

Evidence against the Dorag (mixing-zone) model for dolomitization along the Wisconsin arch—A case for hydrothermal diagenesis

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ABSTRACT

Ordovician carbonates near the Wisconsin arch represent the type locality in ancient rocks for the Dorag, or mixing-zone, model for dolomitization. Field, petrographic, and geochemical evidence suggests a genetic link between the pervasive dolomite, trace Mississippi Valley-type (MVT) minerals, and potassium (K)-silicate minerals in these rocks, which preserve a regional hydrothermal signature. Constraints were placed on the conditions of water-rock interaction using fluid-inclusion methods, cathodoluminescence and plane-light petrography, stable isotopic analyses, and organic maturity data. Homogenization temperatures of two-phase aqueous fluid inclusions in dolomite, sphalerite, and quartz range between 65 and 120°C. Freezing data suggest a Na-Ca-Mg-Cl-H₂O fluid with salinities between 13 and 28 wt.% NaCl equivalent. The pervasive dolomitization of Paleozoic rocks on and adjacent to the Wisconsin arch was the result of water-rock interaction with dense brines at elevated temperatures, and it was coeval with regional trace MVT mineralization and K-silicate diagenesis. A reevaluation of the Dorag (mixing-zone) model for dolomitization, in conjunction with convincing new petrographic and geochemical evidence, has ruled out the Dorag model as the process responsible for pervasive dolomitization along the Wisconsin arch and adds to the abundant body of literature that casts serious doubt about the viability of the Dorag model in general.

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ACKNOWLEDGEMENTS

The author thanks the Department of Earth and Planetary Sciences for funding a part of this research while he was a Ph.D. student at the Johns Hopkins University. Michels Materials, Vulcan Materials, the Milwaukee Public Museum, the Wisconsin Geological and Natural History Survey, and many others generously allowed access to their quarries and materials, without which, this project could not have been accomplished. Rod Norby, Jeff Kuglitsch, and Hope Jahren also aided in the thermal maturity part of the study. Lawrence Hardie and Grant Garven helped refine the ideas presented in the author's doctoral dissertation, from which the bulk of this material was derived. Reviewers Greg Ludvigson, J. Frederick Read, and Langhorne Smith offered constructive and valuable criticisms that improved this manuscript.

INTRODUCTION

The eastern Wisconsin region lies on the extreme western edge of the Michigan Basin and is located to the east of the Wisconsin arch (Figure 1). As much as 500–800 m (1640–2600 ft) of lower and middle Paleozoic quartz sandstone, dolostone, and shale are present there (Figure 1), and the strata thicken toward the Michigan Basin, where they are overlain by younger Paleozoic and Mesozoic sedimentary rocks.

The Upper Ordovician Sinnipee Group carbonates of the Platteville Formation, in particular, were the focus of research by Badiozamani (1973) and others. Several different lithofacies have been recognized in the Platteville Formation of Wisconsin, including argillaceous and nonargillaceous mudstones, bioturbated mudstones, mottled mudstone to wackestone, interbedded mudstone and organic-rich shale, peloidal wackestone to packstone, skeletal wackestone to packstone, quartz packstone, and interbedded nodular carbonate and grainstone (Choi and Simo, 1998). These litho-

facies represent mainly subtidal deposition on a shallow to deep open-marine carbonate ramp.

Most of the diagenetic research on Paleozoic sedimentary rocks in the region has focused separately on three main diagenetic processes: Mississippi Valley–type (MVT) mineralization, dolomitization, and potassium (K)-silicate mineralization. In general, work on these three mineral assemblages has been done by different groups of researchers, and few attempts at investigating a potential relationship between these processes have been made.

Several researchers have proposed models to explain the character and distribution of the dolomite bodies in the Wisconsin region. Although most work has concentrated on the Ordovician dolomites in the upper Mississippi Valley or on the Wisconsin arch (Deininger, 1964; Badiozamani, 1973; Adams, 1975, 1978; Gregg and Sibley, 1984; Smith, 1991; Smith and Simo, 1997), none of these studies has focused on the dolomitized Paleozoic carbonates on and along the eastern side of the Wisconsin arch. Prior to this study, fluid-inclusion

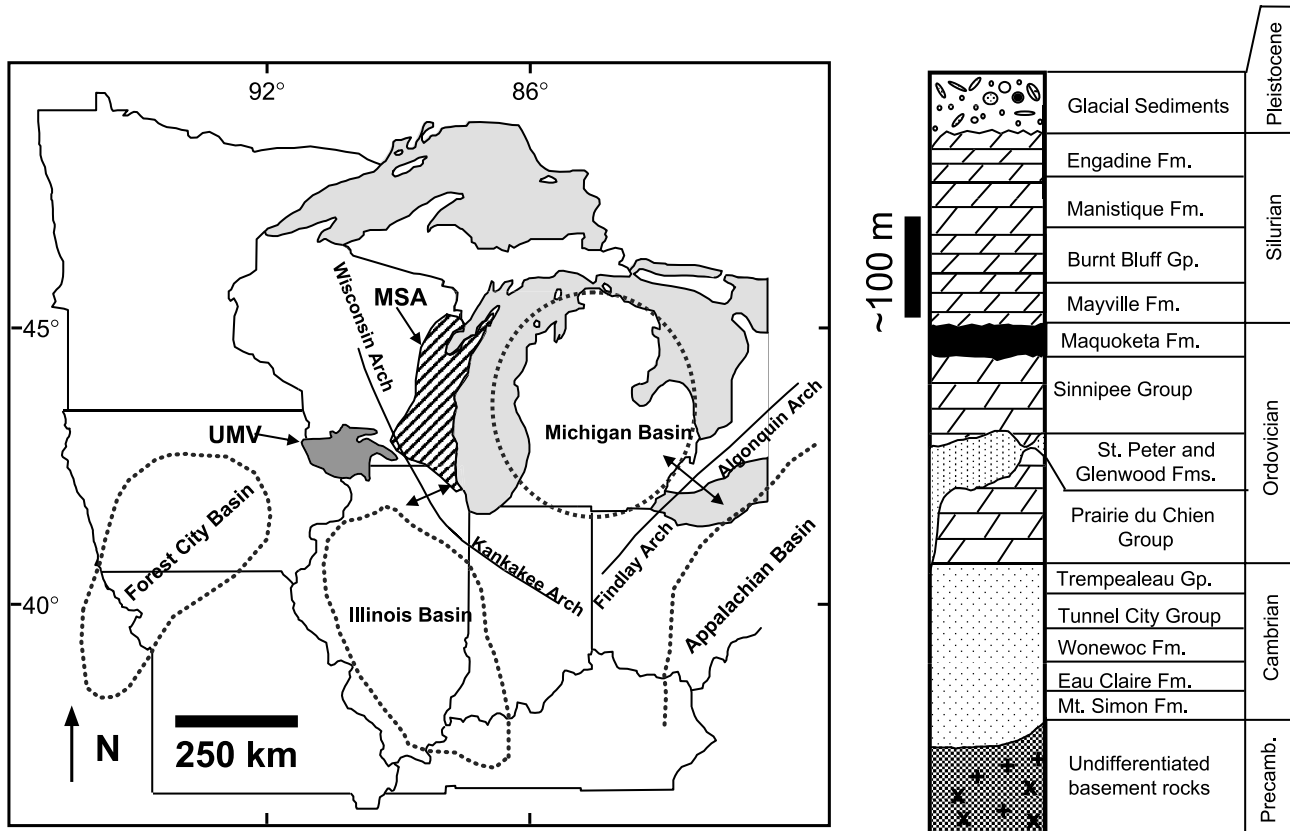


Figure 1. Map of the midwestern United States region showing the positions of the Wisconsin arch and Michigan Basin, relative to the main study area (ruled area, MSA) and the upper Mississippi Valley Pb-Zn ore district (UMV). On the right is a typical stratigraphic column for northeastern Wisconsin (modified from Mugel and Pratt, 1991; Harris et al., 1998).

data had not been used to place constraints on the temperatures or salinities of fluids responsible for dolomitization of these rocks. This article presents strong evidence that the dolomite near and east of the Wisconsin arch is the product of regional hydrothermal fluid flow instead of a low-temperature mixing-zone system, as suggested by Badiozamani (1973). The reexamination of pervasively dolomitized rocks on the western flank of the Michigan Basin in eastern Wisconsin is important and especially relevant, given the recent interest in hydrothermal dolomites as oil and gas reservoirs.

PREVIOUS DOLOMITE MODELS

The first dolomite study of Paleozoic rocks on the Wisconsin arch was by Deiningner (1964), who concentrated on the formation of dolomite in the Ordovician Sinnipee Group carbonates of the Platteville Formation. His hypothesis of hydrothermal dolomitization was not well accepted at the time, and his work went largely unnoticed. He recognized the importance of the experimental work by Baron (1958, cf. Baron, 1960) and even suggested a possible link with the hydrothermal MVT mineralization in the nearby upper Mississippi Valley lead-zinc ore district. Less than a decade later, a new model was developed by Badiozamani (1973) to explain dolomitization of carbonates along the Wisconsin arch.

Badiozamani (1973) proposed what is the most well-known model for pervasive dolomitization in the Wisconsin region, the Dorag model. The term "Dorag" is a Persian word meaning mixed blood or hybrid. It is a mixing-zone model that involves replacement of preexisting calcite by dolomite in a coastal zone where mixing between seawater and meteoric-derived water occurs. The Dorag model was proposed to explain the geochemistry and the distribution of dolomite in Ordovician rocks of the Sinnipee Group, specifically the Mifflin Member of the Platteville Formation along the Wisconsin arch. The Wisconsin arch has served as the type locality of the Dorag model for ancient dolomites. The Dorag model became a paradigm for dolomitization models and remained so throughout much of the 1980s and 1990s. Variants of this mixed-water aquifer model are still favored by some researchers (e.g., Morrow, 1982; Muchez and Viaene, 1994; Dixon and Davis, 1997). Most importantly, Badiozamani suggested that the distribution of dolomite was concentrated along the Wisconsin arch, and that limestone was the principal lithology as one progressed away from the arch to the east or west (see Badiozamani, 1973, his

figure 14). He also used thermodynamic arguments to show that when seawater and fresh water mix, there is a theoretical range of possible compositions where the solution is undersaturated with respect to calcite, but oversaturated with respect to dolomite. Oxygen isotope data for dolomite along the arch yield negative $\delta^{18}\text{O}_{\text{PDB}}$ (Peedee belemnite standard) values, consistent with a meteoric water signature. Finally, he proposed that certain geographic and stratigraphic constraints on the dolomite-limestone transition, such as shifts in the dolomite-limestone transition along unconformity surfaces, could not be produced by hydrothermal dolomitization. Two of Badiozamani's (1973) criticisms of Deiningner's (1964) mechanism for dolomitization at elevated temperatures were the lack of evidence for diagenesis at elevated temperatures ($>50^\circ\text{C}$) and the absence of a mechanism for either heating up the local system or for moving warm fluids into the rocks from another source.

