

Carbon cycle perturbation and stabilization in the wake of the Triassic-Jurassic boundary mass-extinction event

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[1] The Triassic-Jurassic boundary mass-extinction event (T-J; 199.6 Ma) is associated with major perturbations in the carbon cycle recorded in stable carbon isotopes. Two rapid negative isotope excursions in bulk organic carbon ($\delta^{13}\text{C}_{\text{org}}$) occur within the immediate boundary interval at multiple locations and have been linked to the outgassing of ^{12}C -enriched CO_2 from the Central Atlantic Magmatic Province. In British Columbia, a positive $\delta^{13}\text{C}_{\text{org}}$ excursion of +5‰ (Vienna Peedee belemnite (V-PDB)) spans part or all of the subsequent Hettangian stage. Here, we examine the significance of these carbon isotope

excursions as records of global carbon cycle dynamics across the T-J boundary and test the link between carbon cycle perturbation-stabilization and biotic extinction-recovery patterns. A combination of $\delta^{13}\text{C}_{\text{org}}$ and palynological analyses from the Late Triassic to Early Jurassic in the Mingolsheim core (Germany) suggests that organic carbon isotope variations are best explained as the result of both compositional changes in terrestrial versus marine input and disturbance and recovery patterns of major terrestrial plant groups across the T-J boundary. A new high-resolution $\delta^{13}\text{C}_{\text{carb}}$ record from the Val Adrara section in the Southern Alps (Italy) spanning from the uppermost Rhaetian through Lower Sinemurian does not exhibit a negative excursion at the T-J boundary but does record a large positive $\delta^{13}\text{C}_{\text{carb}}$ excursion of +4‰ (V-PDB) in bulk carbonate that begins at the T-J boundary and reaches a local maximum at the Early Late Hettangian boundary. Values then gradually decrease reaching +0.5‰ at the Hettangian-Sinemurian boundary and remain relatively constant into the Early Sinemurian. Complementary $\delta^{13}\text{C}_{\text{carb}}$ data from 4 more sections that span the Hettangian-Sinemurian boundary support carbon cycle stabilization within the Upper Hettangian. Our analyses suggest that isotope changes in organic carbon reservoirs do not necessarily require a shift in the global exogenic carbon reservoir and that the positive excursion in the carbonate carbon isotope record is best explained as the combined result of an increase in atmospheric $p\text{CO}_2$ leading to accelerated carbon cycling, decreased skeletal carbonate production, and increased organic carbon burial lasting several hundred thousand years. The termination of the positive inorganic carbon isotope excursion coincides with the recovery of marine skeletal carbonate producers and coeval changes in terrestrial vegetation and reflects the gradual reduction in $p\text{CO}_2$ and the stabilization of the global carbon cycle during the Sinemurian.

1. Introduction

[2] Earth's chemical and biological histories are inextricably linked. For example, it is increasingly clear that most, if not all, of the major biological extinction events in the Phanerozoic fossil record are associated with rapid carbon cycle perturbations recorded in the stable carbon isotope composition of carbonate rocks and organic matter. The Triassic-Jurassic boundary mass extinction (T-J; 199.6 Ma), one of the “big five” mass-extinction events [Raup and Sepkoski, 1982; Sepkoski, 1996; Tanner *et al.*, 2004], is associated with geologically rapid negative excursions in $\delta^{13}\text{C}$ of carbonates and organic matter that occur in close association with the extinction of Triassic organisms. Two negative C-isotope excursions, often distinguished as the “initial” and “main” excursions, have been identified in bulk organic carbon ($\delta^{13}\text{C}_{\text{org}}$) in T-J boundary sections in the UK [Hesselbo *et al.*, 2002], the United States [Guex *et al.*, 2004; Ward *et al.*, 2007], Spain [Gomez *et al.*, 2007], Austria [Kürschner *et al.*, 2007] and in British Columbia [Wignall *et al.*, 2007]. In some locations evidence for two distinct excursions seems spurious, such as in Greenland [McElwain *et al.*, 1999], Hungary [Palfy *et al.*, 2001] and Canada [Ward *et al.*, 2001; Williford *et al.*, 2007]. Negative C-isotope excursions have also been documented in whole-rock inorganic (carbonate) carbon isotope ($\delta^{13}\text{C}_{\text{carb}}$)

records from Austria [McRoberts *et al.*, 1997], Italy [Galli *et al.*, 2005], Hungary [Palfy *et al.*, 2007], Slovakia [Michalik *et al.*, 2007] and in oyster calcite in the UK [van de Schootbrugge *et al.*, 2007]. In other T-J boundary sections diagenesis appears to have severely overprinted the original $\delta^{13}\text{C}_{\text{carb}}$ signal (e.g., Kennecott Point, British Columbia [Ward *et al.*, 2004]; St Audries Bay, UK [Hallam, 1994]).

[3] Several studies have attributed the negative T-J boundary C-isotope excursions to the effects of CO_2 degassed from the Central Atlantic Magmatic Province (CAMP), a large flood basalt province which erupted over 500 to 1500 ka [McHone, 2002; Hesselbo *et al.*, 2002; Knight *et al.*, 2004]. Stomatal abundance and size data from fossil leaves suggest that $p\text{CO}_2$ may have increased fourfold during that time [McElwain *et al.*, 1999], for which modeling indicates would have required the release of 8000 Gt of volcanic CO_2 and a possible further release of 5000 Gt of methane from gas hydrates [Beerling and Berner, 2002]. The quantitative evaluation of a CAMP-related origin for the C-isotope excursions, however, depends in large part on the magnitude of the excursions, which is still uncertain. In bulk organic matter the excursion ranges from only -2‰ in British Columbia [Ward *et al.*, 2004], to -5‰ in the St Audrie's Bay section in the UK [Hesselbo *et al.*, 2002] and to nearly -8‰ (Vienna Peedee

belemnite (V-PDB)) in Austria [Kürschner *et al.*, 2007]. In carbonate carbon isotope records the negative excursion varies in magnitude from just over -1.5% in Slovakia [Michalik *et al.*, 2007] and Nevada [Ward *et al.*, 2007], to -2.5% in Austria [McRoberts *et al.*, 1997], around -4% in Italy [Galli *et al.*, 2005], and -7% (V-PDB) in Hungary [Palfy *et al.*, 2007].

[4] Further complications for interpreting global carbon cycle events have been introduced by $\delta^{13}\text{C}_{\text{org}}$ data from the Queen Charlotte Islands in British Columbia (Canada). They reveal a large positive carbon isotope excursion of $+5\%$ beginning immediately after the negative T-J boundary excursion and lasting through part or all of the Hettangian Stage of the Early Jurassic [Ward *et al.*, 2007; Williford *et al.*, 2007]. The persistence of carbon isotope excursions beyond the initial boundary event in the Early Jurassic raises two issues. First, if the excursion recorded in bulk organic carbon reflects a global change in the isotope composition of carbon in the oceans and atmosphere, then any adequate T-J scenario must account not only for negative carbon isotope excursions but also for a subsequent positive excursion. Second, carbon isotope excursions in bulk organic carbon do not necessarily require changes in the isotope composition of carbon in the oceans and atmosphere; they can also result from changes in the mixing ratios of organic carbon sources with different isotope compositions [Bechtel *et al.*, 2002; van Bergen and Poole, 2002], potentially explaining some of the variability in timing and magnitude of excursions among localities highlighted above.

