ORIGIN, DISTRIBUTION, MORPHOLOGY, AND CHEMISTRY OF AMPHIBOLES IN THE IRONWOOD IRON-FORMATION, GOGEBIC IRON RANGE, WISCONSIN, U.S.A

by

Carlin J. Green
A Thesis
Submitted to the
Graduate Faculty
of
George Mason University
in Partial Fulfillment of
The Requirements for the Degree
of
Master of Science
Earth Systems Science

Committee:

_____ Dr. Julia Nord, Thesis Director

_____ Dr. Robert Seal, Committee Member

_____ Dr. Robert Hazen, Committee Member

_____ Dr. James Kinter, Department Chairperson

_____ Dr. Donna M. Fox, Associate Dean, Office of Student Affairs & Special Programs, College of Science

_____ Dr. Peggy Agouris, Dean, College of Science

Date: _____ Fall Semester 2017
George Mason University
Fairfax, VA

Origin, Distribution, Morphology, and Chemistry of Amphiboles in the Ironwood Iron-Formation, Gogebic Iron Range, Wisconsin, U.S.A.

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science at George Mason University

By

Carlin J. Green
Bachelor of Science
George Mason University, 2015

Director: Dr. Julia Nord, Professor
Department of Atmospheric, Oceanic and Earth Sciences

Fall Semester 2017
George Mason University
Fairfax, VA

ACKNOWLEDGEMENTS

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

ABSTRACT

ORIGIN, DISTRIBUTION, MORPHOLOGY, AND CHEMISTRY OF AMPHIBOLES IN THE IRONWOOD IRON FORMATION, GOGEBIC IRON RANGE, WISCONSIN, U.S.A.

Carlin J. Green, M.Sc.

George Mason University, 2017

Thesis Director: Dr. Julia Nord

The Ironwood Iron-Formation, located in the Gogebic Iron Range in Wisconsin, is one of the largest undeveloped taconite resources in the United States. Interest in the development of this resource is complicated by potential environmental and health effects related to the presence of amphibole minerals in the Ironwood Iron-Formation, a consequence of Mesoproterozoic contact metamorphism. The purpose of this study is to provide mineralogical information about these amphiboles to aid regulatory, medical, and mining entities in their evaluation of this potential resource. Optical microscopy, X-ray diffraction, scanning electron microscopy, and electron microprobe analysis techniques were utilized to study the origin, distribution, morphology, and chemistry of amphiboles in the Ironwood Iron-Formation. The development of amphiboles from Fe-carbonates and Fe-phyllosilicates at temperatures of approximately 300 - 340º C has long been recognized as a result of regionally extensive contact metamorphism of the Ironwood Iron-Formation by the Mellen Intrusive Complex, however amphiboles related to the emplacement of diabase or gabbro dikes and sills in low-grade iron-formation were also recognized in this study area. Amphiboles in the Ironwood Iron-Formation most commonly

developed in massive and prismatic habits, and locally assumed a fibrous habit. Fibrous

amphiboles were locally recognized in the two potential ore zones of the Ironwood Iron-

Formation, but were not observed in the portion considered to be waste rock. Massive and

prismatic amphiboles show a wide range of Mg# values (0.06 to 0.87), whereas Mg# values of

fibrous amphiboles are restricted from 0.14 to 0.35. Factors that influenced the compositional

variability of amphiboles in the Ironwood Iron-Formation may have included temperature of

formation, the presence of coexisting minerals, morphology, bulk chemistry of the iron-

formation, and variations in prograde and retrograde metamorphism.

INTRODUCTION

The Paleoproterozoic Ironwood Iron-Formation is the principal iron-bearing unit of the

Gogebic Iron Range, which produced approximately 325 billion tons of "natural" (supergene) ore

from 1877 to 1967 (Cannon et al., 2007). The focus of this study is a 35 km-long belt in the

western portion of the Ironwood Iron-Formation in northern Wisconsin that contains

approximately 3.7 billion tons of material constituting one of the nation's largest undeveloped

taconite resources (Mardsen, 1978; Cannon et al., 2007). While the presence of amphiboles in

some taconite deposits resulting from metamorphism has been recognized since at least 1955 in

the Lake Superior region (James, 1955), they became the subject of intense scrutiny in the mid

1970's. At that time, the Reserve Mining Company developed the Peter Mitchell Pit in the

eastern Biwabik iron-formation, Minnesota, producing approximately 11% of US iron (Berndt

and Brice, 2008). Rocks in portions of the Peter Mitchell Pit, having been subjected to intense

contact metamorphism by the intrusion of the Duluth Complex, contained significant amounts of

grunerite-cummingtonite. Reserve Mining's method of disposal of taconite tailings into Lake

Superior eventually resulted in the recognition of amphibole particles in the drinking water

supplies in Duluth, Minnesota, which sparked legal action and a series of investigations into the

nature of the amphibole particles and their potential human-health impacts. In addition to their

presence in the waters of Lake Superior, it was determined that amphibole particles were also

present in the air as a result of mineral processing in Silver Bay, Minnesota. An appeals court

ruling determined that the existence of amphibole particles in air and water gave rise to a

reasonable medical concern for the public health. This resulted in a court order to immediately

reduce the level of airborne particle emissions and provided a "reasonable time" to cease

discharge into Lake Superior as an alternative disposal site was permitted (Berndt and Brice,

2008).

