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In situ geochemistry of middle Ordovician dolomites of the upper Mississippi valley

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Abstract
The dolomitization and diagenetic history of Ordovician carbonates of southern Wisconsin is complex. Previous studies attributed dolomitization to various diagenetic factors and environments. In this study, high-resolution, in situ laser ablation inductively coupled mass spectrometry analysis of rare earth element patterns of dolomite was used to assess the diagenetic fluids responsible for dolomitization of the Ordovician Decorah Formation. Integrated geochemical data and petrographic evidence suggest that the dolostones are formed in two different diagenetic realms: shallow burial and hydrothermal. Shallow burial dolomites exhibit three distinct rare earth element patterns. Dolomite from the middle portion of the Guttenberg Member exhibits light rare earth element enrichment consistent with early burial dolomitization. Dolomites of the Carimona, Specht's Ferry and Lower Guttenberg members are often burrow associated and exhibit medium rare earth element enrichment associated with Fe-oxide desorption in anoxic porewaters. Leaching of Mg from co-occurring volcanic ash during alteration is a probable source that contributed to the dolomitization. Extensively dolomitized samples in the upper Guttenberg and Ion Member exhibit evidence of hydrothermal dolomitization. The relationship of these heavily dolomitized samples to interbedded limestones provides evidence for a recently proposed hydrothermal dolomitization model invoking pressure solution of calcite and precipitation of dolomite. These early burial and hydrothermal depositional models are consistent with models proposed for overlying and underlying Ordovician dolostones.

KEYWORDS
dolostones, laser ablation ICPMS, rare earth elements

1 | INTRODUCTION
Dolomitized strata surrounding the Michigan Basin in northern Illinois and eastern Wisconsin (Figures 1 and 2) have been studied due to the hydrocarbon reservoir production potential of these Ordovician rocks (Luczaj, 2006; Yoo, Gregg, & Shelton, 2000) but no consensus exists on the dolomitization process (Asquith, 1967; Badiozamani, 1973; Deininger, 1964; Luczaj, 2006; Smith & Simo, 1997). Badiozamani (1973) proposed the “Dorag” model that involved mixing of meteoric water from runoff with sea water. According to this model, the mixing of different water masses provided a means of overcoming the kinetic barriers to dolomite formation. This author based
his model on the geometry of dolomitization surrounding the Wisconsin Arch and argued that the dolomitization of Wisconsin Arch strata occurred during regression resulting in subaerial exposure and creation of a freshwater–saltwater mixing zone. However, the mixing zone model in general has been called into question as a model that can lead to widespread dolomitization (Machel, 2004). Hardie (1987) questioned the thermodynamics of this model and noted that mixing zone waters with respect to temperature, pCO₂, pH and initial meteoric water composition are not likely to behave in the ideal manner as argued by Badiozamani (1973). Other Holocene dolomite occurrences that had been attributed to the mixing zone model, like the Hope Gate Formation of Northern Jamaica, have also been shown to be driven by other processes (Land, 1991). Luczaj (2006) provided more evidence against the “Dorag” model when his field observations of the occurrence of dolomite surrounding the Wisconsin Arch did not match the geometry used in the Badiozamani (1973) model. Luczaj (2006) instead demonstrated that the dolomitization zone extended further east towards the margin of the Michigan Basin and proposed that this dolomite formed as the result of hydrothermal fluid flow out of the Michigan Basin.

Studies of carbonate diagenesis have incorporated standard analytical techniques such as inductively coupled plasma mass spectrometry (ICP-MS) major, trace and rare earth element (REE) geochemical analyses to provide insight into the nature of diagenetic conditions (Azmy et al., 2013; Azomani, Azmy, Blamey, Brand, & Al-Aasm, 2013; Banner, Hanson, & Meyers, 1988; Bau, Möller, & Dulski, 1997; Frimmel, 2009; Hecht, Freiburger, Gilg, Grundmann, & Kostitsyn, 1999; Qing & Mountjoy, 1994; Wang, Hu, Wang, Cao, & Chen, 2014; Wang et al., 2009; Zhang, Guan, Jian, Feng, & Zou, 2014). In situ high-resolution analysis via laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) measuring REE has proven to be particularly effective in dolomite studies (Carmichael, Ferry, & McDonough, 2008; Corlett & Jones, 2012; Wang et al., 2009; Xuefeng et al., 2010; Zhang et al., 2014). In this study LA-ICP-MS REE analysis, combined with petrographic and cathodoluminescence analysis, was used to provide new insights into the formation of dolomite in the Upper Mississippi Valley and to test the competing hypotheses of dolomite formation.

2 | GEOLOGICAL SETTING

2.1 | Regional stratigraphy

During the Late Ordovician the majority of Laurentia was situated at a low palaeolatitude in the southern hemisphere (Cocks & Torsvik, 2011). Much of central and eastern North America was inundated by a warm, shallow epicontinental sea (Herrmann & Haupt, 2010; Quinton et al., 2016). Upper Ordovician strata in southern Wisconsin and the surrounding area were deposited in subtidal conditions.

![FIGURE 1](image-url) (a) Regional structural features surrounding the study area in Wisconsin (USA). The red dotted outline is the extent of dolomite surrounding the Wisconsin Arch from the Luczaj (2006) study with large arrows indicating suggested flow directions of basinal hydrothermal fluids. Hydrothermal fluids affecting the Pb–Zn district were probably derived from the Illinois Basin, and dolomitization along the Wisconsin Arch resulted from hydrothermal fluids expelled radially from the Michigan Basin (Luczaj, 2006). (b) Generalized geohistory plot illustrating the burial history of sediments in eastern Wisconsin since the Ordovician (redrawn from Luczaj, 2006). Several geochemical proxies (e.g., organic maturity, oxygen isotopic composition of sandstone cements, oxygen isotopic composition of conodont apatite) and stratigraphic reconstructions suggest that Ordovician rocks in this area were never buried deeper than 1 km and only experience temperatures lower than 40–60°C (Hyodo et al., 2014; Luczaj, 2006; Quinton et al., 2017)
environments ranging from inner ramp to outer ramp depositional settings (Choi & Simo, 1998; Choi, Simo, & Saylor, 1999; Witzke & Ludvigson, 2005).

