

Fluctuations of sea-water chemistry during Gargasian (Middle Aptian) time. Data from trace-element content (Mg, Sr, Mn, Fe) in hemipelagic carbonates from La Marcouline Quarry (Cassis, SE France)

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Fluctuations of sea-water chemistry during Gargasian (Middle Aptian) time. Data from trace-element content (Mg, Sr, Mn, Fe) in hemipelagic carbonates from La Marcouline Quarry (Cassis, SE France)

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Abstract: In the Lower Aptian historical stratotype area (Cassis-La Bédoule, SE France), a geochemical study of the Gargasian (Middle Aptian) marl-limestone alternations of the La Marcouline quarry complements data already obtained from Bedoulian (Early Aptian) sediments there. Nannoconids are the main carbonate producers in both limestones and marls. Although diagenetic minerals, such as ankerite (2.5%) are present in small amounts, the trace-element content of bulk carbonate is very close to that of *Nannoconus* spp. so geochemical sequences can be defined. The long-term evolution of trace-element content was not affected by diagenetic processes, variations in carbonate mineralogy, or a change of carbonate producers. An increase of around 500 ppm in the strontium content of bulk carbonate occurs between the base of the *Cabri* zone (late Bedoulian) and the *Algerianus* zone (late Gargasian). This evolution is linked to fluctuations in seawater Sr/Ca ratios caused by variability in the influx of hydrothermal and river waters, by changes in the ratio of aragonite/calcite production and by shifts in sea level. The eustatic sequence Aptian 4, its parasequences and its key surfaces (sequence boundaries, maximum flooding surface) are clearly reflected in the evolution of the bulk-carbonate contents of manganese.

Key Words: Aptian; Gargasian; pelagic carbonates; magnesium; strontium; manganese; iron; *Nannoconus*; seawater Sr/Ca; chemostratigraphy; sequence stratigraphy

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Résumé : ***Fluctuations de la chimie de l'eau de mer au cours du Gargasien (Aptien Moyen). Apports des teneurs en éléments traces (Mg, Sr, Mn et Fe) des carbonates hémipélagiques de la carrière de La Marcouline (Cassis, Sud-Est France).-*** Dans la région du stratotype historique de l'Aptien inférieur (Cassis-La Bédoule, SE France), les sédiments alternants du Gargasien (Aptien supérieur) de la carrière de la Marcouline ont été étudiés du point de vue géochimique. Le dosage des éléments traces (Sr, Mg, Mn et Fe) du carbonate total a permis de compléter les données déjà obtenues sur le Bédoulien et de définir une zonation chimiostratigraphique du Gargasien. Les *Nannoconus* sont les producteurs carbonatés principaux aussi bien dans les bancs calcaires que dans les bancs marneux. Les différences géochimiques observées entre les marnes (enrichies en Sr et Mg) et les calcaires (enrichis en Mn et Fe) ne peuvent être réduites à une variation des producteurs ou à une

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diagenèse différentielle. En dépit de la présence de traces d'ankérite d'origine diagénétique (2,5%), l'enregistrement des éléments-traces au sein du carbonate total reste très proche de celui des fractions pures en *Nannoconus* et permet de définir les séquences géochimiques. Dans la continuité du processus initié dans le Bédoulien supérieur (base de la zone à *Cabri*), les teneurs en strontium croissent régulièrement durant le Gargasien. Au total une augmentation de l'ordre de 500 ppm survient entre la base de la zone à *Cabri* (Bédoulien supérieur) et la zone à *Algerianus* (Gargasien supérieur). Elle traduit une variation du rapport Sr/Ca de l'eau de mer, à mettre en relation avec le bilan des apports hydrothermaux et fluviatiles, le rapport de la sédimentation aragonitique à la sédimentation calcitique et les variations du niveau marin. Les teneurs en manganèse ont permis de mettre en évidence la séquence eustatique Aptien 4 et les paraséquences qui la composent, ainsi que de localiser ses surfaces clefs (limites de séquence et surface d'inondation maximale).

Mots-Clefs : Aptien ; Gargasien ; carbonates pélagiques ; magnesium ; strontium ; manganèse ; fer ; *Nannoconus* ; Sr/Ca de l'eau de mer ; chimiostratigraphie ; stratigraphie séquentielle

Introduction

MOULLADE & TRONCHETTI (2004) and MOULLADE *et alii* (2004) described the general setting of La Marcouline quarry, where the succession of Gargasian (Middle Aptian) beds is exposed continuously, and they specified its lithostratigraphic and biostratigraphic relationships to the Bedoulian (Lower Aptian) of the Cassis-La Bédoule area. Both the marls and the limestones of the Gargasian beds of La Marcouline quarry were sampled and analyzed for stable carbon and oxygen isotopes (see KUHNT & MOULLADE, 2007) and for the trace elements in bulk carbonate (see results and discussion below). Samples were washed in distilled water, crushed and then dissolved in acetic acid (1N). Trace elements were analyzed by atomic absorption (Hitachi Z8100 spectrometer) using the method described by RENARD & BLANC (1971; 1972) and RICHEBOIS (1990). Analytical accuracy is around 5%. All data are listed in Appendix 1. Gargasian sequences in La Marcouline section are defined geochemically and labeled in continuity with the Bedoulian ones as proposed in the same geographic area by RENARD & de RAFÉLIS (1998).

Results

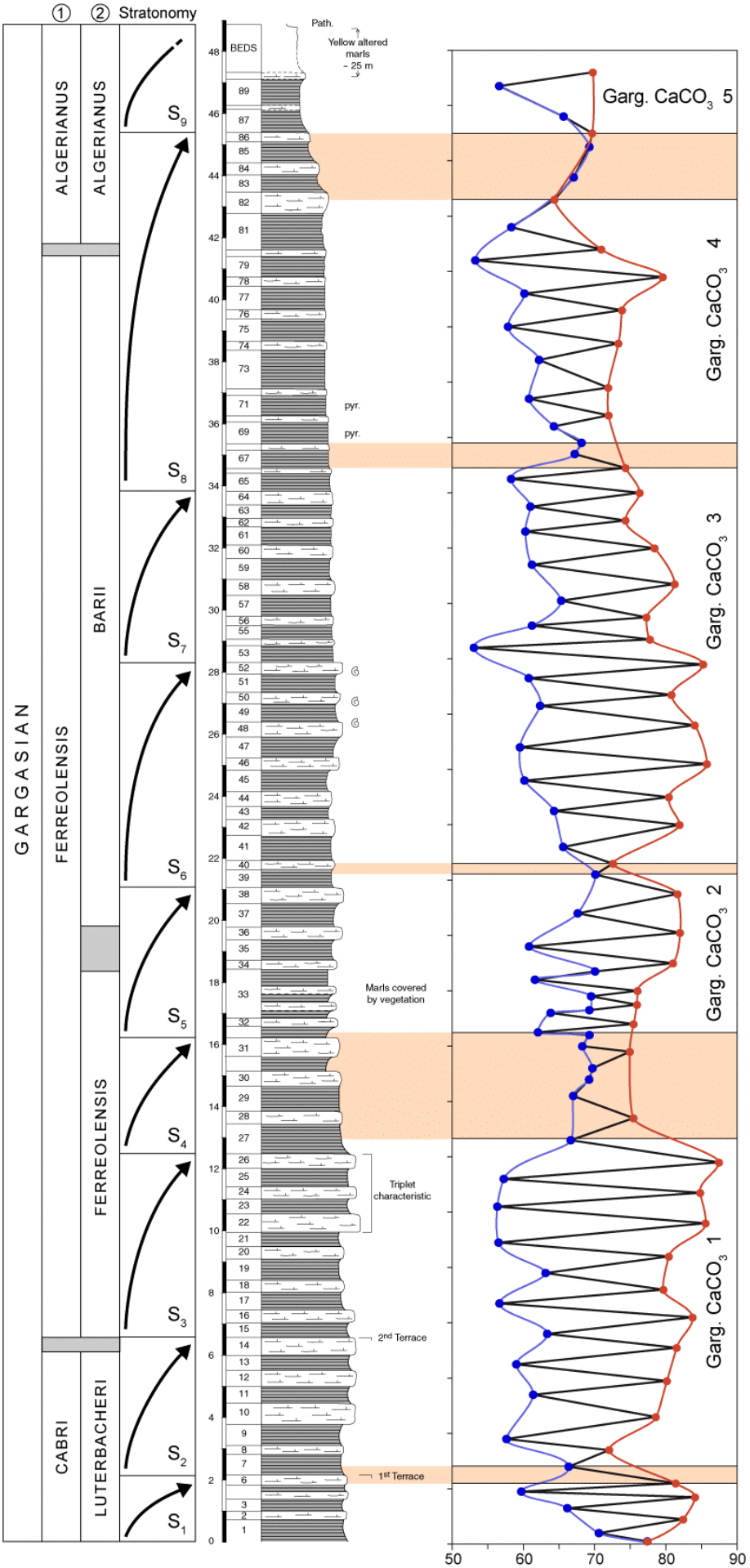
1- $CaCO_3$ contents and relationship with bedding and stratonomy

In La Marcouline quarry, Gargasian sedimentation is of a hemipelagic type in which marl and marly limestone deposits alternate regularly. Contacts between the two lithologies are transitional. Overall, the thickness of limestone beds relative to marly ones decreases upward (Fig. 1). A parasequence pattern is superimposed on this general trend and there are nine parasequences of momentary thickening upward in limestone beds:

- Parasequence S1: Beds 1 to 6 (incomplete sequence),
- Parasequence S2: Beds 7 to 14 (the upper boundary of this sequence corresponds to the transition between the *Cabri* (*Luterbacheri*) and *Ferreolensis* zones (MOULLADE *et alii*, 2005),
- Parasequence S3: Beds 15 to 26 (this parasequence ends with a well-defined triplet of limestone: beds 22, 24, 26),
- Parasequence S4: Beds 27 to 31
- Parasequence S5: Beds 32 to 38 (this sequence includes the *Ferreolensis*/*Barri* zone boundary),
- Parasequence S6: Beds 39 to 52,
- Parasequence S7: Beds 53 to 64,
- Parasequence S8: Beds 65 to 86 (this sequence includes the *Barri*/*Algerianus* zone boundary),
- Parasequence 9: Beds 87 to 90 (the first steps of the last visible parasequence).

We note that the thickness of each parasequence increases upward throughout the observed Gargasian: Parasequence 2 occupies 2.5 m whereas parasequence 8 spans 11 m.

▶ **Figure 1:** Lithology, sequence pattern and $CaCO_3$ content in the Gargasian beds of La Marcouline quarry. Blue line and circles: $CaCO_3$ contents in the marls (soft beds) ; red line and circles: $CaCO_3$ contents in the limestones (hard beds). Biostratigraphic scales from (1) ROBAZYNSKI & CARON (1995) and MOULLADE *et alii* (2002) and (2) from MOULLADE *et alii* (2005).


① ② Stratonomy
GARGASIAN
ALGERIANUS
FERREOLENSIS
CABRI
ALGERIANUS
BARII
FERREOLENSIS
LUTERBACHERI
S9
S8
S7
S6
S5
S4
S3
S2
S1
BEDS
Path.
Yellow altered marls ~ 25 m
pyr.
pyr.
Marls covered by vegetation
Triplet characteristic
2nd Terrace
1st Terrace
Garg. CaCO3 5
Garg. CaCO3 4
Garg. CaCO3 3
Garg. CaCO3 2
Garg. CaCO3 1
50
60
70
80
90

The $CaCO_3$ content of each bed is in accord with the marl/limestone alternations as delineated in the outcrop scale (Fig. 1). The $CaCO_3$ content of the limestone beds ranges from 64.4% to 87.5% (mean 77.6%) and the $CaCO_3$ content of the marly beds from 53% to 77.4% (mean 62.8%). In both limestones and marls, the $CaCO_3$ content decreases upward in the section (more markedly in parasequences 6 through 9). A comparison with Bedoulian data (Fig. 2) from the same area (RENARD & de RAFÉLIS, 1998; RENARD *et alii*, 2005) shows that the $CaCO_3$ content of the Gargasian beds at La Marcouline is intermediate between that of the strata of early Bedoulian age (*Kuznetsovae* and *Blowi* foraminiferal zones) and that of the sequence of late Bedoulian age (*Cabri* zone). $CaCO_3$ content appear to be more variable during the Gargasian than during the Bedoulian. This pattern is caused by the fact that in the Bedoulian interval only limestones were sampled whereas in the Gargasian both limestones and marls were collected.

