



Article scientifique

Article

2012

Published version

Open Access

This is the published version of the publication, made available in accordance with the publisher's policy.

Disentangling the Hettangian carbon isotope record: Implications for the aftermath of the end-Triassic mass extinction

Bartolini, A.; Guex, J.; Spangenberg, Jorge Enrique; Schoene, B.; Taylor, D. G.; Schaltegger, Urs; Atudorei, V.

How to cite

BARTOLINI, A. et al. Disentangling the Hettangian carbon isotope record: Implications for the aftermath of the end-Triassic mass extinction. In: Geochemistry, geophysics, geosystems, 2012, vol. 13, n° 1. doi: 10.1029/2011GC003807

This publication URL: <https://archive-ouverte.unige.ch/unige:21553>

Publication DOI: [10.1029/2011GC003807](https://doi.org/10.1029/2011GC003807)



Disentangling the Hettangian carbon isotope record: Implications for the aftermath of the end-Triassic mass extinction

A. Bartolini

Muséum National d'Histoire Naturelle, CNRS UMR 7207 Paleobiodiversité et Paléoenvironnements, CP38, 8 rue Buffon, F-75005 Paris, France (bartolini@mnhn.fr)

J. Guex

Institute of Geology, University of Lausanne, UNIL-Dorigny, Bâtiment Anthropole 3182, CH-1015 Lausanne, Switzerland (jean.guex@unil.ch)

J. E. Spangenberg

Institute of Mineralogy and Geochemistry, University of Lausanne, Bâtiment Anthropole 3182, CH-1015 Lausanne, Switzerland (jorge.spangenberg@unil.ch)

B. Schoene

Department of Geosciences, Princeton University, 219 Guyot Hall, Princeton, New Jersey 08544, USA (bschoene@princeton.edu)

D. G. Taylor

NW Museum of Natural History, 5004 SW Lowell Street, Portland, Oregon 97221, USA (blitz124@comcast.net)

U. Schaltegger

Section of Earth and Environmental Sciences, University of Geneva, rue des Maraichers 13, CH-1205 Geneva, Switzerland (urs.schaltegger@unige.ch)

V. Atudorei

Department of Earth and Planetary Sciences, University of New Mexico, Albuquerque, New Mexico 87131, USA (atudorei@unm.edu)

[1] This study provides an organic carbon stable isotope ($\delta^{13}\text{C}_{\text{org}}$) record calibrated with detailed ammonite biostratigraphy, following the end-Triassic biological crisis. Precise correlation between this crucial fossil group and the $\delta^{13}\text{C}_{\text{org}}$ record is key to understanding feedbacks between biological and environmental events following mass extinction. The latest Triassic and Hettangian $\delta^{13}\text{C}_{\text{org}}$ record shows several negative and positive excursions. The end-Triassic negative shift coinciding with the mass extinction interval is followed by a positive excursion in the earliest Hettangian *Psiloceras spelae* beds, which marks the onset of recovery in the marine ecosystem. This positive trend is interrupted by a second negative $\delta^{13}\text{C}_{\text{org}}$ excursion in the *P. pacificum* beds related to a minor ammonite extinction event. This pattern of the $\delta^{13}\text{C}_{\text{org}}$ curve culminates in the uppermost Hettangian Angulata Zone major positive excursion. This indicates that both the ecosystem and the carbon cycle remained in a state of perturbation for at least 2 Ma, although the recovery of some pelagic taxa already began at the base of Jurassic. The early and late Hettangian positive $\delta^{13}\text{C}_{\text{org}}$ excursions have been confused in several recent papers. Here, we show that during the Hettangian there are indeed two distinct positive $\delta^{13}\text{C}_{\text{org}}$ excursions. Phases of anoxia and further pulses of

Central Atlantic Magmatic Province volcanism during the Hettangian might have inhibited the full recovery for that interval of time. The main Liasicus–Angulata organic positive CIE (carbon isotope excursion) during the Late Hettangian might be related to gradual decreasing of pCO₂ due to protracted high organic burial, and coincides with a second phase of recovery, as indicated by a pulse of ammonoid diversification.

Components: 6500 words, 2 figures.

Keywords: Triassic–Jurassic; biological crisis; carbon cycle; recovery; stable isotopes.

Index Terms: 0428 Biogeosciences: Carbon cycling (4806); 0454 Biogeosciences: Isotopic composition and chemistry (1041, 4870); 0459 Biogeosciences: Macro- and micropaleontology (3030, 4944).

Received 19 July 2011; **Revised** 1 November 2011; **Accepted** 22 November 2011; **Published** 14 January 2012.

Bartolini, A., J. Guex, J. E. Spangenberg, B. Schoene, D. G. Taylor, U. Schaltegger, and V. Atudorei (2012), Disentangling the Hettangian carbon isotope record: Implications for the aftermath of the end-Triassic mass extinction, *Geochem. Geophys. Geosyst.*, 13, Q01007, doi:10.1029/2011GC003807.

1. Introduction

[2] The end-Triassic represents one of the five most profound Phanerozoic extinction events, and the associated biotic diversity pattern is one of abrupt reduction in diversity just below the system boundary followed by a gradual recovery into the Hettangian. Major global environmental changes coincided with widespread igneous activity in the Central Atlantic Magmatic Province (CAMP), the break-up of the supercontinent Pangea and rapid sea level fluctuations. These biotic-abiotic environmental changes induced significant perturbations in the carbon cycle, as mirrored by a complex pattern of multiple negative and positive carbon isotope anomalies during this time interval. A sharp negative excursion located just below the Triassic–Jurassic (TJ) boundary was first reported by *Ward et al.* [2001] and has been interpreted to have resulted from a productivity “collapse,” CO₂ outgassing associated with the CAMP, or gas hydrate release [*Pálffy et al.*, 2001; *Hesselbo et al.*, 2002; *Ruhl et al.*, 2011]. *Guex et al.* [2004] argued that there are two distinct negative $\delta^{13}\text{C}$ excursions close to the boundary that derived from different environmental causes: the late Rhaetian negative excursion is clearly related to the extinctions, cooling and a regressive phase, while the early Hettangian negative excursion is associated with biotic recovery, the greenhouse effect, and a transgressive phase [*Guex et al.*, 2004; *Schoene et al.*, 2010]. The two negative excursions are separated by a positive excursion that coincides with the first occurrence of the oldest Jurassic ammonite, *Psiloceras spelae*, which defines the base of the Jurassic and is approximately concomitant with the

beginning of the ammonite recovery. More recently, a very large positive $\delta^{13}\text{C}_{\text{org}}$ excursion (5‰ in amplitude) has been documented for the Hettangian at Kennecott Point (KP) in British Columbia [*Williford et al.*, 2007], initially assigned to the early Hettangian.

