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Dolostone units of the Beekmantown Group in the Montreal area, Quebec: diagenesis and constraints on timing of hydrocarbon activities[1]

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Abstract: The dolostone units of the Beekmantown Group in the Montreal area contain multiple generations of dolomite. Early replacement dolomite was followed by late replacement dolomite, pore-filling dolomite, pore-filling quartz, and pore-filling calcite. Homogenization temperatures of aqueous fluid inclusions increased from late replacement dolomite (110–118°C) and early pore-filling dolomite (98–101°C) to late pore-filling dolomite (158–169°C), and then decreased during precipitation of quartz (101–142°C) and calcite (121–135°C). The fluids show very high salinities (17–32 wt.% NaCl equivalent). Solid bitumen coats open pores, postdates late replacement and/or early pore-filling dolomite, and predates late pore-filling dolomite and quartz. Methane inclusions are entrapped in the quartz cement. It is suggested that the dolostone units of the Beekmantown Group may have been charged with liquid hydrocarbons before maximum burial, which were then transformed to gaseous products by overheating with increasing burial. The dolostone units were porous and could have been reservoirs for gaseous hydrocarbons until some time after the maximum burial, when much of the porosity was occluded by calcite cement.

Résumé : Les dolomies du Groupe de Beekmantown dans la région de Montréal renferment de multiples générations de dolomite. À de la dolomite de remplacement précoce, succèdent de la dolomite de remplacement tardive, des dolomites de remplissage de porosité précoce et tardive, du quartz de remplissage de porosité et, enfin, de la calcite de remplissage de porosité. Les températures d'homogénéisation des inclusions fluides aqueuses augmentent en passant de la dolomite de remplacement tardive (110-118 °C) et de la dolomite de remplissage de porosité précoce (98-101 °C) à la dolomite de remplissage de porosité tardive (158-169 °C), pour diminuer par la suite lors de la précipitation du quartz (101-142 °C) et de la calcite (121-135 °C). Les fluides sont caractérisés par des salinités élevées (17-32 % éq. poids NaCl). Du bitume recouvre les parois des pores ouverts et est postérieur à la dolomite de remplacement tardive ou à la dolomite de remplissage de porosité précoce, mais antérieur à la dolomite de remplissage de porosité tardive et au quartz. Des inclusions à méthane sont serties dans le ciment de quartz. Il est suggéré que les dolomies du Groupe de Beekmantown étaient chargées d'hydrocarbures liquides avant l'enfouissement maximal, mais que ceux-ci ont été transformés en gaz lors de la surchauffe associée à l'augmentation de la profondeur d'enfouissement. Les dolomies étaient poreuses et ont pu agir comme réservoirs de gaz naturel pendant un certain temps après l'enfouissement maximal, jusqu'à ce que la majeure partie de la porosité ait été colmatée par le ciment de calcite.

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[1] Contribution to the Appalachian Foreland and St. Lawrence Platform Architectures in Quebec, New Brunswick and Newfoundland NATMAP Project

INTRODUCTION

The dolostone units of the Lower Ordovician Beekmantown Group host a number of occurrences of natural gas and base-metal mineralization in southern Quebec. Because major hydrocarbon and base-metal accumulations have been discovered in stratigraphic equivalents elsewhere along the eastern margin of the Laurentian continental margin, the Beekmantown Group in southern Quebec has attracted the attention of the industry and many researchers. Of particular interest is the reservoir quality of the dolostone, and the timing of hydrocarbon migration. Dykstra and Longman (1995) demonstrated that much of the porosity in the dolostone units of the Beekmantown Group was filled by late-stage calcite cement, but significant porosity was preserved when early and continuous entrapment of hydrocarbons, as indicated by hydrocarbon coatings of pores, prevented later cementation. The nature of the hydrocarbons that filled the pores, and the ages of hydrocarbon migration and late-stage calcite cementation events, which are important in assessing the reservoir quality of the dolostone units, remain unclear. In this paper we use fluid inclusions entrapped in diagenetic phases to address these problems. Similar studies have been carried out in other parts of the Paleozoic Laurentian continental margin of eastern Canada (Chi et al., 1999). The observations reported in this paper are preliminary, and further investigations are ongoing.

The present study constitutes a part of a GSC NATMAP project which consists of five major transects from the St. Lawrence platform to the Appalachian orogen, one of which is from Montreal to Mégantic. The study area of this paper belongs to this transect.

