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Résumé de l'article

La Formation de Macumber, composée de calcaires fins en deux minces unités, représente un marqueur stratigraphique crucial à la base du Groupe de Windsor. À l'île du Cap Breton, la formation encaisse plusieurs indices Pb-Zn et constitue la limite inférieure d'une série d'omissions stratigraphiques à l'intérieur du Groupe de Windsor, l'origine desquelles est fortement débattue.

Cette première investigation de la diagenèse inorganique place neuf processus en une succession post-dépositionnelle incluant la stabilisation des éléments marins, et la précipitation d'évaporites et de ciments calcitiques anhydriques. Les 818O_{carb} (-13,0 à 2,0‰), 87Sr/86Sr (0,7076 à 0,7079) et [Sr] (50 à 10000 ppm) de microéchantillons des unités inférieures et supérieures, et de ciments anhydriques montrent deux tendances enveloppant l'ensemble des résultats. Ces tendances suggèrent qu'un fluide non-radiogénique, évaporitique et un fluide radiogénique dérivé de roches clastiques, auraient affecté les sédiments calcaires au cours de leur enfouissement progressif plus profond. Le fluide évaporitique aurait principalement affecté l'unité supérieure de la formation. Les données de terrain, les observations microscopiques et les résultats géochimiques n'indiquent pas l'empreinte tectonique attendue si une discordance existait au sommet de la formation. L'histoire tectonique ici documentée, ainsi que l'existence de calcite fibreuse développée le long de plans de cisaillement parallèles au litage supportent le modèle de détachement pour expliquer les omissions stratigraphiques du Groupe de Windsor.

Burial diagenesis model for the Macumber Formation on Cape Breton Island - implications for the tectonic evolution of the Windsor Group*

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The Macumber Formation, a finely laminated limestone consisting of two thin units, represents a key stratigraphic marker at the base of the Visean Windsor Group. On Cape Breton Island the formation hosts numerous Pb-Zn occurrences, and its upper boundary is in contact with rocks ranging in age from Visean (early Carboniferous) to Westphalian (middle Carboniferous), the origin of the stratigraphic omissions being debatable.

This first inorganic diagenesis study identifies nine post-depositional processes, including the stabilization of marine components, and evaporite and anhydral calcite precipitation. The $\delta^{18}\text{O}_{\text{PDB}}$ (-13.0 to 2.0‰), $^{87}\text{Sr}/^{86}\text{Sr}$ (0.7076 to 0.7079) and [Sr] (50 to 10000 ppm) of samples, including upper and basal whole-rock units and anhydral calcite cements, show two trends enveloping the entire field of data. The trends suggest that an evaporite-derived, non-radiogenic fluid and a clastic-derived radiogenic fluid mixed and interacted with the limestone sediments, in a progressively deeper burial environment. The evaporite-derived fluid mostly imprinted the top unit of the formation. The field investigations, microscope observations and geochemical results do not indicate a meteoric overprint as would be expected if an unconformity existed along the top of the formation. The burial history documented here, and the presence of fibrous calcite indicating bedding parallel shearing, support a detachment model to explain the stratigraphic omissions within the Windsor Group.

La Formation de Macumber, composée de calcaires fins en deux minces unités, représente un marqueur stratigraphique crucial à la base du Groupe de Windsor. À l'île du Cap Breton, la formation encaisse plusieurs indices Pb-Zn et constitue la limite inférieure d'une série d'omissions stratigraphiques à l'intérieur du Groupe de Windsor, l'origine desquelles est fortement débattue.

Cette première investigation de la diagenèse inorganique place neuf processus en une succession post-dépositionnelle incluant la stabilisation des éléments marins, et la précipitation d'évaporites et de ciments calcitiques anédriques. Les $\delta^{18}\text{O}_{\text{PDB}}$ (-13.0 to 2.0‰), $^{87}\text{Sr}/^{86}\text{Sr}$ (0.7076 to 0.7079) et [Sr] (50 to 10000 ppm) de microéchantillons des unités inférieures et supérieures, et de ciments anédriques montrent deux tendances enveloppant l'ensemble des résultats. Ces tendances suggèrent qu'un fluide non-radiogénique, évaporitique et un fluide radiogénique dérivé de roches clastiques, auraient affecté les sédiments calcaires au cours de leur enfouissement progressif plus profond. Le fluide évaporitique aurait principalement affecté l'unité supérieure de la formation. Les données de terrain, les observations microscopiques et les résultats géochimiques n'indiquent pas l'empreinte météorique attendue si une discordance existait au sommet de la formation. L'histoire diagénétique ici documentée, ainsi que l'existence de calcite fibreuse développée le long de plans de cisaillement parallèles au litage supportent le modèle de détachement pour expliquer les omissions stratigraphiques du Groupe de Windsor.

INTRODUCTION

This paper is the first study of inorganic diagenesis in carbonate rocks of the Macumber Formation, at the base of the Visean Windsor Group (Fig. 1a). The Macumber Formation in Nova Scotia hosts numerous Pb-Zn occurrences and has been an exploration target for base metals for over 50 years on Cape Breton Island (Hein *et al.*, 1993). Previous diagenetic studies of the Windsor Group have focused on organic matter and have established that the thermal alteration indices of palynomorphs are commonly low (-2 to 2+; Utting, 1987), and that the burial depth reached on Cape Breton Island has not exceeded the oil and gas windows (Utting and Hamblin, 1991; Fowler *et al.*, 1993; Héroux *et*

al., 1994). Clastic rocks and shales of the underlying Horton Group are considered to be oil source rocks (Fowler *et al.*, 1993).

Although the carbonate petrography of the formation has been studied (e.g., Schenk, 1992), the inorganic diagenesis profile has never been established even though it is required for distinguishing mineralizing fluids from background diagenetic fluids. Characterization of the diagenetic evolution of carbonates in the basin will help define new approaches for base metal exploration.

The Macumber Formation is a key regional stratigraphic marker at the base of the Windsor Group, and also acts as a lower boundary to significant stratigraphic omissions within the Windsor Group on western Cape Breton Island (Fig. 1b).

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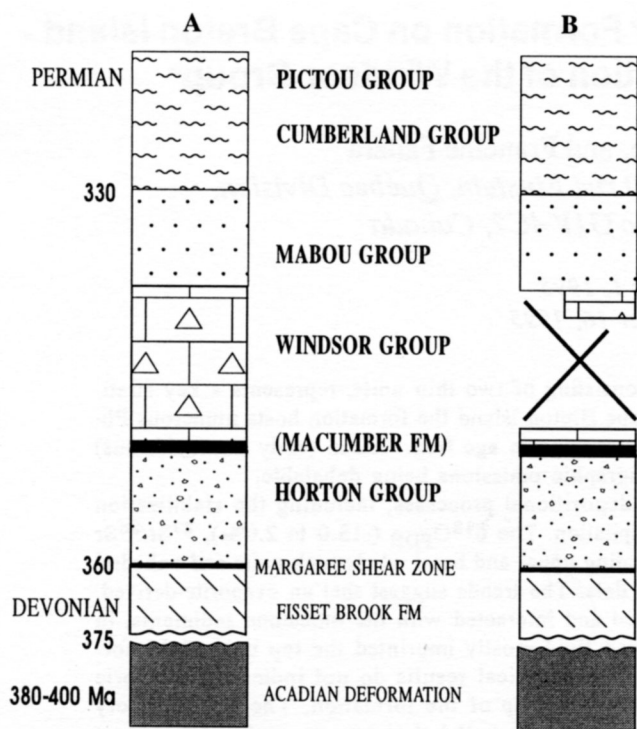


Fig. 1. (A) Stratigraphy of the studied area. The maximum thickness of the Windsor Group has been estimated at 2 km, whereas the Macumber Formation is up to 15 m thick (modified from Boehner, 1986). (B) Stratigraphic column showing major stratigraphic gap, as reported by Kelley (1967) and Lynch and Giles (in press). In most areas where the gaps have been reported, clastic rocks of the Mabou Group or evaporites of the Carrolls Corner Formation directly overlie the top of the Macumber Formation.

