PS Lower Ordovician St. George Group Dolomite: Zoning Investigated by Using Secondary Ion Mass Spectrometer*

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Abstract

Dolomite is an important hydrocarbon reservoir but its origin and mechanism of formation remains a hot debate. Recrystallization to more stoichiometric dolomite is usually accompanied by characteristic textural and geochemical signatures. These factors are primarily studied using multiple populations of crystals, comparison of modern and ancient dolomites, or from results of high temperature dolomite formation experiments.

Representative dolomite samples of Lower Ordovician St. George Group carbonates were chosen for study. The study used multi-proxy high-resolution approaches to carry out imaging and elemental analyses of individual dolomite crystals viz: Scanning Electron Microscopy (SEM), cathodoluminescence (SEM-CL), and Secondary Ion Mass Spectrometer (SIMS). Data obtained were used to characterize the dolomites and also to constrain their condition of formation. Data from the concentric zones of the dolomites indicate that intensities of Cathodoluminescence (CL), Ultra Violet (UV) light, and Blue (BL) light luminescence correlate with the concentration of activator elements (Mn^{2+} and Rare Earth Elements Ce^{3+} and Y^{3+}). Furthermore, data from SIMS show that there is coupled core to rim variations in Mg, Na, Sr, REE, Mn and Fe in the CL-zoned dolomites. This is interpreted to have occurred as a result of successive recrystallization in the ancient dolomites. It is note-worthy that the data obtained from SIMS is largely similar to those obtained from bulk solution analyzed by Inductively Coupled Plasma Mass

Spectrometer. The main implication of this study is that recrystallization and episodes of dolomitization shown by multi-crystal populations is also apparent within dolomite crystals.

Lower Ordovician St. George Group dolomite: Zoning investigated using Secondary Ion Mass Spectrometer

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1 Abstract

- Dolomite is an important hydrocarbon reservoir but its origin and mechanism of formation remains a hot debate. Recrystallization to more stoichiometric dolomite is usually accompanied by characteristic textural and geochemical signatures. These factors are primarily studied using multiple populations of crystals, comparison of modern and ancient dolomites or from results of high temperature dolomite formation experiments.
- Representative dolomite samples of Lower Ordovician St. George Group carbonates were chosen for study. The study used multi-proxy high-resolution approaches to carry out imaging and elemental analyses of individual dolomite crystals viz: Scanning Electron Microscopy (SEM), cathodoluminescence (SEM-CL) and Secondary Ion Mass Spectrometer (SIMS). Data obtained were used to characterize the dolomites and also to constrain their condition of formation.
- Furthermore, data from SIMS show that there is coupled core to rim variations in Mg, Na, Sr, REE, Mn and Fe in the CL-zoned dolomites. This is interpreted to have occurred as a result of successive recrystallization in the ancient dolomites.
- It is note-worthy that the data obtained from SIMS is largely similar to those obtained from bulk solution analyzed by Inductively Coupled Plasma Mass Spectrometer.
- The main implication of this study is that recrystallization and episodes of dolomitization shown by multi-crystal populations is also apparent within dolomite crystals.
- Further work is suggested be done to obtain the $\delta^{18}O$ of the analyzed zones to better constrain the variation in O-isotopic composition of fluids through the course of dolomite precipitation.

2 Study area and Stratigraphic Framework

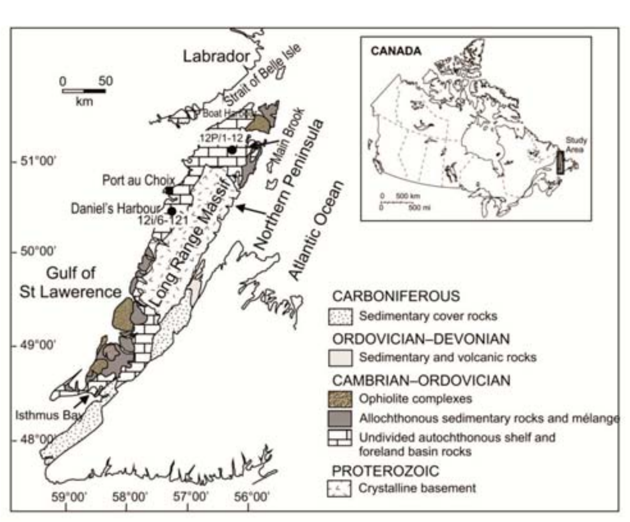


Fig. 1.
Map of study area showing location of the sampled drill holes (modified from Zhang and Barnes, 2004).