Smith (1991) and Smith and Simo (1997) suggest that the dolomitization of the Prairie du Chien Group in southwestern Wisconsin occurred syndepositionally, during shallow burial, and as an early phase of the hydrothermal dolomitization in the region related to the sulfide mineralization in the upper Mississippi Valley ore district. Smith (1991, p. 83–86) and Smith and Simo (1997) documented a complex, multistage cement stratigraphy for the dolomite that was restricted to the Wisconsin arch and was localized in and around the upper Mississippi Valley ore district. Smith (1991) also noted a different cement stratigraphy for these rocks between the Wisconsin arch and upper Mississippi Valley ore district dolomites and those in the Michigan Basin.

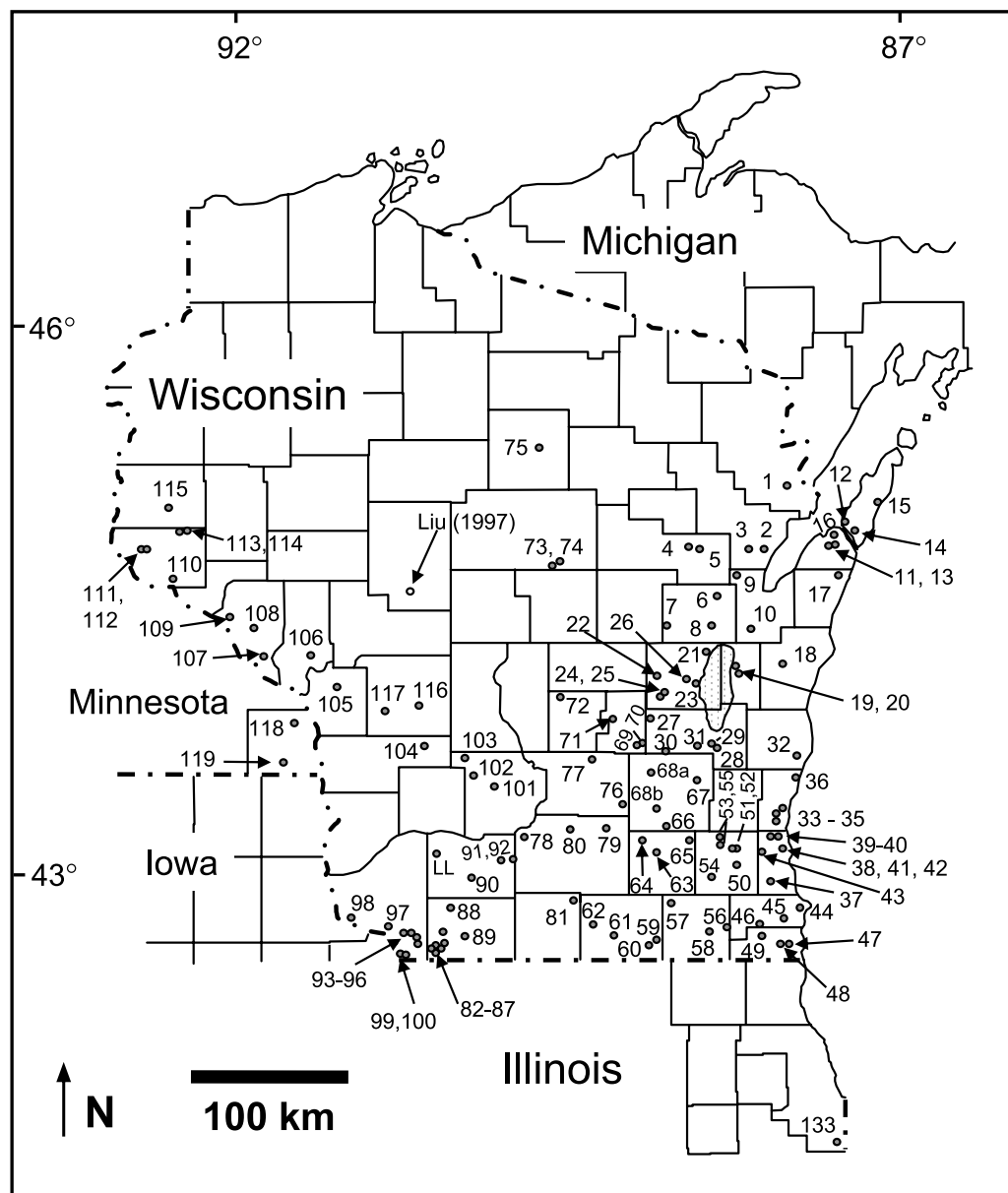
The author recently conducted a regional-scale reconnaissance study (Figure 2) of epigenetic mineralization that culminated in a doctoral dissertation. This research has revealed the existence of a pervasive ancient regional hydrothermal system that operated in eastern Wisconsin during or after the Middle Devonian (Luczaj, 1998, 2000, 2001). Only data relevant to the issue of mixing-zone versus hydrothermal epigenetic dolomitization are presented here.

EVIDENCE FOR REGIONAL HYDROTHERMAL DOLOMITIZATION

Sequence of Mineralization and Petrography

The sequence of mineralization in the study area is presented in Figure 3. Dolomite and quartz occur first, followed by K-feldspar. Dolomite precipitation continues

Figure 2. Numbered localities of samples from Luczaj (2000) in Wisconsin, Minnesota, and Illinois. Thin lines are county municipal boundaries. The stippled area in eastern Wisconsin is Lake Winnebago.



throughout the main stage of sulfide mineralization. K-feldspar is probably coeval with the early to middle stages of sulfide mineralization. The main episode of sulfide mineralization involves marcasite and pyrite, sphalerite, and galena and includes minor amounts of fluorite and dolomite precipitation. The last minerals to precipitate were barite, calcite, and minor amounts of fine-grained Fe-sulfides, principally marcasite.

In transmitted light, most of the dolomite crystals in the study area have cloudy, inclusion-rich cores and clear, inclusion-free rims up to several hundred micrometers thick that are best developed in open pore spaces. In other crystals, especially in areas on the western and southwestern margins of the study area, the clear rims

are thin or absent. Most of the cloudy cores are structureless, but concentric growth zoning is present in some of the dolomite in the study area.

The dolomite in the study area of eastern Wisconsin has been classified into three groups, based on plane-polarized light and cathodoluminescence (CL) petrography. The middle and later stages of dolomitization in eastern Wisconsin were intimately associated with MVT mineralization, especially the precipitation of pyrite and bladed marcasite. All three dolomite types defined in the study show evidence of an intimate association with MVT mineralization because they grow together with the sulfide mineralization. The classification presented below is primarily based on observations

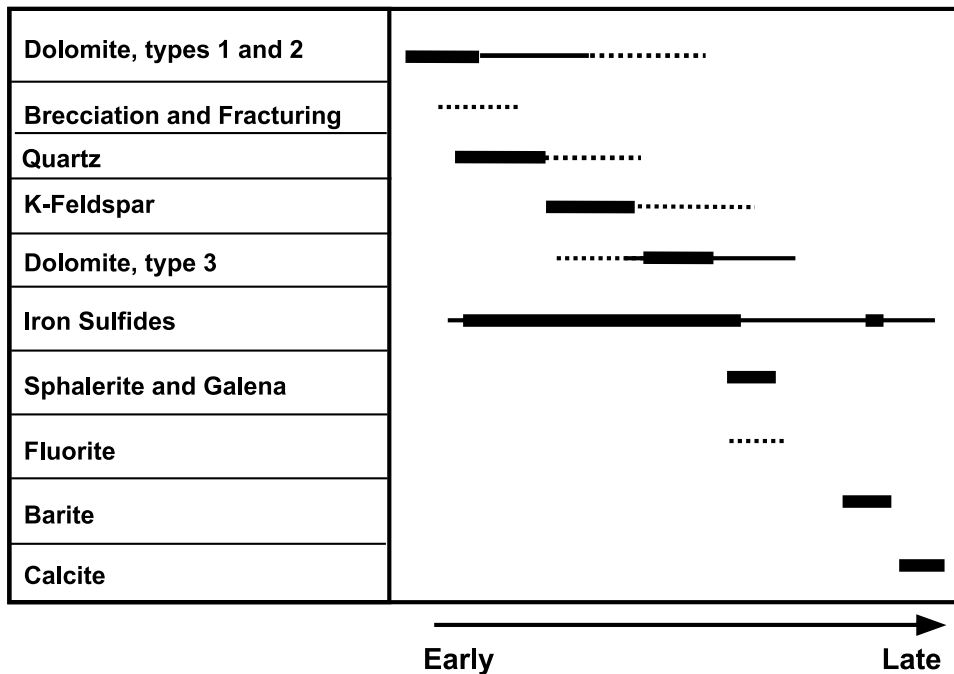


Figure 3. Generalized mineralization sequence observed for the study area in northeastern Wisconsin. Wide bars indicate more intense mineralization, whereas solid lines or dashed lines indicate less significant mineralization or brecciation.

from Ordovician dolostones in the study area, but Silurian and Devonian dolostones show similar characteristics.

Type 1 dolomite makes up nearly all of the dolomite mass in the study area and is defined as planar dolomite that typically displays a cloudy core, rich in solid and fluid inclusions, followed by a clear, inclusion-free cement overgrowth. Type 1 dolomite ranges from tens of micrometers to 1–2 mm (0.04–0.08 in.) in diameter and is present in fractures, vugs, and fossil molds, as well as in the country rock dolomite away from areas with large, well-developed pore spaces. Cathodoluminescence petrography shows that the cloudy core in type 1 dolomite appears to be replacive.

