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Sedimentology and trace element geochemistry of shallow-marine carbonates: an approach to paleoenvironmental analysis along the Pagny-sur-Meuse Section (Upper Jurassic, France)

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Abstract The Middle Oxfordian formations of the eastern edge of the Paris Basin (France) contain mostly shallowmarine carbonate sediments. A detailed sedimentological study of the Pagny-sur-Meuse section reveals five major environments that make up a depositional profile succession grading from tidal-flat to distal lagoon/oolithic shoal. Stratigraphic cycles were established and illustrate variations of the A/S ratio (accommodation rate/sedimentation rate) and hence variations of accommodation space. Geochemical analyses (Sr, Mg, Fe, and Mn) have been conducted along a part of the section. Statistic analysis of the geochemical data (box diagrams and principal component analysis, PCA) are used to investigate similarities between the variations of trace element contents and depositional environments. An analysis of variance (ANOVA) is used to test whether the amounts of trace elements are related to the depositional environments. The relationship is highly significant for Sr, Fe, and Mn. A number of a posteriori tests are performed with this ANOVA to compare the geochemical data for each environment. Tidal-flats and distal lagoon/oolithic shoal transition are the most sig-

an open diagenetic system that explains the low Sr values and (2) the possible influence of clays on Fe-Mn contents in the upper part of the section, some of the variations in Sr and Fe-Mn seem to reflect changes in depositional environment. A number of hypotheses are proposed about the relations between trace elements and paleoenvironmental parameter records: Sr contents may illustrate variations of paleosalinity in depositional environments, whereas Fe and Mn contents seem to record variations of specific low detrital inputs coming from isolated islands submitted to pedogenesis. Low Sr content coupled with relatively high Fe and Mn contents is indicative of low salinity environment near subaerially exposed islands, located in the proximal part of a reconstructed theoretical depositional profile. Conversely, high Sr content coupled with relatively low Fe and Mn contents reflect a more open marine environment in the distal part of the same profile. Such analysis based on trace element geochemistry does not constitute a model but it shows that Sr, Fe, and Mn can partially record indications about paleoenvironmental conditions in shallow-marine carbonates.

nificantly discriminated environments. Differences among

the lagoonal environments are less obvious. Despite (1)

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Introduction

Trace element geochemistry of carbonates from basinal environments can be used as a powerful tool for paleoenvironmental and sequential analysis (Renard 1984; Emmanuel and Renard 1993; Corbin et al. 2000; De Rafelis et al. 2000). Chemostratigraphy is used in the predominantly pelagic deposits to perform sequential analyses, which can provide more detailed informations than standard sedimentologic analyses. Geochemistry is also a valuable source of additional information for biostratigraphic studies (Jan Du Chêne et al. 2000).

On the other hand, chemostratigraphy is not widely used in carbonate platform environments because in most cases geochemical signals are complicated by diagenetic overprinting. However, geochemical data may yield information about the nature of parent water, paleoclimates, and paleohydrology in carbonate environments such as lacustrine (e.g., Calvo et al. 1995), brackish (e.g., Dini et al. 1998), and shallow-marine (e.g., Pascal 1984; Walgenwitz et al. 1992; Vincent et al. 1997; Emmanuel et al. 1999).

This paper presents results of a geochemical analysis of a reference section of Oxfordian shallow-marine carbonates from the eastern edge of the Paris Basin. It was carried out in order to (1) compare the variations in contents of trace elements with sedimentological data, and (2) determine as far as possible the proportion of the geochemical signal caused by paleoenvironmental variations. The treatment of the geochemical data involves both a descriptive presentation of the data, using box diagrams and a principal component analysis (PCA), and an interpretative assessment, utilizing an analysis of variance (ANOVA).

In order to constrain the geochemical approach, the essential first stage of this work consists in a sedimentological study to establish a paleoenvironmental and sequential framework. This study is based on new field observations and also on earlier studies of the Middle-Late Oxfordian (Humbert 1971; Debrand-Passard et al. 1980; Geister and Lathuilière 1991; Lathuilière 1998; Vincent 2001; Olivier et al. 2004).

Geological setting

During the Upper Jurassic, the area corresponding to the eastern edge of the Paris Basin was a carbonate-dominated platform sloping from the London-Brabant landmass (Ardennes Paleozoic massif) to the north and bounded by the Vittel fault to the south (Fig. 1). In the Middle Oxfordian, this carbonate platform is characterised by high facies diversity and well-developed paleotopography, both attributed to the different growth rates of underlying reefs, initiated on a relatively homogeneous marly formation (Debrand-Passard et al. 1980; Geister and Lathuilière 1991; Insalaco 1996; Vincent et al. 2000). These variations in topography became covered and finally buried by sediments during the Middle Oxfordian and a relatively flat shallow platform with high carbonate productivity formed, which extended between the London-Brabant landmass and the Vittel fault (Debrand-Passard et al. 1980). In the Late Oxfordian, pure carbonate sedimentation decreased and mixed carbonate/terrigeneous sedimentation occurred near the London-Brabant landmass in a wide but shallow trough. Carbonate sedimentation was then confined to a narrow area bordering the Vittel fault (Debrand-Passard et al. 1980; Durand et al. 1989).

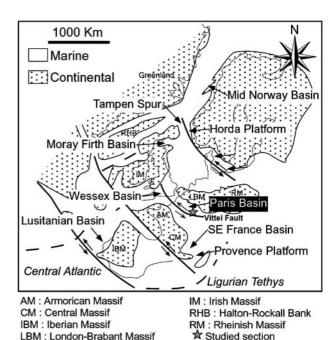


Fig. 1 Location of the studied section on a paleogeographic reconstruction of the northern margin of the Ligurian-Tethys (from Jacquin et al. 1998). This sketch shows the major exposed landmasses, the different basins and platforms as well as the ridges and associated transform faults of both the Central Atlantic and Ligurian Tethys. The London-Brabant massif is the closest exposed landmass to the studied outcrop

Material and methods

The studied section (previously described by Lathuilière 1998 and Olivier et al. 2004), located in an extensively worked quarry near Pagny-sur-Meuse (Fig. 2), is considered as the most representative outcrop of the Oxfordian along the eastern edge of the Paris Basin. This section contains from base to top: (1) Oxfordian reefs of the Plicatilis zone, (2) carbonate-dominated strata attributed to the Transversarium zone of the Middle Oxfordian, and (3) mixed carbonate/terrigeneous formations ascribed



Fig. 2 Pagny-sur-Meuse quarry. Contact between the carbonate formations of the Middle Oxfordian *pro-parte* (Transversarium zone) and the marly formations of the upper Oxfordian (Bifurcatus zone)

to the Bifurcatus zone of the Upper Oxfordian. The biostratigraphic information is taken from Enay and Boullier (1981). The present study concentrates on a 20 m thick carbonate-dominated interval in the middle part of the quarry which is of particular geochemical interest because of its high carbonate contents (mean 98.51%). The section has however been entirely logged (Fig. 3A) to include also mixed carbonate/terrigeneous levels, since they constitute the only biostratigraphic reference level (Enay and Boullier 1981).

