Dolomitization of the Lower Ordovician Catoche Formation:

Implications for Hydrocarbon Exploration in Western Newfoundland

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Reference

Abstract

The lower Ordovician St. George Group in Western Newfoundland consists of a sequence of subtidal and peritidal carbonates, which are extensively dolomitized. The current study investigates the diagenetic evolution of the Catoche Formation from the Port aux Choix and Port au Port peninsulas in order to study the controls on reservoir quality in western Newfoundland. The Catoche Formation dolomites are classified into three main generations. Early and pervasive replacement dolomite (D1) indicates that dolomitization began during early stages of diagenesis. Stable isotope and trace element data indicate significant variations between D1 dolomite on the Port aux Choix and Port au Port peninsulas. The depleted $\delta^{18}O$ signature of D1 dolomite fluids (-8.7 ± 1.3‰ VPBD) on the Port aux Choix Peninsula is consistent with partial dolomitization associated with mixing of seawater and meteoric waters on the flanks of structural highs. In contrast $\delta^{18}O$ values (-6.1 ± 0.7‰ VPBD) and trace element data from the Port au Port Peninsula indicate that pervasive D1 was associated with mixing of possibly post evaporitic brines with meteoric waters.

Later-stage replacement dolomites (D2) are associated with enhancement in porosity through the development of intercrystalline pores, while latest stage saddle dolomite (D3), significantly occluded the pores in some horizons. D2 dolomite formed due to the influx of warm (>100°C), saline (>15 eq. wt% NaCl) fluids. Intercrystalline porosity in D2 formed due to the dolomitization of precursor calcite, due to the lower molar volume of dolomite compared to calcite. Therefore porosity development is lower on the Port au Port Peninsula, with no significant volume change during the recrystallization of the pervasive early (D1) dolomicrite. Similarly, extensive porous horizons on the Port aux Choix Peninsula are related to the limited

extent of D1 dolomitization. This suggests that the quality of a potential dolomite reservoir is strongly controlled by tectonic and diagenetic history of host carbonates.

Keywords: dolomitization, diagenesis, Newfoundland, geochemistry, Appalachians

1 Introduction

Numerous Paleozoic dolomite hosted hydrocarbon reservoirs have been recognized in the Appalachians of Eastern Canada and the United States, and some of these are producing oil and/or oil and gas e.g. Upper Ordovician Trenton-Black River dolomites in New York and Anticosti, Lower Ordovician Garden Hill oil field in western Newfoundland and Lower Devonian Galt gas field on Gaspé Peninsula, Quebec (Cooper et al., 2001; Smith, 2006; Lavoie and Chi, 2010). Recent studies have emphasized the hydrothermal origin of these dolomites (Lavoie et al., 2005; Lavoie and Chi, 2006; Smith, 2006; Azmy et al., 2008, 2009; Conliffe et al., 2009, 2010; Lavoie and Chi, 2010), and argued that the hydrothermal dolomite exploration model described by Davies and Smith (2006) should be applied to these reservoirs. This model suggest that transtensional seismic platform sags associated with major structural features (extensional and/or strike-slip faults), which may have acted as conduits for the hydrothermal fluids, should be targeted in exploration programs. However this model remains controversial, with some authors pointing towards questions and uncertainties about nature and absolute timing of dolomitization, the source of Mg^{2+} rich saline brines and the possible driving mechanisms for hydrothermal circulation (Machel and Lonnee, 2002; Davies and Smith, 2006).

Hydrocarbon exploration in western Newfoundland has been ongoing for more than 140 years of exploration, with a proven petroleum system consisting of organic rich source rocks in the Green

Point Formation and impermeable cap rocks of the Table Point Formation (Cooper et al., 2001). In 1995, drilling encountered a number of oil and gas horizons in the upper part of the St. George Group with the Port au Port 1 Well produced 5012 bbl of oil and 2737 bbl of water during a 7 day test (Cooper et al., 2001). In addition bitumen stained dolomites in the Catoche Formation on the Port aux Choix Peninsula have been interpreted as a major exposed reservoir which form part of a porous body up to 10 km wide (and extending an unknown distance offshore), at least 8 km long, and up to 300 m thick (Cooper et al., 2001).

Previous studies of dolomitization on the Port au Port Peninsula have identified multiple generations of dolomitization, with porosity associated with thin (< 5m) bodies of hydrothermal dolomite (Azmy et al., 2008, 2009; Conliffe et al., 2009). The current study investigates the diagenetic evolution of the Catoche Formation from the proven hydrothermal reservoir on the Port au Port Peninsula and the major exposed reservoir on the Port aux Choix Peninsula, ~250km to the north. The main objectives of this study are: (1) to identify and characterize petrographic and geochemical variations in the dolomitization phases of the Catoche Formation; (2) to determine what factors affect the reservoir quality in both locations; and (3) to establish whether the hydrothermal dolomite exploration model that is currently being used from western Newfoundland is valid for major reservoirs akin to the exposed reservoir on the Port aux Choix Peninsula.

2 Geological Setting

The Lower Paleozoic autochthonous rocks of western Newfoundland were deposited on the passive margin of Laurentia during the Late-Proterozoic break-up of Rodinia and the opening of the Iapetus Ocean (James et al., 1989; Stenzel et al., 1990; Cooper et al., 2001; Waldron and van

Staal, 2001; van Staal, 2005). These rocks comprise a succession of Cambrian to Devonian siliciclastic and carbonate sediments that outcrop over 400km from Cape Norman in the north to the Port au Port Peninsula in the south (Fig. 1) and form part of the Humber Zone, the westernmost of five tectono-stratigraphic zones in the Canadian Appalachians (Fig. 1; Williams, 1979). The St. George Group carbonates forms a sequence of subtidal and peritidal limestones and dolostones, which was deposited as part of a broad, low-energy carbonate platform during the early to middle Ordovician (James et al., 1989). The succession is subdivided, in ascending order, into the Watts Bight, Boat Harbour, Catoche and Aguathuna Formations (Fig. 2). Knight and James (1987) showed that the St George Group represents two long-lived megacycles of Tremadocian and Arenigian age, which consists of a thin lower peritidal layer, a thick middle subtidal layer and a thick upper peritidal layer (Knight and James, 1987). The lower megacycle includes the Watts Bight Formation and most of the Boat Harbour Formation, and is bounded at the top by a regional disconformity, the Boat Harbour Disconformity (BHD). The upper megacycle comprises of the top of the Boat Harbour Formation, and the Catoche and Aguathuna formations. A regional unconformity, the St. George Unconformity, marks the top of the St. George Group and a shift from a passive margin to a foreland basin (Knight et al., 1991).

The Catoche Formation forms the middle subtidal layer of the upper Arenigian megacycle, lying conformable on the Barbace Cove Member of the Boat Harbour Formation. It is approximately 160m thick and is subdivided into three informal units (Fig. 2). A Lower Limestone consists of well-bedded, fossiliferous, bioturbated limestone (Knight et al., 2007). A ~50m thick sequence of dolomitized mound-grainstone facies, termed the Pine Tree Unit, has been mapped on the Port au Port and Northern peninsulas where it replaces the upper levels of the Lower Limestone (Baker and Knight, 1993; Knight et al., 2007). This is overlain by the Costa Bay Member, a

succession of shallowing upwards parasequences of burrow mottled lime mudstones and wackestones to peloidal grainstones.

The Catoche Formation has been mapped throughout western Newfoundland (Knight and James, 1987) and is extensively dolomitized in many areas (Haywick, 1985; Lane, 1990; Knight et al., 2007). Microcrystalline dolomite is common, often replacing sedimentary structures and burrow (Knight et al., 2007). Intercrystalline and vuggy porosity is associated with sucrosic dolomites (Baker and Knight, 1993; Knight et al., 2007) On the Port au Port peninsula, sucrosic dolomitization and associated porosity is most common in the Pine Tree Unit (Knight et al., 2007). Although porosities of up to up to 8.7% over 15m have been reported from the Catoche formation on the Port au Port peninsula (Cooper et al., 2001), porosity is variable and most porous horizons are <5m in thickness. On the Port aux Choix Peninsula the Costa Bay Member is almost totally made of a strataform body of sucrosic and sparry dolomite (Baker and Knight, 1993; Knight et al., 2007). These dolomites are pervasively stained with bitumen (Cooper et al. 2001) and have well developed porosity and permeability (1.0% to 17.8% and 0.02mD to 317mD respectively; Greene 2008). This body can be mapped over more than 10km and in some instance are spatially associated with faults (Cooper et al. 2001; Knight et al. 2007). Cooper et al. (2001) argued that this body represented an exhumed oilfield, with Devonian emplaced oil migrating out of the reservoir after the erosion of Taconic and Salinic cap rock.

3 Methodology

The upper 97m of the Catoche Formation on the Port au Port Peninsula were examined from drillhole 12B/11 44 from the Port au Port Peninsula (Lyn, 1978; longitude 59°02′16″, latitude 48°35′49″). This section represents the Costa Bay Member and Pine Tree Unit, as well as the

upper few metres of the Lower Limestone (Fig. 2). A complete section of the Catoche Formation (160m thick) was examined from outcrop and from core on the Port aux Choix Peninsula. The sampled outcrop is located on the coast of the north-western side of the Port au Choix Peninsula whereas the core (PC 79-2, longitude 57°19′18″, latitude 50°42′07″) is located about 2.5 km inland from the peninsula (Fig. 1). A detailed description Catoche dolomites on the Port au Port and Port aux Choix peninsulas is included in Knight et al.(2007); and Greene (2008). All samples were collected at high resolution (sampling interval of 2 ± 0.5m), and in total 61 samples were collected from Port au Port Peninsula, while 71 samples from Port aux Choix Peninsula were studied. These were analysed following the procedure outlined in detail by Azmy et al. (2008). Thin sections of the samples were stained (Alizarin Red S-potassium ferricyanide; Dickson, 1966) and examined using transmitted light microscopy and cathodoluminescence (CL).

Microthermometric fluid-inclusion analyses were performed using a Linkam THMSG600 heating-freezing stage calibrated with synthetic H_2O and CO_2 fluid inclusion standards at temperatures between -56.6 and 374.1°C. Precision on the measurements is ± 0.2°C at −56.6°C and ± 1°C at 300°C. Homogenization temperatures were recorded first in order to minimise the effects of stretching in relatively soft minerals such as calcite. Following procedures outlined by Shepherd et al. (1985) the initial melting temperatures (T_i), last ice melting ($T_m(ice)$) and the temperature of homogenization (T_h) were measured in two-phase (liquid + vapour) inclusions hosted in dolomite and calcite. Salinities were calculated using a program by Chi and Ni, (2006) for the system of H_2O-$NaCl$-$CaCl_2$

A polished mirror-image slab of each thin section was also prepared for microsampling. For C and O isotope analyses approximately 220µg of powder sample was reacted in an inert

atmosphere with ultrapure concentrated (100%) orthophosphoric acid at 70°C in a Thermo Finnigan Gasbench II and the produced CO2 was automatically delivered to the source of a Thermo Finnegan DELTA V plus isotope ratio mass spectrometer in a stream of helium, where the gas was ionized and measured for isotope ratios. Precision of the data is better than ±0.1‰ Vienna Peedee belemnite (VPDB) for both $\delta^{18}O$ and $\delta^{13}C$ ratios. For major and trace element analyses ~ 4mg of sample powder was digested in 2.5% (v/v) pure H_3PO_4 acid for 70-80 minutes and analysed for Ca, Mg, Sr, Fe and Mn (Coleman et al., 1989) using a HP4500plus inductively coupled plasma – mass spectrometer (ICP-MS). The relative uncertainties of these measurements are less than 5%.

