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Geochemistry and mineralogy of the Wonewoc–Tunnel City contact interval strata in western Wisconsin

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Abstract

In this study we characterize the geochemistry of the Cambrian age (~500 million year old) rocks of the Wonewoc–Tunnel City contact interval (upper Wonewoc Formation and lower Tunnel City Group) in western Wisconsin. Results of groundwater quality testing of private wells near the City of La Crosse that draw groundwater from these rocks (below the water table) as well as preliminary water-quality data from process-water ponds at industrial sand mine sites that extract and process these same rocks (above the water table), have shown elevated concentrations of trace metals and pH levels that fluctuate through time. To aid in understanding the potential source and mechanism(s) for these water-quality issues in both private wells and at industrial sand mining sites, we collected and compiled a geochemical and mineralogical dataset for Wonewoc–Tunnel City contact interval rocks on a regional scale. In this study, trace metal–bearing sulfide minerals are documented in both the Wonewoc Formation and Tunnel City Group, and are most abundant in the west-central region of the study area. The distribution of these sulfides is both spatially and stratigraphically variable, and therefore appears to be site specific in nature. More work is needed to be able to predict their distribution as the current dataset is limited in areal extent and spatial resolution. The regional geochemical and mineralogical database developed in this study provides evidence that the rocks of the Wonewoc–Tunnel City contact interval in west-central Wisconsin are a potential natural source of trace metal concentrations observed in some process-water ponds at industrial sand mines and groundwater in private wells that draw water from these rocks.

Introduction

Wisconsin faces a variety of groundwater quality issues that include both natural sources, such as arsenic from sulfide minerals, as well as human-induced sources, for example nitrate from agricultural land-use practices. In this study we determine if the Cambrian age (~500 million year old) rocks in the Wonewoc–Tunnel City contact interval (lower Tunnel City Group and upper Wonewoc Formation) contain elevated concentrations of trace metals observed in some industrial sand mine process-water ponds and groundwater in western Wisconsin (fig. 1A). Groundwater quality testing of private wells near the City of La Crosse that draw water from these rocks (below the water table) as well as preliminary water quality data from process-water ponds at industrial sand mine sites that extract and process these same rocks (above the water table), have shown elevated concentrations of trace metals (such as cobalt, iron, copper, lead), and pH levels that fluctuate through time. To help understand the potential source and mechanism(s) for these water-quality issues, we collected and compiled a geochemical and mineralogical dataset and reviewed available well geophysical data for Wonewoc–Tunnel City contact interval rocks on a regional scale (fig. 1).

The impetus for this project was the prevalence of groundwater quality issues near La Crosse combined with the rapid expansion of large-scale industrial (frac) sand mines in west-central Wisconsin and associated preliminary process-water pond analyses. Over the past 50 years, western Wisconsin has undergone rapid land-use change related to population increase and suburban sprawl (Radeloff and others, 2005; Mississippi River Regional Planning Commission, 2017), and in the past decade has seen the introduction and growth of industrial (frac) sand mines and processing facilities (Wisconsin Department of Natural Resources, 2016). As population increases and new homes are built in traditionally rural areas, new private drinking water wells are being constructed and their water quality tested. On the highlands east of La Crosse, Wisconsin, groundwater from some private wells that draw water from Wonewoc–Tunnel City contact interval rocks (fig. 1B) has been shown to contain concentrations of aluminum, arsenic, cadmium, chromium, cobalt, copper, iron, lead, manganese, nickel, vanadium, and zinc above advisory levels, as well as low pH (table 1) (Dave Johnson, WDNR, oral communication, 2016). The Wonewoc Formation rocks that form the aquifer supplying these wells also meet the specifications for use as a proppant (frac sand) in hydraulic fracturing, and therefore where these rocks outcrop at the surface in other areas of Wisconsin they have the potential to be an extractable industrial sand resource (Zambito, Haas, and Batten, 2017; Zambito, Mauel, and others, 2018). At the majority of industrial sand mines, resistant rocks of the lower Tunnel City Group cap the Wonewoc Formation sandstone hills being excavated (fig. 1C). Tunnel City Group rocks, which in most cases do not meet the specifications for industrial sand use, are treated as overburden; these rocks are removed, piled on site, and typically used for reclamation. The Wonewoc Formation rocks, which do meet the specifications for industrial sand use (including frac sand, because of the uniform roundness, grain size, and mineralogy of the grains comprising the sandstone), are disaggregated, if necessary, to break apart any cements present, and then washed using on-site groundwater and reclaimed water from processing and stormwater reservoirs to remove any clay minerals present. In the majority of cases, the quartz sand grains are then transported off-site for further processing before being sold for industrial uses. The clay minerals are then removed from the process water in on-site settling ponds or screens/presses and then this water is typically recycled for further sand washing. Preliminary water-quality data from process-water and settling ponds indicates the presence of trace metal concentrations in these ponds as well as variable pH levels through time (table 2) (Roberta Walls, WDNR, oral communication, 2017).

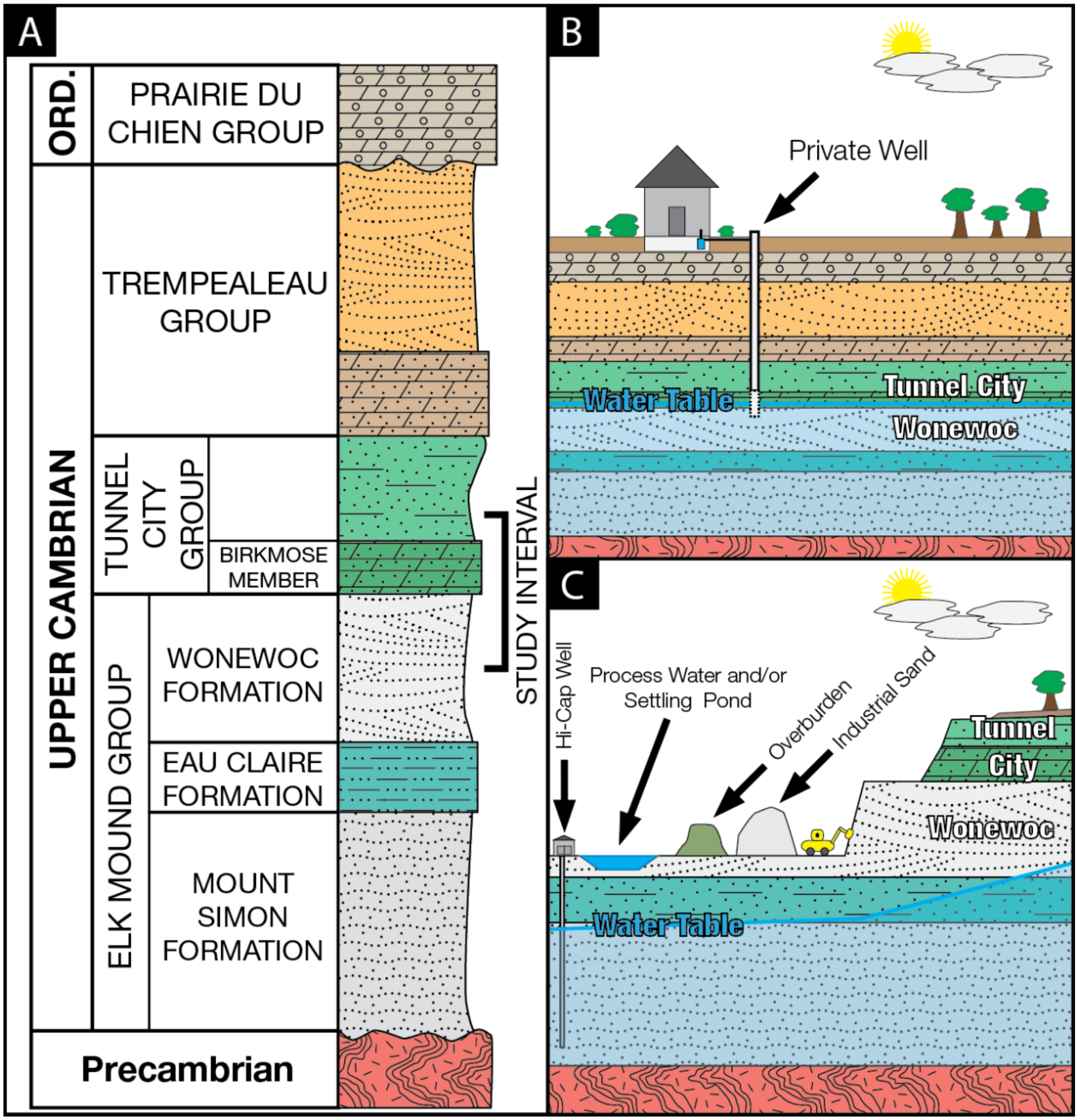

Figure 1. A) Generalized stratigraphic column showing the typical rock succession in west-central Wisconsin.
B) Schematic diagram of a private well (not to scale) that draws groundwater near the water table and from the rocks of the Wonewoc-Tunnel City contact interval. Solid outline of well indicates casing, dashed line indicates where well is open; in this schematic, the well is open to intervals above the water table.
C) Schematic diagram of an industrial sand mine (not to scale) in which the Tunnel City Group overburden is removed and stored onsite and the Wonewoc Formation industrial sand resource is extracted. In this schematic, the high-capacity well is cased throughout the entire depth of the well and only open at the bottom.

Table 1. Concentrations of elements that are known health risks and pH measurements in water produced by private wells near La Crosse, Wisconsin.

	Advisory Level	Private wells—municipality (WUWN)					
		Tomah (ST009)	Bangor (UN859)	Coon Valley (OH527)	Stoddard (CQ196)	La Crosse (RV223)	La Crosse (GC657)
pH		4.6‡	6.97	4.7‡	4.5‡*	4.08‡	6.85
Elements (unit)							
Aluminum (µg/L)	200	22630§	3220§	23900§	67300§	23200§	2320§
Arsenic (µg/L)	10	ND	ND	129§	92§	38§	ND
Cadmium (µg/L)	5	ND	2	1	5§	5§	ND
Chromium (µg/L)	100	2.5	ND	77	220§	56	1
Cobalt (µg/L)	40	244.2§	306§	501§	909§	501§	23
Copper (µg/L)	1300	307.5	1610§	324	1290§	511	16
Iron (mg/L)	0.3	39.19§	53.6§	218§	672§	376§	24.3§
Lead (µg/L)	15	—	ND	109§	80§	47§	ND
Manganese (µg/L)	50	222.8§	142§	921§	2980§	897§	56§
Molybdenum (µg/L)	40	ND	—	20	—	ND	ND
Nickel (µg/L)	100	1232§	419§	771§	1750§	832§	41
Strontium (µg/L)	4000	843.1	70	144	217	219	54
Sulfate (mg/L)	250	1478.5§	—	—	—	—	—
Vanadium (µg/L)	30	ND	5	69§	239§	56§	1
Zinc (µg/L)	2000	574.6	385	52	4460§	706	56

Abbreviations: WUWN = Wisconsin Unique Well Number; — = not measured; ND = not detected.

