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PALEOECOLOGY AND BIOGEOCHEMISTRY OF BRACHIOPODS FROM THE DEVONIAN-CARBONIFEROUS BOUNDARY INTERVAL OF THE GRIOTTE FORMATION, LA SERRE, MONTAGNE NOIRE, FRANCE

by

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(8 figures and 1 table)

ABSTRACT.- Most studied brachiopod shells of the Griotte Formation are microstructurally and geochemically well preserved. Typical microstructural features are bladed calcite fibres and prismatic calcite of the secondary and primary layers, respectively. Microstructural alteration, where evident, is accompanied by geochemical changes in trace element contents and isotopic compositions.

Modelling of geochemical data suggests that the latest Famennian seas were characterized by restricted to mud-bottom brachiopod faunas in generally dysaerobic-aerobic, normal salinity, warm temperature waters with high to reduced productivity. Water depth increased significantly concomitantly with a decrease in temperature during deposition of the middle siliciclastic calcarenite relative to the subjacent lower oolite and the superjacent upper oolite of the Griotte Formation. Oceanographic conditions of the Tournaisian sea were significantly different from those of the Famennian at Montagne Noire. These seas were highlighted by an open, shallow-water brachiopod fauna, which concurs with the slight dysaerobia of the water. Furthermore, the seas experienced only a slight decrease in salinity but marked increases in productivity, temperature and a general shallowing of the water.

KEY-WORDS.- Famennian-Tournaisian brachiopods, geochemistry, paleoecology, paleoceanography, La Serre.

INTRODUCTION

After many years of searching and much discussion (e.g., Paproth & Streel, 1984; Flajs *et al.,* 1988), the IUGS Working Group has finally decided on the section at La Serre to represent the stratotype for the Devonian-Carboniferous boundary. The geochemistry of brachiopods from beds 79 to 93 is deemed important and vital in assessing the paleoecology of the depositional sequence at La Serre. Trace element and stable isotope compositions of brachiopod shell-calcite are invaluable records of depositional conditions within the local/regional environment (e.g., Brand, 1983; 1989b; Popp *et al.,* 1986; Brand & Logan, 1991). Their original low-Mg calcite (LMC) mineralogy plays a major role in the resistance of brachiopod shells to the aggressively catalytic actions/reactions of diagenetic fluids. Furthermore, the geochemical contents and distributions are fairly well understood for brachiopods (Morrison & Brand, 1986; McConnaughey, 1989; Brand & Logan, 1991), and thus, the chemical compositions of pristine material are useful in modelling past depositional conditions (e.g., Veizer, 1977; Brand, 1983, 1987, 1989a; Adlis *et al.,* 1988).

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The objectives of this study are to model paleo-ecological/oceanographic conditions of the sea in the La Serre region during the latest Devonian to earliest Carboniferous. Brachiopods and matrix from a number of sections (trenches) at La Serre form the basis of this geochemical investigation.All samples will be evaluated for their diagenetic state prior to modelling of depositional conditions using a coordinated multi-method approach (cf. Brand, 1987).

GENERAL GEOLOGY

A brief review of the sedimentology suggests that upper Devonian-lower Carboniferous sediments occur in nappes and klippen throughout the southern Montagne Noire. The section at La Serre represents an uninterrupted boundary sequence of fossiliferous nodular limestones and shales : the Griotte Formation (Flajs & Feist, 1988). In ascending order, beds 67-68 are fossiliferous grey-beige micrites and argillaceous marls with calcareous, pyritic nodules (Feist, 1985; Flajs & Feist, 1988). Beds 69-70 are green-grey, arenaceous shales and fossiliferous grain/rudstones with abundant bio- and lithoclasts. Beds 70 to 80 are part of the lower oolite unit (Legrand-Blain & Martinez Chacon, 1988). Beds 81-84 are dark grey-green, fossiliferous, arenaceous marly shales, and are referred to as the middle siliciclastic calcareous unit. Beds 85-98 are medium bedded, dark grey, fossiliferous-ooid grain/rudstones. These beds represent the upper oolite unit.

The Devonian-Carboniferous boundary has been placed at the base of bed 89 of the Griotte Formation at La Serre based on the appearance of *Siphonodella sulcata* and diagnostic trilobites. However, the conodont population represents a mixed fauna of reworked specimens characteristic of the upper Devonian. A sequence of graded layers is conspicuous between the top of bed 88 and the bottom of bed 90 (Flajs & Feist, 1988). In a biodetrital sedimentary sequence of a transgressive pulse, the state of preservation of macrofossils is highly significant in estimating the duration of postmortem transport and diagenesis and their overall value as biostratigraphic indicators.

