Evolution of the marine stable carbon-isotope record during the early Cretaceous: A focus on the late Hauterivian and Barremian in the Tethyan realm

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Abstract

In order to improve our understanding of the relationships between the late Hauterivian oceanic anoxic Faraoni event, contemporaneous platform drowning along the northern Tethyan margin and global environmental change in general, we established high-resolution δ13C and δ18O curves for the late Hauterivian and the entire Barremian stage. These data were obtained from whole-rock carbonate samples from the Veveyse de Châtél-Saint-Denis section (Switzerland), the Fiume-Bosso section and the nearby Gorgo a Cerbara section (central Italy), and the Anges section (Barremian stratotype, France).

We observe an increase of 0.3% in mean δ13C values within sediments from the middle Hauterivian Subsaynella sayni ammonite zone to the Hauterivian–Barremian boundary; δ13C values remain essentially stable during the early Barremian. During the latest early Barremian and most of the late Barremian, δ13C values increase slowly (until the Immites giraudi zone) and the latest Barremian is characterized by a negative trend in δ13C values, with minimal values at the Barremian–Aptian boundary. During the earliest Aptian, δ13C mean values start to rise again and attain +2.25‰.

We interpret the evolution of the δ13C record as resulting from the interaction between changes in the carbon cycle in the Tethyan basin and the adjacent platforms and continents. In particular, changes towards warmer and more humid conditions on the continent and coeval phases of platform drowning along the northern Tethyan margin may have contributed to enhance the oceanic dissolved inorganic carbon (DIC) reservoir which may have pushed the δ13C record towards more negative values and exerted a general attenuation on the δ13C record. From this may have come the general change from a heterozoan to a photozoan carbonate platform community, which influenced the evolution in δ13C values by increasing the export of aragonite and diminishing export of dissolved organic carbon into the basins.

Keywords: Hauterivian; Barremian; Tethys; oceanic anoxic Faraoni event; carbon and oxygen isotopes; paleoceanography

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1. Introduction

Correlated stratigraphic records of stable carbon isotopes measured in marine whole-rock carbonates or on isolated marine carbonate shells and skeletons provide very valuable insight into temporal changes in the global carbon cycle and in paleo-environmental conditions in general. The Cretaceous carbon cycle was perturbed by a series of short-lived oceanic anoxic events (OAEs) and contemporaneous phases of carbonate platform destruction, which are marked in the carbon isotope records of bulk carbonate (δ^{13}C_{\text{carb}}) and organic matter (δ^{13}C_{\text{org}}) (e.g. [1–9]; compare also [10–12]). An exception to these observed links between environmental change and corresponding variations in the δ^{13}C record seems to be exemplified by the Faraoni anoxic event, a black-shale interval recovered in Tethyan (hemi-) pelagic sections of latest Hau terivian age [13,14] and which is coeval to the onset of a major platform drowning episode along the northern Tethyan margin [3]. This event does not appear to be associated with an abrupt change in δ^{13}C values but rather with a long-term increase in the δ^{13}C record (e.g. [15]).

We investigated four hemipelagic to pelagic sections in the Tethyan realm (Angles (SE France), Fiume-Bosso (central Italy), Gorgo a Cerbara (central Italy) and Veveyse de Châtel-Saint-Denis (west Switzerland)), in order to more precisely constrain the δ^{13}C and δ^{18}O record around the Faraoni anoxic event and during the associated platform drowning event, which itself extends well into the early Barremian. We associate the obtained trends with changes in the oceanic carbon cycle, which was influenced by a number of mechanisms, amongst which we count the paleo-ecology of Tethyan carbonate platforms and their influence on the isotope signature of inorganic carbon species. In particular, we suggest that the change between photozoan and heterozoan dominated carbonate-platform ecosystem [3] may influence the isotope signature of the adjacent open ocean.

2. Geological setting

2.1. The sections of Fiume Bosso and Gorgo a Cerbara

The lower Cretaceous sedimentary succession of the Umbria Marche basin (Italy) is composed of the Maiolica (late Tithonian to early Aptian) and the Marne a Fucoidi (early Aptian to late Albian) formations [16].