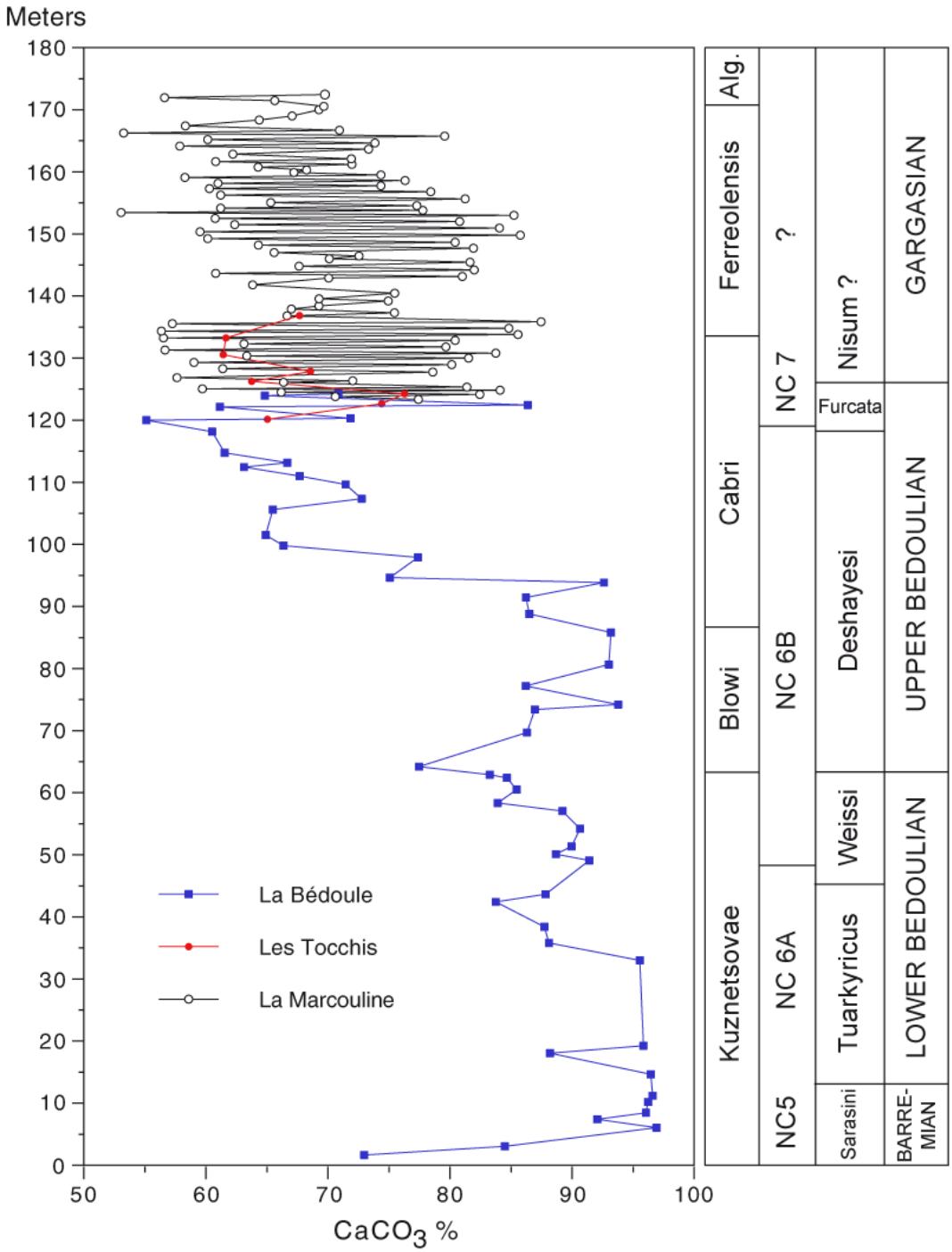


Figure 2: Evolution in the $CaCO_3$ content of Bedoulian and Gargasian sediments from the Cassis area (La Bédoule, Les Tocchis and La Marcouline).

The difference in the amount of $CaCO_3$ in limestone and marl is not constant throughout the Gargasian succession (Fig. 1). The mean difference is about 15% but values range from 30.2% (between beds 25 and 26) to 0.4% (between beds 85 and 86). Sequences with a markedly greater amount of $CaCO_3$ in limestone over that in marl (beds 4-5, 23 to 26, 53-54, 78-79) alternate with sequences in which the difference is slight (beds 7-8, 27 to 33, 39-40, 67-68 and 82 to 86). In these successions, the "hard beds", called "limestones" in outcrop, may have a $CaCO_3$ content nearly the same as or even lower than the "soft beds" (*i.e.* "marls"). These fluctuations define 5 sequences that start with small differences in the $CaCO_3$ content of the two rock types and are more or less related to the pattern of the stratonomic parasequences described above (Fig. 1):

- $CaCO_3$ sequence 1 encompasses stratonomic sequences 2 and 3,
- $CaCO_3$ sequence 2 subsumes stratonomic sequences 3 to 5,
- $CaCO_3$ sequence 3 includes stratonomic sequences 6 and 7,
- $CaCO_3$ sequence 4 takes in stratonomic sequence 8, and
- $CaCO_3$ sequence 5 corresponds with stratonomic sequence 9.

BELTRAN (2006) and KUHNT & MOULLADE (2007) show that these fluctuations in $CaCO_3$ content have a MILANKOVITCH-like frequency. This finding led to their interpretation as reflections of oscillations in the orbit of the earth that affect climate and in turn the rate and characteristics of sedimentation. BELTRAN (2006) and BELTRAN *et alii* (2007) have carried out a detailed sedimentological study focused on the interval spanning beds 29 to 32. In this interval the compositions of marl and limestone beds are very similar in terms of carbonate particles and type of producers (Fig. 3). The carbonate fraction is composed of a heterogeneous assemblage of calcareous nannofossils made up of coccoliths (around 8%, mainly *Watznauearia barnesae* and few *Rhagodiscus* spp., *Biscutum* spp. and *Zeugrhabdotus* spp.), and nannoconids (around 20-25%), a small quantity of planktonic foraminiferal debris, structureless carbonate particles, *i.e.* carbonate macrocrystals (around 8%), and calcitic microcrystals (around 60%).

	Structureless carbonate particles of uncertain origin			Calcareous Nannofossils					
	Ankerite macro-particles	Calcite macro-particles	Micarbs	Coccoliths					*Nannoconus* sp.
Marls	2.5	6	58	8					25.5
				Watznaueria sp.	*Rhagodiscus* sp.	*Biscutum* sp.	Others	Fragments	
				1.2	1	0.1	0.2	5.5	
Limestones	2.5	6	63	8.5					20
				Watznaueria sp.	*Rhagodiscus* sp.	*Biscutum* sp.	Others	Fragments	
				1.8	0.7	0.1	0.1	6	

Figure 3: Mean composition of carbonate fraction in marls and limestones (volume %, from BELTRAN, 2006).

Carbonate macrocrystals (8.5% of the carbonate fraction) range in size from 12 to 5 µm and their mineralogic composition includes calcite (6%) and ankerite (2.5%). MINOLETTI *et alii* (2005) described the same kind of macrocrystals in the Late Cretaceous pelagic sediments ("Marnes de Bidart") under the Bay of Biscay (SW France). In both locations geochemical data suggest that these particles result from early diagenetic processes (see infra). If so, the effects of this diagenesis appear to be quite limited.

Microcrystals are defined as calcitic particles (between < 3 and 5 µm) with no biological shapes or microstructures detectable by optical and electronic microscopy. They correspond to the "micarb" of COOK &

EGBERT (1983), ERBA (1992), NOËL *et alii* (1994) and MATTIOLI & PITTET (2002). Oxygen and carbon isotope ratios and crystallographic data (DTA/TG) show that La Marcouline micarb are mainly minute fragments of *Nannoconus* spp. (BELTRAN, 2006). This shows that the carbonate fraction of La Marcouline sediments is dominanted by biogenic particles (around 90%) and that in both marls and limestones, *Nannoconus* spp. are the main carbonate producers (around 80% by volume).

The non-carbonate portion of the samples is mainly clays and quartz. In both marls and limestones the clay fraction consists of illite (31%) and kaolinite (29%). The lithological contrasts between limestones and marls are caused by dilution cycles which reflect periodic changes in the supply of non-carbonate material during uniform carbonate duction (BELTRAN, 2006; BELTRAN *et alii*, 2007).

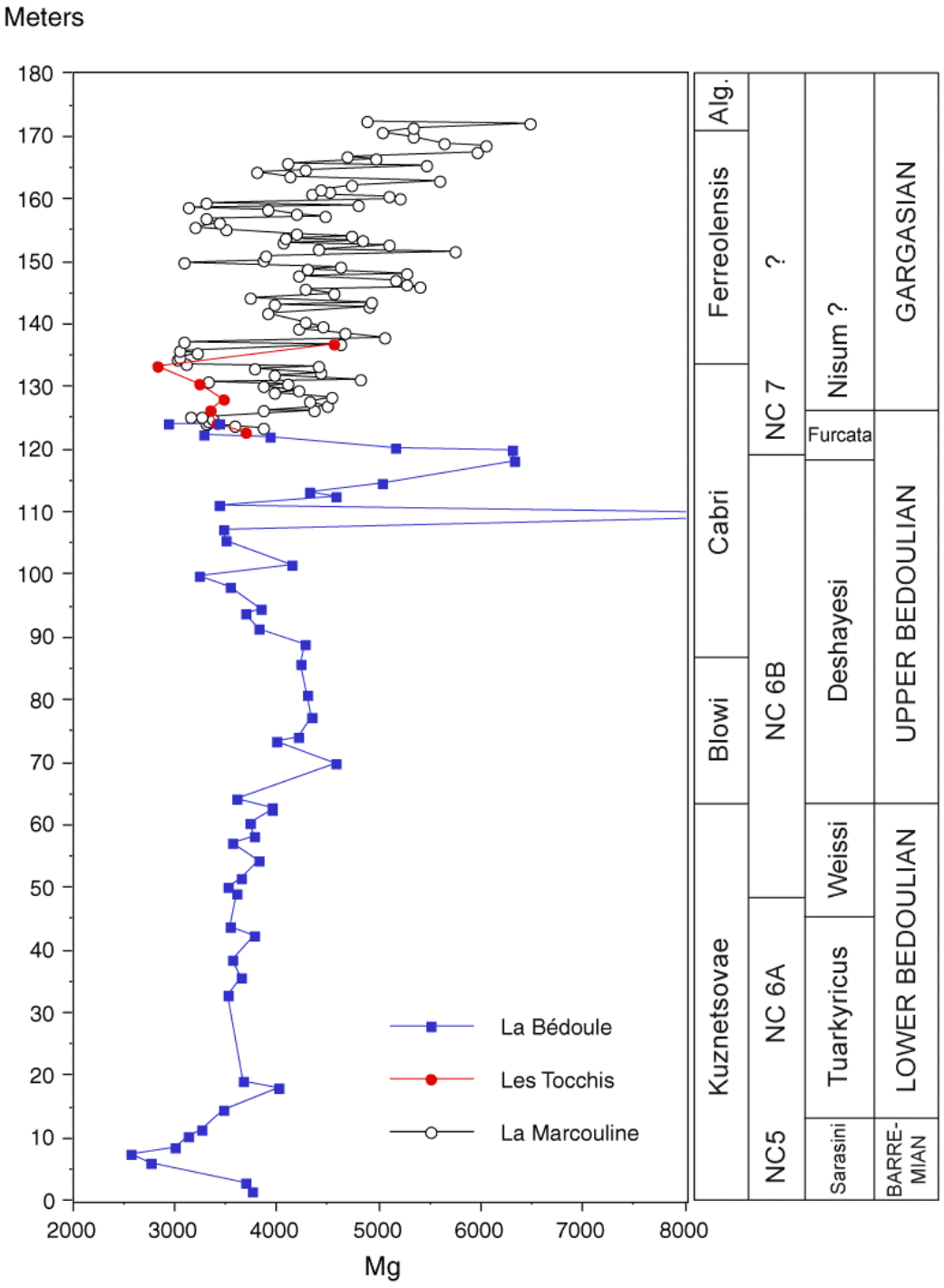


Figure 4: Evolution of Mg content in bulk carbonate in Bedoulian to Gargasian sediments from the Cassis area (La Bédoule, Les Tocchis and La Marcouline). For outcrop locations see MOULLADE *et alii* (2004).

2- Magnesium

2.a- Long-term evolution and comparison with Bedoulian sediment contents

At La Marcouline the magnesium content of the carbonates of Gargasian age is relatively higher (3027-6479 ppm, mean: 4306 ppm) than that of Bedoulian strata in the same Cassis region (Fig. 4, RENARD & de RAFÉLIS, 1998). In these underlying beds the Mg contents ranges consistently from 2500 to 4500 ppm (mean = 3726 ppm), but in the sediments spanning the transition from the *Deshayesi* to the *Furcata* ammonite zones, a higher content (5000 to 6300 ppm) is related to the late Bedoulian anoxic event OAE1a.

Compared to the geochemical data obtained for Bedoulian deposits (RENARD & de RAFÉLIS, 1998), the Gargasian samples show stronger fluctuations in both Mg and carbonate content. These differences may be caused by the different sampling procedures chosen. Indeed, the Bedoulian samples were taken from limestone beds only whereas the Gargasian ones were collected equally from both lithologies.

