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Magnesium isotopes in high-temperature saddle dolomite cements in the lower Paleozoic of Canada

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ABSTRACT

Mg isotopes are used to better understand the genesis of hydrothermal saddle dolomite cements in Lower Paleozoic successions in Canada. These cements occur in fault-bounded dolostones that overlay lithologically diverse basement rocks; Ordovician dolomite lies over the Precambrian craton, whereas the Silurian and Devonian dolomites overlay a succession of tectonically accreted sedimentary, volcanic and ultramafic units of Cambrian to Ordovician age.

Lower Silurian saddle dolomites have the most negative $\delta^{26}Mg_{DSM3}$ values of our dataset (−3.25 to −1.13‰), and plot in two distinct groups: a strongly negative subset that characterizes higher temperature (175 °C) dolomites, and a less negative subset for lower temperature (153 °C) dolomites. Upper Ordovician saddle dolomites precipitated at significantly lower temperatures (102 °C), and their $\delta^{26}Mg_{DSM3}$ values range from −1.26 to −0.71‰. Lower Devonian saddle dolomites formed at very high temperature (350 °C) and have $\delta^{26}Mg_{DSM3}$ values ranging from −1.29 to −0.78‰.

No experimental data on high temperature (100–350 °C) fluid-dolomite Mg isotope fractionation factors have been published, and recent research suggests that no significant fractionation occurs between diagenetic fluids and dolomites at high temperatures in closed to semi-closed diagenetic systems. Our results indicate that the isotopic signature of diagenetic fluid is the primary control for the $\delta^{26}Mg_{DSM3}$ values in these high-temperature dolomites.

1. Introduction

Dolomites and dolomitization have been major research themes since the first scientific description of dolomite by de Dolomieu (1791). Since then, multiple hypotheses for the origin of dolomite have been proposed (van Tuyl, 1914; Hsu, 1966; Machel and Mountjoy, 1986; Machel, 2004; among others). Current models include syn-sedimentary bacteria-mediated precipitation (van Lith et al., 2002; Zhang et al., 2013), marine–meteoric water mixing (Humphrey and Quinn, 1989), shallow burial reflux (Jones and Xiao, 2005), deep burial thermo-chemical sulphate reduction (Machel, 1987) and fault-controlled hydrothermal dolomitization (Davies and Smith, 2006). Dolomite precipitation and dolomitization of precursor carbonates can result from more than one process. Nevertheless, researchers using similar data can arrive at very different conclusions (Humphrey and Quinn, 1989, 1990; Machel and Mountjoy, 1990). Apart from academic interest, an understanding of dolomitization processes is critical because dolostones are one of the most prolific hosts of the world's conventional reserves of hydrocarbons (Braithwaite et al., 2004). The mechanisms of dolomitization have been studied using multiple approaches and techniques, and recent studies incorporate a variety of petrographic (conventional, fluid inclusion microthermometry, cathodoluminescence, UV-excited light, and scanning electron microscopy) and geochemical (major-trace elements, REE, oxygen and carbon stable isotopes, strontium radiogenic isotopes, and ion chemistry of fluid inclusions) approaches in addition to detailed field or core description.

The emergence of new metal isotope systems provides a supplementary tool to better appreciate the various origins of dolomites. The understanding of Mg-isotope values in carbonates is progressing rapidly, with recent contributions on magnesium cycling in deep sea marine sediments (Higgins and Schrag, 2010), on biotic (Hippler et al., 2009) and abiotic (Immenhauser et al., 2010; Li et al., 2012) low-temperature precipitation of Mg-rich calcites and the effects of growth rates on Mg-fractionation factors in low temperature Mg-calcite (Mavromatis et al., 2013). Research on Mg-isotope behaviour in high temperature dolomites is restricted to the detailed studies of an initially

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semi-closed diagenetic system to the late open diagenetic system of Geske et al. (2012) and Azmy et al. (2013), largely based on replacement dolomites.

Here, we focus on trends in Mg isotopes for geologically and geochemically well-characterized, high temperature saddle dolomite cements in Lower Paleozoic Canadian strata (Ordovician, Silurian and Devonian). Mg-isotope values ($^{25}Mg/^{24}Mg$ and $^{26}Mg/^{24}Mg$) of these dolomites are evaluated for their potential for characterizing and contrasting sources of diagenetic fluids and aid in the assessment of Mg-sources for dolomitization.

We restrict our samples to pore- and fracture-filling saddle dolomite cements; this is done in order to minimize the additional complexity of buffering of $\delta^{25}Mg$ and $\delta^{26}Mg$ values with the Mg-isotope signatures of precursor carbonates (Geske et al., 2012; Azmy et al., 2013). The key aims of this study are: 1) to determine whether Mg-isotope values of saddle dolomite cements relate to the temperature of precipitation or to the composition of the diagenetic fluids and 2) to evaluate if Mg-isotope signatures of saddle dolomites are in agreement with the previous interpretations of the nature of hydrothermal fluids responsible for their precipitation.

2. Geological setting

The Lower Paleozoic succession of eastern Canada belongs to two major tectonostratigraphic domains (Fig. 1; Lavoie, 2008): 1) the Cambrian–Ordovician shallow marine platform and adjacent slope and rise successions (St. Lawrence Platform and Humber Zone, respectively) and 2) the Silurian–Devonian shallow to deep marine basin (Gaspé Belt). These host a large number of dolomite-rich units (Lavoie, 2008) and recent field, petrographic and geochemical works on these dolostones have led to the proposition that there are significant hydrothermal imprints on some (Table 1).