- First a sedimentological and paleoenvironmental analysis, based on a study of 40 stained thin sections from the Pagny-sur-Meuse quarry, 30 of which are distributed along the chemically analyzed interval (Fig. 3A), was carried out. Attention was also paid to diagenetic features.
- Subsequently a geochemical analysis of 72 bulk rock samples through the 20 m thick interval following the detailed analytical protocol of Richebois (1990) was carried out. When it was possible, micritic matrix was preferentially sampled. Small amounts of limestone powder (1 g) from each sample were treated with 50 ml of 1 N (1 mol \cdot l⁻¹) acetic acid for 45 min at room temperature. These conditions minimised the alteration of the non-carbonate fraction (clays, oxides) of the bulk rocks. The insoluble residues were then collected on filters to determine the percentage of carbonate by weighing. Carbonate solutions were evaporated after filtering and then treated with hydrochloric acid (x% volume) so as to avoid interactions with acetate ions while measuring trace element contents. All solutions (final hydrochloric acid concentration of 6%) were finally analyzed by atomic absorption spectrometry (Perkin Elmer 3300 spectrometer) to determine Ca contents. To avoid interactions with Ca ions while determining Sr contents, all the solutions were homogenized to the same Ca contents. The solutions were then analyzed to determine Sr, Fe, Mn, and Mg contents, which are the elements classically used in pelagic setting studies (Renard 1984; Emmanuel and Renard 1993; Corbin et al. 2000). An internal standard (Douvrend) was used for these analyses. Lower limits of detection for the five trace elements are: 13.5 ppm for Ca, 16.5 ppm for Sr, 15 ppm for Fe, 5 ppm for Mn, and 1.2 ppm for Mg.

Sedimentological study and sequence analysis

Sedimentology and depositional environments

Facies analysis shows evidence of 25 depositional packages in the section (Fig. 3A, legend Fig. 3B) corresponding to beds or bed sets bounded at their base and top by a discontinuity surface (Hillgärtner 1998). In the geochemically analyzed interval (Fig. 3A), most of the unit boundaries correspond to changes of facies but the occurrence of coarse-grained layers at the base of several units suggests a possible erosive component. In this interval, most of the

carbonates are related to upper subtidal environment except the most proximal, which are interpreted as tidal-flats and related to intertidal. This interpretation can be refined through the subdivision of the upper subtidal into four major shallow-marine depositional environments recognized at the platform scale in the Middle Oxfordian (Vincent 2001). They are (1) Proximal Lagoon, (2) Median Lagoon, (3) Distal Lagoon, and (4) Distal lagoon/Oolithic shoal transition. These environments can be differentiated using a combination of various parameters such as texture, fauna (macro and micro), clasts, and sedimentary structures.

Tidal-flat: fine laminated limestones

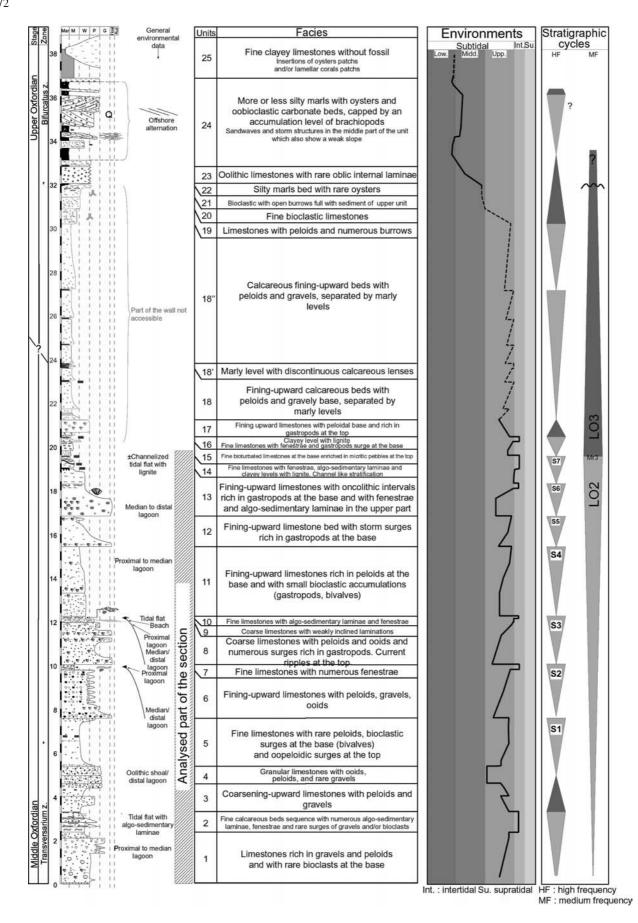
The tidal-flats facies are composed of fine-grained mudstones to wackestones containing fenestral features, ostracods, charophyte oogons, wood debris, and algosedimentary laminae (Fig. 4). These laminated structures are formed by alternating thin dense micritic layers, corresponding to microbial mats and ostracod-rich micritic sediments. These laminae are often bioturbated. This facies is interlayered by granular layers with peloids, fine gravels, and small benthic foraminifera (Miliolidae, Textulariidae). Some coarser granular layers also contain coarser gravels, laminated lithoclasts, and rare micritised ooids (Fig. 4).

Interpretation. The large numbers of ostracods and the presence of charophyte oogons indicate a very shallow, proximal depositional setting. Algo-sedimentary laminae correspond to laminites similar to those on presentday tidal-flats of the Bahamas, Florida, or the Arabian Gulf (Reineck and Singh 1986; Tucker and Wright 1990; Reading 1996). Fenestrae are classically associated with these laminites and indicate exposure and desiccation on tidal-flats. The granular layers were mostly transported and deposited by storm surges over the tidal-flat. The laminated lithoclasts result from in situ reworking during storms. The preservation of a laminated structure results from early hardening of the sediment before reworking, which was caused by desiccation during subaerial exposure in a tidal environment. Consequently, the depositional environment of the above mudstones to wackestones is intertidal.

Sedimentary unit 14 is a tidal-flat facies but showing greenish marly levels separating channel-like depressions. Similar occurrences of greenish marls in very shallow-marine carbonates of Switzerland have already been interpreted by Deconinck and Strasser (1987) and Strasser et al. (1999) as the result of intertidal alteration of smectite-rich soils on small carbonate islands.