The section of Fiume Bosso (FB) is located between Urbino and Gubbio, near Cagli (central Italy, Fig. 1; see also [13]). It represents the type section for the Faraoni

Fig. 1. location of the different studied sections.
Fig. 2. $\delta^{13}$C and $\delta^{18}$O curves obtained from whole-rock carbonate samples ($n$=59) of the Fiume Bosso section. Numbers on top of the columns refer to 1: stages; 2: magnetostratigraphy from Channell et al. [18]; 3: ammonite zonation after Coccioni et al. [16]; 4: nannofossil bioevents (this work). The grey line represents the five point moving average curve.
level [13]. The section is composed of white to grey limestone of the Maiolica Formation which is regularly intercalated with siliceous lenses and layers and contains rare marly and shaly, organic-rich intervals; it was deposited in a pelagic environment near the central zone of the Tethys (paleo-latitude ≈ 17°N for the middle Cretaceous after [17]). The magnetostratigraphy and ammonite biostratigraphy of this section were provided by Channell et al. [18] and by Cecca et al. [13], respectively. Coccioni et al. [16] employed an accurate age model for the middle part of the measured section, where they recognized the *Pseudothurmannia angulicostata* auct., *Pseudothurmannia catulloi* and *Spitidiscus hugii* ammonite zones (Fig. 2).

The section of Gorgo a Cerbara (GC) is located approximately 4 km east of Piobbico, along the Candiigliano River (Fig. 1; cf. [19]). This outcrop represents the type locality for the Barremian–Aptian boundary (e.g. [20]) and consists of a lithology which is comparable to that of the FB section. As the GC section covers the entire Barremian stage (e.g. [21]), it completes the FB section upward.

### 2.2. The section of the Veveyse de Châtel-Saint-Denis

The section at Veveyse de Châtel-Saint-Denis (VCD) is located in the canton of Fribourg, Switzerland (Fig. 1) and is part of the tectonic unit “Ecallle de Riondonnaire” (Ultrahelvetic realm, northern Tethyan shelf margin [22,23]).

The measured VCD section consists of bioturbated limestones alternating with marls, and covers the time interval from the late Hauterivian (*S. sayni* zone) to the early Barremian (*Avramidiscus hugii* zone; [23]). This section lacks chert and the amount of marls is higher, in comparison with the FB and GC sections.

### 2.3. The section of Angles

The section at route d’Angles (RA) is located in the Alpes de Haute Provence region of France (Fig. 1) and represents the stratotype of the Barremian stage [24]. The sediments of this hemipelagic section were deposited in the Vohcontian Trough (e.g. [14]).

For this section, we used the biostratigraphical scheme of Vermeulen [25], who developed an ammonite zonation from the *Balearites balearis* zone (late Hauterivian) up to the *Martellites sarasini* zone (late Barremian); the upper part of the section (early Aptian) is not yet completely prospected, but is thought to belong to the *Deshayesites ogalensis* zone. Lithologically, the Angles section is composed of poorly bioturbated grey limestones alternating with dark marls.

### 3. Methods

We measured all sections in detail sampling each separate limestone bed and, where appropriate, the marl and black-shale levels. The carbonate samples were sawn in order to eliminate weathered surfaces and recrystallized areas or veins. Rock powder was obtained by using a mechanical agate crusher.

The samples of the FB, VCD, and RA sections were analyzed at the stable isotope laboratory of the Department of Mineralogy and Geochemistry at the University of Karlsruhe, Germany, using an Optima (Micromass, UK) ratio mass spectrometer equipped with an online carbonate preparation line (MultiCarb) with separate vials for each sample. Subsequent replicate sample analyses for δ13C were within 0.05‰ to 0.06‰ and for δ18O ranged from 0.06‰ to 0.12‰. Carbonates samples from the GC section were analyzed at the Stable Isotope Laboratory of Hydrology (UMR 8148-IDES, University of Paris Sud, Orsay, France), using a VG SIRA 10 triple collector instrument. The powdered carbonate samples were reacted with anhydrous orthophosphoric acid at 25 °C [26]. Using internal carbonate standards, the reference material NBS 19 as well as replicate analyses of samples, the reproducibility of C and O analyses was better than ±0.05‰ and ±0.08‰, respectively.

### 4. Note on the ammonite biostratigraphy used

During the last ten years, the ammonite zonation of the early Cretaceous has become more and more precise, due to the prospecting of several key sections such as the outcrops at Rio Argos (Spain) or Angles (France), and the correlation of the obtained biozonations (e.g. [27,28]). As a consequence, the ammonite zonation currently proposed by the Kilian Group [28] is not identical with the biostratigraphy published for the FB, VCD and RA sections: the *Pseudothurmannia mortilleti* zone used by Vermeulen [25] in the latest Hauterivian does not exist in the biostratigraphy of the FB section [16], but corresponds to the upper part of the *P. angulicostata* auct. zone used at FB.