GEOLOGICAL SETTING

The stratigraphy of the St. Lawrence platform in the Montreal area comprises, from bottom to top, the Potsdam, Beekmantown, Chazy, Black River, Trenton, and post-Trenton strata (Utica, Sainte Rosalie, Lorraine, and Queenston groups) (Fig. 1), ranging in age from latest Proterozoic to latest Ordovician. The Potsdam Group and the lower part of the Beekmantown Group (the Theresa Formation) are composed of subaerial to shallow marine siliciclastic sediments. The Beekmantown, Chazy, Black River, and Trenton groups are composed predominantly of shallow-marine carbonate strata. The Utica, Sainte Rosalie, and Lorraine groups are composed of deep marine siliciclastic and flyschoid sediments, and the Queenston Group consists of terrestrial sediments (Globensky, 1987). The deposition of the Potsdam and Beekmantown groups took place in a tectonic environment of passive continental margin. The transition from passive margin to convergent margin, as indicated by arc volcanism recorded in the Dunnage Zone, probably took place during

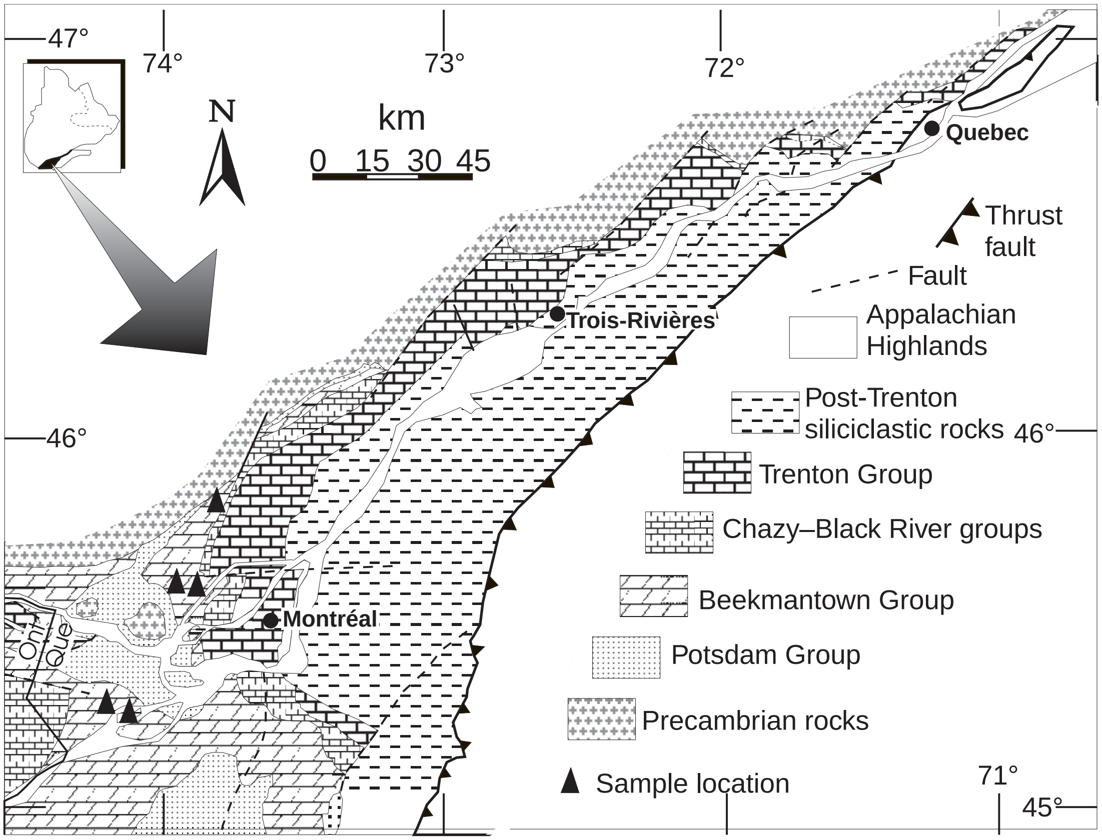

Figure 1. *Geological map of the St. Lawrence platform in southwestern Quebec (*modified from *Globensky, 1987), with sample locations.*

