

The "Schistes carton" of Quercy (Tarn, France): a lithological signature of a methane hydrate dissociation event in the Early Toarcian. Implications for correlations between Boreal and Tethyan realms

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Key words. – Toarcian, Anoxia, Methane hydrates, Stable isotopes, Carbon, Oxygen, Manganese, Subsidence.

Abstract. – The geochemical events (negative shifts in ¹³C and ¹⁸O, and Mn peak) associated with the "Schistes carton" of Quercy (SW France) do not appear to be due only to lithological variations and a differential diagenesis. They correspond to the Lower Toarcian global event and seem to be connected to a destabilization phase of gas hydrates. During its oxidation by seawater, the release of methane gas with a very low carbon isotopic ratio (–60%) led to the production of CO₂ and carbonates with a negative ¹³C. The consumption of oxygen in the seawater resulted in conditions that were first dysoxic and then anoxic. The reduction of burrowing and bioturbation associated with this oxidation resulted in the laminated appearance of the "Schistes carton". The decrease in the oxygen content led to a decrease in MnO₂ microparticles present in the water column and sediments. This created a complementary source of Mn²⁺ that was incorporated into the carbonates produced during this event. Furthermore, an increase in the average seawater temperature (¹⁸O) appears associated with this event. Finally, the apparent diachronism of geochemical events in the Boreal and the Tethyan realms is discussed.

Les "Schistes carton" du Quercy (Tarn-France) : la signature lithologique d'un événement de dissociation d'hydrates de méthane au cours du Toarcien inférieur. Implications sur les corrélations entre les domaines boréaux et téthysiens

Mots clés. – Toarcien, Anoxie, Hydrates de méthane, Isotopes stables, Carbone, Oxygène, Manganèse, Subsidence.

Résumé. – Les événements géochimiques (excursions négatives du ¹³C et du ¹⁸O, pic de Mn) associés aux Schistes carton du Quercy (SW France) ne paraissent pas réductibles aux variations lithologiques et à une diagenèse différentielle. Ils correspondent à l'événement global du Toarcien inférieur et semble en relation avec une phase de déstabilisation d'hydrates de gaz. La libération de méthane gazeux à très faible rapport isotopique du carbone (–60%) conduit, lors de son oxydation par l'eau de mer, à un CO₂ puis à des carbonates à ¹³C négatifs. Cette oxydation en consommant l'oxygène du milieu conduit à des conditions disoxiques puis anoxiques qui permettent, par réduction de la vie fouisseuse et de la bioturbation, l'expression de la lithologie varvée des Schistes carton. La baisse de la teneur en oxygène conduit à une réduction des microparticules de MnO₂ présentes dans la colonne d'eau et les sédiments superficiels, créant ainsi une source complémentaire de Mn²⁺ qui est incorporée dans les carbonates produits au cours de cet événement. Un réchauffement de la température moyenne des eaux marines (¹⁸O) paraît associé à cet événement. Enfin, la réalité du diachronisme apparent des événements géochimiques dans le domaine boréal et téthysien est discutée.

INTRODUCTION

Oceanic anoxic events always correspond to periods during which the carbon isotopic ratio from carbonates (¹³C) shows relatively high values [Schlanger and Jenkyns, 1976; Weissert *et al.*, 1978; Scholle and Arthur, 1980; Renard, 1985; Jenkyns, 1988; Weissert, 1989; Kump and Arthur, 1999]. This is recorded in a huge trapping of ¹²C, accompanied by an increase in fossilized organic matter. These anoxic periods often present very sharp negative shifts in ¹³C, notably in the case of the Toarcian [Jenkyns, 1988; Emmanuel, 1993;

Renard, 1985; Jenkyns and Clayton, 1997; Jones and Jenkyns, 2001; Jenkyns *et al.*, 2002] where the isotopic ratios of carbon in the pelagic carbonates can be lower than –1‰ and even –2‰ at the base of the Falciferum zone and higher than +3‰ to +4‰ at its top.

The coexistence of such different values during such a relatively brief time is difficult to explain. In order to interpret very negative values, the intervention of local upwelling is sometimes postulated [Jenkyns, 1988; Schouten *et al.*, 2000], but most times these are interpreted in terms of diagenesis [Jenkyns and Clayton, 1997]. This is

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notably the case for a series of platforms such as that of Quercy [Emmanuel, 1993], where the negative shift is contemporary with an important change in lithofacies ("Formation de la Barre à Pecten"/"Schistes carton"). The discovery of BSR (Bottom Simulating Reflector) in seismic marine profiles indicating the presence of large quantities of gas hydrates (notably methane hydrates) in the sediments [Kvenvolden, 1988, 2002], puts the traditional interpretations into question. A periodic destabilization of these gas hydrates may have led to an abrupt release into the ocean of a large quantity of methane gas with a very negative ^{13}C . The first investigations on this issue were made by Dickens *et al.* [1995, 1997] for the events in the Late Paleocene, where relatively positive ^{13}C measurements coexist with a very distinctive negative shift [Letolle and Renard, 1980; Shackleton and Hall, 1984; Shackleton, 1986; Stott *et al.*, 1996; Schmitz *et al.*, 1997; Le Callonnec, 1998; Magioncalda *et al.*, 2001]. Indeed, the influence of gas hydrates on the ^{13}C of oceanic carbonates could be much more frequent than initially anticipated [Weissert, 2000] and their intervention is already strongly suspected during the Early Aptian [Jahren *et al.*, 2001; Jahren, 2002; Renard *et al.*, 2005] and in the Oxfordian [Raféllis, 2000; Padden *et al.*, 2001; Hermoso, 2002].

