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Fluid Properties in the Formation of High-Grade Iron Ore in Northern Minnesota

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Abstract

The Mesabi Iron Range in Northern Minnesota has been a major producer of iron ore for over 100 years. Production has been from the 1.85 – billion-year –old Biwabik Iron Formation, an iron-rich sedimentary rock that is tilted gently to the south. Most of the known high-grade ore lies near the surface and has been already mined. Determining whether more high-grade ore may lie at depth could have significant economic impact on the mining industry in northern Minnesota. To evaluate the likelihood of finding more high-grade iron ore deeper underground, it is important to determine the source of the fluids that are responsible for that ore. I have been testing Morey's hypothesis (Econ. Geol. v.94 pp.133-142) that a plate collision event 1.8 billion years ago drove deep fluids upward along faults within the iron formation, and that these fluids dissolved some minerals from the iron formation and increased the grade of the remaining iron ore. In this case, high-grade ore could exist deeper within the iron formation, which is tilted gently beneath the surface. Samples collected in the iron range have been analyzed using various geologic methods. Growth banding, using cathodoluminescence, and the salinity of the fluid from fluid inclusions in minerals associated with high-grade iron ore were used to evaluate the source of the fluid associated with high-grade ore. From this information, we have assessed the likelihood of deeper high-grade ore beneath the surface.

Introduction

The Mesabi Range in Northern Minnesota is about 80 to 100 miles north of Duluth and extends for about 120 miles to the northeast from west of Grand Rapids, MN to Birch Lake (Appendix A1). The formation is about ¼ to 3 miles in width (French 1968). The Mesabi Iron Range is a major producer of taconite in the United States. The term taconite was originally meant to describe low-grade (~30% iron) unoxidized iron formation (French 1968). Before taconite was produced, high-grade iron ore (~60% iron) was mined. Northern Minnesota has produced 3.6 billion metric tons of ore since 1890. Out of that amount 2.3 billion metric tons have been high-grade iron ore. In the 19th and early 20th centuries taconite was considered economically unfeasible to mine, but after World War II the country had almost run out of the high-grade iron ore, and a process was developed for exploiting the taconite ore.

The Mesabi iron range is comprised of rocks that are Paleoproterozoic in age and is part of the Penokean orogeny (mountain building event) that formed between 2200 and 1850 million years ago. This orogen is divided into two tectonic areas: a fold and thrust belt in the southeast and two or more foreland basins in the northwest. The largest of these basins is the Animkie basin. The basin contains three sedimentary units. The first is the Pokegama Quartzite followed by the Biwabik Iron Formation, and finally a thick graywacke-shale known as the Virginia Formation (Morey 1999).

The Pokegama Quartzite consists of quartzites and impure sandstones (French 1968). The Biwabik Iron Formation is about 340 to 750 feet thick and is divided into four units that can be traced across the entire range: the Lower Cherty, the Lower Slaty, the Upper Cherty, and the Upper Slaty (Marsden et. al., 1968). Cherty iron formation

contains abundant cherty (fine-grained) quartz, the bedding is wavy to irregular and massive, and the rock is lacking in fine clastics (Marsden et. al., 1968). The rock's granular texture is produced by iron silicates in rounded, ovoid, or irregular granules. These granules are about 0.5 to 2.0 mm in diameter (French 1968). Cherty taconites usually contain about 28 to 33 percent iron (Marsden et. al., 1968). Slaty iron formation is dark-colored and contains some fine clastic material. The beds are thin and parallel, and there is good parting in the bedding plane (Marsden et. al., 1968). It is composed of mostly iron silicates and carbonates (French 1968). Slaty taconites usually contain about 20 to 30 percent iron (Marsden et. al., 1968). The contacts between the four units are gradual except between the Lower Cherty and Lower Slaty units. This contact is sharp and can be defined within a few feet or inches (Marsden et. al., 1968).

There are two types of taconite that can be mined from the Mesabi Iron Range: oxidized (high-grade) and unoxidized taconite (French 1968). The main minerals of the unoxidized taconite include cherty quartz, magnetite, siderite, stilpnomelane, and minnesotaite with lesser amounts of hematite, calcite, dolomite, chamosite, greenalite, and chlorite (Marsden et. al., 1968). The minerals of the oxidized taconite include cherty quartz, hematite, and goethite with minor amounts of magnetite, manganese oxides, and kaolinite (Marsden et. al., 1968). Greenalite, minnesotaite, and stilpnomelane are iron phyllosilicates (French, 1968). Greenalite contains very little aluminum and can be described as an iron serpentine (French, 1968). Minnesotaite contains a lot of magnesium and can be described as an iron-rich talc, and stilpnomelane is a complicated silicate that can vary in its composition (French 1968).