In Table 1, we propose a correlation between the different biostratigraphical schemes used for the VCD, FB and RA sections. For the VCD section, we use the zonation of Hoedemaeker and Rawson [27] instead of
scheme adopted by Busnardo et al. [23], in order to facilitate the comparison between all studied sections.

5. Results

5.1. The sections of Fiume Bosso and Gorgo a Cerbara

The carbon isotope curve obtained for the FB section (Fig. 2) shows a rather regular behavior for the lower part of the measured section, with $\delta^{13}C$ mean values increasing from 1.7 up to 2.15‰ (P. catulloi zone). The Faraoni level itself is characterized by a positive shift of approximately 0.15‰. In the upper part of the measured section, $\delta^{13}C$ mean values range between 1.8‰ and 1.9‰.

The $\delta^{18}O$ curve displays variations with a similar frequency, and with a range of mean values from $-2.45‰$ to $-2.15‰$.

The $\delta^{13}C$ record in sediments of the GC section displays a slight increase from approximately 2.2‰ to 2.7‰ (Fig. 3). The general trend towards more positive values is superimposed by two negative excursions in sediments corresponding to the middle of the CM3 and to the interval around the Barremian–Aptian boundary.

The $\delta^{18}O$ curve shows a slight decrease from the base of the section up to sediments corresponding to the end of the CM3; in the following, the $\delta^{18}O$ record evolves slowly towards heavier values.

5.2. The section of the Veveyse de Châtel-Saint-Denis

In the lower part of the measured section (S. sayni zone up to the base of the Pseudothurmannia angulicostata zone), a slow and steady increase from 0.85‰ to 1.15‰ characterizes the main trend of the curve (Fig.
4). In the overlying sediments of the *P. angulicostata* zone, the positive gradient in $\delta^{13}C$ curve becomes steeper, with a positive shift of about 0.5‰ in sediments in the vicinity of the “Couche à Poissons,” which is considered as an equivalent of the Faraoni level [23]. The $\delta^{13}C$ curve reaches a maximum of approximately 1.35‰ in sediments just below the Hauterivian–Barremian boundary. In the uppermost part of the measured section the $\delta^{13}C$ curve shows a slight decreasing trend with values diminishing from 1.35‰ to 1.05‰.

The $\delta^{18}O$ curve is characterized by a general trend toward heavier values, from approximately −2.7‰ to
−2.1‰, which seems to be superimposed by a shorter interval in sediments of the early *P. angulicostata* zone, where the trend in $\delta^{18}O$ is stable or even directed towards lighter values.

5.3. The section of Angles

The $\delta^{13}C$ curve displays a slight increase for sediments belonging to the *B. balearis* and *Spathicrioceras*
Fig. 5. $\delta^{13}$C and $\delta^{18}$O curves obtained from whole-rock carbonate samples (black circles: this study, $n=116$; white squares: data from Wissler et al [35]) of the Angles section. Numbers on top of the columns refer to 1: stages; 2: ammonites zonation after Vermeulen [25]; 3: nannofossils bioevents (this work). The grey line represents the five point moving average curve. Note the complementarity of the data of [35] and of this study.
angulicostatum zones (from 1% to 1.4%; Fig. 5); the data corresponding to the Faraoni equivalent display an acceleration of the general increase before a stabilization of the signal. After a decrease of 0.2% in the P. mortilleti and the A. kiliani zones, the δ13C curve displays an irregular evolution from the K. nicklesi to K. compressissima zone. Sediments attributed to the C. darsi zone show an increase in δ13C values from 1.3% to 1.8%, whereas sediments from the Holcodiscus uhitig to Gerharditia sartiouana zones display a more stable albeit a slightly increasing set of values. The δ13C curve shows an increase for sediments of the Hemihoplites feraudianus zone, followed by a decrease from 2.25% to 1.75% for sediments belonging to the I. giraudi and M. sarasini zones. The δ13C trend increases again to 2.25% in sediments of the D. oglanlensis zone, thereby marking a minimum precisely at the Barremian–Aptian boundary.

The evolution of the δ18O curve is more variable, with a double negative peak from −3‰ to −4.15‰ near the base of the measured section. Then, the δ18O record slowly increases in sediments belonging to the latest Hauterivian and remains rather stable for sediments in the remainder of the Hauterivian and the lower part of the early Barremian. In sediments from the N. pulchella to the H. sayni zone, the δ18O trend is negative, with a minimal value of about −4.15‰ reached in sediments of the H. sayni zone. The subsequent positive trend in δ18O values lasts until the base of the L. giraudi zone, where the δ18O curve reaches a value of −2.75‰. The uppermost part of the δ18O curve displays a decrease toward the lowest values of the measured section (−4.18‰).

