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Final report on
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The Porter Well
Seymour, Wisconsin

Final Report
March 23, 1994

Prepared for:
Wisconsin Department of Natural Resources

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EMERG & REMEDIAL RESPONSE SECTION
BUR OF SOLID & HAZRD WASTE

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increasing number of individuals are reporting problems with elevated metals. Of greatest concern, relative to these reported elevated metals, is the presence of arsenic at levels well above recommended drinking water standards. It should be noted that this arsenic problem is suspected to be associated with the St. Peter sandstone and not the underlying Cambrian sandstone.

2.2 Local Geology/Hydrogeology

Information regarding local geology/hydrogeology was obtained from review of logs of wells located within a one mile radius of the Porter site, from the publications referenced at the end of this report, and from drilling conducted in connection with this project.

Glacial soils in the site area consist of clay, sandy clay, sand, sand and gravel, gravel, and till hardpan deposits. Lithology and thickness of these glacial deposits varies between the well locations within a one mile radius of the Porter site. Thickness of the glacial deposits, and thus depth to bedrock, varies from 15 to 62 feet within this radius. Within a one-half mile radius of the Porter site, depth to bedrock varies from 15 to 40 feet. Soil lithology at the Porter well consists of 18 feet of clay underlain by 2 feet of gravel. The lithology of the Marvin Leininger well, located approximately 1500 feet west of the Porter well, is identical. However, greater thicknesses of clay (30 feet) and gravel (10 feet) are present. The surface elevation of the Leininger well is approximately 16 feet higher than that of the Porter well. Thus, the elevation of the bedrock surface at the Porter well is 4 feet higher than at the

Leininger well. Glacial soils at the Maynard Krahn well, located approximately 850 feet east, and slightly south, of the Porter well, consist of 18 feet of sand and gravel. Thus a change in soil lithology exists between the Porter well and the Maynard Krahn well. The elevation of the bedrock surface at the Maynard Krahn well is 1 foot lower than at the Porter well. The bedrock surface elevations are approximate since surface elevations of these wells were interpolated from the USGS 7 1/2 minute topographic map and depth to bedrock data assumes accuracy of the drillers logs.

Between 10 and 60 feet of limestone was generally reported beneath the glacial soils on the drillers logs for wells within a one mile radius of the Porter site. Although logged as limestone, this unit most likely represents the Galena-Platteville dolomite. The varying thickness reported for this unit can be attributed to variations in the elevation of the eroded bedrock surface, greater thicknesses present at down-dip well locations, logging the basal portion of this unit as St. Peter sandstone at some of the wells, inaccuracies in the logging of drill cuttings during well drilling, and natural variation in the thickness of this unit. The thickness of the "limestone" unit was reported as 55 feet (later shown by on-site coring to approximate 40 feet in thickness) at the Porter well and only 32 feet at the Maynard Krahn well. However, a 45 foot thickness of "limestone" was reported in the log of the Steve Krahn well, located approximately 2400 feet east of the Porter well. Con[illegible] difference in surface elevation between the Porter and [illegible] elevation of the base of the "limestone" in both wells is

Nearly all of the wells located within a one mile radius of the Porter site terminate in sandstone underlying the "limestone" unit. A few wells terminate in the "limestone" unit. Wells terminating within sandstone penetrate between 8 and 73 feet of sandstone. The sandstone is generally considered to be the St. Peter sandstone. However, it is possible that upper portions of the sandstone as logged are basal sandstone of the overlying Galena-Platteville unit. This is substantiated by review of the well logs. The Gerald Schaumberg well, located approximately 3200 feet west of the Porter well penetrates 59 feet of interbedded "limestone" and sandstone, terminating in "limestone". The Corniel Skenandore well, located approximately 6000 feet southeast of the Porter well, penetrates black sandstone (Galena-Platteville?) underlain by white sandstone (St. Peter?). The Joyce Phillips well, located approximately one mile north of the Porter well, also penetrates black sandstone. From review of the well logs, it is not believed that any wells within a one radius penetrate the underlying Prairie du Chien group or Cambrian sandstone.

