Dolomitization: Cambrian and Ordovician Formations in the Huron Domain

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ABSTRACT

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Abstract

A preliminary study has been completed to examine the paleogenesis of strata-bound dolomite found occurring in deep-seated Ordovician and Cambrian sediments on the eastern flank of the Michigan Basin. As part of the study seven samples were analyzed for petrographic, stable and Sr isotopic composition, and fluid inclusion microthermometry to characterise dolomitization. The samples represented a range of host rocks from dolomitized limestones, dolostones, sandy dolostones and sandstones within Ordovician Black River Group and underlying Cambrian formation. The petrographic and geochemical attributes have provided a basis to gain insight on the source fluids that modified these rocks, as well as, the possible timing of formation.

Evidence indicates that the formations were subject to higher temperatures than can be explained by burial history alone. This suggests the occurrence and migration of hydrothermal fluids within the low permeability dolomite horizons, possibly during Paleozoic orogenesis. Calcite fracture infill isotopic and fluid inclusion data point to two possibly isolated diagenetic fluid systems; i) an earlier Cambrian system that is characterized by a more radiogenic, cooler and saline signature; and ii) a later Ordovician system that is characterized by hypersaline, more hydrothermal and a less radiogenic fluid system. The observation of highly discrete, strata-bound dolomites combined with only trace quantities of saddle dolomite and its associated geochemical signature suggest that diagenesis, as a result of hydrothermal fluids, was neither pervasive in volume or extent at the Bruce nuclear site.

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1. INTRODUCTION

The purpose of this report is to conduct a preliminary investigation of the nature and occurrence of dolomitization within the Ordovician age Black River Group carbonates and Cambrian sandstones on the eastern flank of the Michigan Basin. As part of the assessment petrographic, isotopic and fluid inclusion analyses were performed on rock core samples obtained from the Coboconk, Gull River and Cambrian formations underlying the Bruce nuclear site, located near Tiverton, Ontario. The analyses provided complementary data sets with which to explore dolomite mineral paragenesis and conditions occurring during mineralization. This has provided a basis to demonstrate a methodology to assess the phenomena responsible for dolomitization. Further it has provided analogue evidence, particularly in the low permeability Black River Group, which has increased understanding of past fluid movement and temperature on geologic time scales.

2. BACKGROUND

Several models have been suggested to explain the formation of dolomite in a broad range of geologic and geochemical processes. These processes lead to a change in formation density that can alter physical properties of the bedrock, including, increased porosity and permeability. In this sense, dolomitization can influence groundwater system evolution through the creation of permeable pathways following lithification and the possibility of localized geologic structure suitable for the accumulation of hydrocarbons. These models include (Tucker et al., 1990; Machel, 2004); 1) sabkha dolomitization model, 2) seepage-reflux dolomitization model, 3) mixing zone dolomitization model, 4) seawater dolomitization model 5) burial-dolomitization model, and 6) structurally-controlled hydrothermal dolomitization model. It is important to recognize that these dynamic models and their applicability to specific geologic settings are dependent on three main criteria (Machel, 2004): 1) Thermodynamics: the fluids must be supersaturated with respect to dolomite and undersaturated with respect to calcite. Thus, dolomite cement will precipitate and calcite cement will dissolve. 2) Kinetics: the rate of dolomite precipitation must be equal or greater than the rate of calcite dissolution; and 3) Hydrologic System: a source of Mg-rich fluids must be available in the limestone pore system, faults and fractures (Machel, 2004).

Within southern Ontario, recent advances in stable and radiogenic isotopes, trace element geochemistry, fluid inclusion analyses and paleomagnetic techniques have improved the ability to characterise and interpret the paleogenesis of dolomites (e.g. Durocher and Al-Aasm, 1997; Wendte et al., 1998, 2009; Lonnee and Al-Aasm, 2000; Machel and Lonnee, 2002; Cioppa et al., 2003; Morad et al., 2010). Haeri-Ardakani et al., (2013a, b). Based on the integration of petrography, stable isotope, Sr isotope, and rare earth elements (REE) these results suggest that within southwestern Ontario, three dolomite types can be identified in Ordovician carbonates: D1 - formed during early diagenesis from Middle Ordovician seawater and recrystallized during progressive burial, D2 - formed by hydrothermal fluids (68 to 99°C) and late-stage saddle dolomite - D3 related to fault controlled, high temperature fluids (>125°C). They also suggested that reflux of seawater younger than Ordovician dissolved Devonian and Silurian evaporites moved downward through the fracture network by density gradients. Hot brines in the central part of the basin migrated through basal Cambrian sandstone (where present) and ascended through the fracture network and precipitated dolomite and late stage calcite while carrying hydrocarbons. A radially outward fluid flow in Michigan Basin is

consistence with occurrence of Middle Ordovician hydrothermal dolomitization in the periphery of Michigan Basin.

Earlier, Coniglio and Williams-Jones (1992), Middleton et al. (1993), Coniglio et al. (1994) indicated that Middle to late Ordovician subtidal carbonates in the Manitoulin area are predominantly limestone, but non-ferroan and ferroan dolomite is a common cement, as well as pervasive replacement dolomite phase. They distinguished cap dolomite and fracture-related saddle dolomite in Trenton and Black River groups in the subsurface. They also suggested that the latter type of dolomite formed from a saline (24-41 wt% NaCl eq.) with temperatures range from 100 to 200°C. The fluid inclusion temperatures obtained by their investigations are higher than the temperatures generated during peak burial (70°C). They suggested that compaction-driven fluids as one of possible fluid sources for fracture-related dolomitization. Upward and lateral movement of Mg-bearing fluids resulting from transformation of clay minerals, originating from younger, older or correlative argillaceous sediments from deeper in the Michigan and Appalachian basins towards the basin margin was considered as a mechanism for migration of dolomitizing fluids (Coniglio and Williams-Jones, 1992; Middleton et al., 1993; Coniglio et al., 1994). Yoo et al. (2000) also considered compaction-driven flow as a working mechanism to carry mass and heat from Michigan Basin.

It is with this knowledge that this study has been devised and was developed to apply complementary techniques to assess dolomitization and gain insight on the phenomena responsible. Where possible a comparison is drawn to dolomitization observed elsewhere in the Paleozoic sediments of the Michigan and Appalachian sedimentary basins as they occur in southwestern Ontario.

3. SAMPLES AND METHODOLOGY

Seven samples from the Ordovician Coboconk and Gull River Formations and basal Cambrian are characterized as listed in Table 1. The location of these samples within the sedimentary stratigraphic column beneath the Bruce nuclear site is shown in Figure 1. The Ordovician carbonate samples were selected purposefully from discrete rock core sections in which dolomite had been identified. The Cambrian samples were chosen from a combination of core logs and where mineral alteration was observed visually.

	Cored Sample	Formation	Age	Depth (m)
1	DGR3 CR 263	Coboconk	Ordovician	790.48
2	DGR3 CR 275	Gull River	Ordovician	829.22
3	DGR4 CR 266	Gull River	Ordovician	825.00
4	DGR4 CR 253	Coboconk	Ordovician	778.29
5	DGR6 CR 239	Coboconk	Ordovician	773.46
6	DGR3 CR 285	Cambrian	Cambrian	856.80
7	DGR3 CR 291	Cambrian	Cambrian	867.47

Table 1: Sample Identification and Depths of Dolomite Samples

Yellow denotes samples taken from the "Tan Dolomite" marker bed - A key marker horizon described in the Descriptive Geosphere Site Model (INTERA, 2011).