[3] We have produced a detailed and extensive $\delta^{13}\text{C}_{\text{org}}$ database in the New York Canyon (NYC), Nevada [cf. *Guex et al.*, 2004, 2009] to calibrate the Hettangian $\delta^{13}\text{C}_{\text{org}}$ record in a robust biostratigraphic framework. Our new data reveal that a major positive $\delta^{13}\text{C}_{\text{org}}$ excursion is also present at NYC. Using the precise ammonoid calibration of the Hettangian $\delta^{13}\text{C}_{\text{org}}$ curve at NYC and a re-examination of the distribution of the ammonites at Kennecott Point established by *Longridge et al.* [2008], we demonstrate that this major positive isotopic event is late Hettangian in age and not early Hettangian as initially assigned [*Williford et al.*, 2007]. We discuss and reinterpret the correlations with Hettangian $\delta^{13}\text{C}$ curves published recently in different parts of the world: Newark Basin, USA [*Whiteside et al.*, 2010]; East Greenland [*McElwain et al.*, 2009]; Southern Alps, Italy [*van de Schootbrugge et al.*, 2008]; St Audrie’s Bay, England [*Ruhl et al.*, 2010]. We also discuss the implication of this major late Hettangian positive carbon isotope event in the light of the post-crisis recovery scenario.

2. Materials and Methods

[4] The stratigraphic interval studied here is located in the upper Gabbs and lower Sunrise Formations first described by *Muller and Ferguson* [1936, 1939]. These formations form one of the most

important Upper Triassic and Lower Jurassic sequences in North America. The studied section (Figure 1) crops out in Muller Canyon, adjacent to the main valley called New York Canyon, where the Triassic/Jurassic boundary beds are comparatively thick and well exposed. The section is in the upper members of the Gabbs Fm (Mt Hyatt Mb and Muller Canyon Mb) and lower Sunrise Formations (Ferguson Hill Mb). Detailed descriptions of the lithostratigraphy and biostratigraphy of that section have been published in several papers [Taylor *et al.*, 1983; Guex, 1995]. Samples were obtained from detailed bed-by-bed collecting.

[5] Powdered samples were decarbonated with concentrated HCl (30%) and then washed with distilled water until neutral. The carbon isotope composition of the bulk organic matter was determined by flash combustion on a Carlo Erba 1108 elemental analyzer (EA) connected to a Thermo Fisher Scientific Delta V isotope ratio mass spectrometer (IRMS) that was operated in the continuous helium flow mode via a ConFlo III split interface (EA-IRMS). The $\delta^{13}\text{C}$ values are reported relative to Vienna-Pee Dee belemnite standard (VPDB). The calibration and assessment of the reproducibility and accuracy of the isotopic analysis were based on replicate analyses of laboratory standard materials and international reference materials. The reproducibility was better than 0.1‰ (1 s).

3. The $\delta^{13}\text{C}_{\text{org}}$ Record and Ammonoid Calibration at New York Canyon

[6] The $\delta^{13}\text{C}_{\text{org}}$ record from NYC section and its relationship to lithological and biological data are given in Figure 1 (see also Data Set S1 in the auxiliary material).¹ The lower 25 m of the $\delta^{13}\text{C}_{\text{org}}$ curve is based on the study by Guex *et al.* [2004, 2009]. The sediments from the transition between the Triassic and lower Hettangian present noise in the $\delta^{13}\text{C}_{\text{org}}$ values, likely due to diagenetic alteration [Guex *et al.*, 2004]. Despite this, after applying a simple moving average to the original measurements, the resulting curve C2, published in the study by Guex *et al.* [2009] can be well correlated with carbon isotope data of Ward *et al.* [2007], which show less variability, possibly because they collected fresher samples at a location within Muller Canyon less altered diagenetically. The curve C2 of Guex *et al.* [2009] is reproduced here (ignoring the outlier “x” at 10 m).

¹Auxiliary materials are available at <ftp://ftp.agu.org/apend/gc/2011gc003807>.

[7] The latest Triassic and Hettangian $\delta^{13}\text{C}_{\text{org}}$ record fluctuates markedly, with several negative and positive excursions. Actually, the dominant feature of the $\delta^{13}\text{C}_{\text{org}}$ curve is a large (~5 per mil amplitude) positive carbon isotopic event at 42 m (Figure 1). The new curve is correlated with the sequence of ammonite-beds and biozones at New York Canyon [Guex, 1995; Guex *et al.*, 2004] (Figure 1). The first negative shift, corresponding with the “initial isotope excursion” of Hesselbo *et al.* [2002], occurs in the *C. crickmayi* beds. This is followed by a positive excursion in the *P. spelae* beds, by a negative shift in the *P. pacificum* beds (correlated to the “main isotope excursion” of Hesselbo *et al.* [2002]), and finally by a major positive excursion in the late Hettangian *Angulaticeras* beds.

4. Interregional Correlations

[8] Williford *et al.* [2007] recognized at Kennecott Point (KP; Queen Charlotte Islands, Canada) a major positive organic carbon excursion (~5‰ in amplitude) in the Hettangian, concomitant with a major $\delta^{34}\text{S}$ excursion reported from the same locality [Williford *et al.*, 2009]. That excursion was interpreted to be early Hettangian in age based on stratigraphic work of Tipper *et al.* [1991].

[9] The discovery of a large positive excursion of similar amplitude in the Angulata Zone (late Hettangian) at New York Canyon (Figure 1) leads us to revise the data by Tipper *et al.* [1991] and Longridge *et al.* [2008] from the Kennecott Point section (Figure 1). The stratigraphic distributions of the ammonites collected by Longridge *et al.* [2008] at Kennecott Point are given in 5 figures (Figures 3 to 7 in the study by Longridge *et al.*) showing the lithology and thickness of each of the sections. The correlation between these is established by Longridge *et al.* [2008] in a synthetic figure. The thicknesses of the sections given in the diagram allows us to have a precise representation of the stratigraphic thicknesses of the ammonite zones and subzones at Kennecott Point. These were reported in the stratigraphic log of Williford *et al.* [2007, 2009] and are reproduced in our Figure 1. The major carbon anomaly is situated entirely above the beds with abundant Alsatitids and yields *Badouxia*. This establishes a late Hettangian Angulata Zone age for the anomaly, which is perfectly synchronous with the major positive carbon isotope excursion (CIE) from NYC found in this study (Figure 1).

