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Geochemical characterization (Mn content) of third order eustatic sequences in Upper Jurassic pelagic carbonates of the Vocontian Trough (SE France).

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Key words: Vocontian basin, geochemistry, manganese, pelagic limestones, Jurassic, Oxfordian-Kimmeridgian boundary, sequence stratigraphy Mots clés: Bassin vocontien, géochimie, manganèse, carbonates pélagiques, Jurassique, limite Oxfordien-Kimméridgien, stratigraphie séquentielle

ABSTRACT

The manganese contents of the Oxfordian-Kimmeridgian pelagic carbonates in the section at Châteauneuf d'Oze (Vocontian Basin, Hautes Alpes, France) are used to define 11 geochemical units. These units are interpreted in terms of sequence stratigraphy and grouped into 6 third-order sequences, which then are compared with those of the sequence-chronostratigraphic chart of Hardenbol et al. (1998). Using this approach, two modifications to the chart are proposed:

(i) the Oxfordian-Kimmeridgian boundary in the Tethyan realm should be set in the upper part of the Hauffianum subzone, as clearly proposed by biostratigraphic studies from Wierzbowski (1991), Atrops et al. (1993), and Schweigert & Callomon (1997),

(ii) a new sequence (Kim2') should be introduced in the Hypselocyclum zone, and the sequence Kim2'' (Hypselocyclum - Divisum zones) becomes the equivalent of the cycle chart Kim2 sequence.

RESUME

Les teneurs en manganèse des carbonates pélagiques de la série oxfordokimméridgienne de Châteauneuf d'Oze (Bassin du Sud-Est, Hautes Alpes, France) permettent de définir 11 unités géochimiques qui sont regroupées en 6 séquences de troisième ordre puis confrontées aux données de la charte chronostratigraphique (Hardenbol et al. 1998). Cette approche montre la nécessité:

(i) de corriger sur la charte la position de la limite Oxfordien-Kimmeridgien en domaine téthysien en accord avec les travaux de Wierzbowski (1991), Atrops et al. (1993) et Schweigert & Callomon, (1997) qui proposent dorénavant de placer la limite au sommet de la sous-zone à Hauffianum.

(ii) d'introduire une séquence supplémentaire au niveau de la zone à Hypselocyclum qui contiendrait alors les limites de deux séquences, Kim2' et Kim2'', cette dernière étant l'équivalent téthysien de la séquence Kim2 de la charte de Hardenbol et al. (1998).

Introduction

In pelagic and hemipelagic series, facies homogeneity makes it difficult to characterize third-order sequences (sensu Vail 1987) by purely sedimentogical observation. Various studies (Accarie et al. 1989, 1993; Emmanuel 1993; Emmanuel & Renard 1993; Corbin 1994) show that the geochemistry of carbonates and, in particular, variations in the content of manganese of the carbonate rocks, could be a powerful tool. When coupled with bedding patterns, this method allows the characterization of sequences and the systems tracts composing them. This geochemical approach is applied to an Oxfordian-Kimmerdigian hemipelagic series in the Vocontian Trough: geochemical units are first identified and interpreted in terms of third-order sequences, and this pattern is then compared to sequence-chronostratigraphic chart of Hardenbol et al. (1998).

This paper is a contribution to a more general project that aims at a sequence-stratigraphic correlation of the Upper Oxfordian and Lower Kimmeridgian between the Boreal and the Tethyan realms. The concept of this multidisciplinary project (De Rafélis et al. 1998; Bombardiere 1998; Bombardiere & Gorin 1998; Jan du Chêne et al. 2000) is similar to the one applied by the same working group for the study of the Berriasian of S-E France (Jan du Chêne et al. 1993).