This study focuses on the Decorah Formation which is the earliest deposition of the Galena Group (Figure 2; McLaughlin, Emerson, Witzke, Sell, & Emsbo, 2011). At the Dickeyville outcrop (Figure 2), the Carimona Member is 0.3 m thick and consists of limestone beds with shale partings. The 1.8 m thick Specht’s Ferry Member is dominated by green to grey-green shale with thin discontinuous interbeds of fossiliferous limestone. Underlying the Specht’s Ferry Member is the Deicke K-bentonite (Emerson, Simo, Byers, & Fournelle, 2004; Kolata, Frost, & Huff, 1986) while the Millbrig K-bentonite is located in the lower portion of the Specht’s Ferry Member. Overlying the Specht’s Ferry Member is the thin phosphatic grain rich Garnavillo limestone bed (McLaughlin et al., 2011). The Elkport K-bentonite lies between the Garnavillo limestone and the overlying Guttenberg Member of the Decorah Formation. The Guttenberg Member is a predominantly limestone unit that is ~4.8 m thick with occasional minor shale partings. The Dickeyville K-bentonite is in the upper portion of the Guttenberg Member. The uppermost 2.5 m of the Dickeyville outcrop consists of the mixed limestone–dolomite Ion Member.

**FIGURE 2** Stratigraphic column, sample horizons (samples DV01 to DV10) and outcrop picture of the Highway 151 roadcut at Dickeyville, Wisconsin. Tentative Midcontinent conodont biozones from Sell et al. (2015) from nearby Hwy. 61 Dickeyville outcrop. Zones were correlated using trace element correlation of apatite from K-bentonites. “?” indicates tentative biostratigraphic boundary. “M” sequence stratigraphic nomenclature from Holland and Patzkowsky (1997) originally developed on the Nashville Dome and correlated to the UMV region by McLaughlin et al. (2011). Abbreviated formations and members include the Platteville (P’ville) Fm, Quimby’s Mill (Q.M.), the Carimona (Car.), and the Garnavillo (G.).
2.2 Application of rare earth elements (REE) and trace element (TE) analysis to dolostones

2.2.1 Application of rare earth elements to dolostones

The REE have very low abundances (ppb) in sea water and calcareous marine organisms, however, they are much more abundant in sea floor and buried carbonate sediments (Banner et al., 1988). This REE enrichment occurs by interaction with pore-waters near the sediment-water interface (Bau & Alexander, 2006; Piper & Bau, 2013; Shields & Webb, 2004). Incorporation of REE can occur by several different means; substitution for Ca$^{2+}$ and Mg$^{2+}$ in the carbonate lattice, filling lattice positions formed by defects, or incorporation by adsorption due to remnant ionic charges (Qing & Mountjoy, 1994). Interaction with later diagenetic fluids can potentially erase or overprint the geochemical signatures of the original carbonate material (Wang et al., 2014; Zhang et al., 2014). Carbonate REE data can also be overprinted by the incorporation into carbonates of non-carbonate phases like Fe or Mn oxides, clay minerals, quartz or sulphides. Due to the high concentration of REE in these phases relative to carbonates, even small amounts of contamination by these phases will overprint the REE pattern of diagenetic fluids in carbonates (Frimmel, 2009; Nothdurft, Webb, & Kamber, 2004; Qing & Mountjoy, 1994; Zhang et al., 2014).

Comparison of REE signatures to potential proxies for sources of REE such as Upper Continental Crust (UCC) (Taylor, McLennan, & McCulloch, 1983) provide a basis for delineating different trends in REE patterns and making inferences regarding the diagenetic history and alteration of carbonate materials. For instance, UCC-normalized REE patterns of sea water and carbonates retaining sea water or sea water-like geochemical signatures exhibit light rare earth element (LREE, i.e., La–Nd) depletion relative to HREE (Ho–Lu) and a distinctly noticeable negative Ce anomaly due to the oxic nature of normal sea water (Piper & Bau, 2013). Variation from this sea water-like REE trend is an indication of influence by fluids with distinctly non-sea water-like geochemical properties (Banner et al., 1988).

Cerium and Europium commonly occur in multiple oxidation states. In the case of Ce (Ce$^{4+}$/Ce$^{3+}$) the oxidation state is controlled by oxidation condition (anoxic vs. oxic fluids). The oxidation state of Eu (Eu$^{3+}$/Eu$^{2+}$) is controlled primarily by temperature, and to a lesser extent by pressure and pH, making it an invaluable tool in the identification of high-temperature burial brines or hydrothermal diagenetic fluids (Frimmel, 2009; Zhang et al., 2014).

2.2.2 Application of trace elements to dolostones

Aluminium and thorium are important indicators of contamination by clay minerals, which can greatly affect the REE patterns of dolomites (Zhang et al., 2014). Concentrations of Ba, Fe and Sr when compared to those of Mn can help in estimating diagenetic fluid characteristics like hydrothermal influence, redox state and recrystallization respectively (Azomani et al., 2013; Frimmel, 2009; Zhang et al., 2014).

3 METHODS

3.1 Sample collection

Thirty-five samples were taken from the Highway 151 roadcut in Dickeyville, WI (Figure 2), described in the 2007 Wisconsin Ground Water Association Fall Field Trip Guide (Brown, 2007), Wright et al. (2017), and McLaughlin et al. (2011).

3.2 Petrographic preparation and analysis

A total of 35 thin sections were made from 32 carbonate intervals. The thin sections were classified using the Dunham carbonate rock classification scheme (Dunham, 1962). The dolomites were classified after Sibley and Gregg (1987). Cathodoluminescence (CL) analysis was conducted with a Relion III cathodoluminescence stage with the conditions of a −4.7−5.7 kV beam voltage, pressure of 32–40 mTorr and a current of 0.51–0.78 mA. Descriptions and interpretations were completed using CL petrography as outlined by Hiatt and Pufahl (2014).

3.3 Laser ablation ICPMS analysis

The LA-ICPMS analyses were performed using a Thermo iCap Qc ICP-MS that was connected to a Cetac G2-213 Nd:YAG laser system. Laser settings are shown in Table 1. Isotopes of individual elements analysed included $^{24}$Mg, $^{27}$Al, $^{43}$Ca, $^{48}$Ti, $^{43}$Ca, $^{55}$Mn, $^{57}$Fe, $^{88}$Sr, $^{89}$Y, $^{90}$Zr, $^{132}$Ba, $^{232}$Th and the lanthanide series (REE) $^{57}$La–$^{71}$La.