Type 2 dolomite makes up a very small fraction of the total dolomite mass and is defined as white or gray saddle dolomite. It is uncommonly found as euhedral crystals in isolated vugs and in planar arrays replacing the cloudy, inclusion-rich parts of type 1 dolomite. Type 2 dolomite has been observed in Ordovician rocks at localities 9, 21, 23, and 26 (Figure 2). Type 2 dolomite crystals are coarser than type 1 dolomite, and they typically range from a few hundred micrometers up to 3–4 mm (0.12–0.16 in.) in diameter.

Type 3 dolomite makes up a small fraction of the total dolomite mass and is found in Ordovician and Silurian rocks of northeastern Wisconsin. Type 3 dolomite is defined as coarse euhedral late-stage planar dolomite crystals and cement overgrowths, which range from a few millimeters to more than 1 cm (0.4 in.) in

diameter and have been found at localities 2, 11, 17, 21, and 26 (Figure 2). It is coeval with sphalerite and galena precipitation at locality 26. Type 3 dolomite is younger than type 1 and type 2 dolomites.

The CL stratigraphy of dolomite was investigated in 26 samples from the study area and in a few samples from outside the main study area. A definitive CL stratigraphy was recognizable for most of the Ordovician Sinnipee Group rocks of northeastern Wisconsin, which is where the most intense mineralization and all three dolomite types are present. Similar CL zonation was seen in the Ordovician Prairie du Chien and Silurian dolomite samples from several localities. Based on this study, the CL stratigraphy in northeastern Wisconsin appears to be different from that described by Smith (1991) and Smith and Simo (1997) for southwestern Wisconsin. In CL, dolomite from the Ordovician of eastern Wisconsin shows that the bulk of the dolomite replacement and cementation were dominated by three main episodes (Figure 4):

- **Zone 1:** A dull- to moderately bright-orange luminescent mottled replacement material that corresponds to the cloudy, inclusion-rich cores of type 1 and type 2 dolomites. The size of the zone typically ranges from approximately 50 to 1000 μm wide. At many localities, CL zone 1 contains poorly developed zoning. This CL zoning is better developed near the outside of CL zone 1 and typically exhibits

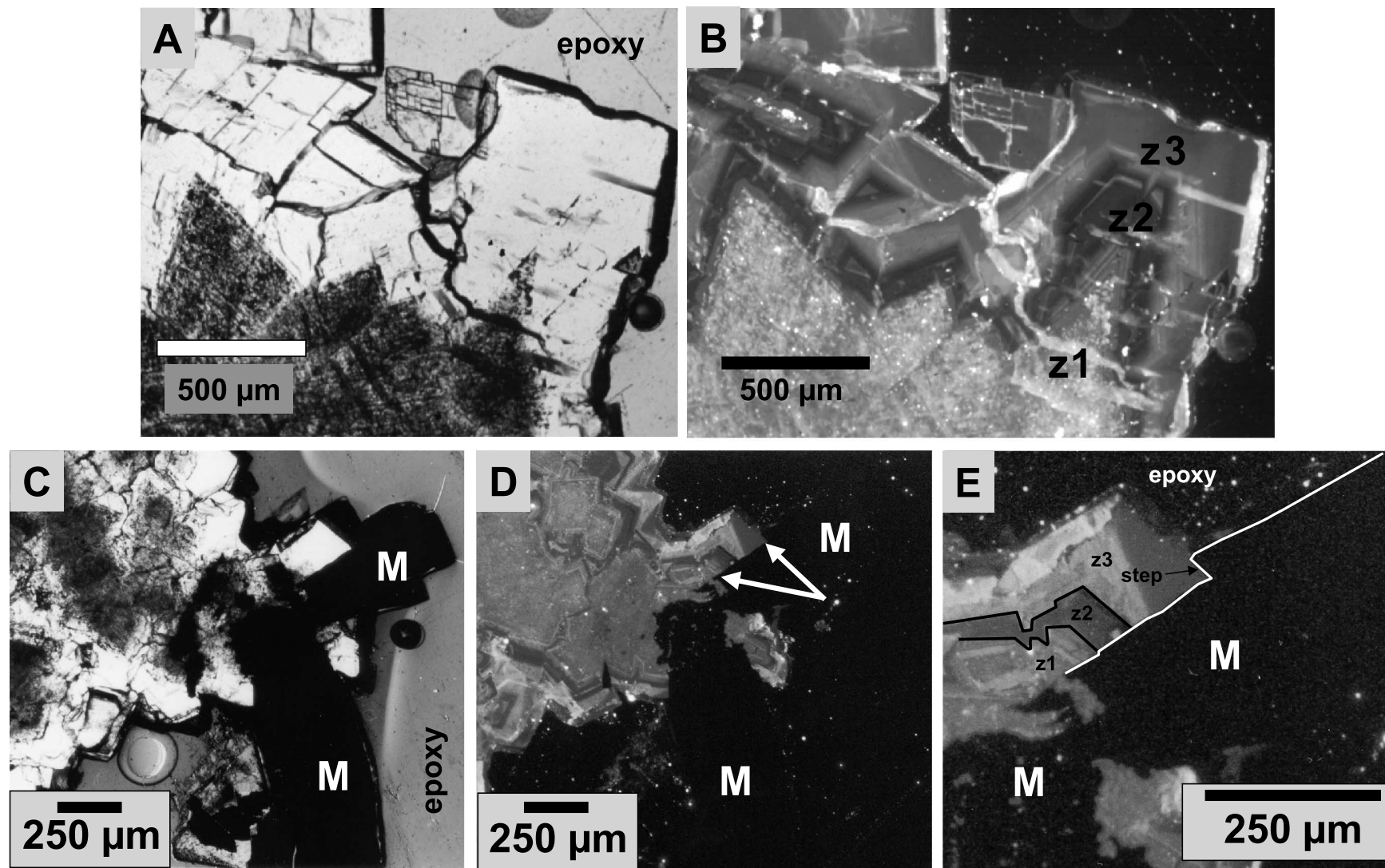


Figure 4. Transmitted-light and cathodoluminescence (CL) photomicrographs of dolomite in northeastern Wisconsin illustrating regionally significant characteristics. (A, B) Transmitted-light and CL images, respectively, of type 2 dolomite from locality 26. Type 2 dolomite has the same CL banding as type 1 dolomite with regard to CL zones 2 and 3, indicating that they are coeval. (C, D) Transmitted-light and CL images of type 1 dolomite from locality 21. Arrows indicate euhedral edge of marcasite crystal. Cathodoluminescence image in (E) is a magnified view of (D) that shows that coarse, bladed euhedral marcasite (M) had formed before the late stages of CL zone 1 and before all of CL zones 2 and 3 because cement growth zones in the dolomite grew up against the euhedral edges of larger bladed marcasite crystals. Minor marcasite precipitation occurred after dolomite growth ended because the marcasite appears to step over the top euhedral edge of the dolomite. Black lines trace the boundaries of CL zones in dolomite, whereas the white line traces the edge of the euhedral marcasite crystal.

the same CL colors as the mottled replacement dolomite in the interior of the crystal.

- Zone 2: A sequence of alternating bright-orange and quenched (black or dark-brown) cement growth zones that are best developed in large pore spaces and in intercrystalline pore spaces. In most cases, there are three quenched zones separating two thin bright-orange luminescent growth zones, although in some cases, only one orange band is present. The quenched zones typically range from about 5 to 40 μm thick, whereas the bright- to very bright-orange luminescent zones range from less than 5 to about 25 μm thick. Zone 2 corresponds to the early part of the clear, inclusion-free type 1 dolomite in transmitted light. Type 2 (saddle) dolomite shows the same CL stratigraphy as type 1 (planar) dolomite in its outer portions at locality 21, suggesting that zone 2 in type 2 dolomite is correlative with zone 2 in type 1 dolomite.
- Zone 3: A dull-orange to dull-red luminescent cement, typically thicker than zone 2. Zone 3 is quite variable and ranges from about 10 μm to hundreds of micrometers thick and is best developed in large pore spaces. This cement is present in most cases where zone 2 dolomite cement is present and is best developed in east central and northeastern Wisconsin. Zone 3 corresponds to the outer part of clear, inclusion-free type 1 and type 2 dolomites.

The distribution of the mottles in the zone 1 interior of type 1 dolomite is irregular and inconsistent with growth zonation (Reeder, 1991). Replacement of the earlier carbonate material may have occurred during later precipitation of dolomite cement. The identity of the precursor carbonate material is unknown and may have been either calcite or dolomite. Dolomite CL zones 2 and 3 only occur as growth bands in pore spaces and do not appear in the mottled parts of the type 1 crystals, suggesting that they are dolomite cements and not replacements (Reeder, 1991).

Zone 1 dolomite formed before zone 2 dolomite because it was encapsulated by zone 2 dolomite cement. The CL character of dolomite crystals in Ordovician rocks throughout the region is generally consistent, especially in the lower part of the Sinnipee Group dolostones, suggesting that most of the dolomitization process was regional in nature. The CL stratigraphy of type 1 (planar) and type 2 (saddle) dolomites is similar, suggesting that they formed at roughly the same stage in the paragenetic sequence of mineralization. Type 3 dolomite is associated with MVT sulfides and appears

in CL as dull red-orange to dull-gray zoned cement that is up to several millimeters thick. Where observed, the luminescence of type 3 dolomite was not as bright as zones 1–3 in type 1 and type 2 dolomites and typically had a translucent grayish appearance.

The CL stratigraphy for type 1 dolomites discussed above was observed in Ordovician Sinnipee Group and Prairie du Chien Group rocks from localities 3, 4, 21, 23, 26, 32, 53, 54, 66, 69, 71, and 76 (Figure 2). In Ordovician rocks from areas to the west and southwest of the study area, a mottled core was typically present, but the CL cement growth zones that formed after zone 1 were either different or were absent, especially for localities 59, 79, 104, and 117.