[10] The abrupt V shape of the positive Angulata CIE at NYC compared with the more U shaped

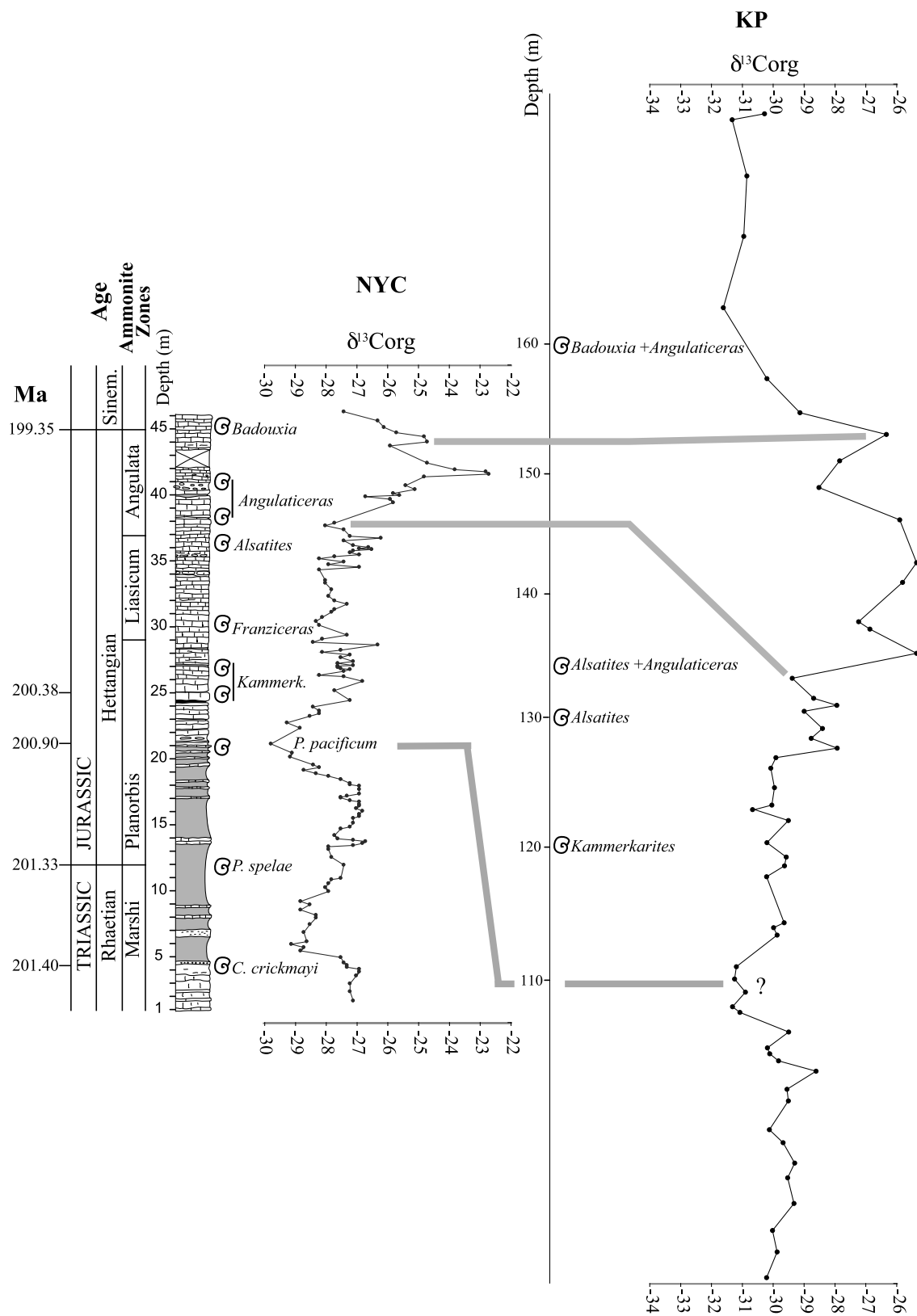


Figure 1. Ammonite biostratigraphical calibration of the organic carbon isotope curve at New York Canyon (NYC) Nevada USA, correlated with the Kennecott Point (KP) curve [Williford *et al.*, 2007] recalibrated with the age diagnostic ammonites identified by Longridge *et al.* [2008]. U-Pb numerical ages are from Schaltegger *et al.* [2008] and Schoene *et al.* [2010].

excursion at KP is likely explained by the presence of a short-duration sedimentary discontinuity and/or high condensation in the acme of positive values at NYC section: the *Angulaticeras* and *Badouxia* beds are condensed in this section. Beyond the above minor dissimilarity, the fact that the general shape of the Hettangian $\delta^{13}\text{C}_{\text{org}}$ curve and its ammonoid calibration are reproducible from two locations within the Pacific province, suggests that they can be used for regional and possibly inter-regional correlation.

[11] It is not easy to correlate the NYC and KP $\delta^{13}\text{C}_{\text{org}}$ curves with records from Newark basin [Whiteside et al., 2010], because the latter fluctuates markedly. Notwithstanding this, Whiteside et al. [2010] correlated one of the positive peaks of Newark basin $\delta^{13}\text{C}_{\text{org}}$ curve with the major positive excursion observed at Kennecott Point by Williford et al. [2007]. According to their cyclostratigraphic interpretation, the duration of the interval spanning the TJB up to the top of the main positive excursion in the Newark basin would have a duration of about 1 Ma. If the correlation of the Newark excursion with the Angulata positive excursion at Kennecott Point was correct, that interval should represent the entire Hettangian stage. This seems too short an interval according to a recent Pb/U radio-isotopic calibration showing a duration of about 2.05 ± 0.25 Ma [Schaltegger et al., 2008] and other cyclostratigraphic estimations [Ruhl et al., 2010]. We suggest that the correlation of the Newark excursion with the Angulata positive excursion at Kennecott Point may not be correct, or, alternatively, that the Newark Hettangian cyclostratigraphic interpretation should be revised.

[12] Ruhl et al. [2010] extended the TJB $\delta^{13}\text{C}_{\text{org}}$ record of St Audrie's Bay to the Hettangian/Sinemurian boundary at East Quantoxhead GSSP (Global Stratotype Section and Point). Ruhl et al. [2010] neither indicated the precise position of ammonite beds in their composite section, nor provided reference to biostratigraphical documentation for the ammonite zonation reported in their figures. However, we can suppose that for St Audrie's Bay they probably referred to the zonation of Ivimey-Cook and Donovan [1983] and for East Quantoxhead-on the ammonite biostratigraphy of Bloos and Page [2002]. Moreover, it is important to stress that they used other biochronological criteria to locate the TJB, placing this last one around the FO of *Psiloceras planorbis*, while the TJB is officially defined by the older FO of *P. spelae*. The development of the earliest Jurassic ammonites occurs within the genus *Psiloceras*, which starts with the occurrence

of *P. spelae* followed by the worldwide development of smooth Psiloceratids of the *P. planorbis* group s.l. [Guex et al., 2004, 2011]. The correlation of the $\delta^{13}\text{C}_{\text{org}}$ curve of the lower part of the NYC section spanning the TJB (*C. crickmayi* to *P. pacificum* beds) can be correlated readily with the curve established at St Audrie's Bay [Hesselbo et al., 2002; Guex et al., 2004], while it is evident that the prominent positive organic CIE in the uppermost Hettangian is missing at St Audrie's Bay-East Quantoxhead composite section (Figure 2). In contrast, the extended post *P. planorbis* $\delta^{13}\text{C}_{\text{org}}$ record at St Audrie's Bay-East Quantoxhead exhibits continuously low values throughout the Hettangian and early Sinemurian. 2‰ shortwave fluctuations have been interpreted as eccentricity controlled climate cycle [Ruhl et al., 2010]. Depleted $\delta^{13}\text{C}_{\text{org}}$ values relate in general with increased total organic carbon (up to 4–10 wt.%) during black-shale intervals and can be related to most extreme anoxic conditions and/or highly stratified conditions of the water column. Clémence et al. [2010a] have already noticed different trends between bulk $\delta^{13}\text{C}_{\text{org}}$ and $\delta^{13}\text{C}_{\text{carb}}$ values in the Planorbis Zone at Doniford section (nearby to St Audrie's Bay, Figure 2), with more positive values of $\delta^{13}\text{C}_{\text{carb}}$ and more negative values of $\delta^{13}\text{C}_{\text{org}}$ during anoxic phases (highest TOC values coupled with absence of microbenthos). The Hettangian $\delta^{13}\text{C}_{\text{org}}$ signal at St Audrie's Bay may therefore have a strong local source control (e.g., change in relative contributions of marine algae and/or bacteria to the bulk organic carbon) linked in this case to recurrent strongly stratified conditions of the water column [Clémence et al., 2010a].