The glass standard NIST SRM 612 was used as the external standard as this reference material has been shown to be useful for carbonate microanalyses (Jochum et al., 2012). IAEA B7 (Tonarini et al., 2003), and NIST SRM 1d (Certificate of Analysis, 2005) were used as secondary standards. Data reduction was conducted using Iolite v2.5 (Hellstrom, Paton, Woodhead, & Hergt, 2008; Paton, Hellstrom, Paul, Woodhead, & Hergt, 2011) with $^{43}$Ca as the internal standard.
TABLE 1 (a) ICP-MS and (b) Laser Ablation System Settings

| Parameter | Setting |
|-----------|---------|
| (a) Thermo iCap Qc ICP-MS | |
| RF power/W | 1,550 |
| Cool gas flow rate (1/min) | 14 |
| Carrier gas (Ar) flow rate (1/min) | 0.74 |
| Carrier gas (He) flow rate (1/min) | 0.67 |
| (b) Cetac G2-213 laser system | |
| Laser type | Nd: YAG |
| Wavelength (nm) | 213 |
| Laser fluence (%) | 3 |
| Pulse repetition rate (Hz) | 4 |
| Shutter delay (s) | 10 |
| Ablation time (s) | 40 |
| Washout time (s) | 30 |
| Spot size (μm) | 100 |

A total of 330 dolomite rhombs were ablated from 10 dolomized horizons that had sufficiently large dolomite rhombs available for laser ablation analysis. The Ba/Ca and Zr/Ca ratios were used to screen for burn through into the underlying glass slide as it has been found that the thin section glass contained high amounts of Zr and Ba. This also aided in eliminating dolomite samples most altered due to terrigenous contaminants (Frimmel, 2009; Zhang et al., 2014). Dolomite crystals that experienced premature burn through, cracked immediately when ablated, or were probably compromised due to laser targeting were eliminated based on observations during the ablation process. Data for 219 dolomites were compiled for this study and element concentration averages were calculated for each sample.

To further evaluate the presence of siliciclastic material within the remaining samples, dolomite REE concentrations were normalized to UCC, a proxy for terrigenous material from the Canadian Shield. The Al and Th concentrations of the UCC are ~8% for Al and 10.5 p.p.m. for Th (Rudnick & Gao, 2003). Clay content of greater than 2% has been shown to be sufficient to alter REE patterns (Frimmel, 2009; Nothdurft et al., 2004; Webb & Kamber, 2000; Zhang et al., 2014). Contamination cut-off limits for this study were 1,600 p.p.m. for Al and 0.2 p.p.m. for Th. Modern sea water and the carbonate standard materials were plotted against samples for comparison. Modern sea water values were magnified by ×10⁶ due to the low concentration of sea water.

Following Bau and Dulski (1996) and Zhang et al. (2014), Eu, Ce and Pr anomalies were calculated using the following formulas: Eu/Eu* = EuN/(0.67EuN + 0.33TbN), Ce/Ce* = CeN/(0.5LaN + 0.5PrN) and Pr/Pr* = PrN/(0.5CeN + 0.5NdN). Error bars for graphs represent standard error of the analysed element or anomaly from each sample set.

4 RESULTS

4.1 Petrography and cathodoluminescence analysis

Samples from the first interval span, the Carimona (DV01), Spechts Ferry (DV02 and DV03) and the lower most Guttenberg Member (DV04) and are all closely stratigraphically associated with the Deicke K-bentonite and Millbrig K-bentonites. The second stratigraphic interval includes samples from the middle and upper portion of the Guttenberg Member (DV05–DV07). The third interval spans samples from the Ion Member (DV08–DV10).

Dolomites were divided into four types (Types 1a, 1b, 2, and 3) based on transmitted light and CL analyses (Figures 3, 4, and 5). The majority of the dolomite crystals are cloudy, light grey in colour, generally exhibiting a Planar-e (euhedral) and less commonly a Planar-s (subhedral) texture. These dolomites are classified as Type 1 (Figure 4). In several samples, these dolomites appear to have been partially dissolved around the rims. These dolomites range from fine to coarse crystalline. The coarser cements range in size from 50 to 200 μm, Type 1a range from occurrence in concentrated portions to occurring sporadically throughout the sample. Type 1a dolomite occasionally contains small cores or pieces of material that often cannot be distinguished from the surrounding dolomite under plain polarized light, but can be differentiated in cross-polarised light and CL (Figure 4). These cores exhibit a brighter, moderate orange–red luminescence compared to the dull red luminescence of the outer portion of the dolomite and the other dolomites of this type. The exception to this is sample DV02. Some of the precursor cores in this sample exhibit some variance in luminescence. The Type 1b dolomite that is similar petrographically to 1a dolomite is finer grained, with individual crystals less than 50 μm, making them too small for in situ geochemical analysis. These dolomites do exhibit slightly higher moderate red luminescence and are often burrow cements or occur in close proximity to bedding surfaces.

Type 2 dolomite is characterized by clear planar-e rhombs with fewer inclusions than Type 1 and range in size from 50 to 125 μm, with the exception of DV06 where individual crystals are ~250 μm in width. These dolomites exhibit either no luminescence or dull red luminescence (Figure 5c). This dolomite occurs only very sporadically, usually consisting of only a few planar-e (euhedral)
rhombs. Type 2 dolomites are often found in samples that have micritic matrices and occur in these matrices or associated with skeletal grains.

Type 3 dolomites account for a very small portion of the total dolomite percentage in the study and are grouped as dolomites that exhibit clear CL zoning. Zoned dolomites are more common in the upper portion of the sampled intervals among the more heavily dolomitized zones (Figures 3d and 5d). These crystals range in size from 75 to 200 μm. In plain polarized petrographic light samples range from clear to cloudy (Figure 4). Although there are some variations in appearance, under CL analysis these samples have similar zoning properties. Samples DV08 and DV10 have a large inner zone that exhibits moderate-bright orange luminescence with dark inclusions (Figure 5), a thin middle zone with very dull red luminescence and an equally thin orange–red, moderately luminescent outer rim (Figure 5d).

The zoning of DV09 is much less consistent, with the inner zone differing between dully luminescent and brightly luminescent, while the outer rim is moderately luminescent. These three examples of Type 3 dolomite exhibit differing petrographic characteristics. Under plain- and cross-polarized light, two of the three samples (DV09 and DV10) show varying degrees of clarity between their inner and outer rims. The third sample (DV08) shows no zoning under plain light. Despite their differing appearances in plain light, the CL zoning in each of these samples is consistent. Type 3 dolomites have a large inner zone that is moderate-brightly luminescent, a thin dull-to nonluminescent middle zone and a dull-bright orange rim.