These core samples were examined and photographed prior to their selection for making thin section and fluid inclusion wafers. Petrographic examination of thin sections was performed under a standard petrographic microscope in order to compliment core descriptions and by cathodoluminescence microscopy (CL) using a Technosyn cold cathodoluminescence stage with a 12-15 kV beam and a current intensity of 0.42-0.43 mA. Oxygen and carbon isotopes were extracted from calcite and dolomite samples (n=25) that were obtained using a microscope mounted drill assembly. The samples were reacted in vacuum with 100% pure phosphoric acid for four hours at 25° and 50°C for calcite and dolomite, respectively. CO₂ gas from samples that contained a mixture of calcite and dolomite was extracted using the chemical separation method of Al-Aasm et al. (1990). The evolved CO₂ gas was analyzed for isotopic ratios on a Delta Plus mass spectrometer. Delta (δ) values for oxygen and carbon are reported in per mil (‰) relative to the PeeDee Belemnite (VPDB) standard. Precision was better than 0.05‰ for both δ^{18} O and δ^{13} C.

For Sr-isotopic determinations 9 microsamples were selected for analyses. These samples represent various calcitic and dolomitic components. Prior to analysis, powdered samples were extracted employing a microscope-mounted drill assembly to extract 1-10 mg of powdered calcite or dolomite from polished slabs. Care was taken to avoid contamination from other components such as later cement fill. These samples were initially dissolved in 2.5 N HCl suprapure for 25 hours in sealed PFA vessels at room temperature. Then they passed through cation exchange quartz columns. In order to remove the eventual pore salts that may contain Sr, these samples were, after crushing and pulverization were washed twice with MilliQ water. Strontium isotopic ratios were measured on a Finnigan MAT 261 mass spectrometer. All analyses were performed in the static multicollector mode using Re filaments. NBS and ocean water were used as standard references and ⁸⁷Sr/⁸⁶Sr ratios were normalized to ⁸⁷Sr/⁸⁶Sr= 8.375209. The mean standard error was 0.00003 for NBS-987.

Seven samples were analyzed for fluid inclusion microthermometric studies. Workable fluid inclusions were found in five samples. Petrographic work was done with a conventional petrographic microscope. Microthermometric analysis was conducted with using a Linkam THMGS600 heating-freezing stage, which was calibrated using synthetic fluid inclusions of known compositions. Homogenization temperatures (Th), halite-melting temperatures (Tm-halite) and ice-melting temperatures (Tm-ice) were measured with a precision (reproducibility) of $\pm 1^{\circ}$ C, $\pm 1^{\circ}$ C and $\pm 0.1^{\circ}$ C, respectively. The microthermometric results are listed in Table 2. The location and occurrences of fluid inclusions examined, together with the raw microthermometric data, are shown in the Appendix for each sample.

The low first melting temperatures and ice-melting temperatures suggest that the fluid within the fluid inclusions may approximate a H_2O -NaCl-CaCl₂ system. The salinities for inclusions in which ice was the last melting phase were calculated with the program of Chi and Ni (2007), and those for inclusions with hydrohalite as the last melting phase was done with the program of Steele-MacInnis et al. (2011). The following steps were followed in the course of micro-thermometric analyses of the fluid inclusions:

- (i) Careful and detailed petrographic examination of size, occurrence habit, and paragenetic contexts of the fluid inclusions in the double polished wafers. Distinction was made between primary, secondary, pseudo-secondary fluid inclusions.
- (ii) Determination of the number of phases (i.e., the liquid to vapor ratio) and their ratios entrapped in each of the fluid inclusions.

- (iii) Determination of the composition (aqueous or hydrocarbon fluids) of the inclusion using fluorescence microscopy; most oil-filled inclusions fluoresce, while the aqueous inclusions do not.
- (v) Micro-thermometric measurements of the homogenization (T_h) and final ice melting temperatures (Tm_{ice}) of fluid inclusions.

Deformation of inclusion walls, necking-down of single inclusions into smaller inclusions, or leakage of fluid can all lead to changes in homogenization temperature. To limit the possibility of measuring deformed aqueous inclusions, only primary inclusions from the same field of view were measured during a single heating or freezing run. By restricting measurements to inclusions within the same field of view, any sudden changes in liquid/vapor ratios due to inclusion deformation could be observed, and removed from consideration. Heating runs were conducted before freezing runs to reduce the possibility of inclusion stretching by freezing (Lawler and Crawford, 1983).



Figure 1: Stratigraphy at the Bruce Nuclear Site with sample location points indicated. (Adapted from AECOM, 2011)

4. **RESULTS**

4.1 PETROGRAPHIC ANALYSIS OF CORED SAMPLES

The diagenetic history of the Ordovician Black River Group and the Cambrian carbonates includes calcite and anhydrite cementation, mechanical and chemical compaction, dissolution, silicification, and dolomitization. It is believed that these diagenetic processes occurred during depositional - related burial in the Paleozoic. A brief description of these diagenetic processes will be presented from the more shallow Coboconk formation to the deeper Cambrian.

<u>Coboconk Formation:</u> The original depositional facies of the formation consists of nodular, bioturbated, micritic facies - now partly dolomitized. A thin fossiliferous layer (grainstone facies) occurs with a sharp contact with the nodular facies. This layer may represent a transition in the depositional system such as a maximum flooding surface, which hence represents a sequence boundary. This layer is also pervasively dolomitized. Skeletal components include bryozoans and echinoderms. These components are recrystallized, dolomitized and show evidence of dissolution as well. Minor hairline fractures are occluded by equant calcite and dolomite cement, which under cathodoluminescence (CL) shows non- to dull CL characteristics (Figs. 3, 5). Some of the allochems were silicified. The silica replacement also observed in some facies within the cored sample. The silicification occurs early replacing part of the muddy calcitic facies, with dolomite (D1) replacing the silicified micrite and fossils.

Very minor anhydrite cement occludes some vuggy pores and are partly replaced by coarse crystalline dolomite. Two principle types of replacive dolomite are recognized: 1) fine crystalline dolomite with crystal size ranging from 25 to 50 μ m (D1), replacing skeletal grains and micrite. 2) replacive matrix dolomite (D2) is fabric destructive and replaces micrite (intranodule). D2 dolomite is volumetrically more abundant than D1. It consists of tightly packed planar-e to planar-s with crystal size ranging from 50 μ m to about 500 μ m, showing non to vey weak dull CL (Figure 5). A very minor presence of saddle dolomite occluding pores and postdates D1 and D2. Stylolites cut across D2, which suggest that D2 formed prior to apprecible chemical compaction.

<u>*Gull River Formation:*</u> This formation is characterized by a nodular, bioturtabed facies. The matrix is highly dolmitized by replacive, euhedral dolomite (D1). However, coarse, euhdral dolomite (D2) that is partly zoned also replaces the matrix (Figs. 8, 9, 10, 11). The intranodule matrix is composed of medium crystalline, zoned, euhdral to subhedral dolomite (D2), which cut by stylolites. Under CL, this dolomite shows non- to very dull CL charateristics. Fossils, such as brachiopods, crinoids and trilobites are dolomitized but their textural integrity is preserved. Coarse, equant calcite cement occludes molds and vugs and shows bright CL. A large fracture is observed where it is occluded by saddle dolmite and succeded by large, equant calcite cement (Figure 12).

<u>Cambrian strata:</u> Cambrian cored sections are charaterized by sandstone and dolostone facies. The dolostone facies is characterized by dolograinstone with large fossils (now dolomitized), such as crinoids, bryozoans and unidentified rounded allochems (Figs. 13-16). The dolomite is medium to coarse crystalline, anhedral and shows dull CL (Figure 14-16). Fractures are occluded by corase, aquant calcite cement with strong, bright CL (Figure 16) and in the sandy facies, which has large detrital quartz cemented by carbonates with bright, red CL.