4 Results

4.1 Petrography

Petrographic examination of the limestones of Catoche Formation has identified multiple phases of sedimentary, diagenetic and void filling calcite and dolomite. The limestones range from packstone and grainstone facies to lime mudstones and wackestones. The earliest calcite identified, C1, is the original sediment and includes the peloidal and intraclastic micrite aggregates and limemuds (Fig. 3a/b). Later calcite generations (C2 and C3) represent cements. Early equant calcite spar (C2), ranging in size from 50 to 250 μm, is present lining grains and filling pores in packstone and grainstone lithofacies (Fig. 3a). A translucent, coarse blocky (100 to 500μm) calcite cement (C3) postdates all C2 cement and dolomitization, filling late fractures and vugs. C1 and C2 phases are dull to non-luminescent under CL, while C3 commonly has bright red to yellow luminescence.

Early dolomitization (D1) is associated with replacement of lime mudstones, wackestone and burrows. D1 is grey in color and commonly mimic the precursor depositional texture of C1. It is typically fine grained (5 to 35 μm) with rare coarser grained D1 (up to 50μm) replacing burrows. D1 exhibits a nonplanar mosaic with irregular intercrystalline boundaries and is dull to non-luminescent under CL, with some compositional zoning noted. Stylolite-associated dolomite (DS) is associated with, and usually bounded by, brown-red stylolites, which postdate the early burial diagenesis (cutting D1). The crystals are sub- to euhedral and range from 70 to 150 μm. DS displays a medium-red luminescence under CL but no compositional zoning is apparent.

A second phase of dolomitization (D2 dolomite) is most common in the Pine Tree Unit on the Port au Port peninsula and the Costa Bay Member on the Port aux Choix peninsula, where D2 almost completely replaces precursor calcite and dolomites. D2 dolomite is grey in hand specimen (rare zebra dolomite) and is easily distinguished from D1 dolomite due to it sucrosic habit and absence of precursor sedimentary fabrics. Contacts between D1 and D2 dolomite are typically sharp. Dolomite rhombs are anhedral to euhedral and range in size from 100 μm to up to 1mm. They are commonly zoned, with inclusion rich cores and clear rims. Under CL, the cloudy cores display a dull red luminescence while the rims are brightly luminescent (Fig. 3j). Three styles of D2 dolomitization have been recorded in the Catoche formation. Mosaic style D2 dolomite is characterized by interlocking anhedral to subhedral dolomite crystals. Euhedral dolomite rhombs are associated with porosity while the most porous horizons on the Port aux Choix Peninsula (>10% porosity) are characterized by a third form of D2 dolomite, which postdates euhedral dolomite rhombs and has a characteristic undulose extinction. D2 dolomite is rarely cut by high amplitude stylolites which are distinctive from lower amplitude stylolites

associated with DS. These stylolites are interpreted to be related to dolomitization (Merino et al., 2006). D2 dolomite rhombs are also commonly coated by bituminous organic material.

The latest void-filling dolomite (D3) is milky white and recorded lining vugs and intercrystalline pores. It displays undulose extinction and commonly has non-planar boundaries, features typical of saddle dolomite (Budd, 1997; Warren, 2000). D3 dolomites are relatively rare on the Port au Port Peninsula, where they are found lining small vugs (<400μm) between D2 dolomite rhombs. On the Port aux Choix Peninsula D3 dolomite is more common, where it forms milky cement crystals (300-600 μm) that line fractures and fill vugs (Fig 3k).When viewed under CL, D3 displays strong zonation with bright and dull luminescence.

4.2 Petrophysical characteristics

Porosity and permeability in the Catoche dolomites and associated reservoir quality is dependant on the type and degree of dolomitization. D1 and DS are not associated with any porosity development. Intercrystalline porosity is associated with D2 dolomite, but development of this porosity is highly variable (Fig. 3). On the Port au Port peninsula, three main porous horizons were associated with D2 dolomitization in the Pine Tree Unit, including about 2m of 10% porosity at 20m from the top of the unit and ~3m of ~12% porosity at 5m from the base of the unit. The rest of the Pine Tree Unit is generally tight (<2% intercrystalline porosity). In contrast, both vuggy and intercrystalline porosity associated with D2 is much more common in the overlying Costa Bay Member on the Port aux Choix peninsula. Porosity values ranging from ~7 to 10 % were documented for the Pointe Blanche section on the Port aux Choix Peninsula with permeability values ranging from 0.02mD to 317mD (Greene, 2008), while up to 20% porosity was visually estimated in some thin sections. D3 dolomite (and C3 calcite) fill pre-existing pores and vugs and are associated with an overall reduction in porosity and reservoir quality. C1-C2

4.3 Fluid Inclusion Studies

Fluid inclusions were examined in D2 and D3 dolomite and C3 calcite and their microthermometric data are summarized in Table 1 and Figure 4. No inclusions were observed in C1- C2 calcite or D1 dolomite. All inclusions are biphase (liquid + vapor; L + V), and range in size from 2-50μm. Fluid inclusions in dolomite are hosted in clusters in the core of dolomite crystals or in discrete zones within dolomite rhombs (termed fluid inclusion assemblages or FIA), and are considered primary in origin (Goldstein, 2003). Primary fluid inclusion assemblages in D2 and D3 dolomite are characterized by a consistent degree of fill (liquid/vapor ratio) indicating little or no post-entrapment re-equilibrium (leaking or necking down of inclusions). Fluid inclusions in C3 calcite are found in clusters in the core of crystals and can be very large with respect to their host crystals (up to 50μm). Some FIA show evidence of post-entrapment leaking and/or stretching (e.g. micro fractures at edge of inclusions) and therefore data was only included if all inclusion in a single FIA had relatively constant liquid vapor ratios and had small T_h variations (usually less than 10°C).

4.3.1 Port au Port Peninsula

Homogenization temperatures of fluid inclusions in D2 dolomite range from 90 to 132°C (average of 106± 11°C). The initial melting temperatures (T_i) ranged from -50.3 to -49°C, corresponding to the eutectic temperature for the H_2O-NaCl-$CaCl_2$ ± $MgCl_2$ system. T_m(ice) of -10.2 to -15.6 equate to fluid salinities of 14.1 to 19.2 eq. wt% NaCl. Fluids responsible for later saddle dolomitization (D3) are NaCl-$CaCl_2$ rich, with T_i ranging from -54.5 to -49.6°C. Ice melting temperatures of -11.2°C to -23.2 were used to calculate fluid salinities of 15.2 to 24.5 eq. wt% NaCl. Homogenization temperatures show a marked bimodal distribution (Fig. 4), with peaks at 80-100°C (early inclusions in the core of D3 crystals) and 120-150°C (later inclusions in

the rims of D3 crystals). Fluid inclusions in C3 calcite have salinities of 5 to 15.6 eq. wt% NaCl and have a wide range of T_h values (52 to 205°C).

4.3.2 Port aux Choix Peninsula

Inclusions in D2 dolomite homogenize to the liquid phase between 87 and 133.5°C (mean = 109°C ± 13°C). T_i in D2 hosted inclusions ranged from -50.3 to -49°C, indicating that with Na^+ and Ca^{2+} are the main ions in solution. Ice melting temperatures ranged from -13.6°C to -24.8, which yield fluid salinities of 17.4 to 25.5 eq. wt% NaCl. Fluid inclusions hosted in D3 dolomite have T_h values ranging from 109 to 118°C (average of 118 ± 10°C). T_i ranged from -54.4 to -51.7°C (close to the eutectic temperature of the H_2O-NaCl-$CaCl_2$±$MgCl_2$). T_m(ice) occurred between -7.8 and -14.6°C corresponding to salinities ranging between 11.5 to18.3 eq. wt% NaCl. Low T_i of -55.2 to -51.2°C of inclusions hosted in C3 calcite again suggests that Na and Ca are the dominant cations in solution. These inclusions have salinities of 22.2 to 25 wt% NaCl and T_h values of 64 to 182°C.

4.4 Carbon and oxygen isotopes

The carbon and oxygen isotopic compositions of calcite (C1-C2, C3) and dolomite (D1, D2, D3) are summarized in Tables 2 and 3 and presented in Figure 5.

4.4.1 Port au Port

C1/C2 calcite yielded $\delta^{13}C$ values from -0.1 to -2.3 ‰ VPDB and $\delta^{18}O$ values of –6.9 to -8.7‰ VPDB. Fifteen samples of C3 cement were analysed, which yielded a wide range of $\delta^{13}C$ values (-0.4 to -7.4‰ VPDB) and $\delta^{18}O$ values (-2.3 to -11.8 ‰ VPDB). Five samples of D1 yielded $\delta^{13}C$ values of -0.5 to -1‰ VPDB and $\delta^{18}O$ values of -5.4 to -6.9‰ VPDB. Twenty six D2 samples were characterized by a narrow range of $\delta^{13}C$ values (-0.4 to -1.4‰ VPDB) and $\delta^{18}O$

values (-5.7 to -7.8‰ VPDB). A single analysis of D3 dolomite gave a $\delta^{13}C$ value of -0.7‰ VPDB and $\delta^{18}O$ value of -7.5‰ VPDB.

4.4.2 Port aux Choix

Isotopic data from C1-C2 samples yield $\delta^{13}C$ values of -1.1 to 2.7‰ VPDB and $\delta^{18}O$ values of -7.9 to -9.7‰ VPDB. D1 has ranges for $\delta^{13}C$ and $\delta^{18}O$ of 0.1 to -1.7‰ VPDB and -6.6 to -10.3‰ VPDB, respectively (n = 12). Twenty samples of D2 were analysed, with $\delta^{13}C$ values of 0.2 to -1.4 VPDB ‰. The oxygen isotope values for D2 dolomite in the Port aux Choix section are depleted in ^{18}O compared with data from the Port au Port section, ranging from -6.9 to -10.7‰ VPDB. Data from five D3 samples yield carbon isotope values of -0.7 to -1.5‰ VPDB and oxygen isotope values of -6.1 to -8.5‰ VPDB.