BRACHIOPOD BEDS AND GENERAL ECOLOGY/OCEANOGRAPHY

Predominance of individual valves in the Griotte sediments infers some transport of the brachiopods. Although the specimens are generally disarticulated, shells are not extensively abraded or show other signs of long-distance transport such as breakage (cf. Legrand-Blain & Martinez Chacon, 1988). A low diversity fauna dominated by rhynchonellids in the top "lower oolitic unit' (beds 79-80; samples ML 844,846) infers a rather restricted environment. This is followed by a less abundant but more diversified fauna in the "middle siliciclastic calcareous unit" representing quiet water conditions (beds 81-84; samples ML 857). A more abundant and diversified brachiopod fauna in the "upper oolitic unit", with a greater degree of disarticulation and breakage, construes a transgressive and higher energy phase for this interval (beds 89-93; samples ML 820, 840, 842 and PS 491/3).

METHODOLOGY

After taxonomic classification, brachiopod specimens were manually separated from their enclosing rock matrix. Further procedures consisted of removing matrix material from within crevices and altered surface layers by physical and chemical methods. A number of cleaned fragments were prepared for microstructural analysis. These were coated with gold/palladium prior to scanning on an I.S.I. scanning electron microscope. Remainder of samples were powdered and about 50 mg of each specimen was digested in 5 mL of 5 % (v/v) HNO_3 for 1h. All samples (23 brachiopods and matrix) were analyzed for Ca, Mg, Sr, Na, Mn, Fe, Zn, Cd and Pb by flame and graphite-furnace atomic absorption spectrometer (cf. Brand & Veizer, 1980). Accuracy and precision of data are within the prescribed elemental limits for N.B.S. standard reference materials 634 and 636 (cf. Brand, 1989a). Samples were also analyzed for $^{18}O/^{16}O$ and $^{13}C/^{12}C$ by mass spectrometer by reacting 10 mg with 100 % phosphoric acid at 25oC for 12h. The isotopic ratios are expressed in the conventional (δ) notation relative to PDB in ‰ and corrected for ^{17}O (Craig, 1957). Accuracy and precision of data compared to recommended values for N.B.S. 20 (Solnhofen Limestone) standard rock were : $\delta^{18}O$ (0.1,0.1) and $\delta^{13}C$ (0.1,0.1) ‰, respectively. Geochemical data are presented in Table 1.

PRESERVATION

Any study of fossil material, requires a detailed evaluation of the state of geochemical and mineralogical preservation. Altered samples and their data may obscure both the large and small-scale picture of the inherently important pristine material which is vital in modelling and evaluating depositional conditions of past seas and oceans (cf. Brand & Veizer, 1980; Popp *et al.*, 1986; Hudson & Anderson, 1989).

Table 1.- Trace element and stable isotope data of brachiopods and matrix from the Devonian-Carboniferous Griotte Formation, La-serre, Montagne Noire, France. The sample numbers are from Legrand-Blain and Martinez Chacon (1988).

Sample #	Taxonomy	Ca	Mg	Sr	Na	Mn	Fe	Zn	Pb	Cd	$\delta^{13}C$	$\delta^{18}O$
		%	ppm						ppb		‰ (PDB)	
PS 491/3	Productids (Spinocarinifera)	34.9	1692	1011	365	689	176	22	13	188		
ML 842	Productids										-1.63	-2.65
"	"										-3.70	-2.65
"	"	35.2	1999	979	368	1582	535	58	17	179	1.27	-3.00
"	"										1.56	-4.05
"	"										2.36	-2.92
"	"										2.32	-5.74
ML 820	Productids (Spinocarinifera)	36.9	2048	1283	550	1025	216	100	18	286	2.14	-4.25
"	"	34.9	2789	880	500	3156	53	41	29	432		
"	"										2.64	-4.16
"	"	36.0	2222	1029	445	1025	228	18	13	125	2.01	-3.00
ML 842m	Matrix	35.8	2807	356	40	2086	711	16	6	311		
ML 840m	Matrix	35.7	2915	418	50	2341	529	16	9	313	1.11	-3.31
ML 820m	Matrix	33.9	3418	356	40	4535	572	1	7	258		
ML 857u	Spiriferids	36.7	936	994	294	137	22	6	12	189	5.02	-0.11
"	"	36.0	1235	916	235	301	142	7	10	169	4.47	-0.49
"	"	36.6	930	1071	294	197	20	7	12	154	4.90	-0.75
"	"	36.6	1022	1306	648	105	57	13	12	74	4.66	0.27
"	"	37.5	986	1104	602	194	110	14	11	136	4.63	-0.18
ML 857l	Spiriferids	37.1	1169	962	293	438	285	9	11	162	4.42	-2.34
"	"	35.4	3527	996	719	213	145	9	12	167	4.71	-2.65
"	"	34.8	2045	787	220	1142	178	7	12	434	2.86	-2.18
"	"	36.9	864	1300	619	77	68	14	12	86		
"	"	37.2	662	1063	308	127	115	17	12	120		
"	"	38.9	601	1148	505	35	51	14	10	63		
ML 857m	Matrix	31.6	2754	280	40	1364	672	1	5	438	1.59	-2.94
ML 844	Rhynchonellids	35.9	1289	1177	359	300	204	28	20	*	3.16	-3.14
ML 844m	Matrix	30.7	2684	301	40	970	968	4	5	554		
ML 846m	Matrix	34.3	2990	336	40	1019	702	21	5	397		

Note: * - anomalous value.