DGR-4 CR-253 (1) Coboconk



DGR-3 CR-263 (2) Coboconk



DGR-4 CR-253 (1) Coboconk



DGR-3 CR-263 (2) Coboconk

Figure 2: Petrographic features of the Coboconk Formation. (A) Optical photomicrographs (PPL) showing intranodular dolomite. The surrounding matrix is micritic with scattered, euhedral microdolomite rhombs. (B) Scattered, euhedral microdolomite replacing bioturbated, silicified matrix. (C) Zoned, medium crystalline dolomite replacing micritric matrix. (D) Coarse euhedral dolomite cement occluding a pore space. Note the medium crystalline, subhedral matrix dolomite



Figure 3: Petrographic features of the Coboconk Formation. (A) Optical photomicrographs (PPL) showing intranodular dolomite. The surrounding matrix is micritic with scattered, euhedral microdolomite rhombs. (B) Same sample under CL. The medium crystalline dolomite inside the nodule is showing dull to non-luminescent while the surrounding internodule matrix has red CL. (C) PPL of the matrix dolomite. (D) The same sample under CL showing the variation in CL intensity in the matrix





DGR-3 CR-263 (2)



DGR-3 CR-263 (2)

Figure 4: Petrographic features of the Coboconk Formation. (A) PPL of intranodule medium crystalline dolomite with calcite cement infilling a vug. (B) Fractures occluded by calcite cement. Note also stylolite cross cutting matrix dolomite. (C) Skeletal fragments replaced by silica. (D) Skeletal components that are silicified early in the diagenetic history



Figure 5: Petrographic features of the Coboconk Formation. (A) Skeletal components showing also syntaxial overgrowth cement. (B) CL image of the same sample as in A showing the bright red CL of the cement and the dark to non-CL of the skeletal fragments. (C) Medium crystalline dolomite and micritic host rock. (D) Same rock under CL. Note the dark to non-CL of the dolomite and the bright CL of the micritic matrix. (E) Hairline fracture, host rock and dolomite matrix. (F) Same under CL. Note the varying intensity of the different components



DGR-3 CR-263 (3) Coboconk

Figure 6: Petrographic features of the Coboconk Formation. (A) Late anhydrite cement filling a vug. Note the medium crystalline matrix dolomite. (B) PPL of medium to coarse crystalline dolomite and later vug-filling euhedral dolomite. (C) Silicified skeletal fragments in the matrix. (D) Vug-filling coarse saddle dolomite. (F) PPL of silicified skeletal components in the grainstone facies. (F) XPL of silicified skeletal components in the grainstone facies



Figure 7: Petrographic features of the Coboconk Formation. (A) PPL of silicified skeletal facies in the formation. (B) XPL of the same rock showing two generations of quartz cement in the allochem. (C) PPL of silicified facies. (D) XPL of the same section as in C showing microdolomite replacing silicified matrix



Figure 8: Petrographic features of the Gull River Formation. (A) PPL of the internodule matrix and the intra-nodule fine crystalline dolomite. Note also the coarse dolomite filling fracture. (B) PPL of medium crystalline, euhedral intra-nodule dolomite. (C) Nodular facies with micritic matrix cut with stylolites. (black fractures) (D) Selective dolomitization in the matrix and associated with stylolites



Figure 9: Petrographic features of the Gull River Formation. (A) PPL of the dolomitized nodular facies. (B) Same section under CL. Note the later generation of cement with bright CL occluding hairline fracture



Figure 10: Petrographic features of the Gull River Formation. (A) PPL of skeletal components replaced by medium crystalline dolomite. (B) Medium crystalline matrix dolomite replacing also the fossil. The dolomite has a dark core and bright outer rim. (C) Medium and coarse crystalline matrix dolomite. (D) Medium crystalline matrix dolomite and later calcite cement in fossil chamber



Figure 11: Petrographic features of the Gull River Formation. (A) Stylolite post-dates cemented hairline fractures. The micritic matrix is dolomitized. (B) Stylolite postdate medium crystalline matrix dolomite. (C) Medium crystalline matrix dolomite and dolomitized fossil. Micrite infills fossil chamber. (D) Medium crystalline matrix dolomite



Figure 12: Petrographic features of the Gull River Formation. (A) Coarse equant calcite cement occluding a fracture. (B) Medium to coarse crystalline dolomite replacing the matrix. (C) Multiple CL zonation in the calcite cement under CL. (D) Dull CL in medium and coarse dolomite. The micritic matrix shows a brighter CL



Figure 13: Petrographic features of Cambrian facies. (A) XPL of dolomitized grainstone facies. Note the fracture filled calcite partly replaced by medium crystalline dolomite rhombs. (B) PPL of dolomitized grainstone facies with calcite cement in vugs. (C) Coarse crystalline, inclusion-rich dolomite replacing calcite cement. (D) Medium crystalline subhedral matrix dolomite



Figure 14: Petrographic features of the Cambrian facies showing both respective PPL and CL images of matrix dolomite and calcite cement in fractures. Note the bright CL characteristics of the calcite cement and the dull CL of matrix dolomite



Figure 15: Petrographic features of the Cambrian facies. (A and B) sandy dolostone facies under PPL and XPL



Figure 16: Petrographic features of the Cambrian facies. PPL and CL images showing both respective PPL and CL images of matrix dolomite and calcite cement in fractures. Note the bright CL characteristics of the calcite cement and the dull CL of matrix dolomite



Figure 17: Petrographic features of the Cambrian facies showing dolomitized matrix by coarse, inclusion-rich dolomite that also show some zoning. The original facies could have been fossiliferous, now dolomitized



Figure 18: Petrographic features of the Cambrian facies showing (A) dolomitized matrix by coarse, inclusion-rich dolomite that also show some zoning. The original facies could have been fossiliferous, now dolomitized. (B) Same section under CL showing the dull to slightly bright CL for the matrix dolomite and the fracture fill, bright calcite cement

4.2 STABLE AND RADIOGENIC ISOTOPIC ANALYSIS

The stable carbon, oxygen and Sr isotopic compositions of the dolomitic and calcitic components of the cored samples are plotted in Figures 19, 20 and 21 (see also Table 2). The dolomitic components represent different generations of dolomite including replacive matrix dolomite D1, D2 and saddle dolomite. The calcitic components include micritic matrix phase, as well as later cement that occludes vugs and fractures.

Fine crystalline (micro) dolomite (D1) δ^{18} O values range from -6.62 to -10.77‰ VPDB and δ^{13} C values from 1.14 to -3.72‰ VPDB. Medium to coarse crystalline (D2) dolomite δ^{18} O values vary from -6.48 to -16.91‰ VPDB and δ^{13} C values from 1.55 to -5.85‰ VPDB. Saddle dolomite cement yields δ^{18} O value of -10.71 ‰ VPDB and δ^{13} C value of -4.21 ‰ VPDB. Calcitic matrix in the Coboconk Formation shows isotopic values varying from -6.12 to -7.79 ‰

VPDB for oxygen and 0.62 to 0.5 % VPDB for carbon. Late-stage vug-filling calcite δ^{18} O values vary from -7.92 to -14.73% VPDB and δ^{13} C values vary from -0.24 to -6.8% VPDB.

In terms of relative age/formation grouping, Figure (20) illustrates the relationship between oxygen and carbon isotopic composition of the three investigated formations. There is a clear overlap in isotopic composition between the Gull River and Coboconk formations. In contrast, the Cambrian dolomite shows more depleted values in both oxygen and carbon isotopes.