[13] Interestingly, the geographically close Lyme Regis (LR) section $\delta^{13}\text{C}_{\text{org}}$ record, published in supporting information in Whiteside et al. [2010], reveals a major positive excursion in the late Hettangian Liasicus and Angulata ammonite Zones, although its amplitude (~4‰) is less important than the ones recorded at NYC and KP (~5‰) during the same period (Figure 2). The LR section $\delta^{13}\text{C}_{\text{carb}}$ data are also reported in the same figure. Such data are of very low resolution, but in the late Hettangian Liasicus and Angulata ammonite Zones it is possible to discern a negative correlation between $\delta^{13}\text{C}_{\text{org}}$ and $\delta^{13}\text{C}_{\text{carb}}$ values.

5. Interpreting the $\delta^{13}\text{C}_{\text{org}}$ Signal

[14] The new results presented here reveal that the organic carbon isotope record of the Triassic-Jurassic transition is more complex than previously recognized, with a protracted instability of

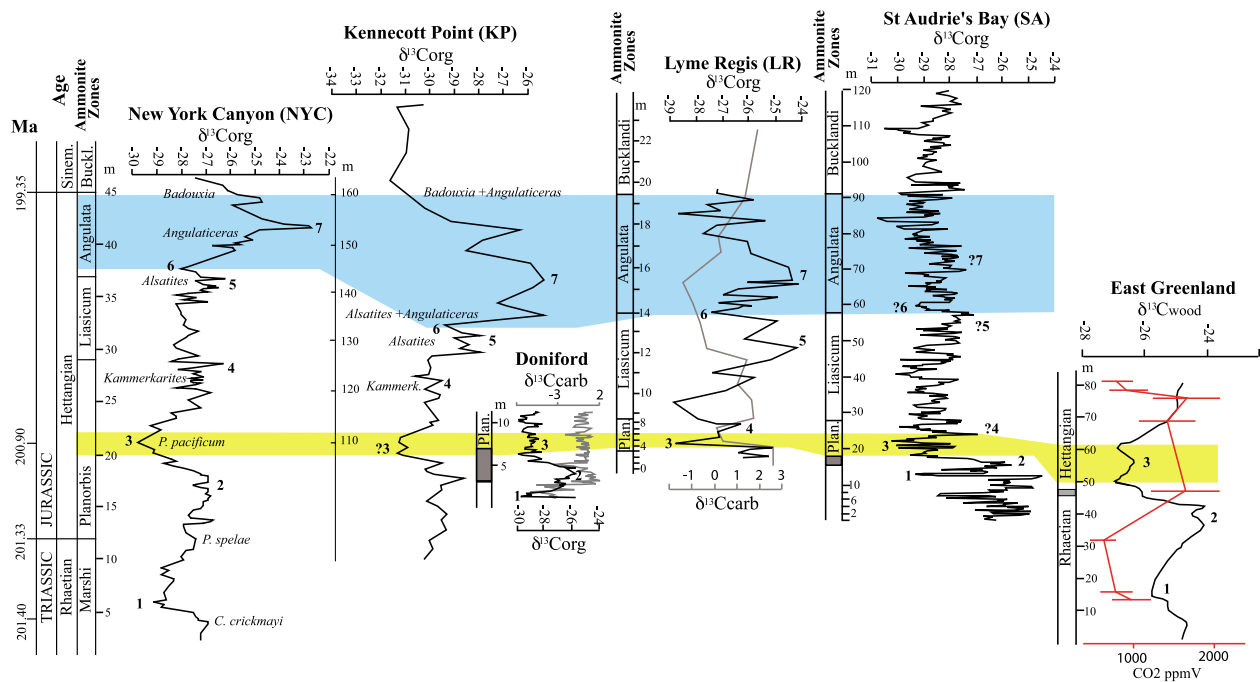


Figure 2. Correlation of Late Rhaetian-Hettangian $\delta^{13}\text{C}_{\text{org}}$ curves from marine sections (NYC, KP, LR, SA) well constrained by ammonite biostratigraphy, and their hypothetical correspondence with trends in $\delta^{13}\text{C}_{\text{wood}}$ from the East Greenland continental record. The numbers 1 to 7 highlight the proposed correlations between excursions. LR data are from *Whiteside et al.* [2010]; SA data from *Hesselbo et al.* [2002] and *Ruhl et al.* [2010]; East Greenland data from *McElwain et al.* [2009]. The record of atmospheric CO_2 concentration in ppmv was derived from stomatal analysis of fossil Ginkgoales leaves [*McElwain et al.*, 2009].

at least about 2 Ma, corresponding to the interval spanning the uppermost Rhaetian *C. crickmayi* beds to the latest Hettangian Angulata Zone [*Schaltegger et al.*, 2008; *Schoene et al.*, 2010]. However, interpreting the perturbations of Hettangian $\delta^{13}\text{C}_{\text{org}}$ signal is not trivial for two primary reasons: First, a diagenetic alteration and thermally induced maturation of the sedimentary organic matter triggering loss of hydrocarbons may change the stable isotope composition of organic carbon [*Hayes et al.*, 1983; *Strauss et al.*, 1997]. A ^{13}C enrichment is generally observed with increasing thermal alteration [*Hayes et al.*, 1983]. Thus, the very high values of $\delta^{13}\text{C}_{\text{org}}$ up to -23‰ in the Angulata positive main excursion at NYC might, at least in part, result from thermal alteration by Tertiary volcanism that impacted the region. However, thermal alteration would have shifted the isotopic values in one direction, preserving the general shape of curve. Second, changes in relative contributions (e.g., bacterial, phytoplankton or terrestrial plant biomass) of bulk organic carbon can explain the changes in the $\delta^{13}\text{C}_{\text{org}}$ values, without necessarily requiring changes in the isotope composition of carbon in the oceans and atmosphere

