GEOCHEMICAL CHARACTERIZATION OF SULFIDE MINERALIZATION IN EASTERN WISCONSIN CARBONATE ROCKS

A final report prepared for the University of Wisconsin Water Resources Institute

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PROJECT SUMMARY (Two pages maximum):

Title: Geochemical characterization of sulfide mineralization in eastern Wisconsin carbonate rocks

Project I.D.: University of Wisconsin System (UWS) Project number WR07R004

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Background/Need:
Characterization of geologic factors affecting groundwater movement, contamination, and aquifer recharge was a stated research priority by the University of Wisconsin System in the Joint Solicitation for Groundwater Research & Monitoring Proposals document for fiscal year 2008.

The chemistry of groundwater systems is controlled in part by the composition of the host rock. Groundwater in eastern Wisconsin carbonate rocks has the potential to be in direct contact with significant quantities of sulfide minerals because of their petrographic location in the host rocks. Sulfide minerals are often found coating the walls of joints, faults, and interconnected vugs in these dolostones. Oxidation of these sulfide minerals has been shown to be the major source of arsenic and other metals of concern in eastern Wisconsin (e.g., Thornburg and Sahai, 2004; Johnson and Riewe, 2006). Because interconnected fractures and bedding planes are important groundwater conduits in carbonate aquifers, the composition of minerals coating these fractures is an important control on groundwater quality.

Objectives:
The objective of the project was to characterize the trace metal composition of the carbonate (and other) rocks from outcrops, quarries, and drill cores in northeastern Wisconsin to gain a better understanding of potential sources of arsenic and other metals of concern.

This information will improve our understanding of the regional, stratigraphic, and petrographic distribution of these elements in the different Paleozoic strata of eastern Wisconsin. These activities will help to create a baseline for follow-up studies and help determine future impacts of arsenic and other metals in Wisconsin's groundwater.

Methods:
Samples were obtained by field work in quarries and at outcrops, from several drill cores, and from existing collections held by the principal investigator. Most field work was performed in Summer 2007, although additional sampling was performed in early Summer 2008. Drill cores that became available in Spring 2008 also benefited the study. The majority of samples used in the study were from various

localities in Marinette, Oconto, Brown, and Shawano counties. Additional samples from several other eastern Wisconsin counties supplemented the study.

Both biased and unbiased sampling methods were used to collect samples for chemical analysis. Samples that were representative of the stratigraphic horizon or those that were taken at random are labeled as "Bulk" specimens. In contrast, sampling that was deliberately biased in an attempt to analyze the most metals-rich materials are labeled as "Concentrate". Samples were submitted to ALS-Chemex in Thunder Bay, Ontario, Canada for Conventional 35-element ICP-AES Analysis after Aqua Regia Digestion to obtain metal concentrations. Petrographic investigations in May 2008 using a Scanning Electron Microscope (SEM) with Energy Dispersive Spectroscopic (EDS) capabilities allowed further characterization of the petrographic distribution of trace metals in the rocks.

Results and Discussion:
Three principal observations have been made during this research. First, it is apparent that the sulfide mineralization observed in Winnebago and Outagamie counties does indeed extend northward into Brown, Shawano, Oconto, and Marinette counties. This mineralization contains metals of concern similar to those in Winnebago and Outagamie counties.

Second, in all of the samples examined in the SEM, none displayed separate mineral phases for arsenic, such as arsenopyrite. However, in one sample, a nickel-iron sulfide phase was identified, suggesting that the distribution of at least some metals of concern is not restricted entirely to the occurrence of pyrite or marcasite (FeS_2).

Third, the distribution of sulfide minerals in the host sedimentary rocks of the region is heterogeneous, but stratigraphically predictable in the region. In addition to the well-documented Sulfide Cement Horizon (SCH) below the base of the Platteville Dolomite, other stratigraphic horizons display a predictable occurrence of sulfides, especially the base of the Silurian Mayville Dolomite and the top of the Maquoketa Shale or Neda Formation.

Conclusions/Implications/Recommendations:
This study provides two major conclusions, both of which can be applied to better understand the water quality in the region. First, the sulfide mineralization observed in Winnebago and Outagamie counties does indeed extend northward into Brown, Shawano, Oconto, and Marinette counties. In addition, abundant quantities of sulfides appear near the contact between the Silurian Mayville Formation and the underlying Maquoketa and/or Neda formations east of the Niagara escarpment. While most water quality issues in wells east of the escarpment are the result of bacteria and nitrate contamination, the possibility of metals contamination might exist for wells that reach a total depth near or at this stratigraphic horizon.

Future water quality studies should focus on these two mineralized stratigraphic horizons, as it seems likely that similar water quality problems should exist near the outcrop belts of these rocks.

Related Publications: None at present (Poster is planned for 2009 Wisconsin Section of AWRA, with peer-reviewed journal manuscript to be submitted at a later date).