6. Discussion

6.1. Stable isotopes and diagenesis

δ18O–δ13C cross plots reveal a lack of correlation between the trends in oxygen and carbon isotopes for all sections (R²=0.0652, 0.0686, 0.4759, and 0.041 for the FB, GC, VCD and RA sections, respectively; Figs. 2–5); the good correlation between the δ18O and the δ13C record at VCD may reflect the comparable evolution of both proxies during the late Hauterivian, as previously described by van de Schootbrugge [15]. Moreover, the results obtained are coherent with values for open marine carbonates from previous studies (e.g., [9,15]; Fig. 8 in Weissert [1]). We assume therefore that for the four studied sections, diagenetic transformations had little impact on the carbon isotope system.

The oxygen isotope record of the RA section, however, appears to be affected by slight diagenetic change: the δ18O values are systematically lighter by approximately 1–1.2% in comparison with the other sections analyzed here or even to the Hauterivian part of the Vergons section [15]. This is consistent with the burial history of the RA section, which is part of the Digne thrust system and has been exposed to higher burial temperatures during alpine deformation (e.g., [15]). Thus, paleotemperatures cannot be deduced from the absolute δ18O values of RA, whereas trends in δ18O may be used for correlation, as diagenesis did not totally reset the isotopic system as shown by the value of R² at RA and by the preservation of the clay mineral assemblage [32].

The δ18O records for the Italian and Swiss sections show rather high and probably only mildly altered oxygen isotopic values, which is again consistent with their tectonic history. We will refrain from an in depth discussion of the trends discerned and only mention the long-term trend in δ18O values.

6.2. Evolution of the δ13C record during the late Hauterivian and Barremian

The integration of geochemical, biostratigraphic and magnetostratigraphic data allows us to correlate and to describe general trends in the evolution of the δ13C record for the time span between the S. sayni and the D. oglanlensis. In Fig. 6, several time lines support our correlation between the Umbria-Marche basin, the Ultrahelvetic realm, and the Vocontian trough: (1) the top of the B. balearis ammonite zone between the VCD, FB, and RA sections; (2) the Faraoni level, which is considered to result from a synchronous anoxic event; this level is well approximated by the LO of nannofossil L. bollii at FB, RA, GC and Cismon; (3) the Hauterivian–Barremian boundary which is defined by means of ammonites in the VCD, RA, and FB sections; (4) the early/late Barremian boundary which is defined by ammonites at RA and by magnetostratigraphy, ammonites and nannofossils at GC and Cismon; and (5) the Barremian–Aptian boundary, which is defined by magnetostratigraphy and nannofossil biostratigraphy (FO of R. irregularis) in the GC section and the Cismon core, and by ammonite and nannofossil biostratigraphy in the RA section.

The trend in δ13C values for the late Hauterivian appears to be marked by a stable long-term trend towards slightly higher values, which becomes more accentuated during the P. angulicostata zone. A maximum in δ13C values for the late Hauterivian is reached in the
Fig. 6. Correlation of the Veveyse de Châtel-Saint-Denis, Fiume Bosso, Angles, Gorgo a Cerbara and Cismontan Aptico δ¹³C curves. Numbers on top of the columns of each section refer to 1: stages; 2: magnetostratigraphy of the FB [18], CG [18,29,30] sections and Cismontan Aptico [33]; 3: ammonite zonation of the VCD [23], FB [16] and RA [25] sections; 4: nanofossils bioevents of the FB, RA (this work), CG [31] sections and Cismontan Aptico [33]. Numbers on the time-lines refer to the numbering used in the text.
upper *P. angulicostata* zone (VCD section), just above the Faraoni level. This implies that this level is placed within the slope of a positive increase in δ¹³C, with an amplitude of 0.5–0.8‰. This positive shift was already observed in the Vergons section, near the RA section [14,15], and is thought to be characteristic of the Faraoni level. The short-lived negative excursion observed within the organic-rich Faraoni level of the FB section (Fig. 2), which exhibits TOC values of up to 25% [16], is interpreted here to reflect a local, early diagenetic signal due to the mineralization of organic carbon during bacterial sulfate reduction (e.g. [34]).