§ Concentration exceeds advisory levels set by Wisconsin DNR (http://dnr.wi.gov/topic/drinkingwater/documents/haltable.pdf, May 2017, last viewed April 5, 2018). (Cells highlighted in blue.)

‡ Low pH measurements (below 6.0). (Cells highlighted in gray.)

* pH was measured separately from when elemental concentrations measured.

Data provided by Dave Johnson (WDNR).

Table 2. Concentrations of select elements in water samples and pH measurements from process-water ponds at industrial (frac) sand mines.

	Jackson County			**Trempealeau County**		**Monroe County**		
	Goose Landing	**Taylor #1**	**Taylor #2**	**Brannt-Guza**	**Preferred**	**Hi-Crush**	**Smart Sand**	**US Silica**
pH	6	7.6	7.6	8.2	9.2	7.4	6.8	7.2
Calcium	3.24	13.3	15	19.2	22.8	31.9	21.6	20.9
Magnesium	2.12	5.68	5.85	6.99	8.01	15.5	16.1	10.5
Aluminum (µg/L)	15100	8660	1050	831	4890	605	35600	3440
Arsenic (µg/L)	—	—	—	—	—	—	—	—
Cadmium* (µg/L)	—	—	—	—	—	—	—	—
Chromium* (µg/L)	13.7[§]	10.2	1.85	—	6.63	1.12	62.7	5.79
Cobalt (µg/L)	9.51	3.92	1.05	—	4.21	3.36	35. 2	3.62
Copper* (µg/L)	34.6[‡]	14[‡]	—	—	14.1[‡]	—	98.7[‡]	9.81[‡]
Iron (mg/L)	11.3	13.8	1.95	1.47	10.6	0.395	32.4	5.58
Lead* (µg/L)	19.5[‡]	6.72	3.55	—	7.03	—	40.6[‡]	4.22
Manganese (µg/L)	154	358	70.3	9.88	220	51.8	206	208
Molybdenum (µg/L)	—	—	—	—	—	—	4.35	—
Nickel* (µg/L)	6.41	14	3.81	—	5.93	9.06	67.1[‡]	4.88
Strontium (µg/L)	179	58.6	38	56.1	81.8	60.7	94.1	59.9
Vanadium (µg/L)	30.4	18.4	2.21	1.99	11.9	3.24	90.9	10.5
Zinc* (µg/L)	31.5[‡]	34.1	8. 37	—	43.7	—	133[§]	12.8

Abbreviation: — = not measured or not detected

*Toxicity measurements calculated.

[‡] Sample exceeds estimated toxicity (acute and/or chronic) for stream biota based on calculated hardness (calcium and magnesium). (Cells highlighted in green.)

[§] Sample is close to estimated toxicity. (Cells highlighted in yellow.)

Data and toxicity calculations provided by Roberta Walls (WDNR).

Similar bedrock geology and high concentrations of trace metals in some La Crosse area wells and also in some industrial sand mine process-water ponds forms the basis for the hypothesis that the Wonewoc–Tunnel City contact interval rocks are a potential natural source of trace metal surface water and groundwater contamination in west-central Wisconsin. Furthermore, data obtained from the UW-Stevens Point Center for Watershed Science and Education suggest that this groundwater quality issue may be of regional concern (fig. 2). Private wells with lower pH tend to be concentrated in west-central Wisconsin, where the Wonewoc–Tunnel City contact is found at or near land surface. In this study, we present geochemical and mineralogical data on the rocks of the Wonewoc–Tunnel City contact interval as the precursor to a future, more detailed project to test the above-mentioned hypothesis.

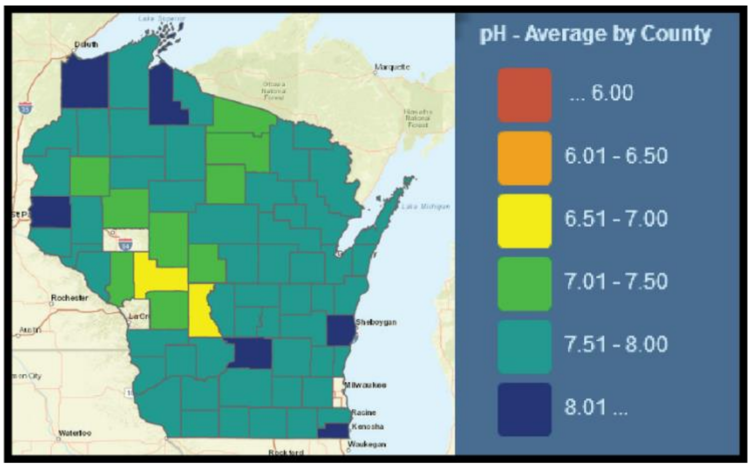

Figure 2. Average pH by county (http://www.uwsp.edu/cnr-ap/watershed/pages/wellwaterviewer.aspx, viewed April 5, 2018). Transparent counties indicate that not enough data was available for analysis.

Previous studies have noted that fluctuating water levels expose rock to variable oxidizing and reducing (redox) conditions, which could increase the rate at which minerals chemically weather and elements go into solution. For example, a model proposed for the release of arsenic from arsenic-bearing sulfide minerals in the St. Peter Formation sandstone in eastern Wisconsin, and resulting poor water quality, is through the drawdown of the water table caused by pumping and the reaction of exposed sulfide minerals with oxygen (Schreiber and others, 2000; Gotkowitz, Schreiber, and Simo, 2004). Variable oxidizing and reducing conditions could also occur if there is preferential flow along horizontal conduits. Previous hydrostratigraphic studies in the Wonewoc–Tunnel City sandstone aquifer of the Upper Midwest have demonstrated that regionally extensive zones of high horizontal hydraulic conductivity within the Tunnel City and near the contact with the Wonewoc create intervals of preferential groundwater flow (Runkel, Tipping, and others, 2006; Swanson 2007; Swanson and others, 2006). Both of these models are possible mechanisms for the chemical weathering of Wonewoc–Tunnel City contact interval rocks (and any sulfides present), and could explain the poor water quality in some private wells near La Crosse. Similar redox reactions, in combination with the physical weathering that occurs during sand mining processes (i.e., disaggregating and washing), may also explain the water quality issues observed in some process-water ponds at some industrial sand mines. It should be noted that there are several other potential abiotic or biotic mechanisms responsible for sulfide mineral dissolution via oxidation that are beyond the scope of this summary, but likely play an important role.

Sulfide minerals are sulfide ions (negatively charged sulfur) ionically bonded to positively-charged metal ions in a solid mineral phase. These metal ions can include elements such as cobalt, nickel, vanadium, arsenic, copper, and zinc. A common example of a sulfide mineral is pyrite, or fool's gold, which is composed of iron and sulfur. Other metal elements can substitute for iron in pyrite, resulting in an iron sulfide crystal composed of trace concentrations of many different metals. Greater enrichment of these metals can result in a different mineral altogether, e.g., zinc sulfide (sphalerite). Sulfide minerals are stable in low oxygen environments but break down in the presence of a strong oxidant, such as oxygen. Clay minerals can also contain cobalt, nickel, vanadium, arsenic, copper and zinc.

Given the correspondence outlined above between Wonewoc Formation and Tunnel City Group rocks and water quality issues, and the plausible redox mechanisms that may be the cause, it has been suggested that the Wonewoc–Tunnel City contact interval rocks are a potential natural source of elevated concentrations of trace metals in some mine process-water ponds and groundwater in western Wisconsin. To date, limited geochemical and mineralogical data exist for these rocks, particularly in western Wisconsin. Gotkowitz, McLaughlin, and Grande (2012) presented chromium data from geologic units in south-central Wisconsin (Madison), noting that chromium concentration corresponded to iron oxyhydroxide minerals within the bedrock, and that the monitoring wells screened only across the Tunnel City Group rocks had higher chromium concentrations, in general, than wells completed in other rock formations. However, they also noted that bedrock geochemistry was variable, with chromium in the Tunnel City Group typically around 5 ppm and as high as 20 ppm, and concentrations in the Wonewoc Formation observed at less than 5 ppm and also as high as 30 ppm.

Because the water-quality data collected to date is also highly variable among wells and mine process-water ponds (tables 1 and 2), we anticipated observing variable trace metal composition, and probably also mineralogy, in this study. We also anticipated that trace metal composition and mineralogy would vary regionally, dependent upon the geologic history of a given area. Therefore, we focused on samples from three regions: south-central, southwest, and west-central Wisconsin (figs. 3 and 4). To increase sample density within these regions, we incorporated drill core, outcrop, and well cutting material in our analysis (see fig. 4). We used these different sample types with the understanding that different sampling methods and processing techniques from the same rock units have been shown to have different trace metal concentrations (Gotkowitz, McLaughlin, and Grande, 2012; Zambito, McLaughlin, Haas, and others, 2016). Furthermore, we focused on identifying the presence of redox sensitive minerals, such as sulfides, near the Wonewoc–Tunnel City contact interval as the likely source of the observed water-quality issues because (1) sulfides are common hosts for trace metals, (2) they have been shown to cause water-quality problems in other Wisconsin sandstone aquifers, (3) they are extremely unstable under oxygenated conditions, and (4) the oxidation of sulfides can lower water pH.

