Preliminary Results of a Magnesium Isotope Study of Dolomite in Upper Ordovician Strata, Southeastern Saskatchewan, Northern Williston Basin

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Abstract

In this paper, we report preliminary findings of a magnesium (Mg) isotope study of Upper Ordovician dolomite in the Yeoman and Herald formations in the subsurface of southeastern Saskatchewan (northern portion of the Williston Basin). Three types of dolomite have been previously described: 1) burrows, 2) matrix, and 3) saddle dolomite, representing multiple stages of dolomitization. Samples from each type were collected from four depths in the core selected for this study, but only two distinct groupings of δ^{26}Mg values were found: -1.38 ±0.10‰ ($2\sigma_{mean}$) and -1.67 ±0.01‰ ($2\sigma_{mean}$). These groupings are unrelated to the type of dolomite sampled, indicating that: 1) the three types of dolomite were formed from a single dolomitizing fluid with a uniform δ^{26}Mg value, or 2) the dolomitizing fluid from each successive stage of dolomitization overprinted the δ^{26}Mg value of the earlier-formed dolomite. Small differences in δ^{26}Mg values of dolomite at different depths in the core may be attributed to local-scale conditions of dolomitization, such as changes in precipitation rate, temperature, and the δ^{26}Mg value of the migrating subsurface dolomitizing fluid.

Keywords: *magnesium isotopes, dolomitization, Upper Ordovician, Yeoman Formation, southeastern Saskatchewan, Williston Basin.*

1. Introduction

The Upper Ordovician Red River Formation (Herald and Yeoman formations in southeastern Saskatchewan) is an economically important unit of the Williston Basin, producing oil from reservoirs located in Saskatchewan, North Dakota, and Montana. To the end of 2012, Red River reservoirs in Saskatchewan had produced 4.2 million m^3 of oil (Haidl *et al.*, 2013).

Complex and discontinuous dolomitization patterns in the Yeoman and lower Herald formations are responsible for the reservoir-quality porosity and permeability of the Red River strata (*e.g.*, Kendall, 1976, 1977; Longman and Haidl, 1996; Kreis and Kent, 2000). The Herald Formation consists of interbedded limestone, dolostone, and anhydrite strata of the Lake Alma and Coronach members, and the upper Redvers unit. The Yeoman Formation consists of variably dolomitized packstone, wackestone and mudstone, and contains abundant macrofossils such as brachiopods, corals, stromatoporoids, and a characteristic burrow-mottled fabric reminiscent of *Thalassinoides* (*e.g.*, Kendall, 1976), but more recently interpreted as smaller diameter burrows of *Palaeophycus* and *Chondrites* that have been broadened in appearance by diagenetic halos of dolomite (Gingras *et al.*, 2004). In a portion of southeastern Saskatchewan and in North Dakota, Montana and into South Dakota, kukersitic beds and laminae are present in Yeoman strata and, where they are thermally mature, the kukersites are the source rock for most Red River oil (Fowler *et al.*, 1998).

Striking characteristics of the Yeoman, and its stratigraphic equivalents in the Williston Basin succession, involve several types and patterns of dolomitization, including: 1) preferential dolomitization of the burrow network, 2) complete dolomitization of burrows and matrix carbonate, and 3) carbonate sediment that has evaded dolomitization entirely. Deposits where the carbonate sediment associated with the burrows is the only dolomitized fabric in the rock led researchers to propose that seawater flowed preferentially through the burrow network, thus resulting in the early dolomitization of the burrows (Kendall, 1977; Longman *et al.*, 1983). Gingras *et al.* (2004) offered an alternative hypothesis. These authors presented evidence that the centimetre-scale burrows are actually diagenetic halos of dolomite formed around millimetre-scale worm burrows. Recognizing that smaller burrows would be less likely to channelize fluid flow through the sediment, these authors suggested that the dolomite halos formed as a

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by-product of the metabolic activity of sulphate-reducing bacteria. The bacteria colonized the burrows, rather than the matrix sediment, due to the organic matter accumulated by the feeding activities of the burrowing organisms.