4.5 Major and trace element geochemistry

The distribution of major and trace elements in calcite and dolomite analysed are summarized in Tables 2 and 3 and Figure 6

4.5.1 Port au Port

The Catoche dolomites from the Port au Port peninsula are non-stoichiometric, with Ca concentrations ranging from 66 to 55.2%. C1-C2 calcite is characterized by Sr concentrations of 211 ± 166ppm and low Mn and Fe values (393 ± 253 pm and 253 ± 158ppm, respectively). D1 dolomites have lower Sr contents than C1-C2 (106 ± 60ppm) but are relatively enriched in Fe (1706 ± 465). D2 and D3 dolomite have similar Fe concentrations (1584 ± 1001ppm and 1178ppm respectively) but are depleted in Sr (68 ± 21ppm and 65ppm respectively). Although the average Mn concentration of D1, D2 and D3 dolomite remains relatively constant, Fe/Mn ratios can vary. (Fig 6c). C3 calcite is relatively depleted in Sr (122 ± 87ppm) and Fe (402 ± 244ppm) and enriched in Mn (798 ± 963ppm).

4.5.2 Port aux Choix

The Ca concentrations of D1 to D3 dolomites from the Port aux Choix peninsula range from 53.5 to 63.8%. C1-C2 calcite has Sr concentration of 362 ± 61ppm, Fe of 1607 ± 626ppm and Mn of 53 ± 17ppm. D1 to D3 dolomite have significantly lower Sr values (<161ppm), while the Fe content of dolomites ranges from 4001 ± 1939ppm in D1, 1751 ± 1008ppm in D2 and 14934 ± 10287ppm in D3 (Fig. 6b). The Mn content of the dolomites increases from 100 ± 40 ppm in D1 to 178 ± 90 ppm in D2 and 316 ± 115 ppm in D3, with Fe/Mn ratios reflect the oxidising state of dolomitizing fluids (Fig. 6d).

5 Discussion

5.1 Early dolomitization (D1 to DS)

D1 dolomite in the Catoche formation commonly occurs as replacement of lime mudstones, wackestone and burrows (Haywick 1984, Lane, 1990, Green, 2008, this study).. Although D1 dolomite replacing lime mudstones is generally finer grained than D1 dolomite partially replacing wackestones and burrows they are geochemically indistinct and are interpreted to represent a single dolomitization event. These dolomites predate significant burial and formation of stylolites (frequently crosscut by stylolites). In addition dolomitized fragments are recorded in collapse breccia associated with the St George Unconformity (directly after deposition of the Aguthuna Formation: Knight et al., 1991). Therefore D1 dolomites are interpreted as essentially syn-sedimentary to early burial in origin (>300m) and dolomitization is believed to have occurred at near surface temperatures (<50°C)The carbon isotope values from D1 dolomite on the Port au Port and Port aux Choix peninsulas are similar and most likely represent the carbon isotope signature of the precursor carbonates (C1 and C2) and that bacterial sulfate reduction of

organic material, and/or oxidation of subsurface methane were not responsible for early dolomitization. However variations in the $\delta^{18}O$ and trace element (Sr, Fe) composition of D1 dolomites on the Port au Port and Port aux Choix reflect variations in the style of dolomitization at both locations. The $\delta^{18}O$ composition of D1 dolomite can be used to calculate an estimate for the $\delta^{18}O$ value of the dolomitizing fluids (e.g., Azmy et al., 2008), using the well calibrated calcite-water fractionation curve of O'Neil et al. (1969) and fractionation of 3.8‰ coexisting calcite and dolomite (calculated by Land, 1985). The results of these empirical dolomite-water equations of Land (1985) at 25 and 30°C are shown in Figure 7. Also included are the $\delta^{18}O$ values of D1 dolomites and the calculated $\delta^{18}O$ signature of Arenig seawater and meteoric water. The documented $\delta^{18}O$ of the best preserved primary calcite precipitated from the Arenig seawater is estimated at -8.2 to -11.1‰ (Shields et al., 2003), which translate into $\delta^{18}O_{seawater}$ of a warm (25 to 30°C) tropical zone of ~-4.4 to -7.3‰ VSMOW (Shields et al., 2003). Assuming that the relationship between the $\delta^{18}O$ of Arenig meteoric and seawaters were similar to those of our present day environment (i.e., the meteoric water is approximately depleted by ~4‰ compared with seawater), the $\delta^{18}O$ of meteoric fluids is calculated to be -8.4 to -11.3‰ VSMOW.

Previous studies of D1 dolomites in the St George Group have argued that D1 dolomites formed due to the mixing of seawater and meteoric waters possibly in a mixing zone environment (Azmy et al., 2008, 2009; Conliffe et al., 2010). However numerous authors have shown that thick bodies of dolomite are unlikely to form in mixing zones (Machel and Mountjoy, 1986; Hardie, 1987), with recent examples of mixing zone dolomites confined to isolated regions with limited extent (Melim et al., 2004). Figure 7 shows that the $\delta^{18}O$ of D1 dolomite of the Port au Port Peninsula fall within the range calculated for Arenig seawater. This may indicate that

dolomitization was associated with slightly modified seawater or mixing between isotopically heavy post-evaporitic brines and isotopically light meteoric water. The relatively high Cl content (444 to 988 ppm) of D1 dolomites from the Port au Port Peninsula argues for brine involvement, with the high Fe content (1175 to 2248 ppm) due to the influx of Fe-rich meteoric fluids. The $\delta^{18}O$ values of D1 dolomite on the Port aux Choix Peninsula are much lower and fall close the calculated range for Arenig meteoric water (Fig. 7). This indicates that dolomitizing fluids had relatively higher meteoric-water contents compared with those of their Port au Port counterparts. Such an interpretation is supported by the lower Sr and elevated Fe contents of D1 dolomite on the Port aux Choix Peninsula (Tables 2 and 3, 31 to 161 ppm and 1721 to 7389 ppm respectively).

These varying styles of early dolomitization may be related to the tectonic architecture of western Newfoundland after the deposition of the Catoche limestones. This period was marked by the exhumation of the St. George Group and the formation of the St. George Unconformity (Knight et al., 1991). However this exhumation was not uniform and led to the formation of numerous upfaulted structural highs, with the Aguathuna Formation deposited in downfaulted basins (Knight et al., 1991). The Port au Port Peninsula represents a downfaulted basin, with a thick sequence of Aguathuna limestones overlying the Catoche Formation. The Aguathuna Formation contains an evidence of evaporates and numerous exposure surfaces (Knight et al., 1991), consistent with a peritidal setting with restricted water circulation and hypersaline sedimentation. D1 dolomitization on the Port au Port Peninsula is likely associated with the downward percolation of dense, post-evaporitic seawater into the underlying Catoche limestone (brine reflux). These sediments would have already been saturated with meteoric fluids (or mixed seawater and meteoric fluids) originating on the exposed structural highs, similar to

models of strand-zone dolomitization from the Nijar Dolomite, Spain (Meyers et al., 1997). This mixing zone interpretation is supported by oxygen isotope data from the St George Group D1 dolomites on the Port au Port Peninsula. These data show a lightening trend from the uppermost Aguathuna Formation (-4.0 ± 0.6‰; Azmy et al., 2008) top to the underlying Catoche (-6.1 ± 0.7‰; this study), Boat Harbour (-6.2 ± 0.8‰; Azmy et al., 2009) and Watts Bight (-6.7 ± 0.8‰; Conliffe et al., 2009) formations.

The Port aux Choix oilfield is believed to represent a structural high, which formed a barrier between downfaulted basins (Knight et al., 1991; Cooper et al., 2001; Knight et al., 2007). As such the infiltration of any post-evaporitic brines into the Catoche formation would have been limited (Fig. 8). D1 dolomitization on the Port aux Choix Peninsula may be related to the formation of seawater-meteoric water mixing zones during exhumation. However mixing zone dolomitization was restricted to isolated regions with limited extent, similar to modern mixing zone environments (Melim et al., 2004).

Dolomites associated with stylolites and solutions seams (DS) postdate early D1 dolomitization and represent the earliest phase of burial dolomitization. Increase in chemical compaction during early burial resulted in the release of Mg^{2+}-rich connate fluids, which traveled along pressure seams and reacted with the host limestones, causing dolomite precipitation in and around stylolites (cf. Wanless, 1979). Insoluble residues such as clays usually accumulate along those stylolites which cause inconsistent variations in the chemistry of the related fluids, due leaching elements out of clays, and consequently the chemical signatures of DS.

5.2 Burial dolomite (D2)

D2 dolomite is most common dolomite type in the Catoche Formation, and almost totally replaces the Pine Tree Unit on the Port au Port peninsula and the Costa Bay Member on the Port

aux Choix peninsula. D2 crystals are interpreted to represent dolomitization during burial (cf. Warren, 2000). The Sr content is low (<108ppm), much lower than would be expected from dolomites associated with hypersaline waters (<550ppm; Tucker and Wright, 1990). D2 crystals have inclusion rich, cloudy cores with inclusion poor, clear rims and display distinct zoning under CL. D2 dolomite in the Catoche formation is non-stoichiometric (63.7 to 53.5% $CaCO_3$) and is locally associated significant intercrystalline porosity (up to 20%). This is consistent with dolomitization in a relatively close and rock-buffered diagenetic system with a low fluid/rock ratio and a limited local supply of Mg^{2+} ions (Sperber et al., 1984; Warren, 2000; Kirmaci and Akdag, 2005).

Fluid inclusion and isotopic data from D2 dolomites provide constraints on the nature of dolomitizing fluids in the Catoche Formation. T_i and T_m(ice) indicate that fluids are high salinity $NaCl$-$CaCl_2$ rich, with slightly higher salinities recorded from the Port aux Choix Peninsula. Conliffe et al. (2010) reported crush leach data on D2 dolomites from the Catoche formation on the Port aux Choix Peninsula and the Aguathuna Formation on the Port au Port Peninsula, which showed that that these fluids represent post-evaporitic brines. The similarities in the petrographic, fluid inclusion and trace element characteristics of D2 dolomite suggest that dolomitization is associated with a regional scale event late in the diagenetic history of these carbonates. However, D2 dolomite from the Port aux Choix Peninsula is more depleted in $\delta^{18}O$ by ~2-3‰ (Fig. 5b). This may be related to the isotopic composition of dolomitizing fluids, with a relatively greater degree of evaporation of precursor brines and/or influxes of ^{18}O enriched magmatic fluids associated with D2 on the Port au Port Peninsula. Alternatively, the more negative $\delta^{18}O$ values on the Port aux Choix Peninsula may reflect higher temperatures of dolomitization. For fluids with the same or similar isotopic compositions, an ^{18}O depletion of

2−3‰ corresponds to a temperature increase of 20 to 30°C (according to the equation of Land, 1985).