For the Toarcian, Hesselbo *et al.* [2000] showed a widespread occurrence of negative shifts in the ^{13}C of carbonates for various sedimentary environments on the west side of European continent (Wales, England, Denmark, Portugal, Spain). For some of the mentioned countries, a concomitant negative excursion is also recorded in the carbon-isotope values for wood ($^{13}\text{C}_{\text{wood}}$) and marine organic matter ($^{13}\text{C}_{\text{org}}$), and accounted for the observation by dissociation of gas hydrate. In addition, Hesselbo *et al.* [2000] and Beerling *et al.* [2002] modelled the quantities of hydrated methane necessary in order to account for the negative shift in ^{13}C . These results prompted us to investigate the facts more thoroughly and to complete the preliminary geochemical study of the Penne-Château Granier section (Tarn, France) [Emmanuel, 1993].

LITHOSTRATIGRAPHY

The Penne-Château Granier section (fig. 1) is situated along the D33 road to the northeast of the village of Penne (Tarn). The sedimentology and paleontology have already been studied by Cubaynes [1986], Rey *et al.* [1988], Cubaynes and Rey [1994] and Gardin and Manivít [1994]. The biozonation has been reviewed taking into account the works of Elmi *et al.* [1997]. This section (fig. 2) enabled sampling of the "Formation de la Barre à Pecten" (Late Domerian) and the "Penne Formation" (Late Domerian and Early Toarcian).

"Formation de la Barre à Pecten" (18 m thick)

Bioclastic carbonates in decimetric beds dating from the Late Domerian (spinatum zone) to the basal Toarcian (Tenuicostatum zone, Paltus sub-zone and horizon); they can be divided into 4 facies:

- (i) at the base, 6 m of bioclastic carbonates (calcareous biomicrites; wackestone to packstone), alternating with dark laminated marls (sample P1 to P17). This group of beds dates from the Solare sub-zone;

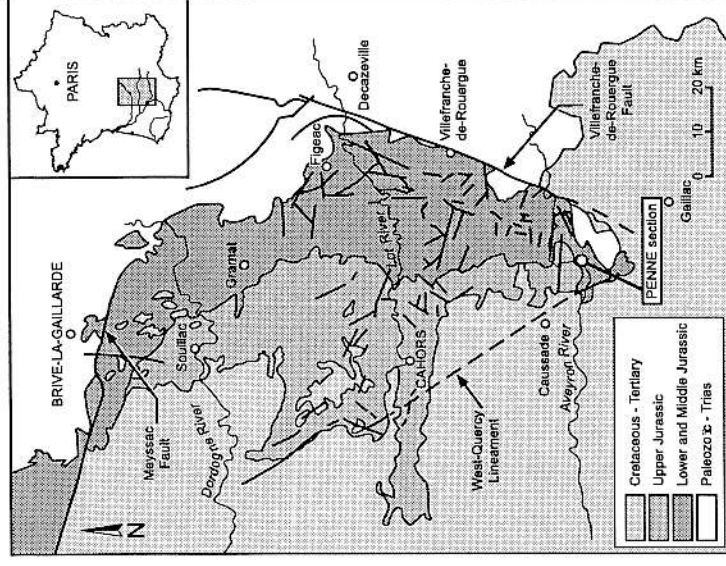


FIG. 1. – Geological framework of the Quercy area and location of the Penne Château-Granier section.

FIG. 1. – Cadre géologique du Quercy et localisation de la coupe de Penne Château-Granier.

- (ii) in the middle, 11.5 m of decimetric fossil-rich beds with cherts and sponge spicules (samples P21 to P63). The presence of *Isocrinus cf. jurensis* indicates a decrease in water depth;
- (iii) in the upper part, 2 m of decimetric beds with cross bedding (samples P65 to P 69) overlain by a hardground [discontinuity D7a, Rey *et al.*, 1988], which was interpreted as a maximum flooding surface;
- (iv) the formation is capped by a layer of red bioclastic marly carbonates (sample P70), overlain by a second hardground, affected by microkarst structures (discontinuity D7b). This layer corresponds to the base of the Toarcian (Tenuicostatum zone, Paltus sub-zone and horizon – horizon 1).

"Formation de Penne"

Toarcian in age, it comprises 3 members ("Schistes carton", "Marnes et Calcaires à Hildoceras", "Marnes noires à Pseudogrammoceras"), only the first two of which are observable in the studied section.

"Schistes carton"

Sapropelic algal facies mainly formed in the Serpentinum zone, *Elegantulum* sub-zone. In this member, the following facies can be distinguished (fig. 3):

- a) a thin lenticular layer of crumby limestone (2 to 5 cm in thickness, sample P71) identified as belonging to the Semiclaturum sub-zone and horizon;

scarce, but very diversified, whereas the terrestrial microflora is almost monospecific [80% *Spheripollenites*; Boutet, 1981]. Four beds can be distinguished from the base to the top:

- (i) 1.80 m of grey Schistes carton (samples P74 to P76) identified as belonging to the elegantulum horizon III. The laminae show millimetric-thick whitish amygdaloides rich in coccoliths and grouped in clusters (crustacean fecal pellets);
- (ii) a reference bed (0.15 to 0.20 m thick, sample P77) of calcareous nodules (biolomicrites: 75 to 80% CaCO₃) with internal stratification parallel to those of the enveloping Schistes carton;
- (iii) 1 m of grey Schistes carton (sample P78), changing to brown with millimetric bedding (sample P79, horizon III);
- (iv) a bed of decimetric condensation [sample P80, discontinuity D8, Rey *et al.* 1988], with a Strangewaysi horizon (horizon IV) fauna and Pseudoserpentinum horizon fauna at the top (extreme base of horizon V).

"Marnes et Calcaires à Hildoceras" (15 m)

At the base of this member there is a condensation layer containing dactyloceratid ammonites (sample Pe7d). The lower part (samples Pe7 to Pe22) is composed of alternating marls and clayey limestones (mudstone-type biomicrites). The marly layers are strato-decreasing until layer 13, where they become strato-increasing. This part of the formation is dated as Falciferum (samples Pe7 to 19) and Sublevisoni (samples Pe 21 to 22) sub-zones.