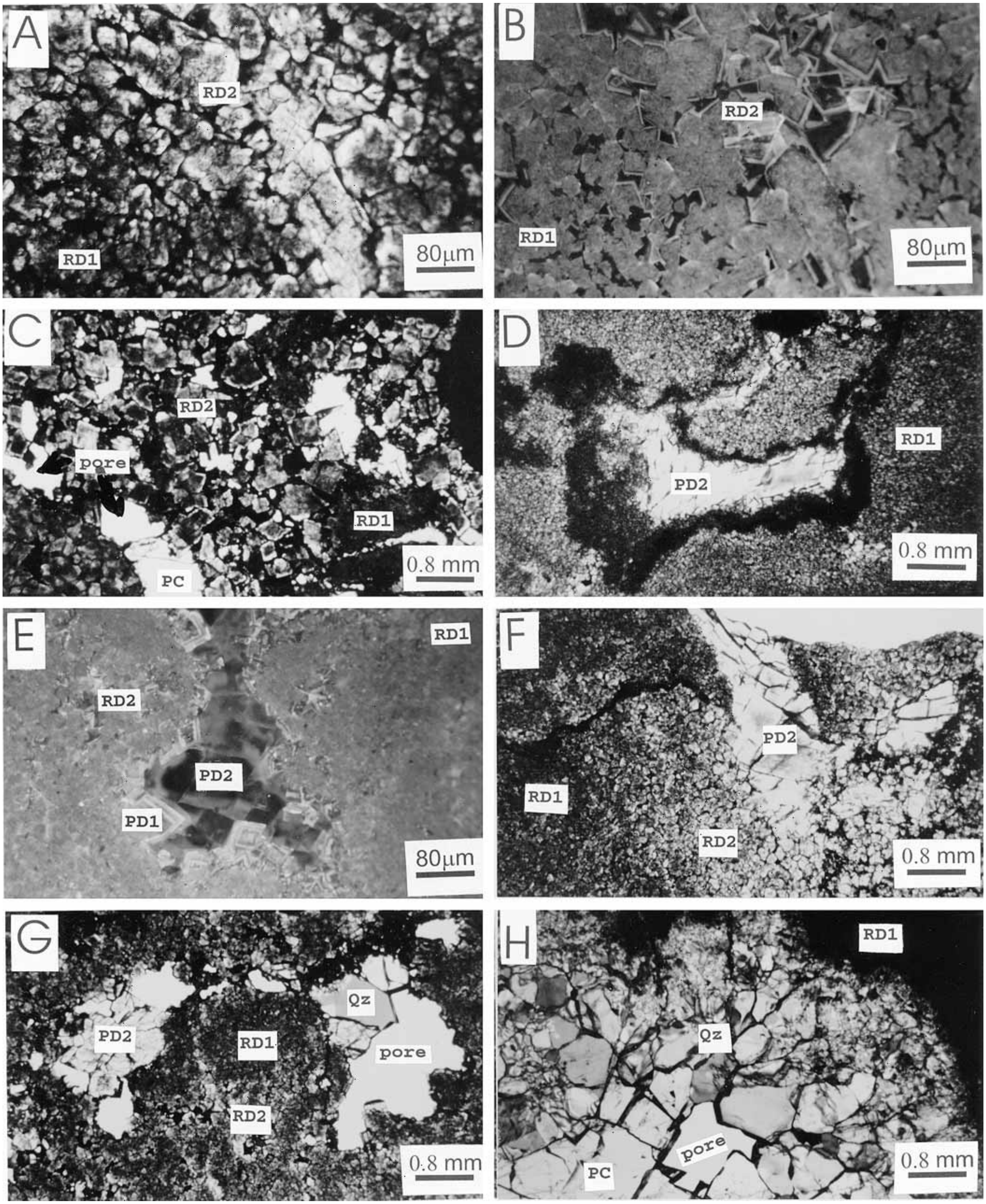

Figure 2. A) *Early replacement dolomite (RD1) and later replacement dolomite (RD2), the latter having an inclusion-rich core and a relatively inclusion-free rim.* ***B)*** *Same view as A; RD1 showing dull reddish-orange cathodoluminescence, and RD2 showing zoned dull alternating with relatively bright orange cathodoluminescence.* ***C)*** *Intercrystal and dissolution porosity associated with RD2; part of the porosity is filled by calcite (PC).* ***D)*** *Dissolution pores in RD1 surrounded by a finer grained halo.* ***E)*** *Early pore-filling dolomite (PD1) with zoned dull reddish-orange cathodoluminescence alternating with relatively bright orange cathodoluminescence, and late pore-filing dolomite (PD2) with very dull cathodoluminescence.* ***F)*** *A stylolite cuts RD2 and is cut by PD2.* ***G)*** *Quartz cement (Qz) coating pores with PD2.* ***H)*** *Quartz cement (Qz) predates pore-filling calcite (PC).*

