CARBONATE DIAGENESIS AND DOLOMITIZATION OF THE LOWER ORDOVICIAN PRAIRIE DU CHIEN GROUP

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ABSTRACT

The carbonate diagenetic history of the Lower Ordovician Prairie du Chien Group includes syndepositional diagenesis, shallow-burial diagenesis, hydrothermal diagenesis, and near-surface weathering. Syndepositional diagenesis included calcium carbonate and dolomite cementation, micritic fabric-retentive replacement dolomitization, and anhydrite precipitation. Shallow-burial diagenesis was associated with the development of at least two regional disconformities. Shallow-burial diagenesis included carbonate dissolution and karst development, patchy silicification, and possibly the early phases of coarse, fabric-destructive replacement dolomitization and dolomite cementation. Hydrothermal diagenesis included pervasive dolomite cementation and fabric-destructive replacement dolomitization, minor dedolomitization and calcite cementation, and patchy Mississippi Valley-type sulfide mineralization. Near surface weathering has included karst development and the precipitation of aragonitic and calcitic speleothems.

This study illustrates some of the difficulties of interpreting the mechanisms responsible for the dolomitization of ancient dolostone, many of which have complicated diagenetic histories that include multiple episodes of dolomitization. In the case of the Prairie du Chien Group, hydrothermal dolomitization has petrographically overprinted many of the earlier diagenetic events but has not markedly shifted bulk-rock $\delta^{18}O$ and $\delta^{13}C$ values from Early Ordovician marine carbonate values. Thus, the history of carbonate diagenesis and dolomitization in the Prairie du Chien Group is based primarily on detailed petrography and cathodoluminescence petrography, but is not strongly supported by trace element or stable isotope geochemistry.

INTRODUCTION

Lower-Middle Ordovician dolostone of the upper Mississippi Valley region has been studied intermittently since the early 1900s (for example, Steidtmann, 1911; Van Tuyl, 1914) as part of a continuing, broader effort to develop a general model for regional fabric-destructive dolomitization. To date, regional dolomitization in the study area has been variously attributed to seawater or evaporative brines (Calvin and Bain, 1900; Leonard, 1905; Asquith, 1967), meteoric water and/or hydrothermal fluids (Deininger, 1964), and mixed meteoric-marine water (Badiozamani, 1973). Other than Deininger (1964), studies of hydrothermal minerals in the Upper Mississippi Lead-Zinc District (for example, Bain, 1906; Agnew and others, 1956; Heyl and others, 1959) have generally ignored the problem of dolomitization outside of ore deposits.

Our study examines the dolomitization and other carbonate diagenesis of the Lower Ordovician Prairie du Chien Group throughout the upper Mississippi Valley-southern Wisconsin outcrop area (fig. 1). Throughout this area the Prairie du Chien Group exhibits a complex diagenetic history, and multiple episodes of dolomite cementation and fabric-destructive replacement dolomitization are a major feature of this diagenetic history. In the Prairie du Chien Group, regional hydrothermal dolomitization has overprinted many of the earlier diagenetic events (Smith, 1990; Smith and Simo, 1991), resulting in somewhat ambiguous stable-isotope and trace-element signatures. Detailed petrography and cathodoluminescence petrography have been essential to placing Prairie du Chien Group dolomite fabrics in sequence. This study illustrates some of the difficulties of interpreting the mechanisms responsible for the dolomitization of ancient dolostone.

SEDIMENTOLOGY AND STRATIGRAPHY

The Lower Ordovician Prairie du Chien Group crops out from Minnesota to Michigan (fig. 1). The carbon-

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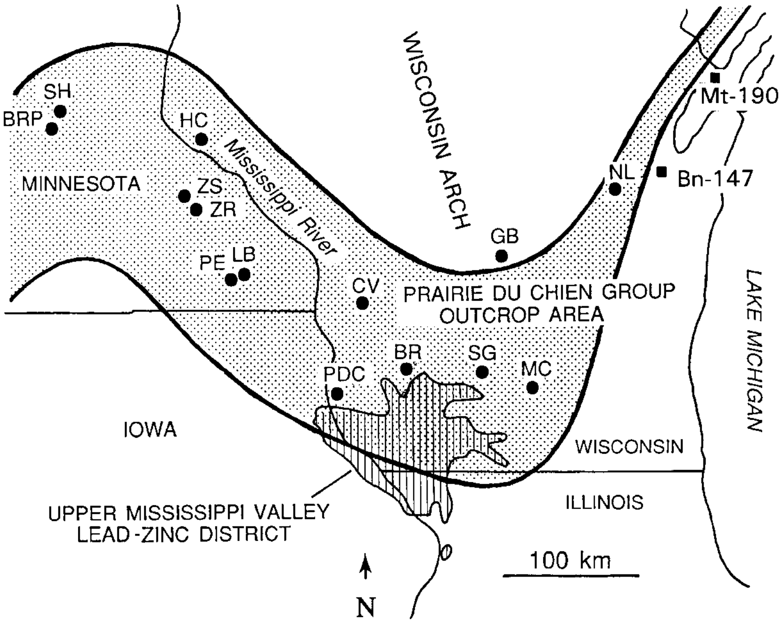


Figure 1. *Map showing location of study area, Prairie du Chien outcrop area, Wisconsin arch, and Upper Mississippi Valley Lead-Zinc district. Alphabetical abbreviations identify locations of measured sections (all Wisconsin, unless otherwise noted): BR-Blue River; BRP-Bryant Rock Products, Shakopee, Minnesota; CV-Coon Valley; GB-Glovers Bluff (Plainfield); HC-Hager City; LB-Lanesboro, Minnesota; MC-Millers Curve (Cross Plains); NL-New London; PDC-Prairie du Chien; PE-Preston, Minnesota; SG-Spring Green; SH-Shakopee, Minnesota; ZR-Zumbro River (Zumbrota, Minnesota); ZS-Zumbrota, Minnesota. Water wells are identified by Wisconsin Geological and Natural History Survey number: Bn-147 (Brown County), Mt-190 (Marinette County).*

ate-dominated, mixed carbonate-siliciclastic sediment of the Prairie du Chien Group correspond mainly to the "restricted platform" carbonate facies belts of Wilson (1974; for example, Adams, 1978; Austin, 1971; Davis, 1966, 1970, 1971; Ostrom, 1970; Raasch, 1952; Shea, 1960; Smith, 1991; Smith and others, 1993, 1996). Abundant oolites, mudcracks, and moldic nodular anhydrite, and a moderately diverse macrofauna (Smith and others, 1993, 1996) and conodont microfauna (Smith and Clark, in press) indicate deposition in a variety of shallow-subtidal to supratidal, marine to hypersaline settings.

The Prairie du Chien Group consists of the Oneota and Shakopee Formations (fig. 2), deposited during two major relative highstands of sea level that flooded the central North American craton during the Early Ordovician (Smith and others, 1993, 1996). The Prairie du Chien Group and correlative units mark the end of regional siliciclastic deposition and the inception of widespread Ordovician carbonate deposition. The Prairie du Chien Group is underlain by the Upper Cambrian Jordan Formation and overlain by the Middle Ordovician St. Peter Formation (fig. 2).

