jurassic transition. However, a distinct and abrupt lithological change from basinal

carbonates of the Eiberg Member to marls and clays of the Tiefengraben Member (lower Kendlbach Formation) occurred, possibly in response to a sea-level drop. This stratigraphic horizon has also been suggested to coincide with the onset of extrusive CAMP emplacement, partly based on elemental geochemistry and mineralogy for the bituminous topmost layer of the Kössen Formation (Pálfy & Zajzon, 2012). Observed lithological change at this time may alternatively therefore also reflect changing climatic and environmental conditions, leading to increased precipitation and weathering, and the associated enhanced supply of siliciclastic materials into the Eiberg Basin.

The lithological transition at the top of the Kössen Formation is marked by the development of a thin (1–5cm) bituminous layer, with total organic carbon (TOC) values up to 10% (Ruhl et al., 2009). The following reddish grey and faintly laminated mudstones of the Schattwald Beds are marked by low TOC and low carbonate concentrations, and gradually transition into greyish brown marls of the remainder of the Tiefengraben Member (Ruhl et al., 2009). The Tiefengraben Member (and Kendlbach Formation) is replaced up-section by Lower Jurassic (upper Hettangian to Sinemurian) carbonate strata of the Adnet Formation, representing increasing water-depths and a more pelagic influence.

All sections within the Eiberg Basin show similar sedimentary records across the T-J boundary, with only minor variations in carbonate and clay contents depending on more proximal *vs* more distal positions. The Karwendel Syncline exposures arguably provide one of the most expanded and complete marine Triassic-Jurassic boundary sequences worldwide, which is one of the reasons the Kuhjoch locality was selected as Global Stratotype Section and Point (GSSP) for the base of the Jurassic.

The abrupt lithological change from the predominantly carbonate Kössen Formation to the marly sediments of the lower Tiefengraben Mb (locally known as the ‘Grenzmergel’, which includes the reddish-grey colored Schattwald Beds) was traditionally considered to represent the T-J boundary (Golebiowski, 1990; Hallam & Goodfellow, 1990), as it is marked by the disappearance of typical Triassic ammonoid and conodont fossils. More recent studies however showed that the lowest metres of the Tiefengraben Member still yield Triassic microflora and nannoflora (Kürschner et al., 2007).

Newly described psiloceratids in the Triassic–Jurassic boundary successions of the Eiberg Basin, including *Psiloceras spelae tirolicum*, stratigraphically precede the well-known earliest *Psiloceras* of England (*P. erugatum*, *P. planorbis*) and the Alps (*P. calliphyllum*) (Hillebrandt et al., 2013). The first occurrence of

Psiloceras spelae tirolicum was selected as marker for the base of the Jurassic System (Hillebrandt et al., 2013). Within the GSSP succession, ammonites of the bed with *P. calliphyllum* can be compared with the earliest *Psiloceras* in England (Bloos, 2004; Page, 2003; Hillebrandt and Krystyn, 2009; Page et al., 2010).

The GSSP for the base of the Jurassic and several other Triassic–Jurassic boundary sections of the Eiberg Basin were studied in detail for micro- and macrofossil occurrences (McRoberts et al., 1997; Kürschner et al., 2007; Bonis et al., 2009a, 2009b; Hillebrandt & Krystyn, 2009; Bonis & Kürschner, 2012; Hillebrandt et al., 2013; and references therein). Notably, the first occurrence of terrestrial biological markers (pollen/spores) stratigraphically close to the base of the Jurassic allow also for correlation to continental sedimentary sequences of this age (Kürschner et al., 2007; Bonis et al., 2009a; Bonis & Kürschner, 2012). Carbon-isotope analyses of bulk sedimentary organic matter as well as individual higher-plant derived leaf-wax *n*-alkanes, show a pronounced $\delta^{13}C$ negative excursion of ~6 and ~8 ‰, respectively, in the studied sections of the Eiberg Basin (Ruhl et al., 2009; Ruhl et al., 2011). This negative carbon isotope excursion (CIE) occurs at the very base of the Tiefengraben Member, directly coinciding with the end-Triassic mass extinction, and it is marked by a TOC-rich bituminous black shale at its onset (Bonis et al., 2009b). Further to the west, in theLechtal nappe of the Bajuvaric nappe group, in the western NCA (western Austria), the Triassic–Jurassic transition is represented in extensive carbonate platform sedimentary sequences (Felber et al., 2015). Also here, the upper Triassic Kössen Formation was deposited on top of the Hauptdolomit (of which the upper part is informally known as ‘Plattenkalk’), and followed by prograding siliciclastic sedimentation (Berra et al., 2010). The transitional Schattwald Beds, including the T–J boundary are here followed by the Hettangian ‘Lorüns oolite’ (Felber et al., 2015).

Specific clay mineralogies and (REE) elemental concentrations and ratios in the lower Tiefengraben Member of the Eiberg Basin were suggested to have been associated with the onset of CAMP volcanism and the associated atmospheric dispersal of volcanic ash and weathering of clays (Pálfy & Zajzon, 2012). The combined bio- and chemostratigraphic framework of the Triassic–Jurassic boundary sections in the Austrian Eiberg Basin provide an excellent framework for the stratigraphical correlation to marine and continental Triassic–Jurassic sedimentary sequences elsewhere, for the study of oceanographic, climatic and environmental changes at that time, and for understanding their temporal and potentially causative link to CAMP volcanism.

10.3.2. Bristol Channel Basin at St Audries Bay (UK)

The Triassic–Jurassic sedimentary succession in the Bristol Channel Basin has long been studied for micro- and macrofossil composition, and the outcrops at St Audries Bay were proposed as GSSP for the base of the Jurassic (Warrington et al., 1994, 2008, and references therein). The recognition of a negative excursion in $\delta^{13}C_{TOC}$ coinciding with the end-Triassic mass extinction event in this sedimentary record, sparked the study of the potential (temporal) link between CAMP volcanism, global carbon cycle change and biotic response at this time-interval (Hesselbo et al., 2002). The ~5 ‰ negative CIE, informally called the 'initial negative CIE' at the end–Triassic mass extinction interval is followed by a return to more positive values and a subsequent long-term shift to yet more negative values (the 'main CIE') (Hesselbo et al., 2002). This evolution in $\delta^{13}C_{TOC}$ is also mirrored in the $\delta^{13}C_{fossil\text{-}calcite}$ record from the same section (Korte et al., 2009). Facies analysis in the Bristol Channel Basin sedimentary succession suggests a sea-level lowstand stratigraphically shortly preceding the end-Triassic mass extinction and 'initial' negative CIE (Hesselbo et al., 2004).