The missing sequences are at the origin of conceptual debates about the Upper Paleozoic tectono-stratigraphic evolution of Cape Breton Island. Two explanations advocated are an unconformity caused by uplift and erosion (e.g., Kelley, 1967; Gibling *et al.*, 1987) and a flat detachment faulting in an extensional regime (Lynch and Giles, in press; Lynch and Tremblay, 1994). Distinct diagenetic histories can be expected for each structural model: burial diagenesis should be first recorded in both cases, but followed by a meteoric imprint for the uplift/erosion model, or by shearing under shallow burial conditions in the case of the detachment model. Consequently, documenting the diagenetic evolution of the Macumber Formation may help constrain the tectono-stratigraphic evolution of the Windsor Group.

The objectives of the present paper are to document the regional diagenetic evolution of the Macumber Formation through the use of petrography and stable isotope geochemistry, to infer the nature of the fluids involved in its post-depositional history, and to discuss the implications of the diagenetic model for the tectono-stratigraphic evolution of the Windsor Group. At least nine post-depositional processes have affected the Macumber Formation. These are described here, characterized geochemically and related to their tectonic context.

METHODS

Macumber Formation samples from outcrops were selected at 17 locations (Fig. 2). One hundred thin sections and corresponding blocks were stained with Red Alizarin and potassium ferricyanide, and microsampled for stable isotopes. The limestone is generally too fine grained for the separation of clasts from cements. However, late calcite cements were sampled with a Jansen drill stage from large cavity fills such as nodules and veins. Results related to the Jubilee and Sugar Camp Zn-Pb occurrences and the description of their hydrothermal systems are reported in other papers (Paradis *et al.*, 1993; Fallara *et al.*, 1994; Chi and Savard, 1995; Chi *et al.*, 1995; Fallara, 1996).

The 109 carbon and oxygen isotope analyses were performed on micritic and stromatolitic limestones and late coarse anhedral calcite cements. CO₂ gas was extracted by reacting 5 mg of calcite powders for twelve hours with phosphoric acid at 25°C. The liberated CO₂ gases were analyzed on a VG-SIRA 12 mass spectrometer at the δ-Lab of the Quebec Geoscience Centre, Geological Survey of Canada. The results are expressed in the usual delta notation and given in per mil (‰) relative to the Peedee Belemnite standard (PDB). All values are corrected for the presence of ¹⁷O and for internal linear deviation. Precision (2σ) of the data is ±0.1‰.

Samples for Sr isotopic ratio were analyzed at the Geological Institute of the Ruhr University-Bochum, Germany. Eighteen powdered samples (splits from stable isotope samples), weighing from 2.0 to 4.4 mg, were dissolved in 2.5 N supra pure HCl. Sr was separated by a standard ion exchange technique and loaded on a single Ta filament. Mass spectrometry was performed on a 5 collector FINNIGAN MAT 262 and the data normalized to ⁸⁸Sr/⁸⁶Sr of 8.375209. The standards, NBS 987 and EN-1 (USGS) gave average values of 0.710193 ± 12 (±2σ) and 0.709121 ± 9 (±2σ), respectively, in 1991, and of 0.710286 ± 8 and 0.709207 ± 8 (±2σ) in 1993. The σ for single measurement was better than 2 × 10⁻⁵. The samples analyzed in 1993 were corrected for correspondence with the 1991 ones.

GEOLOGICAL CONTEXT

The Maritimes Basin is a large intracontinental basin featuring thick accumulations of Devonian to Permian sediments deposited during rifting and strike-slip faulting (Belt, 1968; Sheridan and Drake, 1968; Howie and Barss, 1975; Fralick and Schenk, 1981; Giles, 1981). The Macumber Formation occurs in the first of five transgressive-regressive cycles that formed the Windsor Group, the only marine interval in the Maritimes Basin (Giles, 1981). The Windsor Group is made up of carbonates, evaporites and siltstones of Viséan age, and is underlain by non-marine conglomerates, sandstones, and siltstones of the Tournaisian Horton Group. The Windsor Group is either conformably overlain by siliclastic rocks from the Namurian Mabou Group or unconformably by the

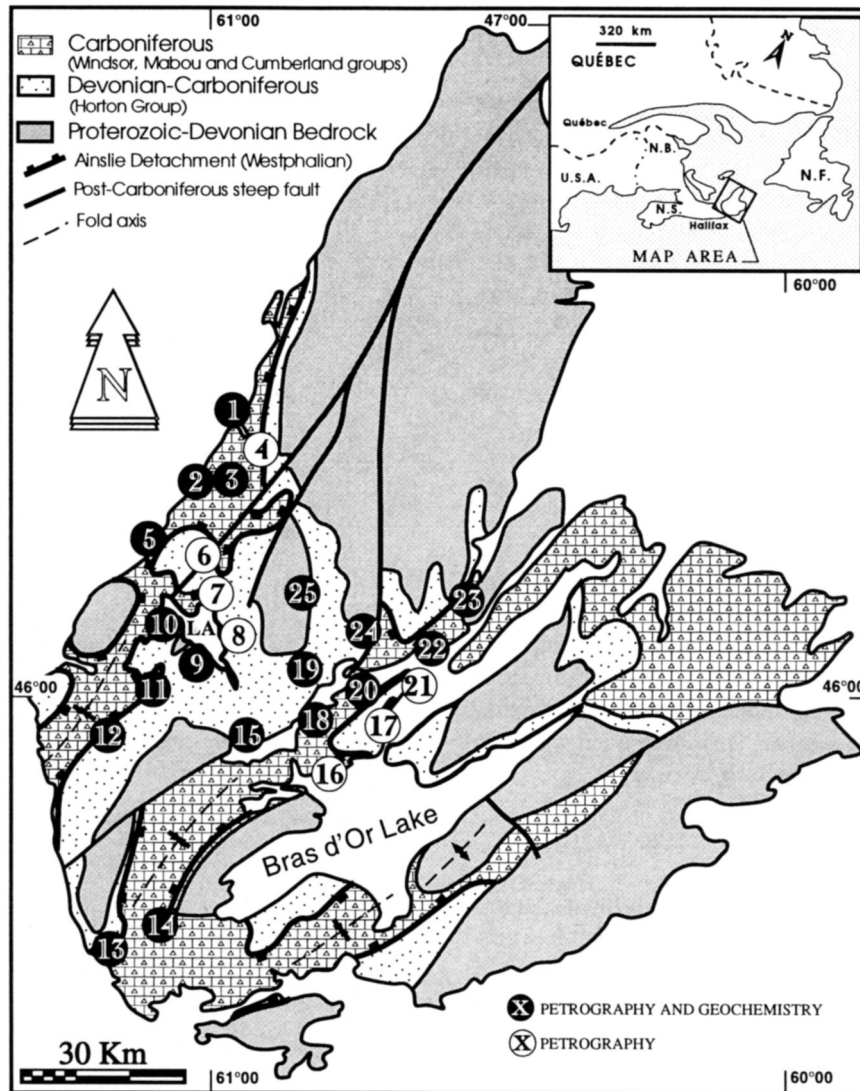


Fig. 2. Simplified map showing the geology of Cape Breton Island and the sampled locations. Mineralized sections from Jubilee and Sugar Camp (18 and 14) are not discussed in the present paper (see Chi and Savard, 1995; Fallara *et al.*, 1994). 1 = Margaree Harbour, 2 = Beatons Brook, 3 = Southeast Margaree, 4 = Margaree Forks, 5 = Big Brook, 6 = Inverness, 7 = Upper Margaree, 8 = East Lake Ainslie, 9 = Mount Pleasant, 10 = West Lake Ainslie, 11 = Mabou, 12 = Meander River, 13 = Port Hastings, 14 = Sugar Camp, 15 = Whyocomagh, 16 = Red Point East, 17 = Iona, 18 = Jubilee and Cains Mountain, 19 = Yankee Line, 20 = Lower Washabuck, 21 = John Alex Cove, 22 = Beinn Bhreagh, 23 = Big Bill, 24 = Baddeck Forks and South Side Baddeck, 25 = Upper Middle River. The distribution of the Horton Group and Carboniferous units and trace of the Ainslie Detachment are from Lynch and Giles (in press).