[*van de Schootbrugge et al.*, 2008; *Fio et al.*, 2010]. For example, in the interval containing the positive excursion in $\delta^{13}\text{C}_{\text{org}}$ at Kenecott Point a lithological change from black-shales to siltstones and turbiditic sandstones accompanied by an increase of woody debris was observed [*Williford et al.*, 2009]. At NYC such an important lithological change in the upper Hettangian positive excursion interval has not been observed. However, we cannot exclude that in these Pacific sections, an increased terrigenous input may have amplified the positive shift in bulk organic carbon isotope ratios, as terrestrial organic matter was generally enriched in ^{13}C relative to marine organic matter prior to the mid-Cretaceous [*Arthur et al.*, 1985; *Popp et al.*, 1989]. Other $\delta^{13}\text{C}_{\text{org}}$ records recently published (e.g., St Audrie's Bay) do not reveal a prominent Late Hettangian $\delta^{13}\text{C}_{\text{org}}$ positive excursion (Figure 2), probably because of a strong influence of recurrent extreme anoxic conditions during the Hettangian and early Sinemurian. This depletion might be explained by a higher proportion of biomass derived from isotopically depleted chemoautotrophic bacteria and green algal groups (e.g., acritarchs and prasinophytes), which likely develop during anoxic

conditions [Joachimski, 1997; van de Schootbrugge et al., 2008].

[15] Nevertheless, the robust correlation of a major positive excursion of $\delta^{13}\text{C}_{\text{org}}$ record in the Late Hettangian Liasicus-Angulata Zones between geographically distant locations (NYC, KP and LR, Figure 2) argues for a global interpretation. As discussed above, the amplitude and absolute values of the positive excursion might have been amplified by local environmental conditions, source control and/or local diagenetic/thermal history, but the general shape of the curve likely traces a more global history.

[16] Even though there are few documented paired organic and carbonate carbon isotope data sets from the same Hettangian section [Clémence et al., 2010a, 2010b; Whiteside et al., 2010], this information is important to help evaluate whether or not the Late Hettangian positive excursion resulted from a global carbon cycle perturbation. The uppermost Triassic is marked by a pronounced negative excursion in both $\delta^{13}\text{C}_{\text{org}}$ and $\delta^{13}\text{C}_{\text{carb}}$ (Figure 2) that coincides with biotic extinctions of several marine organisms, such as ammonites, radiolarians, calcareous nannofossils [Guex et al., 2004; Clémence et al., 2010b]. A high-resolution micropaleontological study combined with geochemical analyses in the Austrian Alps for the end of the Triassic revealed a dramatic calcareous phytoplankton crisis and disturbance of the biological pump associated with regression, cooling and/or seawater acidification episodes [Clémence et al., 2010b]. As interpreted for other mass-extinction intervals, the $\delta^{13}\text{C}$ negative excursion at the end of the Triassic can also be explained, at least in part, by the primary productivity crisis and a loss of the efficiency of the CO_2 biological pump [Ward et al., 2001; Guex et al., 2004; Clémence et al., 2010b]. The succeeding post-crisis interval, corresponding with lowermost Hettangian Spelae Beds, is marked by a parallel trend toward more positive values both of $\delta^{13}\text{C}_{\text{org}}$ and $\delta^{13}\text{C}_{\text{carb}}$ records, correlated with the initial phases of recovery of the pelagic carbonate producers [Clémence et al., 2010a], as well as with a first pulse of diversification of ammonites [Guex et al., 2011].

[17] From the *P. planorbis* beds (correlative with the *P. pacificum* beds) up to the Angulata Zone, the organic and carbonate carbon isotope records seem to be generally decoupled: as observed in Doniford and Lyme Regis sections (Figure 2), the $\delta^{13}\text{C}_{\text{org}}$ curve is negatively correlated with the $\delta^{13}\text{C}_{\text{carb}}$ curve ([Clémence et al., 2010a] see Whiteside et al.

[2010] supporting information). Such phenomena have already been documented for other time intervals [Joachimski, 1997; Kump and Arthur, 1999]. Kump and Arthur [1999] showed by model simulations comparing isotopic records of carbonate and organic carbon, that the timing of the peaks and valleys of the two secular carbon isotope records might not coincide, even when they are subject to the same forcing. Thus, such carbon isotope curves without biostratigraphical control cannot be used infallibly as a correlation tool.

[18] According to the simulations of Kump and Arthur [1999], we can interpret the Planorbis negative excursion in $\delta^{13}\text{C}_{\text{org}}$ unaccompanied by a response in $\delta^{13}\text{C}_{\text{carb}}$, as due to a dramatic increase in pCO_2 (e.g., volcanically induced). It is also possible that the two are not coupled at Doniford because of peculiar conditions of the water column: the $\delta^{13}\text{C}_{\text{carb}}$ mirroring the increase of sea-surface primary productivity and the $\delta^{13}\text{C}_{\text{org}}$ responding to low oxygen conditions at sea-bottom [Clémence et al., 2010a]. Note that the Planorbis negative excursion coincides with a minor ammonite extinction event: the last Choristocerataceae (i.e., *Choristeras minutum* and *Odoghertyceras*) surviving the mass extinction were finally extinguished at this time [Guex et al., 2004, 2011]. The following Liasicus-Angulata major positive excursion is recorded only in the organic carbon and apparently not in the carbonates, if we admit that there was not a strong diagenetic impact on the $\delta^{13}\text{C}_{\text{carb}}$ values at LR (Figure 2). The total duration of the organic positive shift from the minimum values in the Planorbis beds to maximum values in the Angulaticeras beds can be estimated at about 1 My, according to the high resolution radiometric calibration of Hettangian ammonite beds in the Levanto section in Peru [Guex et al., 2011]. Such duration is much longer than the residence time of carbon in the ocean-atmosphere system, and it might imply, according to the model of Kump and Arthur [1999], an organic burial event that began at highly elevated atmospheric pCO_2 . Their model, in addition to standard considerations of carbon mass and isotopic fluxes to the ocean-atmosphere system from weathering and volcanism and fluxes of organic carbon and carbonate-carbon to sediments, incorporates sensitivity of the photosynthetic carbon isotope effect to change in pCO_2 . In the modern ocean, the photosynthetic isotope effect for marine algae against CO_2 concentration varies by nearly 8‰ as a function primarily of variations in surface water pCO_2 , temperature and growth rate [Rau et al., 1997]. As high rates of

organic burial proceed in time, this causes $p\text{CO}_2$ to fall, inducing a reduction in the photosynthetic isotope effect and an increase in ^{13}C in phytoplankton organic matter. The counterintuitive overall result is that the carbonate carbon isotopic composition actually decreases because of enhanced burial of phytoplankton organic matter enriched in ^{13}C . Alternatively, during recovery phases, the turnover and resulting change in contribution of the main taxonomic components of the phytoplankton and plants with different photosynthetic carbon isotope fractionations, might explain the negative and positive excursions observed in the organic record [van de Schootbrugge *et al.*, 2008] without necessarily involving the isotopic composition of ocean dissolved inorganic carbon (DIC).