The evolution of the δ¹³C record during the early Barremian is illustrated by a trend toward more negative values in the *A. kiliani* zone (RA section), which is followed by an irregular long-term trend with no discernible gradient. The top of the early Barremian (*C. darsi* zone) is again marked by a positive gradient of about 0.4‰ (RA section).

The δ¹³C record during the late Barremian shows an irregular long-term trend towards more positive values followed by a negative gradient. The Barremian–Aptian boundary is marked by a minimum in δ¹³C values in both the RA and GC sections.

We also compared our results with the δ¹³C record established for the Cismon Apticore (Fig. 6; [33]) and from this correlation it appears that the identification of the early–late Barremian boundary in the RA, GC and Cismon sections is not coherent. At RA, this boundary is defined by ammonites, and corresponds to the end of a positive shift of the δ¹³C, whereas at GC this boundary is located in the upper part of the CM3 chron [18], just below the beginning of a positive shift, which seems comparable to the positive shift observed at RA. At Cismon, the location of the early–late Barremian boundary with respect to the positive shift of the δ¹³C curve is identical to RA; however a discrepancy occurs between the magnetostratigraphic records from GC and Cismon, as the early-late Barremian boundary is located several meters above the boundary between the CM3 and CM2 magnetozones at Cismon.

The correlation of the RA and GC sections with the Cismon record shows a further discrepancy: Wissler et al. [35] already called into question the continuity of the record at RA and, in particular, proposed the presence of a significant hiatus in sediments attributed to the *I. giraudi* zone, and inferred the absence of up to 50% of the entire Barremian stage in the stratotype of the Barremian. In the RA section, the *I. giraudi* zone is characterized by a positive shift (Δδ¹³C = 0.35‰), which is also easily recognizable at GC and Cismon with amplitudes of 0.28‰ and 0.45‰, respectively. On the other hand, just below the above-mentioned positive shift, the δ¹³C curve at Cismon displays a negative excursion, which is not recorded at RA. Based on these observations, it seems that either condensation or omission may have occurred in sediments belonging to the *G. sartousiana* or the *H. feraudianus* zones of the RA section. These phenomena may be linked to the maximum flooding surface of the B3 sequence, which is expressed by a glauconitic level within the *G. sartousiana* zone, or to the sequence boundary B4, a major sequence boundary in south-eastern France located in the *H. feraudianus* zone [36].

Alternatively, normal (syn-sedimentary?) faults led to the formation of a decametric graben in the *H. sayni* zone of the Angles section. It is therefore possible that a hiatus, coinciding with the first positive excursion of the Cismon section, is present within this zone. Further investigations are needed to solve this question.

6.3. Evolution of the δ¹⁸O record during the late Hauterivian and Barremian

In Fig. 7, the correlation of the δ¹⁸O curves from the RA, VCD, and GC sections allows to define major trends in the evolution of the δ¹⁸O during the late Hauterivian and the Barremian. We do not consider the FB section because it covers a relatively short time-period, and does not add essential information with regards to the long-term trend in δ¹⁸O values. The late Hauterivian and a part of the early Barremian (until the *K. nicklesi* zone; data from the VCD and the RA sections) are characterized by an increase of approximately 1.1‰. The latter is followed by a decreasing trend which lasted until the base of the *H. sayni* zone, with values reaching −4.1‰ at Angles. The beginning of the late Barremian is characterized by a positive trend (Δδ¹⁸O = 1.1‰) with a maximum located near the base of the *I. giraudi* zone (RA section). Finally, the δ¹⁸O record shows a decreasing trend for the latest Barremian and the earliest Aptian.

The increasing trend during the late Hauterivian may be linked to the installation of a marine passage between the boreal and the Tethyan realms. Indeed, Mutterlose and Bornemann [37] described the arrival of Tethyan faunas in lower Cretaceous sediments from northern Germany, in particular in the latest Hauterivian. This implies that a connection came into place between the Tethys and the boreal region during the late Hauterivian (Fig. 20 in [37]), which through the exchange of water masses may have led to relatively high δ¹⁸O values.
observed in the late Hauterivian–early Barremian. This hypothesis is also supported by the presence of boreal nannofossil species at Angles in sediments of the *P. mortilleti* and *A. kiliani* zones. Alternatively, the δ¹⁸O trend may reflect an increased salinity which would be in agreement with the enhanced evaporation and the subsequent increased continental weathering deduced from the kaolinite evolution during the latest Hauterivian and the early Barremian [32].