Lagoon

Proximal lagoon: muddy micro-packstones/wackestones with Cayeuxia. This environment is represented by poorly sorted fine packstones (rarely wackestones) to grainstones with peloids, pellets, and gravels (Fig. 5, photo C3). Micritised ooids are uncommon. These limestones contain numerous cyanobacteria of the genus Cayeuxia encrusted



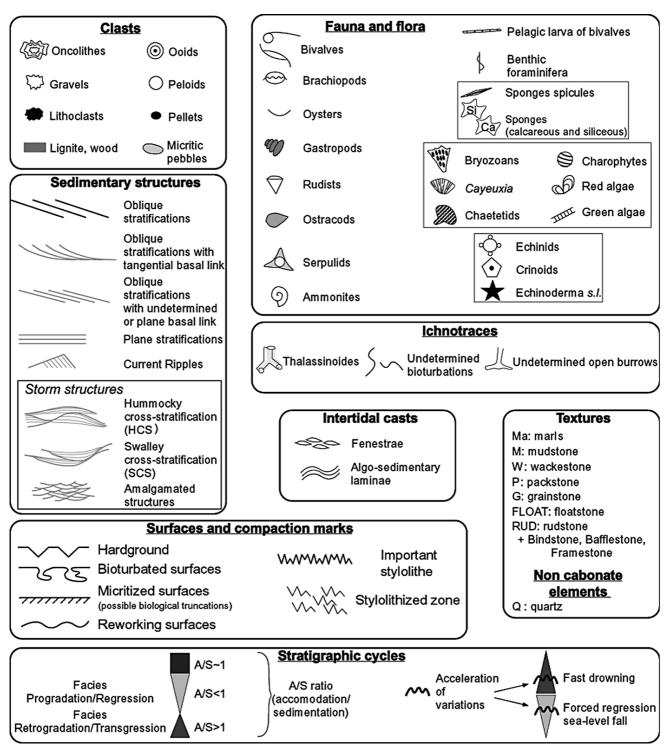


Fig. 3 A Sedimentological log, facies description of the sedimentary units, environmental variations, and stratigraphic cycles along the Pagny-sur-Meuse section (Meuse, France). This section shows the carbonate-dominated interval used in the geochemical approach and also the marly levels in the upper part used to date this succession from biostratigraphic data (Enay and Boullier 1981). The

high-frequency stratigraphic cycles are arranged into two medium frequency cycles LO2 and LO3 according to Vincent et al. (2000). The analyzed part for geochemistry of this section is highlighted in Fig. 6. **B** Legend of the sedimentological logs and stratigraphic interpretations used in Figs. 3A and 4

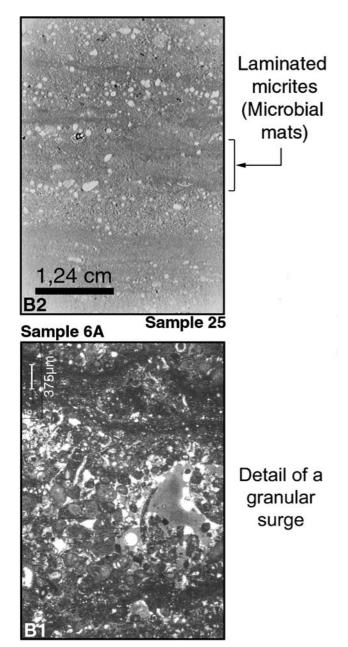


Fig. 4 Facies of the tidal-flat environment both at microscopic (B1) and at macroscopic scale (B2)

clasts, and rare small nubecularian oncoids. The fauna consists of small benthic foraminifera (Miliolidae, Textularidae) and rarely by bivalve and gastropod debris.

Interpretation. The texture of the sediments and the poor sorting indicate moderate hydrodynamic conditions and winnowing. The scarcity of ooids suggests a limited supply from distant sources. The abundance of *Cayeuxia* encrusting clasts suggests that they formed *in situ*, in a nearshore environment (Bernier 1984). Consequently, the depositional environment corresponds to the proximal area of the lagoon.

Median laoon: muddy packstones/grainstones with Cayeuxia debris. These deposits consist of poorly sorted packstones to grainstones with peloids, pellets, and nubecu-

larian oncoids of various sizes. These limestones also contain some rare gravels, lithoclasts, and micritised ooids. Numerous *Cayeuxia* debris (not encrusting; Fig. 5, photo C2) occur along with Miliolidae and Textulariidae (exceptionally Lituolidae) foraminifera. Some rare bivalve and gastropod debris also occur.

Interpretation. The occurrence of gravels, lithoclasts, ooids, and the presence of a scarce micritic matrix indicate an alternating environment with variable winnowing. Nubecularian oncoids indicate a luminous, oxygenated, but also agitated environment. The scarcity and heterometry of the ooids suggest that their source, which is assumed to be an oolithic carbonate shoal, is somewhat distant from the considered depositional environment (Loreau

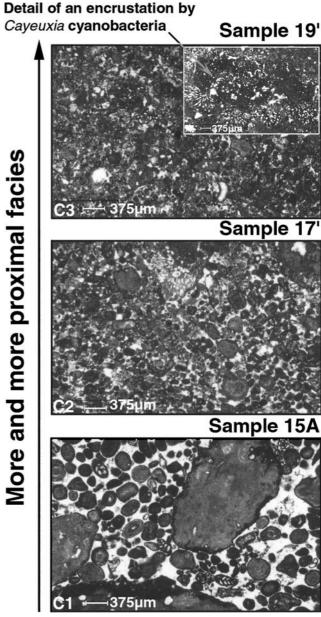


Fig. 5 Microfacies of the lagoonal environments from more distal (C1) to more proximal (C3). See main text for detailed descriptions

1982). The *Cayeuxia* debris indicate transport from their life environment, but their abundance also reflects its proximity to the area of origin. Consequently, the depositional environment corresponds to the median area of the lagoon.

Distal lagoon: grainstones/packstones with heterometric micritised ooids. These poorly sorted grainstones and packstones are rich in peloids. They are also rich in micritised ooids with heterogeneous size, and contain variable amounts of grapestones, gravels, and lithoclasts (Fig. 5, photo C1), as well as large nubecularian oncoids (several millimetres in diameter). Pellets are also present, and are locally abundant when a micritic matrix is present. Fossils consist of foraminifera: Lituolidae (Pseudocyclamina, Nautiloculina), Miliolidae, Textulariidae, Nodosariidae (Lenticulina). Debris of gastropods, bryozoans, echinoderms, dasycladacean algae, and bivalves complete this inventory.

Interpretation. The predominance of grainstones indicates strong winnowing, although scarce micritic matrix suggest some local intermittent quiet deposition. The heterometry of the ooids means they were transported from their place of origin (Loreau 1982), but their abundance indicates that this environment was nearby. As in the median lagoon, nubecularian oncoids indicate luminous, oxygenated, and agitated conditions. The dominant foraminifera are a classical association in lagoonal environments (Zaninetti et al. 1996), but the presence of Lenticulina and ooids indicate input from nearby shoals of the shoreface. Consequently, the depositional environment corresponds to a more or less agitated lagoon, near an ooid source, meaning a distal lagoonal area.