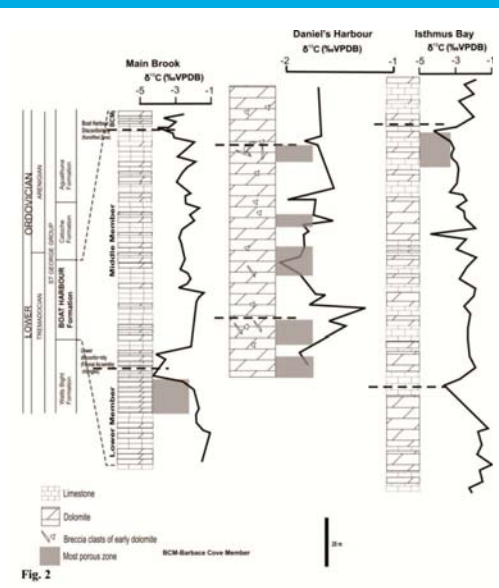


Fig. 2
Stratigraphic log showing dolomite distribution in the cores. It also shows $\delta^{13}C$ that also delineates the disconformity zones. (Olanipekun et al., 2014).

3 Methods

Representative samples of epigenetic dolostones of the Boat Harbour Formation (two drillholes from Main Brook and Daniel's Harbour localities; Fig 1) were selected for ion microprobe analyses on Cameca IMS 4f Secondary Ion Mass Spectrometer (SIMS; Fig. 3a).

Petrographic examination was done using Scanning Electron Microscope (SEM) and its associated Energy Dispersive X-Ray Spectrometer (EDX) and cathodoluminescence (SEM-CL) .

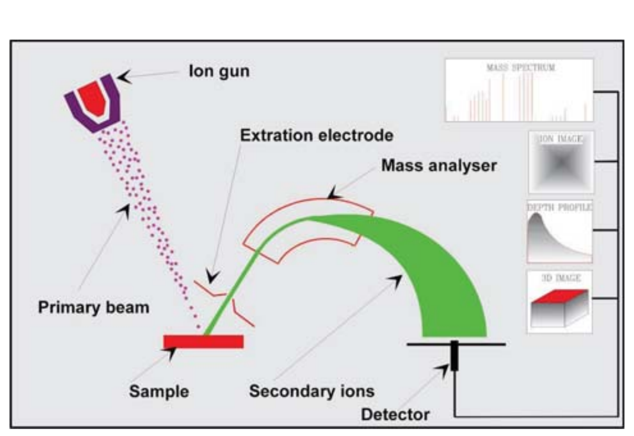
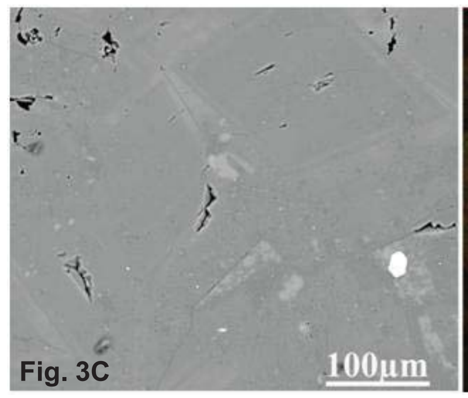


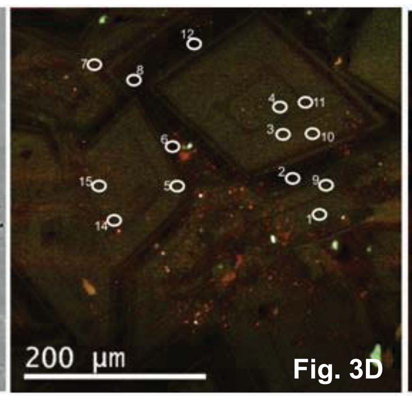
Fig. 3A.Schematic of SIMS. (http://www.geos.ed.ac.uk/facilities/ionprobe/SIMS4.pdf).

Fig. 3B. Cameca IMS 4F SIMS.

