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Silica Distribution in Oxidized Biwabik Iron Formation: Ore-Waste Cutoff Prediction

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ABSTRACT

Silica Distribution in Oxidized Biwabik Iron Formation: Ore-Waste Cutoff Prediction

Oxidation of iron formation in the Mesabi Iron Range, Minnesota, has negatively impacted recovery of the main ore mineral, magnetite, by two mechanisms. First, magnetite has been partially or completely oxidized to hematite (martite), which is not magnetically separable. Second, silica has been remobilized during the oxidation process, and comprises a higher percentage of the ore concentrate than is desirable due to its altered grain size, making it difficult to grind sufficiently. Fluid inclusion data showed that fault-channeled, diagenesis-stage fluids (mean T homog = 154° C; mean salinity = 9.5 wt% NaCl equivalent) were responsible for early oxidation of iron formation: this event is distinct from later, widespread, shallow-level supergene (lateritic) oxidation.

Petrographic and SEM examination of rocks from early-oxidized zones show rims of recrystallized quartz around variably-oxidized magnetite in samples in which Fe-talc and/or minnesotaite have been oxidized to goethite, indicating silica redistribution during oxidation. No such rims have been noted in later (supergene)-oxidized iron formation, implying they may have formed only under diagenetic conditions. Additionally, quartz micro veins have filled fractures formed in magnetite grains caused by faulting in some ore zones. This study focuses on the cause and effect of silica remobilization with an eye to enabling prediction of the ore-waste cutoff in a mine from visual inspection of variably oxidized iron formation.

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Banded iron formations are the world's primary source of iron, and their geology has been studied for over a century (Leith, 1903). A classic example of a Banded Iron Formation that has been metamorphosed (altered) by the dissolution and recrystallization of silica is the Mesabi Iron Range of northern Minnesota (Leith, 1903; Gruner, 1946; Marsden et al., 1968). The Mesabi Iron Range forms a 150 km long by 6 km wide outcrop of 1.85 billon year old rock, known as the Biwabik Iron Formation.

The range has been economically affected by the oxidation of iron formation, negatively impacting the efficiency at which the mine can magnetically separate the main ore mineral, magnetite. In places throughout the mines, magnetite has been partly to completely oxidized to the mineral hematite, which is not amenable to magnetic separation (Losh and Rague, 2011). Additionally, silica has been remobilized by fluid flow during the oxidation process, recrystallizing quartz 'halos' around the perimeter of magnetite grains, resulting in less magnetic iron-ore. Near fault zones, silica recrystallization occurs in micro-fractures in magnetite grains, posing an issue when separating quartz and amenable iron-ore. The goal of my geologic research at Minnesota State University was to develop more efficient methods of silica prediction in oxidized ore zones in the Mesabi Iron Range.

From an economic standpoint, the issue is simple: silica concentration in oxidized iron ore concentrate is unacceptably high (>5% conc. wt.). Iron ore is pulverized and then magnetically separated to extract the greatest amount of iron-bearing minerals. The smallest size of pulverized ore is \sim 40µm, resulting in excess silica content in the iron ore concentrate if the quartz is less than 40µm in size. The excess silica lowers the quality of the taconite pellets that are produced from the iron ore concentrate, to manufacture steel. In summary, the more silica that remains connected to magnetite grains when pulverized and magnetically separated, the lower the profit margin of the mining operation.

There are three primary mine locations on the Mesabi Range that we sampled (appendix 1). The primary site of study was the Hibbtac Mine, located in Hibbing, Minnesota, on the southwest section of the iron range. The second and third sites of study are the Thunderbird and Fayal Mines, located within close proximity to each other, in the center of the iron range. These mine sites allowed increased accessibility and represent the greatest amount of rock samples analyzed. Samples from the LTV #6 deposit were also analyzed, however fewer samples were collected.

Oxidation in the Biwabik Iron Formation occurs in two major processes: near surface-lateritic oxidation and deep oxidation. Near surface oxidation (appendix 2) is characterized by chert peloid dissolution. The remaining voids are lined with red, microplaty hematite. Magnetite in

these lateritic ore systems is locally overgrown by goethite, resulting in the formation of 'Natural' Ore, the primary iron source of the 20^{th} century.

Deeply oxidized ore zones (appendix 3) are characterized by the oxidation of iron-talc to a fibrous, distinctly high temperature goethite that is indicative by early oxidation, determined by fluid inclusion analysis (Losh & Rague, 2011). The reaction between iron-talc, water and oxygen, produces equal volumes of goethite and quartz. Most notably, quartz has been remobilized at depth during deep oxidation, however it has not been completely dissolved, as documented with chert peloid dissolution during near surface oxidation.