Distal lagoon/oolithic shoal transition: oolithic grainstone

These deposits consist of sorted onlithic grainstones containing peloids and rare gravels. The fauna consists of porcelaneous foraminiferans (Miliolidae), rare gastropods, and broken bivalves, which occur mostly as ooid nuclei. Ooids display heterogeneous size.

Interpretation. The grainstone texture indicates strong agitated conditions and winnowing of mud. The heterogeneous sizes of ooids indicate that they are transported and do not occur at their original location (Loreau 1982), but their dominance reflects the proximity of their source area. Consequently, the depositional environment of these sediments corresponds to the most distal part of the lagoon, near oolithic shoal barriers.

Deeper water facies occur in the upper part of the section. Terrigeneous input strongly reduces carbonate productivity leading to regional slight drowning of the platform (e.g., Debrand-Passard et al. 1980; Vincent 2001).

Vertical changes in depositional environment are shown as a curve in Fig. 3A, where it oscillates from intertidal (tidal-flat facies) to lower subtidal (top of the section). In the lower half of the section (units 1–17; see Fig. 3A), this curve

is restricted to intertidal and upper subtidal environments, here subdivided in four distinct settings (see above).

Sedimentary stratigraphic cycles

The vertical stacking patterns of the facies are interpreted in terms of retrogradation (transgressive) and progradation (regressive) cycles. These cycles reflect the variations of the ratio between accommodation space (A) and sedimentation rates (S). The prograding phases correspond to periods with A/S of <1 and retrograding phases to periods with A/S of >1. Consequently, these cycles can be interpreted to be due to the variations in available accommodation space (Homewood et al. 1999). Seven high-frequency cycles (HF; see Fig. 3A), termed S1-S7, were identified in the lower half of the section, which corresponds to the geochemically analyzed units 1–15 (see Fig. 3A). Cycles S2-S7 are clearly asymmetrical because there is no expressed transgressive phase, while cycle S1 is symmetrical. Previous papers (Osleger 1991; Strasser 1991; Strasser et al. 1999) argue that this asymmetry is characteristic of stratigraphic cycles in shallow-marine carbonate systems. Based on their thickness and stacking arrangements the seven high-frequency cycles are assigned to a lower frequency prograding phase defined at the regional scale (LO2) of Vincent 2001; see Fig. 3A). Three indicators reflect the maximum of regression of this cycle around 19.6 m: (1) concentrations of greenish marly levels occurring in channels which cut in tidal-flat facies between 19 and 20 m (sedimentary unit 14), (2) the abundance of fenestral structures between 18 and 19.5 m, and (3) the presence near 18.2 m of a bed of *Cayeuxia* which is a nearshore fauna. The LO2 prograding phase is overlain by an inferred retrograding phase termed LO3 (Vincent et al. 2000; Vincent 2001).

Diagenesis

Despite the intertidal attribution of some of the carbonates of the lower half of section, neither early dissolution nor early cementation was observed. There is also any indication of even a subtle pedogenetic evolution. The only early diagenetic feature is a hardground near 32 m, just below the terrigeneous levels, corresponding to an undulated erosional surface (see Fig. 3A). But it affects micritic sediments and just displays some boring and a classic iron stain. It is a subtidal hardground.

In fact, modifications of studied carbonates mainly occurred during burial with the precipitation of blocky calcite cements that were observed in the grainstone levels. Isotopic study of these cements in the Oxfordian formations at the scale of the eastern edge of the Paris Basin shows that they precipitated from either mixed marine/meteoric fluids or slightly buffered meteoric waters (Buschaert 2002; Vincent et al. 2005). The Middle Oxfordian micrites were also affected by late diagenesis, but later during the uplift of the Paris Basin in the Tertiary (telogenesis). They acquired a chalky aspect (smoothed

crystals joint by thin calcitic bridges observed under SEM) through dissolution and reprecipitation during freshwater flowing in the Oxfordian formations, here again at the scale of the eastern edge of the Paris Basin (Vincent et al. 2004).

Geochemistry

Sr, Mn, Fe, and Mg are the elements classically selected for analyzing platform carbonate facies in terms of pale-oenvironments and diagenesis (Veizer et al. 1971; Veizer and Demovič 1974; Renard 1975; Walgenwitz et al. 1992; Vincent et al. 1997; Emmanuel et al. 1999). The purpose is to understand the variations in these trace element contents in the previously interpreted and determined paleoenvironments, taking into account both sedimentological data and diagenetic context.

Description of the variations in element contents

Variations in trace element contents are illustrated in Fig. 6. Comparing these variations with the depositional environments and/or stratigraphic cycles (Fig. 6) suggests the following. The Sr, Fe, and Mn curves exhibit shifts as in the depositional environments. Likewise, the stratigraphic cycle boundaries correspond to trend reversals and shifts in the geochemical elements. However, the Mg curve does not show such a relationship.

Respectively high Fe and Mn contents and low Sr contents are related to the more proximal restricted environments, except near 11.8 m in the S3 stratigraphic cycle and near 18 m in the S6 cycle where Sr contents are relatively high (Fig. 6). Conversely, in the inferred more distal open environments, Fe and Mn contents are low whereas Sr contents are high (Fig. 6). Despite the fact that the highest Sr values correspond to the lowest Fe-Mn contents and inversely, there is no significant linear correlation between Fe and Sr (r=0.33), and Mn and Sr (r=0.31). The Fe and Mn variations are similar (r=0.91) because they are derived from the same source and are interpreted in the same manner into the carbonate lattice (Emmanuel and Renard 1993; Calvo et al. 1995). In the upper part of the geochemically analyzed interval, above 12 m, percentage of insoluble residue increases slowly (Fig. 6). In the same way, Fe and Mn contents increase slowly and more abruptly above 17 m (Fig. 6). In fact, linear correlations exist between carbonate contents, thus insoluble residue, and respectively Fe contents (r=0.54; Fig. 7a) and Mn contents (r=0.62; Fig. 7b). But in detail, such correlations are significant in the uppermost 8 m (from 12 to 20 m, 22 samples; Fig. 7c, d) and weak to non-significant in the lower 12 m (50 first samples; Fig. 7c, d). Despite the applied protocol was developed in order to minimise the leaching of non-carbonate constituents, it is not possible to completely rule out a contribution of either clays or oxides in the analysis, which would explain this Fe-Mn and IR correlation. On the other hand, this relationship in the upper part of the analyzed interval does not completely rule out the possibility for the Fe and Mn signal to reflect an increase of initial seawater contents.

Statistics

Therefore statistical analysis, used in order to test a possible relationship between variations of depositional environments and geochemical contents, were performed on the 50 samples of the first 12 m of section for which we assume no contribution from leached non-carbonate phase. The controversial 22 samples of the upper 8 m are not included.