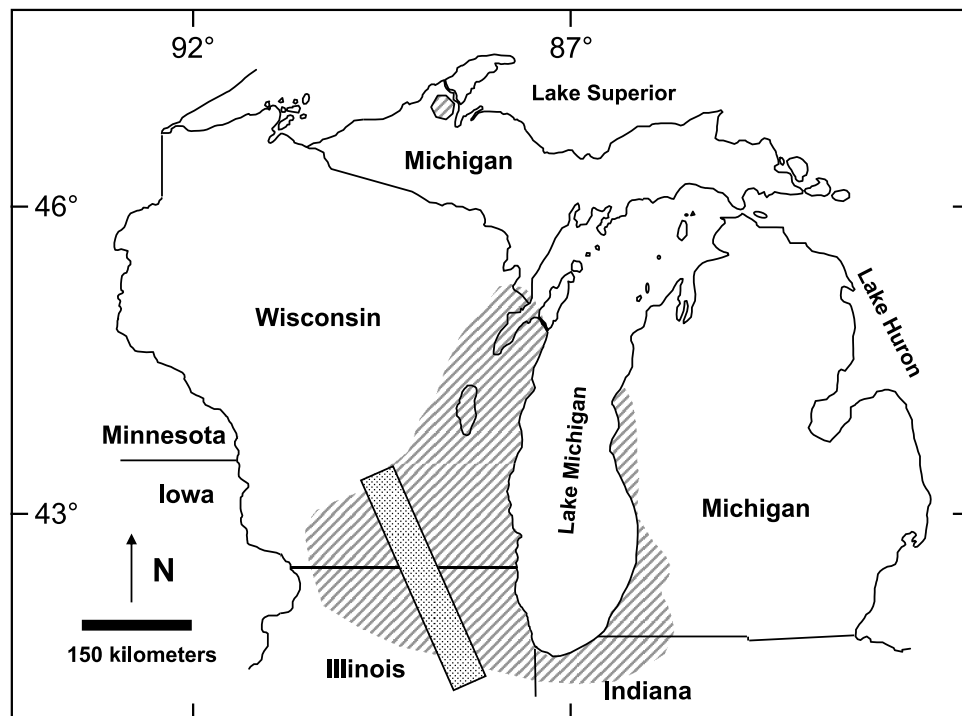
Petrographic evidence exists that regional trace sulfide mineralization occurred along with widespread dolomite precipitation and replacement in types 1–3 dolomites throughout the study area. For example, Figure 4C–E detail the relationship observed between type 1 dolomite and marcasite at locality 21. Bladed marcasite either replaced or coprecipitated with the early or middle stages of CL zone 1. The final stage of CL zone 1 at this locality contains cement growth banding and indicates that at least some CL zone 1 growth occurred after marcasite precipitation and replacement. After precipitation of the euhedral bladed marcasite crystal, dolomite CL zones 2 and 3 were precipitated. This interpretation is made because the dolomite CL growth zones appear to have grown up against the edge of the euhedral marcasite crystal. Minor growth of marcasite followed dolomite CL zone 3 and steps over the top edge of the final dolomite cement growth zone (Figure 4E). Similar relationships were observed with Fe, Pb, and Zn sulfide minerals in type 2 and type 3 dolomites.

Regional Distribution of Dolomite

Figure 5 shows the regional distribution of dolomite for the Ordovician Sinnipee Group/Trenton and Black River formations. Complete dolomitization of this part of the Ordovician section has occurred in the western and southwestern Michigan Basin and eastern Wisconsin, whereas the percentage of limestone increases to the south and west of the study area and to the east toward the center of the Michigan Basin. Limited information was available for the upper peninsula of Michigan and will be addressed in future research.

The hypothetical distribution of dolomite near the Wisconsin arch that would be consistent with the mixing-zone hypothesis of Badiozamani (1973) is shown

Figure 5. Regional distribution of dolomite in Ordovician rocks in the eastern Wisconsin–western Michigan Basin region. Data for the Michigan Basin and Indiana are from Taylor and Sibley (1986) and Yoo et al. (2000), respectively. Complete dolomitization of the carbonate section has occurred in the western and southwestern Michigan Basin and in eastern Wisconsin, whereas the percentage of limestone increases to the south and west of the study area and to the east in the center of the Michigan Basin. Dolomite distribution in the upper peninsula of Michigan is not well known. Stippled box represents the hypothetical dolomite distribution expected from the mixing-zone dolomitization process along the Wisconsin arch.



for comparison in Figure 5. Note that the observed dolomite distribution does not match the arch-centered dolomite distribution predicted by the mixing-zone hypothesis. In fact, the first limestone-to-dolostone transition observed west of the Michigan Basin (locality 79) occurs near the Wisconsin arch, instead of away from the arch toward the east. Throughout most of central Wisconsin, the Ordovician and younger parts of the section have been eroded, and the location of the limestone-to-dolostone transition cannot be evaluated. Therefore, the western edge of the dolostone in Figure 5 is the outcrop belt of exposed carbonate rocks throughout much of northeastern Wisconsin.

Faults are present within the study area, based on well records, but few are directly observed. This is because the primary study area in eastern Wisconsin is covered by Pleistocene glacial deposits, and the choice of field locations was limited to quarries and a few isolated outcrops. The carbonate rocks throughout the primary study area (Figure 2) are dolomitized, with the exception of locality 79, and, therefore, show no particular relationship to the faults. Faults and joints were certainly conduits for mineralizing fluids, and sulfide minerals were preferentially precipitated along these surfaces throughout most of the study area. One exception to the lack of a notable relationship between

dolomitization and faults or joints is at locality 79, where some original limestone and two different episodes of epigenetic dolomite were observed, at least one of which is focused along preexisting joints (see below). West of the main study area, however, fault-controlled dolomitization in Sinnipee Group limestones was reported by Heyl et al. (1959), and a close association to sulfide mineralization was reported.

The precise identity of the precursor carbonate material throughout the study area is not well known and may have been either calcite or dolomite. As noted by others who have worked in the region (e.g., Smith and Simo, 1997; Choi and Simo, 1998), textural and compositional characteristics in Ordovician dolostones of Wisconsin are commonly obliterated by the late-stage dolomitization. Note the possibility of preexisting nonhydrothermal dolomite in the carbonates of eastern Wisconsin and the western Michigan Basin, the origins of which may have varied between the stratigraphic units. If a precursor low-temperature dolomite existed or is still partially preserved, type 1 dolomite with the character of CL zone 1 is the most likely candidate.

The regional and stratigraphic distribution of dolomite suggests that if these rocks were partially or completely dolomitized before the hydrothermal system

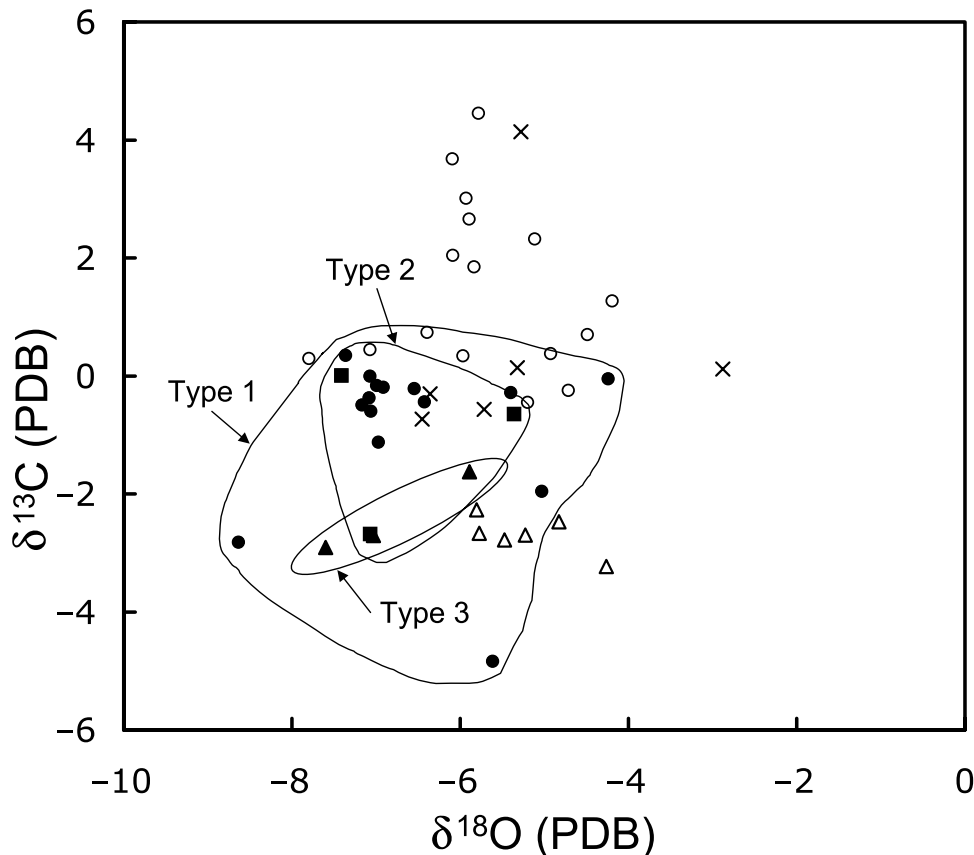


Figure 6. Crossplot of carbon ($\delta^{13}\text{C}_{\text{PDB}}$) and oxygen ($\delta^{18}\text{O}_{\text{PDB}}$) stable isotopic data for dolomite in Ordovician through Devonian rocks in the study area. Open triangles represent type 1 dolomite from the Lower Ordovician Prairie du Chien Group. Solid circles, squares, and triangles outlined by black lines represent type 1, type 2, and type 3 dolomites, respectively, from the Upper Ordovician Sinnipee Group. Open circles represent dolomite from a variety of Silurian units, whereas crosses indicate dolomites from Devonian units.

operated, then a dolomitization process that was focused along the western edge of the Michigan Basin would be required. Similar regional patterns of dolomitization along the western margin of the basin have been observed in younger units. For example, the Devonian Dundee Formation is regionally dolomitized only in the western one-third of the Michigan Basin (Gardner, 1974). Evaporite reflux dolomitization systems operating along the western edge of the Michigan Basin during the Silurian and/or Devonian might have been responsible for the formation of a precursor dolomite in the study area and would be consistent with the reflux dolomitization interpretations in parts of the Silurian of the Michigan Basin (e.g., Sears and Lucia, 1980) and the evidence for Devonian coastal sabkha environments in eastern Wisconsin (e.g., Mikulic and Kluessendorf, 1988).