Litho- and biostratigraphic framework

The Châteauneuf d'Oze section is located along the road D20 (geological map n°869, Gap, 1/50000, 44°31' N-5°53' E; Fig. 1). It is a reference section of the Oxfordian-Kimmeridgian boundary and Lower Kimmeridgian in the subalpine domain because it contains a large quantity of ammonites. Located north of the Serres shoal, it is representative of sections with moderate sedimentation rates: a 7m-long interval correspond-

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Fig. 1. Location map of the Vocontian trough, SE France, showing the Châteauneuf d'Oze section.

ing to the Lothari subzone (Fig. 2) for a 300 ky duration estimated by cyclostratigraphy compared to numerous sections as Serres (condensed section with a 3m-long sedimentary interval corresponding to the Lothari subzone) and La Cluse (expanded section with an up to 30m-long interval corresponding to the Lothari subzone) studied by Moussine-Pouchkine et al. (1998) in the same area.

The studied interval (Fig. 3) extends from the early Oxfordian (Bimammatum zone) to the base of the late Kimmeridgian (Acanthicum zone ; Atrops 1982). At the base of the section, a marly interval (beds 44 to 58) provides a rich ammonite fauna which characterizes the upper part of the Bimammatum subzone. At the top of the series, sediments of Berriasian age (bed 196b) discomformably overly sediments of late Kimmeridgian age (bed 196a ; Remane 1966, 1970). The intervening hiatus is attributed to the erosive activity of a submarine canyon (Beaudoin 1977).

The 96 m-long section is composed of marl-limestone alternations. A 3 m-thick slump deposit (bed 150) extends over several kilometers (Pederneiras Raja Gabaglia 1995) and is situated within the Hippolytense subzone (early Kimmeridgian). At Châteauneuf d'Oze, the erosional gap related to the slump event is limited to a part of the Hippolytense subzone, but on a regional scale, the erosion can include sediments belonging to the Bimammatum zone sediment (late Oxfordian).

Two major lithological units are distinguished:

- a lower group (beds 37-127), in which the alternating beds are generally dominated by limestones;
- an upper group (beds 128-196a), in which the marly intervals are generally thicker than the limestones.



Fig. 2. Correlation between the Tethyan and boreal ammonite zonation (from Wierzbowski 1991, Atrops et al. 1993, Hantzpergue et al. 1997 and Schweigert & Callomon 1997) and location of the sequence boundaries proposed by Hardenbol et al. (1998).

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Fig. 3. Biostratigraphy, lithostratigraphy and trends of manganese contents of pelagic limestones in the section of Châteauneuf d'Oze: (A) Biostratigraphic framework according to the recent studies of Wierzbowski 1991, Atrops et al. 1993 and Schweigert & Callomon 1997; (B) Biostratigraphic framework used in the sequence-chronostratigraphic chart (Hardenbol et al. 1998); (1) geochemical units ; (2) sequence stratigraphic framework based on stratonomy and biostratigraphy (from Jan du Chêne et al. 2000) ; (3) systems tracts and (4) sequences established by Mn record ; (5) third order sequences of the cycle chart after Hardenbol et al. 1998 ; (6) proposed sequence stratigraphic framework.

Solid line: sequence boundary (SB) - Dotted line: maximum flooding surface (MFS)

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Fig. 4. Mn-contents evolution curve in pelagic limestones during a third-order sequence (from Emmanuel 1993).

The homogeneity of carbonate mineralogy (low magnesian calcite) and facies (moderately bioturbated micrites with low TOC contents (< 0,2% wt., Bombardiere 1998) makes this series well suited to geochemical studies. All limestone beds were systematically sampled (145 samples). The carbonate fraction from the samples has been dissolved in 0,5 M acetic acid for one hour (Richebois 1990). Manganese analyses were performed on a Hitachi Z-8100 model polarized Zeeman atomic absorption spectrophotometer. The average standard deviation of the manganese analyses is 2%. It is obtained by systematic measurements of an internal standard (chalk of the late Cenomanian of France) comparable to Châteauneuf d'Oze samples for CaCO₃ and Mn contents (90% and 500 ppm respectively).

In addition to this method, several samples were analysed using sequential leaching and cathodoluminescence (see below) in order to verify the location and the oxydation state of manganese.

Manganese and sequence stratigraphy

The behaviour of manganese is complex in the sedimentary environment (Michard 1969). It can easily be:

- precipitated directly in the form of Mn dioxide (MnO₂) and various oxy-hydroxides (MNOOH),
- incorporated into the calcite lattice by the substitution of calcium atoms, according to the formula Ca_(1-x)Mn_xCO₃ (with x<<1).