Key Words: arsenic, nickel, iron, metals, sulfide, pyrite, stratigraphic, northeast Wisconsin, carbonate, sulfide cement horizon, Neda Formation, Sinnipee Group, Prairie du Chien Group, Silurian, Ordovician

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INTRODUCTION

Much attention has been given to the problem of arsenic contamination in groundwater from northeastern Wisconsin. The focus of previous research (e.g., Pelczar, 1996; Johnson and Riewe, 2006; Burkel and Stoll, 1999; Schreiber et al., 2000; Schreiber et al., 2003; Gotkowitz et al., 2003; Thornburg and Sahai, 2004) has been to characterize the distribution of arsenic in well waters and aquifer rocks, primarily in parts of Winnebago and Outagamie Counties. Little information is known about the trace element signature of the carbonates in those two counties that also host these sulfide minerals (pyrite, marcasite, galena, sphalerite, and others). Even less is known about the potential for arsenic and other metals contamination in Paleozoic rocks from other areas, such as those along the northern part of this outcrop belt in Marinette, Oconto, and Shawano Counties. With parts of northeastern Wisconsin expecting significant population growth over the next 25 years (Egan-Robertson et al., 2004), a better understanding of potential sources of groundwater contamination is needed, especially in rural areas where domestic well supplies are prevalent. It is apparent from existing well data that arsenic contamination exists in areas outside of Winnebago and Outagamie Counties, even in areas away from the St. Peter Sandstone outcrop belt (e.g., Johnson and Riewe, 2006). However, because of fewer wells and more limited screening for arsenic and other metals of concern in these areas, it is unclear whether the potential for arsenic and other metals contamination differs from the well-studied area in Winnebago and Outagamie Counties.

Luczaj (2000, 2006) characterized the ancient hydrothermal groundwater flow system responsible for water-rock interaction in eastern Wisconsin Paleozoic rocks. This ancient system was responsible for precipitation and replacement of a suite of Mississippi Valley-type (MVT) sulfide minerals that includes pyrite, marcasite, galena, sphalerite, millerite, and chalcopyrite. It is this hydrothermal system that precipitated the arsenic and nickel-bearing sulfide minerals in the region, including those in the uppermost meter of the St. Peter Sandstone.

Field, petrographic, and geochemical evidence suggests a link between the late-stage dolomite, trace MVT minerals, and authigenic potassium (K)-silicate minerals in eastern Wisconsin rocks, which preserve a regional hydrothermal signature. Constraints placed on the conditions of water-rock interaction using fluid-inclusion techniques indicate replacement and precipitation of dolomite, quartz, and sphalerite between 65 and 120°C in the presence of dense brines with salinities between 13 and 28 weight %, NaCl equivalent (Luczaj, 2000, 2006).

The chemistry of a groundwater system is controlled in part by the composition of the host rock. Groundwater in eastern Wisconsin carbonate rocks has the potential to be in direct contact with significant quantities of sulfide minerals, depending upon their abundance and spatial distribution in the host rocks. Sulfide minerals are often found coating the walls of joints, faults, and interconnected vugs in these dolostones. Oxidation of these sulfide minerals has been shown to be the major source of arsenic and other metals of concern in eastern Wisconsin (e.g., Gotkowitz et al., 1996; Thornburg and Sahai, 2004; Johnson and Riewe, 2006). Because interconnected fractures are important groundwater conduits in carbonate aquifers, the composition of minerals coating these fractures is an important contributing component of groundwater quality.

This study had three principal objectives. The first objective was to examine the stratigraphic and regional distribution of sulfide mineralization in Paleozoic rocks throughout northeastern Wisconsin (Figure 1). While the carbonate portions of the section received the most attention, sampling of sandstones, shales, and iron formation (Neda) was also conducted. The primary sources of rock samples were quarries and outcrops. This effort was supplemented by examination of numerous drill cores from throughout the region that became available after the project funding was awarded. Additional samples from an existing collection held by principal investigator Luczaj were also incorporated, where appropriate. The rocks examined and analyzed ranged in age from Cambrian through Silurian, representing most of the stratigraphic range of Paleozoic sedimentary rocks in the region.