The return to more negative values in sediments from the *N. pulchella* to the *H. sayni* zones at RA (i.e., middle of CM3 to the base of CM2 at GC) may

Fig. 7. Correlation of the δ¹⁸O curves from the Angles, Veveyse de Châtel-Saint-Denis and Gorgo a Cerbara sections. Numbers on top of the columns of each section refer to: 1: stages; 2: ammonite zonations of the RA [25] and VCD (modified after [23]) sections; 3: nannofossils bioevents (this work); 4: magnetostratigraphy of GC [18,21,29,30]; 5: nannofossils bioevents of the CG section [31]. The dark grey lines represent the five points moving average curves. The light grey areas represent the scattering of the minima and maxima values.
indicate the end of the interaction between boreal and Tethyan water masses, and consequently the return to warmer oceanic temperatures; this would be in agreement with a short-term eustatic minimum [38].

Finally, the δ18O curve forms a maximum which is located in the I. giraudi zone (RA section). This appears to be synchronous with a short-term eustatic maximum that would have led to the arrival of cooler water in the Tethys and a corresponding positive shift of the δ18O curve. However, boreal nanofloras were not detected in this interval and therefore the trend towards higher values may also be due to climate cooling, in the absence of water-mass exchange between the Tethyan and the boreal realms.

These observed trends are in agreement with the trends of the δ18O curve obtained from belemnites by Podlaha et al. [39], van de Schootbrugge et al. [15] or by Veizer et al. [6], who observed the heaviest δ18O values of the entire early Cretaceous during the Hauterivian, whereas the Barremian is characterized by an initial warming phase followed by a cooling phase. Moreover, the trend we observe is coherent with published early Cretaceous δ18O curve [9]. This thermal evolution during the Barremian is also reported from fish tooth enamels analysis by Pucéat et al. [40], although the low-resolution of their study – probably due to the scarcity of fish teeth in sediments – does not allow a precise correlation between their results and the curves presented therein. Finally, the shift toward more negative values recorded at Angles from the I. giraudi zone to the top of the section, may correspond to the lower part of the negative shift recorded by rudists in the latest Barremian – earliest Aptian [41].

6.4. Possible mechanisms driving the evolution of the δ13C values during the late Hauterivian and Barremian

In a classical sense, the evolution of the carbonate δ13C record is interpreted as an approximation of the ratio between carbonate carbon and organic carbon burial fluxes in marine environments and their associated changes (e.g., [1,5,42]). External factors such as the release of methane from clathrate dissociation in slope environments (e.g., [43,44]), atmosphere–ocean exchange of CO2 (including volcanic activity; e.g., [9]), and the influx of terrestrial organic matter may also influence this record as well (e.g., [45]).

A new approach in the interpretation of marine carbonate δ13C records is given by a linkage in the style and intensity of shallow-water carbonate production and the rate of export of shallow-water carbonates into the basin environment, levels of dissolved inorganic carbon (DIC) in open oceans, and the δ13C record (e.g., [46,47]).

The latest Hauterivian is characterized by an increase in the δ13C record (Δδ13C=0.5–1‰), which reaches a maximum just before the Hauterivian–Barremian boundary. The Faraoni level and its equivalents are localized in the middle of this positive gradient. Even if the δ13C excursion does not have the same amplitude as the excursions associated with the oceanic anoxic events during the Valanginian, Aptian, and late Cenomanian (e.g. [2,48,49], respectively), the trend towards more positive values could still be explained by a shift in the burial ratio of organic carbon and carbonate carbon, as is suggested by the Faraoni anoxic event and the coeval onset in platform demise along the northern Tethyan margin. It remains, however, to be seen in how far this event has had an impact on the global carbon cycle. The Faraoni level is mainly known from the western Tethyan realm [14,50]. Recently, a possible equivalent was described from the northwestem Pacific realm [51], which would imply that the extent of this event is more important than previously assumed. If indeed the Faraoni oceanic anoxic event is implied in this small positive shift in δ13C values, an explanation for the attenuated isotope signature needs to be found. In following Bartley and Kah [46] we suggest that the attenuating effect may have been related to the increased size of the oceanic DIC reservoir.