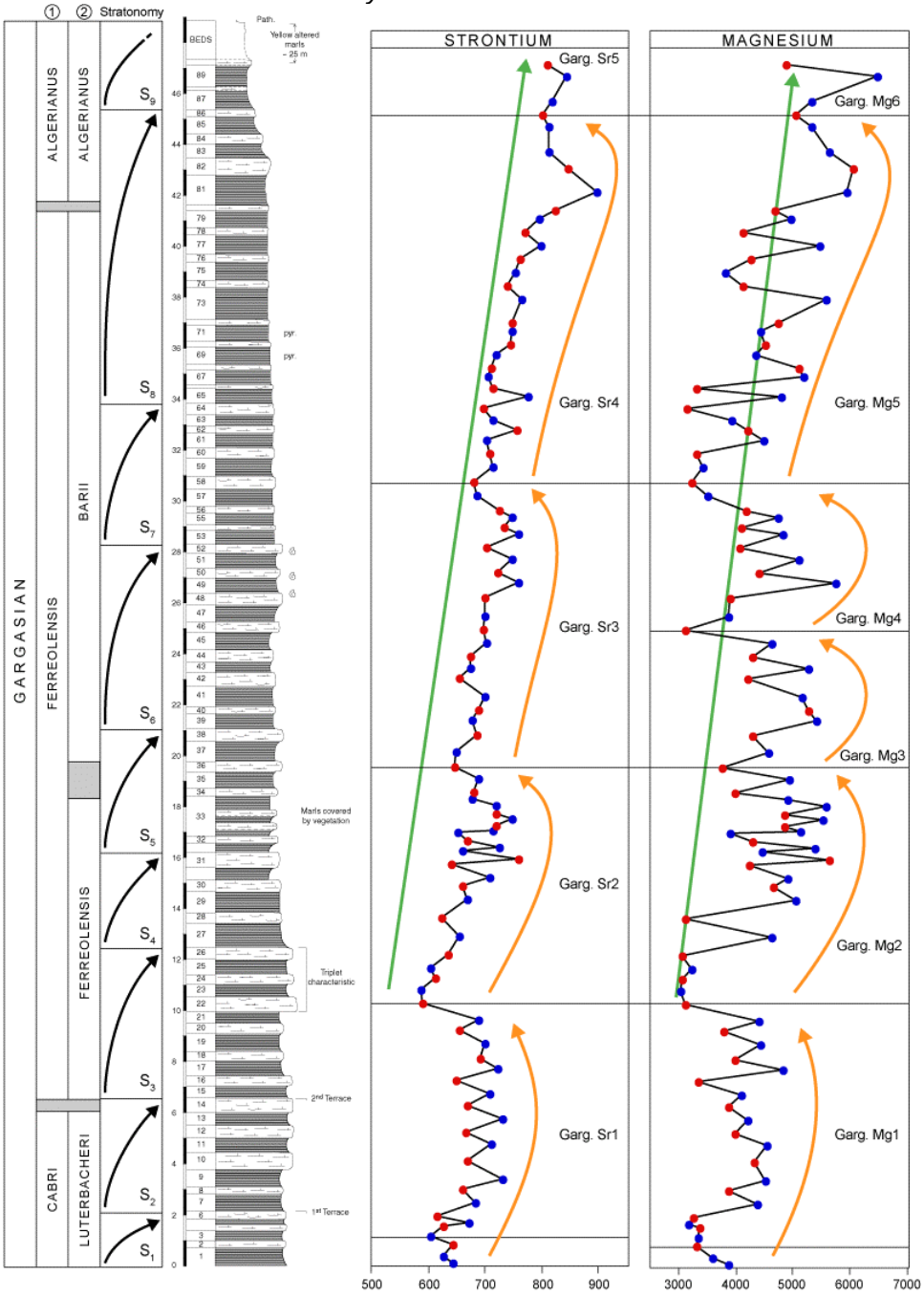


Figure 5: Sr and Mg contents in the bulk carbonate of Gargasian beds in the La Marcouline quarry. Blue circles: Marls (soft beds); red circles: Limestones (hard beds).

2.b- Relationships between Mg content and lithology

In a general way the evolution of the Mg content of the bulk carbonate is in phase with changes in lithology (Fig. 5): Marls have a higher contents (mean 4557 ppm, average 3027-6479 ppm) than limestones (mean 4039 ppm, average 3035-6046 ppm). Nevertheless, the long-term evolution of Mg content throughout the Gargasian succession may not be related to lithology alone. In the lower part of the sequences (beds 2 to 6, 22 to 26, 46 to 48, 57 to 60) many samples of both marl and limestone are low in magnesium while in the uppermost portion (from bed 64 to top) the content of magnesium in both marl and limestone increases in a similar manner.

2.c- Mg geochemical sequences in the La Marcouline succession.

Throughout the Gargasian succession at La Marcouline there is an overall trend toward an increase in Mg contents from 3000-4000 ppm at the base to 5000-6000 ppm at the top (Fig. 5). The Mg content increases in five positive excursions, each ended by a negative shift. The lowest samples figured are the uppermost portion of the last geochemical sequence described by RENARD & de RAFÉLIS (1998) in Bedoulian outcrops. The first Gargasian Mg sequence runs from bed 3 (3313 ppm) to bed 22 (base of a well-characterized triplet in outcrop, 3113 ppm) and reaches its highest reading, 4818 ppm, in bed 17. This first sequence is attributed to the *Cabri* (*Luterbacheri*) and early *Ferreolensis* zones and is labelled Garg.Mg1, in accordance with the numbering system of RENARD & de RAFÉLIS (1998). In the second sequence, (Garg.Mg2), from bed 22 to 36 (3738 ppm), the Mg content reaches a maxinum of 4447 ppm in the upper part of bed 31. The third Mg sequence (Garg.Mg3) spans beds 36 to 46 (3098 ppm) with a maximum in bed 39 (5402 ppm). In the Garg.Mg4 sequence, Mg values rise to 5748 ppm in bed 46 and the upper boundary is again a negative shift, recorded in bed 58 (3206 ppm). The last well-exposed Mg sequence (Garg.Mg5) spans beds 58 to 86 (5041 ppm) with the highest Mg content (6046 ppm) in bed 82. At La Marcouline quarry, only the initial stages of the Garg.Mg6 sequence are accessible.

3- Strontium

3.a- Long-term evolution and comparison with Bedoulian sediment contents

The increase in Sr in the sediments of the Bedoulian type locality (Fig. 6, RENARD & de RAFÉLIS, 1998) from the base of the *Cabri* Zone upward continues throughout the La Marcouline Gargasian series, rising from 626 ppm in bed 1 to 896 ppm in bed 81.

3.b- Relationship between Sr content and lithology

The correlation of Sr content with variations in lithology is less obvious than it is for Mg (Fig. 5). Nevertheless, in marls the content is slightly higher (mean 711 ppm, average 588–896 ppm) than in limestones (mean 699 ppm, average 590 – 845 ppm). The effects of lithology are clear only at and near the base of the outcrop (base to bed 22) where the difference in the Sr content of marls and limestones is on the order of 40/50 ppm. In the higher sequences the long-term increase in Sr content screens difference caused by changes in lithology.

3.c- Sr geochemical sequences at La Marcouline (Fig. 5)

As for Mg, the overall increase in Sr upward is supplemented by positive excursions marking the geochemical sequences. The first (Garg.Sr1) indicates an increase in Sr from 605 ppm (bed 3) to maxima of 732 ppm in beds 9 and 13 followed by a decrease to 588 ppm (bed 22). The negative shift in bed 22 (base of the outcrop triplet) seems to be a major geochemical break. The second positive excursion (Garg.Sr2) extends from bed 23 to bed 36 (646 ppm) with a maximum in bed 31 (759 ppm). The highest value of Garg.Sr3 is in bed 49 (758 ppm) and the sequence ends in bed 58 (681 ppm). We note that this sequence covers two magnesium sequences (Garg.Mg3 and 4). The upper boundary of sequence Garg.Sr4 is located at bed 86 (800 ppm). Its maximum content is recorded in bed 81 (896 ppm).

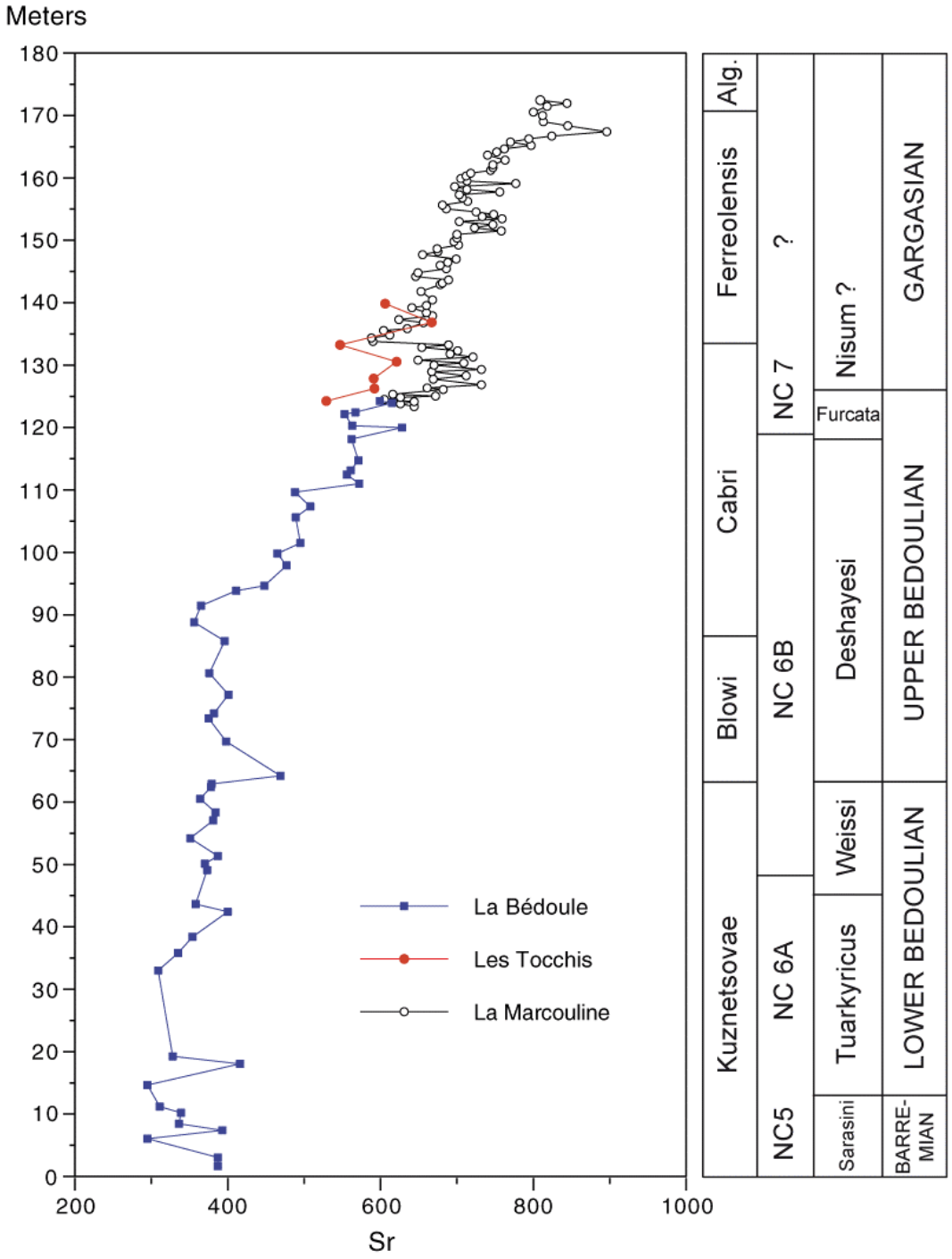


Figure 6: Evolution of Sr content in bulk carbonate in Bedoulian to Gargasian sediments from the Cassis area (La Bédoule, Les Tocchis and La Marcouline).

3.d- Correlation of Sr and Mg contents

The development of the Sr and Mg profiles follow a similar course, so are easily comparable (Fig. 7); the long-term trends both show an upward rise but lithology had a greater effect on Mg than on Sr. Figure 4shows the correlation between these two trace elements. The correlation coefficient (r) is 0.69 for 96 samples and the equation of the correlation line is:

[Sr] ppm = 0.074 [Mg] ppm + 381

The overlap of the areas of marl and limestone data on Figure 4shows that the diagenesis of marls and limestones differs slightly, but may not play a major role in the quantification of Sr and Mg.

