

# Hydrothermal Dolomitization and a Fluid Flow Model: An Example from the Middle Ordovician Trenton Group, Southwestern Ontario, Canada\*

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## Abstract

Middle Ordovician Trenton Group carbonates are fractured and extensively dolomitized along the axis of the Algonquin Arch in southwestern Ontario. Hydrocarbon reservoirs formed where these dolomitized fracture zones penetrate otherwise impermeable host limestones.

Three different types of dolomite (D1, D2, and D3) are distinguished. Petrographic characteristics and  $\delta^{18}\text{O}$  values indicate that D1 formed during early diagenesis from Middle Ordovician seawater and recrystallized during progressive burial, whereas fracture-related, replacive matrix dolomite (D2) formed by hydrothermal fluids (68 to 99°C). Late-stage saddle dolomite (D3) and calcite (C3) cements occlude fractures. Based on petrographic, fluid inclusion, and stable isotope data, D3 dolomite and C3 calcite formed from warm (68 to 144°C), saline (22 to 24 wt. % NaCl+CaCl<sub>2</sub>) hydrothermal fluids.

Magnesium required for dolomite precipitation was supplied by Mg-rich seawater-derived (Silurian and/or Devonian) saline waters from the dissolution of Silurian evaporites which became heated during their descent along faults and fractures to reservoir depths at the center of the basin. Hot basinal brines migrated laterally through basal sandstones and ascended into the network of faults and fractures and precipitated fracture-related dolomite.

## Introduction

Middle Ordovician Trenton and Black River carbonates in southwestern Ontario and neighboring regions form one of the most important hydrocarbon exploration targets and oil reservoirs in Lower Paleozoic strata of North America (e.g., Davies and Smith, 2006). Laterally equivalent carbonates in New York, Ohio, Indiana, and Wisconsin have also produced large amounts of hydrocarbons and some are host to lead-zinc-fluorite mineralization.

Hydrocarbons are produced where these carbonates have been fractured and dolomitized and laterally sealed by tight, undolomitized limestone (e.g., Smith 2006; Yoo et al., 2000; Coniglio et al., 1994). Numerous studies have focused on diagenetic aspects of these carbonates as well as hydrothermal dolomites in the Lower Paleozoic rocks of eastern Canada and the United States (e.g., Conliffe et al., 2010; Luczaj, 2006; Smith, 2006; Yoo et al., 2000; Coniglio et al., 1994).

Some of these studies suggested dolomitizing fluids originated from crystalline basement rocks that flowed up through basement-rooted faults and associated fractures (e.g., Smith, 2006; Davis and Smith, 2006). Other studies have suggested that downward migration of seawater-derived (Silurian and/or Devonian) fluids and their circulation through a network of fractures due to buoyancy-derived fluid flow is responsible for dolomitization (Coniglio et al., 1994).

The purpose of the present work is to critically review and refine the current fluid flow models to document the diagenetic processes, in particular dolomitization of Trenton carbonates, by detailed petrography, stable isotope and strontium isotope analysis and fluid inclusion study.

### **Geologic Setting**

The study area is located between the Michigan and Appalachian basins. These two differentially subsiding basins, the Michigan Basin in the west and the Appalachian Basin to the southeast ([Figure 1](#)), were separated by the Algonquin and Findlay arches which formed a broad platform. The arches formed in the Late Precambrian and remained intermittently active throughout the Paleozoic, controlling patterns of sedimentation (Sanford et al., 1985).

The region is underlain by an essentially undisturbed Phanerozoic sedimentary succession resting unconformably on Precambrian basement rocks (Armstrong and Carter, 2006). Sedimentation of the Paleozoic cover in the area commenced with transgression over the Precambrian basement. The Middle Ordovician consists of the Black River and Trenton groups, which together range up to 280 m in thickness. These strata consist of fossiliferous carbonates underlying the deeper-water shales of the Blue Mountain Formation (Armstrong and Carter, 2006).