The presence of amphibole minerals in the ~1.87 Ga Ironwood Iron-Formation has been a

cause of controversy due to conflicting claims about the prevalence of fibrous amphibole

minerals in proposed mining areas. The potential human-health risks of mining rocks that bear

fibrous amphiboles necessitate a more detailed understanding of amphibole minerals in the

Ironwood Iron-Formation. This study was conducted to provide unbiased information regarding

the origin, distribution, morphology, and quantitative chemistry of amphibole minerals in the

Ironwood Iron-Formation.

STUDY AREA

The Ironwood Iron-Formation, is a classic banded iron formation (BIF) in the Lake Superior Region,which formed in a shallow sea that resulted from extension and subsidence of the Superior craton associated with the 1.88 Ga Penokean Orogeny (Schulz and Cannon, 2007). The study area is an approximately 35-kilometer east-west trending portion of the western Gogebic Iron Range, bounded in the east by the town of Upson and in the west by Mineral Lake (Figure 1). The Ironwood Iron-Formation was divided by Hotchkiss (1919) into five members: from the base upward, these are the Plymouth, Yale, Norrie, Pence, and Anvil members. The Anvil member is absent from the study area. The Ironwood Iron-Formation conformably overlies the Palms Formation, which was deposited in a tidal environment and grades upward over several meters into the Ironwood Iron-Formation, marking the transition from clastic to chemical sedimentation (Ojakangas, 1983; Cannon et al., 2007). Together, these formations comprise the Menominee Group in the western portion of the Ironwood Iron-Formation. The Ironwood Iron-Formation is unconformably overlain by Tyler Formation in the study area, a turbiditic unit primarily composed of black shale and greywacke (Cannon et al., 2007).

In the western portion of the study area, the Ironwood Iron-Formation is truncated by Mesoproterozoic gabbro of the 1.1 Ga Mellen Intrusive Complex. The primary effect of this intrusion was the formation of a broad contact metamorphic aureole, with metamorphic grade being most intense in the west, and diminishing eastward as the distance between the Ironwood Iron-Formation and the Mellen Intrusive Complex increases (Cannon et al., 2007). Laybourn

3

(1979) divided the Ironwood Iron-Formation into four metamorphic zones, which are defined by the degree of contact metamorphism and the resulting mineral assemblages. These zones closely parallel the progressive contact metamorphism found in the Biwabik Iron-Formation due to the intrusion of the Duluth Complex in Minnesota as described by French (1968). Zone 1 experienced diagenetic alteration/low-grade metamorphism and is defined by the presence of the Fe-phyllosilicates minnesotaite and stilpnomelane and Fe-bearing carbonates such as siderite, dolomite, and ankerite. Zone 2 is characterized by medium-grade metamorphic conditions that resulted in the disappearance of Fe-phyllosilicates and Fe-bearing carbonates and the appearance of amphibole. Zone 3 underwent high-grade metamorphism and is defined by the presence of pyroxenes that develop from amphiboles. Zone 4 represents the highest grade of metamorphism where the development of fayalite is observed, and occurs in close proximity to the intrusive contact.