METHODS

Field data and samples were obtained from 14 measured outcrop sections and 2 water-wells (fig. 1). Dolomite associated with Mississippi Valley-type ores from the Upper Mississippi Lead-Zinc District (fig. 1) was sampled from a collection at the University of Wisconsin-Madison. Approximately 350 thin sections were examined petrographically, including approximately 50 examined using cathodoluminescence. Dolomite phases with distinctive and correlatable cathodoluminescence colors were analyzed by electron microprobe in order to determine Ca:Mg ratios and weight-percentages of Fe, Mn, Sr, and Na. Electron beam width was 0.015 mm; beam voltage was 15 Kv; count times were 20-30 s.

Forty-three dolomite samples were analyzed for oxygen and carbon stable-isotopic ratios at the Stable Isotope Laboratory of the University of Wisconsin-Madison. Whole-rock samples (5-50 mg) were drilled and chipped from parts of thin section chips containing representative mixtures of dolomite types based on cathodoluminescence petrography of matching thin sections. Powdered samples were reacted for approximately 12 hours with phosphoric acid at 50^{o}C in an evacuated reaction vessel. Carbon dioxide was drawn off, cryogenically purified, and analyzed in a Finnigan/MAT 251 mass spectrometer.

SYNDEPOSITIONAL DIAGENESIS

Overview

Evidence of syndepositional diagenesis is partially overprinted by later diagenetic events. Evidence of syndepositional diagenesis includes moldic and silicified nodular anhydrite, moldic halite, platy cm-thick intraclasts, intraclasts consisting of decimeter-thick grainstone slabs, grapestone clasts, ooids, stromatolites, and micritic envelopes and cement. Nodular anhydrite and minor halite precipitated within peloidal packstone and wackestone deposited in supratidal settings. Platy cm-thick intraclasts composed of peloidal packstone probably formed as supratidal crusts and were later reworked into both supratidal and shallow-subtidal deposits. Syndepositional cement within supratidal crusts may have included halite, gypsum, anhydrite, calcite, aragonite, and dolomite. Decimeter-thick slabs of oolitic grainstone are weakly imbricated within an oolitic grainstone matrix, and are interpreted as reworked beachrock. Ooids and stromatolites indicate a range of shallow-subtidal to intertidal, marine to hypersaline settings.

Internal fabrics of ooids are commonly well preserved (for example, figs. 3 and 4), suggesting that many non-skeletal grains were originally calcite instead of aragonite (for example, Sandberg, 1983). In contrast, the aragonitic skeletal fragments of molluscs are preserved as molds. Grapestone clasts and micritic envelopes and cement (fig. 3) probably formed in shallow-subtidal settings.

Syndepositional dolomite and dolomitization

Based on petrography on stained thin sections and petrography using cathodoluminescence, the earliest dolomite within the Prairie du Chien Group is finely-crystalline (<0.02-0.1 mm) dolomite crystals with unzoned red-orange cathodoluminescence. These small dolomite crystals are ubiquitous, and are overgrown and partially replaced by later dolomite phases. Syndepositional dolomite crystals are best preserved within mud-rich rocks, such as peloidal micrites, peloidal wackestone, and boundstone. Perhaps partially-dolomitized micritic carbonates were protected from extensive later replacement dolomitization by their relatively low initial porosity and permeability.

Tidal pumping and evaporation are known produce supratidal dolomitic crusts in some modern, tropical, supratidal settings (Carballo and others, 1987; Mazzullo and others, 1987; Lasemi and others, 1989). Syndepositional dolomite also precipitates in association with microbial, mat-forming communities on supratidal sabkhas (Patterson and Kinsman, 1977; McKenzie and others, 1980; Muller and others, 1990; Illing and Taylor, 1993). Abundant platy intraclasts are the best candidates for supratidal dolomitic crusts in the Prairie du Chien Group. In addition, muddy-peloidal sabkha sediment containing laminae and moldic anhydrite and gypsum are also likely to have been partially dolomitized syndepositionally.

Petrographic evidence suggests that reducing microenvironments within grains and micritic sediment may have facilitated syndepositional dolomitization of Prairie du Chien Group sediment. Syndepositional dolomite crystals are commonly similar in size to the peloids that contain them (fig. 5), like the "one-per-peloid" pattern observed in Holocene sediment (Gunatilaka and others, 1984). In contrast, larger grains such as ooids typically contain remnants of multiple 0.02-0.1 mm-size syndepositional dolomite crystals overgrown by late-stage dolomite (fig. 6). In some cases, Prairie du Chien Group peloids are entirely replaced by dolomicrite (fig. 6, righthand part of figure), much of which may be of syndepositional origin.

Dolomite is likely to have also precipitated within subtidally-deposited Prairie du Chien Group sediment without the replacement of aragonite or calcite. Dolo-

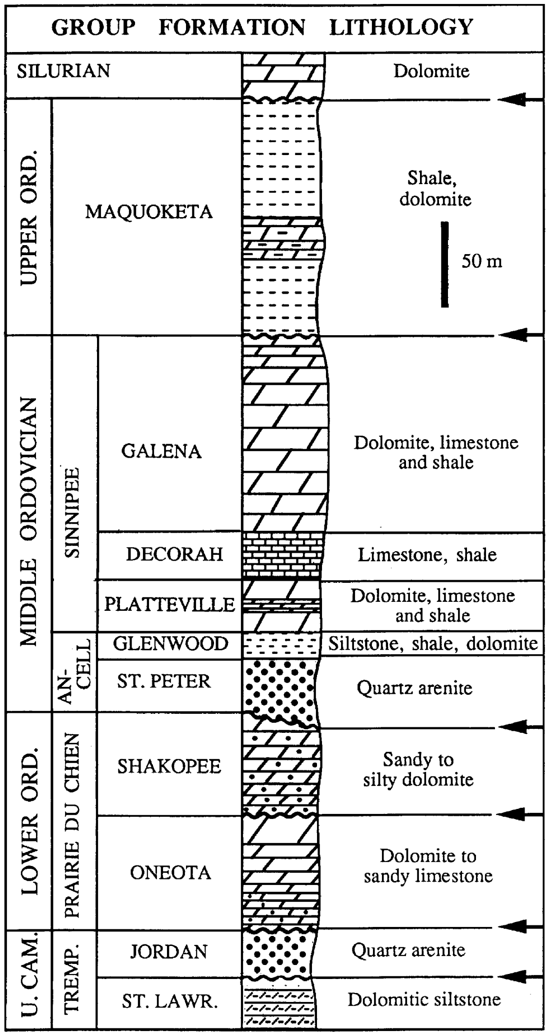


Figure 2. *Generalized stratigraphic column for Prairie du Chien Group and associated Upper Cambrian to Upper Ordovician strata. Arrows indicate the positions of major subaerial unconformities.*

Figure 3. *Dolomitized grapestone from lower Oneota Formation at Glovers Bluff (GB), Wisconsin. Grapestone and ooids indicate pervasive early cementation. Note dolomitized micritic envelopes. Scale bar = 1 mm.*