The Trenton Group includes the Cobourg, Sherman Fall (the focus of this investigation), and Kirkfield formations, in descending order. These strata represent the upper part of a widespread carbonate platform developed during the Middle Ordovician over a vast area of the North American craton (Wilson and Segupta, 1985).

Most of the faults in southern Ontario are basement faults extending upward into the overlying strata. Displacement along these faults formed channelways for fluid movement, resulting in dissolution of Silurian evaporites and hydrothermal dolomitization in Middle Ordovician strata (Sanford et al., 1985).

The majority of fracture-related Ordovician reservoirs in southwestern Ontario are located along fractures.

## Materials and Methods

For  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  analysis, approximately 5 mg of selected calcite and dolomite were micro-drilled and reacted with 100% pure phosphoric acid for four hours at 25°C for calcite and 50°C for dolomite, respectively (Al-Aasm et al., 1990). The resultant  $\text{CO}_2$  was measured for its oxygen and carbon isotopic ratios on a Delta plus mass spectrometer. Isotopic values are given in  $\delta$ -notation and reported relative to the VPDB standard. Reproducibility of isotopic measurements is better than  $\pm 0.05\%$ .

Fluid inclusion microthermometry measurements were carried out using a Linkam THMG 600 heating-freezing stage at the University of Windsor. Calibration with precision of  $\pm 1^\circ\text{C}$  at 300°C and  $\pm 0.1^\circ\text{C}$ , at  $-56.6^\circ\text{C}$  was conducted using synthetic  $\text{H}_2\text{O}$  and  $\text{CO}_2$  fluid inclusion standards. Heating experiments were conducted prior to conducting cooling experiments so as to reduce the risk of stretching or decrepitating the fluid inclusions.

## Results

Three principal types of dolomite are recognized:

- Replacive fine crystalline dolomite with crystal size ranging from 25 to 50  $\mu\text{m}$  (D1), replacing skeletal grains, calcite cement and microspar. D1 dolomite consists of tightly packed planar-e to planar-s, non-luminescent ferroan rhombs ([Figure 2A](#)).
- Replacive matrix dolomite (D2) is fabric destructive and replaces skeletal grains, and calcite cements. D2 forms medium to coarse planar-s to nonplanar crystals (100-700  $\mu\text{m}$ ) and is non-luminescent ([Figure 2B](#)). D2 crystals shows sweeping extinction similar to saddle dolomite.
- The third type of dolomite is vug- or fracture-filling saddle dolomite and it postdates matrix dolomite (D2). D3 forms coarse planar-e to non-planar crystals with curved faces and ranges in size from 300  $\mu\text{m}$  to 3 mm, showing strong zonation with cloudy centers and clear rims ([Figure 2C](#)).

Fluid inclusions observed in D2 dolomite are very small, ranging from 2 to 8  $\mu\text{m}$ . This dolomite (D2) shows a narrow range of  $T_h$  values from 67.6° to 98.9°C. It was not possible to measure the last ice melting temperature due to the small size of the inclusions. Fluid inclusions in D3 (saddle dolomite) range from 15 to 30  $\mu\text{m}$ . Homogenization temperatures ( $T_h$ ) in D3 cement show a wider range than D2 from 96.7° to 143.5°, with the last ice-melting temperatures ( $T_m$ ) ranging from  $-28.8^\circ$  to  $-21.9^\circ\text{C}$ . These values corresponds to salinities of 24.4 to 21.5 wt.% (NaCl+CaCl<sub>2</sub>) equivalent.

D1 dolomite  $\delta^{18}\text{O}$  values ranging from  $-2.6\%$  to  $-8.6\%$  and  $\delta^{13}\text{C}$  values of 1.3‰ to  $-0.2\%$  VPDB. D2 samples giving  $\delta^{13}\text{C}$  values of  $-1.0\%$  to 1.3‰ and  $\delta^{18}\text{O}$  values of  $-11.5\%$  to  $-7.8\%$  VPDB. D3 dolomite yielded  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values ranging from 1.3‰ to  $-0.9\%$ , and  $-7.1\%$  to  $-11.8\%$  VPDB, respectively ([Figure 3](#)).

