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

Maurice RENARD$^1$
Marc de RAFÉLIS$^2$
Laurent EMMANUEL$^3$
Michel MOULLADE$^4$
Jean-Pierre MASSE$^5$
Wolfgang KUHNT$^6$
Jim A. BERGEN$^7$
Guy TRONCHETTI$^8$

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 fluviatile 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 Bédoule 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

Citation: RENARD M., RAFELIS M. de, EMMANUEL L., MOULLADE M., MASSE J.-P., KUHNT W., BERGEN J.A. & TRONCHETTI G.(2005).- 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.- Carnets de Géologie / Notebooks on Geology, Brest, Article 2005/04 (CG2005_A04)

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 oixiques régnant au début du Bédoulien, le second aux conditions dysoxiques/anoxiques liées à la dissociation.

---

1 Université P. et M. CURIE, Département de Géologie Sédimentaire (J.E. Biominéralisations et Paléoenvironnements), Case 116, 4 pl. Jussieu, 75252 Paris Cédex 05 (France)
renard@ccr.jussieu.fr

2 Université P. et M. CURIE, Département de Géologie Sédimentaire (J.E. Biominéralisations et Paléoenvironnements), Case 116, 4 pl. Jussieu, 75252 Paris Cédex 05 (France)

3 Université P. et M. CURIE, Département de Géologie Sédimentaire (J.E. Biominéralisations et Paléoenvironnements), Case 116, 4 pl. Jussieu, 75252 Paris Cédex 05 (France)

4 Université de Provence, Centre de Sédimentologie & Paléontologie, CNRS UMR 6019, Centre Saint-Charles, 13331 Marseille Cedex 3 & Museum d'Histoire naturelle de Nice, 60 bd Risso, 06300 Nice (France)

5 Université de Provence, Centre de Sédimentologie & Paléontologie, CNRS UMR 6019, Centre Saint-Charles, 13331 Marseille Cedex 3 (France)

6 Christian-Albrechts-Universität, Institut und Museum für Geologie und Paläontologie, Olshausenstraße 40, D-24118 Kiel, F.R. (Germany)

7 University of North Carolina, Dept of Geological Sciences Rm228, Mitchell Hall, Chapel Hill, NC 27599-3315 (U.S.A.)

8 Universitè de Provence, Centre de Sédimentologie & Paléontologie, CNRS UMR 6019, Centre Saint-Charles, 13331 Marseille Cedex 3 (France)
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 (Renaud & Raféis, 1998) in the bulk carbonate. Whereas the isotope study concentrated on the positive excursion of δ13C 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 δ13C 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 & Renaud, 1980; Renaud, 1985, 1986; Shackleton & Hall, 1990; Strauss & Peters-Köttig, 2003; Pearson et alii, 2005). During these extended periods, heavy carbon isotope ratios are often associated with large amplitude short term (hundred of thousands of years) δ13C 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 CO₂ is then enriched in carbon-13 and the δ13C of the carbonates rises during this period. The effects of volcanism (Weissert & Erba, 2004) and those of continental weathering (Chen 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; Renaud, 1986; Weissert, 1989; Weissert & Channell, 1989; Shackleton & Hall, 1990; Corfield et alii, 1991; Magaritz, 1991; Jenkyns et alii, 1994 & 2002; Bartolini et alii, 1996; Renaud 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 & Knivvolden, 1985; Gornitz & Fung, 1994). As these complexes are stable only over a given range of pressure and temperature (Field & Knivvolden, 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 m3 of methane hydrate produces on the order of 140 m3 of methane gas with very low δ13C (-60‰) values (Dickens et alii, 1995). This methane is then oxidized to form CO₂ (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 δ13C.

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 Callonpec, 1998). There is much more
evidence suggesting that such events occurred at various widely disparate times (WEISSELT, 2000): Proterozoic (KENNEDY et alii, 2001), Toarcian (EMMANNUEL, 1993; JENKYS & 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 Marl’ (MASSE et alii, 1998). The biozonations used in this work (Fig. 2) are those of ROPOL 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 WESSERT & BRÉHERET (1991) from the Vocontian basin, WESSERT & LINI (1991) from the Cismon section, ERBACHER & THUROW (1997) from the Gorgo 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
Figure 5: Detailed comparison of the $\delta^{13}$C record from the La Bédoule and the Cismon section (ERAA & 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 Bédoule 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‰ to -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 -2.4‰).

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...
phenomenon. This pattern is characterized by a relatively large rise throughout the upper Barremian (bed 38, [Mn] = 31 ppm) and lowest Barremian (bed 73, [Mn] = 216 ppm). During the lower Barremian and in the lower part of the upper Barremian 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 Barremian (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 Barremian 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 an hiatus or an intense sedimentary condensation at this level.

III - Interpretation and discussion

The lower part of the upper Barremian (D. deshayesi and base of the R. hambrowi ammonite zones, B. blowi and base of the S. cabri foraminifer zones, nanzone N6b) seems to be the site of substantial geochemical anomalies: a negative excusion of the carbon isotope ratios, two positive excursions of carbonate Mn contents and in a less obvious way an increase of δ18O 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 δ13C values at the Bédoulien/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 Barremian temporarily interrupts this trend. The Δ13C 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 (δ13C ≈ 1%) and increased with fluctuations throughout the early Barremian (δ13C ≈ 1.5%) and late Barremian (δ13C ≈ 2.25‰). The Barremian-Aptian boundary is marked by a decrease in the phenomenon (δ13C ≈ 1.75‰). The record of this decrease is exaggerated in the Cassis stratotype (δ13C ≈ 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 CH4 into CO2 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 Barremian and is recorded both in the Angles section (δ13C ≈ 2.5‰) and the Cassis section. The phenomenon is more marked in the stratotype series (δ13C ≈ 3‰ in the D. tuarayricus 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).