Stable Isotope Data

Stable isotopes of carbon and oxygen from selected calcite and dolomite samples from throughout eastern Wisconsin were analyzed at the University of Michi-

gan Stable Isotope Laboratory using standard methods. Forty-nine dolomite samples and 25 calcite samples from Ordovician to Devonian age were analyzed for carbon ($\delta^{13}\text{C}$) and oxygen ($\delta^{18}\text{O}$) isotopic ratios, relative to the PDB standard. Figure 6 is a crossplot showing stable isotopic data for dolomite from Ordovician to Devonian age units. Although considerable variability is present in the carbon isotopic ($\delta^{13}\text{C}$) data, the oxygen isotopic ($\delta^{18}\text{O}$) data are consistently negative. For all samples analyzed, the stable isotopic composition of dolomite has a $\delta^{13}\text{C}$ range from -4.84 to $+4.45$ ‰ and a $\delta^{18}\text{O}$ range from -8.64 to -2.88 ‰. Although differences with regard to $\delta^{13}\text{C}$ are evident in the crossplot, especially for Silurian and Devonian dolomite, there is no significant difference with respect to $\delta^{18}\text{O}$ for the dolomites analyzed. The Ordovician Sinnipee Group types 1–3 dolomites exhibit substantial overlap for both $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$. For reference, the estimated marine calcite value for brachiopods in the overlying Ordovician Decorah Formation is about $+1$ ‰ for $\delta^{13}\text{C}_{\text{PDB}}$ and -5 to -3.5 ‰ for $\delta^{18}\text{O}_{\text{PDB}}$ (Ludvigson et al., 1996).

Note that all of the data for dolomite fall in the field for high-temperature dolomite or in the overlap

between the high-temperature and low-temperature dolomite fields as defined by Allan and Wiggins (1993). The data from this study also overlap those reported by Badiozamani (1973) for both the Mifflin Member of the Platteville Formation and for hydrothermally altered limestone. Although not plotted in Figure 6, the stable isotopic data for late-stage epigenetic calcite crystals occur in a group with a $\delta^{13}\text{C}$ range between -12.4 and -2.46‰ and a $\delta^{18}\text{O}$ range between -11.28 and -4.48‰ . These calcite crystals have a $\delta^{18}\text{O}$ composition that is similar to the dolomite.

Fluid-Inclusion Data and Interpretations

Homogenization Temperature Data

Fluid inclusions were observed in crystals of dolomite, quartz, sphalerite, calcite, and barite throughout the region. Most of the fluid inclusions are aqueous and two phase, although all-liquid fluid inclusions were observed in late calcite fluid-inclusion assemblages (FIAs).

Dolomite from Ordovician, Silurian, and Devonian carbonates from throughout the eastern Wisconsin region was examined qualitatively, and fluid inclusions from a selected number of Ordovician dolomite samples were measured quantitatively. Petrographic characteristics of dolomite FIAs were generally consistent throughout eastern Wisconsin, especially for dolomite in the Sippewicet and Prairie du Chien groups. In most cases, each dolomite FIA is treated as all fluid inclusions inside each cloudy, inclusion-rich dolomite core. All dolomite crystals contain a clear, inclusion-poor or inclusion-free dolomite cement overgrowth that surrounds the inclusion-rich dolomite cores. Most of the fluid inclusions in the cloudy cores are irregularly shaped, range in size from about 2 to 30 μm , and have relatively consistent low vapor/liquid ratios. Note that two-phase aqueous fluid inclusions were observed in dolomite from throughout the region, suggesting that the dolomite was replaced and/or precipitated above approximately 50°C (Goldstein and Reynolds, 1994).

Planar assemblages of both primary and secondary fluid inclusions were observed in sphalerite from throughout the region. The primary FIAs in sphalerite contain 10–50- μm pyramid-shaped inclusions that occur in planar arrays along growth banding in the sphalerite. Secondary FIAs are more abundant and contain irregularly shaped, approximately 2–100- μm fluid inclusions that occur along planar or curved-planar arrays that cut across or have no relationship to growth banding in sphalerite.

Homogenization temperature measurements (T_h) were obtained from fluid inclusions in dolomite, sphalerite, and quartz from localities throughout the study area (Table 1). In general, dolomite FIAs exhibit a more variable T_h distribution than primary or secondary FIAs from sphalerite. All three types of dolomite record similar T_h values in the fluid inclusions. In all of the dolomite samples, two-phase inclusions with low vapor/liquid ratios (most of the inclusions) homogenized to liquid between about 60 and 152°C, although most inclusions homogenized between about 75 and 115°C. Average T_h values for dolomite FIAs range from 81.9 to 100.5°C. All two-phase inclusions in sphalerite homogenized to liquid between 63 and 132°C, although most homogenized between 85 and 110°C. The average T_h values for sphalerite FIAs range between 78.7 and 109.2°C. The primary FIAs in sphalerite from two localities yielded average T_h values of 78.7 (locality 69) and 95.8°C (locality 23) and had the narrowest temperature range in each FIAs of T_h data recorded in this study. Sphalerite secondary FIAs from 11 localities yielded average T_h values between 81.4 and 109.2°C. T_h values from primary or pseudo-secondary inclusions in quartz from locality 71 ranged from 59.5 to 91.1°C, with an average of 77.0°C.

Freezing Data

Observations of the final melting temperature of ice ($T_{m\text{ ice}}$), the temperature at which hydrohalite breaks down (T_{hh}), and the eutectic temperature (T_e) were made. All reported $T_{m\text{ ice}}$ and T_{hh} data were recorded with the presence of the vapor phase in each inclusion. In dolomite from locality 21, $T_{m\text{ ice}}$ values ranged from -27.4 to -13.7°C and averaged -19.8°C (Table 1). Ice appeared to be the last phase to break down in the inclusions. In dolomite from locality 26, both the $T_{m\text{ ice}}$ and T_{hh} could be determined for one inclusion. Hydrohalite was the last phase to break down in three of the inclusions, and ice was the last phase to break down in five inclusions. $T_{m\text{ ice}}$ was between -20.3 and -13.2°C , with an average of -16.9°C . T_{hh} was observed in three inclusions at temperatures of approximately -18 , -0.9 , and -0.6°C . $T_{m\text{ ice}}$ in sphalerite primary FIAs ranged from -19.0 to -9.1°C and averaged -9.8 (locality 23) and -18.5°C (locality 69). The average $T_{m\text{ ice}}$ in sphalerite secondary FIAs ranged from -21.7 to -14.8°C . In quartz, $T_{m\text{ ice}}$ was -28.5 to -22.7°C , with an average of -25.9°C , and T_{hh} occurred between -14.6 and -2.5°C .

Fluid inclusions from all samples of sphalerite, dolomite, and quartz in the study exhibit similar behavior

Table 1. Fluid-Inclusion Microthermometric Data from Dolomite, Quartz, and Sphalerite from the Study Area along the Eastern Margin of the Wisconsin Arch

Locality	Host Rock	Mineral	FIA Type	Heating Data		Freezing Data			
				Number of Inclusions Measured	Average T_h ($^{\circ}\text{C}$)	Number of Inclusions Measured	Average $T_{m\text{ ice}}$ ($^{\circ}\text{C}$)* or T_{hh} ($^{\circ}\text{C}$)**	Salinity in Weight% NaCl Equivalent	Eutectic Temperature
3 [†]	SG ^{††}	Dolomite	Primary	19	81.9	0	–	–	–
21 [†]	SG	Dolomite	Primary	60	97.1	6*	– 19.8 $^{\circ}\text{C}$ *	22.2 wt.%	– 59 to – 51 $^{\circ}\text{C}$
21 [‡]	SG	Dolomite	Primary	15	100.5	0	–	–	–
26 ^{‡‡}	SG	Dolomite	Primary	31	97.3	5 of 8*	– 16.9 $^{\circ}\text{C}$ *	20.2 wt.%	– 58 to – 56 $^{\circ}\text{C}$
						3 of 8 **	– 18, – 0.9, – 0.6 $^{\circ}\text{C}$ **	~23 to 26 wt.%	– 58 to – 56 $^{\circ}\text{C}$
71	PDC [§]	Quartz	Primary or pseudosecondary	25	77.0	1 of 10*	– 22.7 $^{\circ}\text{C}$ *	24.10 wt.%	– 58 to – 56 $^{\circ}\text{C}$
						9 of 10**	– 10.5 $^{\circ}\text{C}$ **	~23 to 26 wt.%	– 58 to – 56 $^{\circ}\text{C}$
3	SG	Sphalerite	Secondary	36	84.3	0	–	–	–
8	SG	Sphalerite	Secondary	12	81.4	0	–	–	–
8	SG	Sphalerite	Secondary	21	93.2	0	–	–	–
9	SG	Sphalerite	Secondary	41	103.3	4*	– 21.7 $^{\circ}\text{C}$ *	23.5 wt.%	– 57 $^{\circ}\text{C}$
23	SG	Sphalerite	Primary	25	95.8	5*	– 9.84 $^{\circ}\text{C}$ *	13.8 wt.%	n/a
23	SG	Sphalerite	Secondary	28	98.1	>3*	– 14.8 $^{\circ}\text{C}$ *	18.5 wt.%	– 59, – 56 $^{\circ}\text{C}$
28	Silurian	Sphalerite	Secondary	79	96.4	3*	– 19.3 $^{\circ}\text{C}$ *	21.9 wt.%	mid-50s
38	Devonian	Sphalerite	Secondary	37	109.2	0	–	–	–
44	Silurian	Sphalerite	Secondary	19	91.0	0	–	–	–
44	Silurian	Sphalerite	Secondary	30	97.4	0	–	–	–
63	SG	Sphalerite	Secondary	15	81.4	0	–	–	–
65	SG	Sphalerite	Secondary	45	104.8	0	–	–	–
69	PDC	Sphalerite	Primary	23	78.7	3*	– 18.5 $^{\circ}\text{C}$ *	21.3 wt.%	– 55, – 57 $^{\circ}\text{C}$
79	SG	Sphalerite	Secondary	14	108.8	0	–	–	–
133	Silurian	Sphalerite	Secondary	22	96.6	0	–	–	–

*Refers to data in which the ice was the last to break down.