In cases where the matrix carbonate was also dolomitized, a second episode of dolomitization must have occurred, driven by a different mechanism. Indeed, matrix dolomite is theorized to have formed later than the burrow dolomite, by the downward flux of seawater into the sediment (concentrated through evaporation) (Longman *et al.*, 1983; Qing *et al.*, 2004). The 'brining upward' conditions of deposition recorded in the Yeoman/Herald succession supports this interpretation. However, the brine reflux hypothesis does not explain why completely dolomitized strata (burrows and matrix) are interbedded with limestone units or strata with dolomitized burrows and limestone matrix. Kendall (1977) and Longman and Haidl (1996) discuss the possibility that the distribution of dolomite reflects patterns in the deposition of high-magnesium calcite in the original limestone deposits. These authors hypothesized that the units that were dolomitized contained higher concentrations of magnesium than the surrounding carbonate lithologies, which aided the formation of dolomite when this magnesium was released during diagenesis. Recent work by Nash *et al.* (2011) supports this idea by demonstrating that high concentrations of magnesium can be achieved through biologically mediated activity in the formation of protodolomite from magnesite in modern calcifying algae.

The last stage of dolomitization of the Yeoman carbonates is represented by saddle dolomite, which is interpreted to reflect the passage of a hydrothermal fluid through the succession sometime after the matrix dolomite had formed (*e.g.*, Qing *et al.*, 2001).

The seawater hypothesis for the source of the dolomitizing fluid, whether it was seawater of normal salinity in sedimentary pore fluids (*e.g.*, burrows), or evaporated seawater with potentially elevated Mg/Ca ratios (*e.g.*, matrix dolomite), was tested for each type of dolomite using $^{87}Sr/^{86}Sr$ as a tracer (Qing *et al.*, 2001). Due to the long residence time of strontium in the modern ocean (~2.5 million years), the $^{87}Sr/^{86}Sr$ ratio of seawater is effectively constant on million-year time scales. Accordingly, if seawater was the source of the magnesium that dolomitized the Herald and Yeoman formations, then the $^{87}Sr/^{86}Sr$ ratio of the dolomites should be nearly uniform, in the likelihood that the diagenetic time frame for dolomitization was no more than a few million years. The $^{87}Sr/^{86}Sr$ ratio of seawater at the time of Yeoman and Herald deposition is 0.7080, as measured by Holmden (2009). By contrast, the $^{87}Sr/^{86}Sr$ ratios of Yeoman and Herald dolomite are higher than this (Qing *et al.*, 2001; Holmden, 2009), ranging between 0.7084 and 0.7091, suggesting that contemporaneous seawater was not the dolomitizing fluid. Qing *et al.* (2001) offered three hypotheses for sources of dolomitizing fluid that could potentially explain the results: 1) Late Silurian seawater that filtered downward into the succession when seawater $^{87}Sr/^{86}Sr$ ratios were higher; 2) formation waters expelled from Cambro-Ordovician formations located lower in the succession, also with high $^{87}Sr/^{86}Sr$ ratios (0.7085 to 0.7090); and 3) connate waters whose $^{87}Sr/^{86}Sr$ ratios were modified by strontium exchange reactions with Precambrian basement rocks. Note that for the second and third hypotheses the dolomitizing fluids would have flowed upward through the succession.

In this study, we use magnesium isotopes to study the process of dolomitization. In contrast to $^{87}Sr/^{86}Sr$, which is an indirect tracer of dolomitization, the isotopes of magnesium ($^{26}Mg/^{24}Mg$ and $^{25}Mg/^{24}Mg$) have the potential to trace the dolomitizing fluids directly. By obtaining magnesium isotope data ($\delta^{26}Mg$ values) from samples within dolomitized burrows, matrix, and saddle dolomite, we aim to improve understanding of the sources of the dolomitizing fluids, the paleo-flowpaths taken by the dolomitizing fluids, and the general process of dolomitization.

