Early Aptian δ13C and manganese anomalies from the historical Cassis-La Bédoule stratotype sections (S.E. France): relationship with a methane hydrate dissociation event and stratigraphic implications

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Early Aptian $\delta^{13}C$ and manganese anomalies from the historical Cassis-La Bédoule stratotype sections (S.E. France): relationship with a methane hydrate dissociation event and stratigraphic implications

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Abstract: Comparison of oxygen and carbon isotope and manganese evolution curves in bulk carbonate from the historical Bedoulian stratotype (Cassis-La Bédoule area, Provence, France) reveals an important geochemical event (negative $\delta^{13}C$ and high Mn content) located within the *D. deshayesi* ammonite Zone and at the base of the *R. hambrowi* ammonite Subzone. This worldwide event, which can be observed in environments ranging from the fluvial to the pelagic realm (Selli/Goguel level), seems to be related to methane hydrate destabilization. Scenarios for manganese, carbon and oxygen evolutions are proposed for early Bedoulian oxic conditions and for dysoxic/anoxic conditions related to methane hydrate destabilization at the early/late Bedoulian transition. The impacts of this global event on the biosphere (nannoconid crisis) and its stratigraphic implications are considered. Comparison of geochemical and biostratigraphical data from the Cassis-La Bédoule stratotype with that of the Cismon-Apticore reference borehole shows that the La Bedoule sequence records geochemical evolution during the Goguel/Selli Event in more detail than that of any other previously published section.

Key Words: Lower Aptian; Bedoulian; carbon and oxygen isotopes; manganese; methane hydrates; nannoconid crisis; Selli and Goguel levels

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Résumé : *Anomalies géochimiques ($\delta^{13}C$ et manganèse) dans l'Aptien inférieur du stratotype historique de Cassis-La Bédoule (S.E. France) : relation avec un événement de dissociation d'hydrates de méthane et implications stratigraphiques*.- La comparaison des courbes isotopiques (carbone et oxygène) et des teneurs en manganèse de la série du stratotype historique du Bédoulien (coupes de Cassis-La Bédoule, Provence, France) met en évidence des anomalies géochimiques (accident négatif du $\delta^{13}C$ et pic des teneurs en Mn) se développant dans les zones d'ammonites à *D. deshayesi* et à *R. hambrowi*. Cet événement, d'occurrence mondiale, qui s'enregistre dans tous les environnements sédimentaires (niveau Selli/Goguel), parait lié à une période de déstabilisation des hydrates de méthane. Deux modèles de comportement du manganèse et des isotopes du carbone et de l'oxygène sont proposés. Le premier correspond aux conditions oxiques régnant au début du Bédoulien, le second aux conditions dysoxiques/anoxiques liées à la dissociation

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des hydrates de méthane au cours de la transition Bédoulien inférieur/Bédoulien supérieur. L'impact sur la biosphère (crises des nannoconidés) et les implications stratigraphiques sont discutés. La comparaison des données biostratigraphiques et géochimiques issues de la région stratotypique et du sondage de référence de Cismon-Apticore (Italie) montre que la série de la Bédoule enregistre les évolutions géochimiques au cours de l'événement Selli/Goguel d'une façon plus complète que les autres coupes précédemment publiées.

Mots-Clefs : Aptien inférieur ; Bédoulien ; isotopes du carbone et de l'oxygène ; hydrates de méthane ; crise des nannoconidés ; niveau Selli/Goguel

Introduction

A revision (MOULLADE *et alii*, 1998a) of the historical stratotype of the lower Aptian (Bedoulian) has provided the opportunity for a multidisciplinary review of various sections in the Cassis-La Bédoule area (Provence, France: Fig. 1A). This review includes a study of stable oxygen and carbon isotopes (KUHNT *et alii*, 1998; MOULLADE *et alii*, 1998b) and trace elements (RENARD & RAFÉLIS, 1998) in the bulk carbonate. Whereas the isotope study concentrated on the positive excursion of $\delta^{13}C$ subsequent to the anoxic episode, the analysis of trace elements focused on their relationship with the sequence stratigraphy of the stratotype.

The aim of this new work is a comparison of the two geochemical approaches and the integration of these data into those already available concerning the long term geochemical evolution of the Lower Cretaceous of the Vocontian Trough (Angles and Vergons sections, Alpes de Haute Provence: EMMANUEL, 1993 and new data). This comparison reveals an important geochemical break during the lower Aptian within the *D. deshayesi* ammonite Zone and at the base of the *R. hambrowi* ammonite Subzone. These geochemical anomalies may be related to methane hydrate destabilization and this study attempts to understand $\delta^{13}C$ and Mn behaviours during such an event and to underline the importance of geochemical anomalies of this kind as a stratigraphic tool.

During Mesozoic and Cenozoic times the long-term evolution of carbon isotope ratios presents lengthy (several million years) positive excursions that increased gradually throughout their term (LETOLLE & RENARD, 1980; RENARD, 1985, 1986; SHACKLETON & HALL, 1990; STRAUSS & PETERS-KOTTIG, 2003; PEARCE *et alii*, 2005). During these extended periods, heavy carbon isotope ratios are often associated with large amplitude short term (hundred of thousands of years) $\delta^{13}C$ negative shifts.

These lengthy positive excursions were rather soon understood and interpreted as being related to an increase in the production of organic matter together with a rise in the percentage fossilized because they coincide with oceanic anoxic events (OAE: JENKYNS, 1980). As organic matter preferentially incorporates carbon-12 during photosynthesis, this isotope is trapped in larger amounts during periods of increased productivity, in particular when a greater percentage of the organic matter produced is fossilized. Oceanic CO_2 is then enriched in carbon-13 and the $\delta^{13}C$ of the carbonates rises during this period. The effects of volcanism (WEISSERT & ERBA, 2004) and those of continental weathering (COHEN *et alii*, 2004) have been evaluated.

The shorter negative shifts associated with the long term trend are classically used in chemostratigraphy (SCHOLLE & ARTHUR, 1980; ZACHOS & ARTHUR, 1986; RENARD, 1986; WEISSERT, 1989; WEISSERT & CHANNELL, 1989; SHACKLETON & HALL, 1990; CORFIELD *et alii*, 1991; MAGARITZ, 1991; JENKYNS *et alii*, 1994 & 2002; BARTOLINI *et alii*, 1996; RENARD *et alii*, 1997; REY & DELGADO, 2002) because they are short-lived and synchronous phenomena. However their causes were in dispute for a considerable time: temporary oxygenation of the environment with consequent oxidation of the excess organic matter produced; sharp decrease in the quantity of organic matter produced. Discovery and recognition in many localities of BSR (bottom simulating reflectors: STOLL *et alii*, 1972; DILLON *et alii*, 1983; TINIVELLA & LODOLO, 2000) attesting to the widespread occurrence of methane hydrates in marine sediments has led to another interpretation (FIELD & KVENVOLDEN, 1985; GORNITZ & FUNG, 1994). As these complexes are stable only over a given range of pressure and temperature (FIELD & KVENVOLDEN, 1985; SLOAN, 1990; DICKENS *et alii*, 1995), the periodic destabilization of these gas hydrates (formed thermogenically or more probably biogenically by methane-producing bacteria from organic matter in sediments: PAULL *et alii*, 1994) causes the sudden release of methane into the ocean (destabilization of 1 m^3 of methane hydrate produces on the order of 140 m^3 of methane gas with very low $\delta^{13}C$ (-60‰) values (DICKENS *et alii*, 1995). This methane is then oxidized to form CO_2 (possibly forcing the environment towards anoxia, see below), which in turn influences the isotopic composition of oceanic carbonates. The more methane released the more negative the carbonate $\delta^{13}C$.

The first convincing evidence that such a process had occurred in a fossil sedimentary sequence was found with respect to the negative shift occurring at the Paleocene/Eocene boundary (DICKENS *et alii*, 1995; DICKENS, 2001), the release of methane having been caused by bottom water warming (KENNETT & STOTT, 1995; SCHMITZ *et alii*, 1997; LE CALLONNEC, 1998). There is much more