The emplacement of the Mellen Intrusive Complex is approximately coeval with northward tilting of the region during events related to the Midcontinent Rift at about 1.1 Ga (Cannon et al., 1993; 2007). As a result of this tilting, the surficial geology of the region offers an oblique cross-sectional view of the Paleoproterozoic strata at the surface(Cannon et al., 2007). An additional effect of tilting is the change between true distance and geographic distance with respect to the Ironwood Iron-Formation and the Mellen Intrusive Complex. The conversion from geographic distance to true distance is detailed in Figure 2.
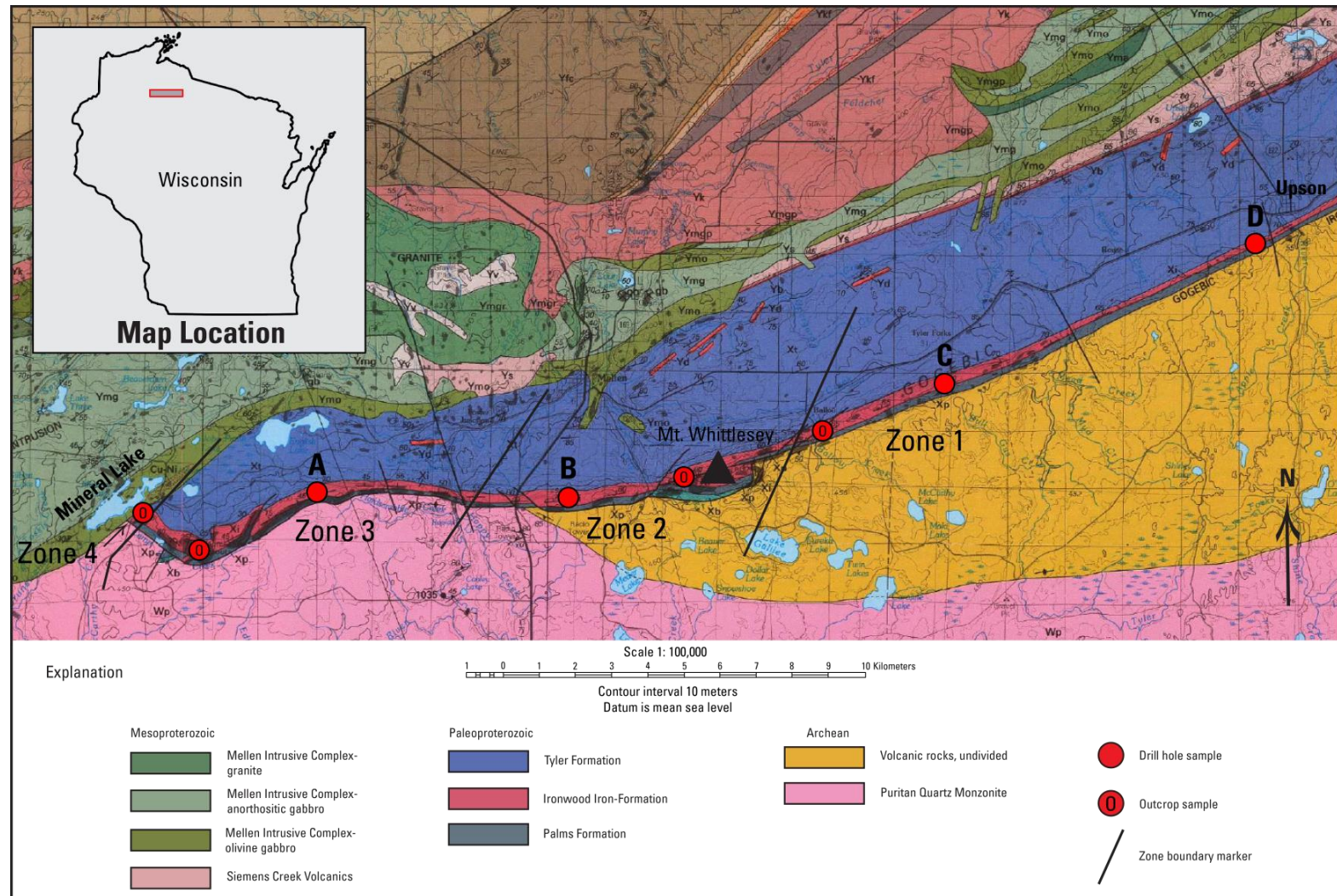
Figure 1. Geologic map of the study area and sampling locations within the Ironwood Iron-Formation, after Cannon et al. (1996).
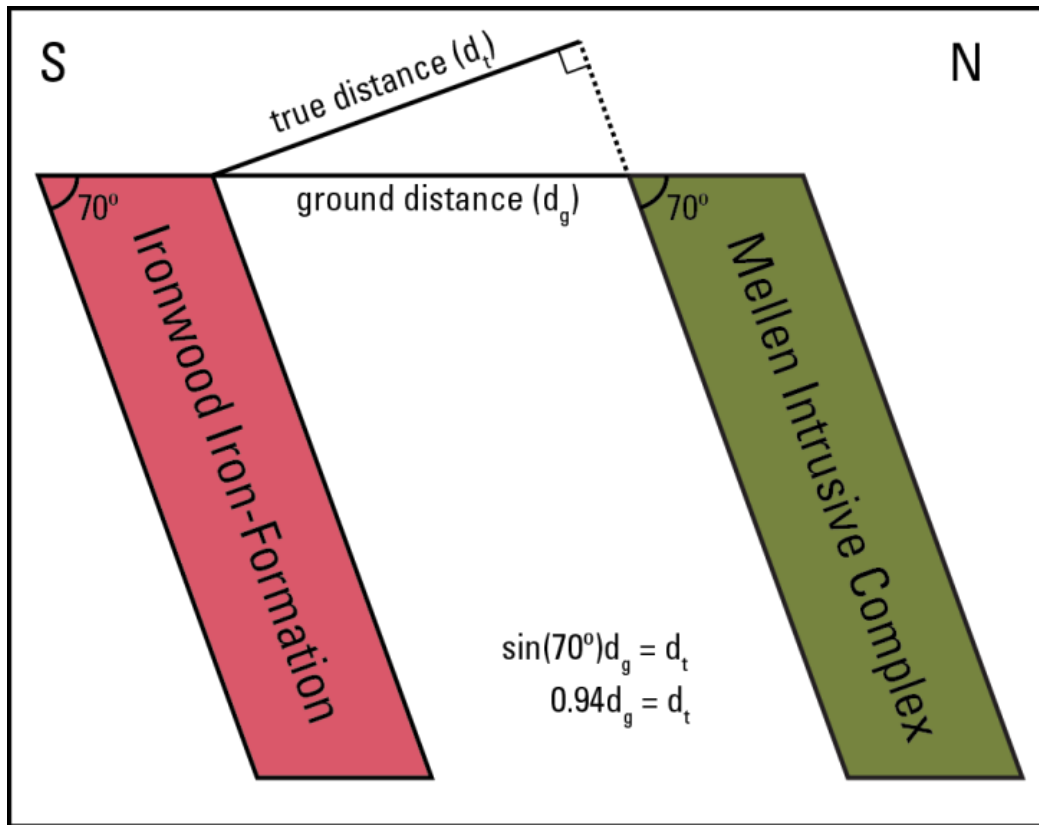
Figure 2. Method for the calculation of true distance between the Ironwood Iron-Formation and the Mellen Intrusive Complex. Average dip of 70º is assumed for both units (Cannon et al., 1996).