## Discussion

The finely crystalline nature, planar texture, and  $\delta^{18}\text{O}$  values of D1 suggest an early-stage replacement of marine carbonates. However, the negative shift in  $\delta^{18}\text{O}$  values of D1 can be attributed to the effect of recrystallization during burial although, petrographically, it is still fine-crystalline with planar texture. The coarse crystal size, non-planar texture, presence of saddle dolomite cement, negative  $\delta^{18}\text{O}$  values of D2 and D3, and high homogenization temperature ( $82 \pm 9.5^\circ\text{C}$  and  $121 \pm 13.3^\circ\text{C}$ , respectively) are strong evidence of dolomitization at higher temperature conditions (Machel, 2004) either during burial or from hydrothermal fluids.

Maximum burial temperature for lower Ordovician strata in southwestern Ontario, based on conodont and acritarch alteration index estimated to be  $60^\circ\text{C}$ . The average homogenization temperature of D2 and D3 is significantly higher than the estimated maximum burial temperature which is an indication of the involvement of hydrothermal fluids in replacement and precipitation of D2 and D3, respectively. Integration of dolomite (D2 and D3)  $\delta^{18}\text{O}$  values with measured microthermometry data was used to determine the  $\delta^{18}\text{O}_{\text{fluid}}$  responsible for dolomitization of Middle Ordovician Trenton Group carbonates (Figure 4). The  $\delta^{18}\text{O}_{\text{fluid}}$  for D2 ranges from  $-6$  to  $+2\text{‰}$  SMOW, and for D3 range from  $-2$  to  $+5\text{‰}$  SMOW. Calculated  $\delta^{18}\text{O}_{\text{fluid}}$  for D2 varies from values similar to Middle Ordovician seawater ( $-6.3\text{‰}$  SMOW; Shields et al., 2003) to values more positive ( $+2\text{‰}$  SMOW) than estimated Middle Ordovician seawater.

Silurian seawater ( $-3.5\text{‰}$  SMOW, Azmy et al., 1998) or Devonian seawater ( $-1\text{‰}$  SMOW, Joachimsky et al., 2009) could be considered as sources of  $^{18}\text{O}$ -enriched waters relative to Middle Ordovician seawater (Figure 4), assuming downward migration through network of fractures in the Paleozoic succession. Reflux of Mg-bearing (Silurian and/or Devonian) seawater or seawater-derived brines through fractures are likely to have been involved in the precipitation of D2 and D3 dolomite.

The  $\delta^{18}\text{O}$  values of Canadian Shield brines varies from  $-10$  to  $-17\text{‰}$  VSMOW (Frape et al., 2005; Bottomley et al., 2003), whereas the  $\delta^{18}\text{O}_{\text{fluid}}$  for D2 ranges from  $-6$  to  $+2\text{‰}$  VSMOW, and for D3 range from  $-2$  to  $+5\text{‰}$  VSMOW (Figure 4). This indicates that fluids originated from the crystalline basement were not involved in dolomitization of D2 and D3. Contoured crossplots for Ordovician-hosted, matrix-replacive, and fracture-fill saddle dolomite from outcrop and subsurface locations in southwestern Ontario, Canada (Figure 4) show that the dolomite was formed from fluids that originated from mixing of younger seawater (Devonian and/or Silurian) and Ordovician connate waters. Reflux of seawater and dissolution of the Salina evaporites produced  $^{18}\text{O}$ -enriched saline fluids that were involved in precipitation of fracture-filling saddle dolomite cement (D3).

