

**Geochemical, mineralogical and structural characterization of the
Tyler Formation and Ironwood Iron Formation,
Gogebic Range, Wisconsin**

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by

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Overview

The purpose of this report is to provide baseline geologic information about the physical and chemical character of the Ironwood Iron Formation, a potential mining target, and the overlying shale or slate, known as the Tyler Formation, in the Gogebic Range of Iron and Ashland Counties, Wisconsin. These rock units have been known to geologists since the late 1800's, and there is a considerable body of scientific literature on their outcrop-scale characteristics, summarized in the accompanying annotated bibliography by Tom Fitz of Northland College (Ashland, Wisconsin). This report will review the existing information in brief but focus primarily on new geochemical analyses done in the geology department at Lawrence University (Appleton, Wisconsin).

Introduction: Geologic context

The Tyler Formation and Ironwood Iron Formation are tilted, metamorphosed sedimentary rock strata exposed in the Gogebic Range of northwestern-most Wisconsin, an ancient mountain belt formed by Precambrian tectonic events in the Lake Superior region. These rocks were originally deposited in a shallow continental shelf setting about 1.9 billion years ago, in early Proterozoic time, when free oxygen (O₂) first began to accumulate in Earth's atmosphere. At this time, the shallow oceans contained some dissolved oxygen, at least on a seasonal basis when photosynthesizing microorganisms released oxygen into the water. Deeper waters tended to contain little or no oxygen, but were sometimes aerated by turbulent mixing during storm events. The geochemistry of the Ironwood and Tyler Formations reflects their deposition in waters that fluctuated between oxidizing and reducing conditions. In particular, the level of oxygen dictated whether iron in the rocks occurs as oxide minerals (magnetite and hematite) or sulfide minerals (primarily pyrite). This important distinction is discussed at length in the section on Geochemical Analyses below.

As a result of two ancient tectonic events -- the Penokean Orogeny and the Midcontinent Rift (approximately 1.85 and 1.1 billion years ago, respectively) -- the originally horizontal rocks were folded and faulted and now dip, or tilt, 55-70° toward the north-northwest (Bjornerud and Cannon, 2011). As shown in Figure 1, a geologic map of the area around Mellen (from Cannon et al., 2008), the Ironwood and Tyler strata strike, or trend, east-northeast, with the Ironwood formation (red on map) exposed in only a relatively

narrow band compared with the larger near-surface exposure of the thicker overlying Tyler formation (blue) to the northwest. The present topographic expression and outcrop extent of these rock units also reflect hundreds of millions of years of erosion, most recently by glaciers of the Pleistocene epoch. The Ironwood Formation is a relatively hard, resistant unit and forms prominent ridges including Mount Whittlesey, the highest bedrock peak in Wisconsin. In contrast, the Tyler Formation, especially the lowermost part, is soft and easily eroded and is not well exposed because it tends to occur in low areas where it is obscured by vegetation and wetlands.

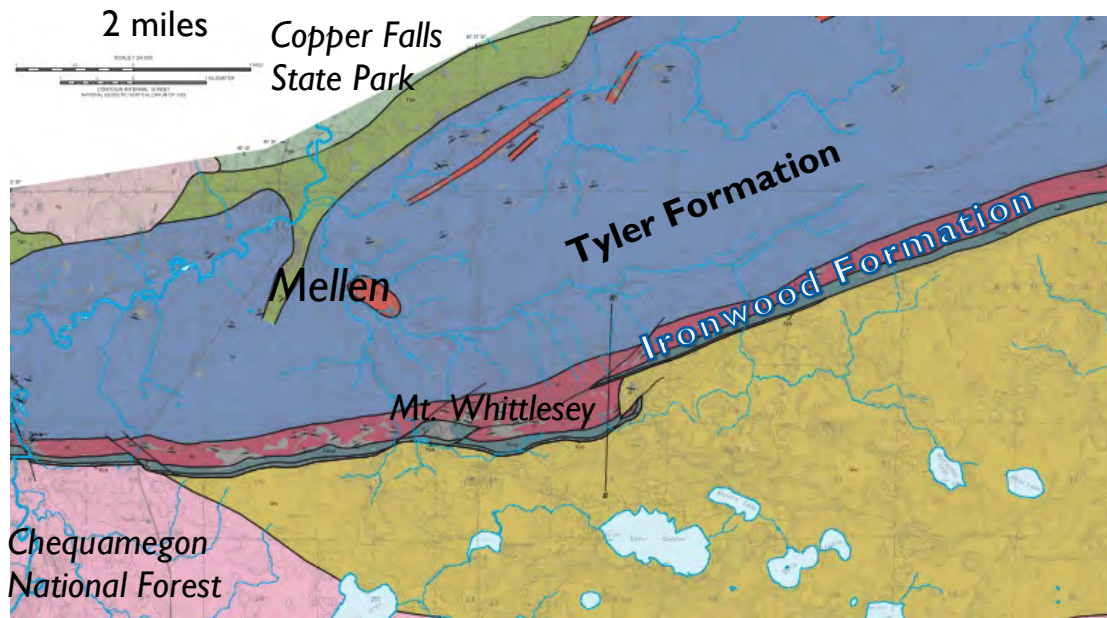


Figure 1. Bedrock geologic map of the Mellen, WI area (detail from map by Cannon et al., 2008, USGS Prof. Paper no. 1730). Colors indicate where different rock units reach the surface. Blue = Tyler Formation; Red/Maroon = Ironwood Iron Fm.; Grey = Palms Quartzite; Pink and gold in southern part of map: Archean rocks (Puritan Quartz Monzonite and Ramsay Lake Fm.); Pale pink, green in northern part of map, and orange areas within Tyler Formation: Igneous rocks related to the Mid-continent rift.

Stratigraphy of the Gogebic range

Open pit iron mining would involve blasting and removal primarily of the lower Tyler Formation together with the target Ironwood Formation, but the larger stratigraphic context of these units (Figure 2) is also relevant to understanding the potential impacts of mining. The oldest rocks in the region are exposed on the southern part of the map in Figure 1. These are late Archean rocks, approximately 2.6 billion years old, which include a weakly deformed granitic massif called the Puritan Quartz Monzonite (pink on map) and a complex suite of volcanic rocks ranging from basalt to andesite, known as the Ramsay Lake Formation (gold).

The Puritan Batholith is a hard, crystalline, chemically inert and quite impermeable rock composed mainly of alkali feldspar, quartz and biotite. The Ramsay Lake Formation is more schistose (banded or foliated due to deformation) and has scattered quartz veins containing minor amounts of pyrite and other sulfide minerals. This unit is also quite massive and impermeable (Schmidt, 1976).

Overlying the Archean rocks, above an unconformity surface that represents almost 700 million years of erosion, is a unit called the Palms Quartzite, ca. 130 m (430 ft) thick, a metamorphosed sandstone with some interbedded clay-rich layers, thought to have been laid down in a near-shore or intertidal environment by the same ancient sea that deposited the overlying Ironwood Formations (Ojakangas 1983). Mineralogically, this unit consists mainly of quartz and fine-grained micas, primarily muscovite.