SAMPLE COLLECTION AND METHODS

In order to observe changes in mineralogy related to varying degrees of contact metamorphism, sampling locations were selected at distances ranging from 0 to approximately 5 kilometers between the Ironwood Iron-Formation and the Mellen Intrusive Complex. Sampling consisted of several outcrop locations and four diamond drill-cores (designated A-D) which extend throughout the entirety of the Ironwood Iron-Formation, ranging from 171 to 237 meters of continuous drill-core. Each drill-core was collared in the Pence member and ended in the upper quartzite unit of the Palms Formation. Two different types of drill-core samples were taken: a set of samples from each lithologic sub-unit intended to be representative of the section, and a topical set that could potentially yield insights about the paragenesis of amphiboles in the iron formation.

A variety of methods were used to qualitatively and quantitatively characterize samples collected from the Ironwood Iron-Formation. Polarized light microscopy was used to examine thin sections, and areas of interest were observed using a Hitachi SU5000 field emission scanning electron microscope equipped with energy dispersive X-ray spectroscopy (SEM/EDS). Using SEM imagery, amphiboles were systematically observed and measured to provide morphological and geometric data. In order to limit selective bias, a standardized grid of ten uniform areas per thin section was utilized (Figure 3), and the amphiboles within these areas were categorized according to definitions adapted from Campbell et al. (1977). These categories are: massive, equant, prismatic, and fibrous. Massive amphibole particles are tightly packed with scarcely

7

distinguishable grain boundaries and are arranged in a homogenous structure. Equant particles are those with three approximately equally spaced dimensions, whereas prismatic particles are those with one elongate dimension and two approximately equal shorter dimensions. Fibrous particles are those with high aspect ratios, often displaying curvature and occurring in bundles. The minimum aspect ratio necessary to apply the term "fibrous" is generally 3:1 according to most regulatory bodies such as the International Organization for Standardization, National Institute for Occupational Safety and Health, and National Bureau of Standards, but this is often constrained by a maximum particle width of 3 μm (Lowers and Meeker, 2002). This width requirement allows for the distinction between prismatic particles that may have aspect ratios of greater than 3:1 but are generally much wider than fibrous particles. Using these morphological definitions and the standardized grid method, seventeen thin sections in which amphibole minerals are a major constituent were examined. Of the 170 areas observed, 158 of them contained amphibole minerals.
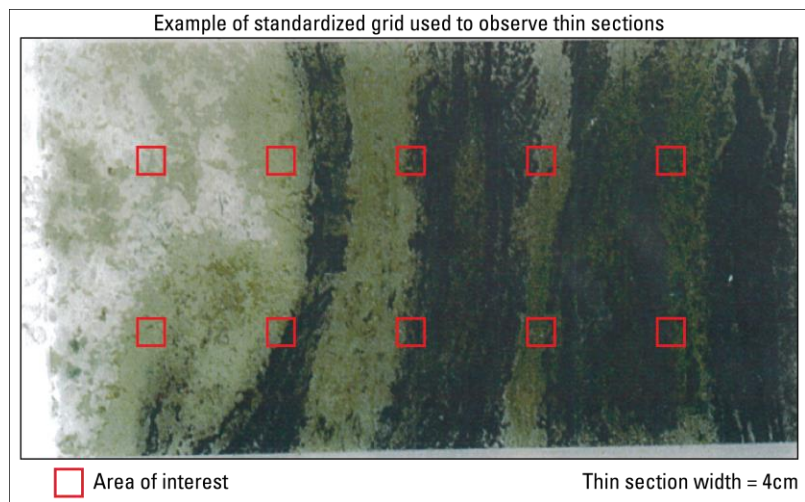
Figure 3. An example of the standardized grid of points or areas used to observe multiple thin sections in an unbiased manner. Sample A-276 shown.

A total of 437 amphibole particles of prismatic, equant, and fibrous morphologies were measured using QuartzPCI, an SEM imaging software, in order to determine geometric parameters such as length, width, and aspect ratio. Massive particles were not measured because by definition, their boundaries were indistinct. These data are shown in Figures 12-14, which display the properties of fibrous amphibole particles superimposed on the entire set. Fibrous amphiboles were identified using ISO 10312 criteria for phase-contrast microscopy equivalent fibers which are the basis for most health studies related to cancers in humans caused by asbestos exposure. These criteria are: length of greater than 5 µm, width between 0.25 and 3 µm, and aspect ratio of greater than 3:1 (Ecology and Environment, Inc., 2005).