The T_h recorded from primary fluid inclusions in D2 dolomites are similar on the Port au Port and Port aux Choix peninsulas (106 ± 11°C and 109 ± 13°C respectively). However, these represent estimates of minimum entrapment temperatures and at greater pressures (and depths) true trapping temperatures could be higher. However, Conliffe et al. (2010) showed that temperature of dolomitization on the Port au Port peninsula was higher than maximum burial temperatures (hydrothermal dolomitization) and occurred at shallow crustal levels (<2km). Therefore the T_h values recorded for D2 dolomite are likely close to the true trapping temperatures, and little or no pressure correction is needed. The elevated trapping temperatures estimated from T_h and $\delta^{18}O$ values for D2 hosted inclusions on the Port aux Choix peninsula (~120 to 150°C) are similar to maximum burial temperatures of 120 to 130°C from the Catoche formation of the Port aux Choix peninsula, estimated from acritarch alteration indices (AAI) and graptolite reflectance data (Williams et al., 1998). Therefore D2 dolomite on the Port aux Choix peninsula did not form at temperatures higher than the ambient rock temperatures and can be classified as geothermal dolomitization at deeper crustal levels (Machel and Lonnee, 2002).

A suggested model for the development of D2 dolomitization is shown in Figure 9. Cooper et al. (2001) argued that D2 dolomitization on the Port au Port Peninsula was Devonian in age, consistent with radiometric and paleomagnetic data from coeval Pb-Zn mineralization at Daniels Harbor (Lane, 1990; Pan and Symons, 1993; Nakai et al., 1993). During the Late Devonian lithospheric flexure associated with the Acadian orogeny led to the deposition of the Clam Bank Formation in a foreland basin in western Newfoundland (Waldron at el., 1993). The Clam Bank Formation show evidence of periodic episodes of evaporation (Burden et al., 2002) and may be

the source of post-evaporitic brines responsible for D2 dolomitization (Conliffe et al., 2010). These dense brines were drawn into the underlying sediments via brine reflux and were subsequently entrained in hydrothermal convection cells (driven by Devonian igneous activity associated with the Acadian Orogeny). D2 dolomitization on the Port aux Choix Peninsula was geothermal, where hot Mg-rich basinal brines are likely to cause extensive dolomitization of pre-existing carbonates. These brines may have travelled to shallow crustal levels along major faults (e.g. Round Head Fault) which were reactivated during Acadian shortening (Waldron et al., 1993; Cooper et al., 2001), causing hydrothermal dolomitization on the Port au Port Peninsula.

5.3 Late stage dolomite and calcite (D3 and C3)

D3 dolomite represents the final dolomite phase in the Catoche formation, where it occludes late pores and vugs. D3 dolomite on the Port au Port Peninsula is rare and is geochemically similar to D2 dolomite (Table 2). Homogenization temperatures and salinities of inclusions hosted in the core of D3 crystals are identical to those hosted in D2 dolomite. This indicates that D2 and D3 dolomite on the Port au Port Peninsula are akin to non-saddle and saddle D2 dolomite on the Port aux Choix Peninsula and were formed during a single hydrothermal event, with the saddle dolomite forming due to the increased space created during early hydrothermal dolomitization. Higher T_h values from the rims of D3 crystals may represent recrystallization by later hydrothermal fluids at higher temperatures.

On the Port aux Choix peninsula, coarse grained saddle dolomite is relatively more abundant. It is similar to megacrystic saddle dolomite reported from Daniel's Harbour (Type VI of Lane, 1990) which postdates major ore deposition. The lower salinities (14 ± 1.8 eq. wt% NaCl) and higher Fe-contents (Fig. 6) recorded from D3 dolomites on the Port aux Choix indicate that this

fluid was geochemically distinct from D2 dolomitizing fluids associated with porosity development and ore-deposition.

C3 calcite postdates all other carbonates in the Catoche formation. Wide variations in carbon and oxygen isotope, trace element and fluid inclusion data (Tables 1, 2, 3; Figs. 4, 5, 6) indicates that C3 calcite represents a number of separate episodes of calcite precipitation associated with regional uplift after hydrocarbon emplacement and ore deposition. This is consistent with data from elsewhere in western Newfoundland (Lane, 1990; Azmy et al., 2008, 2009; Conliffe et al., 2009, 2010, Azmy and Conliffe, 2010).

5.4 Implications for hydrocarbon exploration in western Newfoundland

The distribution of intercrystalline porosity associated with D2 dolomite in the Catoche Formation is patchy, which has important implications for hydrocarbon exploration in western Newfoundland. This distribution is controlled by the relative degree of early D1 dolomitization. Intercrystalline porosity is formed due to the dolomitization of precursor C1-C2 calcite, with the porosity forming due to the lower molar volume of dolomite compared to calcite (Warren, 2000). In contrast no significant volume change is expected with the recrystallization of the precursor (D1) dolomicrite. Although thick horizons of D2 dolomite are encountered on the Port au Port Peninsula, the porous horizons are generally thin (<5m). This suggests that D1 dolomitization on the Port au Port Peninsula was relatively pervasive, with only thin horizons of undolomitized limestone. On the Port aux Choix Peninsula porous horizons in the St George Group carbonates are much thicker, (up to 300m; Cooper et al., 2001), consistent with little early D1 dolomitization. The variations in porosity on the Port au Port and Port aux Choix Peninsula the style and volume of early dolomitization in the Catoche Formation (see 5.1). D1 dolomitization on the Port au Port Peninsula is associated with the downward percolation of post-evaporitic

brines and is likely to have been extensive. Therefore little or no porosity would have been created during subsequent dolomitization events. In contrast the Catoche Formation on the Port aux Choix Peninsula would have been relatively undolomitized prior to D2 dolomitization, and therefore significant intercrystalline porosity developed during to the D2 dolomitization of precursor C1-C2 calcite. Therefore, the quality of any potential dolomite reservoir is strongly controlled by diagenetic history of carbonates prior to burial.

6 Conclusions

This study identifies multiple dolomite generations (D1, DS, D2 and D3) in the Catoche Formation on the Port au Port and Port aux Choix peninsulas, western Newfoundland.

1. On the Port au Port Peninsula pervasive fabric-retentive D1 dolomicrite probably formed due to the mixing of post-evaporitic brines sourced in shallow overlying basins and meteoric waters from nearby structural highs. In contrast, dolomitizing fluids responsible for D1 dolomite on the Port aux Choix Peninsula had relatively higher contributions by meteoric fluids (depleted in ^{18}O) and therefore D1 dolomitization was relatively minor.

2. Burial dolomitization during the Devonian is likely hydrothermal on the Port au Port Peninsula and geothermal on the Port aux Choix Peninsula, and is associated with intercrystalline porosity development in the Catoche Formation (D2). However, the distribution of this porosity is patchy and the best preserved reservoirs are likely associated with the replacement of previously undolomitized carbonates (i.e. structural highs akin to the Port aux Choix Peninsula).

3. Late stage dolomite cement precipitation (D3) postdate porosity development and ore-deposition in the St George Group and in some locations significantly occlude porosity.

Previous studies have argued that hydrocarbon exploration in western Newfoundland should focus on hydrothermal dolomites associated with major structural features (extensional and/or strike-slip faults) which act as a focus for the dolomitizing fluids (Cooper et al., 2001). Although some producing reservoirs are undoubtedly associated with hydrothermal dolomites (e.g. the Garden Hill oil field on the Port au Port Peninsula), the current study shows that the extensive exhumed oilfield on the Port aux Choix Peninsula is geothermal in origin, and therefore the hydrothermal dolomite exploration model proposed by Davies and Smith (2006) may not be suitable for western Newfoundland. In contrast, we argue that the quality of a potential dolomite reservoir is strongly controlled by tectonic and diagenetic history of host carbonates prior to burial and future hydrocarbon exploration in western Newfoundland should focus on structural highs, which have the best chance of showing significant porosity. On a global scale this project illustrates the importance of understanding the sedimentological, diagenetic and tectonic history of any potential dolomite reservoir.