High-grade ore (natural ore) is extracted from hematite (Fe_2O_3) or goethite rich deposits ($Fe_2O_3 \bullet H_2O$), which are formed by oxidation, hydration, and the leaching of minerals from low-grade iron formation (taconite) by water (Peterson, Jirsa, & Hudak 2005). Along with the hematite and goethite small amounts of cherty quartz, magnetite, manganese oxides, and kaolinite can also be found (Marsden et. al., 1968). The oxidation and hydration make the rocks more porous and more permeable which allows the water to remove more silica, phosphate, magnesium, and calcium. The removal of these substances concentrates the residual iron oxides into high-grade ore.

The major structure of the Mesabi Range is a gently dipping monocline that strikes northeast and dips from 5° to 15° southeast (Marsden et. al., 1968). There are several minor structural features located throughout the range. Small folds and monoclines can cause steep dips in the iron formation locally. The faults along the range have a common strike of N75W or N20W (Marsden et. al., 1968). The displacement along these faults is commonly less than 50 feet (Marsden et. al., 1968). There is a correlation between the location of the ore bodies and the location of faults and folds. About 75 percent of the natural ore is related to various folds and 15 percent to faults (Marsden et. al., 1968). The development of high-grade ore could be controlled by minor structural features throughout the range. Fold and some faults appear to have been formed in response to slumping which was caused by the volume loss in the iron formation that had lost its chert and other minerals.

There are two conflicting hypothesis to how the high-grade ore formed. Leith (1903) explained that water entered the iron formation from a highland that was associated with the Giants range. The highland provided enough hydraulic head to allow

the water to enter the iron formation and to leach silicates and to hydrate and oxidize the iron into high-grade iron ore quality (Appendix A2 figure A2). The evidence for this model is the chemical weathering profile. At the surface, the meteoric water has weathered a majority of the rocks. From this profile, Leith concluded that the necessary fluid to concentrate the residue iron material came from above. If this hypothesis is correct, then the implication for finding more high-grade iron ore is not very plausible, as its abundance would be expected to diminish with depth.

In contrast to Leith's downward-percolating waters, Gruner (1930) suggested that heated fluids from a magmatic source could circulate and dissolve the minerals necessary to concentrate iron formation into high-grade iron ore (Gruner 1930). If this hypothesis is correct then the implication for finding more high-grade ore is great. Both of these researchers recognized that a large volume is required to circulate for a long period of time in order for the silica to dissolve out. If the water is heated or contains alkali metals such as sodium, the silica can dissolve faster.

In addition to these hypotheses another model was introduced. Morey (1999) proposed that regional ground water flow systems with flow paths tens of kilometers long existed in Precambrian time. Many of the flow paths extended to several kilometers in depth. He suggested that groundwater recharge took place in an elevated region centered on the Penokean collision zone at the south end of the Animkie Basin. From this point the waters flowed downward to the basal Penokean quartzite (then a porous and permeable sandstone) to depths of several kilometers, where the water was heated. The hydraulic gradient formed by topography drove the water upward to the north, along the dip of the Penokean quartzite to the northern margin of the Animkie basin. Open

fractures extending from the older Archean igneous rocks to the bedrock surface allowed the water to escape, probably as artesian springs. These fractures channeled the water upward through the overlying iron formation. The flow was continuously supplied with fresh water, which promoted oxidation and the dissolving of minerals (Appendix A2 figure A3), (Morey 1999). Two lines of evidence support this model. First, about 80% of the ore bodies are located on faults (Morey 1999), some of which are thrust faults (Jirsa 2006), unrelated to slumping caused by dissolution of iron formation. The fluids were driven up along these faults. Second, as stated earlier, the removal of silica concentrates the iron oxides to high-grade iron ore. Even in the most extreme weathering conditions, silica does not weather easily. This suggests that ascending, warm fluids were responsible for its removal and reprecipitation into quartz veins, which are common in faults associated with high-grade ore.

This study evaluated the source of the fluids that were involved in the formation of high-grade ore, in particular testing Morey's (1999) model. If high-grade ore was formed from the water coming from deep underground then there is reason to believe that more high-grade ore exists under the glacial deposits or younger sedimentary rocks. By characterizing the fluids that transformed the iron formation into high-grade iron ore. I can address the possibility of finding more high-grade iron ore, which could make mining ore much more economically feasible again.

Methods and Materials

The samples for this study came from Aurora, and Hibbing, Minnesota at the Hibbtac Mine. In order to characterize the fluids, quartz veins from faults associated with high-grade ore were sampled. The quartz veins are believed to be of the same age as the

high-grade iron ore and thus are suited for fluid studies. The samples that were collected from Aurora contained both pyrite and hematite in bedding –parallel veins to 4 inches wide associated with a thrust fault mapped by Jirsa (2006, personal comm.) at the southwest corner of the Number 6 pit. The Hibbtac samples were from a brecciated 1-inch wide quartz vein in a high-angle fault zone that also contained oxidized ore.