The ca. 150 m (500 ft) thick Ironwood Formation contains sedimentary structures that suggest somewhat deeper, but fluctuating, water depths, with zones of granular 'ferruginous chert' (jasper) and finer iron-oxide-rich layers alternating with still finer-grained 'ferruginous slate'. The 'cherty' intervals appear to represent agitated waters of the surf zone, while the 'slaty' intervals presumably accumulated in somewhat deeper, quieter water. Based on samples obtained from drilling and underground mining in the early 20th century, Hotchkiss (1919), Aldrich (1929), Huber (1959) and Marsden (1978) describe five subunits, or members, within the Ironwood Formation. Beginning from the lowest, these are the Plymouth (40-46 m; cherty), Yale (14-22 m; slaty), Norrie (34-36 m; cherty), Pence (30-37 m; slaty) and Anvil (16 m; cherty) members (Fig. 2). Owing to discontinuous outcrop, it is not easy to define the boundaries of these units in the field. Also, the zones of potential economic interest as ores do not correspond exactly with the sedimentologically defined subunits. This reflects post-depositional (hydrothermal and metamorphic) processes that affected the local magnetite content of the rock. Marsden identified a "lower ore" zone in the middle Plymouth member and an "upper ore" that occurs primarily in the Norrie, and Pence members, based on a minimum value 20% iron content for taconite ore. The Yale member is notable for a 3 m thick basal layer that is rich in pyrite (iron sulfide). A sample of this layer was obtained for this study from drill core IR-201 at the Wisconsin Geological and Natural History Survey (WGNHS) core repository in Mount Horeb. According to the WGNHS, this core came from just west of Pence WI, ca. 20 km east of the Mellen area. The other Ironwood samples

analyzed for this study came from surface outcrops of the Ironwood Formation in the Mellen area (Figs. 2, 3, and 4a; Table 1).

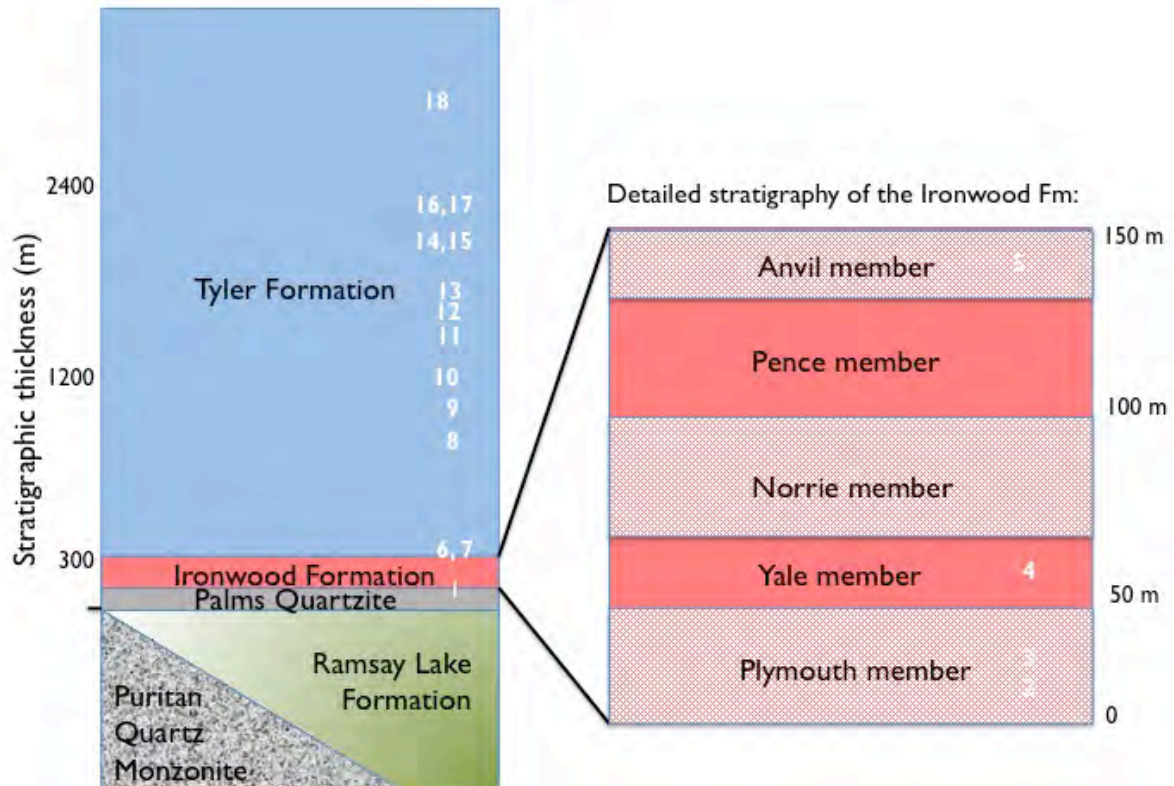
Iron mining in the Gogebic Range in the early twentieth century focused on zones within the upper and lower ores where hydrothermal fluids had locally concentrated iron to 40-65% of the rock mass by preferentially removing silica from the rocks (Huber, 1959). These mines were either shallow surface pits or underground mines that followed bedding planes at a steep pitch. Most of the remaining iron formation in the Gogebic Range is taconite with only 15-30% iron, and would likely be economic only through open pit mining.

The Tyler Formation is nearly 3000 m thick in the Gogebic Range and originated as fine-grained siltstones and mudstones in a deep water setting. It is weakly metamorphosed and variously described in the literature as either a shale or slate. The contact with the underlying Ironwood Formation is not well exposed, and there has been disagreement about whether or not there was uninterrupted sedimentation between the accumulation of the uppermost Ironwood and lowermost Tyler. Based on regional studies of early Proterozoic units in the western Upper Peninsula and northern Wisconsin, Cannon et al. (2008) concluded that there is an unconformity, or erosional gap, between the Ironwood and Tyler Formations, and that the Tyler Formation represents a deeper basin with different water chemistry than that in which the Ironwood Formation accumulated. In particular, the Tyler Formation appears to have accumulated in anoxic to 'euxinic' (sulfidic) waters in which iron combined with sulfur to form pyrite and related minerals, rather than combining with oxygen to form magnetite and hematite as in the Ironwood Formation. The lowermost Tyler formation, known primarily from old drill cores, is especially fine grained and is described by Cannon et al. (2008, Plate 1) as a "black pyritic shale or slate".

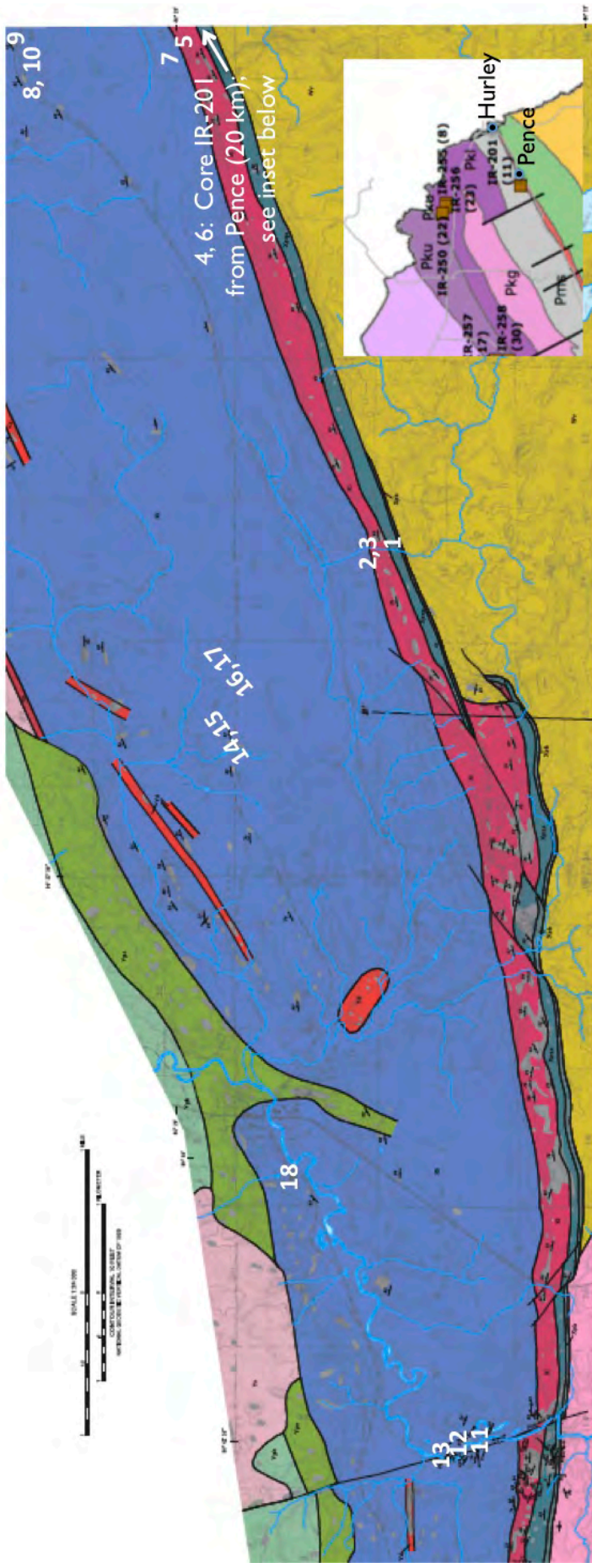
The upper, better exposed parts of the Tyler formation have the sedimentary characteristics of turbidite deposits, formed by distal density currents -- slurries of clay-to silt-sized sediment that travel at high velocity down submarine slopes to the deep ocean floor. Fine, disseminated pyrite occurs in these rocks as well. Figure 4b shows a typical outcrop view of the middle Tyler formation, along the railroad track at Penokee Gap. The orangish weathering reflects oxidation of iron sulfides to form an iron hydroxide mineral, limonite. There are no outcrops of the lowermost Tyler formation, but we were able to obtain one sample from close to the contact with the Ironwood Formation from WGNHS core IR-201.