In all analyzed dolomite samples from both Cambrian and Ordovician samples, these dolomites differ in their oxygen isotopic signatures from the postulated values for dolomite precipitated with Ordovician and Cambrian dolomites, respectively (Veizer et al, 1999; Land, 1983). This raises the possibility that dolomitized material in the Cambrian sandstones may have a separate thermal history to the Ordovician carbonates through either a packaging (partitioning) of the Cambrian sandstones, or overprinting at a later date by a separate fluid.



Figure 19: Cross plot of $\delta^{13}C_{VPDB}$ versus $\delta^{18}O_{VPDB}$ values of different generations of dolomite and of matrix calcite and cement. Note the overlap in many values and the departure from the postulated values for respective seawater composition.



Figure 20: Cross plot of $\delta^{13}C_{VPDB}$ versus $\delta^{18}O_{VPDB}$ values of dolomite from the three age groups. Note the negative correlation between the C- and O-isotopic values of the Cambrian dolomite. The two arrows show the possible trends for the Ordovician vs. the Cambrian samples

Selected dolomite and calcite from all the three formations were analyzed for ⁸⁷Sr/⁸⁶Sr ratios (Table 2, Figure 21). These samples encompass fine crystalline matrix dolomite (D1), medium to coarse crystalline matrix dolomite (D2), and coarse calcite cement. Samples of matrix dolomite yields ⁸⁷Sr/⁸⁶Sr ratios ranging from 0.70813 to 0.71015. Later precipitated calcite cement show more radiogenic ratios (0.71006). Some of the Coboconk and Gull River samples fall very close to the Ordovician seawater Sr isotopic signature. However, others and Cambrian carbonates are more radiogenic than the postulated values for seawater at that time (Veizer et al, 1999).



Figure 21: Cross plot of δ^{18}_{VPDB} versus ${}^{87}Sr/{}^{86}Sr$ ratios values of carbonate components from the three investigated formations. Cambrian samples and some of the Coboconk dolomite show departure from the postulated ratios for marine carbonates at their respective ages. This reflects a younger relative age for the precipitation of these cements and/or more radiogenic attributes

Sample	Well – Core	Lithology	Age/Formation	$\delta^{13}C_{VPDB}$	$\delta^{18}O_{VSMOW}$	$\delta^{18}O_{VPDB}$	Sr ⁸⁷ /Sr ⁸⁶
ID	run			(‰)	(‰)	(‰)	
8-1	DGR3-CR285	vug-filling calcite	Cambrian	-4.00	16.67	-13.81	
8-2	DGR3-CR285	Medium crystalline dolomite (D2) matrix	Cambrian	-1.76	22.71	-7.95	
8-3	DGR3-CR285	vug-rimming saddle dolomite	Cambrian	-4.21	19.87	-10.71	
11-1	DGR3-CR291	algal laminated microdolomite (D1)	Cambrian	-3.18	19.80	-10.77	0.709770
11-2	DGR3-CR291 Poiklotopic calcite cement		Cambrian	-6.80	15.72	-14.73	
11-3	DGR3-CR291	micro to medium crystalline dolomite in sandy matrix	Cambrian	-4.80	13.48	-16.91	
9-1	DGR3-CR285	vug-filling calcite	Cambrian	-3.75	17.07	-13.43	0.710060
9-2	DGR3-CR285	micro to medium crystalline dolomite matrix	Cambrian	-5.85	21.15	-9.47	
9-3	DGR3-CR285	medium crystalline dolomite matrix, less saddle	Cambrian	-2.15	23.74	-6.95	0.710159
101	DGR3-CR285	micro to medium crystalline dolomite	Cambrian	-3.72	22.96	-7.71	
102	DGR3-CR285	medium crystalline dolomite (D2) matrix	Cambrian	-2.96	22.45	-8.20	
2-1	DGR3-CR263	coarse crystalline dolomite (D2) tabular body	Coboconk	0.57	21.53	-9.10	0.708135
2-2	DGR3-CR263	fine crystalline internodule matrix (D1)	Coboconk	-0.55	21.03	-9.58	

 Table 2: Isotopic analysis of Ordovician and Cambrian carbonates

Sample	Well – Core	Lithology	Age/Formation	$\delta^{13}C_{VPDB}$	δ ¹⁸ Ovsmow	$\delta^{18}O_{VPDB}$	Sr ⁸⁷ /Sr ⁸⁶
ID	run			(‰)	(‰)	(‰)	
2-2	DGR3-CR263	fine crystalline internodule matrix (D1)	Coboconk	-0.55	21.03	-9.58	
2-2	DGR3-CR263	fine crystalline internodule matrix (D1)	Coboconk	-0.55	21.03	-9.58	
2-4	DGR3-CR263	internodule calcite matrix	Coboconk	0.50	24.60		
2-5	DGR3-CR263	Coarse calcite cement	Coboconk	0.06	22.94		
1-1	DGR4-CR253	fine crystalline internodule matrix (D1)	Coboconk	0.46	21.32	-9.30	
1-2	DGR4-CR253	Medium crystalline dolomite nodule (D2)	Coboconk	1.21	24.23	-6.48	
1-3	DGR4-CR253	inclusion-rich medium crystalline dolomite layer (D2)	Coboconk	1.55	21.96	-8.68	
1-4	DGR4-CR253	Internodule calcite matrix	Coboconk	0.62	22.87		
12-1	DGR6-CR239	microdolomite, selective replacive (D1)	Coboconk	1.14	20.61	-9.99	0.709564
3-1	DGR3-CR263	white dolomitic marker unit fossiliferous silicified	Coboconk	-0.55	18.04	-12.48	0.710000
5-1	DGR4-CR266	nodular medium crystalline matrix dolomite (D2)	Gull River	0.64	23.87	-6.83	0.708466
5-2	DGR4-CR266	fine crystalline internodular dolomite matrix (D1)	Gull River	-0.23	21.53	-9.09	0.708180
5-2	DGR4-CR266	fine crystalline internodule dolomite matrix (D1)	Gull River	-0.23	21.53	-9.09	0.708180
61	DGR3-CR275	Coarse blocky calcite cement filling vug	Gull River	-0.24	22.74	-7.92	
62	DGR3-CR275	Medium crystalline dolomite (D2)	Gull River	1.05	22.90	-7.77	

Table 2: Isotopic analysis of Ordovician and Cambrian carbonates

Sample	Well – Core	Lithology	Age/Formation	$\delta^{13}C_{VPDB}$	δ ¹⁸ Ovsmow	$\delta^{18}O_{VPDB}$	Sr ⁸⁷ /Sr ⁸⁶
ID	run		_	(‰)	(‰)	(‰)	
63	DGR3-CR275	microdolomite replacive (D1)	Gull River	0.74	24.08	-6.62	
71	DGR3-CR275	microdolomite nodule (D1)	Gull River	1.11	23.73	-6.96	
72	DGR3-CR275	mesodolomite nodule (D2)	Gull River	0.49	23.18	-7.50	
2-2	DGR3-CR263	fine crystalline internodule matrix (D1)	Coboconk	-0.55	21.03	-9.58	
2-2	DGR3-CR263	fine crystalline internodule matrix (D1)	Coboconk	-0.55	21.03	-9.58	
2-2	DGR3-CR263	fine crystalline internodule matrix (D1)	Coboconk	-0.55	21.03	-9.58	
2-4	DGR3-CR263	internodule calcite matrix	Coboconk	0.50	24.60		
2-5	DGR3-CR263	Coarse calcite cement	Coboconk	0.06	22.94		
1-1	DGR4-CR253	fine crystalline internodule matrix (D1)	Coboconk	0.46	21.32	-9.30	
1-2	DGR4-CR253	Medium crystalline dolomite nodule (D2)	Coboconk	1.21	24.23	-6.48	
1-3	DGR4-CR253	inclusion-rich medium crystalline dolomite layer (D2)	Coboconk	1.55	21.96	-8.68	
1-4	DGR4-CR253	Internodule calcite matrix	Coboconk	0.62	22.87		
12-1	DGR6-CR239	microdolomite, selective replacive (D1)	Coboconk	1.14	20.61	-9.99	0.709564
3-1	DGR3-CR263	white dolomitic marker unit fossiliferous silicified	Coboconk	-0.55	18.04	-12.48	0.710000
5-1	DGR4-CR266	nodular medium crystalline matrix dolomite (D2)	Gull River	0.64	23.87	-6.83	0.708466
5-2	DGR4-CR266	fine crystalline internodule dolomite matrix (D1)	Gull River	-0.23	21.53	-9.09	0.708180