A layer of grey marls (Pe 23), starting with a bed of bioclastic sand with lignite and reworked fauna, cuts off the underlying beds. A double bed (samples Pe24-26), visible on the regional scale of Quercy, corresponds to a condensed interval very rich in hildoceratids ammonites (base of the Bifrons sub-zone, top of the Lusitanicum horizon). The series continues with alternating marls and clayey limestones with micro-filaments (beds Pe27 to 41) belonging to the Bifrons sub-zone.

GEOCHEMICAL DATA

Materials and methods

After crushing, 1 gram of rock is solubilized using 1N acetic acid for one hour at room temperature. After filtration, the solution is left to evaporate and the residue is put into a hydrochloric acid solution in order to remove the acetates which could interfere with analysis by atomic absorption. The solutions are analysed using a Hitachi Z8100 flame atomic absorption spectrometer. An internal standard is analysed on a routine basis with the series. The margin of analytical error is < 10% for measurements lower than 500 ppm and 5% for measurements between 500 and 1000 ppm.

Isotopic analyses have been carried out using a VG609 mass spectrometer coupled with a configuration for automatic preparation at 50°C of CO₂ by the individual addition of acid for each sample. The analytical precision is ± 0.05‰ for carbon and ± 0.08‰ for oxygen.

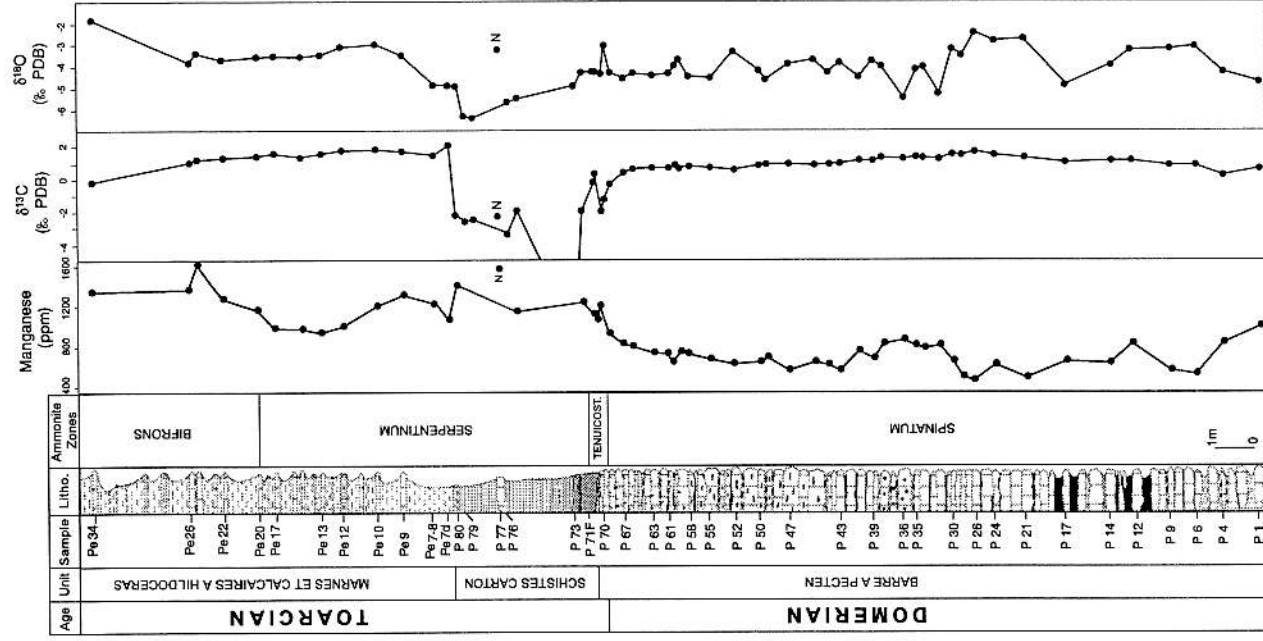


FIG. 2. – The Penne Château-Granier section. Lithologic log and evolution of manganese content and of bulk carbonate ¹⁸O and ¹³C curves. N = nodular limestone.

FIG. 2. – La coupe de Penne Château-Granier. Log lithologique et évolution des teneurs en manganèse et des rapports isotopiques du carbone et de l'oxygène des carbonates. N = nodules.

b) 0.30 m of dark pyritic sandy marls (sample P72) with relatively abundant bioclasts;

c) 0.25 to 0.30 m of pyritic argillites, with a very low carbonate content (8.14% CaCO₃, sample P73);

d) 3 m of Schistes carton (ss): grey to brown laminated argillite, mainly composed of illite, chlorites and a very small proportion of kaolinite, with a carbonate content higher than the previous facies (13 to 14%). The microplankton is

Stable isotopes

Carbon isotopic ratios

A double evolution of carbon isotopic ratios can be observed in the "Formation de la Barre à Pecten". The lower part is characterized by a positive trend from +0.23‰ in sample P2 to +1.52‰ in sample P30. After this point, the trend reverses and the isotopic ratios decrease progressively until sample P52 (+0.58‰). It can be noted that the facies transition between the alternating and lumachella members (sample P17) of this formation is almost unnoticeable in the evolution of ^{13}C . After this, the values stabilize between +0.6 and +0.8‰ until sample P65 and then fall quite sharply at the member with oblique stratifications (-0.28‰ in sample P69) to reach -1.23‰ in the upper limit of "Formation de la Barre à Pecten" (P70s).

The base of the Schistes carton member (granular limestone, horizon II) shows an increase in ^{13}C (+0.32 at the base of bed P71), followed by another abrupt decrease (-1.94‰, sample P72). The pyritic marls in bed P73 (horizon III) have a particularly negative ^{13}C (-9.8‰) then the values stay very low, lower than -2‰ for all of the Schistes carton formation (horizon III, IV and base of V) until bed 80. The carbonate nodules of bed P77 do not have a fundamentally different isotopic ratio than those of the enveloping Schistes carton (fig. 3).