Palaeomagnetic, chemo-, bio- and cyclostratigraphic analyses of the sedimentary record at St Audries Bay has provided a detailed stratigraphic framework for correlation to marine and continental sedimentary records elsewhere, and to the CAMP magmatic records of Morocco and North America (Hounslow et al., 2004; Warrington et al., 2008; Bonis et al., 2010; Deenen et al., 2010; Ruhl et al., 2010; Bonis & Kürschner, 2012; Mander et al., 2013; Hüsing et al., 2014; Xu et al., 2017).

10.3.3. Csővár section in the Transdanubian Range Unit (Hungary)

The sections near the village of Csővár are located in north-central Hungary (Fig. 1), near the northeastern end of the Transdanubian Range Unit segment of the Tethyan shelf (Haas et al., 2010). The Triassic-Jurassic transition is recorded in open marine, basinal to toe-of-slope carbonates of the Norian to Sinemurian Csővár Limestone Formation (Pálfy & Haas, 2012) deposited in a periplatform basin. Dark grey, bituminous and partly graded calcarenite (containing shallow water fossils and clasts supplied from the adjacent platform) and marl are predominant in the lower part and well bedded, light-yellow to light-brown micritic limestone and cherty limestone characterize the upper part (Haas et al., 1997; Haas & Tardy-Filácz, 2004) (note that

Kozur (1993) suggested to distinguish the upper unit as a separate formation, the Várhegy Cherty Limestone Fm.). Two different sections of partly overlapping age are exposed on both sides of the Pokol-völgy (Hell Valley) northwest of village: the Pokol-völgy quarry and the Vár-hegy (Castle Hill) section (see map e.g. in Pálfy et al., 2007). An uppermost Rhaetian marker bed containing abundant lithoclasts and platform-derived bioclasts helps establishing lithologic correlation between the two sections. Synsedimentary slump structures occur at several levels in the lowermost Jurassic.

Ammonoid biostratigraphy provides broad constraints for drawing the T–J boundary between occurrences of Rhaetian *Choristoceras* sp. and an early Hettangian psiloceratid, with the intervening 17 m only yielding an *ex situ* specimen of *Nevadaphyllites* (Pálfy & Dosztály, 2000; Pálfy et al., 2007). Radiolarians indicating the *Globolaxtorum tozeri* and *Canoptum merum* zones (latest Rhaetian and earliest Hettangian, respectively) also bracket a ~25 m barren interval (Pálfy et al., 2007). The staggered disappearance of conodonts falls into this interval, subdivided into the *Misikella ultima* and *Neohindeodella* zones (Pálfy et al., 2001, 2007; Korte & Kozur, 2011). However, as Kozur (1993) already noted, the Csővár section may be unique in preserving the last and youngest conodont taxa, with rare survivors reaching into the earliest Jurassic. On palynological grounds, a synchronous marine and terrestrial T–J boundary event is suggested by correlated spikes in the abundance of prasynophyte algae and fern spores (Götz et al., 2009)

The Vár-hegy section provided one of the first detailed C isotope curves across the T–J boundary, and the first one where a T–J boundary negative anomaly was simultaneously documented in both $\delta^{13}C_{carb}$ and $\delta^{13}C_{org}$, with a magnitude of -3.5‰ and -2‰, respectively, over a stratigraphic interval of ~2 m within the available biostratigraphic brackets of the system boundary (Pálfy et al., 2001). Despite some noise in the $\delta^{13}C_{carb}$ data attributed to minor diagenetic overprint, this anomaly stands out and is verified by the $\delta^{13}C_{org}$ data, lending support to its primary character. Carbon isotope ratios are not significantly correlated with either TOC or hydrogen index values. Another, comparably minor negative anomaly is observed somewhat lower in the upper Rhaetian. A subsequent study extended the $\delta^{13}C_{carb}$ curve for an additional 20 m into the middle Hettangian, and analysed the T–J boundary negative anomaly at a higher resolution (Pálfy et al., 2007). Here the T–J boundary anomaly appears to contain a series of short-term oscillations, whereas no clear trend was found after the curve levelled off returning to the pre-excursion values. A $\delta^{13}C_{carb}$ curve was also obtained from a 16 m thick Upper Rhaetian part of the Pokol Valley quarry section by Korte & Kozur

(2011). Although a <1‰ negative excursion followed by a stepped ~2‰ positive shift is recognized, its correlation to the nearby Vár-hegy section is not straightforward. Additional geochemical investigations targeted Rhaetian conodonts from the Pokol Valley quarry to help refine the $^{87}Sr/^{86}Sr$ reference curve in the lead-up to the T–J boundary (Korte, 1999; Korte et al., 2003).

Although the Csővár sections yield important data for our understanding of the carbon cycle perturbation at the TJB, they also challenge our ability to interpret the raw curves and unambiguously correlate them with other sections. The main negative anomaly in the Vár-hegy section is best equated with the initial CIE, whereas the precursor anomaly also appears to be recorded. However, the main negative anomaly reported from other sections remains difficult to prove here.

10.3.4. Kennecott Point in Haida Gwaii (Queen Charlotte Islands, Canada)

Studies of an expanded TJB section at Kennecott Point yielded $\delta^{13}C$ curves with one of the earliest recognized anomalies across the TJB (Ward et al., 2001). Haida Gwaii (also known as the Queen Charlotte Islands), a Pacific archipelago in British Columbia, forms part of the accreted terrane of Wrangellia and preserves a relatively continuous and unmetamorphosed Middle Triassic to Middle Jurassic sedimentary sequence (Lewis et al., 1991). Kennecott Point is located on the northwestern shore of Graham Island, with excellent exposures on a wave-cut intertidal platform. Fine-grained siliciclastics (thin-bedded, organic-rich shale and siltstone with fine to medium-grained sandstone interbeds) of the Rhaetian to Sinemurian Sandilands Formation were deposited in deep marine, outer shelf to basinal environment (Desrochers & Orchard, 1991).

