

Link between long-lasting evaporitic basins and the development of thick and massive phreatic calcrete hardpans in the Mississippian Windsor and Percé groups of eastern Canada

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Abstract

Part of the Viséan (upper Mississippian) succession in the upper Paleozoic Maritimes Basin of eastern Canada is overprinted by massive phreatic calcrete hardpans that can exceed 10 m in thickness and that are characterized by the thorough mineral replacement of most of their host sediment by calcite, similar to those that are currently forming around salt lakes in Quaternary sediments of central Australia. The precise timing and paleogeography of this Carboniferous event was until now poorly known, but lateral correlations over a large study area indicate that phreatic calcitization occurred in the vicinity of large evaporitic basins following a marine transgression and regression cycle in Chadian to Holkerian times. This relation confirms that the previously proposed model for modern analogs in central Australia, which states a genetic link between the salt lakes and the thick and massive phreatic calcrete hardpans, can be applied to ancient environments, and that such occurrences may be used to infer the former presence of an evaporitic basin in their vicinity. Finally, our relatively large dataset indicates that the stable isotopes of carbon and oxygen are successful in differentiating ancient marine carbonates from ancient phreatic calcretes.

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1. Introduction

Thick and massive phreatic calcrete hardpans such as those reported in Quaternary sediments of central Australia, which result from thorough mineral replacement along the entire thickness of an aquifer, have been associated with the mixing zone between a fresh groundwater discharge and the salty groundwater that surrounds evaporitic basins in arid environments (Mann

and Horwitz, 1979; Arakel and McConchie, 1982; Jacobson et al., 1988; Arakel et al., 1989). The mixing generates an increase in alkalinity within the fresh groundwater discharge, which creates a significant increase in silica solubility paired with a substantial decrease in calcium carbonate solubility, thus favouring replacement of silicate minerals by calcite (Arakel and McConchie, 1982). However, a possible analog in Portugal (Pimentel et al., 1996) was more recently reinterpreted as a palustrine carbonate, potentially casting doubt on the Australian model (Pimentel and Alonso-Zarza, 1999; Alonso-Zarza, 2003). Moreover,

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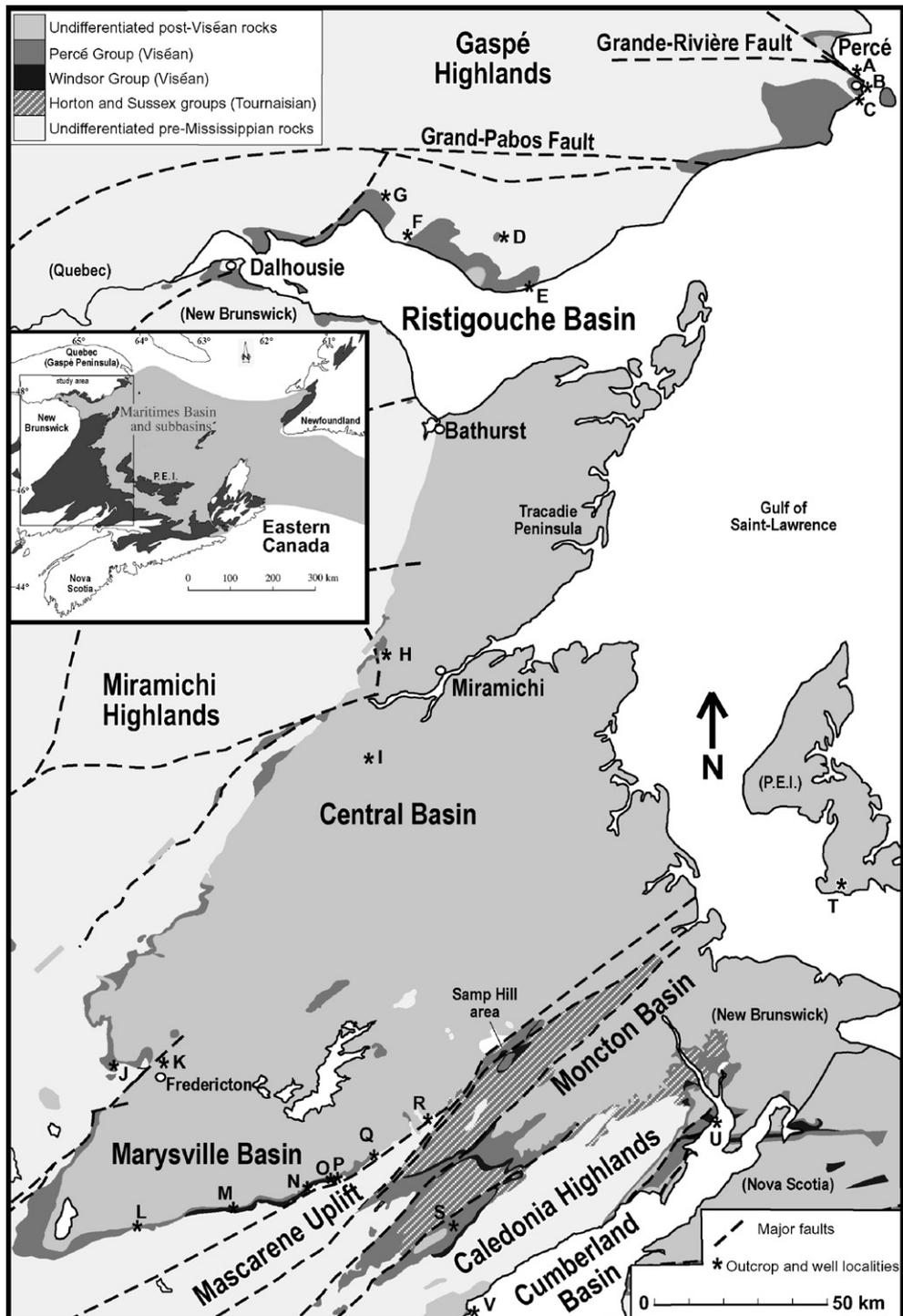


Fig. 1. Simplified post-Acadian (post-Middle Devonian) geology of the study area (modified from the [New Brunswick Department of Natural Resources and Energy, 2000](#)). Localities A: Cannes-de Roches; B: La Coulée Creek; C: Percé-Beach; D: Saint-Elzéar; E: New-Carlisle; F: Black Cape; G: Saint-Jules; H: Sevogle; I: Blackville; J: Mactaquac Dam; K: Killarney; L: Shin Creek; M: Irving Brook; N: Hampstead; O: Albright Brook west; P: Albright Brook east; Q: Stewarton; R: Snider Mountain; S: Salt Springs; T: Wellington; U: Hopewell Cape; V: Quaco Head. Inset: location of the study area within eastern Canada (Dark grey: onshore extent of upper Paleozoic rocks; light grey: offshore extent of upper Paleozoic rocks; modified from [Gibling et al., 1992](#)). P.E.I. is an acronym for the Province of Prince Edward Island.

the evaporitic basin connection was suggested but not demonstrated in the only reported case of an ancient equivalent of such calcretes (the La Coulée Calcrete) in the Viséan (late Mississippian) Percé Group of eastern Canada (Jutras et al., 1999, 2001, submitted for publication; Jutras and Prichonnet, 2002, 2005).

In order to identify the diagenetic paleoenvironment of the Viséan phreatic calcrete hardpans of eastern Canada, they are here studied in the context of their broad lateral variations and stratigraphic relationships. To achieve this goal, some inter-regional correlations of Viséan units had to be made. New field, well and stable isotopes data from the southern part of the Province of New Brunswick are compared and correlated with new and published data from the eastern part of the Province of Quebec, northern New Brunswick and the Province of Prince Edward Island (Jutras et al., 1999, 2001, submitted for publication; Jutras and Prichonnet, 2002, 2005) (Fig. 1, inset). The paper also tests the constraints that can be provided by stable isotopes in terms of differentiating ancient phreatic calcrete hardpans from other forms of ancient carbonate.

