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C-ISOTOPE STRATIGRAPHY, A CALIBRATION TOOL BETWEEN AMMONITE- AND MAGNETOSTRATIGRAPHY: THE VALANGINIAN-HAUTERIVIAN TRANSITION

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Abstract: Detailed carbon isotope stratigraphy was calibrated with standard ammonite stratigraphy for two Valanginian to Lower Hauterivian sections in Southern France, La Charce in the Vocontian Basin and Pont de Carajuan on the Provence platform margin. The excellent correspondence of ammonite zonation and carbon isotope composition between the two sections allowed us to create a composite C-isotope curve. The Valanginian carbon isotope excursion starts with a positive $\delta^{13}C$-shift of ca. +1.3 ‰ in the upper Campylotoxus Zone. $\delta^{13}C$-values culminate in the Verrucosum Zone and decrease from the upper Verrucosum Zone to the Hauterivian Loryi Zone where they reach pre-excursion values again. Correlation of the Valanginian to Lower Hauterivian standard ammonite zonation of Southern France (N. Tethys) with other bio- and chronostratigraphies, such as the South Alpine nannofossil- and magnetostratigraphy (S. Tethys) is significantly improved by the link via carbon isotope stratigraphy.

Key words: Lower Cretaceous, Tethys, Southern France, Valanginian-Hauterivian transition, carbon isotope excursion, ammonite stratigraphy.

Introduction

Over the last decades C-isotope stratigraphy has been established as a powerful tool in stratigraphy (e.g. Scholle & Arthur 1980; Renard 1986; Weissert & Lini 1991; Weissert et al. 1998). If combined with biostratigraphy and magnetostratigraphy it can contribute to a higher resolution of the sedimentary record and it may serve as a correlation tool in basin-shelf studies. In addition, the use of C-isotope stratigraphy may help to solve correlation problems between biostratigraphy and magnetostratigraphy and it may also provide a link between biostratigraphies considered as uncorrelatable. In this study we establish a link between the Valanginian-Hauterivian C-isotope stratigraphy of the southern Tethyan margin (Lini et al. 1992; Lini 1994) and the hypostratotype ammonite stratigraphy recently revised for the Valanginian northern Tethyan margin (Busnardo & Thieuloy 1979; Bulot et al. 1992; Bulot et al. 1996). We analysed bulk samples from the hemipelagic section La Charce (Vocontian Trough, S. France) which was chosen as the boundary stratotype for the Valanginian-Hauterivian boundary (Thieuloy 1977; Bulot et al. 1992; Mutterlose et al. 1996). In order to test the correlation potential of C-isotope stratigraphy, we also measured bulk carbonate samples from the outer platform sequence Pont de Carajuan, located in the Provence region (S. France), (Ferry & Rubino 1989; Walter 1991; Arnaud & Bulot 1992). We compared this new C-isotope stratigraphy with the magnetostratigraphically calibrated C-isotope curve for the Valanginian-Hauterivian (Lini et al. 1992; Channell et al. 1993). The comparison allows us to propose a new, isotopically calibrated correlation between Valanginian-Early Hauterivian ammonite stratigraphy and magnetostratigraphy.

The studied sections

Two sections, La Charce and Pont de Carajuan, both located in Southern France (Drôme and Alpes de Haute Provence) have been used for this C-isotope study (Fig. 1). The ammonite-rich section La Charce in the basinal part of the Vocontian domain is described in Bulot et al. (1992). It is now used as the stratotype for the Upper Valanginian to Lower Hauterivian ammonite zonation (Mutterlose et al. 1996). Its lithology consists of hemipelagic, fossiliferous, cyclic marl-limestone alternations (Fig. 2). The Lower Valanginian and the Lower Hauterivian parts of the section are more calcareous than the Upper Valanginian interval, where marls predominate. The section used for C-isotope stratigraphy covers the Late Valanginian and Early Hauterivian (Verrucosum Zone–Loryi Zone, Fig. 2).