The base of the "Marnes et Calcaires à Hildoceras" unit is marked by an abrupt increase in ^{13}C , which reaches a higher level than that observed in "Formation de la Barre à Pecten" (+2.07‰ in the condensed layer of bed Pe7d).

Afterwards, these values then decrease, first progressively to +1.03‰ in layer Pe26 and then more rapidly (-0.16‰ in layer Pe34).

The extent and rapidity of the increase in ^{13}C between samples P80 and Pe7d indicate the existence of a hiatus which can be confirmed by the thinness of the pseudoserpentinum sub-zone.

Oxygen isotopic ratios

In the "Formation de la Barre à Pecten", the oxygen isotopic ratios have a fairly high variability that attenuates as the beds get younger. In the lower member (mean $\text{d}^{18}\text{O} = -3.90\text{‰}$) and at the base of the middle one (mean $\text{d}^{18}\text{O} = -3.97\text{‰}$), the values fluctuate between -2.44‰ and -5.28‰, whereas in the upper part the fluctuation is limited between -3.35‰ and -5.43‰. In the upper member, the values are very stable (-4.29 to -4.54‰). Finally, the top condensed layer (P70s) is marked by an increase in ^{18}O (-3.08‰). The Schistes carton Formation is characterized by an important drop in the oxygen isotopic ratio, reaching a minimum in layer P79 (-6.4‰). Contrary to what was observed for the ^{13}C , the nodules show a very different ^{18}O (-3.22‰) from those of the enveloping Schistes carton (mean $^{13}\text{C} = -5.98\text{‰}$).

Afterwards, the oxygen isotopic ratios increase very abruptly between samples P80 (-6.3‰) and Pe7d (-4.96‰) at the transition from the Schistes carton to the "Marnes à Hildoceras" (Pseudoserpentinum horizon); then more progressively at the base of the Douvillei horizon until -2.99‰ (sample Pe10). The values then slightly decrease,

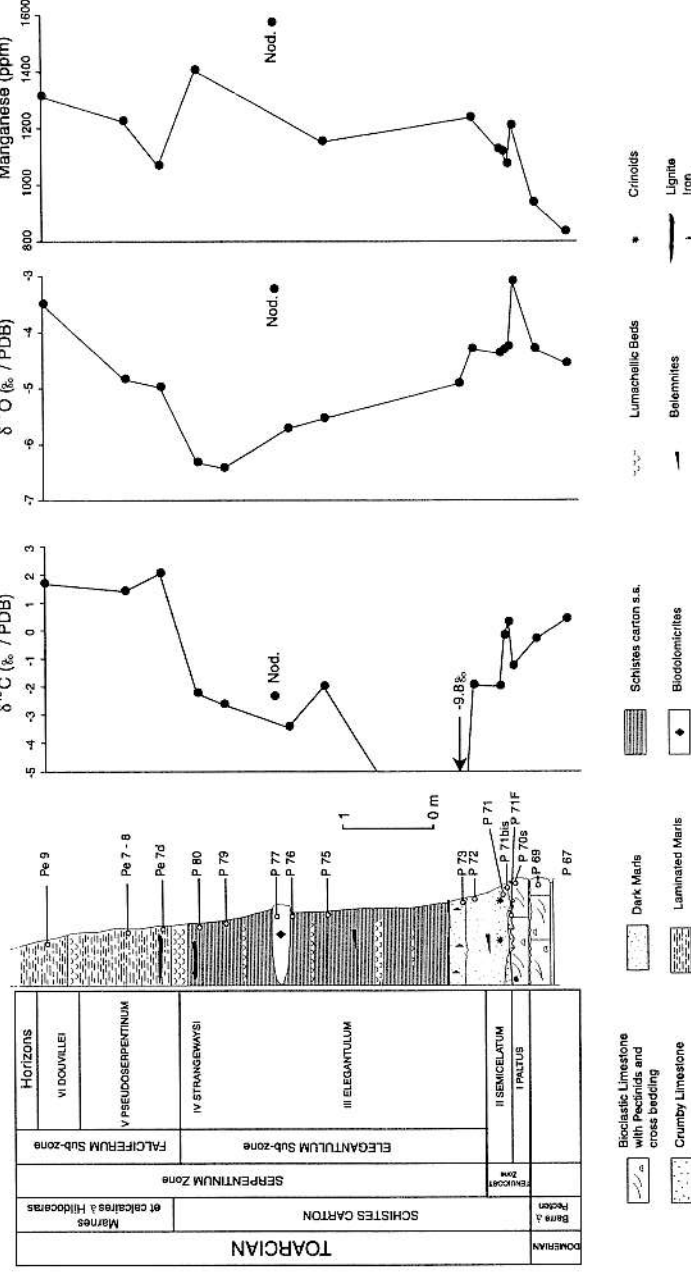


FIG. 3. - Detailed geochemical evolution of the "Schistes carton" formation, N = nodular limestone.
 FIG. 3. - *Détail des évolutions géochimiques au niveau de la formation des Schistes carton. N = nodules.*

stabilizing around -3.50% , before an increase in the Bifrons sub-zone (-1.87%).

Manganese content

The section is characterized by fairly high manganese contents, between 500 and 1500 ppm. The "Formation de la Barre à Pecten" has the lowest values, with a negative trend at the base of the section from 900 ppm (P1) to 469 ppm (P26). A positive shift, centered around sample P36 (868 ppm), develops until sample P43 (569 ppm). A progressive increase then follows until the top of the part of the section studied (top of the Bifrons sub-zone). This progressive evolution is interrupted by positive shifts used by Emmanuel [1993] to geochemically define third order sequences (*sensu* Vail). However, one of these shifts, which corresponds to the Schistes carton member (between samples P70 and P80), clearly interrupts the progressive trends and leads to values that are among the highest in the series (1408 ppm, sample P80). Therefore, we think that the interpretation of this trend in Mn content cannot be restricted to eustatic control alone. Finally, it should be noted that the nodules of the Schistes carton have even higher values (1578 ppm, sample P76).