Westphalian Cumberland Group (Fig. 1a). At numerous studied locations, 1 to 1.5 km of the Windsor group is missing, and strata of the Mabou Group or of the upper Windsor Group directly overlie limestones of the Macumber Formation (Fig. 1b). These various contacts have been folded, faulted and exposed during late to post-Carboniferous Alleghenian deformation (Fig. 2).

SEDIMENTOLOGY AND PETROGRAPHY

At the locations studied, the thickness of the Macumber Formation varies between 10 and 15 m. The formation is divided into two main lithofacies, in ascending order: (1) micritic and intramicritic bioturbated lithofacies, and (2),

stromatolitic lithofacies (sometimes brecciated). These two lithofacies correspond to the strandline lithofacies A and B, respectively, of Schenk (1967), although deposition under chemosynthetic conditions (Schenk, 1992) or below fairweather wave base, under a restricted and highly saline regime (e.g., Lavoie and Savard, 1995) have been proposed.

The basal and top units consist of fine grained wackestones, packstones and bindstones characterized by overall low primary porosity and permeability. Secondary porosity as molds of evaporite nodules and fractures is very localized (under 5% where it occurs). Breccias occur at the top of the Macumber Formation at numerous locations, including Jubilee and Sugar Camp where limestone fragments of the Macumber Formation are cemented by calcite and Zn-Pb sulfides (locations

18 and 14, Fig. 2). The interpretation of Macumber breccia types in Nova Scotia are discussed in Lavoie *et al.* (1995) and Fallara (1996).

The micritic and intramicritic basal lithofacies consists of thin-bedded (10–40 cm), finely laminated, dark grey-brown limestones. For the micritic facies, the near absence of open marine fauna and wave-induced structures with, however, intense bioturbation suggest a relatively deep water environment (for a detailed description, see Lavoie, 1994 and Lavoie *et al.*, 1995). The intramicritic facies contains a high percentage of sub-angular to rounded intraclasts (Fig. 3a), as well as oolites, peloids, and calcimicrobial clast fragments. Graded (normally and inversely) bedding suggests deposition from waning flow currents of storm origin. The micritic and the intramicritic units alternate and the transition between the two is gradational. Their total thickness is between one and ten metres.

The stromatolitic (summital) facies is dominated by flat laminites devoid of clastic sediments, sometimes containing coproliths (Fig. 3b), algal fragments and ostracods. The stromatolites (laminites) never show columnar forms, but are stratiform. In thin section (Fig. 3b), they consist of mosaics of anhedral crystals forming fine layers with a *grumeleuse* texture (Bathurst, 1975). Laminites are interbedded with fine grained wackestones, sometimes rich in ooids.

POST-DEPOSITIONAL FEATURES

Post-depositional features include recrystallization (stabilization) of metastable marine carbonates, which has produced mosaics of inclusion-rich, anhedral crystals within oolites and stromatolites (Fig. 3), and pseudosparite after micrite. The allochems are cemented by inclusion-free, anhedral calcite which fills primary pores (Fig. 4a).

In the case of the stromatolitic unit, postdepositional features also include precipitation of evaporites as nodules between laminites, or isolated crystals within laminae, later replaced by inclusion-free, anhedral calcite forming pseudomorphs after evaporites (Fig. 4b,c).

Mechanical compaction affected the coarse components of the formation, which show indented contacts due to vertical displacement prior to anhedral calcite cementation and stylolitization (Figs. 3a, 4a). Mechanical compaction formed bedding-parallel solution seams and stylolites, which are ubiquitous and post-dated the anhedral calcite cement (Figs. 3, 4a, 5).

Shear-related calcite fibres are found as a late feature in the upper unit. Bedding-parallel shear is indicated by the calcite fibres, which occur along slip planes or between fragmented intraclasts and peloids. Tension gashes oriented perpendicular to bedding also contain calcite fibres, indicating bedding-parallel shear as well. Some local recrystallization appears to be related to the shearing. Rotated nodules and intrafolial folds within the recrystallized laminae demonstrate a non-coaxial component to the shear. Shearing and late recrystallization crosscut solution seams and therefore must postdate chemical compaction (Fig. 5).

There is no field evidence of karsting, surficial clastic

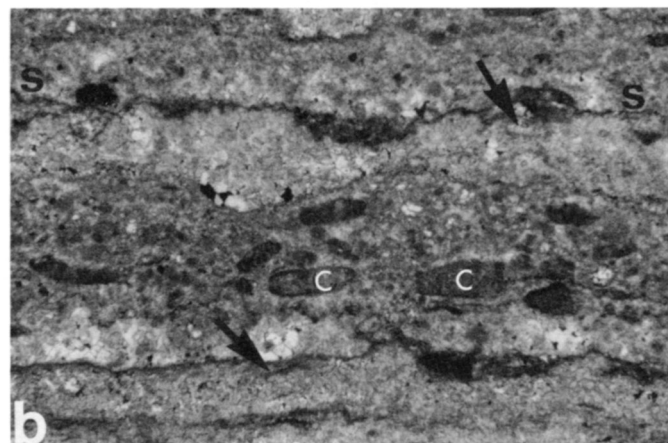
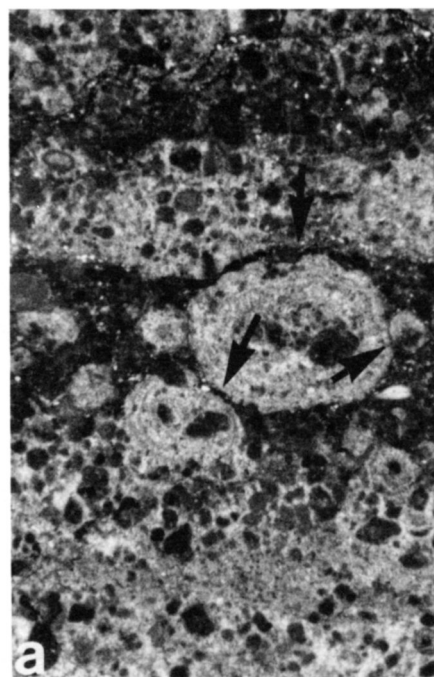


Fig. 3. (a) Photomicrograph showing oolites from the lower Macumber Formation, and compactional features (arrows). Plane polarized light, long axis of the picture is 9.5 mm. Sampling site #15, Whycocomagh. Sample skb93-56. (b) Photomicrograph showing stromatolitic laminites with grumeleuse texture (arrows). Laminite boundaries are accentuated by solution seams "S". The central layer is rich in coproliths "C". Plane polarized light, long axis of the picture is 7.2 mm. Sampling site #8, east Lake Ainslie. Sample skb93-60.

sedimentation or collapse breccia in the outcrops examined. Detailed petrography of thin sections does not reveal drastic dissolution or a cement fabric characteristic of meteoric diagenesis.