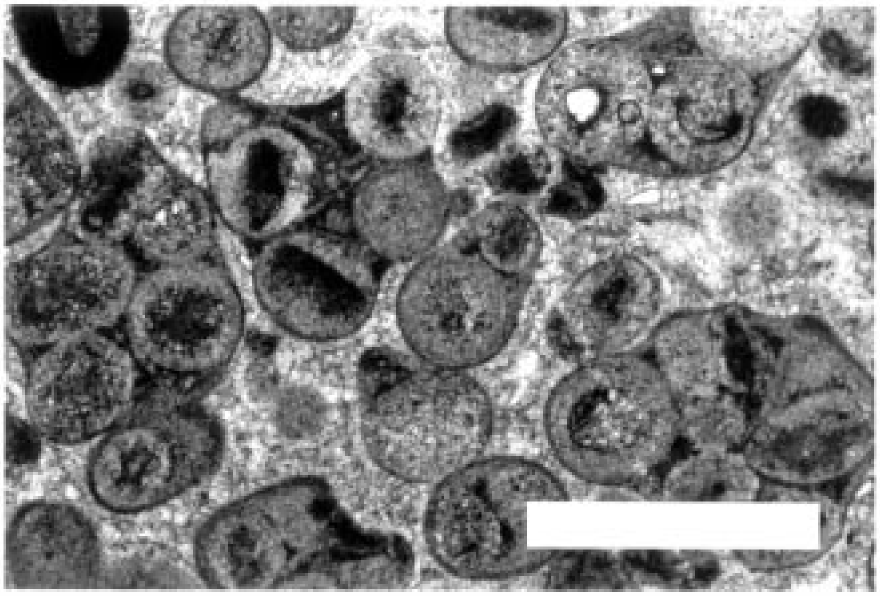
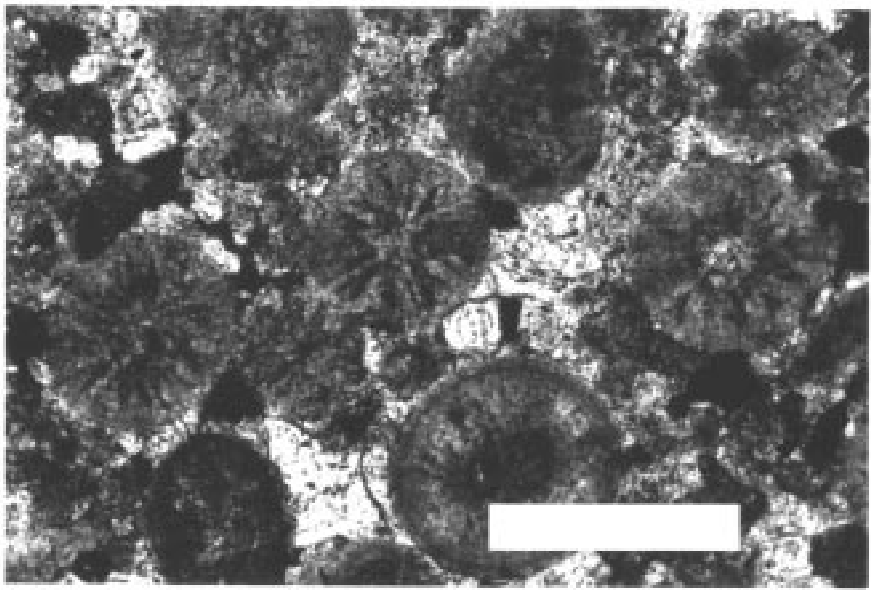


Figure 4. *Dolomitized ooid from lower Oneota Formation at Prairie du Chien, Wisconsin, showing preserved primary fabric. Lack of petrographic evidence for neomorphic recrystallization into coarse calcite suggests primary mineralogy was calcite instead of aragonite. Scale bar = 0.5 mm.*



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mite precipitation in marine sediment appears to be in part thermodynamically driven by bacterially-mediated organic carbon oxidation and sulfate reduction according to the general reaction:

$2CH_2O$ (organic) + $SO_4^{2-} \longrightarrow H_2S + 2HCO_3^-$ (Burns and others, 1988).

Assuming a diffusion-limited seawater source of Mg^{2+} and SO_4^{2-}, marine dolomitization should occur preferentially at shallow burial depths beneath the sediment-water interface (Baker and Burns, 1985; Compton and Siever, 1986; Burns and Baker, 1987). This model for syndepositional dolomitization is supported by evidence from a variety of modern and ancient carbonate marine sediment (Behrens and Land, 1972; Bone and others, 1991, 1992; Gebelein and others, 1980; Gunatilaka and others, 1984; James and others, 1991; Sass and Katz, 1982; Bein and Land, 1983). Bone and others (1992) suggest that dolomite crystals of marine origin may nucleate later dolomite, although the marine origin of these nuclei could easily be obscured by recrystallization, replacement, and overgrowth.

By inference, much of the finely-crystalline (<0.02-0.1 mm), red-orange luminescent dolomite dispersed within subtidal Prairie du Chien Group sediment is interpreted as marine in origin.

SHALLOW-BURIAL DIAGENESIS

Overview

Shallow-burial diagenesis included carbonate dissolution and karst development, patchy silicification, and possibly the early phases of coarse, fabric-destructive replacement dolomitization and dolomite cementation. Aside from possible dolomitization, these diagenetic events occurred during prolonged subaerial exposure associated with unconformity development (Smith 1989, 1992; Smith and others, 1993, 1996).

The large-scale paleokarst features formed during the development of the Oneota-Shakopee and Shakopee-St. Peter unconformities have been mapped regionally (summarized in Smith and others, 1996). In contrast, the microscale carbonate fabrics associated with shallow burial and unconformity development are the least well-documented aspect of Prairie du Chien Group diagenesis, in part because later diagenetic overprinting such as regional hydrothermal dolomitization preferentially altered carbonate fabrics associated with high-permeability.

Examples of calcium-carbonate cement fabrics

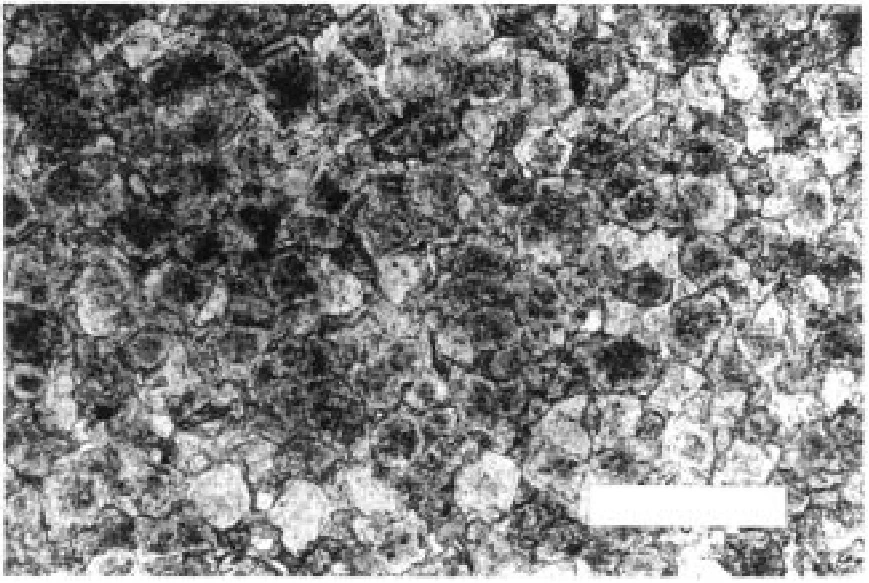


Figure 5. *Dolomitized peloidal packstone-wackestone from basal Shakopee Formation at Preston (PE), Minnesota. Dolomite crystal size and peloid size are similar. Scale bar = 0.5 mm.*