Description of statistical data

The first step of this approach consists in interpreting and assigning each sample analyzed to a depositional environment. It is easy to determine the samples attributed to either tidal-flat or distal lagoon/oolithic shoal environments, but since there is not one thin section for each geochemical sample this is sometimes more difficult in the lagoonal setting. The six environmental classes available for the allocations of the samples are: (1) Tidal-Flat (TF), (2) Proximal Lagoon (PL), (3) Median Lagoon (ML), (4) Distal Lagoon (DL), (5) distal lagoon/oolithic Shoal Transition (ST), and (6) Storm Surge on Tidal-Flat (SSTF). This last specific category introduced here corresponds to the thickest (pluri-centimetric) granular layers interbedded in the tidalflat sediments. Even if these layers are part of the tidal-flat environment, their thickness allow us to distinguish them from the tidal-flat sets as being different sedimentological features and are of different origin.

Box diagrams for each element and insoluble residue (Fig. 8) illustrate both the median and interquartile of all depositional classes placed side-by-side along an inferred opening and deepening trend from the most proximal (TF) to the most distal class (ST). Fe and Mn contents decrease continuously from shallow proximal to more distal environments. Insoluble residue does not show any similar trend which confirm here that for this part of the section, Fe and Mn come actually from the carbonate phase. Notice that the quartiles of PL samples for Fe contents is relatively extended even if the median is part of the trend noted above. On the other hand, Sr content increases from TF to PL, stays more or less constant from PL to DL, and increases again in ST. Mg content displays only minor change as environments become more open. It begins by decreasing slightly from TF to DL and then increasing slightly to ST.

Principal component analysis (PCA)

In addition to this simple statistical approach confirming the initial observations, a PCA was performed including all of the first 50 samples, so as to illustrate the variance of the total geochemical system.

Two primary PCs (principal components) make up 87.5% of the total variance (Fig. 9). PC1 contributes 55.3% and is

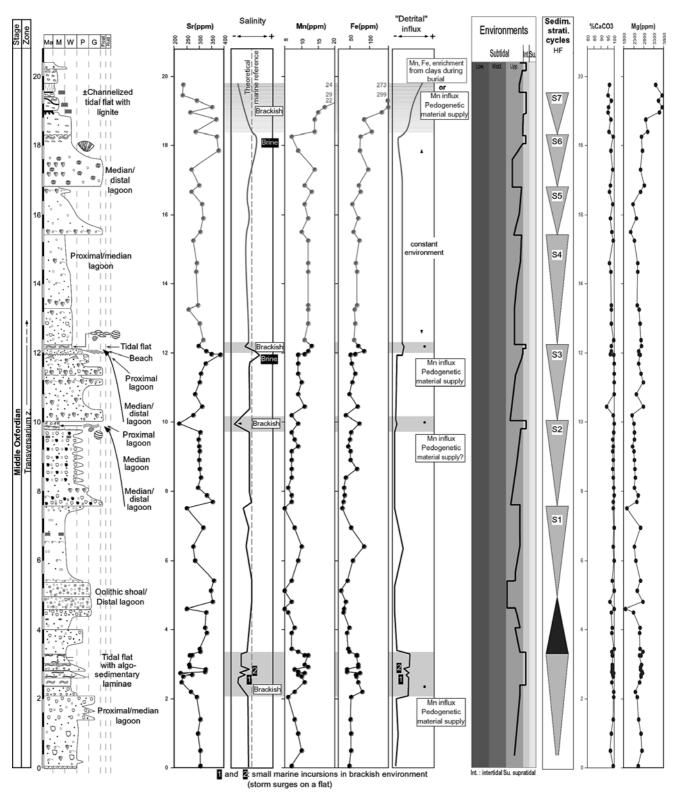


Fig. 6 Trace element curves along the Pagny-sur-Meuse section. Paleoenvironmental interpretation of the Sr and Fe–Mn curves. The black part of the curves and associated geochemical cycles correspond to the interval covered by the statistical analysis. The grey

upper part is also interpreted in terms of paleoenvironments even in there is a probable influence of insoluble residue on Fe-Mn contents

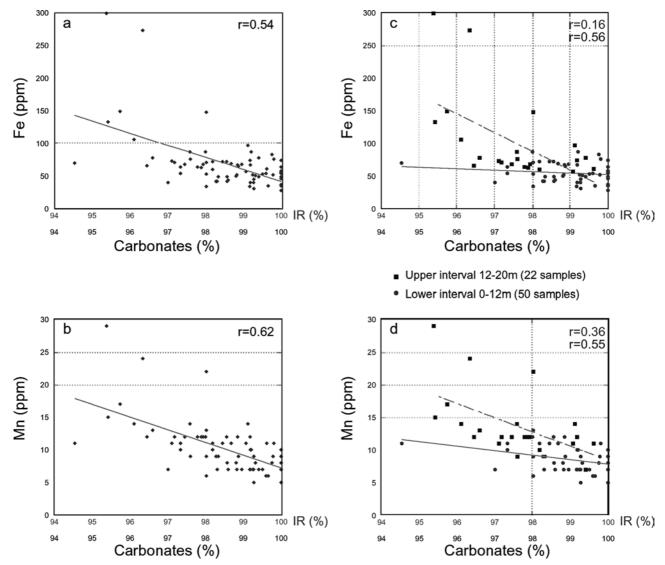


Fig. 7 IR% (insoluble residue) vs. Fe–Mn (ppm) cross-plots. **a** IR/Fe cross-plot including all the 72 samples. **b** IR/Mn cross-plot including all the 72 samples. **c** IR/Fe cross-plot for two distinct sets of

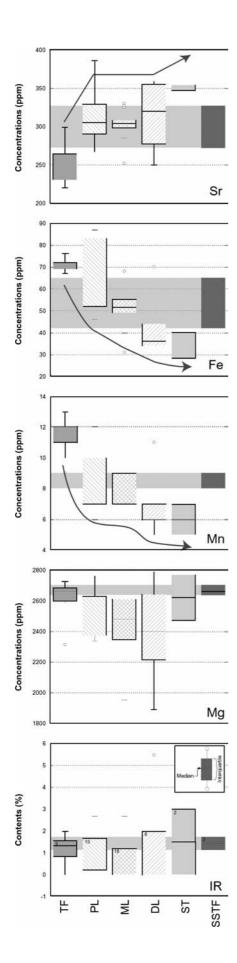
samples: 0–12 m interval with 50 samples, 12–20 m interval with 22 samples. **d** IR/Mn cross-plot for two distinct sets of samples: 0–12 m interval with 50 samples, 12–20 m interval with 22 samples

related to Mn, Fe, and to a lesser extent Mg. PC2 accounts for 32.2% of the variance and is related to Sr and to Mg. The four variables are plotted in the two-dimensional PC space (Fig. 9). Whereas Sr and the Fe-Mn pairing are clearly differentiated, Mg loadings are similar and relatively high for the two PCs (Fig. 9), giving it an intermediate position. The samples, arranged in their corresponding depositional class, are plotted in two-dimensional PC (Fig. 10). In this bivariate diagram, some fields corresponding to the different depositional classes, can be differentiated. TF and ST environments are well discriminated, like with the box diagrams (see Fig. 8), and all the fields are arranged along a trend of increasingly open environments ranging between these two extremes (Fig. 10). However, all the other fields for lagoonal environments show some overlap (Fig. 10). Only Sr and Fe-Mn contents control the arrangement of the fields in the PC space. Mg contents do not seem to affect this arrangement.

