

# **<sup>PS</sup>Understanding Hydrothermal Dolostone through Combined New Stable Isotope ( $\delta\text{Mg}$ ) Analyses with Conventional Field, Petrographic and Isotopic Data\***

**Denis Lavoie<sup>1</sup>, Simon Jackson<sup>2</sup>, and Isabelle Girard<sup>2</sup>**

Search and Discovery Article #50521 (2011)

Posted December 12, 2011

\*Adapted from poster presentation at AAPG International Conference and Exhibition, Milan, Italy, October 23-26, 2011. Update of article, "<sup>PS</sup>Mg Isotopes in Hydrothermal Saddle Dolomites; Current Data for Paleozoic Dolomites of Eastern Canada and Implications for Mg Source", Search and Discovery article #50350.

<sup>1</sup>Geological Survey of Canada, Natural Resources Canada, Quebec City, QC, Canada ([delavoie@nrcan.gc.ca](mailto:delavoie@nrcan.gc.ca))

<sup>2</sup>Geological Survey of Canada, Natural Resources Canada, Ottawa, ON, Canada

## **Abstract**

The processes that form high temperature dolomites are controversial, with end-members of: 1) tectonically controlled early processes with rapid upward migration of high temperature fluids, and 2) burial-dominated late processes with regional slow migration of high-temperature brines. Magnesium stable isotope ratios in saddle dolomites, ultramafics and shales are presented and offer critical new data in the ongoing debate.

Hydrothermal saddle dolomites in eastern Canada overly diverse Precambrian and Paleozoic basements, which may have acted as Mg sources. The dolomites and potential Mg sources were chemically characterized (ICP-ES) and their  $\delta^{26}\text{Mg}_{\text{DSM3}}$  and  $\delta^{25}\text{Mg}_{\text{DSM3}}$  ratios measured (MC-ICP-MS). Column chemistry was used to purify the Mg in the digested samples prior to isotopic analysis.

The Lower Silurian dolomites ( $T_h$  of 150-200°C) are related to fluid flow along foreland faults. The  $\text{Mg}^{2+}$  is interpreted to originate from Ordovician ultramafic sivers. Near the Silurian occurrences, Lower Ordovician dolomitized slope carbonates are associated with a transpressional fault. These dolomites have yielded negative  $\delta^{26}\text{Mg}_{\text{DSM3}}$  values ranging from -3.2 to -1.5‰.

Middle Ordovician platform dolomites ( $T_h$  of 90 to 120°C) are associated with foreland faults that reach the Precambrian metamorphic basement. They yielded  $\delta^{26}\text{Mg}_{\text{DSM3}}$  ratios of -1 to -0.7‰. Lower Devonian reef with massive replacement dolomite of magmatic origin ( $T_h$  of 300 to 350°C) occurs at the junction of two transpressional faults. Even though the reef neighbours the ultramafic sivers, the dolomite has  $\delta^{26}\text{Mg}_{\text{DSM3}}$  ratios around -1‰.

Linear relationships between dolomite  $\delta^{26}\text{Mg}_{\text{DSM3}}$  and 1)  $\delta^{18}\text{O}_{\text{VSMOW}}$  of the fluid, and 2)  $^{87}\text{Sr}/^{86}\text{Sr}$  in the dolomite suggest a link with the nature of the fluid and its source. Linear relationships