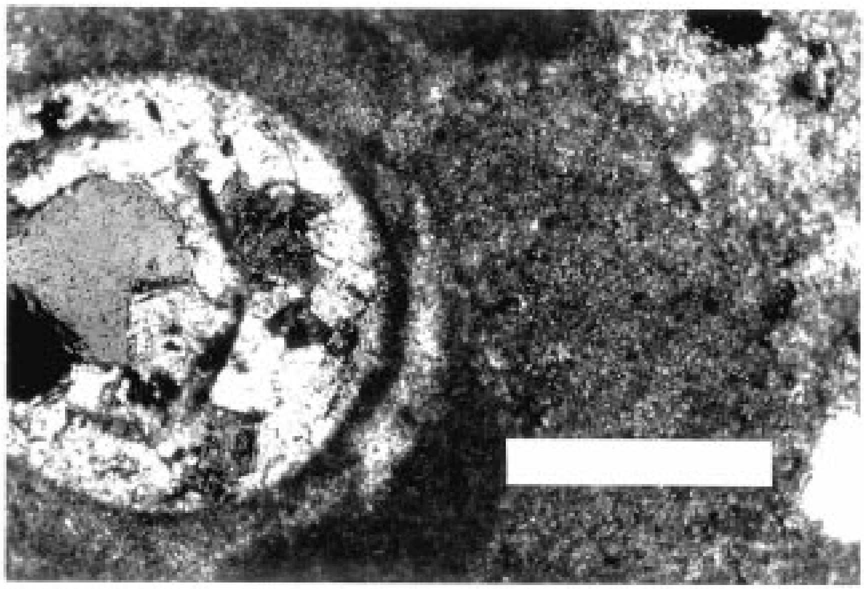


Figure 6. *Dolomitized ooid within dolomitized peloidal packstone-wackestone matrix, from lower Oneota Formation at Madison, Wisconsin. Note relatively coarse dolomite crystals within ooid (left) and finer dolomite crystals within micritic-textured peloidal packstone-wackestone (right). Ooid core is a grain of quartz silt. Scale bar = 0.2 mm.*

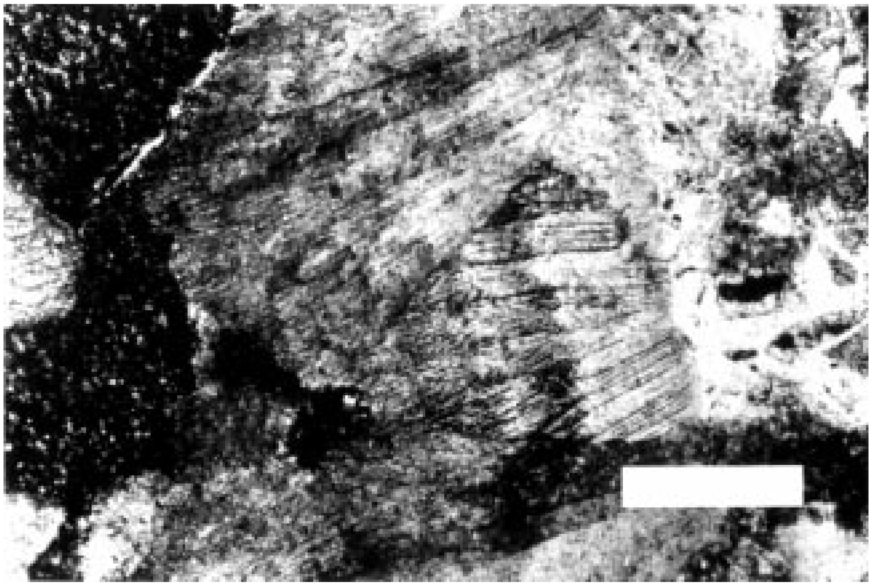


Figure 7. *Dolomitized fibrous (formerly aragonite?) fracture-filling cement, from lower Oneota Formation at Spring Green (SG), Wisconsin. Scale bar = 0.5 mm.*

formed during shallow-burial diagenesis are exceedingly rare within the Prairie du Chien Group. One example contains the ghosts of fibrous cement within later dolomite (fig. 7). The fibrous cement is interpreted as aragonitic fracture-filling cement precipitated within centimeter-wide fractures during paleokarst development. Alternatively, the fibrous cement may have been fibrous high-magnesium calcite precipitated during marine transgression across a karsted land surface.

Shallow-burial dolomite and dolomitization

The Prairie du Chien Group contains a somewhat heterogeneous assortment of dolomite cement and replacement phases unified by the fact that they postdate syndepositional diagenetic features and some paleokarst development, and precede the main events of regional hydrothermal mineralization. Shallow-burial dolomite, as they are termed here, forms cement and fabric-destructive replacement fabrics composed of idiotopic, subhedral-to-euhedral crystals. Shallow-burial dolomite crystals (0.1-0.5 mm) are larger than the syndepositional dolomite crystals (<0.02-0.1 mm) upon which they nucleated. Under cathodoluminescence, shallow-burial dolomite typically exhibits a distinctive microzoning composed of red-orange and orange microzones, quite unlike the relatively uniform red-orange color of early dolomite, and unlike the blocky microzoning of later hydrothermal dolomite (fig. 8). The distinctively microzoned dolomite is best developed in vuggy pores of the Oneota Formation. Smaller dolomite crystals without distinct microzones but with similar petrographic relationships and cathodoluminescence colors are present in the overlying Shakopee Formation.

The earliest work on the regional dolomitization of Ordovician carbonates in the study area attributed dolomitization to seawater or evaporative brine (for example, Calvin and Bain, 1900; Leonard, 1905). This work was later corroborated by Asquith (1967) and Deininger (1964), both of whom also primarily examined Middle Ordovician dolostone of the Sinnipee Group. Alternative dolomitization mechanisms that have been proposed include mixing-zone dolomitization (Badiozamani, 1973) and dolomitization by hydrothermal fluids (Deininger, 1964; Sheppard, 1982).

Finely microzoned shallow-burial dolomite from the Prairie du Chien Group is similar in cathodoluminescence pattern to detrital dolomite obtained from the continental shelf of South Australia by Bone and others (1991, 1992). Trace element composition and stable isotopic data suggest that the microzoned Australian dolomite precipitated from seawater below the sediment-water interface (Bone and others, 1992). In contrast, geochemical analyses of Prairie du Chien Group dolomite are inconclusive regarding physiochemical conditions, and Prairie du Chien Group petrography suggests dolomitization of well-lithified strata, not unconsolidated sediment. In addition, the extensive fabric-destructive replacement of precursor carbonate material by shallow-burial dolomite in the Prairie du Chien Group suggest dolomitization by a fluid more corrosive than seawater.

Alternatively, shallow-burial dolomite may have precipitated within a coastal mixing zone. Mixing zones would have been widespread across our study area during the marine transgressions that followed the regional development of formation-bounding disconformities. The concept of mixing-zone dolomitization (Hanshaw and others, 1971) was first applied to Ordovician carbonates of the study area by Badiozamani (1973), who used it to explain partial dolomitization of the Middle Ordovician Platteville Formation. The chemical underpinning of the mixing-zone model have since been severely questioned (for example, Hardie, 1987). Recent work suggests that modern mixing zones are typically dominated by carbonate dissolution instead of pervasive dolomitization (for example, Back and others, 1986; Sanford and Konikow, 1989), although some dolomite has been shown to precipitate within the seawater-dominated parts of mixing zones (for example, Ward and Halley, 1985).