Early to Middle Ordovician (Tremblay, 1992). This transition broadly corresponds to the end of the deposition of the Beekmantown Group, when a regional unconformity and/or disconformity was formed. This unconformity and/or disconformity is recorded along the whole Laurentian continental margin, from western Newfoundland (Knight et al., 1991) to southern United States (Mussman et al., 1988). It probably resulted from upward flexure or peripheral bulge accompanying the collapse of the shelf in relation to the onset of plate convergence. With continued plate subduction, some parts of the Laurentian continental margin (promontories) entered the stage of continent-island collision, whereas other parts of the continental margin (re-entrants) remained relatively unaffected. As a result, when the St. Lawrence Promontory was experiencing collision with accompanying formation of foreland-basin siliciclastic sediments (Middle–Upper Ordovician), the St. Lawrence platform in the Montreal area was still the site of shallow-marine carbonate sediments (Lavoie, 1994). As compression progressed, the St. Lawrence platform in the Montreal area experienced the transition from

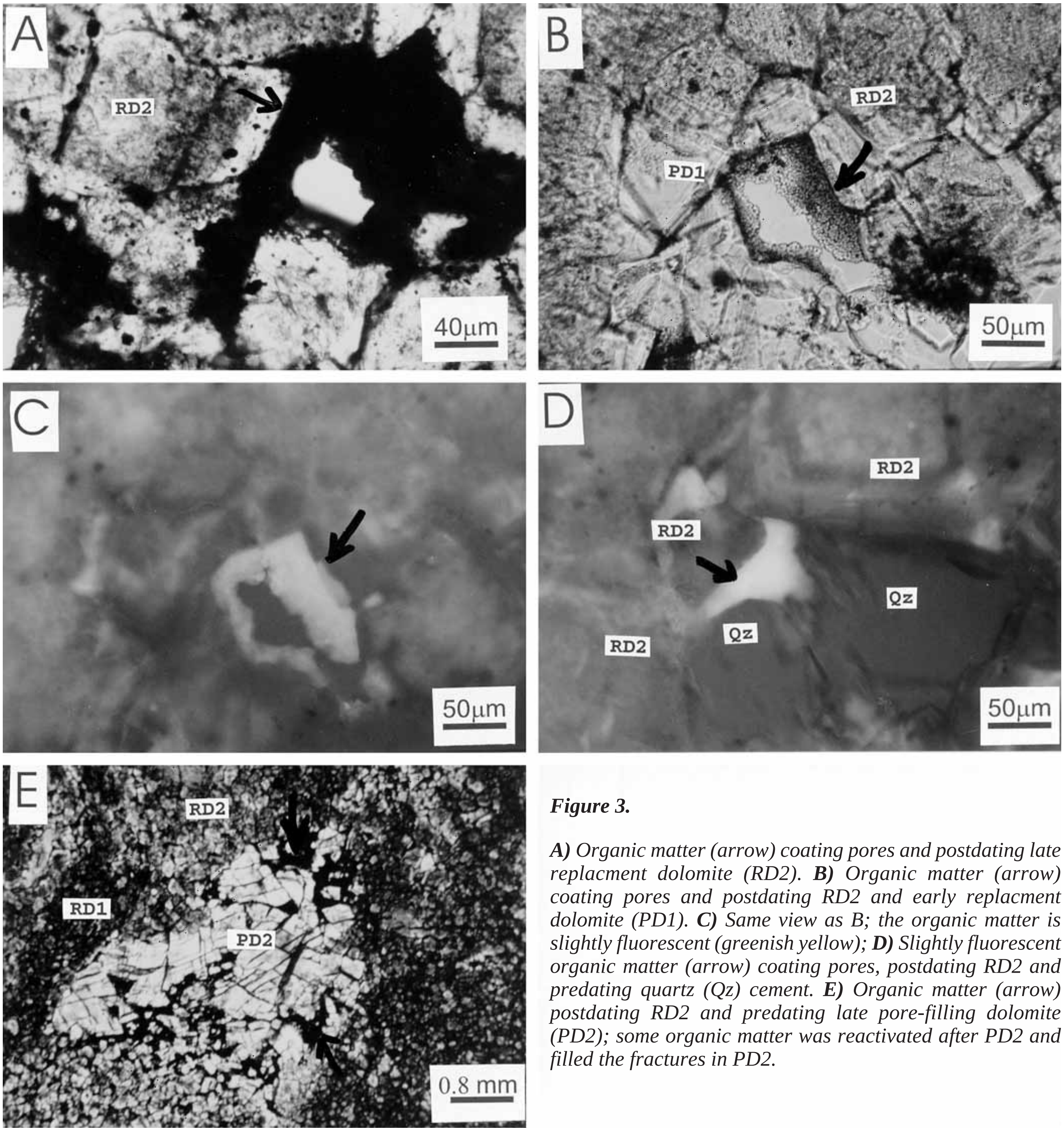

Figure 3.

A) *Organic matter (arrow) coating pores and postdating late replacment dolomite (RD2).* ***B)*** *Organic matter (arrow) coating pores and postdating RD2 and early replacment dolomite (PD1).* ***C)*** *Same view as B; the organic matter is slightly fluorescent (greenish yellow);* ***D)*** *Slightly fluorescent organic matter (arrow) coating pores, postdating RD2 and predating quartz (Qz) cement.* ***E)*** *Organic matter (arrow) postdating RD2 and predating late pore-filling dolomite (PD2); some organic matter was reactivated after PD2 and filled the fractures in PD2.*

shallow-marine carbonate to foreland-basin silisiclastic sedimentation (Utica, Sainte Rosalie, and Lorraine groups) in late Ordovician. During the Silurian the area was probably subject to erosion (Globensky, 1987). Additional sedimentation took place during the Devonian, as indicated by local occurrence of fragments of Devonian limestone breccia, but have been entirely eroded later (Globensky, 1987).

During the sedimentation of the Lower Ordovician shallow-marine carbonates (Beekmantown, Knox, and St. George groups), frequent sea-level fluctuations favored synsedimentary to early diagenetic dolomitization of the shallow-marine carbonates (Montanez and Read, 1992). Karst features related to the unconformity between the Beekmantown and Chazy groups were developed in many places along the eastern Laurentian continental margin, including the Quebec City area (Bertrand et al., 1995) and the Ottawa and Montreal areas (Dix et al., 1998). As the Beekmantown Group was buried to increasing depths, the dolostone units experienced various diagenetic processes, including further dolomitization, dissolution, and cementation. These features are studied in this paper.