## Conclusions

Petrographic and oxygen isotopic composition suggest that D1 dolomite formed in the early stages of diagenesis from Middle Ordovician seawater and recrystallized during the early stages of burial. Reflux of seawater younger than Ordovician (i.e., Silurian and/or Devonian) dissolved Devonian and Silurian evaporites and moved downward through the fracture network by density driven fluid flow. A thermal anomaly along the mid-continent rift during Devonian to Mississippian (Alleghanian orogeny) time likely was the source of excess heat in the Michigan Basin. The potential thermal buoyancy of hot brines was the driving force for migration of hydrothermal fluids. Hot brines in the

central part of the basin migrated through basal Cambrian sandstones and ascended through the fracture network and precipitated dolomite and late stage calcite while carrying hydrocarbons.

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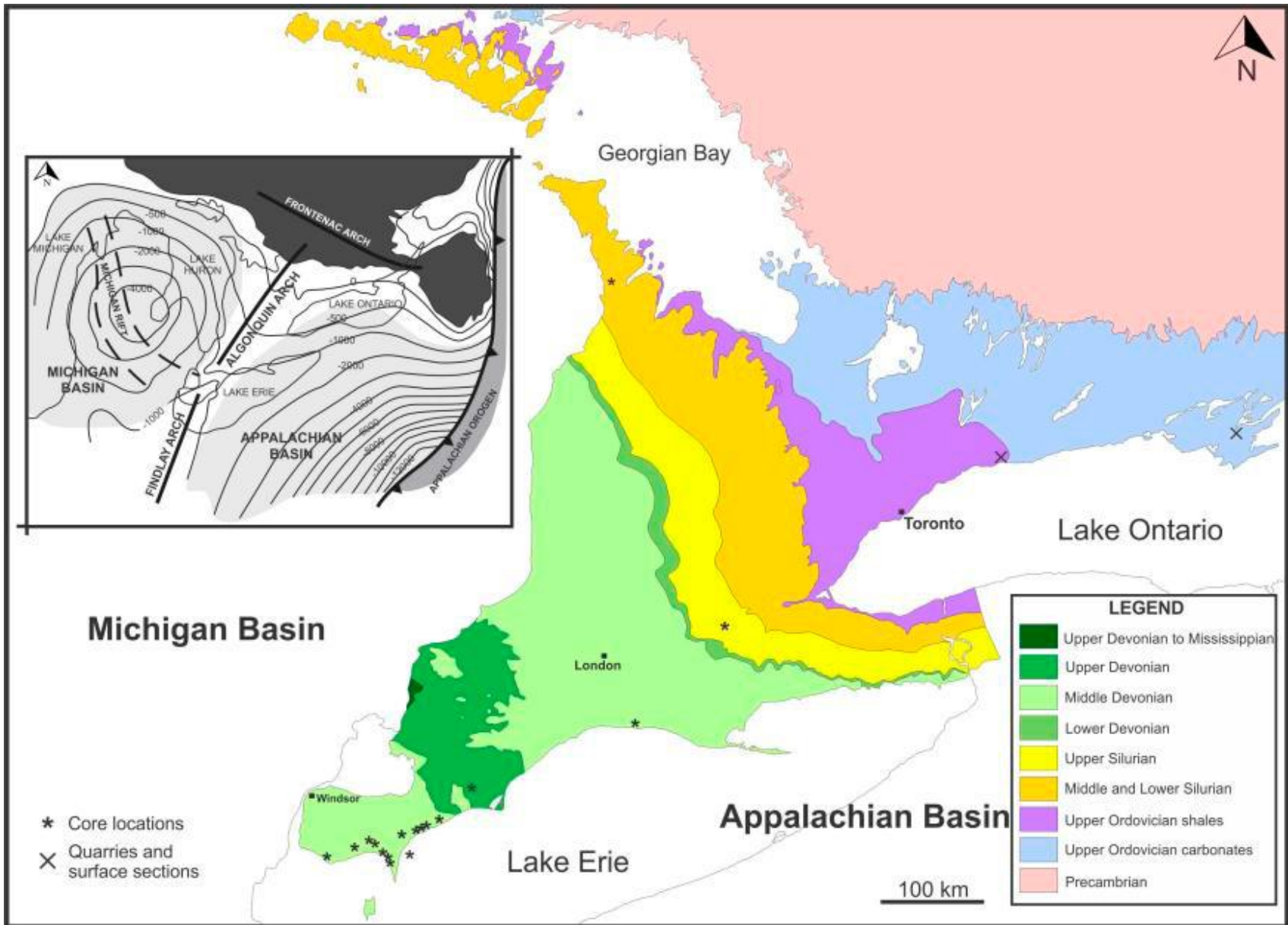