To evaluate the effects of oxidation and quartz recrystallization in the iron formation, fluid inclusion thermometry and petrographic and scanning electron microscopic analysis was performed. Analyzed rock includes a traverse of samples collected from oxidized and unoxidized iron formation (appendix 4), including several fault zones (appendix 4 & 5). The mineralogical, chemical and structural variations between ore zones were analyzed to determine where zones of iron formation were impacted by silica recrystallization. The results of this study also conclude an additional event in the known geologic history of the Biwabik Iron Formation.

Fluid inclusion analysis was conducted to determine some of the fluid sources responsible for depositing quartz in the iron formation. Fluid inclusions are pockets of fluid and vapor that were trapped as the mineral precipitated into solid form (appendix 6). Fluid included into quartz varies chemically, depending upon the conditions from which the dissolved silica was deposited. Temperature manipulation was performed on primary and secondary inclusions to determine where the silica was derived. Heating the fluid inclusions to the point of fluid and vapor homogenization determined the minimum temperature of the fluid present during the time of mineral crystallization. Freezing the inclusion with liquid nitrogen and allowing it to thaw provides the melting temperature from which salinity (amount of dissolved salts) of the fluid inside the inclusion can be calculated (Bodnar, 1993). Higher homogenization temperatures (compared to surficial fluid temperature) and salinities are expected in oxidizing recrystallized quartz halos and recrystallized quartz veins.

The analysis of hundreds of fluid inclusions concluded a cumulative average homogenization temperature of 155.1°C, with a fault quartz average homogenization temperature of 157°C and a recrystallized quartz average homogenization temperature of 147.4°C (appendix 7).

The cumulative average inclusion salinity was 8.3 wt. % NaCl and the fault quartz average inclusion salinity was 9.5 wt. % NaCl (appendix 8). The results of the fluid inclusion analysis concluded that near surface, lateritic oxidation, responsible for the deposition of natural ore, was not the only oxidation and quartz remobilization episode in the history of the Biwabik Iron Formation. The high homogenization temperature and salinities provide evidence of an early oxidation and alteration event in which hot fluids, derived from depth flowed upward in the iron formation, recrystallizing quartz, particularly in fault zones. In addition to high temperature and

salinities, cooler homogenization temperature and lower salinities were also documented, insisting that near surface, lateritic oxidation occurred after a deep alteration event at depth.

The lithostatic depth temperature/pressure correction (~50°C/km depth) concludes that the iron formation was buried between 3-4 km below the earth's surface at the time of first oxidation and alteration. Oxygen was likely incorporated into upward flowing fluids via early faulting in the Biwabik Iron Formation. Faults are conduits for fluid rising upward and fluid percolating downward, explaining the mix of high and low temperature and salinity fluid inclusions. Recrystallized quartz was determined to be the product of deep fluid interaction with the iron formation. The extent of the recrystallized quartz halos occurs primarily in oxidized iron formation, determined by using petrographic microscopy to view samples at high magnification.

Mineralogical variations were analyzed using the Scanning Electron Microscope at Minnesota State University. Scanning electron microscopy (SEM) images the texture of mineral assemblages and alterations that occurred due to oxidation, such as quartz-goethite intergrowths resulting in pitting magnetite grains. The SEM can perform up to 300,000x optical zoom, making it ideal for close range analysis of iron-bearing minerals. Energy Dispersive Spectroscopy (EDS) was used to identify the chemical composition (by atomic weight percentage) and chart chemical variations in oxidized versus unoxidized iron formation, especially with regard to the composition of iron oxide-silica intergrowths (appendix 9).

Recrystallized quartz halos were identified in oxidized ore zones using petrographic imagery, energy dispersive spectroscopy (EDS) and scanning electron microscopy (appendix 10). The width of documented recrystallize quartz rims is 10μ m- 50μ m, making adequate pulverization and magnetic separation extremely difficult. Upon closer examination, micro-fractures in magnetite grains were filled with recrystallized quartz veins, ranging in size between 1μ m- 25μ m, in oxidized ore zones (appendix 11). Due to stress fracturing from faulting, fault-adjacent ore zones showed significantly more magnetite micro-fractures filled in with recrystallized quartz (appendix 12). Samples closest to the fault had the highest percentage of quartz halos and quartz micro-veins, decreasing with distance from the fault. It is important that mine geologists are aware of this correlation so that ore excavation can continue up to a predetermined point near fault zones, as examined by the mine geologist.