6. Possible Extinction-Recovery Scenario

[19] A consensus in the literature points to flood volcanism of the CAMP as the major trigger of biotic and carbon cycle disturbance across the T-J [Marzoli *et al.*, 1999, 2004]. Recent precise radiometric age correlations between basalts of CAMP and marine T-J boundary help to affirm this possible causal link [Schoene *et al.*, 2010]. Two interpretations exist regarding the role and effects of volcanic impact: (1) On one hand, the carbon dioxide (CO_2) degassing and clathrate escape, or thermogenic methane related to CAMP sill intrusion, have been invoked as triggers of a catastrophic greenhouse effect, anoxia, and seawater acidification, resulting in mass extinction [McElwain *et al.*, 1999; Pálffy *et al.*, 2001; Hesselbo *et al.*, 2002; Korte *et al.*, 2009; Bonis *et al.*, 2010; Ruhl *et al.*, 2011]; (2) on the other hand, CAMP-related sulphuric emissions might have been the trigger for cooling episodes, light reduction, and seawater acidification leading to collapse of marine ecosystems, mass extinctions, and reduction in biomass [Tanner *et al.*, 2001; Guex *et al.*, 2004; van de Schootbrugge *et al.*, 2009; Clémence *et al.*, 2010b].

[20] McElwain *et al.* [1999, 2009] infer a major $p\text{CO}_2$ increase from the analysis of the stomatal index of fossil Ginkgoales leaves. From this they concluded that the end-Triassic extinction was caused by a super-greenhouse effect. This interpretation of the stomatal index has been debated because SO_2 increase may also cause changes in stomatal density [Tanner *et al.*, 2007]. Nonetheless, if the increase in stomatal index relates to increased atmospheric CO_2 , the low-resolution data available [McElwain *et al.*, 1999, 2009] leave considerable

uncertainty as to the precise timing of the increase in atmospheric CO_2 concentration. It is plausible that the first sample showing increased CO_2 in the studies by McElwain *et al.* [1999, 2009] corresponds to the second negative anomaly (also called the “main” excursion) in the Planorbis Zone (Figure 2), making their model compatible with a post-crisis warming proposed by Guex *et al.* [2004]. The interpretation of an Early Jurassic post-crisis super-greenhouse time is strengthened by new $p\text{CO}_2$ estimations from high-resolution stable isotopic data of pedogenic carbonates interbedded with volcanics of CAMP in the Newark Basin [Schaller *et al.*, 2011]. Considering that the eruption of North Mountain Basalt has been radiometrically correlated with the FO of TJB boundary primary marker *P. spelae* [Schoene *et al.*, 2010], it is clear that the calculated $p\text{CO}_2$ increased by pulses corresponding with lava flows during the early Jurassic, while during the Late Triassic the calculated $p\text{CO}_2$ are low, according to Figure 1 in the study by Schaller *et al.* [2011].

[21] The impact of CAMP volcanism on the ecosystems could have been twofold: first short-term repeated releases of SO_2 (cooling and acidification) during the end-Triassic, and second a long-term CO_2 release (greenhouse and anoxia) during the Early Hettangian post-crisis, see the cooling-warming scenario in the study by Guex *et al.* [2004]. An inefficient biological CO_2 pumping mechanism due to the productivity crisis, coupled with volcanogenic (or thermogenic) accumulation of CO_2 in the atmosphere resulting from the CAMP activity could have produced a super greenhouse effect during the Early Hettangian.

[22] Super-greenhouse promoted an acceleration of continental weathering, runoff and increased the input of nutrients into the ocean. This may have, in turn, promoted biotic radiations in marine environments stimulating primary productivity as well the initial recovery of zooplankton and nekton in the Spelae Beds [Guex *et al.*, 2004; Clémence *et al.*, 2010b], <290 ka after the end-Triassic mass extinction [Schoene *et al.*, 2010]. On the other hand, the restoration of marine primary production sustained by elevated CO_2 levels in the aftermath of a mass extinction can induce water anoxia, a pattern also suggested for the aftermath of the Permo-Triassic crisis [Grard *et al.*, 2005; Payne and Kump, 2007; Hermann *et al.*, 2010]. Anoxia and possible water column stratification in several basins likely hindered in turn the full recovery of marine ecosystems

[Clémence *et al.*, 2010a], as also evidenced by a minor ammonite extinction event coupled with the organic negative Planorbis (Pacificum) CIE. As high rates of organic burial proceeded in time, this caused pCO₂ to fall and therefore reduced the basinal area affected by water anoxia, favoring a main pulse of diversification of ammonites in coincidence with the Angulata organic positive excursion [Guex *et al.*, 2011].

7. Conclusions

[23] In several recent paper papers, the early and late Hettangian positive $\delta^{13}\text{C}$ excursions have been confused. Here, we show that the lowermost Hettangian positive Spelae excursion is indeed dissimilar in magnitude and time from the uppermost Hettangian Angulata positive excursion. The FO of *P. spelae* marks the base of the Hettangian stage (and of the Jurassic System) and the onset of post-extinction ecological recovery <290 ka after the end-Triassic mass extinction. The fluctuating pattern of the $\delta^{13}\text{C}_{\text{org}}$ curve culminating with the uppermost Hettangian Angulata positive excursion, indicates that although the recovery of some pelagic taxa (ammonites, radiolarians, calcareous nannofossils, etc.) already began at the base of Jurassic, the ecosystem and the carbon cycle remained highly perturbed for at least 2 Ma.

[24] An inefficient biological CO₂ pumping mechanism due to the productivity crisis, coupled with volcanogenic accumulation of CO₂ in the atmosphere resulting from the continuing CAMP could have produced a super-greenhouse effect during the early Hettangian. Pulses of CAMP volcanism and phases of anoxia might have perturbed the full recovery. The main Angulata organic positive CIE might be related to gradual decreasing of pCO₂ due to protracted high organic burial, and coincides with a second phase of recovery, as indicated by a pulse of diversification of ammonites. Alternatively, during the recovery phases, the turnover and resulting change in contribution of the main taxonomic components of the phytoplankton and plants with different carbon isotope fractionation factors, might explain this positive excursion observed in the organic record. For this latter scenario, invoking the entire global carbon cycle would not be required.

[25] These can be considered as a working-hypothesis, and further work on the carbon isotopic record from both organic matter and carbonates from more sections worldwide, coupled with micropaleontological, palynological and possibly

biomarker analyses, is needed to better understand this major positive late Hettangian organic CIE.

Acknowledgments

[26] This study was supported by the Swiss National Foundation (project 124375) and by the MNHN ATM Biodiversité et rôle des microorganismes dans les écosystèmes actuels et passés. The paper has benefited from the constructive comments of Louis Derry, Hugo Bucher, Bas van de Schootbrugge and an anonymous reviewer, who are gratefully thanked.