Figure 1. Generalized Paleozoic bedrock geology map of southern Ontario (adapted from Armstrong and Carter, 2006). Inset shows generalized basement structural contours (meters above sea level datum) and location of structural arches and basins (adapted from Johnson et al., 1992). Core (\*) and surface sampling locations (x) are shown on the map.

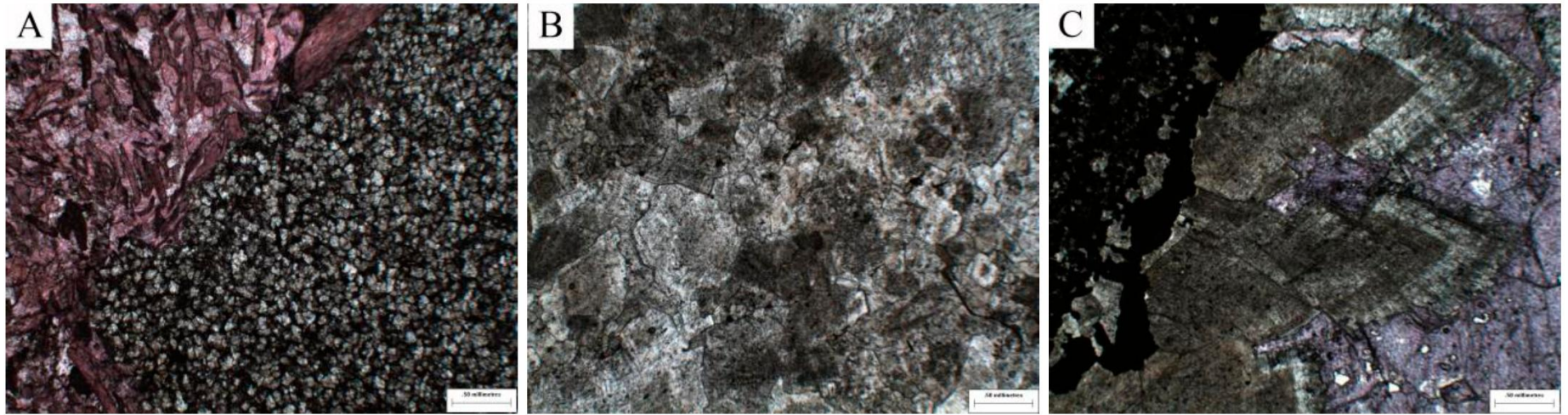


Figure 2. A) Ferroan planar-e to planar-s replacive dolomite (D1), scale bar 250  $\mu\text{m}$ . B) Coarse planar-s to non-planar crystals of D2 dolomite, scale bar 500  $\mu\text{m}$ . C) Saddle Dolomite (D3) filled fracture followed by late stage calcite (C3), scale bar 500  $\mu\text{m}$ .