2. General tectonostratigraphic framework of Viséan units in eastern Canada

Mississippian rocks in eastern Quebec, western New Brunswick and Prince Edward Island occur in subbasins of the composite Late Devonian to Early Permian Maritimes Basin of Atlantic Canada (Fig. 1). Viséan rocks in these basins belong to the time-equivalent Windsor and Percé groups (Fig. 2), which were both affected by phreatic calcretization at their base in marginal areas of the Cannes-de-Roches, Ristigouche,

Central and Marysville basins (Fig. 1). These rocks were mildly deformed in Viséan (Jutras and Prichonnet, 2005) and Pennsylvanian (Jutras et al., 2003a,b, 2005, submitted for publication) times.

The Maritimes Basin is largely dominated by continental clastics, but accommodated 28 epicontinental sea incursions during the Viséan (late Mississippian) (Giles, 1981), leaving the successive marine limestones and lowstand evaporites of the Windsor Group (Fig. 2). These sea incursions mainly affected the southwestern half of the composite basin, in the Province of Nova Scotia (Fig. 1, inset), whereas only the first few reached southern New Brunswick (McCutcheon, 1981; Plint and van de Poll, 1983), and perhaps only one transgression made it as far as northern New Brunswick and eastern Quebec (Jutras and Schroeder, 1999; Jutras et al., 1999, 2001) (Fig. 1). The Upper Windsor Group of Giles (1981) is not represented in eastern Quebec and New Brunswick, and the Middle Windsor Group is only represented in the southern part of New Brunswick. According to Utting and Giles (2004), based on macrofossils, spores and conodonts, the Lower Windsor Group is Chadian to Holkerian, whereas the Middle Windsor Group is Asbian (Viséan time-scale in Fig. 3).

2.1. The Lower Windsor Group

The base of the Lower Windsor Group in the study area is characterized by carbonate laminites of the Macumber Formation in central parts of Carboniferous basins, above Tournaisian clastic graben-fills (Giles and Boehner, in press). The Macumber Formation is time-equivalent to the Gays River Formation carbonate bank

Period	Epoch	Ma	Nova Scotia	Southern NB	Central NB	Northern NB	Eastern QC
Mississippian	Namurian	327	Mabou Gp	Mabou Gp			Mabou Gp
			Upper Windsor Gp	Percé Gp	Percé Gp	Percé Gp	Percé Gp
	Viséan	342	Middle Windsor Gp	Lower Windsor Gp	Percé Gp	Percé Gp	Percé Gp
			Lower Windsor Gp	Lower Windsor Gp			
Tournaisian	355	Horton Gp	Sussex Gp Horton Gp			?	
Devonian	Late	376	Fountain Lake Gp		Piskahegan Gp		Saint-Jules Fm ?
		383					Miguasha Gp
	Middle		Syn-Acadian units				

Fig. 2. General Mississippian stratigraphy in eastern Canada. Time-scale after Okulitch (2004).

Period	Epoch	Stages	Age (Ma)	Ristigouche and Cannes-de-Roches basins		Central Basin		Marysville Basin		Moncton Basin		Cumberland Basin (west of Shepody Bay)		
Mississippian	Viséan	(Pendlean)	327	Juras and Prichonnet (2005)	This study	Juras et al. (submitted)	This study	McLeod et al. (1998)	This study	McCutcheon (1981)	This study	St. Peter and Johnson (1997)	This study	
		Brigantian	329	Bonaventure Fm	Bonaventure Fm	Bonaventure Fm	Bonaventure Fm	Shin Fm	Bonaventure Fm	Scoodic Brook Fm	Bonaventure Fm	Hopewell Cape Fm	Bonaventure Fm	
		Asbian	331	Cap d'Espoir Fm	Poodiac Fm	Cap d'Espoir Fm?	Poodiac Fm	Shin Fm	Lime Kiln Brook Fm	Wanamaker Fm	Poodiac Fm	Poodiac Fm	Lime Kiln Brook Fm	Lime Kiln Brook Fm
		Holkerian	334	La Coulée Fm and Calcrete	La Coulée Fm and Calcrete	La Coulée Calcrete	La Coulée Calcrete	Shin Fm	Clover Hill Fm?	Clover Hill Fm	Clover Hill Fm	Clover Hill Fm	Lime Kiln Brook Fm	Lime Kiln Brook Fm
		Arundian	338	La Coulée Fm and Calcrete	La Coulée Fm and Calcrete	La Coulée Calcrete	La Coulée Calcrete	Parleeville Fm	Cassidy Lake Fm?	Cassidy Lake Fm	Cassidy Lake Fm	Cassidy Lake Fm	Upperton Fm	Upperton Fm
								Parleeville Fm	Meaghers Grant Fm	Upperton Fm?	Upperton Fm	Meaghers Grant Fm	Upperton Fm	Upperton Fm
		Chadian						Parleeville Fm	La Coulée Calcrete (*)	Macumber Fm	Macumber Fm	Macumber Fm	Gays River Fm	Gays River Fm
							Macumber Fm	Gays River Fm	Gays River Fm	Gays River Fm	Macumber Fm	Gays River Fm	Macumber Fm	

Fig. 3. Proposed framework for the Viséan stratigraphy of eastern Quebec and western New Brunswick. Time-scale after Okulitch (2004).

and mound facies, which is found along basin margins or on knobs of basement highs. Large inputs of clastic sediments in some areas of the basin margins resulted in the deposition of the mixed carbonates and siliciclastics of the Meaghers Grant Formation (Boehner, 1977), which was formerly referred to as the Parleeville Formation in southern New Brunswick (McCutcheon, 1981). This unit is time-equivalent to the Macumber and Gays River formations, as well as to the lower part of the Upperton Formation, an up to 300 m thick sulphate unit overlain by up to 1 km of halite assigned to the Cassidy Lake Formation. Conformably overlying the Cassidy Lake Formation, the Clover Hill Formation (Fig. 3) marks a return to sulphate deposition, but it is characterized by more siliciclastics than the Upperton Formation.

2.2. The Middle Windsor Group

Conformably overlying the Lower Windsor Group evaporites in the Cumberland Basin are the marine limestones and clastic rocks of the Lime Kiln Brook Formation. This unit was identified for the first time within the limits of the Marysville Basin in the present study (Fig. 3). It is differentiated from the petrographically similar Meaghers Grant Formation by more fossiliferous and brachiopod-rich limestones, and by the occasional presence of *K. stephanephorus* (diagnostic of the Asbian *K. stephanephorus* Concurrent Range Zone of Utting and Giles, 2004) in its spore assemblage.

2.3. The Percé Group

Whereas grey continental clastic rocks of the early Namurian Mabou Group are directly underlain by marine rocks of the Viséan Windsor Group in central Nova Scotia, continental red beds of the Percé Group separate these two successions in northwest Nova Scotia and in southern New Brunswick, where only older Windsor Group rocks are represented (Fig. 2). In eastern Quebec, only continental clastic rocks of the Percé Group are found in the Viséan successions below the Mabou Group, with no Windsor Group rocks identified to date, apart from occurrences in the Magdalen Islands in the Gulf of Saint-Lawrence (Barr et al., 1985).

The Percé Group includes (1) grey fanglomerates of the La Coulée Formation, which are affected by a 10–12 m thick phreatic calcrete hardpan at their base (the “La Coulée Calcrete”), (2) fine red beds of the Cap d’Espoir Formation, and (3) coarse red beds of the

Bonaventure Formation. In the present study, the Cap d’Espoir Formation of eastern Quebec (Jutras and Prichonnet, 2005) was found to be the petrographic and stratigraphic equivalent of the Poodiac Formation of southern New Brunswick (Anderle et al., 1979), to which it is now correlated with on the basis of precedence.

Similar red beds to those of the Bonaventure Formation are found throughout eastern Canada at the same stratigraphic position, but bear different names from one area to the next. For the purpose of producing large paleogeographic reconstructions and to better constrain the stratigraphic position of the Viséan phreatic calcrete hardpans in the region, formal correlation of these red beds with the Bonaventure Formation is here proposed based on the following stratigraphic and petrographic criteria:

- Jutras et al. (2001) stratigraphically defined the Bonaventure Formation as a red bed unit that is conformably to disconformably below early Namurian grey clastics of the Mabou Group (the Pointe Sawyer Formation in eastern Quebec).
- Petrographically, the Bonaventure Formation includes mudstone, sandstone, conglomerate, breccia and pedogenic calcretes, but is mainly defined by its gravel fraction, which is polymictic and includes far-derived quartz pebbles as a minor component amongst more locally derived sedimentary, igneous and metamorphic clasts (Jutras et al., 1999, 2001, 2005; Jutras and Prichonnet, 2002, 2004, 2005). The Bonaventure Formation is also characterized by arid features such as desiccation cracks, pedogenic calcretes and an apparent absence of carbonaceous plant remains.