In summary, based on petrography, post-depositional processes that have affected the Macumber Formation include by nine distinct events which occurred in the following order: (1) precipitation of evaporites (nodules and isolated crystals); (2) mineralogical stabilization of metastable sedimented carbonates; (3) dissolution of evaporites; (4) mechanical compaction; (5) cementation by anhedral calcite; (6) chemical

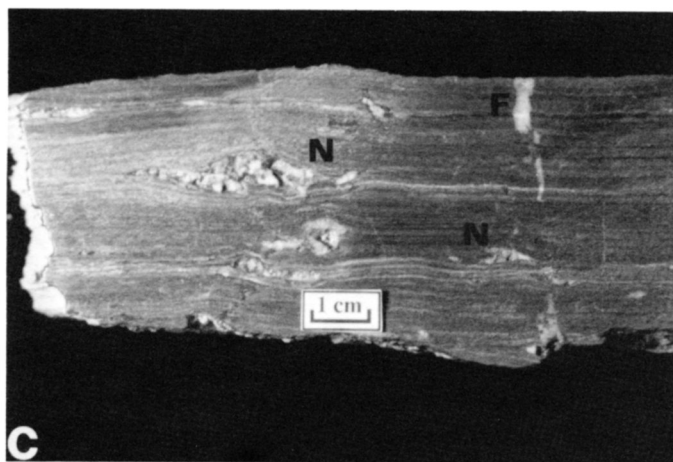
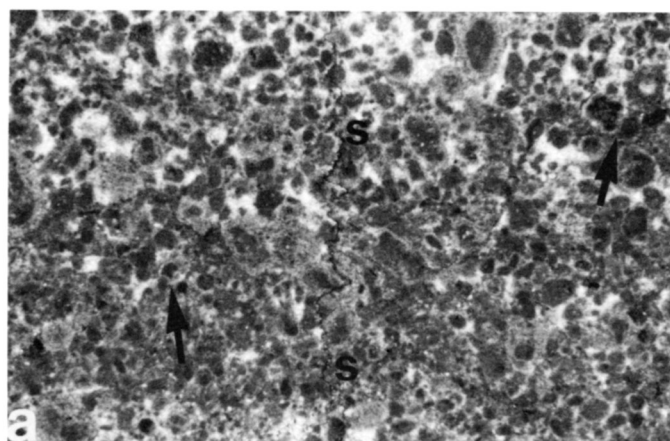


Fig. 4. (a) Photomicrograph of the peloidal and oolitic basal unit showing mechanical compaction features (arrows), cemented by late calcite (white) and later affected by vertical stylolites "S". Plane polarized light, long axis of the picture is 7.2 mm. Sampling site #8, east Lake Ainslie. Sample skb93-63. (b) Photomicrograph of stromatolitic layers from the upper unit, showing evaporite pseudomorphs (arrows) replaced by calcite. Plane polarized light, long axis of the picture is 7.2 mm. Sampling site #12, Meander River. Sample skb93-48. (c) Photograph of a slab showing compacted evaporite nodules "N", partly dissolved and filled with late calcite. A vertical fracture "F" filled with calcite, has been affected by horizontal displacement. Sampling site #25, Upper Middle River. Sample 93FF-284.

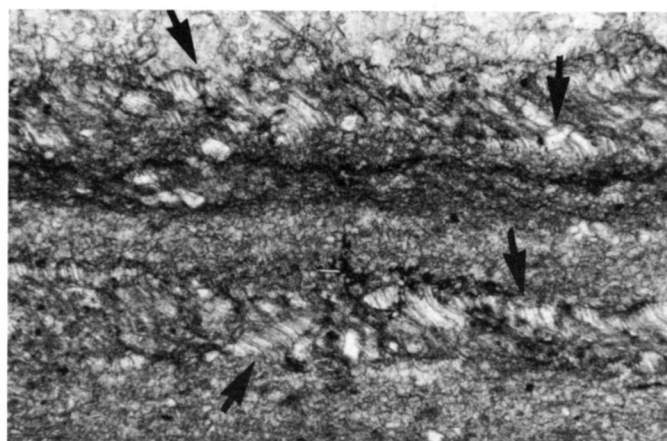


Fig. 5. Photomicrograph showing shear-related fibrous calcite (arrows). Displacement of solution seams by fibrous calcite (lower right arrow) suggest that shearing is post-chemical compaction. Plane polarized light, long axis of the picture is 1.8 mm. Sampling site #13, Port Hasting. Sample skb93-26.

compaction (solution seams and stylolites); (7) shearing; (8) vertical fracturing; and (9) final cementation by anhedral calcite.

ISOTOPE GEOCHEMISTRY - RESULTS

$\delta^{18}\text{O}_{\text{PDB}}$ -values of whole rock samples from the stromatolitic (top) and oolitic (basal) units, and microsamples of the anhedral, inclusion-free calcite cement have been compared on histograms (Fig. 6). Whole rock samples show a broad range of values (Fig. 6a,b). Eighty-six percent of the values obtained for the top unit are above the minimum theoretical (Popp *et al.*, 1986; Lohmann and Walker, 1989), marine Visean calcite signal (-4.0‰) whereas 60% of the basal unit samples are above this value. The heaviest ratios are also found in samples from the top unit (Table 1, Fig. 6). The results obtained for the late cements fall in a range of values exclusively under the marine Visean signal (-4.8 to -13.0‰, Fig. 6c, Table 1), regardless of their stratigraphic position.

In $\delta^{18}\text{O}$ - $\delta^{13}\text{C}$ space (Fig. 7a), the data set has been separated into two populations on the basis of distinctive $\delta^{13}\text{C}$ results. Population 1 groups analyses from the lower oolitic unit, the upper stromatolitic unit and calcite cements, and is recorded from western to eastern outcrops indicating no regional systematic variations (Table 1, Fig. 7a). The trend is characterized by a large variation of $\delta^{18}\text{O}_{\text{PDB}}$ values (-12.8 to +1.2‰) and typically heavy $\delta^{13}\text{C}$ values (+3 to +5.8‰). For the same $\delta^{18}\text{O}_{\text{PDB}}$ range, population 2 has a lower mean $\delta^{13}\text{C}$ value (0.5‰); it is restricted to the western domain (see Figs. 2, 7a), suggesting the presence of a local source of isotopically light carbon. The most depleted $\delta^{13}\text{C}$ samples do not carry the highest oxygen or the highest $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (Fig. 7, Table 1).

Many samples have $\delta^{18}\text{O}_{\text{PDB}}$ values within the expected range for calcite in equilibrium with Visean seawater but 23 samples are heavier (-1.5 to +1.2‰) than the marine