**Refers to data in which the hydrohalite was the last phase to break down.

[†]Saddle dolomite.^{††}SG = Ordovician Sinnipee Group.[‡]Early vug filling dolomite.^{‡‡}Late planar dolomite.[§]PDC = Ordovician Prairie du Chien Group.

at low temperatures. T_e was about -57°C for most inclusions and was between -59 and -51°C for all of the rest of the inclusions measured.

Interpretations

The presence of two-phase fluid inclusions entrapped during dolomite replacement and precipitation that homogenize in the range of 60 to at least 110°C indicates that rocks were exposed to temperatures of that magnitude during dolomitization (Barker and Goldstein, 1990). A few homogenization temperatures approaching 150°C for dolomite suggest that rocks may have been exposed to temperatures well above 100°C . However, because these very high T_h values are only a small proportion of the data sets, unrecognized necking down after a phase change or heterogeneous entrapment of a relatively small fraction of the vapor phase cannot be ruled out for these few inclusions. All three types of dolomite (type 1 planar dolomite, type 2 saddle dolomite, and type 3 late planar dolomite) yield data over a similar T_h range. In general, most T_h data for dolomite are not as consistent as those for sphalerite. However, the dolomite data still provide important information regarding the temperature history of the rocks. Dolomite T_h data from each crystal typically span a $30\text{--}40^\circ\text{C}$ range. No obvious correlation was observed between the size of an inclusion and its homogenization temperature, which would be expected if reequilibration of existing inclusions caused by stretching had occurred (Goldstein and Reynolds, 1994). In two dolomite crystals, the inclusions can be segregated petrographically into different FIAs that each have different T_h ranges (localities 21 and 26). For those bimodal cases, T_h data are more consistent, which suggests that dolomite formed over a range of temperatures. Together, the T_h , $T_{m\text{ ice}}$, and T_{hh} data suggest that replacement and precipitation of dolomite occurred over a range of temperatures from about 60 to about 115°C as ambient conditions changed. In the case of the late clear dolomite cement that is associated with MVT mineralization (locality 21, FIA 2), temperatures may have even reached $125\text{--}145^\circ\text{C}$ because all three inclusions in that FIA homogenized in that temperature range.

T_h data from primary or pseudosecondary FIAs in quartz suggest the entrapment of inclusions over a moderate range of temperatures between 65 and 91°C . In addition to the petrographic association between the dolomite and quartz from several different localities, these data are consistent with the T_h data from dolomite in eastern Wisconsin. T_h data from primary inclu-

sions in sphalerite are similar and suggest that during precipitation of sphalerite, temperatures were between about 79 and 96°C in the region (Table 1). Data from the secondary inclusions are also similar and suggest that during and/or after precipitation of the sphalerite, temperatures in the region were at least between 81 and 110°C . Fluid-inclusion data from secondary FIAs in sphalerite are extremely important because they allow insight into the thermal history of the rocks that may not have been recorded by primary FIAs in any mineral phase. No obvious regional temperature trends were observed in any of the T_h data.

For inclusions in dolomite, in which ice was the last solid phase to break down, salinities calculated from $T_{m\text{ ice}}$ data range from 17.1 to 27.0 wt.% NaCl equivalent. For samples in which hydrohalite was the last phase to break down, salinities fall between about 23 and 26 wt.% NaCl equivalent (Goldstein and Reynolds, 1994). For primary inclusions in sphalerite, salinities ranged from 13.0 to 21.7 wt.% NaCl equivalent. For secondary inclusions in sphalerite, salinity values ranged from 18.5 to 23.6 wt.% NaCl equivalent. In quartz, only one inclusion in the recorded FIAs exhibited ice as the last solid phase to break down. This yielded a salinity of 24.1 wt.% NaCl equivalent. For all of the other inclusions, hydrohalite was the last phase to break down on some or all of the runs, yielding salinities between about 23 and 26 wt.% NaCl equivalent (Goldstein and Reynolds, 1994). The observed eutectic at approximately -57°C is consistent with the stable T_e for a model NaCl-CaCl₂-MgCl₂-H₂O system (Goldstein and Reynolds, 1994). No regional salinity gradient is apparent from the freezing data.

Burial Constraints

The youngest rocks preserved in Wisconsin are equivalent to the Late Devonian (middle Frasnian to early Famennian) Antrim Shale of the Michigan Basin (Mikulic and Kluessendorf, 1988). Although the Devonian, Mississippian, and parts of the Pennsylvanian section in the Michigan Basin are well preserved, the precise thickness of Upper Devonian and younger strata that were present in eastern Wisconsin is not known because they have been partly removed by erosion. Several methods can be used to estimate the thickness of rocks that may have existed in the Wisconsin-Michigan region during the latest Devonian through the early Mesozoic.

Beaumont et al. (1987) presented results from geodynamic modeling experiments that numerically predict

Eastern Wisconsin Burial-History Curve

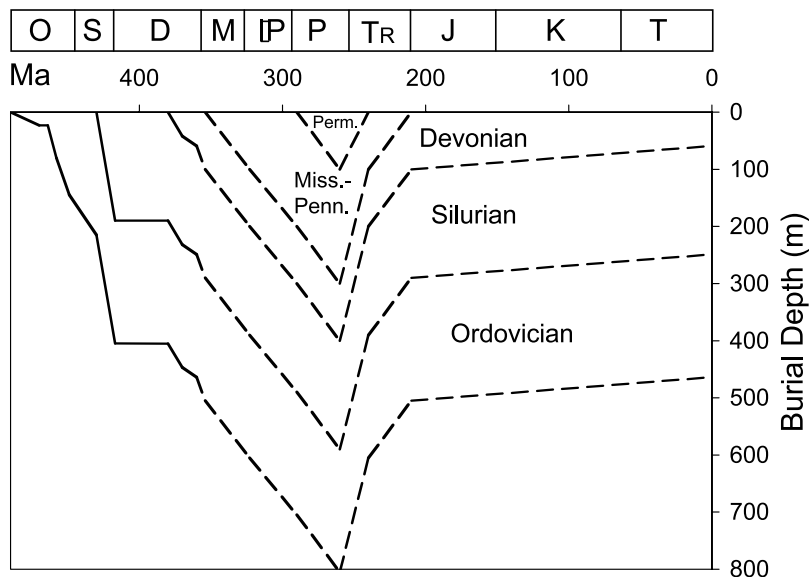


Figure 7. Generalized burial-history curve for eastern Wisconsin. Dashed lines indicate estimated burial depths for various units using predictions from stratigraphic reconstructions and other sources. The depth curve illustrates that Ordovician rocks likely have not been buried more than 1 km (0.6 mi) deep at any time since their deposition.

a stratigraphy for a given study area as a result of mountain building during the Taconic, Acadian, and Alleghenian orogenies. Their predictions of the sediment thicknesses resulting from the Taconic and Acadian orogenies match the observed regional thickness patterns fairly well. Beaumont et al. (1987) predicted fairly low thicknesses of sediments in eastern Wisconsin as a result of the Acadian orogeny (200 m [660 ft] or less). The late Paleozoic Appalachian–Ouachita orogenic belt is probably the only source for significant thicknesses of sediment that could have buried the region after the early Pennsylvanian. They also predicted maximum thicknesses of Pennsylvanian–Permian sediments on the order of less than 300 m (985 ft) for most of the Michigan Basin and less than 100 meters (330 ft) in Wisconsin.

Vugrinovich (1988) used a measure of shale compaction to estimate the amount of additional burial that was present in the Michigan Basin between the early Pennsylvanian and the Late Jurassic. He estimated that at most, 850 m (2790 ft) of additional sediment were present in the central part of the lower peninsula of Michigan, and that those thicknesses dramatically decreased to less than 200 m (660 ft) toward the edges of the basin.

Together, stratigraphic reconstructions and sediment modeling predictions suggest that only a few hundred meters of sediment were likely deposited on top of the present-day rocks in eastern Wisconsin. Even if these burial depths are doubled or tripled, the thick-

ness of eroded rocks in eastern Wisconsin would not have been more than about 1 km (0.6 mi).

Organic maturity data, including conodont alteration index (CAI) and vitrinite reflectance (R_o) data, are consistent with a burial depth limited to less than 1–1.5 km (0.6–0.9 mi). Observations of conodont elements (locality 2) indicate CAI values of 1.0 for Ordovician rocks in northeastern Wisconsin (R. Norby, 1999, personal communication). Vitrinite reflectance data from Devonian rocks and Devonian sediment fills in Silurian karst from eastern Wisconsin (localities 36 and 52) were measured by DGSi of The Woodlands, Texas. Analyses of vitrinite and cutinite yielded R_o values of 0.32–0.6%. DGSi concluded that the thermal maturity data were not precise, but they appear to indicate a maturity level between 0.5 and 0.6% R_o , based on several lines of evidence (W. Dow, 1998 and 1999, personal communication). Together, these organic maturity data suggest that these rocks were not deeply buried for an extended period of time.

Stratigraphic reconstructions and organic maturity data suggest that the thickness of eroded sediments in eastern Wisconsin was probably much less than 1–1.5 km (0.6–0.9 mi) (Figure 7). Assuming a mean annual surface temperature of 20°C and a 20–25°C/km geothermal gradient, a simple burial model would require a minimum of 3–4 km (1.8–2.5 mi) of missing sediments to satisfy the T_h data presented in this study. Together with available field, petrographic, and fluid-inclusion data, this indicates that the epigenetic dolomitization

and MVT mineralization were part of a regional hydrothermal fluid-flow system instead of part of a simple burial heating system.

