Hydrothermal dolomitization in the Lower Silurian La Vieille Formation in northern New Brunswick: geological context and significance for hydrocarbon exploration

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ABSTRACT

Hydrothermal dolomites are potential hydrocarbon reservoirs in the Late Ordovician–Middle Devonian Gaspé Belt in eastern Canada. These dolomites are recognized in the Lower Silurian Sayabec Formation, Upper Silurian–lowermost Devonian West Point Formation and Lower Devonian Upper Gaspé Limestones and are also recognized in the Lower Silurian La Vieille Formation in northeastern New Brunswick. Hydrothermal dolomitization is expressed in local pervasive dolomitization fronts originating from fracture feeders and by saddle dolomite and high temperature late calcite cements filling fractures and associated dissolution voids. Field evidence such as dolomite clasts in a post-Salinic (early Ludlovian) conglomerate indicates a dolomitization event early in the burial history. Petrographic study documents a complex history of multiple fracture generation and saddle dolomite and/or calcite cement precipitation. Saddle dolomite is locally brecciated and cemented by a later phase of dull luminescent, mm-sized calcite crystals (calcite 1), the latter, in some cases, also completely filling fractures. Saddle dolomite is locally dedolomitized which is expressed as bright luminescent sub-millimetre-sized calcitic zones. Dedolomitization is associated with calcite-cemented (calcite 2), late stage fractures. $\delta^{18}O_{VPDB}$ values of the saddle dolomite ($–17.3$ to $–10.0\%$) and calcite 1 ($–13.8$ to $–8.8\%$) cements indicate precipitation from an $^{18}O$-depleted fluid and/or at relatively high temperatures. Fluid inclusion homogenization temperatures ($86$ to $212^\circ$C, average of $132^\circ$C) support a high temperature origin for calcite 1 from very saline fluids (from $12$ to $23$ wt\% NaCl$_{equiv}$). Calcite 2 is characterized by similar $\delta^{18}O_{VPDB}$ values ($–9.5$ to $–8.7\%$) with notably different $\delta^{13}C_{VPDB}$ values ($–4.1$ to $–3.1\%$ and $0.9$ to $3.0\%$ for calcite 2 and 1, respectively). Moreover, calcite 2 is characterized by fluid inclusions with very low salinities (about $0$ wt\% NaCl$_{equiv}$) and is interpreted as late meteoric calcite cement likely precipitated during the Late Silurian global sea level lowstand (Salinic Unconformity) or following the Middle Devonian (Acadian Orogeny) subaerial exposure of the Lower Silurian ramp.

The Early Silurian tectono-magmatic setting of the Gaspé Belt basin played a significant role in the regional hydrothermal alteration of the carbonates. The occurrence of hydrothermal dolomite suggests previously unrecognized reservoir potential of Silurian carbonates that should be considered along with the presence of good Middle and Upper Ordovician source rocks and favourable thermal maturation.

RÉSUMÉ

Les dolomies hydrothermales sont de potentiels réservoirs à hydrocarbures pour la Ceinture de Gaspé de l’Ordovicien tardif au Dévonien médian dans l’est canadien. Ces dolomies ont été décrites dans les unités du Silurien inférieur de la Formation de Sayabec, du Silurien supérieur–Dévonien basal de la Formation de West Point et du Dévonien inférieur du Groupe des Calcaires supérieurs de Gaspé de la Gaspésie et sont également reconnues dans la Formation de La Vieille du Silurien inférieur du nord-est du Nouveau-Brunswick. La dolomitisation hydrothermale s’exprime par la présence locale de fronts de dolomitisation intense associés à des fractures nourricières et par la présence de dolomite baroque et/ou de ciments de calcite de haute température en remplissage de fractures et de cavités de dissolution associées. Des arguments de terrain tels que des fragments de dolomite dans un conglomerat du post-Salinique (Ludlovien précoce) suggèrent une dolomitisation importante peu de temps après l’initiation de l’enfouissement. L’étude pétrographique indique une évolution complexe de fracturation et de remplissage de ciments de dolomite-calcite. La dolomie baroque est parfois...
The drilling of a hydrocarbon-filled hydrothermal dolomite reservoir in the Lower Ordovician St. George Group of the passive margin succession in western Newfoundland (Cooper et al., 2001) spurred significant interest for similar reservoirs in eastern Canada (Eaton, 2004a, b, and c). Hydrothermal alteration of the Lower Ordovician Romaine Formation on Anticosti Island has been documented (Lavoie et al., 2005). The industry interest has been further fuelled by the major production of natural gas (>115 MMcf/day) in Middle Ordovician hydrothermal dolomites of the Black River Group in the Taconian (‘Appalachian’) foreland basin of New York State (Smith, 2006).

The recognition of hydrothermal alteration of carbonates in the Lower Silurian Sayabec (Lavoie and Morin, 2004) and Upper Silurian–lowermost Devonian Devonian West Point (Lavoie, 2005a) formations and, in the Lower Devonian Upper Gaspé Limestones Group (Galt gas field; Lavoie, 2005b) in the Gaspé Peninsula has demonstrated that hydrothermal alteration and dolomitization of carbonates along the paleosouthern margin of Laurentia was not restricted to the Ordovician passive margin and Taconian foreland basin carbonates. Silurian-Devonian Salinic-Acadian foreland basin carbonates of the Gaspé Belt (sensu Bourque et al., 2001; Fig. 1) are also regionally altered. Most of this initial research was focussed on the successions on Gaspé Peninsula and, until recently, the extension of that belt in the adjacent northern New Brunswick was largely ignored. Renewed interest for New Brunswick relies on the recent proposal of a unified stratigraphic nomenclature and the linking of structural elements on both sides of the provincial border (Castonguay et al., 2004; 2005) made possible through the recent joint federal-provincial Lower Paleozoic NATMAP project in eastern Canada (Lavoie et al., 2004). It was on this improved tectono-stratigraphic framework that detailed hydrocarbon systems studies were initiated, first on thermal maturation and source rocks (Bertrand and Malo, 2004) followed by initial appraisal of potential reservoir units (Lavoie, 2005c).