From the information gathered during this analysis, a proposed burial history and fluid event plot was developed (appendix 13). The Biwabik Iron Formation was initially deposited in a shallow, temperate sea, 1.85 billion years ago. Shortly after deposition the iron formation was buried underneath the erosional sediments of the Penokean Orogeny (erosional mountain sediments). Around 1.65 billion years ago, subsequent uplift from the Duluth Complex and overlaying erosion began the ascent of the Biwabik Iron Formation toward the surface. Around 1.6 billion years ago, between 3-4 km below the earth's surface, the first high-angle faulting and oxidation (diagenetic) events occurred, responsible for the deep oxidation and alteration of iron formation. Continued uplift of the Biwabik Iron Formation and erosion of overbearing sediments over the

next 1.5 billion years brought the iron formation back to the surface, where lateritic (near surface) oxidation and the creation of 'natural' ore occurred.

The results from my undergraduate research of the Mesabi Iron Range conclude that the Biwabik Iron Formation had two distinctly separate oxidation events. The first oxidation occurred ~1.65 billion years ago and was diagenetic (first occurrence). The second oxidation occurred between 100 million years ago and present day, at or near the earth's surface, after uplift and erosion occurred.

The economic solutions to counteracting the ore processing effects of quartz halos and quartz micro veins in magnetite fractures are quite simple, and enormously beneficial. Grinding early oxidized ore zones to 20μ m, rather than 40μ m, will reduce the silica content in oxidized ore zones by up to 3% (determined using SEM and data calculations). Reducing the silica content in early oxidized zones by 3% widely permits the concentration of iron ore to include less than 5% silica, the cutoff mark for economical excavation and processing of iron ore to taconite. The economic iron concentration of deeply oxidized ore is viable, granted the research and pulverization efforts are made as advised through this research.

The results from this research may assist mine geologists to more accurately predict silica abundance in ore zones in Northern Minnesota. Examining the Mesabi Iron Range has resulted in an early mineralogical prediction system, particularly near fault zones and an updated geological history of the Biwabik Iron Formation. This project has been performed accurately, with a high degree of analysis, in the development of conclusive results.

Appendix



1.) Mine sampling sites: Hibbtac Mine, Thunderbird & Fayal Mines, and the LTV #6 deposit.



2.) Near Surface-Lateritic Oxidation: Chert Peloid dissolution filled with red, microplaty hematite.



3.) Deep oxidation: goethite and quartz intergrown; quartz is recrystallized but not completely dissolved.



4.) Oxidized ore zones highlighted in red; fault zones signified by black lines.



5.) Petrographic image of breccia inside of faults indicated in appendix 4. Recrystallized quartz cements larger quartz clasts together. Recrystallized quartz is intergrown with goethite (brown mineral), indicating that fluids had oxidizing properties.



6.) Fluid inclusions are bubbles of fluid and vapor trapped as the mineral was precipitated.



7.) Fluid inclusion thermometry chart indicates temperatures of low-angle quartz vein inclusions, fault breccia inclusions in oxidized zones, high-angle quartz vein inclusions without oxidation and septarian (diagenetic) quartz vein fluid inclusion temperatures.



- 8.) Salinity plot of fluid inclusions analyzed from conditions state above in adjacent table.
- 9.) Point and Shoot function lists elements by atomic weight percentage.



СК	3.29 +/-0.15
ОК	29.19 +/-0.31
FΚ	0.00 +/-0.00
Mg K	0.53 +/-0.08
Al K	0.49 +/-0.08
Si K	8.54 +/-0.17
Fe K	<u> 57.97 +/-1.23</u>
	Total 100.00



10.) Recrystallized quartz halos seen in petrographic view (left) and SEM & EDS (right), highlighted in green



11.)Quartz micro fractures in magnetite, highlighted in green.



12.)Magnetite closest to a fault shows the greatest amount of micro fracturing in which silica can recrystallize quartz micro veins within.



13.) Proposed burial history and fluid event plot of the Biwabik Iron Formation.

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Ryan Rague is 2013 graduate and recipient of a Bachelor of Science Degree in Earth Science from Minnesota State University-Mankato. While completing his academic curriculum, he focused on researching quartz and magnetite distribution in oxidized iron deposits in the Mesabi Iron Range of Northern Minnesota (2010-2013). His research was presented nationwide, in large part to encouragement and funding from the Undergraduate Research Center, the College of Science, Engineering and Technology, the Department of Chemstry & Geology, and Minnesota State University-Mankato. He was the president of the MNSU Geology Club from 2010-2012 and enjoys promoting progressive and responsible mine geology research and consulting.

Faculty Mentor:

Steven Losh is a Professor of Geology in the Department of Chemistry and Geology. He obtained his B.S. in Geological Engineering at the Colorado School of Mines and his PhD in Geology at Yale University. His research focuses on fluid flow in faults, a topic that has led into research on gold and iron deposits, fluid sources and movement in oilfields and processes that affect oil chemistry, and fault mechanics that bear on earthquake occurrence. He enjoys research and passing on the excitement of it to the next generation of geologists.