The Porter well penetrates 48 feet of sandstone. The Maynard Krahn well penetrates 73 feet of sandstone and the neighboring Steve Krahn well 41 feet of sandstone. The Marvin Leininger well terminates in "limestone".

Review of constant yield test data for wells located within a one mile radius of the Porter site indicates that, in terms of well performance, the Porter well is the poorest performing well within this area. When pumped for two hours at 10 gallons per minute (GPM), the well experienced 40 feet of drawdown.

In contrast, the Steve Krahn well experienced 30 feet of drawdown when pumped for two hours at 20 GPM and the Maynard Krahn well experienced 50 feet of drawdown when pumped for two hours at 50 GPM.

The Porter site is located south of the potentiometric surface divide which extends from the southwestern to the northwestern corner of the county. Bedrock groundwater movement in the Porter site area is expected to be to the east-southeast. Static water level in the Porter well was at 60 feet below ground surface upon completion of the well in October 1977, and at 62 feet below ground surface in September 1991.

2.3 Site Geology

During the months of February and August, 1993, soil boring and rock core drilling was conducted by Eichleay at the Porter site. A total of nine soil borings were drilled through the unconsolidated glacial till to the top of rock. In addition, a total of four rock core borings were drilled on site. Two of the rock core borings were continuously sampled while the other two were sampled at the interface between the Galena-Platteville and the St. Peters Sandstone formation. The field investigations are summarized in Section 3, Subsurface Investigation.

The typical soil profile was a thin organic layer which overlies a glacial till. The till was predominantly a red/brown silty clay. In some of the borings the clay was underlain by a thin gray silty sand and/or silt. The top of rock was

generally encountered between 14 and 17.5 feet below existing grade. Groundwater was encountered in five of the seven borings while sampling.

Underlying the unconsolidated glacial till was the Galena-Platteville dolomite. Large quantities of water were encountered during drilling in the upper dolomite. The Galena was found to be a gray, massive, non-weathered, very resistant dolomite. The dolomite reacted mildly with a dilute solution of hydrochloric acid (HCL) when applied to scratched surfaces. The basal portions of the dolomite had numerous thin alternating layers of sand, poorly cemented sandstone, and silty zones with shale partings. Also encountered in the same area were thin lenses of brass to black colored, apparent sulfide minerals. The sulfides appeared to be randomly dispersed through the basal portions of the dolomite down into the top of the St. Peters Sandstone below. The nodules encountered ranged in size from a solid band several inches thick down to the size of a coarse sand grain.

The St. Peter sandstone was found below the Galena-Platteville dolomite. The St. Peter was found to be a soft, poorly cemented well sorted medium grained sandstone. The sandstone did not react to a dilute solution of HCL. Scattered sulfide mineralization was detected in the upper portions of the sandstone. The formation further contained red bands at depths 100 or more feet below existing grade. The red banding appeared to be associated with individual sand grains. Moderate volumes of drilling fluid were lost to the St. Peter sandstone. Figure 2-1 presents a site specific cross section derived from borings drilled in connection with this investigation. Copies of the soil boring and rock coring logs are attached as Appendix B.

Summary of the PAL Results from the Porter Well -- Boring/Monitoring well Groundwater Sampling, July through September, 1993. The PAL data is presented in Appendix F.

4.5.4 Mineralogical Analysis

Core samples were selected for optical mineralogical analysis based on the visual presence of sulfides as identified in the field. The samples were selected from the basal portion of the Galena-Platteville dolomite and the upper portion of the St. Peter sandstone. Two samples from each of four cores for a total of eight samples were sent to the University of Wisconsin Madison for optical mineralogical analysis. The results of these analyses are included in Appendix G.

The mineralogical analysis of the sulfides within the dolomite revealed the presents of marcasite (FeS_2) with traces of pyrite (FeS_2) and limonite [goethite] ($FeO \cdot OH \cdot nH_2O$). The marcasite crystalline structures were lath-shaped and rounded; the latter was more common. The marcasite was found in irregularly distributed ragged patches with no distinct shape; therefore it was not possible to tell if there was an organic precursor. However, some marcasite replaced fossil fragments such as crinoid, brachiopod, or pelecypod were noted.