Based on the above-mentioned stratigraphic and petrographic criteria, beds that were mistakenly assigned to the Shin (van de Poll, 1967), McKinley (Anderson and Poole, 1959), Gelder (van de Poll, 1967), Wanamaker (Anderle et al., 1979), Scoodic Brook (Anderle et al., 1979) and Hopewell Cape (Ami, 1902) formations of central and southern New Brunswick are correlated with the Bonaventure Formation of Logan (1845) and therefore abandoned on the basis of stratigraphic and petrographic equivalence, as well as precedence (Fig. 3).

3. The Viséan phreatic calcrete hardpans of eastern Canada versus other types of carbonate or calcrete

In the field, the phreatic calcrete hardpans are differentiated from marine or lacustrine limestone by

their massive appearance and the absence of sedimentary structures. In terms of geochemistry, they differ from marine limestone by their consistently negative carbon isotope ratios (δC^{13} VPDB), mostly lower than -2 (Jutras et al., 1999). They are differentiated from pedogenic calcretes by (1) their stratigraphic position, lying directly on basement rocks as opposed to within a soil profile; (2) their thickness, which can exceed 3 m (*sensu* Wright and Tucker, 1991); (3) the paucity of iron oxides, due to their position below the water table, and (4) their *alpha* (i.e., massive) microfabric (*sensu* Wright, 1990), due to the lack of biogenic influence.

We agree with Nash and McLaren (2003) that the popular term “groundwater calcrete” is a vague term that could be understood to encompass all types of calcretes, even pedogenic ones. We are here specifically referring to the Viséan groundwater calcretes of eastern Canada as “thick and massive phreatic calcrete hardpans” to differentiate them from other types of groundwater calcretes that may not share the same diagenetic environment. The Viséan occurrences in eastern Canada are characterized by the thorough mineral replacement of a regolith or a sedimentary column by calcite along several metres in thickness. They typically have a relatively sharp lower boundary corresponding to the lower limit of the paleo-aquifer in contact with the aquiclude that constrained it (Jutras et al., 1999, 2001, submitted for publication; Jutras and Prichonnet, 2002) (Fig. 4A). The upper boundary of these calcretes has been eroded at all localities except one (Figs. 1 and 5, locality B), where it is diffused along a thickness of 20 m, possibly due to frequent water table readjustments in an active basin with high sedimentation rates (Jutras et al., 1999). The calcretes are typically composed of 90–100% calcite, and very little clues usually remain on the nature of the host sediment, apart from the occasional presence of partly preserved silicified clasts floating in a massive calcite matrix (Fig. 4B). In some cases, the calcrete may be thoroughly auto-brecciated (Fig. 4C). The calcite can be micritic, microsparitic or macrosparitic, but earlier formed calcrete that is overprinted or reworked by younger calcite is always darker and finer grained than the calcite from subsequent events (Fig. 4C, D). Our geochemical study of these calcretes is limited to the earliest generation of calcrete material in comparison with the seemingly undisturbed host material when the latter is composed of carbonate.

In our view, the groundwater (or “valley”) calcretes and dolocretes described around modern salt lakes in central Australia (Butt et al., 1977; Mann and Horwitz, 1979; Arakel and McConchie, 1982; Jacobson et al., 1988; Arakel et al., 1989) are the only ones described in

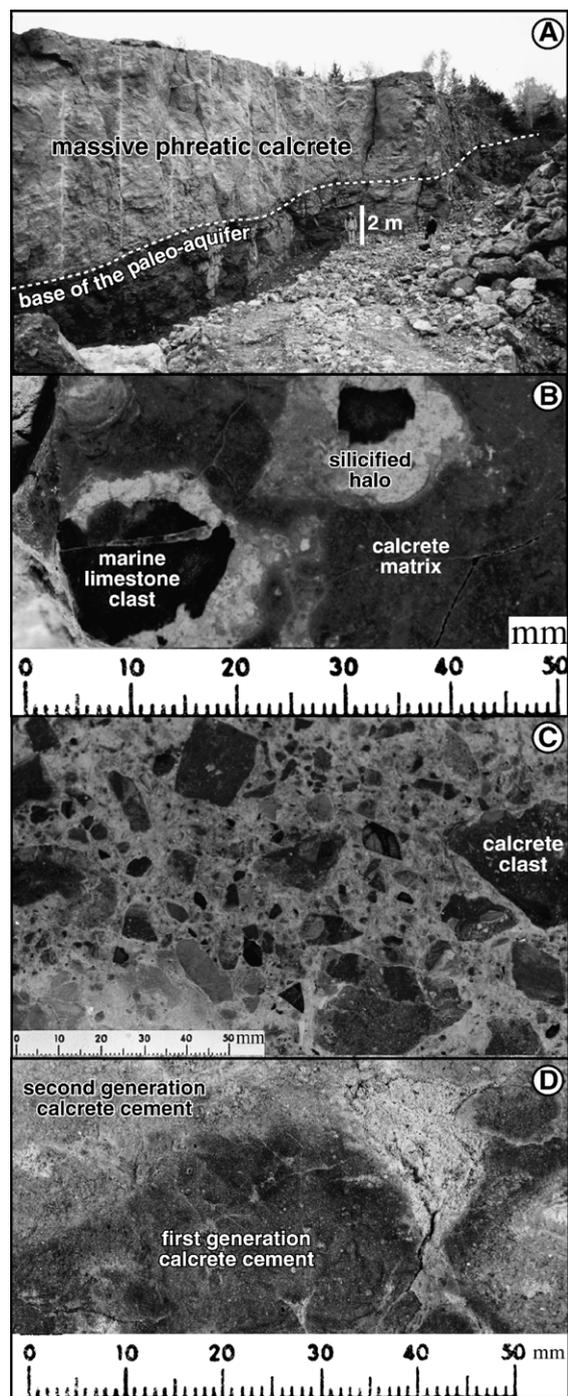


Fig. 4. A: Quarry section of the massive La Coulée Calcrete at Saint-Jules (Figs. 1 and 5, locality G; modified from Jutras and Prichonnet, 2002). B–D: Cut-sections of the La Coulée Calcrete from the La Coulée Creek section (Figs. 1 and 5, locality B; modified from Jutras et al., 1999); B: Dark marine limestone clasts with siliceous halos floating in massive calcrete; C: Multiple generations of auto-brecciated calcrete material; D: Dark microsparitic calcrete material overprinted by a younger and paler macrosparitic cement.