[5] In this study, we evaluate the negative T-J boundary carbon isotope excursions and the ensuing Hettangian positive carbon isotope excursion in two independent ways. First, we use high-resolution palynological data to evaluate the potential role of varying sources of organic carbon in generating the observed C-isotope excursions in bulk $\delta^{13}\text{C}_{\text{org}}$. We find that negative and positive organic carbon isotope variations across the T-J boundary in Germany can be explained simply by changes in relative contributions of a few groups of marine algae and terrestrial plants to the bulk organic carbon and do not require any change in the isotope composition of the global exogenic carbon reservoir. Second, we use a high-resolution $\delta^{13}\text{C}_{\text{carb}}$ record from an expanded marine section in carbonate strata at Val Adrara in the Southern Alps of Italy to test whether or not the positive excursion in $\delta^{13}\text{C}_{\text{org}}$ is supported as global by a

parallel excursion in the isotope composition of inorganic carbon. Carbon isotope data from Val Adrara are at best equivocal in replicating a T-J boundary negative excursion but clearly reveal a $+4\%$ positive excursion in $\delta^{13}\text{C}_{\text{carb}}$ during the earliest Hettangian and ending in the latest Hettangian that is independent of local variations in lithofacies. Finally, we show that after the major early Hettangian perturbation, the carbon cycle became stabilized across the Hettangian-Sinemurian boundary. We base this conclusion on the examination of $\delta^{13}\text{C}_{\text{carb}}$ data from four more Italian sections that encompass the Hettangian-Sinemurian boundary. Stabilization of the carbon cycle appears to have coincided with a recovery of skeletal carbonate producing biota.

2. Materials and Methods

2.1. Materials

[6] The strata drilled in the Mingolsheim core (Germany) and the investigated sections in Italy (Val Adrara, La Spezia, Montecatini, Portirone and Pozzo Glaziale) were all situated in the Tethyan realm (Figure 1) and represent two distinct, but complementary sedimentological end-members: The Mingolsheim core is dominated by siliciclastic sedimentation with intercalated carbonate beds, whereas the Italian sections are entirely dominated by shallow marine carbonate deposition. Because of the absence of carbonate in the uppermost Rhaetian and lowermost Hettangian at Mingolsheim, carbon isotope analyses are limited to bulk organic carbon. For similar reasons, the absence of abundant organic carbon in Italy limits our carbon isotope analyses there to bulk carbonate.

[7] The Mingolsheim core was drilled in 1968 near the town of Bad Mingolsheim in Southern Germany [Hettich, 1974]. Compared to neighboring areas, the Mingolsheim core contains a more expanded Upper Triassic to Lower Jurassic succession from the depocenter of a local shallow marine basin (the Langenbrückener Trough). Drilling reached a total depth of 220 m covering the uppermost Triassic Keuper marls up to the Lower Jurassic Toarcian black shales. The investigated interval comprises the uppermost Rhaetian to lowermost Sinemurian. On the basis of the presence of marine phytoplankton (dinoflagellate cysts, acritarchs, and prasinophytes) remains throughout the studied interval, the uppermost Rhaetian to Sinemurian strata are interpreted to reflect exclusively marine sedimentation. We place the T-J boundary

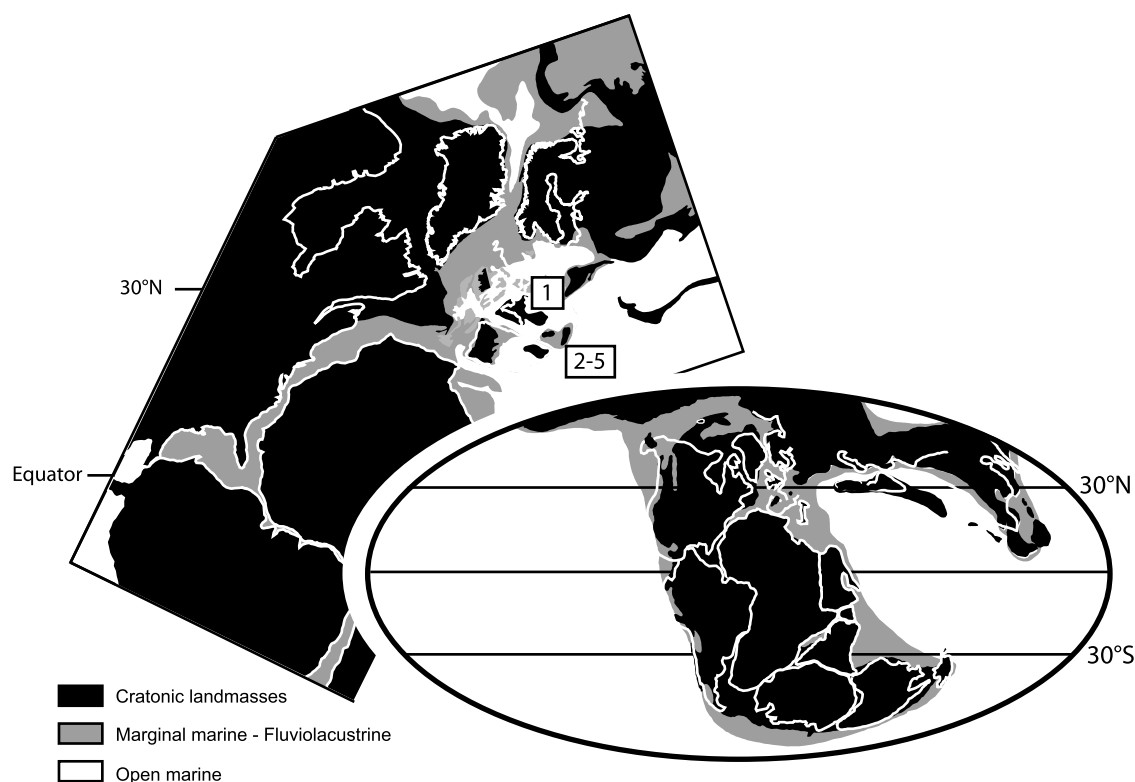


Figure 1. Paleogeography for the Early Jurassic modified after Scotese Paleomap Project 2000 (<http://www.scotese.com/jurassic.htm>) and Ziegler [1990]: 1, Mingolsheim Core; 2–5, location of Italian sections (Val Adrara, Portirone, La Spezia, Montecatini, Pozzo Glaziale).

at the base of the so-called “Triletes Beds,” a peculiar unit of carbonate poor, unfossiliferous claystones that are extremely rich in trilete fern spores (B. van de Schootbrugge et al., Acid rain and the demise of terrestrial ecosystems at the Triassic-Jurassic boundary, submitted to *Geology*, 2008). Characteristic Rhaetian pollen and dinoflagellate cysts, such as *Rhaetipollis germanicus* and *Suessia swabiana*, respectively, disappear at its base. The duration of the Triletes Beds is difficult to constrain. Two previous studies [Fowell et al., 1994; Olsen et al., 2002] recognized a similar “fern spike” interval in the Newark Basin and estimated its duration to be less than 20 Ka on the basis of cyclostratigraphy. In Mingolsheim this interval comprises more than 7 m and the finely laminated thin-bedded appearance suggests a much longer duration. On the basis of palynological evidence (e.g., last occurrence of *Rhaetipollis germanicus*), the Triletes Beds seem to correspond to the Zu-4 Member in Italy (see also below), an azoic, finely laminated limestone unit that has a variable thickness of up to 30 m and contains the T-J boundary at its base [Galli et al., 2005].