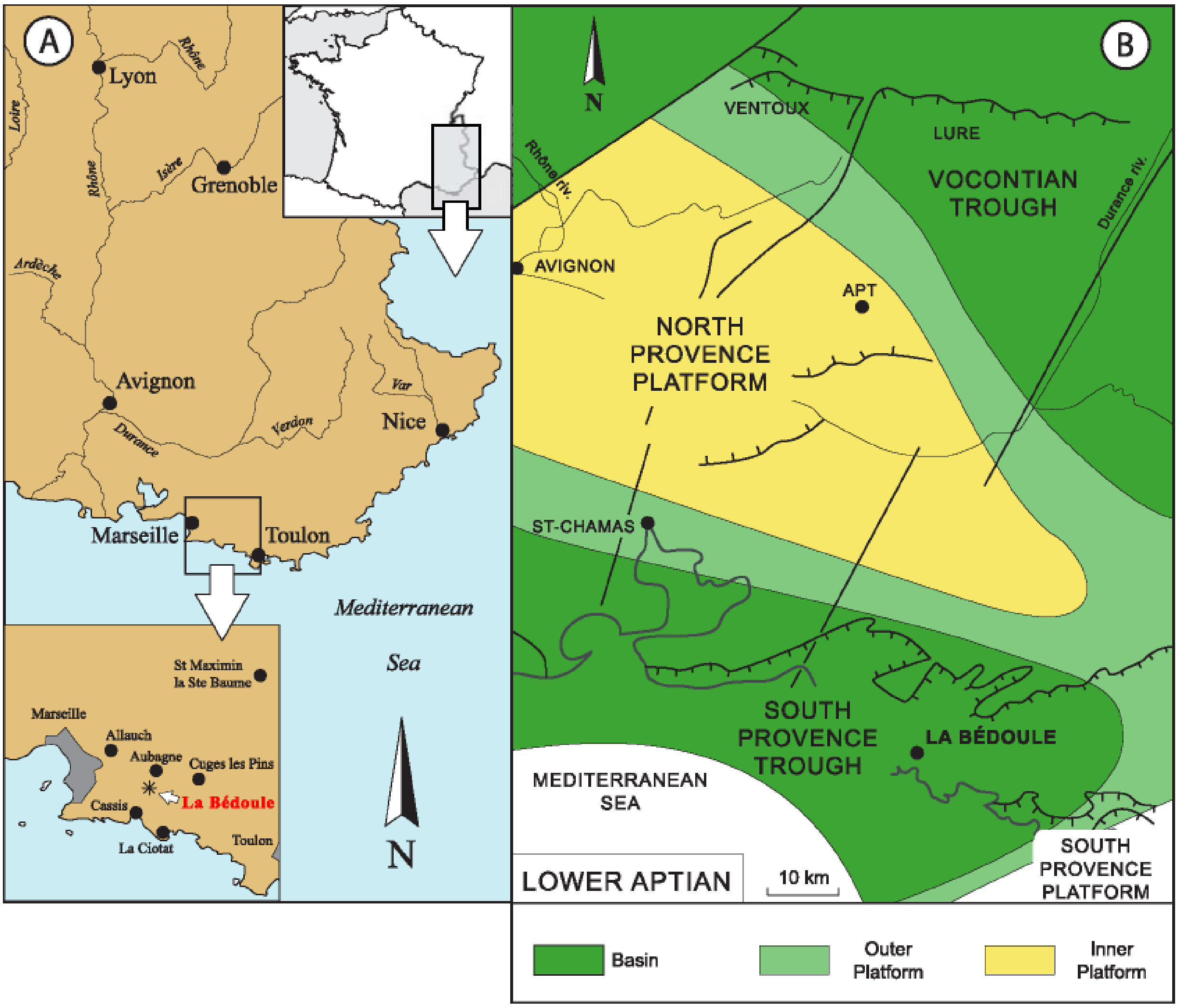


Figure 1: 1A: Location of the La Bédoule-Cassis area. **1B**: Paleogeographical scheme of the South Provence intrashelf basin during the Lower Aptian.

evidence suggesting that such events occurred at various widely disparate times (WEISSERT, 2000): Proterozoic (KENNEDY *et alii*, 2001), Toarcian (EMMANUEL, 1993; JENKYNS & CLAYTON, 1997; SCHOUTEN *et alii*, 2000; HESSELBO *et alii*, 2000; BEERLING *et alii*, 2002), Mid-Late Oxfordian (PADDEN *et alii*, 2001; WIERZBOWSKI, 2002). In 1994, JAHREN & ARENS were the first to report the possibility of a methane event during the Aptian OAE (AGU, Abstract) but their proposal was published only later (JAHREN *et alii*, 2001; JAHREN, 2002; BEERLING *et alii*, 2002). We opine here that the negative excursion of $\delta^{13}C$ recorded in the lower part of the upper Bedoulian in the historical stratotype section may be related to such an event because of its large amplitude (more than 2 ‰), its strong occurrence and short duration (*D. deshayesi* Zone and base of the *R. hambrowi* Subzone), its synchronism with other geochemical (Mn, $\delta^{18}O$) and biological anomalies and its global character.

I - The Bedoulian historical stratotype

The regional and palaeogeographic setting of the stratotype (Fig. 1B) is that of an intrashelf basin - the South Provence Trough - that formed in the Urgonian Platform during late Barremian times (MASSE *et alii*, 1998). It was isolated from the Vocontian Basin to the north by the North Provence Platform (Monts de Vaucluse - Mont Ventoux) and bounded to the southeast by the South Provence Platform (Mont Faron). Although quite restricted in extent initially, this trough extended westward during Lower Aptian times to join the North Pyrenean Basin of the '*Deshayesites* Marls' (MASSE *et alii*, 1998). The biozonations used in this work (Fig. 2) are those of ROPOLO *et alii* (1998) for ammonites, MOULLADE *et alii* (1998e) for foraminifers and BERGEN (1998) for nannofossils. As described by MOULLADE *et alii* (1998c-d) and MASSE (1998) the stratotype presents three members (Fig. 2):

- Upper Barremian-lower Bedoulian limestone member (beds 36-129) overlying the Urgonian Platform deposits;
- Upper Bedoulian alternating marls and limestones member ranging from bed 129 (major unconformity of MASSE, 1998) to bed 170;
- Top Bedoulian - lower Gargasian marly member above bed 170.

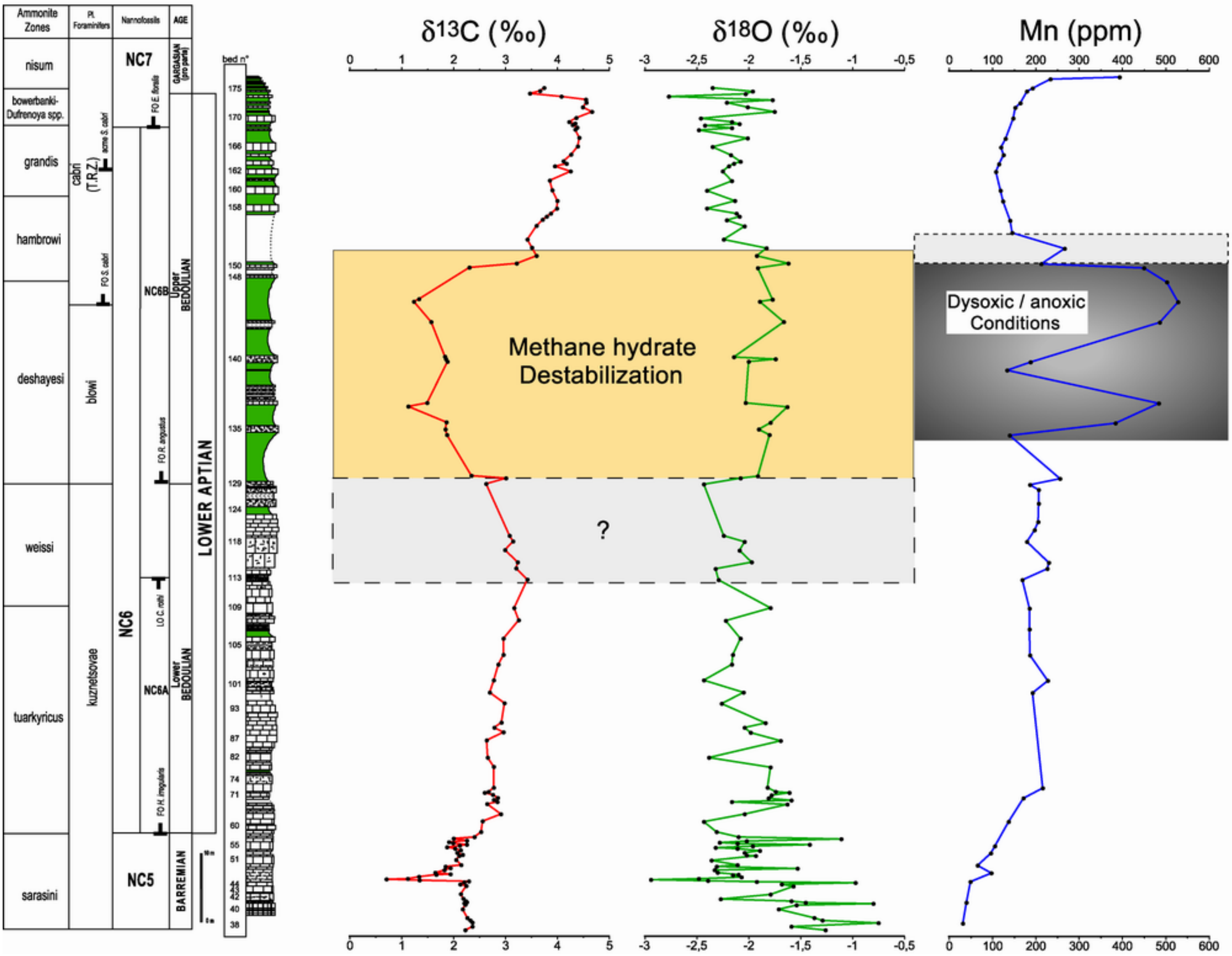


Figure 2: $\delta^{13}C$, $\delta^{18}O$ and Mn evolution curves from La Bédoule-Cassis sections (Gare de Cassis, Les Sardons and Camping outcrops) and biostratigraphic framework (Moullade *et alii*, 1998). Shaded area underlines geochemical anomalies related to dysoxic / anoxic events possibly linked to methane hydrate dissociation.