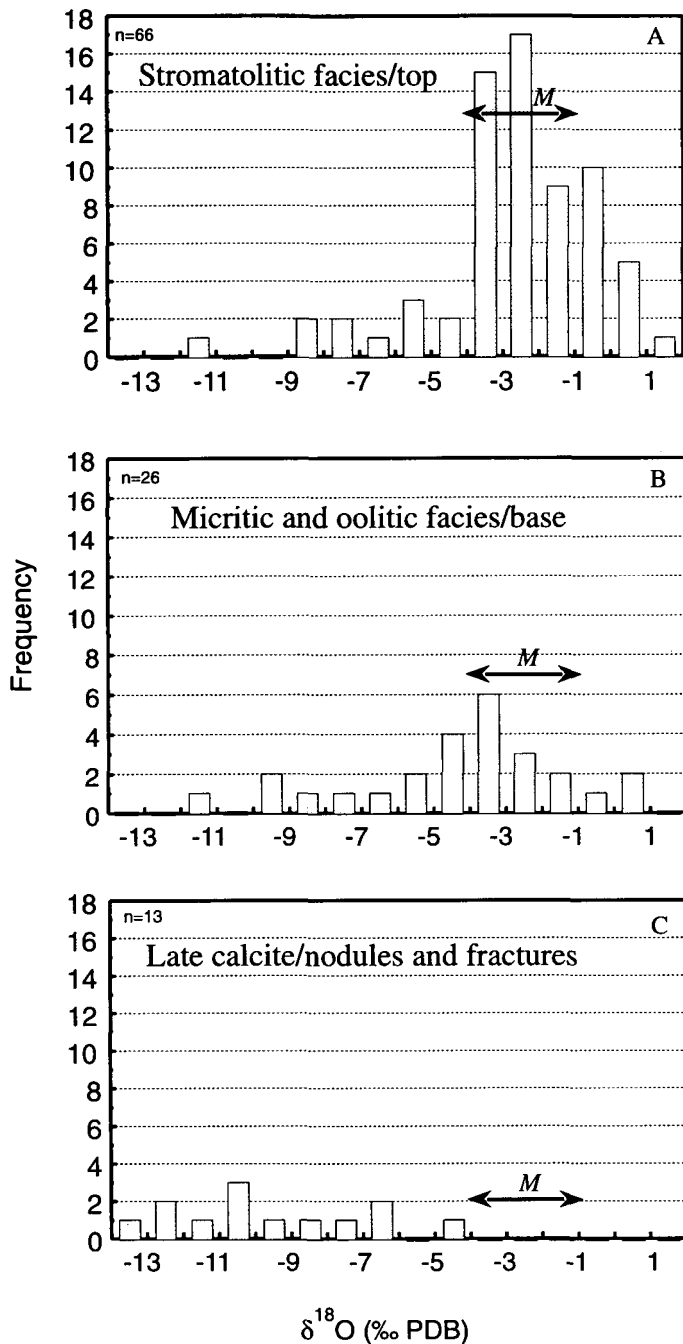


Fig. 6. Histograms showing $\delta^{18}\text{O}$ values relative to PDB of the Macumber Formation for (A) stromatolitic facies (upper unit), (B) oolitic facies (basal unit) and (C) for separated late calcite cement from all units of the Macumber Formation. "M" represents the isotopic field for calcite in equilibrium with Visean seawater (Popp *et al.*, 1986; Lohmann and Walker, 1989).

signals, and 28 samples are lighter (-13.0 to -5.4‰) than the hypothetical meteoric water signal (HMWL, Fig. 7a). Within individual samples, late calcite cements show $\delta^{18}\text{O}_{\text{PDB}}$ values lower than the whole rock values by 5 to 8‰, but similar $\delta^{13}\text{C}$ values (Table 1, e.g., location 11, sample 213; location 13, samples 210, 211 and 212). This is also visible regionally in the overall trend of the late cements (Table 1). Two samples of late anhedral cement extracted from the same nodule show very distinct signals: -6.0 and -10.6‰ $\delta^{18}\text{O}_{\text{PDB}}$

Table 1. Geochemical results.

Location	Sample	Phase	$\delta^{18}\text{O}_{\text{VPDB}}$	$\delta^{13}\text{C}$	$^{87}\text{Sr}/^{86}\text{Sr}$	Sr (ppm)
2	tr-620	c-fract	-8.0	0.6		
2	G1	m	-2.6	4.6		
2	H	m	-3.1	3.9	0.707701	3818
2	H1	m	-1.3	4.2		
2	J	m	-0.2	4.1		
2	J1	m	0.2	4.2	0.707652	2997
3	ly-658	c-fract	-10.9	0.8		
3	B	m	-3.4	3.1		
3	B1	m	-3.3	3.5		
3	E	m	-2.3	5.5		
3	E1	m	-3.6	4.5		
3	G	m	-3.0	4.4		
3	I	m	-2.2	3.5		
3	I1	m	-2.3	3.5		
3	93-402A	o	-0.7	3.6	0.707759	308
3	93-402B	o	-1.7	3.3		
3	A	o	-5.7	2.4	0.708577	247
3	A1	o	-5.9	2.4		
3	93-402C	m	-2.5	2.5		
3	93-402D	m	-2.1	3.4		
5	tr-665a	m	-4.4	3.5		
5	tr-666a	c-nod	-9.1	3.4		
5	tr-666c	c-fract	-7.2	2.8		
5	K	m	-2.0	4.3		
5	K1	m	-1.7	4.4		
5	L	m	-2.4	4.2		
5	L1	m	-2.5	4.3		
5	M	m	-3.3	4.1		
5	M1	m	-3.4	4.1		
5	N	m	-3.2	4.4		
5	N1	m	-2.7	4.2		
5	O	m	-3.1	4.2		
5	O1	m	-3.1	4.1		
9	63	o	-2.9	2.2		
9	93-73	c-nod	-4.8	0.5		
9	T	m	0.3	2.7		
9	U	m	-0.7	-1.7	0.707741	395
9	60	m	-1.8	3.6		
9	65	o	-4.9	3.2	0.708200	285
9	68	m	-2.7	4.1	0.707764	515
9	93-72	o	-2.6	2.1		
9	93-68	m	-3.9	0.7		
9	93-71	o	-3.7	3.9		
9	93-73	m	-1.6	3.9		
10	33b	m	-2.1	4.2		
10	mull	c	-6.4	3.2		
10	V	m	-0.4	4.0		
10	W	m	-1.1	4.3		
10	28	o	-6.3	0.3	0.708033	404
10	32	o	0.2	4.6		
10	34	o	-4.1	3.6	0.707771	497
10	42	o	-2.5	2.5		
10	33a	m	-2.0	4.3		
10	44	m	0.9	4.1		
11	212	c-fract	-13.0	3.7		
11	94-213a	c-fract	-11.7	4.0		
11	94-213b	c-fract	-12.5	0.9		
11	X	m	-1.0	4.5		
11	Y	m	-0.6	3.6		
11	212	st	-8.0	4.1		
11	94-213a	m	-5.9	4.2		
11	94-213b	m	-5.4	4.1		
12	46	o	-3.1	3.6	0.708017	322
12	48	m	0.4	3.9		
12	50	m	1.2	4.1	0.707661	50
13	26	m	-7.4	4.4	0.707899	498
13	23b	c-fract	-10.1	3.3		
13	211	c-nod	-10.6	3.2		
13	211	c-nod	-6.0	3.2		

at 3.2‰ $\delta^{13}\text{C}$ (Table 1, sample 211), suggesting a progressive depletion in ^{18}O during calcite cementation.

Most $^{87}\text{Sr}/^{86}\text{Sr}$ ratios obtained (Fig. 7b,c) are lower than the global Visean seawater ratios (Smalley *et al.*, 1994), suggesting that the Sr pool was locally influenced by a non-

Table 1...

Location	Sample	Phase	$\delta^{18}O_{VPDB}$	$\delta^{13}C$	$^{87}Sr/^{86}Sr$	Sr (ppm)
13	210	c-fract	-12.4	3.3		
13	23a	o	-11.7	3.6	0.707739	423
13	25	o	-8.2	3.7	0.707847	373
13	26-1	o	-7.6	5.8	0.708171	893
13	23	m	-11.4	3.1		
13	210	m	-6.3	3.1		
13	211	m	-2.7	4.2		
15	57	m	-8.3	4.1	0.707966	466
15	56a	o	-9.4	4.2		
15	56b	o	-9.7	4.3	0.707749	301
19	93FF-217B2	m	-1.5	3.9		
19	93FF-221A	o	-3.0	4.2		
19	93FF-222A	o	-3.7	4.3		
19	93FF-223B	m	-3.0	4.3		
19	93FF-223B	m	-0.9	4.7		
19	93FF-224	m	-3.1	4.5		
20	93FF-019A	o	-1.9	4.6		
20	93FF-019b	m	-2.2	4.7		
20	93FF-039D	o	-3.5	4.4		
20	93FF-039e	m	-2.5	4.3		
20	93FF-060B	m	-1.2	4.5		
20	93FF-2	o	-3.2	3.0		
22	93FF-120C	m	-5.8	4.7		
22	93FF-120b	m	-7.9	4.4		
23	93FF-084B	o	-4.5	4.2		
24	93FF-122	m	-4.3	4.3		
24	93FF-137B1	m	-0.4	4.5		
24	93FF-159B	m	-2.9	4.3		
24	93FF-161b	m	-3.9	4.2		
24	93FF-165B	m	-3.3	4.1		
24	93FF-216	o	-4.2	4.5		
24	52	o			0.707823	531
24	51	m	-0.6	4.4		
24	54	o	0.1	4.9	0.707747	10175
24	207	m	0.4	3.8		
24	208	m	-0.2	4.2		
25	93FF-255B	o	-1.8	4.7		
25	93FF-256B	m	-0.5	4.5		
25	93FF-258A	m	-0.4	4.5		

radiogenic source and was isolated from the global oceanic reservoir. This suggestion implies that the sedimentary environment was not an open sea but a restricted body of marine water and is supported by the faunal assemblage of subzone A (Mamet, 1970; Geldsetzer, 1977), and by the importance of the overlying evaporite succession in the Windsor Group.