Regional reconnaissance survey, which targeted the Silurian carbonate units in northern New Brunswick, documented field evidence for hydrothermal dolomitization in the Lower Silurian La Vieille Formation (Lavoie, 2005c) and possible hydrothermal events in the Upper Silurian Laplante Formation (Lavoie, work in progress). This contribution builds on the previously reported field evidence for hydrothermal dolomitization of the La Vieille Formation and presents petrographic and geochemical data to support this assertion. This paper documents the extension of regional hydrothermal alteration of Lower Silurian carbonates over significant segments of the Gaspé Belt in eastern Canada, from northern Gaspé (Sayabec Formation; Lavoie and Morin, 2004) to northern New Brunswick and provides a model for the anomalous high geothermal gradient that prevailed over large segments of the Gaspé Belt in Early Silurian time. The conclusions of this paper indicate significant reservoir potential in northern New Brunswick, in an area that was recently shown to have a favourable thermal maturation history and good hydrocarbon source rocks (Wilson et al., 2004; Bertrand and Malo, 2004).

INTRODUCTION

The drilling of a hydrocarbon-filled hydrothermal dolomite reservoir in the Lower Ordovician St. George Group of the passive margin succession in western Newfoundland (Cooper et al., 2001) spurred significant interest for similar reservoirs in eastern Canada (Eaton, 2004a, b, and c). Hydrothermal alteration of the Lower Ordovician Romaine Formation on Anticosti Island has been documented (Lavoie et al., 2005). The industry interest has been further fuelled by the major production of natural gas (>115 MMcf/day) in Middle Ordovician hydrothermal dolomites of the Black River Group in the Taconian (‘Appalachian’) foreland basin of New York State (Smith, 2006).

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GEOLOGIC AND STRATIGRAPHIC SETTINGS

The Gaspé Belt extends from eastern Gaspé Peninsula, southwest through northwestern New Brunswick to northeastern Maine (Fig. 1). The basement of the Acadian Gaspé Belt is quite variable. In northern New Brunswick, early Paleozoic rocks that belong to the Dunnage oceanic (Fournier Group) and island arc (Balmoral Group) domains are sandwiched between paleo-continental margin rocks that belong to the Laurentia Humber Zone (to the north) and Ganderia (to the south). In most cases, the lowermost units assigned to the Gaspé Belt overlie either disconformably or, with a more or less pronounced unconformity, the various Lower–Middle Ordovician mafic volcanic and/or sedimentary units (Figs. 1 and 2). The Gaspé Belt encompasses Upper Ordovician to Middle Devonian rocks that outcrop in three major structural divisions: the Connecticut...
Valley–Gaspé synclinorium; the Aroostook–Percé anticlinorium; and the Chaleurs Bay synclinorium (Bourque et al., 2001; Wilson et al., 2004) (Fig. 1).

The Gaspé Belt in northern New Brunswick comprises three stratigraphic successions separated by Late Silurian (Salinic) and Early Devonian unconformities and the upper succession is capped by a Middle Devonian (Acadian) unconformity (Wilson et al., 2004). The lower succession records post-Taconian basin infilling and is expressed in the Upper Ordovician to Lower Silurian siliciclastic turbidites of the Grog Brook Group, overlain by calcareous turbidites of the Matapédia Group. The regressive phase culminated in slope and shelf deposits of the lower part of the Chaleurs Group and is represented by the deep subtidal Upsilonch and Limestone Point formations that are laterally equivalent to the subtidal–peritidal La Vieille Formation (Lee and Noble, 1977; Wilson et al., 2004; Lavoie

Fig. 1. Simplified geological map of northern New Brunswick (modified from Map NR-1; New Brunswick Department of Natural Resources, 2000) with the location of the six studied stratigraphic sections of the La Vieille Formation. Refer to the inset map for the overall tectonostratigraphic setting of the study area. “T” refers to Témiscouata and “E.I.” to Elmire Inlier.
and Asselin, 2004) (Fig. 2). The upper beds of the La Vieille Formation are locally eroded (Fig. 2) and in a few places, sub-aerial volcanics of the Bryan Point Formation sit above the Wenlockian La Vieille Formation (Wilson et al., 2004).

Above the Salinic Unconformity in northeastern New Brunswick, the middle succession consists in the upper part of the Chaleurs and the Dalhousie groups which record a complete transgressive-regressive cycle. The upper part of the Chaleurs Group consists first of Ludlovian coarse- to medium-grained shallow marine to continental clastics of the Simpsons Field Formation, followed by mixed outer shelf clastics and carbonates of the reefal Pridolian Laplante Formation (Noble, 1985) and then by the Lower Devonian Free Grant Formation (McCutcheon, 2006). McCutcheon (2006) reported the presence of a carbonate-clast conglomerate at the base of the Ludlovian Simpsons Field Formation, which immediately overlies the La Vieille Formation. Limestone clasts are dominated by shallow marine facies which can only be linked with the La Vieille Formation both locally and regionally; this conglomerate provides more evidence for Salinic-related erosion (Lavoie and Asselin, 2004). In northernmost New Brunswick, Wilson et al. (2004) recognized the Pridolian reefal facies of the West Point Formation (=Laplante Formation) and overlying open marine Pridolian to Lochkovian sedimentary rocks of the Indian Point Formation (=Free Grant Formation). The Lochkovian to lower Emsian subaerial volcanic and subordinate siliciclastic rocks of the Dalhousie Group conformably overlie the Chaleurs Group and mark the end of the regressive event with its uppermost unit capped by a disconformity. The alluvial-lacustrine deposits of the upper Emsian Campbellton Formation (Wilson et al., 2004) form the upper succession and unconformably overlie the Dalhousie Group. Finally, post-Acadian (post Middle Devonian) coarse-grained reddish sandstones and conglomerates of the Bonaventure Formation unconformably overlie various Ordovician to Lower Devonian units of both the Early Paleozoic Dunnage Zone and Middle Paleozoic Gaspé Belt.