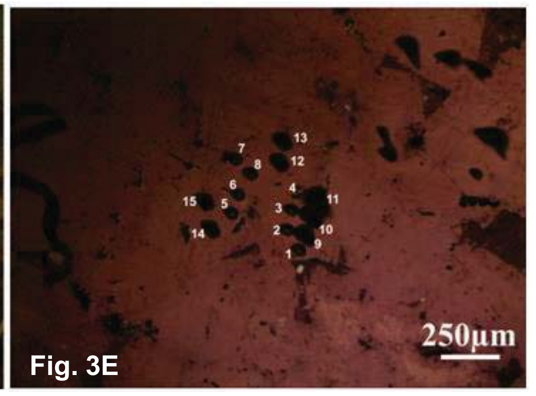
3 Methods



SEM image of Boat Harbour formation epigenetic dolomite.



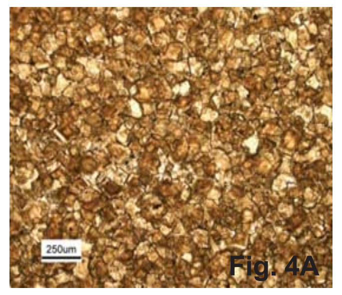
Same area of view as 3C under SEM-CL, showing correlated spots on zoned dolomite crystals.



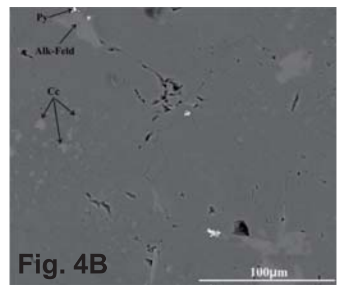
Same area of view as 3C showing spots sputtered by SIMS. Wavy lines are marker scratches.

4 Petrography

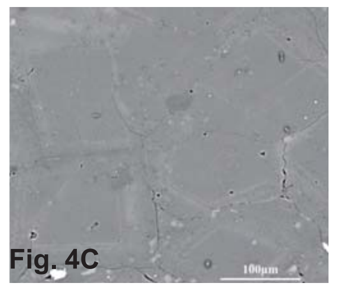
Main Brook locality



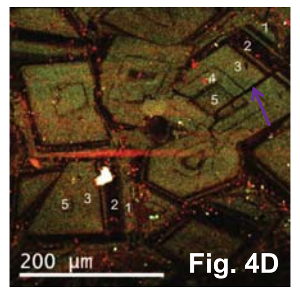
Plain light image of a typical epigenetic dolomite.



SEM image of a typical epigenetic dolomite. Py-Pyrite; Alk-Feld-Alkali feldspar cement; Cc Calcite inclusions.

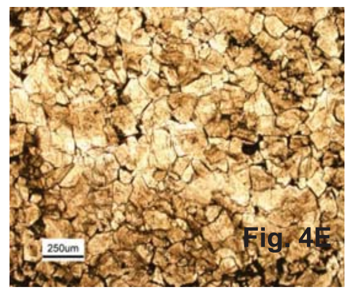


SEM image of sampled area of the dolomite.

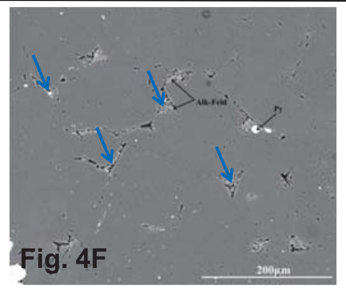


Same field of view as 4C under SEM-CL showing concentric zoning and zone identities. Purple arrow-healed intra-crystalline fracture.

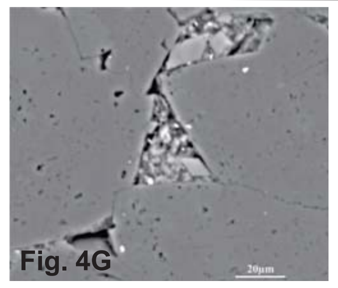
Daniel's Harbour locality



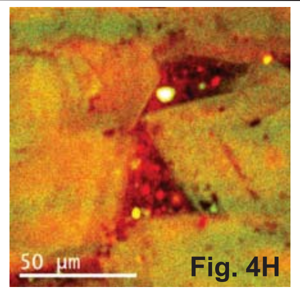
Plain light image of a typical epigenetic dolomite.



SEM image of a typical epigenetic dolomite. Py-Pyrite; Alk-Feld-Alkal feldspar cement; blue arrows-intercrystalline pores. Cc- Calcite inclusions.



SEM image of sampled area.



Same field of view as 4G under SEM-CL showing subtle concentric core-rim zoning.