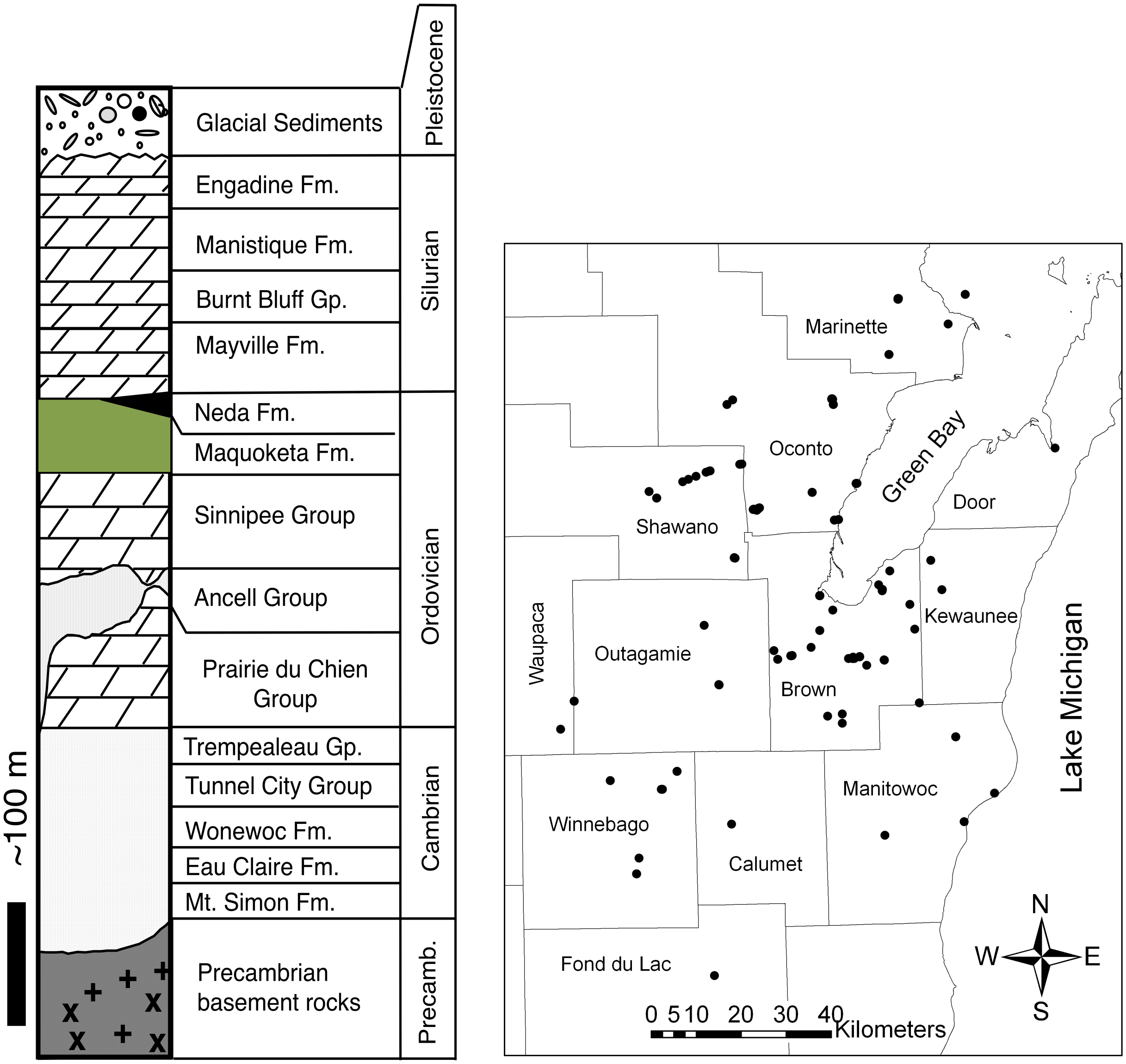

Figure 1. A (left). Generalized Stratigraphic column for northeastern Wisconsin (modified after Luczaj, 2006). B (right). Map showing the locations of samples analyzed in this study.

The second objective included Scanning Electron Microscopy (SEM) with Energy Dispersive Spectroscopy (EDS). This technique was used to explore the chemistry and petrographic distribution of metal sulfide minerals and associated minerals in 18 selected samples.

The third objective was to characterize the bulk geochemistry of both representative and non-representative (sulfide-rich or otherwise visually biased) samples. In total, 212 samples were submitted for 35 Element Aqua Regia ICP-AES analysis by ALS Chemex in Thunder Bay, Ontario. Unanticipated delays occurred due to negotiation with a major corporation to obtain core samples and locations. In addition, the final round of analytical results was not received until September 2008 due to unexpected laboratory delays.

PROCEDURES AND METHODS

Design of a sampling strategy was affected by two major limitations. First, the distribution of outcrop and core samples is not random in either the stratigraphic or the regional sense. Outcrops in the region are more common near either the Silurian or the Ordovician escarpments. Quarry locations also tend to be preferentially distributed near the base of the Silurian Mayville Formation, near the base of the Platteville Formation, and near the base of the Prairie du Chien Group carbonates. This outcrop distribution leads to a biased stratigraphic sampling. A second limitation is that physical access to samples near quarry high walls is often restricted for safety reasons related to MSHA regulations. We made reasonable attempts to sample multiple stratigraphic levels where possible.

We collected and processed two principal types of samples. Samples that were representative of the stratigraphic horizon or those that were taken at random are labeled as “Bulk” specimens (See Appendix B1). In contrast, sampling that was deliberately biased in an attempt to analyze the most metals-rich materials are labeled as “Concentrate”. Bulk samples collected were typically 1-2 kilograms, except for drill cores, which had a mass of at least 0.25 kilogram. Specimens labeled as “Concentrate” were as large as possible, but generally were at least 0.2 kilogram.