The other samples analyzed for this study came from surface outcrops at various levels in the Tyler Formation (Figs. 2 and 3; Table 1).

Figure 2. Stratigraphy of the Gogebic Range. White numbers show stratigraphic levels from which samples were collected for geochemical analyses. See Table 1 for more information.



Next page: **Figure 3.** Map showing sample locations. See Table 1 for more information.



Geochemical analyses

Sampling localities: Samples of the Ironwood and Tyler formations were obtained from outcrops in the Mellen area and also from a drill core (#IR-201) stored at the Wisconsin Geological and Natural History Survey. Because samples were collected at different times by different people, they were not initially assigned numbers according to a single scheme. For this report, samples have been renumbered in stratigraphic order. Figures 2 and 3 and Table I summarize the sources and stratigraphic positions of the samples analyzed.

Figure 4. The Ironwood and Tyler Formations in outcrop



	<p>a. Outcrop of magnetite-rich layers alternating with chert in the Ironwood Iron Formation near the top of Mount Whittlesey.</p>
	<p>b. Outcrop of the Tyler Formation along the railroad grade at Penokee Gap (source of Sample #11 in this study). Orange color of weathered surfaces is caused by the mineral limonite ($\text{FeO}(\text{OH}) \cdot n\text{H}_2\text{O}$), which typically forms by oxidation of iron sulfide minerals like pyrite.</p>

Table I. Samples collected for geochemical analysis, listed stratigraphically from lowest.

Final sample #	Temporary LU Sample ID	Original sample # if different	Collector	Location	Stratigraphic level
1	Ironwood - A	11-12-5	Tom Fitz	Lake Drive/Ballou Cr	Lower Ironwood or uppermost Palms Fm
2	Ironwood - B	11-12-6	Tom Fitz	Lake Drive/Ballou Cr	Lower Ironwood (Plymouth member)
3	Ironwood - C	11-12-7	Tom Fitz	Lake Drive/Ballou Cr	Lower Ironwood (Plymouth member)
4	Pyritic Ironwood	IR-201-977	M. Bjornerud	Drill core taken near Pence - WGNHS	Middle Ironwood (Yale member)
5	Ian #4		Ian Shackelford	Moore Park Road	Upper Ironwood
6	Lowermost Tyler	IR-201-T	M. Bjornerud	Drill core - Pence	Base of Tyler
7	Ian #3		Ian Shackelford	Moore Park Road	Lower Tyler
8	Hwy 77 S		Ian Shackelford	Hwy 77 E of Moore Pk Rd	Lower middle Tyler
9	Hwy 77 N		Ian Shackelford	Hwy 77 E of Moore Pk Rd	Lower middle Tyler
10	Tyler-B	11-12-9	Tom Fitz	Hwy 77 E of Moore Pk Rd	Lower middle Tyler
11	Tyler-MB		M. Bjornerud	RR - Penokee Gap	Middle Tyler
12	Tyler-H		M. Bjornerud	RR - Penokee Gap	Middle Tyler
13	Tyler-I		M. Bjornerud	RR - Penokee Gap	Middle Tyler
14	Tyler-C	11-12-10	Tom Fitz	Hwy 77/Revie Rd	Upper middle Tyler
15	Tyler-D	11-12-11	Tom Fitz	Hwy 77/Revie Rd	Upper middle Tyler
16	Tyler-E	11-12-12	Tom Fitz	Hwy 77/Revie Rd	Upper middle Tyler
17	Tyler-F	11-12-13	Tom Fitz	Hwy 77/Revie Rd	Upper middle Tyler
18	Tyler-A	11-12-3	Tom Fitz	Hwy 77/W Mellen	Upper Tyler

These samples are typical of the Tyler and Ironwood Formations in the area of the proposed mine. Efforts were made to gain access to drill cores taken in the Mellen area by US Steel, and now owned by RGGGS Land and Minerals Ltd, but these were unsuccessful.

Methods of geochemical analysis

In addition to using standard techniques for identifying minerals in hand specimen and microscopic thin section, we analyzed samples from the Ironwood and Tyler Formations with both x-ray fluorescence (XRF) spectroscopy to determine elemental compositions and x-ray diffractometry (XRD) to identify major and minor minerals present in the rocks. XRF spectroscopy is based on the characteristic spectrum of electromagnetic energy that different elements give off when they are bombarded with high-energy electrons. X-ray diffractometry uses the known geometries of the lattices of minerals at the molecular scale to identify minerals present in a particular rock. More technical details about these methods can be found at the websites listed in Appendices A and B.

For both types of analyses, samples were crushed to 125 micron powders following a standard protocol to ensure that the material analyzed was homogeneous and representative of the bulk rock composition:

- 1) A water-cooled rock saw was used to remove weathered surface rinds to ensure that analyses represent bulk compositions of fresh rock. The samples were then cut into ca. 5 cm cubes.
- 2) Samples were placed in a carefully cleaned jaw crusher, yielding gravel-sized rock fragments.
- 3) Samples were sieved to 5/8 cm. Any larger fragments were run through the jaw crusher again and then sieved again.
- 4) Using a SPEX Mixer Mill, the gravel-sized samples were crushed into a fine powder.
- 5) Samples were sieved to 125 μm . Any larger powder was run through the Mixer Mill again and sieved once more.

The XRF analyses for element concentrations were conducted with a Rigaku ZSXMini II wavelength-dispersive XRF at the Lawrence University Geology Department. Technical specifications for this instrument can be found at www.rigaku.com/products/xrf/miniz. This XRF system has been recommended for environmental analyses by the US EPA: www.epa.gov/nrmrl/lrpcd/site/reports/540r06001.html

For all XRF analyses, a 10 g aliquot of each sample was transferred to a plastic cup and sealed with mylar. The scanning chamber of the XRF was filled with helium gas and

sealed. The XRF was standardized for phosphorous and sulfur detection, yielding a precision from 10 to 1000 ppm for those elements. In this mode, results for major elements, usually expressed as oxides (SiO_2 , Fe_2O_3), are somewhat less accurate (on the order of +/-1%), but these were not the primary focus of the analyses.