The lower succession of the Gaspé Belt (Upper Ordovician to uppermost Lower Silurian) is affected by the Salinic Orogeny (van Staal, 2005) which is marked by synsedimentary extensional block faulting, within-plate mafic volcanism, local uplift and deep erosion of pre-Gaspé Belt basement and Upper Ordovician to Lower Silurian strata (Wilson et al., 2004). Early Silurian mafic volcanism is recognized in the Témiscouata area (David and Gariepy, 1990), some 200 km to the northwest of the study area in northern New Brunswick (Fig. 1). The tectonic instability created by the Salinic Orogeny, which started in latest Early Silurian, was proposed as a critical element in the development of hydrothermal dolomite in the Lower Silurian carbonates of northern Gaspé Peninsula (Lavoie and Morin, 2004). The Salinic Orogeny should not be confused with the Salinic Unconformity, which resulted from a Late Silurian global sea level lowstand (Lavoie and Chi, 2001; Bourque et al., 2001).

**LA VIEILLE FORMATION**

The type-area of the La Vieille Formation is in the Port Daniel–Gascons area in southern Gaspé Peninsula (Schuchert and Dart, 1926). These authors also recognized that unit in northeastern New Brunswick. Stratigraphic descriptions for the New Brunswick occurrences were provided by Noble (1976) and Lee and Noble (1977).

In the Gaspé Peninsula and northern New Brunswick, the La Vieille Formation typically consists of three informal members (Figs. 3 and 4; Lavoie et al., 1992). These consists of: 1) a lower nodular, locally highly fossiliferous limestone member of outer shelf origin (Fig. 3A); 2) a middle well-bedded wackestone to packstone calcarenite of subtidal origin with a local (southern Gaspé) algal–metazoan bioherms and biostromes belt that rims a wide spectrum of algal and cryptobacterial facies (laminites, stromatolites, thrombolites and oncolites) of peritidal origin (Figs. 3B and C); and 3) an upper nodular, poorly fossiliferous limestone member that records an abrupt and rapid return to outer shelf conditions. Dolomitic facies are
uncommon in the La Vieille Formation of northern New Brunswick, a situation already noted for the La Vieille in the southern Gaspé Peninsula.

In northern New Brunswick, the typical three informal members of the La Vieille Formation are recognized in sections adjacent to the Elmtree Inlier (Dunnage Zone; Fig. 1, sections 2, 3, 4 and 5), whereas at some distance of this inlier, the middle unit is apparently absent (Fig. 1, sections 1 and 6) and the formation is represented only by the nodular limestone facies. Further to the west, the La Vieille is replaced by the coeval deeper subtidal open marine facies of the Upsalquitch and Limestone Point formations (Wilson et al., 2004).

For the shallower paleogeographic areas (i.e. where the middle peritidal member is developed), the La Vieille Formation has been subaerially eroded at least twice. The first event is associated with combined Salinic (Late Silurian) global sea level lowstand and tectonic activity. The resulting unconformity is recognized in local carbonate-clast conglomerates that overlie the La Vieille and in discordant map relationships displayed by Lower and Upper Silurian units (Wilson et al., 2004; McCutcheon, 2006). The second subaerial erosion event in these Lower Silurian carbonates is not restricted to palaeogeographically shallower successions; rather, it is related to the Acadian Orogeny with the siliciclastic continental red facies of the Bonaventure Formation that unconformably overlies the La Vieille facies (Figs. 4A and B).

Biostratigraphic data for the La Vieille Formation in northern New Brunswick is abundant, and the age of the unit is fairly well constrained to be Llandoverian C6 (late Telychian) to early to middle Wenlock based on brachiopods (Noble, 1976; Lee and Noble, 1977) or late Telychian based on chitinozoans (Asselin, 2001).

METHODS

During the summer of 2004, six stratigraphic sections (Fig. 1) of the Lower Silurian La Vieille Formation were carefully examined for facies architecture and evidence for hydrothermal alteration of the limestone facies (Lavoie, 2005c). Forty-five thin sections were examined under transmitted light microscopy and cathodoluminescence (CL). Distinct cement generations were recognized and micro-sampled for carbon and oxygen isotope analysis (11 analyses). Samples were micro-drilled from parent rock slabs and homogeneity of cement samples was confirmed through CL examination of milled areas. The carbonate powders were then treated and analyzed at the GSC Delta-Lab. Data are reported in the usual permil (‰) notation relative to the standard VPDB for carbon and oxygen. Precision of the data is always better than 0.1‰ for both δ18OVPDB and δ13CVPDB. Eight thin sections were examined for fluid inclusion microthermometry using a Linkam THMS 600 heating/freezing stage. Homogenization (Thom) and final ice-melting (Tm-ice) temperatures of aqueous fluid inclusions were measured with a precision of ±1°C and ±0.2°C, respectively. The thin sections for fluid inclusions were stained with a mixture of Alizarin Red-S and potassium ferricyanide (Dickson, 1965) to document presence or absence of iron in the various carbonate phases.

FIELD EVIDENCE FOR SHALLOW BURIAL HYDROTHERMAL ALTERATION OF THE LA VIEILLE FORMATION

Lavoie (2005c) reported multiple lines of field evidence that point to a significant fault-controlled shallow burial hydrothermal alteration of the limestone facies of the La Vieille Formation. A depositional model for the Lower Silurian carbonate ramp in the Gaspé Belt with the major sedimentary belts illustrated in the companion field photographs of lithofacies of the La Vieille Formation: A) Nodular lime mudstone set in a black mudstone matrix. From section 1. Hammer (30 cm) for scale; B) Well-bedded middle facies composed of subtidal peloidal and bio-intraclastic calcarenite. From section 4. 1.2 m-high back-pack (circled) for scale; C) Plane-bedding view of shallow subtidal thrombolite mounds in the well-bedded middle facies. From section 5. Hammer (30 cm) for scale.
Formation in northern New Brunswick. The most critical evidence for timing of dolomitization is the presence of siliceous, dolomite-rich clasts which are found in a carbonate conglomerate at the base of the Ludlovian Simpsons Field Formation (Fig. 5A; Wilson et al., 2004; McCutcheon, 2006). The Simpsons Field Formation overlies the Late Silurian Salinic Unconformity in the Pointe Rochette to Petit Rocher areas in northwestern New Brunswick (Fig. 1; McCutcheon, 2006). The conglomerate is clast-supported and reaches up to 5 m in thickness. Limestone fragments dominate the conglomerate and consist (in decreasing abundance) of bioclastics (gastropod, brachiopod, tabulate corals), packstone to wackestone, oncolite packstone, stromatolite and thrombolite boundstone; all of which can only be linked (because of time constraints) with the Lower Silurian La Vieille Formation locally and regionally. Of critical importance for this contribution is the presence of silica-rich dolomite clasts in the limestone conglomerate (Fig. 5A). These clasts are petrographically identical to facies that are pervasively dolomitized in the La Vieille Formation at locality 4 (Fig. 4C). Dolomite facies are unknown in pre-Late Silurian strata in northern New Brunswick (Wilson et al., 2004; Lavoie and Asselin, 2004). Other field evidence includes:

Fig. 4. Simplified stratigraphic column of the La Vieille Formation in northern New Brunswick with lower and upper outer shelf nodular limestone members and a middle member of peritidal limestones. Companion field photographs illustrate: A) The Acadian Unconformity with strongly discordant nearly horizontal coarse clastics of the Bonaventure Formation overlying the well-bedded vertical limestones of the La Vieille Formation. From section 5. Width of the exposure is 8 m; B) Calcite- and red clastic-filled fracture cutting through the La Vieille limestones. The fracture originates from the Acadian Unconformity shown in A. Hammer (30 cm) for scale; C) Massive dolomitization of carbonate facies of the La Vieille Formation, the bedding-discordant dolomitization (within the dashed white outline) is centred on a middle feeder. From section 4. 30 cm hammer (circled) for scale.
1) coarse-grained saddle dolomite cement that fills the youngest secondary voids (Fig. 5B and C); 2) dolomitized fault-brecciated zones, which were folded by later tectonic events; and 3) pervasive dolomitization of the precursor limestone host that resulted in a highly irregular, bedding-discordant dolomitic zone with a central feeder (Fig. 4C). The relatively early timing of the hydrothermal alteration is suggested by the total lack of preferred orientation of the fractures that controlled the dolomitic alteration, in contrast to later tectonic calcite-only filled fractures that characterize the regional Acadian (Middle Devonian) deformation in northeastern New Brunswick (N65° ±15°; Walker et al., 1993).

Based on limited outcrops information (Fig. 1), pervasive dolomitization of the La Vieille Formation seems to be restricted as it was only observed at one locality (section 4; Fig. 1). Elsewhere, dolomite occurs as a void filling phase and as isolated replacement saddle dolomite crystals in well-bedded limestone facies.

**PETROGRAPHY OF THE LA VIEILLE FORMATION DOLOMITES**

Samples for petrographic study were mainly dolomite cements in fractures and dissolution voids, which commonly also contain calcite cements. Cathodoluminescence petrography revealed two distinct calcite cement phases; these are designated as calcite 1 and calcite 2.

**DOLOMITE**

Void-filling dolomite is medium (sub-mm) to coarsely-crystalline (mm) (Fig. 6A) and coats the walls of secondary pores. These voids are locally filled with variable percentages of bitumen (Fig. 6A) and minute amounts of sphalerite as well as by some calcite and silica cements. The dolomite (+bitumen/calcite/silica)-filled voids are commonly cut by younger calcite-only filled fractures. The coarser dolomite crystals are characterized by the typical curved faces and sweeping extinction of saddle dolomite (Fig. 6B). A deep blue stain indicates Fe-rich dolomite or ankerite. In most cases, the dolomite crystals have well-preserved tips that project toward the centre of the pore space (Fig. 6C). The dolomite can also be fractured and brecciated with dolomite clasts surrounded by calcite cement (Fig. 6D).

Under cathodoluminescence (CL), saddle dolomite crystals are predominantly composed of dull, reddish, luminescent crystals without any significant internal zoning (Fig. 6E). In areas where brecciation and chemical corrosion (scalloped surfaces) of the dolomite crystals is observed, a patchy luminescence texture is visible, which results from multiple small spots of bright luminescent calcite engulfed in the dolomite (Fig. 6D). This texture is likely the result of dedolomitization.

**CALCITE 1**

This first calcite cement occurs in the same dolomite-bearing pores (Fig. 6A). The calcite 1 occurs as small (sub-mm-sized) idiomorphic to large (mm-sized) xenomorphic
limpid crystals. Similar crystals also occur in dolomite-free secondary voids. This calcite cement stains purple, which indicates an Fe-rich composition.

Under CL, calcite 1 is characterized by orange, dull to brown, luminescent crystals that are mostly devoid of any internal zoning (Fig. 7A). Where these dull luminescent crystals coat dolomite crystals, no evidence of corrosion can be seen even if the dolomite crystals can be prominently fractured (Fig. 7A).

**CALCITE 2**

This type of calcite cannot be easily distinguished from calcite 1 on the sole basis of conventional transmitted light petrography. From field relationships complemented by CL discrimination of calcites, the fractures filled by calcite 2 cross-cut fractures filled by the dolomite-calcite 1 couple. Calcite 2 is Fe-poor, stains red and commonly occurs in mm- to cm-wide fractures that locally reach dm width (Fig. 4B). Calcite 2 consists
of small to large idiomorphic crystals that range from 0.1 to 5 mm in size. When in contact with the dolomite crystals, the calcite 2 precipitated over micro-scalloped surfaces, and these corroded dolomite crystals are characterized by the patchy luminescent fabric described previously (Fig. 6D).

Calcite 2 consists of non-luminescent to very dull luminescent crystals with some bright to dull internal zones (Fig. 7B). The abundance and width of the luminescent zones vary significantly between individual thin sections, although it is always subordinate to the dominant non- to very dull-luminescent phase. In some thin sections, pores are floored by clasts of the predominantly non-luminescent calcite crystals cemented by bright luminescent calcite (Fig. 7C).