4.2 | Dolomite and standards geochemical results

4.2.1 | Carimona–Lower Guttenberg interval REE data

The ∑REE values range between 36.33 and 102.45 p.p.m. (see supplementary online material for Data Table S1), some of the highest values in the study (Figure 6a). There is no clear grouping with regard to Ce anomalies (Figure 6d). Sample DV04 exhibits a negative La anomaly and
no Ce anomaly, while sample DV01 has neither La nor Ce anomaly. None of the samples exhibit significant Eu anomalies (0.92–1.15) (Figure 6e). The lowermost set of dolomite REE patterns (DV01–DV04) are consistent with MREE enrichment (Figure 7a), also called a “MREE-bulge” (Corlett & Jones, 2012; Haley & Klinkhammer, 2003; Haley, Klinkhammer, & McManus, 2004; Johanneson & Zhou, 1999).

### 4.2.2 | Middle–Upper Guttenberg Member interval REE data

The samples from DV06 were divided based on two different REE patterns. The first REE pattern includes sample spots (spots 1–4 and 7) from dolomite formed within a trilobite fossil. The second pattern type came from sample spots (spots 5, 6 and 8–10) formed in the micritic matrix infilling a fossil cavity.

| Class. | Dolomite Texture | Dolomite PPL Char. | Dolomite CL Char. | Schematic |
|--------|-----------------|--------------------|-------------------|-----------|
| Type 1 | Often planar-e seldom planar-s, 50–200µm (1a) <50 µm (1b) | Cloudy, inclusion-rich with precursor carbonate, occasionally partially dissolved | No to dull red luminescence, precursor material more brightly luminescent | ![Schematic](image1.png) |
| Type 2 | Very sparse planar-e, most commonly 50–125µm | Clear, few inclusions | No to dull red luminescence | ![Schematic](image2.png) |
| Type 3 | Packed planar-e to planar-s 75–200 µm | Moderately cloudy, occasional inclusions | 1. moderate-bright orange with dark inclusions, 2. dull red, 3. moderate orange-red luminescence | ![Schematic](image3.png) |

**FIGURE 4** Dolomite classification chart with characteristics (Char.) of each dolomite classification (Class.). Schematic representations represent appearance under plain polarized (PPL) and cathodoluminescence (CL) microscopy.

**FIGURE 5** (a) Image of DV02 (Type 1a) with Planar-e rhombs that are dully luminescent with some examples having a brighter core. (b) Sample DV05 (Type 1a) shows partially dully luminescent dolomite rhombs and fragments with some portions of moderately luminescent precursor material with a similar luminescence to the moderately luminescent micrite matrix. (c) Sample DV06 (Type 2) CL exhibiting moderate luminescence of micrite and the trilobite and dull-no luminescence by dolomite. (d) Sample DV08 (Type 3) with zoomed in CL image which shows zoned rhombs with three zones, a bright inner zone, dull middle zone and thin outer zone surrounded by blue luminescent grains that are probably quartz.
This interval includes several REE patterns. The first pattern shows a very slight LREE enrichment trend (e.g., DV05 and several dolomites from DV06, namely sample spots 5, 6, 8–10) (Figure 7b). These samples have the lowest $\Sigma$REE values of the sampled intervals, 11.43 p.p.m. and 11.58 p.p.m., with the exception of the ablation spots within the fossil (DV06, sample spots 1–4, 7) (7.91 p.p.m.). Neither sample has a Ce anomaly, and plots on the line between no La anomaly and a negative La anomaly (Figure 6d). These samples also have neutral Eu anomaly values of 1.02 and 1.05 (Figure 6e). DV07, the highest sample in this stratigraphic interval exhibits a flat pattern (Figure 7b) and has a relatively low $\Sigma$REE value of 14.30 p.p.m. (Figure 6a). This sample plots within the field of neither Ce nor La anomalies (Figure 6d).

The other pattern in this stratigraphic interval is one of higher HREE values compared to LREE, or HREE enrichment, from laser ablation of two dolomites within a skeletal grain from DV06 (sample spots 1–4, 7) (Figure 7c). These samples have the lowest HREE Tm, Yb and Lu values. The CL zoning of these dolomites, however, indicates definite fluctuations in fluid chemistry, indicating mainly redox conditions and/or changing Mn/Fe ratio of fluids (Machel, 1985).

### 4.2.3 Ion Member interval REE data

The third interval samples (DV08–DV10) are overprinted by terrigenous contaminants, thus REE patterns and $\Sigma$REE values cannot be used. Dolomites DV08 and DV10 exhibit similar geochemical properties of true positive Ce anomalies (Figure 6d) while a positive Ce anomaly is not exhibited by DV09. Sample DV09 has the highest recorded Eu anomaly value of 1.19, while DV08 and DV10 have moderate values of 1.06 and 0.94 (Figure 6e). The CL zoning of these dolomites, however, indicates definite fluctuations in fluid chemistry, indicating mainly redox conditions and/ or changing Mn/Fe ratio of fluids (Machel, 1985).

### 5 INTERPRETATION AND DISCUSSION

#### 5.1 REE patterns and evaluation of contamination by terrigenous material

Nothdurft et al. (2004) demonstrated that even 2% contamination by shale can obliterate diagenetic elemental anomalies and result in relatively flat REE patterns. Due to the...
high REE concentration of shales and clays, a positive correlation between these incompatible elements and $\sum$REE should be present if contamination has occurred (Bolhar, Kamber, Moorbath, Fedo, & Whitehouse, 2004; Frimmel, 2009; Zhang et al., 2014). Thorium values for dolomite range between 0.02 and 1.14 p.p.m., and Al values range from 87 to 6220 p.p.m. There appears to be a positive relationship between both Al and Th and $\sum$REE concentration among the dolomite samples (Figure 6a,b). Statistical analysis using linear regression yielded values of $R^2 = 0.27$ for the Al crossplot and $R^2 = 0.44$ for the Th crossplot. This indicates at least a moderate positive correlation between REE concentrations and Al/Th concentrations for the studied dolomite samples.

Carimona–Lower Guttenberg samples (DV01 to DV04) have the highest $\sum$REE, Al and Th values of any stratigraphic interval and REE patterns for this interval are distinctly nonlinear. This suggests that the expected linear REE pattern from siliciclastic material has been overprinted by a stronger signal source.

Samples from the Middle Guttenberg to Upper Guttenberg exhibit percentages at (DV07) or below (DV05 and DV06) cut-off values for both elements. The $\sum$REE concentrations and the shape of the curves of this interval are not greatly different despite DV07 samples being closer to the contamination cut-off. The REE patterns for this interval are interpreted as being the result of diagenetic fluids instead of contamination.

The Ion Member samples (DV08 to DV10) plot near or above the contamination cut-off for Al and above the cut-off for Th (5.2%–6.2%). These REE patterns are interpreted as being the result of contamination which is supported by their flat REE patterns (Figure 7d). The enrichment could be the result of hydrothermal fluids (Read, Andreoli, Knope, Williams, & Jarvis, 2002).