5 Compositional zoning

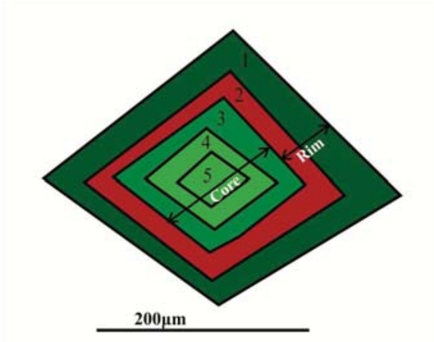


Fig. 5A. Schematic of typical zoned dolomite crystal in Boat Harbour Formation.

5 Compositional zoning

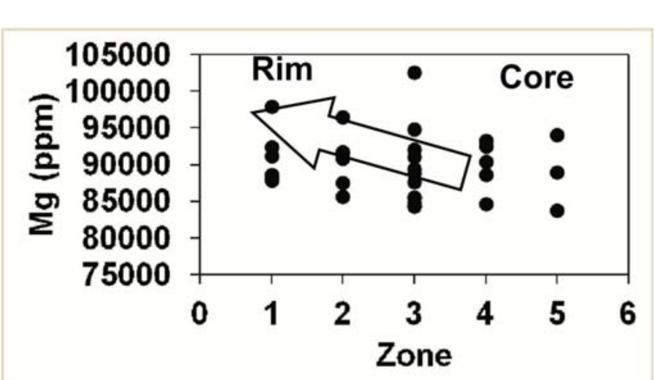


Fig 5B. Scatter diagram of Mg against zone identity within the dolomite crystals. Note increasing trend from core (5) to the rim (1).

5 Compositional zoning

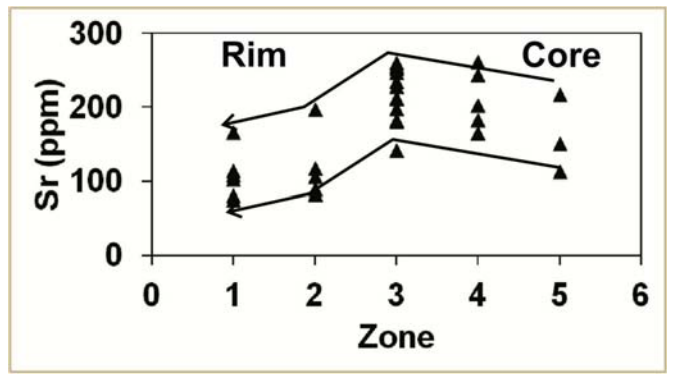


Figure 5C. Plot of Sr (ppm) against zone identity showing decreasing trend from the crystals' cores to their rims.

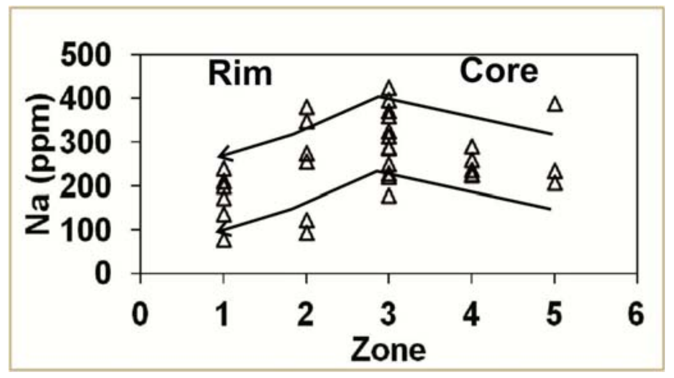


Figure 5D – Plot of Na (ppm) against zone identity showing decreasing trend from the crystal's cores to their rims.