**MICROTHERMOMETRIC ANALYSES**

Doubly-polished thin sections were prepared with the aim to measure fluid inclusions in the dolomite, but unfortunately the fluid inclusions are all smaller than 2 micrometres and the dark brown colour of the dolomite crystals makes it impossible to see phase changes in heating and freezing runs. Fluid inclusion data for calcite cements were acquired on 4 doubly polished thin sections (Table 1 and Fig. 8). Fluid inclusions that occur as isolated inclusions, in clusters, or randomly distributed in three dimensions are considered as primary or pseudosecondary inclusions (Roedder, 1984).

**CALCITE 1**

The workable fluid inclusions in the calcite 1 range in size from 2 to 10 µm. They are characterized by homogenization temperature (T_h) values ranging from 87º to 212ºC (Table 1; Fig. 8) with an average of 127ºC. First melting temperatures were measured for a few inclusions and range from −58.2 to −43ºC, suggesting an H_2O–NaCl–CaCl_2–MgCl_2 system typical of basinal brines. Ice-melting temperatures range from −21.5 to −8.6ºC, corresponding to salinities ranging from 12.4 to 23.3 wt% NaCl-equiv., with an average of 17.7 wt% NaCl-equiv. (Table 1). The occurrence of some all-liquid inclusions with similar salinities suggests that the minimum homogenization temperatures could be lower than 87ºC.

**CALCITE 2**

The fluid inclusions in calcite 2 consist of two types; monophase (all-liquid) and biphase (liquid + vapour), and both occur as isolated inclusions and in clusters. The biphase inclusions have T_h values that range from 66º to 106ºC (Table 1) with an average of 91ºC. Ice-melting temperatures range from −0.2 to 0ºC, with calculated salinities from 0 to 0.4 wt% NaCl-equiv. The monophase inclusions are also characterized by low salinities (Table 1).

**CARBON AND OXYGEN STABLE ISOTOPES**

The results from dolomite, calcite 1 and calcite 2 cements are presented in Table 2 and Figure 9. The isotopic ratios of the coeval hydrothermally-altered carbonates of the Sayabec
Table 1. Fluid-inclusion microthermometric data of samples from La Vieille Formation

<table>
<thead>
<tr>
<th>Host mineral</th>
<th>Occurrence</th>
<th>Size (mm)</th>
<th>Vapor%</th>
<th>Tm-first (°C)</th>
<th>Tm-H₂O (°C)</th>
<th>Th-total Range</th>
<th>Mean (n)</th>
<th>Salinity (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcite 1</td>
<td>Random</td>
<td>2 – 5</td>
<td>5</td>
<td>-</td>
<td>−15.4 (1)</td>
<td>145</td>
<td>145 (2)</td>
<td>19.0</td>
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<tr>
<td></td>
<td>#5403 - 3</td>
<td>2 – 4</td>
<td>8</td>
<td>-</td>
<td>-</td>
<td>140 – 154</td>
<td>147 (2)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>4 – 5</td>
<td>5</td>
<td>−14.7 (1)</td>
<td>123 – 124</td>
<td>123 (2)</td>
<td>18.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>5</td>
<td>5</td>
<td>≤ −1.9 (1)</td>
<td>132</td>
<td>132 (1)</td>
<td>-</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td>3 – 5</td>
<td>5</td>
<td>≤ −5.2 (1)</td>
<td>146 – 163</td>
<td>155 (2)</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>4</td>
<td>5</td>
<td>-</td>
<td>111</td>
<td>111 (1)</td>
<td>-</td>
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</tr>
<tr>
<td></td>
<td></td>
<td>3 – 7</td>
<td>8</td>
<td>−15.3 (1)</td>
<td>127 – 193</td>
<td>183 (2)</td>
<td>18.9</td>
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<td>3</td>
<td>-</td>
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<td>3</td>
<td>-</td>
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<td>8</td>
<td>0</td>
<td>-</td>
<td>−0.2 (1)</td>
<td>all-liquid</td>
<td>all-liquid</td>
<td>0.4</td>
</tr>
</tbody>
</table>
Formation in northern Gaspé (Lavoie and Morin, 2004) are also shown in Figure 9 for comparison.

**Dolomite**

The saddle dolomite cements were collected from five different samples; the material was selected in samples not affected by the dedolomitization event. The $\delta^{18}O_{VPDB}$ and $\delta^{13}C_{VPDB}$ values range between $-9.9$ to $-17.3‰$ (average of $-13.9‰$) and $1.3$ to $-2.6‰$ (average of $-0.4‰$), respectively (Fig. 9).

**Calcite 1**

The calcite 1 cements were collected from three different samples. The $\delta^{18}O_{VPDB}$ and $\delta^{13}C_{VPDB}$ values range from $-8.8$ to $-13.8‰$ (average of $-10.5‰$) and $3$ to $0.9‰$ (average of $1.6‰$), respectively (Fig. 9).

**Calcite 2**

The calcite 2 cements were collected from three different samples. The $\delta^{18}O_{VPDB}$ and $\delta^{13}C_{VPDB}$ values fall in a narrow range from $-8.7$ to $-9.5‰$ (average of $-9‰$) and $-3.1$ to $-4.1‰$ (average of $-3.5‰$), respectively (Fig. 9).

**TECTONO-DIAGENETIC EVENTS IN THE LA VIEILLE FORMATION**

The field evidence (see above in text and Lavoie, 2005c) suggests a likely shallow burial origin for the dolomitization. This field evidence is here combined with the petrographic and geochemical data to support the interpretation of shallow burial hydrothermal alteration of the limestone facies of the Lower Silurian La Vieille Formation in northern New Brunswick. The

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**Table 2. Oxygen and carbon stable isotope ratios**

<table>
<thead>
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<th>Sample</th>
<th>Section</th>
<th>$\delta^{18}O_{VPDB}$</th>
<th>$\delta^{13}C_{VPDB}$</th>
</tr>
</thead>
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<td>$-17, 3$</td>
<td>$-0, 8$</td>
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<tr>
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<td>#5401</td>
<td>5</td>
<td>$-16, 2$</td>
<td>$1, 3$</td>
</tr>
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<td></td>
<td>#5435</td>
<td>4</td>
<td>$-9, 9$</td>
<td>$0, 7$</td>
</tr>
<tr>
<td></td>
<td>#5433</td>
<td>4</td>
<td>$-12, 1$</td>
<td>$-2, 6$</td>
</tr>
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<td></td>
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<td>Average</td>
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<td>$-13, 9$</td>
<td>$-0, 4$</td>
</tr>
<tr>
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<td>4</td>
<td>$-8, 8$</td>
<td>$1$</td>
</tr>
<tr>
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</tr>
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<td>#5403</td>
<td>3</td>
<td>$-13, 8$</td>
<td>$3$</td>
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<td>Average</td>
<td></td>
<td>$-10, 5$</td>
<td>$1, 6$</td>
</tr>
<tr>
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<td>Average</td>
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following section discusses the likely composition and origin of the fluids responsible for the precipitation of the cement phases recognized in fractures and pore space in the La Vieille Formation.