5.2 | Modern sea water REE patterns compared to studied dolostones

The REE geochemistry of sea water has remained similar through the Phanerozoic and that Phanerozoic carbonates can retain sea water-like REE patterns (Shields & Webb, 2004; Wang et al., 2009; Zhang et al., 2014). This suggests that a sea water-like diagenetic fluid mediating dolomitization would maintain the sea water-like REE pattern of precursor carbonate material (Banner et al., 1988; Bau & Alexander, 2006; Qing & Mountjoy, 1994).

A comparison of modern sea water REE patterns to the dolomite and carbonate standard REE patterns of this study demonstrate that only dolomite sample DV06 exhibits a
sea water-like REE pattern (Figure 7c). The REE patterns of all other dolomites in this study were formed by nonsea water diagenetic fluids or were overprinted by incorporation of contaminants such as Fe-oxides and siliciclastic material.

5.3 | Cerium and europium anomalies as redox and temperature indicators

Cerium is a redox-sensitive element, causing it to act differently than the rest of the REEs. Ce\(^{3+}\) in a dissolved state can be oxidized to Ce\(^{4+}\) in particulate form, which preferentially takes place in shallow water (Piper & Bau, 2013) and results in the negative Ce anomaly (Ce/Ce\(^*\)<1) of oxygenated sea water, an indicator of the oxygenation state of fluids. Negative Ce anomalies are absent in all of the tested samples (Figure 6d), indicating that either none of these dolomites were formed in oxic conditions, or that contamination overprinted these signatures. Contaminated dolomites DV08 and DV10 are the only samples that have positive Ce anomalies (Figure 6d). Despite overprinting by siliciclastic contamination, this anomaly potentially indicates anoxic conditions or warm temperatures of diagenetic fluids because contamination should flatten the pattern and not result in anomalies.

The Eu\(^{3+}/\text{Eu}^{2+}\) redox potential is highly dependent on temperature, thus high-temperature hydrothermal or basinal diagenetic fluid can result in Eu anomalies (Frimmel, 2009). Positive Eu anomalies are associated with pyrite-bearing carbonates and acidic, reducing hydrothermal fluids, while negative Eu anomalies occur in Fe-oxide–rich carbonates. The lack of significant positive Eu anomalies (Figure 6e) in any sample can either be attributed to these dolomites having no interaction with high temperature hydrothermal fluids (>200–250°C) (Bau & Dulski, 1996) or terrigenous overprinting from contamination. Assuming that this anomaly is still indicative of diagenetic fluids, it is possible that heated diagenetic fluids could have interacted with these rocks assuming they were no warmer than 90–130°C, as positive Eu anomalies require higher temperature (Zhang et al., 2014). This is consistent with mineralization studies in the Upper Mississippi Valley where Bailey and Cameron (1951) and Heyl, Agnew, Lyons, Behre, and Flint (1959) proposed temperatures of 50–121°C and 50–121°C respectively, based on liquid inclusions in sphalerite and calcite. Similarly, based on the oxygen isotopic composition of sandstone cements, Hyodo, Kozdon, Pollington, and Valley (2014) demonstrated that quartz cements of Ordovician sandstones that underlie the studied limestones formed in a near-surface environment at low temperatures (~40°C), lending support to the interpretation that the Ordovician rocks never experienced burial depths greater than 500 m (Figure 1b; Luczaj, 2006). Furthermore, the conodont alteration index of conodonts extracted from this outcrop is between 1 and 1.5 and supports these temperature estimates (Quinton et al., 2017), indicating that no alteration of Ce or Eu anomalies occurred due to elevated temperatures.

As reported by Zhang et al. (2017), Eu anomalies in carbonates can also occur where plagioclase weathering or dissolution contributes to a positive Eu anomaly in “inland limestones.” The Eu anomalies reported by Zhang et al. (2017), however, are larger than the Eu anomaly observed here and appear to not fall in this category.

5.4 | Stratigraphic control on geochemistry and sedimentology

5.4.1 | Carimona–Lower Guttenberg Interval

The association of dolomites with burrows in this interval is probably the result of the higher permeability created by bioturbation, allowing greater water/sediment interaction, and also acting as a sink for organic matter, clays and Fe-oxides (Baniak, Gingras, & Pemberton, 2013; Freiburg, Fouke, & Lasemi, 2012; Gingras, Pemberton, Muelenbachs, & Machel, 2004). The close relationship between greater dolomite occurrence, burrows and K-bentonites is potentially due to weathering converting volcanic ash to K-bentonite, providing Mg\(^{2+}\) ions that could promote dolomitization via diagenetic fluids. Witham, Oppenheimer, and Horwell (2005) showed that Mg\(^{2+}\), together with other ions including Ca\(^{2+}\), Na\(^{+}\), SO\(_4^{2-}\) and Cl\(^{-}\), is released following the interaction of volcanic ash with sea water and the resulting supersaturation of pore fluids with Mg\(^{2+}\) can be expected to promote dolomitization. Another possible cause is that SO\(_4^{2-}\) released from the K-bentonites bound with available free Mg\(^{2+}\) and later interacted with sulphate-reducing bacteria (SRB), resulting in the release of Mg\(^{2+}\). This interaction has been attributed to the promotion of dolomitization, particularly in burrows (Corlett & Jones, 2012; Wright, 2000):

This interval exhibits geochemical evidence of siliciclastic material and this contamination appears to be overprinted by Fe-oxide signal contamination. This signal could be the result of Fe-oxides contained inside the dolomite, however, Fe-oxide contaminated carbonates in another study exhibited a flatter REE pattern than the samples of this interval (Frimmel, 2009). Therefore, this pattern is interpreted as Fe-oxides becoming reduced under anoxic porewater conditions causing them to release their preferentially scavenged REEs, as similarly demonstrated by Corlett and Jones (2012).

These samples exhibit what has been called the “MREE” bulge (Haley et al., 2004; Johannesson & Zhou, 1999). Haley et al. (2004) attributed this pattern to the presence of Fe-oxides in the porewaters. This pattern has
been recorded in previous studies of dolomite-filled burrows from a Devonian ramp setting in the Northwest Territory, Canada (Corlett & Jones, 2012). The MREE bulge was interpreted as a sign of fully anoxic conditions below the sediment–water interface where Fe-oxides preferentially scavenge MREEs in the water column only to subsequently release them in carbonates forming under reducing conditions (Haley et al., 2004). In these samples, the existence of fully anoxic conditions capable of reducing Fe-oxides is supported by the very dull, quenched luminescence exhibited by these dolomites under CL. The rare occurrence of more moderately luminescent nonzoned cores are probable remnants of previous carbonate material that were largely replaced when dolomitization occurred, similar to Smith and Simo (1997). Navarro-Ciurana et al. (2017) described dolomites from SE Spain that display a MREE bulge that looks similar to the dolomites from Wisconsin. Navarro-Ciurana et al. (2017) showed that those dolomites formed through high-temperature fluid–rock interaction and exhibit a strong Eu anomaly. While the MREE patterns of the Spanish dolomites look similar to the data reported here, the lack of Eu anomaly in the dolomites from Wisconsin argue against a similar dolomitization process.