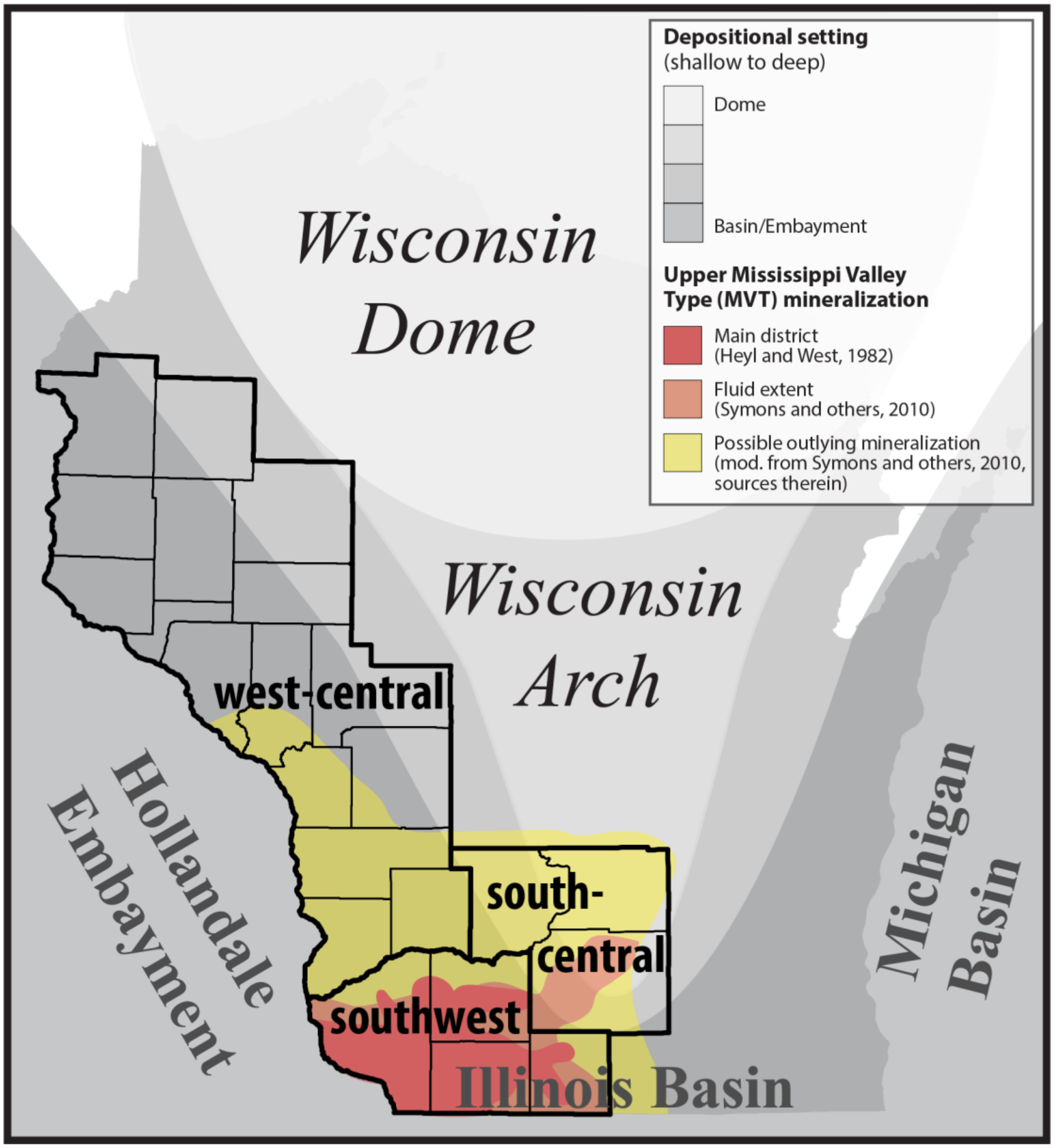

Figure 3. Generalized geologic setting and concentration of Mississippi Valley Type (MVT) ore deposits in the study area. Grayscale gradient represents submarine depositional settings with the shallowest areas (pale gray) over the Wisconsin Dome and Arch in northern and central Wisconsin and becoming progressively deeper to the southwest and southeast. During deposition of the Wonewoc Formation and Tunnel City Group rocks, the source of siliciclastic sediment (primarily quartz grains) was from modern north, and may have included the Wisconsin Arch and Dome (Dott and others, 1986; Runkel, McKay, and Palmer, 1998; Runkel, McKay, and others, 2012).

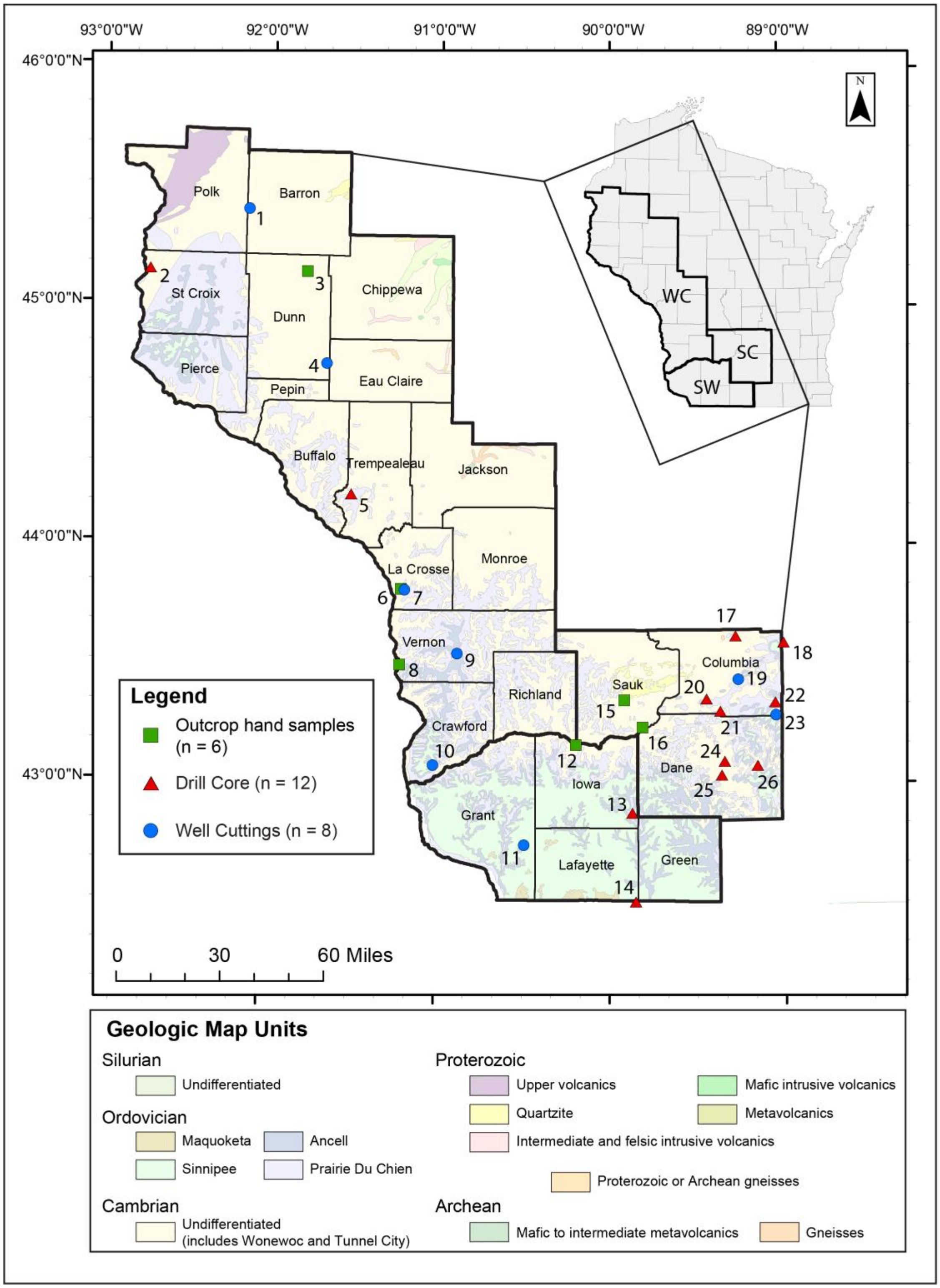

Figure 4. Location of borehole (drill core and well cuttings) and outcrop samples analyzed in this study. Region abbreviations: SC = south-central, SW = southwest, and WC = west-central. Geologic map adapted from Mudrey and others, 1982.

Geologic setting

The Paleozoic rocks of the Upper Mississippi River Valley have a long history of geologic study; a detailed examination of this previous work is beyond the scope of this open-file report. Below, we give a basic outline of geologic setting and encourage the reader to see the references cited for further details. Based on bedrock geology, glacial history, and geomorphology we divided the counties of this study into three regions: south-central, southwest, and west-central Wisconsin (figs. 3 and 4). The rocks examined in this study were deposited about 500 million years ago during the late Cambrian on a broad submarine depositional ramp with an onshore-offshore profile from modern day northeast to southwest (fig. 3) (Runkel, McKay, and others, 2012).

The south-central region is distinct in that the Wonewoc Formation and Tunnel City Group rocks were deposited on the Wisconsin Arch (a paleotopographic high surrounded by the Hollandale Embayment, Illinois Basin, and Michigan Basin), in a relatively shallower, more onshore depositional setting than the rest of the study area (fig. 3). (See Runkel, McKay, and others, 2012, for a regional depositional model; Dott and others, 1986, and Runkel, McKay, and Palmer, 1998, provide a detailed examination of Wonewoc Formation depositional environments; and Eoff, 2014, provides the same for the Tunnel City Group.) In this relatively shallow depositional setting, sulfide minerals forming from Cambrian seawater sulfate may have been less common relative to offshore areas (west-central and southwestern Wisconsin). Likewise, the Tunnel City Group rocks in south-central Wisconsin contain much less glauconite (a green iron potassium phyllosilicate mineral) than the Tunnel City rocks in western Wisconsin (see Eoff, 2014; i.e., Mazomanie Formation vs. Lone Rock Formation). Both the west-central and southwest regions of this study were deposited in offshore settings in which glauconite and Cambrian seawater-derived pyrite (observed in this study) is more common.

The southwest region is differentiated from the other two regions by the presence of thick Ordovician carbonate rock (Prairie du Chien and Sinnipee Groups) that cap the Cambrian sandstone succession, thus burying the Wonewoc Formation and Tunnel City Group at depths of several hundred feet (fig. 4); in the south-central and west-central regions, the Sinnipee Group is generally absent and the Prairie du Chien Group is less common. Additionally, the Driftless Area, a part of Wisconsin that has no evidence of subglacial deposits, covers most of the southwest region of this study and the southwestern portion of the west-central region. Almost all of the south-central region has experienced post-depositional glaciation.

A final but important note is that Mississippi Valley Type (MVT) ore deposits, which include the sulfide minerals galena (PbS), sphalerite ($[Zn,Fe]S$), marcasite (FeS_2), and pyrite (FeS_2), are present in the study area (fig. 3). These minerals are unstable under oxidizing conditions and contain trace metals of interest. The southwest region of this study lies almost entirely within the classic upper MVT mineral district (Heyl and West, 1982), the southern portion of the south-central study region is within the upper MVT mineral district fluid extent (Symons and others, 2010), and the northern portion of the south-central study area and the southern portion of the west-central study area are both within the outlying zone of MVT mineralization (Symons and others, 2010, and references therein) (fig. 3).

Materials and methods

The distribution and location of the boreholes (drill core and well cuttings) and outcrops studied is shown in figure 4 and analyses undertaken for each are shown in table 3. WGNHS identification numbers (WIDs), listed in table 3, are used for internal WGNHS sample and data management. In addition to studying existing geologic materials, we drilled a borehole in Trempealeau County, Wisconsin, just south of the City of Arcadia on Arcadia Ridge (WGNHS Arcadia Quarry) to collect drill core near the center of industrial sand mining in Wisconsin. We also investigated and sampled six outcrops throughout the study area (fig. 4).

Preliminary elemental data were collected from drill core, outcrop, and well cuttings using portable x-ray fluorescence (pXRF) (appendix A). Geological and geophysical logs of boreholes (including a suite of tools such as natural gamma radiation, spontaneous potential, fluid conductivity, rock resistivity, borehole diameter [caliper], temperature, optical borehole imaging, and flow meter) were collected by the WGNHS or compiled from the WGNHS subsurface database if available (appendices B and C). These were used to help identify stratigraphic units and contacts in the subsurface, as well as reconstruct the relationship between the water table, water conductivity, and groundwater flow to the stratigraphy in the vicinity of the Wonewoc–Tunnel City contact interval. Additional data were then collected on a subset of samples using inductively coupled plasma mass spectrometry (ICP-MS) (appendix D) for elemental analysis, and x-ray diffraction (XRD) (appendix E) for mineralogical analysis.