Thin sections of quartz veins were examined under cathodoluminescence (CL). In addition, doubly polished thin sections at a thickness of 30 microns were used for fluid inclusion analysis.

Fluid inclusions are microscopic bubbles of fluid trapped inside minerals during the time of mineral growth and that preserve the original physical and chemical properties of the parent fluid (Roedder, 1984). Appendix A3 shows a picture of fluid inclusions containing liquid plus vapor in a sample from Aurora. By heating and freezing the samples and measuring the temperatures at which phase changes take place in the fluid inclusions, determination of the temperature at which mineralization took place as well as the dissolved salt content (salinity) of the fluid can be found. The amount of variation in the freezing point will depend on the concentration of the salt (Brown, LeMay, & Bursten, 2003); freezing point decreases with increasing solute concentration. This is known as freezing-point depression (Brown, LeMay, & Bursten, 2003). In the Iron Range, meteoric water percolating downward from above should have a lower salinity and therefore have a higher freezing point relative to water that ascended from below and that was presumably saltier.

As noted, quartz vein samples were also viewed under cathodoluminescence (CL). A mineral luminesces when it is struck by energy of a shorter wavelength. For

cathodoluminescence, x-rays are shot at the mineral. This causes the electrons in the atoms that make up the mineral jump up to a higher energy state. Because this excited state is unstable, the electrons fall back a lower-energy state. As they fall back, the electrons emit a photon. The wavelength of the light that we see corresponds to the energy gap (Marshall 1988).

The amount that a mineral or rock luminesces results from the activator and quencher ions. In silicates the activator ion is commonly Mn^{2+} (Pagel et. al., 2000). There are many other different cations that can activate CL. About 15-30 ppm of manganese is enough to activate cathodoluminescence (Marshall 1988). Lack of luminescence in silicates can be caused by a low concentration of activator ions or large amounts of quencher ions. In silicates these quencher ions can be Fe^{3+}, Fe^{2+}, Ni^{2+}, or Co^{2+} (Pagel et. al., 2000). Quenchers modify the energy level arrangement so that energy gap does not correspond to the wavelength of visible light (Marshall 1988). It is possible for a mineral to accept more than one activator. If this happens, each activator will exhibit a different luminescence color (Marshall 1988). A common feature in silicate minerals is growth zoning (Pagel et. al., 2000), which results from pulses of fluids from different sources, hence having differing trace element chemistry, being involved in the growth of the mineral grain.

In order to view quartz luminescence I used cold plate CL. In this method a copper plate is cooled with liquid nitrogen. The sample can then be placed onto this plate and placed into the CL apparatus. The cold temperature enhances the cathodoluminescence of the quartz.

The CL technique highlights features in the rock such as growth zoning or banding. If these features are part of quartz or calcite veins that are associated with high-grade ore, I can conclude that the fluid responsible for precipitating these minerals arrived at the site in pulses. These pulses would give rise to banding that might be observed.

Cathles and Smith (1983) interpreted banding in the mineral sphalerite in terms of fluid pulses coming out of a sedimentary basin not unlike the Animkie basin in the Mesabi Iron Range. They concluded that the color banding occurred due to the variations in the iron content. The minerals were not deposited all at once but rather in many pulses (Cathles and Smith, 1983). In order for fluids to flow in pulses there is a rupture of pressured fluid that accumulates in low permeability units. Fluid coming up from depth must have ascended episodically, not as a continuous event (Cathles and Smith, 1983). In addition, Cathles and Smith (1983) noted that pulses of pressured fluid, passing through ore, could account for the tectonic features of the deposits (Cathles and Smith, 1983). As explained earlier, some of the samples that were collected are from fault zones. If fluid pulses coming up from depth are the cause of high-grade ore, there is a high probability of finding this type of banding in fault zones.

Results

The preliminary results that were obtained from cathodoluminescence show evidence of growth banding in the vein quartz (Appendix A4). There does seem to be a difference in the banding between the Hibbing and Aurora samples. The growth banding in the Hibbing samples tends to be more linear (Appendix A4 figure A5), while the growth banding in the Aurora samples tends to be more geometric (Appendix A4 figure

A6), appearing to illustrate the standard hexagonal growth of quartz crystals. The presence of growth banding in both the Hibbing and Aurora samples indicates that the fluids involved in quartz vein growth arrived in pulses. Although pulsed fluid flow could also characterize descending meteoric waters, the existence of growth banding is consistent with the involvement of deeply-sourced fluid that flowed episodically, and that perhaps may have mixed with another fluid at the site.