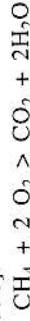
INTERPRETATION

$\delta^{13}\text{C}$: paleoproductivity, methane hydrate dissociation and anoxia

The values of carbon isotopic ratios appear to be very dependent on the lithology (fig. 2). The Schistes carton (fig. 3) are characterized by carbon isotopic ratios that are much more negative (-2.60% on average) than those of the formations enveloping the "Formation de la Barre à Pecten" ($+0.89\%$) and the "Marnes à Hildoceras" ($+1.40\%$). The same is true for oxygen because the Schistes carton have a mean ^{18}O value which is less than that of the "Formation de la Barre à Pecten" (a difference of about 1.15%) and less than the "Marnes à Hildoceras" (a difference of about 1.5%). These data led Emmanuel [1993] to ascribe an important role to differential diagenesis in the interpretation of the negative shift of ^{13}C recorded at the level of the Schistes carton Formation. Moreover, Rosales *et al.* [2001, 2003, 2004] and Bailey *et al.* [2003], by comparison with the isotopic signature of belemnites, have postulated that Toarcian bulk carbonates have not retained their primary marine geochemical composition after burial diagenesis. In a recent work in progress, Hermoso *et al.* [2005], by using the nannofossil isotopic record, argue against this idea. The generalization of observations of such a shift at the base of the Falciferum sub-zone [Hesselbo *et al.*, 2000; Schouten *et al.*, 2000, Jenkyns *et al.*, 2002] is recorded both in the carbonates and the organic matter. Its occurrence in marine to terrestrial environments and the models making an interpretation plausible in terms of a methane hydrate dissociation phase [Beerling *et al.*, 2002], led to minimizing the influence of the lithology and differential diagenesis. Therefore, a negative shift recorded in the Quercy Schistes carton does indeed correspond to a global event in the Early Toarcian. It is also important to note that in Quercy, the shift is not, in a detailed sense, totally in phase with the lithological change because it starts (fig. 2) in the uppermost beds of the "Formation

de la Barre à Pecten" and is preceded by a slow negative shift from the middle of the "Formation de la Barre à Pecten".

During the Domerian ("Formation de la Barre à Pecten"), the organic productivity and fossilization of the organic material in Quercy was very high but not exceptional, because ^{13}C is never above $+1.7\%$, whereas values above $+3\%$ are frequent in the Tethyan realm [Emmanuel, 1988; Monaco *et al.*, 1994; Parisi *et al.*, 1998, fig. 5]. At the base of the Toarcian, a destabilization phase of methane hydrate culminated in a release of methane gas that was rapidly oxidized in seawater and then transformed into CO_2 [Sloan, 1990]:



There are three consequences to this reaction:

- (i) it leads to the production of dissolved CO_2 , and thus to carbonates with a very low carbon isotopic ratio since the ^{13}C of free methane gas is in the order of -60% ,
- (ii) by producing CO_2 , it acidifies the environment and limits the production of carbonates, resulting in very low content (20%) in the Schistes carton Formation.
- (iii) it consumes a large part of the dissolved oxygen, thus allowing the fossilization of the organic matter and the development of an anoxia that makes the activity of burrowing organisms impossible and leads to the laminar facies of the Schistes carton.

After this episode, the organic productivity and the fossilization of organic matter remains at a level higher than during the Domerian, the ^{13}C is more positive ($+2.07\%$) but never reaches values recorded in the Tethys ($>$ to $+4\%$).

$\delta^{18}\text{O}$: mean seawater temperature

We have already pointed out (fig. 2) that the oxygen isotopic ratios recorded in the Schistes carton were on average more negative by about 1 to 1.5% than those recorded in the enveloping formations. In a platform environment such as Quercy, carbonates show a wide range of variations in lithology, types of producers and mineralogic composition. In addition, diagenesis under the influence of continental water can be important, and it is therefore difficult to use this marker in terms of paleoenvironment and paleotemperature reconstructions. Nevertheless, three facts lead us to think that the initial origin of at least one part of this difference is related to an environmental fluctuation:

- (i) such a shift exists in much more open environments, i.e. the Umbria-Marche basin [Emmanuel, 1988];
- (ii) the "Formation de la Barre à Pecten" exhibits the maximum amount of cementation and diagenetic recrystallization. Therefore, it should have the most negative ^{18}O , which has not been observed;
- (iii) in the Schistes carton, the limestone nodules, whose diagenetic origin is not in doubt, have ^{18}O values close to those of samples from the "Formation de la Barre à Pecten", which are much more negative than those of the enveloping Schistes carton.

It seems that at least a part of the negative ^{18}O shift is related to a variation in temperature and/or isotopic ratio of seawater during the Toarcian in the Quercy basin. By using the conventional equations for paleotemperatures [Craig, 1953, 1965; Shackleton, 1973] and considering that the ^{18}O of seawater varied only a little between the Domerian

and the Lower Toarcian, an increase in the mean seawater temperature in the order of 4°C is plausible.

Methane hydrates are only stable under given temperature and pressure conditions [Sloan, 1990; Dickens *et al.*, 1995]. Therefore, this increase in seawater temperature could be one of the causes of the destabilization of its components. It must also have contributed to the development of the anoxia by decreasing the oxygen solubility in seawater. It can be noted that for the Paleocene/Eocene limit event, Dickens *et al.* [1995] assumed an increase of deep seawater temperature of the same order of magnitude.