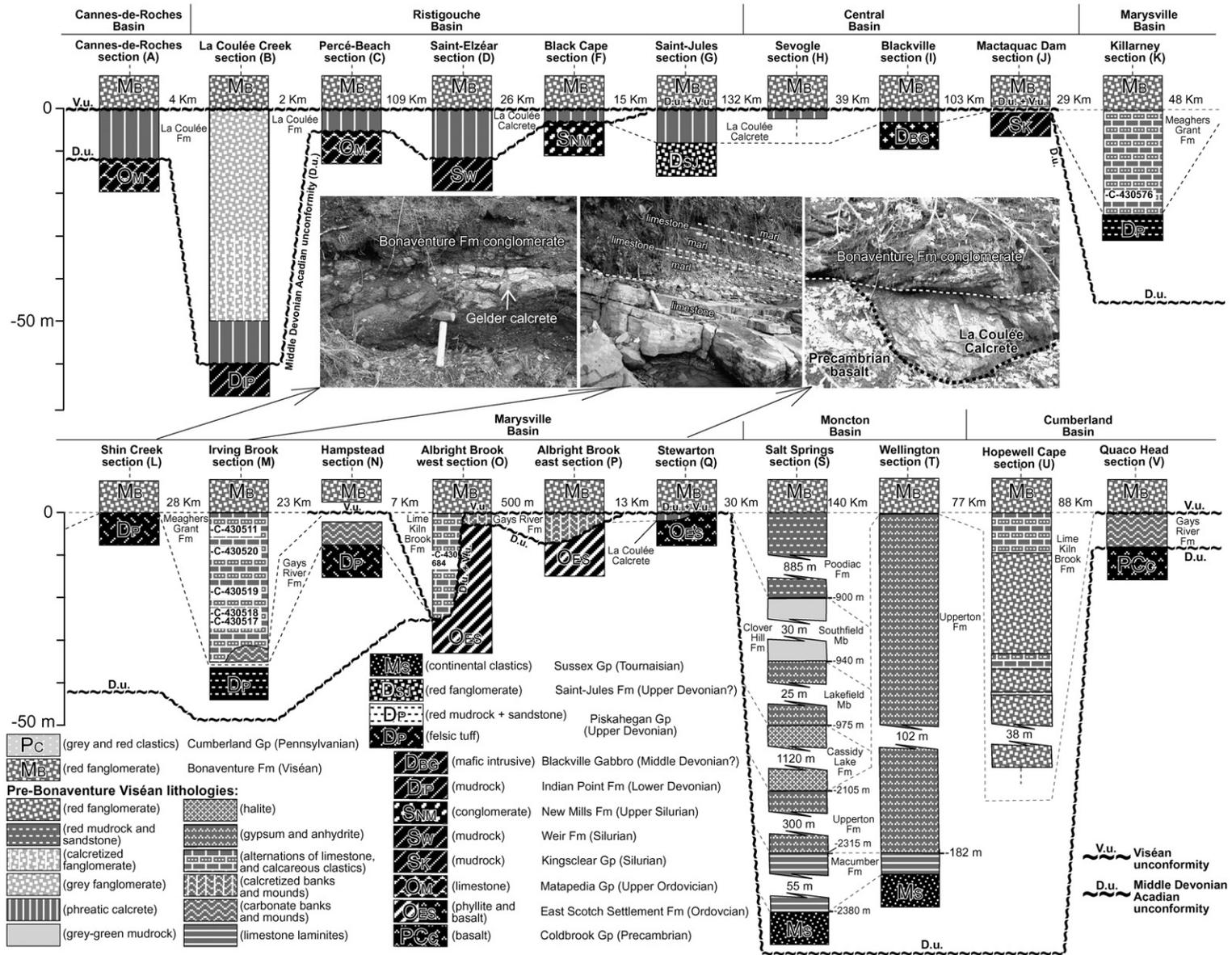


Fig. 5. Stratigraphic sections from the Cannes-de-Roches, Ristigouche, Central, Marysville, Moncton and Cumberland basins. The location of successful samples for palynology is indicated on the sections (e.g., C-430511). Section A is modified from Juras et al. (2001); B, C and D from Juras et al. (1999); F and G from Juras and Prichonnet (2002); H and I from Juras et al. (submitted); S from Anderle et al. (1979); T from Giles and Utting (1999); U from McCutcheon (1981); V from Plint and van de Poll (1983).

the literature that present a similar facies to that of the Viséan phreatic calcrete hardpans of eastern Canada. Apart from the mineralogy, the latter are also similar to massive groundwater dolocretes developed in late Paleogene to Neogene sediments of Kuwait (Khalaf, 1990; El-Sayed et al., 1991), in Upper Triassic sediments of the Paris Basin in central France (Spötl and Wright, 1992), and in Paleogene sediments of the Provence Basin in southern France (Colson and Cojan, 1996), which are all attributed to the mixing of fresh and saline groundwaters around salt lakes or restricted marine bodies under arid conditions.

What is here referred to as thick and massive phreatic calcrete hardpans implies extensive and penetrative mineral replacement. It should therefore not be confused with the small groundwater calcrete lenses described by Tandon and Gibling (1997) in Pennsylvanian sandstones of eastern Canada; the thin calcrete sheets and columnar rhizoconcretions described by Purvis and Wright (1991) in Middle Triassic sandstones of southwest England; the nodular groundwater calcretes described by Lang et al. (1990) in coarse Mesozoic sediments of Morocco and by Khadkikar et al. (1998, 2000) in Quaternary alluvium of Gujarat; nor with the pore-filling groundwater calcrete cements described by Tandon and Narayan (1981), Sassi et al. (1984), Maizels (1987), Kaemmerer and Revel (1991), Nash and Smith (1998, 2003) and Nash and MacLaren (2003) in coarse Cenozoic alluvium of respectively Punjab, Tunisia, Oman, Morocco, Spain and Botswana, in which the original host sediment material is largely preserved. Finally, thick and massive phreatic calcrete hardpans should not be confused with palustrine carbonates, which are lacustrine carbonates overprinted by pedogenic processes (Alonso-Zarza, 2003).

4. Stratigraphic relationships between phreatic calcrete hardpans, host sediments, lateral equivalents and bounding units

The phreatic calcrete hardpan occurrences in the Maritimes Basin, and the host material that hosts them, are all constrained to the same relative stratigraphic position, unconformably beneath the Bonaventure Formation red beds (Figs. 1 and 5, localities A–D, F–I and O–Q). Because they are demonstrably coeval with alluvial fan deposition of the La Coulée Formation (Jutras et al., 1999) (Figs. 1 and 5, localities A–C), they have been formally referred to as the “La Coulée Calcrete” (Jutras and Prichonnet, 2005), but are in no way bound to this unit, as they are also hosted by basement regolith (Jutras and Prichonnet, 2002; Jutras et al., submitted for

publication) (Figs. 1 and 5, localities G–I, Q), and by marginal carbonate banks and mounds of the Gays River Formation (this study) (Figs. 1 and 5, localities O, P). Because the La Coulée Calcrete belongs to a group of continental rocks, the phreatic calcrete is here informally referred to as “calcretized Gays River Formation bank” when the host sediment can be identified as such based on the presence of diagnostic Lower Windsor Group fossils preserved within the calcrete matrix.

Although no clasts could be found in them, apart from occasional quartz silts that are aligned parallel-to-bedding, the host sediment of the calcrete at the Saint-Elzéar and Black Cape localities in eastern Quebec (Figs. 1 and 5, localities D and F) is suspected to be a penecontemporaneous marine sediment because the calcrete sits directly on what was identified as an exhumed Carboniferous paleoshore platform (Jutras and Schroeder, 1999; Jutras et al., 1999). The calcrete also bears a negative cerium anomaly in the distribution of its rare earths content (Jutras et al., 1999), which suggests that the host sediment is either marine or composed of reworked marine sediments (Haskin et al., 1966). Moreover, the Black Cape locality includes well defined stromatolitic structures near the base of the calcrete profile. Because no marine fossils were identified in the 63 thin-sections that were studied from these two localities, no formal correlation with the Gays River Formation was made, and these two calcrete profiles are still included in the La Coulée Calcrete of the Percé Group (*sensu* Jutras and Prichonnet, 2005).

Due to a mild deformation and erosion event that followed phreatic calcretization and preceded deposition of the Bonaventure Formation, the latter unit sometimes sits directly on basement rocks (Figs. 1 and 5, localities J and L). In other areas, phreatic calcretization seemingly never occurred, and the Bonaventure Formation sits directly on a non-calcretized succession of Viséan rocks (Figs. 1 and 5, localities K, M, N, S–V).

Phreatic calcretization only affected the eastern part of the Marysville Basin (Figs. 1 and 5, localities O–Q), whereas the western part of this basin remained unaffected (Figs. 1 and 5, localities K–N). Conversely, occurrences of Meaghers Grant Formation beds are limited to the western part of this basin (Figs. 1 and 5, localities K and M). The well-exposed succession of the Meaghers Grant Formation at Irving Brook (Figs. 1 and 5, locality M) is characterized by alternations of micritic limestone, marl and sandstones with abundant coaly fragments. Similar to Meaghers Grant Formation occurrences in Nova Scotia (Harnish, 1978), the marine micrite and marl are poorly fossiliferous and include no brachiopods. In the area of Hampstead (Figs. 1 and 5,

locality N), the Meaghers Grant Formation is absent and the Gays River Formation bank facies is paraconformably overlain by the Bonaventure Formation, with some pedogenic overprints identified in the upper part of the bank material at one outcrop.