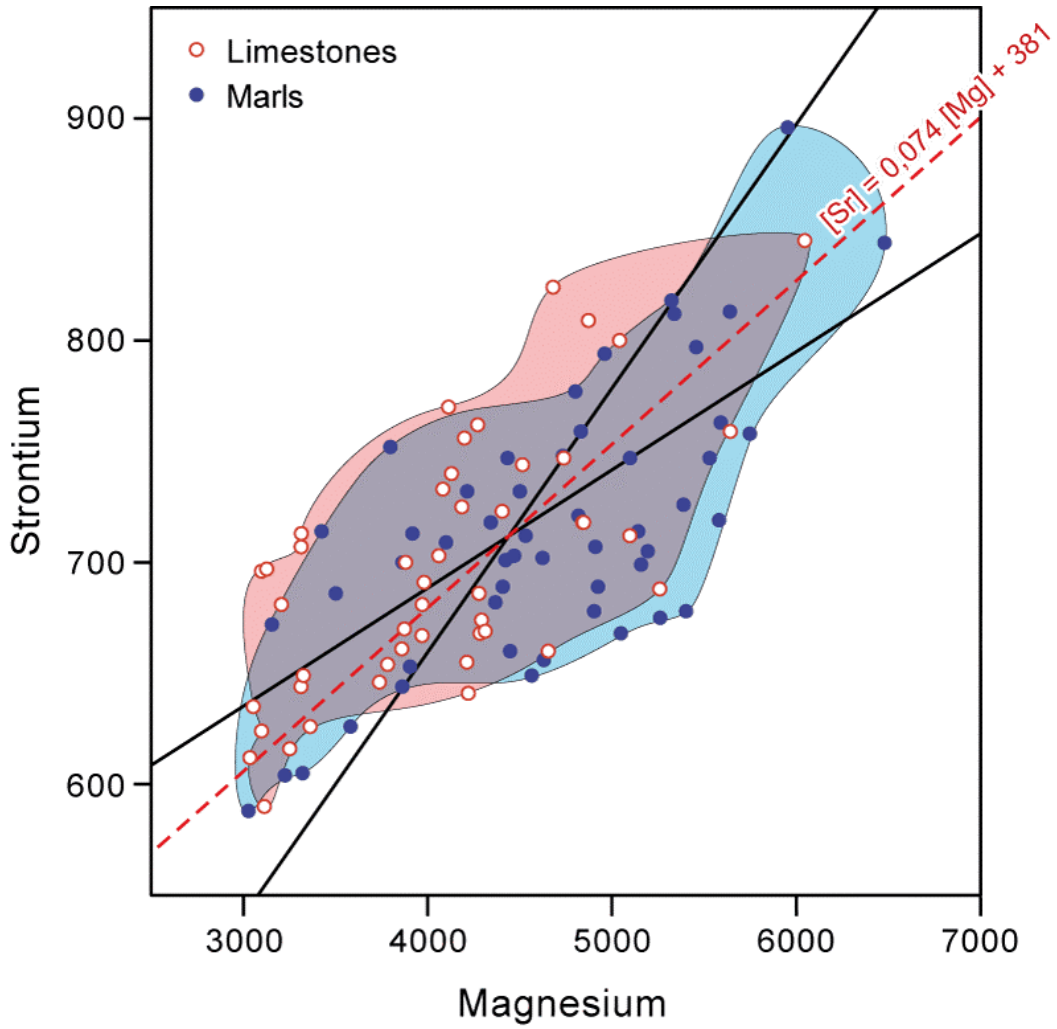


Figure 7: Relationship between the Sr and Mg content of Gargasian beds in La Marcouline quarry. Blue circles: Marls (soft beds); red circles: Limestones (hard beds).

4- Manganese

4.a- Long-term evolution and comparison with Bedoulian sediment contents

The quantities of Mn in the bulk carbonates of the Gargasian strata of La Marcouline (Fig. 8, mean 285 ppm, average 175-399 ppm) are higher than those of Bedoulian age, excluding high values (up to 450 ppm) in beds at the base of the Upper Bedoulian (base of the *Deshayesi* ammonite Zone) which are linked to an anoxic and methane hydrate event (JAHREN *et alii*, 2001; BEERLING *et alii*, 2002; RENARD & de RAFÉLIS, 1998; RENARD *et alii*, 2005).

4.b- Relationship between Mn content and lithology

As noted above for Sr, lithology influences the quantity of Mn slightly (Fig. 9) but its effect is contrary to that made on strontium: Limestones have a higher content of Mn than marls. The effect of lithology on Mn content is well expressed only in the first sequence of the La Marcouline series where a difference of 20 to 60 ppm is measured. In the other sequences, long-term increasing or decreasing trends tend to mask the role of lithology.

4.c- La Marcouline Mn geochemical sequences (Fig. 9)

Three Mn geochemical sequences are defined. During the first (Garg.Mn1) the Mn content rises slightly, through its variations related to lithology, from bed 5 (229 ppm) to a maximum of 319 ppm and decreases to 227 ppm (bed 25-26). The second sequence (Garg.Mn2) presents a more obvious positive excursion (maximum: 381 ppm in beds 31-33). Its upper boundary is located in bed 47 (244 ppm). The third (Garg.Mn3) reaches a maximum value in bed 62 (399 ppm) and ends in bed 81 or 83 (175 ppm). Low values (around 170-180 ppm) in the interval comprising beds 84 to 89 connote the beginning of the fourth sequence (Garg.Mn4).

5- Iron

5.a- Long-term evolution and comparison with Bedoulian sediment contents

The Gargasian portion of the La Marcouline series has a very high content of Fe. It increases from 1600 to 2000 ppm at the base to 2000-3000 ppm at the top.

This increase is continuous with that of the acceleration of its trend in Bedoulian strata which began in sediments attributed to the base of the *Cabri* foraminiferal Zone and becomes more prominent in the upper part of the *Deshayesi* ammonite Zone. The sedimentological study on the interval comprising beds 29 to 32 (BELTRAN, 2006; BELTRAN *et alii*, 2007) has shown that an important part of the Fe content of bulk carbonates is related to the presence of ankerite macroparticles (Fig. 3).

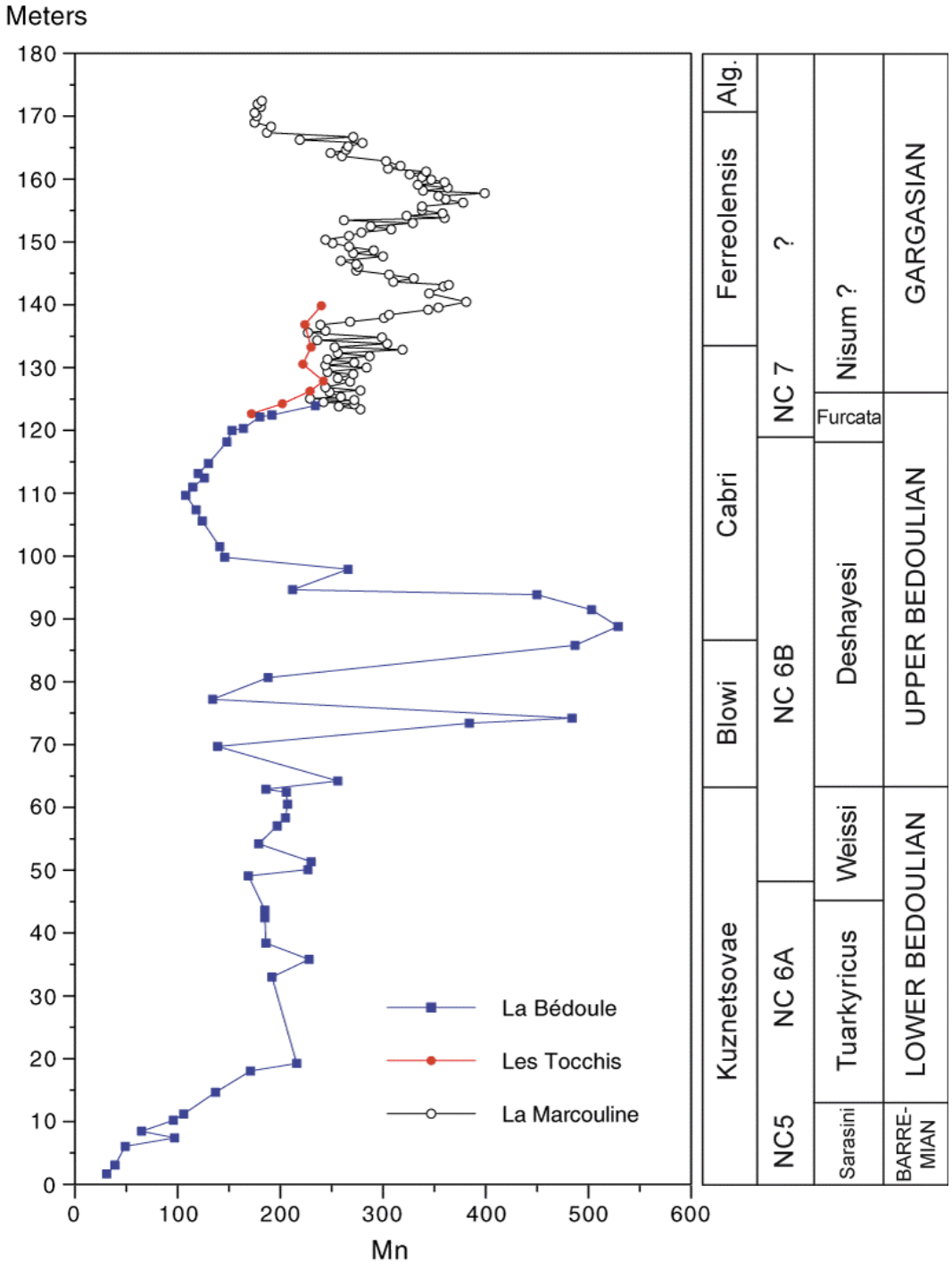


Figure 8: Evolution of bulk carbonate Mn content in Bedoulian to Gargasian sediments from the Cassis area (La Bédoule, Les Tocchis and La Marcouline).

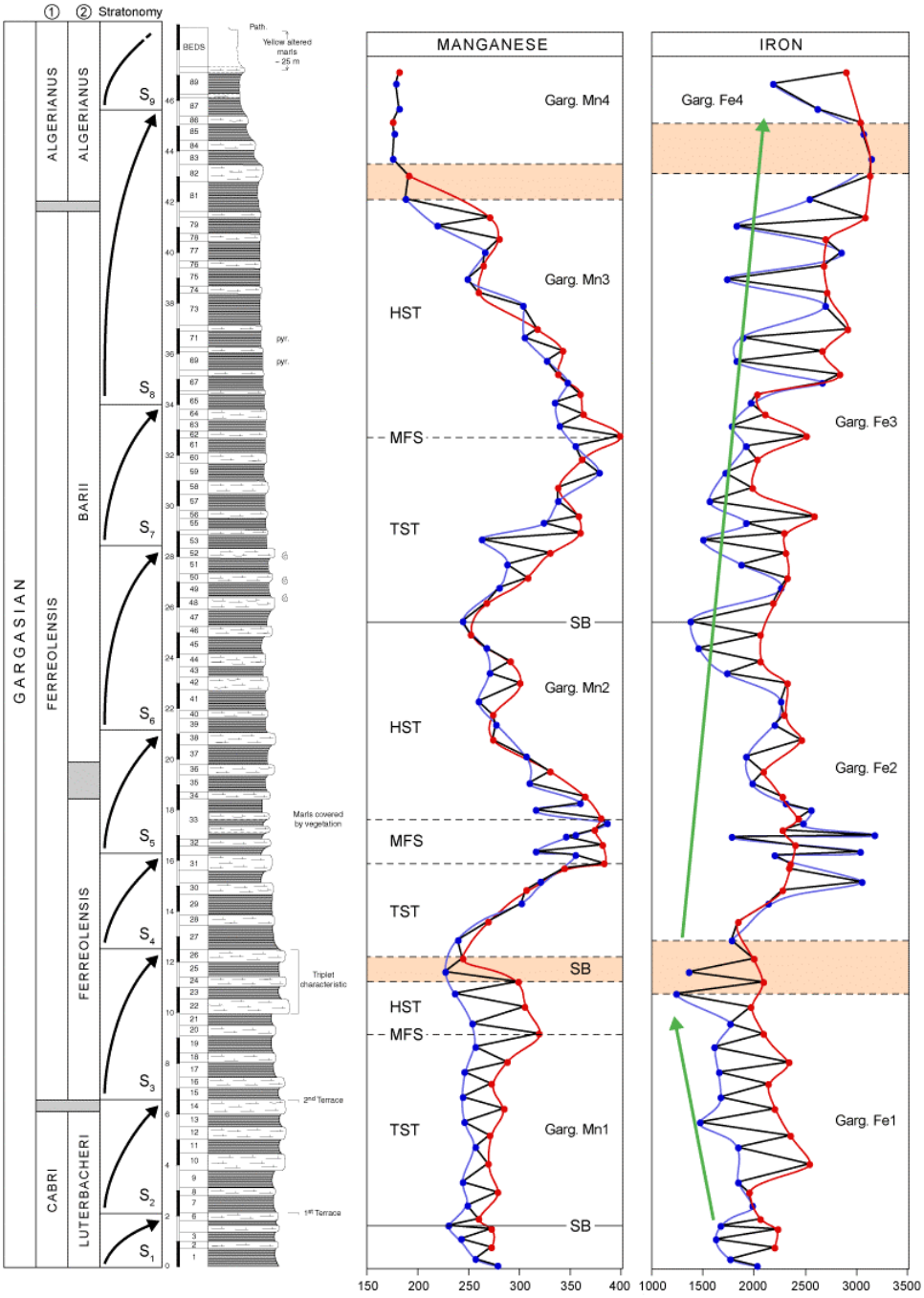


Figure 9: Mn and Fe content of bulk carbonates in the Gargasian beds of La Marcouline quarry. Blue line and circles: Marls (soft beds); red line and circles: Limestones (hard beds).