Two methods were employed to investigate the chemical composition of the rocks:

1. Digestion of whole-rock samples was performed by ALS Chemex of Thunder Bay, Ontario using Conventional 35-element ICP-AES Analysis after Aqua Regia Digestion. The results of these analyses yielded concentrations for 35 different elements, including arsenic (As), cadmium (Cd), cobalt (Co), chromium (Cr), copper (Cu), nickel (Ni), lead (Pb), zinc (Zn), molybdenum (Mo), and vanadium (V). This suite of elements was chosen because it is part of a standard ICP-AES analysis package supplied by commercial labs. Additional “overlimit” analyses, conducted with standard laboratory methods, were required for certain samples in which sulfur (S), iron (Fe), and phosphorous (P) exceeded instrument limits. Results for all analytical work are available in Appendix B.
2. Selected polished rock sections and crystal-lined vugs were analyzed with a Scanning Electron Microscope (SEM) with Energy Dispersive Spectroscopy (EDS) available at UW Green Bay. This technique was used to explore the chemistry and petrographic distribution of metal sulfide minerals and associated minerals in 18 selected samples. While the instrument available had X-ray mapping capability, the specimens for which this was attempted did not show significant concentrations of trace elements.

RESULTS AND DISCUSSION

The Paleozoic stratigraphic section (Figure 1) was divided into six principal stratigraphic units for this study. They are the Cambrian sandstones, the Prairie du Chien Group (PDC) carbonates, the Ancell Group sandstones and shales, the Sinnipee Group carbonates, the Maquoketa Shale/Neda Ironstone, and the Silurian carbonates. Multiple samples from each of these stratigraphic units were included in the study, with an emphasis on the carbonate portions of the section.

Field and Core Observations

Observations made at quarries and outcrops clearly indicate that the trend of sulfide mineralization observed in Winnebago and Outagamie counties definitely extends northward into Brown, Shawano, Oconto, and Marinette Counties. The sulfide mineralization was dominated by pyrite or marcasite (FeS_2 polymorphs), but sphalerite (ZnS), chalcopyrite ($CuFeS_2$), and galena (PbS) were also observed in hand specimens.

The distribution of sulfide minerals in the host sedimentary rocks of the region is heterogeneous, but stratigraphically predictable in the region. Regionally, the unit with the most sulfide mineralization was the top of the Ordovician Ancell Group (St. Peter and Glenwood formations). This zone of concentrated iron sulfide mineralization, known as the Sulfide Cement Horizon (SCH), is exposed on the floor or in sump trenches in several quarries in Shawano, Oconto, and Marinette counties. Nodules and intergranular cements of FeS_2 are abundant where this group of rocks is exposed. A thin (~10-50 cm) layer of dark brown shale above the St. Peter Sandstone is interpreted to be the Glenwood Shale. It contains abundant fine-grained sulfides, including pyritized arthropod and bryozoan fossils in some quarries.

The next most mineralized zone is the contact between the Silurian Mayville Dolomite and the underlying Ordovician Maquoketa Shale and Neda Formations. Where present, the Upper Ordovician Neda Ironstone and related strata appear to have sulfides associated with the upper extent of those units. In places, the mass of sulfides is striking, with large (10-40 cm thick) accumulations of pyrite easily identified. This sulfide mineralization often extends in to the lower few meters of the Silurian Mayville Dolomite. In at least one case, a local quarry operator has problems with the "aesthetic" quality of aggregate materials due to rust stains from weathering of pyrite fragments in asphalt and concrete products. This interval is best exposed in quarries and natural outcrops along Scray Hill in the towns of Ledgeview and Glenmore, southeast of Green Bay. Significant, but lesser amounts of pyrite are present at this contact and within the upper part of the Maquoketa Formation where the Neda Formation is missing.

The Ordovician Sinnipee Group carbonates contained significant quantities of metal sulfides, even at stratigraphic intervals farther away from the SCH in the Ancell Group. Sulfide mineralization was abundant along hardgrounds (a carbonate depositional surface), in vertical fractures and joints, and as vug fillings and intercrystalline cements (Figure 2). The mineralization was recognized throughout the Sinnipee Group, and some vertical fractures were mineralized by pyrite and calcite cements throughout 50+ feet of vertical exposure.

The carbonate units with the least amount of mineralization are the Silurian dolostones and the Prairie du Chien Group (PDC) dolostones. Some minor mineralization was identified in the PDC Group, especially in an outcrop and quarry south of New London on Highway 45. Chalcopyrite, pyrite, and galena were observed at this location along with a number of other non-sulfide minerals. Cores and outcrops of the Silurian dolostones indicate that most sulfides are restricted to the lower few meters of the Mayville Formation.

Scanning Electron Microscopy

Eighteen samples of polished rock slabs or crystal-lined vugs were carbon coated before analysis in an SEM with EDS capabilities at UW Green Bay. The main focus of the SEM work was to identify whether or not separate mineral phases could be identified for metals of concern or if FeS_2 phases (pyrite or marcasite) were the likely host materials for certain metals.