Table 2: Isotopic analysis of Ordovician and Cambrian carbonates

Sample	Well – Core	Lithology	Age/Formation	$\delta^{13}C_{VPDB}$	δ ¹⁸ Ovsmow	$\delta^{18}O_{VPDB}$	Sr ⁸⁷ /Sr ⁸⁶
ID	run			(‰)	(‰)	(‰)	
5-2	DGR4-CR266	fine crystalline	Gull River	-0.23	21.53	-9.09	0.708180
		internodule dolomite matrix (D1)					
61	DGR3-CR275	Coarse blocky calcite	Gull River	-0.24	22.74	-7.92	
		cement filling vug					
62	DGR3-CR275	Medium crystalline	Gull River	1.05	22.90	-7.77	
		dolomite (D2)					
63	DGR3-CR275	microdolomite replacive	Gull River	0.74	24.08	-6.62	
		(D1)					
71	DGR3-CR275	microdolomite nodule	Gull River	1.11	23.73	-6.96	
		(D1)					
72	DGR3-CR275	mesodolomite nodule	Gull River	0.49	23.18	-7.50	
		(D2)					

 Table 2: Isotopic analysis of Ordovician and Cambrian carbonates

4.3 FLUID INCLUSION THERMOMETRY ANALYSIS

Table 3 shows a summary of the fluid inclusion analysis. Figure 22 shows homogenization temperature (Th) distribution among the analyzed mineral phases and Figure 23 shows salinity distribution among the same analyzed mineral phases in the investigated successions. Figure 24 shows a comparative analysis of Th values in dolomite in both Cambrian and Ordovician rocks. Microthermetric measurements were conducted on both medium (100-200 μ m) and coarse crystalline (>200 μ m) replacive dolomite, as well as coarse crystalline dolomite cement occluding vugs. For calcite and anhydrite cements, measurements were taken for coarse crystalline cements in vugs and fractures. Overall, the fluid inclusions in dolomite, calcite and anhydrite are characterized by a wide range of homogenization temperatures (67-153°C) and high salinities (22.4 to 30.5 wt.% NaCl eq.), as well as low NaCl/(NaCl+CaCl₂) ratios. Figures (22, 23) show the distribution of Th and Tm among the investigated mineral phases.

In the Coboconk Formation, the range of (Th) of the liquid-vapor inclusions in medium to coarse crystalline matrix dolomite (D2) is 85-90 °C and in coarse crystalline dolomite cement occluding pores is 91-126 °C. The salinity range of the latter type is 22.4-25 wt.% NaCl eq. Salinity measurement in replacive matrix dolomite was not possible. For coarse crystalline, equant calcite cement, Th ranges from 96-144 °C and salinity from 27.7 to 29.8 wt% NaCl eq. For anhydrite cement, Th ranges from 75-132 °C and 25.2-25.9 wt% NaCl eq., respectively.

In the Gull River Formation, the homogenization temperatures and salinity in coarse crystalline replacive and dolomite cement range from 97-103 °C and 29.9-30.1 wt % NaCl eq., respectively. For calcite cement, Th and salinity values range from 66-124 °C and 26.4-30.5 wt% NaCl eq.

In the Cambrian replacive matrix dolomite (D2), Th values range from 67-105°C. The coarse crystalline equant calcite cement occluding porosity in this formation records Th values ranging from 85-141°C.

Most of the samples show fluorescence in the interstitial spaces; a few samples (Coboconk DGR-3 CR-263 and DGR-6 CR-239) have minor inclusions that fluoresce along with the coarse dolomite crystals. Many of these inclusions however, are so small that a positive identification of oil inclusions is inconclusive.

 Table 3: Microthermometric results

No.	Sample	FI	Host	Occurrence	V%	Tfz (°C)	T _{fm}	T _{hh}	T _{m,ice}	T _h	Salinity	X _{NaCI}
	NO.		mineral				(°C)	(°C)	(°C)	(°C)	(%)	
1		A-1	dolomite	Isolated	12	-80	-70	41.0	-23.2	91 L	22.4	0.12
2		C-1	dolomite	Isolated	10					102 L		
3	DGR-6 CR-239	D-1	dolomite	Random	10	-95			-26	120 L	24.6	0.54
4	Coboconk RV12	D-2	dolomite	Random	10					120 L		
5		D-3	dolomite	Random	10	-70	-68	-49	-30	125 L	25	0.06
6		D-4	dolomite	Random	10					123 L		
7		C-2	coarse calcite	Isolated	10	-100 (reheat)	-75	45.9	-39	144 L	28.4	0.08
8		D-1	coarse calcite	Short trail	10					96 L		
10	DGR-3	D-3	coarse calcite	Short trail	10					118 L		
11	CR-263 Coboconk RV2f	E-2	coarse calcite	Cluster	6.5	-94 (reheat)	-74		-44.3	110 L	29.8	0.09
12		E-3	coarse calcite	Cluster	5	-93 (reheat)	-74		-43.7	114 L	29.6	0.1
13		F-3	coarse calcite	Isolated	10					153 L		
14		G- 1	calcite	Cluster	8	-87 (reheat)	-70		-42.4	112 L	29.3	0.11

No.	Sample	FI	Host	Occurrence	V%	Tfz (°C)	T _{fm}	T _{hh}	T _{m,ice}	T _h	Salinity	X _{NaCI}
	No.		mineral				(°C)	(°C)	(°C)	(°C)	(%)	
					1.0							1
15	DGR-3	G-	calcite	Cluster	10					113		
16	CR-203	2	aglaita	Cluster	0							
10	RV2f	3	calcite	Cluster	Ö					104 L		
17		H-1	dolomite	Cluster	10					110 L		
18		H-2	dolomite	Cluster	8					123		
10			l - :4 -	Davadava	<u> </u>							
19	CR-263	1-2	calcite	Random	6					103 L		
20	Coboconk	I-3	calcite	Random	6	-92	-73	45.1	-36.5	131	27.7	0.09
	RV3f					(reheat)				L		
21		A-1	dolomite	Random	10					99 L		
22		A-2	dolomite	Random	10					119		
										L		
23		A-3	dolomite	Random	12					114 L		
24		A-4	dolomite	Random	8					82		
										L		
25		A-5	dolomite	Random	8					108		
	DGR-3									L		
26	CR-263 Coboconk	A-6	dolomite	Random	8					122 L		
27	RV3f	A-7	dolomite	Random	10					126		
										L		
28		B-1	dolomite	Random	10					90		
	ļ											
29		B-2	dolomite	Random	10					97		
1		1			1			1		I L		