In order to perform powder X-ray diffraction (XRD), drill-core samples were crushed by hand, micronized for 5 minutes, and ran as sideloaded mounts using Co K-α radiation at 60 seconds per step on a a PANalytical X`Pert PRO diffractometer. XRD was used to determine the presence of amphiboles and modal mineral abundance, aided by Reitveld refinement using HighScore Plus v.4.5. A JEOL JXA-8900 electron microprobe analyzer utilizing wavelength-dispersive spectroscopy (EPMA-WDS) was employed to determine the chemistry of various minerals. Amphiboles were analyzed using a 1 µm spot size for Na, Mn, Si, Ti, Mg, Al, Fe, Ca, K, Cr, F, and Cl. The $Fe^{3+}/\Sigma Fe$ ratio was estimated using cation normalization schemes selected based on the smallest maximum deviations from the criteria discussed in Appendix III of Hawthorne et al. (2012) (Locock, 2014). Pyroxenes were analyzed using a 1 µm spot size for Na, Mn, Ni, Ca, Al, Cr, Si, Mg, Fe, K, and Ti, whereas carbonates were analzyed using a 20 µm spot size for Ca, Mn, Fe, Mg, and Sr.

ORIGIN OF AMPHIBOLES IN THE IRONWOOD IRON-FORMATION

The Ironwood Iron-Formation experienced progressive contact metamorphism due to the emplacement of the Mesoproterozoic Mellen Intrusive Complex. The effects of the formation of a broad contact metamorphic aureole are first observed near Upson, in the eastern portion of the study area. The degree of metamorphism increases westward, reaching a maximum near Mineral Lake in the western portion of the study area where the Ironwood Iron-Formation is truncated by the Mellen Intrusive Complex (Figure 1).

The Ironwood Iron-Formation can be divided into four zones, which are defined by the degree of contact metamorphism and the resulting mineral assemblages (Figure 1; Laybourn, 1979). These zones closely parallel the progressive contact metamorphism of the Biwabik Iron-Formation by the Duluth Complex in Minnesota as described by French (1968). Zone 1 experienced low-grade/diagenetic metamorphism and is characterized by the presence of the Fe-phyllosilicates minnesotaite and stilpnomelane and Fe-bearing carbonates such as siderite, dolomite, and ankerite. This zone extends to within approximately 3.5 km distance from the body of the Mellen Intrusive Complex. In this zone, temperatures reached approximately 300-340° C, which is the upper stability limit of these minerals (French, 1973; Frost et al., 2007).

The transition to Zone 2 occurs approximately 2.5 km east of Mount Whittlesey. It lies between approximately 2.5 and 3.5 km distance from the body of the Mellen Intrusive Complex. In this zone, amphibole minerals in the cummingtonite – grunerite and actinolite – ferro-actinolite series develop as Fe-phyllosilicates and Fe-carbonates undergo a variety of dehydration and

decarbonation reactions (French, 1968; Bonnichsen, 1975; Laybourn, 1979; Frost, 1979), for example:

1) $7Fe_3Si_4O_{10}(OH)_2 = 3Fe_7Si_8O_{22}(OH)_2 + 4SiO_2 + 4H_2O$
   minnesotaite   grunerite   quartz

2) $5Ca(Fe,Mg)(CO_3)_2 + 8SiO_2 + H_2O = Ca_2(Fe,Mg)_5Si_8O_{22}(OH)_2 + 3CaCO_3 + 7CO_2$
   ankerite   quartz   actinolite   calcite