The TJB has been defined by integrated ammonoid, radiolarian and conodont biostratigraphy (Tipper et al., 1994). Radiolarians occur abundantly throughout the section, enabling the most highly resolved biostratigraphy, where a marked faunal turnover leads to recognition of the boundary between *Globolaxtorum tozeri* and *Canoptum merum* zones, equated to the system boundary (Carter & Hori, 2005; Longridge et al., 2007). The Norian-Rhaetian boundary is approximated by the base of the *Parvicingula moniliformis* radiolarian zone (Carter, 1993) or the last appearance of the distinctive bivalve *Monotis* (Ward et al., 2004). Sparse latest Triassic ammonoids include *Choristoceras rhaeticum* and *C. nobile*, assigned to the North American Crickmayi Zone (Tozer 1994; Ward et al., 2001), whereas the *Minutus* Zone, the second

lowest Jurassic ammonoid zone, is documented by the index species *C. minutus*, appearing ~8 m higher than the earliest Jurassic radiolarians, and followed by *Psiloceras* ex gr. *tilmanni*, indicative of the next higher Pacificum Zone of the Lower Hettangian (Longridge et al., 2007). The Rhaetian zonal index conodont *Misikella posthernsteini* was found in a single sample in the uppermost Triassic part of the section and the highest conodont occurrence is recorded close to the radiolarian-defined TJB (Tipper et al., 1994). Significantly, there is no change in lithology at the TJB in the Kennecott Point section.

Ward et al. (2001) obtained a $\delta^{13}C_{org}$ curve from a ~120 m part of the section, from the uppermost Norian through the lowermost Hettangian. This study was among the first ones to document a significant, -2‰ excursion over <5 m of strata directly at the TJB, following the Rhaetian with no obvious trend in the C isotopic evolution. No significant correlation was found between TOC and $\delta^{13}C_{org}$ values, lending support to the interpretation as a primary signal. Subsequent work at higher sampling resolution confirmed the presence of the TJB negative anomaly, and described it as a series of short-term oscillations with up to six local minima (Ward et al., 2004). On the other hand, isotopic values measured on bulk carbonate appeared diagenetically overprinted and were not considered for further interpretation. Williford et al. (2007) extended the isotopic analyses to the higher, Lower Jurassic part of the section, doubling the sampled stratigraphic thickness to 250 m, through the entire Hettangian well into the Sinemurian. (However, as faulting is known to cause tectonic repetitions at Kennecott Point (Pálfy et al., 1994; Longridge et al., 2008), caution is needed as the measured and sampled section may include some overlooked tectonically duplicated parts.) The key feature of the extended $\delta^{13}C_{org}$ curve is the presence of a pronounced, 5‰ positive excursion in the Hettangian, closely following a transient return from the TJB negative spike to pre-excursion values. Although correlation of this Lower Jurassic isotope curve with existing ammonoid and radiolarian biostratigraphic data is not tightly constrained, the positive anomaly appears early to mid-Hettangian in age. Post-excursion $\delta^{13}C_{org}$ values in the upper part of the Hettangian and Sinemurian section are ~1‰ more negative than the long-term Rhaetian average and the values during transient return after the T–J boundary negative anomaly.

Sulfur isotopic analyses of a suite of samples revealed a major positive $\delta^{34}S$ anomaly coincident with the Hettangian positive $\delta^{13}C_{org}$ excursion (Williford et al., 2009). On the other hand, the T–J boundary negative

carbon isotope excursion was shown to correspond to a significant, protracted negative $\delta^{34}S$ anomaly, as well as the occurrence of lipid biomarkers suggestive of photic zone euxinia (Kasprak et al., 2015).

In summary, the Kennecott Point section with continuous, deep marine sedimentation in the East Pacific realm is an important archive of geochemical data to detect perturbation of the global carbon, sulphur and nitrogen cycles, whereas the fossil record is utilized for both biostratigraphic constraints and assessment of biotic changes at the mass extinction.

10.3.5. New York Canyon section (Nevada, USA)

One of the best known and most intensively studied T–J boundary sections in North America (and the world) is at Ferguson Hill and Muller Canyon in the New York Canyon area of the Gabbs Valley Range (Mineral County, Nevada), ~170 km SE of Reno. The significance of this continuous, marine T–J boundary section was first recognized by Muller & Ferguson (1936) who subdivided the predominantly dark shale, siltstone and limestone strata encompassing the system boundary into the Gabbs and Sunrise Formations, with a gradational contact between them. Further lithostratigraphic subdivision led to the introduction of members (Taylor et al., 1983), of which, in ascending order, the limestone-dominated Mount Hyatt and siltstone-dominated Muller Canyon Members of the Gabbs Fm. and the limestone-dominated Ferguson Hill Member of the Sunrise Fm. were subjected to several bio- and chemostratigraphic studies. The continuous, shallow marine sedimentary succession was deposited in a foreland basin east of the Sonoma allochton, following Permian-Triassic thrusting related to the Sonoma orogeny at the Cordilleran margin of North America (Dickinson, 2004). Magmatism related to a later, Cretaceous phase of tectonic evolution led to a low-grade metamorphic overprint hindering magnetostratigraphic studies and destroying palynomorphs (Lucas et al., 2007).

The macrofossil record across the T–J boundary is particularly rich in ammonoids (Guex, 1995) and bivalves (Laws, 1982), which served as the basis for the GSSP candidacy of the section (Guex et al., 1997, Lucas et al., 2007, McRoberts et al., 2007). Latest Triassic *Choristoceras* spp. occur up to the lowermost Mount Hyatt Member, below a 7-m-thick barren interval, followed by the first occurrence of *Psiloceras spelae* and *P. tilmanni*, regarded as the oldest Jurassic ammonoid species and zonal indices of the lowermost Hettangian ammonoid biozone. The first occurrence of pectinid bivalve *Agerchlamys boellingi* is also of stratigraphic

significance near the system boundary (McRoberts et al., 2007). The age of latest Triassic strata is also well-supported by conodont and radiolarian biostratigraphy (Orchard et al., 2007). A high-precision U-Pb zircon age of 201.33±0.13 Ma provides a numeric tie-point to calibrate other stratigraphic schemes and the geological time scale, and to correlate with other radioisotopically dated sections (Schoene et al., 2010).

The first $\delta^{13}C_{org}$ curve from the New York Canyon area was produced by Guex et al. (2003, 2004), documenting two negative excursions of similar, ~2‰ amplitude, the first one near the last occurrence of *Choristoceras crickmayi*, and the higher one between the first occurrence of *Psiloceras spelae* and *P. tilmanni,* and *P. pacificum*. Despite some scatter in the data, a return to pre-excursion values is observed between the anomalies. Ward et al. (2007) reported a new set of $\delta^{13}C_{org}$ data from an independently collected suite of samples. Although it confirmed the presence of two negative anomalies in a curve with less scatter, it also led to controversies regarding the position of the negative anomalies with regard to lithostratigraphy and biostratigraphic markers, recording a positive peak in the earliest Jurassic, and an apparently offset absolute values of isotopic ratios. Although Guex et al. (2009) argued that part of these discrepancies are explained by differing views on the definition of lithostratigraphic units and overlooking a fault by the other authors, comparison of positions of both negative anomalies remains ambiguous. Repeated measurements on five samples yielded values >0.3‰ different from the originally reported ones. A third independent sampling was carried out and new measurements were reported by Thibodeau et al. (2016), with the resultant curve in good agreement with a corrected version of that of Ward et al. (2007). These data were obtained by a geochemical study which also documented elevated Hg concentrations with a peak at the termination of the first negative C isotope anomaly, supporting the inference of a volcanic trigger for the environmental changes (Thibodeau et al., 2016). An additional 20 m was sampled upsection to the Hettangian-Sinemurian boundary, and the extended curve features a prominent, 5‰ positive anomaly in the Upper Hettangian (Bartolini et al., 2012). Thus the New York Canyon section also contributes to our understanding of the Hettangian carbon isotope record, where correlation of positive anomalies remains controversial.