The distinction of these members is of practical value in the field but does not accurately reflect the $CaCO_3$ content which always remains high (mostly 80-95%: Masse, 1998). The distinction between marl and limestone lithofacies is therefore more closely associated with induration than carbonate content.

II - Geochemical results

II.1 - Methods

Samples were washed in distilled water, crushed, then dissolved in acetic acid (1N). Trace elements were analysed by atomic absorption (Hitachi Z8100 Zeeman spectrometer) using the method described by Renard & Blanc (1971; 1972) and Richebois (1990). Analytical accuracy is around 5%. Stable isotopes were measured with a Finnigan MAT 251 mass spectrometer coupled to a Carbo-Kiel device for automated CO_2 preparation from carbonate samples. Reactions were produced by adding acid to individual samples. The system is accurate to ±0.05‰ for carbon isotopes and ±0.08‰ for oxygen isotopes.

II.2 - Isotope data

II.2a - Carbon isotope ratio

Overall, the carbon isotope ratio of carbonates is high in the stratotype section (Fig. 2), rising from 2‰ at the top of the Barremian to around 4.5‰ in the uppermost Bedoulian (4.66‰ in bed 171). This general trend is interrupted by a brief negative shift (0.70‰ in bed 45, top of the Barremian) and a longer negative excursion at the base of upper Bedoulian between beds 129 and 157 (base of the *D. deshayesi* Zone and the *R. hambrowi* Subzone). This excursion reaches its minimum values between beds 136 and 146 where the $\delta^{13}C$ values scarcely overpass 1‰.

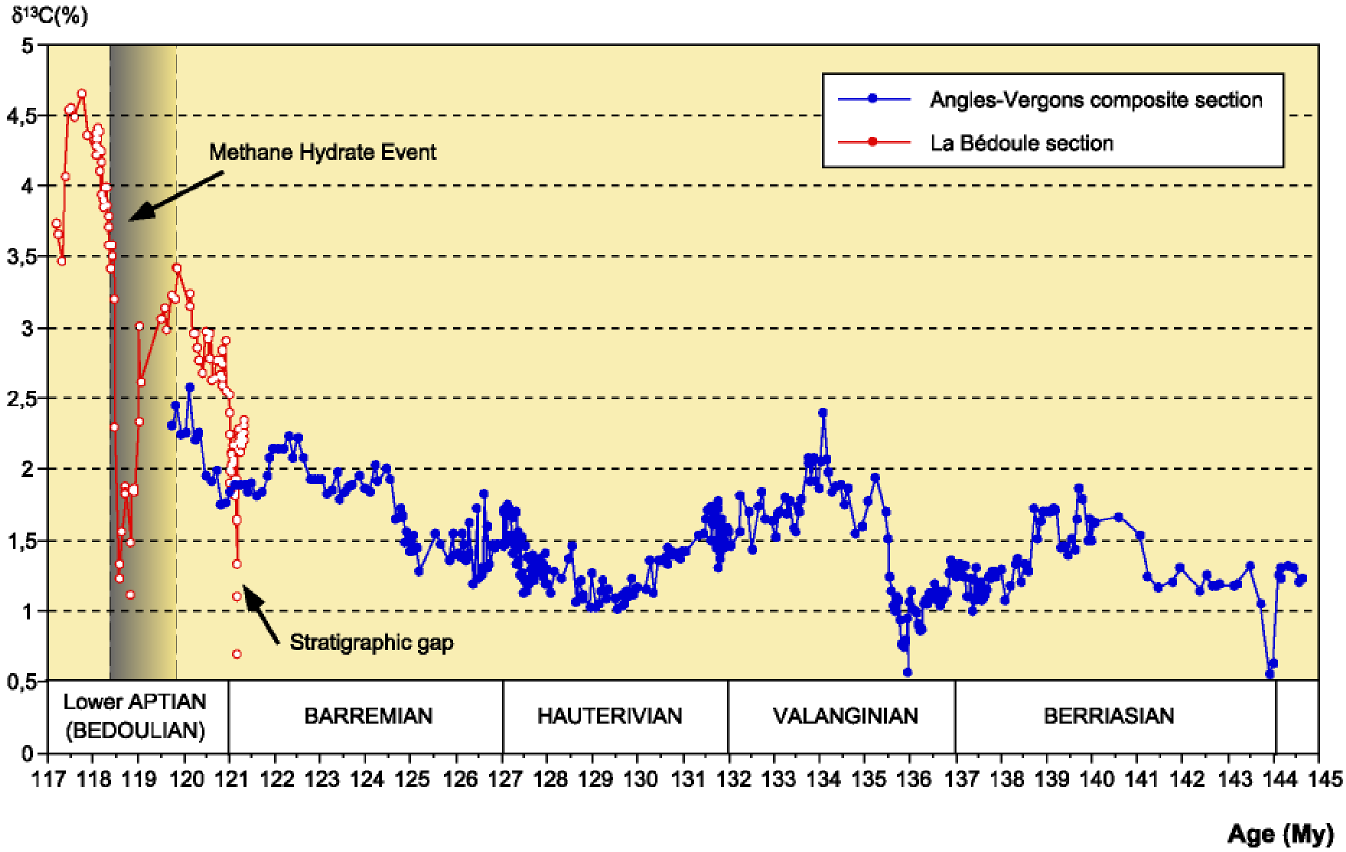


Figure 3: Lower Cretaceous long term evolution of bulk carbonate $\delta^{13}C$. This composite curve includes isotopic data from the La Bédoule stratotype and from the Vocontian trough (Angles and Vergons sections, EMMANUEL, 1993). Note that the positive excursion ranging from middle Hauterivian to Aptien is cutted by two negative shifts. The first one, located at the Barremain/Aptian boundary is related to a stratigraphic hiatus. The second one, in the base of the upper Bédoulian is related to a methane hydrate dissociation event (see text).

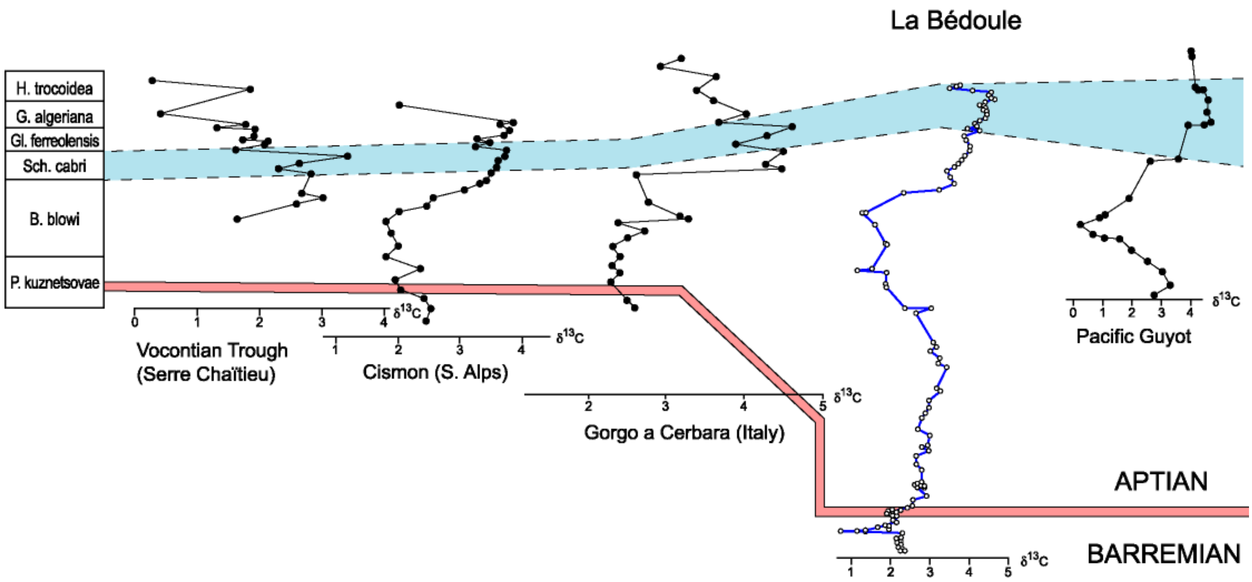
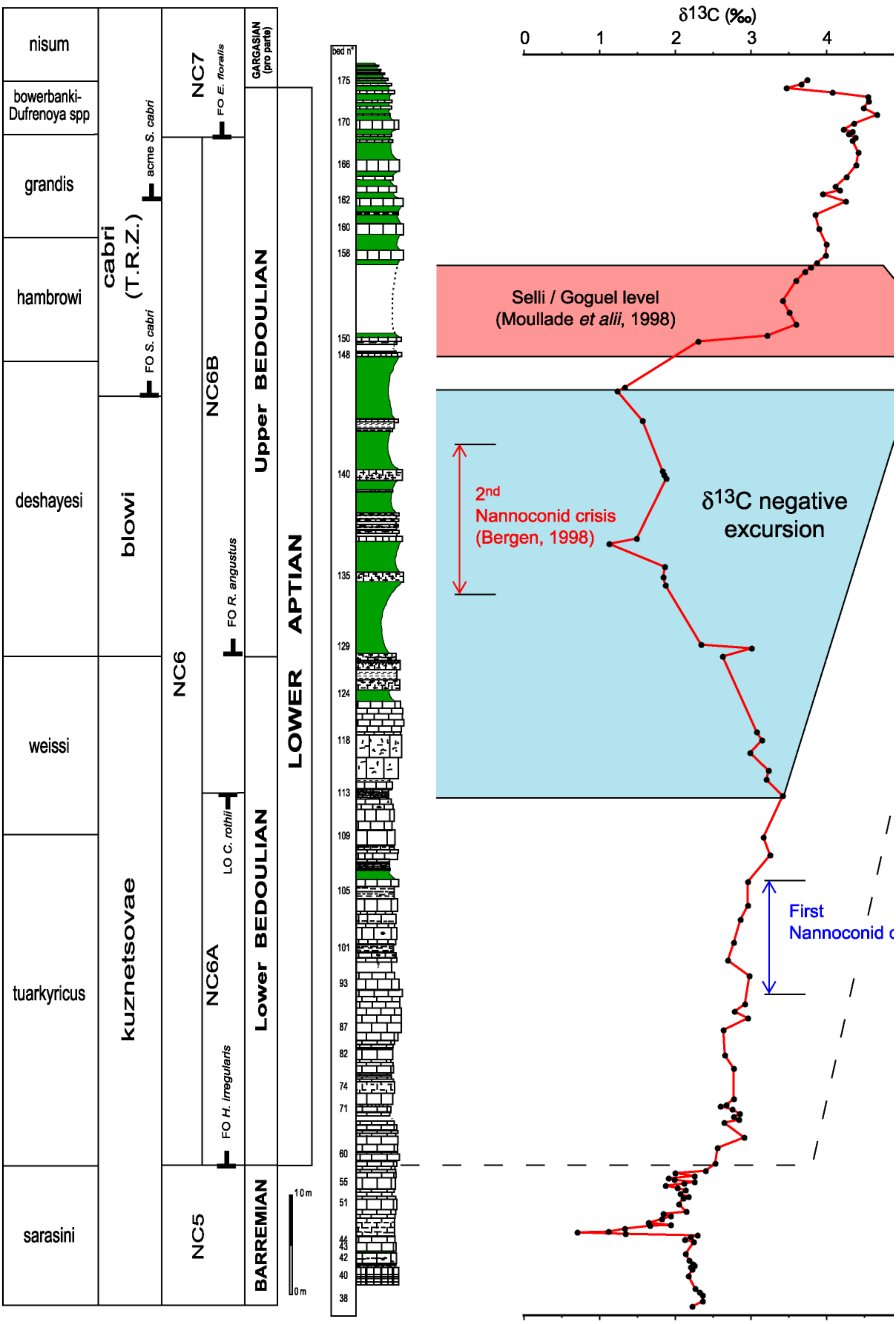