Manganese: variations in sea level vs anoxia

Oceanic geochemistry of manganese in its soluble form is characterized by the predominance of hydrothermal flux [Bostrom and Peterson, 1969; Bender *et al.*, 1970 and 1977; Lyle, 1976; Klinkhammer, 1980; Klinkhammer and Bender, 1980; Thomson *et al.*, 1986; Von Damm, 1995; Corbin *et al.*, 2000]. Nevertheless, the interpretation of Mn contents in carbonates is complex since this element can be extracted from seawater using two processes:

– (i) the direct precipitation of MnO₂ and MnOOH mixed with the carbonate sediment. These micronodules are partially solubilized during an acid dissolution of carbonates, which introduces a bias in the atomic absorption analysis;

– (ii) The co-precipitation of Mn²⁺ in calcite [Pingitore, 1988] according to the equation:

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

In an oxidizing environment, the first process can play an important role whereas, in a reducing environment only the second intervenes [Michard, 1969]. Nevertheless, studies of manganese speciation in carbonates either by cathodoluminescence [Rafélis *et al.*, 2000] or RPE [Rafélis, 2000] have shown that in the majority of cases, the Mn contents of pelagic carbonates were mainly due to Mn²⁺ co-precipitated in the calcite lattice.

Following the initial studies of Pomerol [1976, 1984], Renard and Letolle [1983], Accarie *et al.* [1989 and 1993] and Pratt *et al.* [1991] that relate manganese fluctuations to variations in sea level, Emmanuel [1993] and Emmanuel and Renard [1993] proposed a geochemical model allowing the characterization of pelagic series into 3rd order sequences [sensu Vail *et al.*, 1977]. The lowstand systems tract is characterized by low, relatively stable contents and the transgressive interval by increasing amounts that culminate at the level of the maximum flooding surface. The highstand systems tract has decreasing contents until a minimum, corresponding to the sequence boundary. Improved Mn speciation by Rafélis [2000] indicates a hydrothermal oceanic origin of manganese and a tectono-eustatic control of the majority of 3rd order sequences during the Mesozoic.

The sequential analysis of the Penne series (fig. 2), based on the fluctuations of manganese contents, was then proposed by Emmanuel [1993]. He had already pointed out the problem posed by the Schistes carton in which a manganese peak, contemporary with the negative ¹³C shift, appeared to be superimposed on the general trend related to the hydrothermal/eustatic control. Figure 4 shows the peculiar geochemical composition of the Schistes carton facies. It should be noted that the processes involved begin at the summit of the "Formation de la Barre à Pecten" (beds P69 and P70s)

and therefore, in order to explain variations in both ¹³C and Mn, the process cannot be restricted to the change in lithology. Compatibility between the negative shift of ¹³C and an important peak of Mn contents in carbonates has already been pointed out for the Early Toarcian at the Valdorbia section (Umbria, Italy) by Emmanuel [1988] and in the Early Aptian of the "la Bédoule" stratotype section (France) by Renard and Rafélis [1998] and Renard *et al.* [2005].

Therefore, the high Mn contents do not correspond to a simple increase in hydrothermal input during the most active expansion phase of the mid-oceanic rifts but imply an additional source of sedimentary or early diagenetic Mn related to the event responsible for the negative ¹³C shift. The following scenario can be envisaged: during the Domesian, productivity is average in the Quercy basin. A consequential amount of the organic matter produced is not oxidized. This fossilization of organic material traps the ¹²C, inducing positive values of ¹³C. The decomposition of organic matter does not consume enough oxygen to cause anoxia, therefore the redox front is situated inside the sediment, at several decimeters or centimeters depth. The amount of dissolved manganese (Mn²⁺) in seawater fluctuates depending on mid-oceanic rift hydrothermal activity. A part is oxidized into Mn⁴⁺ and precipitates in the form of MnO₂ particles. However, most of the Mn²⁺ co-precipitates

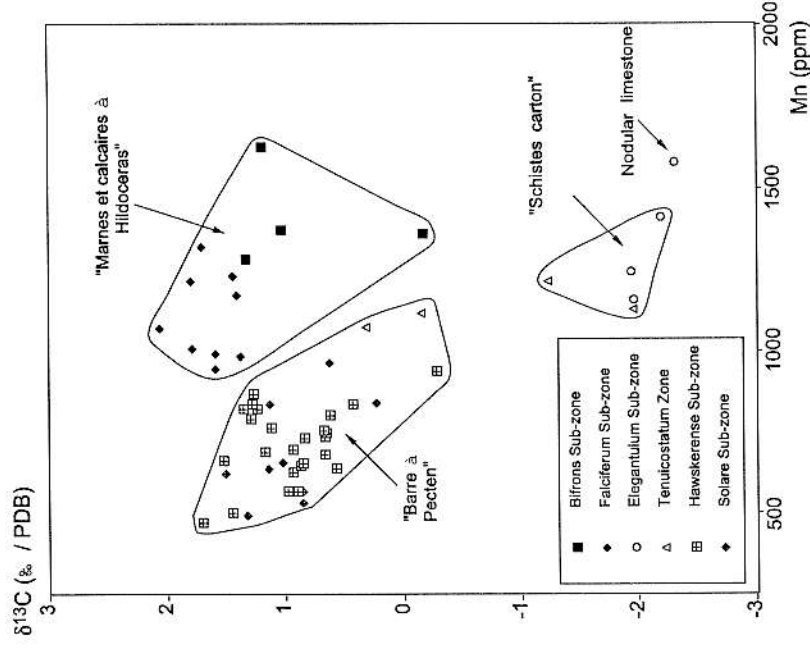


FIG. 4. – Relationship between Mn content and carbon isotope ratios for the various facies of the Penne Château-Granier section. Note the particularity of the Schistes carton facies and the associated nodular limestone.

FIG. 4. – *Teneurs en Mn et rapport isotopique du carbone dans les différents faciès de la coupe de Penne Château-Granier. On notera les particularités du faciès Schistes carton et les nodules associés.*

with calcite synthesized by carbonate producers. During sedimentation, particles of MnO₂ pass under the redox front and, a relatively small part of them is reduced, thus releasing Mn²⁺ that is retroceded by diffusion inside the sediment to the oceanic system and incorporated in the calcite [Burdige, 1993].