The lower MREE enrichment in sample DV04 is potentially indicative of lower Fe-oxide concentrations in the water column and in porewaters. There exist two possibilities for the lower Fe-oxide concentrations. Sediment input into the midcontinent sea slowed, indicated by the shift in lithologies from the shale facies of the Specht’s Ferry Member (DV01 to DV03) to the carbonate facies of the overlying Guttenberg Member (DV04). This would result in fewer terrigenous grains for Fe-oxides to coat and could potentially result in lower MREE enrichment. Alternatively, subduction-related volcanic ash has proven capable of quickly releasing large amounts of adsorbed Fe into sea water (Duggen, Croot, Schacht, & Hoffmann, 2007; Frognar, Reynir Gislason, & Óskarsson, 2001). Iron released can be in the order of 0.01–91 mg/kg ash (Witham et al., 2005). If Fe concentrations contributing to the formation of Fe-oxides in sea water were controlled by immediate leaching from volcanic ash, the fact that this sample postdated ash deposition makes any Fe-oxide enrichment of diagenetic fluids due to ash–water interaction less probable.

The shallow burial model of dolomitization in this interval supports the model of Smith and Simo (1997) for this area. That study revealed that these dolomites occasionally nucleated on precursor protodolomite seed crystals. These cores are not always present or are unidentifiable in many of the dolomites of this study. Although the dolomitization realms and some characteristics of the dolomites in these studies are the same, the mechanisms for dolomitization are different. The burrow or bioturbation-related nature of these dolomites, as well as the Fe-oxide–influenced REE pattern have been identified in oxides elsewhere (Baniak et al., 2013; Corlett & Jones, 2012; Freiburg et al., 2012; Gingras et al., 2004 Haley et al., 2004). A novel finding from this interval is the association of larger burrow-related dolomite in this interval with K-bentonites, and a potential cause could be Mg$^{2+}$ leached from K-bentonites which promoted dolomite growth.

5.4.2 | Middle–Upper Guttenberg Interval

Dolomites from DV06 (spots 1–4, 7) are the only dolomites in this study that exhibit sea water-like REE patterns (Figure 7c) and also have the lowest $\sum$REE values and Al and Th concentrations (Figure 6a,b). The HREE enrichment pattern of sea water is tracked well by this sample except for the HREE Tm, Yb and Lu. Thus, this deviation from commonly applied sea water patterns is interpreted as being indicative of a shallow water sea water REE pattern consistent with the shallowing upward interpretation of Guttenberg Member deposition (Ludvigson, Jacobson, Witzke, & González, 1996; Ludvigson et al., 2004).

These samples do not exhibit the negative Ce anomaly that should be present for normal sea water-derived carbonates (Figure 6c,d). This suggests that diagenetic fluid conditions were probably sub-oxic to anoxic (Bau & Alexander, 2006). The dark nature of luminescence in this sample suggests that this dolomite was probably formed under anoxic conditions, supporting the Ce anomaly data (Hiatt & Pufahl, 2014). Trace element Mn versus Fe plots of these samples, however, record the most oxidizing signatures of any sample. In this case REE and trace element data are potentially contradicting regarding the redox nature of the diagenetic fluid. Other studies support periodic dysoxia or anoxia of sea water during this time period (Ludvigson et al., 1996, 2004; McLaughlin et al., 2011).

Dolomitized fossils in UMV strata were also identified by Van Tuyl (1914) and were likewise attributed to burial dolomitization. It is possible that the Mg necessary for the formation of this dolomite was caused by the remobilization of Mg due to leaching surrounding high Mg fossils and carbonate grains, as Van Tuyl (1914) proposed.

Samples DV05 and DV06 (spots 5–6, 8–10) exhibit LREE enrichment patterns (Figure 7b). The LREE enrichment in dolomite has been attributed to dolomitization by hydrothermal fluids, however, in many cases when LREE is present there is also a strong positive Eu anomaly due to the temperature of the hydrothermal fluids (Bolhar & Vankranendonk, 2007; Zhang et al., 2014). Low Ba values (Figure 8) in DV06 preclude hydrothermal diagenetic fluid interaction. Hydrothermal fluids also generally exhibit high $\sum$REE values, but these samples exhibit very low values. Furthermore, these samples also lack any other petrographic evidence of hydrothermal diagenesis associated...
with UMV-type mineralization. These samples are also micrites of low porosity and permeability where hydrothermal fluid is unlikely to have been able to penetrate the samples effectively (Figure 3). Thus hydrothermal fluid seems unlikely to be the diagenetic mediating fluid. High Mn–Sr ratios (∼8) indicate recrystallization as opposed to direct precipitation, ruling out any syndepositional dolomitization. Ferroan dolomite, which these samples exhibit with high Fe concentrations (DV06, spots 5–6, 8–10) and dull luminescence (all samples of this interval), has been interpreted to have been of burial origin (McHargue & Pri, 1982; Yoo et al., 2000). Taken together, the diagenetic realm for these dolomites appears to be burial. The dolomites from DV06 in micritic matrices are most closely related to what Asquith (1967) considered to be shallow burial dolomite often protected in fossils. The samples from DV05 with precursor cores are more closely related to the shallow burial dolomite described by Smith and Simo (1997).

A modest LREE enrichment and lack of Ce anomaly of carbonates has been identified in other studies (Azmy et al., 2011; Nothdurft et al., 2004). It has been shown that suspended ocean particles and estuarine colloids preferentially uptake LREE (Sholkovitz, 1993; Sholkovitz, Landing, & Lewis, 1994) resulting in the relative HREE enrichment of sea water. Nothdurft et al. (2004) suggested that these samples had incorporated estuarine colloids, resulting in a pattern that displayed LREE enrichment. Furthermore, Nothdurft et al. (2004) showed that contamination evaluations did not reveal contamination, as those samples exhibited low ∑REE and Al concentrations, even given colloidal incorporation that affected the REE pattern. If these dolomites were formed contemporaneously with the dolomites inside the fossil in DV06 (spots 1–4, 7), incorporation of colloidal material in the dolomite during recrystallization of the micrite is the cause of their differing REE signatures. However, if these dolomites formed during slightly later burial than those from DV06 (spots 1–4, 7), the diagenetic fluids could have been different, resulting in a different REE pattern.