Less than 1% sulfides were identified within the samples of St. Peter sandstone submitted for analysis. The sulfides present in the St. Peter

appears to be primarily pyrite (FeS_2). The pyrite occurs as both well formed cubes and anhedral masses. The pyrite formed between the sand grains and the presence of organic residues may have provided a reducing environment for the sulfide development.

Sulfides appear to be present due to diagenetic processes. Diagenesis is loosely defined as a process and or processes by which minerals form after initial deposition of the parent rock. The chemical, physical, and biological, modifications or transformations occur within the parent rock (replacement of existing minerals) or within pore spaces to form the sulfide mineral(s). These changes can occur during and/or after lithification; however, weathering and metamorphism are not included in the process.

The sulfide minerals at the base of the Galena-Platteville and upper portion of the St. Peter likely formed from a secondary enrichment process. The sulfides associated with the site possibly developed when water containing dissolved oxygen and carbon dioxide percolated through the formation and contacted reducing conditions in the organic rich/mineral rich shale/clay layer at the base of the Galena Platteville. These percolating waters became enriched by minerals contained in the shale/clay and, coupled with other chemical/biological processes, formed the secondary sulfide minerals.

5.0 DISCUSSION OF RESULTS

In summary, based upon the work conducted to date at the Porter site the following can be concluded: 1). The Porter's well developed low pH conditions as a result of the oxidation/reduction of sulfide minerals associated with the interface of the Galena-Platteville and St. Peter formations. 2). The sulfide minerals present at this interface include marcasite, pyrite and sphalerite. Other sulfide minerals are suspected, such as arsenopyrite, that at this stage have not been identified in samples of core collected from the site. 3). The pH phenomenon to the degree experienced by the Porters is rare. It can be inferred, on the basis of the evidence collected, that the primary reason for the rare nature of the phenomenon is the discontinuous nature of the sulfide mineralization and/or localized differences in aquifer properties and/or differences in well construction.

This section presents a discussion of the mineralogy/petrology of the site and region, and the natural processes that appear to have acted upon the site geology to cause the low pH conditions in the Porter well. It is known from the examination of the cores collected at the Porter property that significant sulfide mineralization is associated with the interface of the Galena-Platteville dolomite and the St. Peter sandstone. This sulfide mineralization was shown to consist of primarily marcasite (FeS_2) and pyrite (FeS_2) with possible traces of limonite ($FeO \cdot OH \cdot nH_2O$) and sphalerite (ZnS). The sulfides were determined through optical mineralogy performed by the Department of Geology and Geophysics at the University of Wisconsin-Madison. Arsenic is also present in area groundwater. Although not specifically identified by the optical mineralogy, traces of the sulfide arsenopyrite are suspected to be present in the area as an explanation of the arsenic in area groundwater. Arsenopyrite ($FeAsS$) is essentially marcasite with somewhat variable portions of the sulfur

replaced by arsenic. Arsenopyrite, the most common mineral containing arsenic, is reported to exist in combination with other sulfides in Wisconsin.

5.1 Literature Review

Although the presence of groundwater with pH as low as that encountered at the Porter site appears to be isolated, evidence for the presence of geologic conditions, apparently responsible in part for the generation of low pH, exists. This evidence is contained in the following apparently analogous situations.

5.1.1 NURE Data

A report compiled by the Wisconsin Geological and Natural History Survey (WGNHS) titled "Evaluation of NURE Hydrogeochemical Data for Use in Wisconsin Groundwater Studies". The WGNHS report plotted existing data compiled by the National Uranium Resources Evaluation (NURE). The NURE data had been compiled by the United States Department of Energy and its predecessors in an effort to map the uranium resources of the conterminous United States and Alaska. The NURE project attempted to determine the location of uranium deposits through the analysis of ground, lake, and stream water samples collected on a 3-mile grid. A wide range of parameters were analyzed including arsenic, copper, iron, zinc, sulfate, conductivity, pH, and alkalinity.

conclusion that the sulfide minerals are a primary factor in the generation of the acid conditions, but does not necessarily establish the mineralization as the only factor. As discussed in greater detail in following sections, other conditions, or combination of conditions, are suspected to be required in order for the acid problem to proceed to the extremes observed in the Porter and Spreeman wells.