δ13C 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 Barremian, 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 “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 (δ13C = 1.12‰) and at the base of bed 146 (δ13C = 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 (δ13C = 2.30‰) and 151 (δ13C = 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 Barremian (δ13C = 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 Chaîteau: Weisert & Bréheret, 1991), Southern Alps (Cismon: Weisert & 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 δ13C in the late Barremian is a worldwide phenomenon recorded in all sections studied. The negative excusion of the D. deshayesi Zone is more difficult to identify elsewhere because in many Tethyan sections gaps at the base of the Aptian (Delany, 1996) or major slumps (Umbria-Marche Basin: Cresta et alii, 1989; Hadji, 1991) mask the initial phase of δ13C 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 Apticoare 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 nanozoone NC6) in the Cismon Apticoare 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 Hyblla Formation in Sicily show that the equivalent of the Selli level records a negative $\delta^{13}C$ excursion that 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: Brolower 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: Grocke et alii, 1999), from northern Japan marine sediments (Ando et alii, 2002), from Algarve basin coastal 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 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; Rafelis, 2000).

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

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

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 (Rafelis et alii, 2000) or by ESR (Rafelis, 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; Rafelis 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 & Rafelis (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 δ¹³C (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 centimeters or decimeters. The concentration of dissolved manganese in seawater (Mn⁴⁺) fluctuated with the hydrothermal activity at the ocean ridges with some of the element being oxidized as Mn³⁺ and precipitated as MnO₂ particles. However, most of the Mn²⁺ available coprecipitated with the calcite synthesized by pelagic carbonate producers. In the course of sedimentation, the MnO₂ particles are trapped below the redox front where a relatively small proportion is reduced, thereby releasing Mn²⁺ (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 δ¹³C) of the carbonate from the D. deshayesi Zone and the base of the R. hambrovi Subzone with regard to other Bedoulian carbonates.](image)

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 CO₂ 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 MnO₂ particles to be reduced thus releasing a large quantity of Mn³⁺ 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 δ¹³C marking the release of CH₄ 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 δ¹³C 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 δ¹³C 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 (COCCHIONI et alii, 1987) in the lower part of the S. cabri foraminifer level and the upper part of nannozone NC6. In the Cassis-La Bèdoule 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 Grantinarhabdus 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 δ¹³C values are lowest. A similar pattern is observed at Cassis-La Bèdoule 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 δ¹³C excursion and thus appears to correlate, in part at least, with the “nannocyst 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 δ¹³C excursion (MOULLADE et alii, 1998; Fig. 5) owing to the reduced
**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 alli, 1998e). These bioevents, involving the abundance and diversity of - both planktonic and benthic - foraminifers and nannofossils, were contemporaneous with the end of the negative δ13C 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 alli, 1990), may be determined by comparing the record of the evolution of the δ13C 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 δ13C 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 δ13C 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 alli (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 δ13C 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 alli, 1998e). At Cismon, the nannoconid crisis (ERBA, 1994) is coeval with the decrease in δ13C 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 δ13C (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 (RENAUD & RAFLÉS, 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 & RAFLÉS (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 RAFLÉS et alli (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 δ13C excursions. So the sequences proposed in the B. blowi and S. cabri zones (RENAUD et alli, 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 δ¹³C, oxygen isotope data could shed light on this problem. δ¹⁸O evolution indicates surface water warming in the early Bedoulian (of the order of 3° C, KUHN 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, KUHN 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 δ¹³C 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 compatible with the amplitude of the negative excursion in 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 & PEYBERNÉS, 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 δ¹³C 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 CO₂, which was then used by organisms to form pelagic carbonates characterized by low δ¹³C ratios. This oxidation of the methane led to anoxic trends in the environment and many of the MnO₂ particles became unstable. The Mn⁴⁺ released thereby was also incorporated in the pelagic carbonates that developed a positive peak for manganese during the negative excursions of δ¹³C.

The δ¹³C excursion is developed over a length of time (D. deshayesi and base of the R. hambrowi ammonite zones, B. bloi 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 δ¹³C excursion. The Cassis-La Bédoule stratotype appears to be one of the rare series that recorded the entire phenomenon.

Acknowledgements

The authors would like to thank the reviewers for carefully reading the preliminary version of this paper and for their useful advices to improve it. Special thanks are due to N.J. SANDER for his assistance in improving the English text.

Bibliographic references

BERGEN J.A. (1998).- Calcareous nannofossils
BENDER M.L., TEH-LUNG KU & BROECKER W.S.
ANDO A., KAKEGAWA T., TAKASHIMA R. & SAITO T.
BARTOLINI A., BAUMGARTNER P. & HUNZIKER J.
ACCARIE H., RENARD M. & JØRGENSEN N.O.
BOSTROM K. & Petersen M.N.A. (1969).- The
p. 227-255.
BENGUELA D.J., LOMAS M.R. & GRÖCKE D.R.
BARTOLINI A., BAUMGARTNER P. & HUNZIKER J.
BARTOLINI A., BAUMGARTNER P. & HUNZIKER J. (1996).- Middle and Late Jurassic carbon
BERGEN J.A. (1998).- Calcareous nannofossils from the lower Aptian historical stratotype at Cassis-La Bédoule (SE, France).- Géologie Méditerranéenne, Marseille, t. XXV, n° 3-4, p. 227-255.
DICKENS G.R. (2001).- The potential volume of oceanic methane hydrates with external
Paleocene mass extinction in deep sea:


SHACKLETON N. & HALL M. (1990).- Carbon isotope stratigraphy of bulk sediments.-
Proceedings of the Ocean Drilling Program, Initial Reports, College Station, DSDP 113, p. 985-989.