[8] The Lower Jurassic at Mingolsheim is better constrained than the Upper Triassic by the use of

ammonites [von Hildebrandt and Schweizer, 1992] and comprises the Lower Hettangian *Caloceras johnstoni* Subzone (of the *Psiloceras planorbis* Zone), lowermost Middle Hettangian (*Alsatites liassicus* Zone), Upper Hettangian (*Schlotheimia angulata* Zone) and lowermost Sinemurian (*Arietites bucklandi* Zone). The appearance of Lower Jurassic ammonites at Mingolsheim coincides with palynological evidence for a change from a flora dominated by ferns toward one dominated by conifers (*Classopollis*) and lycopods (*Kraeuselisporites reissingeri* (van de Schootbrugge et al., submitted manuscript, 2008)). Although there is no evidence for a major erosional unconformity, the Jurassic ammonite fauna lacks representatives typical of the lowermost Jurassic *Psiloceras planorbis* Subzone. Therefore, we cannot exclude a paraconformity between the top of the Triletes Beds and the base of the Pilonoten Limestone (Figure 2). However, conditions may have been too shallow during deposition of the Triletes Beds to allow psiloceratid ammonites to migrate from the open Tethys into the Germanic Basin. Another explanation could be that the Pilonoten Limestone is highly condensed, marking the onset of a major flooding event [Bloos, 1976, 1999].

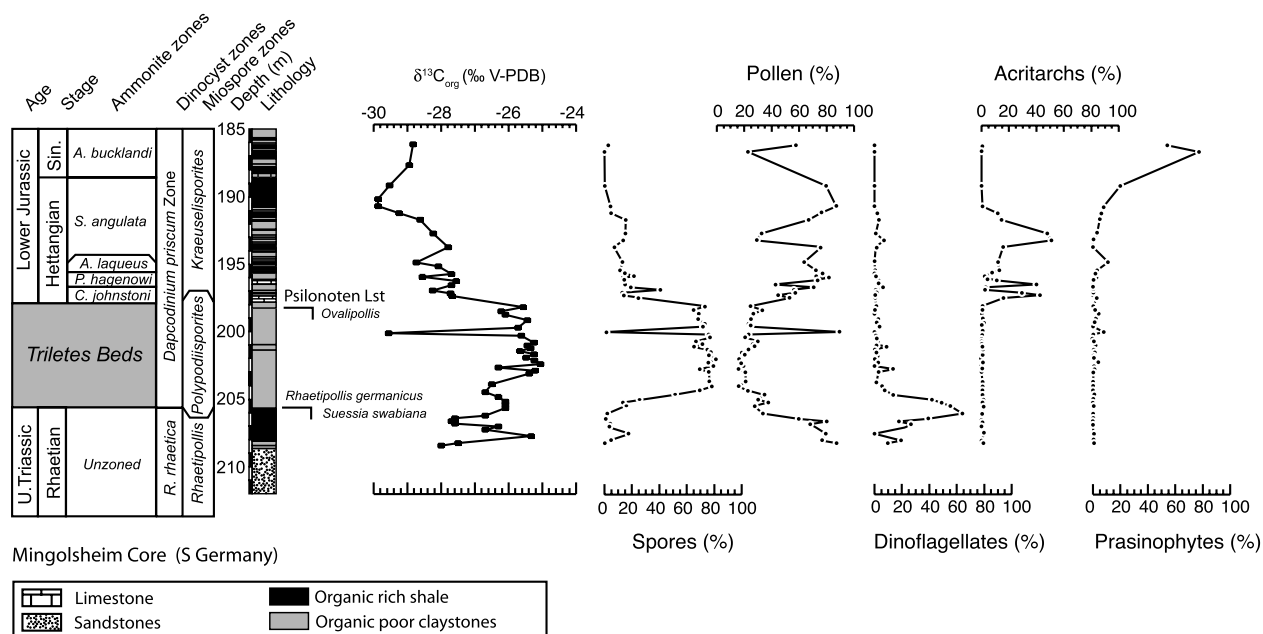


Figure 2. Mingolsheim Core biostratigraphy based on palynomorphs (*Rhaetipollis germanicus* and *Suessia swabiana*; this study) and ammonites [von Hildebrandt and Schweizer, 1992]. Measured $\delta^{13}\text{C}_{\text{org}}$ isotope data from Mingolsheim from Quan *et al.* [2008]. Abundance of individual palynomorph groups as percentages of the total palynomorph fraction (this study).

[9] For $\delta^{13}\text{C}_{\text{carb}}$ we sampled the Val Adrara section near the town of Sarnico in the Southern Alps of Italy (Figure 1). The Val Adrara section is one of the most expanded Late Triassic to Early Jurassic successions in the Southern Alps and was studied in detail for its sedimentology and macropaleontology by Gaetani [1970], Jadoul *et al.* [1992] and McRoberts [1994]. The sampled interval (422 m) comprises the transition from the Rhaetian Zu Limestone Formation to the Hettangian-Sinemurian Conchodon Dolomite and Sedrina Limestone Formations (Figure 3). Using micropaleontological and carbon isotope evidence, Galli *et al.* [2005, 2007] recently identified the T-J boundary at the base of the Zu-4 Member, which they renamed as Malanotte Fm. The transition from the Zu Limestone to Malanotte Fm is characterized by a sharp decline in the density of bioclastic grains; the Zu Limestone Fm consists primarily of bioclastic packstones with subordinate scleractinian coral framestone, whereas the Malanotte Fm consists of thinly bedded micritic limestones devoid of macrofossils. Overlying the Malanotte Fm, the base of the Conchodon Dolomite Fm is marked by a 20 m thick, cross-bedded unit of oolitic grainstones followed by nearly 150 m of monotonous, laminated to massively bedded unfossiliferous carbonate mudstones, that are partly pervasively dolomitized. The Conchodon Dolomite Fm grades upward into mixed bioclastic and oolitic grain-packstones of the Sedrina Limestone Fm that

turn increasingly cherty and change gradually into hemipelagic marl-limestone alternations. Although biostratigraphic control for sections in the Southern Alps is generally poor, the finding of a *Schlotheimia* sp. ammonite by Gaetani [1970] at Val Adrara 100 m above the base of the Sedrina Limestone Fm, suggest that hemipelagic sedimentation began in the latest Hettangian or earliest Sinemurian.

[10] The measured section to the west of La Spezia (Ligurian coast, Italy) includes the upper Hettangian Feriera Formation and the lower Sinemurian “Ammonitico Rosso” (Figures 1 and 4). The Feriera Formation consists of a well-bedded, pelagic, darkly colored limestone, which in the middle part of the measured section changes into marl-limestone alternation. The boundary with the overlying “Ammonitico Rosso” is marked by an angular unconformity, probably induced by slumping. The basal part of the “Ammonitico Rosso” is composed of a well-bedded, pelagic, red limestone, which includes two massive conglomeratic intervals [Ciarapica, 2007]. The section at Montecatini (Tuscany, Italy) starts with the upper Hettangian “Calcare massiccio,” which includes a light-colored siliceous limestone that is nodular and well bedded in its lower part and massively bedded at its top. This formation is overlain by the “Ammonitico Rosso” of Sinemurian age, which consists of a finely bedded, gray to