PETROGRAPHY AND PARAGENESIS

Dolostone units from the Theresa Formation (two samples) and the Beauharnois Formation (18 samples) of the Beekmantown Group, collected from the Montreal area (Fig. 1), were studied using light microscopy, fluoroscopy, and cathodoluminoscopy. In all the samples studied, at least two generations of replacement dolomite can be distinguished, an earlier, relatively fine-grained, inclusion-rich, anhedral dolomite and a later, relatively coarse-grained, anhedral to euhedral dolomite that often has an inclusion-rich core and a relatively inclusion-free rim (Fig. 2A). The earlier-formed replacement dolomite shows uniform, dull reddish-orange cathodoluminescence, whereas the later replacement dolomite shows either uniform dull reddish-orange or zoned dull orange alternating with relatively bright orange cathodoluminescence (Fig. 2B). The cathodoluminescence zonation of the latter dolomite appears to be better developed where intercrystal spaces are filled by organic matter. Significant intercrystal and dissolution porosity was created during the formation of the later replacement dolomite (Fig. 2C, G). In most cases, dissolution is accompanied by the formation of the later replacment dolomite which is coarser than the earlier replacement dolomite (Fig. 2C, G). In one sample, however, dissolution pores are surrounded by a finer grained halo (Fig. 2D). We suspect that this dissolution feature is related to the karstification events after the deposition of the Beauharnois Formation. The various dissolution pores are filled, to different extents, by dolomite, quartz, calcite, and occasionally anhedrite and/or gypsum. Two different pore-filling dolomite types can be distinguished, an earlier, relatively fine-grained, euhedral dolomite and a later, coarse-grained, anhedral dolomite. The earlier pore-filling dolomite shows zoned dull reddish-orange cathodoluminescence alternating with relatively bright orange cathodoluminescence, and the later pore-filling dolomite shows very dull cathodoluminescence (Fig. 2E). The later-formed pore-filling dolomite commonly shows undulatory extinction. Stylolites cut both replacement dolomite types, but are truncated by the later pore-filling dolomite (Fig. 2F). Quartz cement is contemporaneous with or slightly later than the later pore-filling dolomite (Fig. 2G), and is earlier than pore-filling calcite (Fig. 2H). Anhydrite and/or gypsum is contemporaneous with or slightly earlier than pore-filling calcite.