In summary, geochemical studies from the New York Canyon area (i) span the T–J transition and the entire Hettangian, (ii) benefited from good ammonoid biostratigraphical control, (iii) are important in establishing the succession of two separate negative carbon isotope anomalies, separated by a mild and followed by a prominent positive anomaly, and (iv) are unparalleled in being based on three independent sets of samples and measurements by different teams.

10.3.6. Astartekløft (East Greenland)

Astartekløft is the best studied of several localities in the Hurry Inlet (Scoresby Sund) area of East Greenland, part of the Jameson Land Basin, that have been subject to intensive palaeobotanical study. Within the Jameson Land Basin, the T-J boundary occurs in largely lacustrine strata of the Kap Stewart Group (Surlyk, 2003), which range from basin centre shales to marginal fluvial sandstone. The Hurry Inlet localities show a marginal fluival succession comprising coarse sandy channels, commonly multi-story, with thinner overbank deposits, which include plant bearing crevasse splays (Dam & Surlyk, 1992; McElwain et al., 2007). Initial painstaking stratigraphic work by Harris (1937) documented in the Hurry Inlet localities a significant turnover of floras from the supposed Triassic *Lepidopteris* flora to the Jurassic *Thaumatopteris* flora. Harris' work was subsequently expanded upon by McElwain et al. (2007, 2009) who amassed large collections of plant macrofossils from Harris's plant beds at Astartekløft. Several studies have built upon this palaeobotanical framework to suggest significant changes in plant ecosystems across the T-J boundary in response to LIP forcing (e.g. Belcher et al., 2010; Bacon et al., 2013; Mander et al., 2013; Steinthorsdottir et al., 2015), and the Astartekløft fossil plant (stomatal density/index) record has been the principal basis for reconstruction of atmospheric CO_2 changes across T-J boundary (McElwain et al., 1999; Steinthorsdottir et al., 2011, 2012). A carbon-isotope stratigraphy was constructed by Hesselbo et al. (2002), which was used to suggest a precise correlation to St Audries Bay in southern England. The carbon isotope stratigraphy of Hesselbo et al. (2002), based on macrofossil wood, was corroborated by analysis of specifically identified leaf cuticles (Bacon et al., 2011). On the basis of detailed palynological study, Mander et al. (2013) suggested a revised correlation to St Audries Bay in which strata equivalent to the 'initial' carbon-isotope excursion at are missing or undetected at Astartekløft.

10.4. Chemostratigraphy

10.4.1. Carbon-isotope stratigraphy and total organic carbon (TOC) variation

Following on the pioneering work by McRoberts et al. (1997) and McElwain et al. (1999), many studies investigated the carbon isotope trend across the T–J boundary. A negative carbon isotope excursion was indeed confirmed from other marine (e.g., Ward et al., 2001; Pálfy et al., 2001; Hesselbo et al., 2002; Guex et al., 2004; Galli et al., 2005; Kuerschner et al., 2007; Williford et al., 2007; McRoberts et al., 2007; Ruhl et al., 2009) and terrestrial (Hesselbo et al., 2002; Pieńkowski et al., 2012; Steinthorsdottir et al., 2011) T–J boundary key sections and have been related to the end-Triassic mass extinction. In the western NCA the isotope excursion is marked by a ~3 ‰ negative shift in bulk carbonate $\delta^{13}C$ (Felber et al., 2015), and this is similar in magnitude as observed in $\delta^{13}C_{carb}$ records from northern Italy (3–5 ‰ negative CIE), the Budva Basin in Montenegro (1–2 ‰ negative CIE) and the United Arab Emirates (~5 ‰ negative CIE) (Galli et al., 2005; Crne et al., 2011; Al-Suwaidi et al., 2016).

The negative CIE in the Eiberg Basin is followed by a return to pre-excursion values throughout the Schattwald Beds (lower Tiefengraben Member) and the subsequent grey marls of the upper Tiefengraben Member (Fig. 2), with 1–2 ‰ reduced $\delta^{13}C$ values broadly coinciding with the first occurrence of *Psiloceras spelae tirolicum* at the base of the Jurassic (Ruhl et al., 2009). A shift to the continuously lower $\delta^{13}C$ values of the Hettangian Stage, as for example observed in the marine Bristol Channel Basin (Hesselbo et al., 2002; Korte et al., 2009; Ruhl et al., 2010), the Danish Basin (Lindström et al., 2012), in the New York Canyon section of Nevada (Bartolini et al., 2012) and the continental Newark and Hartford Basins (Whiteside et al., 2010), occurs in the Eiberg Basin broadly at the level of the first occurrence of the *Psiloceras* cf. *pacificum* (Hillebrandt et al., 2013).

Several studies have suggested a minor carbon-cycle perturbation, and associated negative CIE to precede the end-Triassic mass extinction (sometimes referred to as the precursor CIE) (Deenen et al., 2011; Ruhl & Kürschner, 2011; Lindström et al., 2012; Dal Corso et al., 2014; Davies et al., 2017). The upper Triassic sequences in the Eiberg Basin have only been studied extensively in the Eiberg quarry (Korte et al., 2017). An even earlier carbon cycle perturbation was, based on this succession, suggested to have occurred in the late Rhaetian (the Late Rhaetian CIE; Mette et al., 2012).