X-ray diffraction (XRD) analyses for mineral composition were conducted with a Rigaku Ultima-IV powder diffractometer in the Lawrence University Geology Department. Technical specification for the Ultima IV can be found at <http://www.rigaku.com/products/xrd/ultima>. Scans were collected using Cu-K α radiation over a 2θ range from 2° - 70° . Two sets of scans were collected, the first set was a faster 68 minute scan, the second scan was a longer 12-hour scan to increase the resolution for the investigation of minor phases. Mineral phases were identified using the PDXL software package, which allows identification of minerals containing specific elements such as sulfur. For a subset of samples the mineralogy was quantified using the Rietveld whole powder pattern fitting method in the PDXL software. Results of the diffraction data are presented in the next section and the full results are included in Appendix B.

Mineralogy and geochemistry of the Ironwood and Tyler Formations

Ironwood Formation mineralogy: XRD analyses of the Ironwood samples (#1-5) indicates that the primary minerals are magnetite, quartz, biotite/phlogopite (iron-rich mica) and chlorite (a mica-like mineral formed by hydrothermal alteration of biotite). Figure 5 shows a typical XRD diffractogram for the Ironwood Formation (Sample #5).

A notable exception to this mineralogy is the pyritic horizon from the Yale member. A sample from this layer (from WGNHS core IR-201) was analyzed using back-scattered electron (BSE) microscopy by Joseph Skulan, staff scientist in the Geology Museum at the University of Wisconsin-Madison Department of Geoscience. Two of the resulting images are shown in Figure 6. In BSE analysis, which is done by bombarding a thin section with an electron beam in a scanning electron microscope, minerals composed of elements with high atomic numbers show up as bright spots. BSE results for samples from this layer indicate that pyrite constitutes up to 20% of the rock volume (J. Skulan, email communication, 4 April 2012). All of the diffractograms for the Ironwood samples are included in Appendix B.

Figure 5. X-ray diffractogram for Ironwood Fm sample #5. Horizontal axis is scanning angle 2θ .

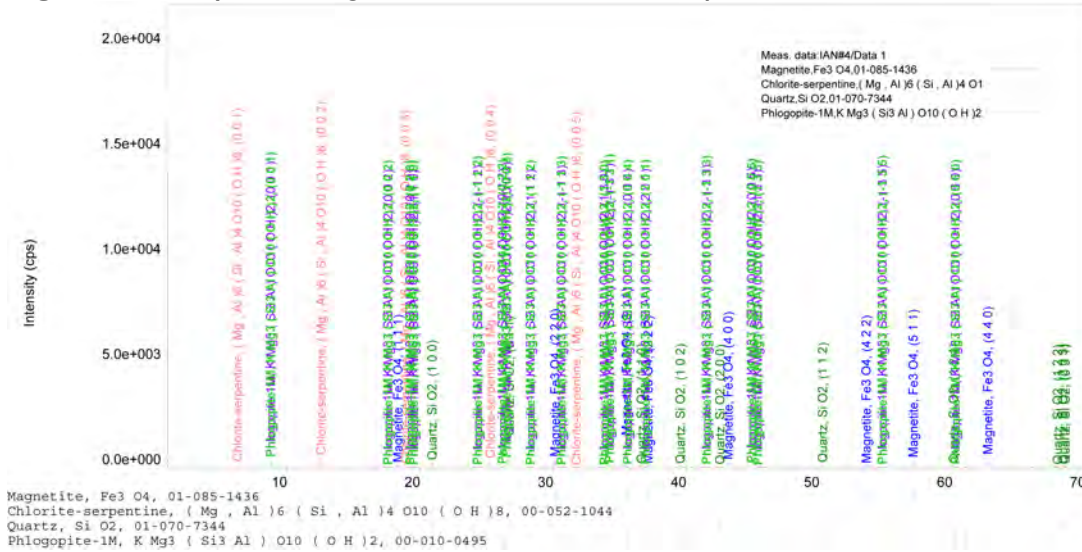
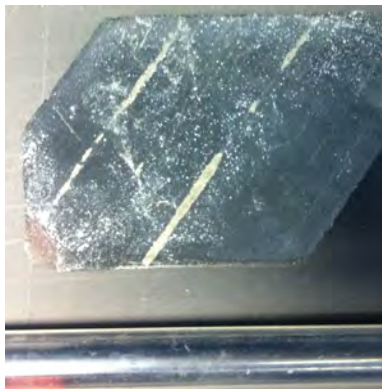
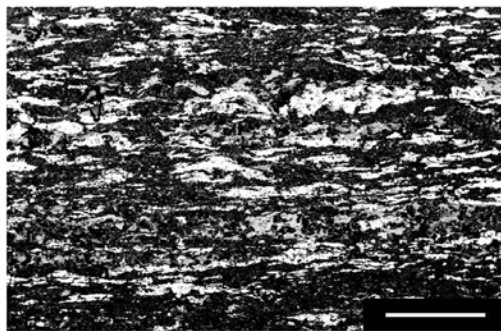


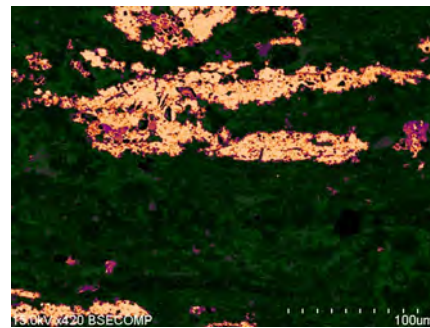
Figure 6. Images of pyrite-rich layer within Yale Member of Ironwood Formation, from drill core IR-201 (Wisconsin Geological and Natural History Survey Core Repository). a) Photograph of small section of core; b) and c) Backscattered electron (BSE) micrographs, courtesy J. Skulan, UW-Madison.



a. Pyritic bands in slaty iron formation; pen at bottom indicates scale



b. Grey-scale BSE image of core sample; lightest patches are pyrite; silicate minerals (quartz, bitoite) take up most of remaining field of view. Scale bar is 100 microns.



c. False color BSE image of same sample at slightly higher magnification. Orange: Pyrite; Pink: Apatite (a phosphate mineral); Dark: Silicates. Scale bar is 100 microns.

Tyler Formation mineralogy: The Tyler formation is very fine-grained and in most samples, few minerals can be seen at the hand specimen scale. Exceptions include layers in the middle and upper Tyler with sand-sized quartz grains and, at all stratigraphic levels, scattered pyrite crystals 2-4 mm in diameter (Figure 7a). In thin section, the silhouettes of pyrite cubes are readily seen (Figure 7b), and finer pyrite is disseminated throughout the rock mass. XRD analyses of Tyler samples (#6-18) in exploratory mode show that the primary minerals, found in all Tyler samples, are quartz, muscovite or phengite ('white' micas), and chlorite (Figure 8a). Major minerals found in some, but not all, of the samples include magnetite, sodium feldspar, and siderite (iron carbonate). Notably, only two samples (13 and 14) contained detectable amounts of other carbonate minerals (ferroan [iron-rich] dolomite).

All of the Tyler samples were found to have some pyrite and/or other sulfide minerals present as secondary phases (Figure 8b; Table 2). For two samples (14 and 17), the Rietveld fitting method showed that the pyrite content is about 2% by weight. In other samples, sulfide content is close to the detection limit (1%), but consistent with the elemental sulfur content determined by XRF (next section). The iron sulfides pyrrhotite, mackinawite, greigite, troilite, and other unnamed species are probably alteration products of original pyrite. Although we attempted to remove weathering rinds from the samples, many outcrops have been at the surface since the end of the ice age and are deeply weathered.