MICROSTRUCTURES

Despite the minor transport inferred for the La Serre brachiopods (Legrand-Blain & Martinez Chacon, 1988), most specimens chosen for this study were microstructurally well-preserved. Specimen #2 (Fig. 1, Plate A) shows the typical prismatic nature of the primary layer found in modern and ancient brachiopods. Bladed and elongated fibres typical of the secondary calcite layer is demonstrated by specimen #4 (Fig. 1, Plate B). In specimen #18, both the primary and secondary layers are preserved in their pristine condition (Fig. 1, Plate C). However, in some small areas of a few specimens, the primary bladed calcite has been replaced by diagenetic calcite rhombs (Fig. 1, Plate D). Overall though, most of the studied specimens show few signs of alteration at the macro- and microstructural levels.

GEOCHEMISTRY

Geochemical data support the excellent preservation of the studied brachiopods from La Serre. Most of the specimens fall well within the limits defined by data of modern brachiopods (Fig. 2; Brand & Logan, 1991). The matrix material in all cases shows the effects of post-depositional alteration by diagenetic fluids. Minor alteration is detected in two of the studied specimens, and one Famennian brachiopod has an anomalous Mg content. However, based on other geochemical and microstructural data, this specimen is not considered altered but included for completeness sake.

Interestingly enough no significant difference was detected in the Sr content between the Devonian and Carboniferous brachiopods. At the same time though, a noticeable difference in Mg is apparent for the Devonian (933 ± 208 ppm) and Carboniferous specimens (1990 ± 220; Fig. 2). A similar Mg trend at the generic level was noted by Bates & Brand (1991) for coeval brachiopods from the Demissa bed of the mid-Devonian Hamilton Group. Although it is difficult to decode the exact cause of this differentiation in our specimens, perhaps calcification/growth rate influenced by changing nutrient levels may be