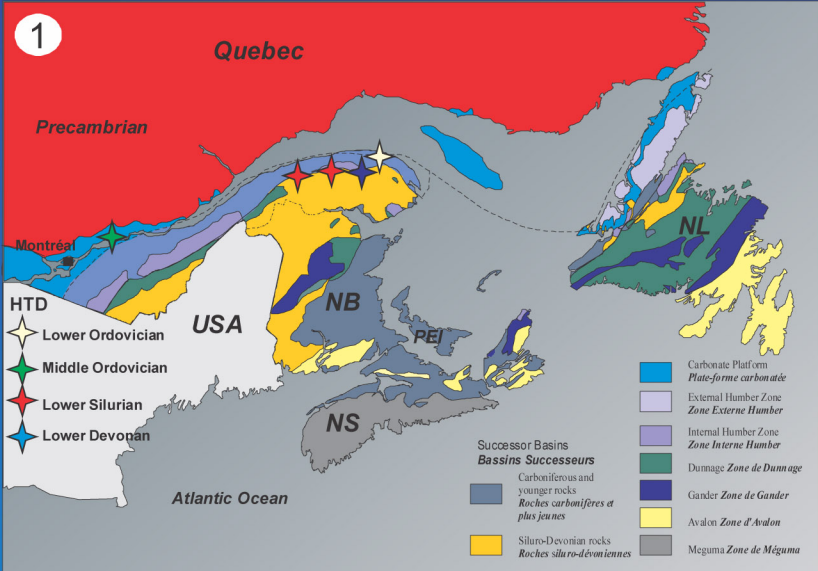
between  $\delta^{26}\text{Mg}_{\text{DSM3}}$  and  $T_h$  of fluid inclusions indicate a thermal kinetic effect on  $\text{Mg}^{2+}$  incorporation in the dolomite.

There are no Lower Paleozoic evaporites in these eastern Canada basins, as such  $\text{Mg}^{2+}$  cannot be derived from that source. Data from other potential Mg sources are being gathered. Lower Ordovician ultramafics are serpentinized; the altered material has a tight range of  $\delta^{26}\text{Mg}_{\text{DSM3}}$  values of -0.4 to -0.2‰. Lower and Upper Ordovician shales abound in the Lower Paleozoic basin. The shales have Mg isotope ratios that differ with age; the Lower Ordovician has yielded  $\delta^{26}\text{Mg}_{\text{DSM3}}$  values of -0.8 and +0.1‰ whereas the Upper Ordovician has given  $\delta^{26}\text{Mg}_{\text{DSM3}}$  values of -1.2 and -1‰.

### References

- Lavoie, D., and C. Morin, 2004, Hydrothermal dolomitization in the Lower Silurian Sayabec Formation in northern Gaspé-Matapédia (Quebec): First constraint on timing of porosity and regional significance for hydrocarbon reservoirs: *Bulletin of Canadian Petroleum Geology*, v. 52, p. 256-269.
- Lavoie, D., and G. Chi, 2010, Lower Paleozoic foreland basins in eastern Canada: tectono-thermal events recorded by faults, fluids and hydrothermal dolomites: *Bulletin of Canadian Petroleum Geology*, v. 58, p. 17-35.
- Lavoie, D., G. Chi, M. Urbatsch, and B. Davis, 2010, Massive dolomitization of a pinnacle reef in the lower Devonian West Point Formation (Gaspé Peninsula, Québec) – An extreme case of hydrothermal dolomitization through fault-focussed circulation of magmatic fluids: *Bulletin of American Association of Petroleum Geologists*, v. 94, p. 513-531.
- Lavoie, D., and G. Chi, 2006, Hydrothermal dolomitization in the Lower Silurian La Vieille Formation in northern New Brunswick: Geological context and significance for hydrocarbon exploration: *Bulletin of Canadian Petroleum Geology*, v. 54, p. 380-395.