The first process dominates the oxidizing environment, the second occurs mainly under suboxic or reducing conditions (associated with diagenetic MnCO₃ precipitation under highanoxic conditions). It is generally accepted that variations in Mn-content of pelagic carbonates record the levels of oxidation in seawater and/or interstitial waters. Initially, attention was mainly given to diagenetic processes (Brand & Veizer 1980) at the water-sediment interface and the redox transition zone of marine sediments (Pingitore 1978; Calvert & Pedersen 1993).

Despite the numerous studies of natural environments and laboratory experiments, the coefficient of Mn²⁺ incorporation into carbonates is still poorly understood. It seems to be controlled by the rate of precipitation and the Mn/Ca ratio of the parent solution (Pingitore 1978; Lorens 1981; Franklin & Morse 1983; Mucci 1988; Pingitore et al. 1988). The Mn-content of seawater varies from 0.2 to 15 ppb with an average of 3 ppb, and the oceanic residence time is short (in the order of 1000 years ; Brown 1989). In oceanic environments, Mn is mainly of hydrothermal origin, hydrothermal input (1.4 x 10¹¹ moles-year) being about 30 times higher than that of rivers (4.9 x 10⁹ moles-year; Von Damm 1995). In addition, the major part of terrestrial manganese is trapped inside estuaries and coastal sediments. The hydrothermal influence on Mn contents of pelagic sediments is detected up to 2,000 km away on either side of the spreading ridge (Lyle 1976; Klinkhammer 1980). Consequently, manganese concentrations in pelagic sediments depend directly on the distance of the sedimentation area from the ridge, and on the spreading rate (Bostrom & Peterson 1969; Bender et al. 1970; Andrianiazy & Renard 1984; Emmanuel & Renard 1993).

Using examples from the Lower Cretaceous sediments of the Vocontian Trough, Emmanuel (1993) characterized sedimentary systems tracts composing third-order sequences using the Mn content of the carbonate phase (Fig. 4): (1) the lowstand systems tract (LST) is characterized by low and relatively constant contents, (2) the transgressive systems tract (TST) by an increase in Mn content, (3) the maximum flooding surface (MFS) by maximum concentrations, (4) the highstand systems tract (HST) by a decrease in concentrations, and (5) the sequence boundary (SB) at the end of this decreasing trend. A similar pattern was found in various pelagic series, e.g. in the Middle Jurassic of the Vocontian Trough (Corbin 1994), the Late Cretaceous of the London and Paris Basins (Barchi 1995), the Paleocene of the Biscave Bay (Le Callonnec 1998), the Cenomanian deposits of the Vocontian Trough (Morel 1998), and the Isle of Wight (Jarvis & Murphy 1999). Because of the predominance of hydrothermal control on the chemistry of marine manganese, this model implicitly assumes that the

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control on third-order sequences is of tectono-eustatic origin. This concurs with propositions made by Harrison (1990) who correlates variations in spreading rate of oceanic ridges with third-order sea-level cycles.

Using samples from Châteauneuf d'Oze section, we have developped a parallel approach using cathodoluminescence (de Rafelis 2000; de Rafélis et al. 2000). The results have shown that almost all the manganese obtained after acid leaching corresponds to Mn^{2+} co-precipited into calcite lattice. Therefore, Mn-variations shown in figure 3 cannot be solely related to sedimentary condensations but also reflect fluctuations of the amount of disolved manganese in seawater.

Results: identification of geochemical units

Manganese contents of Oxfordian-Kimmeridgian limestones at Châteauneuf d'Oze fluctuate between 170-866 ppm (Fig. 3). Two major geochemical zones are distinguished:

the first corresponds to the base of the section (beds 37–127), where the Mn content is low, between 180-350 ppm with minor variations;

the second, from bed 128 to the top of the outcrop (bed 196), is characterized by much higher amounts of Mn (430–866 ppm) and variations of higher amplitude.