3) $7FeCO_3 + 8SiO_2 + H_2O = Fe_7Si_8O_{22}(OH)_2 + 7CO_2$
   siderite   quartz   grunerite
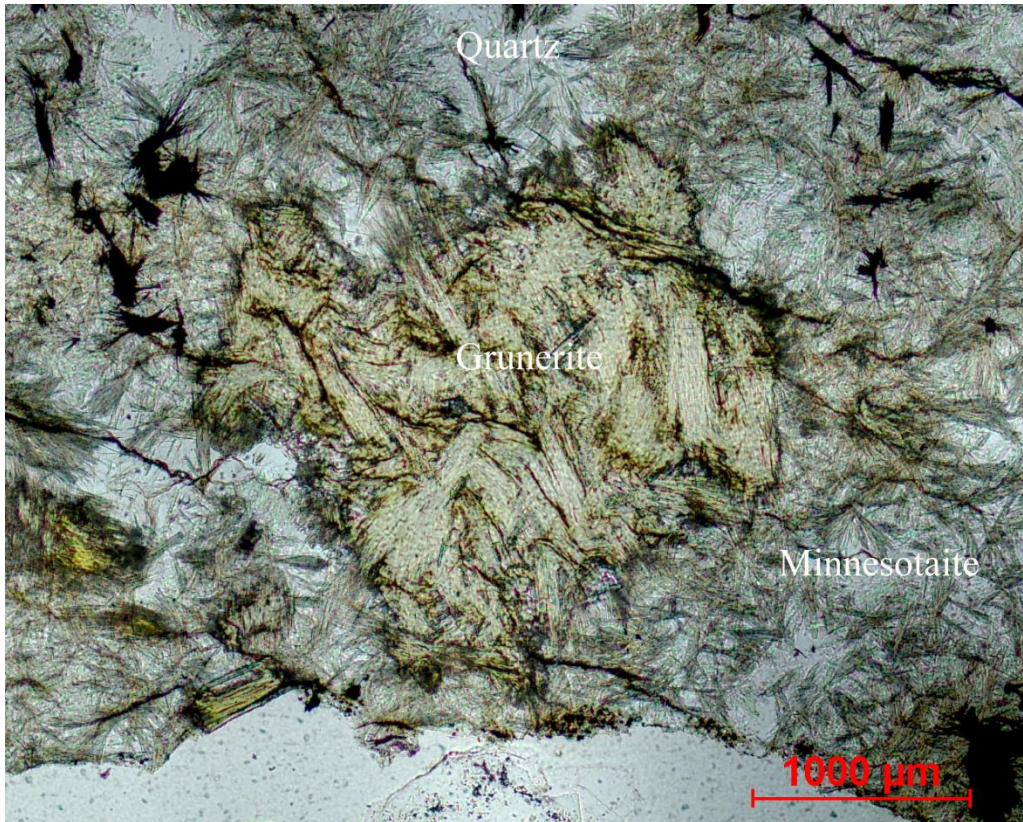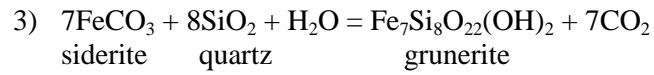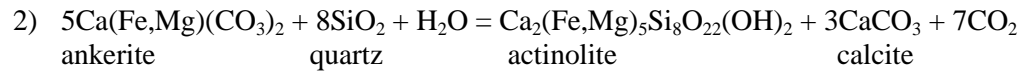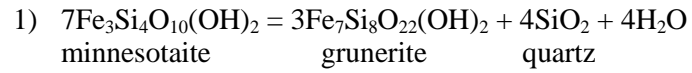
Figure 4. Mass of grunerite surrounded by sheaves of minnesotaite in sample D-64.0
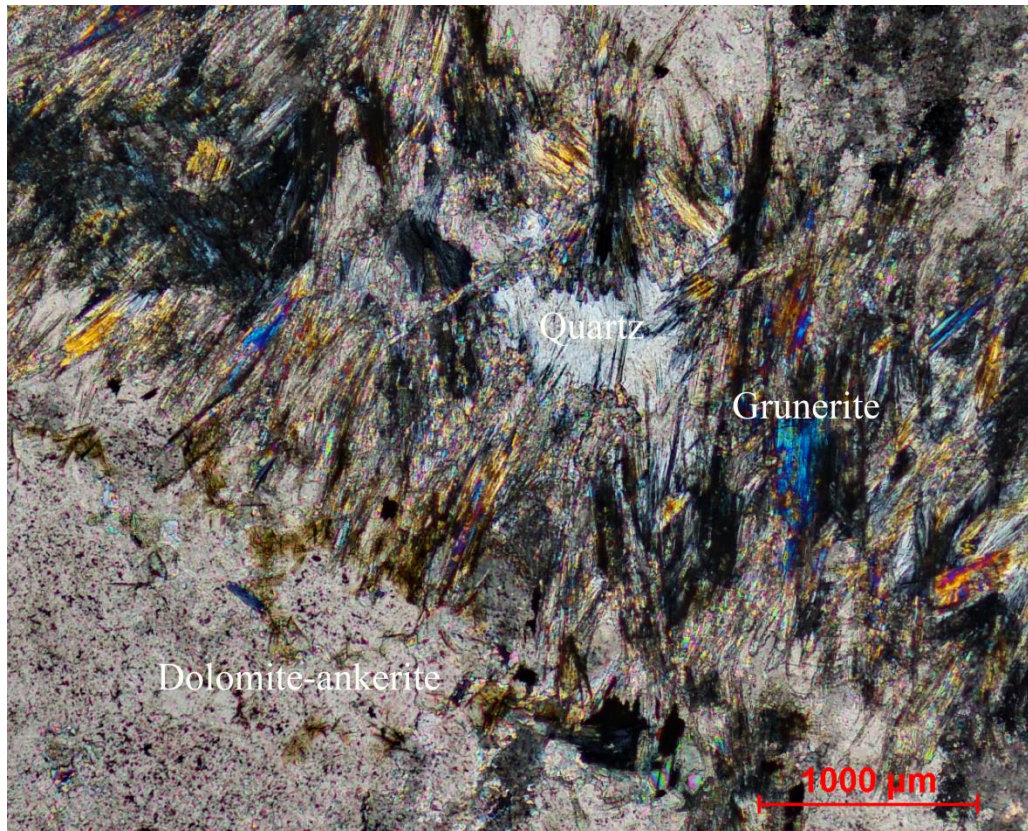
Figure 5. Grunerite developing from carbonates of the dolomite-ankerite series in sample C-813.5.