Two principal processes may have enhanced the DIC reservoir during the late Hauterivian: (1) clay mineral studies in sections of late Hauterivian and Barremian age of the northern and the southern Tethyan margin in western Europe show systematic increases in kaolinite contents in the late Hauterivian, which may indicate a change of the climate towards warmer and more humid conditions for this time period [32,52,53]. Such climate conditions are favorable for increasing rates of DIC mobilization via biogeochemical weathering and throughput of DIC into the ocean by enhanced river transport [54]. During the late Hauterivian, the threefold evolution of ammonite fauna linked to sea-level fluctuations [55] may reflect the enhanced and facilitated export of DIC; (2) a widespread platform drowning event that started during the latest Hauterivian along the northern Tethyan margin may also have contributed to an increase in the oceanic DIC reservoir through the decrease in shallow-water carbonate production – a potential sink of DIC – and a corresponding increase in ocean alkalinity (e.g., [56]). The increased oceanic DIC reservoir may have been sustained throughout most of the early Barremian, paralleled by persisting drowning conditions on the northern Tethyan platform,
and this may explain the rather steady evolution in the \( \delta^{13}C \) record throughout the early Barremian.

The positive shift in the \( \delta^{13}C \) record close to the early–late Barremian transition (\( \Delta \delta^{13}C = 0.5 - 0.7\%o \)) is more difficult to be explained in terms of changes in the burial ratio of organic and carbonate carbon, since to our knowledge no major change in organic carbon output has been documented from this time interval. We propose to link this shift to an important change in the shallow-water platform carbonate factory, which is documented from the northern Tethyan margin and elsewhere: the platform drowning episode that started in the latest Hauterivian and ended near the early–late Barremian boundary (S. Bodin, personal communication) marks the transition between carbonate production dominated by heterozoans (“green water” or foraminal facies, [3,57]) and photozoans (“blue water” or chlorozoan facies). This transition is documented by the widespread installation of the so-called “Urgonian” facies in France and Switzerland, which is, for example, also documented from the Cupido and Coahuila carbonate platforms of northeastern Mexico, where peritidal shelf-lagoonal carbonate deposits are formed during the late Barremian and Aptian ([58,59]; see also [60]), and from the Jebel Akhdar in northeastern Oman where the installation and subsequent progradation of shallow-water carbonate platforms is observed during the Barremian [61,62].

The principal carbonate mineral produced by heterozoan assemblages, which – in the helvetic realm – are dominated by crinoidal remains, is calcite, whereas photozoan assemblages also produced aragonite during the early Cretaceous (corals and associated rudists, green algae, etc.; e.g., [63,64]). Aragonite tends to be enriched in \( ^{13}C \) relative to calcite and \( \delta^{13}C_{\text{aragonite}} \) may reach values of up to 5\%o (e.g., [47,65]). If produced by green algae, aragonite consists of a fine-grained material that is readily transported and exported into adjacent basins, where it is either dissolved in the water column or integrated into peri-platform sediments (e.g., [47,66]). The increased export of meta-stable, \( ^{13}C \)-enriched particulate inorganic carbon (PIC) in the form of aragonite with the renewal of photozoan assemblages may have influenced the \( \delta^{13}C \) record from the early–late Barremian transition, in particular through the installation of the Urgonian-type platforms in the G. sartousiana zone. This is coherent with the Phosphorus Mass Accumulation Rate evolution during this period [67]: the onset of photozoans may be coeval with oligotrophic conditions, which is in agreement with Mutti and Hallock [57]. Moreover, the arrival of photozoan carbonate platforms around the Tethys in the middle late Barremian may have led to a decrease in the oceanic DIC reservoir implicitly diminishing the DIC buffering effect. This we relate to the possible reduction in the throughput of DIC via the platform because of its transformation and storage by carbonate-producing organisms and because of the rather closed architecture of the platform, which is usually rimmed towards the basin by patch reefs and/or oolithic shoals. Consequently, the oceanic C-system would have become more sensitive to paleoceanographic and/or paleocological perturbations, in particular to the export of material that holds a more positive \( \delta^{13}C \) signature.

The negative excursion in \( \delta^{13}C \) values of approximately 0.5\%o at the Barremian–Aptian boundary is in our view related to a widespread decrease in kaolinite and an increase of detrital input in general registered along the northern Tethyan margin and elsewhere, and a corresponding temporary disappearance of the Urgonian facies (e.g., [52,68]). The corresponding increase in continentally derived DIC and decrease in shallow-water carbonate production may have contributed to this negative excursion. The involvement of increased methane release from slope environments cannot be excluded either (e.g., [7,43]), even though direct evidence is lacking.

6.5. Quantification of the carbonate platform exportation and its influence on the pelagic record

In order to quantify the impact of the export of aragonite and/or calcite from the platform to the basin, we calculated theoretical \( \delta^{13}C \) values that would result from an increasing input of platform-derived calcite or aragonite into the pelagic environment.