It is frequently observed that brownish organic matter, presumably solid bitumen, coats open pores. The emplacement of the solid bitumen postdates late replacement dolomite (Fig. 3A) and early pore-filling dolomite (Fig. 3B, C), but predates quartz (Fig. 3D). The solid bitumen likely predates late pore-filling dolomite, but may have been reactivated after its precipitation (Fig. 3E). The solid bitumen is slightly fluorescent in some samples (greenish yellow) (Fig. 3C, D).

The paragenetic sequence (Fig. 4) can be summarized as follows. The carbonate minerals of the Beekmantown Group were dolomitized during and immediately after deposition, forming early replacment dolomite. The dolostone units were then exposed to the surface and underwent karstification, and some dissolution porosities may have been created. The dolostone units were then increasingly buried, and subject to further dolomitization (late replacment and early pore-filling events) and dissolution, with generation of pore space. Some of the secondary porosity was probably filled by liquid hydrocarbons, which were later altered to solid bitumen, and followed by precipitation of late pore-filling dolomite and quartz. The remaining secondary dissolution and fracturing porosities were filled by calcite.

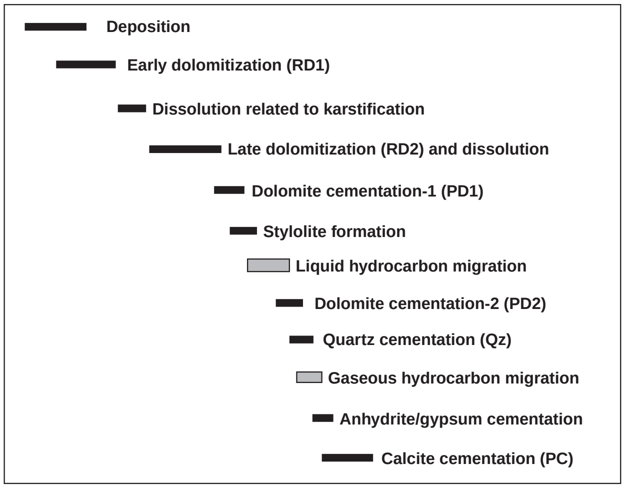

Figure 4. *Summary of paragenetic sequence.*

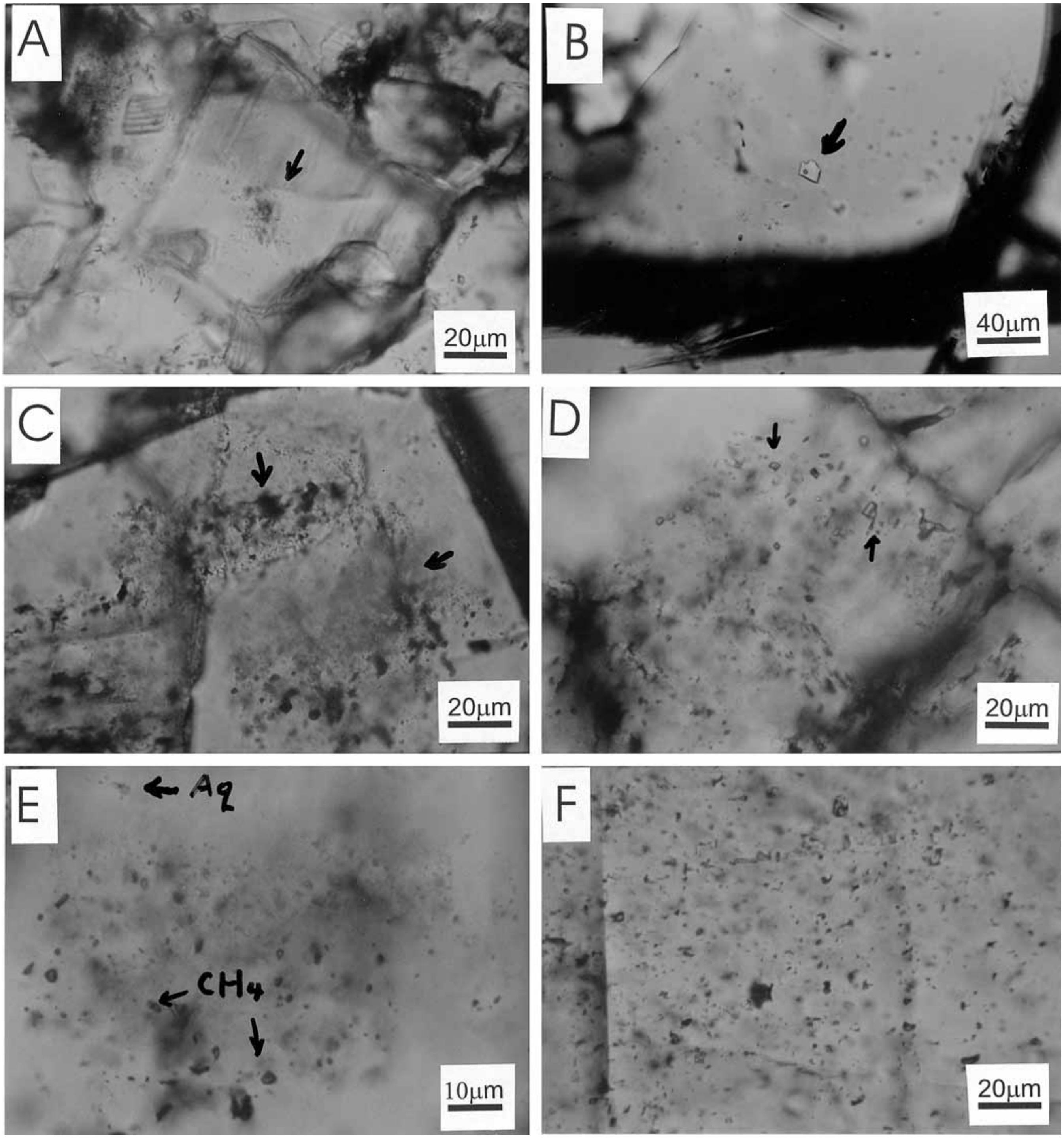

Figure 5. A) *Fluid inclusions in early pore-filling dolomite (PD1) occurring in cloudy cores (arrow) surrounded by a relatively clean rim.* ***B)*** *An isolated fluid inclusion (arrow) in quartz cement.* ***C)*** *Fluid inclusions distributed along growth zones (arrow) of quartz cement.* ***D)*** *Methane inclusions (arrow) in quartz cement.* ***E)*** *Methane (CH_4) and aqueous fluid inclusions (Aq) occurring in the same crystal of quartz, but apparently not belonging to the same group.* ***F)*** *Randomly distributed fluid inclusions in pore-filling calcite.*