Figure 4: Correlation of the $\delta^{13}C$ record from the La Bédoule section with the curves of WEISSERT & BRÉHERET (1991) from the Vocontian basin, WEISSERT & LINI (1991) from the Cismon section, ERBACHER & THUROW (1997) from the Corgo a Cerbara section and JENKYNS (1995) from the Resolution Guyot in the Pacific (from KUHNT *et alii*, 1998).

II.2b - Oxygen isotope ratio

KUHNT *et alii* (1998) have already discussed the quality of the isotope signals recorded by bulk carbonates in this series by showing the slight effect of late burial diagenesis. However, the high variability of oxygen isotope ratios (on the order of 1‰) reported for nearby samples (Fig. 2) suggests that early diagenesis may be involved in bed formation and in the alternating pattern of the outcrop. Although their great variability obscures the signal to a degree, a general pattern can be observed for



nisum
bowerbanki-Dufrenoya spp
grandis
hambrowi
deshayesi
weissi
tuarkyricus
sarasini
cabri (T.R.Z.)
acme S. cabri
FO S. cabri
blowi
kuznetsovae
NC7
FO E. floralis
NC6
NC6B
FO R. angustus
NC6A
LO C. rothii
FO H. irregularis
NC5
GARGASIAN (pro parte)
Upper BEDOULIAN
Lower BEDOULIAN
LOWER APTIAN
BARREMIAN
10 m
0 m
bed n°
δ13C (‰)
Selli / Goguel level
(Moullade et alii, 1998)
2nd Nannoconid crisis
(Bergen, 1998)
δ13C negative excursion
First Nannoconid c

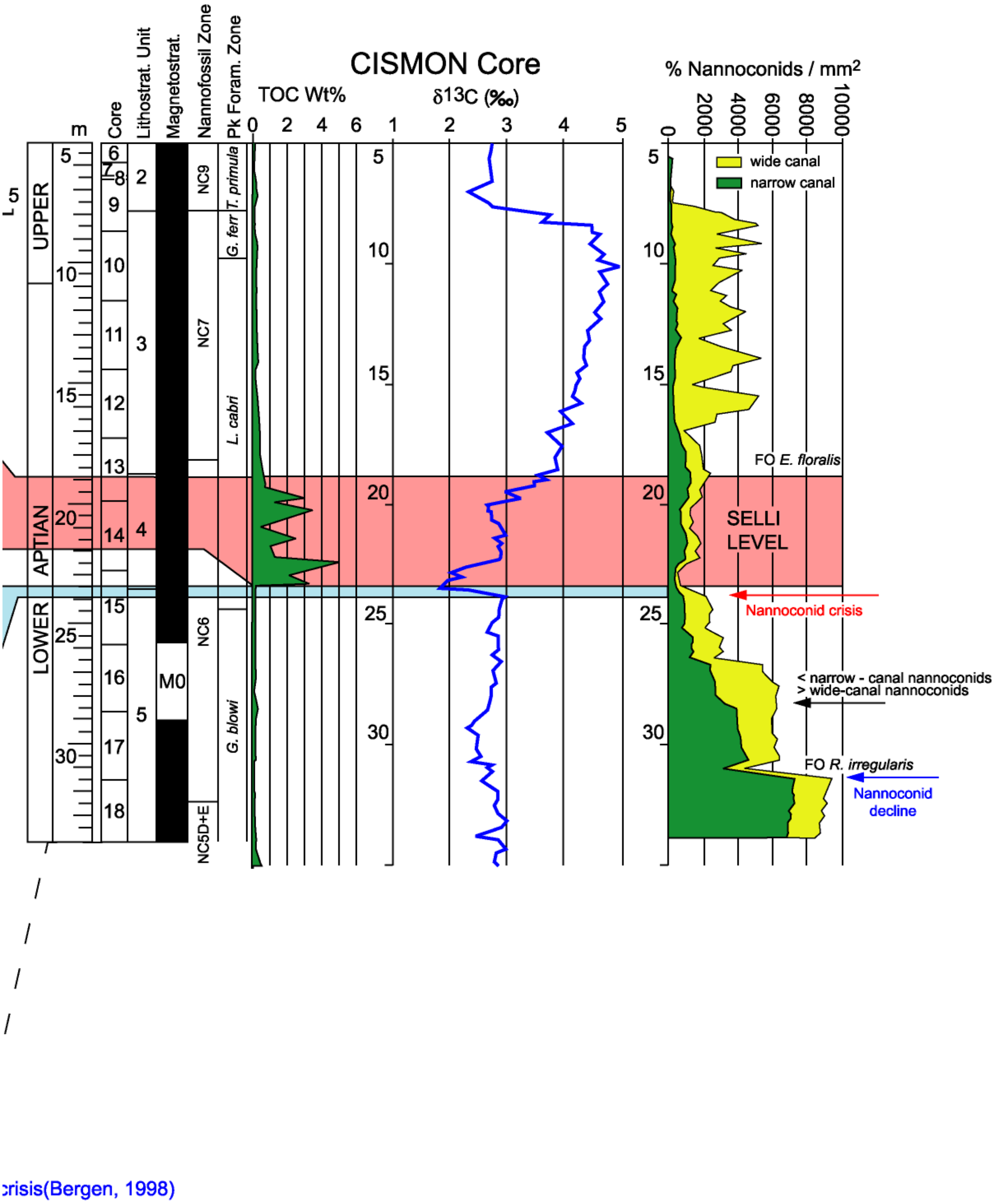


Figure 5: Detailed comparison of the $\delta^{13}C$ record from the La Bédoule and the Cismon section (Erba & Larson, 1999). Cismon section stratigraphy has been reinterpreted in this study for the definition of the base and the top of the Aptian (see text). This comparison involves the existence of a major sedimentary gap or of extreme condensation of the *B. blowi* Zone at Cismon and of a minor gap at the base of this zone in the La Bedoule stratotype section (Bed 129).

the oxygen isotope ratios (Fig. 2) that shows two negative trends. In the first one (top of the Barremian - lower Bedoulian), ratios decrease from values ranging between -0.7‰ -1.5‰ to values around -2,4‰ (bed 128). Furthermore bed 45 (site of the negative $\delta^{13}C$ shift) also records a negative $\delta^{18}O$ shift (-2.94‰).