References

- Arthur, M. A., W. E. Dean, and G. E. Claypool (1985), Anomalous ¹³C enrichment in modern marine organic carbon, *Nature*, *315*, 216–218, doi:10.1038/315216a0.
- Bloos, G., and K. N. Page (2002), Global Stratotype Section and Point for base of the Sinemurian Stage (Lower Jurassic), *Episodes*, *25*, 22–28.
- Bonis, N. R., M. Ruhl, and W. M. Kürschner (2010), Climate change driven black-shale deposition during the end-Triassic in the western Tethys, *Palaeogeogr. Palaeoclimatol. Palaeoecol.*, *290*, 151–159, doi:10.1016/j.palaeo.2009.06.016.
- Clémence, M. E., A. Bartolini, S. Gardin, G. Paris, V. Beaumont, and K. N. Page (2010a), Early Hettangian benthic–planktonic coupling at Doniford (SW England) Palaeoenvironmental implications for the aftermath of the end-Triassic crisis, *Palaeogeogr. Palaeoclimatol. Palaeoecol.*, *295*, 102–115.
- Clémence, M. E., S. Gardin, A. Bartolini, G. Paris, V. Beaumont, and J. Guex (2010b), Benthic–planktonic evidence from the Austrian Alps for a decline in sea-surface carbonate production at the end of the Triassic, *Swiss J. Geosci.*, *103*, 293–315, doi:10.1007/s00015-010-0019-z.
- Fio, K., J. E. Spangenberg, I. Vlahović, J. Sremac, I. Velić, and E. Mrinjek (2010), Stable isotope and trace element stratigraphy across the Permian–Triassic transition: A redefinition of the boundary in the Velebit Mountain, Croatia, *Chem. Geol.*, *278*, 38–57, doi:10.1016/j.chemgeo.2010.09.001.
- Grard, A., L. M. Francois, C. Dessert, B. Dupre, and Y. Godderis (2005), Basaltic volcanism and mass extinction at the Permian–Triassic boundary: Environmental impact and modeling of the global carbon cycle, *Earth Planet. Sci. Lett.*, *234*, 207–221, doi:10.1016/j.epsl.2005.02.027.
- Guex, J. (1995), *Ammonites Hettangiennes de la Gabbs Valley Range (Nevada)*, *Mém. de Géol.*, vol. 27, Univ. Lausanne, Lausanne, Switzerland.
- Guex, J., A. Bartolini, V. Atudorei, and D. G. Taylor (2004), High-resolution ammonite and carbon-isotope stratigraphy across the Triassic–Jurassic Boundary at New York Canyon (Nevada), *Earth Planet. Sci. Lett.*, *225*, 29–41, doi:10.1016/j.epsl.2004.06.006.
- Guex, J., A. Bartolini, D. Taylor, V. Atudorei, P. Thelin, S. Bruchez, L. H. Tanner, and S. G. Lucas (2009), The organic carbon isotopic and paleontological record across the Triassic–Jurassic boundary at the candidate GSSP section at Ferguson Hill, Muller Canyon, Nevada, USA, Comment, *Palaeogeogr. Palaeoclimatol. Palaeoecol.*, *273*, 200–204, doi:10.1016/j.palaeo.2008.01.010.
- Guex, J., B. Schoene, A. Bartolini, J. Spangenberg, U. Schaltegger, L. O’Dogherly, D. Taylor, V. Atudorei, and H. Bucher (2011), Geochronological constraints on the post-extinction recovery