Our workflow began with identifying drill core and borehole cuttings samples available in the WGNHS research collections as well as any corresponding geophysical data (from that borehole or, in some cases, a neighboring one). From this dataset we identified a drill site (site 5, WGNHS Arcadia Quarry; fig. 4) and six outcrops that would improve the spatial resolution of geological materials to be studied. We performed fieldwork and drilling between June and August 2015 (fig. 4, table 3).

Practical methods were used to prepare “clean” samples for analysis. We removed any obvious case-hardening or other rock surface alteration prior to sampling outcrops. In the laboratory, we collected pXRF elemental data for a first look at the composition of the geological materials studied with a focus on sulfide minerals (appendices A and B). Fresh cut, rock saw slabbed core and hand sample faces were analyzed when possible. Rock core that had not been slabbed was cleaned, using sandpaper, if necessary, to remove any drilling mud or post-drilling surface oxidation, and analyzed on the outer surface.

Cuttings and unconsolidated hand samples were analyzed in a sample holder using polypropylene XRF film. (Details of sample preparation with different sample types are available in Zambito, McLaughlin, Haas, and others, 2016.) For a given sample or core depth, we often performed multiple pXRF analyses to capture any lithological or mineralogical variability observed at the centimeter-scale. We previously undertook a case study of the effects of sample type and preparation on pXRF elemental analysis (see appendix 5 of Zambito, McLaughlin, Haas, and others, 2016).

Elemental analysis by pXRF, lithologic logs, and geophysical data for each borehole or outcrop studied were plotted alongside one another (appendix B). Major rock forming elements that could be a proxy for lithology (silicon, calcium, and aluminum for quartz sandstone, carbonate cement, and clay minerals, respectively) (Zambito, McLaughlin, and Bremmer, 2017), elements indicative of pyrite (co-variance of iron and sulfur), trace metals related to MVT mineralization (lead and zinc), and arsenic (a known groundwater contaminant in Wisconsin) were plotted stratigraphically. Elements that are lithologic proxies were used to inform stratigraphic divisions shown in the lithologic logs (appendix B). Since we used the pXRF analysis to obtain relative elemental composition (and sample type is variable, i.e., core, hand samples, and cuttings, along with variable lithologies) we did not calibrate the pXRF data presented herein; we instead used it as a “first look” (see Zambito, McLaughlin, Haas, and others, 2016, for further details on calibration). For elemental analyses that were below the instrument’s limit of detection, we converted those values to zero and include them on the stratigraphic plots to signify the location of these analyses (appendix B). The error bars shown for pXRF measurements are the instrument’s uncertainty in the measurement, and not the error based on instrument accuracy.

Part of this first look was to examine possible relationships between sulfur and the elements calcium, aluminum, and iron using cross-plots to get an idea if any sulfur present was hosted in carbonates, clays, or pyrite, respectively. Similarly, we also cross-plotted arsenic, lead, and zinc with calcium, aluminum, and sulfur to understand if these trace metals were bound to carbonates, clays, or sulfides, respectively. However, these cross-plots are only meaningful if there is enough data available to plot for each lithology (Wonewoc vs. Tunnel City) that is greater than the pXRF instrument limit of detection (element specific; see Zambito, McLaughlin, Haas, and others, 2016). The pXRF datasets from core, in which we did collect high-resolution analyses that represent cm-scale lithologic variation, is robust and large enough to cross-plot as described above; we did this for one core with abundant data from each region (see appendix B). In this study, we generally had limited samples from outcrops and therefore do not undertake cross-plots for those sections. Similarly, well cuttings samples, which represent some mixture of material drillers collect typically for each 5-ft stratigraphic interval tended to have lower trace metal concentrations and more measurements that were less than the instrument’s limit of detection; therefore, we do not cross-plot this data herein either. For these cross-plots, if sulfur is associated with lead or zinc (suggesting galena or sphalerite, respectively) it could indicate MVT sulfide mineralization within the rocks sampled. We looked for the presence of arsenic because it is associated with sulfides in northeastern Wisconsin in the Ordovician St. Peter sandstone (Schreiber and others, 2000; Gotkowitz, Schreiber, and Simo, 2004). Herein, we chose the cut-off of $r^2 \geq 0.45$ as suggestive of correspondence between cross-plotted elements; this r^2-value is low in order to account for mm-scale lithologic variability observed in cores, which results in a large amount of “noise” in the pXRF data (see appendix B plots).

Analysis of the pXRF and geophysical data was then used to select a subset of samples that represented the elemental variability observed in the studied successions for further elemental analysis (ICP-MS; appendix D) and mineralogical composition (XRD; appendix E). We reviewed any down-hole geophysical data collected as part of this study or available from the WGNHS subsurface database to understand hydrogeologic conditions at the Wonewoc–Tunnel City contact interval in the studied successions. Detailed ICP-MS and XRD analysis was then preferentially applied to regions where the Wonewoc–Tunnel City contact interval was close to the water table. Therefore, we did not undertake detailed geochemical or mineralogical analysis on samples from the southwest region because this interval is well below the water table or potentiometric surface and likely never exposed to redox conditions. Sample powders for ICP-MS were drilled from rock material using a tungsten carbide drill bit, or were powdered using a mortar and pestle for poorly lithified materials. This subset of samples for ICP-MS and XRD analysis came mostly from drill core (site 2, Belisle Quarry; site 5, Arcadia Quarry; and site 17, Triemstra Quarry; representing each of the three regions studied), but also included outcrop (site 6, Granddad Bluff La Crosse) and cuttings (site 7, Arbor Hills Addition Well); see table 3 for sample details. Elemental data collected using ICP-MS and mineralogical data collected using XRD is presented below by region for all sites (see also appendices D and E for further details).

For discussion of XRD mineralogical results, we focus only on major rock forming minerals (i.e., quartz, glauconite, dolomite, etc.) as well as sulfide mineral phases (i.e., pyrite, sphalerite, etc.). To summarize ICP-MS elemental data in this study, we calculated the median and mean concentration for trace metals of interest. This report focuses on those values that are above the median value for either the Tunnel City or Wonewoc, and, therefore, are values signifying relative enrichment observed for each rock unit. More robust statistical analyses are beyond the scope of this report, which only aims to identify potential natural sources for unusually high concentrations of trace metals found in some water wells and some sand mine process-water ponds in western Wisconsin (i.e., the natural occurrence of trace metals and in what mineral phases).

Table 3. Details of the spatial and stratigraphic location, and analysis undertaken, for the samples investigated in this study. Site locations are shown in figure 4.

Site number, name		WID	County	Sample interval*	Sample type	Geo-phys. data	Analyses	Lati-tude	Longi-tude
West-Central									
1	Village of Turtle Lake #2	3000192	Barron	350 to 550 ft	Well cutting	Nearby well	XRF	45.3981	-92.1436
2	WGNHS Belisle Quarry	56000829	St. Croix	140 to 200 ft	Core	No	XRF, XRD, ICP-MS	45.1400	-92.7210
3	Hwy W Hay Creek	—	Dunn	1.0 to –1.0 m	Hand sample	No	XRF	45.1395	-91.7892
4	Duane Welch Well	17000274	Dunn	20 to 125 ft	Well cutting	No	XRF	44.7556	-91.6667
5	WGNHS Arcadia Quarry	62000166	Trempealeau	288.5 to 450 ft	Core	Yes	XRF	44.2020	-91.4580
6	Granddad Bluff La Crosse	—	La Crosse	4.6 to –3.8 m	Hand sample	No	XRF	43.8140	-91.2127
7	Arbor Hills Addition Well (S.D. 2)	32000107	La Crosse	250 to 450 ft	Well cutting	Yes	XRF, XRD, ICP-MS	43.8103	-91.1919
8	Victory North	—	Vernon	1.9 to –1.1 ft	Hand sample	No	XRF	43.4956	-91.2159
9	Viroqua City Well #6	63000165	Vernon	405 to 635 ft	Well cutting	Yes	XRF	43.5444	-90.8823
10	Aherns Bros. Farm	12000001	Crawford	250 to 445 ft	Well cutting	No	XRF	43.0750	-91.0150
Southwest									
11	Platteville City Well 4	22000143	Grant	650 to 955 ft	Well cutting	Yes	XRF	42.7422	-90.4911
12	Lone Rock Type Area	—	Iowa	0.3 to –1.0 ft	Hand sample	No	XRF	43.1640	-90.1960
13	WGNHS Hwy A 2	25000529	Iowa	292 to 357 ft	Core	Nearby well	XRF	42.8780	-89.8720

Site number, name		WID	County	Sample interval*	Sample type	Geo-phys. data	Analyses	Lati-tude	Longi-tude
14	Commonwealth Edison UPH-1	33000331	Illinois (state)	667 to 735 ft	Core	No	XRF	42.5050	-89.8520
South-Central									
15	Hwy C Leland	—	Sauk	1.4 to 1.5 m	Hand sample	No	XRF	43.3516	-89.9183
16	Ferry Bluff West	—	Sauk	2.3 to –2.6 m	Hand sample	No	XRF	43.2362	-89.8130
17	WGNHS Triemstra Quarry	11005900	Columbia	133 to 209.0 ft	Core	Yes	XRF, XRD, ICP-MS	43.6206	-89.2749
18	WGNHS Alsum 4	14001384	Dodge	232 to 325.2 ft	Core	Yes	XRF	43.5939	-88.9977
19	WGNHS Rio 1	11000783	Columbia	100 to 305 ft	Well cutting	Yes	XRF	43.4374	-89.2605
20	WGNHS Stevenson 2	11005908	Columbia	160 to 238.5 ft	Core	Yes	XRF	43.3574	-89.4443
21	WGNHS Arlington Quarry	11005901	Columbia	181.5 to 238.5 ft	Core	Yes	XRF	43.3050	-89.3650
22	WGNHS Columbus 2	11000782	Columbia	150 to 258.5 ft	Core	Yes	XRF	43.3423	-89.0497
23	WGNHS Manke Farm Test Hole	11000784	Columbia	221 to 400 ft	Well cutting	Yes	XRF	43.2882	-89.0447
24	Arcadis Madison Kipp MW-5D3	13005716	Dane	38 to 151.5 ft	Core	No	XRF	43.0950	-89.3420
25	Nine Springs Core Hole 2 (NS-2)	13001466	Dane	109 to 158 ft	Core	Yes	XRF	43.0364	-89.3597
26	Cottage Grove Hydrite MP-18	13001216	Dane	200 to 300 ft	Core	Yes	XRF	43.0770	-89.1540

Abbreviations: WID = WGNHS identification number, — = none.

*Sample interval for subsurface data is depth below surface in feet; for hand samples from outcrops the sample interval is relative to the Wonewoc–Tunnel City contact in meters.

Results

The analyses and borehole observations of this study are summarized below:

1. For each borehole and outcrop studied the presence of MVT and sulfide-related elemental enrichments (elevated concentrations of sulfur, arsenic, lead, and zinc) as measured by pXRF is noted relative to the Wonewoc–Tunnel City stratigraphic contact (table 4). The maximum concentration measured using pXRF is also shown using percent sulfur, and ppm (rounded to the nearest increment of 5 ppm) arsenic, lead, and zinc (see appendices A and B for details of data and sample position relative to contact).
2. Where available, we describe well-construction specifics and borehole characteristics gathered from borehole geophysical logs that may influence water chemistry in the well (see also appendices B and C).
3. For select samples in which ICP-MS and XRD data are available, we present additional elemental concentration and mineralogical data obtained using these analyses, with a focus on the ICP-MS elemental concentrations above the median values for each unit in order to convey samples of relative enrichment (table 5, full results in appendices D and E).
4. Finally, we include photographs of representative samples from ICP-MS and XRD analyses to show centimeter-scale lithological and mineralogical variability (figs. 5–9).