Table 1. Preliminary microthermometric data of fluid inclusions.

Host mineral	$T_{m\text{-}ice}$ (°C)	Salinity (wt% NaCl equiv.)	T_h (°C)
RD2	-17.2 (n=1)	20.4 (n=1)	110.4 to 118.1 (n=3)
PD1	-30.6 to -33.7 (n=2)	25.8 to 26.7 (n=2)	97.6 to 100.7 (n=4)
PD2	-30.1 to -31.4 (n=2)	25.6 to 26.0 (n=2)	157.5 to 168.5 (n=9)
Qz	-27.4 to -37.4 (n=2)	24.7 to 27.6 (n=2)	101.3 to 141.8 (n=11)
		Methane inclusions:	-81.2 to -87.5 (n=14) (to liquid)
PC	-13.0 to -50.0 (n=7)	16.9 to 32.0 (n=7)	121.4 to 134.6 (n=17)

Notes:
RD2 = late replacement dolomite, PD1 = early pore-filling dolomite, PD2 = late pore-filling dolomite, Qz = quartz, PC = pore-filling calcite.
$T_{m\text{-}ice}$ = final ice-melting temperature; T_h = homogenization temperature.

FLUID INCLUSIONS

Fluid inclusions were examined in late replacment dolomite, early pore-filling dolomite, late pore-filling dolomite, quartz, and pore-filling calcite. The primary purpose of studying the fluid inclusions is to seek records of hydrocarbon activities and to estimate the T-P conditions and timing of these events.

Fluid inclusions in late replacement and early pore-filling dolomite occur in cloudy cores surrounded by a relatively clean rim (Fig. 5A). Fluid inclusions in late pore-filling dolomite are densely and randomly distributed in three dimensions, and are usually limited by relatively clean, irregular rim. The quartz cement contains many workable fluid inclusions, some of which are well isolated (Fig. 5B) or distributed along growth zones (Fig. 5C), and are considered as primary fluid inclusions. The calcite cement contains workable fluid inclusions which are isolated or randomly distributed (Fig. 5F).