In the deep and narrow Moncton Basin, phreatic calcretes are absent and the pre-Bonaventure succession is instead characterized by thick evaporites above deepwater carbonate of the Macumber Formation (Figs. 1 and 5, localities S and T). A thick succession of fine Poodiac Formation red beds separates the evaporites from the overlying Bonaventure Formation in the most central part of the basin (the Marchbank Syncline of Anderle et al., 1979). The basin-centre evaporite succession evolves laterally into siliciclastic and carbonate material of the Meaghers Grant (formerly Parleeville) Formation along the northern margin of that basin (McCutcheon, 1981).

Viséan rocks are not affected by phreatic calcification in the Cumberland Basin either. Undisturbed stromatolitic mounds of the Gays River Formation (Macumber Formation according to Plint and van de Poll, 1983) overlie basement regolith and are unconformably overlain by coarse red fanglomerate of the Bonaventure Formation at Quaco Head (Figs. 1 and 5, locality V), but a thick succession of Lower Windsor Group evaporites and Middle Windsor Group carbonates and siliciclastics is known to exist between these two units in other areas of the basin, although poorly exposed (McLeod and Johnson, 1999). At Hopewell Cape, Middle Windsor Group rocks of the Lime Kiln Brook Formation interdigitate with red conglomerates of the Bonaventure Formation (Figs. 1 and 5, locality U).

At Albright Brook west, below the Bonaventure Formation, a ~50 m wide channel of brachiopod-rich limestone and siliciclastic rocks of the Lime Kiln Brook Formation (Middle Windsor Group) cuts through a calcified Gays River Formation bank and the underlying basement rocks (Figs. 1 and 5, locality O). This observation constrains the phreatic calcification event to pre-Asbian times.

5. The calcified banks of the Gays River Formation in the Marysville Basin

Only 7 km separate a non-calcified bank of the Gays River Formation at Hampstead from a partially calcified bank at Albright Brook (Figs. 1 and 5, localities N–P), which encroaches steep basement highs. On outcrop, the bank at Hampstead is crudely bedded, whereas the calcified bank at Albright Brook is massive. On thin-sections, the bank at Hampstead is characterized by a peloidal texture with flat-lying

brachiopod shells, whereas such textures are only preserved in small pockets (0–20% of the rock volume) in the calcified bank at Albright Brook, which is mainly characterized by globular bodies of calcite ranging from micrite to macrospar, and representing several generations of recrystallization. In the calcified bank, brachiopod shells and other fossil remains are not flat-lying, but randomly oriented.

In the Stewarton section (13 km to the east of Albright Brook) and further east within large floats near Snider Mountain (Figs. 1 and 5, localities Q and R), phreatic calcification is complete and no clasts are preserved, except at the very base of the Stewarton profile, where it can be inferred that the host material for the calcite was a regolith developed in the basaltic basement rocks. Although it is possible that bank material was overlying the regolith prior to the calcification event, the host sediment is here assumed to be basement regolith.

6. Stable isotope data

Within the Viséan successions of eastern Canada, carbonate samples that were identified as marine limestone, phreatic calcite hardpan or pedogenic calcite hardpan through outcrop and thin-section analyses are compared in terms of their stable isotope compositions (δC^{13} VPDB and δO^{18} VPDB) (Fig. 6). A total of 46 phreatic calcite hardpan samples, 21 marine carbonate samples (*in situ* Carboniferous limestone except for the four samples at locality B, which are Siluro-Devonian limestone clasts within calcified Carboniferous conglomerate of the La Coulée Formation) and five pedogenic calcite samples were analyzed by dual inlet mass spectrometry at the GEOTOP (Université du Québec à Montréal, Canada) using a GV Instruments Multicarb preparation system connected to an Isoprime Dual Inlet mass spectrometer.

As can be observed in Fig. 6A, the marine carbonate and phreatic calcite hardpan samples are mainly distinguished by their δC^{13} VPDB values, which show very little overlap. They range from +4.05 to –1.53 in the marine carbonate samples, and from –1.00 to –5.52 in the phreatic calcite hardpan samples, which is altogether consistent with the range of values summarized by Brownlow (1996) for marine *versus* freshwater carbonate. However, the two types of carbonate do not overlap when δC^{13} VPDB and δO^{18} VPDB values are plotted together, as calcite samples with unusually high δC^{13} VPDB values tend to have unusually high δO^{18} VPDB values as well, which brings them away from the marine carbonate cluster, thus allowing ranges that bear

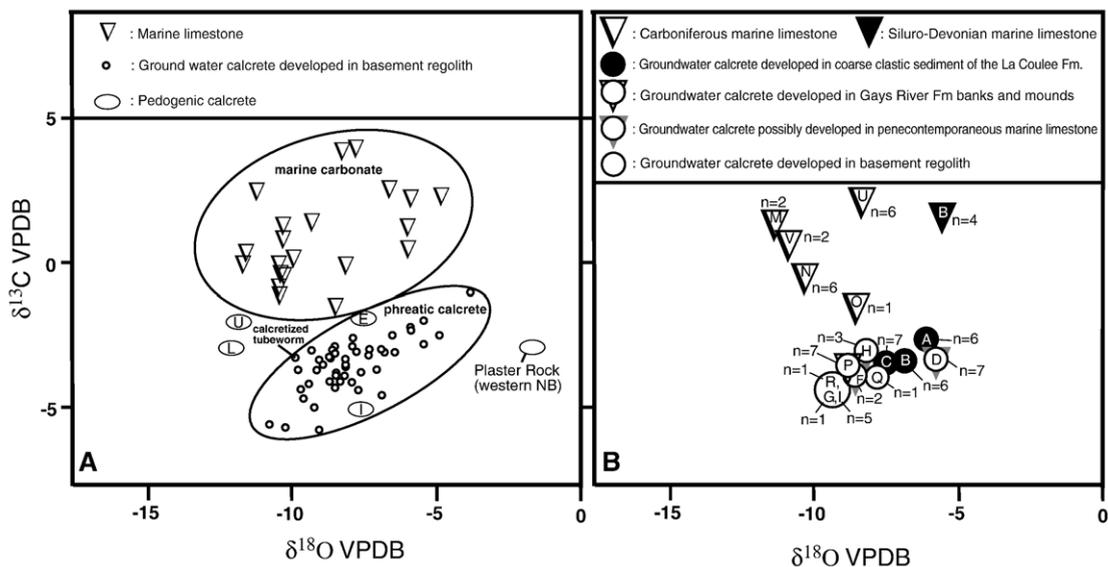


Fig. 6. A: stable isotopes of carbon and oxygen in individual samples of marine carbonate, phreatic calcrete hardpan and pedogenic calcrete hardpan. B: Nature of the marine carbonates or of the host sediment of phreatic calcrete hardpans, and average stable isotope values for various localities (refer to Figs. 1 and 5 for the localities). Data for B, C and D were previously published by Jutras et al. (1999), and for E by Jutras et al. (2006).

no overlap to be drawn (Fig. 6A). As was pointed out by Drever et al. (1987), high evaporation rates cause a concurrent increase of $\delta^{13}\text{C VPDB}$ and $\delta^{18}\text{O VPDB}$ values due to the higher volatility of lighter isotopes, which explains the sloping distribution of phreatic calcrete hardpan samples on the $\delta^{13}\text{C VPDB}$ – $\delta^{18}\text{O VPDB}$ variation diagram (Fig. 6A).

There are no obvious differences in the stable isotope composition of the studied phreatic calcrete hardpans that can be attributed to the nature of the host sediment (Fig. 6B). The calcretized marine limestones at localities D, F (assumed from indirect evidence) and T (determined by the presence of remnant fossils) have values that closely resemble those of phreatic calcrete hardpans that were rather developed in penecontemporaneous conglomerate (localities A, B and C) or basement regolith (localities G–I, V, W) (Fig. 6B). A tubeworm fossil (a typical occurrence in the Gays River Formation mounds according to von Bitter et al., 1990, 1992) from the calcretized limestone of the Albright Brook east section (locality T) was also analyzed and shows stable isotope values that plot in a marginal area of the phreatic calcrete hardpan cluster, but still quite far from the cluster of marine carbonates (Fig. 6B), suggesting thorough recrystallization by fresh groundwaters. Moreover, two of the samples from Albright Brook (Figs. 1 and 5, locality T) were taken from pockets of material in which the original peloidal texture of the bank is preserved, but these

samples show similar stable isotope values as the rest of the calcretized bank, suggesting thorough recrystallization by fresh groundwater in this material as well.