2. Sampling and Analytical Procedures

Small powdered samples of Yeoman carbonate were collected from core of the Home Dome Torquay S 41/03-08-001-11W2M; 85B212 well in southeastern Saskatchewan (Figures 1 and 2) using a power drill and carbide cutter bit. All three types of dolomite (burrow, matrix, and saddle) are present in this core. The sampling of the burrows and matrix dolomite was performed on hand-sample–scale slabs of core. One sample of saddle dolomite was collected (precipitated as infill vug cement) (Figure 3). Analyses of elemental concentrations were carried out at the Saskatchewan Research Council's (SRC) Geoanalytical Laboratories. Magnesium isotopic analyses were conducted at the Saskatchewan Isotope Laboratory in the Department of Geological Sciences, University of Saskatchewan.

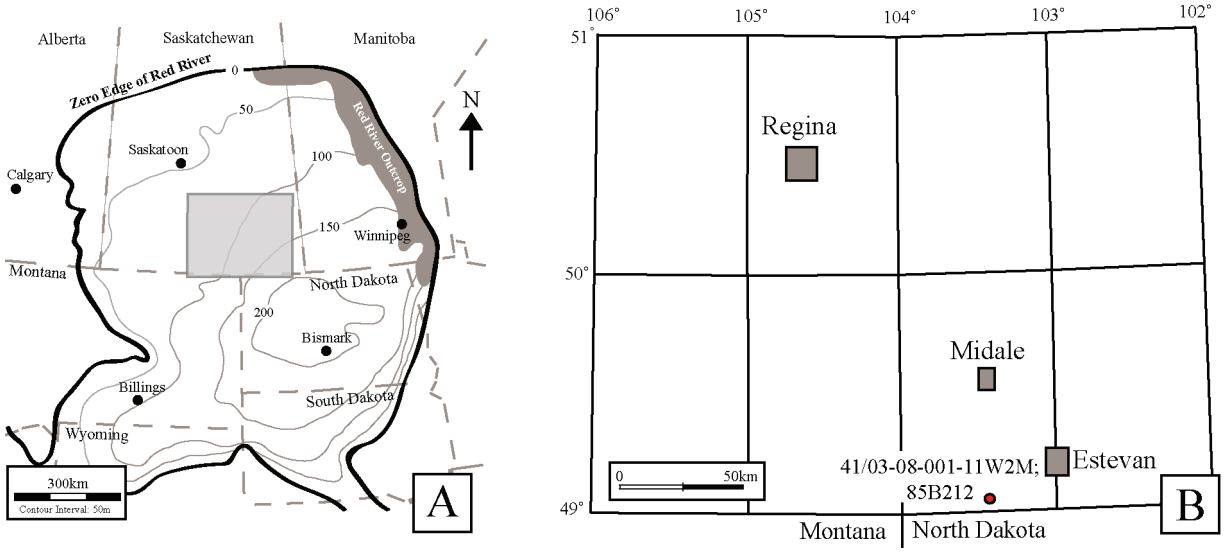

Figure 1 – Map showing the distribution of Red River strata in central North America. A) Isopachs of the Red River strata in the Williston Basin, indicating the centre of the basin located in North Dakota. The grey shaded box represents the study area in Figure 1B. **Modified from** ***Pratt and Haidl (2008) and Norford*** **et al.** ***(1994). B) Detail view of southeastern Saskatchewan and location of the Home Dome Torquay S 41/03-08-001-11W2M; 85B212 well.***