Studies have shown that porewaters only several tens of centimetres below the sediment–water interface can lose a sea water-like signature (Elderfield & Sholkovitz, 1987), exhibiting flat or more linear patterns as POC (particulate organic carbons) remineralizes (Haley et al., 2004). Azmy et al. (2011) described Ordovician lime mudstones and burial cements with similar modest LREE enrichment. Dolomites with similar REE concentrations and patterns were also interpreted as having been formed during early burial and replacement (Azmy et al., 2013; Azomani et al., 2013). Non-marine Ce signatures of subsurface fluids have been proven to be obtained from interaction with detrital sediments, which would also erase any negative Ce anomaly because in the subsurface Ce is more likely to remain in its trivalent state due to anoxic conditions (Piper & Bau, 2013). Although the exact reason for the REE pattern exhibited by these samples is unclear, it is probable that these dolomites are formed in a relatively early burial environment.

DV07 with the “flat” REE pattern (Figure 7b) is interpreted as having been the result of later stage burial fluids, more specifically hydrothermal fluids, as will be explained. Pressure solution seams have been tied to dolomitization previously (Wanless, 1979) as the dissolution of limestone provides sufficient Mg²⁺ to promote dolomitization in proximal strata. Solution seams above the dolomite in this petrographic thin section (Figure 3e) is thus proposed as a source of Mg²⁺ for the formation of dolomite (Wanless, 1979). Merino and Canals (2011) proposed a different dolomitization model linking pressure solution, dolomitization and Mississippi Valley-type mineralization. In this model, calcite dissolution supersaturates these brines with respect to dolomite and dolomite forms. This reaction forms a positive feedback loop and causes self-acceleration until the available Mg is scavenged too quickly, resulting
in the process shutting down. This results in abrupt contacts between limestone and dolomite. The abrupt transition (0.2 m) between this less altered portion and the heavily dolomitized sample DV08, attributed to hydrothermal interaction, serves as evidence that this process has occurred at least at this outcrop if not regionally. Merino and Canals (2011) note that many petrographic analyses reveal that replacement cannot occur by dissolution–precipitation (but see Morrow, 2014 for a different view). In this study, the petrographic evidence seems to fit the Merino and Canals (2011) model.

The application of this model and its mechanics of abrupt limestone–dolostone transitions serve to act as an argument against Badiozamani’s (1973) distinct limestone–dolomite transitions that argument necessarily of being indicative of Dorag dolomitization. The application of this mechanism to the hydrothermal dolomitization model at this outcrop may serve to provide greater insight into dolomite–limestone contacts and their formation in the UMV given more study.

5.4.3 | Ion Member

Several studies have attributed the Ion Member and overlying Galena Group strata to hydrothermal dolomitization (Agniewski, Heyl, Behre, & Lyons, 1956; Gregg & Sibley, 1984). It is probable that these hydrothermal fluids flowed from the Illinois Basin in the south updip into the Wisconsin strata (Hall & Friedman, 1963). These fluids were probably high-salinity basinal brines (Heyl, Landis, & Zartman, 1974). Timing can be constrained by Rb–Sr dating to Early Permian hydrothermal mineralization (270 Ma) associated with the Alleghenian/Ouachita orogeny (Branconnier, Podosek, & McLimans, 1992; Rowan & Goldhaber, 1995).

Samples DV08, DV09 and DV10 all exhibit high Al, Th and ΣREE consistent with contamination, therefore their REE patterns might not reliably indicate the geochemistry of the diagenetic fluids (Figure 6a,b). However, the petrographic analysis demonstrates that the Ion interval samples DV08 and DV10 are extensively dolomitized, suggesting large volumes of fluid flow to support such extensive alteration. Within the REE suite, DV08 and DV10 are the only samples with a positive Ce anomaly (Figure 6d). There exists no cause for Ce fractionation in siliciclastic contaminants, therefore this positive anomaly is probably not the result of contamination (Bayon et al., 2015). A positive Ce anomaly is indicative of heavily reducing conditions, which can occur as the Ce⁴⁺/Ce³⁺ redox equilibrium shifts towards higher oxygen fugacity with warmer diagenetic fluid temperatures (Frimmel, 2009). The moderate to brightly luminescent inner zones of the dolomite in these samples are caused by relatively high concentrations of Mn²⁺ and relatively low concentrations of Fe²⁺, indicative of low oxygen levels (Hiatt & Pufahl, 2014). The CL patterns of these samples are similar to the dolomite patterns of type 1 (dull orange) and type 3 (red/no luminescence) hydrothermal dolomite identified by Smith and Simon (1997) in the Prairie du Chien Group. In this study, however, these samples occasionally exhibit a third outer zone of orange luminescence (Figure 5). Petrographic analysis shows sulphide mineral replacement of many skeletal grains. Pyrite and marcasite are identified as minerals commonly precipitated by regional hydrothermal fluids (Heyl et al., 1959; Tupas, 1950), and the dark matter filling the intercrystalline pore space is potentially hydrothermally precipitated Fe-oxide, a feature noted in the overlying Galena Group (Gregg & Sibley, 1984). Furthermore, Ion Member strata have been shown to be influenced by hydrothermal fluids in many parts of the UMV (Agniewski et al., 1956). These lines of evidence suggest that these dolomites are hydrothermal in nature and support the earlier studies (Agniewski et al., 1956; Gregg & Sibley, 1984).

The sample between these two, DV09, is not as extensively dolomitized. Dolomites in this sample are largely concentrated towards the upper portion of the sample. Thus, hydrothermal fluids were probably flowing through the rock directly overlying this sample, and this sample represents the lower edge of the limestone–dolomite replacement front. These differing characteristics and the extent of dolomitization were probably controlled by the lithology and the extent and speed with which diagenetic fluids could penetrate due to permeability differences in the original rock (Deininger, 1964). Alternatively, the hydrothermal fluids could have followed higher permeability fractures or seams, leading to this interbedding of heavily dolomitized samples with samples not completely dolomitized.