5.b- Relationship between Fe content and lithology

The amount of Fe ranges widely in function of the lithology (Fig. 9). Limestones have a greater amount of Fe than marls, a fact already noted for Mn. The difference ranges between 400 and 1000 ppm. Beds 30 to 33 (the interval in which the maxima of the Garg.Fe2 sequence is reached) are an exception because marls are richer in Fe than limestones.

5.c- La Marcouline Fe geochemical sequences

Three Fe sequences are distinguished (Fig. 9): The first (Garg.Fe1) records a decrease in contents from 2000 ppm (bed 1) to 1219 ppm (bed 23, the base of the characteristic triplet). The second (Garg.Fe2) shows a positive excursion with a maximum at the base of bed 33 (3179 ppm) and is bounded upward by bed 47 (1369 ppm). The last sequence (Garg.Fe3) shows an increase of Fe up to 3000 ppm in beds 82-86.

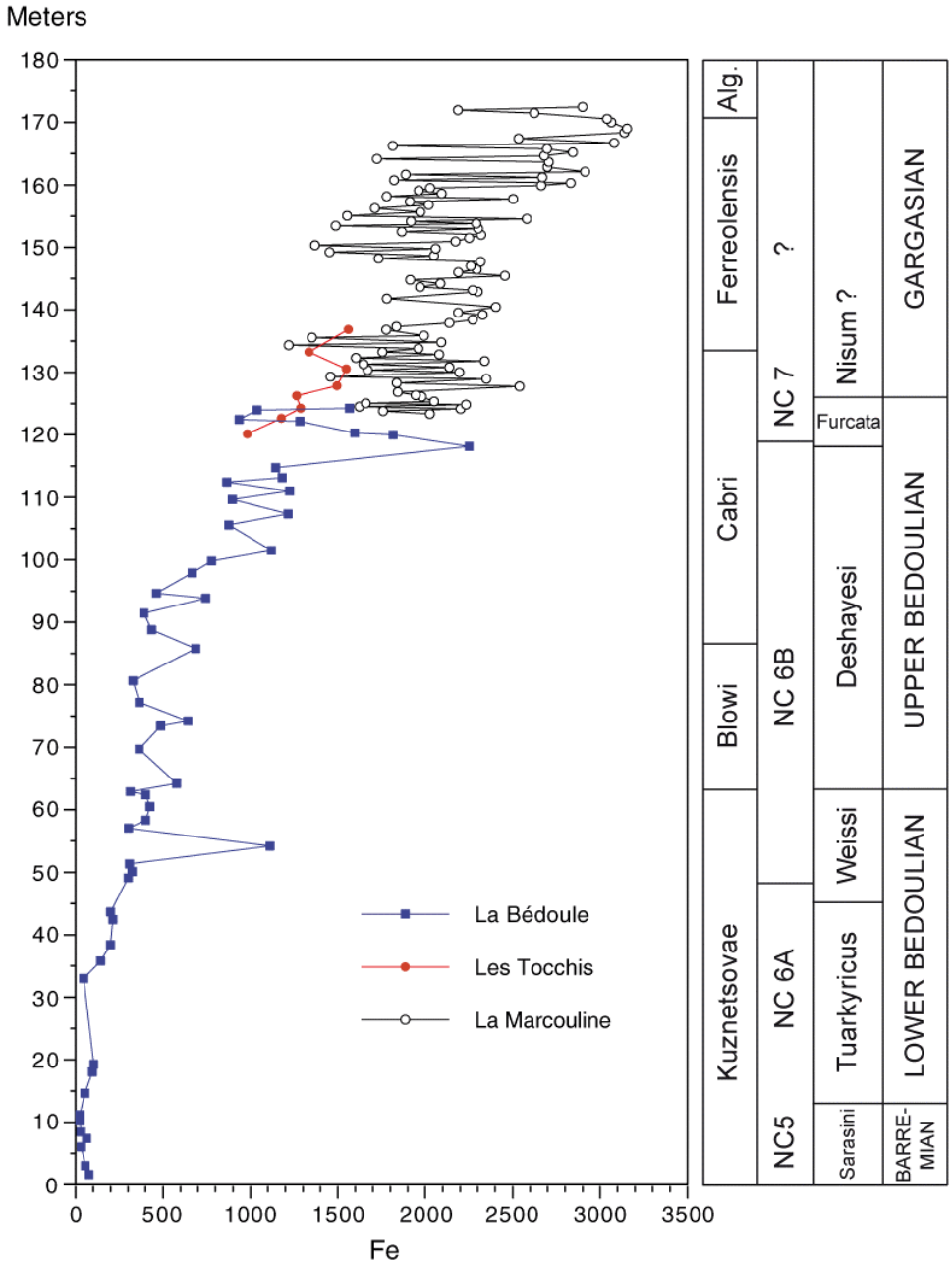


Figure 10: Evolution of Fe in the bulk carbonate of Bedoulian to Gargasian sediments from the Cassis area (La Bédoule, Les Tocchis and La Marcouline).

Discussion

1- Chemostratigraphy of the Gargasian section from La Marcouline quarry (Fig. 11)

The stratigraphic evolution of trace elements in the La Marcouline section (Figs. 5and 9) and the frame provided by these geochemical sequences (Fig. 11) highlight five geochemical breaks, of which the first (G1) is the most important. It is manifested very well in the values of the four trace elements and corresponds to the characteristic limestone triplet visible in outcrop. There are some slight differences in the location of the break for the various trace elements: Limestone bed 22 for Sr and Mg, limestone bed 24 for Mn and marl beds 23 to 26 for Fe. Note that the transition between $CaCO_3$ zone 1 and zone 2 starts in bed 26. This important geochemical shift does not coincide precisely with any of the bio-events recorded recently by MOULLADE *et alii* (2005). It corresponds only to the upper part of stratonomic sequence S3. No geochemical anomaly is associated with the boundary (bed 14) between the *Luterbacheri* and *Ferreolensis* foraminiferal zones which, nevertheless, is the location of stratonomy sequence boundary S2/S3.

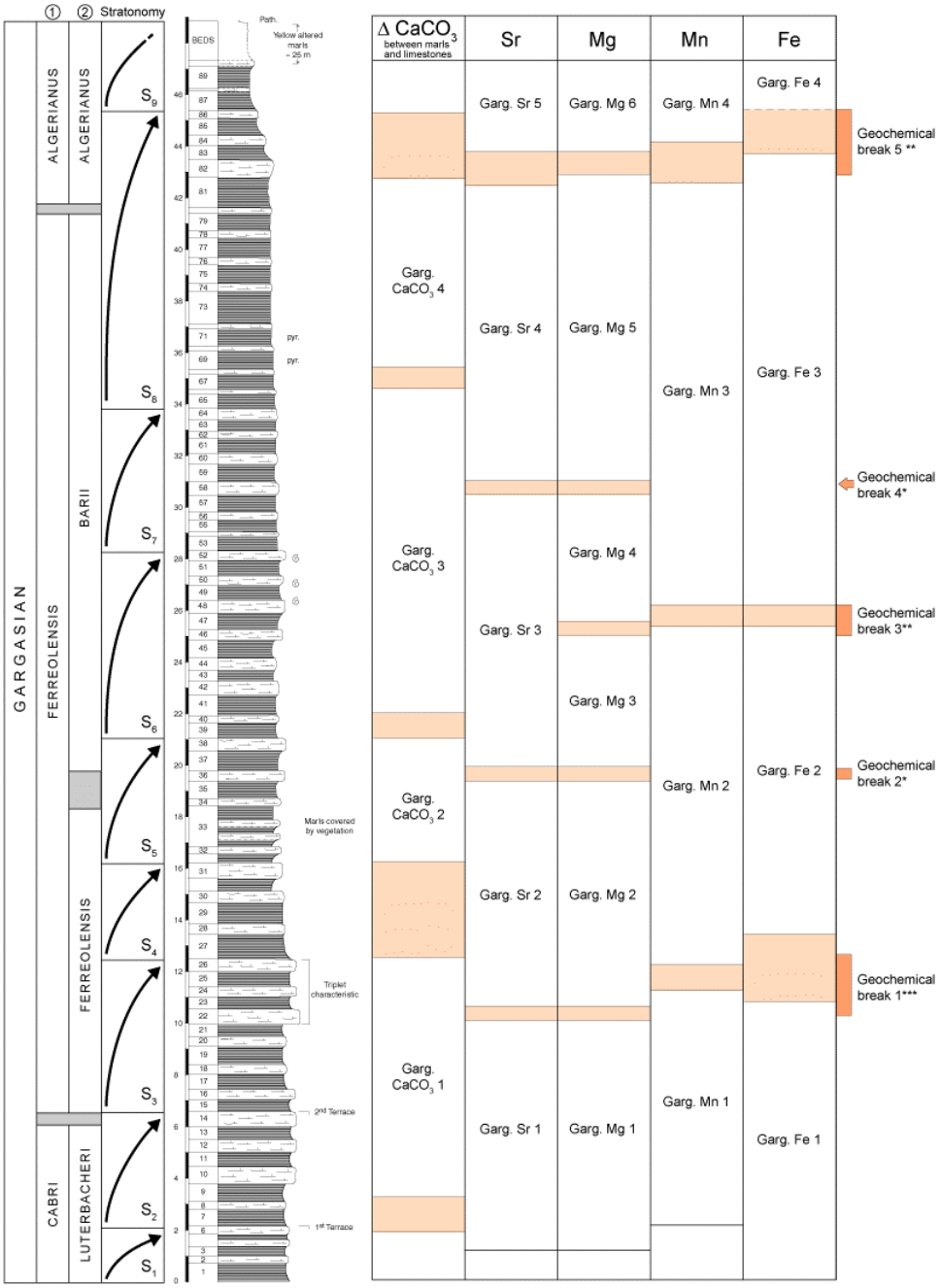


Figure 11: Schematic pattern of the chemostratigraphic zonation of the La Marcouline Gargasian section. Comparison with the stratonomy (1) and the biostratigraphic zonations (2) - (1) from ROBAZYNSKI & CARON (1995) and MOULLADE *et alii* (2002) and (2) from MOULLADE *et alii* (2005).

The second break (G2), located in bed 36, is less important and involves only Sr and Mg. Located in stratonomic sequence S5, this anomaly coincides with the *Ferreolensis*/*Barri* zonal boundary.

The third break (G3) is of moderate importance; for Mg it is located in bed 46 and for Mn and Fe in bed 47. The fourth boundary (G4) is of little importance and is located in bed 58 (Sr and Mg). The last break (G5) is in beds 81- 83 for Sr, Mg and Mn, and in beds 83-86 for Fe. This break is near (slightly later than) the transition between the *Ferreolensis* and *Algerianus* zones (bed 80).

2- Sr evolution: Hydrothermal supply, platform developments, aragonite/calcite production and nannofossil productivity

Following the pioneer work of KINSMAN (1969) bulk carbonate strontium has been used as a classical proxy of seawater chemistry in both pelagic (CRONBLAD & MALGREN, 1981; GRAHAM *et alii*, 1982; RENARD, 1986; STOLL *et alii*, 1999) and in neritic realms (VEIZER *et alii*, 1971, 1978;

BRAND, 1981; STEUBER, 1999). In neritic environments, carbonate Sr/Ca are correlated with sea water Sr/Ca and salinity (LORENS & BENDER, 1980; RENARD, 1985) but late diagenesis often masks the primary record (VEIZER, 1978, 1983). For pelagic carbonates, RENARD (1985, 1986) has shown that the effects of late diagenesis on pelagic carbonates is reduced, so the Sr content of bulk carbonate provides a reliable approximation of the Sr content of nannofossils. This view is confirmed by Sr isotope studies made by RICHTER & LIANG (1993) who consider that 80% of the geochemical signal of upper Cretaceous pelagic carbonate is of primary origin. On the other hand FRANK *et alii* (1999) and ANDO *et alii* (2006) consider that diagenesis obscured paleoceanographic signals in Lower Cretaceous sediments of the North Atlantic, because of the addition of diagenetic cements during burial compaction. In the La Marcouline Gargasian sediments, the use of granulometric separation (see BELTRAN *et alii*, 2007, for detail of the method) does not confirm this point of view. The Sr content of the 5 µm fraction, composed mainly of nannoconids (up to 80%), is very similar to that of bulk carbonate (Fig. 12). In Beds 29 to 32, the mean Sr content of bulk carbonate is 753 ppm (ranging between 650 and 924 ppm) and the mean Sr content of the *Nannoconus* spp. fraction is 743 ppm (range 669 to 927 ppm). In marls the Sr content of bulk carbonate fluctuates between 710 and 924 ppm (mean: 772 ppm) and the Sr content of the nannoconid-rich fraction between 705 and 927 (mean: 772 ppm). In the limestones bulk Sr content fluctuates from 650 to 772 ppm (mean: 728 ppm) and the Sr content of nannoconids from 669 to 759 (mean: 694).