Then, it appears that Sr, Fe, and Mn contents of the carbonates vary with the interpreted paleogeographic position of their depositional environment along the depositional profile described in the sedimentological approach.

Testing the relationship between depositional environments and geochemistry: analysis of variance (ANOVA)

An ANOVA was conducted on the same set of 50 samples arranged into the six environmental classes in order to evaluate the effect of the depositional environment on the geochemical contents. One test was carried out for each element separately. The results confirm the visual observations: the effect of the environment on Sr, Fe, and Mn contents is highly significant (p<.0001; Fig. 11), whereas this effect on Mg contents is not significant (p<.1097; Fig. 11).



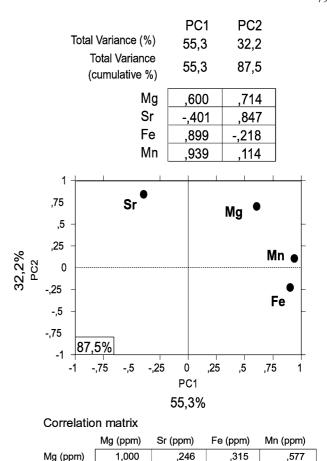


Fig. 9 Bivariate diagrams of the PCA: projection of the variables in the principal component (PC) space

1,000

-,443

-,250

-,443

1,000

,770

-,250

,770 1,000

,246

,315

,577

Sr (ppm)

Fe (ppm)

Mn (ppm)

Within this ANOVA, a number of *a posteriori* tests (Fischer PLSD, significance level of 5%) were also performed for each element revealing the significance of the difference between the geochemical contents of the environmental classes (Fig. 11). TF is the most distinctive class as its Sr, Fe, and Mn contents are significantly different from those of all the other classes, except PL which is the nearest to it

Fig. 8 Box diagrams showing the evolution of the median values of Sr, Fe, Mn, Mg, and IR (insoluble residue) contents along an environmental opening trend from the most proximal/shallowest environments (tidal-flat, TF) to the most distal/deepest ones (distal lagoon/oolithic shoal transition, ST). Medians are preferred to means because they are less influenced by extreme values. This graphic representation shows the relation between geochemical contents of sediments and their depositional environment. Number of samples is indicated in the IR box diagram. Samples corresponding to the most proximal/shallowest environments show relatively low Sr contents and relatively high Fe and Mn contents, whereas samples from more distal/deeper environments show relatively high Sr contents and low Fe and Mn contents. Mg and IR contents do not display the same evolution. Notice that SSTF geochemical values are similar to the lagoon ones (grey band)

and only exhibit significantly different Sr and Mn contents (Fig. 11). For the results of these *a posteriori* tests, the ST class is the second most distinct class (Fig. 11).

The lagoonal classes (PL, ML, DL) do not display significantly different geochemical contents, except DL/PL with respectively highly significantly different Fe contents and significantly different Mn contents (Fig. 11). The visual continuous evolution of Fe and Mn contents (see Fig. 8) is not statistically confirmed. The SSTF category is a particular case. Even if these deposits are related to tidal-flat systems, Sr, Fe, and Mn contents differ significantly between SSTF and TF (Fig. 11). On the other hand, Sr, Fe, and Mn contents of SSTF samples are never significantly different from the lagoon ones. In fact, the sediments of the SSTF levels are reworked by storms from their environment of production, thus the lagoon s.l., and deposited again as allochthonous layers in the tidal-flat areas. The significant difference between SSTF and TF shows that reworked SSTF material preserve the geochemical signature of its depositional environment. This particularity was predictable from the box diagrams of Fig. 8 where SSTF quartile fits with lagoon quartiles.

Effect of diagenesis on the trace element contents

Geochemistry shows distinct differences in Sr, Fe, and Mn contents between lithologies reflecting different depositional environments. Before expressing hypotheses about the use of trace elements as potential paleoenvironmental indicators, the diagenetic context needs to be considered to constrain the possible alterations of the primary, i.e., marine chemical signal.

First of all, the studied carbonates are almost totally in low magnesian calcite (LMC), meaning variations in trace element contents should not be attributed to different distribution coefficients.

The Sr and Mg absolute values are very low and do not represent initial marine contents of carbonate sediments. The depletion of Sr and Mg contents can be classically caused by water-rock interactions involving freshwater fluids with very low Sr and Mg contents (Banner and Hanson 1990; Cicero and Lohmann 2001) either during burial or stripping. Vincent (2001) provides clear evidences of such interactions for the Oxfordian carbonates of the eastern edge of the Paris Basin. However, the low Mn and Fe values are compatible with initial marine calcite contents and are not characteristic of a freshwater fluid dominated system (Brand and Veizer 1981; Banner and Hanson 1990). In the same way, altered Oxfordian shallow-marine micrites of the eastern edge of the Paris Basin display marine δ^{13} C values and freshwater influenced δ^{18} O values (Vincent et al. 2004). All these data joined together seem to rather indicate an open partially rock buffered system than a fluid dominated system (Brand and Veizer 1981; Banner and Hanson 1990; Cicero and Lohmann 2001). If late diagenesis modified the primary Sr and Mg absolute values (discussed by Frank and Lohmann 1996), it shifts the entire curve of one considered element and does not erase the variations in this curve.

The specific behavior of Mg compared with that of Sr, Fe, and Mn cannot be ascribed to dolomitisation/dedolomitisation processes since no dolomite (crystals or ghosts) has been observed. It is more likely to be related to high magnesian calcite (HMC) to LMC replacement in an open system. Because of (1) the behavior of Mg is considered to be sensitive to this early diagenetic processes, and (2) Mg contents appear to be unrelated to paleoenvironment variations, Mg is excluded from further discussion.