Table 4. Enrichments relative to the Wonewoc–Tunnel City contact and maximum concentrations of sulfur, arsenic, lead, and zinc for each locality as determined by pXRF. *(Refer to appendices A and B for full details.)*

			Sulfur (%)		Arsenic (ppm)		Lead (ppm)		Zinc (ppm)	
Site number, name		**Sample type**	**Location[a]**	**Max[b]**	**Location[a]**	**Max[b]**	**Location[a]**	**Max[b]**	**Location[a]**	**Max[b]**
WEST-CENTRAL										
1	Village of Turtle Lake #2	well cuttings	near, above	1.2	near	15	near, above	15	throughout	30
2	WGNHS Belisle Quarry	core	throughout, esp. Wonewoc	3.0	throughout	60	throughout	15	throughout	950
3	Hwy W Hay Creek	hand sample	near, above	0.02	near, above	10	above	15	throughout	90
4	Duane Welch Well	well cuttings	below	0.7	above	10	rare	5	above	60
5	WGNHS Arcadia Quarry	core	throughout	30.0	near, above	600	throughout	50	throughout	40*
6	Granddad Bluff La Crosse	hand sample	above	33.0	near, above	40	throughout	30	near, above	200
7	Arbor Hills Addition Well (S.D. 2)	well cuttings	throughout, esp. Wonewoc	0.8	near, above	30	near, above	15	throughout	40
8	Victory North	hand sample	near, above	0.5	near, above	125	near, above	100	near, above	150
9	Viroqua City Well #6	well cuttings	near, above	1.0	near, above	10	near, above	10	throughout	50
10	Aherns Bros. Farm	well cuttings	throughout	0.4	above	10	above	15	throughout	20
SOUTHWEST										
11	Platteville City Well #4	well cuttings	throughout, esp. near/above	0.8	throughout, esp. near/above	20	throughout, esp. near/above	20	throughout, esp. near/above	40
12	Lone Rock Type Area	hand sample	near	0.2	near	15	—	—	near	20
13	WGNHS Hwy A 2	core	near, above	8.0	near, above	40	near, above	20	throughout	60
14	Commonwealth Edison UPH-1	core	throughout, esp. near/above	5.0	near, above	50	near, above	40	throughout	40
SOUTH-CENTRAL										
15	Hwy C Leland	hand sample	near, above	0.8	near, above	8	—	—	near, above	15
16	Ferry Bluff West	hand sample	above	0.2	above	5	—	—	above	40
17	WGNHS Triemstra Quarry	core	throughout	0.6	rare	10	near	15	throughout	50
18	WGNHS Alsum 4	core	throughout	0.6	—	—	throughout	60	throughout	80
19	WGNHS Rio 1	well cuttings	throughout	0.05	—	—	near	5	throughout	70
20	WGNHS Stevenson 2	core	throughout	0.3	rare	5	throughout	15	throughout	175
21	WGNHS Arlington Quarry	core	throughout	0.5	—	—	—	—	throughout	20
22	WGNHS Columbus 2	core	throughout, esp. near	1.0	near	100	near	80	throughout, esp. near/above	100
23	WGNHS Manke Farm Test Hole	well cuttings	rare	<0.05	rare	5	above	5	throughout	20
24	Arcadis Madison Kipp MW-5D3	core	above	8.0	near, above	10	above	100	throughout	80
25	Nine Springs Core Hole 2 (NS-2)	core	throughout	0.8	near, above	10	near, above	30	throughout	50
26	Cottage Grove Hydrite MP-18	core	throughout	0.3	rare	10	near, above	10	throughout	50

[a]Location of enriched samples relative to contact between Wonewoc and Tunnel City, unless noted as throughout.
[b]Maximum pXRF concentrations, reported in % sulfur, or for arsenic, lead, and zinc, in ppm rounded to the nearest increment of 5 for ease of comparison.
*one anomalously high value of 2,686 ppm obtained

Well-construction specifics and borehole characteristics from borehole geophysical logs.
(Only sites with logs are included.)

West-Central

Site 1: Village of Turtle Lake Well #2 (municipal well, cuttings)

Shallow water table in unlithified material above the Prairie du Chien Group; well is cased to ~100 ft below water table in the Trempealeau Group. Borehole water electrical conductivity is elevated in the upper Tunnel City (uncased) above a zone of enhanced borehole flow; below this flow zone, relatively uniform low borehole water conductivity is observed.

Site 5: WGNHS Arcadia Quarry (core hole)

Water table located in the St. Lawrence Formation, above the Tunnel City Group; fully 100 ft below the bottom of shallow temporary casing finished in the Prairie du Chien. Borehole abandoned following geophysical data collection. Water conductivity increases downhole, with inflections toward increasing values at the top of the Tunnel City, at the Tunnel City–Wonewoc contact, and the highest conductivity readings occurring within the Wonewoc near the presumed contact with the Eau Claire Formation.

Site 7: Arbor Hills Addition Well [S.D. 2] (municipal well, cuttings)

Potentiometric surface is located in the lower Wonewoc; well is cased more than 100 ft deeper into the lower Eau Claire Formation.

Site 9: Viroqua City Well #6 (municipal well, cuttings)

The static water table is located just above the Tunnel City Wonewoc contact, but the well is cased ~400 ft deeper into the Elk Mound Group. Water conductivity increases at the contact, though this part of the well is cased; this conductivity increase is likely an artifact of temperature change.

Southwest

Site 11: Platteville City Well #4 (municipal well, cuttings)

Water table located at the Prairie du Chien–Ancell Group contact; well is cased to just below the water table. Borehole water conductivity measurements not collected.

Site 13: WGNHS Hwy A #2 (core hole)

Shallow static water level fluctuates near land surface and is in the Prairie du Chien Group; well cased ~50 ft deep in the Prairie du Chien. Decreased water conductivity seen at the Tunnel City–Wonewoc contact coincident with increased temperature. Well is open across Eau Claire shale confining unit into Mt. Simon. Well noted to be flowing occasionally.

South-Central

Site 17: WGNHS Triemstra Quarry (core hole)

The water table is located near the Tunnel City–Wonewoc contact; borehole has shallow casing far above water table. This borehole was abandoned following collection of geophysical data. Water conductivity is highest at the water table, decreasing but elevated through the Tunnel City and Wonewoc, and lowest at and below the Wonewoc equivalent (cannot differentiate the Eau Claire Formation), where an interval of increased borehole flow is observed.

Site 18: WGNHS Alsum 4 (core hole)

Water table is located within the Prairie du Chien Group; borehole is cased to water table. This borehole was abandoned following collection of geophysical data. No change in water conductivity at the Tunnel City–Wonewoc contact interval. Increased borehole flow throughout the Tunnel City.

Site 19: WGNHS Rio 1 (borehole, cuttings)

The water table is located near the St. Lawrence (Black Earth)–Tunnel City contact; bottom of shallow casing far above water table. This well was abandoned following collection of geophysical data. Water conductivity shows some variation near the Tunnel City–Wonewoc contact interval.

Site 20: WGNHS Stevenson 2 core

The water table is located within the Tunnel City; borehole has shallow casing far above water table. This borehole was abandoned following collection of geophysical data. Water conductivity increases slightly downhole, with a marked increase near the bottom of the borehole; since log stops shortly thereafter it is possible that this increase is an artifact.

Site 21: WGNHS Arlington Quarry (core hole)

The water table is located near the St. Lawrence (Black Earth)–Tunnel City contact; borehole has shallow casing far above water table. This borehole was abandoned following collection of geophysical data. Water conductivity increases downhole, with a marked increase in the Tunnel City, but log stops shortly thereafter.

Site 22: WGNHS Columbus 2 (core hole)

The water table is located near land surface near the Prairie du Chien Group–Ancell Group contact; no casing installed. This borehole was abandoned following collection of geophysical data. Slightly increased water conductivity observed just above the Tunnel City–Wonewoc contact interval, but log stops shortly thereafter.

Site 23: WGNHS Manke Farm Test Hole (borehole, cuttings)

The water table is located near the Ancell Group–Sinnipee (Platteville–Galena) Group contact; well is cased to just above water table. This well was abandoned following geophysical data collection. No change in water conductivity observed at the Tunnel City–Wonewoc contact interval.

Site 25: Nine Springs Core Hole 2 (NS-2) (core hole)

Water table located within the Tunnel City Group; well is cased to water table. Water conductivity elevated throughout. Log ends near Tunnel City–Wonewoc contact interval.

Site 26: Cottage Grove Hydrite MP-18 (core hole)

The water table is located above the base of the Prairie du Chien Group; borehole is cased to water table. Water conductivity data not available.

Table 5. Trace element concentrations (ppm, as determined by ICP-MS) above the median value and mineralogy (as determined by XRD), for selected samples. *(Refer to appendices B and C for full details.)*

Location, sample unit	Interval (ft)	Trace elements[a] (ppm)												Mineralogy[b]
		As	Cd	Co	Cr	Cu	Mn	Mo	Ni	Pb	U	V	Zn	
WEST-CENTRAL														
Site 2—WGNHS Belisle Quarry														
Tunnel City	132.0	—	0.048	11.95	37.30	—	1940.00	0.38	12.95	—	1.35	40.20	15.50	Qts, *Kspar*, Glauc
	146.0	—	—	—	19.30	—	—	—	—	—	—	—	—	Qtz, Kspar, Glauc
Wonewoc	182.0	—	**0.034**	32.00	11.60	22.20	—	—	5.19	—	—	15.00	**13.50**	Qtz
	199.0	1.42	—	—	—	—	—	—	—	—	**2.64**	—	2.90	Qtz
Site 5—Arcadia Quarry														
Tunnel City	290.0	—	—	13.10	29.70	—	—	—	12.25	—	1.35	34.00	10.10	Qtz, Glauc, Dol
	293.7	—	—	27.50	—	64.20	—	—	—	—	—	—	—	