Zone 3 comprises the area of the Ironwood Iron-Formation that is less than 2.5 km from the Mellen Intrusive Complex, and up to within 100 meters of the contact between the two in the western portion of the study area. It is characterized by the development of pyroxene from amphiboles by the following reactions (Bonnichsen, 1975; Laybourn, 1979):

1) $Ca_2(Fe,Mg)_5Si_8O_{22}(OH)_2 + 3CaCO_3 + 2SiO_2 = 5Ca(Fe,Mg)Si_2O_6 + 3CO_2 + H_2O$
   actinolite   calcite   quartz   hedenbergite

2) $Fe_7Si_8O_{22}(OH)_2 = 7FeSiO_3 + SiO_2 + H_2O$
   grunerite   ferrosilite   quartz
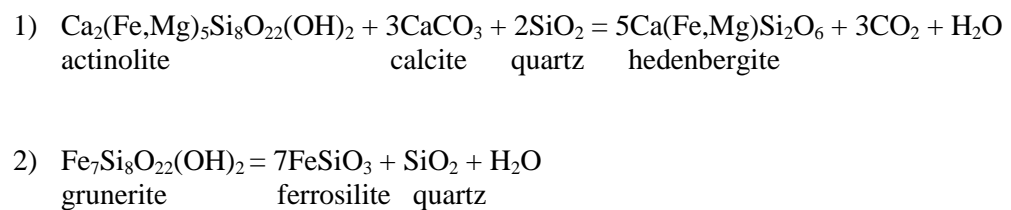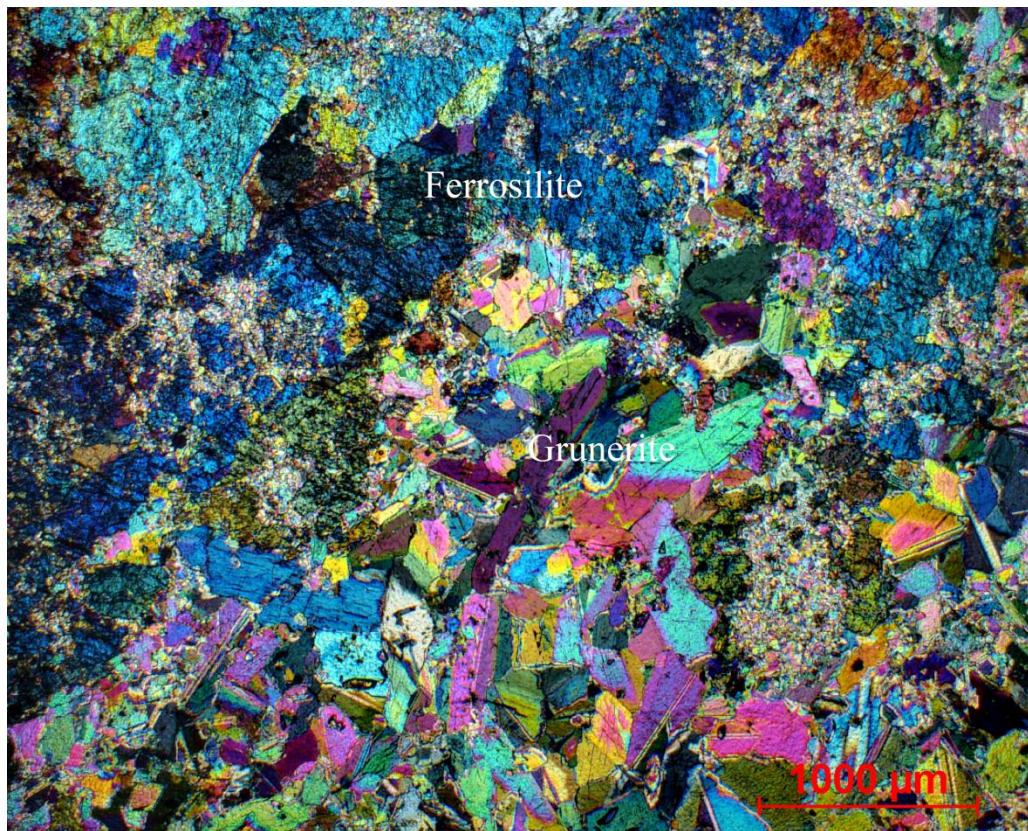
Figure 6. Ferrosilite and grunerite in sample A-532.5.

A retrograde metamorphic event is documented in Zone 3 by the presence of fine-grained grunerite exhibiting a secondary replacement texture after large, prismatic crystals (Figure 7), and by the development of grunerite from orthopyroxene (Figure 8), which proceeds by the following reaction (Bonnichsen, 1969):