GEOLOGICAL AND STRATIGRAPHIC SETTINGS

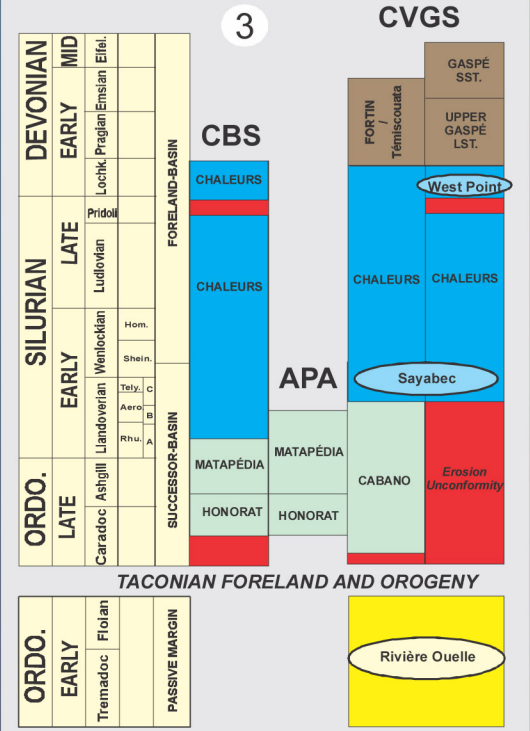
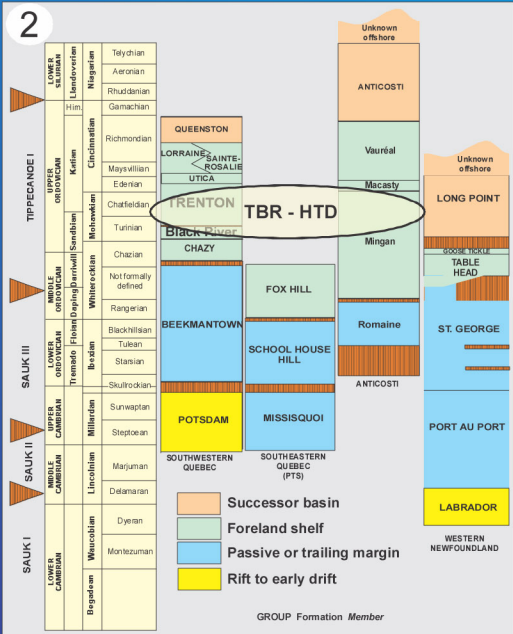


GEOLOGICAL, STRATIGRAPHIC AND TECTONIC SETTING

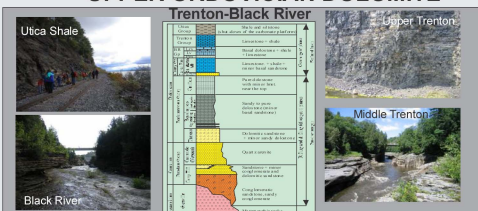
The Paleozoic successions of eastern Canada consists of 3 major domains (Fig. 1); the Cambrian-Ordovician deformed by the Taconian Orogeny, the Silurian-Devonian deformed by the Acadian Orogeny and the Carboniferous-Permian deformed by the Alleghanian Orogeny. This poster presents field and geochemical data on hydrothermal dolomites found in the first two geological domains of eastern Canada (Fig. 1).

The Middle to Late Ordovician Trenton-Black River of southern Québec (Fig. 2) represents the youngest Taconian foreland basin carbonates. Equivalent units are found in the Anticosti basin (Mingan; Fig. 2) whereas similar but older facies are present in western Newfoundland (Table Head Group; Fig. 2). The Trenton-Black River hydrothermal dolomites are major hydrocarbon reservoirs in the various intracratonic basins in the USA (Michigan) but also in the Appalachian basin of New York and in the St. Lawrence platform of southern Ontario. Recent drilling in the St. Lawrence platform in southern Quebec has confirmed the presence of dolomite-breccia, the distribution of which is controlled by faults. These dolomite breccia have yielded some significant gas flows (up to 9 mmcf/d).