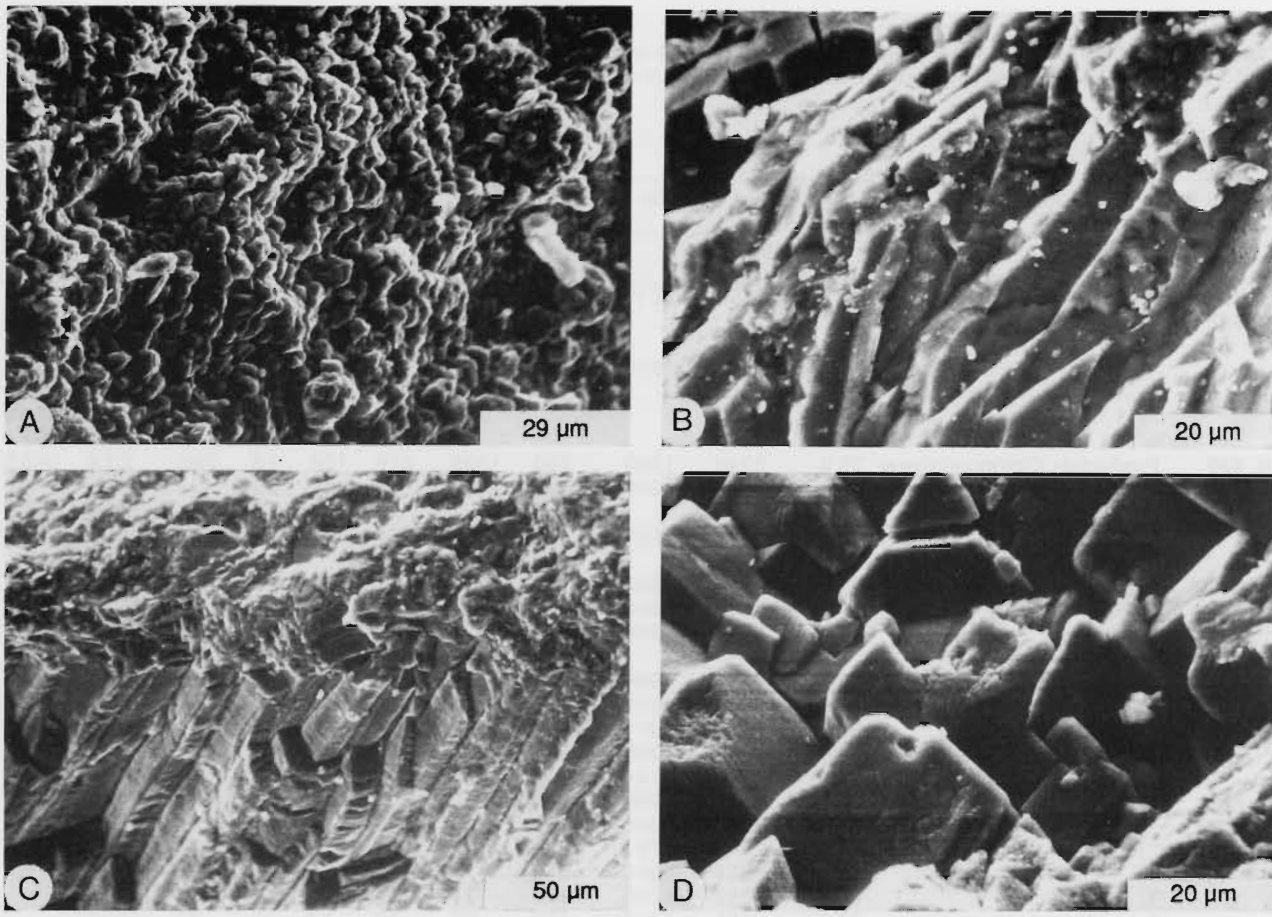

Fig. 1.- Microstructures in brachiopods from the Griotte Formation at La Serre, Montagne Noire.
Plate A shows the well-preserved texture of the primary prismatic layer (#2; ML 857, spiriferid). Plate B shows the bladed fibrous calcite of the secondary layer (#4; ML 857, spiriferid). Plate C shows the boundary between the well-preserved primary (prismatic) and secondary (bladed) layers (# 18; ML 857, spiriferid). Plate D shows that in some areas the primary fibres are replaced by calcite cement (#18).

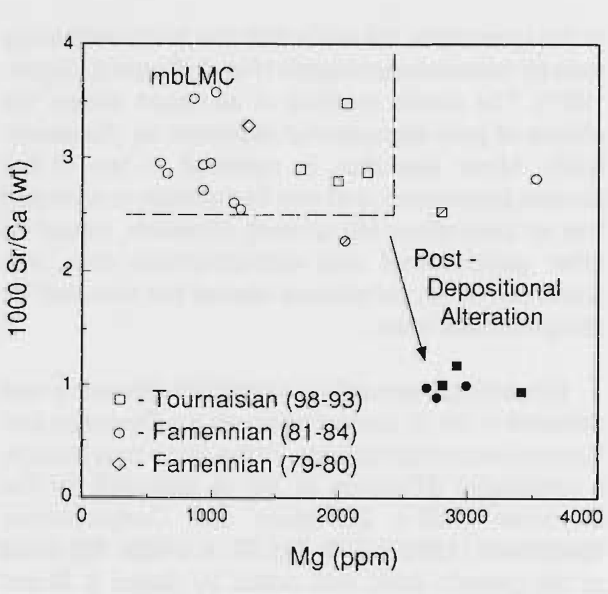

Fig. 2.- Elemental diagenetic evaluation of brachiopods and matrix from the Devonian-Carboniferous Griotte Formation. Brachiopods are well preserved (open symbols) or partially altered (modified open), and matrix material is completely altered (solid symbols). Field defines geochemical range of pristine modern-brachiopod low-Mg calcite (mbLMC).

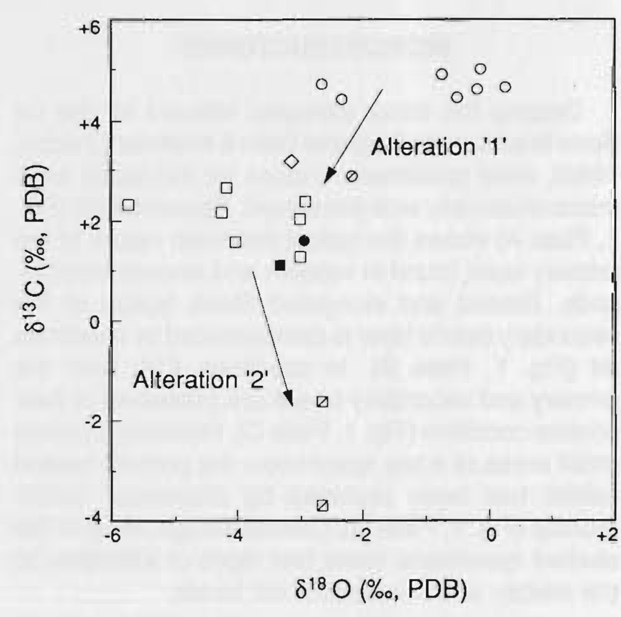

Fig. 3.- Isotopic diagenetic evaluation of brachiopods and matrix from the Devonian-Carboniferous Griotte Formation. Symbols and explanations as in fig. 2.