In Late Domerian and Early Toarcian, for a reason that has yet to be elucidated (cf infra), an abrupt destabilization of gas hydrates released methane gas with a very low carbon isotopic ratio (–60‰). In the seawater, this methane is oxidized to CO₂ that participates in the production of carbonates with the lowest carbon isotopic ratios. Methane oxidation involves an increased consumption of oxygen and the environment becomes dysoxic or even anoxic. This agrees with Pancost *et al.* [2004] who discuss the occurrence of a photic zone anoxia on the base of chlorophyll and bacteriochlorophyll degradation product analysis. The redox front moves up to the sediment/water interface or even into the water column. The majority of MnO₂ particles are then reduced, thus releasing a large additional quantity of Mn²⁺ that is integrated into the lattice of carbonates produced during this period. It can be noted that a time lag exists between the two processes (fig. 2 and 3): the maximum amplitude of the negative ¹³C shift (marking the release of CH₄) is situated at the base of the Schistes carton, whereas the manganese peak (related to a lowering of oxygenation in the environment) only culminates at the top of this formation. A scenario of this type is also proposed by Vető *et al.* [1997] to account for the manganese ore deposits at this time in the Bakony Mounts (Hungary) and by Renard *et al.* [2005] in order to explain the Mn peak in the Upper Bedoulian of the stratotype region.

CAUSES OF THE DESTABILIZATION OF GAS HYDRATES DURING THE TOARCIAN

Even if the present-day estimations of hydrated gas reservoirs [Paull *et al.*, 2000; Hovland *et al.*, 1999; Sloan *et al.*, 1999] tend to be downsized, models [Beerling *et al.*, 2002] show the likelihood of scenarios proposed for both the Toarcian and the Aptian. The main problem remains the identification of the cause of the destabilization of gas hydrates. We have already pointed out that these compounds, trapped in the sediments, were only stable in a limited domain of temperatures and pressures. In the case of the Late Paleocene event, the warming of bottom waters that seem to be a trigger for the release of methane gas, appear to be related to a modification of the circulation of bottom waters (high vs low latitude deep water formation). In the case of the Toarcian, it is difficult to question an oceanic event of this type because the oceanic circulation is totally different and the sedimentation develops in a group of small subsiding basins [Bassoulet *et al.*, 1993]. Therefore, we think that a combination of phenomena exist, and this cast doubts on the role of a minor controlling factor such as oceanic warming (cf oxygen isotopes) and a major controlling factor of tectonic origin such as suggested by Hesselbo *et al.*, [2000].

Palfy and Smith [2000] and Jahren [2002] have also attempted this type of explanation for the Toarcian and the Bedoulian, respectively, by interpreting the negative ¹³C event as a result of super plumes. These plumes initiated the formation of the Karoo-Ferrar basalts during the Toarcian and the oceanic volcanic plateaus of Kerguelen and

Ontong-Java during the Aptian-Albian [Larson, 1991a and b]. The epigenesis of the ocean floor related to the super plume (because of the decrease in hydrostatic pressure) resulted in a release of a quantity of methane compatible with the negative shift in amplitude in the Bedoulian. Nevertheless, Jahren [2002] recognizes that such a process stretches over a period of time that is not compatible with the brevity of the negative ¹³C shift observed. Two other hypotheses are proposed by this author, the first consisting of a very rapid and local epigenesis in an hypothetical oceanic region, particularly rich in methane hydrate. The second involves sediment warming during a depositional phase of a particularly large quantity of basalts during the formation of the Kerguelen and Ontong-Java plateaus (120-80 Ma). Renard *et al.* [2005] noted that a period of tectono-seismic instability in the Tethyan, Atlantic [Masse *et al.*, 1993] and Pacific [Vaughan, 1995] could signal a tectonic controlling factor for the Aptian event.

The case of the Early Toarcian seems fairly similar because it is also an important period of structural rearrangements resulting in the fragmentation of Lower Lias carbonate platforms in both the Boreal and Tethyan realms [Bassoulet *et al.*, 1993]. The preliminary data of Le Solleuz [2003] and Le Solleuz *et al.* [2004] support the Hesselbo *et al.* [2000] idea that tectonic control (variations in subsidence) must be invoked as an explanation. An increase of temperature of several degrees (induced by an advection of hydrothermal fluids) and a fault disruption of the sedimentary pile would lead to the destabilization of gas hydrates.

In comparison with purely thermal deep mantle superplume-type hypotheses [Palfy and Smith, 2000; Jahren, 2002], the proposed hypothesis has the advantage of being compatible with the relative brevity of the isotopic event and its apparent synchronism in different western European and Tethyan regions (cf infra). However, an alternative explanation is recently proposed by Mc Elwain *et al.* [2005]. These authors suggest that injection of isotopically light carbon from the release of thermogenic methane occurred owing to the intrusion of Gondwana coals by Toarcian-aged Karoo-Ferrar dolerites.

STRATIGRAPHIC IMPLICATIONS: CORRELATIONS FOR THE BOREAL AND TETHYAN REALMS

The problem of synchronism in the Lower Toarcian anoxic event and more precisely the ¹³C negative shift becomes obvious when the data obtained in Quercy and the Tethyan reference section in Valdorbria [Umbria, Italy; Emmanuel, 1988 and unpublished data] are compared (fig. 5). This problem has already been raised in a study made by Macchioni [2002], which includes references on what is to follow. All the studies on the Umbria-Marche basin identify an anoxic event and a ¹³C negative shift as belonging to the Tenuicostatum zone (cf Valdorbria, fig. 5). In contrast, in the majority of cases, the authors working on northern Europe sites place them in the Serpentinum zone. Elegantulum sub-zone (cf Quercy, fig. 5).