5 Compositional zoning

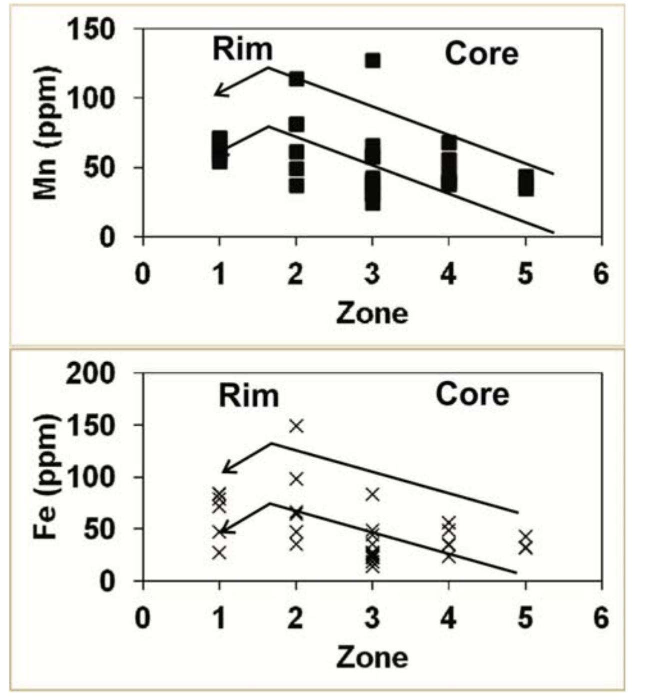


Fig 5E. Mn (ppm) and Fe (ppm) against zone identity. Showing increasing trend from core to rim except at the cortex (see text for explanation).

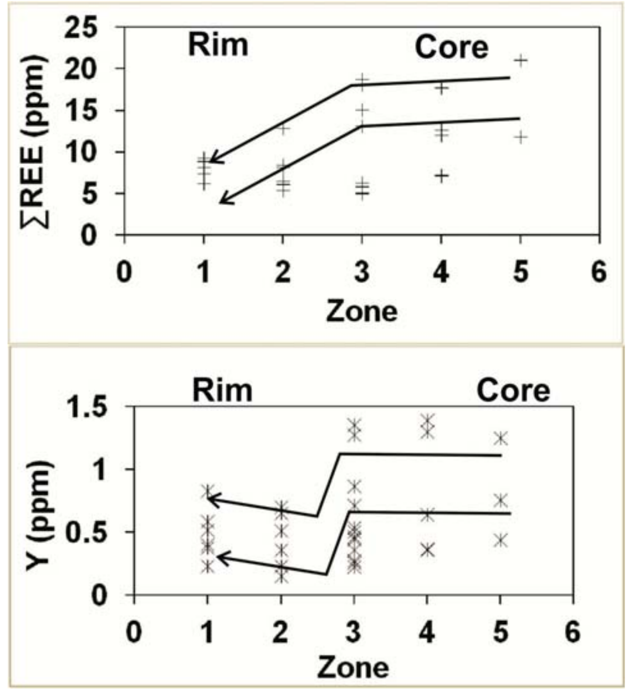


Fig 5F. REE (ppm) and Y (ppm) against zone identity showing decreasing trend from the crystals' core to their rim.

6 Conclusions and Implications

- Mg concentration increases from core to rim (Fig. 5B):
- Consistent with process of dolomite 'ripening' from unstable to stable form;
- Sr and Na concentrations decrease from core to rim (Fig. 5C and 5D)
- Later dolomitizing fluid low in salinity (mixed source formation fluid) OR
- Kinetic effects due to recrystallization of dolomite crystals (partitioning coefficient of Sr and Na is less than 1 (Veizer, 1983).
- Fe and Mn concentrations broadly increase from core to rim (Fig. 5E):
- Due to reducing condition at the rim. Implies precipitation in a deeper burial setting. Note crack-heal feature on Fig 4D.
- The lesser reducing condition at the outermost cortex might be an influence of more oxidizing fluid that fluxed through disconformity-related (see Fig. 2) dissolution zones.
- REE and Y concentrations decrease from core to rim (Fig. 5F):
- Large water/rock reaction is required to alter Y and REE concentrations in carbonate rocks during diagenesis (Banner et al., 1988). Hence core and rim likely formed from fluids of different chemistries. Implying core and rim formation are likely separated in time.
- Further indicates that rim formed from fluid of lower salinity (Sholkovitz, 2000) as supported low Na and Sr.

Implications

- Trace element variations across the crystal traverses reflect changing fluid chemistry and environmental setting.
- The crystals studied preserves multiple episodes of dolomitization during crystal growth.

7 Works Cited

Banner, J. L., Hanson, G. N., & Meyers, W. J. (1988). Rare Earth Element and Nd isotopic variations in regionally extensive dolomites from the Burlington-Keokuk formation (Mississippian); Implications for REE mobility during carbonate diagenesis. *Journal of Sedimentary Petrology, 58*(3; 3), 415-432

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