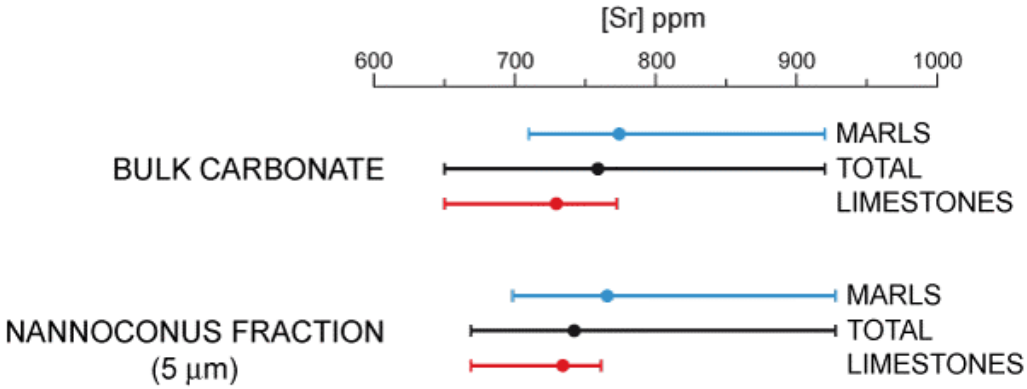


Figure 12: Comparison of the content of Sr in bulk carbonates and the Sr content of the 5 µm fraction in beds 29 to 32. The 5 µm fraction is mainly *Nannoconus* (up to 80%). Neither cementation nor diagenesis appears to have played a significant role. The Sr content of limestones is lower than that of marls in both bulk carbonate and in the *Nannoconus* fraction. Consequently, this relationship cannot be attributed to lithologic factors that might influence diagenesis.

Trace-element content in carbonates is controlled by the following equation:

$$[A/Ca]_{crystal} = K.[A/Ca]_{sea\ water}$$

where A and Ca are the concentrations of the trace-element and calcium and K the apparent distribution coefficient. For Sr and Mg, the content of carbonate is mainly the outcome of a *sensu stricto* co-precipitation process (substitution of Ca in the carbonate lattice) but other processes such as inclusion or absorption are not excluded. So the apparent distribution coefficient may include various processes of co-precipitation.

Three factors control the K_{Sr} value: Carbonate mineralogy, temperature and nature of the $CaCO_3$ producer (vital effect) if the carbonate is biogenic. Carbonate mineralogy plays a major role. For example, at typical temperatures for sedimentary environments, the distribution coefficients of strontium are 1.1 for aragonite, 0.1 for calcite, 0.09 for magnesian calcite and 0.01 for dolomite (KINSMANN, 1972; KITANO *et alii*, 1979; RENARD, 1985; MOORE, 2001).

In hemipelagic deposits such as the La Marcouline sediments, the mineralogy is mainly calcitic. Ankerite is not concentrated enough (< 3%, BELTRAN, 2006) to affect Sr concentrations in bulk carbonate (Fig. 12). As a result, the distribution of Sr in Bedoulian-Gargasian times cannot be explained by fluctuations in carbonate mineralogy.

Temperature plays a minor role in the incorporation of strontium into inorganic calcite. $K_{Sr}^{calcite}$ fluctuates very little: From 0.12 at 40°C to 0.076 at 98°C (HOLLAND *et alii*, 1964). For organic calcite the relationship to temperature works inversely from that for molluscs (see LANGLET, 2002; LANGLET *et alii*, 2006) or sometime does not work at all (*e.g.* benthic foraminifera, RAJA *et alii*, 2005).

Although potentially temperature could have exerted a control during the deposition of La Marcouline sediments, a direct comparison with isotopic data shows that this factor had no significant effect. The Sr content (Fig. 6) begins to increase in strata of late Bedoulian age (earliest *Cabri* foraminiferal Zone) while $\delta^{18}O$ is declining from around -1,75 ‰ to -2,25 ‰ (MOULLADE *et alii*, 1998) (thus indicating in first approximation a rise in temperature of roughly 2°C). Sr content keeps on increasing from the late *Cabri* Zone until the end of the Gargasian while during the same time interval $\delta^{18}O$ records a rise up to -1.75% followed by a new phase of decrease reaching values around –2,20 ‰ (KUHNT & MOULLADE, 2007). Thus it is obvious that the increase in Sr during the late Bedoulian and the Gargasian cannot have been affected only by a thermic factor.

Vital effects may be important too. The best known case is molluscs's production of aragonite which in comparison to inorganic aragonite contains much less Sr (KINSMAN, 1969). In hemipelagic deposits the carbonate producers are limited to foraminifera and nannofossils, so the force of various vital effects should be reduced.

RENARD (1986), using Tethyan outcrops and DSDP oceanic drilling holes, has shown that during the last 140 Ma the Sr content of pelagic carbonate may differ in amount by as much as 700 ppm. This was confirmed by a recent and more precise study (STOLL & SCHRAG, 2001), in which it was shown that carbonate Sr/Ca varies by up to 80% over both long and short periods of time. For example during the Late Berriasian and the Early Valanginian (EMMANUEL, 1993; EMMANUEL & RENARD, 1993; STOLL & SCHRAG, 2001) an important increase in the Sr content of pelagic bulk carbonates occurs in the Tethys (Vocontian Basin) and various DSDP sites between the *Otopeta* ([Sr] = 400 ppm) and the *Verrucosum* ([Sr] = 1100 ppm) ammonite zones. In the same way, during the Barremian an increase of 600 ppm (600 to 1200 ppm) occurs in the *Hugii* Zone. Increases in Sr are of the same amplitude in the La Bédoule/La Marcouline sections with values of around 400 ppm in sediments of Barremian, early Bedoulian and early late Bedoulian ages (*Blowi* Zone) and around 850 ppm in sediments of the Gargasian (*Ferreolensis*/ *Algerianus* zone boundary, Fig. 6). This increase takes place in two steps: The first, which occurs in the *Cabri* Zone, ends at a negative shift of around 100 ppm at the *Cabri*/ *Ferreolensis* boundary. The second spans the *Ferreolensis* and *Algerianus* zones.

Such variations may reflect either changes in the Sr/Ca content of seawater over time, or variations in Sr partitioning in biogenic carbonates. RENARD (1986) proposed that long-term fluctuations in seawater Sr/Ca are related to mid-ocean ridge activity and the hydrothermal budget of the ocean, while short-term variations are related to changes in sea-level, platform development (drowning vs emersion) and neritic carbonate mineralogy. STEUBER & VEIZER (2002) insisted on this point by taking into account the alternation of calcite and aragonite periods in seawater (SANDBERG, 1975; MACKENZIE & PIGOTT, 1981; MORSE *et alii*, 1997; STANLEY & HARDIE, 1998; STANLEY, 2006). As the Sr partitioning coefficient is very different in calcite ($K_{Sr}^{calcite}$ = 0.1) and aragonite ($K_{Sr}^{aragonite}$ = 1), the ratio of aragonite to calcite production is important in the control of the Sr/Ca of seawater. This occurs through fluctuations in the amount of aragonite-rich neritic sedimentation (dependent on sea level) as well as the chemistry of seawater (the rate of precipitation of calcite changes in relation to the quantity of Mg).

Nevertheless variations through time of Sr partitioning in biogenic carbonate cannot be excluded (STOLL & SCHRAG, 2001; BILLUPS *et alii*, 2004; STOLL, 2005). Experimental coccolithophorid cultures have shown that the Sr partitioning coefficient is higher ($D_{Sr}^{calcite}$ = 0.39, LANGER *et alii*, 2006) for this biogenic calcite than for inorganic precipitation. These new data confirm the previous work of RENARD (1985): Analysis of modern coccolith oozes and sea water yielded $0.25 \leq K_{Sr}^{calcite} \leq 0.28$ for ooze, versus 0.148 for

inorganic calcite at the temperature of the Eastern Mediterranean Sea.

If nannoconid populations increased during Aptian time, the Sr content of bulk carbonate may have increased as well. Moreover, the nannofossil Sr coefficient appears to correlate with growth and calcification rates (STOLL *et alii*, 2002; STOLL, 2003; STOLL & BAINS, 2003; BILLUPS *et alii*, 2004; ANDREA *et alii*, 2005; WAITE *et alii*, 2005). Thus carbonate Sr/Ca measurements may provide valuable information on changes in the productivity of calcareous nannoplankton through time. But population growth does not explain the long-term increase in Sr at La Marcouline for the $\delta^{13}C$ record shows that pelagic productivity regularly decreased through the early-middle Gargasian (see KUHNT & MOULLADE, 2007).

An important part of the increase in Sr content in the late Bedoulian and the Gargasian appears to be linked to an increase in the Sr/Ca ratio of the seawater. A consensus exists concerning a molar Sr/Ca ratio value of $0.86 \pm 0.04 \times 10^{-2}$ in normal modern seawater (KINSMAN, 1969). However, RENARD (1985) has shown that this ratio may be more variable in relation to salinity and the nature of the adjacent continent (limestones vs silicates). Values of $0.938 \pm 0.04*10^{-2}$ are proposed for the surface seawater of the western English Channel (mean chlorinity = 19.49 ‰); $0.796 \pm 0.04*10^{-2}$ for the Eastern Mediterranean Sea (at a depth of –200m, mean chlorinity = 21.636 ‰) and $0.809 \pm 0.03*10^{-2}$ for the Western Mediterranean Sea (from surface to –2085 m; mean chlorinity = 21.303 ‰). The Sr/Ca ratio of seawater does not vary in an important way with depth; nevertheless, in numerous sites Sr content was seen to increase between –500 and –800m because of the dissolution of *Acantharia* tests (celestine).

If we consider the data obtained from the *Nannoconus* spp. fractions of beds 29 to 32, the mean Sr/Ca of Aptian calcite is around $0.872*10^{-2}$ (0.787 to $0.967*10^{-2}$). The use of the inorganic calcite K_{Sr} value determines an Aptian seawater Sr/Ca of around $0.793*10^{-2}$ which is consistent with the modern value. The use of $K_{Sr}^{\text{calcite pelagic ooze}}$ of RENARD (1986) or of $K_{Sr}^{\text{coccoliths}}$ of LANGER *et alii* (2006) leads to a very low Sr/Ca ratio ($0.329*10^{-2}$ or $0.224*10^{-2}$) compared to the modern value. Due to the absence of *Nannoconus* spp. in the modern ocean we cannot choose between these various options.

Although the absolute value of Gargasian seawater Sr/Ca is not determinable, it is probable that this ratio increased by 40–50% during the time between the early *Cabri* Zone and the *Algerianus* Zone. This confirms the results of STEUBER & VEIZER (2002) obtained through the analysis of brachiopods and rudists. On a geological time scale, four processes can be invoked to explain the increase of the Sr content of bulk carbonate during late Bedoulian and Gargasian times:

1. Variations in the relative input of Ca and Sr in the ocean by rivers and hydrothermal sources (duration up to 10Ma),
2. Changes in sea level as they affect the relative proportions of carbonate production from platform and pelagic environments,
3. Change in the chemistry of sea water (Mg content) and change from photozoan (*i.e.* including aragonite) to heterozoan (calcite) carbonate production on platforms as they affect the aragonite/calcite ratio,
4. Change in the pelagic producers of carbonates, each with a discrete Sr distribution coefficient.

The second process does not seem realistic as the growth of Tethyan platforms (MASSE & PHILIP, 1981; FUNK *et alii*, 1993; WEISSERT *et alii*, 1998) is not coincident, at this scale of frequency, with the Aptian long-term Sr fluctuations. Process 4 does not appear to play a significant role during this period, for nannoconids were the main pelagic producer of carbonate.