Regional, fabric-destructive dolomitization of well-lithified limestone by seawater and/or seawater-derived fluids has also been hypothesized (for example, Saller, 1984; Pleydell and others, 1990; Goldstein and others, 1991; James and others, 1991). In all of these cases the dolomitizing fluid appears to have been seawater or seawater-derived evaporative brines, although the actual conditions of dolomitization are not well constrained in all cases.

The Prairie du Chien Group would have been thoroughly flushed by seawater, brackish water, and fresh water during the sea level changes that accompanied development of formation-bounding disconformities. Some mixing-zone dolomitization, and dolomitization by seawater and evaporatively-derived brines probably accompanied marine regressions and transgressions. However it is also possible that the dolomite represents an initial phase (that is, warm, not hot) of hydrothermal dolomitization, and do not represent dolomitization by these other mechanisms. Once again, relevant geochemical evidence is lacking in the Prairie du Chien Group because of extensive replacement by later dolomite phases. All that is certain is that shallow-burial dolomitization followed syndepositional diagenesis and lithification, and preceded further dolomitization by hydrothermal brines.

HYDROTHERMAL DIAGENESIS

Overview

Non-economic occurrences of hydrothermal minerals indicate that regional hydrothermal mineralization affected a 100,000 km^2 area surrounding the Upper Mississippi Lead-Zinc District, including the study area (Jenkins, 1968; Heyl and West, 1982). Petrographic and geochemical similarities between the ores and disseminated sulfides from outlying locations support the hypothesis of regional hydrothermal mineralization by the same fluids (Garvin and others, 1987).

Rubidium-strontium dating indicates that hydrothermal mineralization of the Upper Mississippi District occured during the Early Permian (269 +/- 4 Ma, Rowan and others, 1995). Maximum burial of the district during hydrothermal mineralization is estimated at approximately 1 km, based on apatite fission-track analysis (Zimmerman, 1986).

The following paragenetic sequence has been documented for Mississippi Valley-type ores of the Upper Mississippi Valley: dolomitization, cherty silicification, marcasite and pyrite precipitation, sphalerite and galena precipitation, and calcite precipitation (Tupas, 1950; Heyl and others, 1959). Although the homogenization and final-melting temperatures of fluid inclusions in sphalerite and late-stage calcite have been studied, the earliest hydrothermal mineral phase (dolomite) lacks comparable documentation.

Homogenization temperatures of two-phase fluid inclusions in sphalerite indicate ore precipitation at 75-220^{o}C in the main Upper Mississippi Valley mining district (Newhouse, 1933; Bailey and Cameron, 1951; McLimans, 1977), and precipitation of outlying ores at lower temperatures: 57-116^{o}C (Jenkins, 1968; Coveney and Goebel, 1983; Coveney and others, 1987; Kutz and Spry, 1989). Final melting temperatures of two-phase fluid inclusions in sphalerite indicate precipitation from brines containing 16-24 equiv wt percent NaCl (McLimans, 1977; Kutz and Spry, 1989).

Homogenization temperatures of 38-78^{o}C from late-stage calcite indicate that temperatures decreased toward the end of hydrothermal mineralization (Bailey and Cameron, 1951; Erickson, 1965; Kutz and Spry, 1989). Late-stage calcite precipitated from brine containing 5-23 equiv wt percent NaCl (Hall and Friedman, 1963; Erickson, 1965; Kutz and Spry, 1989), also suggesting local dilution of mineralizing brine by meteoric water (Hall and Friedman, 1963).

Hydrothermal dolomite and dolomitization

Hydrothermal dolomite is a relatively late diagenetic feature and is the youngest dolomite within the Prairie du Chien Group. Hydrothermal dolomite crystals are mainly subhedral to euhedral, idiotopic (mainly) to xenotopic, and up to 2 mm in size (figs. 8 and 9). In general, xenotopic dolomite crystal textures indicate

Figure 8.
Cathodoluminescence photomicrograph of finely-microzoned dolomite within lower Oneota Formation at Cazenovia (CZ), Wisconsin. Finely microzoned dolomite (B) overgrow poorly-defined earlier dolomite (A), which are overgrown by hydrothermal dolomite (C). Solid black color indicates open porosity. Scale bar = 0.2 mm.

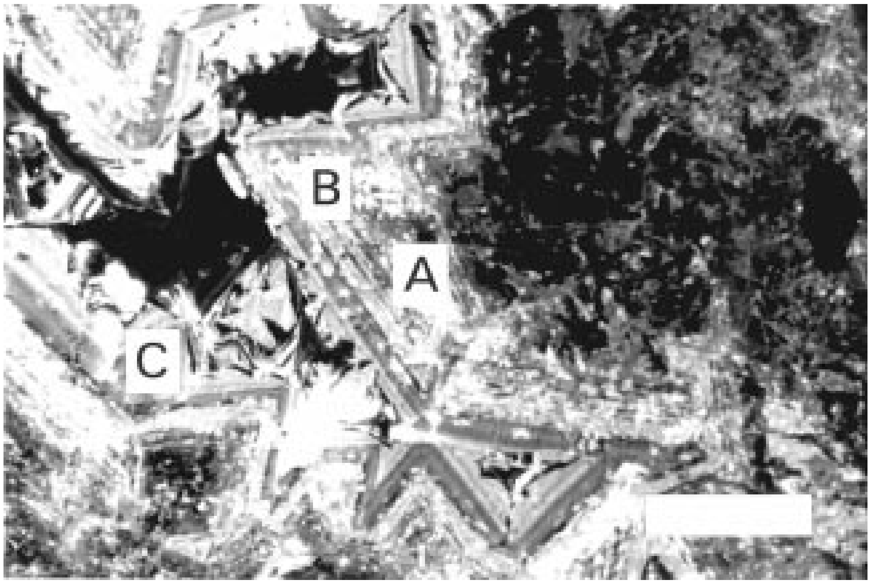
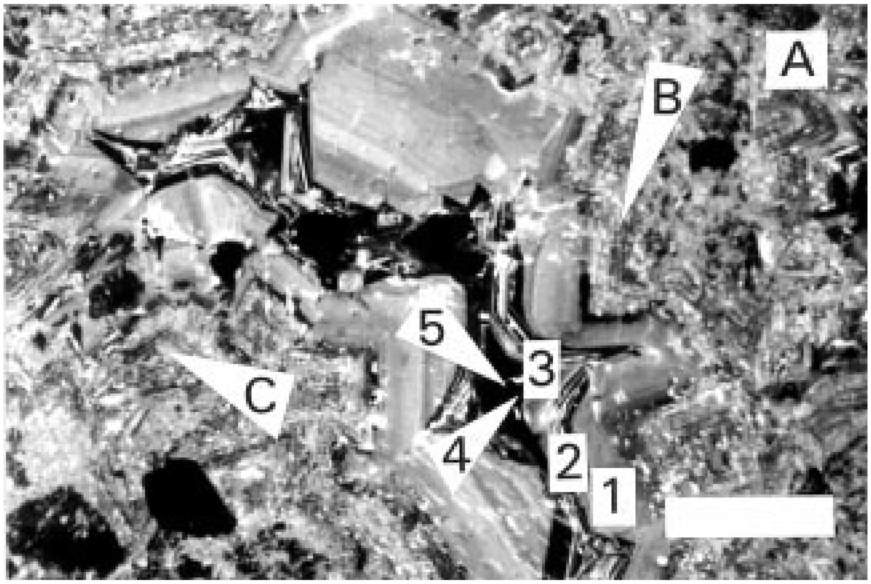


Figure 9.
Cathodoluminescence photomicrograph of hydrothermal dolomite 1-5 filling vuggy pore within lower Oneota Formation at Cazenovia, Wisconsin. Earlier dolomite (A), parts of which contain fine microzones (B), are overgrown and patchily replaced by hydrothermal dolomite 1-5. Note dolomite 3 replacing earlier dolomite at C. Scale bar = 0.2 mm.