	296.6	43.80	**3.700**	**100.00**	41.40	**269.00**	—	1.10	149.00	22.80	1.72	31.90	**4860.0**	Qtz, Kspar, Glauc, Dol
	309.4	**547.00**	—	19.60	34.00	21.50	—	2.38	42.30	17.30	1.80	34.10	—	
	309.5	5.56	—	—	44.00	—	—	—	—	10.25	1.95	47.20	11.70	
	310.5	—	—	—	40.50	—	—	—	—	10.90	2.29	42.10	—	
	313.5	—	—	—	28.20	—	—	—	—	9.77	1.45	22.40	—	Qtz, *Calc*
	313.7	30.40	—	62.20	32.00	174.50	1700.00	—	**158.00**	11.50	—	107.50	16.70	
	313.8	42.70	—	14.15	—	—	1885.00	0.47	20.70	13.00	—	51.90	17.00	Qtz, Glauc, Dol
	313.9	5.93	—	—	—	—	**2630.00**	—	—	—	—	—	—	Qtz, Glauc, Dol
	314.0	23.60	—	15.20	—	25.10	1935.00	—	12.80	8.56	—	23.20	11.50	
	314.1	—	—	—	—	—	1150.00	0.73	—	8.52	—	—	9.50	Qtz, Kspar, Glauc, Dol
	314.2	5.03	—	—	—	12.50	1075.00	0.72	—	—	—	—	10.70	
	314.3	19.60	—	12.20	28.50	—	1610.00	—	16.70	—	—	41.20	17.00	
	314.4	7.62	—	—	38.10	—	1190.00	—	—	—	1.39	23.20	16.00	
	320.0	—	—	—	31.50	8.40	1100.00	—	—	—	—	21.80	10.60	
	323.9	5.18	—	—	23.30	—	1680.00	—	—	—	1.14	21.90	—	Qtz, Kspar, Glauc, Dol, *Pyr*
	325.8	—	—	19.85	21.50	15.70	931.00	0.75	17.40	17.80	1.39	—	10.90	
	334.9	—	—	—	—	—	—	—	—	—	—	—	—	
	338.4	139.50	—	17.55	—	88.10	—	1.30	17.30	14.65	—	—	—	Qtz, Glauc, *Sph*
	339.7	19.55	0.011	25.30	—	11.05	—	1.54	15.45	**49.60**	3.34	—	—	Qtz, *Sph*, *Cov*
	345.5	—	—	—	—	11.90	—	—	—	11.60	—	—	—	
	346.5	—	—	—	**90.60**	26.50	—	0.64	16.40	29.90	**4.01**	**113.00**	11.60	
	347.7	—	—	—	—	—	—	0.57	—	9.79	—	—	—	
Wonewoc	350.9	3.96	—	10.60	**54.00**	19.65	83.40	0.63	13.80	33.10	2.28	53.30	8.00	
	353.2	—	—	—	—	—	—	—	—	—	—	—	—	
	357.1	—	—	—	—	9.65	—	0.29	—	—	—	—	—	
	359.8	3.90	0.031	**94.60**	14.30	**645.00**	—	1.44	7.14	9.04	—	—	—	
	375.7	0.90	—	21.50	16.00	37.20	30.90	0.30	9.62	7.33	1.30	15.90	2.60	
	376.5	1.61	—	18.70	38.90	31.50	38.70	0.57	12.20	15.60	2.21	48.90	7.90	
	383.1	1.44	—	10.55	—	5.06	—	0.19	4.52	16.20	0.67	—	—	Qtz, Kspar, *Calc* , *Pyr*
	384.5	2.70	—	10.95	18.10	12.10	75.40	0.75	10.90	30.10	1.13	16.70	2.70	
	394.0	—	—	—	—	—	36.20	—	—	—	—	—	—	
	395.5	**8.21**	0.012	13.60	26.30	21.50	39.00	**3.18**	**16.50**	**42.50**	1.94	**62.60**	2.90	Qtz, Kspar, *Calc* , *Pyr*, *Sph*
	398.0	—	—	—	—	—	—	—	—	—	—	—	—	
	405.5	3.98	0.012	—	14.20	16.40	78.10	0.41	9.31	23.70	1.47	13.10	—	Qtz, Kspar, *Calc* , *Pyr*, *Sph*
	430.5	1.77	—	—	13.50	6.35	74.20	0.76	8.82	15.70	1.20	13.80	3.70	
	442.5	2.65	—	—	9.40	6.02	**3790.00**	0.41	8.54	20.50	—	8.40	6.30	
	445.0	1.42	0.009	—	7.40	—	48.20	0.22	5.89	11.15	—	4.60	—	
Site 6—Granddad Bluff, La Crosse														
Tunnel City	3.95a	—	—	—	—	19.10	2160.00	1.11	14.80	—	—	—	—	Qtz, *Glauc*, Dol
	3.95b	13.40	—	30.60	—	13.60	1140.00	**5.47**	123.50	21.20	2.07	—	—	Qtz, Glauc, Dol, *Pyr*
	3.95c	5.65	—	16.50	—	—	1765.00	2.45	34.70	11.20	1.07	—	—	Qtz, Glauc, Dol
	3.95d	7.82	—	19.25	—	45.10	1185.00	2.40	73.30	15.30	—	—	13.10	Qtz, Dol, Pyr
	3.25a	—	0.042	—	—	—	1860.00	—	—	—	—	—	31.40	Qtz, Glauc, Dol
	0.95	—	—	21.50	—	25.30	—	0.43	—	11.65	1.21	—	—	Qtz
Wonewoc	–0.65	—	—	—	—	—	—	—	—	5.78	1.34	3.70	—	Qtz, *Kspar*
	–3.55	—	—	—	—	—	—	—	—	8.76	—	—	—	Qtz
Site 7—Arbor Hills Addition Well (S.D. 2)														
Tunnel City	255–260	10.35	0.015	—	31.40	8.03	—	0.40	15.20	—	1.25	34.50	11.70	Qtz, Glauc, Dol, *Pyr*
Wonewoc	400–405	—	—	—	—	—	—	—	—	—	—	—	2.60	Qtz
SOUTH-CENTRAL														
Site 17—WGNHS Triemstra Quarry														
Tunnel City	165.0	—	0.023	11.40	48.60	—	—	—	—	—	1.82	28.50	9.40	Qtz, Kspar, Glauc
	166.0	—	0.091	—	—	—	—	—	—	—	—	—	—	Qtz, Glauc
Wonewoc	171.0	—	0.009	57.80	—	—	43.50	—	—	—	—	—	—	Qtz, *Kspar*, *Calc*
	176.0	—	0.032	12.45	19.80	—	337.00	—	—	—	0.79	13.20	5.60	Qtz, Kspar, Glauc
	180.0	—	—	26.70	—	—	—	—	—	—	—	—	—	Qtz
	202.9	—	—	41.00	—	—	—	—	—	—	1.38	—	2.40	Qtz

[a] **Trace elements**
Abbreviations: As = arsenic, **Cd** = cadmium, **Co** = cobalt, **Cr** = chromium, **Cu** = copper, **Mn** = manganese, **Mo** = molybdenum, **Ni** = nickel, **Pb** = lead, **U** = uranium, **V** = vanadium, **Zn** = zinc.
Bold values = highest observed concentration of a particular trace element in either the Wonewoc Formation or Tunnel City Group.
— = Concentrations below the median value

[b] **Mineralogy**
Abbreviations: Calc = calcite/aragonite, **Chal** = chalcopyrite, **Cov** = covellite, **Dol** = dolomite, **Glauc** = glauconite, **Kspar** = potassium feldspar, **Pyr** = pyrite, **Qtz** = quartz, **Sph** = sphalerite.
Italicized abbreviations indicate XRD patterns suggestive of the mineral, though identification is tentative.
If no abbreviations are listed, then XRD was not performed on that sample.

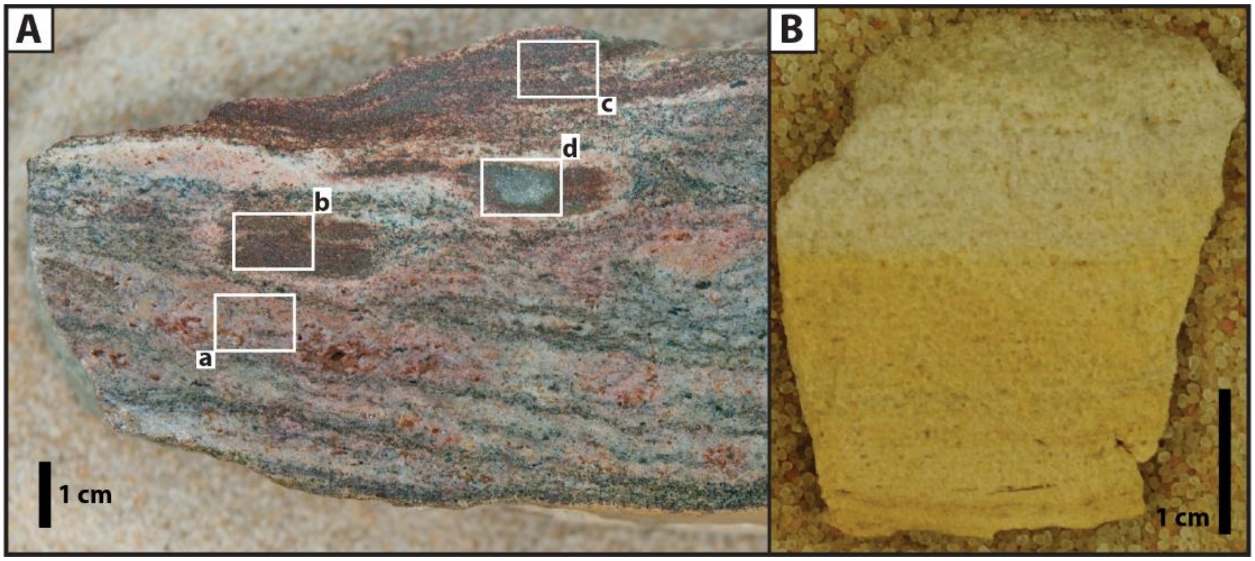

Figure 5. Hand samples from Granddad Bluff, City of La Crosse. **A)** +3.95 m, location of subsamples denoted by lowercase letters and white squares. **B)** –0.65 m.

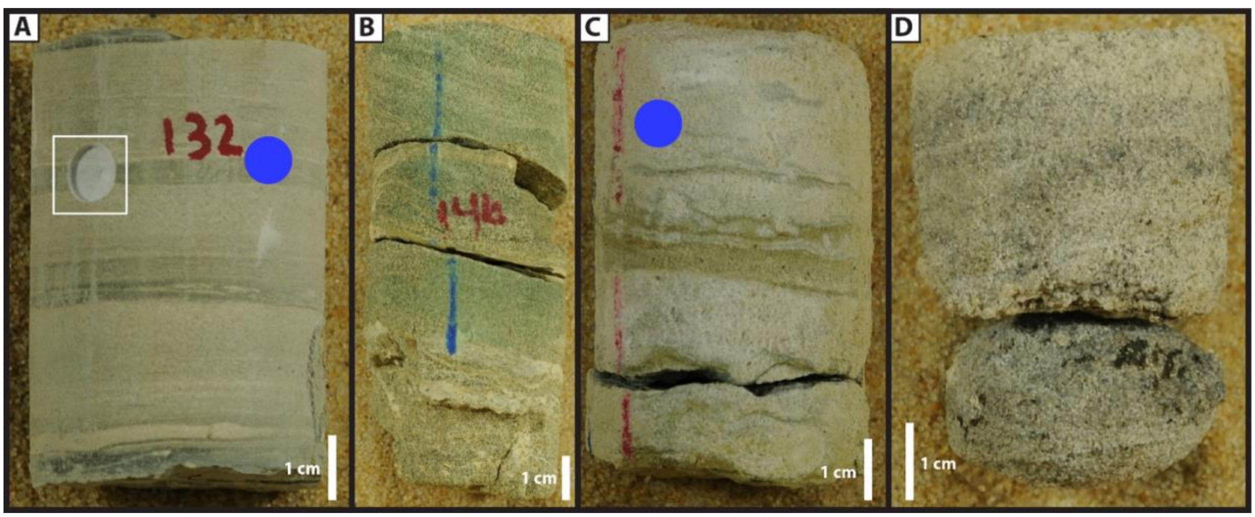

Figure 6. Pictures of sampled intervals of drill core WGNHS Belisle Quarry. Drill hole from sample powder collection is noted by white square, blue circles denote location of pXRF analysis. **A)** 132.0 ft; **B)** 146.0 ft; **C)** 182.0 ft; **D)** 199.0 ft, note dark mineralized material on lower right side of sample.