**Dolomite and Calcite 1 Cement Association**

Saddle dolomite is assumed to record rapid precipitation from a high temperature and saline fluid (Radke and Mathis, 1980; Searl, 1989) and is taken as a common (although not diagnostic) indicator of hydrothermal conditions (Davies and Smith, 2006). Fracture- and void-filling dolomite in the La Vieille samples is of the saddle type, although the lack of workable fluid inclusions prevented a direct assessment of fluid temperature and salinity. The petrographic, fluid inclusion microthermometric ($T_h$ and $T_{m-ice}$) data for the calcite 1 and very negative $\delta^{18}O_{VPDB}$ values for saddle dolomite in the void space indicate the likely presence of high temperature and very saline diagenetic fluids. The transition between saddle dolomite and calcite 1 is abrupt and at places, calcite 1 fills microfractures in the saddle dolomite. However, there is no evidence of chemical corrosion between the saddle dolomite and calcite 1.

The $\delta^{18}O_{SMOW}$ values of the diagenetic fluids from which calcite 1 was precipitated, calculated from the average $T_h$ values and $\delta^{18}O_{VPDB}$ values of calcite 1 fall between $+2$ and $+3$‰ (Fig. 10). Such values could indicate: 1) $^{18}O$ enrichment of marine waters through evaporation; 2) fluid-rock interaction in the deeper parts of the basin or basement; or 3) some input of magmatic water ($\delta^{18}O_{SMOW}$ of +5.5 to +10‰; Taylor, 1979) in the diagenetic fluid. Enrichment through evaporation of marine waters is highly unlikely given the normal marine fauna and lack of other saline condition indicators (sulphate nodules for example). This is also the case for the lower Silurian La Vieille and Sayabec formations in the adjacent Gaspé Peninsula where open marine fauna and $\delta^{18}O_{VPDB}$ normal marine cements are recorded (Lavoie et al., 1992; Lavoie and Bourque, 1993). It is therefore more probable that some fluids derived from deeper parts of the basin or fluids of magmatic origin were responsible for the precipitation of calcite 1 and most likely for the saddle dolomite, as well.

Calcite 1 is characterized by less negative $\delta^{18}O_{VPDB}$ values compared to the saddle dolomite (Table 2 and Fig.9). Dolomite should be enriched by $+3$ to $+4$‰ in $\delta^{18}O_{VPDB}$ compared to consanguineous calcite (Land, 1985). If both cements originated from a relatively similar diagenetic fluid ($\delta^{18}O_{SMOW}$), it follows that calcite 1 cement was precipitated at lower temperature compared to the saddle dolomite. Fluid inclusions in calcite 1 have high $T_h$ values (up to 212°C, average of 127°C). If one takes $\delta^{18}O_{SMOW}$ of $+2.5$‰ as the likely value of the fluid also responsible for the precipitation of the associated saddle dolomite, it follows that the saddle dolomite ($\delta^{18}O_{VPDB}$ of $-9.9$ to $-17.3$‰) precipitated at temperatures that possibly ranged between 125°C to 210°C, based on the dolomite-water fractionation equation of Land (1985).

**Fig. 9.** Cross-plot of individual oxygen and carbon stable isotope ratios of calcite 1 and 2 and saddle dolomite phases in the La Vieille Formation. The grey fields show distribution of oxygen and carbon stable isotope values from the coeval Sayabec Formation in northern Gaspé Peninsula (Lavoie and Morin, 2004). Data are listed in Table 2. The Lower Silurian marine calcite field is from Lavoie and Bourque (1993). Say: Sayabec, S.D.: saddle dolomite, M.D.: matrix dolomite, M.C.: meteoric calcite. Samples from section 3 are shown by black symbols, those from section 4 are white, those from section 5 are grey and calcite 2 samples from section 6 are white.

**Fig. 10.** $\delta^{18}O_{VPDB}$ composition of calcite 1 versus precipitation temperatures based on $T_h$ values of individual samples; the $\delta^{18}O_{SMOW}$ of the diagenetic fluid in equilibrium with the calcite is indicated by the values of the curves. Equilibrium lines from Friedman and O’Neill (1977). Assumed $\delta^{18}O_{SMOW}$ values of magmatic water are from Taylor (1979) and that of Lower Silurian marine water is from Azmy et al. (1998).
Regional considerations

The presence of dolomite clasts in a Ludlovian (Upper Silurian) conglomerate that overlies the Lower Silurian La Vieille Formation is a strong argument for an early dolomitization of the facies shortly after the inception of burial (Fig. 5A). Therefore, the high temperature events recorded in the δ13OVPDB values of the dolomite and the T_h of fluid inclusions of calcite 1 (average of 127°C) was most likely much higher than the temperature of the interstitial early burial fluid at that time, a prerequisite for hydrothermal designation (Machel and Lonee, 2002).