Above the unconformity of bed 129, $\delta^{18}O$ increases at the base of the upper Bedoulian (*D. deshayesi* Zone). Then a second negative trend occurs in the upper Bedoulian with values falling from around -1.6‰ (bed 136) to less than -2.4‰ (beds 170 and 174). So the negative excursion of $\delta^{13}C$ in the *D. deshayesi* Zone corresponds rather closely with an increase of $\delta^{18}O$ values (ranging from -1.6 to-2‰).

II.3 - Manganese content

The manganese concentration of carbonate fluctuates considerably: from less than 50 ppm at the top of the Barremian to more than 500 ppm over the middle part of the upper Bedoulian (Fig. 2). This pattern is characterized by a relatively large rise throughout the upper Barremian (bed 38, [Mn] = 31 ppm) and lowest Bedoulian (bed 73, [Mn] = 216 ppm). During the lower Bedoulian and in the lower part of the upper Bedoulian Mn values level out at around 200 ppm. These observations are the basis for a proposed 3rd order geochemical sequence pattern (RENARD & RAFÉLIS, 1998), according to the model of EMMANUEL (1993) and EMMANUEL & RENARD (1993), supplemented by RAFÉLIS (2000) and RAFÉLIS *et alii* (2000).

The lower part of the upper Bedoulian (*D. deshayesi* and *R. hambrowi* zones) is characterized by very high values rising suddenly above the otherwise fairly level curve. There are two Mn-rich intervals: beds 136-137 (384 ≤ [Mn] ≤ 484 ppm) and beds 144-150 (450 ≤ [Mn] ≤ 529 ppm). The second part of the upper Bedoulian is characterized by low values (108 ≤ [Mn] ≤ 212 ppm). The sudden decrease in Mn content at the end of the Mn-rich zone (bed 150, [Mn] = 450 ppm; bed 151, [Mn] = 212 ppm) suggests either a hiatus or an intense sedimentary condensation at this level.

III - Interpretation and discussion

The lower part of the upper Bedoulian (*D. deshayesi* and base of the *R. hambrowi* ammonite zones, *B. blowi* and base of the *S. cabri* foraminifer zones, nannozone N6b) seems to be the site of substantial geochemical anomalies: a negative excursion of the carbon isotope ratios, two positive excursions of carbonate Mn contents and in a less obvious way an increase of $\delta^{18}O$ values.

III.1 - Carbon isotope ratio

Juxtaposition of the carbon isotope data from the La Bédoule stratotype with data from the Vocontian area (Berriasian to Barremian in the Angles and Vergons sections, EMMANUEL, 1993; Fig. 3) shows that high $\delta^{13}C$ values at the Bedoulian/Gargasian transition correspond to the end of a long-term positive trend that began in the middle Hauterivian. The negative excursion at the base of the upper Bedoulian temporarily interrupts this trend. The $\delta^{13}C$ negative shifts observed at the Barremian-Aptian transition in the Angles section are not of the same order of magnitude as those recorded in the La Bédoule stratotype, but they confirm the occurrence of a sedimentary gap at bed 45, which may reflect a major drowning phase (MASSE & MACHHOUR, 1998).

During Hauterivian to Gargasian (middle Aptian) times the following series of processes could be detected (Fig. 3). A phase of increased organic productivity developed gradually during the mid-Hauterivian ($\delta^{13}C$ ≈ 1‰) and increased with fluctuations throughout the early Barremian ($\delta^{13}C$ ≈ 1.5‰) and late Barremian ($\delta^{13}C$ ≈ 2.25‰). The Barremian-Aptian boundary is marked by a decrease in the phenomenon ($\delta^{13}C$ ≈ 1.75‰). The record of this decrease is exaggerated in the Cassis stratotype ($\delta^{13}C$ ≈ 0.70‰) because of sedimentary gaps in the late Barremian associated with a regional drowning phase (MASSE & MACHHOUR, 1998). However, it cannot be completely ruled out that a first regional methane hydrate release occurred at that time. The oxidation of CH_4 into CO_2 would decrease the availability of oxygen and thus allow increased fossilization of organic matter (2% ≤ TOC ≤ 10%, in beds 41-49, MASSE & MACHHOUR, 1998). The increase in organic productivity continued into the early Bedoulian and is recorded both in the Angles section ($\delta^{13}C$ ≈ 2.5‰) and the Cassis section. The phenomenon is more marked in the stratotypic series ($\delta^{13}C$ ≈ 3‰ in the *D. tuarkyricus* Zone and ≈ 3.4‰ at the base of the *D. weissi* Zone). This peak corresponds to the first positive excursion reported by KUHNT *et alii* (1998).

$\delta^{13}C$ decreases progressively at the top of the *D. weissi* Zone and then abruptly at the transition from the limestone to the marl-limestone member (lower Bedoulian/upper Bedoulian, *D. weissi* Zone / *D. deshayesi* Zone). The methane hydrate release may have begun at bed 114 in the *D. weissi* Zone or more probably at bed 129 coincident with the *D. weissi* / *D. deshayesi* boundary (the first part of the negative trend is considered to be a "normal" fluctuation in productivity). Methane hydrate release leads to very low carbon isotope ratios in the carbonates with two minima in the *D. deshayesi* Zone: at the top of bed 136 ($\delta^{13}C$ = 1.12‰) and at the base of bed 146 ($\delta^{13}C$ = 1.23‰; bottom of the *S. cabri* foraminifer Zone, top of the *D. deshayesi* ammonite Zone). The phenomenon ends at the base of the *R. hambrowi* ammonite Subzone (lower part of the *S. cabri* Zone) between beds 150 ($\delta^{13}C$ = 2.30‰) and 151 ($\delta^{13}C$ = 3.21‰). The second positive excursion (identified by KUHNT *et alii*, 1998) corresponds to a renewed increase in the productivity and fossilization of organic matter during the late Bedoulian ($\delta^{13}C$ = 4‰ in bed 159 at the top of the *R. hambrowi* Subzone and = 4.66‰ in bed 171 in the *T. bowerbanki* Zone).

By comparison between isotope data from the Cassis-La Bédoule section (Fig. 4) with those from the Vocontian domain (Serre Chaïtieu: WEISSERT & BRÉHERET, 1991), Southern Alps (Cismon: WEISSERT & LINI, 1991), Umbria-Marche Basin (Corgo Cerbera: ERBACHER & THUROW, 1997) and Pacific Ocean (Guyot du Resolution: JENKYNS, 1995), KUHNT *et alii* (1998) show that the positive trend of $\delta^{13}C$ in the late Bedoulian is a worldwide phenomenon recorded in all sections studied. The negative excursion of the *D. deshayesi* Zone is more difficult to identify elsewhere because in many Tethyan sections gaps at the base of the Aptian (DELANOY, 1996) or major slumps (Umbria-Marche Basin: CRESTA *et alii*, 1989; HADJI, 1991) mask the initial phase of $\delta^{13}C$ evolution (first positive excursion of KUHNT *et alii*, 1998). So the isotopic minimum in these sections is taken to be the $\delta^{13}C$ base level of the Aptian. However, more recent isotope data on the Cismon outcrops (MENEGATTI *et alii*, 1998) and above all the Apticore borehole in the same region (ERBA *et alii*, 1999; LARSON & ERBA, 1999) show a pattern identical to that recorded in the historical stratotype, *i.e.* a negative excursion of 1-2‰ at the Selli level (Fig. 5). However, with regard to fine-scale correlation a problem still exists because the negative excursion, much more abrupt at its base, has but a single minimum in the lower part of the *S. cabri* foraminifer Zone (upper part of nannozone NC6) in the Cismon Apticore borehole (Fig. 5; LARSON & ERBA, 1999) and at the top of the *B. blowi* Zone in the outcrops of the area (MENEGATTI *et alii*, 1998). The causes and the stratigraphic implications of this apparent diachronism between the Cismon and La Bédoule sections are discussed below. MENEGATTI *et alii* (1998) also indicate a single event at the top of the *B. blowi* Zone at Rotter Sattel (Swiss Prealps) where the isotope curve displays sudden breaks suggesting gaps in sedimentation. However, the La Bédoule section displays a much more extensive excursion, with two minima. The earlier one is located in the *B. blowi* Zone and the second at the base of the *S. cabri* Zone (zone NC6b). Data from the Hybla Formation in Sicily show that the equivalent of the Selli level records a negative $\delta^{13}C$ excursion that there too extends from the top of the *B. blowi* Zone to the base of the *S. cabri* Zone (BELLANCA *et alii*, 2002). Various studies show that the negative excursion of $\delta^{13}C$ is clearly recorded in shallow shoal series in the Pacific (Fig. 4) and carbonate platform such as the Sierra Madre (Mexico: BRALOWER *et alii*, 1999) or the Urgonian Platform (Vaucluse, France: MASSE *et alii*, 1999) suggesting a general oceanic phenomenon. Moreover, JAHREN *et alii* (2001) and JAHREN (2002) recorded a $\delta^{13}C$ negative accident of this type in the total organic matter, in the vitrinite and in the Aptian sediment cuticles of estuarine and coastal facies (Andes, Colombia). Numerous authors have described a similar record in terrestrial organic matter from the Isle of Wight (southern Britain: GRÖCKE *et alii*, 1999), from northern Japan marine sediments (ANDO *et alii*, 2002), from Algarve basin costal series (Portugal: HEIMHOFER *et alii*, 2003). These studies clearly show that all carbon reservoirs, both marine and continental, were almost synchronously disturbed by the event, which is consistent with the hypothesis of an important gas hydrate dissociation.