Concerning the platform, we estimated the volume of carbonates produced by using the surface covered by nertic carbonates during the early Aptian [69], and assuming a sedimentation rate of 5 cm ky\(^{-1} \) ([3,62]). Using paleomaps of the Tethyan realm, Philip [69] estimated that the deposition of nertic carbonates was mainly limited to intertropical seas, and that they covered an area of approximately \( 4.63 \times 10^6 \) km\(^2 \) in the early Aptian. Presently, reefs are estimated to represent an area of only 247,000 km\(^2 \) [70]. The importance of late early Cretaceous shallow-water carbonate production relative to today points to a potentially significant influence on the oceanic carbon-cycle during the early Cretaceous. In this estimation, we used a \( \delta^{13}C_{\text{calcite}} \) value of 1\%o and a \( \delta^{13}C_{\text{aragonite}} \) value of 5\%o [47].

For the pelagic production, we estimated the area covered by the Tethys as the average of the late Tithonian and early Aptian areas [71,72]. Then, the volume
of carbonate produced per kiloyear and per square kilometer was estimated from the sedimentation rate recorded during the late Barremian in the RA section, assuming that CaCO₃ represents on average, approximately 73% of the total pelagic sedimentation [73].

For both parts of the model we quantify both the quantity of ¹²C and ¹³C produced, then we calculate a theoretical δ¹³C (noted δ¹³Cₜₜ) that takes into account the influence of the platforms. So the variable parameters are the rate of export (τ) under particulate or dissolved form, and the δ¹³C that would be recorded in the basin without any influence from the platforms (δ¹³Cᵢᵣᵢ). The results (Fig. 8) show that during time of aragonite production, the δ¹³C increases; even with a τ of 20% and with a δ¹³Cᵢᵣᵢ of 2‰, the δ¹³Cₜₜ reaches a value of 2.20‰. Such a shift is recorded in RA sediments attributed to the G. sartousiana zone, which corresponds to the onset of the Urgonian platform. In comparison, storms can remove up to 50% of present-day reefs [74].

In contrast, the δ¹³Cₜₜ values decrease in the theoretical case that platform carbonate is mainly produced as calcite. With a δ¹³Cᵢᵣᵢ value of 2‰ and a τ of 30%, the δ¹³Cₜₜ value corresponds to 1.90‰. This suggests that photozoan carbonate factories such as the Urgonian platforms and their potential to produce and export aragonite into the pelagic realm may have had a considerable effect on the pelagic δ¹³C signal, whereas shallow-water carbonate production in the heterozoan mode would be less influential.

7. Conclusions

The carbon and oxygen stable isotope records of selected sections representative for the northern and southern Tethyan margins give a consistent image of environmental change during the late Hauterivian and Barremian. The late Hauterivian is characterized by a long-term increase in the δ¹³C record, which becomes accentuated during the latest part of this stage. This trend is explained here in a classical sense, with a shift in the burial ratio of organic and inorganic carbon in favor of organic carbon, which culminated in the widespread deposition of organic-rich sediments during the Faraoi oceanic anoxic event during the latest Hauterivian. This anoxic event is coeval with the onset of a platform drowning episode along the northern Tethyan margin, which lasted until the latest early Barremian. This was also a period of relative climate stability albeit with a tendency towards warmer conditions as is shown by the δ¹⁸O record. The general stability of the δ¹³C record during the early Barremian is explained by a buffering effect of the increased oceanic DIC reservoir, which is sustained by increased continental DIC input and diminished carbonate sedimentation rates along the northern Tethyan margin.

Near the transition from the early to the late Barremian, a shift toward more positive values is seen in the δ¹³C record, which is explained here by the installation of widespread photozoan-type shallow-water carbonates of the so-called Urgonian platforms. This type of

![Fig. 8. Predicted δ¹³C values recorded in pelagic settings (δ¹³Cₜₜ, as a function of the exportation rate (τ), of the δ¹³C in the basin without platform influence (δ¹³Cᵢᵣᵢ) and of the mineralogy of the exported material (δ¹³C(calcite) = 1‰; δ¹³C(aragonite) = 5‰, after Swart and Eberli [47]).](image-url)
carbonate production likely favored the production of aragonite, which may have been a source of heavy $\Delta^{13}C$ material in the adjacent basins, once exported into those realms.

The negative excursion in $\Delta^{13}C$ values at the Barremian–Aptian boundary is explained by a widespread decrease in the production of photozoan carbonates and an increase in detritus, which both may have contributed to an increase in the transfer of DIC towards the ocean.

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