The primary sizes of the inclusions were about ten microns in diameter. Only two phase (liquid and vapor) inclusions were observed (Appendix A3). The temperature data was recorded when the vapor bubble homogenized in the liquid phase. Preliminary fluid inclusion homogenization temperatures show a bimodal distribution (Figure 1). One cluster of temperatures spans about 40-60 ℃ and another cluster at about 70-100 ℃. Table 1 shows the temperatures that were gathered.
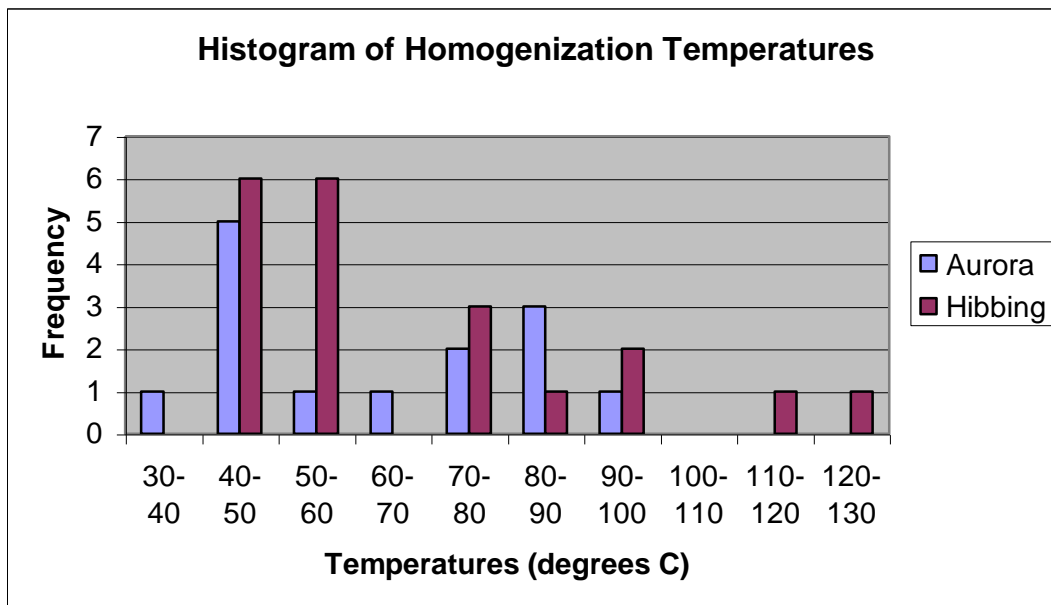

Figure 1. Histogram of homogenization of vapor bubble inside fluid inclusions.

The salinity data that was obtained from freezing the fluid inclusions shows salinities at about 4 wt% NaCl (Table 1). In comparison seawater is about 3.5 wt% NaCl. These high salinities indicate that the fluid responsible for forming the high-grade ore is not meteoric. If it were meteoric (fresh water), the salinities would be much lower. In addition, one fluid inclusion exhibited a final ice melting temperature of 0.8 °C, suggestive of the presence of a clathrate, which contains dissolved gases such as methane and carbon dioxide inside the fluid inclusion.

Table 1

Homogenization Temperatures		Hibbing Salinity Data		
Aurora	Hibbing	Homogenization Temp	Ice Melting Temp	wt% NaCl
32.5	43.6	59.6	-2.6	4.8967
42.9	46.1	114.5	-2.4	4.49842
44.1	47.8	122.5	-2.6	4.8967
47.1	48.2	95.1	0.8 (clathrate)	
48.7	48.5			
49.5	49.3			
53.5	50.9			
69.7	51.7			
75.1	52			
78.9	52.2			
83.5	58.2			
88.1	59.6			
88.3	70.5			
90.1	72.5			
	76			
	82.2			
	90.2			
	95.1			
	114.5			
	122.5			

Discussion

To evaluate the likelihood of finding more high-grade iron ore deeper underground, the fluids that are responsible for forming this high-grade ore have been

evaluated. The CL analysis indicated features such as banding. The banding that was present in the samples collected from two different areas could represent fluids coming up from depth in pulses.

The fluid inclusions homogenization temperatures indicate that fluid could have come from up from depth and/or percolated in from above. Homogenization temperatures have been found as high as 125 ℃, which is nowhere near a surface environment. The descending model would require homogenization temperatures that are cold when compared to these extremely hot temperatures, which support the ascending fluid model. Two data clusters of homogenization temperatures could mean that there was an alternation of fluid, one pulse of fluid coming up from depth giving rise to the high homogenization temperatures, and another source of fluid from above, shown by the low homogenization temperatures. The salinity data suggests that the fluid was considerably more saline than near-surface meteoric water and is more compatible with an ascending, far-traveled fluid.