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crystallization at temperatures >50-60°C (Gregg, 1982; Gregg and Sibley, 1983, 1984; Radke and Mathis, 1980), however, the dominance of the idiotopic dolomite crystal growth form in the Prairie du Chien Group suggests 50-60°C as the upper limit of fluid temperatures during Prairie du Chien Group dolomitization. These modest temperatures are consistent with petrographic evidence that dolomitization was an early phase of hydrothermal mineralization.

Hydrothermal dolomite replaces and overgrows part of all precursor carbonate material (figs. 8 and 9). This observed replacement of parts of lower-temperature dolomite by higher-temperature dolomite is generally expected because of the relative thermodynamic instability of calcium-rich, relatively disordered lower-temperature dolomite (for example, Land, 1980, 1985). Hydrothermal dolomite is itself locally replaced and/or overgrown by hydrothermal calcite (fig. 10), the last phase of regional hydrothermal mineralization in the Upper Mississippi Valley (Tupas, 1950).

Hydrothermal dolomite from Prairie du Chien Group outcrops displays a consistent sequence of cathodoluminescence colors (fig. 9): dull orange (dolomite 1), microzoned red and black (dolomite 2), red (dolomite 3), dark red (dolomite 4), and black (dolomite 5). Dolomite 1, 2 (where present), and 3 are generally separated by microdissolution surfaces. Dolomite 1 is the most abundant hydrothermal dolomite phase (for example, fig. 9). The trend toward darker ("quenched") cathodoluminescence is accompanied by an increase in Fe/Mn ratios from 1.3 to 12.8 (table 1). Dolomite 4 and 5 are particularly ferroan and average 5600 to 12,800 ppm Fe (table 1).

Dolomite 1 (dull orange) and 3 (red) can be visually correlated between ore bodies and dolomitized parts of the Prairie du Chien Group and Sinnipee Groups. Dolomite from Upper Mississippi Valley lead-zinc ore typically consists of dolomite 1 and a thin, discontinuous rim of dolomite 3. Within ore deposits, dolomite 3 precipitated just prior to sulfide precipitation and is commonly overgrown by marcasite or sphalerite (Heyl and others, 1959).

Dolomite 4 (dark red) and 5 (black) was only identified in Prairie du Chien Group samples from outside of ore deposits, although these ferroan dolomite phases also occur as isolated vein- and mold-filling cement in relatively unaltered limestone of the Platteville Formation (Sheppard, 1982). Precipitation of the ferroan dolomite throughout the outcrop area probably overlapped with precipitation of marcasite and pyrite in the ore bodies (for example, Tupas, 1950; Heyl and others, 1959), and with precipitation of disseminated epigenetic iron sulfide identified by Heyl and West (1982) and Garvin and others (1987).

Late-stage hydrothermal calcite

Four phases of progressively less-ferroan calcite precipitated after the peak of sulfide precipitation (fig. 10, table 1; Calcites I-IV of Tupas, 1950). Although each calcite phase partially replaces precursor carbonate phases, the hydrothermal calcite primarily form cement and are best developed within centimeter-scale vuggy pores containing marcasite and pyrite.

Calcites I and II typically occur as isolated millimeter-scale cement crystals (fig. 10A). Calcite III forms larger, centimeter-scale scalenohedral cement crystals that are typically overgrown but not replaced by calcite IV (fig. 10B). Where these late-stage calcites are abundant, calcite IV commonly occludes remaining pore space. Calcites I-IV are locally abundant within the Prairie du Chien Group and have also been documented within the Platteville Formation (Sheppard, 1982).

NEAR-SURFACE WEATHERING

Based on the absence of Mesozoic and Tertiary sediment, the study area has experienced nondeposition and/or erosion throughout most of the Mesozoic and Cenozoic. Karst development continues to the present. Other, relatively recent paleokarst is buried beneath Pleistocene glacial sediment. Post-hydrothermal carbonate diagenesis has been dominated by near-surface weathering and karst development, accompanied by the precipitation of aragonitic and calcitic speleothems.

STABLE ISOTOPE GEOCHEMISTRY

The results of 43 whole-rock analyses of Prairie du Chien Group dolomite, dolomite from Upper Mississippi Valley District ores, and other Upper Cambrian and Middle Ordovician dolomite are shown in figure 11 and table 2. Oxygen isotope values of Prairie du Chien Group dolomite ranges from $\delta^{18}O = -6.39$ to -3.49, whereas carbon isotopic values range from $\delta^{13}C = -5.91$ to -1.50. Isotopic values for oxygen and carbon do not display consistent geographic or stratigraphic trends, and do not vary consistently based on rock type. The oxygen and carbon stable isotopic values of Upper Cambrian and Middle Ordovician dolo-

Table 1. *Dolomite trace element data obtained by electron microprobe analysis. Values in parentheses indicate 95% confidence intervals.*

Color*	Fe/Mn	Ca/Mg (moles)	Fe (ppm, wt)	Mn (ppm, wt)	Sr (ppm, wt)	Na (ppm, wt)
A. Pre-hydrothermal dolomite (bulk composition)						
orange and red	1.6	1.05 (1.04, 1.06)	450 (340, 570)	290 (230, 340)	120 (60, 180)	210 (72, 350)
B. Hydrothermal dolomites 1-5						
1- orange	3	1.03 (1.02, 1.04)	450 (370, 530)	350 (290, 410)	80 (40, 120)	40 (0, 170)
2- red/blk	0.9	1.05 (1.04, 1.06)	120 (50, 180)	130 (70, 190)	90 (40, 140)	150 (20, 290)
3- red	2.8	1.04 (1.03, 1.05)	2310 (1880, 2750)	820 (480, 1160)	90 (40, 150)	40 (0, 70)
4- dark red	7.5	1.04 (1.02, 1.05)	5630 (4860, 6410)	750 (550, 950)	30 (-30, 90)	30 (-20, 90)
5- black	12.8	1.00 (1.00, 1.02)	12780 (10560, 15010)	1000 (570, 1420)	110 (20, 200)	30 (-10, 70)

*Color = cathodoluminescence color

mite sampled from outcrops are generally similar to Prairie du Chien Group values.