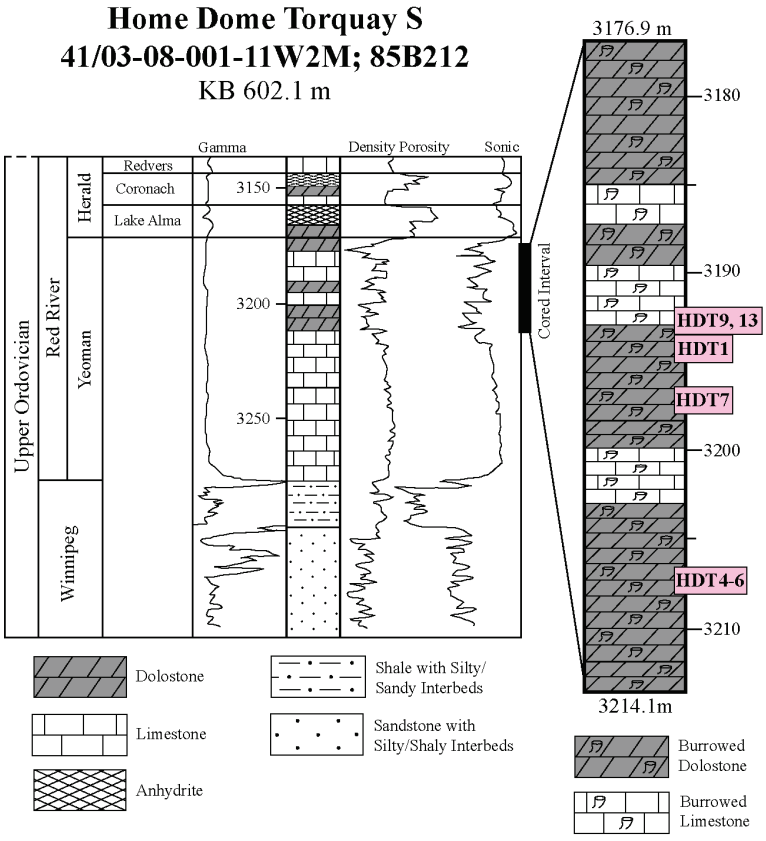

Figure 2 – General stratigraphy of Upper Ordovician Red River strata in southeastern Saskatchewan, and the lithologies identified in core of the Home Dome Torquay S 41/03-08-001-11W2M; 85B212 well (KB=kelly bushing). Sampling locations of rock powders for magnesium isotope analyses are indicated on the close-up of the cored interval. **Modified from** ***Qing*** **et al.** ***(2001). Note: Burrow features indicated on the close-up cored interval have been dolomitized. Refer to Figure 3 for sample details.***