Conclusion

Preliminary data does seem to indicate a fluid source that originated deep underground. Further data collection needs to be completed before more conclusive findings can be stated. More samples throughout the Mesabi Iron Range should also be collected to look for the same trends that are present in those samples from Hibbing and Aurora. Once more data has been collected and x-ray crystallography has been performed, a more definitive statement about the fluid source can be made.

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Appendix A1
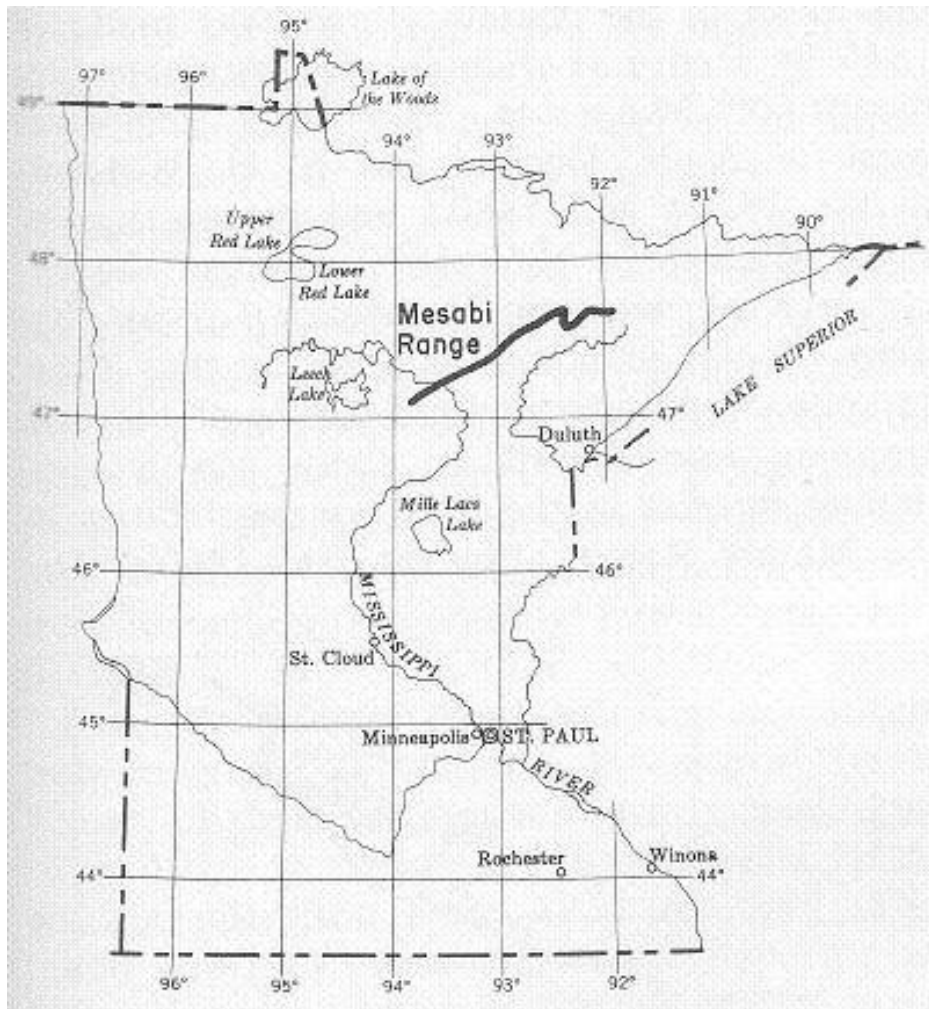
Figure A1: Location of Mesabi Iron Range in Minnesota

Source:

Marsden, R.W., Emanuelson, J.W., Owens, J.S., Walker, N.E., and Werner, R.F., 1968, The Mesabi iron range, Minnesota, *in* Ridge, J.D., ed., Ore deposits of the United States, 1933-1967: New York, Amer. Inst. of Min. Metal. & Petrol. Engrs., p. 518-537.
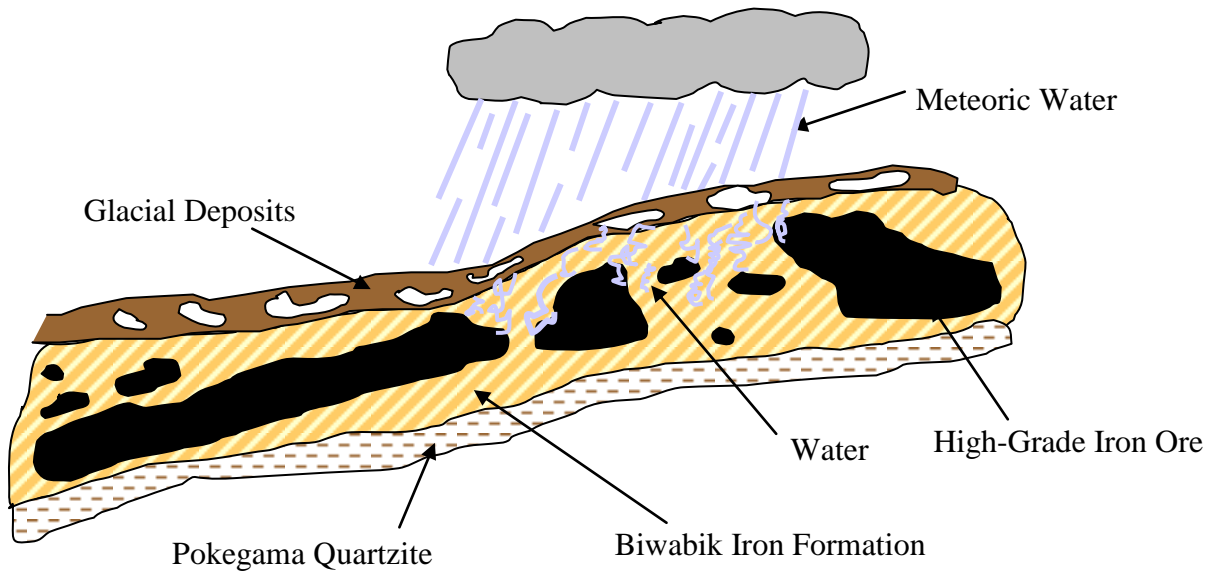
Appendix A2

Figure A2. Rainwater enters the iron formation from above and leaches silica, phosphate, magnesium, and calcium (Leith 1903). The remaining rock is an iron oxide of ore-grade material.
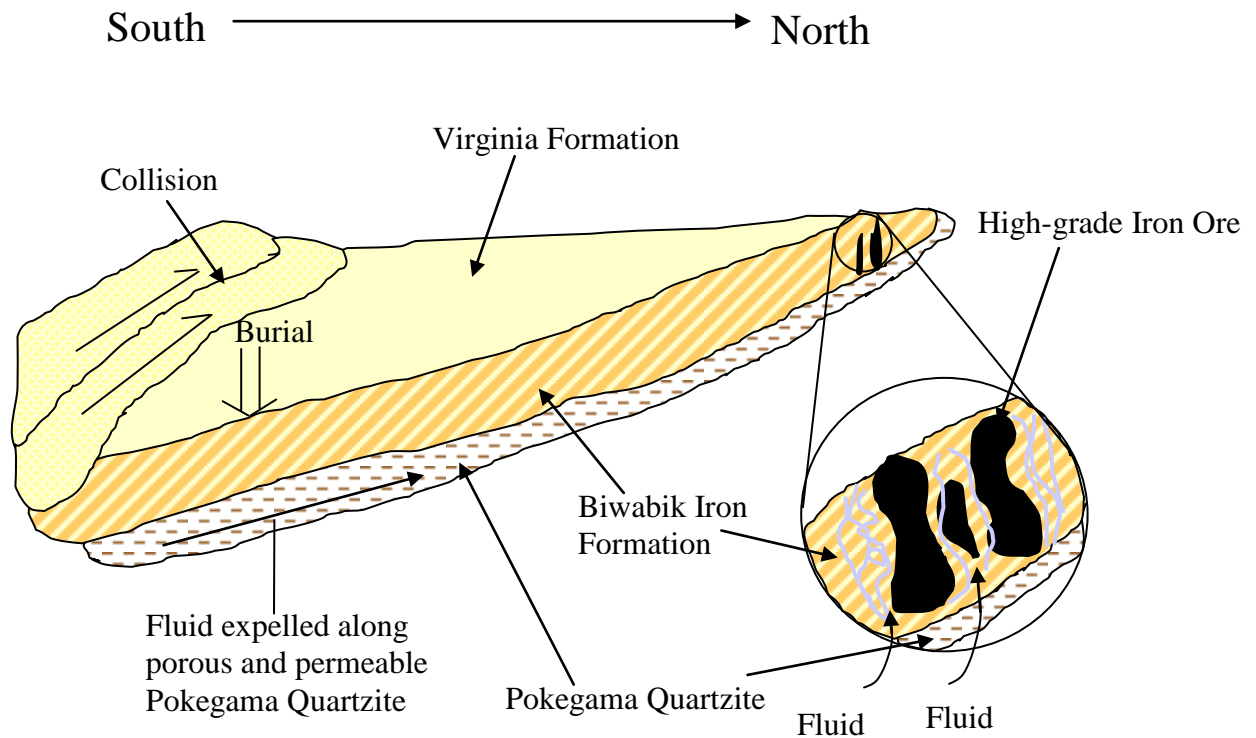