The section Pont de Carajuan has been studied previously by various authors (Ferry & Rubino 1989; Walter 1991; Arnaud & Bulot 1992). It is located within the "réserve géologique de Haute Provence", in the Verdon Valley near Castellane. The section is paleogeographically situated at the transition of the Provence platform to the Vocontian domain. The sequence consists of fossiliferous shallow water limestones and marls. The studied section starts in the upper Campylotoxus Zone with the "Karakaschiceras Beds", ammonite and bivalve-bearing marly limestones. These limestones are overlain by a thick, marly sequence, the "Marnes à Toxaster", containing

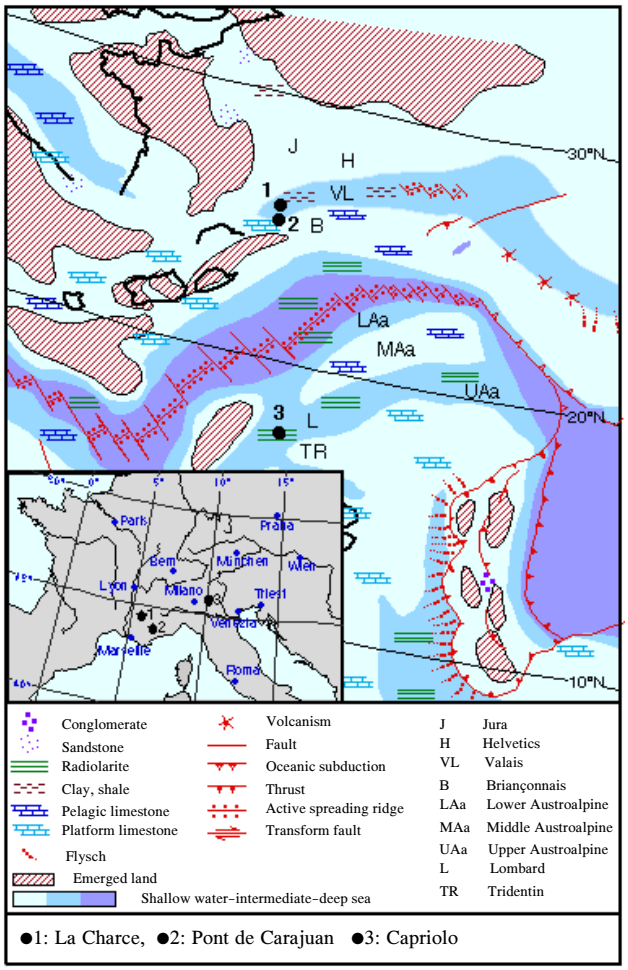

Fig. 1. Geographical and paleogeographical situation of the sections. Paleogeography after Dercourt et. al. (1986).

mainly *Toxaster*, bivalves, brachiopods and some ammonites, and getting marlier and more fossiliferous towards the top. The "Petite Lumachelle" represents a calcarenitic interruption within these marls. The "Grande Lumachelle" lies on top of the "Marnes à Toxaster" and consists of bioclastic Alectryonia-limestones alternating with marls containing *Alectryonia*, bivalves, serpulids, brachiopods, bryozoans and crinoids. The "Grande Lumachelle" represents the peak of a shallowing upward trend and is dated to the Verrucosum Zone (Arnaud & Bulot 1992). After an outcrop gap, calcareous marls with limestone beds and thin-bedded white nodular limestones with numerous, large ammonites mark the transition to the Hauterivian. Blue marls with few fossils form the top of the studied Pont de Carajuan section. The detailed ammonite stratigraphy for the Pont de Carajuan section is published in Arnaud & Bulot (1992).

Methods

On the basis of positive experience with other pelagic, hemipelagic and shallow water sediments of Early Cretaceous age (Lini 1994; Jenkyns 1995; Ferreri et al. 1997), bulk samples were used for this C-isotope study. The samples from the section La Charce were drilled at the University of Grenoble from the ammonite bearing rocks collected for ammonite stratigraphy at the recommended boundary stratotype (Bulot et al. 1992; Bulot & Thieuloy 1993). The samples from the section Pont de Carajuan were prepared at ETH Zürich.

The powdered samples were reacted with 100 % H_3PO_4 at 90 °C, or 50 °C. The carbon and oxygen isotope composition of the gas liberated was analysed at ETH Zürich with a VG Isocarb device coupled with a Prism inlet mass spectrometer, or with a VG 903 mass spectrometer. The isotope data are expressed in per mill (‰) deviation relative to the Cretaceous Pee Dee Belemnite (PDB) standard (McCrea 1950; Craig 1957). The working standard used in the Zürich laboratory is MS2 (Carrara Marble, $\delta^{13}C$ = 2.10 ‰; $\delta^{18}O$ = –1.82 ‰). The reproducibility of replicate analyses was ±0.1 ‰ for both carbon and oxygen isotope ratios.