III.2 - Manganese content of the carbonates

The oceanic geochemistry of manganese is characterized by the prevalence of its association with a hydrothermal source (BOSTROM & PETERSON, 1969; BENDER *et alii*, 1970; LYLE, 1976; KLINKHAMMER, 1980; KLINKHAMMER & BENDER, 1980; THOMSON *et alii*, 1986; VON DAMM, 1995; CORBIN *et alii*, 2000). However, the interpretation of the significance of the Mn content of pelagic carbonates is complex for this element can be extracted from seawater by either of two processes:

(i) Direct precipitation of MnO_2 as micronodules within carbonate sediments. These micronodules are soluble in part by acid that may thus introduce bias in estimates of original Mn carbonate content (EMMANUEL, 1993; RAFÉLIS, 2000).

(ii) Co-precipitation of Mn^{2+} in the calcite lattice (PINGITORE *et alii*, 1988):

$$[Mn/Ca]_{crystal} = k^{Mn}_{calcite} \, [Mn/Ca]_{seawater}$$

The first process may be important in oxidizing environments while the second is active in reducing environments (MICHARD, 1969). However, studies of manganese speciation in pelagic carbonates either by cathodoluminescence (RAFÉLIS *et alii*, 2000) or by ESR (RAFÉLIS, 2000) show that in most cases the Mn content of pelagic carbonates is due to Mn^{2+} co-precipitated in the calcite lattice.

Following pioneer works of POMEROL (1976, 1984), RENARD & LETOLLE (1983), ACCARIE *et alii* (1989, 1993) and PRATT *et alii* (1991) associating manganese fluctuations with sea-level variations, EMMANUEL (1993) and EMMANUEL & RENARD (1993) have proposed the use of the Mn content of pelagic carbonates as a geochemical tool to characterize 3rd order sequences (*sensu* VAIL *et alii*, 1977). Lowstand systems tracts are characterized by a low and relatively stable Mn content. Transgressive episodes correspond to an increase of Mn content that peaks at the level of the maximum flooding surface. Highstand systems tracts display Mn values that decrease to a minimum at the sequence boundary. This model, first developed for the Tethyan Lower Cretaceous, has now been found applicable in the Middle and Upper Jurassic (CORBIN, 1994; CORBIN *et alii*, 2000; RAFÉLIS *et alii*, 2000) and in the Upper Cretaceous (BARCHI, 1995; JARVIS & MURPHY, 1999).

The La Bédoule stratotypic section was divided into sequences based on variations in manganese content by RENARD & RAFÉLIS (1998). This proposed tectono-eustatic interpretation is problematic in the lower portion of the upper Bedoulian where the correlation of manganese peaks with the negative $\delta^{13}C$ excursion seems to indicate that another phenomenon is superimposed on the hydrothermal/eustatic control. Figure 6 illustrates the geochemical specificity of the *D. deshayesi* Zone and the base of the *R. hambrowi* Subzone (beds 136, 137, 144, 146, 147 and 150). As oceanic hydrothermal events do not generate lighter carbon (only -7‰), a high Mn content cannot be linked straightforwardly to an increase in hydrothermal input during a more active phase of ridge spreading. This implies that an additional source of Mn must be related in some way to the event that caused the negative $\delta^{13}C$ excursion.

The following scenario can be envisaged (Fig. 7A). The increased productivity of organic remains that began in the mid-Hauterivian (Fig. 3) continued during the early Bedoulian. A large proportion of the produced organic matter escaped oxidation, was fossilized and consequently trapped a large quantity of carbon-12, thus inducing a first positive excursion of $\delta^{13}C$ (KUHNT *et alii*, 1998). The decomposition of organic matter did not consume enough oxygen to cause anoxia in the environment, so the redox front is located in the sediments at a depth of a few centimetres or decimetres. The concentration of dissolved manganese in seawater (Mn^{2+}) fluctuated with the hydrothermal activity at the ocean ridges with some of the element being oxidized as Mn^{4+} and precipitated as MnO_2 particles. However, most of the Mn^{2+} available co-precipitated with the calcite synthesized by pelagic carbonate producers. In the course of sedimentation, the MnO_2 particles are trapped below the redox front where a relatively small proportion is reduced, thereby releasing Mn^{2+} (diffused in the sediment) which is returned to the ocean system and incorporated in the pelagic calcites (BURDIGE, 1993).

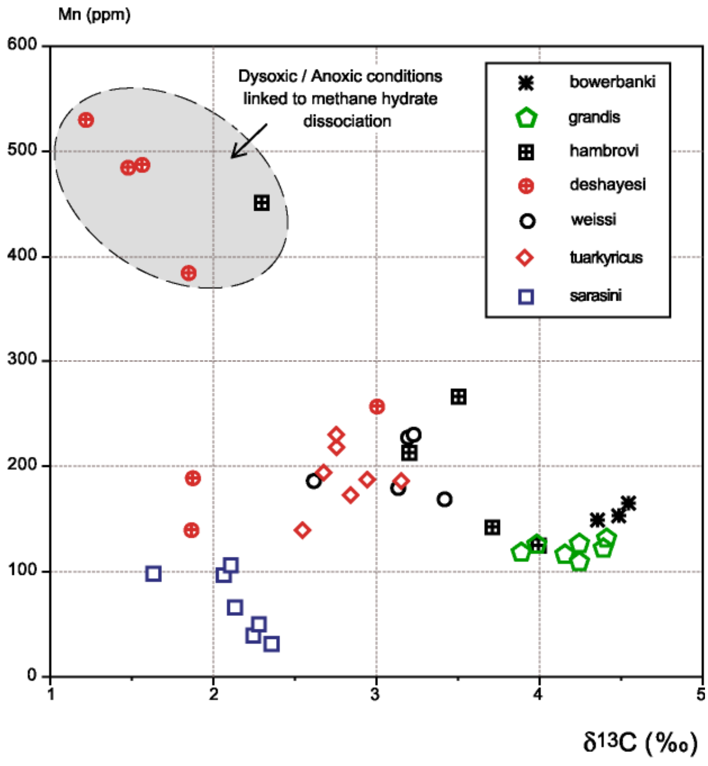


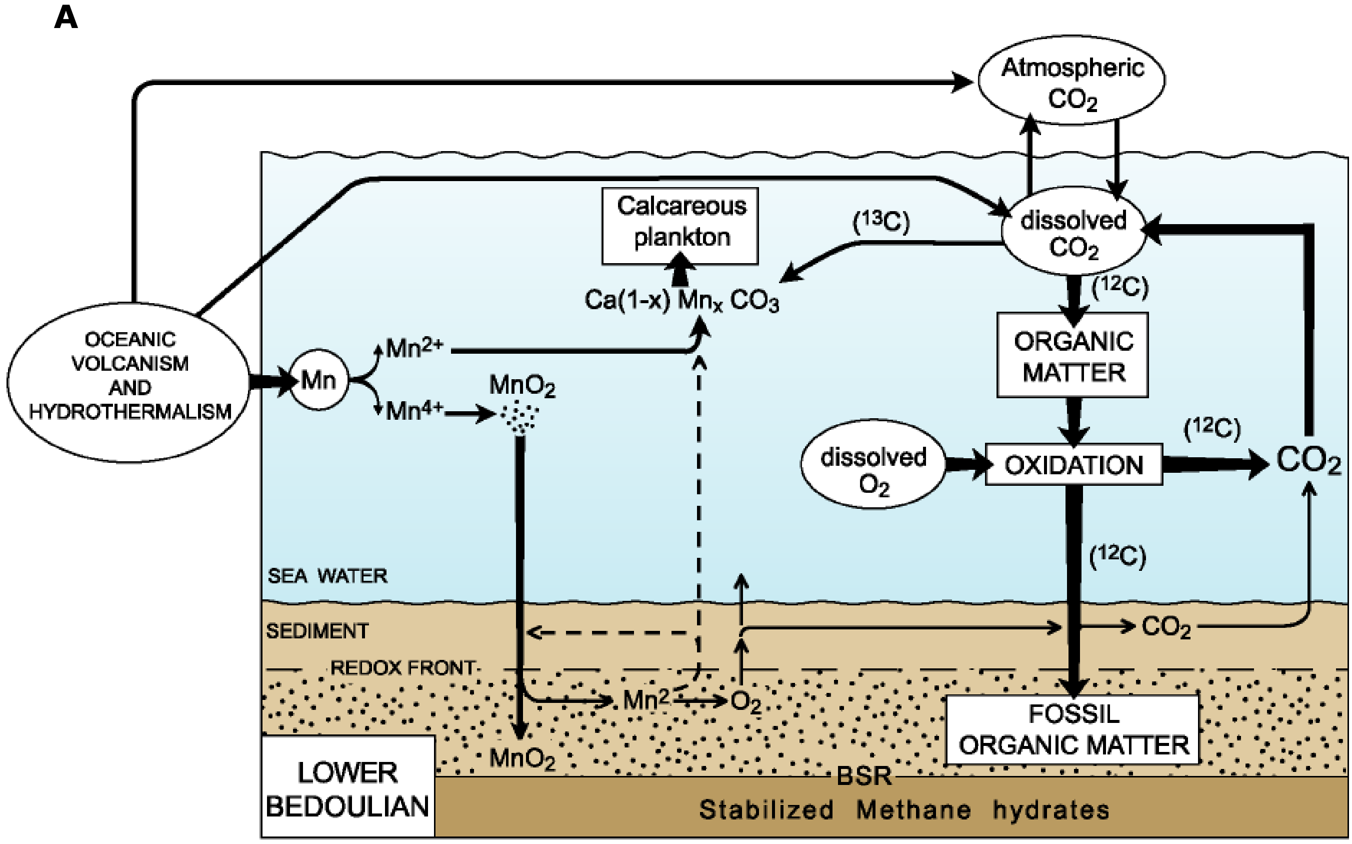
Figure 6: Carbon isotope ratio and Mn content of bulk carbonate relationships. Note the geochemical originality (high Mn content and low $\delta^{13}C$) of the carbonate from the *D. deshayesi* Zone and the base of the *R. hambrowi* Subzone with regard to other Bedoulian carbonates.