responsible for the observed Mg trends. Cadmium and lead are approximate indicators of oceanic productivity (e.g., Boyle, 1986), and the levels in the specimens are significantly different between the unaltered Devonian (Cd, 128 ± 45 ppb; Pb, 11 ± 1 ppm) and Carboniferous (Cd, 194 ± 67 ppb; Pb, 15 ±3 ppm) brachiopods from La Serre. Thus differences in either nutrient levels between Devonian and Carboniferous La Serre seawater, or some other unidentified factor(s) may be responsible for the observed differences in Mg contents. More studies of Cd and Pb as paleoproductivity/nutrient/terrestrial flux indicators and of Mg as growth/calcification rate indicator are warranted before a final assessment is made of these observed trends in the La Serre brachiopods (cf. Boyle, 1986); Cd and Pb trends are further discussed in a subsequent section.

Stable isotope evaluation further confirms the excellent state of preservation of many of the brachiopod specimens (Fig. 3). Post-depositional alteration of the samples falls into two regimes. Altered brachiopod and matrix (81-84) of the Famennian Griotte are characterized by more negative $\delta^{13}C$ and $\delta^{18}O$ values than their unaltered counterparts. This alteration process probably took place in a partly-closed system in the presence of mixed waters. The light $\delta^{13}C$ and $\delta^{18}O$ values of the Famennian specimen from beds 79-80 (Fig. 3) are considered primary based on trace element and microstructural data. Alteration of the younger Tournaisian sediments and brachiopods show a dramatic increase in ^{12}C (Fig. 3). In conjunction with other geochemical data, alteration of these specimens probably also took place in a partly-closed diagenetic system but in the presence of CO_2-charged waters. The coordinated microstructural and geochemical approach was able to isolate and depict the least-altered specimens for the subsequent paleoceanographic modelling.

REDOX POTENTIAL

The late Famennian specimens fall within the natural chemical range observed in modern brachiopod shell calcite from seas with generally aerobic conditions (Fig. 4; Veizer, 1977; Morrison & Brand, 1986; Brand & Logan, 1991). Slight dysaerobia is indicated by increased levels of Mn and Fe in the brachiopods from beds 79-80 (Fig. 4). The equally well-preserved early Tournaisian specimens contain more Mn with high-end Fe contents suggesting moderate dysaerobic water conditions during the transgressive phase for the La Serre sea. The increased Mn and Fe levels of the matrix and variable contents of the altered specimens, in contrast infer

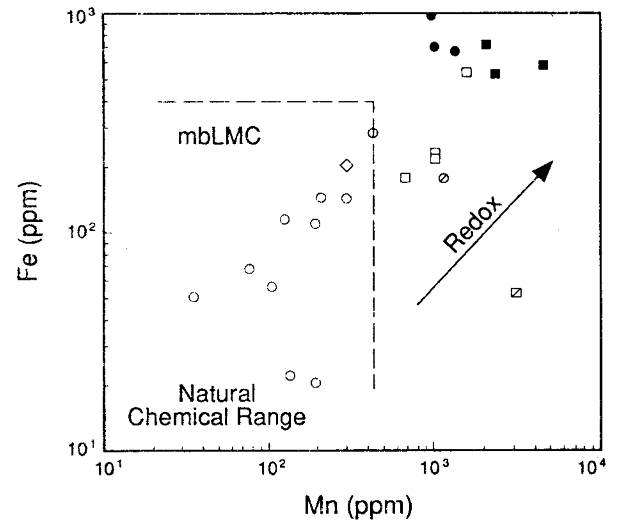

Fig. 4.- Redox potential of La Serre seawater and paleoecology of Griotte brachiopods. Redox potential is controlled in part by the original depositional environment for the pristine samples, and in part by that of the diagenetic fluid(s) for the altered brachiopods and matrix. Symbols and explanations as in fig. 2.

diagenetic fluids with higher elemental content under reducing conditions.

TEMPERATURE/DEPTH

Water temperatures based on unadjusted $\delta^{18}O$ values (Table 1) are reasonable for a "shallow" sea near the equator during the Famennian-Tournaisian. Postulated water temperatures for the sea during the latest Famennian ranged from 12-24oC, whereas more "normal" tropical temperatures of 22-36oC were modelled for the Tournaisian seas. It is unreasonable to expect such large temperature fluctuations in a sequence covering a short interval of time. Thus, it is postulated that changes in water depth, in large part, probably can account for this variation, with extensive solar heating of the shallower waters during the Tournaisian. This variation in water depth may be intricately linked to the transgressive-regressive nature of the seas during this time postulated by Flajs & Feist (1988).