The carbonate content was analysed on some of the same samples of the Pont de Carajuan section. The analysis were effected on a Coulometer 5011 (Laborlux S. A.) at EAWAG, Dübendorf. The standard for calibration was pure Na_2CO_3, reproduction error was ±1 % $CaCO_3$.

Data

The oxygen isotope data were used as indicators of diagenetic overprint. At la Charce, the $\delta^{18}O$-values fluctuate around –1 ± 0.2 ‰ throughout the section. The values indicate that burial diagenetic overprint is minor and that potential alteration by meteoric waters may be neglected. The $\delta^{13}C$-values range between +1.0 ‰ and +2.6 ‰ (Fig. 2). The $\delta^{13}C$-curve starts with values of about +2.0 ‰. More positive values of up to +2.6 ‰ were measured at 25 m, in the lower part of the ammonite horizon V3. Within the upper part of ammonite horizon V3, and part of ammonite horizon T1, $\delta^{13}C$-values decrease by 1 ‰ to +1.6 ‰. The curve fluctuates around +1.7 ‰ for the rest of the Trinodosum-Zone, then it decreases to lower values varying between 1.1 ‰ and 1.6 ‰ in the Callidiscus and Radiatus- zones. A small positive shift marks the transition from the Radiatus to the Loryi- zones. In the uppermost part of the section the measured $\delta^{13}C$-values decrease to ca. +1.0 ‰.

The outer platform section Pont de Carajuan is marked by less stable $\delta^{18}O$-values varying between –4 ‰ and –1.2 ‰. Carbonate concretions with pyrite have a maximal deviation of –0.4 ‰ in $\delta^{13}C$ corresponding to a shift of –1 ‰ in $\delta^{18}O$. All data of the section together, however, show no covariance of $\delta^{13}C$-values with $\delta^{18}O$-values. Nor is there any correlation of the carbonate content ranging from 60 % to 95 % with $\delta^{13}C$ or $\delta^{18}O$. The negative shift of $\delta^{18}O$ to non-marine values is most probably due to meteoric diagenesis and had little or no effect on the $\delta^{13}C$-values (see also James & Choquette 1990). Therefore, the established $\delta^{13}C$-curves with values ranging from +1 ‰ to +3 ‰ probably preserve an original paleoceanographic pattern (Fig. 2). This observation is in agreement with earlier studies made in neritic carbonate sequences (e.g. Jenkyns 1995).

The measured curve starts with values of +1.4 ‰ interrupted by a small but remarkable negative excursion to +1.1 ‰