No.	Sample	FI	Host	Occurrence	V%	Tfz (°C)	T _{fm}	T _{hh}	T _{m,ice}	T _h	Salinity	X _{NaCI}
	NO.		mineral				(°C)	(°C)	(°C)	(°C)	(%)	
30		B-3	dolomite	Random	10					123		
00	DGR-3		dolorinto		10					L		
31	CR-263	B-4	dolomite	Random	10					119		
32	RV3f	B-5	dolomite	Random	8					93 L		
33		B-6	dolomite	Random	10					85 L		
34		C-1	anhydrite	Cluster	5	-105	-78	46.1	-32.2	75 L	25.9	0.08
35		C-2	anhydrite	Cluster	7	-105	-78		-30.2	132 L	25.9	0.34
36		C-4	anhydrite	Cluster	9	-103	-78		-31	107 L	26.1	0.31
37		C-7	anhydrite	Cluster	8	-105	-78	-50	-30.5	76 L	25.2	0.06
38	DGR-3 CR-263	D-1	anhydrite	Cluster	4	-45			-30	78 L	25.8	0.34
39	Coboconk RV3f	D-2	anhydrite	Cluster	8				-30.6	110 L	25.8	0.32
40		A-1	calcite	Isolated	5	-90		-50	-46.5	86 L	30.3	0.06
41		A-4	calcite	Isolated	6	-90	-80		-32	98 L	26.4	0.28
42		A-5	calcite	Cluster	8					107 L		
43		A-8	calcite	Cluster	7					107 L		
44		A- 10	calcite	Cluster	8					104 L		

 Table 3: Microthermometric results

No.	Sample No.	FI	Host mineral	Occurrence	V%	Tfz (°C)	T _{fm} (°C)	T _{hh} (⁰C)	T _{m,ice} (°C)	T _h (⁰C)	Salinity (%)	X _{NaCI}
45		A- 11	calcite	Cluster	8	-90			-36	124 L	27.5	0.19
46	DGR-3 CR-275	A- 13	calcite	Cluster	7	-90		-60	-47.5	111 L	30.5	0.05
47	Gull River RV6f	A- 16	calcite	Cluster	6					66 L		
48		A- 17	calcite	Cluster	5					92 L		
49	-	A- 18	calcite	Cluster	7					91 L		
50		A- 20	calcite	Cluster	7	-90			-43.9	113 L	29.7	0.1
51		D-1	dolomite	Isolated	5					97 L		
52	DGR-3 CR-275	D-2	dolomite	Isolated	8	-100 (reheat)	-72	43.8	-44.2	132 L	29.9	0.08
53	Gull River RV6f	E-1	dolomite	Isolated	10					111 L		
54		F-2	dolomite	Isolated	10	-90 (reheat)			-45.2	115 L	30	0.09
55	-	F-3	dolomite	Isolated	7	-90 (reheat)		56.7	-45.7	103 L	30.1	0.05
56		F-4	dolomite	Isolated	5					111 L		
57	DGR-3	E	coarse calcite	Isolated	11					85 L		
58	CR-285 Cambrian	I-1	coarse calcite	Cluster	5	-69			-33.1	93 L		
59	RV9I	I-2	coarse calcite	Cluster	9	-67			-33.3	93 L		

No.		FI	Host mineral	Occurrence	V%	Tfz (oC)	Tfm (oC)	Thh (oC)	Tm,ice	Th (oC)	Salinity	XNaCI
			Innoru				(00)	(00)	(00)	(00)	(70)	
60	DGR-3 CR-285 Cambrian RV9f	0- 1	coarse calcite	Cluster	7					121 L		
61		O- 2	coarse calcite	Cluster	8					141 L		
62		Cd	dolomite	Isolated	11					67 L		
63		Gd	dolomite	Isolated	14					91 L		
64		Md	dolomite	Random	9	-90 (reheat)	-55		-32	87 L		
65												
66		Nd- 2	dolomite	Cluster	11					89 L		
67		Pd	dolomite	Isolated	16					105 L		
68		Ac	calcite	Isolated	7					91 L		

 Table 3: Microthermometric results

Key

-	treezing	
l _{fz}	temperature	
	lemperature	
T _{fm}	first melting temperature	
_	hydrahalite melting	
Thh	ing a cancer moting	
	temperature	
	ice melting	
Tmice	loo molang	
- 111,100	temperature	
Т.	homogenization temperature	
• n	nomogenization temperature	
	Liquid	



Figure 22: Histogram plot showing homogenization temperature for analyzed mineral phases showing a unimodal distribution of Th for both calcite and dolomite



Figure 23: Homogenization temperature vs. salinity cross plot for analyzed mineral phases showing overlap between the three analyzed mineral phases with no clear separation





5. DISCUSSION AND INTERPRETATION

The integrated petrographic, stable and radiogenic Sr isotopes and fluid-inclusion microthermometry provided understanding to the geochemical conditions during the formation of diagenetic phases in Ordovician carbonates and Cambrian sandstones. These conditions

contributed to the origin, geochemical composition and migration of diagenetic fluids, responsible for dolomitization and cementation by dolomite, calcite and anhydrite.

5.1 CONSTRAINTS FROM PETROGRAPHY

A summary displaying the paragenetic sequence of identified diagenetic events from the samples is shown in Figure (25). Based on the petrographic observations and cross cutting relationships, both early (marine to shallow burial) and deeper burial diagenetic processes are recognized.

Diagenetic processes	Early	Late
Nodular Substratal cementation		
Equant Calcite Cement		
Silicification		
Dissolution		
Fine Crystalline Dolomite (D1)		
Medium-Coarse Crystalline Dolomite(D2)		
Saddle Dolomite	·	
Hairline fracture		
Stylolites / Solution Seams		
Fracture Fill Calcite		

Figure 25: Partial paragenetic sequence of the main diagenetic event for the Ordovician and Cambrian successions

The depositional environment of the Ordovician and Cambrian carbonates encompass various facies assemblages, including supratidal, lagoonal to subtidal environments (e.g. Middleton et al., 2000; AECOM and ITASCA, 2011). The diverse facies changes observed in these formations are directly controlled by relative sea-level changes and sources of detritus. Ultimately, these depositional processes also affected the diagenetic changes encountered in these sediments during shallow and deeper burial stages.

In the Coboconk Formation diagenesis was initiated by early cementation that produced the nodular facies on the seafloor. Burial and compaction affected the formation of these nodules and may have created hair line fractures, later occluded by dolomite. Dolomitization also occurred by selective replacement of the micritic matrix, as well as, pervasively replacing the intra-nodule matrix during shallow burial. These dolomites were cross cut by stylolites during burial at a later stage. Silicification, which occurs in some facies of the Coboconk Formation occurred prior to dolomitization as evidenced by silica replacing the matrix and fossils that later were selectively dolomitized (Figure. 7).

In the Gull River Formation, a similar paragenetic sequence to the Coboconk Formation is observed. Initially, dolomitization proceeded with fine crystalline (D1) and medium to coarse crystalline matrix replacement dolomite (D2). The minor saddle dolomite cement postdates

earlier dolomite formation and occludes vugs and fractures and is also postdated by late calcite cement. Other compaction features such as stylolites postdate or sometimes appear to be contemporaneous with the coarse crystalline dolomite (D2).

In both the Coboconk and Gull River formations, the intra and internodule dolomites typically present as petrographically distinct. These distinctions reflect differences in the underlying substrate that was originally dolomitized and relate to permeability, not fluid chemistry or timing (notwithstanding some evolution of brine chemistry over time). An early, shallow burial origin is suggested for the fine crystalline (D1) dolomite as evidenced by the selective replacement of this dolomite, its shape and size and it predates stylolite formation. In contrast, the medium and coarse crystalline (D2) dolomite may have formed at medium burial stages as evidenced by its increasing crystal size, subhedral and anhedral shape (e. g. Al-Aasm et al, 2003) and close association sometimes with compaction features, such as stylolites. The styolites observed in the samples all occur at ~90° to the fractures (Figures 4, 8 and 11). This relationship may be explained by compressive stress, imposed by the Taconic Orogeny, which was occurring concurrently with deposition.