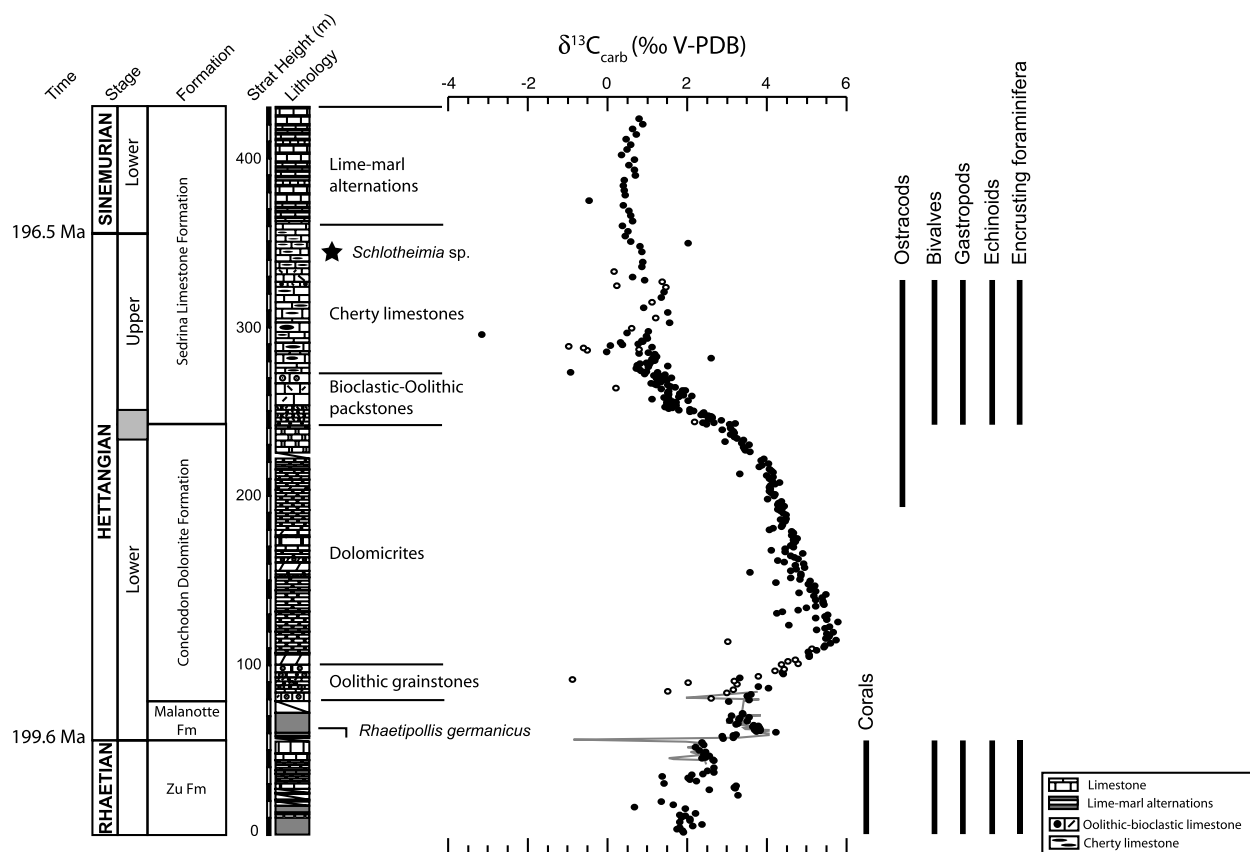


Figure 3. Carbonate carbon isotope record from the Val Adrara section. Open circles indicate aberrant C-isotope values that deviate from the main trend. Grey line is a redrawn C-isotope curve from *Galli et al.* [2007] and shows the sharp negative excursion at the base of the Malanotte Formation (Zu-4 Member) that we failed to capture, possibly because this interval was covered at the time of sampling. The occurrence of *Schlotheimia* sp. is after *Gaetani* [1970].

reddish, pelagic limestone with marl alternations. The section of Portirone (Lago d’Iseo, Lombardian Alps, Italy) consists of thick bedded, siliceous limestone of upper Hettangian age (Sedrina Formation), which are followed by lower Sinemurian thinly to thickly bedded, pelagic siliceous limestone [Gaetani, 1970; Faure et al., 1978]. The section of Pozzo Glaciale (Lago d’Iseo, Lombardian Alps, Italy), which is situated 5 km to the south of Portirone, shows thickly bedded, oolitic and oncolithic carbonates of late Hettangian age at its measured base, which are topped by thinly bedded, marly and partly siliceous limestones of early Sinemurian age [Gaetani, 1970; Faure et al., 1978].

2.2. Methods

2.2.1. Palynology

[11] For palynological analyses, 56 samples from the Mingolsheim core were treated in alternating steps with concentrated HCl and HF to remove

mineral carbonate and silicate phases, washed with distilled water and sieved with a 15 μm mesh sieve. Strew mounts were investigated with a compound light microscope and up to 300 palynomorphs per sample were identified to genus and/or species level and counted.

2.2.2. Organic Carbon Isotopes

[12] For organic carbon isotope analyses, samples from the Mingolsheim core were treated with HCl prior to carbon isotopic analysis to remove all carbonate. The residues were rinsed several times with distilled water, dried for 3d at 80°C and subsequently ground to a homogeneous powder using an agate mortar. Depending on their TOC content sample aliquots of 3–10 mg were weighed and wrapped into tin capsules. At least two aliquots were prepared per sample. Carbon isotope analysis of TOC was subsequently performed using a Flash Elemental Analyzer 1112 (Thermoquest), connected to the continuous flow inlet system of a MAT 253 gas source mass spectrometer (Thermoquest) at the

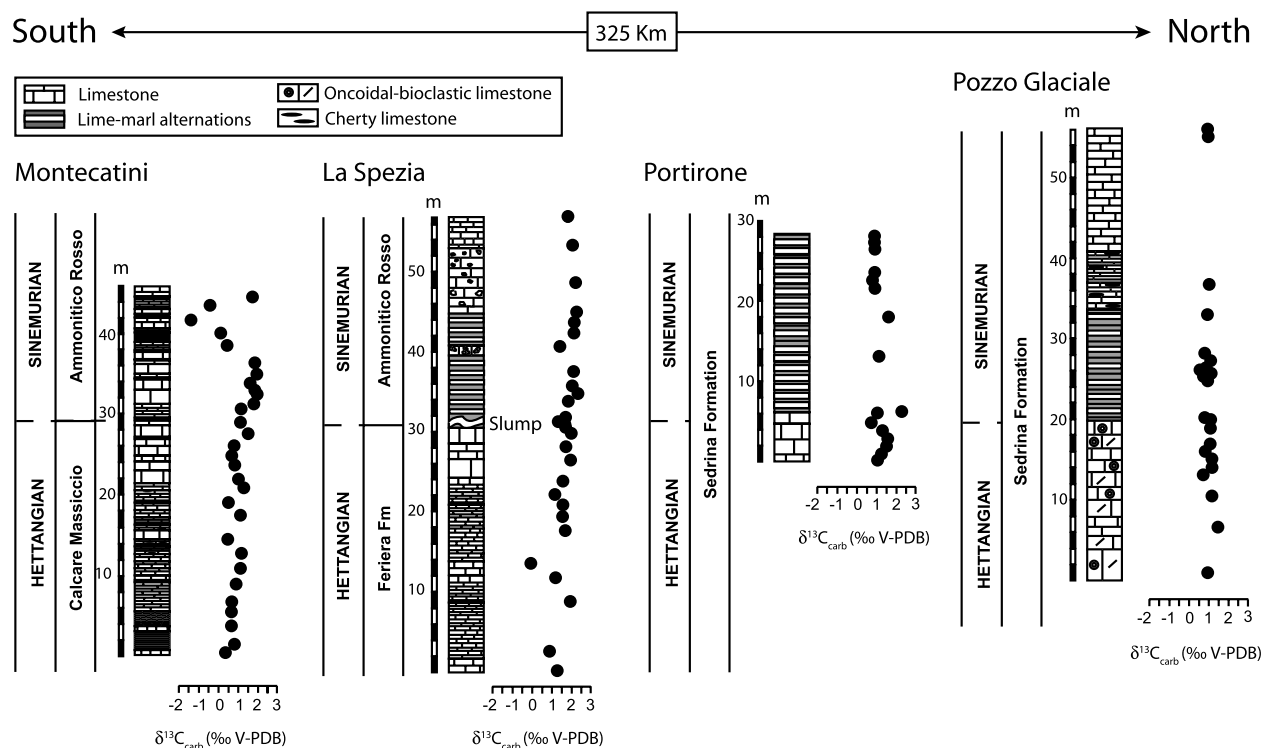


Figure 4. Hettangian-Sinemurian carbon isotope data from four sections in Italy. Carbon isotope values are similar for all four sections across the Hettangian-Sinemurian boundary and are well comparable with our results from Val Adrara.