There is no simple explanation for this diachronism because it is superimposed on a biostratigraphical problem. Macchioni [2002] points out dating ambiguities in numerous studies, i.e. the species used to assign the anoxic event to the Serpentinum zone is not always indicated. In addition,

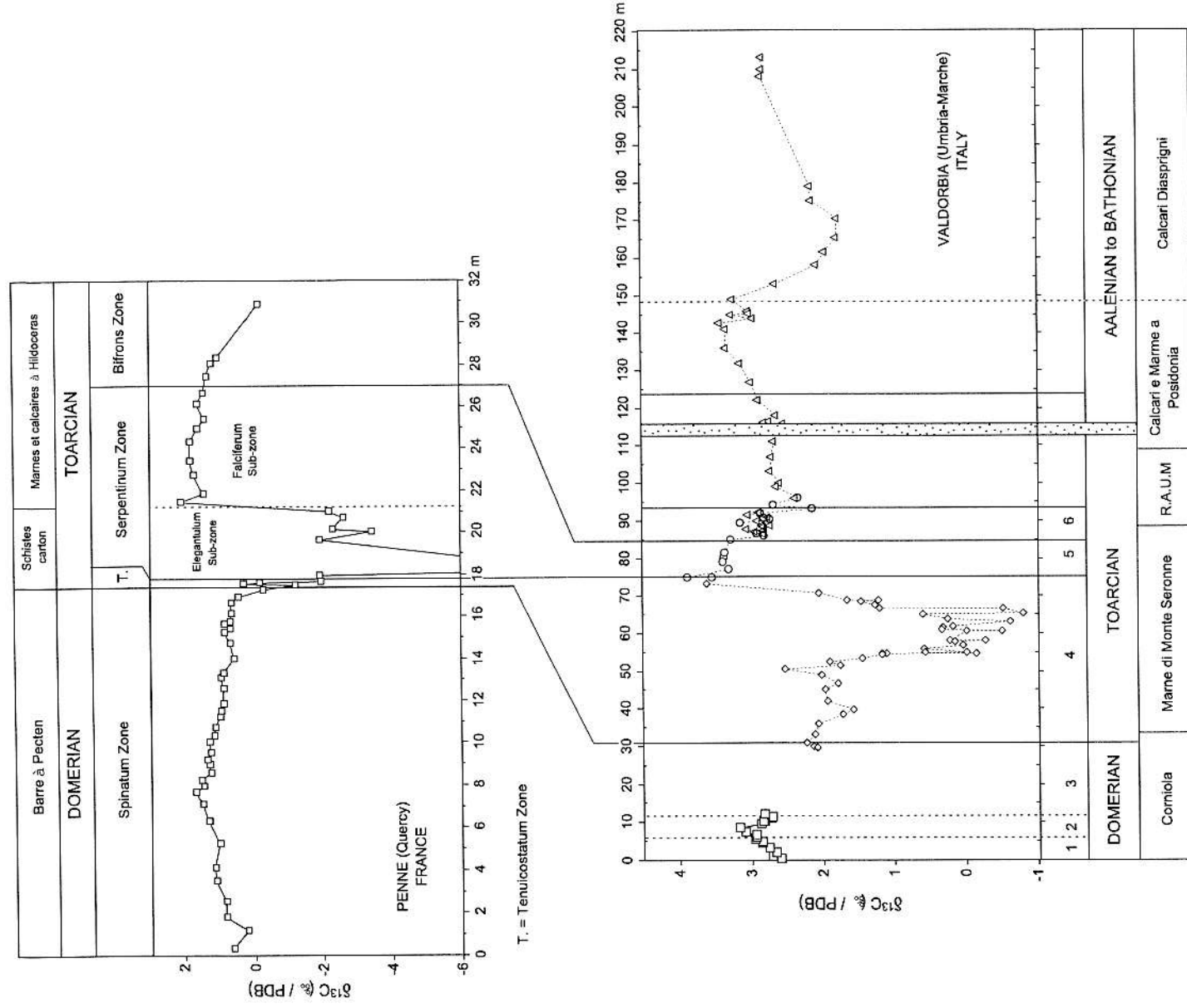


FIG. 5. — Comparison between the evolution of ^{13}C curves for Penne Château-Granier section (Quercy, France) and Valdorbria section (Umbria-Marches basin, Italy). Note the stratigraphic discrepancy of the isotopic minimum between the two realms. Biostratigraphic zonation for Valdorbria section: 1: Lavinianum Zone, 2: Algovianum Zone, 3: Emaciatium Zone, 4: Tenuicostatium Zone, 5: Serpentinum Zone, and 6: Bifrons Zone; R.A.U.M.: Ammonitico Rosso of Umbria-Marches area (Rosso Ammonitico Umbrò Marchigiano).

FIG. 5. — Comparaison de l'évolution des rapports isotopiques du carbone dans la coupe de Penne Château-Granier (Quercy, France) et dans celle de Valdorbria (Ombrie-Marches, Italie). On notera le décalage stratigraphique du minimum isotopique entre les deux domaines. Zonation biostratigraphique pour la coupe de Valdorbria: 1: zone à Lavinianum, 2: zone à Algovianum, 3: zone à Emaciatium, 4: zone à Tenuicostatium, 5: zone à Serpentinum et 6: zone à Bifrons; R.A.U.M.: Ammonitico Rosso d'Ombrie Marches (Rosso Ammonitico Umbrò Marchigiano).

he insists on the presence of frequent hiatuses in the sections studied in the West European realm (like at Penne

where the Tenuicostatium zone is very poorly represented). For this author, the apparent diachronism between the two

realms is not as important as has been thought in the past and it originates mainly from the erroneous interpretation of data in the Mediterranean realm. It is precisely here (in the Migiana di Monte di Malbe section, Italy) that the occurrence of species common to both realms puts into question for the first time correlations established between Boreal and Mediterranean scales. This study, which is still in progress, is crucial for the elucidation of explanatory scenarios for the Toarcian crisis. Does the apparent diachronism of geochemical records (fig. 5) correspond to a true diachronism of the events or is it only an artifact related to a stratigraphical bias in the correlation of paleontological Boreal and Mesogean scales?

In the first case, within the boundaries of the proposed scenario, this leads to the admission of a slight lag in different subsidence regimes between the Boreal and Mesogean realms. In the second case, variations in subsidence regimes are in phase with the two realms.

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