The CL zonation of overgrowths creating the dullly luminescent middle zone and the occasionally occurring, more brightly luminescent outer zone are probably the result of the evolution of the hydrothermal fluid as dolomite overgrowth occurred. The dull/dark middle zone to moderately luminescent outer zone could be caused by removal of Fe²⁺ from the hydrothermal fluids before this zone. This could be the result of sulphide mineral precipitation or replacement, either marcasite or pyrite, removing Fe²⁺ from the fluids and shifting zoning characteristics from quenched luminescence to moderate luminescence (Hiatt & Pufahl, 2014). Deininger (1964) also found Fe zoning in hydrothermal dolomite of south-west Wisconsin in the Platteville Formation, stratigraphically lower than these samples.

5.4.4 | Insights into dolomitization and relationship to previous studies

Petrographic and geochemical evidence from this study points to two depositional realms with dolomitization
driven by several different mechanisms in the shallow burial realm (Figure 9). The second dolomitization model is that of hydrothermal dolomite. The first stage, early burial dolomite, can be divided into several categories. Dolomites in the Carimona–Lower Guttenberg interval are burrow-associated and occur in larger crystal size near K-bentonite beds. This study argues that the K-bentonites provided a potential source of Mg from water–ash interaction to aid in dolomitization, and that burrow conditions, specifically sulphate-reducing bacteria, probably contributed to the formation of these dolomites. The REE released from Fe-oxides during changing porewater redox conditions from oxic to anoxic, occurred in the shallow burial realm. This dolomitization model is consistent with burrow-related dolomitization presented by Corlett and Jones (2012) as well as the Fe-oxide–associated REE pattern presented by (Baniak et al., 2013; Corlett & Jones, 2012; Freiburg et al., 2012; Gingras et al., 2004 Haley et al., 2004). The early burial dolomitization model, including precursor carbonate cores, is consistent with the interpretation of Smith and Simo (1997).

A similar early burial depositional model was applied to the two lower Guttenberg samples (DV05 and DV06). A portion of the dolomite inside a fossil in DV06 probably formed very near the sediment–water interface, as indicated by the REE pattern. It also seems probable that this REE pattern is consistent with relatively sluggish water that was potentially anoxic, sea water conditions supported by palaeoceanographic and sequence stratigraphic studies (Ludvigson et al., 1996, 2004). The sourcing of Mg and the nature of the water is problematic, however. Dolomite in fossils was recognized by Van Tuyl (1914) who also attributed this dolomitization to a burial realm. The remaining dolomites of this interval, which are found in micritic matrices, were also attributed to a relatively early burial origin, matching the burial interpretation and petrographic and CL appearances of Platteville Formation dolomites from Asquith (1967) and Smith and Simo (1997).

Hydrothermal dolomitization is exhibited in the upper portion of the sampled interval, the upper portion of the Guttenberg Member and the sampled portion of the Ion Member. Hydrothermal dolomitization of these strata has been discussed previously (Agnew et al., 1956; Smith & Simo, 1997). These portions are unique in that it seems that hydrothermal fluid selectively penetrated layers. Unlike the overlying Galena Group hydrothermal dolomite (Gregg & Sibley, 1984), this dolomite is interpreted as having replaced carbonates and not overgrowing or neomorphosing precursor dolomite. Furthermore, these samples exhibit evidence supporting the hydrothermal dolomitization model of Merino and Canals (2011) that invokes pressure-solution replacement rather than dissolution–precipitation.

Due to the location of this outcrop in relation to the Wisconsin Arch, this study cannot directly disprove that dolomitization on the Wisconsin Arch is not the result of Badiozamani’s (1973) Dorag dolomitization model. Based on Badiozamani’s limestone–dolostone transition argument and the stratal geometries he used, if Dorag-type dolomitization were to have occurred at this outcrop, it would probably have been below the contact between the Quimby’s
Mill Member and the Carimona Member or the Specht's Ferry Formation and the Guttenberg Member. There is no large-scale dolomitization of the lower interval, however, and the occurrence of the burrow-associated dolomite is primarily above the Specht's Ferry–Guttenberg contact. This could be because the location of this outcrop was too distal to the Wisconsin Arch to have experienced extensive dolomitization by mixing zone diagenesis. Furthermore, this study has found evidence of hydrothermal alteration by pressure-solution replacement which potentially overcomes Badiozamani’s argument that distinct limestone–dolomite boundaries are only indicative of mixing zone dolomitization. More work regarding the importance and application of this dolomitization model is necessary. Taken together, however, there exists no dolomite formed at this outcrop that was interpreted as having formed by Dorag-type dolomitization and it seems appropriate to suggest that the Dorag model should not have been widely applied to dolomites of the southern Wisconsin area (Luczaj, 2006).

6 | CONCLUSIONS

The petrographic and geochemical study of dolomites from the upper portion of the Platteville Formation and the Decorah Formation of the Upper Mississippi Valley in south-western Wisconsin has yielded additional evidence to support multiple phases of dolomitization. Petrographic and CL characteristics were combined with in situ geochemical REE analysis techniques of LA-ICP-MS on these dolomites to provide a new means of interpreting the history of dolomitization.

Although REE data can be a powerful tool in the analysis of palaeoceanographic and diagenetic conditions in carbonates, this study, as with similar investigations, revealed that even minor contamination can greatly hinder the utility of the geochemical diagenetic proxy. Despite this issue, petrographic and geochemical results were combined to reveal that the dolomite in the Carimona Member, Specht’s Ferry Member, Guttenberg Member and Ion Member were largely formed in two realms, shallow burial and hydrothermal. These interpretations are similar to other studies of overlying and underlying Ordovician strata in the southern Wisconsin region.

The application of new analytical techniques and the evaluation of dolomitization in formations that had not previously been extensively studied have provided new insight into dolomitization, and particularly some mechanisms for dolomitization not previously applied. The findings of greatest note are the apparent link between dolomitization, particularly in those dolomites that are more abundant and more coarsely crystalline than the surrounding strata, and K-bentonites in the studied samples. This paper argues for a genetic link due to Mg release into water by ash–water leaching. These dolomites also exhibit “MREE” typical of Fe-oxide desorption in anoxic porewater. Furthermore, evidence for a relatively new model for hydrothermal alteration seems to be applicable here. This pressure-solution replacement model of hydrothermal dolomitization will need more work before it can be more generally applied. While it is impossible to disprove the Badiozamani (1973) “Dorag” model of dolomitization for all dolomites in the area given the distance of this outcrop from the Wisconsin Arch, none of these dolomites were attributed to a mixing zone diagenetic realm. Thus Luczaj’s (2006) argument that the “Dorag” model of deposition should not be widely applied to the majority of Lower and Middle Ordovician dolomites seems fair.

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**SUPPORTING INFORMATION**

Additional supporting information may be found online in the Supporting Information section at the end of the article.

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