Institute of Geosciences (Goethe University Frankfurt). USGS 24 standard was analyzed along with the samples in order to prove for accuracy and precision. Both samples and standards reproduced within $\pm 0.2\%$.

2.2.3. Carbonate Carbon Isotopes

[13] We analyzed a total of 367 bulk rock carbonate samples from the Val Adrara section for $\delta^{13}\text{C}_{\text{carb}}$ at the Institute of Geosciences of Goethe University Frankfurt. Samples were cut to obtain clean surfaces and ground to powder in an agate mortar prior to isotopic analysis. For carbon isotope analyses, a Gas Bench II (Thermoquest) was connected to the continuous flow inlet system of the MAT 253 mass spectrometer. A detailed description of the analytical setup and the analytical method itself has been given by [Spötl and Vennemann, 2003]. Each sample was analyzed in duplicates, ranging from 50 to 100 μg in size. An internal standard, calibrated against NBS18 and NBS19, was run along with the samples [Fiebig *et al.*, 2005]. Internal precision was better than ± 0.05 for $\delta^{13}\text{C}$ and ± 0.08 for $\delta^{18}\text{O}$.

[14] Carbonate carbon isotope data from the four Italian sections spanning the Hettangian-Sinemur-

ian boundary were generated at the Geological Institute of the University of Berne (Switzerland) using a VG Prism II ratio mass spectrometer. Approximately 10 mg of powder was reacted with 100% H_3PO_4 at 90°C in an online-automated preparation system. The resulting CO_2 was analyzed. The error margin is 0.1‰ for the oxygen isotope analyses and 0.05‰ for the carbon isotope analyses. The results are expressed relative to the V-PDB standard.

3. Results

[15] The $\delta^{13}\text{C}_{\text{org}}$ record from the Mingolsheim core shows large variations of up to -5% . A positive excursion from -28.0% to -25.4% (V-PDB) is followed by a (initial) rapid negative shift of approximately the same magnitude close to the Triassic-Jurassic boundary (Figure 2; see auxiliary material¹ for data). Across the Triletes Beds organic carbon isotopes are significantly more positive and show a stable isotopic signature around -25.5% , except for one sample at 200 m (Ming-52), which has a composition of -30% . The

¹Auxiliary materials are available at <ftp://ftp.agu.org/apend/gc/2007gc001914>.

Table 1. Results of Simple and Multiple Linear Regression Models With Organic Carbon Isotopes as the Response Variable, and Proportional Abundances of Palynomorph Groups as the Predictor Variables^a

Predictor Variable	Degrees of Freedom (Number of Variables)	Sum of Squares	Mean Square Error	F Value	p Value	Adjusted R2
Pollen grains	1	53.9	53.9	67.8	<0.0001	0.59
Spores	1	51.4	51.4	60.5	<0.0001	0.56
Green algae	1	26.75	26.75	19.1	<0.0001	0.28
Dinoflagellates	1	1.7	1.7	0.86	0.36	0
Pollen and green algae	2	67.5	33.7	66.9	<0.0001	0.74
Pollen and spores	2	57.3	28.6	38.8	<0.0001	0.62
Spores and greens	2	57	28.5	38.4	<0.0001	0.62
Pollen, greens, and spores	3	67.5	22.5	43.6	<0.0001	0.74
All four variables	4	67.6	16.9	32.1	<0.0001	0.73

Composition Estimates for 1- and 4-Variable Models	Slope (1-Variable Model)	St. Error (1-Variable Model)	t Value (1-Variable Model)	p Value (1-Variable Model)	Estimate: 1-Variable Model	Estimate: 4-Variable Model
Pollen estimate	-0.044	0.005	-8.23	<0.0001	-29.3	-28.6
Spores estimate	0.033	0.004	7.78	<0.0001	-24.8	-24.72
Greens estimate	-0.055	0.012	-4.37	<0.0001	-31.9	-28.95
Dinos estimate	0.012	0.013	0.93	0.36	-25.8	-24.86

^aF-test evaluates whether models explain a significant portion of variance. Predicted organic carbon composition of four palynomorph groups is shown for 1-variable and 4-variable models. The adjusted R-squared value adjusts the multiple R-squared value to the degrees of freedom of the regression model.

$\delta^{13}\text{C}_{\text{org}}$ values rapidly decrease above the Triletes Beds, becoming as light as -30‰ in the Upper Hettangian *Schlotheimia angulata* Zone and lowermost Sinemurian *Arietites bucklandi* Zone. The positive excursion within the Triletes Beds is associated with an increase in the proportional abundance of spores and a decrease in the proportional abundance of pollen. Moreover, the sample with the unusually light $\delta^{13}\text{C}_{\text{org}}$ composition also differs from surrounding samples in the palynological composition, with higher abundance of pollen, lower abundance of spores, and a slightly elevated abundance of prasinophyte phycmata.

[16] Overall, there is a strong association between the composition of the palynoflora and the bulk $\delta^{13}\text{C}_{\text{org}}$ values. Quantitative evaluation of the correlation between palynological assemblage composition and bulk $\delta^{13}\text{C}_{\text{org}}$ using simple and multiple linear regression reveals highly significant correlations between the proportional abundances of pollen, spores, and green algae (acritarchs and prasinophytes) and the bulk carbon isotope composition. The abundances of pollen grains correlate negatively and abundances of spores correlate positively with $\delta^{13}\text{C}_{\text{org}}$ and the abundances of green algae correlate negatively with $\delta^{13}\text{C}_{\text{org}}$. The proportional abundances of dinoflagellates do not correlate with the bulk carbon isotope composition (Table 1).