All the samples were examined under UV fluoroscope. No fluorescent liquid hydrocarbon inclusions were found. Abundant methane inclusions were found in the quartz cement (Fig. 5C, D, E). Aqueous fluid inclusions were found in the same quartz crystals that contain methane inclusions (Fig. 5E), but there is no concrete evidence that indicates contemporaneous entrapment of methane and aqueous fluid inclusions. No methane inclusions have been found in the calcite cement.

Preliminary microthermometric data obtained from late replacment dolomite, early pore-filling dolomite, late pore-filling dolomite, quartz, and pore-filling calcite are summarized in Table 1. Although no data have been obtained from early replacement dolomite and earlier events, it appears evident that the dolostone units were subject to increasingly high temperatures from early replacement dolomite through late replacement dolomite (T_h = 110–118°C; T_h is homogenization temperature), early pore-filling dolomite (T_h = 98–101°C), to late pore-filling dolomite (T_h = 158–169°C), and then experienced cooling processes from late pore-filling dolomite through quartz (T_h = 101–142°C) to pore-filling calcite (T_h = 121–135°C). The fluids involved in the diagenesis are brines with very high salinity (17–32 wt % NaCl equivalent). Diagenetic phases that may be related to paleokarstification were dolomitized, and no record of meteoric water has been recognized.

The methane inclusions homogenized to the liquid phase near the critical point (-82.1°C), indicating moderate density. Some of the homogenization temperatures of the methane inclusions are slightly higher than the critical temperature, probably indicating the existence of other light hydrocarbons in addition to CH_4. An isochore is calculated for the methane inclusions, using the mean T_h value of methane inclusions (-83.6°C, to liquid) with the Flincor program (Brown, 1989). Using this isochore, fluid pressures corresponding to the homogenization temperatures of aqueous fluid inclusions in the same mineral (quartz) (i.e. 101–135°C) are calculated to be 460–529 bars. These probably represent the minimum pressures because the aqueous fluid inclusions may not have been saturated with CH_4 at trapping. The depths corresponding to these pressure values are 2039–2345 m if a lithostatic system is assumed (density of burden = 2.3 g/cm^3), or 4690–5394 m if a hydrostatic system is assumed (density of water = 1.0 g/cm^3).

DISCUSSION ON TIMING OF HYDROCARBON ACTIVITIES

It is well known that the dolostone units of the Beekmantown Group are reservoirs of natural gas, but it is not clear when the reservoirs were charged with hydrocarbons and whether the hydrocarbons were originally gaseous or liquid. This uncertainty influences the strategy of hydrocarbon exploration because the selection of exploration targets depends on assumptions of the timing and nature of hydrocarbon emplacement. The results of this study have provided some constraints on the timing and nature of hydrocarbon activities.

Dykstra and Longman (1995) have shown that much of the porosity in the dolostone units of the Beekmantown Group was filled by late-stage calcite cement, and suggested that early and continuous entrapment of hydrocarbons may have prevented later cementation. Our observations and fluid-inclusion data in this study further constrain the timing of hydrocarbon activities. The fact that solid bitumen predates late pore-filling dolomite and quartz cement suggests that hydrocarbons were emplaced in open pores (associated with late replacement dolomite) before maximum heating (recorded by late pore-filling dolomite), probably in the form of liquid hydrocarbons, although no liquid hydrocarbon fluid inclusions have been found. The liquid hydrocarbons were then transformed to gaseous products by overheating, which were entrapped as methane inclusions in the quartz cement. The cause of the weak fluorescence of the solid bitumen in some samples has not been understood, because the high degree of heating, as indicated by pyrobitumen reflectance values of more than 2.5% (Héroux and Bertrand, 1991), could have minimized the fluorescence intensity (Bustin et al., 1983). The cementation of quartz and calcite probably took place after maximum burial, but nevertheless at considerable depths (>2000 m). The brines that precipitated the pore-filling dolomite minerals and the quartz and calcite cements appear to belong to the same system. The fluid- inclusion data suggest that the cementation of quartz and calcite, which occluded most of the porosities of the dolostone units of the Beekmantown Group, took place after liquid hydrocarbons were transformed to gaseous products. The absolute ages of liquid hydrocarbon emplacement, liquid-to-gas transformation, and the subsequent cementation, need to be further determined.

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