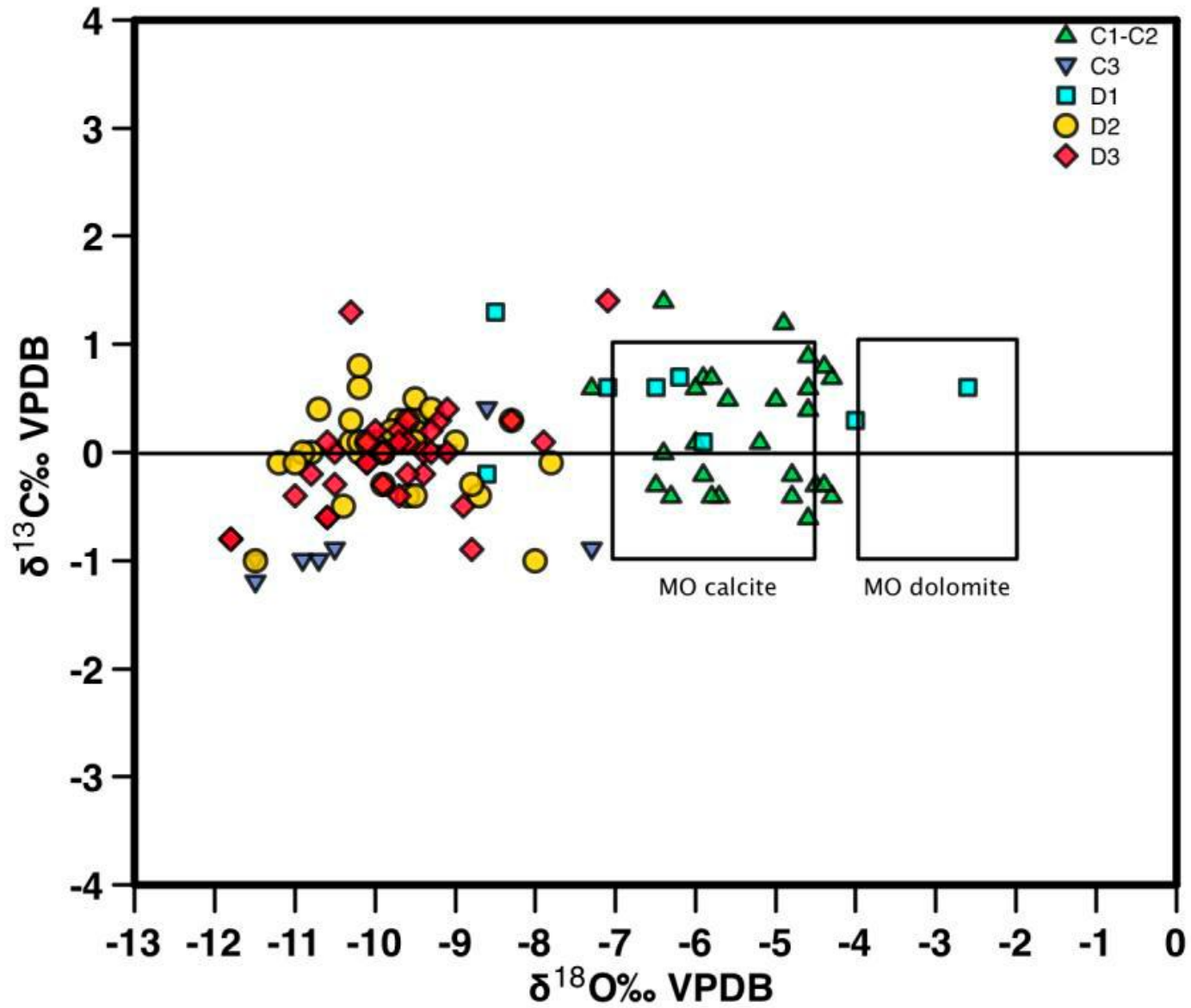


Figure 3.  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  values of replacive dolomite, dolomite cement from the Sherman Fall Formation, southwestern Ontario. The two rectangles show the estimated values for marine calcite (Shields et al., 2003) and dolomite precipitated from Middle Ordovician (MO) seawater.