Figure 7. Pyrite in the Tyler Formation in a) hand specimen and b) thin section (plane polarized light). In (a), irregular pyrite crystals can be seen inside and to the left of the black circle, in a relatively coarse layer in the Tyler Fm. In (b), field of view is about 5 mm across. Black pyrite crystals can be seen at lower right and also in reddish vein (stained by oxidation) near top. Finer dark material throughout sample may also be pyrite.

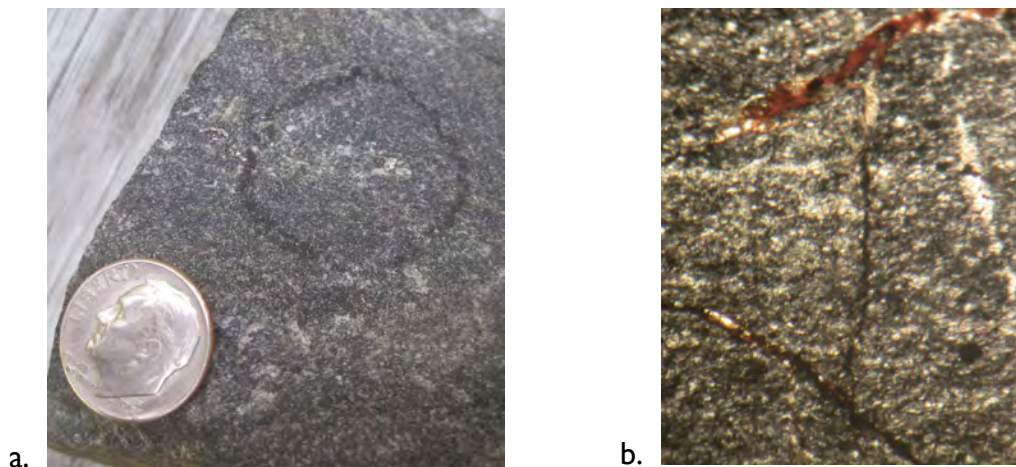
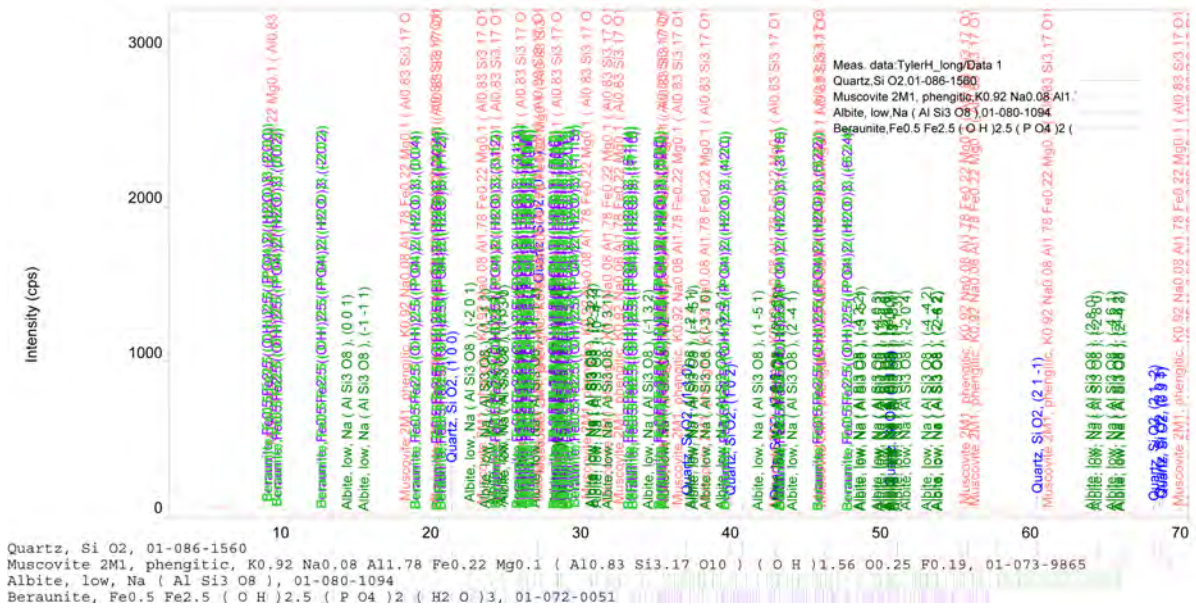
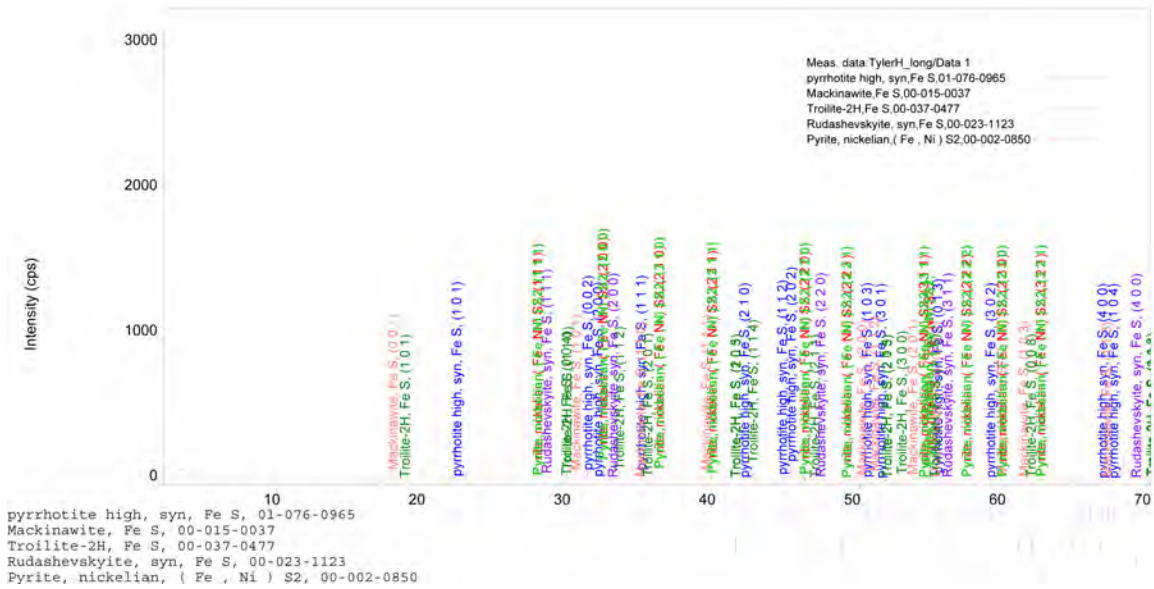


Figure 8. X-ray diffractograms for Tyler Fm sample #12. Horizontal axis is scanning angle 2θ.