Observed trends in $\delta^{13}C$ records led to the suggestion of a characteristic $\delta^{13}C$ geometry for the T–J boundary interval including a short-term 'initial' negative excursion, followed by a longer lasting positive excursion and the long lasting 'main' negative excursion in marine successions (Hesselbo et al., 2002; Ward et al., 2007; Kuerschner et al., 2007; Williford et al., 2007; McRoberts et al., 2007; Korte et al., 2009; Ruhl et al., 2009, 2010, 2011; Korte & Kozur, 2011), and that the end-Triassic mass extinction is coeval with the 'initial' negative peak (e.g., Guex et al., 2004; McRoberts et al., 2007; Hesselbo et al., 2007; Ruhl et al., 2009; Korte & Kozur, 2011). This trend and evolution in $\delta^{13}C$ has also been identified in some terrestrial successions (Deenen et al., 2010; Whiteside et al., 2010; Dal Corso et al., 2014) certifying that it is likely global in nature, reflecting changes in $\delta^{13}C$ values of the global ocean-atmosphere system. Additional potential excursions, predating that across the T–J boundary have been also discovered (Cleveland et al., 2008; Schaller et al., 2011; Ruhl & Kürschner, 2011; Mette et al., 2012; Korte et al., 2017). The 'main' negative T–J boundary excursion,however, has not be identified in all marine sections (e.g. see Pálfy et al., 2007; Galli et al., 2007; van de Schootbrugge et al., 2008; Götz et al., 2009). This has led some others to suggest that the amplitude, shape, duration and even the stratigraphic position of the 'initial' $\delta^{13}C$ minimum is different between sections and therefore does not represent a clear chemostratigraphic marker (Lindström et al., 2017). This inference, however, largely stems from limited data on the absolute abundance of, often scarce, pollen and spores species and sometimes neglects all other available stratigraphic markers, such as ammonites.

If the observed changes in $\delta^{13}C$ across the Triassic–Jurassic transition are indeed global in nature, and because of the short residence time of carbon in the ocean-atmosphere system, peaks and troughs in carbon isotope records should represent coeval markers for trans-continental correlations.

Only a limited amount of compound-specific $\delta^{13}C$ data has to date been published, and only on leaf-wax derived long-chain *n*-alkanes (Whiteside et al., 2010; Ruhl et al., 2011).

The observed changes in these organic geochemical compounds are suggested to largely reflect changes in Triassic–Jurassic atmospheric $\delta^{13}C$, and they do directly correspond to changes in bulk organic $\delta^{13}C$ ($\delta^{13}C_{TOC}$ and $\delta^{13}C_{wood}$) in the same sedimentary successions (Whiteside et al., 2010; Ruhl et al., 2011). Further similar work spanning the upper Triassic and lower Jurassic is highly desirable, but has to date been limited by e.g. thermal maturity, low sedimentary TOC values, and poor organic sedimentary preservation in studied successions.

10.4.2. Mercury chemostratigraphy

The concentration of Hg in the ocean-atmosphere system is largely controlled by emission as a trace volcanic gas from continental volcanoes or mid-ocean spreading ridge systems (Pyle & Mather, 2003; Bowman et al., 2015). Gaseous elemental Hg has a typical residence time of 0.5–2 years, allowing for global atmospheric dispersal before eventual drawdown into marine and continental sediments (Blum et al., 2014). Importantly, Hg is typically drawn down into sediments bound with organic matter (Benoit et al., 2001; Outridge et al., 2007), although chemical binding to sulphides and clays may also be of some importance (Benoit et al., 1999; Niessen et al., 2003; Kongchum et al., 2011; Bergquist, 2017). Sedimentary Hg concentrations are therefore typically normalized against total organic carbon (TOC) content of the sediment (Percival et al., 2017). The timing of activity and impact of several Phanerozoic large igneous provinces (LIPs), and their potential relationships to global change (e.g. such as oceanic anoxic events (OAEs)) and mass extinction events, including in the end-Permian, the Early Toarcian, the mid-Cretaceous (Cenomanian–Turonian) OAE2 and the end-Cretaceous events, was previously already studied (Sanei et al., 2012; Percival et al., 2015; 2016; Font et al., 2016; Sial et al., 2016; Scaife et al., in press).

The potential temporal correlation between events at the Triassic–Jurassic transition, including the end-Triassic mass extinction event, and the emplacement of CAMP was recently extensively studied in marine and continental sedimentary records from both hemispheres and from different palaeo-latitudes (Thibodeau et al., 2016; Percival et al., 2017). The onset of peaks in sedimentary Hg concentrations, possibly reflecting the onset of Hg emissions, directly coincides with the end-Triassic mass extinction event (Percival et al., 2017) (Fig. 3). More importantly, however, individual major CAMP basalt flows preserved in the continental basins of North America (US and Canada) and North Africa (Morocco) can potentially be temporally (and perhaps causatively) linked to peaks in sedimentary Hg accumulation (Percival et al., 2017).

A recent study suggests that extrusive emplacement of CAMP may have been preceded, by ~100 kyrs, by the intrusive emplacement of dyke and sill systems, partly in sedimentary basins, which potentially perturbed the Earth's climate and environment already earlier (Davies et al., 2017). The analyses of sedimentary Hg have so far been largely constrained to the T–J transition interval. Future studies may provide further insights on

Hg release, possibly also indirectly from the thermogenic release from dyke and sill intruded sedimentary basins, already in the latest Triassic.

10.4.3. Oxygen-isotope stratigraphy

The oxygen isotopic composition of marine carbonates is generally controlled by seawater temperature (Urey et al., 1951) as well as by seawater $\delta^{18}O$ and pH (Zeebe & Wolf-Gladrow, 2001). The temperature dependence, leading to lighter oxygen isotope ratios in carbonates secreted in warmer water and *vice versa*, enables the use of $\delta^{18}O_{carb}$ as palaeothermometer for ancient oceans. In addition, the carbonate carbon isotope (chapter 10.4.1) measurements are performed parallel and on the same aliquots as those from the oxygen isotopes, allowing a direct comparison to each other, e.g. reconstructing temperature (climate) change together with atmosphere/ocean fluctuations of carbon dioxide. Oxygen isotope ratios – especially those from bulk carbonates – are, in comparison to carbon isotopes, more prone to diagenesis (e.g., Veizer 1983; Marshall, 1992). A careful evaluation of the data is therefore necessary to interpret seawater temperature changes of the past. On the basis of a dataset from which potentially altered bulk carbonate $\delta^{18}O$ data were culled Pálfy et al. (2001, 2007), an extreme temperature increase of more than 10°C across the T–J boundary at the Csővár section in Hungary is suggested, and this is quite dramatic for palaeolatitudes of about 30°N (Fig. 1). A similar bulk carbonate $\delta^{18}O$ negative shift is also evidenced in other successions, such as the Doniford section in SW England (Clémence et al., 2010) suggesting climate change with a superregional extent. Pálfy et al. (2001, 2007) pointed out that this severe apparent temperature increase occurred during the period when the initial negative carbon isotope excursion happened (see Fig. 2), and this during a time span when an injection of isotopically light carbon from volcanic exhalation of CO_2 or/and a methane hydrate releases occurred, which potentially triggered a global warming (Pálfy et al., 2001; Hesselbo et al., 2002, Ruhl et al., 2011). This hypothesis of climate warming has also been suggested by model data (e.g. Huynh & Poulsen, 2005), and the findings of shelf-sea photic zone anoxia or even euxinia (Jaraula et al., 2013; Kasprak et al., 2015). However, bulk carbonate $\delta^{18}O$ from the Lorüns section in Austria (even if some data only), show heavier values in the interval of the negative $\delta^{13}C$ excursion, and other data showing the negative bulk carbonate oxygen isotope excursion havebeen interpreted as the result of diagenetic alteration (Morante & Hallam, 1996). For a robust evaluation of a global temperature rise more proxy data from pristine samples across the T–J boundary are still highly desirable.