In contrast, the siliciclastic-carbonate facies in the Cambrian strata impose a control over the diagenetic pathways of these sediments. In carbonate-rich units, the grainstone bioclastic facies has been affected by early stabilization and dolomite replacement onto coarse crystalline dolomite, possibly at burial. The siliciclastic-dominated facies was cemented earlier by carbonate cement later to be compacted with creation of some minor fractures occluded by equant calcite cement, which was partly dolomitized. The basal Cambrian sandstone is assumed to have been a major migratory path for digenetic fluids (Harper et al. 1995; Ziegler and Longstaffe 2000). Strata in the eastern region of basin pinches out towards the margins. These thin fingers of clastic material which have large amounts of bioclastic material increase the likelihood for extensive dolomitization of a thin layer.

5.2 CONSTRAINTS FROM STABLE AND SR ISOTOPES

Many of the analyzed calcitic and dolomitic components of the Ordovician carbonates and Cambrian sandstones show comparable values to the postulated values of carbonate deposited in equilibrium with respective-age seawater composition (Figure 19, e.g. Veizer et al., 1999). This can be interpreted to imply that carbon isotopes have been buffered by the precursor marine limestones (Al-Aasm, 2003). The δ^{13} C values of the D1 and D2 in the Ordovician samples (Figure 20) are interpreted to reflect the carbon isotopic composition of the precursor limestone. Dolomite carbon isotopic composition is generally buffered by the precursor limestone (Fritz and Smith, 1970; Banner and Hanson, 1990; Warren, 2000). It appears that the carbon content of the dolomitizing fluids of all generations were buffered by marine carbon. In contrast, some of D1, D2 and saddle dolomite from the Cambrian samples (Figure 20) show a clear negative departure from the equilibrium values. This reflects another input of oxidized organic carbon, which can be related to a hybrid carbon source including both seawater and hydrocarbons. These samples also show a co-variant trend between carbon and oxygen isotopes and may reflect increasing water-rock interaction at burial (cf. Frank and Lohmann, 1996; Al-Aasm et al, 2009). This linear trend may also indicate that the isoptopic composition of oxygen and carbon were controlled by temperature dependent fractionation (Ghazban and Al-Aasm, 2007).

For dolomite precipitated in equilibrium with its ambient seawater, it is generally enriched in ¹⁸O relative to coexisting calcite by $3\pm1\%$ (e.g. Land, 1980; McKenzie 1981; Major et al., 1992). Undolomitized calcitic matrix in the Coboconk Formation has δ^{18} O values ranging from -6.12 to -7.79 ‰ VPDB and are in the range of postulated Ordovician marine calcite δ^{18} O values (-4 to -8 ‰ PDB; Veizer et al., 1999; Shields et al., 2003). If the Ordovician seawater (-6.3‰ SMOW; Shields et al., 2003) is considered as the source of dolomitizing fluid for fine crystalline dolomite (D1), then the δ^{18} O values of dolomite precipitated from seawater should be between -4.4 and - 1.3‰ VPDB with an average of -2.9‰ corresponding to a precipitation temperature of 19°C. Most of the samples from D1 dolomite fall outside this range (Figure 19), and display a negative shift by ca. 4-6‰ compared with the expected average δ^{18} O values for Ordovician dolomite (-2.9‰). The more negative δ^{18} O values of dolomite could be related to recrystallization or later alteration at elevated hydrothermal temperatures (e.g., Dorobek et al. 1993; Durocher and Al-Aasm 1997, Al-Aasm, 2000).

This is certainly more evident for Cambrian carbonates as they show a more radiogenic signature in comparison with the postulated range for Cambrian seawater. The source of this radiogenic fluid can be traced to the presence of more siliciclastic (e.g. clays and feldspars) in the Cambrian strata, with possible contribution from Precambrian rocks (cf. Ziegler and Longstaffe, 2000). Brines may also incorporate radiogenic ⁸⁷Sr during passage through siliciclastic sequences (Mountjoy et al, 1992).



O Vs C (Dolomites)

Figure 26: Cross plot of $\delta^{13}C_{VPDB}$ versus $\delta^{18}O_{VPDB}$ range of dolomite from the current study in comparison to previous study on Ordovician dolomite in southern Ontario. Note the overlap in the isotopic ranges for all studies. However, Cambrian dolomites from the current study show a clear departure from the Ordovician samples

5.3 CONSTRAINTS FROM FLUID INCLUSIONS

Fluid inclusion analysis of the medium to coarse crystalline matrix dolomite (D2) and coarse crystalline dolomite cement in the Coboconk Formation yield average homogenization temperatures of 109°C. The average homogenization temperatures of the late calcite is 118°C, and in the anhydrite cement 96°C. In the Gull River Formation the average homogenization temperature is 115 °C, while it is 100°C for the calcite cement. In both formations the salinity values for the measured fluid inclusions in both calcite and dolomite are quite high (ca. 22-30 wt% NaCl). Coniglio et al. (1994) and Middleton et al., (1993) reported homogenization temperatures of fluid inclusions hosted in Ordovician dolomite with modes at 149 and 206°C (Figure. 27). Fluid inclusions hosted within late calcite in these other studies also display a bimodal distribution in homogenization temperatures, with peaks at 96°C and 156°C (Middleton et al., 1993; Coniglio et al., 1994). The medium to coarse crystal size, negative δ^{18} O values of D2, and moderate homogenization temperatures and salinity are strong evidence of dolomitization at higher temperature conditions from saline brines. Such temperature values could be responsible for depleted oxygen isotope values of replacive dolomite.

Vug and fracture-filling calcite, which paragenetically postdates replacive and dolomite cement show a fairly comparable homogenization temperature to dolomite, which suggest that this cement precipitated from similar fluids under comparable diagenetic conditions. Comparing the results of fluid inclusions of dolomite from the Ordovician samples from the current investigation with previous work on Ordovician dolomite in southern Ontario (Figure. 26), demonstrates an overlapping pattern between the three studies on Ordovician dolomite. A notable exception is that Th and salinity values reported by Middleton et al (2000) show wider ranges of values.

In general, homogenization temperatures of the Cambrian dolomites record lower values than in the Ordovician strata (Figure. 24). This can be explained by two possibilities: (1) The presence of two different phases of fluid migration in the Paleozoic that are responsible for the dolomitization of those strata, although we don't have strong evidence for which one formed first; or (2) the nature of the conduits for fluid migration may be different. All Ordovician late stage mineralization and dolomitization (Haire-Ardakani et al., 2013a, b) were in the vicinity of major fractures demonstrating that fluid movement is significantly faster in a fracture network. Consequently, the heat transfer with the wall rock was lower in comparison than with similar fluid conduits through porous sandstone, which has a higher thermal exchange potential with the host rock. Considering that dolomitization from the same fluid, at the same time is unlikely based on isotopic results, then a difference in the rate of fluid movement and heat transfer with host rock can be major factors in controlling the temperature of fluids.