Petrographic and geochemical data have been reported from hydrothermally-altered Lower Silurian Sayabec Formation in nearby northern Gaspé Peninsula, where this correlative unit of the La Vieille Formation (Lavoie, 1988; Lavoie et al., 1992; Lavoie and Asselin, 2004) was altered early in the burial history (Lavoie and Chi, 2001; Lavoie and Morin, 2004). The saddle dolomites in the coeval Sayabec Formation in northern Gaspé Peninsula are characterized by high T_h fluid inclusions (114 to 218°C; Lavoie and Chi, 2001 and work in progress) as well as very high salinities (21.1 to 28 wt% NaCl equiv.; Lavoie and Chi, 2001 and work in progress). Very negative δ18OVPDB values were also reported for the saddle dolomites in Lower Silurian carbonates in the Gaspé Belt, ranging from −14.5 to −17.9‰ for the Sayabec Formation (Lavoie and Chi, 2001; Lavoie and Morin, 2004) to the herein reported −9.9 to −17.3‰ for the La Vieille Formation. In other nearby Paleozoic settings, hydrothermal dolomite is also characterized by negative δ18OVPDB values that range from −10 to −12‰ for the Middle Ordovician Trenton-Black River HTD in New York (Smith, 2006) and between −6.4 to −13.8‰ for the Lower Ordovician Romaine HTD in Anticosti (Lavoie et al., 2005).

Calcite 2

The later calcite 2 recorded a very different diagenetic fluid. The T_m-ice data indicates a non-saline fluid and the calcite is also characterized by negative δ13CVPDB values. These signatures are commonly found in calcites derived from meteoric waters. The interpretation of meteoric fluid responsible for the precipitation of the calcite 2 cement is also supported by the petrographic attributes of that cement such as strongly zoned non-luminescent crystals with bright luminescent zones which is common for meteoric calcites (James and Choquette, 1990; Meyers, 1991). Similar luminescence patterns are also observed in other meteoric calcite cements found as a later phase associated with hydrothermal dolomites in the Lower Silurian Sayabec Formations of the Gaspé Belt (Lavoie and Morin, 2004) as well as in the Upper Carboniferous carbonates in Northern Spain (Gasparrini et al., 2006).

The occurrence of monophase (liquid-only) fluid inclusions in calcite 2 is consistent with a shallow meteoric water environment. The co-existence of two-phase inclusions (T_h from 66 to 106°C) in the same crystals is interpreted to indicate the vadose zone where either only water (the liquid-only inclusions) or both water and air (the two phases inclusions) were entrapped. The T_h values are therefore invalid and cannot be used to indicate a high temperature environment. Similar observation and interpretation are reported in Pleistocene limestones partly cemented in the vadose zone (Barker and Halley, 1988).

Regional considerations

In samples from the Lower Silurian Sayabec Formation, where vugs in dolomite are filled by late calcite cement which has been interpreted as meteoric calcite on the basis of petrographic habit and δ18OVPDB - δ13CVPDB values (Lavoie and Morin, 2004), fluid inclusions are mainly liquid-only, and two-phase inclusions with highly variable vapour/liquid ratios are present (Chi and Lavoie, work in progress). Such fluid inclusion occurrences are indicative of the vadose zone environments.

In the case of the Lower Silurian Sayabec Formation of the northern Gaspé Peninsula, the subaerial event responsible for the precipitation of the late meteoric calcite cement has been ascribed to the Late Silurian Salinic Unconformity (Lavoie and Morin, 2004). There is no absolute age dating on this meteoric calcite cement and the assignment to the Late Silurian subaerial event is supported by the significant erosion of pre-Late Silurian strata in many places in the Gaspé Peninsula as well as by the total lack of post-Acadian sediment record in northern Gaspé leaving no evidence for Acadian erosion of the Silurian strata. In northern New Brunswick, undisputed evidence for Salinic (Late Silurian) and Acadian (Middle Devonian) subaerial exposure and erosion of the La Vieille Formation is present. It is currently unknown to which unconformity the meteoric cements relate as both unconformities are present in the area where the samples were collected.

Hydrothermal Dolomitization of the Lower Silurian Units – Constraints on Plumbing System, and Mg2+ and Heat Sources

Mafic Basement – the Potential Source of Mg2+ for Hydrothermal Dolomitization

Known outcrops of interpreted hydrothermal dolomites in the La Vieille Formation in northern New Brunswick occur in areas where mafic volcanic units of the Early Paleozoic Dunnage Zone constitute the basement of the Gaspé Belt (Fourier Group in the Elmtree Inlier; Spray et al., 1990; Fig. 1). The La Vieille Formation is separated from these mafic volcanics by less than 100 m of lowermost Silurian strata that unconformably drape the Dunnage Zone volcanic units of Llandeilian (=Darriwilian) age (461 +3/–2 Ma, Spray et al., 1990) (Figs. 1 and 2). The presence of nearby Ordovician oceanic slivers has been demonstrated for the hydrothermally altered Lower Silurian Sayabec Formation in the northern Gaspé Peninsula (Lavoie and Morin, 2004). These tectonic slivers of Middle Ordovician sea floor ultramafic (456 ±5 Ma, Trzcienski et al., 1995) and mafic volcanics have been proposed as the source of Mg2+-needed for the extensive hydrothermal dolomitization of the Sayabec Formation in northern
Gaspé (Lavoie and Morin, 2004); such mafic basement likely played a similar role for Mg$^{2+}$ supply for the dolomitization of the La Vieille Formation in northern New Brunswick.

**EARLY EXTENSIONAL TECTONISM OF THE SALINIC OROGENY – THE PLUMBING SYSTEM**

Lavoie and Morin (2004) proposed that late Early Silurian extensional movement of the Shickshock Sud fault in the northern Gaspé Peninsula generated the plumbing system for hydrothermal fluid migration and alteration of the Sayabec Formation. The late Early Silurian motion of that fault has been documented on recent seismic lines in northern Gaspé (Kirkwood et al., 2004a, b), which supported previous stratigraphy (Bourque et al., 2001) and structural (Sacks et al., 2004) evidence. Other faults in Gaspé Peninsula with a Middle Devonian Acadian dextral transpressional movement, i.e. the Bassin Nord-Ouest and Troisième Lac faults, also show seismic and field stratigraphic evidence for a pre-Late Silurian extensional (transensional?) history (Lavoie, 1992; Malo, 2001; Kirkwood et al., 2002; Kirkwood et al., 2004a).