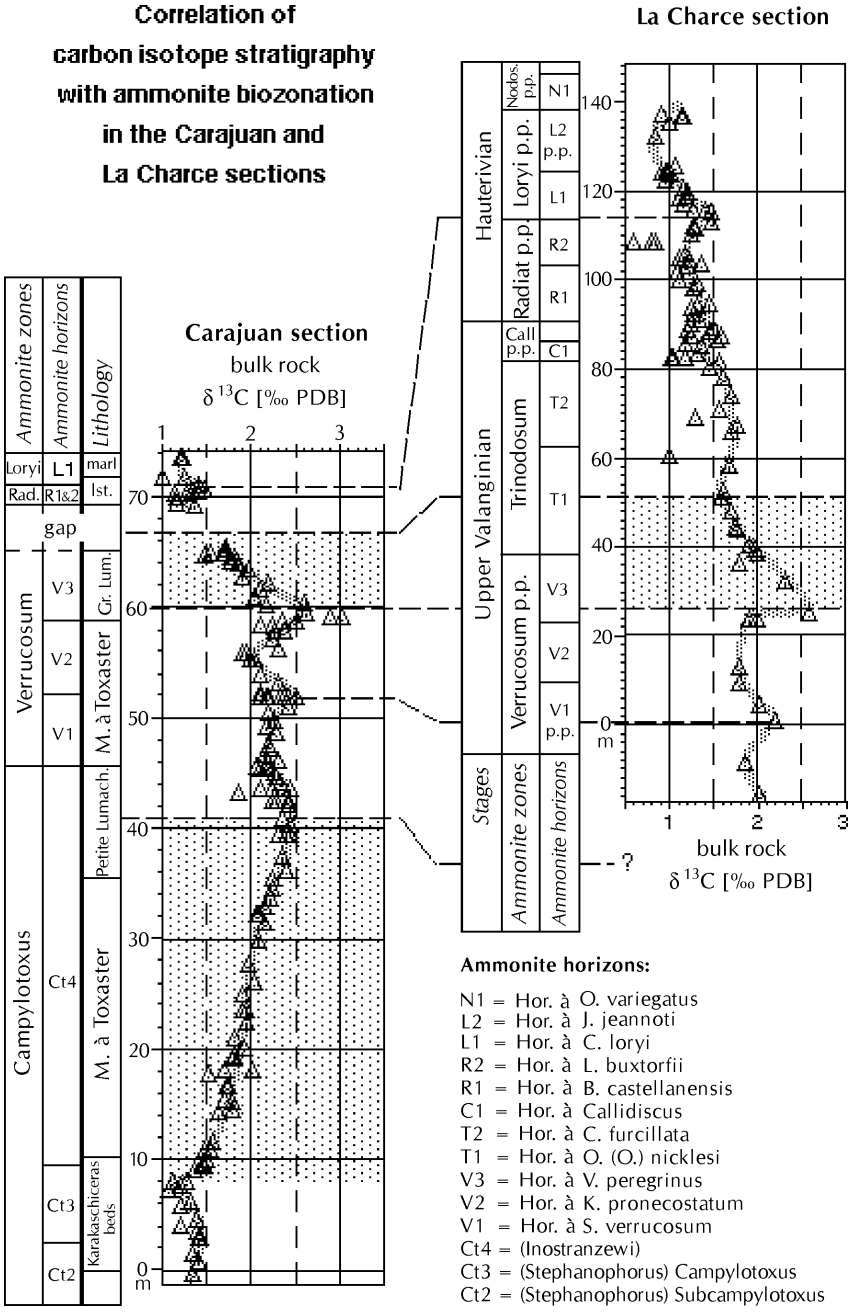

Fig. 2. Correlation of carbon isotope stratigraphy with ammonite biozonation in the Pont de Carajuan and La Charce sections. Carajuan ammonite zonation amended after Arnaud & Bulot (1992). La Charce ammonite zonation from Bulot et al. (1992). Lower shaded area: positive carbon isotope shift of +1.3 ‰ in the Pont de Carajuan section. Upper shaded area: rapid decrease of carbon isotope values by ca. 1 ‰ in the Pont de Carajuan and La Charce sections.

within ammonite horizon Ct3 (Fig. 2). Within Ct4 the $\delta^{13}C$-values steadily increase by +1.3 ‰ and they reach a first peak at the top of the Campylotoxus Zone (+2.4 ‰). The C-isotope curve is marked by a second peak (+2.5 ‰) in the ammonite horizon V1, and a third, most positive peak (+2.6 ‰) in the lower part of V3. The rapid decrease of $\delta^{13}C$-values within V3 to +1.6 ‰ is interrupted by an outcrop gap between 65 m and 69 m. In the uppermost, Lower Hauterivian part of the section the $\delta^{13}C$-values vary between +1 ‰ and +1.5 ‰, with a small positive peak at the boundary of the Radiatus to the Loryi-Zone.

Discussion

Both the Pont de Carajuan and the La Charce sections are accurately dated with ammonites (Arnaud & Bulot 1992; Bulot et al. 1992). The C-isotope curve established at the two localities La Charce and Pont de Carajuan shows a remarkable pattern which can be described as follows (Fig. 3):

(1) A minor negative $\delta^{13}C$-event within the *campylotoxus* ammonite horizon (Ct3) marks the base of the Valanginian C-isotope excursion. The positive shift of +1.3 ‰ to the first