During Aptian-Albian times the $^{87}Sr/^{86}Sr$ curve shows a negative excursion related to sea-floor hydrothermal activity (JONES & JENKYNS, 2002). Consequently, we think that the increase in the Sr content of late Bedoulian/Gargasian carbonates is due to an increase in the supply of Sr from hydrothermal sources and the development of conditions favoring the formation of calcite, thus indicating a limited production of aragonite on the shelves (STANLEY & HARDIE, 1998; STEUBER & VEIZER, 2002).

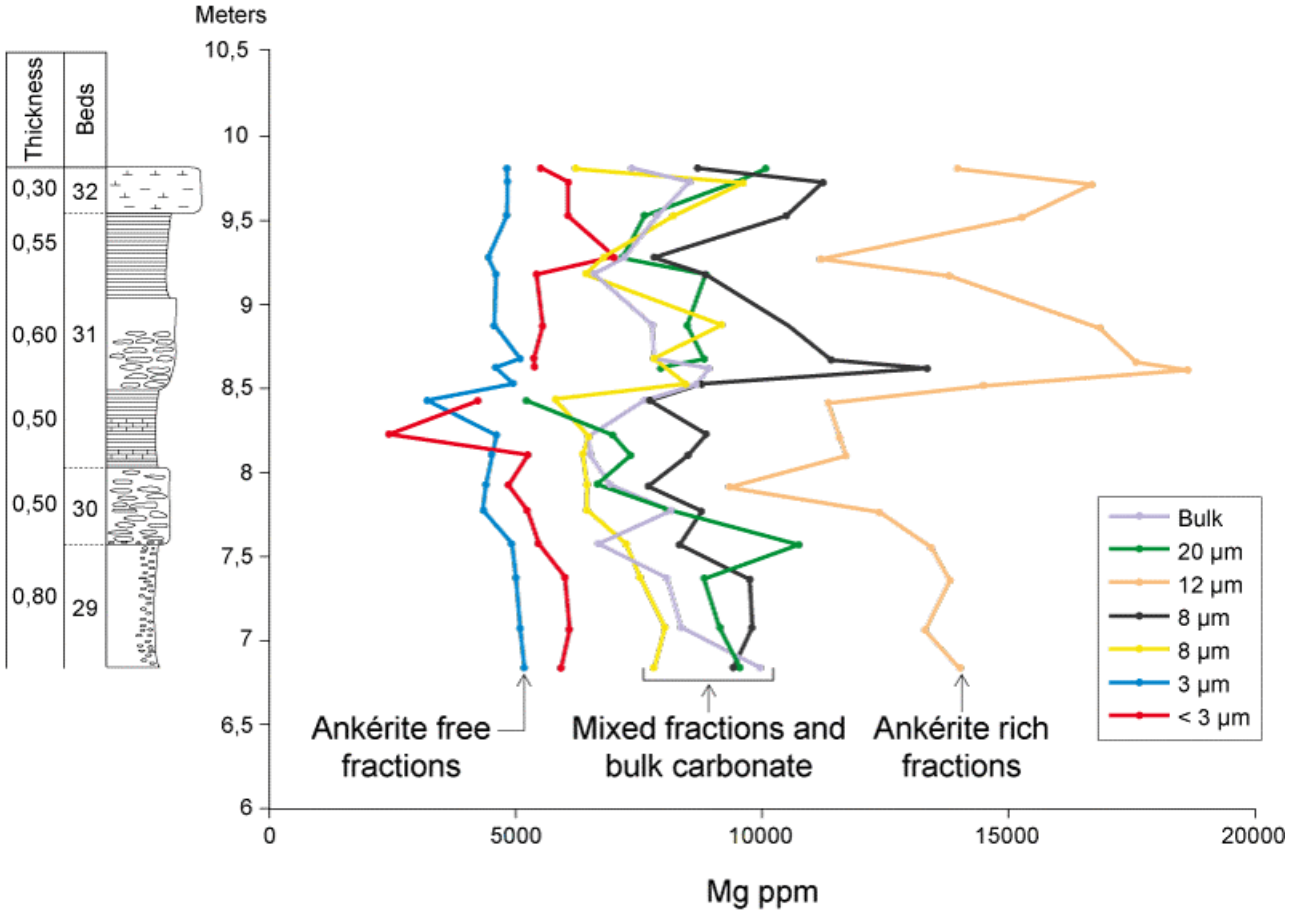


Figure 13: Comparison of the Mg content of bulk carbonate in beds 29 to 32 with that of various granulometric fractions. The fraction 12 µm concentrates ankerite macroparticles. Only fine fractions are more or less ankerite-free.

The difference in the Sr content of marls and limestones may be due to a change in the Sr incorporation coefficient of *Nannoconus* as it relates to growth and calcification rate (STOLL *et alii*, 2002; STOLL, 2003; STOLL & BAINS, 2003; BILLUPS *et alii*, 2004; ANDREA *et alii*, 2005; WAITE *et alii*, 2005). This hypothesis of a higher $K_{Sr}^{Nannoconus}$, that causes a greater productivity during the deposition of marls, may be congruent with the long-term carbon isotope data ($\delta^{13}C$ higher in marls, KUHNT & MOULLADE, 2007) and with short-term data (BELTRAN, 2006; BELTRAN *et alii*, 2007).

3- Mg and Fe evolution: Role of ankerite macroparticles

The presence of traces of an Mg and Fe-rich mineral (ankerite, Fig. 3) introduces an important bias and renders impossible the use of bulk carbonate Fe and Mg content to define the chemical conditions of the La Marcouline sedimentary environment. This does not mean that the presence of this early diagenetic mineral is not influenced by the environment, but the link is not clear and the Mg and Fe content of the bulk carbonate is mainly a guide to the percentage of ankerite in the sediment.

A comparison of the Mg and Fe contents of the separated granulometric fractions obtained from the samples of beds 29 to 32 shows that the fraction 12 µm, in which ankerite macroparticles are concentrated, has an Mg content of 10000–15000 ppm (Fig. 13, BELTRAN, 2006). The Mg content of fractions 20, 8 and 5 µm and bulk carbonate is lower but has a broad range like that of the fraction 12 µm. These observations bring out the correlation between the amount of ankerite and the Mg-Fe content. Only fine fractions (3 and < 3 µm) seem to be more or less ankerite free.

Since MINOLETTI *et alii* (2005) described the same kind of ankerite crystals in Late Cretaceous pelagic sediments, the occurrence of this mineral phase seems more common than was thought previously and in the pelagic realm limits the potential use of Mg as a paleotemperature tool.

In spite of the presence of ankerite in Gargasian sediments, a surprisingly high degree of correlation exits between their

Mg and Sr content (Figs. 5 and 7). As ankerite is an important carrier of Mg and not of Sr, this means that the existence of long-term coeval Sr and Mg fluctuations in the Aptian marine environment in no way depended on the existence of this product of early diagenesis.

The same can be said for the larger part of the fluctuations of iron and Mn (even ankerite may contain traces of Mn). From the base of the measured section to bed 62-63, the plotted traces of Fe and Mn fluctuate more or less in phase, but in the upper part of the section they fluctuate in opposite directions: Fe content rises as Mn content decreases. As ankerite commonly forms by diagenesis under early redox conditions, a change in the redox environment may have occurred during late *Ferreolensis* Zone times (this hypothesis is consistent with a general decrease of $\delta^{13}C$ during the Gargasian (KUHNT & MOULLADE, 2007)).

4- Mn evolution: Role of sea-level fluctuations

Numerous studies (POMEROL, 1983; ACCARIE *et alii*, 1989, 1993; CORBIN *et alii*, 2000) led to the suggestion that the Mn content of pelagic bulk carbonates varies in response to a change in sea level. EMMANUEL (1993), EMMANUEL & RENARD (1993), de RAFÉLIS (2000) and de RAFÉLIS *et alii* (2000, 2001) have established geochemical criteria for the identification of systems tracts and sea-level changes from an analysis of sediments in the Vocontian Trough (SE France): Sequence boundaries are marked by a minimum in Mn content. That content increases in transgressive systems and reaches a maximum at the level of maximum flooding surfaces (*mfs*). Highstand systems have a lower amount of Mn. JARVIS *et alii* (2001) used this method to identify sequence boundaries in upper Cretaceous chalks on the Isle of Wight (England).

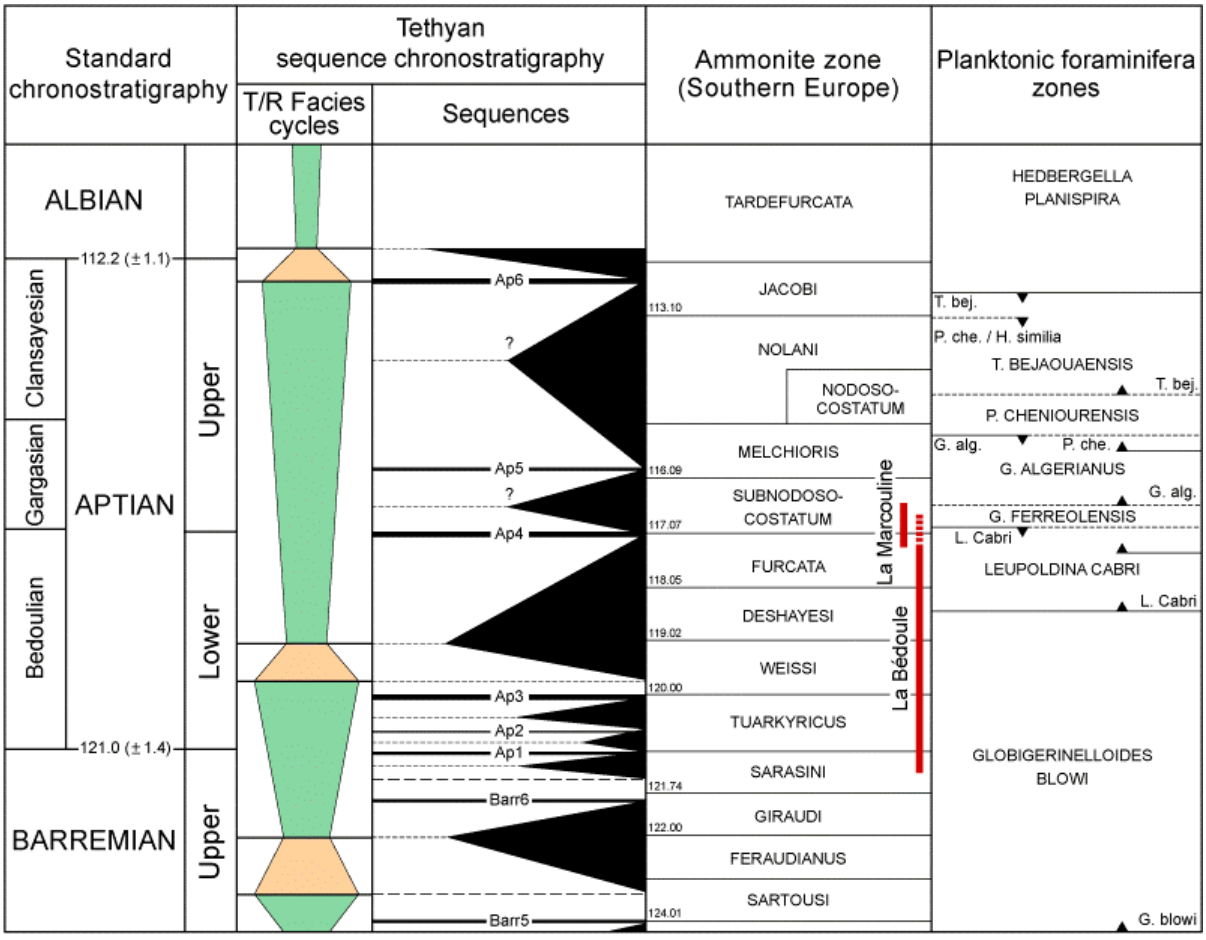


Figure 14: Chronostratigraphic chart for the Aptian from HARDENBOL *et alii* (1998): Location of 2nd and 3rd order sequences relative to ammonitic and planktonic foraminiferal zones.

Using these geochemical criteria, three eustatic sequences are recognized in La Marcouline section. They correspond with the Gargasian Mn sequences 1 to 3 (Fig. 9). The candidate for the maximum flooding surface of the first eustatic sequence may be Bed 20 (high Mn content). Bed 14 (*Luterbacheri*/ *Ferreolensis* zone boundary) may indicate a transgressive surface (increase of Mn content). The lower limit of the second sequence (lower Mn content) is in the upper part of the characteristic triplet (Bed 25-26). Its *mfs* is in the marly part of the series between bed 32 and the base of bed 33; the highstand systems tract includes two parasequences characterized by Mn fluctuations and ends in bed 47. The *mfs* of the third eustatic sequence is in bed 62 and ends in bed 82, in the lowest part of the *Algerianus* Zone.