Pedogenic calcretes show a much less focused distribution of stable isotope values (Fig. 6A), perhaps due to a more direct influence of the immediate vegetation cover in the vadose zone than in the phreatic zone. Separate patches of varying plant assemblages will bear differently on the isotopic signature of the surrounding and underlying vadose water, whereas water composition would tend to be more homogenized below the water table. However, none of our pedogenic calcrete samples overlap with marine carbonates in terms of their $\delta^{13}\text{C VPDB}$ values (Fig. 6A), including the sample from the Shin Creek locality (Fig. 5, locality L; inset), which was formally referred to as the Gelder Limestone by van de Poll (1967), but identified as a pedogenic calcrete by McCutcheon (1981).

7. Discussion

Correlations across the 20 studied sections provide new constraints concerning the tectonostratigraphic and diagenetic history of Viséan rocks in eastern Quebec, western New Brunswick and Prince Edward Island. Recrystallization of the Chadian to Holkerian Gays River Formation limestone by groundwaters at the Albright Brook localities is indicated by field, thin-

section and stable isotope analyses, suggesting that the La Coulée Calcrete is younger than the basal carbonates of the Lower Windsor Group. The disconformable contact between the calcretized bank and the overlying Lime Kiln Brook Formation (Asbian) indicates that phreatic calcretization preceded deposition of the Middle Windsor Group and therefore occurred at the same time as the deposition of the Lower Windsor Group evaporites. The latter observation supports the hypothesis of Jutras et al. (2001) that the paleoshore platform on which the La Coulée Calcrete is sitting at Saint-Elzéar (Fig. 1, locality D; Jutras and Schroeder, 1999) was carved by the first transgression of the Windsor Sea (Fig. 7). However, the north-westernmost occurrences of sedimentary rocks associated with this transgression were intercepted in the Killarney Oil and Gas #3 Borehole (Figs. 1 and 5, locality K) within the limits of the Marysville Basin of southern New Brunswick, 250 km away from Saint-Elzéar. It is postulated that this rapid transgression was accommodated by transtension along the same NW-trending paleostress regime that is found to have controlled underlying Tournaisian rocks of the Horton Group (Wilson and White, 2006) and overlying rocks of the Percé Group (Jutras and Prichonnet, 2005), although the detail of fault activities remains highly speculative at this stage (Fig. 9).

Abundant inputs of clastic and ligneous material into the marine succession at Irving Brook (Figs. 1 and 5, locality M) suggests a deltaic environment and the nearby presence of a sub-aerial source area. Although no paleocurrent data could be obtained from the Irving Brook section, it is postulated that the nearby Mascarene Uplift, which separates the Marysville and Moncton basins (Fig. 1), was already in existence at that time, providing terrigenous material to the marine basin (Fig. 9). Moreover, McCutcheon (1981) notes that the clastic material of the Parleeville (now Meaghers Grant) Formation is restricted to the northern margin of the Moncton Basin, on the southern side of the Mascarene Uplift (Fig. 9). However, marine beds of the Lower Windsor Group overlap the eastern extension of the fault convergence that limits the Mascarene Uplift in the area of Samp Hill (Fig. 1), suggesting that the Marysville and Moncton basins were only separated by a small wedge of source area (Fig. 9). A shallow marine facies is inferred for the Lower Windsor Group carbonates in the Cumberland Basin of southern New Brunswick, but with no significant input of clastic material (McCutcheon, 1981; Plint and van de Poll, 1983), suggesting that the Caledonia Highlands were no more than a large shoal at the time of deposition (Fig. 9).

7.1. Phreatic calcretization around evaporitic basins during deposition of the Lower Windsor Group and the La Coulée Formation (Fig. 8)

7.1.1. The Ristigouche and Cannes-de-Roches basins

In the Percé and Cannes-de-Roches areas of eastern Quebec (Fig. 1, localities A–C), fault-controlled fanglomerates were being deposited at the margin of evaporitic basins and were being simultaneously calcretized by saturated groundwaters (Jutras et al., 1999). Based on the geometry of the fault-controlled source areas of the La Coulée Formation and on syn-sedimentary structural data from the rest of the Percé Group, Jutras and Prichonnet (2005) concluded that this time-slice was affected by NW compression (Fig. 8).

7.1.2. The Central Basin

Phreatic calcretization of regolith below the Bonaventure Formation in the Sevogle and Blackville areas (Fig. 1, localities H and I) suggests the former presence of an evaporitic basin to the east (Fig. 8) (Jutras et al., submitted for publication).

7.1.3. The Marysville Basin

Below the Bonaventure Formation, along the southern margin of the Marysville Basin, we observe a west-to-east lateral evolution from non-calcretized marine limestone at Irving Brook and Hampstead (Figs. 1 and 4, localities M and N), to partially calcretized limestone at Albright Brook (Figs. 1 and 4, localities O and P), and to thoroughly calcretized regolith near Stewarton and Snider Mountain (Figs. 1 and 4, localities Q and R), suggesting the presence of an evaporitic basin to the east or to the northeast (Fig. 8). This is supported by well data in Prince Edward Island (Figs. 1 and 4, locality T), in which Lower Windsor Group evaporites are represented. It is postulated that this evaporitic basin is the same as the one responsible for phreatic calcretization in the Sevogle and Blackville areas (Figs. 1 and 4, localities H and I).

Above the basal Gays River Formation mound, the overall paucity of marine fauna in the carbonate rocks of the Meaghers Grant Formation at Irving Brook (Figs. 1 and 4, locality M) and the notable absence or rarity of brachiopods, which dominate most of the Windsor Group fauna (Moore and Ryan, 1976), suggest high salinity conditions at the time of deposition. For this reason, and because of the observed lateral variation between Lower Windsor Group calcareous clastics and evaporites in the Moncton Basin (McCutcheon, 1981), it is postulated that deposition of the Meaghers Grant Formation was in part coeval with evaporitic deposition

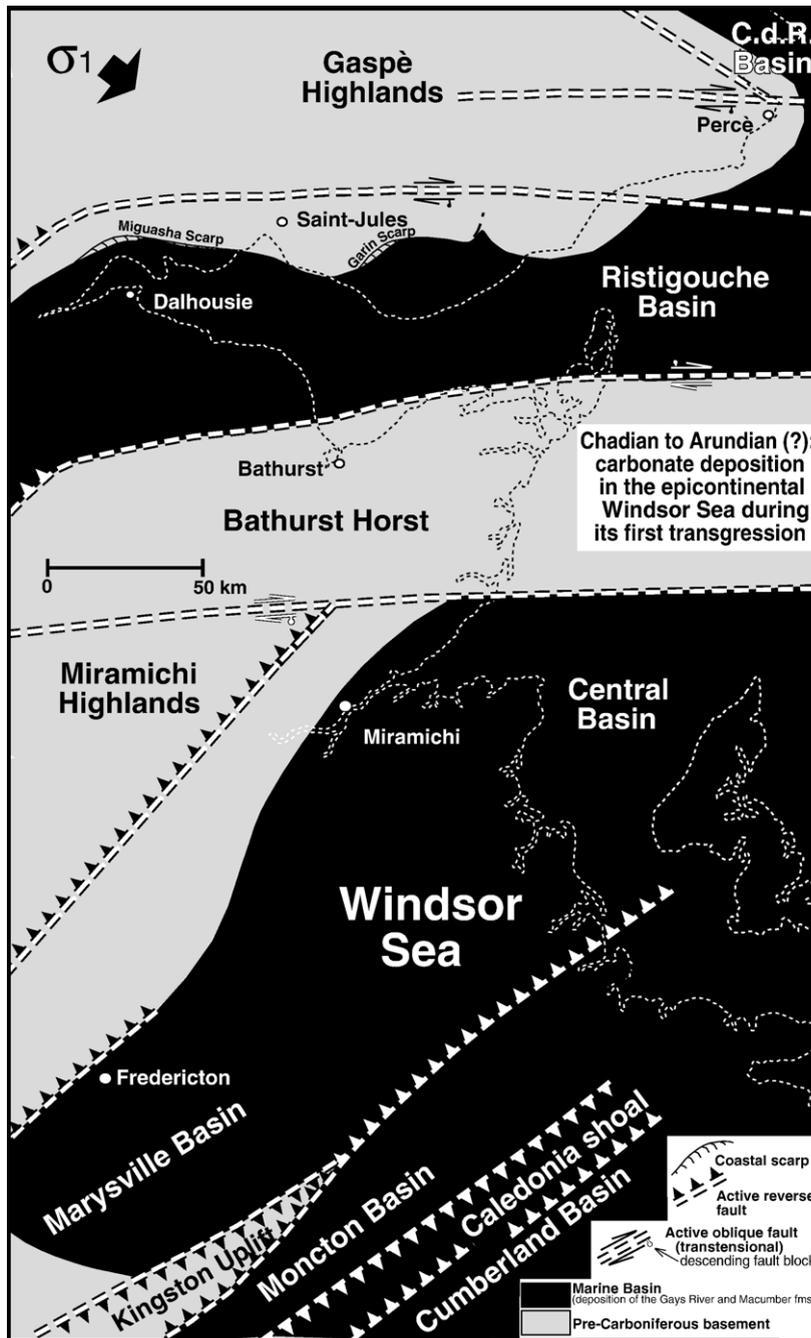


Fig. 7. Hypothetical paleogeography and tectonic context of the Windsor Sea in the study area during Chadian to Arundian (?) times.