Oxygen and carbon isotopes from Upper Mississippi Valley district ore samples are generally greater than values from outcrop samples. Oxygen isotopic values from Upper Mississippi samples range from $\delta^{18}O$ = -3.74 to -2.42, and carbon isotopic values vary from $\delta^{13}C$ = -0.29 to -0.18 (table 2). These numbers fall within the range of previously published isotopic values of Upper Mississippi Valley ores (for example, fig. 11; Hall and Friedman, 1969; Garvin and others, 1987; $\delta^{18}O$ = -4 to -2, $\delta^{13}C$ = -0.5 to +0.5) and are consistent with precipitation from hypersaline, evaporite-derived brines (for example, Kutz and Spry, 1989).

Because of their history of partial replacement and overgrowth, dolomite from Prairie du Chien Group outcrops is heterogeneous in composition (for example, fig. 9). Therefore, the $\delta^{18}O$ and $\delta^{13}C$ values of Prairie du Chien Group dolomite represent compositional averages of syndepositional, shallow-burial, and hydrothermal dolomite. The $\delta^{18}O$ values of Prairie du Chien Group dolomite are consistent with mainly seawater-derived, Early Ordovician calcium carbonate (for example, fig. 11; Lohmann, 1988, p. 67). The $\delta^{13}C$ values of Prairie du Chien Group dolomite is somewhat lower than Early Ordovician seawater-derived carbonate (for example, Lohmann, 1988, p. 67), but biogenic grains commonly display ^{12}C enrichment (for example, Tucker and Wright, 1990, p. 325). In spite of petrographic evidence for pervasive hydrothermal dolomitization, Prairie du Chien Group dolomite does not appear to have acquired the heavier $\delta^{18}O$ and $\delta^{13}C$ values characteristic of Upper Mississippi Valley dolomite. This combination of hydrothermally-overprinted microfabrics and non-Upper Mississippi Valley $\delta^{18}O$ and $\delta^{13}C$ values suggests that much of the replacive dolomitization in the Prairie du Chien Group has involved local dissolution and reprecipitation of precursor carbonate material.

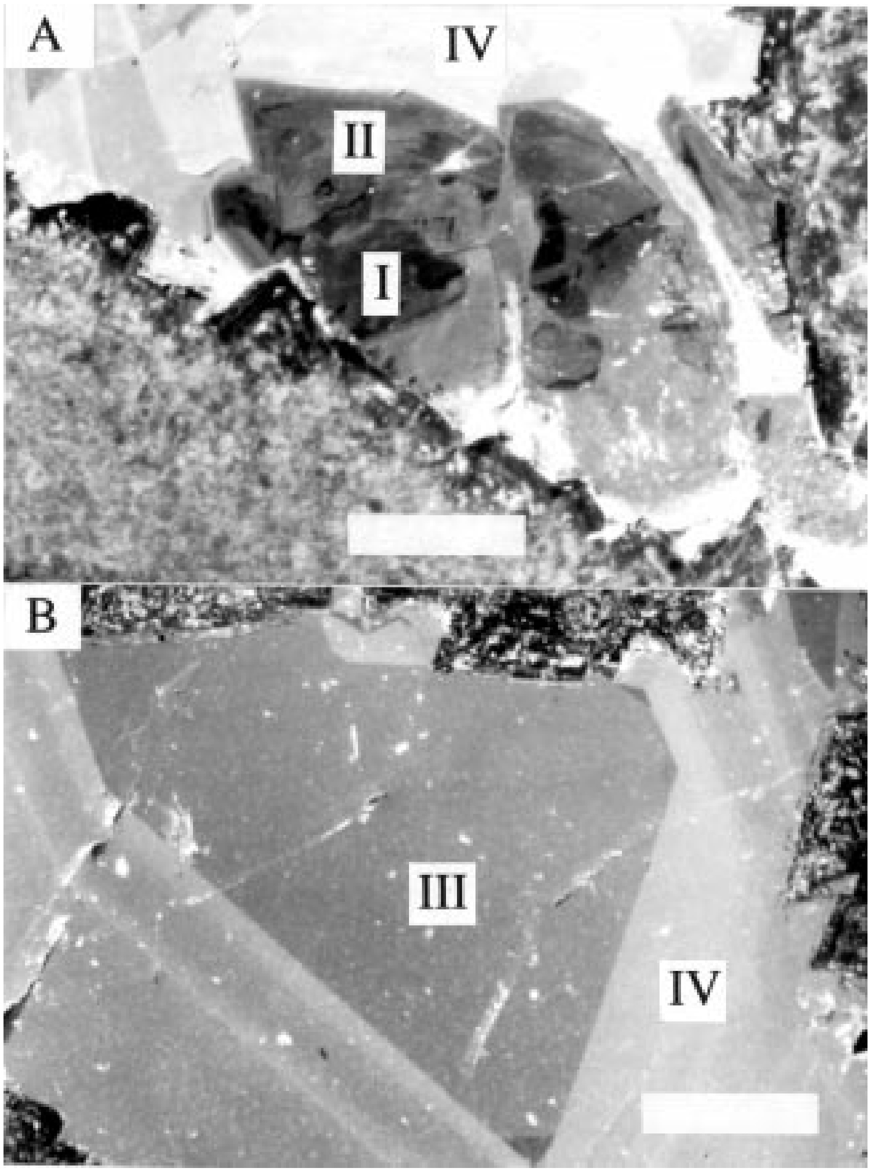

Figure 10. *Examples of hydrothermal calcites I-IV, lower Oneota Formation, Preston (PE), Minnesota. Roman numerals I-IV from Tupas (1950). A. Scale bar = 0.2 mm. B. Scale bar = 0.5 mm.*

Table 2. *Values of $\delta^{13}C$ and $\delta^{18}O$ from Upper Cambrian to Middle Ordovician dolomite analyzed in this study. Values shown relative to the PDB standard. Samples are archived at the University of Wisconsin-Madison under "U.W.1866/number."*