In the Gaspé Peninsula of eastern Québec, interpreted hydrothermal dolomites are found in the Lower Ordovician Rivière-Quelle Formation of the Taconian fold and thrust belt (Fig. 3). Hydrothermal dolomites are also found in all major shallow marine carbonate units of the Silurian-Devonian Gaspé Belt, these include the shallow marine carbonate ramp of the Early Silurian Sayabec Formation and the major reef platform of the Late Silurian-Early Devonian West Point Formation (Fig. 3). These dolomite bodies in the Gaspé Peninsula are all associated with major Acadian dextral strike-slip faults although their mode of formation is documented to vary from one case to the other. It is noteworthy that the known occurrences of hydrothermal dolomites in the Silurian-Devonian Gaspé Belt are closely associated with both magnetic and gravity highs in the basin. There is no current hydrocarbon production from the Sayabec and West Point formations, however, a small gas field (Galt Field) is hosted in a fault-controlled dolomitic breccia in the Lower Devonian Upper Gaspé Limestones in eastern Gaspé (Fig. 3).

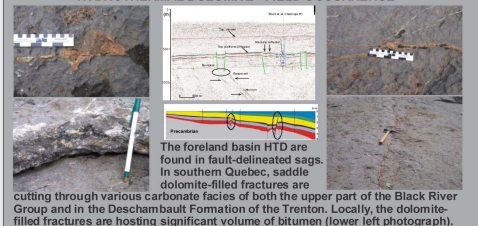


# UPPER ORDOVICIAN DOLOMITE

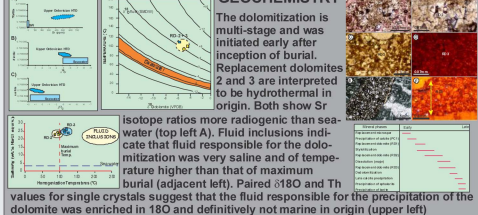


The Middle-Upper Ordovician Black River and Trenton groups are host to world-class hydrocarbon reservoirs in hydrothermal dolomites. They both represent shallow-marine carbonate units deposited in the Taconian foreland basin.

## HYDROTHERMAL DOLOMITE - FIELD OCCURRENCE



## GEOCHEMISTRY



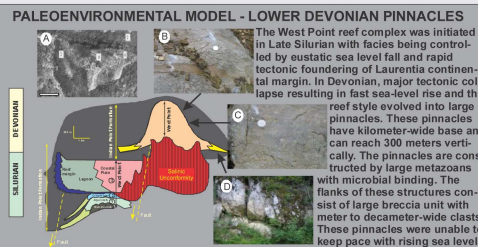
LAVOIE AND CHI, 2010

# HIGH-TEMPERATURE FAULT-CONTROLLED

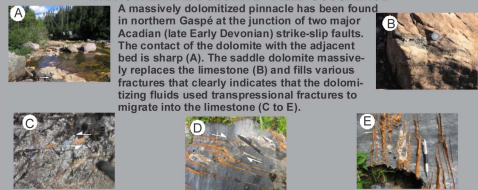
## HYDROTHERMAL DOLOMITES:

# FIELD, PETROGRAPHIC AND GEOCHEMICAL EVIDENCE

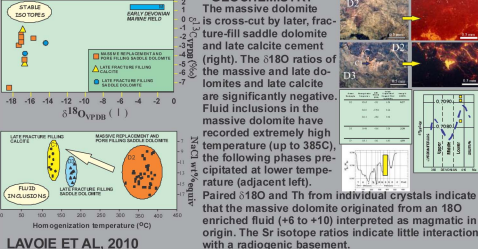
## LOWER DEVONIAN DOLOMITE



## HYDROTHERMAL DOLOMITE - FIELD OCCURRENCE

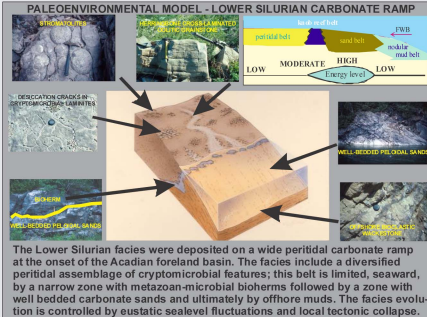


## GEOCHEMISTRY

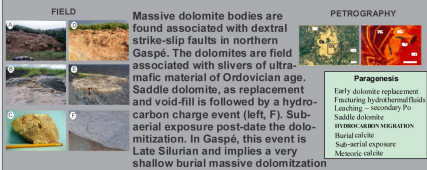


LAVOIE ET AL, 2010

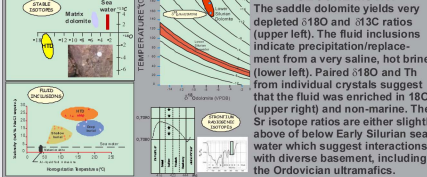
## LOWER SILURIAN DOLOMITE



## HYDROTHERMAL DOLOMITE - FIELD AND PETROGRAPHY



## GEOCHEMISTRY



LAVOIE AND MORIN, 2004

LAVOIE AND CHI, 2006, 2010



# MAGNESIUM ISOTOPES IN SADDLE DOLOMITE CEMENT

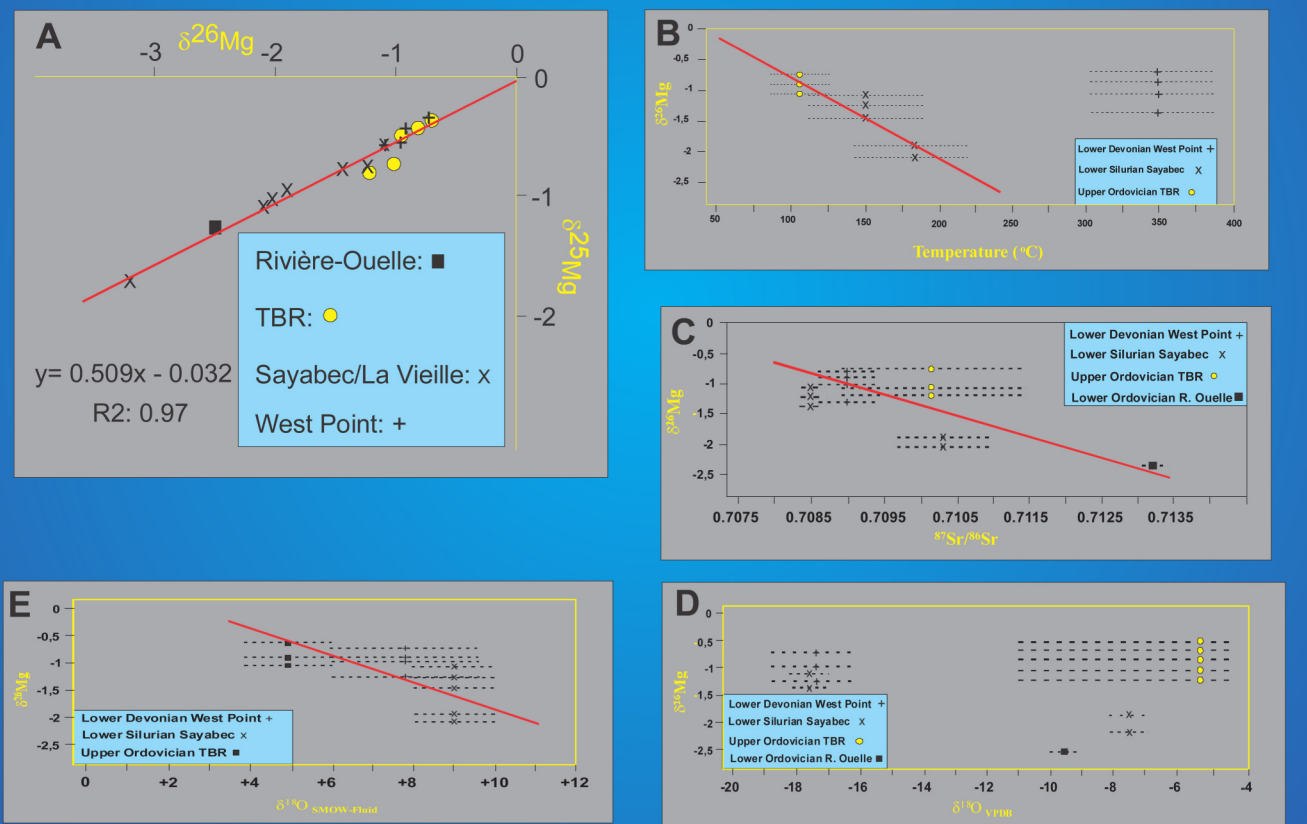
Saddle dolomites from the Lower Ordovician Riviere Ouelle Formation, the Middle Ordovician Black River and Trenton groups, the Lower Silurian Sayabec Formation and the Lower Devonian West Point Formation were analyzed with ICP-MS for their  $\delta^{26}\text{Mg}$  and  $\delta^{25}\text{Mg}$  ratios. The  $\delta^{26}\text{Mg}$  and  $\delta^{25}\text{Mg}$  ratios vary from -3,25 to -0,71 permil and from -1,71 to -0,38 permil, respectively.