in the Marysville Basin (Fig. 8). The Meaghers Grant was probably deposited in deltaic areas of the marine basin that were well fed by fluvial inputs, while brines were sufficiently concentrating in the rest of the basin for evaporitic deposition to occur (Fig. 8). A similar scenario was proposed for the Lower Windsor Group in central Nova Scotia (Jutras et al., 2006).

We therefore postulate that, while evaporitic deposition was occurring to the east and northeast, the Albright Brook, Stewarton and Snider Mountain localities (Figs. 1 and 4, localities O–R) were sub-aerially exposed and affected by phreatic calcretization in the mixing zone between fresh groundwater issued from the Mascarene Uplift and saline groundwater surrounding the evaporitic

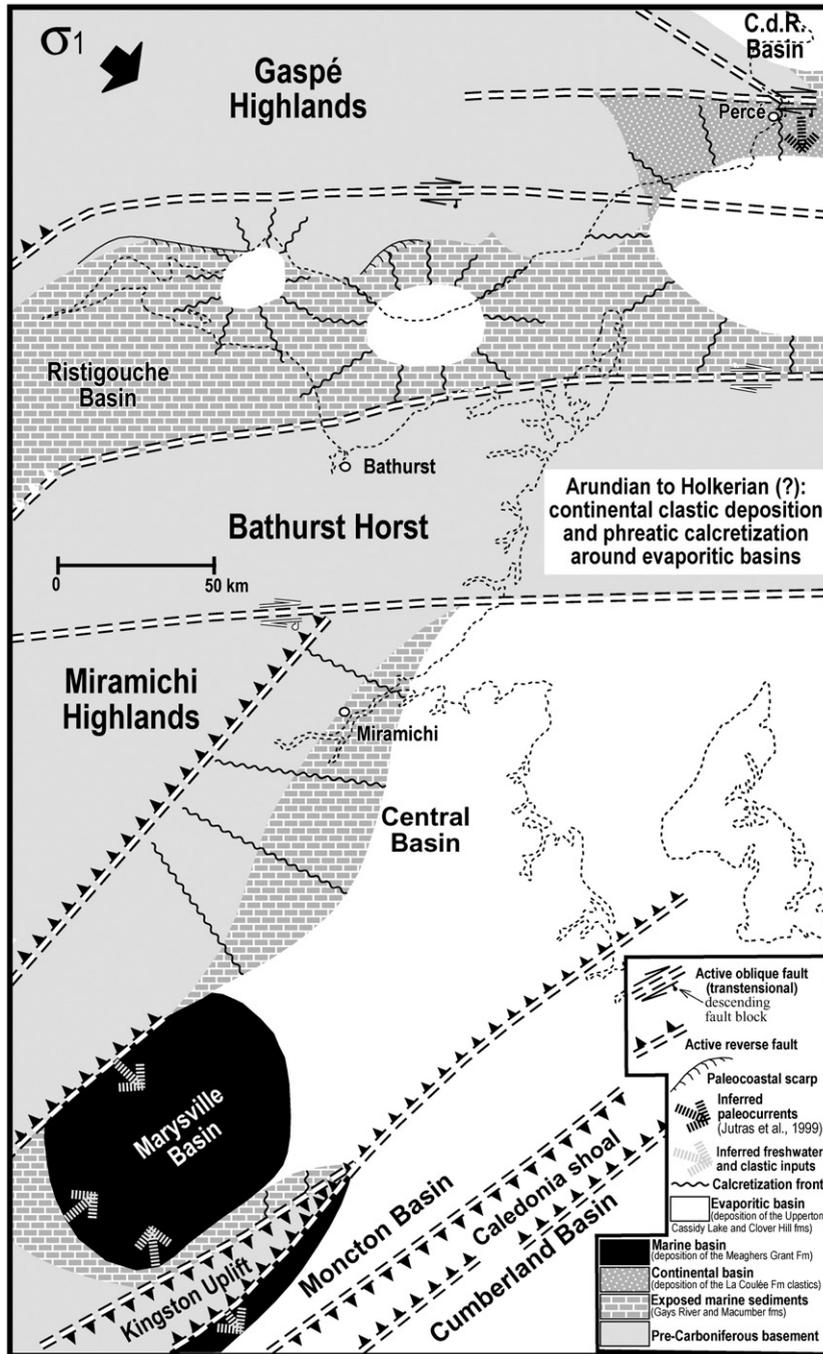


Fig. 8. Hypothetical paleogeography and tectonic context of the La Coulée, Meaghers Grant, Upperton, Cassidy Lake and Clover Hill formations during Arundian to Holkerian (?) times.

basin (Fig. 8). During the same time period, the Hampstead locality (Figs. 1 and 4, locality N) was also sub-aerially exposed, but far enough from the evaporitic basin to avoid phreatic calcretization, whereas the Killarney and Irving Brook localities were still experiencing marine deposition, deeper into the basin (Fig. 8).

7.1.4. The Moncton Basin

In contrast with the Marysville Basin, the presence of Lower Windsor Group evaporites is well documented in the Moncton Basin (McCutcheon (1981)). Prior to the Asbian, this basin was undergoing evaporitic deposition away from the Mascarene Uplift, where

McCutcheon (1981) infers a north-to-south lateral transition from the Parleeville (now Meaghers Grant) Formation to the Upperton Formation. It is interpreted that the upward transition from Macumber Formation

limestone to Upperton Formation anhydrite and Cassidy Hill Formation halite (Fig. 4, locality S) reflects the gradual concentration of brines in a restricted marine basin.