Separate mineral phases containing Zn, Pb, Ni and Cu were identified in a few samples (Figure 2). As expected, pyrite and marcasite (FeS_2) were the dominant sulfide phases present in most specimens. Zn and Pb sulfide phases were sphalerite and galena, respectively. The crystal morphology and EDS spectrum of the Cu-bearing phase suggests that it is chalcopyrite ($CuFeS_2$), but the Ni-bearing phase is less obvious. In one sample, an apparently cubic nickel-iron sulfide phase was identified, suggesting that the distribution of at least some Ni is not restricted entirely to the occurrence of pyrite or marcasite (FeS_2). The Ni-bearing phase contained significant amounts of Fe, and because of its cubic shape, the mineral pentlandite ($(Fe, Ni)_9S_8$) is a possibility. The identified Ni-phase was microscopic, so it was not possible to use X-ray powder diffraction to identify the mineral.

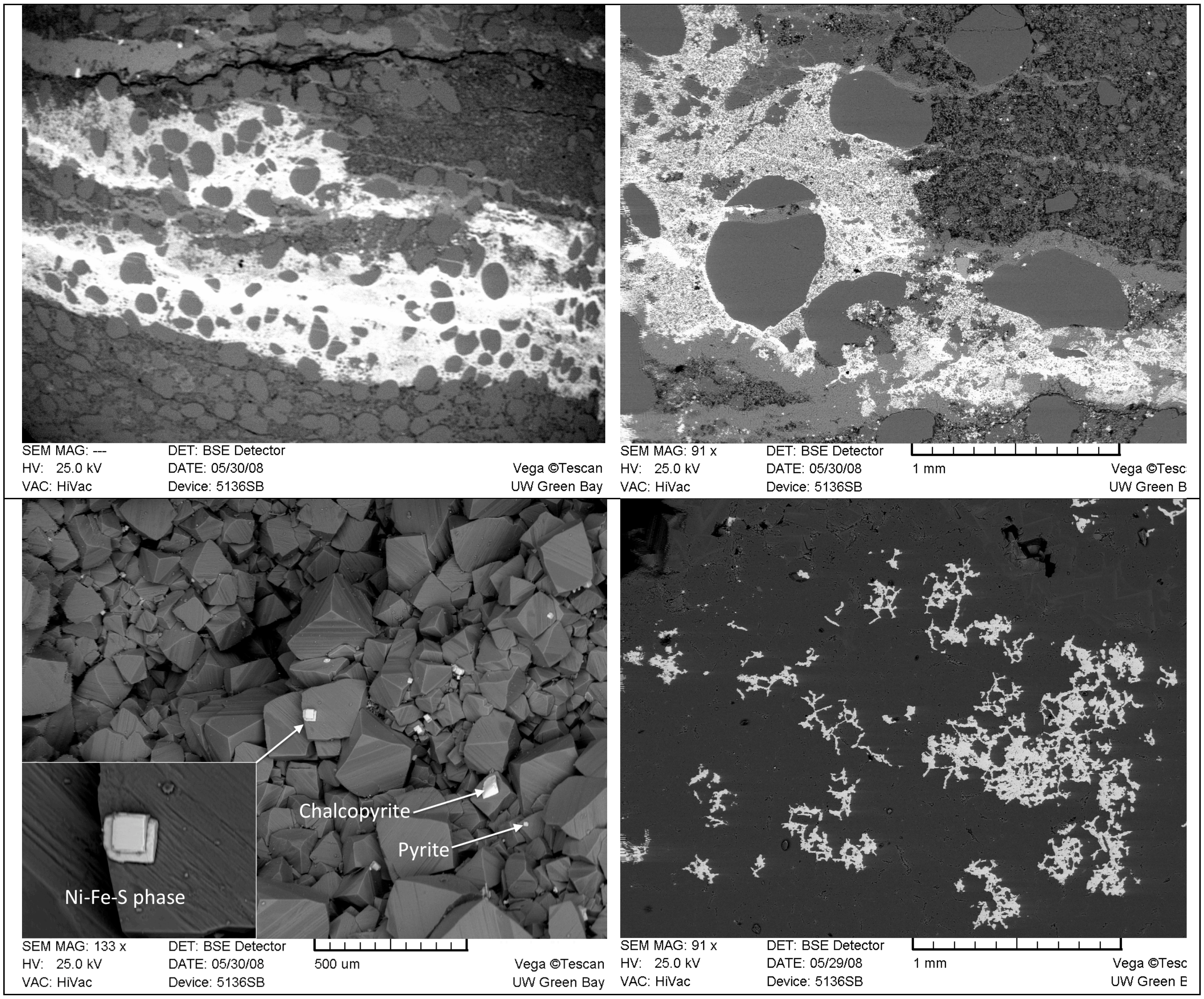

Figure 2. Scanning electron microscope images of polished sections and vug filling cements illustrating the character of sulfide mineralization in the region. A and B. (upper left and upper right) Sample 07-MT-FP-2 (Marinette County) from a quartz sandstone layer in lower Platteville Formation with fracture-filling cements. Round grains are quartz sand. Bright white areas in fracture are FeS_2 cements, whereas gray cements are calcite. Gray spotted areas in B are crystals of an unknown K-Al-Silicate mineral cement, possibly illite or K-feldspar. C. (lower left) Sample 07-OCO-MTV-2 (Oconto County) showing euhedral vug-filling dolomite crystals with associated pyrite, chalcopyrite, and cubic Ni-Fe-sulfide crystals from the Sinnipee Group dolostone. Inset shows the ~40µm crystal that is possibly pentlandite. D. (lower right) Sample 07-BN-LQ-1 (Brown County) exhibiting partial replacement and filling of intercrystalline pore spaces between dolomite crystals in the Sinnipee Group dolostone.