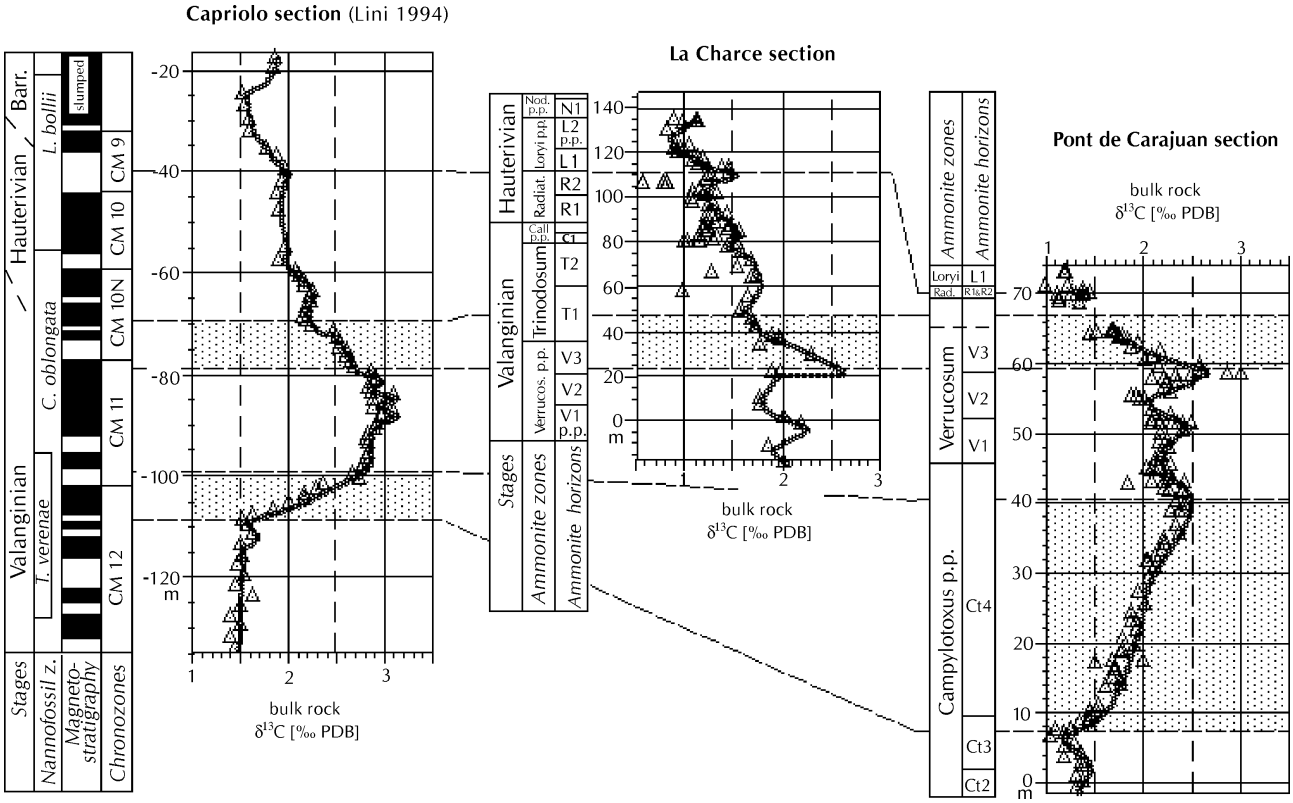

Fig. 3. Correlation of the Southern Tethyan margin (Lombardian Basin) carbon isotope stratigraphy (Lini 1994) with the Northern Tethyan margin (Provence) carbon isotope stratigraphy. Lower shaded area: positive carbon isotope shift of +1.3 ‰ in the Capriolo and Pont de Carajuan sections. Upper shaded area: rapid decrease of carbon isotope values by ca. 1 ‰ in the Capriolo, Pont de Carajuan and La Charce sections.

maximum in the $\delta^{13}C$-record falls within the upper part of the Campylotoxus Zone. The first maximum is measured in the upper part of the Inostranzewi Subzone (Ct4).

(2) An interval of very positive $\delta^{13}C$-values of up to +2.6 ‰ extends from the uppermost Campylotoxus to the lower to middle Verrucosum zones. The second positive peak (+2.5 ‰) occurs within the *verrucosum* horizon (V1) and the highest peak is measured at the base of the *peregrinus* horizon (V3).

(3)The $\delta^{13}C$-values decrease rapidly by 1 ‰ within the upper Verrucosum and lower Trinodosum zones. Then, they decrease irregularly and finally reach pre-excursion values in the Loryi Zone.