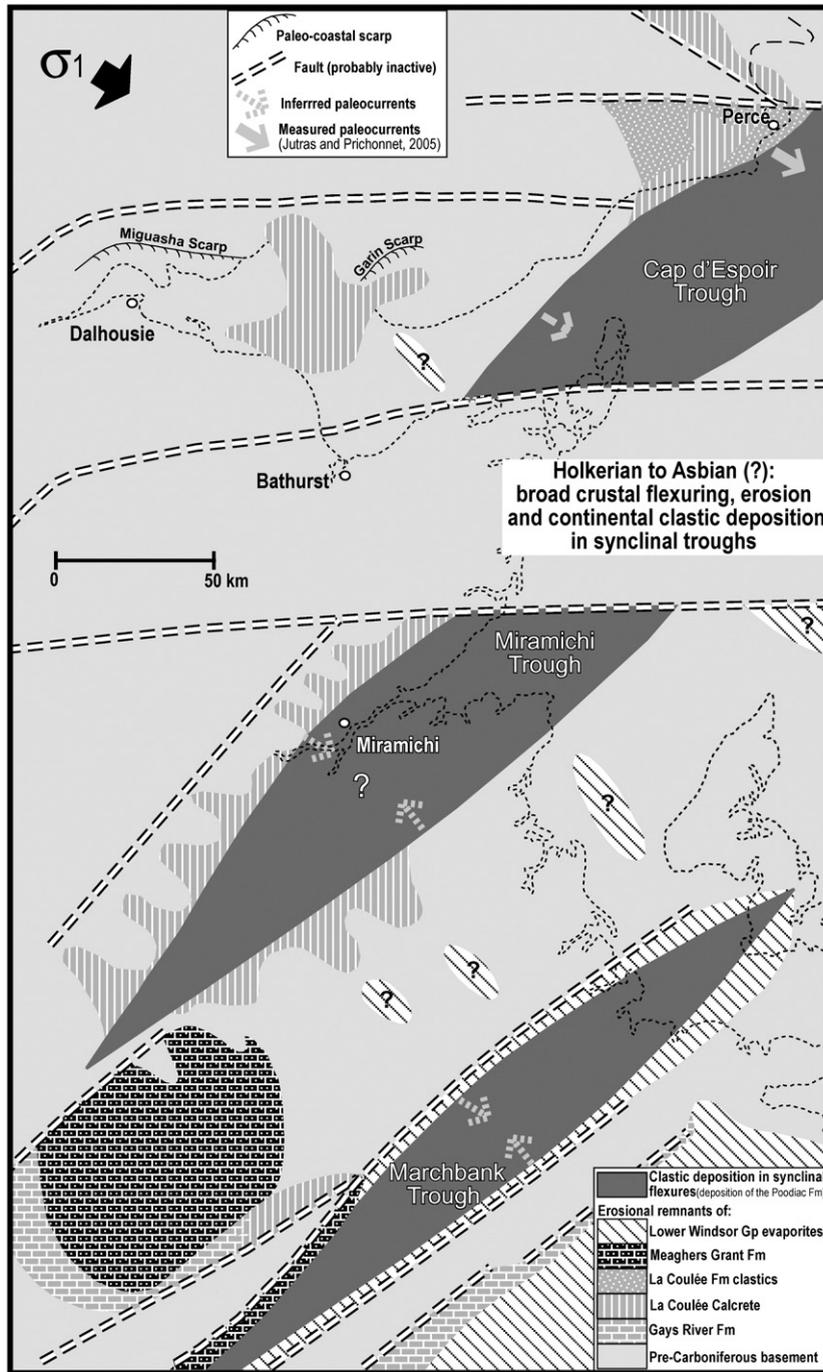


Fig. 9. Pre-Bonaventure erosion of basin margins and associated deposition of the Poodiac Formation in broad synclinal troughs in Holkerian to Asbian (?) time.

7.1.5. The Cumberland Basin

The concentration of salt in the centre of the Moncton Basin (McCutcheon, 1981) suggests that the Caledonian shoal still separated the latter from the Cumberland Basin, although this topographic high was never prominent enough to act as a source area during Lower Windsor Group deposition (McCutcheon, 1981).

7.2. Partial erosion of the phreatic calcrete hardpans and contemporaneous evaporites (Fig. 9)

As in the Cannes-de-Roches, Ristigouche and Central basins (Jutras et al., 1999, 2001, submitted for publication; Jutras and Prichonnet, 2002, 2004, 2005), a period of broad uplift and erosion occurred between the phreatic calcretization event and deposition of the Bonaventure Formation in the Marysville Basin (Fig. 9). This erosional event potentially eradicated phreatic calcretes or Lower Windsor Group marine beds from the Mactaquac and Shin Creek areas (Figs. 1 and 4, localities J and L), although non-deposition is also a possibility in each case. Along the eastern part of the southern margin of the Marysville Basin, this erosion event is indicated by the paraconformable to unconformable contact between the phreatic calcrete hardpan (including the calcretized bank at Albright Brook) and the overlying Bonaventure Formation fanglomerates (Figs. 1 and 4, localities O–Q). The Marysville and Cumberland basins may have experienced basin inversion and sourced the Poodiac Formation in the Moncton Basin during this time frame (Fig. 9). This unit is characterized by a monotonous succession of fine red beds that were more likely sourced from broad uplifts than from sharp fault scarps. Anderle et al. (1979) noted that the Poodiac Formation thickens along the Marchbank syncline in the Moncton Basin, which may represent the original depocentre of this unit in southern New Brunswick (Marchbank Trough in Fig. 9). Deposition along broad crustal flexures is also inferred for this unit in the Percé area (Cap d'Espoir Trough) of eastern Quebec (Jutras and Prichonnet, 2005) and the Miramichi City area (Miramichi Trough) of central New Brunswick (Jutras et al., submitted for publication).

This period of uplift and erosion is probably responsible for the erosion of much of the Lower Windsor Group evaporites, which may be now mainly preserved below broad trough-fills of Poodiac Formation clastic rocks, such as in the Moncton Basin area (Fig. 9). The more dolomitic or sulphatic transitional compositions that are observed between pure phreatic calcretes and evaporites in Australia (Arakel and McConchie, 1982) may also have been formerly

present in eastern Canada, but eroded during this event. Finally, the disconformable contact between the calcretized banks of the Gays River Formation and the grey marine beds of the Lime Kiln Brook Formation at Albright Brook west (Figs. 1 and 5, locality O), below red beds of the Bonaventure Formation, suffices to conclude that the pre-Bonaventure Formation erosion event that is observed throughout the Cannes-de-Roches, Ristigouche, Central and Marysville basins occurred prior to the onset of Middle Windsor Group sedimentation.

8. Conclusion

Large tectonostratigraphic reconstructions in eastern Canada allow to better constrain the paleogeographic, paleoenvironmental and diagenetic settings of the thick Mississippian phreatic calcrete hardpans that are found in that area, which are mainly limited to erosional remnants unconformably below red beds of the Bonaventure Formation. Evidence for the recrystallization of Lower Windsor Group limestone by saturated groundwater indicates that the phreatic calcretization event is no older than Chadian to Holkerian, and the disconformable contact between this calcretized limestone and the grey marine beds of the Lime Kiln Brook Formation (Middle Windsor Group) in the Marysville Basin suggests that it is pre-Asbian. The phreatic calcrete hardpans therefore correlate with a long-lasting event of extensive evaporitic deposition that occurred throughout the Maritimes Basin in Chadian to Holkerian times, thus confirming that the genetic connection between thick and massive phreatic calcrete hardpans and evaporitic basins that was suggested by Arakel and McConchie (1982) for modern analogs in central Australia applies to ancient environments as well, although the link may be obscured by subsequent events of deformation and erosion in ancient cases. This has considerable implications regarding the petroleum potential of relatively unexplored areas, such as Chaleur Bay, which was never drilled, but which must have at least formerly included large evaporite deposits to justify the presence of Mississippian occurrences of such calcretes along its northern shore (Jutras et al., 1999, 2001; Jutras and Prichonnet, 2002).

Although phreatic calcretization can occur in non-evaporitic settings (Tandon and Narayan, 1981; Sassi et al., 1984; Maizels, 1987; Lang et al., 1990; Kaemmerer and Revel, 1991; Purvis and Wright, 1991; Tandon and Gibling, 1997; Khadkikar et al., 1998, 2000; Nash and Smith, 1998, 2003; Nash and

McLaren, 2003), the presence of a long-lasting evaporitic basin seems to be required for the development of thick and massive phreatic calcrete hardpans, which result from the thorough mineral replacement of all or most of the original host material. To date, such extreme cases of phreatic calcretization have only been observed in Quaternary sediments of central Australia (Butt et al., 1977; Mann and Horwitz, 1979; Arakel and McConchie, 1982; Jacobson et al., 1988; Arakel et al., 1989) and in Carboniferous sediments of eastern Canada (Jutras et al., 1999, 2001; Jutras and Prichonnet, 2002; this study), although dolomitic equivalents that are similarly associated to the vicinity of evaporitic basins are also known (Khalaf, 1990; El-Sayed et al., 1991; Spötl and Wright, 1992; Colson and Cojan, 1996).

Stable isotopes of carbon and oxygen prove to be very useful in differentiating ancient phreatic calcrete hardpans from ancient marine carbonates, but not for differentiating them from pedogenic calcretes. The small degree of overlap in δC^{13} VPDB values between phreatic calcretes and marine carbonates is compensated by the tendency for calcretes with high δC^{13} VPDB values to also have unusually high δO^{18} VPDB values, higher than those of marine carbonates. However, it should be pointed out that a wider database of stable isotope values for both ancient phreatic calcretes and ancient marine carbonates would be needed to produce realistic ranges for both types of carbonate on δC^{13} – δO^{18} variation diagrams.

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