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Figures
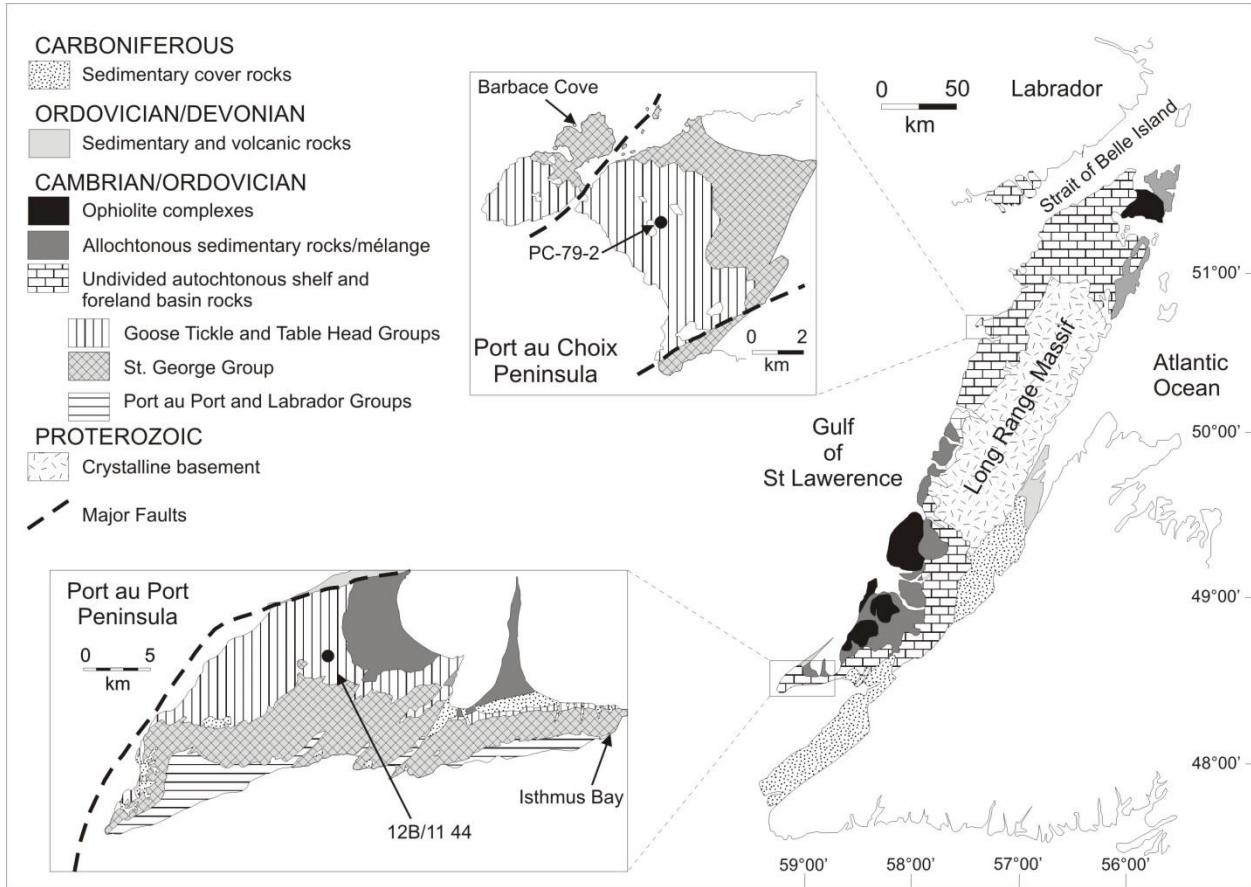
Figure 1: Simplified map of the geology of Western Newfoundland, with insets showing the geology of the Port au Port and Port aux Choix peninsulas (adapted from Zhang and Barnes, 2004 and Knight et al., 2007).
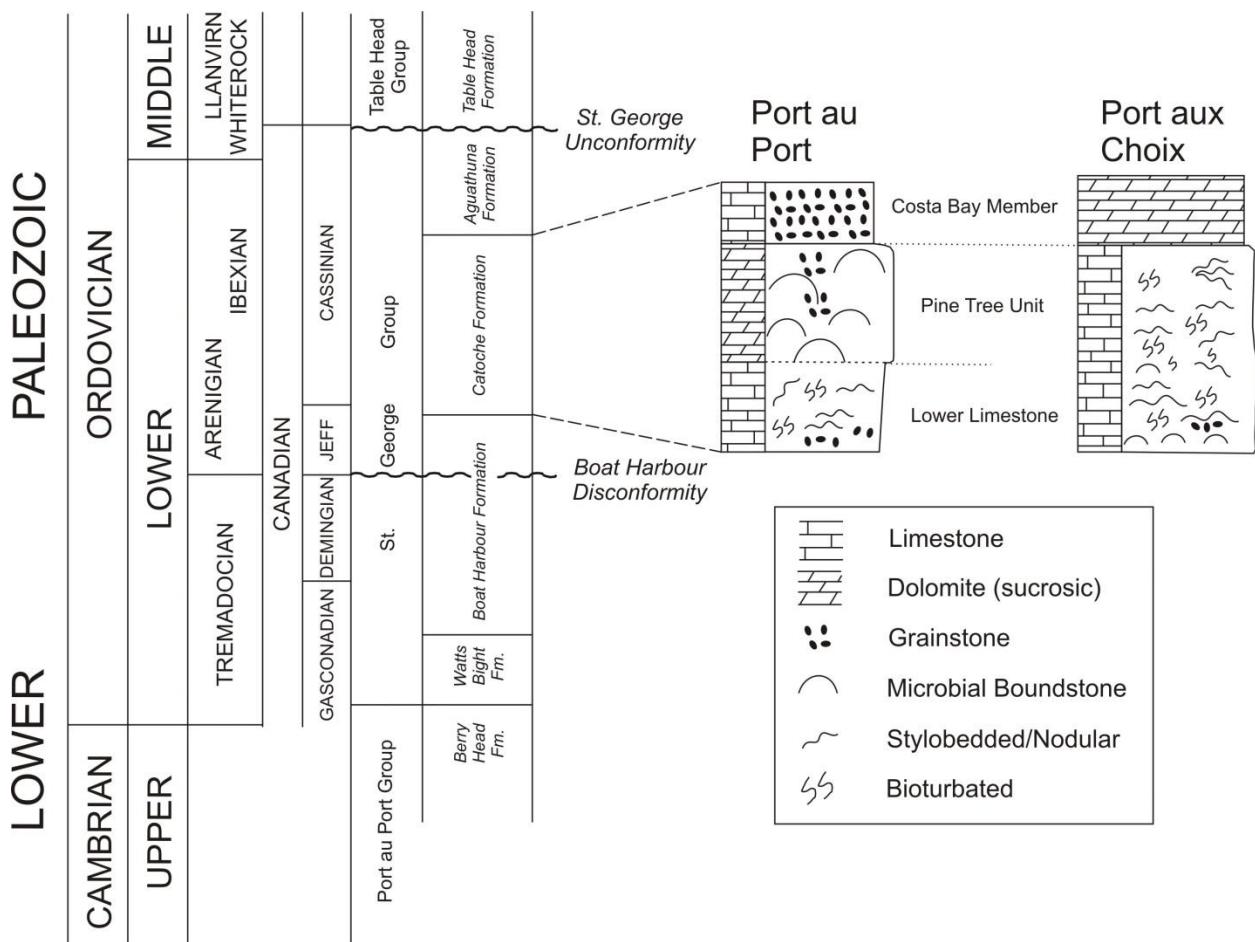
Figure 2: Simplified lithostratigraphy of the St. George Group, with detailed section of the Catoche Formation on the Port au Port and Port aux Choix peninsulas (adapted from Knight et al., 2007).
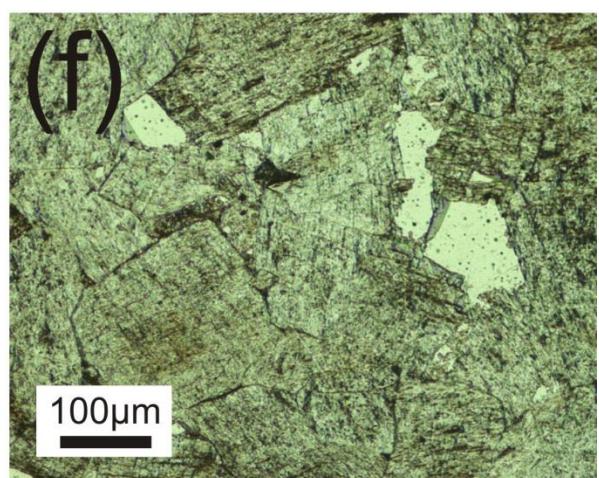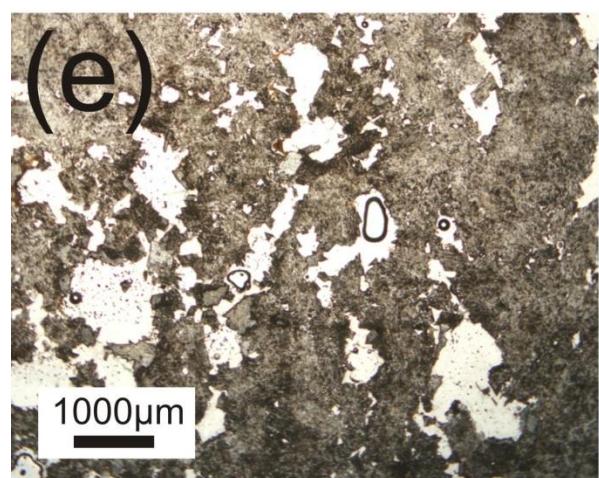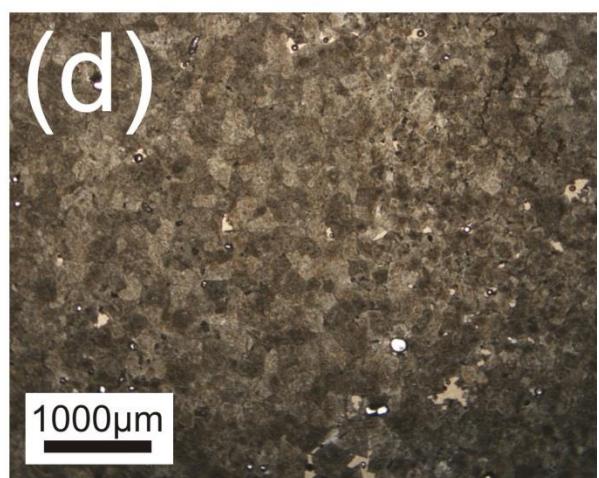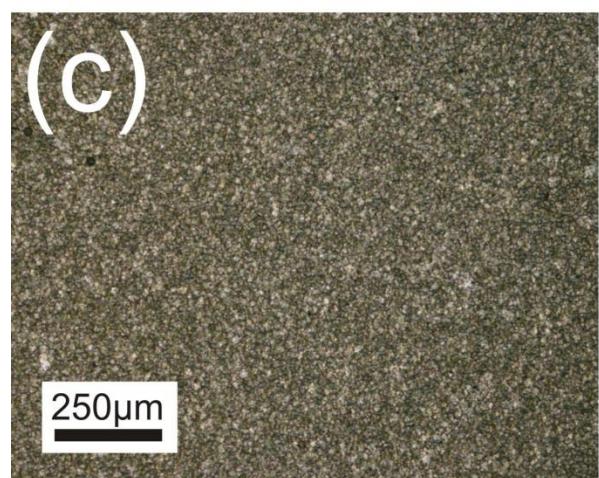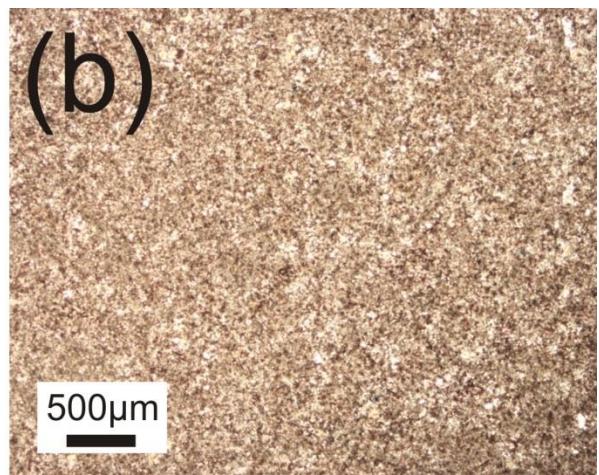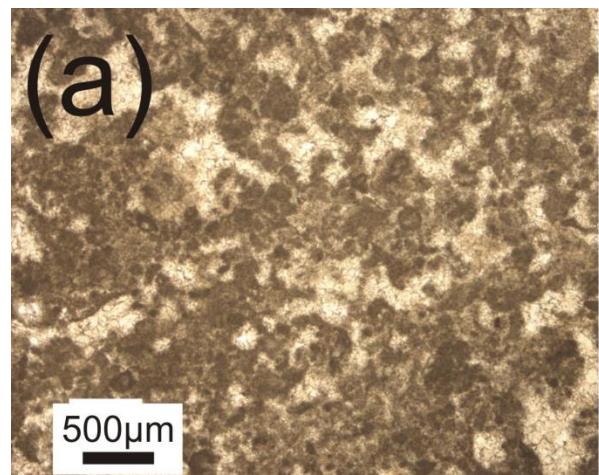
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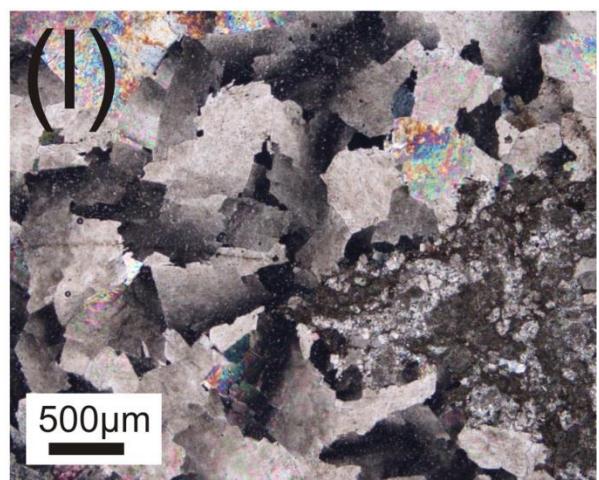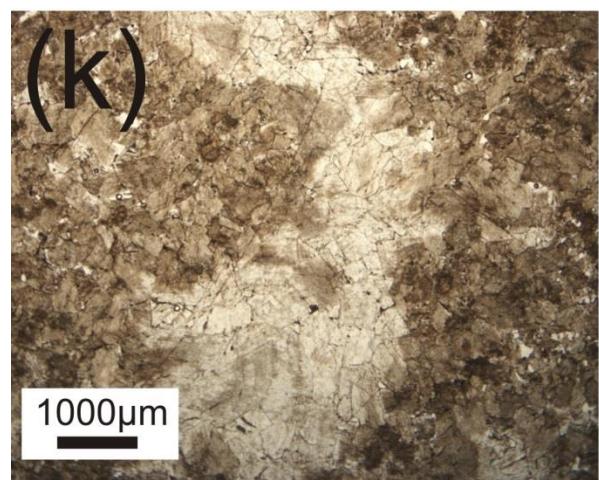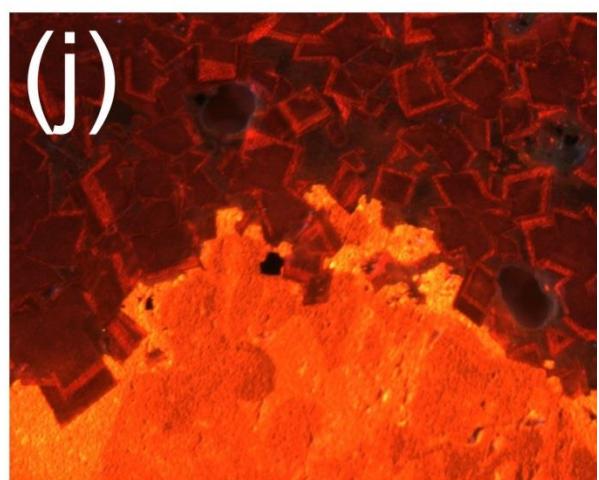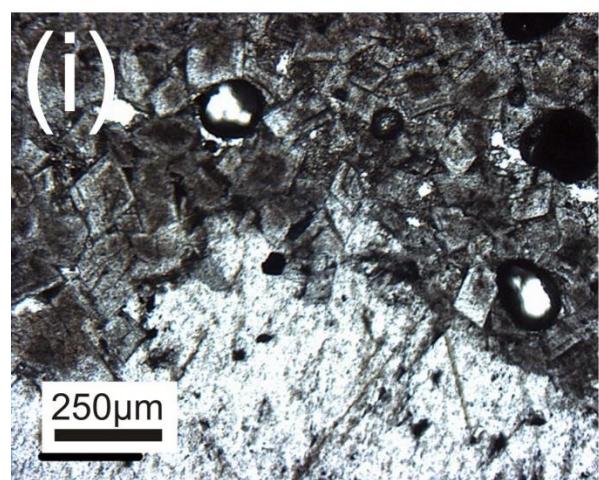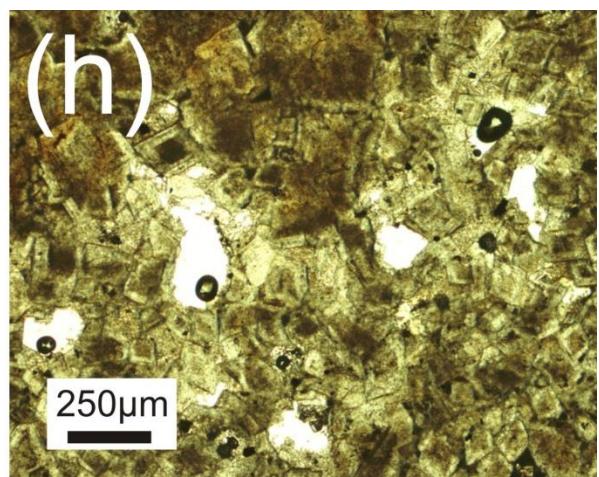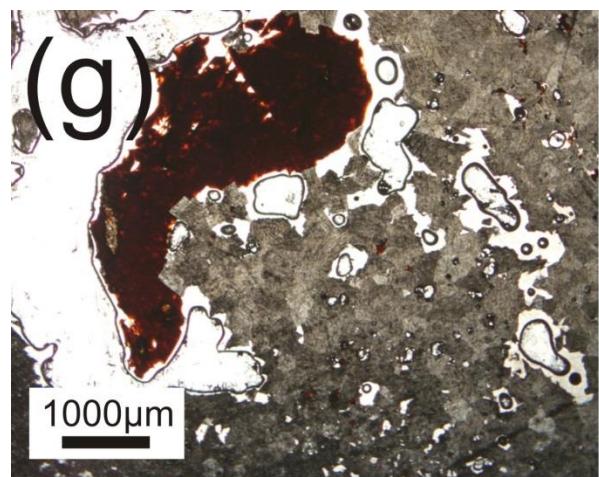
Figure 3b