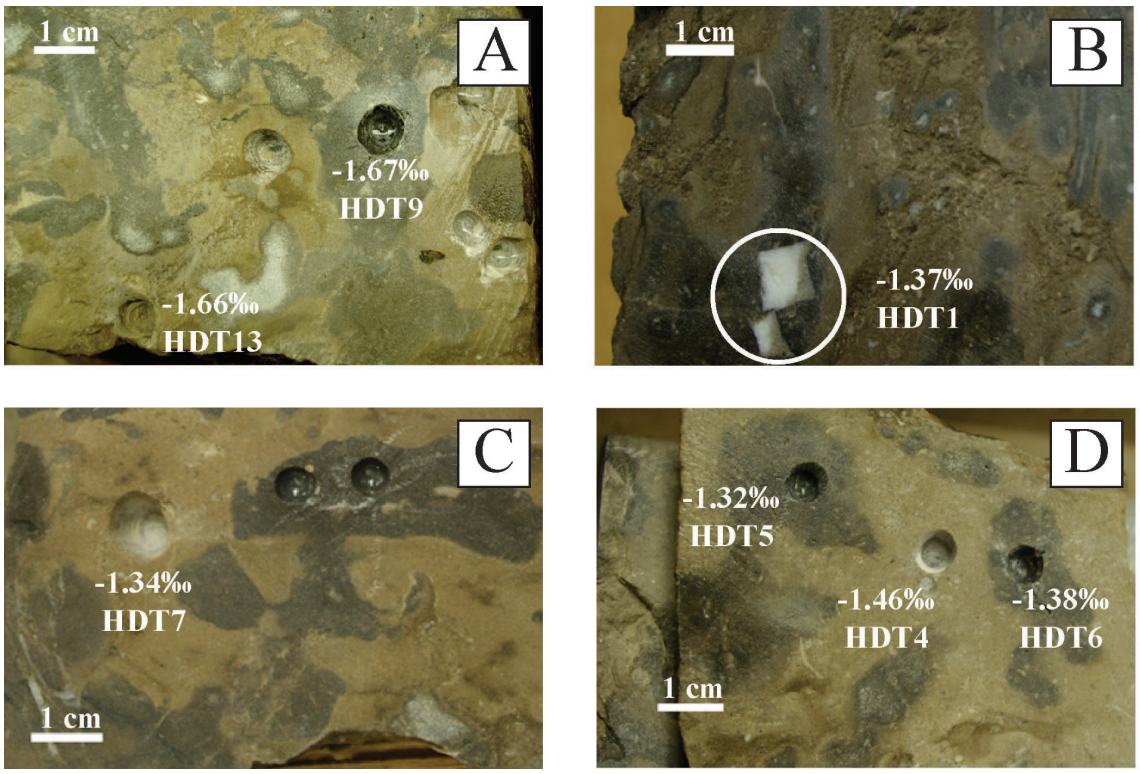

Figure 3 – Photographs showing sampling locations of burrow, matrix, and saddle dolomite within core taken from the Home Dome Torquay (HDT) S 41/03-08-001-11W2M; 85B212 well. Magnesium isotope (δ^{26}Mg (‰)) values are reported with sample IDs. A) Burrow HDT9 and matrix HDT13 dolomite at ~3192 m depth. B) Saddle dolomite (circled) precipitated within a rectangular-shaped vug, occurring within a burrow at ~3194 m depth. Saddle dolomite HDT1 was sampled from the other side of the slab in order to preserve this pristine example. C) Matrix HDT7 dolomite at ~3197 m depth. D) Matrix HDT4, burrow 1 HDT5, and burrow 2 HDT6 dolomite at ~3207 m depth.

Rock powders were dissolved drop-wise with ultrapure 6 M HCl and brought up to 50 ml total solution volume with deionized water (18.2 MΩ cm^{-1}). Elemental concentrations of the solutions were measured by inductively coupled plasma mass spectrometry (ICP-MS) at SRC's Geoanalytical lab. The magnesium was purified prior to mass spectrometry using traditional gravity flow cation exchange columns filled with 2 ml of BioRad AG-MP-50 resin. Aliquots were taken before and after the magnesium elution from the column to ensure that more than 98% of the magnesium was collected, in order to avoid isotopic fractionation during the purification procedure. The purified magnesium solutions were dried down and treated with ultrapure H_2O_2 and concentrated HNO_3 to destroy residual organics. Magnesium isotope ratios were measured with a Thermo Fisher Scientific Neptune multicollector ICP-MS using a cyclonic glass spray chamber sample introduction system. Samples of approximately 1 ppm Mg dissolved in 0.3 M HNO_3 were measured using the low-resolution slit with an uptake rate of 100 µl/min, yielding 8-10V signals on mass 24. Magnesium isotope ratios were measured using a standard-sample bracketing technique. Sample intensities were matched to within 5% of the intensity of the bracketing standard (DSM3). The quality of the measurements was monitored using an interlaboratory standard (CAM-1) and an internal magnesium standard (Mg Specpure), which is isotopically distinct from CAM-1.