- of the ammonoids and on the carbon isotope cycle during the Early Jurassic, *Geophys. Res. Abstr.*, **13**, EGU2011-1851.
- Hayes, J. M., I. R. Kaplan, and K. W. Wedeking (1983), Precambrian organic geochemistry, preservation of the record, in *Earth's Earliest Biosphere, its Origin and Evolution*, edited by J. W. Schopf, pp. 93–134, Princeton Univ. Press, Princeton, N. J.
- Hermann, E., P. A. Hochuli, H. Bucher, J. O. Vigran, H. Weissert, and S. M. Bernasconi (2010), A close-up view of the Permian–Triassic boundary based on expanded organic carbon isotope records from Norway (Trondelag and Finnmark Platform), *Global Planet. Change*, **74**, 156–167, doi:10.1016/j.gloplacha.2010.10.007.
- Hesselbo, S. P., S. A. Robinson, F. Surlyk, and S. Piasecki (2002), Terrestrial and marine extinction at the Triassic–Jurassic boundary synchronized with major carbon-cycle perturbation: A link to initiation of massive volcanism?, *Geology*, **30**, 251–254, doi:10.1130/0091-7613(2002)030<0251:TAMEAT>2.0.CO;2.
- Ivimey-Cook, H. C., and D. T. Donovan (1983), Appendix 3: The fauna of the Lower Jurassic, in *Geology of the Country Around Weston-Super-Mare*, edited by A. Whittaker and G. W. Green, *Mem. Geol. Surv. G. B.*, **279**, 126–130.
- Joachimski, M. M. (1997), Comparison of organic and inorganic carbon isotope patterns across the Frasnian–Famennian boundary, *Palaeogeogr. Palaeoclimatol. Palaeoecol.*, **132**, 133–145, doi:10.1016/S0031-0182(97)00051-5.
- Korte, C., S. P. Hesselbo, H. C. Jenkyns, R. E. M. Rickaby, and C. Spotl (2009), Palaeoenvironmental significance of carbon- and oxygen-isotope stratigraphy of marine Triassic–Jurassic boundary sections in SW Britain, *J. Geol. Soc.*, **166**, 431–445, doi:10.1144/0016-76492007-177.
- Kump, L. R., and M. A. Arthur (1999), Interpreting carbon-isotope excursions: Carbonates and organic matter, *Chem. Geol.*, **161**, 181–198, doi:10.1016/S0009-2541(99)00086-8.
- Longridge, L. M., J. Pálffy, P. L. Smith, and H. W. Tipper (2008), Middle and late Hettangian (Early Jurassic) ammonites from the Queen Charlotte Island, British Columbia, Canada, *Rev. Paléobiologie*, **27**, 191–248.
- Marzoli, A., P. R. Renne, E. M. Piccirillo, M. Ernesto, G. Bellieni, and A. De Min (1999), Extensive 200-million-year-old continental flood basalts of the Central Atlantic magmatic province, *Science*, **284**, 616–618, doi:10.1126/science.284.5414.616.
- Marzoli, A., et al. (2004), Synchrony of the Central Atlantic magmatic province and the Triassic–Jurassic boundary climatic and biotic crisis, *Geology*, **32**, 973–976, doi:10.1130/G20652.1.
- McElwain, J. C., D. J. Beerling, and F. I. Woodward (1999), Fossil plants and global warming at the Triassic–Jurassic Boundary, *Science*, **285**, 1386–1390, doi:10.1126/science.285.5432.1386.
- McElwain, J. C., P. J. Wagner, and S. P. Hesselbo (2009), Fossil plant relative abundances indicate sudden loss of Late Triassic biodiversity in East Greenland, *Science*, **324**, 1554–1556, doi:10.1126/science.1171706.
- Muller, S. W., and H. G. Ferguson (1936), Triassic and lower Jurassic formations of west central Nevada, *Geol. Soc. Am. Bull.*, **47**, 241–252.
- Muller, S. W., and H. G. Ferguson (1939), Mesozoic stratigraphy of the Hawthorne and Tonopah quadrangles, Nevada, *Geol. Soc. Am. Bull.*, **50**, 1573–1624.
- Pálffy, J., A. Demeny, J. Haas, M. Htenyi, M. J. Orchard, and I. Veto (2001), Carbon isotope anomaly at the Triassic–Jurassic boundary from a marine section in Hungary, *Geology*, **29**, 1047–1050, doi:10.1130/0091-7613(2001)029<1047: CIAAOG>2.0.CO;2.
- Payne, J. L., and L. R. Kump (2007), Evidence for recurrent Early Triassic massive volcanism from quantitative interpretation of carbon isotope fluctuations, *Earth Planet. Sci. Lett.*, **256**, 264–277, doi:10.1016/j.epsl.2007.01.034.
- Popp, B. N., R. Takigiku, J. M. Hayes, J. W. Louda, and E. W. Baker (1989), The post-Paleozoic chronology and mechanism of ¹³C depletion in primary marine organic matter, *Am. J. Sci.*, **289**, 436–454, doi:10.2475/ajs.289.4.436.
- Rau, G. H., U. Riebesell, and D. Wolf-Gladrow (1997), CO₂,_{aq}-dependent photosynthetic ¹³C fractionation in the ocean: A model versus measurements, *Global Biogeochem. Cycles*, **11**, 267–278, doi:10.1029/97GB00328.
- Ruhl, M., M. H. L. Deenen, H. A. Abels, N. R. Bonis, W. Krijgsman, and W. M. Kürschner (2010), Astronomical constraints on the duration of the early Jurassic Hettangian stage and recovery rates following the end-Triassic mass extinction (St Audrie's Bay/East Quantoxhead, UK), *Earth Planet. Sci. Lett.*, **295**, 262–276, doi:10.1016/j.epsl.2010.04.008.
- Ruhl, M., N. R. Bonis, G.-J. Reichert, J. S. Sinninghe Damsté, and W. M. Kürschner (2011), Atmospheric Carbon Injection Linked to End-Triassic Mass Extinction, *Science*, **333**, 430–434, doi:10.1126/science.1204255.
- Schaller, M. F., J. D. Wright, and D. V. Kent (2011), Atmospheric PCO₂ perturbations associated with the Central Atlantic Magmatic Province, *Science*, **331**, doi:10.1126/science.1199011.
- Schaltegger, U., J. Guex, A. Bartolini, B. Schoene, and M. Ovtcharova (2008), Precise U–Pb age constraints for end-Triassic mass extinction, its correlation to volcanism and Hettangian post-extinction recovery, *Earth Planet. Sci. Lett.*, **267**, 266–275, doi:10.1016/j.epsl.2007.11.031.
- Schoene, B., J. Guex, A. Bartolini, U. Schaltegger, and T. J. Blackburn (2010), Correlating the end-Triassic mass extinction and flood basalt volcanism at the 100,000-year level, *Geology*, **38**, 387–390, doi:10.1130/G30683.1.
- Strauss, H., G. Vidal, M. Moczydlowska, and J. Paczesnaet (1997), Carbon isotope geochemistry and palaeontology of Neoproterozoic to early Cambrian siliciclastic successions in the East European Platform, Poland, *Geol. Mag.*, **134**, 1–16, doi:10.1017/S0016756897006602.
- Tanner, L. H., J. F. Hubert, B. P. Coffey, and D. P. Mcinerney (2001), Stability of atmospheric CO₂ levels across the Triassic/Jurassic boundary, *Nature*, **411**, 675–677, doi:10.1038/35079548.
- Tanner, L. H., D. L. Smith, and A. Allan (2007), Stomal response of swordfern to volcanogenic CO₂ and SO₂ from Kilauea volcano, *Geophys. Res. Lett.*, **34**, L15807, doi:10.1029/2007GL030320.
- Taylor, D. G., P. L. Smith, R. A. Laws, and J. Guex (1983), The stratigraphy and biofacies trends of the lower Mesozoic Gabbs and Sunrise formations, west-central Nevada, *Can. J. Earth Sci.*, **20**, 1598–1608, doi:10.1139/e83-149.
- Tipper, H. W., P. L. Smith, B. E. B. Cameron, E. S. Carter, G. K. Jakobs, and M. J. Johns (1991), Biostratigraphy of the Lower Jurassic formations of the Queen Charlotte Islands, British Columbia, in *Evolution and Hydrocarbon Potential of the Queen Charlotte Basin, British Columbia*, edited by G. J. Woodsworth, *Pap. Geol. Surv. Can.*, **90-10**, 203–235.
- van de Schootbrugge, B., J. L. Payne, A. Tomasovych, J. Pross, J. Fiebig, M. Benbrahim, K. B. Föllmi, and T. M. Quan (2008), Carbon cycle perturbation and stabilisation in



- the wake of the Triassic–Jurassic mass-extinction event, *Geochem. Geophys. Geosyst.*, **9**, Q04028, doi:10.1029/2007GC001914.
- van de Schootbrugge, B., et al. (2009), Floral changes across the Triassic/Jurassic boundary linked to flood basalt volcanism, *Nat. Geosci.*, **2**, 589–594, doi:10.1038/ngeo577.
- Ward, P. D., J. W. Haggart, E. S. Carter, D. Wilbur, H. W. Tipper, and T. Evans (2001), Sudden productivity collapse associated with the Triassic–Jurassic boundary mass extinction, *Science*, **292**, 1148–1151, doi:10.1126/science.1058574.
- Ward, P. D., G. H. Garrison, K. H. Williford, D. A. Kring, D. Goodwin, M. J. Beattie, and C. A. McRoberts (2007), The organic carbon isotopic and paleontological record across the Triassic–Jurassic boundary at the candidate GSSP section at Ferguson Hill, Muller Canyon, Nevada, USA, *Palaeogeogr. Palaeoclimatol. Palaeoecol.*, **244**, 281–289, doi:10.1016/j.palaeo.2006.06.042.
- Whiteside, J. H., P. E. Olsen, T. Eglinton, M. E. Brookfield, and R. N. Sambrotto (2010), Compound-specific carbon isotopes from Earth’s largest flood basalt eruptions directly linked to the end-Triassic mass extinction, *Proc. Natl. Acad. Sci. U. S. A.*, **107**, 6721–6725, doi:10.1073/pnas.1001706107.
- Williford, K. H., P. D. Ward, G. H. Garrison, and R. Buick (2007), An extended organic carbon-isotope record across the Triassic–Jurassic boundary in the Queen Charlotte Islands, British Columbia, Canada, *Palaeogeogr. Palaeoclimatol. Palaeoecol.*, **244**, 290–296, doi:10.1016/j.palaeo.2006.06.032.
- Williford, K. H., J. Foriel, P. D. Ward, and E. J. Steig (2009), Major perturbation in sulfur cycling at the Triassic–Jurassic boundary, *Geology*, **37**, 835–838, doi:10.1130/G30054A.1.