There is no seismic data in northern New Brunswick and our current understanding of the subsurface architecture of the Gaspé Belt there is based on field relationships and some fault kinematic indicators (Wilson et al., 2004). The regional Early Silurian tectonic environment may have been characterized by fault-bounded tectonic blocks with highly variable tectonic subsidence rates, with rapidly subsiding areas as suggested by the local absence of the middle peritidal member of La Vieille and the rapid westward transition to slope deposits of the Upsalquitch Formation. Such geometry is compatible with field structural observations that identify a number of major faults that cut through the stratigraphic pile and, more significantly, this explanation is also supported by the recent organic matter maturation studies of the area (Bertrand and Malo, 2004).

The thermal maturation map has helped in recognizing three major tectonic blocks in northern New Brunswick separated by NNE-oriented faults (Bertrand and Malo, 2004). All of these blocks are characterized by a northwestern domain with lower thermal maturation that passes southeastwardly to an area with higher thermal maturation for the same stratigraphic level and in particular for the La Vieille Formation. The organic matter in many samples located close to the major faults that delineate the above discussed tectonic block is characterized by abundant coke microstructures indicative of anomalous rapid heat flow (Bertrand and Malo, 2004). These thermal maturation relationships are used as indirect arguments for syn-sedimentary tectonic activity in the late Early Silurian depositional basin in northern New Brunswick; these faults are likely open conduits for focussing hydrothermal fluids flows.

**EARLY SILURIAN MAGMATISM – A REGIONAL ANOMALOUSLY HIGH HEAT GRADIENT**

The homogenization temperatures of the fluid inclusions for the Sayabec Formation saddle dolomite range from 114 to 194°C in northern Gaspé (Lavoie and Chi, 2001) and from 141 to 218°C in northwestern Gaspé (Chi and Lavoie, unpublished data). No saddle dolomite fluid inclusion data is available for the La Vieille Formation in northern New Brunswick although, based on the assumption that the saddle dolomite was precipitated from a fluid similar to that for calcite 1 as discussed above, the saddle dolomite cement in the La Vieille Formation of northern New Brunswick may have precipitated under temperature conditions from 125 to 210°C.

A recent summary of fluid inclusion $T_h$ data (Davies and Smith, 2006) shows that very high $T_h$ values (routinely above 150°C) are uncommon in other known cases of Phanerozoic hydrothermal dolomites (HTD). The nearby Ordovician HTD in eastern North America are all characterized by lower $T_h$ values for saddle dolomite; these include the Middle Ordovician Trenton-Black River of New York (usually less than 150°C; Smith, 2006), the Lower Ordovician St. George Group in western Newfoundland (less than 130°C, Lane, 1990) and the Lower Ordovician Romaine Formation on Anticosti (less than 150°C, Lavoie et al., 2005).

A relationship between arc volcanism and elevated heat flow is reported in some Paleozoic HTD cases (Davies and Smith, 2006). For example, the Middle Ordovician bentonites within the Trenton carbonate succession in the eastern US are proposed as an indicator for such a link between active arc volcanism, elevated heat flow and hydrothermal dolomitization (Davies and Smith, 2006). Significant volumes of arc to back-arc mafic volcanism of Early Silurian age are known in northern New Brunswick (Bryan Point Formation; Gower and McCutcheon, 1997; van Staal et al., 2003), in adjacent southern Gaspé Peninsula (Restigouche volcanites; Bourque et al., 2001) and in the Témiscouata region (Pointe-aux-Trembles Formation; David and Gariepy, 1990). In Early Silurian, the Tetagouche-Exploits arc (now preserved in central New Brunswick) had a NW-oriented subduction (van Staal et al., 2003) and the final accretion of that composite arc is no younger than Late Silurian (Salinic Orogeny; van Staal, 2005). This regional tectono-magmatic event, related to the Salinic Orogeny, may have been a critical element in generating a significant regional thermal gradient that enhanced fluid circulation and hence hydrothermal dolomitization of the roughly coeval Lower Silurian carbonate platforms of the Gaspé Belt.

**CONCLUSIONS**

The Lower Silurian La Vieille Formation in northern New Brunswick is characterized by hydrothermal alteration of its facies during the early stages of its burial. The field evidence includes: 1) dolomite clasts (most likely derived from the La Vieille) in the Ludlovian Simpsons Field conglomerate that unconformably overlies the La Vieille Formation; and 2) early fractures (pre-Acadian) and dissolution voids filled by saddle dolomite and calcite cements. Petrographic, fluid inclusions and stable isotope data suggest that the early saddle dolomite and calcite cements were precipitated from a high temperature...
and very saline fluid of hydrothermal origin, and later fracture-fill calcite cement formed from meteoric water related to subaerial exposure of the hydrothermally-altered La Vieille facies.

The Early Silurian Gaspé depositional basin was tectonically active as Ganderia progressively accreted to the continental margin of Laurentia (Salinic Orogeny) along the northwestward prograding subduction zone of the Tetagouche–Exploits arc, now preserved in central New Brunswick. The active tectonism generated significant basin-scale extensional faulting in late Early Silurian time with significant evidence from regional seismic profiles, fault kinematic indicators and, in northern New Brunswick, thermal maturation patterns. This tectonic activity was instrumental in creating an efficient plumbing system for upward migration of deep-seated fluids. The progressive subduction generated Early Silurian arc and back-arc magmatism expressed in mafic volcanic units in northern New Brunswick, southern Gaspé Peninsula and Témiscouata. The regional magmatic event resulted in high thermal gradients and enhanced upward convection.

The combined tectono-magmatic events in Early Silurian time created favourable conditions for episodic, fault-controlled upward flow of high temperature saline fluids to interact with shallowly buried Lower Silurian limestones. These very high temperature events are clearly expressed in the anomalously high fluid inclusions $T_I$ values of both saddle dolomite and associated calcite cements. In areas where Ordovician ultramafic and mafic volcanics were intercepted along flow patterns of these high temperature fluids, they became charged with significant amount Mg$^{2+}$ and were thus able to pervasively dolomitize limestones and precipitate loads of dolomite cements in fractures and voids.

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**REFERENCES**


Canadian Society of Petroleum Geologists, Diamond Jubilee Convention, Program with abstracts, p. 186.


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