The plot of  $\delta^{26}\text{Mg}$  versus  $\delta^{25}\text{Mg}$  (A) shows a linear relationship with a correlation equation of  $y=0,509x-0,032$  ( $R^2=0,97$ ). The correlation indicate that the fractionation of the magnesium isotope is controlled by kinematic processes. It is noteworthy that two major groupings are recognized; the first one consists of saddle dolomites of the Lower Ordovician Rivière Ouelle and the Lower Silurian Sayabec Formation with more negative  $\delta^{26}\text{Mg}$  and  $\delta^{25}\text{Mg}$  ratios and a second group made of the Middle Ordovician TBR and the Lower Devonian West Point with less negative ratios.

Discarding the very high temperature saddle dolomite of the Lower Devonian West Point Formation, a strong relationship exists between  $\delta^{26}\text{Mg}$  and temperature of precipitation (based on fluid inclusion Th) of saddle dolomite (B). For a diagenetic fluid of fairly constant Mg-Isotope composition, higher temperatures of precipitation are associated with negative  $\delta^{26}\text{Mg}$  ratios.

A less convincing relationship seems to link the  $\delta^{26}\text{Mg}$  and the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of saddle dolomite (C). However, this relationship (decreasing  $\delta^{26}\text{Mg}$  ratios with increasing radiogenic values) is only valid if the data point from the Riviere Ouelle Formation is valid. Such relationship would link the magnesium isotopic ratios of void-filling and replacement saddle dolomite with the nature of the dolomitizing fluid.

Finally, if there is no clear relationship is detectable between  $\delta^{26}\text{Mg}$  and  $\delta^{18}\text{O}$  of saddle dolomite (D), a relationship is developed between the  $\delta^{26}\text{Mg}$  ratio of saddle dolomite and the  $\delta^{18}\text{O}$  value of the diagenetic fluid responsible for dolomitization (E)



## SUMMARY OF GEOCHEMICAL DATA

Age - Unit	Fluid Inclusions (Th- $^{\circ}\text{C}$ )	$^{87}\text{Sr}/^{86}\text{Sr}$	$\delta^{18}\text{O}_{\text{VPDB-Dol}}$ (‰)	$\delta^{18}\text{O}_{\text{VSMOW-Fluid}}$ (‰)	$\delta^{25}\text{Mg}_{\text{DSM3}}$ (‰)	$\delta^{26}\text{Mg}_{\text{DSM3}}$ (‰)
Lower Ordovician - Riviere Ouelle		0.7131 - 0.7132	-10 to -9		-1.3	-2.5
Middle Ordovician - TBR	80 - 130	0.7088 - 0.7115	-11 to -7	+4 to +6	-0.8 to -0.3	-1.3 to -0.71
Lower Silurian - Sayabec						
- Ruisseau Isabelle section	110 - 200	0.7082 - 0.7085	-18 to -17		-1.7 to -0.6	-3.3 to -1.1
- Lac Matapedia section	140 - 220	0.7096 - 0.7101	-8 to -7	+8 to +10		
Lower Devonian - West Point	300 - 380	0.7084 - 0.7092	-19 to -16	+6 to +10	-0.7 to -0.4	-1.3 to -0.8