a. Major minerals in Tyler Formation Sample #12



b. Iron sulfide minerals detected in Tyler Formation Sample #12

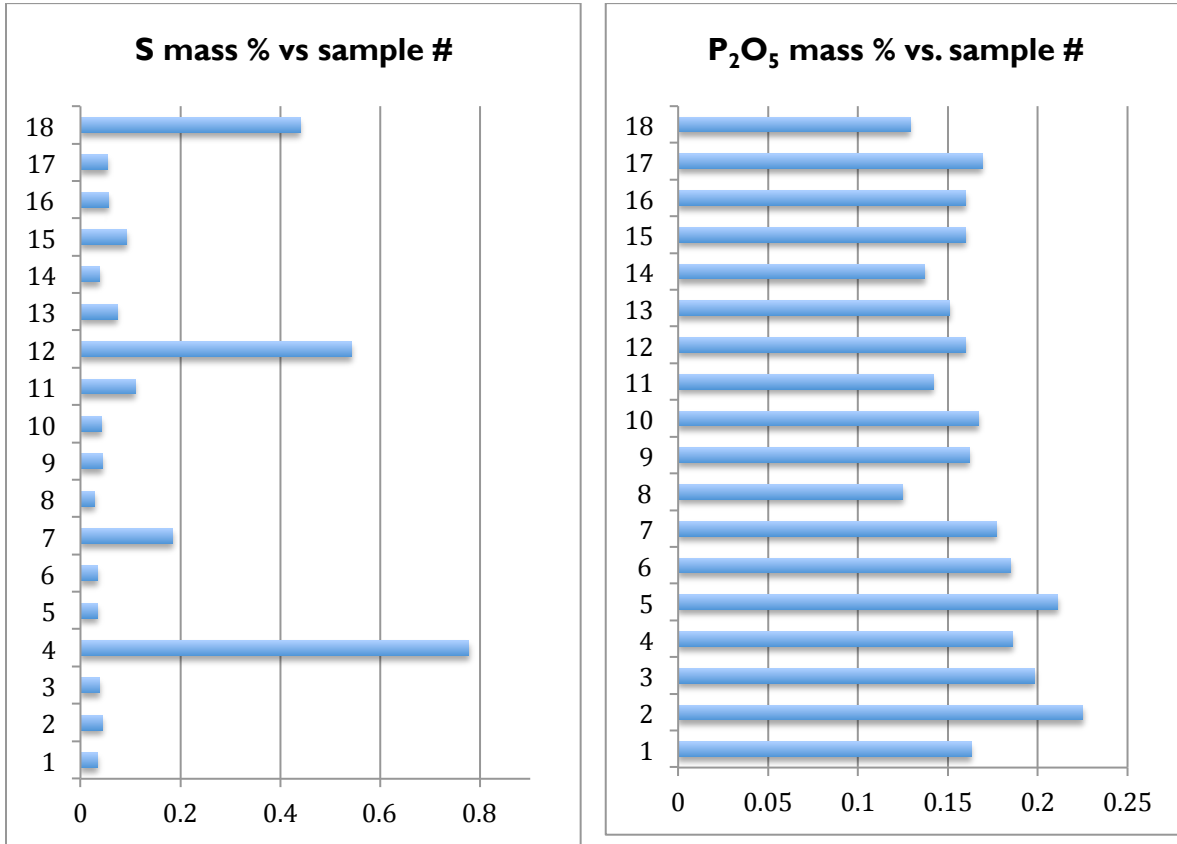
Table 2. Sulfide minerals detected in more than one sample of the Tyler formation.

Mineral name	Formula	Samples in which found
Pyrite/Marcasite	FeS ₂	11, 12, 14, 15, 16, 17, 18
Pyrrhotite	FeS	10, 11, 12, 14, 15, 17
Mackinawite	FeS	12, 15, 16, 17, 18
Greigite	Fe ₃ S ₄	9, 13, 15, 16
Other iron sulfide	Fe ₃ S; Fe ₉ S ₁₁	13, 14, 17
Troilite	2HFeS	11, 15, 16, 18
Metacinnabar	HgSe _{0.6} S _{0.4}	6, 16

Elemental (XRF) analyses of Ironwood and Tyler Formations. The results of the XRF analyses for all samples are given in Appendix A. In the Ironwood samples, SiO₂, Fe₂O₃, and Al₂O₃, in that order, are the three most abundant elements (as oxides) and together make up 70-91% of the rock by mass. Fe₂O₃ content ranges from 5 to 40 mass percent with an average of 23%, or about 16% pure Fe. (Most of the iron in the Ironwood Fm. occurs as magnetite -- Fe₃O₄ -- but it is conventional to report Fe content as Fe₂O₃). SiO₂, Al₂O₃ and Fe₂O₃ are also the most abundant elements in the Tyler Formation, but, unsurprisingly, iron content is typically lower than in the Ironwood and ranks third in abundance.

Sulfur and phosphorous content in both the Ironwood and Tyler Formations were measured to a precision of a few ppm. The results are shown in Figures 9a and b and also reported in Appendix A. In the two formations, elemental sulfur content ranges from 0.034 to 0.777 mass percent, with an average of 0.148. Phosphorous content (as P₂O₅) was also significant and surprisingly consistent across all the samples, with an average of 0.167 mass percent. Given the great volume of waste rock from the Ironwood and Tyler Formations that would be generated in an open pit mine (see next section), a large amount of both S and P could be oxidized and mobilized via interaction with air and water.

Figure 9. Sulfur (S) and phosphate (P_2O_5) content of samples from the Ironwood and Tyler Formations from XRF analyses. Samples are plotted by number in stratigraphic order (1-5= Ironwood; 6-18 = Tyler). Horizontal axes have different ranges in the plots.



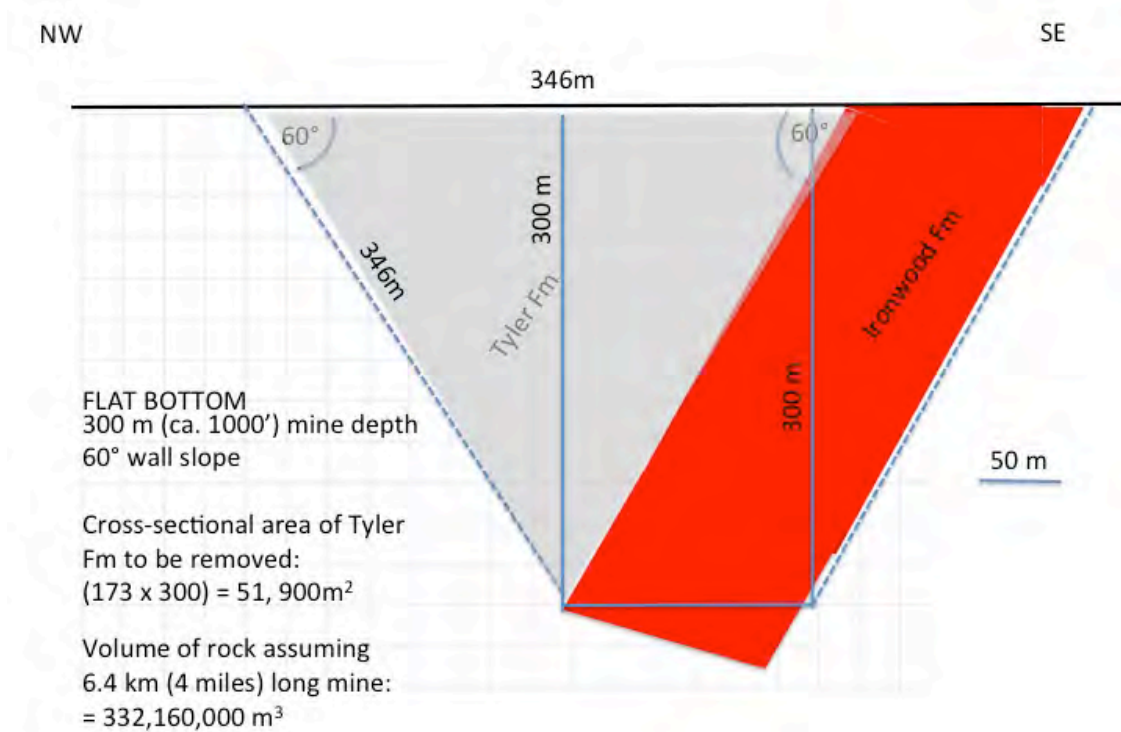
Estimates of volume of waste rock from an open pit mine in the Ironwood Fm.