Evidence for Overlapping Regional Systems

Most of the radiometric ages of authigenic K-feldspar and illite in Wisconsin and the Michigan Basin range from Devonian to Mississippian (448–322 Ma) (Marshall et al., 1986; Hay et al., 1988; Matthews, 1988; Girard and Barnes, 1995; Liu, 1997), but some of the late illite in northwestern Illinois yields a Permian age of 265 Ma (Duffin et al., 1989). In addition, sphalerite from the upper Mississippi Valley lead-zinc district yielded a Rb-Sr age of 270 Ma (Brannon et al., 1992). Other research has suggested that the middle Paleozoic authigenic K-silicate mineralization occurred over a range of temperatures, similar to those presented in this study. For example, T_h data reported by Liu (1997) for primary fluid inclusions from 360 Ma authigenic K-feldspar in central Wisconsin (Figure 2) suggest that the Cambrian quartz sandstone and uppermost Precambrian basement in central Wisconsin were heated to at least 100°C during the middle Paleozoic.

These data indicate that two separate water-rock interaction systems likely operated in the Wisconsin region at different times. The predominant middle Paleozoic-age K-feldspar suggests that the middle Paleozoic episode of mineralization was far reaching and may have set the stage for later mineralization by altering the permeability pathways during regional dolomitization.

One locality that may still preserve evidence of both systems is locality 79 in Sun Prairie, Wisconsin. In general, Ordovician Sinnipee Group dolostones in the western and southwestern parts of Wisconsin are buff or yellow tan in color on outcrop and in quarries, whereas the same dolostones east of the Wisconsin arch are bluish gray or brown in color. At locality 79, however, both dolostone colors are present, and well-developed joints were present before at least one episode of dolomitization (Figure 8). This locality was one of the same localities visited by Deininger (1964), who noticed similar relationships, and was also Badiozamani's (1973) locality 44. Observations during the present study show evidence for two episodes of dolomitization at this locality. This is especially well developed in the lowermost 2 m (6.6 ft) of the Platteville Formation, above the permeable St. Peter Sandstone, which appears to have been one of the main regional conduits for hydrothermal fluid flow. The center of each of the joint-bounded blocks contains blue-gray dolo-

stone, whereas the edges of the joint-bounded blocks have a tan or buff color. A thin section made along this dolostone boundary shows that the color difference is not purely caused by weathering on the outcrop. Instead, there is a difference in the grain size and texture of the dolomite, suggesting that the solutions that reacted with and precipitated dolomite near the edges of the joint blocks were focused along the fractures and were not able to penetrate far into the interior of the blocks. The difference in color probably translates to a compositional difference between the two dolomites. Badiozamani (1973, p. 973) also noted that dolomite along a joint at locality 79 had "a much lower oxygen isotopic value than other dolomites. . . and are indicative of a late stage of dolomitization postdating the jointing."

The blue-gray dolomite has a very dull to dull-orange mottled appearance in CL, with little or no CL growth zoning. In contrast, the buff dolomite has an increased crystal size and has moderately bright-orange mottled and weakly zoned dolomite cores, followed by a 5–50- μm -thick dull-red CL growth zone that is not present in the blue-gray dolomite. Clearly, there has been alteration and precipitation of different dolomititic material near the joint faces, as opposed to the centers of the joint blocks away from fractures at this locality. This buff-weathering dolomite may correspond to the late Fe-rich cement (CL growth zone 4) described by Smith and Simo (1997) for Ordovician dolostones surrounding the upper Mississippi Valley ore district west of the Wisconsin arch. Based on the information available at the present time, it seems that the Wisconsin arch is the eastern limit of the upper Mississippi Valley hydrothermal system that was responsible for mineralization west of the Wisconsin arch. Locality 79 may record elements of both the middle Paleozoic dolomitization that dominated in eastern Wisconsin and the late Paleozoic dolomitization that dominated in western and southwestern Wisconsin.

Evidence for Fluid Flow Out of the Michigan Basin into Eastern Wisconsin

Several lines of evidence support fluid flow out of the Michigan Basin as the source of some or all of the fluids responsible for hydrothermal dolomitization and sulfide mineralization in the primary study area of eastern Wisconsin, although a partial contribution of fluids and heat from the Precambrian basement cannot be ruled out. The Michigan Basin is the closest large source of hot brines that could have invaded these rocks. Paleozoic



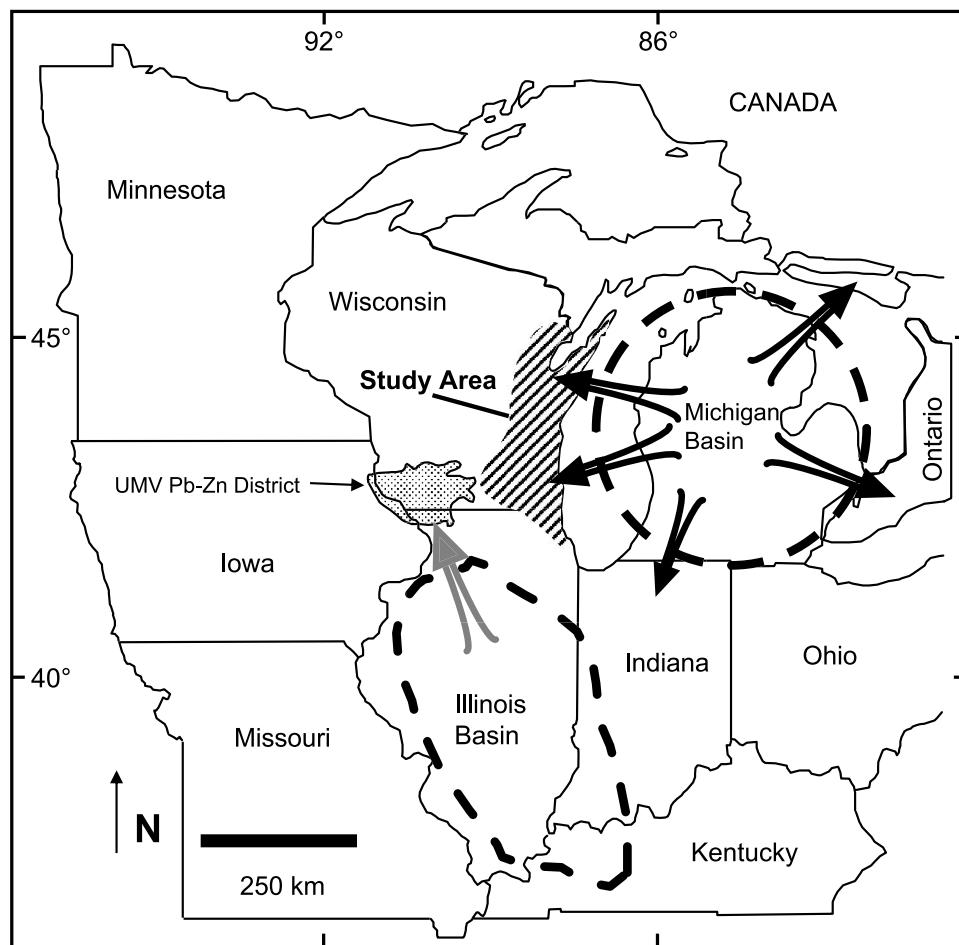
Figure 8. Photograph of joint-controlled dolomitization in the Ordovician Platteville Formation of the Sinnipee Group at locality 79. Lighter buff-colored dolostone occurs near joints and bedding planes (arrows) and has different petrographic and CL characteristics than the blue-gray dolostone away from the joints and bedding planes. The black line has been added to better differentiate the two different dolomites. Field book is 19 cm (7.5 in.) long.

carbonates along the western margin of the Michigan Basin have been completely dolomitized, especially in the case of Ordovician carbonates. The regionally correlative CL zoning pattern that was observed in dolomite throughout eastern Wisconsin, but that was not observed to the west of the Wisconsin arch, suggests a consistent source to the east. In addition, a prominent sulfide cement horizon in the uppermost 1 m (3.3 ft) of the Ordovician St. Peter Sandstone was observed in outcrop and drill core from north to south throughout the entire eastern Wisconsin region and as far west as locality 79 along the Wisconsin arch. Middle Paleozoic ages for K-silicate mineralization in eastern Wisconsin and the Michigan Basin show consistent timing. This differs from the documented Permian age for fluid flow out of the Illinois Basin that was responsible for

the formation of the upper Mississippi Valley lead-zinc ore district. Together, these mineralogical characteristics indicate that a distinct water-rock interaction system operated on the western edge of the Michigan Basin in eastern Wisconsin.

Small quantities of crude oil were found at a depth of 315 ft (~96 m) in a well drilled by the Wisconsin Geological and Natural History Survey at Minooka County Park in Waukesha County, Wisconsin (R. Peters, 1998, personal communication). Three compositionally distinct types of crude oil have been identified in the Michigan Basin. These are the Devonian Traverse, Silurian Niagaran, and Ordovician Trenton-Black River oils (Illich and Grizzle, 1985; Catacosinos et al., 1990). Whole oil gas chromatography-mass spectrometry of the Waukesha County, Wisconsin, oil

Figure 9. Map of the northern mid-continent region of the United States showing the directions of fluid flow out of the Michigan and Illinois basins during the Paleozoic. Evidence collected from the margins of the Michigan Basin (Coniglio and Williams-Jones, 1992; Coniglio et al., 1994; Yoo et al., 2000; and this study) suggests that fluid flow was directed radially outward from the center of the basin and probably occurred during the middle Paleozoic. A separate fluid flow event during the Permian, associated with northwestward fluid flow out of the Illinois Basin, was responsible for mineralization in the upper Mississippi Valley (UMV) Pb-Zn ore district in southwestern Wisconsin.



sample reveals that the oil is similar to the Devonian Traverse-type oil and is unlike any known Silurian or Ordovician oils in the mid-continent. In addition, the mass-to-charge ratio (m/z) 191 and 217 mass chromatograms are very similar to oils derived from the Antrim Shale in the Michigan Basin (W. Dow, 1999, personal communication). These data, along with the thermal maturity data for eastern Wisconsin rocks described above, suggest that the oil has migrated to its current position, most likely from the Michigan Basin.

Previous research has suggested fluid flow out of the Michigan Basin (Figure 9). Yoo et al. (2000) suggested fluid flow out of the Michigan Basin into northern Indiana to explain dolomitization in the Trenton and Black River formations. Coniglio and Williams-Jones (1992) and Coniglio et al. (1994) suggested fluid flow to the east out of the Michigan Basin to explain hydrothermal dolomitization of Ordovician carbonates along the northeastern and southeastern margins of the basin, respectively. When combined with the results from this study, a clearer picture is emerging regarding

hydrothermal diagenesis along the margins of the Michigan Basin (Figure 9). The mechanism for driving fluids out of the Michigan Basin is still unresolved, but available evidence strongly suggests a radial fluid-flow pattern out of the Michigan Basin. This issue of the driving mechanism is beyond the scope of this article and will be addressed in a forthcoming publication.