In contrast to the above metals, none of the samples examined with the SEM displayed separate mineral phases for arsenic (As), such as arsenopyrite. While the presence of arsenopyrite cannot be ruled out in these rocks, it seems likely that As is substituting for Fe as a trace element in the iron sulfides as has been suggested by others (e.g., Thornburg and Sahai, 2004).

ICP-AES Analytical Results

Analytical results for all 212 samples are presented in Appendix B. Nearly all specimens were obtained from northeastern Wisconsin, but four samples (96-RA-1.1, 97-RA-2, Stop 2 Rohl, 07-UWGB-TS-1.1) were from other parts of the state and were used for comparison purposes only.

The main purpose for analyzing the metals content of these rocks was to look for regional and stratigraphic trends in the character of the mineralization. We examined the concentrations of these metals and made certain comparisons between Fe, La, Mo, V, and the 8 metals of concern (As, Cd, Co, Cr, Cu, Ni, Pb, and Zn).

Table 1 presents the range of metals concentrations for all samples in the study (Bulk and Concentrate). Averages were not calculated because an unbiased sampling strategy is not possible for the region across all stratigraphic intervals.

Table 1. Minimum and maximum concentration values for iron and trace metals in Paleozoic rocks of northeastern Wisconsin. Concentrations for Fe are in %, while all other concentrations are in parts per million (ppm).

	Fe (%)	As	Cd	Co	Cr	Cu	Mo	Ni	Pb	V	Zn
Minimum	0.06	< 2	< 0.5	< 1	< 1	< 1	< 1	< 1	< 2	< 1	< 2
Maximum	28.4	499	4.2	133	38	1620	25	1110	1660	353	25200

Discussion

Various graphing methods were employed to determine possible correlations between the different metals. Many of these correlations were best expressed when plotted as separate stratigraphic populations. The most obvious trends include a correlation between As and Ni, As and Co, and between Cr and V. Weak correlations may exist between As and Cu, and Co and Ni. The Sinnipee Group samples showed a particularly good correlation between As and Co, as well as between As and Ni.

After graphical analysis of all data, it is apparent that three stratigraphic horizons showed the most significant mineralization. These were the top of the Ancell Group, the Ordovician – Silurian contact, and the Sinnipee Group dolostones. All three of these zones showed the potential for relatively high As concentrations (Figure 3a).

Positive correlations were found between several of the metals of concern. Some of these correlations hold for all stratigraphic intervals, whereas others are stronger for some units than for others. For example, while a general correlation exists for V and Cr over all stratigraphic intervals, the mineralized zone near the Ordovician-Silurian contact showed a particularly unexpected and interesting relationship due to enrichment of V relative to Cr (Figure 3b). While some scatter exists on As vs. Co plots, there is a well-defined positive linear correlation for samples hosted by Sinnipee Group dolostone (Figure 3c).

Ni vs. Fe plots show a weak correlation, if any. One stratigraphic difference noted is that FeS_2-rich samples from the Maquoketa/Neda contact and the Silurian dolostones just above this contact are depleted in Ni, relative to samples from the Ancell and Sinnipee groups (Figure 3d). Samples near the Ordovician-Silurian contact are also depleted in Ni, but appear to be enriched in V and La (lanthanum) (see Figure 3b and Appendix B1).

Some variations appear to be regional in nature. For example, Mo appeared to vary in a significant way regionally, with higher concentrations found in samples from Oconto County. The As vs. Ni plot (Figure

3e) shows a positive correlation for two distinct populations. Samples from all stratigraphic intervals fall into only one of these populations, except for the Ancell Group samples, which are split between the two populations. The population branch that shows significantly elevated Ni concentrations, relative to As, is represented by some Ancell Group samples from three Oconto County quarries (Duame Quarry, Chase Quarry, and Montevideo Quarry). An enlargement of the As vs. Ni plot shows that a similar split might occur for samples from the Sinnipee Group (Figure 3f).

We think that metals such as As, Fe, and Co correlate well with each other because As and Co are likely substituting for Fe in pyrite or marcasite. The reasons for a correlation between Cr and V are unknown, and most samples with appreciable quantities of these materials are located near the contact between the Silurian dolostones and the Ordovician Neda Ironstone. Poor correlation between Fe and Zn, Pb, and Cu are probably because those metals precipitate in separate phases, such as sphalerite, galena, and chalcopyrite, and are independent of the presence of pyrite or marcasite in any particular sample.

Rocks near the Ordovician-Silurian contact were somewhat deficient in Ni relative to Fe, as compared to the Ancell and Sinnipee Groups. These differences are likely due to the source of metals in the hydrothermal fluids that passed through the rocks. The Maquoketa Shale is a regional confining unit that likely isolated the Silurian dolostone units above it from the Ordovician sandstones and carbonates below it during the mineralization period in the Paleozoic.