5.2 Chemical/Biological Processes

The chemical processes generating the acidic conditions relative to the above and the Porter well are postulated to be similar to those responsible for the generation of acid conditions in coal mining regions. Acid drainage in coal regions is an extremely acidic, iron sulfate rich drainage formed under natural conditions when certain types of coal is mined. When the coal is mined, iron disulfides, occurring primarily either as marcasite or pyrite, that are commonly associated with the coal and/or associated strata, are exposed to the atmosphere and oxidize in the presence of humidity and oxygen to form soluble hydrous iron sulfates. Subsequent natural water movement dissolves these compounds which chemically react to produce a highly acidic drainage that is high in iron and sulfate.

As previously stated, the iron disulfides (FeS_2) found at the Porter site were primarily marcasite and pyrite. The marcasite and/or pyrite present oxidize in the presence of groundwater (instead of meteoric water as in the mining scenario) and oxygen that was introduced in sufficient quantities only after the

well was drilled. It is likely this process initially formed the hydrous iron sulfates. Groundwater reacts with these compounds to form acidic conditions with the high levels of iron and sulfate. The general chemical reactions are given in the following equations:

$$FeS_2(s) + \frac{7}{2} O_2 + H_2O = Fe^{++} + 2SO_4^{=} + 2H^+ \qquad (1)$$

$$Fe^{++} + \frac{1}{4}O_2 + H^+ = Fe^{+++} + \frac{1}{2}H_2O \qquad (2)$$

$$Fe^{+++} + 3H_2O = Fe(OH)_3(s) + 3H^+ \qquad (3)$$

$$FeS_2(s) + 14Fe^{+++} + 8H_2O = 15Fe^{++} + 2SO_4^{=} + 16H^+ \qquad (4)$$

More specifically the oxidation of pyrite or marcasite can be written as:

$$FeS_2 + H_2O + 3\frac{1}{2}O_2 = FeSO_4 + H_2SO_4 \qquad (5)$$

The ferrous sulfate formed by this reaction may oxidize further to highly soluble ferric sulfate and dissolve in the groundwater as follows:

$$Fe_2(SO_4)_3 \rightarrow 2Fe^{+++} + 3SO_4^{=} \qquad (6)$$

The resulting iron can hydrolyze as in equation 3 above.

This results in the formation of acidity and iron hydroxides. The ferric iron formed in above equations can then react with more pyrite or marcasite to

form additional acidity, ferrous and sulfate ions as in equation 4 above.

The oxidation/hydrolysis of iron disulfides as outlined above yields more than acidity and elevated iron and sulfide. It also results in an alteration of the mineralogy of the parent sulfide. The oxidation products of the iron disulfides include the iron hydroxides and minerals such as melanterite (white crystals of ferrous sulfate), halotrichite (white crystals of iron or magnesium sulfate, and alunogenite (white crystals of aluminum sulfate).

Most of the chemical processes postulated to be responsible for the acid conditions in the Porter well require microbial action in order for the reaction to occur. Without the action of microbes, many of the above chemical reactions would occur too slowly to represent a problem. An effort was made to sample for sulfur and iron reducing microbes in the Porter well. The results did not indicate significant reducing microbes present. The well probably should also have been sampled for the presence of iron and sulfur oxidizing bacteria. In retrospect it is unlikely that reducing conditions exist in the Porter well under normal conditions. If reducing conditions exist they would likely only be present, to any significant degree, at the base of the well after the well had been allowed to stagnate. Reducing environments, and the chemicals and many of the bacteria associated with them, can only exist or function under strict anaerobic conditions (no oxygen). In the presence of oxygen, chemicals formed under reducing conditions are often spontaneously converted to an oxidized state, and obligate anaerobic bacterial activity is reduced or eliminated. The same is often true when oxygen is removed from

the environments of aerobic chemicals and bacteria.