SALINITY

At Sr/Ca ratios of 2.5 to 3.5, modern brachiopods contain about 2000 ppm Na, whereas those from the Griotte Formation at La Serre have invariant Na contents (Fig. 5). Brachiopods as a group biologically regulate the Na content of their shell calcite (Brand

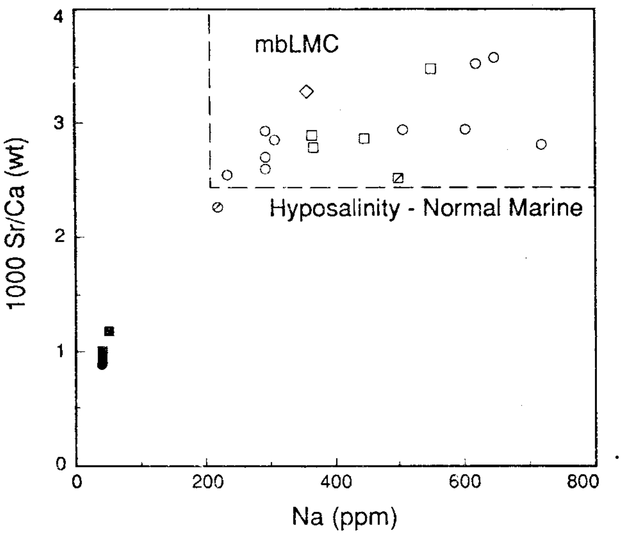

Fig. 5.- Salinity of La Serre seawater and paleoecology of Griotte brachiopods.The Na content of modern brachiopods from normal marine conditions is about 2000 ppm; those from brackish marine environments tend to have lower contents (cf. Brand & Logan, 1991; Flajs & Feist, 1988). Other symbols and explanations as in fig. 2.

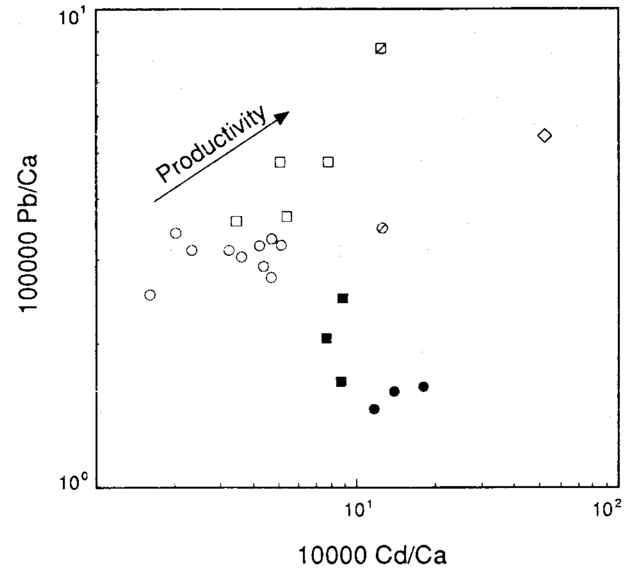

Fig. 6.- Element-based nutrient level and productivity of La Serre seawater. Relative productivity levels are based on work by Boyle (1986). Symbols and explanations as in fig. 2.

& Veizer, 1980; Bates & Brand, 1991), and have the capability to strive in a wide range of salinity regimes (e.g., Fürsich & Hurst, 1980). Thus, it is difficult to ascertain the precise meaning of the lower Na contents in the Griotte brachiopods, but they correspond to levels measured in modern shallow-water counterparts from Sao Paulo, Brazil (Brand & Logan, 1991). Modelling based on $\delta^{18}O$ values suggest only slight variation in water salinity throughout deposition of the sediments of the Griotte Formation.

NUTRIENT AND PRODUCTIVITY LEVELS

Cd contents of ocean waters relate positively with oceanic P and productivity, which ultimately should be reflected in shell calcite of the ambient invertebrate fauna (Shen & Boyle, 1988). The potential of Cd in marine invertebrates as a biomonitor of oceanic productivity is still largely unexploited, and precise trends and interpretations await further studies on modern counterparts (e.g., Brand & Logan, 1991). In contrast, Shen & Boyle (1988) demonstrated a pollution influence on Cd and Pb contents in modern scleractinian corals of Bermuda. The Pb contents encountered in the Griotte brachiopods correspond to the high spectrum of Pb measured in modern specimens from shallow waters of the northern hemisphere with significant anthropogenic influence.