The isotopic ratios represented in the $\delta^{18}O$ - $^{87}Sr/^{86}Sr$ plot show two end-member trends enveloping the entire spread of data (Fig. 7b). Trend 1 has uniform $^{87}Sr/^{86}Sr$ and highly variable $\delta^{18}O_{PDB}$ values, and trend 2 shows highly variable ratios for both tracers. Samples most depleted in ^{18}O , possibly representing a high water/rock ratio (W/R), show non-radiogenic $^{87}Sr/^{86}Sr$ in trend 1, but radiogenic ratios in trend 2. The most radiogenic $^{87}Sr/^{86}Sr$ ratios belong to the basal unit (Fig. 7b,c). Two sources of Sr clearly

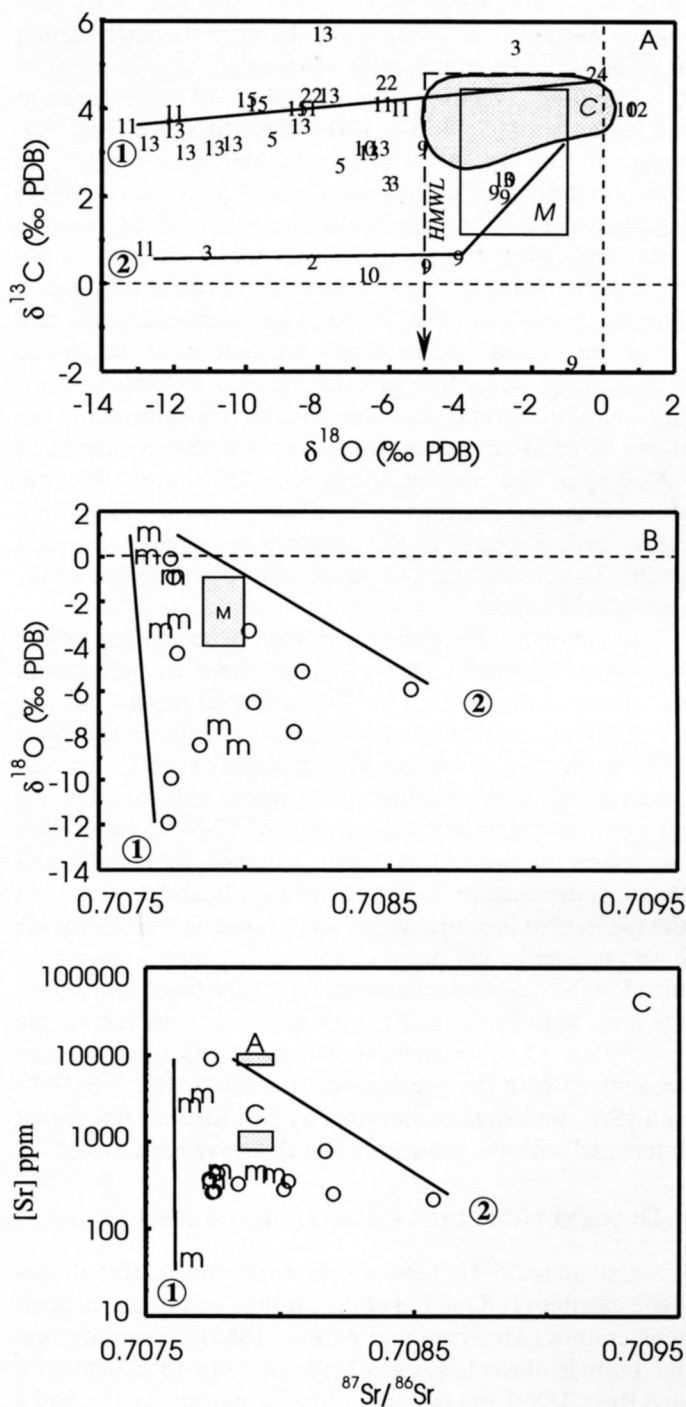


Fig. 7. (A) Scatterplot of $\delta^{13}C$ vs $\delta^{18}O$. Sampling locations are indicated as data labels. A cluster of 66 points for samples from all sites is represented by the "C" field. A broad range of $\delta^{18}O$ values is recorded, with a relatively narrower variation of $\delta^{13}C$ values. For population 1 the $\delta^{13}C$ values cluster around the marine carbon signal of +3 to +4‰, whereas for population 2, the value is lower, at around 0.5‰. Grey box "M" indicates isotopic composition of calcites in equilibrium with Viséan seawater (Lohmann and Walker, 1989; Popp *et al.*, 1986). The hypothetical meteoric water line (HMWL) is calculated for a paleolatitude of 10 to 15°S (Hamblin and Rust, 1989), and for a surficial temperature

of 20°C (Anderson and Arthur, 1983). (B) Scatterplot of $\delta^{18}O$ vs $^{87}Sr/^{86}Sr$ for micritic "m" and oolitic "o" samples of the Macumber units. Trend 1 shows significant variations of $\delta^{18}O$ values with practically no changes in $^{87}Sr/^{86}Sr$, whereas trend 2 represents an end-member where both tracers vary significantly. Grey box indicates isotopic composition of calcites in equilibrium with Viséan seawater (Lohmann and Walker, 1989; Smalley *et al.*, 1994). (C) Scatterplot of [Sr] vs $^{87}Sr/^{86}Sr$ for samples of the micritic "m" and oolitic "o" units. End-member trends 1 and 2 enclose the entire field of data. Trend 1 shows no variation of $^{87}Sr/^{86}Sr$ for drastic changes in [Sr], whereas trend 2 shows significant variations for both tracers. Grey boxes indicate Sr concentrations and isotopic ratios for aragonite "A" and calcite "C" in equilibrium with Viséan seawater (Veizer, 1983; Smalley *et al.*, 1994).

influenced the diagenetic evolution of the Macumber Formation, the effect of radiogenic Sr being particularly strong at its base and geographically widespread.

The radiogenic tail of trend 2 (Fig. 7b) corresponds to the lowest bulk [Sr] in the [Sr]- $^{87}\text{Sr}/^{86}\text{Sr}$ space (Fig. 7c), suggesting incorporation of allochthonous (non-marine) Sr during stabilization of the limestones. A broad range of [Sr] is obtained for $^{87}\text{Sr}/^{86}\text{Sr}$ below and at the Visean marine ratio, suggesting that many samples contain marine Sr derived either from the sediments or from interstitial water. The [Sr] range (<100 to 10000 ppm) is characteristic of a mixed mineralogy assemblage that underwent diagenetic stabilization. According to Veizer (1983), calcites in equilibrium with normal seawater have Sr concentrations between 800 and 1200 ppm whereas aragonite can have up to 10000 ppm. The concentrations near 10000 ppm likely resulted from the transformation of aragonite to calcite in a closed system and/or in the presence of saline, non-radiogenic, Sr-rich waters. The lower values are typical of recrystallized calcite.

In summary, the regional isotope geochemistry of the Macumber Formation shows that: (1) there are no regional variations in the $\delta^{18}\text{O}$, $^{87}\text{Sr}/^{86}\text{Sr}$ and [Sr] trends, but low $\delta^{13}\text{C}$ values are restricted to western locations; (2) many $\delta^{18}\text{O}$ values are above the Visean marine signal, this tendency being more pronounced for upper unit samples; (3) all samples considered, the overall $\delta^{13}\text{C}$ - $\delta^{18}\text{O}$ trend does not match the theoretical meteoric diagenesis pattern, and the most depleted $\delta^{18}\text{O}$ values are significantly lower than the theoretical meteoric water signal (see next section); (4) both radiogenic and non-radiogenic Sr sources are recognized in the diagenetic carbonates; (5) the basal unit shows the most radiogenic, and the top unit, the least radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$; (6) end-member populations and trends can be recognized with the geochemical tracers ($\delta^{18}\text{O}$, $^{87}\text{Sr}/^{86}\text{Sr}$ and [Sr]), and suggest imprints by two distinct fluids that interacted with the sediments and that may have mixed.