Figure 7. Drill core WGNHS Arcadia Quarry. **A)** Core photograph. Note that the Wonewoc–Tunnel City contact is not clear; tentatively placed at unconformity overlying coarse-grained non-glauconitic sandstone.
B) Vials of sample powder from this interval (not all powders were analyzed in this study).

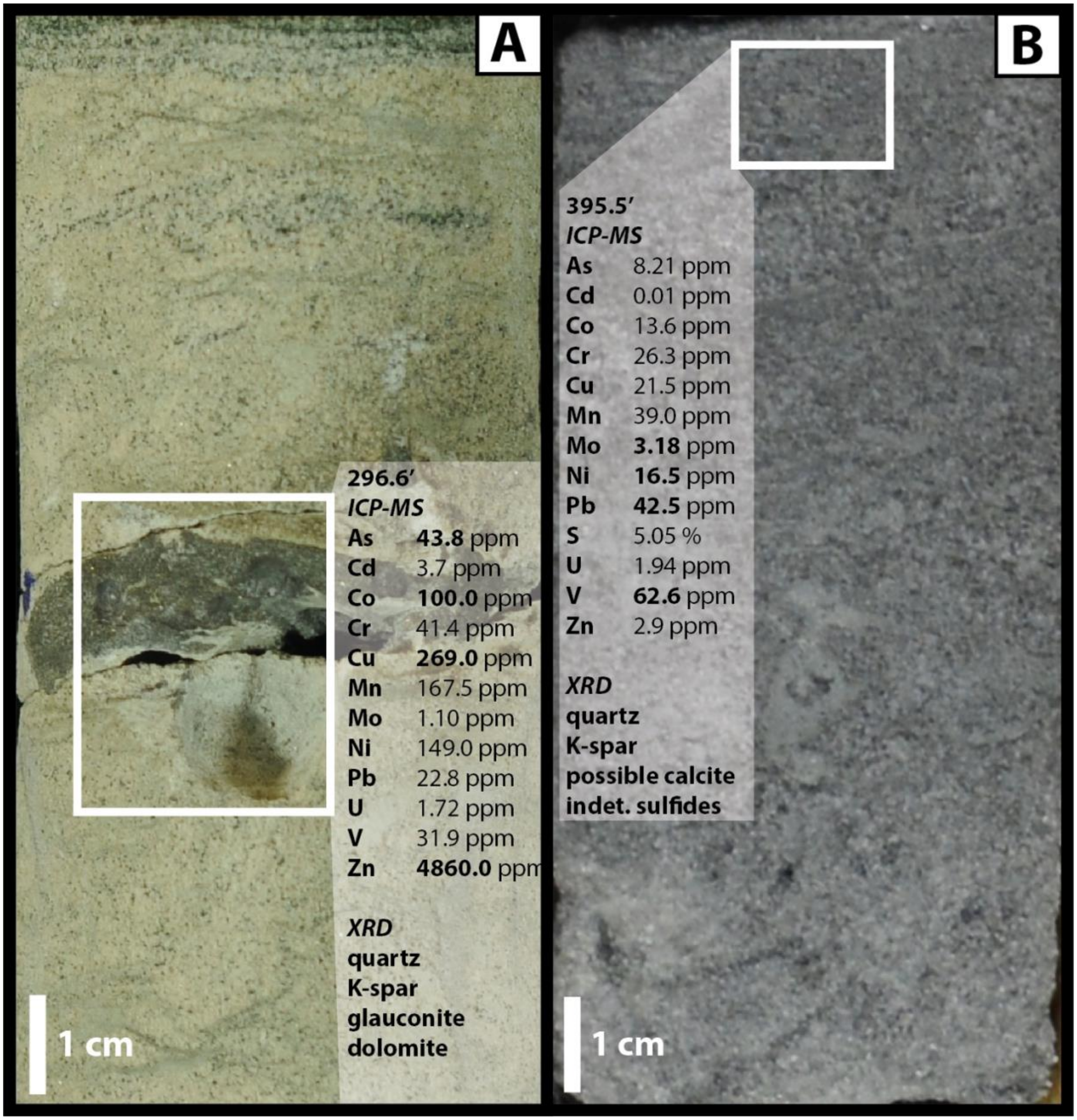

Figure 8. Select drill core samples from WGNHS Arcadia Quarry core showing results of ICP-MS and XRD analysis. White boxes indicate the area from which sample powders were collected. Elemental concentrations in bold are the highest observed in this study for each rock unit (data also presented in table 5).

A) Tunnel City, 296.6 ft; powder collected from both glauconitic quartz sandstone matrix and sulfide nodule. This is an example of how identification of the sulfide was difficult because of the strong quartz signal in XRD (appendix E). The zinc concentration (4860 ppm) was the highest observed in this study and well above the second highest observed (31.4 ppm), suggesting the sulfide nodule is likely sphalerite (ZnS_2) and therefore MVT in origin.

B) Wonewoc, 395.5 ft; powder collected from dark gray, bioturbated sulfide-cemented quartz sandstone. Although both pyrite and sphalerite are possibly present in this sample (appendix E), the strong quartz signal in XRD analysis of this sandstone made identification of these sulfides indeterminate.

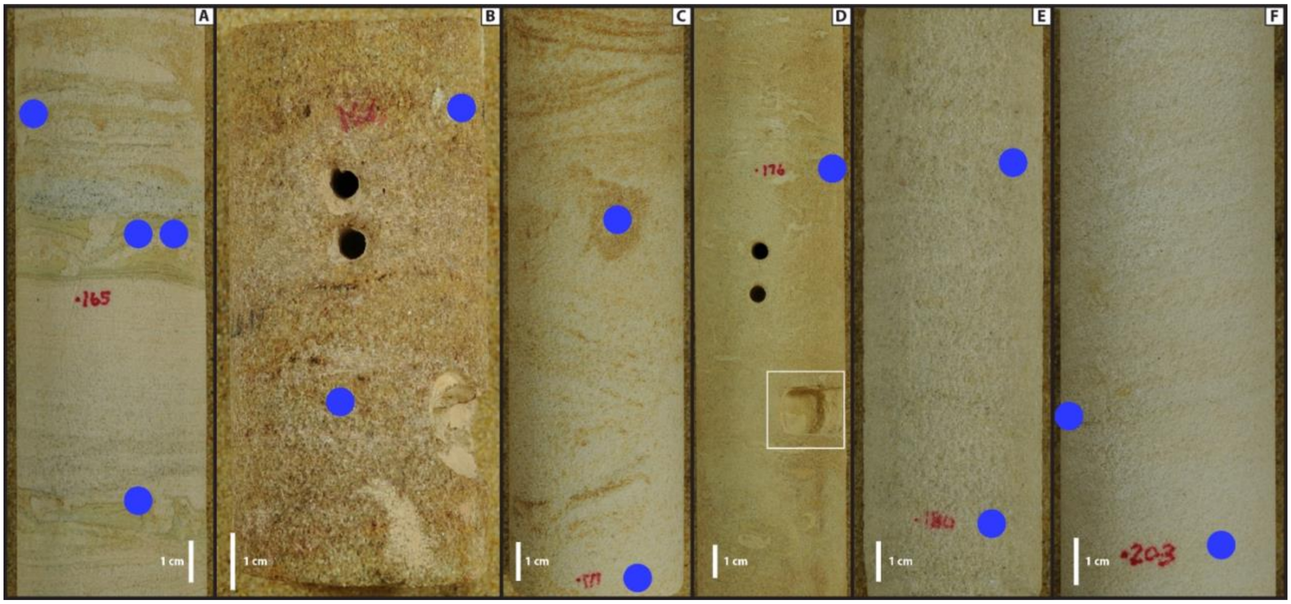

Figure 9. Sampled intervals of drill core WGNHS Triemstra Quarry. Blue circles represent location of pXRF analyses, white square represents powder collected for ICP-MS/XRD analysis, small drill holes represent sampling from a different study. **A)** 165.0 ft; **B)** 166.0 ft; **C)** 171.0 ft; **D)** 176.0 ft; **E)** 180.0 ft; **F)** 202.9 ft.

Discussion

Direct comparison between the different data types is difficult because of the sample type and scale of sampling. Analyses of core were directed at discrete ~1 cm^2 spots and undertaken at a resolution of 0.1–1.0 ft, hand samples were collected at the decimeter to meter scale, and cuttings are essentially a "grab sample" of material collected by drillers for each 5-ft interval encountered while drilling (figs. 5–9; appendix B). In general, higher concentrations for trace metals were observed in core and hand samples than in cuttings; this is most likely an artifact of the sampling resolution inherent to sample type, as well as the sampling method. Drill cuttings are commonly biased coarse-grained as a result of the preferential removal of fines during the drilling process. Another complication is that outcrops are far more weathered compared to subsurface samples. This was most obvious in the Wonewoc, which in most cases could be removed from the outcrops in the west-central region with your bare hand, but was cemented in core. This suggests that some cements, including sulfide minerals, have been removed by weathering and oxidation at earth's surface in this region. In the case of the Driftless Area, this weathering and oxidation has likely been occurring for millions of years. Furthermore, uncertainty in where the Wonewoc–Tunnel City contact should be placed in some successions (for example, Site 5, WGNHS Arcadia Quarry; see fig. 7) complicates attempts to treat these units separately in some cases. Regardless, our observations indicate that both geologic units contain sulfides that host a variety of trace metals (tables 4 and 5).

Elemental analysis by pXRF provided a useful first look at the geochemistry of Wonewoc–Tunnel City interval rocks. Furthermore, for core and hand samples, the ability to collect elemental data at discrete ~1 cm^2 spots using pXRF allowed us to better observe, and characterize, the centimeter-scale lithologic, mineralogical, and trace metal variations present in our samples. In general, sulfur, arsenic, lead, and zinc concentrations as measured by pXRF were highest in Wonewoc–Tunnel City Group contact interval rocks in the west-central region, lower in the southwest region, and lowest in south-central region samples. Furthermore, elemental cross-plots to test for MVT relationships or common trace constituents show regional differences in the three cores for which this was done. For example, correlations are observed in the plots of sulfur versus iron (r^2 = 0.9252) and sulfur versus arsenic (r^2 = 0.7035) in the west-central region (Wonewoc Formation, Site 5, WGNHS Arcadia Quarry core), suggesting the presence of arsenic-bearing pyrite. Conversely, in the southwest region core (Site 13, WGNHS Hwy A #2) we only observed a correlation between aluminum and arsenic (r^2 = 0.4877) in the Tunnel City Group, suggesting the presence of arsenic-bearing glauconite and/or some other clay mineral. No correlations were observed in elemental cross plots for the south-central core (Site 17, WGNHS Triemstra Quarry). A lack of correlation ($r^2 < 0.3$) between sulfur and zinc/lead suggests that at least some of these sulfides are not MVT-related, but rather precipitated from Cambrian seawater or related pore fluids during early diagenesis and/or lithification.