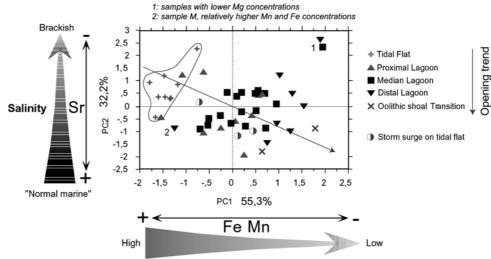
Fe-Mn increase in the shallowest environments could be ascribed to the concentration of clay due to a weak pedogenetic evolution near the top surface of the considered sedimentary units. However, there is no evidence for any pedogenesis in this section, and as we discussed above there is no correlation between Fe-Mn contents and IR in the lower part of the section. Conversely, we consider that relative variations of Sr, Fe, and Mn contents illustrate variations of the concentrations in the carbonate phase, which traduce at least partially the primary chemical signal.

Discussion: trace elements as indicators of paleoenvironmental parameters

The main sources of Mn and Fe in marine carbonates are: (1) the hydrothermal activity of the oceanic ridges (Emmanuel and Renard 1993; Von Damm 1995; Corbin et al. 2000; De Rafelis et al. 2000), and (2) detrital inputs from the erosion of exposed landmasses (Pascal 1984) even if this flux is trapped in coastal shelf sediments. However, hydrothermal sources can be here ruled out for three reasons: (1) the ridges are a long way from the study area, even if Mn is easily transported in seawater (Klinkhammer 1980), (2) analyzed carbonates have low Mn contents in comparison with basin carbonates, and above all, (3) the highest contents of Fe and Mn are associated with very proximal shallow environments (tidal-flat) and not with the more distal ones (distal lagoon to shoal transition). If, the most open marine should contain the highest amounts of Fe and Mn. In this case, the most probable sources of Fe and Mn should be the input of detrital sediments derived from exposed, weathered land areas. Here the restricted supply of detritus comes more probably from isolated exposed carbonate islands subjected to pedogenesis (Fig. 12) than from the nearest exposed continental landmass located 200 km to the north (see Fig. 1). Weathering of soils, either intertidal or trough rainfalls, would allow small amounts of Fe and Mn to be reworked and possibly to be incorporated in the carbonates precipitated in nearby shallow-marine environments (Fig. 12). Such exposed carbonates, with pedogenetic alteration, have been documented in the same stratigraphic levels, laterally to the southwest of Pagny-Meuse (Vincent 2001).

The decrease in Sr content toward proximal restricted environments could be the result of exposure-related early diagenesis involving freshwater associated cementation

Fig. 10 Samples plotted in the PC space polarized according to trace element contents. Certain environmental fields seem to stand out when the samples are arranged with their environmental attributions and the fields are ranked from the most proximal environment to the most distal one. Environmental parameters explaining geochemical variations are shown parallel to each PC



Pedogenetic material supply (clays and/or associated trace elements)

	DF	Sum of squares	Mean square	F value	p value
Environnments	5	29035,453	5807,091	7,603	€,0001
Residus	44	33606,067	763,774		

PLSD Fisher for Sr (ppm) Effects: Environnement Significance level: 5%

	Mean deviation	Critical deviation	p value	
Distal Lagoon, Median Lagoon	11,222	23,667	,3445	1
Distal Lagoon, Oolithic Shoal Transition	-37,000	44,033	,0974	1
Distal Lagoon, Proximal Lagoon	,900	26,420	,9456	1
Distal Lagoon, Storm surge on TF	5,833	37,707	,7567	1
Distal Lagoon, Tidal Flat	61,389	27,064	<,0001	нѕ
Median Lagoon, Oolithic Shoal Transition	-48,222	41,515	,0238	s
Median Lagoon, Proximal Lagoon	-10,322	21,967	,3488	1
Median Lagoon, Storm surge on TF	-5,389	34,734	,7560	1
Median Lagoon, Tidal Flat	50,167	22,738	<,0001	нѕ
Oolithic Shoal Transition, Proximal Lagoon	37,900	43,143	,0836	1
Oolithic Shoal Transition, Storm surge on TF	42,833	50,845	,0966	1
Oolithic Shoal Transition, Tidal Flat	98,389	43,541	<,0001	HS
Proximal Lagoon, Storm surge on TF	4,933	36,665	,7875	1
Proximal Lagoon, Tidal Flat	60,489	25,591	<,0001	нѕ
Storm surge on TF, Tidal Flat	55,556	37,132	,0043	s

	DF	Sum of squares	Mean square	F value	p value
Environnments	5	5749,889	1149,978	9,788	€,0001
Residus	44	5169,331	117,485		

PLSD Fisher for Fe (ppm) Effects: Environnement Significance level: 5%

	Mean deviation	Critical deviation	p value	
Distal Lagoon, Median Lagoon	-9,875	9,282	,0376	s
Distal Lagoon, Colithic Shoal Transition	7,125	17,270	,4102	1
Distal Lagoon, Proximal Lagoon	-21,775	10,362	,0001	HS
Distal Lagoon, Storm surge on TF	-8,542	14,789	,2507	1
Distal Lagoon, Tidal Flat	-29,986	10,615	<,0001	HS
Median Lagoon, Oolithic Shoal Transition	17,000	16,282	,0411	s
Median Lagoon, Proximal Lagoon	-11,900	8,616	,0079	s
Median Lagoon, Storm surge on TF	1,333	13,623	,8445	1
Median Lagoon, Tidal Flat	-20,111	8,918	<,0001	HS
Oolithic Shoal Transition, Proximal Lagoon	-28,900	16,921	,0013	s
Oolithic Shoal Transition, Storm surge on TF	-15,667	19,941	,1205	1
Oolithic Shoal Transition, Tidal Flat	-37,111	17,077	<,0001	HS
Proximal Lagoon, Storm surge on TF	13,233	14,380	,0704	1
Proximal Lagoon, Tidal Flat	-8,211	10,037	,1063	l
Storm surge on TF, Tidal Flat	-21,444	14,563	,0048	s

Significant (or highly significant)	for the 3 major elements
difference	for 2 of the 3 major element

Fig. 11 Results of the ANOVA (analysis of variance). Effect of the environment on the contents of each element, and associated *a posteriori* tests comparing the different geochemical contents of all the environmental classes among themselves for each element sepa-

	DF	Sum of squares	Mean square	F value	p value	
Environnments	5	343081,680	68616,336	1,923	,1097	
Residus	44	1569750,100	35676,139			

PLSD Fisher for Mg (ppm) Effects: Environnement Significance level: 5%

Distal Lagoon, Median Lagoon
Distal Lagoon, Oolithic Shoal Transition
Distal Lagoon, Proximal Lagoon
Distal Lagoon, Storm surge on TF
Distal Lagoon, Tidal Flat
Median Lagoon, Oolithic Shoal Transition
Median Lagoon, Proximal Lagoon
Median Lagoon, Storm surge on TF
Median Lagoon, Tidal Flat
Oolithic Shoal Transition, Proximal Lagoon
Oolithic Shoal Transition, Storm surge on T
Oolithic Shoal Transition, Tidal Flat
Proximal Lagoon, Storm surge on TF
Proximal Lagoon, Tidal Flat
Storm surge on TF, Tidal Flat