Although these sequences deduced from Mn fluctuations are clearly expressed, it is difficult to determine to which order of sea-level variation they correspond. The chronostratigraphic chart of HARDENBOL *et alii* (1998) has only one third-order sequence *sensu* VAIL (Ap. 4) during the time span of the *Ferreolensis*/ *Algerianus* zones (Fig. 14). Thus two possibilities exist: Either the Gargasian Mn sequences are fourth-order sea-level parasequences of the Ap.4 third-order sequence, or one Middle Aptian third-order sequence is missing in the chart.

The question is: Which of these two possibilities is the correct one? It can be answered by integrating the evolution of the Mn content of the Gargasian in that of the long-term evolution of Mn at La Bédoule - La Marcouline (Figs. 8 and 15). The positive excursions of Mn during the Gargasian clearly appear as parasequences in a third-order sequence that starts in the upper part of the *Cabri* Zone and ends at the lower boundary of the *Algerianus* Zone. So this third-order sequence, including its three parasequences, seems to represent the fourth Aptian sequence in the chart of HARDENBOL *et alii* (1998). The maximum flooding surface may be located in beds 32-33, or in bed 62. The latter seems to be the better candidate when the long-term evolution of Mn values is the criterion (Fig. 14).

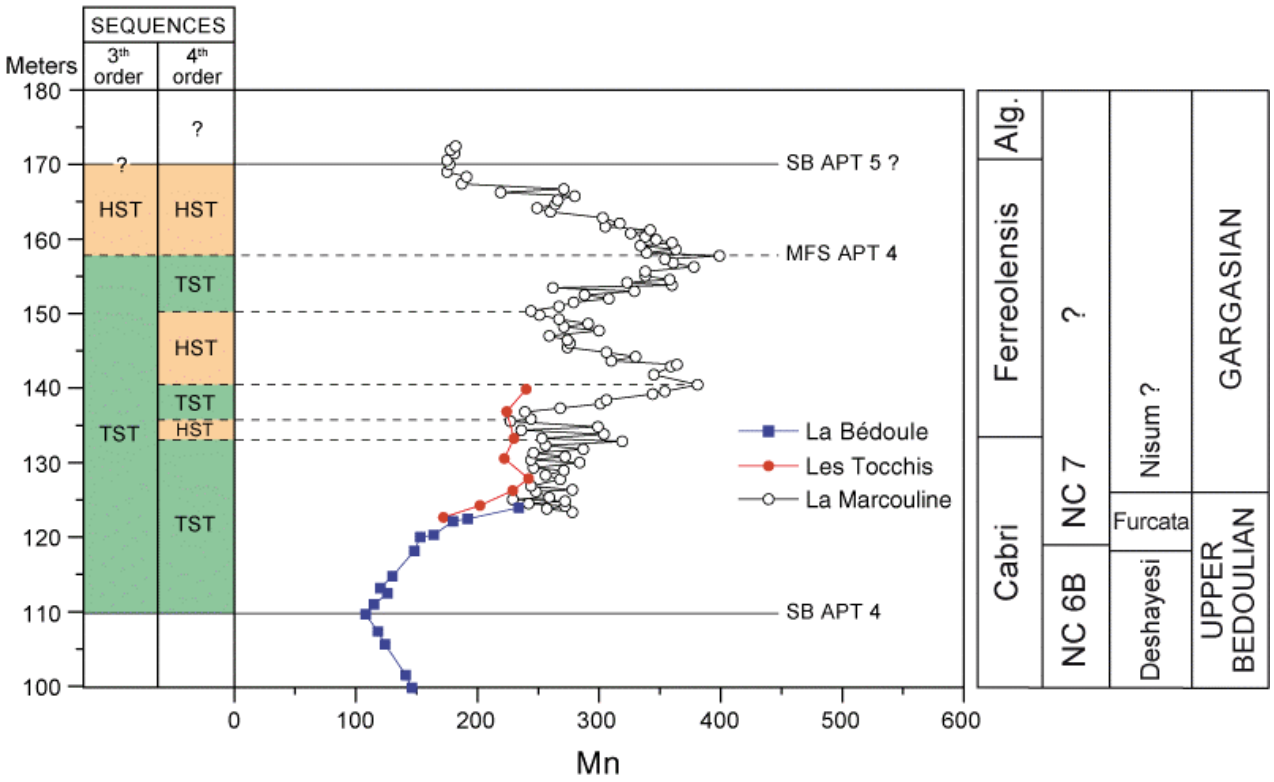


Figure 15: Evolution of bulk carbonate Mn during the late Bedoulian and early Gargasian. Relationship with the Aptian 4 eustatic sequence of HARDENBOL *et alii* (1998). SB = sequence boundary, TST = transgressive system tract, MFS = maximum flooding surface and HST = highstand system tract.

However, the limits of our scheme, based on geochemistry, are not precisely coincident with those of HARDENBOL *et alii* chart (1998). In this chart, the fourth Aptian sequence begins in the uppermost part of the *Cabri* Zone, just below the *Cabri*/*Ferreolensis* boundary and ends in the upper *Algerianus* Zone. From a geochemical point of view, the fourth Aptian sequence starts in the middle of the *Cabri* Zone and ends at the boundary between the *Ferreolensis* and *Algerianus* zones. Such discrepancies might also be a result of the fact that the zonal boundaries of the chart of HARDENBOL *et alii* (1998) were defined on the basis of taxonomic and biostratigraphic concepts which differ slightly from those of MOULLADE *et alii* (2002, 2005).

Nevertheless the succession in the La Marcouline outcrop does not preclude the presence of other highstand parasequences in the time represented by the *Algerianus* Zone. To locate and to define precisely the limits of the Aptian 5 sequence complementary upper Gargasian outcrops must be selected to carry out further Mn analyses.

Conclusions

This geochemical study of the Gargasian beds of La Marcouline quarry (Cassis-La Bédoule, SE France) complements data previously obtained from the Bedoulian historical stratotype area and leads to a comprehensive knowledge of geochemical fluctuations during the Early and Middle Aptian. Nannoconids are the main carbonate producers in both limestones and marls. Because of their low content of diagenetic minerals (such as ankerite), the trace-element records of the bulk carbonate closely approach those of *Nannoconus* spp. so geochemical sequences can be defined. The long-term evolution of Sr and Mn content is linked to fluctuations in the chemistry of sea-water due to differences in the rate of their supply by rivers and hydrothermal sources, to changes in sea level and to variation in the ratio of aragonite to calcite production on the platforms. Diagenetic processes are not involved, nor are variations in carbonate mineralogy or changes in the number or nature of pelagic carbonate producers in the hemipelagic sediments of La Marcouline quarry.

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Appendix 1: Trace element contents of bulk carbonates from La Marcouline Quarry.

Bed	Echantillons	Lithology	CaCO3	Ca	Mg	Sr	Mn	Fe
1	MAR.1	marl	77.41	402269	3862	644	278	2027
1	MAR.2	marl	70.60	389243	3581	626	257	1759
2	MAR.3	limestone	82.44	413993	3312	644	272	2202
3	MAR.4	marl	66.17	392512	3321	605	242	1623
4	MAR.5	limestone	84.10	400189	3362	626	272	2233
5	MAR.6	marl	59.71	390936	3154	672	229	1660
6	MAR.7	limestone	81.38	387065	3251	616	259	2051
7	MAR.8	marl	66.36	389249	4367	682	248	1980
8	MAR.9	limestone	72.03	385941	3859	661	278	1945
9	MAR.10	marl	57.63	389408	4500	732	244	1843
10	MAR.11	limestone	78.59	399268	4312	669	268	2539
11	MAR.12	marl	61.38	396504	4531	712	256	1837
12	MAR.13	limestone	80.14	396924	3969	667	271	2350
13	MAR.14	marl	59.02	392785	4214	732	246	1458
14	MAR.15	limestone	81.52	403453	3873	670	284	2195
15	MAR.16	marl	63.35	393347	4099	709	244	1671
16	MAR.17	limestone	83.75	395846	3325	649	272	2138
17	MAR.18	marl	56.65	388558	4818	721	246	1647
18	MAR.19	limestone	79.66	398004	3980	691	287	2340
19	MAR.20	marl	63.12	382975	4422	701	256	1603
20	MAR.21	limestone	80.42	411078	3782	654	319	2080
21	MAR.22	marl	56.52	393486	4407	689	253	1755
22	MAR.23	limestone	85.57	389148	3113	590	304	1961
23	MAR.24	marl	56.35	398327	3027	588	236	1219
24	MAR.25	limestone	84.82	399297	3035	612	299	2092
25	MAR.26	marl	57.25	383978	3225	604	227	1352
26	MAR.27	limestone	87.46	401760	3053	635	244	1993
27	MAR.28	marl	66.65	385305	4630	656	239	1777
28	MAR.29	limestone	75.45	387194	3098	624	268	1835
29	MAR.30	marl	67.00	380048	5048	668	301	2138
30	MAR.31	limestone	69.26	401177	4654	660	306	2271
31	MAR.32	marl	74.94	390698	4220	641	344	2329
31	MAR.33	marl	69.27	382298	4447	660	354	2188
32	MAR.34	limestone	75.47	396647	4284	668	381	2404
33	MAR.35	marl	63.83	393504	3904	653	345	1780
33	MAR.36	marl	70.06	395392	4903	678	359	2301
34	MAR.37	limestone	81.01	396952	3970	681	364	2271
35	MAR.38	marl	60.80	381648	4924	689	310	1970

36	MAR.39	limestone	81.98	389342	3738	646	330	2087
37	MAR.40	marl	67.63	385691	4564	649	306	1914
38	MAR.41	limestone	81.64	396100	4278	686	274	2456
39	MAR.42	marl	70.11	389537	5402	678	276	2189
40	MAR.43	limestone	72.54	398431	5259	688	274	2295
41	MAR.44	marl	65.59	375455	5158	699	259	2260
42	MAR.45	limestone	81.92	390028	4212	655	300	2317
43	MAR.46	marl	64.30	381402	5261	675	271	1733
44	MAR.47	limestone	80.42	397367	4292	674	291	2050
45	MAR.48	marl	60.15	382202	4623	702	267	1453
46	MAR.49	limestone	85.76	387303	3098	696	251	2060
47	MAR.50	marl	59.52	387974	3863	700	244	1369
48	MAR.51	limestone	84.05	387977	3880	700	267	2173
49	MAR.52	marl	62.36	411943	5748	758	279	2251
50	MAR.53	limestone	80.79	393196	4404	723	308	2320
51	MAR.54	marl	60.76	392205	5098	747	288	1866
52	MAR.55	limestone	85.24	390380	4060	703	329	2303
53	MAR.56	marl	53.05	389568	4831	759	262	1488
54	MAR.57	limestone	77.77	392509	4082	733	360	2292
55	MAR.58	marl	61.21	392525	4733	748	323	1918
56	MAR.59	limestone	77.28	387537	4185	725	358	2581
57	MAR.60	marl	65.31	390411	3501	686	338	1553
58	MAR.61	limestone	81.24	400759	3206	681	338	1972
59	MAR.62	marl	61.21	423052	3424	714	378	1712
60	MAR.63	limestone	78.42	394436	3313	707	361	2020
61	MAR.64	marl	60.29	388117	4469	703	354	1912
62	MAR.65	limestone	74.34	403756	4199	756	399	2503
63	MAR.66	marl	60.99	390893	3917	713	339	1779
64	MAR.67	limestone	76.32	390707	3126	697	363	2094
65	MAR.68	marl	58.28	390947	4801	777	334	1963
66	MAR.69	limestone	74.34	394561	3314	713	360	2028
67	MAR.70	marl	67.21	383645	5194	705	347	2664
68	MAR.71	limestone	68.25	385904	5097	712	338	2832
69	MAR.72	marl	64.28	387657	4342	718	326	1822
70	MAR.73	limestone	71.96	389180	4514	744	342	2670
71	MAR.74	marl	60.80	392382	4433	747	305	1888
72	MAR.75	limestone	71.91	394810	4738	747	317	2914
73	MAR.76	marl	62.21	386520	5590	763	303	2699
74	MAR.77	limestone	73.33	396977	4129	740	260	2707
75	MAR.78	marl	57.86	379660	3797	752	249	1724
76	MAR.79	limestone	73.85	395465	4271	762	264	2681

77	MAR.80	marl	60.15	386142	5457	797	266	2844
78	MAR.81	limestone	79.56	395477	4113	770	280	2697
79	MAR.82	marl	53.26	387535	4960	794	219	1814
80	MAR.83	limestone	70.94	390031	4680	824	271	3081
81	MAR.84	marl	58.32	386971	5953	896	187	2534
82	MAR.85	limestone	64.37	384437	6046	845	191	3139
83	MAR.86	marl	67.06	389581	5640	813	175	3154
84								
85	MAR.87	marl	69.26	385892	5338	812	177	3065
86	MAR.88	limestone	69.66	393814	5041	800	175	3040
87								
88	MAR.89	marl	65.64	384791	5323	818	181	2624
89	MAR.90	marl	56.61	368112	6479	844	178	2187
90	MAR.91	marl	69.75	392938	4872	809	182	2900