Immediately before the carbonate platform drowning phase at the onset of the late Bedoulian (*D. deshayesi* Zone, Fig. 7B; MASSE, 1998), by a mechanism not yet precisely determined (see below), gas hydrate was destabilized, releasing methane with a very low carbon isotope ratio (-60‰). In seawater, this methane was oxidized to form CO_2 that ultimately was used to produce carbonates with low carbon isotope ratios. As the oxidation of methane required much oxygen, the seafloor became dysoxic or anoxic. The redox front rose to the water/sediment interface or even higher in the water column. This caused most MnO_2 particles to be reduced thus releasing a large quantity of Mn^{2+} which was then integrated into the lattice of the produced pelagic carbonates. The two processes are out of phase (Fig. 2): the negative excursion of $\delta^{13}C$ marking the release of CH_4 began at the base of the late Bedoulian (*D. deshayesi* Zone) at bed 129 whereas the manganese peak resulting from the lower oxygenation of the environment did not appear until bed 136. In the same manner of succession, the $\delta^{13}C$ event ends at bed 150 before the Mn event took place (bed 151c). These events completed, organic productivity continued to rise as a preliminary to the second positive $\delta^{13}C$ excursion reported by KUHNT *et alii* (1998).

IV - The response of the planktonic and benthic biosphere of the basin

An early Aptian nannoconid crisis (chron M0) associated with oceanic volcanic events was described by ERBA (1994) in the Italian series. This crisis took place below the base of the Selli level (COCCIONI *et alii*, 1987) in the lower part of the *S. cabri* foraminifer level and the upper part of nannozone NC6. In the Cassis-La Bédoule stratotype the effects of this crisis are not obvious. However, BERGEN (1998) reported two periods of decrease in the abundance of nannoconids (Fig. 5). The first occurs within the *Conusphaera mexicana* Subzone (NC6A, beds 92-106, *D. tuarkyricus* / *P. kuznetsovae* Zone) and the second in the *Grantarhabdus coronadventis* Subzone (NC6B, beds 133-143, *D. deshayesi* / *B. blowi* Zone). New data from the Cismon region (Italy: ERBA *et alii*, 1999; LARSON & ERBA, 1999, Fig. 5) help to demonstrate the pattern of the crisis: fluctuation in the nannoconid population began with a severe depletion at the base of zone NC6; a partial recovery took place thereafter, but reached a minimum in the upper third of this zone at the base of the Selli level, where the $\delta^{13}C$ values are lowest. A similar pattern is observed at Cassis-La Bédoule although the events are spaced farther apart and interrupted because of the high rates of sedimentation in the stratotype area. The second event described by BERGEN (1998) coincides with the minimum of the negative $\delta^{13}C$ excursion and thus appears to correlate, in part at least, with the "nannoconid crisis" reported by ERBA (1994) at the base of the Selli level. In the stratotype foraminifers too have been disturbed at the time of the negative $\delta^{13}C$ excursion (MOULLADE *et alii*, 1998e; Fig. 5) owing to the reduced

A



B

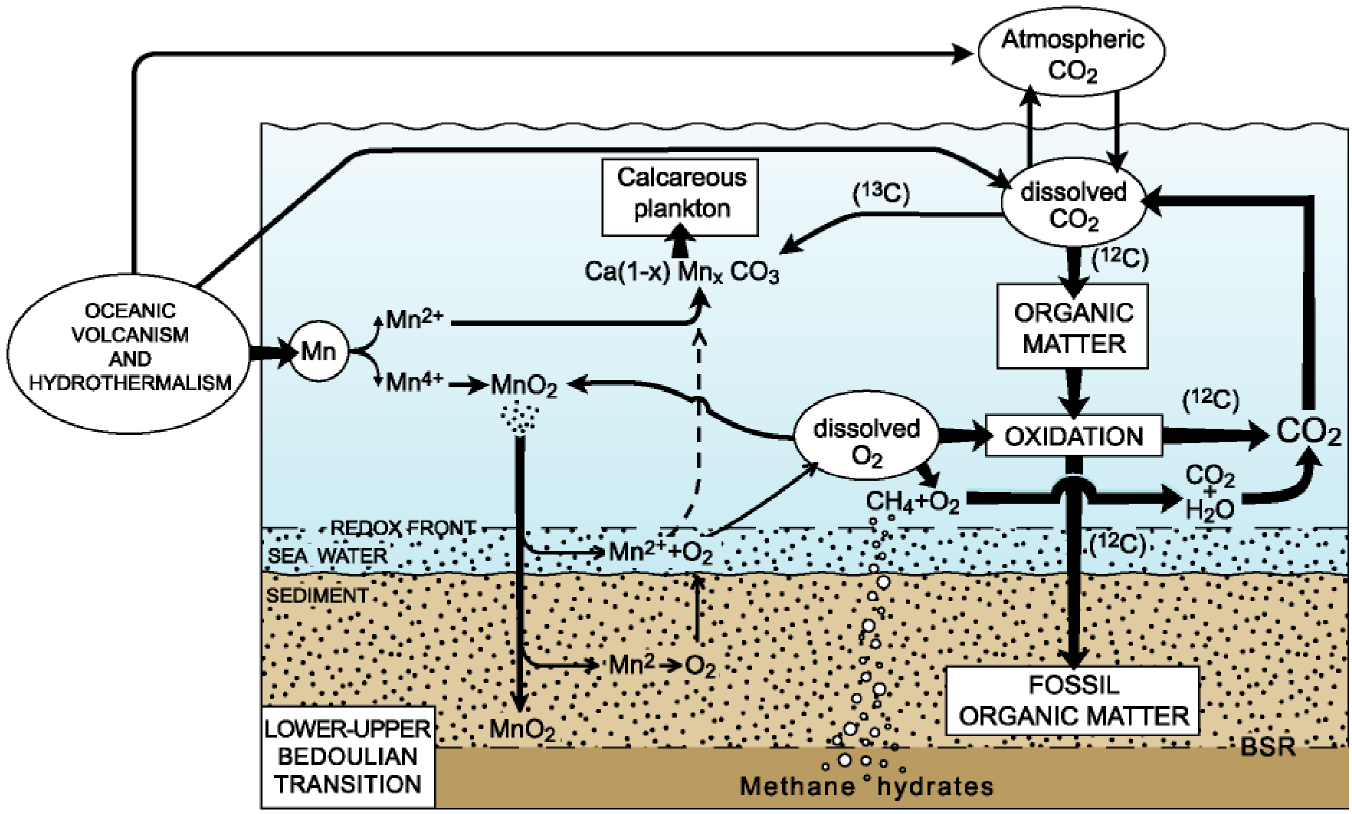


Figure 7: Behaviour of CO_2, O_2, and Mn in sea water and sediments:
7A: Oxic conditions during the Lower Bedoulian. Increasing of productivity and trapping of organic matter induce a $\delta^{13}C$ positive excursion.
7B: Anoxic / dysoxic conditions related to methane hydrate dissociation during the Lower - Upper Bedoulian transition. Oxidation of methane produces CO_2 with very low $\delta^{13}C$ and MnO_2 particles are reduced under this anoxic conditions resulting from this phenomena. Released Mn^{2+} is incorporated in the lattice of pelagic calcite.

oxygenation of the environment. Because of its stratigraphic position in the *R. hambrowi* Subzone (beds 153-157), this crisis was correlated with the Selli level (MOULLADE *et alii*, 1998e). These bioevents, involving the abundance and diversity of - both planktonic and benthic - foraminifers and nannofossils, were contemporaneous with the end of the negative $\delta^{13}C$ excursion and with the Mn-rich period (nannofossils) and consequently with the back to "normal" phase of the oceanic environment (foraminifers). They are consistent with a period of oxygen depletion subsequent to the release of gas hydrates.