(4) A minor positive peak is measured at the boundary between the Radiatus and the Loryi zones.

The Pont de Carajuan section apparently contains the entire Valanginian-Hauterivian C-isotope event, while the La Charce section covers only the upper part of it. In the overlapping part, however, the $\delta^{13}C$-stratigraphy of the two sections coincides precisely with the ammonite zonation. This C-isotope curve can therefore be regarded as an ammonite-calibrated standard for stratigraphic correlations.

In a further step we correlate the La Charce-Pont de Carajuan curve with the southern Alpine $\delta^{13}C$-record (Fig. 3) (Lini et al. 1992; Channell et al. 1993; Lini 1994). In the Southern Alps, (e.g. Capriolo section, Lombardian Basin) the Valanginian $\delta^{13}C$-excursion was dated with calcareous nannoplankton and with magnetostratigraphy. The excursion falls within the C. oblongata and the C. bollii nannofossil zones. Paleomagnetic data document a beginning of the $\delta^{13}C$-event within magnetozone CM12. Peak values are reached in CM11. Between CM10N and CM8 the $\delta^{13}C$-curve returns to pre-excursion conditions.

C-isotope stratigraphy allows us to link the new Valanginian-Hauterivian ammonite stratigraphy with magnetostratigraphy and with southern Alpine nannofossil zonation. Our data indicate that:

(1) The beginning of the $\delta^{13}C$-excursion occurs within the *campylotoxus* horizon Ct3 of the Campylotoxus Zone. Therefore, the ammonite horizon Ct3 falls within magnetozone CM12.

(2) The Inostranzewi Subzone (Ct4) containing the positive shift can be correlated with the upper CM12 and lowermost CM11.

(3) Peak values of the *verrucosum* (V1) and *pronecostatum* (V2) horizons entirely lie within CM11.

(4) The decreasing $\delta^{13}C$-values marking the end of the Valanginian $\delta^{13}C$-excursion allow us to place the uppermost Verrucosum zone horizon *peregrinus* (V3) into magnetozone CM10N. The Trinodosum, Callidiscus, Radiatus and the basal part of the Loryi zones coincide with magnetozones CM10N–CM9.

The correlation of the Southern French composite $\delta^{13}C$-stratigraphy with the reference $\delta^{13}C$-stratigraphy in the Southern Alps offers the opportunity to link ammonite stratigraphy with magnetostratigraphy. The new correlation differs by about one magnetozone from earlier published correlations.

Channell et al. (1995) placed the top of the Campylotoxus Zone into CM12A. With our new correlation we place the boundary between Campylotoxus and Verrucosum Zone into CM11. Channell et al. (1995) correlated the Verrucosum Zone into CM12A–CM11A. Our data document that the Verrucosum Zone falls within CM11, and possibly the lower part of CM10N. Channell et al. (1995) and Mutterlose et al. (1996) place the Radiatus Zone into CM11–CM10N. In our correlations we can place the Radiatus Zone into CM10 to CM9. The base of the Radiatus Zone is proposed as the stage boundary between the Valanginian and the Hauterivian (Busnardo & Thieuloy 1979; Bulot & Thieuloy 1993; Mutterlose et al. 1996). According to our correlation, this boundary falls into the normally magnetized zone of CM10, while Channell et al. (1995) and Mutterlose et al. (1996) placed it into CM11. The lower Loryi Zone is shifted from a CM10N position (Channell et al. 1995; Mutterlose et al. 1996) into CM9.

Conclusions

We established a $\delta^{13}C$-stratigraphy for the Late Valanginian to Early Hauterivian in a hemipelagic (La Charce) and in an outer carbonate platform section (Pont de Carajuan) in Southern France. Both sections are accurately dated with ammonite stratigraphy and the section La Charce has been proposed as the boundary stratotype for the Valanginian-Hauterivian transition (Mutterlose et al. 1996). The C-isotope record seems to preserve an original paleoceanographic isotope signal. This allows us to use the $\delta^{13}C$-curves as a stratigraphic tool to establish a composite Southern French curve covering a time span between the Campylotoxus Zone (Valanginian) and the Loryi Zone (Hauterivian).

Based on our study of the Valanginian-Hauterivian transition we conclude that C-isotope stratigraphy will provide extremely useful information for stratigraphy which will result in a significant improvement of the stratigraphic timescale.

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