Because of the steep (ca. 60°) dip of the strata in the Gogebic Range, a large amount of the overlying Tyler Formation would have to be blasted and removed for an open pit mine in the Ironwood Formation. Table 3 and Figure 10 show the basis for simple estimates of the minimum amount of waste rock that would be generated from the Tyler Formation for a mine 200 or 300 m (650 or 1000 feet) deep and 6.4 km (4 miles) long. These estimates are conservative because 1) they are based on uninterrupted, and unrealistically steep, mine wall slopes (the walls would actually need to be benched for stability; see next section) and 2) they do not include the volume of waste rock from the Ironwood Formation, which could be one-third to one-half the total amount of the Ironwood removed (Marsden, 1978).

Table 3. Estimates of volume of waste rock from Tyler Fm for different mine geometries

Mine Depth	Wall slope	Area of waste rock from Tyler Fm	Length	Total volume of waste rock from Tyler Fm
200 m (ca. 650')	60°	23,000 m ²	6400 m (4 miles)	147,200,000 m ³
200 m (ca. 650')	45°	30,000 m ²	6400 m (4 miles)	192,000,000 m ³
300 m (ca. 1000')	60°	51,900 m ²	6400 m (4 miles)	332,160,000 m ³

Figure 10. Scaled cross section illustrating amount of Tyler Formation that would need to be removed for a 300 m deep mine. Dashed line shows mine profile with 60° walls.



Geotechnical considerations

The natural outcrop tendencies of the Ironwood and Tyler Formations reflect the relative strength and durability of the two rock units. The Ironwood, especially the cherty intervals, forms resistant outcrops, while the Tyler is generally a recessive unit. It seems reasonable to consider the strongest parts of the Ironwood formation comparable to quartzite in geotechnical properties, and the Tyler formation comparable to other shales and slates. Table 4 lists typical physical properties for these rock types (Waltham, 2002).

Table 4. Physical properties of rock types similar to the Ironwood and Tyler Fms.

Rock type	Dry unconfined compressive strength range (MPa)	Average dry unconfined compressive strength (MPa)	Tensile strength (MPa)	Density (g/cm³)
Quartzite	150-300	200	20	2.7
Shale	5-30	20	0.5	2.3
Slate	20-250	90	10	2.7

Using these values, and the assumption that the Ironwood Formation is about 20% magnetite, which has a density of 5.15 g/cm³, there would be no danger of exceeding the unconfined compressive strength of the rock even at the base of a 300 m mine. The vertical load would be equal to $\rho g h$, where ρ is rock density (ca. 3.19 g/cm³ or 3190 kg/m³), g the acceleration due to gravity (9.8 m/s²) and h the depth (and 1 Pa = 1 kg/m s²). In contrast, if the lower values for shale are used as representative of the Tyler Formation, the unconfined compressive strength of the rock would be exceeded at 221 m. Realistically, however, the mine walls would be benched for stability. For shales and other easily weathered rocks, Waltham (2002) recommends slopes of 25°-40° and no unbroken heights greater than 20 m with similarly spaced benches. This would make the width of a 300 m deep open pit mine at least 800 m and make the volume of Tyler Formation that would have to be removed considerably greater than that shown in Fig 10.

Descriptions and cross sections of early twentieth century mines also provide insight into the physical characteristics of the Tyler Formation (Hotchkiss, 1919; Aldrich, 1929; Huber, 1959). These early mines were principally local, underground mines that targeted high-grade ores in the upper Ironwood Formation, yet the Tyler Formation was consistently avoided in excavating the mine shafts, presumably because of its low strength. In some cases, such as the Plummer Mine, the shaft was actually dug in the underlying Palms Quartzite (Information plaque at Plummer Mine site near Pence). This suggests that the walls of a deep open pit mine in the Tyler Formation may be difficult to stabilize without extensive engineering.

Other geotechnical considerations specific to the Gogebic Range include 1) the likelihood of dip-slope failure on the high (southeast) wall of the mine, where the mine walls would likely be cut parallel to the bedding planes (Fig. 10); and 2) the fact that virtually the entire mine would be below the water table. With a hydrostatic pressure gradient of 9.8 MPa/km ($= \rho_{\text{water}} g$), there would be high pore pressures (ca. 3 MPa) in the lower parts of a 300 m deep mine. Although the pore pressure values would probably not exceed the tensile strength of the rocks, they could lead to rock failure by causing the horizontal effective stress to be tensile and commensurately reducing the magnitude of the vertical effective stress, thereby shifting the state of stress closer to a typical brittle failure envelope (Jaeger et al., 2007). The severity of pore pressure problems would depend on the permeability of the Tyler Formation at depth, which is not well characterized at present.

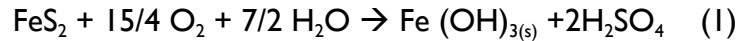
Acid drainage potential

Although the Ironwood Formation itself contains primarily iron oxide minerals (especially magnetite) rather than sulfides (with the important exception of the pyrite-rich layer within the Yale member), the presence of disseminated sulfide minerals at all levels within the overlying Tyler formation makes the potential for acid drainage from an open pit mine a serious concern. In a recent review of acid mine drainage studies, Jamieson (2011) identifies the primary factors governing acid generation at mine sites:

- 1) The balance between acid-producing sulfide minerals (pyrite, pyrrhotite, etc.) and acid-neutralizing minerals (primarily the carbonate minerals calcite and dolomite);
- 2) The average size and size range of mine waste rock fragments (smaller average sizes mean larger surface area for potential acid generation, and size distribution influences waste pile permeability);
- 3) The hydrology of the waste site (annual precipitation and runoff patterns, elevation relative to water table, etc.)
- 4) Microbial action within the waste rock (a function of climate and hydrology as well as the chemistry of the rocks).

This section will focus primarily on the first of these factors.

In simplified form, the reaction that generates acid by oxidation of pyrite in the presence of water (Nordstrom, 2011) is:

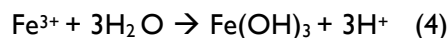
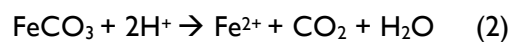


In reality, this reaction occurs in several steps, but in any case the result is the generation of sulfuric acid (H_2SO_4). Carbonate minerals, especially calcite (CaCO_3) and to some extent dolomite ($\text{CaMg}(\text{CO}_3)_2$) can help to neutralize acidic aqueous solutions, both through the direct buffering effect and by the inhibition of acid-generating bacterial activity under alkaline conditions (Perry, 1999).

Several approaches can be used to assess the net chemical reactivity of mine wastes (Jamieson, 2011). The simplest of these are ‘static tests’ – essentially acid-base accounting -- in which the acid –producing potential (AP) is compared with the neutralization potential (NP). The AP value is based on sulfide content, and the NP is determined by titrating samples (ideally, hundreds from a given mine site) with sulfuric acid. Samples for which $\text{NP/AP} < 1$ are considered acid generating. A more rigorous approach to determining acid generation potential is to use kinetic tests using ‘humidity cells’ of crushed rock that are subjected to alternating wetting and drying over weeks or months to simulate varying hydrological conditions. The drainage from these cells is analyzed over time for pH and solutes.

Using the conservative estimate of 332 million m^3 of mine waste from the Tyler Formation, an average S content of 0.15 mass percent, and an assumed bulk density of 2.3 g/cm^3 (2300 kg/m^3), the waste rock from a 6.4 km (4 mile) long, 300 m (1000 foot) deep mine would contain 1150 million (1.15 billion) kg of oxidizable sulfur.