Mean deviation	Critical deviation	p value	
-74,861	161,752	,3560	
-225,250	300,942	,1386	
-136,550	180,565	,1346	
-272,250	257,712	,0389	\$
-223,694	184,970	,0189	5
-150,389	283,731	,2912	
-61,689	150,136	,4121	
-197,389	237,386	,1009	
-148,833	155,406	,0601	
88,700	294,862	,5475	
-47,000	347,498	,7864	
1,556	297,580	,9916	
-135,700	250,585	,2810	
-87,144	174,904	,3208	
48,556	253,777	,7016	

	DF	Sum of squares	Mean square	F value	p value
Environnments	5	95,880	19,176	8,734	<,0001
Residus	44	96,600	2,195		

PLSD Fisher for Mn (ppm) Effects: Environnement Significance level: 5%

	Mean deviation	Critical deviation	p value	
Distal Lagoon, Median Lagoon	-1,056	1,269	,1007	1
Distal Lagoon, Colithic Shoal Transition	1,000	2,361	,3979	1
Distal Lagoon, Proximal Lagoon	-1,700	1,416	,0198	s
Distal Lagoon, Storm surge on TF	-1,667	2,022	,1037	1
Distal Lagoon, Tidal Flat	-4,111	1,451	<,0001	HS
Median Lagoon, Oolithic Shoal Transition	2,056	2,226	,0694	1
Median Lagoon, Proximal Lagoon	-,644	1,178	,2761	1
Median Lagoon, Storm surge on TF	-,611	1,862	,5118	1
Median Lagoon, Tidal Flat	-3,056	1,219	<,0001	HS
Oolithic Shoal Transition, Proximal Lagoon	-2,700	2,313	,0232	s
Oolithic Shoal Transition, Storm surge on TF	-2,667	2,726	,0550	1
Oolithic Shoal Transition, Tidal Flat	-5,111	2,334	<,0001	не
Proximal Lagoon, Storm surge on TF	,033	1,966	,9729	1
Proximal Lagoon, Tidal Flat	-2,411	1,372	,0010	s
Storm surge on TF, Tidal Flat	-2,444	1,991	,0173	s

HS: Highly significant difference between environmental classes according to the means for one considered element S: Significant difference

rately. The effect of the depositional environment is highly significant on Sr, Fe, and Mn contents, and not significant on Mg contents. TF and ST, which are the extreme positions of the opening trend, are the most significantly discriminated environmental classes

and/or dissolution (Dini et al. 1998; Strasser et al. 1999). None of the observations performed on the microfacies corroborate such a direct freshwater-related diagenesis in the shallowest facies. However, transgressive erosion could have removed sedimentological features (Hillgärtner 1998), and in this case Sr contents could be the only indication of exposure events, like it has been illustrated for the stable isotopes (Joachimski 1994). But variations in Sr contents are also known to reflect the paleosalinity of the seawater in which carbonates precipitate (Renard 1975; Pascal 1984), with increasing Sr contents reflecting increasing salinity. Lower Sr contents in proximal environments could illustrate brackish conditions, without involving exposure- and freshwater-related diagenesis, whereas higher contents in more distal environments could reflect open marine conditions. This environmental interpretation is consistent with that proposed for the Fe–Mn pair. The weathering of soils and associated detrital supplies may be the result of rainfall on the exposed islands (Fig. 12). But rainfall should also affect nearby proximal shallow-marine environments, which are then brackish. Therefore, the Sr contents of the carbonates precipitating in these proximal environments may decrease (Fig. 12). The rainfall weathering is consistent with the proposed warm and humid climate of the Late Jurassic at the paleolatitude of the study area (Read et al. 1995; Price 1999). However, depositional environments may be not always subjected to rainfall but could also be subjected locally in space and time to less humid conditions (Fig. 12). Then, the more proximal and shallowest environments may suffer high salinity by evaporation (brine environments) and record corresponding increases in Sr content of the carbonates rather than the expected low contents. In fact, restricted stratigraphic levels with chicken-wire structures (anhydrite pseudomorphs) have been reported in the Middle Oxfordian formations, to the southwest of the section site (Vincent 2001).

With such hypotheses, it is possible to traduce the variations in Sr and Fe–Mn contents in variations of paleoenvironmental conditions along the section (see Fig. 6). These geochemical/environmental relationships are summarised on the bivariate scatter diagram of samples (see Fig. 10), and the opening trend depicted by the distribution of the different environmental fields can also be explained in terms of paleoenvironmental parameters.

Conclusions

To summarise, it appears that geochemistry shows distinct differences in Sr, Fe, and Mn contents between some shallow-marine environments. Along a depositional profile defined by the sedimentologic study, the evolutions of Sr, Fe, and Mn contents observed in the descriptive statistical stage, are significant between tidal-flat and lagoon, and between lagoon and distal lagoon/oolithic shoal transition. Within the lagoon, Sr, Fe, and Mn contents are not significantly different between the various depositional environments, but Fe and Mn display a progressive shift from one environment to the other. Finally, Mg contents appear to not reflect variations of depositional environments.

Trace element geochemistry in Oxfordian neritic carbonates along the Pagny-sur-Meuse section thus still record

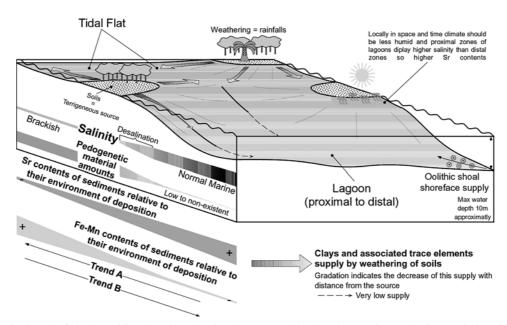


Fig. 12 Schematic sketch of the depositional setting showing the environments described in the sedimentological study. Variations of the environmental parameters (salinity and pedogenetic material amounts) as well as changes in Sr, Fe, and Mn contents are shown alongside this profile. Evolution of the geochemical contents along the section mirrors the evolution of the environmental parameters and so the shift in the profile. These shifts in the profile are

recorded along the section and reflect variations in available space. A decrease in available space leads to a facies progradation. Along a vertical section, increasingly proximal facies (lagoon to tidal-flat) are recorded together with an increasingly proximal chemical signal. Conversely, an increase in available space results in increasingly distal facies (tidal-flat to lagoon) and an increasingly distal chemical signal

part of an initial signal influenced by paleoenvironment. Geochemical data obtained give precisions about paleoenvironmental parameters such as salinity, here related to Sr contents, detrital input, here related to Fe and Mn contents, and so about some of the climatic conditions during deposition of the sediments.

There is however one important point to bear in mind: contrary to the situation with pelagic carbonates, geochemical studies of neritic carbonates cannot yet be dissociated from sedimentological and diagenetic studies.

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