Magnesium has three naturally occurring stable isotopes: ^{24}Mg (78.99%), ^{25}Mg (10.00%), and ^{26}Mg (11.01%). ^{26}Mg/^{24}Mg and ^{25}Mg/^{24}Mg ratios are reported as δ^{26}Mg and δ^{25}Mg values, respectively, in the conventional delta notation as per mil (‰) deviations of the sample isotope ratio relative to the standard DSM3 (Galy *et al.*, 2003), as shown in equation (1) for δ^{26}Mg.

$$\delta^{26}Mg = \left(\frac{(^{26}Mg/^{24}Mg)_{sample}}{(^{26}Mg/^{24}Mg)_{DSM\,3}} - 1 \right) \times 1000 \qquad \text{(Eq. 1)}$$

The total range of variation in magnesium isotopes in Earth materials is approximately 5 to 6‰. The analytical uncertainty for δ^{26}Mg is ±0.10‰ (2σ), and for δ^{25}Mg it is ±0.05‰ (2σ), which is determined on the basis of repeated analyses of CAM-1 (n=48) from different mass spectrometry sessions. Uncertainties associated with measurements of samples within the same mass spectrometry session are reported as two standard errors of the mean (2 SE). In

cases where sample measurements are repeated between different mass spectrometry sessions, the average value is reported, along with the 2σ uncertainty.

3. Results

δ^{26}Mg and $^{87}Sr/^{86}Sr$ data are listed in Table 1. Dolomite from the Home Dome Torquay S 41/03-08-001-11W2M; 85B212 well core yielded δ^{26}Mg values ranging from -1.32‰ to -1.67‰, showing significant variability considering the uncertainty of the measurements (±0.10‰, 2σ). The results are broadly consistent with previously reported δ^{26}Mg values for dolomite ranging from Mississippian to Jurassic in age (-1.63‰ to -1.40‰) (Young and Galy, 2004; Brenot *et al.*, 2008; Jacobson *et al.*, 2010). A modern Atlantic seawater standard measured in our laboratory yielded -0.84‰ ±0.08‰ ($2\sigma_{mean}$), which is within the uncertainty of the values reported for modern seawater measured in other laboratories (-0.82‰) (*e.g.*, Chang *et al.*, 2003; Carder *et al.*, 2004; Young and Galy, 2004; De Villiers *et al.*, 2005; Tipper *et al.*, 2006). The average $^{87}Sr/^{86}Sr$ ratio for SRM987 measured over the course of this work is 0.710288 ±0.000014 ($2\sigma_{mean}$). There is no correlation between δ^{26}Mg and $^{87}Sr/^{86}Sr$ in the dolomite samples (R^2=0.11).

The δ^{26}Mg values for the burrow dolomite and matrix dolomite are nearly identical when sampled from the same slab of core, but differ significantly between slabs sampled at different depths. The first four samples (HDT4 to 6 and HDT7), which were collected at depths of 3207 m (HDT4 to 6) and 3197 m (HDT7) (Figure 2, Table 1), yielded an average δ^{26}Mg value of -1.38 ±0.10‰ ($2\sigma_{mean}$) for the combined burrow and matrix dolomite, whereas the last two samples (HDT9 and 13), which were collected higher in the core at ~3192 m, yielded an average value of -1.67 ±0.01‰ ($2\sigma_{mean}$). Saddle dolomite (HDT1) collected at ~3194 m yielded an average value of -1.37 ±0.14‰ ($2\sigma_{mean}$).

Table 1 – Magnesium isotope data for single element magnesium standards (CAM-1, DSM3, Mg Specpure), as well as magnesium isotope and Mg/Ca molar ratios for a modern Atlantic seawater standard (OSIL) and Upper Ordovician dolomite samples collected for this study (HDT1, 4 to 7, 9, 13). $^{87}Sr/^{86}Sr$ ratios are also reported for the modern Atlantic seawater standard, strontium isotope standard SRM987, and the Upper Ordovician dolomite samples. All dolomite samples were collected from core taken from the Home Dome Torquay S 41/03-08-001-11W2M; 85B212 well. N is the number of separate instrument sessions by mass spectrometry. 2σ (two standard deviations) is the external (Ext) analytical uncertainty based on replicates of standards and samples measured in more than one instrument session. 2SE (two standard deviations divided by the square root of the number of runs) is the internal (Int) uncertainty based on multiple runs of each sample during one instrument session.