2.1. Hydrothermal dolomite occurrences and petrography

2.1.1. Upper Ordovician foreland carbonate ramp

The Upper Ordovician Taconian foreland carbonate ramp in eastern North America is known as the Trenton–Black River (TBR) interval from which hydrothermal dolomite was initially recognized as a major hydrocarbon exploration target (Hurley and Budros, 1990). These units recorded high temperature hydrothermal events in southern Quebec (TBR, Lavoie et al., 2009), Anticosti Island (Mingan Formation; Lavoie and Chi, 2010) and Hudson Bay (Red Head Rapids Formation; Lavoie et al., 2011).

The Deschambault Formation (Trenton Group) is characterized by initial calcite cementation that commonly fills most of available primary pore space. Replacement dolomitization initiated before the onset of stylolitization and continued afterwards, and the replacement dolomite occurs near small fractures that cut through the limestone facies. The replacement dolomite consists of sub-mm (0.01 to 0.15 mm) crystal size of planar-e type (Sibley and Greg, 1987), dull reddish to non-luminescence under CL (Fig. 2A, B). Saddle dolomite cements are found coating small fracture walls and within secondary dissolution pore space, the dolomite is subhedral to euhedral, planar to saddle, and 0.1 to 0.8 mm in crystal size; it is very dull reddish orange luminescent with fine very dull luminescent crystal tips (Fig. 2A, B). A late calcite phase fills most of the remaining void spaces and locally, sphalerite is observed as the last diagenetic phase.

2.1.2. Lower Silurian foreland carbonate ramp

The Lower Silurian peritidal carbonate ramp of the Gaspé Belt, comprising the Sayabec and La Vieille formations, evolved during the inception of the Acadian foreland basin (Lavoie, 2008). Locally, the carbonate ramp succession contains extensive dolostone bodies where dextral strike-slip faults juxtapose the carbonates with the Ordovician ultramafic and mafic volcanic rock units in the northern Gaspé and northern New Brunswick. Detailed field, petrographic and geochemical studies support the hydrothermal origin of these dolomites (Lavoie and Chi, 2001; Lavoie and Morin, 2004; Lavoie and Chi, 2006, 2010). Previous work on the Lower Silurian Sayabec Formation dolostones suggests that diagenetic fluids differed in composition among the western and central Gaspé locations (Table 1).

In the intensively dolomitized outcrops of the Sayabec Formation, matrix-replacive dolomite that consists of interlocking, 0.05 to 0.5 mm dolomite rhombs form the groundmass of all samples (Lavoie and Morin, 2004). The fine-grained groundmass dolomite is locally corroded at the margin of some mm- to cm-sized dissolution vugs and fractures. Pore-filling coarsely crystalline saddle dolomite lines the walls of the secondary pores. The saddle dolomite can entirely fill some small pores and fractures although, in most cases, it partially fills the largest pores. This dolomite consists of 0.5 to 2 mm, inclusion-rich euhedral to subhedral saddle crystals (Fig. 2C, D). Under CL, the crystals are red luminescent with common sub-mm non-luminescent tips (Fig. 2C, D). In some larger pores, calcite cements overlie the saddle dolomite; the calcite consists of anhedral crystals.

2.1.3. Lower Devonian pinnacle reefs

Lower Devonian pinnacle reefs of the West Point Formation in the northern Gaspé grew in response to rapid sea level rise (Bourque et al., 1986). One of these pinnacles is exposed at the junction of two major dextral transpressive faults where magmatic activity and high heat flux are recorded (Pinet et al., 2008). The pinnacle is intensively dolomitized; early saddle dolomite records very high precipitation temperatures, with homogenization temperatures of primary fluid inclusions ranging between 301 and 382 °C. Petrographic and geochemical data suggest a major hydrothermal imprint on the carbonate facies (Lavoie et al., 2010).

The massively dolomitized section of the West Point Formation contains three phases of dolomite as well as a late calcite phase; the second phase of saddle dolomite has been analysed for its Mg isotope values. The first dolomite phase is rare (volumetrically less than 1%) and consists of anhedral crystals that range in size from 0.005 to 0.05 mm (0.0002 to 0.002 in). The second dolomite is the most abundant phase in the pinnacle reef, making up over 90% of the total rock volume; it is represented by euhedral, iron-rich crystals that range from 0.5 to 8 mm (0.02 to 0.3 in) in size (Fig. 2E, F). This pore-filling dolomite is dull red luminescent. The last saddle dolomite is restricted to fractures cutting through the pinnacle and makes up roughly 5% of the total rock volume.

3. Interpretation of hydrothermal fluids from geochemical tracers

Based on the data available from the previous studies (Table 1), we provide some interpretations as to the origin of the hydrothermal fluids responsible for the precipitation of saddle dolomites in the Upper Ordovician, Lower Silurian and Lower Devonian dolostones. More details can be found in the above-cited literature. $\delta^{18}O_{VSMOW}$ values of the dolomitizing fluids can be determined from fluid inclusion homogenization temperatures (T_h) and $\delta^{18}O_{VPDB}$ value of the same dolomite crystal (Table 2 and Fig. 2); the stable isotope fractionation between dolomite and water has been calculated using Zheng's (1999) equation. The data indicate that the Upper Ordovician, Lower Silurian (western Gaspé), and Lower Devonian saddle dolomites precipitated over a wide range of temperatures from ^{18}O-enriched brines (+4 to +12‰) with the Upper Ordovician examples being slightly less enriched. Lower Silurian saddle dolomites from central Gaspé precipitated from a near marine fluid (−1 to 0.8‰).

Calculated fluid $\delta^{18}O_{VSMOW}$ values and $^{87}Sr/^{86}Sr$ ratios of saddle dolomite samples (Fig. 3) suggest that Upper Ordovician saddle dolomites are more radiogenic that contemporaneous seawater (Denison et al., 1997; Shields et al., 2003). Lower Silurian saddle dolomite parent fluid