Figure A3. A collision event drove deep fluids up along the Pokegama Quartzite through sedimentary rocks toward the iron formation where minerals were leached out (Morey 1999).
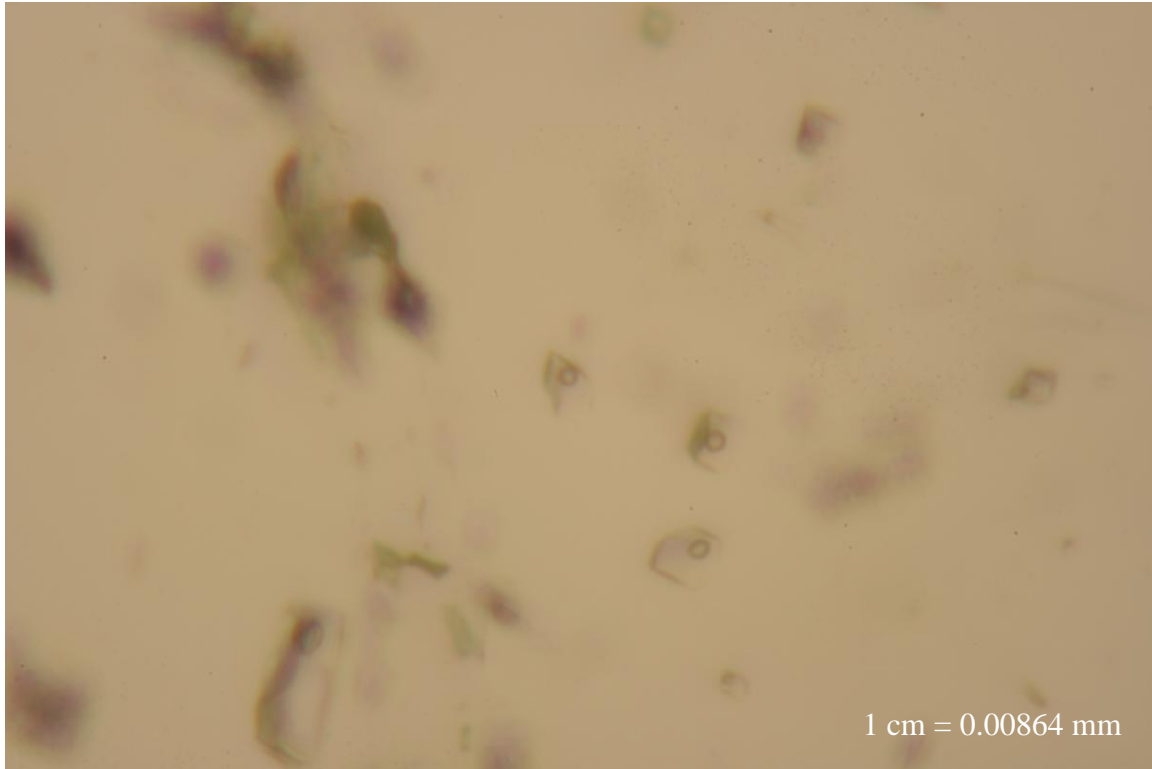
Appendix A3