The transition between these two zones is indicated by a sharp increase at bed 128 ($\Delta = 210$ ppm). These two geochemical zones correspond to the two lithological groups previously described (Fig. 3).

The short-term evolution is obtained by subdividing Mncontent curve into geochemical units defined by successive positive to negative excursions. Following this method, 11 geochemical units are identified in the Châteauneuf d'Oze section (Fig. 3, col. 1). The general evolution of Mn contents is often surimposed by high frequency fluctuations (i.e. units 8 and 10).

Geochemical unit 1 is incomplete, its base not having been sampled. The Mn content increases slowly at first, and then abruptly from the upper part of bed 41, reaching a maximum (356 ppm) at bed 48. Its upper boundary (bed 51) has of low Mn content (178 ppm).

Unit 2 (beds 52-61) shows a symmetric evolution, but the contents are less than in the previous unit (maximum 328 ppm in bed 56).

The Mn concentrations in the carbonate phase of the following four units are uniformly low.

Unit 3 (beds 61 to the top of bed 83): the variability is very low (maximum 282 ppm in bed 67 and minimum 157 in bed 83).

Unit 4 (beds 84-89a): the Mn content remains low (maximum 239 ppm).

Unit 5 (beds 89a-113a): despite the low values, the Mn-content curve once again becomes symmetrical on either side of the maximum of 368 ppm (bed 100a).

Unit 6 (beds 113-127c): the values remain very homogeneous, averaging around 270 ppm.

Unit 7 (beds 127c-135): this unit is characterized by an increase in values starting at the abrupt shift in the curve between beds 127 (270 ppm) and 128 (483 ppm). This represents the major geochemical shift of the series. It corresponds to the boundary between the two lithological groups previously described. The maximum value (643 ppm) is located in bed 134, but the upper boundary is poorly defined because of the absence of sampling in bed 135.

Unit 8 (bed 135 to the base of bed 150): after the relative lower values

(500-580 ppm) of beds 135-139, which allow the identification of the boundary of this geochemical unit, the values increase until bed 147 (725 ppm). They decrease until the base of bed 150 (601 ppm), directly under the slump.

Unit 9 (beds 150-160): Its basal part is poorly defined from a geochemical point of view, because of the presence of the slump. The beds capping the slump (151–154) continue to have relatively low values (around 520 ppm). Concentrations increase regularly until bed 159 (803 ppm) and then drop abruptly (549 ppm) at the overlying bed, which marks the upper boundary of the unit.

Unit 10 (beds 160–176top) displays three fluctuations of increasing amplitude (671 ppm for bed 163; 801 ppm for bed 165; 866 ppm - maximum value for the series - bed 172). This unit ends with a drastic drop in concentrations (385 ppm);

Unit 11 (beds 176top–196a): the values remain relatively constant (around 400 ppm) until bed 184, after which the concentrations progressively decrease from 661 ppm (bed 185) to 307 ppm (bed 196a).

Discussion:

Significance of geochemical units related to sequence stratigraphy

Jan du Chêne et al. (2000) propose a sequential analysis (thirdorder sensu Vail) of the Chateâuneuf d'Oze section based on stratonomy and biostratigraphy (Fig. 3, col. 2). The aim of the present study is the comparison of this sequential framework with the one based on the evolution of a geochemical marker linked to the sealevel variations: manganese. A similar approach using sedimentary organic matter has already been made on the same section (Bombardiere & Gorin 2000).

Using the model established by Emmanuel (1993) and Emmanuel & Renard (1993), we propose an interpretation of the previously described geochemical units (Fig. 2, col. 3 and 4) in terms of sequence stratigraphy (third-order sequences wich are indexed OZE). This proposition is compared both to the stacking patterns approach (fig. 3, col. 2) and to the sequencechronostratigraphic chart of Hardenbol et al. (1998, Fig. 3, col. 5).

- Third-order sequence OZE 1:

Geochemical units 1 and 2 may represent the same depositional sequence OZE 1. Therefore, geochemical unit 1 contains the maximum-flooding surface (bed 48), whereas the geochemical unit 2 represents a parasequence of the corresponding HST. The boundary of this third-order sequence is at bed 61.