Sample ID	Depth (m)	Type	N	δ^{26}Mg DSM3 (‰)	Uncertainties *Int* 2SE	Uncertainties *Ext* 2σ	δ^{25}Mg DSM3 (‰)	Uncertainties *Int* 2SE	Uncertainties *Ext* 2σ	$^{87}Sr/^{86}Sr$	Mg/Ca (mol/mol)
CAM-1		Cambridge-1 Standard	48	-2.62		0.10	-1.35		0.05		
DSM3		Dead Sea Metal 3 Standard	39	-0.03		0.06	-0.02		0.05		
Mg Specpure		Alfa Aesar Mg Single Element Standard	47	-3.79		0.10	-1.95		0.06		
SRM987		Sr Carbonate Isotopic Standard	19							0.710288	
OSIL		Modern Atlantic Seawater Standard	2	-0.84		0.08	-0.42		0.04	0.7092	5.136
Slab 1											
HDT9	3192	Burrow	1	-1.67	0.06		-0.86	0.04			0.923
HDT13	3192	Matrix	1	-1.66	0.03		-0.88	0.01		0.70848	0.822
Slab 2											
HDT1	3194	Saddle Dolomite	2	-1.37		0.14	-0.72		0.08	0.70824	0.764
Slab 3											
HDT7	3197	Matrix	1	-1.34	0.03		-0.69	0.03		0.70883	0.852
Slab 4											
HDT4	3207	Matrix	1	-1.46	0.05		-0.77	0.03		0.70909	0.933
HDT5	3207	Burrow 1	1	-1.32	0.02		-0.68	0.01		0.70902	0.935
HDT6	3207	Burrow 2	1	-1.38	0.02		-0.71	0.02		0.70907	0.840

4. Discussion

The burrow and matrix dolomite in this study yielded nearly identical δ^{26}Mg values when sampled from the same slab of core (centimetre-scale distances between burrow and matrix dolomite). Taken at face value, this finding suggests that a single dolomitizing fluid is responsible for both types of dolomite, which seems at odds with the petrographic evidence for separate episodes of dolomitization (*e.g.*, Kendall, 1976). Equally puzzling are the high $^{87}Sr/^{86}Sr$ ratios, which suggest that the dolomitizing fluid cannot be Upper Ordovician seawater (Qing *et al.*, 2001; Holmden, 2009). If the earlier-formed burrow and matrix dolomite were susceptible to overprinting by later-stage dolomitizing fluids, then it is possible to reconcile the geochemical and petrographic constraints. In this scenario, the last major stage of dolomitization of the Yeoman and Herald formations caused both the homogenization of δ^{26}Mg values between burrow and matrix dolomite in the same slab of core, and the increase in $^{87}Sr/^{86}Sr$ ratios. In support of this hypothesis, Malone *et al.* (1996) reported that dolomite is very susceptible to magnesium exchange with fluids at high temperature, based on laboratory experiments. Field support for the overprinting hypothesis comes from a recent study of a thick succession of Triassic dolomites by Geske *et al.* (2012), who reported a decrease in δ^{26}Mg variability between four phases of dolomite with an increase in stratigraphic depth correlating with increased burial temperature.

If the overprinting hypothesis is correct, it remains to be explained why pervasively dolomitized strata are interbedded with limestone beds or units in which the burrows are dolomitized and the matrix is not. Could late-stage dolomitizing fluids have travelled through the succession without passing through the limestones? One promising explanation is that earlier-formed burrow and bedded dolomite resulted in channelization of later-stage dolomitizing fluids, which protected the limestone units from being dolomitized.