Figure 3: Photomicrographs of Catoche Formation Carbonates. (a) Peoloidal grainstone with grey C1 calcite after peloids and clear C2 cement (from Port au Port Peninsula); (b) Lime mudstone from Port au Port Peninsula; (c) Fine grained D1 dolomicrite after lime mudstone (from Port au Port Peninsula); (d) Sucrosic D2 dolomite with low porosity (from Port au Port Peninsula); (e) Sucrosic D2 dolomite with low porosity (from Port aux Choix Peninsula); (f) Large zoned D2 rhombs from the Port aux Choix Peninsula; (g) Bitumen infilling vug between D2 dolomite (from Port au Port Peninsula); (h) Zoned D2 dolomite rhombs from the Port au Port Peninsula with intercrystalline porosity; (i) D2 dolomite and C3 calcite infilling vug; (j) Same view as (i) under cathodoluminescence showing zoned orange/red luminescence of D2 dolomite and bright fluorescence of C3 infilling pores; (k) Clear D3 dolomite infilling fracture in D2 dolomite (from Port aux Choix Peninsula); (l) Anhedral D3 saddle dolomite, showing undulose extinction.
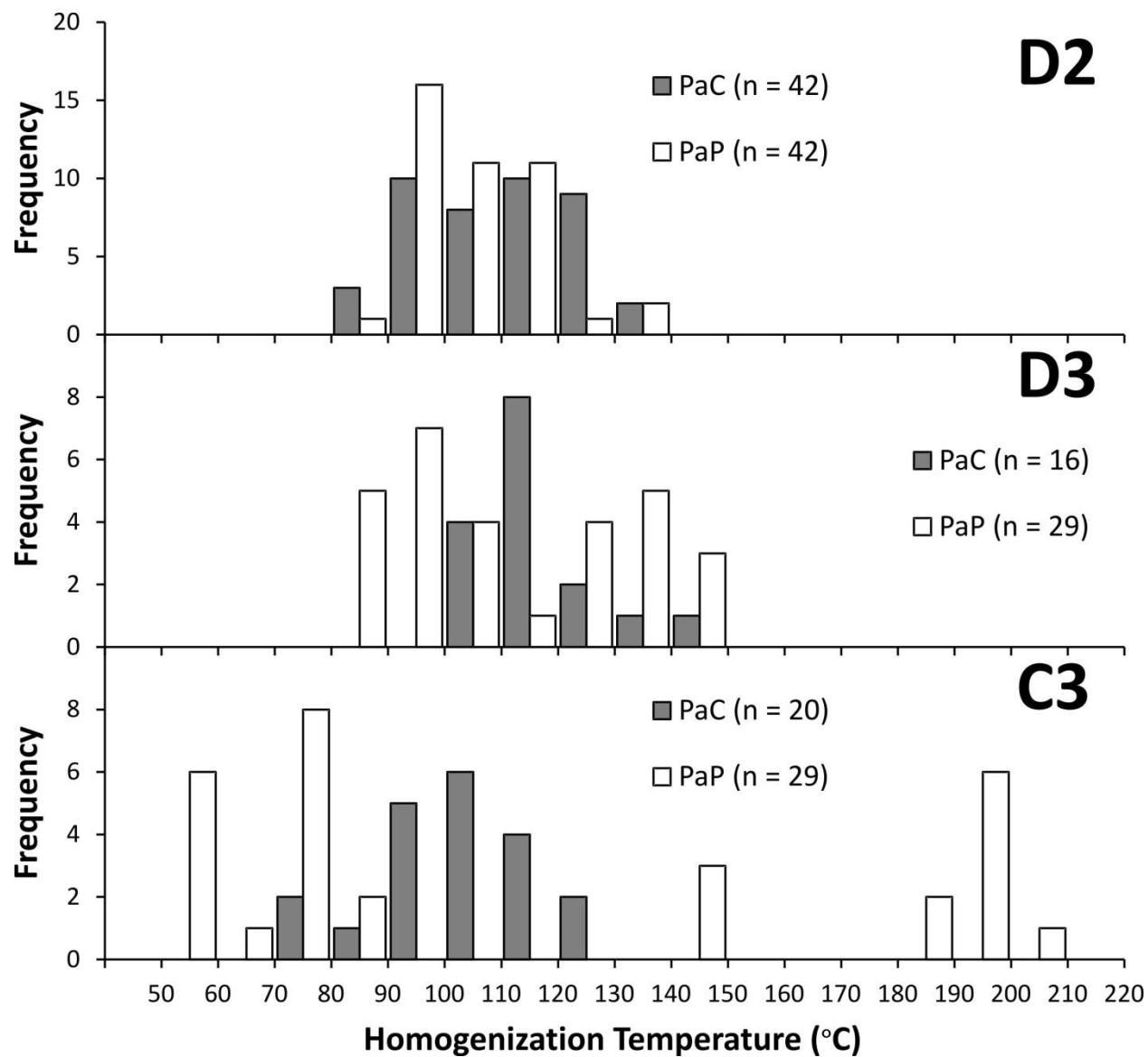
Figure 4: Histogram of homogenization temperatures for fluid inclusions in the D2 and D3 dolomites and C3 calcite of the Catoche Formation. PaC = Port aux Choix Peninsula, PaP = Port au Port Peninsula.
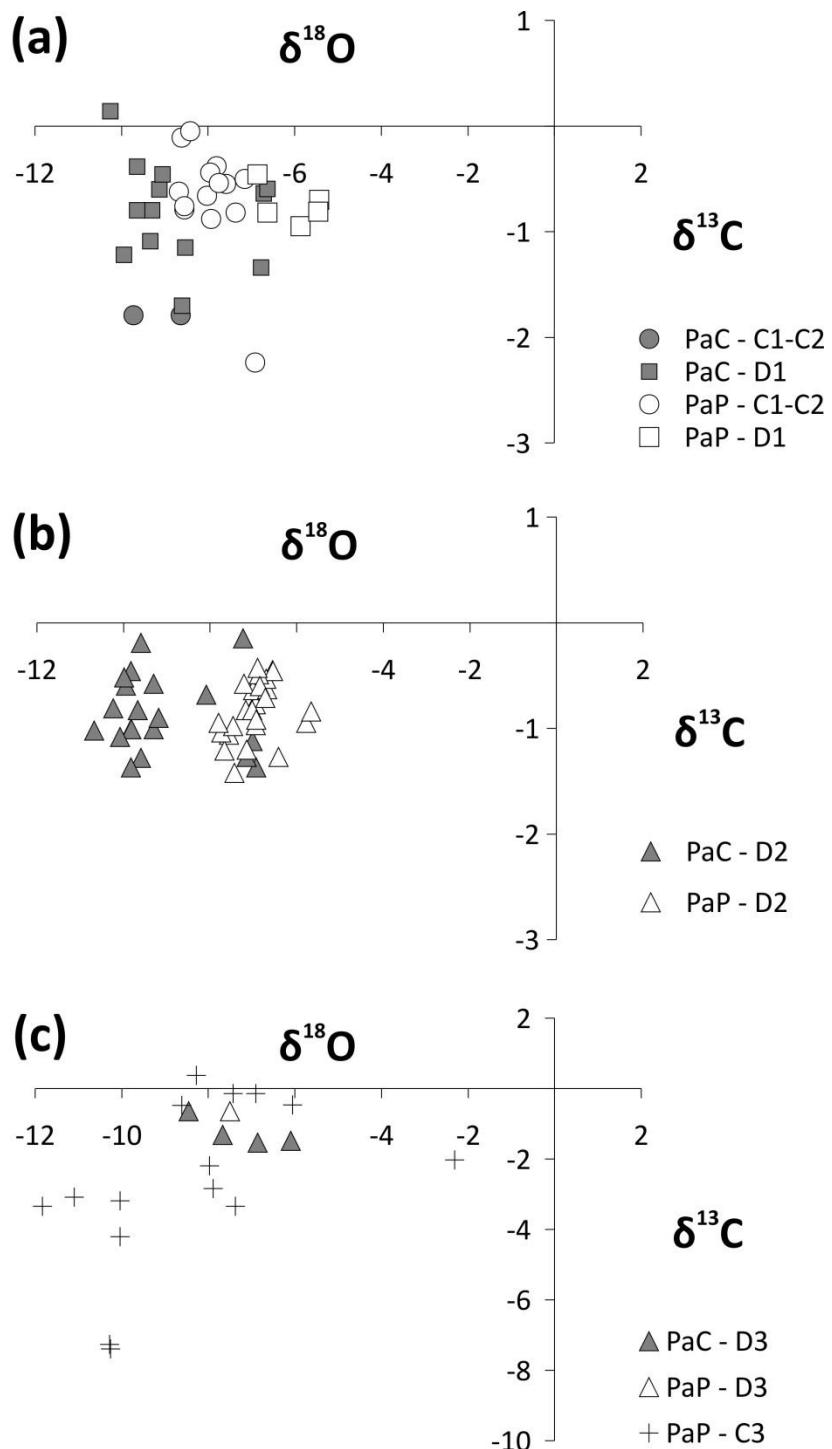
Figure 5: Oxygen vs. Carbon isotope values for: (a) C1-C2 calcite and D1 dolomite; (b) D2 dolomite; and (c) D3 dolomite and C3 calcite. PaC = Port aux Choix Peninsula, PaP = Port au Port Peninsula.
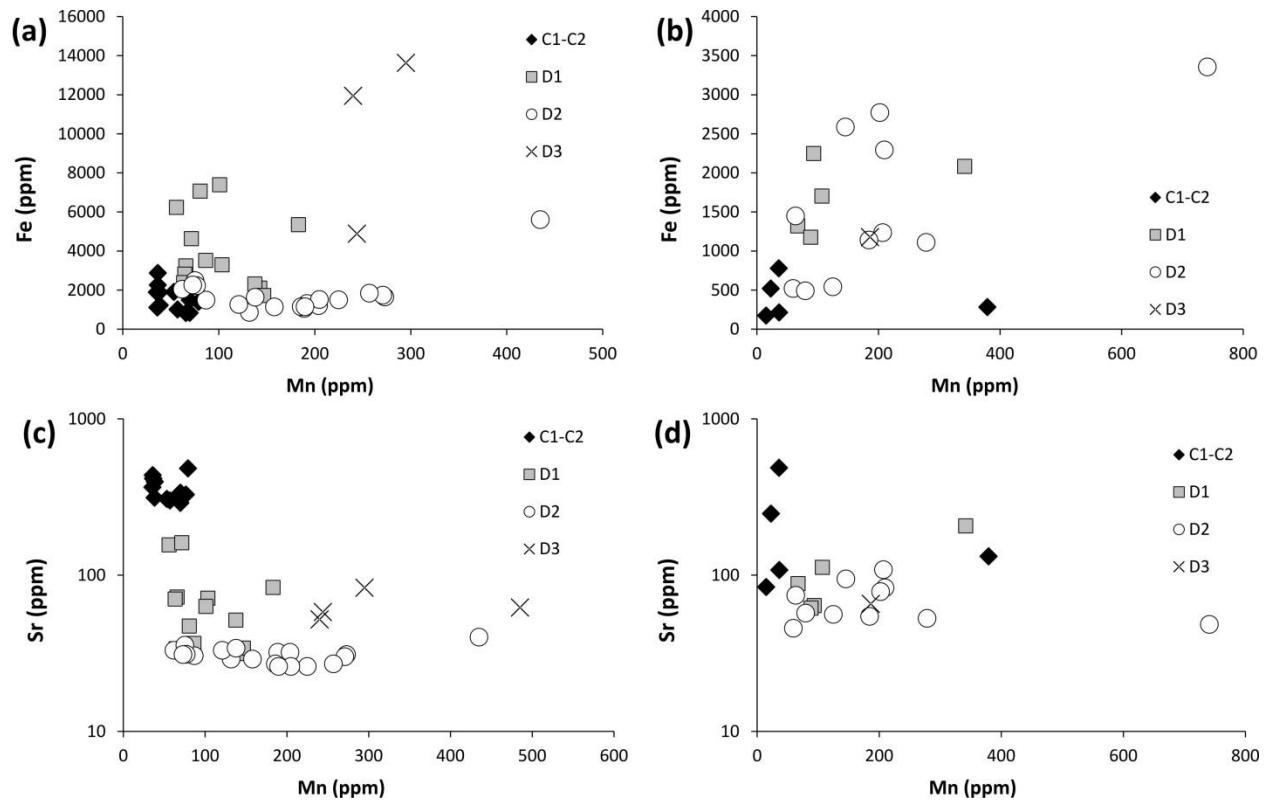
Figure 6: Geochemistry of carbonate phase from the Catoche Formation. (a) Fe vs. Mn from the Port aux Choix Peninsula; (b) Fe vs. Mn from the Port au Port Peninsula; (c) Sr vs. Mn from the Port aux Choix Peninsula; (d) Sr vs. Mn from the Port au Port Peninsula.