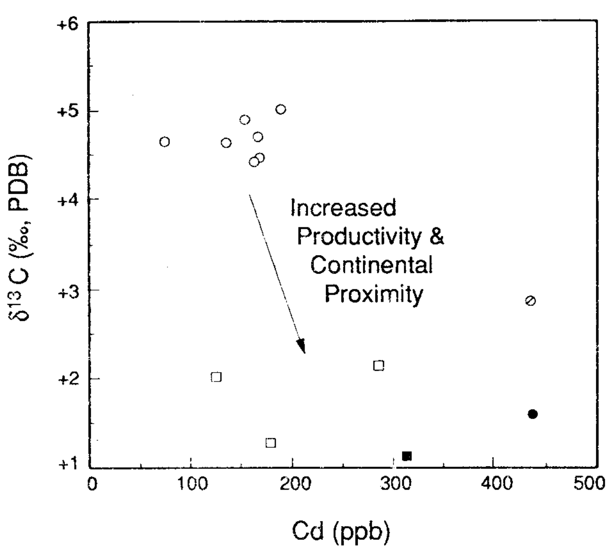

Fig. 7.- Isotope-based nutrient level and productivity of La Serre seawater. Symbols and explanations as in fig. 2.

Since anthropogenic pollution can be discounted during the Famennian-Tournaisian, another factor must be responsible for these "high" Pb levels in the Griotte brachiopods. On average, modern river water contains about thirty times more Pb than seawater (Drever, 1982), thus it is possible that the La Serre sea was subject to greater continental freshwater influx than any of the modern localities which were not influenced by anthropogenic perturbations. The preferred interpretation is that more solubilized Pb was available for incorporation into shell calcite due

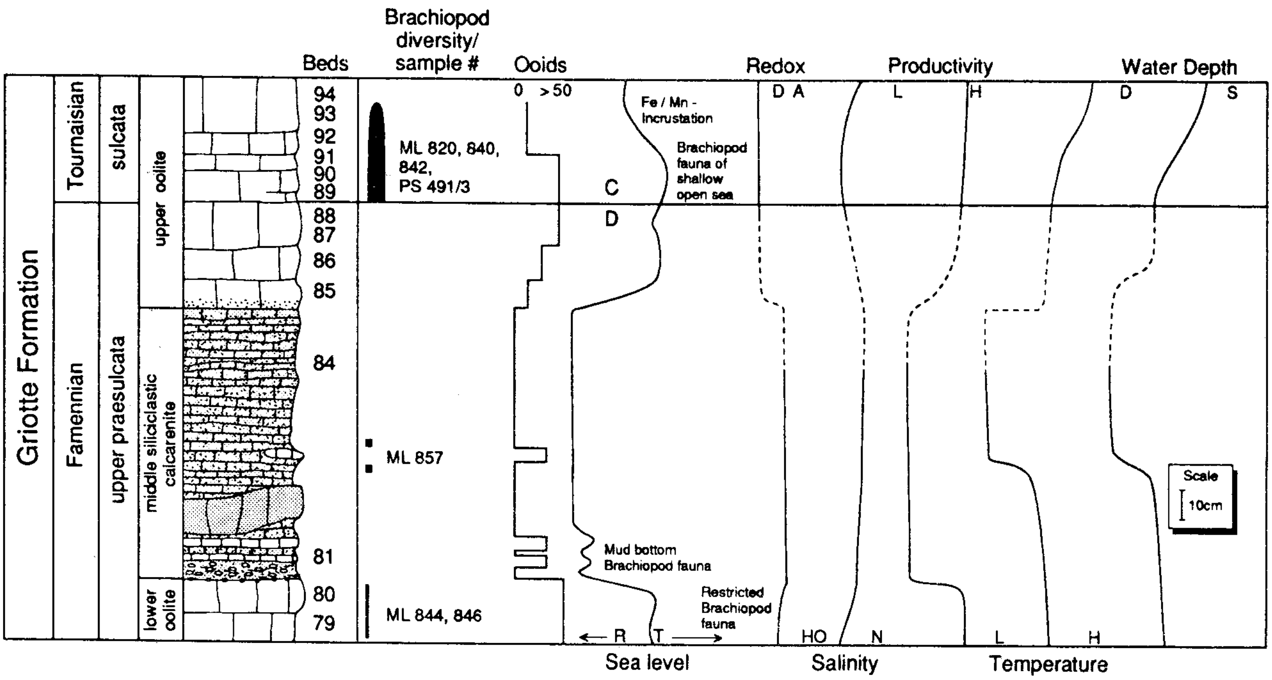

Fig. 8.- Summary sedimentological and paleoecological evaluation of Griotte Formation at La Serre.
Sedimentological data are from Flajs & Feist (1988), and brachiopod faunal information is from Legrand-Blain & Martinez Chacon (1988). Paleoecological interpretation for section : ooids (0 to >50 %), sealevel (R-regression, T-transgression), redox (D-dysaerobic, A-aerobic), salinity (Ho-hyposaline, N-normal marine), productivity (L-low, H-high), water temperature (L-low, H-high) and water depth (D-deep, S-shallow).

to the invarient redox conditions during the Tournaisian (Fig. 4).