[17] Figure 3 illustrates the $\delta^{13}\text{C}_{\text{carb}}$ data from the Val Adrara section (see auxiliary material for data table). Rhaetian limestones of the Zu-3 member are characterized by values near $+2\text{‰}$ (V-PDB), but exhibit inter-sample variability of as much as 1‰ . Beginning above the contact between the Zu-3 Member and Malanotte Formation, $\delta^{13}\text{C}$ values increase over an interval of 80 m to a peak near $+6\text{‰}$ within the lower Conchodon Dolomite Fm. Values then decrease gradually over 200 m to near 0.5‰ within the basal Sedrina Limestone and remain near this value through the remainder of the measured section. The data do not reveal a negative excursion in the base of the Malanotte Fm, but do show a possible negative excursion near the contact between the Malanotte and Conchodon Formations. A crossplot of all the C- and O-isotope data for Val Adrara shows no clear discernable trends that point to diagenetic overprint (Figure 5). Some of the data points that deviate most from the overall trend (especially samples with light C-isotope values near the base of the Conchodon Dolomite) also tend to be characterized by the lightest $\delta^{18}\text{O}$ values, suggesting their C-isotope compositions may have been altered during diagenesis. However, other light C-isotope values are not easily recognizable as altered. We use a cutoff value of -5.5‰ for oxygen isotope values; this eliminates approximately 10% of our

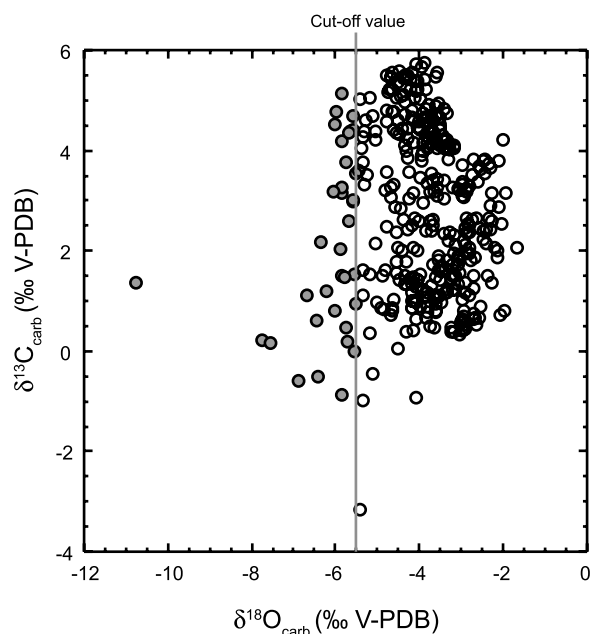


Figure 5. Crossplot of all stable carbonate carbon isotope data from the Val Adrara section showing the absence of a correlation between oxygen and carbon isotope values. We used a $\delta^{18}\text{O}$ value of -5.5‰ as a cutoff value to distinguish between altered and unaltered carbon isotope values. TMQ thank the ICMS post doctoral fellowship program.

measured values and most, but not all, of the outliers (identified as white dots in Figure 3).

[18] Carbonate C-isotope data from the Hettangian-Sinemurian transition in the four investigated Italian sections (La Spezia, Portirone, Montecatini, Pozzo Glaziale) are remarkably stable (Figure 4 and auxiliary material for data table). The $\delta^{13}\text{C}_{\text{carb}}$ values are also very similar between all four sections despite significant variations in lithology and range from 0 to +1%. These results correspond well to those $\delta^{13}\text{C}_{\text{carb}}$ values obtained from the Val Adrara section for the Hettangian-Sinemurian transition (Figure 3).

4. Discussion

4.1. Organic Carbon Isotopes

[19] Bulk $\delta^{13}\text{C}_{\text{org}}$ records are increasingly being debated as reliable proxies for the isotope composition of atmospheric and upper ocean $p\text{CO}_2$. The large negative excursion of up to -7‰ in bulk organic carbon across the Toarcian Oceanic Anoxic Event has been taken to reflect the sudden release of methane from gas hydrates to the atmosphere [Hesselbo et al., 2000, 2007; McElwain et al.,

2005]. However, as shown by van de Schootbrugge et al. [2005] and Gomez et al. [2008], pristine $\delta^{13}\text{C}_{\text{carb}}$ records derived from belemnite calcite lack large negative excursions, therefore suggesting that Toarcian bulk organic carbon was more likely influenced by regional recycling of respired CO_2 or possibly reflects the substantial contribution of amorphous organic matter produced by sulfur and/or methanogenic bacteria with a very light isotopic signature. A recent assessment of terrestrial C-isotope records across the Paleocene-Eocene boundary, which is also marked by a pronounced carbon cycle perturbation, shows that the negative C-isotope excursion across that boundary is modulated by the type of vegetation; angiosperm biomarkers show a much larger negative excursion than compounds derived from conifers [Schouten et al., 2007]. Whereas compound-specific carbon isotope analyses of alkanes indicate that various groups of plants fractionate differently toward ^{13}C [Lockheart et al., 1997], many extrinsic factors, such as temperature and humidity, may also affect the C-isotope fractionation by land plants.

[20] Additional confounding factors in the interpretation of bulk $\delta^{13}\text{C}_{\text{org}}$ records are the effects of changes in the contribution of marine relative to terrestrial organic matter, and profound changes in the composition of standing biomass, i.e., terrestrial floras or phytoplankton communities. The T-J boundary witnessed large changes in both macrofloral and microfloral composition [McElwain et al., 2007; McElwain and Punyasena, 2007; van de Schootbrugge et al., 2007] with potentially large effects on bulk organic C-isotope records. Compound specific carbon isotope analyses of the Permian-Triassic boundary indicate that large negative carbon isotope excursions associated with that mass-extinction event are influenced by a proportional increase in the burial of marine organic carbon with a lighter isotopic signature [Grice et al., 2007].

[21] It is tempting to interpret the “initial” and “main” negative C-isotope excursions in the Mingolsheim record as reflecting perturbations in the global carbon cycle, as many have done before us for isotope records derived from sections elsewhere [Hesselbo et al., 2002; Ward et al., 2004; Kürschner et al., 2007]. However, a comparison of these organic carbon isotope variations with detailed palynological analyses from the Mingolsheim core (Figure 2) suggests that isotopic variations are more likely explained as variations in the composition of

the bulk organic matter measured. The negative excursion of about -4.5‰ that occurs at 200 m is highly correlated with a spike in conifer pollen (*Corollina* spp.), whereas the higher $\delta^{13}\text{C}_{\text{org}}$ values below and above are from sediments that are entirely dominated by fern spores.

[22] We used linear regression to quantitatively evaluate the correlation between the taxonomic composition of identifiable palynomorphs and the isotope composition of bulk organic carbon. Highly significant correlation between taxonomic composition of the palynological assemblage and bulk $\delta^{13}\text{C}_{\text{org}}$ would suggest that isotope variation could be explained without any variation in isotope composition of individual organic components. The model provides a further test of the link between varying taxonomic input and isotope variation because it also produces estimates of the isotope composition of each component that can be compared to direct observations. The $\delta^{13}\text{C}$ value for gymnosperm (conifer) pollen appears to average around -28‰ [Jahren, 2004]. Although ferns are C_3 plants that utilize the Calvin Cycle with Rubisco to fix CO_2 , tropical epiphytic and lithophytic ferns have been shown to use mechanisms for carbon acquisition resembling the Crassulacean Acid Metabolism (CAM) pathway [Holtum and Winter, 1999]. Such a carbon metabolism is thought to be more efficient in habitats where water availability is limited. CAM plants discriminate less effectively against ^{13}C resulting in generally higher tissue $\delta^{13}\text{C}$ values. More than 60% of fern spores in the Triletes Beds belong to two groups of ferns: the Schizeaceae-Polypodiaceae (*Polypodiisporites* spp.) and the Dipteridaceae (*Concavisporites* spp.). Several of the Polypodiaceous ferns investigated by Holtum and Winter [1999] showed signs of weak CAM metabolism with corresponding tissue $\delta^{13}\text{C}$ values ranging from -25 to -22‰ . Several Triassic ferns (e.g., *Lepidopteris ottonis*) were analyzed for their C-isotopic composition by Bocherens et al. [1993] and showed values ranging from -26.9 to -25.5‰ . The green algal group, in this study composed of acritarchs and prasinophytes, is harder to constrain. Empirical evidence from ion microprobe analyses [Kaufman and Xiao, 2003] suggests that acritarchs show a maximal fractionation factor (ϵ_p) of 25‰ , indicating that their organic carbon isotope values are on the order of -33‰ (assuming atmospheric CO_2 in the Early Jurassic had a composition similar as today, i.e., -8‰). Wong and Sackett [1978] measured carbon isotope fractionation by the prasinophyte green

alga *Platymonas*, showing that it fractionates by -19‰ . Hence, for the green algal group (acritarchs + prasinophytes) one would predict an overall isotope composition near -29‰ . Dinoflagellates are well studied in the present-day oceans and are known to fractionate in the range from -18‰ to -24‰ . For the isotopic composition of dinoflagellates we thus expect an average value of -26‰ .