In the chemical reactions presented above, the iron disulfide is oxidized/hydrolyzed yielding ferrous iron (Fe^{++}) and ferric iron (Fe^{+++}). It is important to note that pH is a driving factor in determining how rapidly ferrous iron oxidizes to ferric iron with a resulting increase in acidity. In neutral pH conditions, ferrous iron will spontaneously oxidize in air to ferric iron, which then forms a highly insoluble ferric hydroxide. Under neutral conditions ferric iron is reduced to ferrous iron by microorganisms which lower the redox potential of their habitat by consuming O_2. Thus, at neutral pH ferrous iron exists only in anaerobic environments. As stated, anaerobic, i.e. reducing, conditions would likely only be created at the base of the Porter well. If a reducing environment exists under neutral pH conditions, waters from the reduced environment which contact aerobic environments would spontaneously alter the ferrous iron to ferric hydroxides. It is possible that, prior to disturbing the contact of the Galena and St. Peter, a reducing environment existed, in particular at the shale/clay layer. Once this zone was disturbed and waters/minerals associated with the zone were brought to the surface where they contacted oxygen, significant alteration due to oxidation occurred. This is possibly the explanation of the brown to black precipitate encountered in most of the borings at the contact of the Galena and St. Peter formations. It also likely explains the rapid proliferation of rust staining observed on the cores upon exposure to oxygen at the surface.

The ultimate negative outcome of the oxidation/reduction/microbial

alteration of the sulfides present in the Porter well is an increase in acidity and a dramatic lowering of the pH. Once the pH is lowered, the ferrous-ferric iron processes change. At acid pH values, ferrous iron will not oxidize spontaneously to the ferric state. Under acid conditions, the oxidation of ferrous iron will only occur biologically from the action of certain autotrophic sulfur-iron bacteria (*Thiobacillus ferrooxidans, Ferrobacillus ferrooxidans*). These bacteria are acidophiles and will only proliferate under extremely acid conditions. Thus, for these sulfide/ferrous/ferric iron oxidation/reduction processes to maintain themselves in the Porter well, bacterial activity must be present.

The action of bacteria may also have contributed to the original deposition of the sulfides. The apparent diagenetic state of the sulfides present in the formation may in part be due to the microbial degradation of compounds associated with the shale/clay layer. Bacteria generate H_2S under reducing conditions. H_2S is highly reactive with and precipitates many metal ions, in particular iron sulfides. (The black color encountered in the formation water may be due to iron sulfide) Reducing conditions could have existed relative to the shale/clay. Thus, the biological oxidation/reduction of the shale/clay may have created iron-sulfide enriched water that, in conjunction with other geo-chemical processes, resulted in the deposition of the iron disulfides present. The apparent appearance of sulfides in framboidal aggregates may be indicative of this microbial involvement in the deposition. It is theorized that the microscopic sulfide grains composing a framboid resulted from the filling of bacterial cells with sulfide crystals. (The presence of the iron

disulfides in microscopic concretions, such as fromboids, will be important later in Section 5.3 in discussions on acidity generation).

Sulfur oxidizing bacteria can also convert H_2S to sulfuric acid. As stated above, it is not expected that large quantities of H_2S were generated relative to the Porter well due to a suspected lack of the reducing conditions. In the case of the Porter well, it is more likely that the acid conditions are the result of ferrous-ferric iron reactions and the direct oxidation of the sulfides. It should be noted that H_2S generation is suspected to exist relative to the geology at the site. This is based upon the olfactory sensing of the distinctive H_2S "rotten egg" odor in some of the borings.