DISCUSSION

This study shows clear evidence that Paleozoic sedimentary rocks in eastern Wisconsin preserve a hydrothermal signature and contain abundant epigenetic dolomite and ubiquitous trace MVT mineralization. The term ‘hydrothermal dolomite’ is applied to these rocks because of the relatively high temperature of dolomite precipitation relative to what is expected from heating by burial alone. A similar sequence of mineralization is present throughout the region in rocks

ranging in age from Early Ordovician to Late Devonian. Petrographic and geochemical evidence suggests a genetic link between the dolomite, MVT minerals, and K-silicate minerals in these rocks. Constraints were placed on the conditions of water-rock interaction using fluid-inclusion methods, CL and plane-light petrography, stable isotopic analyses, and organic maturity data.

There are problems with the regional distribution of dolostone presented by Badiozamani (1973, his figure 14). The 1973 article indicated that all of the rocks are limestone to the east of the Wisconsin arch by using one data point (locality 44) as a constraint. After visiting this quarry near Sun Prairie, Wisconsin, which was also the same quarry visited by Deininger (1964), it appears that most of the carbonate material in the present quarry exposure is dolomite. Dozens of Ordovician through Devonian outcrops and cores along the eastern side of the Wisconsin arch were examined as part of this study (see Figure 2). In all cases, with the exception of the partially dolomitized rocks of the Sun Prairie quarry, the Ordovician section in eastern Wisconsin is completely dolomitized. This observation removes a critical regional geometric argument supporting the mixing-zone hypothesis, which suggests that dolomitization was focused along the arch. Instead, the distribution of dolomite only decreases to

the west of the arch, away from the Michigan Basin. Figure 5 compares the hypothetical regional distribution of mixing-zone dolomite predicted by the mixing-zone model with the known regional distribution of dolomite for the Sinnipee Group/Trenton and Black River formations. Table 2 shows a comparison and contrast of some important geochemical and physical attributes of the mixing-zone model and of the rocks observed in the study area.

Hardie (1987) used several geochemical and thermodynamic arguments to reveal serious weaknesses with the Dorag model. He showed that the range of fluid compositions theoretically capable of producing ordered, stoichiometric dolomite in a seawater-freshwater mixing-zone environment was greatly restricted compared to what was originally suggested for the Dorag model. This means that although the Dorag model still predicts that mixing-zone fluids are capable of producing dolomite, the likelihood that the Dorag model can explain the pervasive dolomite in the region has been greatly diminished. In fact, dolomitization is kinetically favored by warm fluids (above $\sim 60^\circ\text{C}$) and is more likely to occur over a much larger range of fluid compositions under these conditions, including those with a $\text{Ca}^{2+}/\text{Mg}^{2+}$ ratio greater than 1.0 (Hardie, 1987).

Table 2. Comparison and Contrast of Some Important Geochemical and Physical Attributes of the Mixing-Zone Model and of the Rocks Observed in the Study Area

Mixing-Zone Dolomitization Model	Observations and Interpretations for Study Area
Partial regional dolomitization along bands parallel to the Wisconsin arch, where subaerial exposure and mixing zones are developed along structural highs.	Complete (100%) regional dolomitization east of the arch, regardless of structural position, partial to complete dolomitization along the arch, and sporadic dolomitization west of the arch. Dolomitized region extends well into the Michigan Basin.
Dolomite replacement and precipitation with simultaneous calcite dissolution in mixing zone.	Dolomite replacement and precipitation is intimately associated with Mississippi Valley-type mineralization.
CL zoning different for each subaerial exposure event; CL zoning should occur in patterns restricted to areas exposed parallel to arch.	Regionally correlative CL zoning in eastern Wisconsin can be traced through Prairie du Chien and Sinnipee groups, with some record found in Silurian units; A different CL zoning has been observed in southwest Wisconsin (Smith and Simo, 1997).
Fluid inclusions in dolomite should record low temperatures (all liquid inclusions; $T_h < 50^\circ\text{C}$).	Fluid inclusions in dolomite record high temperatures (two-phase FIAs with average T_h between 82 and 100°C).
Fluid inclusions in dolomite should contain water with a salinity between fresh water and seawater ($T_{m\text{ ice}} = 0$ to -1.9°C).	Fluid inclusions in dolomite and associated hydrothermal minerals contain dense brine with salinities of 13–28 wt.% (NaCl equivalent) ($T_{m\text{ ice}} = -16.9$ to -19.8°C ; or hydrohalite was the last phase to break down).
A $\delta^{18}\text{O}$ range of about -4 to -5.5‰ was reported by Badiozamani (1973) for the Mifflin Member.	A $\delta^{18}\text{O}$ data range from -8.64 to -2.88‰ is consistent with the range for hydrothermal dolomite (Allan and Wiggins, 1993).

Badiozamani (1973, p. 974) stated that "because major shifts in (the) dolostone-limestone boundary are associated with unconformity surfaces and marked differences in lithology, it is unlikely that the distribution of the facies boundary can be explained by hydrothermal dolomitization." However, field evidence has shown that fluids preferentially travel along bedding-plane fractures and other surfaces of relatively high permeability, in addition to vertical faults and fractures. Therefore, the conclusion that the limestone-dolostone transition geometry is solely caused by sea level fluctuations and other syndepositional elements is not required.

Oxygen isotopic data reported by Badiozamani (1973) are consistent with both mixing-zone and hydrothermal dolomitization models. Badiozamani (1973, his figure 6) showed that dolomite from the Mifflin Member of the Platteville Formation plots completely within the zone of hydrothermally altered limestone with regard to stable isotopic data, despite his interpretation of a nonhydrothermal origin for the dolomite. Data obtained in this study for Ordovician dolomites adjacent to the Wisconsin arch show a similar oxygen isotopic signature to that presented by Badiozamani (1973). Therefore, carbon and oxygen stable isotopic data alone cannot be used with confidence to distinguish between mixing-zone and hydrothermal dolomite in this region and must be accompanied by other petrographic and geochemical data to provide a thorough understanding of the origin of the dolomite.

The mixing-zone model was based on the paleogeographic requirement that the Wisconsin arch was the principal location of subaerial exposure and mixing of meteoric water with marine water occurred within the Platteville Formation. Sequence-stratigraphic research may not support the idea of subaerial exposure and early meteoric or mixing-zone dolomitization. Unconformities in the Platteville and Decorah formations of the Sinnipee Group west of the Wisconsin arch have been interpreted as submarine disconformities that punctuated an entirely subtidal depositional history (Ludvigson et al., 1996; Ludvigson et al., 2004). Although Choi and Simo (1998) interpreted the lithofacies of the Platteville Formation in southern and eastern Wisconsin to indicate inner-ramp to deep subtidal outer-ramp environments with very limited evidence of subaerial exposure, it is difficult to see support for the paleogeographic and paleohydrologic system proposed by Badiozamani (1973).

The mixing-zone model, which involves dolomitization along a linear band (shoreline) during the Ordovician, is also inconsistent with the observed CL stratigraphy for much of the dolomite that can be cor-

related over a large part of eastern Wisconsin in different stratigraphic units. Early work from 26 localities has shown that the CL stratigraphy can be correlated over most of the study area in parts of the underlying Prairie du Chien Group, in the Sinnipee Group, and, at least locally, in the overlying Silurian dolostones. This same CL stratigraphy was used to petrographically demonstrate the genetic relationship between MVT mineralization and dolomitization (e.g., Figure 4).

The mixing-zone model requires dolomitization at temperatures less than approximately 30°C in the presence of a fluid with salinities between that of fresh water and seawater. In contrast, the fluids responsible for dolomite replacement and precipitation in the study area were at temperatures between 65 and 120°C and had salinities between 13 and 28 wt. % NaCl equivalent. This study has shown that the dolomite and MVT minerals present in the study area were formed at elevated temperatures in the presence of dense brine as part of a regional hydrothermal system that was responsible for dolomitization and trace MVT mineralization.

It is significant that the only region where the Ordovician carbonates are completely dolomitized is the area stretching from the Wisconsin arch into the western Michigan Basin. To the east, west, and south of the study area, limestone comprises part or all of the carbonate section. The lack of abundant dolomite mass west of Platteville, Wisconsin, was noted by Badiozamani and was used as evidence against hydrothermal dolomitization of arch sediments during the upper Mississippi Valley lead-zinc ore district emplacement. A reevaluation of the regional dolomite distribution as part of this study suggests that the hydrologic process or processes that were responsible for regionally dolomitizing the Ordovician rocks operated most effectively on the western edge of the Michigan Basin in eastern Wisconsin, but diminished westward and were probably overprinted by one or more later episodes of hydrothermal alteration.

SUMMARY

If the carbonate rocks in eastern Wisconsin were partly or completely dolomitized by early low-temperature processes, they have been strongly overprinted by a late hydrothermal dolomite signature. Much or all of the evidence used by Badiozamani (1973) to support mixing-zone dolomitization in the Sinnipee Group was influenced by this hydrothermal overprint. Even if there was some vestige of a mixing-zone or other

low-temperature signature present in these rocks, this signature has been largely or completely removed. The present study adds to the abundant body of evidence against the mixing-zone model for pervasive dolomitization (e.g., Hardie, 1987; Land, 1998, Melim et al., 2004). The field, petrographic, and fluid-inclusion evidence presented in this study have undercut the foundations of the mixing-zone model for dolomitization to the point where it is no longer valid in its type locality.

This study has revealed the existence of a regional hydrothermal system that was active during the Late Devonian–Mississippian in eastern Wisconsin. The rocks preserve a pervasive hydrothermal signature and contain abundant epigenetic dolomite and ubiquitous trace MVT mineralization. Available evidence suggests that the MVT mineralization, K-silicate mineralization, and the dolomites found in eastern Wisconsin are genetically related to the same regional hydrothermal system that operated at temperatures between about 60 and 120°C.

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