- Third-order sequence OZE 2:

Very low values of Mn persist in geochemical units 3 to 6. However, a slightly increase of Mn-content starts at geochemical unit 4. Two sequential interpretations are possible: the manganese-poor geochemical units (3 to 6) represent one large LST, the transgressive surface being situated at the level of the major geochemical shift of the series (base of bed 128); the slightly progressive increase of values observed in geochemical units 4, 5 and 6 represents parasequences of a TST. In this interpretation, the LST would be limited to geochemical unit 3 (which could also include unit 4). The best candidate for a transgressive surface is bed 83 (the minimum Mn value not being observed at the boundary of the sequence, as is commonly the case, but at the top of the next LST). Geochemical unit 7 corresponds to the two last parasequences of the TST (with a maximum-flooding surface at around bed 134). The HST is limited to bed 135. The top of bed 135 corresponds to the boundary of this third-order sequence.

- Third-order sequence OZE 3:

Geochemical unit 8 appears to represent a new third-order sequence composed of a thin lowstand systems tract (beds 135-139), a TST (with at least 3 parasequences), a maximum-flooding surface in bed 147 (Mn = 727 ppm) and a HST, probably incomplete, due to the gullying of the slump at bed 150. Associated with the low Mn values of the underlying beds, this provides an argument for the location of the boundary of the next sequence.

- Third-order sequences OZE 4 and OZE 5:

Two interpretations are possible for geochemical units 9 and 10: they can be considered together as one third order sequence (OZE 4) whose transgressive surface is situated around bed 154 in geochemical unit 9 and the maximum flooding surface around bed 172 in geochemical unit 10; however, considering the small-scale fluctuations of the manganese curve, it seems more likely that geochemical units 9 and 10 correspond to two third-order sequences. The first (OZE 4) has its maximum-flooding surface located at level 159 (803 ppm) and ends at the top of bed 160 (549 ppm). The second (OZE 5) does not present a lowstand systems tract but has a well-developed TST with three clearly identifiable parasequences. – Third-order sequence OZE 6:

Unit 11 seems, at least in part, to represent a third-order sequence whose maximum-flooding surface is located at level 185, but the gullying by the overlying Berriasian sediments does not allow its upper boundary to be clearly identified.

The biostratigraphic framework and comparison of sequence interpretations based on geochemistry with the sequencechronostratigraphic chart of Hardenbol et al. (1998)

The position of the Oxfordian-Kimmeridgian boundary in the Tethyan realm in relation to boreal ammonite zones has long been the object of discussions (see synthesis in Hantzpergue et al. 1997). In the Tethyan realm, the boundary is usually placed at the base of the Platynota zone, making it equivalent to the base of the Baylei zone in the Boreal area. Recent studies (Wierzbowski 1991 ; Atrops et al. 1993 ; Schweigert & Callomon 1997) suggest, however, that the complete Planula zone already belongs to the Kimmeridgian (Fig. 2) and that the Oxfordian-Kimmeridgian boundary should be located in the upper part of the Hauffianum subzone (Bauhini horizon). As a matter of fact, the association in northern Germany, of Amoeboceras bauhini (Boreal species which commonly occurs at the base of Baylei zone) and Taramelliceras hauffianum (Tethyan species) suggests that the base of Baylei zone and, therefore, the Oxfordian-Kimmeridgian boundary, corresponds in the

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Tethyan realm to the appearance of *T. hauffianum*. This species being missing at Châteauneuf d'Oze, the position of Hauffianum subzone can not be identified precisely in the studied section. Precise lithological correlations with the Crussol section (Ardèche), where *T. hauffianum* has been observed are possible. This leads us to locate the base of the Kimmeridgian at the top of bed 65 at Châteauneuf d'Oze (Atrops, work in progress).