5.3 Physical/Geological Factors

The question remains as to why the acid conditions occur only at discontinuous locations, such as the Porter's. For example, a neighbor, Maynard Krahn, appears to be exploiting a similar portion of the Galena-St. Peter, yet water from the Krahn well has to date not exhibited similar quality problems. The initial clue to answering this question is offered in an examination of the cores collected at the Porter site. The core drilling conducted at the Porter property suggests that the sulfide body, apparently responsible for the water quality problems, is discontinuous. Coring conducted at boring SB-300, located between the Porter well and the Krahn well, did not contain nearly the extent of the sulfide mineralization that was contained in cores SB-100 and SB-200 that were collected nearer the Porter

well. It is interesting to note at this point that this discontinuous sulfide body may be precisely what was being mapped during the geophysical survey conducted at early stages of site investigations. Coupled with the increased mineralization of the Porter well water, the anomaly reported around the Porter well likely would record on an EM survey. The plot generated during this earlier geophysical survey is included as Figure 5-4.

The problem may also have been exacerbated by factors such as well construction. Other wells in the area may have been constructed in a manner that cased the interface of the Galena-Platteville and St. Peter out of production. Alternately, other area wells may have been completed to depths that provide enough water to dilute interface-induced problems. Alternatively, aquifer yield in the area of the Porter well may not provide adequate dilution when compared with other areas.

If the sulfides originated, as theorized, from biological/geochemical alteration of the shale/clay layer encountered on the Porter property, the discontinuous nature of the sulfide mineralization may be linked to the reported discontinuous nature of the shale/clay layer itself. Alternately, there may be alterations in the mineralogy of the shale/clay that resulted from factors such as a facies change. These mineralogical alterations, if they exist, could have affected the composition of the shale/clay and also affected the generation of the sulfide minerals.

Other factors may also have influenced the discontinuous nature of the acid

generation/sulfides. Necessary biological/geochemical factors, as discussed in part above, probably don't universally exist in proper proportions. For instance, marcasite usually disintegrates more rapidly than pyrite in the presence of O_2, with an accompanying formation of ferrous sulfate and sulfuric acid. One determining factor in the generation of acidity in the area thus may be the ratio of pyrite vs marcasite. Additionally, as was stated above, the generation of the acid conditions is dependent upon oxygen. Natural levels of dissolved oxygen in groundwater are insufficient to produce adequate acidity. Approximately 1 mole of O_2 is required to generate 1 mole of acidity. Soil/groundwater normally contains less than 0.6 mmoles of O_2 per liter. When the Porter well was drilled, additional O_2 was introduced to the formation and the movement of water through the formation was increased. The dewatering of the formation created by the pumping introduced additional oxygen. The oxidation was no longer limited by the transport of oxygen in the groundwater, and acidity resulted. As noted above, most of the bacteria responsible for catalyzing the acidity-producing reactions thrive only under acid conditions. Thus, once the pH drops below certain levels, the process accelerates in response to the proliferation of the bacteria.

Once the pH drops, the stability of metals in solution also increases. This results in the dissolution of other associated trace metals, such as arsenic, cadmium, copper and zinc, with an associated rise of their levels in the groundwater. Thus, in the case of the Porter well, the elevated metals observed are mostly a function of the generated acid waters reacting with the associated formations.

Other factors could be influencing the discontinuous nature of the acid generating problem. It has been demonstrated that only certain forms of sulfide mineralization will produce appreciable amounts of acidity. In strata associated with coal seams, sulfide occurs in euhedral grains, as coarse grained replacement of original plant matter, as coarse grained platy masses filling joints in strata, and as framboidal sulfide. Studies conducted in connection with the generation of acid drainage relative to the mining of coal demonstrated that it is only the framboidal form of the sulfides that decomposes rapidly enough to create sufficient acidity. The other forms of sulfide decompose too slowly to represent a significant problem. Thus, as the levels and/or the dissemination of the framboidal sulfide exposed to oxidation decreases, the acid generation potential of the formation decreases.

5.4 Recommendations for Further Research

Questions do remain that may warrant further research at the site. The chemical processes that generated the acidity can, with a high degree of confidence, be postulated to be the same as those responsible for the generation of acid conditions at coal mines. However, without further geochemical/biological analysis a complete understanding of the process is not possible. For example, are the processes entirely driven as discussed above or are other factors such as galvanic decomposition of the sulfides at least partly involved?