## MAGNESIUM SOURCE FOR DOLOMITIZATION THEIR Mg-ISOTOPE SIGNATURE

Significant sources of Mg are needed to explain the major volumes of dolomites present in the Paleozoic of eastern Canada. Given the geological nature of the basements, the most likely sources are: 1) Cambrian to Ordovician mafic and ultramafic volcanic rocks and 2) Lower and Upper Ordovician black shales. Recycling Mg from replaced precursor carbonates is not considered as significant because of our restriction to dolomite cements, no replacement dolomites have been selected for this first phase of research.

Figure A presents the Mg-isotope ratios of the potential sources. The Lower Ordovician (Rivière-Ouelle) and Upper Ordovician (Utica) shales have ratios that are totally different. The Cambrian (Saint-Damase) and Ordovician (Pointe Verte) basalts are also occupying two mutually exclusive domains. Finally, the Ordovician ultramafic (Lady Step) ratios are in the same domain as the Ordovician mafics. At first approximation, differences exist in Mg-isotopes for Lower Paleozoic potential sources.

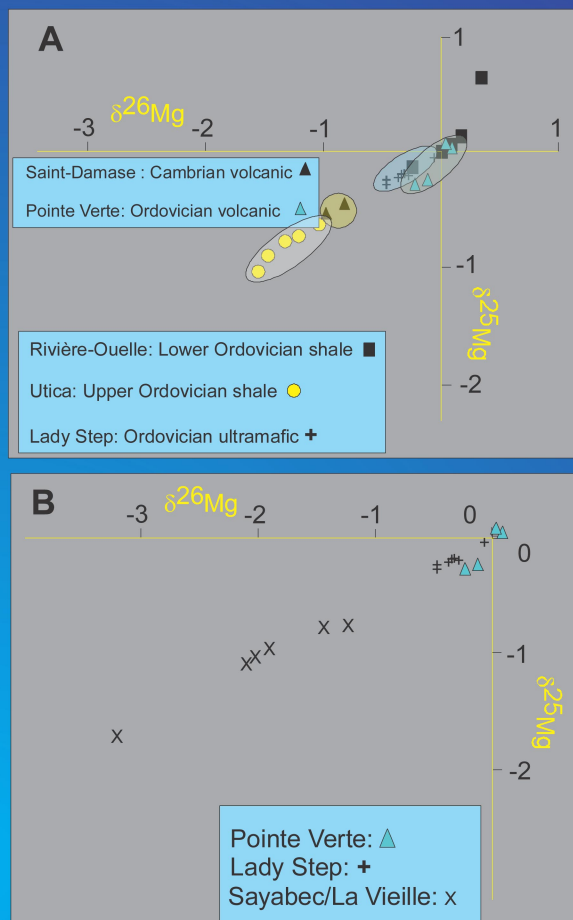


Figure B displays the Mg-isotope ratios for saddle dolomite cements in the Lower Silurian Sayabec and La Vieille formations and those of the Ordovician mafic and ultramafic volcanics that form the geological basement beneath the carbonate platform. It has been hypothesized that the Mg for dolomitization was derived from this basement. There is a significant isotopic difference between the relatively clustered Ordovician volcanic ratios and those widespread of the Silurian dolomite. We interpret this as the result of significant thermal isotopic fractionation between the diagenetic fluid (Mg-isotope largely derived from the mafic minerals) and in the high-temperature (Th of 110 - 220°C) saddle dolomite.

Ongoing and future research projects will target a complete diagenetic dolomitization history from very early burial to late burial and hydrothermal dolomite precipitation and replacement. More potential sources of Mg will be analyzed from different Paleozoic ages and tectonostratigraphic settings.