Regardless of region, we observed a common, though not universal, trend that groundwater near or in the Tunnel City and Wonewoc has an inflection in, or increase in water electrical conductivity where data was available (appendix B). More data are needed to investigate this pattern, which may be attributable to a high concentration of dissolved material (for example, trace metals, chloride, and/or sulfate) entering the borehole within this discrete rock interval. We hypothesize that this would be most pronounced in wells where the water table is at or close to the Wonewoc–Tunnel City contact based on the geochemical and mineralogical data presented in this report. As the water table fluctuates at or near the Wonewoc–Tunnel City contact interval, it would create variable redox conditions that would likely increase the chemical weathering of trace metal-bearing minerals. In both the west-central and south-central regions, the water table is commonly observed near the Wonewoc–Tunnel City contact interval, while in the southwest region the geologic contact is considerably below the water table, such that oxidation expedited by a fluctuating water table is unlikely (see appendix B and fig. 4 for regional geology).

Based on the pXRF and geophysical log observations outlined above (see also appendices A–C), we decided to focus ICP-MS elemental and XRD mineralogical sampling in the west-central region, with some additional sampling of the south-central region core WGNHS Triemstra Quarry for comparison (see results above, and appendices D and E). Further analysis in the southwest region was deemed a lower priority since the Wonewoc–Tunnel City contact interval is well below the water table, and presumably is less likely to contribute metals to increased concentrations of trace metals in groundwater relative to the west-central and south-central regions. The mineralogical analysis undertaken confirmed that the majority of these rocks are (glauconitic) dolomite-cemented quartz sandstones. From the XRD results, pyrite was confidently identified in only one sample (Tunnel City, sample +3.95d at Granddad Bluff; see appendix E and fig. 5). Other sulfide samples that were analyzed for mineralogy came back with uncertain results. While a variety of sulfide minerals are possible (for example pyrite, sphalerite, chalcopyrite, and covellite, which are MVT type minerals), the XRD data obtained should be interpreted with caution because the signal for more abundant minerals, such as quartz, made it difficult to interpret the signals for less abundant minerals. This signal bias may be mitigated in future work by micro-sampling sulfide materials and limiting the incorporation of extraneous rock matrix into the sample (see fig. 8; H. Xu, oral communication, 2016). Although not a focus of this study, it should be noted that a suite of minerals that could form during sulfide alteration were also observed, and these were often associated with sulfides (or indications of sulfides based on XRD analysis; appendix E). These include gypsum, goethite, bernalite, and szomolnokite, all of which were associated with ICP-MS measurements of trace metal enrichment. Future work should look at the trace metal composition of both sulfides and iron oxide minerals, as well as geochemical pathways for trace metals from these different mineral phases to surface and groundwater.

Elemental analysis by ICP-MS indicates that, in general, trace metal enrichment is lower in the south-central region core WGNHS Triemstra Quarry than in samples analyzed from the west-central region although we focused on, and analyzed more samples from the west-central region (see appendix D and figs. 7-9). None of the maximum elemental concentrations obtained by ICP-MS are observed in the south-central region WGNHS Triemstra Quarry core, though the rocks of the Wonewoc–Tunnel City contact interval are almost uniformly enriched in cadmium and cobalt in samples from this core (table 4; appendix D). Furthermore, sulfide minerals were absent in the WGNHS Triemstra Quarry core samples analyzed with the exception of one sample with possible chalcopyrite (appendix E). It is not clear if this relative lack of sulfides is related to depositional environment (fig. 3), distance from the MVT mineral district (fig. 3; Heyl and West, 1982; Symons and others, 2010), post-depositional oxidative weathering, or some combination of the three.

Almost all of the maximum elemental concentrations we observed occur in the west-central region drill core WGNHS Arcadia Quarry, which was the focus of our ICP-MS and XRD analyses (appendices B, D, and E; table 5, figs. 7 and 8). For example, in this core, the highest concentrations in each rock unit for a variety of elements, as determined by ICP-MS, occurred within 10 feet of the (tentatively placed) Wonewoc–Tunnel City contact. The highest measured concentrations included cobalt (94.6 ppm), chromium (54.0 ppm), and copper (645.0 ppm) in the Wonewoc Formation, and chromium (90.6 ppm), lead (49.6 ppm), uranium (4.01 ppm), and vanadium (113.0 ppm) in the Tunnel City Group. The highest concentrations for other trace metals observed in this study were observed within 50 ft of the Wonewoc–Tunnel City contact, associated with or in close proximity to sulfide mineralization (table 5, fig. 8; appendices D and E).

As mentioned above, we noticed that, in general, pXRF trace metal concentrations were higher in drill core than in either well cuttings or hand samples, and, most outcrop samples appeared to have undergone oxidation processes. In contrast, the majority of the rocks in the Wonewoc–Tunnel City contact interval of the WGNHS Arcadia Quarry core were located well below the water table and are primarily dark gray in color suggesting that the minerals present are in reduced phases (see core pictures in fig. 7 and appendix B, and compare to the Wonewoc in fig. 5B; note also that a number of possible sulfides were identified as shown in table 5 and appendix E). We suggest that the preponderance of reduced-phase mineralogies in the Wonewoc Formation as observed in this core (Arcadia Quarry) is relatively rare for this region or may be the result of a set of hydrogeologic factors specific to this site. This core was drilled upon a topographic high (Arcadia Ridge), and the core samples from the center of this ridge are relatively isolated from any present-day oxidation processes, and presumably any that may have occurred in the past as well. Indeed, the only oxidation we observed in the Wonewoc–Tunnel City contact interval in this core is at a depth of approximately 314 ft, at the top of the Birkmose Member of the Tunnel City Group; this lithologic change would be a likely conduit for horizontal groundwater flow and the introduction of oxygen (see color change in fig. 7; Swanson, 2007; Swanson and others, 2006). Interestingly, this depth is approximately 150 ft below the water table, suggesting that oxidation can occur independent of the water table. Our observations during recent mapping are that oxidized mineralogies in the Wonewoc Formation are more common in west-central Wisconsin where these rocks are close to the surface (Zambito, Haas, and Batten, 2017; Zambito, Mauel, and others, 2018). However, sulfides do occur in proximity to oxides in outcrop (see Granddad Bluff discussion below) and we document in this report that trace metals are present in both the Wonewoc Formation and Tunnel City Group and are associated with both oxidized and reduced mineral phases (appendices D and E).

The samples from Granddad Bluff are a good example of trace metal enrichment in both oxidized and reduced mineral phases, and they show centimeter-scale geochemical and mineralogical variation. As seen in figure 5 and appendix E, subsamples from +3.95 m come from a dolomite and pyrite cemented glauconitic quartz sandstone that varies in color from greenish white to pinkish red (the latter suggests the presence of iron-oxides). All subsamples studied are relatively enriched in manganese, molybdenum, and nickel compared to other Tunnel City Group samples analyzed in this study by ICP-MS. Furthermore, some of these subsamples also show relative enrichments in arsenic, cobalt, copper, lead, uranium and zinc (appendix D). Indeed, the highest molybdenum value found in this study by ICP-MS analysis is 5.47 ppm and comes from subsample B (fig. 5A). The presence of enrichments in both lead and zinc associated with pyrite may indicate an MVT origin. These observations are of further note because they come from an outcrop along a roadcut. Although this outcrop was likely freshly exposed during road construction and/or subsequent maintenance, the road is along Granddad Bluff and presumably this bluff has been undergoing physical and chemical weathering in an oxidizing environment for a substantial period of time (millions of years?). Conversely, the Wonewoc Formation samples from this same outcrop have low concentrations for most trace metals relative to concentrations measured in other Wonewoc samples analyzed in this study by ICP-MS. However, relative enrichments in lead, uranium, and vanadium are observed in samples from this site (table 5). This may suggest that oxidation potential for these rocks is related to grain size and cementation, such that cleaner quartz sandstones of the Wonewoc Formation are more easily oxidized than the dolomite cemented, glauconitic sandstones of the Tunnel City Group. Oxidation potential may also be related to the size of sulfide crystals; subsample D of sample +3.95 at Granddad Bluff is a pyrite nodule displaying an oxidation halo (fig. 5A), whereas the sulfides in sample 395.5 ft in the WGNHS Arcadia Quarry core are finer grained and disseminated in a coarse-grained sandstone (fig. 8). Finally, it should be noted that this outcrop is directly west of an area where water quality issues have been observed in numerous private wells (table 1), and provides further evidence that the rocks of the Tunnel City–Wonewoc contact interval are a potential natural source of the trace metal concentrations observed in groundwater.

Conclusions, future work, and remaining questions

Trace metal-bearing sulfide minerals are documented in both the Wonewoc Formation and Tunnel City Group, and are most abundant in west-central Wisconsin. The regional geochemical and mineralogical database presented in this report provides evidence that the rocks of the Wonewoc–Tunnel City contact interval in west-central Wisconsin are a potential natural source of high concentrations of trace metals in process-water ponds at industrial sand mines and in groundwater in some private wells. Given the association between low and/or fluctuating pH and elevated trace metal concentration (tables 1 and 2), the most likely source of high trace-metal concentrations in surface and groundwater is through the oxidation of the observed trace-metal-bearing sulfides. However, we have also observed that the presence of sulfides is spatially variable, both at the scale of hand samples (fig. 5) and that of landscape geomorphologic features such as large ridges (see discussion of drill core WGNHS

Arcadia Quarry above, figs. 7 and 8; further discussion in Zambito, Mauel, and others, 2018). This suggests that sulfide mineralization in these rocks is essentially site-specific or is influenced by a combination of hydrogeologic factors not fully understood. Furthermore, we also note trace-metal enrichment associated with the mineral glauconite and with iron oxide mineralization. While we have focused in this report on trace metal input to water via sulfide oxidation, future studies should also consider glauconite and iron oxide alteration and any resultant trace metal release.

Future work could also focus on isolating sulfide materials for geochemical and mineralogical analysis. In the XRD mineralogical analysis performed in this study, the mineralogy of sulfides could not be confidently identified if the sample was so quartz-dominated (sandstone) that the quartz signal inhibited confident interpretation of the sulfide signal (appendix B). Once sulfide minerals are isolated for mineralogical analysis, an additional step would be to undertake sulfur isotopic analysis to determine the source of the sulfides (MVT vs. Cambrian seawater). With a better understanding of sulfide origin, one could better predict where sulfides will be encountered or had originally occurred prior to weathering. In addition to sulfide origin, systematic differences in sulfide trace metal composition related to origin should also be investigated. For example, one could test if MVT sulfides are enriched in different or the same trace metals as Cambrian seawater-derived sulfides.

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