Assuming that in FeS_2-rich samples, all As is hosted by pyrite or marcasite, then an estimate of the range in concentrations of As in pure FeS_2 can be made. The estimated concentration of As in FeS_2 varies from low values (~25 ppm) to a maximum of about 1,400 ppm.

Comparison With Existing Research Results

Results of the whole-rock analyses from this study were compared with published concentrations for metals in the St. Peter Sandstone of Winnebago and Outagamie Counties and other localities in northeastern Wisconsin (Pelczar, 1996, CH2M Hill, 2000; Gotkowitz et al., 2003). This procedure allowed generalized comparisons to be made between rocks in the Oshkosh to Green Bay corridor versus those in the Green Bay to Marinette corridor. It is worth mentioning that most previous work was limited to a smaller number of samples because those studies were mostly focused on detailed water quality research in a few locations. We compared our results with previously reported values, but those data tables and graphs are not presented here due to space constraints.

Arsenic concentrations relative to iron in this study were compared to those from the studies mentioned above. In general, whole-rock arsenic concentrations varied between 0 ppm and 500 ppm for all studies. However, three samples from Winnebago and Outagamie counties reported in previous studies had As concentrations that ranged between 500 and 743 ppm. While a few samples reported by Gotkowitz et al. (2003) had higher maximum Co concentrations than those in this study, a comparison of As vs. Co data also shows general overlap between the studies.

There were, however, some differences noted between the studies. First, the Cr concentrations in all samples in this study were below 40 ppm (Table 1). In contrast, 18 of 21 samples analyzed in previous studies (Simo et al., 1996; Gotkowitz et al., 2003) were reported to have Cr concentrations between 100 and 764 ppm, regardless of location, with most concentrations above 200 ppm. Because the locations of some of these data overlap those in our study, these high Cr values seem anomalous. One value reported by Gotkowitz et al. (2003) for an unmineralized sample of St. Peter Sandstone had a Cr concentration above 500 ppm, even though the sample had no sulfur and less than 1% Fe. Because of this anomalous behavior of Cr, we did not attempt to draw any conclusions about the difference in Cr between our studies and previous studies as they relate to rock geochemistry. It might be possible, however, that samples in the previous studies were submitted to a laboratory that crushed the samples with high Cr-steel, which is an alloy known for its toughness and which would be a suitable material for crushing rocks.

A comparison of As vs. Ni shows general agreement between most samples analyzed in our study and those of Gotkowitz et al. (2003) and Pelczar (1996), except for a few samples of Ancell Group sulfides from Oconto County (Figures 3e and f).