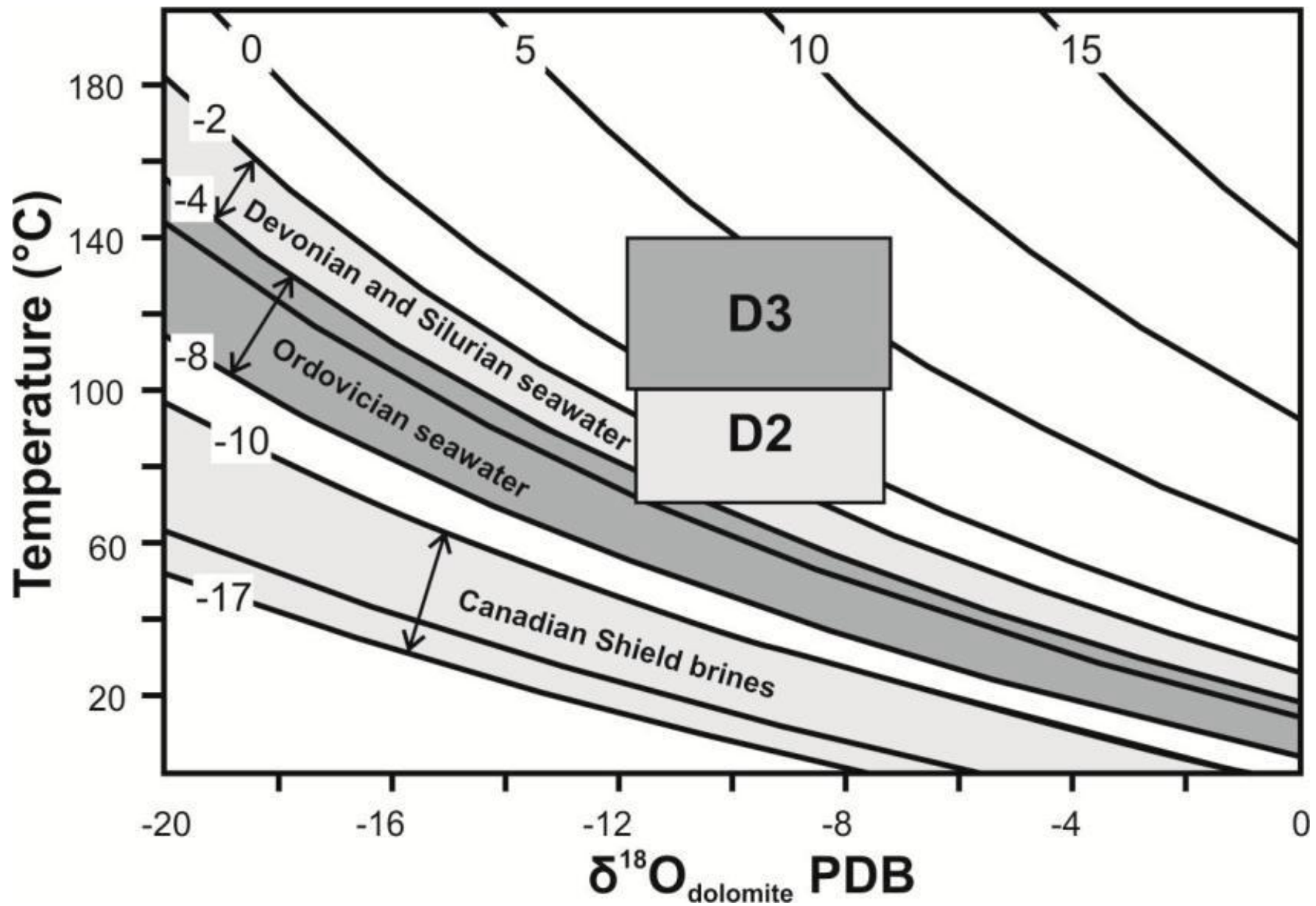


Figure 4. Temperature vs.  $\delta^{18}\text{O}$  fluid for various  $\delta^{18}\text{O}$  values of dolomite derived from the fractionation equation:  $10^3 \ln \alpha_{\text{dolomite} - \text{water}} = 3.2 \times 10^6 T^{-2} - 3.3$  (Land 1985). Shaded areas represent range of  $\delta^{18}\text{O}$  values of Devonian, Silurian, and Ordovician seawater and Canadian Shield brines (Bottomley et al., 2003) and boxes shows the range of homogenization temperatures and  $\delta^{18}\text{O}$  values of D2 and D3.