Th Vs Salinity (dolomites)



Figure 27: Salinity vs. homogenization temperature cross plot for dolomite for the current study in comparison to previous studies from southern Ontario. Note the wide range in both Th and salinity in Middleton et al. 1993 investigations and the close and overlapping ranges from both the current study and Haeri-Ardakani (2013) investigation

5.4 PORE FLUID EVOLUTION

Petrographic and isotope data can be used to infer changes in the oxygen isotope composition of diagenetic fluids in the investigated Ordovician and Cambrian carbonates during progressive diagenesis. The relationships among mineral δ^{18} O values, pore water δ^{18} O values and temperature for diagenetic phases from the investigated carbonates are shown in Figures 28 and 29. The range of temperatures used were obtained from the fluid inclusion analysis. Figure 28 shows a plot of oxygen isotope values of dolomite from Ordovician and Cambrian strata on the temperature dependent, dolomite-water oxygen fractionation curve (e.g. Land, 1983). There is an overlap in the isotopic composition of fluids responsible for the formation of dolomite from both Coboconk and Gull River formations with more enriched $\delta^{18}O_{SMOW}$ values for the latter formation. However, Cambrian dolomite precipitated at lower temperatures from less enriched $\delta^{18}O_{SMOW}$ values.

Using the most negative D2 δ^{18} O values of Coboconk dolomite (-12.4‰ VPDB), and assuming Middle Ordovician seawater of -6.3‰ SMOW (Shields et al., 2003) yields a precipitation temperature of 72°C, which is lower than the average homogenization temperature of D2 dolomite (109°C) (Figure 28). Higher temperatures are possible if dolomitizing fluids had more positive δ^{18} O values relative to Middle Ordovician seawater. The same applies if we use the most negative D2 δ^{18} O values of the Gull River dolomite (-9.09‰ VPDB), where the precipitation temperature will be around 50°C, which is even lower than the average homogenization temperature of D2 dolomite (115°C). Possible sources of ¹⁸O enriched waters are basinal brines, waters from gypsum dehydration, waters from salt dissolution, isotopic exchange reactions between waters and associated carbonate minerals or mixtures of the above (e.g., Clayton 1966; Hitchon and Friedman, 1969; Knauth and Beeunas,1986). For Cambrian dolomite, using the most negative D2 δ^{18} O values (-16.9‰ VPDB), and assuming Cambrian seawater ca. -8.0‰ SMOW (Veizer and Prokoph, 2015) yields a precipitation temperature of D2 dolomite (91.5°C) (Figure. 28). This illustrates the divergence in fluid composition between that precipitated in the Cambrian vs. the Ordovician dolomites.

The thermal history of the Michigan Basin has been investigated by a number of researchers: (Cercone, 1984, Vugrinovich, 1988; Cercone and Pollack, 1991; Crowley, 1991; Coniglio et al., 1994; Luczaj et al., 2006). These investigations used a variety of proxies (e.g., organic maturity data, stable isotopes, fluid inclusions), which point to the occurrence of high temperatures (up to 200°C) in the past (Ma et al., 2009). Two burial curves were suggested for the basin. including the Bruce Nuclear site (Figure. 30; INTERA, 2011). They differ in their interpretation in terms of rate of erosion and timing. Legall et al. (1981) suggested a minimum burial temperatures between 60 and 90°C for Ordovician strata in southwestern Ontario using conodont alteration index. Reconstruction of burial depth for Middle Ordovician sequence resulting in a maximum burial depth of 1500 m for this sequence in Manitoulin Island (Coniglio and Williams-Jones, 1992). However, Cercone (1984) estimated a 2000 m burial depth by extrapolating stratigraphic data from Michigan. Considering a normal intracratonic geothermal gradient (23°C/km) suggested by Hogarth and Sibley (1985) and a 20°C surface temperature, the maximum burial temperature for southwestern Ontario is 66°C. However, a higher geothermal gradient (35 to 45°C/km) was proposed by Cercone (1984), using the Lopatin method for the Michigan Basin.

The high temperature fluids of the basinal brines can be related to hydrothermal fluids sourced from deeper part of the centre of Michigan basin as suggested by Haeri-Ardakani et al., (2013) migrated up dip to basin margins. The Th of fluid inclusions from Ordovician matrix dolomite and saddle dolomite from the central part of Michigan Basin record higher values (155-175 °C) compared to the lower Th values reported from the margin of the basin (90-121 °C); Haeri-Ardakani et al., 2013). These values place the homogenization temperatures of the dolomites above those of the burial-related temperatures.



Figure 28: Oxygen isotope values of dolomite from Ordovician and Cambrian strata are plotted on the temperature dependent, dolomite-water oxygen fractionation curve. The formation temperatures of dolomite are based on fluid inclusion microthermometry. There is an overlap in the isotopic composition of the formation of dolomite from both the Coboconk and Gull River formations with more enriched $\delta^{18}O_{SMOW}$ values. However, the Cambrian dolomite precipitated at lower temperatures from less enriched $\delta^{18}O_{SMOW}$ values



Figure 29: Oxygen isotope values of calcite cements from Gull River and Cambrian samples are plotted on the temperature dependent, calcite-water oxygen fractionation curve. The formation temperatures of calcite are based on fluid inclusion micro-thermometry. The range of homogenization temperatures from the late diagenetic calcite (dark blue) indicates formation from evolved brines for the Gull River calcite cement, while Cambrian calcite cement records high formation temperatures from less enriched $\delta^{18}O_{SMOW}$ values



Figure 30: Hypothetical burial history curves for Michigan Basin. The Orange curve is based on Coniglio and Williams-Jones (1992) after Cercone (1984). Black curve is based on Wang et al. (1994). (a) Indicates the present day burial depth of approximately 675 m for the middle of the Ordovician sedimentary succession at the Bruce nuclear site (INTERA, 2011)

6. SUMMARY AND CONCLUSIONS

A preliminary study was completed to examine the paleogenesis of dolomite occurring within Ordovician carbonates and Cambrian clastics on the eastern flank of the Michigan Basin in southwestern Ontario. The study involved integrated petrographic, stable and Sr isotope, and microthermometry fluid-inclusion analyzes of seven rock core samples from the Ordovician Black River Group and underlying Cambrian formation. The petrographic and geochemical attributes have provided a basis to gain insight on the source fluids that modified these rocks, as well as, the possible timing of formation.

Key findings of this study include:

- Fluid inclusion homogenization temperatures indicate secondary mineral temperatures exceeding those estimated by burial history. As such the occurrence of hydrothermal events is indicated. Higher temperature diagenetic minerals near the center of the Michigan Basin suggest a basin center origin for the hydrothermal fluids, possibly associated with mid-continent rifting during late Devonian-Mississippian.
- Ordovician dolomite stable water isotope signatures overlap with those of previous studies in southern Ontario. Depleted δ¹⁸O values may have resulted from later precipitation at higher temperatures from basinal brines as cited by Taylor and Sibley, (1986), Middleton et al., (1993); Coniglio et al., (1994); Yoo et al., (2000); Smith (2006).

- Cambrian isotopic δ¹⁸O signatures are clearly different than found in the Ordovician carbonates providing evidence that a different fluid was responsible for dolomitization. There appear to be two isolated fluid systems recorded in the samples; one older marine or slightly modified marine system (Cambrian) and the other, an evolved basinal brine (Ordovician)
- Within the Ordovician carbonates the D2 dolomite appears related to: i) shallow to intermediate burial from modified seawater brines; or ii) replacive dolomite recrystallized by the incursion of hydrothermal fluids. The time of emplacement may have been during either the Taconic or Acadian Orogenies, where large horizontal compressive stresses and associated elevated temperatures (from nearby subduction) created conditions suitable for dolomitization.
- The results of ⁸⁷Sr/⁸⁶Sr ratios for matrix dolomite and later precipitated calcite cement demonstrate both a marine fluid composition for the Ordovician carbonates and an external, more radiogenic source for the Cambrian

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