[23] The full linear model explains 73% of the variance in bulk $\delta^{13}\text{C}_{\text{org}}$, and abundances of all components other than dinoflagellates are significantly correlated with bulk $\delta^{13}\text{C}_{\text{org}}$ when analyzed individually (Table 1). Moreover, the model predictions of isotope compositions for individual components are compatible with estimates from studies of biological fractionations in living organisms and individual microfossils: conifer pollen is predicted by the model to have a composition near -29‰ , green algae between -29‰ and -32‰ , fern spores and dinoflagellate cysts close to -25‰ . Obviously, palynological analyses only characterize the structured, recognizable fraction of organic matter. Especially in the Hettangian amorphous organic matter may exert an additional effect on the isotopic composition of bulk organic matter.

[24] Because the model passes tests both of significant correlation between taxonomic composition and correspondence between modeled isotope composition and that predicted from plant and algal physiology, we suggest that observed excursions in the organic carbon isotope record from Mingolsheim are best interpreted to reflect variations in the relative importance of organic matter sources and may not require any change in the isotope composition of individual components. Moreover, strong variations in palynological composition also line up with carbon isotope excursions in sections elsewhere, such as in Austria [Kürschner et al., 2007]. There, negative C-isotope excursions coincide with a proportional increase in the abundance of marine organic matter, much like as is observed for the Mingolsheim Core. We suggest that bulk organic carbon isotopes should be interpreted with caution, particularly as a proxy for the isotope composition of atmospheric CO_2 , without detailed parallel investigations of the organic matter measured.

4.2. Carbonate Carbon Isotopes

[25] On the basis of our high-resolution $\delta^{13}\text{C}_{\text{carb}}$ isotope record from Val Adrara we are able to put

other carbon isotope records from that section and from T-J boundary sections elsewhere into a new perspective. Our data do not replicate the negative C-isotope excursion recognized by *Galli et al.* [2005, 2007]. Our failure to capture the negative excursion may reflect insufficient sample resolution in our study. However, the occurrence of several samples with $\delta^{13}\text{C}_{\text{carb}}$ values that deviate by as much as 3‰ from the general trend of our data at horizons close to and far from the extinction horizon suggests many of these points reflect local, diagenetic incorporation of isotopically light carbon, likely due to remineralization of organic carbon. In our data set, most of these points with light C-isotope values are clearly identifiable from oxygen isotope values, indicating at least some such unreliable points can be identified easily with simple geochemical indicators of diagenesis.

[26] Data from the Mingolsheim core and the Val Adrara section appear potentially contradictory. The former data set suggests the Hettangian positive excursion may be artifactual whereas the latter supports a global carbon isotope event. There are several possible routes to reconciling these findings. First, the bulk organic carbon analyzed in most studies may reflect unchanging proportions of marine and terrestrial organic carbon despite the variation in proportions of identifiable palynomorphs. Second, the Val Adrara data may reflect a genuine carbon isotope event whose magnitude was muted in the organic carbon isotope compositions of individual taxa because increased $p\text{CO}_2$ during the excursion caused an increase in the fractionation between CO_2 and organic carbon. If so, the occurrence of an excursion in bulk organic carbon records at many widely separated localities could reflect the global sedimentary consequences of the event, even though it only fortuitously records a positive carbon isotope excursion. Third, the carbonate carbon isotope excursion in the Val Adrara data may also be an artifact of variations in depositional environment or varying water circulation over the carbonate platform through the study interval [cf. *Immenhauser et al.*, 2003]. However, we deem this last explanation unlikely, because carbon isotope values first increase across ooidal grainstones of the lower Conchodon Fm and then decrease across a similar lithology and facies higher up in the Conchodon Fm (Figure 3). The most positive $\delta^{13}\text{C}$ values occur in an interval dominated by microbial laminated facies that appear to reflect deposition in a more restricted platform interior environment whereas less positive $\delta^{13}\text{C}$ values occur in more fossiliferous facies

indicative of open shelf environments. Although other studies have generally found more negative $\delta^{13}\text{C}$ values moving from open marine to platform interior environments [*Immenhauser et al.*, 2003], it is plausible that platform interior environments with restricted water flow may develop heavy or light $\delta^{13}\text{C}$ signatures depending on the relative influence of photosynthesis and respiration in the water mass over the platform.

[27] The positive carbonate carbon isotope excursion was unlikely to be the result of changes in the prevalent mode of carbonate deposition, such as a change from predominant aragonite to calcite deposition [*Hautmann*, 2004]. The T-J boundary witnessed a major reef crisis with exceptionally high extinction rates among aragonite producers, such as scleractinian corals [*Stanley*, 2003] and calcareous green algae [*Barattolo and Romano*, 2005], and a shift in shell mineralogy within bivalves toward calcitic shells [*Hautmann*, 2004]. Aragonite is isotopically heavier than calcite and a local breakdown in aragonite deposition would therefore lead to lower $\delta^{13}\text{C}_{\text{carb}}$ values [*Swart and Eberli*, 2005; *Godet et al.*, 2006; *Föllmi et al.*, 2006], the opposite of what we observe across the T-J boundary at Val Adrara.

[28] Because the $\delta^{13}\text{C}_{\text{carb}}$ excursion at Val Adrara is gradual over hundreds of meters and smoothly crosses lithofacies boundaries, we prefer to interpret the Val Adrara record to reflect global change in the isotope composition of carbon, rather than local influences. Consequently, we suggest that the events responsible for the positive carbon isotope excursion also affected sedimentological patterns and the relative abundances of organic sources with differing isotope values. As a consequence the bulk organic carbon record contains a positive excursion at many localities that mimics the inorganic carbon isotope record. We view the alternative that the taxonomic composition of bulk organic carbon was relatively constant despite the marked variation in the palynological assemblages as less likely. Following the former interpretation, the positive excursion in bulk organic carbon is a reliable indicator of global events, but primarily as a recorder of shifting taxonomic compositions of land floras and proportions of terrestrial versus marine organic carbon in studied sections rather than a recorder of the isotope composition of carbon in the oceans and atmosphere.

[29] We suggest that elevated $p\text{CO}_2$ during the Hettangian increased fractionation factors between organic matter and CO_2 such that the magnitude of

the carbon isotope event was greatly muted within any given organic matter source. Alternatively, the isotope shift in the bulk organic carbon also reflects a global isotope event and the palynological shifts are not representative of shifting taxonomic sourcing of the bulk organic carbon, but this then requires that the changing proportions of spores versus pollen that correlate with isotope shifts in the bulk organic carbon are merely fortuitous, a scenario that appears highly unlikely.