The small but significant variability in δ^{26}Mg values between slabs sampled at different depths may be evidence for differences in local-scale conditions of dolomitization, such as temperature, precipitation rate, and fluid migration rate. Although the magnitude of the fractionation factor ($\Delta^{dolomite}_{Mg(aq)}$) is not well established (-2.0‰ to -2.7‰, as stated by Higgins and Schrag, 2010), the sign of the fractionation factor indicates that dolomite is preferentially enriched in the light isotopes of magnesium compared to the dolomitizing fluid. Accordingly, if the precipitation rate is high and fluid migration rate is low, such that a significant fraction of the aqueous magnesium is used up before it can be replenished, the dolomite will record progressively higher δ^{26}Mg values, *i.e.*, the δ^{26}Mg value of the dolomite will be closer to the δ^{26}Mg value of the fluid. The opposite is the case where precipitation rate is low and fluid migration rate is high; these dolomites will record the maximum fractionation between dolomite and fluid. This local reservoir effect may explain the small differences in δ^{26}Mg values between different slabs of core measured in this study.

If the dolomitizing fluids experience changes in δ^{26}Mg values along fluid migration flow paths due to the process of dolomitization, then δ^{26}Mg gradients may be recorded in large dolomite bodies. These hypothetical gradients could reveal the direction of fluid flow during dolomitization—the flow direction being recorded by increasing δ^{26}Mg values in the dolomite. The fluid migration hypothesis is testable with additional work aimed at documenting whether spatial gradients in δ^{26}Mg values exist within the Yeoman and Herald dolomite. The presence of gradients could help to resolve whether seawater percolating downward through the sedimentary succession, or connate water flowing upward through the succession, is the source of the dolomitizing fluid, bearing in mind the possibility that magnesium isotope signatures of early-stage fluid migration events might be overprinted by later-stage events.

5. Conclusions

Preliminary results of a magnesium isotope study of dolomite within core of the Home Dome Torquay S 41/03-08-001-11W2M; 85B212 well exhibit small but significant variability in δ^{26}Mg values, ranging from -1.32‰ to -1.67‰. Three types of dolomite have been described in the studied core, including burrow, matrix, and saddle dolomite (Qing *et al.*, 2001). Nevertheless, only two distinct groupings of δ^{26}Mg values emerge from the dolomite samples analyzed in this study, regardless of which type is measured: -1.38 ±0.10‰ ($2\sigma_{mean}$) and -1.67 ±0.01‰ ($2\sigma_{mean}$). It was also found that burrow and matrix dolomite from the same slab of core gave identical results, and that the two groupings of δ^{26}Mg values correlate to slabs sampled at different depths in the core. It is possible that the uniformity in δ^{26}Mg values reflects one source of dolomitizing fluid for both the burrow and matrix dolomite. On the other hand, magnesium exchange with a late-stage dolomitizing fluid might overprint the isotopic signatures of the earlier-formed dolomite. If this hypothesis is correct, then the high $^{87}Sr/^{86}Sr$ ratios recorded in these dolomites might also be the product of overprinting by late-stage fluids, and the high $^{87}Sr/^{86}Sr$ ratios do not necessarily preclude Upper Ordovician seawater as the source of the fluid that dolomitized the Yeoman Formation burrow and matrix carbonate.

By contrast, the difference in δ^{26}Mg values between slabs from different depths in the core may reflect differences in local-scale processes of dolomitization, in particular, differences in dolomite formation rate *vs.* fluid migration rate. These data also suggest the possibility that large dolomite bodies might record subsurface gradients in dolomite δ^{26}Mg values. If gradients exist, then it may be possible to use them to determine paleoflow directions of

dolomitizing fluids. Petroleum industry workers could use magnesium isotope gradients in dolomite bodies to target new exploration wells, as migrating petroleum systems might be expected to follow the same subsurface pathways in the Williston Basin as the dolomitizing fluids. The gradient hypothesis is testable with further work aimed at sampling many more core slabs from spatially distributed wells.

6. Acknowledgements

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7. References

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