V - Stratigraphic implications

V.1 - Occurrence of sedimentary gaps in the B. blowi Zone in reference sections and in boreholes of the Cismon area (Italy)

A detailed stratigraphy of the Selli level (equivalent to the Goguel level of the Vocontian Basin: BRÉHERET, 1988), which represents the major anoxic peak OAE1a (ARTHUR *et alii*, 1990), may be determined by comparing the record of the evolution of the $\delta^{13}C$ content at Cismon (Italy) with that at La Bédoule. As Italian stratigraphers do not use the same reference markers as their French counterparts to define the base (*H. irregularis*) and top (*E. floralis*) of the Aptian stage, the stratigraphy of Cismon has been reinterpreted using these reference markers (Fig. 5).

The first thing to keep in mind is the enormous difference in sedimentation rates. The Selli level (1% ≤ TOC ≤ 5%) at Cismon is some 3.5 m thick, while the negative $\delta^{13}C$ excursion occupies 1.5 to 3 m (depending on the boundaries ascribed to it) at the base of the *S. cabri* Zone. The Selli level starts at the isotopic minimum and develops throughout the rise in the carbon isotope ratio. At La Bédoule, the negative $\delta^{13}C$ excursion occupies some 35-38 m, that is the entire *B. blowi* Zone and the base of the *S. cabri* Zone. The equivalent to the Selli/Goguel level (beds 153-157) suggested by MOULLADE *et alii* (1998e) on the basis of a strongly decreasing foraminiferal diversity extends more than 5 m into the *S. cabri* Zone. This uppermost level corresponds only to the very end of the rise in the $\delta^{13}C$ curve. Comparison with fluctuations in isotope values recorded at Cismon necessitates setting the base of the equivalent of the Selli/Goguel level lower down, at least to bed 146 and occupying 8-10 m at the base of the *S. cabri* Zone in La Bédoule section. This interpretation is consistent with the occurrence of black shale facies in the sequence from beds 151c to 157c (camping section: MOULLADE *et alii*, 1998e). At Cismon, the nannoconid crisis (ERBA, 1994) is coeval with the decrease in $\delta^{13}C$ and with the minimum (base of the *S. cabri* Zone); it extends over one or two metres of sediment. At La Bédoule, the second phase of nannoconid depletion reported by BERGEN (1998), which may be the equivalent of the *ERBA nannoconid crisis*, occupies 16-17 m at the top of the *B. blowi* Zone.

The only way to make these data consistent is to postulate the existence of a hiatus in sedimentation or an extreme condensation of the *B. blowi* Zone at Cismon (Fig. 5). The isotopic minimum recorded at Cismon (at the base of the *S. cabri* Zone) then is equivalent to the second negative event at La Bédoule (bed 146, base of the *S. cabri* Zone) or, considering the absolute values of $\delta^{13}C$ (Cismon 2‰, La Bédoule 1.23‰), might be placed at the base of the rising phase of the isotope curve. The drastic decrease in isotope values at Cismon appears to be indicative of an important hiatus (most of the *B. blowi* Zone) at this level, which would mask the first part of the negative excursion recorded at La Bédoule at the top of the *B. blowi* Zone. The ERBA's nannoconid crisis would then correspond to a condensation of the second event described by BERGEN (1998) at La Bédoule.

On the other hand it seems likely that there is a minor gap in sedimentation at the base of the *B. blowi* Zone in the stratotype sequence at bed 129. This unconformity (expressed in the transition from the limestone to the marl-limestone member) is coincident with the largest geochemical break in the series (RENARD & RAFÉLIS, 1998). It can be correlated with the intra-Urgonian discontinuity U2/U3 of the Monts de Vaucluse, an event that has also been identified in the northern Sub-Alpine domain (MASSE, 1998). In Provence, this tectonically-controlled event (MASSE, 1994) was followed by a substantial drowning phase. RENARD & RAFÉLIS (1998) also interpret bed 129 as a major transgressive surface. This sedimentary gap, already suspected by BERGEN (1998) from nannofossil assemblages, is the result of a two-stage phenomenon: an initial regressive impulse of tectonic origin followed by a tectono-eustatic major drowning phase.

V.2 - Implications for the use of manganese fluctuations as a tool in sequence stratigraphy.

Detailed study of the La Bédoule stratotype reveals a phenomenon already suspected by EMMANUEL (1993) and RAFÉLIS *et alii* (2000), namely that Mn peaks can be caused during anoxic periods by phenomena not directly related to eustacy. Therefore, care should be taken when using the Mn content of carbonates as a tool for sequence stratigraphy during anoxic periods, in particular by searching for correlations between Mn peaks and negative $\delta^{13}C$ excursions. So the sequences proposed in the *B. blowi* and *S. cabri* zones (RENARD *et alii*, 1998) and in particular the interpretation of level 146 as a maximum flooding surface of the Aptian 3 sequence should be topics for additional discussion.

VI - Origin and causes of hydrate gas destabilization

We have already indicated that methane hydrates trapped in sediments are stable only over a relatively narrow range of temperatures and pressures. As regards the Palaeocene/Eocene boundary event, warming of bottom water at mid and high latitudes (attested by benthic foraminifers and stable oxygen isotopes) appears to have triggered the release of methane gas. For the Aptian event, it is difficult to invoke a thermal trigger of this type as there was relatively little disruption in the benthic foraminifer community. Although differential diagenesis could bias bulk carbonate $\delta^{18}O$, oxygen isotope data could shed light on this problem. $\delta^{18}O$ evolution indicates surface water warming in the early Bedoulian (of the order of 3° C, KUHNT *et alii*, 1998, fig. 1) but this trend was progressive. In addition, during the period corresponding to the carbon isotope excursion, oxygen isotopes display a positive trend reflecting either a cooling (2° C, KUHNT *et alii*, 1998) or a change in the isotope ratio of seawater because of the fluids released during the hydrate destabilization.

JAHREN (2002) attempted to interpret the negative $\delta^{13}C$ event of the Aptian as the consequence of the late Hauterivian superplume development (LARSON, 1991a-b). During the Aptian and Albian, this plume brought about the formation of the Kerguelen Islands and of the Ontong-Java oceanic volcanic province, along with the emergence of numerous seamounts and deformation of the circum-Pacific rim (VAUGHAN, 1995). Models of epirogenesis of the ocean floor related to this superplume (JAHREN, 2002) suggest that through reduction of hydrostatic pressure a quantity of methane may have been released compatible with the amplitude of the negative excursion in the Bedoulian. Models of epirogenesis of the ocean floor related to this superplume (JAHREN, 2002) suggest that through reduction of hydrostatic pressure a quantity of methane may have been released, which is compatible with the amplitude of the negative excursion of the Bedoulian. However, JAHREN acknowledges that such a process is lengthy and therefore is incompatible with the brief negative excursion reported. Against this hypothesis too is the fact that during the Hauterivian-Aptian the long-term pattern of the carbon isotope ratio of pelagic carbonates (Fig. 1) is the reverse of that caused by a gradual release of methane. Two other hypotheses are proposed by JAHREN (2002). The first involves very rapid and localized epirogenesis in a hypothetical oceanic region rich in methane hydrate. The second requires large-scale warming of sediments when a major extrusion of basalts accompanied the formation of the Kerguelen and Ontong-Java plateaux (120-80 Ma).

We too lean toward a tectonic cause of destabilization. The Aptian stage was a tectonically and seismically unstable time because of a major structuring phase along the continental margins in the Tethyan and Atlantic (MASSE *et alii*, 1993) and Pacific domains (VAUGHAN, 1995). We have mentioned the episode of exposure at the onset of the early Aptian identified in Provence and in the Vercors (MASSE, 1998). In many regions (Pyrenean Trough, Hungary, Bosnia) bauxites are evidence of movement on tilted blocks (COMBES & PEYBERNÈS, 1987). Many small interruptions in sedimentation developed on the margins of the Central Atlantic and Western Alps and in basins (Austrian-Alpine, Pindus-Olonos, Hawasina: MASSE *et alii*, 1993). However, the question remains unanswered as to whether or not so brief and synchronous events can be demonstrated to have occurred in all of these areas.

Conclusion

Comparative analyses of geochemical and biostratigraphic data of lower Aptian series suggest that the negative $\delta^{13}C$ excursion at the base of the upper Bedoulian may be related to a destabilization of gas hydrates trapped in sediments. The methane thus released, with its very low carbon isotope ratio, was oxidized to form CO_2, which was then used by organisms to form pelagic carbonates characterized by low $\delta^{13}C$ ratios. This oxidation of the methane led to anoxic trends in the environment and many of the MnO_2 particles became unstable. The Mn^{2+} released thereby was also incorporated in the pelagic carbonates that developed a positive peak for manganese during the negative excursions of $\delta^{13}C$.

The $\delta^{13}C$ excursion is developed over a length of time (*D. deshayesi* and base of the *R. hambrowi* ammonite zones, *B. blowi* and base of the *S. cabri* foraminifer zones, nannozone N6b) that possibly includes two episodes of methane hydrate release. Because of gaps, most sites record either the beginning or (more commonly) the end of the $\delta^{13}C$ excursion. The Cassis-La Bédoule stratotype appears to be one of the rare series that recorded the entire phenomenon.

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