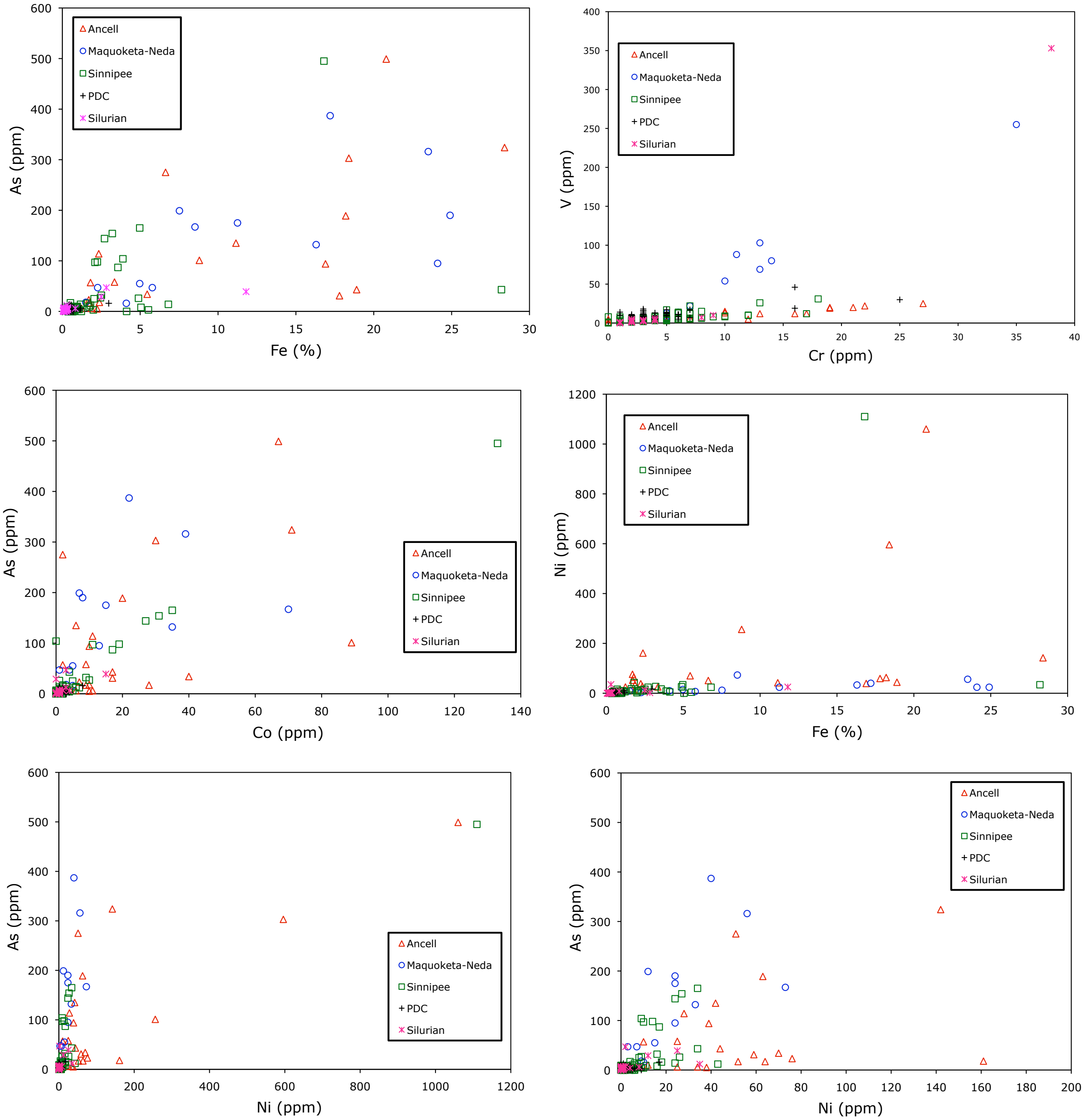

Figure 3. Scatter plots of selected metal concentrations from ICP-AES analyses on rock specimens from this study. Reported values for metals are in parts per million (ppm), except for iron, which is in percent (%). Legends in each graph indicate the particular stratigraphic unit sampled. A. (upper left) Arsenic (As) vs. iron (Fe). B. (upper right) Vanadium (V) vs. chromium (Cr). C. (middle left) Arsenic (As) vs. cobalt (Co). D. (middle right) Nickel (Ni) vs. iron (Fe). E. (lower left) Arsenic (As) vs. nickel (Ni). F. (lower right) Expanded view of E for arsenic (As) vs. nickel (Ni).

It is important to consider the potential impact of this mineralization on groundwater quality in the region north of Winnebago and Outagamie Counties. While the upper Ancell Group is likely to be the most significant source of metals due to the abundance of sulfides and the fact that porous media flow dominates, water quality in the Sinnipee Group should also be studied more carefully in the future. Because the distribution of sulfide minerals is very heterogeneous, their locations along fractures, faults, bedding planes, and in vugs is important. Fracture and bedding plane dominated flow are likely to greatly amplify the interaction between groundwater and sulfide minerals under the right redox conditions. In addition, certain stratigraphic zones of dolostone with high intercrystalline porosity, such as one about 20 feet above the base of the Platteville Formation, also contain abundant Fe-sulfides. For these reasons, the "average" concentration of metals within the Sinnipee Group as a whole are probably not so important – rather, the complex distribution of sulfide minerals and fluid flow pathways likely has a much larger influence on water quality in the carbonate units.

Because receipt of some analytical results was delayed by the contracted laboratory, some results were received in September 2008. Intensive analysis of all data is ongoing, and we will present further details and interpretations in a future publication.

CONCLUSIONS AND RECOMMENDATIONS

This study provides two major conclusions, both of which can be applied to better understand the water quality in the region. First, the sulfide mineralization observed in Winnebago and Outagamie counties definitely extends northward into Brown, Shawano, Oconto, and Marinette counties. This includes both the highly concentrated SCH at the top of the St. Peter Formation, as well as the disseminated iron and other metal sulfides in other parts of the section.

Abundant quantities of sulfides also appear near the contact between the Silurian Mayville Formation and the underlying Maquoketa and/or Neda formations east of the Niagara escarpment. While most water quality concerns in these wells has been focused on bacteria and nitrate contamination, the possibility of metals contamination might exist for wells that reach a total depth near or at this stratigraphic horizon.

Future water quality studies should focus on these two mineralized stratigraphic horizons, as it seems likely that similar water quality problems would exist at and near the outcrop belts of these rocks. However, the dominance of bedding plane and fracture flow pathways throughout the Sinnipee Group means that groundwater impact from metals could occur throughout this unit. We recommend that a detailed domestic well sampling program for all metals of concern be considered for areas near and east of the SCH in Marinette, Oconto, Shawano and western Brown counties.

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APPENDIX A: Awards, Publications, Reports, Patents and Presentations

There are no finished publications or manuscripts at this time. We are planning to present this work at the March 2009 Wisconsin Section of AWRA, with submittal of a peer-reviewed publication during the summer of 2009.

APPENDIX B:

Appendix B1 (Pages 1-18)
Summaries of sample numbers, locations, descriptions, and analytical results.

Appendix B2 (11 reports, 8 shipments and 3 overlimit analyses)
35 Element ICP-AES results from ALS Chemex.