Oxygen-isotope values from low-Mg-calcite fossils, such as brachiopods and oysters, represent a robust dataset usable for reconstruction of past seawater temperatures because this material is relatively resistant to diagenesis (e.g., Popp et al., 1986; Veizer et al., 1986), and because the alteration degree can be assessed by a multitude of physical and chemical techniques (see Veizer 1983; Marshall, 1992; Ullmann & Korte 2015 for reviews). From different regions in Europe, $\delta^{18}O$ (and $\delta^{13}C$) data exist from well-preserved brachiopods of the Late Triassic (Korte et al., 2005, 2017; *Mette* et al., 2012) and pristine oysters of the earliest Jurassic (Jones et al., 1994; Korte et al., 2009). Unfortunately, no continuous datasets over the T–J boundary is available from the same locality. A combination of datasets from different regions, and especially a lack of data in the latest Triassic and earliest Jurassic (Korte et al., 2009, 2017), is a relatively poor basis for reconstructing the temperature evolution across the whole period of interest. However, the dataset from Korte et al. (2009) provides insights into the bottom water temperature changes during the earliest Jurassic in the Bristol Channel Basin, UK (Fig. 4). Relatively cool seawater temperatures between < 7 and 14°C existed for the period of deposition of the upper Langport Member, just above the T–J boundary. The temperatures increased then distinctly by more than 8°C reaching values ~12 and 22°C in the first three ammonite subzones of the Jurassic. Extreme changes in seawater $\delta^{18}O$ (evaporation, melting of continental ice, meteoric water dilution) as a trigger for these severe oxygen isotope fluctuation(s) have been excluded by Korte et al. (2009). This oxygen isotope signal therefore potentially reflects a true climate signal in which the warming (Fig. 4) occurred together with the trend towards to lighter carbon isotope values (main negative carbon isotope excursion sensu Hesselbo et al., 2002). The data are compatible with the suggestion that heavy carbon isotope values correspond to periods of lower *p*CO2 contentsand *vice versa*. However, the detailed comparison between the $\delta^{18}O$ and the $\delta^{13}C$ curves show small differences in the positions of the positive peaks (Fig. 4). The $\delta^{18}O$ decrease (i.e. increase in temperature) in this case began earlier than the $\delta^{13}C$ decline, and with it the inferred increase in CO_2 levels, and this suggests that factors other than CO_2 may have contributed to the warming in this area, such as opening up of the seaway to marine currents derived from warmer more equatorial waters (Korte et al., 2015).

We note, however, that the oxygen isotope values in the upper Langport Member just above the T-J boundary reflect similarly cool temperatures evidenced for the Aalenian stage in the Hebrides Basin of Scotland (Korte et al., 2015). These data indicate that a “Cold Mode” interval existed around the T–J boundary – at least equivalent to the upper Langport Member just above the T–J boundary – at Mid-European palaeolatitudes,

which were below 40°N (Fig. 1). Cool temperatures close to the T–J transition were also identified by sporomorph associations from several successions in central and north-western Europe and in north-east Greenland (Hubbard & Boulter, 2000). Although this was later challenged by McElwain et al. (1999), pollen data do suggest initial warming at the end-Triassic mass extinction interval to be followed by a short cooling phase at or directly preceding the T-J boundary and a long term-warming into the Hettangian Stage (Bonis & Kürschner, 2012).

The cool interval in the period just above the T–J boundary (upper Langport Member) occurs during the interval of subaerial basaltic volcanism from theCAMP evidenced by the Hg peaks (Figs 3 and 4; chapter 10.4.2.), and effects of the volcanism likely induced this cool interval (Guex et al., 2004, 2012; Schoene et al., 2010). It has been shown that volcanic eruptions have triggered short-term climate cooling events (Lamb, 1970; Kennett & Thunell, 1975; Rampino et al., 1988), when exhaled ashes, sulphur dioxide and hydrogen sulphide (hydrogen sulphide rapidly oxidises to SO_2 in the atmosphere) reaches the stratosphere. Ashes fall down rapidly, whereas SO_2 reacts with hydroxyl (OH^-) and water to sulphuric acid and generates aerosol clouds which circulate for several years around the planet (Pollack et al., 1976; Cadle et al., 1976; Rampino et al., 1988). These clouds reduce the transparency for light and, in addition, reflect solar radiation, and these factors cause that the troposphere and Earth's surface cool down (Devine et al., 1984; Sigurdsson, 1990). Volcanic cooling events, induced by short-term felsic (high SiO_2) or intermediate volcanic eruptions, are usually of short duration and lasting not longer than two years (e.g., Mt Pinatubo eruption in 1991, Genin et al., 1995) and it was therefore debated whether volcanically-induced cool periods can last over hundreds of years (Bryson & Goodman, 1980; Rampino et al., 1988). CAMP emplacement, however, represents the most extensive subaerial LIP in Earth's history (McHone, 2003; Blackburn et al., 2013). Its emplacement spanned 600–800 kyr (Kent et al., 2017 and references therein) and occurred likely recurrent and on multitude eruption centres along the Atlantic rift basin (Davies et al., 2017). Potentially, volcanic aerosol enrichments in the atmosphere maintained over a longer period and triggered the cool interval in the upper Langport Member (Fig. 4).

Basaltic magma eruptions, such as the fissure eruptions at Laki on Iceland, usually generate aerosol clouds in the troposphere reaching the stratosphere only occasionally (Devine et al., 1984; Walker et al., 1984; Palais & Sigurdsson, 1989, 2013). It could be shown, however, that even the Laki eruption which was several magnitudes smaller than those of the CAMP, caused a recognisable cooler period over even several years (Sigurdsson, 1982; Rampino et al., 1988). Moreover, aerosols originating from basaltic eruptions contain 10

to 50 times more H_2SO_4 than those from felsic eruptions and influence climate much more effectively (Rampino et al., 1988; Palais & Sigurdsson, 1989. 2013).