DIAGENETIC FLUIDS - BURIAL DIAGENESIS MODEL

Calculated $\delta^{18}\text{O}$ between meteoric and marine diagenetic calcites is a function of the latitude and mean surficial temperature (Anderson and Arthur, 1983). Assuming that the latitude of the basin was between 10 to 15°S (Hamblin and Rust, 1989) and that early Visean marine calcites had a $\delta^{18}\text{O}_{\text{PDB}}$ value of -2‰ (Lohmann and Walker, 1989), their coeval meteoric counterparts should not be depleted by more than 3‰ (Anderson and Arthur, 1983), i.e., they should not have $\delta^{18}\text{O}_{\text{PDB}}$ values lower than -5‰ (HMWL, Fig. 7a). This constitutes a conservative estimate because the Visean marine signal in the study area could have been even heavier than -2‰ due to evaporative effects. An accurate estimate of the exact composition of ancient meteoric waters depends on knowledge of nearby relief. However, because a large part of our trend falls considerably below -5‰, and does not show affinities with meteoric systems such as the well known "J" curve of Lohmann (1988) or the "L" curve of Al-Aasm and Veizer (1986), a meteoric influence in the diagenesis of the Macumber Formation is not indicated. The

trends instead show the typical profile of burial diagenetic systems, evolving from surficial marine signals, to progressively lighter $\delta^{18}\text{O}$ values, without marked depletion of $\delta^{13}\text{C}$ values at high W/R (low $\delta^{18}\text{O}$ values) (i.e., Choquette and James, 1990).

With $\delta^{18}\text{O}$ being a good indicator of parent fluid salinity and temperature of precipitation, the clear tendency towards heavier values for the top unit likely reflects conditions of precipitation and/or recrystallization distinct from its basal counterpart. These conditions could have been governed by circulation of hypersaline waters from the evaporites to the top unit, and of fluids mainly derived from the permeable clastic rocks of the Horton Group to the basal unit.

Samples with low $\delta^{13}\text{C}$ values suggest incorporation of light carbon bicarbonates through shallow-burial decarboxylation of organic components (Tissot and Welte, 1984). These samples are restricted to the western domain (Fig. 7a, population 2). This, together with traces of hydrocarbons and bitumen common on thin sections, indicates that the Macumber Formation was locally rich in organic components. Numerous hydrocarbon seeps sourced to the Horton Group exist near Lake Ainslie and constitute a likely source of light carbon (Utting and Hamblin, 1991; Fowler *et al.*, 1993).

The covariations of $\delta^{18}\text{O}$ with $^{87}\text{Sr}/^{86}\text{Sr}$ and [Sr] suggest two sources for Sr: seawater and the interstitial waters of evaporites represent a non-radiogenic source, and the clastic rocks of the Horton Group, mainly derived from plutonic rocks, represent a radiogenic source (e.g., White *et al.*, 1990).

Incorporation of heavy $\delta^{18}\text{O}_{\text{PDB}}$ and non-radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ during growth of biogenic components in a restricted and saline environment, coupled with early diagenetic processes such as evaporite precipitation and possibly early cementation, have produced the heavy $\delta^{18}\text{O}_{\text{PDB}}$ and non-radiogenic character of the Macumber Formation. Burial has produced limestones with lighter $\delta^{18}\text{O}_{\text{PDB}}$ due to the decrease of fractionation at higher temperatures, and with higher $^{87}\text{Sr}/^{86}\text{Sr}$ in the basal unit due to its exposure to hot fluids expelled from the underlying radiogenic clastic sediments. Hot fluids can leach Sr from clastic components and inherit a radiogenic signal.

Mixing of non-radiogenic, evaporitic fluids with radiogenic basal waters and water/rock interaction during burial possibly produced intermediate isotopic values (Fig. 7). The uniformity of the O and Sr isotope trends throughout the study area suggests that the burial diagenetic system was relatively homogeneous on a regional scale (Table 1, Fig. 7a,b).

In summary, the petrographic and isotopic diagenetic features described above can all be explained by a simple burial model (Fig. 8). After sedimentation, seawater produced early precipitation of calcite cement and evaporites (Fig. 8a). As thicker evaporites were being deposited, formation water expelled from the Horton Group started to stabilize limestones, dissolve evaporites, precipitate calcite cement, and mix slowly with evaporite-related brines (Fig. 8b). At deeper burial depths (and higher temperatures), stabilization and cementation continued, producing carbonates with lower $\delta^{18}\text{O}$ and higher $^{87}\text{Sr}/^{86}\text{Sr}$ (Fig. 8c).

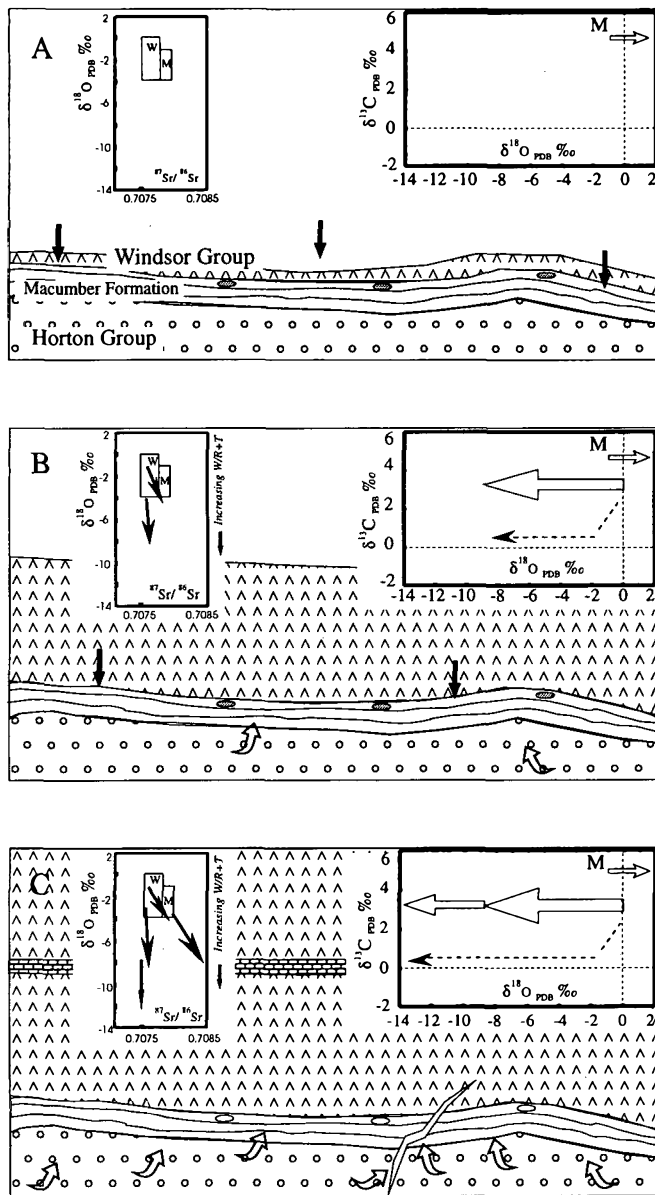


Fig. 8. Diagenetic model for the Macumber Formation (not to scale). Departures from Viséan marine $\delta^{18}\text{O}$ signals by Macumber carbonates were caused both by evaporitic enrichment in ^{18}O and lowering of oxygen fractionation factor at high temperature. The produced trends are illustrated by arrows on $\delta^{18}\text{O}_{\text{PDB}}-^{87}\text{Sr}/^{86}\text{Sr}$ and $\delta^{13}\text{C}-\delta^{18}\text{O}_{\text{PDB}}$ plots. (A) Evaporite-derived brines directly precipitated calcite and evaporite nodules in the top unit, and/or shifted the signals of metastable marine carbonates to the "W" box, to the left of the expected Viséan marine values "M". (B) Recrystallization and precipitation of carbonates in the top and basal units during progressively increasing temperature and burial caused a lowering of $\delta^{18}\text{O}$ values. Samples depleted in ^{13}C probably derived some light carbon from oxidation of organic matter, the Macumber Formation being locally rich in petroleum (see text). (C) At high temperature, radiogenic water was expelled from the Horton Group producing the end-member isotope ratios of the carbonates, and low $\delta^{18}\text{O}$ values resulted from lower oxygen fractionation at higher temperatures.