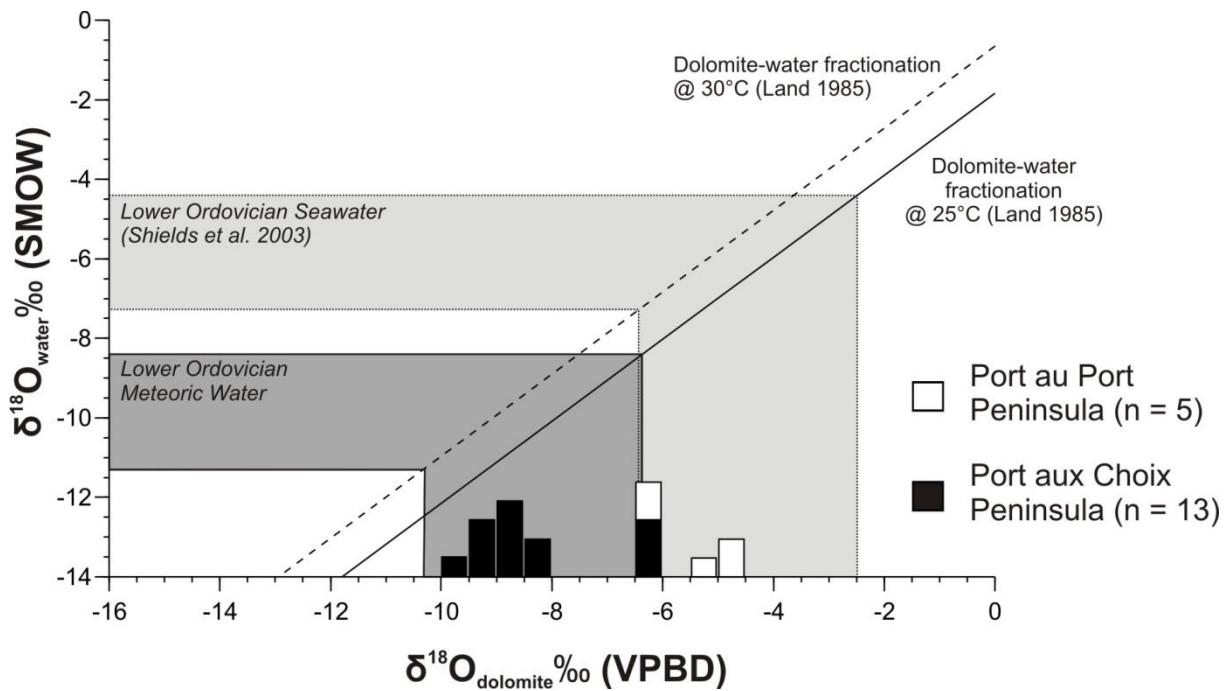
Figure 7: Histogram of oxygen isotope compositions of D1 dolomite from the Port au Port and Port aux Choix peninsulas. These data are plotted on a fractionation diagram showing empirical dolomite-water equations at 25°C and 30°C from Land (1985). Shaded areas mark the composition of Arenig seawater and meteoric water (from Shields et al., 2003). See text for further discussion.
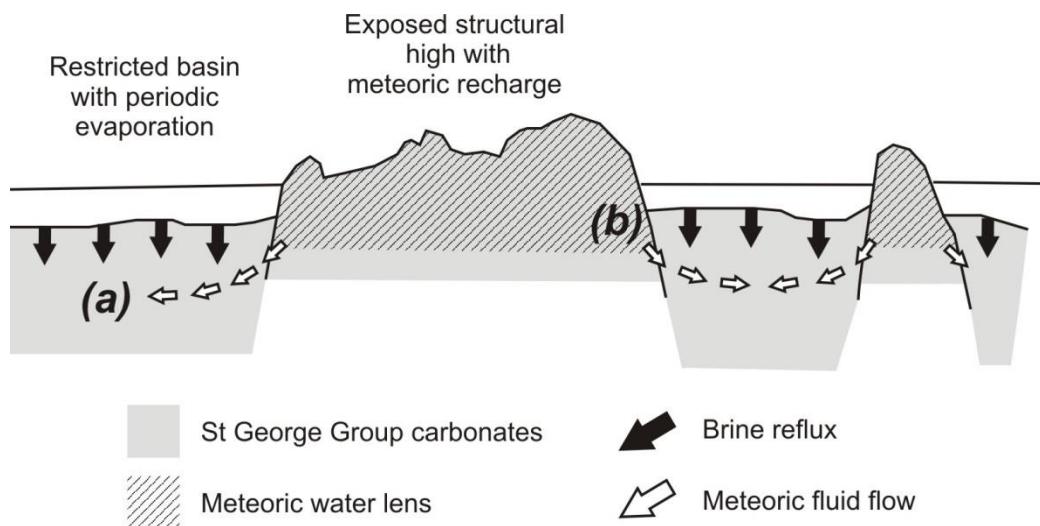
Figure 8: Schematic diagram showing a model of D1 dolomitization in St. George Group carbonates during the deposition of the Aguathuna Formation. (a) Catoche Formation on the Port au Port Peninsula - D1 dolomitization associated with the mixing of post evaporitic brines with meteoric water; (b) Catoche Formation on the Port aux Choix Peninsula – minor mixing zone dolomitization on structural highs.
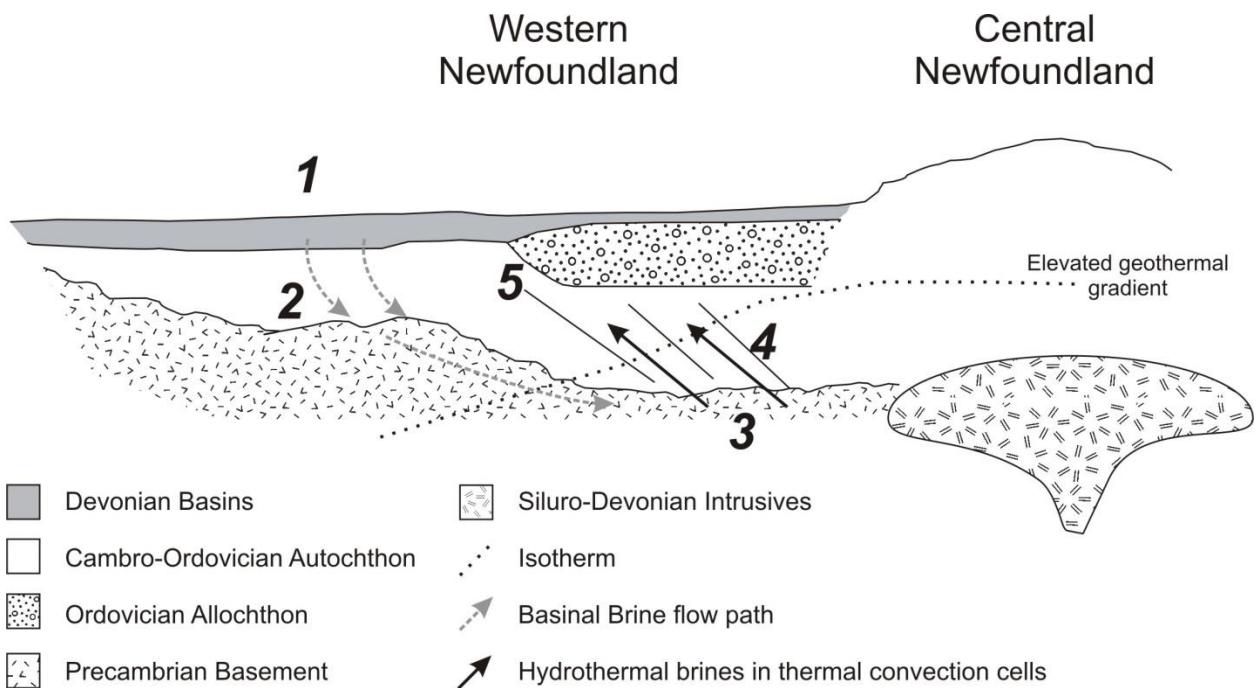
Figure 9: Schematic model of western Newfoundland during the Devonian, illustrating possible fluid flow associated with D2 dolomitization: (1) Evaporation of seawater in shallow foreland basins (Clam Bank Formation); (2) Infiltration of dense post-evaporitic seawater into basement rocks via brine reflux; (3) Circulation of fluids in hydrothermal convection cells, possible riven by heat from Devonian intrusions; (4) Geothermal dolomitization of Catoche Formation buried under Ordovician allochthonous rocks (Port aux Choix Peninsula); (5) Ascent of fluids along extensional faults to shallow crustal levels causing hydrothermal dolomitization (Port au Port Peninsula).