10.4.4. Strontium- and osmium-isotope stratigraphy

The T-J boundary falls into an interval of a ca. 30 Myr long, gradual decline ofthe marine $^{87}Sr/^{86}Sr$ curve which commenced in the Norian (Late Triassic) at a ratio near 0.7080 (Korte et al., 2003). This decreasing trend was terminated by a rebound to more radiogenic values in the earliest Toarcian (Early Jurassic) after reaching a ratio close to 0.7070 (Jones et al., 1994). The finer structure of the marine $^{87}Sr/^{86}Sr$ curve across the TJ-boundary where values are near 0.7077 (Jones et al., 1994; Korte et al., 2003) is not defined with great confidence at present.

It has been suggested that a rapid decrease of marine $^{87}Sr/^{86}Sr$ in the Rhaetian was briefly inverted in the latest Rhaetian and followed by a phase of zero net change (Cohen & Coe, 2007) or even to brief increase (Callegaro et al., 2012) in the marine $^{87}Sr/^{86}Sr$ ratio that lasted throughout the entire Hettangian Stage (Cohen & Coe, 2007). This interpretation hinges on the accuracy of the geological timescale, the direct comparability of $^{87}Sr/^{86}Sr$ ratios from Late Triassic Austrian shelf seas to latest Triassic and earliest Jurassic UK shelf seas, and the pristine preservation state of two oyster specimens from the Rhaetian of the UK. Opposing this scenario stands the current marine Sr isotope curve (McArthur et al., 2012) which adds four Rhaetian conodont values from the Hungarian Csővár section to Rhaetian brachiopod data from the Austrian Weißloferbach section (Korte et al., 2003), but discards earliest Jurassic oyster data from Jones et al. (1994). A statistical fit through these data suggests a minor slowdown of the marine $^{87}Sr/^{86}Sr$ decline during the latest Rhaetian and Hettangian. This slowdown, however, is not constrained by any tie point in the critical time interval of the T-J boundary due to the choice of which fossil materials can be regarded as trustworthy.

Regardless of the adopted model, at some point shortly preceding the Triassic-Jurassic boundary, the seawater Sr reservoir appears to have been affected by a more or less substantial shift in the balance of unradiogenic (mantle) and radiogenic (continental) Sr sources to the oceans. This shift has been tied to fluctuations in Os isotope ratios as measured in organic-rich mudrocks in the UK (Cohen et al., 1999) and related to the emplacement of the CAMP (Cohen & Coe, 2007). Such a shift could either be related to a more

important flux of continent-derived Sr, e.g. by way of globally increased weathering rate or by reducing the importance of riverine drainage from catchments with unradiogenic $^{87}Sr/^{86}Sr$ ratio. Alternatively, this effect could also have been brought about by a reduction of mid ocean ridge activity. CAMP rocks themselves, emplaced at low latitudes and likely highly susceptible to weathering (Cohen & Coe, 2007), would rather have counteracted the observed change in slope of the marine $^{87}Sr/^{86}Sr$ curve. CAMP weathering would have led to the injection of somewhat more unradiogenic Sr into the coeval seawater, as most reconstructed initial $^{87}Sr/^{86}Sr$ ratios for CAMP igneous rocks fall within a range from 0.705 to 0.708 (Whalen et al., 2015), slightly lower than the ratio of coeval seawater. CAMP's direct influence on the marine $^{87}Sr/^{86}Sr$ must thus have been overwhelmed by more potent environmental changes brought about by CAMP emplacement and changes to the Earth surface system that happened simultaneously. Potentially enhanced hydrological cycling as well as elevated sulphuric acid rain may have increased weathering of more radiogenic continental/crustal rocks, delivering relatively more positive Sr to the global ocean, resulting in an Early Jurassic (Hettangian) plateau in seawater $^{87}Sr/^{86}Sr$ values (Jenkyns et al., 2002 and references therein).

10.4.5. Redox changes across the Triassic–Jurassic transition

Major global change events in Earth's history are often associated with oceanic anoxic events (OAEs), in which significant parts of globally distributed marine basins developed anoxic and/or euxinic conditions (Jenkyns, 2010; Percival et al., 2016). Much discussion has focused on the causes, consequences and timing of Mesozoic OAEs, and associated changes in global (bio)geochemical cycles, biotic and ecosystem response and carbon drawdown, on local, regional and global scales (Jenkyns, 2010, and references therein). The end-Triassic mass extinction and Triassic–Jurassic transition interval has generally not been considered to be an OAE, but recent studies do suggest anoxic/euxinic conditions developing at this time. Several studies suggest the increased flux to and/or preservation of organic carbon in marine sediments, commonly associated with the deposition of laminated (organic-rich) black shales (Bonis et al., 2010; Clemence et al., 2010; Ruhl et al., 2010; Thibodeau et al., 2016; Xu et al., 2017). In addition, organic geochemical analyses of Triassic–Jurassic sediments in multiple marginal marine basins suggests the increased abundance of isorenieratane and gammacerane biomarkers, derived from bacteria living in a euxinic photic zone or at the boundary between watermasses in a stratified water-column, respectively (Richoz et al., 2012; Jaraula et al., 2013; Kasprak et al., 2015).

Elevated sedimentary TOC values, suggestive of increased carbon burial potentially under sub- or anoxic conditions, in many Triassic–Jurassic marginal marine basins, combined with geochemical evidence for a change in water-column redox-conditions, potentially suggests more widespread anoxia also at the Triassic–Jurassic transition.

10.5. Conclusions

The Triassic–Jurassic transition is marked by significant changes in $\delta^{13}C$ values in organic and inorganic substrates, from marine and continental (terrestrial and lacustrine) sedimentary records. A (major) negative carbon isotope excursion (CIE) predates the T–J boundary by ~100-200 kyr and directly coincides with the end-Triassic mass extinction. The observed $\delta^{13}C$ signature at that time suggests the release of isotopically light carbon into the ocean-atmosphere system. The temporal relationship between Triassic–Jurassic carbon cycle change and the emplacement of the Central Atlantic Magmatic Province (CAMP) suggests a potentially causative effect. Different mechanisms of carbon release have been proposed, including (1) carbon degassing directly from CAMP basalts, (2) thermogenic carbon (methane) release from subsurface organic rich sediments by intruding dykes and sills related to CAMP emplacement, and (3) methane clathrate release from seafloor sediments in response to initial CAMP carbon release which might be associated with global warming.