TECTONO-STRATIGRAPHIC EVOLUTION - DISCUSSION

The stratigraphic succession of the Maritimes Basin in western Cape Breton Island is marked by important and conspicuous gaps in the stratigraphy which occur systematically above the Macumber Formation. The missing stratigraphy may be accounted for by either: (1) an extensional detachment fault running along the contact between the limestones of the Macumber Formation and overlying evaporites, which have highly contrasting rheologic properties (Lynch and Giles, in press); or (2) a local unconformity. The diagenetic history of the Macumber Formation as documented here provides important new data which can distinguish between the presence of a detachment fault or unconformity along the top of the Macumber Formation.

The unconformity processes should produce collapse breccias and weathering (e.g., Kelley, 1967; Gibling *et al.*, 1987). Field evidence such as soil formation, calcrete, karsts and surface breccia could also indicate erosion. The Macumber Formation underlying unconformities, especially where covered with continental rocks of the Mabou Group, should show karsting and petrographic features such as solution pipes, pendant and meniscus cements, and a geochemical profile typical of marine and burial diagenesis with a meteoric diagenesis overprint.

During the present study, field and petrographic features characteristic of sub-aerial erosion were not found (see also Lynch and Giles, in press; Lynch and Tremblay, 1994), and the diagenetic succession recognized by petrography and geochemistry does not include a meteoric component. Hence, the absence of features diagnostic of meteoric diagenesis is inconsistent with the presence of an important unconformity at the top of the Macumber Formation.

The detachment model proposes that the detachment plane occurs along the top of the Macumber Formation on Cape Breton Island, where it is in contact with a thick evaporite succession, and is referred to as the Ainslie detachment (Lynch and Giles, in press). The carbonates of the Macumber Formation would have acted as an upper crustal stress guide, controlling the propagation of the detachment which was active in Westphalian times (Lynch and Giles, in press). This mechanism should produce typical burial diagenetic features, followed by shearing in the Macumber Formation. The overall geochemical trends, from stabilization of fine grained sediments to late cementation, should indicate initial marine and progressive burial diagenesis. This model is fully supported by field and petrographic observations, and the geochemical characterization of the Macumber units is consistent with a burial diagenetic succession. Moreover, the observation of cleavage, shear-related, fibrous calcite along horizontal planes, recumbent folds and rotated nodules can all be interpreted as effects of bedding-parallel shear. These features post-date numerous burial processes as suggested by their cross-cutting solution seams (Fig. 5). Relative chronology (based on petrography) of shear-related fibrous calcite and

fracture-filling late calcites ($\delta^{18}\text{O}_{\text{PDB}}$ down to -12.4% , Table 1, location 13) indicate that extension took place prior to thermal peaks of 75 to 95°C (i.e., at an estimated maximum burial depth of 2.0 km (Fig. 9)).

CONCLUSION

The Macumber Formation consists of fine grained carbonate sediments that were mostly impermeable throughout its diagenetic history. However, during and after lithification, evaporite dissolution, shearing and fracturing produced a heterogeneous secondary porosity in the formation. The succession of diagenetic events consists in precipitation of evaporites (nodules and isolated crystals), recrystallization (stabilization) of metastable marine carbonates, dissolution of evaporites, mechanical and chemical compaction (stylolitization) and late cementation. Petrography and isotope geochemistry indicate that all the processes have taken place in the marine and burial environments. Whole-rock samples from a few western locations have yielded $\delta^{13}\text{C}$ values around -0.5% interpreted as resulting from incorporation of light carbon through shallow-burial decarboxylation of hydrocarbons, concentrated in the western Macumber Formation.

The formation can be divided into two units, a top unit dominated by stromatolitic laminites and a basal unit dominated by ooid limestones. Non-radiogenic ($\delta^{18}\text{O}_{\text{PDB}}$ between 1.5 and -13% , $^{87}\text{Sr}/^{86}\text{Sr}$ around 0.7075) and radiogenic ($\delta^{18}\text{O}_{\text{PDB}}$ between 1.0 and -8% , $^{87}\text{Sr}/^{86}\text{Sr}$ between 0.7076 and 0.7085) diagenetic systems (1 and 2 in order), have largely affected the top and basal units, respectively. The recognized diagenetic fluids are marine brines (system 1) from the overlying evaporites, and formation waters (system 2) from the underlying Horton Group. These two fluids have mixed and dominated during the diagenetic evolution of the Macumber Formation, from near surface to maximum burial. This, in addition to the lack of erosional and meteoric diagenetic features, gives indirect support for the occurrence of a detachment fault along the upper contact of the Macumber Formation.

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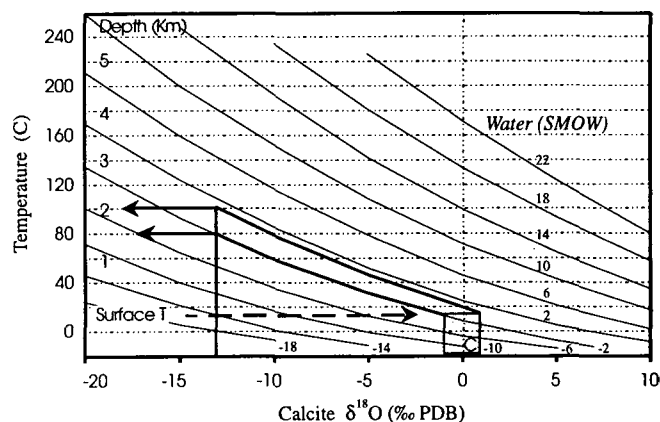


Fig. 9. Temperature of precipitation vs $\delta^{18}\text{O}_{\text{PDB}}$ of diagenetic calcites. Curves are constructed with the equation of Craig (1965):

$$T(^{\circ}\text{C}) = 16.9 - 4.2 (\delta^{18}\text{O}_{\text{cal}} (\text{PDB}) - \delta^{18}\text{O}_{\text{wat}} (\text{SMOW})) + 0.13 (\delta^{18}\text{O}_{\text{cal}} (\text{PDB}) - \delta^{18}\text{O}_{\text{wat}} (\text{SMOW}))^2.$$

The translation to burial depths (km) is based on a geothermal gradient of 40°C/km as suggested by the curve of Lister *et al.* (1991) for uniform stretching of the lithosphere in an extensional tectonic regime.

Assuming that the heavy marine $\delta^{18}\text{O}_{\text{PDB}}$ values (-1.5 to 1.5%) of Macumber carbonates precipitated at 15°C, a likely temperature for the advocated sedimentary environment, parent waters of the diagenetic carbonates had a calculated $\delta^{18}\text{O}_{\text{SMOW}}$ of -2 to -1% . Using this estimated signal for diagenetic waters (assuming it did not change with burial), temperatures needed to precipitate the most depleted calcite ($\delta^{18}\text{O}_{\text{PDB}}$ value of -13%) range between 80 and 100°C, which correspond to estimated burial depths of 1.5 to 2.0 km. These values are minimal because the salinity of fluids generally increase with burial and the parent waters could have had a higher ratio from the start (see text). Thus simple heating due to burial in the presence of a high geothermal gradient can generate carbonates with the range of $\delta^{18}\text{O}_{\text{PDB}}$ values obtained.

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