Additionally, a statistical evaluation of available geologic, hydrogeologic, chemical, and well construction data may yield further clues to the pattern of this phenomenon. For example, sulfide deposition along linear features such as fractures and solution channels may in part explain the randomness of the phenomenon. The secondary hydrothermal deposition of sulfides along such features is common. Many major sulfide ore deposits are identified through wide scale lineation studies. Such a study conducted in the area of the Porter well may provide additional clues to the form of the sulfide distribution in this area. One of the factors controlling the expression of the acid problem at the Porter's may be the location of the well through or near such a highly mineralized lineation. It should be noted that drilling conducted at the site to date did not reveal such a linear trend to the sulfide mineralization. Some of the above information may be available from sources such as the NURE data evaluated by WGNHS, other WGNHS studies, United States Geological Survey (USGS) reports, and other WDNR directed area groundwater studies.

Finally, with the knowledge gained from this study it would be interesting to conduct another geophysical evaluation of the site designed at determining the nature and extent of the sulfide deposits. There are geophysical methods and individuals available that are adept at identifying sulfide mineral deposits. Instead of the geophysical EM (Electromagnetic) methods employed during the earlier study, a survey utilizing what is known as VLFEM (Very Low Frequency Electromagnetics) equipment could be attempted. This technique utilizes very low frequency radio stations operated by the U.S. Navy to augment the search capabilities of the instrument. This system has proven to be quite successful at quickly and economically delineating ore deposits.

There are distinct differences between the opaque mineralogies of the St. Peter Sandstone and the contacting carbonate rock. The sharp contact is generally marked by a thin shale band that also contains opaque phases.

The sandstone contains much less than 1% sulfide which appears to be invariably pyrite. The pyrite is not distributed randomly throughout the sandstone but is commonly concentrated in small areas where it may fill 50+% of the available inter granular space. The pyrite occurs as both well formed cubes and anhedral masses. Some of the masses completely coat the grain boundaries. The pyrite shows no visible internal structure. The pyrite grew between the sand grains during diagenesis and may well have been localized by the presence of minor organic residues providing a slightly more reducing environment.

The carbonate rock contains two important opaque phases: marcasite and more minor limonite (goethite). Marcasite has essentially the same color as pyrite but is distinctly anisotropic under high magnification. The marcasite in these samples occurs in two habits: lath-shaped crystals and more massive, rounded grains. Both habits can occur together, the lath morphology is more common. The marcasite is found as either minor concentrations irregularly distributed through the carbonate or completely replacing fossil fragments. The replaced fossils appear under the microscope as either rings or crescents suggesting crinoid, brachiopod, or pelecypod precursors. The replacement marcasite is very fine grained and occurs in both the lath and more rounded morphologies. The irregularly distributed marcasite occurs as ragged patches with no distinct shape that would suggest whether or not it had any organic precursor. The marcasite must have formed in the carbonate host during diagenesis. Limonite occurs sporadically in the carbonate host and appears to be secondary in nature.

There are a few rounded grains in the carbonate host that may be pyrite- they are too small to be sure that they are isotropic or anisotropic. Both pyrite and marcasite have the same composition, FeS_2, and so even compositional data will not easily sort out this question for sure. I observed two or three grains in the carbonate portions of the thin sections that may be sphalerite. They again are too small for definite optical identification and it has not been possible to use the Department's new electron microprobe to confirm or deny the identity of these grains. Their gray color and isotropic character are permissive of the sphalerite identification.

The thin (1-5mm) shale-rich band at the contact contains dominantly marcasite but also small amounts of pyrite. The sulfides occur as stringers parallel to the foliation of the shale. Most of the marcasite has the lath-like habit.

In summary, observation of 8 thin sections cut from the provided drill cores shows a consistent relationship between the host rock and the nature of the opaque accessory phases present. It has not been possible to obtain trace element compositional data on the sulfides present as our new electron microprobe has just been installed and is usage is still restricted for general purposes.

Phil Brown