Table 1: Summary of the microthermometric data from D2, D3 and C3 carbonates in the Catoche Formation

Host Mineral		Port au Port Peninsula				Port aux Choix Peninsula			
		T_i (°C)	$T_m$ice (°C)	Eq. wt% NaCl	T_h (°C)	T_i (°C)	$T_m$ice (°C)	Eq. wt% NaCl	T_h (°C)
D2	*Mean*	-49.8	-12.6	16.5	106	-54.9	-19.7	22.0	109
	Max	-49.0	-10.2	19.1	132	-54.2	-13.6	25.5	134
	Min	-50.3	-15.6	14.1	90	-55.3	-24.8	17.4	87
	Stdev	0.7	1.7	1.6	11	0.5	3.4	2.4	13
	n	3	8	8	42	4	17	17	42
D3	*Mean*	-51.0	-17.8	20.7	112	-53.1	-10.1	14.0	118
	Max	-49.6	-11.2	24.5	147	-51.7	-7.8	18.3	140
	Min	-54.5	-23.2	15.2	85	-54.4	-14.6	11.5	109
	Stdev	2.3	3.5	2.7	21	1.0	1.8	1.8	10
	n	4	10	10	29	6	11	11	16
C3	*Mean*	-46.9	-10.2	13.7	116	-52.8	-21.8	23.6	102
	Max	-23.2	-5.0	19.1	205	-51.2	-19.7	25.0	129
	Min	-53.7	-15.6	7.9	52	-55.2	-24.0	22.2	72
	Stdev	13.3	3.9	4.2	60	1.7	1.6	1.1	15
	n	5	20	20	29	5	14	14	20

Table 2: Ca, Mg, Sr, Fe, Mn, $\delta^{13}C$ and $\delta^{18}O$ data for the Catoche Formation on the Port au Port Peninsula

Phase		CaCO$_3$ (%)	MgCO$_3$ (%)	Sr (ppm)	Fe (ppm)	Mn (ppm)	$\delta^{18}O$	$\delta^{13}C$	Fe/Mn
C1-C2	*Mean*	99.4	0.6	211	393	98	-7.9	-0.7	13.0
	Max	99.7	1.2	486	777	379	-6.9	-0.1	23.6
	Min	98.8	0.3	84	174	15	-8.7	-2.2	0.8
	SD	0.4	0.4	166	253	158	0.6	0.5	10.0
	n	5	5	5	5	5	14	14	5
C3	*Mean*	99.1	0.9	122	402	798	-8.4	-2.6	6.8
	Max	99.8	3.2	303	813	2282	-2.3	0.4	40.1
	Min	96.8	0.2	41	109	11	-11.8	-7.4	0.3
	SD	1.0	1.0	87	244	963	2.4	2.4	13.1
	n	8	8	8	8	8	15	15	9
D1	*Mean*	60.9	39.1	106	1706	140	-6.1	-0.7	16.4
	Max	66.0	44.8	206	2248	342	-5.4	-0.5	25.0
	Min	55.2	34.0	61	1175	67	-6.9	-1.0	6.3
	SD	5.0	5.0	60	465	114	0.7	0.2	7.0
	n	5	5	5	5	5	5	5	5
D2	*Mean*	61.7	38.3	68	1589	209	-7.0	-0.8	9.5
	Max	63.7	41.5	108	3354	741	-5.7	-0.4	23.7
	Min	58.5	36.3	46	490	60	-7.8	-1.4	4.1
	SD	1.8	1.8	21	1001	190	0.5	0.3	6.3
	n	11	11	11	11	11	26	26	12
D3	*Mean*	63.0	37.0	65	1178	186	-7.5	-0.6	6.6
	Max								
	Min								
	SD								
	n	1	1	1	1	1	1	1	1

Table 3: Ca, Mg, Sr, Fe, Mn, δ^{13}C and δ^{18}O data for the Catoche Formation on the Port aux Choix Peninsula

Phase		CaCO$_3$ (%)	MgCO$_3$ (%)	Sr (ppm)	Fe (ppm)	Mn (ppm)	δ^{18}O	δ^{13}C	Fe/Mn
C1-C2	*Mean*	97.3	2.7	362	1607	53	-9.2	-1.8	36.1
	Max	98.8	6.1	482	2874	79	-8.6	-1.8	81.8
	Min	93.9	1.2	290	822	36	-9.7	-1.8	12.3
	SD	1.9	1.9	61	626	17	0.8	0.0	21.4
	n	13	13	13	13	13	2	2	13
D1	*Mean*	57.9	42.1	70	4001	100	-8.7	-0.8	49.0
	Max	62.1	45.0	161	7389	183	-6.6	0.1	115.8
	Min	55.0	37.9	31	1721	56	-10.3	-1.7	12.2
	SD	2.0	2.0	43	1939	40	1.3	0.5	31.0
	n	13	13	13	13	13	13	13	13
D2	*Mean*	55.6	44.4	31	1751	178	-9.2	-0.9	13.3
	Max	57.0	46.5	40	5600	435	-6.9	-0.2	34.3
	Min	53.5	43.0	26	853	62	-10.7	-1.4	5.8
	SD	1.0	1.0	4	1008	90	1.2	0.4	10.4
	n	20	20	20	20	20	20	20	20
D3	*Mean*	60.9	39.1	64	14934	316	-7.3	-1.2	45.8
	Max	63.8	40.6	83	29279	485	-6.1	-0.7	62.8
	Min	59.5	36.2	52	4881	240	-8.5	-1.5	20.8
	SD	2.0	2.0	13	10287	115	1.0	0.4	17.8
	n	4	4	4	4	4	4	4	4