4.3. Early Jurassic Carbon Cycle Dynamics

[30] If the Hettangian positive $\delta^{13}\text{C}_{\text{carb}}$ isotope excursion does indeed reflect a global carbon isotope event, what are the potential causes? *Williford et al.* [2007] suggested widespread cyanobacterial blooms could cause a positive excursion because these primary producers fractionate carbon less than most marine algae. However, *Williford et al.* [2007] rejected this scenario due to the absence of widespread microbial mounds preserved in lower Hettangian strata. This scenario also fails to account for the positive excursion in $\delta^{13}\text{C}_{\text{carb}}$; mass balance requires a decrease in $\delta^{13}\text{C}_{\text{carb}}$ if the fractionation between carbonates and organics decreases. For the same reason, the positive excursion in carbonate rocks also rules out a shift to primary production dominated by isotopically heavy photosynthetic green sulfur bacteria [*van Breugel et al.*, 2005]. *Williford et al.* [2007] favor a shift to a greater fraction of carbon buried as organic carbon rather than in carbonate rocks, arguing that the extinction of skeletal carbonate producing organisms led to a reduction in global rates of carbonate sedimentation. Although skeletal carbonate production was indeed severely eclipsed, as is also evident in the Val Adrara section (Figure 3), this does not require that overall carbonate sedimentation was similarly impeded; in fact, rates of carbonate sedimentation appear to have remained high throughout the Hettangian as indicated by the more than 400 m of carbonate sampled during the course of this study at Val Adrara. Extinction of carbonate producers may have merely shifted carbonate production to a nonskeletal mode, as seen after the end-Permian mass extinction [*Payne et al.*, 2006].

[31] Alternatively, the positive excursion could reflect an increase in the rate of organic carbon burial even if the rate of carbonate sedimentation remained unchanged [*Kump and Arthur*, 1999]. We favor this latter interpretation for several reasons. First, over timescales greater than approximately 200 ka the delivery of carbonate alkalinity via

silicate and carbonate weathering will increase the saturation state of the oceans and cause carbonate burial to continue even in the absence of biomineralizing organisms; any episode of reduced saturation and reduced carbonate sedimentation is likely to have been short-lived relative to the likely duration of the positive carbon isotope excursion [*Archer et al.*, 1997; *Zachos et al.*, 2005]. A continued delivery of carbonate alkalinity into an ocean sparsely populated by biomineralizing animals and algae may partly explain the widespread occurrence of carbonate deposition in a Conchodon modus, i.e., laminated dolomicrites that bear all the hallmarks of microbial and/or chemical precipitates. Oolitic carbonates covering carbonate platforms across the Southern Alps and Appennines also accord with changes in carbonate saturation state [*Ciarapica*, 2007].

[32] Second, the release of CO_2 during CAMP eruptions would, if anything, increase the rate of silicate weathering and lead to the burial of greater quantities of organic and carbonate carbon. Modeling the effects of massive volcanism on the carbon isotope record suggests episodes where carbon is released rapidly from the Earth's mantle can drive positive carbon isotope excursions by generating marine anoxia, leading to more efficient organic carbon burial with continuing high rates of primary production due to the liberation of phosphate from organic matter in anoxic bottom waters [*Payne and Kump*, 2007]. Evidence for the widespread development of oxygen-restricted facies across Europe has been discussed by *Hallam* [1995].

4.4. Stabilization of the Carbon Cycle and Biotic Recovery

[33] The positive carbon isotope excursion terminated during the Upper Hettangian and rapid and large fluctuations in $\delta^{13}\text{C}_{\text{carb}}$ records in Italy are absent, suggesting that the carbon cycle stabilized across the Hettangian-Sinemurian boundary. In the Val Adrara section the positive carbon isotope excursions span an interval that is strikingly devoid of macrofossil remains, whereas stabilization of the carbon cycle coincides with a return of skeletal carbonate producers, including bivalves, gastropods and echinoids (Figure 3) [*McRoberts*, 1994]. In addition, the abundance of cherts and the deposition of spiculitic carbonates during the Upper Hettangian and Early Sinemurian, indicates that the conditions governing the biotic recovery initially favored sponges. Although the abundance of

cherty carbonates could also reflect a progressive deepening due to the continued Early Jurassic sea level rise [Delecat and Reitner, 2005], spiculitic carbonates are widespread along both the Southern (Southern Alps, Appennines) and Northern margins of the Tethys (Northern Calcareous Alps) during this time and testify to an overall increase in metazoan activity. Williford *et al.* [2007] commented on the return to background isotope values in British Columbia at the same time that abundant ammonites and other shelly fossils reappear in the Queen Charlotte Island section. Interestingly, a similar pattern is observed in Mingolsheim, where decreasing carbon isotope values during the Hettangian and Sinemurian correspond to a surge in psiloceratid ammonite diversity (Figure 2). The onset of widespread deposition of bioclastic carbonates and the recovery of skeletal carbonate producers (e.g., bivalves, brachiopods, echinoderms, cephalopods) in the Middle Hettangian is well documented from southern Germany [Bloos, 1976, 1982], the Eastern Alps [Golebiowski and Braunstein, 1988; Tomasovych and Siblik, 2007], and the West Carpathians [Gazdzicki *et al.*, 1979]. The observed increase in marine skeletal abundance in Germany and Italy appears to coincide with a simultaneous change in terrestrial floras from those composed mainly of pteridophytes toward those dominated by cheirolepid conifers as recorded in the Mingolsheim core. The congruence in floral changes on land and the timing of recovery of skeletal carbonate producers in shallow seas during the Middle-Upper Hettangian implies that they shared a mutual environmental control. What could be the reason for this congruence?

[34] The shape and duration of the Hettangian carbonate carbon isotope excursion bears similarity to other Mesozoic carbon isotope events, such as the Early Cretaceous Valanginian and Aptian positive carbon isotope excursions that have also been linked to episodes of destabilized carbonate production during emplacement of large igneous provinces [Lini *et al.*, 1992; Föllmi *et al.*, 1994; Menegatti *et al.*, 1998; Weissert *et al.*, 1998]. A scenario established for these Cretaceous carbon cycle perturbations [Weissert *et al.*, 1998] may likewise explain several of the features of the Hettangian carbon isotope excursion, such as the rapid shift to peak values and the slow return to background values. Peak values in the lower part of the Conchodon Fm could reflect accelerated biogeochemical cycling under high atmospheric $p\text{CO}_2$. In analogy, the gradual decrease to lower

carbon isotope values appears to mark the stabilization of carbonate production and decreased export of excess carbon into organic reservoirs under decreased atmospheric $p\text{CO}_2$.

5. Conclusions

[35] A high-resolution Rhaetian (Late Triassic) to Sinemurian (Early Jurassic) carbonate carbon isotope curve from southern Italy contains a large Early Jurassic Hettangian positive carbon isotope excursion that correlates with a similar excursion previously observed by Williford *et al.* [2007] in bulk organic matter from British Columbia. However, detailed palynological investigation of the positive excursion in $\delta^{13}\text{C}_{\text{org}}$ from Mingolsheim, Germany, reveals that the excursion occurs in an interval dominated by fern spores, which are isotopically heavy relative to other sources of organic carbon. In fact, palynological data demonstrate that most of the variation in the organic carbon isotope record can be accounted for via changing contributions of organic matter sources with different fractionation factors and does not require a global carbon isotope event. Hence, correlative positive excursions during the Hettangian in bulk organic carbon and carbonate rocks may be largely fortuitous. Instead, the large positive C-isotope excursion observed in bulk carbonate in the Val Adrara section does not monitor a change in the C-isotopic composition of atmospheric CO_2 , but rather reflects elevated $p\text{CO}_2$, likely resulting from CAMP eruptions. A return to background carbonate carbon isotope values appears to coincide with a resurgence of shelly fossils during the Middle to Late Hettangian and likely marks a decrease in $p\text{CO}_2$.

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