The chart of Hardenbol et al. (1998) proposes five sequences for the studied interval: two in the Upper Oxfordian (Ox7 and 8) and three in the Lower Kimmeridgian (Kim1, 2, and 3). For editorial reasons, this new chart does not include the recent progress in Upper Jurassic biostratigraphy. Consequently, the five sequence boundaries of the studied interval appear with a diachronism between the Boreal and Tethyan realms. Figure 2 attempts to rectify this stratigraphic bias of the chart. Thus, the sequences appear subsynchronous in the two realms, with the exception of the sequence boundary Ox8, placed at the boundary of Bimammatum and Planula zones in the Tethyan realm, and in the upper part of the Pseudocordata zone in the boreal realm.

Sequence OZE 1 (whose base was not sampled), which is located in the Bimammatum zone (Fig. 2 and 3), is taken here to be equivalent to the Ox7 sequence of Hardenbol et al. (1998).

The OZE 2 sequence boundary is located in the upper part of the Bimammatum zone (Fig. 2 and 3) and appears slightly earlier than the Ox8 SB of the chart, which is situated at the Bimammatum-Planula boundary (Fig. 2 and 3). If we correlate OZE 2 with Ox8, the boundary of this sequence should be located, based on geochemical arguments, in the upper part of the Bimammatum zone, making it subsynchronous in the boreal and Tethyan realms. The Ox8 sequence boundary, as defined in the chart for the Tethyan realm, corresponds in fact to the first transgressive surface of this sequence (OZE 2).

The OZE 3 sequence boundary is located in the upper part of the Polygyratus subzone (Platynota zone), making it equivalent to the first boundary of the Kimmeridgian sequence (Kim1) of the chart.

The correlation between the boundaries of sequences OZE 4 (base of the Hypselocyclum zone, Hippolytense subzone), OZE 5 (top of Hypselocyclum zone, Lothari subzone) and OZE 6 (upper part of Divisum zone) with those of the chart of Hardenbol et al. (1998) is more complex.

Although there is a good correlation between OZE 6 and Kim3 (upper part of the Divisum zone), geochemical arguments suggest the existence of two sequences inside the in the Hypselocyclum and Divisum zones, whereas, the chart of Hardenbol et al. (1998) proposes only one (in the Lothari subzone and part of the Divisum zone). Indeed, the high manganese values of beds 159 and 172 may correspond only to two distinct maximum-flooding surfaces. Thus, an additional sequence (Kim2' = OZE 4) in the Hypselocyclum zone could be proposed, with its boundary in the lower part of Hippolytense subzone and its maximum-flooding surface at the base of the

Lothari subzone. This sequence is followed by sequence Kim2" (= OZE 5), with its boundary inside the Lothari subzone and its maximum-flooding surface in the upper part of the Divisum zone. Such a division of the Kim2 sequence is also supported by regional litho- and biostratigraphy:

in the Vocontian realm, in the Crussol (Atrops 1982, p. 284) and La-Roche-sur-le-Buis sections (Atrops 1982, p. 317) and in the Louyre, Gorges de l'Eygues and Châteauneuf d'Oze sections (Bombadiere 1998, Bombardiere & Gorin 2000),

in the boreal realm, at sites on the seashore of Normandy and Charentes (Hantzpergue 1993; Jan du Chêne et al. 1995).

Conclusion

Manganese geochemistry seems to be a complementary powerful tool which assists to the identification of third-order sequences in Upper Jurassic pelagic deposits of the Vocontian realm. The application of this method to Upper Oxfordian-Lower Kimmeridgian series leads to a sequence-stratigraphic framework that is in general agreement with the sequencechronostratigraphic chart of Hardenbol et al. (1998) when using the corrected definition of the Oxfordian-Kimmeridgian boundary of Wierzbowski (1991), Atrops et al. (1993) and Schweigert & Callomon (1997) in the Tethyan realm. Thus, this geochemical approach supports the conclusions of the biostratigraphic work of these authors concerning the position of this boundary and the correlation of ammonite biozones in the Boreal and Tethyan realms. Furthermore, the sequential interpretation, based on the manganese content of the pelagic carbonates, lead us to confirm the proposed subdivisions of Jan du Chene et al. (2000) based on stratonomy, and the presence of an additional third-order sequence (Kim 2' and Kim 2") in the Hypselocyclum zone, Kim 2" being equivalent to the Kim 2 of the Hardenbol et al. (1998) chart.

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