Overall the brachiopods from the late Famennian of the Griotte Formation have lower Pb and Cd levels compared to those from the transgressive/higher energy seas of the early Tournaisian (Fig. 6). Thus, it appears that the transgressive waters of the upper oolite unit had either greater nutrient levels or were subject to an increased continental flux than the seas which deposited the underlying siliciclastic calcarenite. Only the specimen from the lower oolite unit of the Famennian has anomalous Pb and Cd, which may reflect either unusual productivity levels during this time period or some other unknown factor(s). Paucity of data precludes any further speculation on this point.

According to Boyle (1986) the underlying assumptions are that "... phosphorus, cadmium and $\delta^{13}C$ are linearly related at all times, and phosphorous and cadmium are depleted to negligible levels in subtropical surface waters...". Thus, the $\delta^{13}C$ trends and interpretations (Fig. 7) concur with the Cd and Pb conclusions (Fig. 6) and support a shallowing and increase in productivity of the seas from the Famennian to the Tournaisian at La Serre.

SUMMARY

Figure 8 summarizes the major faunal (brachiopod), sedimentological and chemo-ecological aspects recognized in the latest Famennian-earliest Tournaisian horizons of the Griotte Formation at La Serre, Montagne Noire. Interpretations of ooid distribution, brachiopod faunal and sealevel changes are based on the data from Flajs & Feist (1988) and Legrand-Blain & Martinez Chacon (1988). A restricted brachiopod faunule of the lower oolite was replaced by a mud-bottom dwelling one in the siliciclastic calcarenite, which in turn was replaced by a shallow and open sea fauna in the upper oolite (Fig. 8). The oceanographic conditions for this interval correspond to normalizing of conditions in the transition from the Devonian to the Carboniferous.

La Serre seawater for the late Famennian (lower oolite) was characterized by slightly dysaerobic and normal salinity conditions, which was complemented by generally modest (to high ?) productivity levels and warm temperatures. A deepening sequence from the lower oolite to the middle siliciclastic calcarenite units is suggested by modelling of the $\delta^{18}O$ based water temperatures and salinities (Fig. 8). This is complemented by aerobic redox associated with decreased productivity and water temperatures for the latest Famennian.

Oceanographic conditions possibly changed with deposition of the upper oolite unit and definitely persisted into the Tournaisian (Fig. 8). Redox potential of the seas became marginal with slightly dysaerobic conditions coupled with slightly lower salinities than during deposition of the preceding units. However, productivity increased dramatically to new levels accompanied by warmer temperatures and shallowing of the sea. Upwelling currents warmed over a shallower shelf can possibly account for the oceanographic transition and changes recorded by the Griotte brachiopods during the latest Famennian-earliest Tournaisian at La Serre, Montagne Noire, France.

CONCLUSIONS

Based on a combined sedimentological, paleontological and geochemical analysis of the brachiopods and matrix, the following conclusions can be reached about the depositional conditions at La Serre during the Famennian-Tournaisian.

1. Most studied brachiopod shells are microstructurally and geochemically well preserved. Typical microstructural features are bladed calcite fibres and prismatic calcite of the secondary and primary layers, respectively. Microstructural alteration is accompanied by geochemical changes in trace element content and isotopic compositions. These microstructural and geochemical data further support a minimum of reworking, postmortem transport and most importantly post-depositional diagenesis for the Griotte brachiopods.

2. Modelling of geochemical data suggests that some significant oceanographic changes accompanied the deposition of sediments and allochems from the latest Famennian to the earliest Tournaisian in the Montagne Noire region. The latest Famennian seas were characterized by restricted to mud-bottom brachiopod faunas in generally dysaerobic-aerobic, normal salinity, warm-cool temperatures, and reduced productivity waters. Water depth increased and temperature decreased significantly during deposition of the middle siliciclastic calcarenite relative to the subjacent lower oolite and the superjacent upper oolite units.

3. Oceanographic conditions of the Tournaisian sea at Montagne Noire as modelled by geochemical data were different from those of the Famennian. Seas were characterized by an open, shallow-water brachiopod fauna, which concurs with the slight dysaerobia of the water. Otherwise the seas experienced only a slight decrease in salinity but marked increases in productivity, temperature and a general shallowing of the water.

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