Sample	$\delta^{13}C$ (PDB)	$\delta^{18}O$ (PDB)	Comments
A. Galena and Decorah Formations			
MVT-2A, U.W.1866/30	-0.22	-3.74	sulfide ore, zoned dolomite
MVT-2B-1, U.W.1866/31	-0.18	-3.68	sulfide ore, saddle dolomite
MVT-2A-2, U.W.1866/32	-0.29	-3.61	sulfide ore, zoned dolomite
MVT-15B, U.W.1866/33	-0.22	-2.42	sulfide ore, zoned dolomite
BV-GAL, U.W.1866/29	-1.49	-5.32	outcrop,peloidal-bioclastic packstone
B. Platteville Formation			
PE-PL, U.W.1866/36	-2.50	-6.24	outcrop, peloidal-bioclastic packstone
PDC-PL-D, U.W.1866/35	-1.34	-5.48	outcrop, peloidal-bioclastic packstone
C. Shakopee Formation (west to east, arranged stratigraphically for each location)			
PE-58, U.W.1866/47	-3.94	-4.82	outcrop, peloidal dolomicrite
PE-50-OO, U.W.1866/45	-3.41	-3.49	outcrop, oolitic grainstone
PE-50-ST, U.W.1866/46	-3.11	-5.10	outcrop, stromatolite
PDC-120, U.W.1866/44	-2.97	-5.22	outcrop, oolitic grainstone
PDC-74, U.W.1866/43	-2.90	-5.28	outcrop, peloidal dolomicrite
CZ-1, U.W.1866/37	-2.17	-5.98	outcrop, oolitic grainstone
CZ-33, U.W.1866/40	-2.73	-5.84	outcrop, oolitic grainstone
CZ-30, U.W.1866/39	-2.09	-5.51	outcrop, peloidal dolomicrite
CZ-2, U.W.1866/38	-2.59	-5.68	outcrop, oolitic packstone
HR-21, U.W.1866/41	-2.92	-5.46	outcrop, peloidal wackestone
HR-NR, U.W.1866/42	-4.68	-5.07	outcrop, peloidal wackestone
BN-2-1, U.W.1866/64	-5.91	-5.20	cuttings, oo-peloidal packstone
BN-2-2, U.W.1866/65	-5.79	-5.00	cuttings, oo-peloidal packstone
BN-3, U.W.1866/66	-5.55	-5.10	cuttings, oo-peloidal packstone
D. Oneota Formation (west to east, arranged stratigraphically for each location)			
PE-16-1, U.W.1866/57	-3.02	-4.86	outcrop, peloidal wackestone
PE-16-2, U.W.1866/58	-3.07	-4.87	outcrop, peloidal wackestone
PE-11, U.W.1866/56	-2.77	-5.15	outcrop, oolitic grainstone
PDC-7, U.W.1866/55	-3.16	-4.86	outcrop, peloidal dolomicrite
PDC-5, U.W.1866/54	-3.58	-4.90	outcrop, oolitic grainstone
CZ-3-1, U.W.1866/48	-1.84	-6.23	outcrop, oo-peloidal packstone
CZ-3-2, U.W.1866/49	-1.78	-6.39	outcrop, oo-peloidal packstone
CZ-9, U.W.1866/53	-2.37	-5.84	outcrop, oo-peloidal packstone
CZ-6, U.W.1866/52	-2.51	-5.79	outcrop, peloidal packstone
CZ-4-1, U.W.1866/50	-2.74	-5.55	outcrop, oolitic packstone
CZ-4-2, U.W.1866/51	-2.73	-5.61	outcrop, oolitic packstone
SW-7, U.W.1866/59	-2.36	-5.63	outcrop, stromatolite
BN-4, U.W.1866/67	-4.95	-5.39	cuttings, oolitic packstone
BN-5, U.W.1866/68	-3.61	-5.56	cuttings, oo-peloidal packstone
BN-6-1, U.W.1866/69	-1.57	-5.74	cuttings, oolitic grainstone
BN-6-2, U.W.1866/70	-1.50	-5.84	cuttings, oolitic grainstone
BN-7, U.W.1866/71	-2.47	-5.76	cuttings, oolitic grainstone
E. Trempealeau Group (St. Lawrence Formation, west to east)			
RW-STL-1, U.W.1866/62	-0.47	-5.48	outcrop, dolomitic siltstone
RW-STL-2, U.W.1866/63	-0.48	-5.46	outcrop, dolomitic siltstone
BE-STL, U.W.1866/60	-0.56	-5.48	outcrop, stromatolite
M-STL, U.W.1866/61	-1.45	-4.91	outcrop, stromatolite
BN-8, U.W.1866/72	-2.27	-6.11	cuttings, dolomitic siltstone

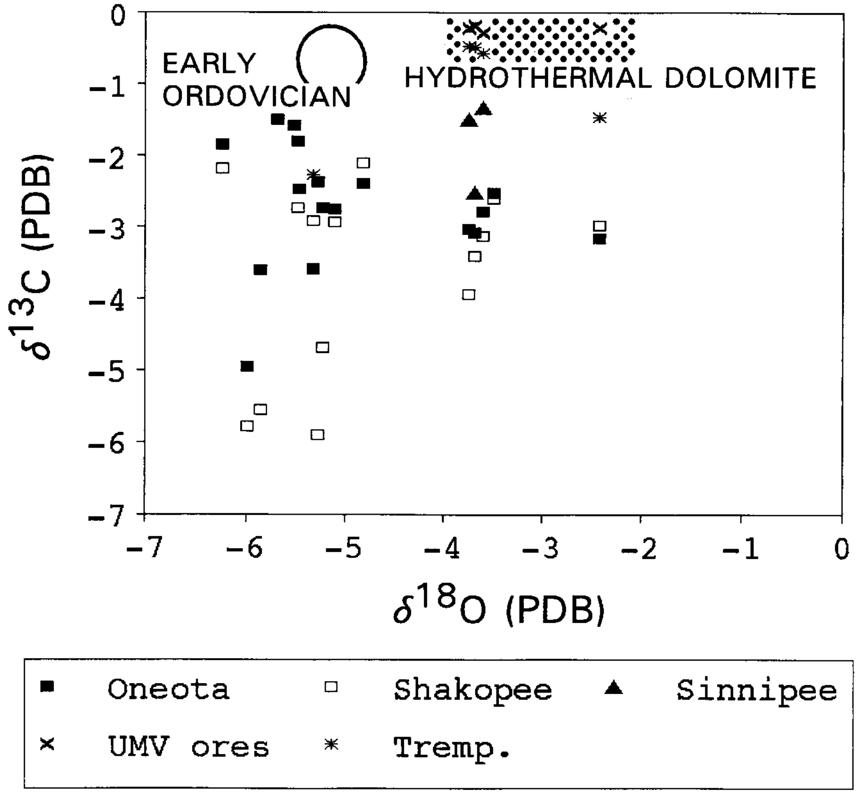

Figure 11. *Scatter plot of δ^{18}O and δ^{13}C values from Upper Cambrian-Middle Ordovician dolomite analyzed in this study. Circle labeled "Early Ordovician" indicates estimate of seawater composition based on primary calcite compositions (Lohmann, 1988). Rectangular field labeled "hydrothermal dolomite" indicates range of values obtained by Hall and Friedman (1969) and Garvin and others (1987) from dolomite associated with Upper Mississippi Valley district ores.*

CONCLUSIONS

Carbonate diagenesis of the Prairie du Chien Group included syndepositional diagenesis, shallow-burial diagenesis, hydrothermal diagenesis, and near-surface weathering. Dolomitization has been a prominent aspect of carbonate diagenesis, and occurred during syndepositional, shallow-burial, and hydrothermal diagenesis, although shallow-burial dolomitization may actually be an early, relatively low-temperature phase of hydrothermal diagenesis.

The sequence of diagenetic events within the Prairie du Chien Group is well-constrained by petrography and cathodoluminescence petrography. Iron and magnesium trace-element data corroborate previous work on Upper Mississippi Valley ore paragenesis, and support a more detailed interpretation of the timing of hydrothermal dolomitization and late-stage hydrothermal calcite precipitation relative to the main phases of Upper Mississippi Valley ore precipitation. Values of δ^{18}O and δ^{13}C are consistent with precipitation of most Prairie du Chien Group carbonate from Early Ordovician seawater. Although petrography and cathodoluminescence petrography indicate pervasive hydrothermal dolomite cementation and replacement of precursor carbonate, differences between the values of δ^{18}O and δ^{13}C for Prairie du Chien Group dolomite and dolomite from Upper Mississippi Valley ore deposits suggest that most hydrothermal dolomitization within the Prairie du Chien Group involved the dissolution and local reprecipitation of precursor carbonate material. In summary, because of sequential, partial, patchy replacement of preexisting carbonate phases by later phases, the diagenetic history of the Prairie du Chien Group is supported primarily by petrography and cathodoluminescence petrography, not by geochemical data.

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