Temporal and magnitudinal differences in observed Triassic–Jurassic changes in $\delta^{13}C$ values, between localities, depositional environments and proxy-records, however, for now prohibit a full consensus on carbon-cycle evolution at that time.

Changes in the global exogenic carbon-cycle across the Triassic-Jurassic transition and related changes in atmopsheric and oceanic pCO_2 did likely impact on local, regional and global climates, environments and depositional conditions. Changes in marine $\delta^{18}O$ values are suggestive of global warming, seawater $^{87}Sr/^{86}Sr$ and $^{188}Os/^{187}Os$ signatures suggest a change to higher continentalweathering rates, and other geochemical and sedimentological markers suggest changes in the redox-state of, at least, marginal marine basins. Macrofossil and microfossils furthermore suggest changing conditions, both on land and in the oceans, including changing *p*H values in the shallow marine realm as well as changing temperatures and humidity on land. The global warming in the early Jurassic, however, could also reflect a shift back to

normal conditions after a cool interval, the latter triggered by aerosol clouds originating from sulphuric acid exhaled from the CAMP volcanism. This sulphuric acid would acidify the rain and could also explain enhanced weathering at that time.

Bio- and chemostratigraphically well-constrained Triassic–Jurassic sedimentary records, especially from the open marine realm, are relatively scarce compared to other Early Jurassic, Cretaceous or Cenozoic global change events (such as OAEs). The Triassic–Jurassic, however, stands out as it arguably has one of the best constrained stratigraphic framework linking contintental LIP emplacement with the marine sedimentary environments.

Recent and increasing interest in the mechanistic (causative) processes controlling events at the Triassic–Jurassic transition and the increasing amount of marine and terrestrial, and globally distributed, sedimentary records being studied, strongly increase our understanding of the drivers of marine and continental paleoclimatic and paleoenvironmental and paleobiotic change across this highly enigmatic interval in Earth history.

Acknowledgements

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Figure captions

Fig. 1: Palaeogeographic map of discussed and cited T–J boundary sections. Rocks of CAMP are marked in dark red and the reconstructed CAMP area is coloured light and dark Red and taken from McHone (2003). 1: Fundy Basin (Blackburn et al., 2013; Schoene et al., 2006); 2: Hartford Basin (Whiteside et al., 2010); 3: Newark Basin (Blackburn et al., 2013; Marzoli et al., 2011; Schaller et al., 2011; Whiteside et al., 2010); 4: Culpeper Basin (Marzoli et al., 2011); 5: Argana Basin (Blackburn et al., 2013; Deenen et al., 2010); 6: High Atlas Basin (Marzoli et al., 2004); 7: Northern Calcareous Alps(Kuerschner et al., 2007; Ruhl & Kürschner, 2011; Ruhl et al., 2009, 2011); 8: Pelso Unit, Hungary (Pálfy et al., 2001, 2007); 9: Western Carpathians (Michalík et al., 2007, 2010); 10: Southern Alps (Bachan et al., 2012; Galli et al., 2007; van de Schootbrugge et al., 2008); 11: Apennines (Bachan et al., 2012; van de Schootbrugge et al., 2008); 12: Southern Germany (van de Schootbrugge et al., 2008; Ruhl & Kürschner, 2011); 13: Polish Trough (Pieńkowski et al., 2012); 14: Northern Germany (van de Schootbrugge et al., 2013); 15: Danish Basin (Lindström et al., 2012); 16: Southwest Britain (Clémence et al., 2010; Hesselbo et al., 2002; Korte et al., 2009; Ruhl et al., 2010); 17: East Greenland (McElwain et al., 1999; Hesselbo et al., 2002); 18: Queen Charlotte Islands (Friedman et al., 2008; Pálfy et al., 2000; Ward et al., 2001; Williford et al., 2007); 19: New York Canyon, Nevada (Bartolini et al., 2012; Guex et al., 2004, 2012; Schoene et al., 2010; Ward et al., 2004); 20: Utcubamba Valley, Peru (Schaltegger et al., 2008; Schoene et al., 2010); 21: Arroyo Malo, Argentina (Damborenea & Manceñido, 2012; Percival et al., 2017). Map modified after Ruiz-Martínez et al. (2012) and Pálfy & Kocsis (2014).

Fig. 2: Comparison of Triassic–Jurassic $\delta^{13}C_{CARB}$, $\delta^{13}C_{TOC}$ and $\delta^{13}C_{WOOD}$ data from geographically distributed marine and terrestrial sections, with Hg/TOC ratios and atmospheric pCO_2. Atmospheric pCO_2 estimates are based on stomatal density analyses (Astartekløft, Greenland) and $\delta^{13}C$ analyses

of pedogenic carbonate sequences (Newark and Hartford basins). Note that this compilation is by no means exhaustive and that many more Triassic-Jurassicboundary sections have been studied. Data in Figure 2 comes from: Newark and Hartford basins, USA: Kent et al. (2017) and references therein, Schaller et al. (2011, 2012, 2015); St Audries Bay, UK: Hesselbo et al. (2002), Korte et al. (2009), Ruhl et al. (2010), Hüsing et al. (2014), Xu et al. (2017); Canj, Montenegro: Crne et al. (2011); Kuhjoch, Austria: Ruhl et al. (2009), Hillebrandt et al. (2013), Percival et al. (2017); New York Canyon, Nevada, USA: Bartolini et al. (2012), Thibodeau et al. (2016); Astartekløft, Greenland: Hesselbo et al. (2002), Steinthorsdottir et al. (2011), Percival et al. (2017); Csővár, Hungary: Pálfy et al. (2001).

Fig. 3: Compilation of continental Triassic–Jurassic sequences, which have been analyzed for $\delta^{13}C_{TOC}$ and $\delta^{13}C_{WOOD}$ and which record Central Atlantic Magmatic Province (CAMP) basalt emplacement. Data in Figure 3 comes from: Hartford Basin, USA: Schaller et al. (2012), Kent et al. (2017) and references therein; Newark Basin, USA: Schaller et al. (2011), Kent et al. (2017) and references therein; Fundy Basin, Canada: Deenen et al. (2011); Argana Basin, Morocco: Deenen et al. (2010); High Atlas Mountains, Morocco: Dal Corso et al. (2014), El Ghilani et al. (2017).

Fig. 4: Oxygen and carbon isotope values from pristine oysters originating from the earliest Jurassic successions Lavernock Point, St Audries Bay and Watchet from Korte et al. (2009; including results from van de Schrootbrugge et al., 2007) and bulk organic $\delta^{13}C$ data from Hesselbo et al., 2002) plotted against stratigraphy. Figure modified after Korte et al. (2009).