1 cm = 0.00864 mm

Figure A4. Fluid inclusions with vapor bubble from a sample collected at the Number 6 pit 2 miles NE of Aurora, MN. Width of picture is 0.132 mm.
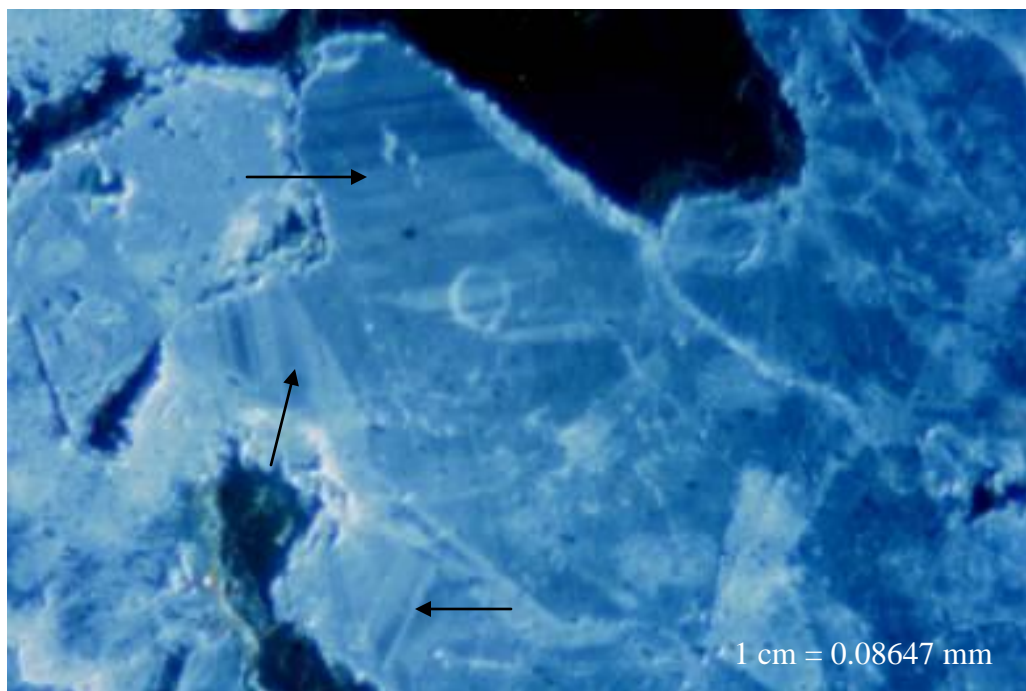
Appendix A4

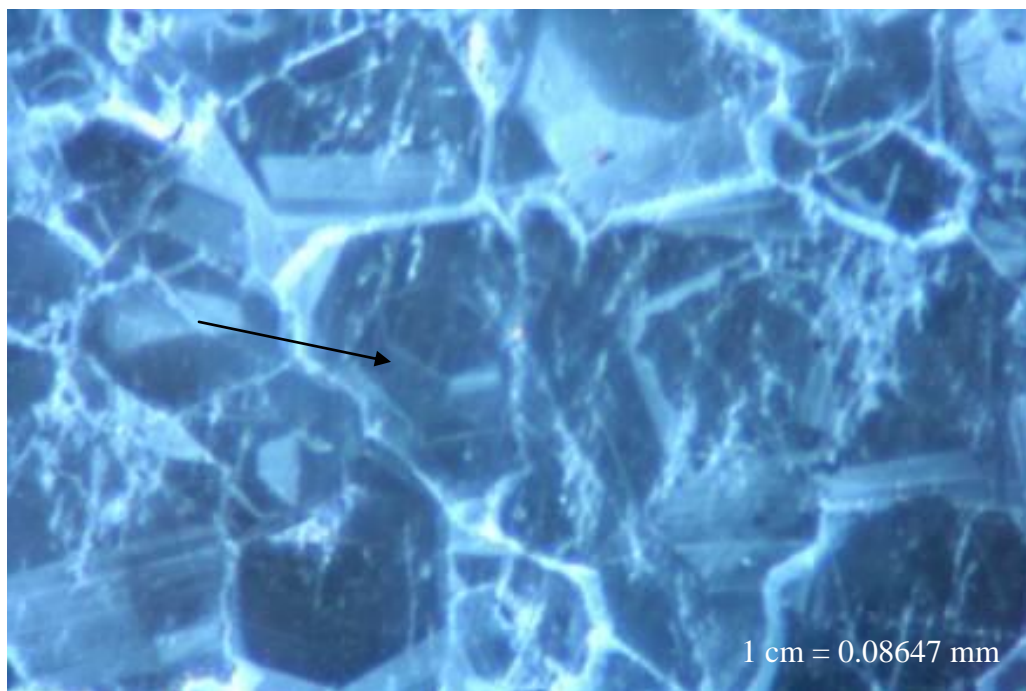**Figure A5.** Growth banding in a quartz vein sample from Hibbing, MN.

Figure A6. Growth banding in a quartz vein sample from Aurora, MN.

Author's Biography:

Elizabeth Drommerhausen was born and raised in New Prague, MN. After graduating from New Prague High School in 2003, she started attending Minnesota State University, Mankato. Elizabeth is pursuing a double major in Chemistry and Earth Science Secondary Education with a minor in Geology. She will be graduating in the spring of 2008. After graduation, Elizabeth plans to be employed at a secondary school teaching science.

Mentor's Biography

Dr. Steven Losh received a B.S. in Geological Engineering from the Colorado School of Mines and a Ph.D in Geology from Yale University. Over the past 20+ years, he has conducted research in fluid flow in a variety of geological settings from the oil and gas fields of the Gulf of Mexico to regional low-angle normal faults in Nevada to ore deposits in California and elsewhere. Dr. Losh has served as an assistant professor at MSU Mankato since 2005.