Although siderite, a carbonate mineral (FeCO_3), does occur in some samples of the Ironwood and Tyler Formations, it would likely not help to neutralize acidic solutions in the rock waste piles. This is because 1) siderite has much lower solubility than calcite and dolomite and is thus slow to provide buffering, but also 2) the iron released by siderite dissolution can later *produce* acid under oxidizing conditions according to the following sequence of reactions (Skousen et al., Perry, 1999):



As stated by Perry (1999), “The initial dissolution of siderite and ferrous iron oxidation consumes acid and may provide temporary neutralization. However, iron hydrolysis ultimately generates acidity equal to that initially consumed, resulting in no net neutralization”. Based on this fact, the Pennsylvania Department of Environmental Protection does not include siderite in its calculation of neutralization potential in evaluating acid drainage generation potential from coal mines in Pennsylvania. It would thus appear that there would be little or no intrinsic acid buffering capacity within the Tyler Formation, and waste rock would need to be mixed with volumes of imported limestone commensurate with at least 1.15 billion kg of oxidizable sulfur to avoid acid drainage.

The very fine grain size and disseminated nature of the sulfides in the Tyler Formation (Fig. 7) could act to exacerbate the production of acidic solutions. Low pH solutions could also mobilize heavy metals present as trace elements in the Tyler formation, including mercury (Hg), arsenic (As), copper (Cu), and zinc (Zn) (Table 2; Appendix A) (Jamieson, 2012).

As noted above, historic mines in the Gogebic Range were small, primarily underground operations that avoided excavation of the Tyler Formation. Most of the existing waste rock piles in the area represent high-silica, iron-poor material from the Ironwood Formation that is relatively chemically inert. The volume and composition of waste rock from a large open pit mine in the Gogebic Range would be entirely different.

Although the pyritic horizon within the lower Ironwood Formation is comparatively thin (ca. 3 m), it would constitute more than 6.6 million m³ of material for a 300 m (ca. 1000 ft) deep, 6400 m (4 mile) long mine (cross sectional area of 3 m x 346 m, over a distance of 6400 m). Moreover, because rock from the Ironwood Formation would be crushed onsite as part of the magnetic separation process, this material would be left as especially fine-grained waste rock with very high acid generation potential unless it was carefully identified and isolated on a continuous basis as the mine excavation progressed.

Summary

Unlike the Precambrian iron formations mined in Minnesota and Michigan, the Ironwood Iron Formation in the Gogebic Range is steeply tilted (ca. 60° to NNW) and has limited natural exposure at the surface. A stably benched 200-300 m deep open pit mine in the Ironwood would therefore have a very large surface area and would require the removal of an immense volume (on the order of 330 million m³) of waste rock. Responsible monitoring and managing such a volume of waste rock, and a pit of such depth, over the long term would pose significant engineering challenges.

Although the economic target mineral in the Ironwood Formation is an iron oxide (magnetite), the overburden rock that would be stockpiled as waste (the Tyler Formation) contains significant amounts of reduced iron as sulfide (pyrite, pyrrhotite and related minerals), which could react with oxygen to generate acid mine drainage. The iron carbonate (siderite) present in small quantities in the Tyler Formation would not help to mitigate acid production, and the fine grain size of the rock would accelerate the generation of acidic solutions. A 3-meter thick pyrite-bearing layer within the Ironwood Formation itself also has the potential to generate acid drainage, given the fine grain size to which the Ironwood would be crushed onsite for the magnetic separation process. The Tyler and Ironwood Formations also have surprisingly high phosphate concentrations, and mobilization of this material could lead to eutrophication of water bodies.

Elevated pore pressure at the base of a deep open pit could cause the slaty rock of the Tyler Formation on the northwest wall to be close to failure in the tensile realm. The high wall in the stronger Ironwood Formation could be prone to dip-slip failure since the natural layering would lie parallel to the excavated face.

The scale of a modern open pit mine in the Gogebic Range would be completely different from historic mines in the region, which were localized, primarily underground mines that targeted high grade ore and did not involve excavation of the Tyler Formation.

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Appendix A: XRF analyses of samples from the Ironwood and Tyler Formations

For an overview of the principles of x-ray fluorescence spectrometry (XRF), see: http://serc.carleton.edu/research_education/geochemsheets/techniques/XRF.html

	A	B	C	D	E	F	G	H	I	J	K
	Final sample #	LU sample #	Stratigraphic level	SiO2	Al2O3	Fe2O3	P2O5	As	Cu	Zn	S
				mass%	mass%	mass%	mass%	mass%	mass%	mass%	mass%
1	1	Ironwood A	Lower Ironwood/Upper Tyler	70.563	14.146	3.407	0.163	ND	ND	ND	0.034
2	2	Ironwood B	Lower Ironwood - Pymouth	ND	1.629	60.121	0.225	ND	ND	ND	0.044
3	3	Ironwood C	Lower Ironwood - Pymouth	63.726	1.177	19.976	0.198	ND	ND	ND	0.038
4	4	Pyritic Ironwood (R-201)	Middle Ironwood - R26	66.313	5.491	15.654	0.386	0.001	0.001	0.001	0.777
5	5	IAN 44	Upper Ironwood	29.928	3.364	33.983	0.211	-0.002	-0.006	-0.008	0.035
6	6	Lowermost Tyler (R-201)	Base of Tyler	50.587	14.335	13.703	0.185	-0.001	-0.001	-0.003	0.033
7	7	IAN 83	Lower Tyler	27.727	3.113	33.792	0.177	-0.001	-0.006	-0.009	0.184
8	8	HWY 77 S	Lower middle Tyler	66.542	11.479	3.729	0.125	0	-0.001	0.001	0.029
9	9	HWY 77 N	Lower middle Tyler	54.142	14.352	2.219	0.162	0	0	0.005	0.044
10	10	Tyler B	Lower middle Tyler	ND	9.208	2.802	0.167	0.001	0	0.003	0.043
11	11	Tyler MB	Middle Tyler	54.182	12.53	6.651	0.142	0.002	0.006	0.024	0.11
12	12	Tyler H	Middle Tyler	68.912	13.938	4.842	0.16	0.001	0.014	0.063	0.543
13	13	Tyler I	Middle Tyler	58.206	13.044	5.563	0.151	0.003	0.005	0.022	0.074
14	14	Tyler C	Upper middle Tyler	ND	8.358	2.7	0.137	0.001	0.001	0.002	0.038
15	15	Tyler D	Upper middle Tyler	78.813	12.683	4.832	0.16	0	0.001	0.003	0.093
16	16	Tyler E	Upper middle Tyler	70.425	15.424	4.772	0.16	0.001	0	0.008	0.057
17	17	Tyler F	Upper middle Tyler	54.977	16.305	6.546	0.169	0.001	0	0.003	0.054
18	18	Tyler A	Upper Tyler	50.844	15.603	8.095	0.129	0	0.007	0.009	0.44
21				AVE			0.167055556			AVE	0.148444
22				SD			0.026818502			SD	0.213491

Appendix B: XRD analyses of samples from the Ironwood and Tyler Formations

Diffraction patterns for all XRD analysis are included as jpg files on the CD that includes this report.

Explanation of file names:

XRD results for primary minerals are named by Final sample number (1-18) + LU sample ID + run length (e.g. I8_TylerA_long; see Table 1).

XRD results using a filter for detecting sulfide minerals begin with S, followed by the same sample numbering format (e.g., S18_TylerA_long).

XRD results for Ironwood samples 1-3 show all detected minerals.

For an overview of x-ray powder diffraction (XRD) analysis, see:

http://serc.carleton.edu/research_education/geochemsheets/techniques/XRD.html