1) $7FeSiO_3 + SiO_2 + H_2O = Fe_7Si_8O_{22}(OH)_2$
   ferrosilite   quartz   grunerite
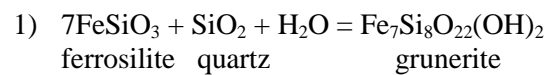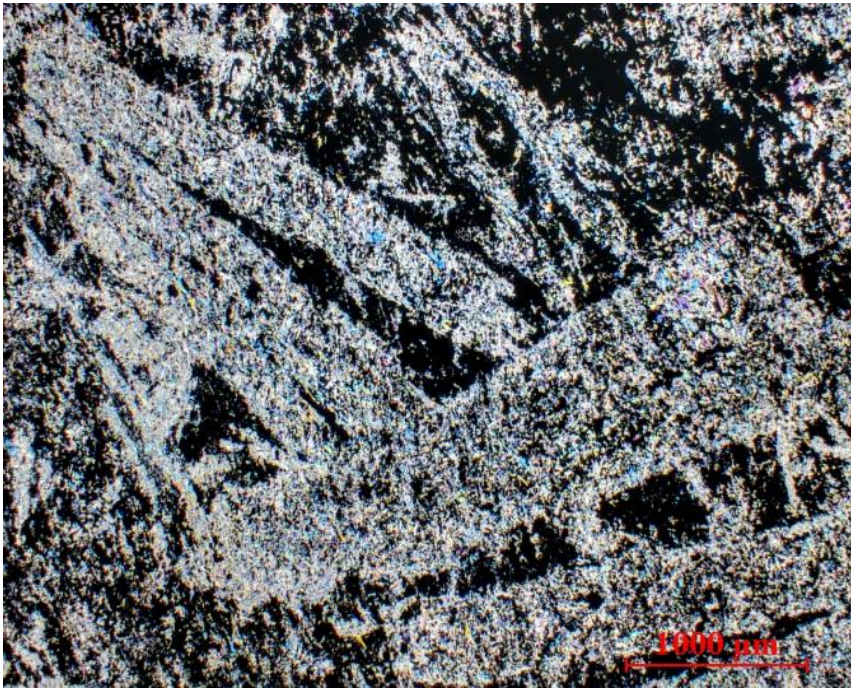
Figure 7. Replacement of prograde prismatic grunerite by fine-grained retrograde grunerite in sample A-395.5.
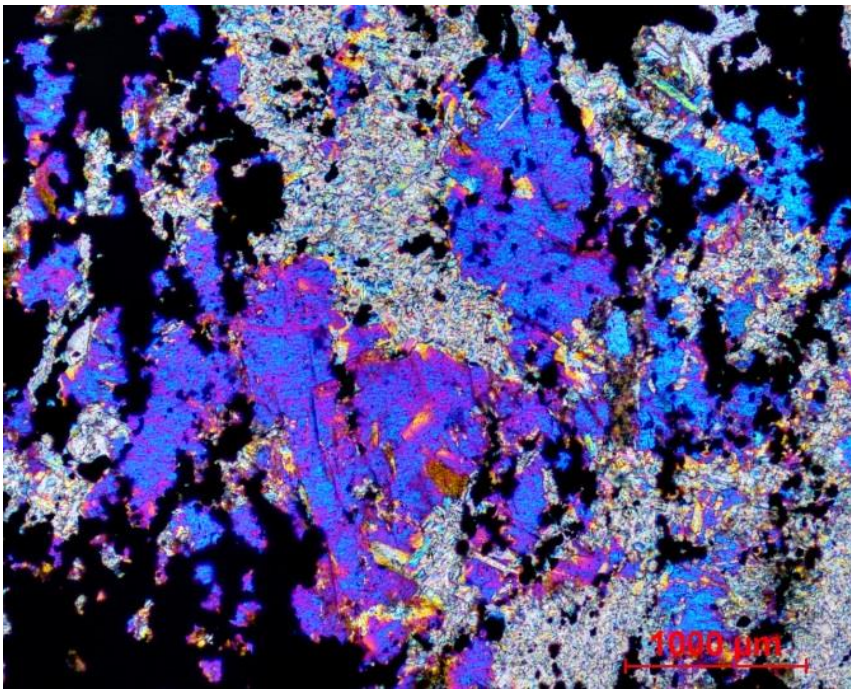
Figure 8. Development of retrograde grunerite from orthopyroxene in sample A-205.0.

Zone 4, which occurs in the westernmost portion of the study area, lies within 100 meters of the contact between the Ironwood Iron-Formation and the Mellen Intrusive Complex. The development of fayalite is unique to this zone, where maximum temperatures reached approximately 700° C (Laybourn, 1979). Fayalite is formed from amphibole by the following reaction (French, 1968):

1) $2Fe_7Si_8O_{22}(OH)_2 = 7Fe_2SiO_4 + 9SiO_2 + 2H_2O$
   grunerite   fayalite   quartz
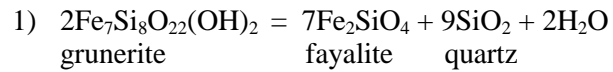
Retrograde amphibole is observed in association with pyroxene and fayalite. Prograde amphibole was not observed in these samples, although it has been reported in Zone 4 by Laybourn (1979). Based on these well-documented changes in mineralogy due to contact metamorphism, the development of amphibole minerals in the Ironwood Iron-Formation is shown to occur in areas where temperatures reach or exceed 300-340° C.

DISTRIBUTION OF AMPHIBOLES IN THE IRONWOOD IRON-FORMATION

The location of all samples containing amphibole minerals is displayed in Figure 9. In Zones 2, 3, and 4, in which temperatures exceeded 300-340º C, amphiboles are present in abundance. In drill-holes A and B, located in Zones 3 and 2, respectively, amphibole minerals are found in each member of the Ironwood Iron-Formation. Their widespread occurrence sharply contrasts with the amphiboles found in drill-holes C and D, both located in Zone 1. These drill-holes contain amphiboles in relatively localized areas, an observation that is not predicted by the zoned model of progressive contact metamorphism first described by James (1955) and applied to the Ironwood Iron-Formation by Laybourn (1979). XRD data show that the most common minerals present in drill-holes C and D (not including quartz and Fe-oxides, which are ubiquitous in the iron-formation) are dolomite-ankerite, siderite, minnesotaite, and chlorite. The presence of these low-grade minerals is indicative of temperatures less than approximately 300-340º C.
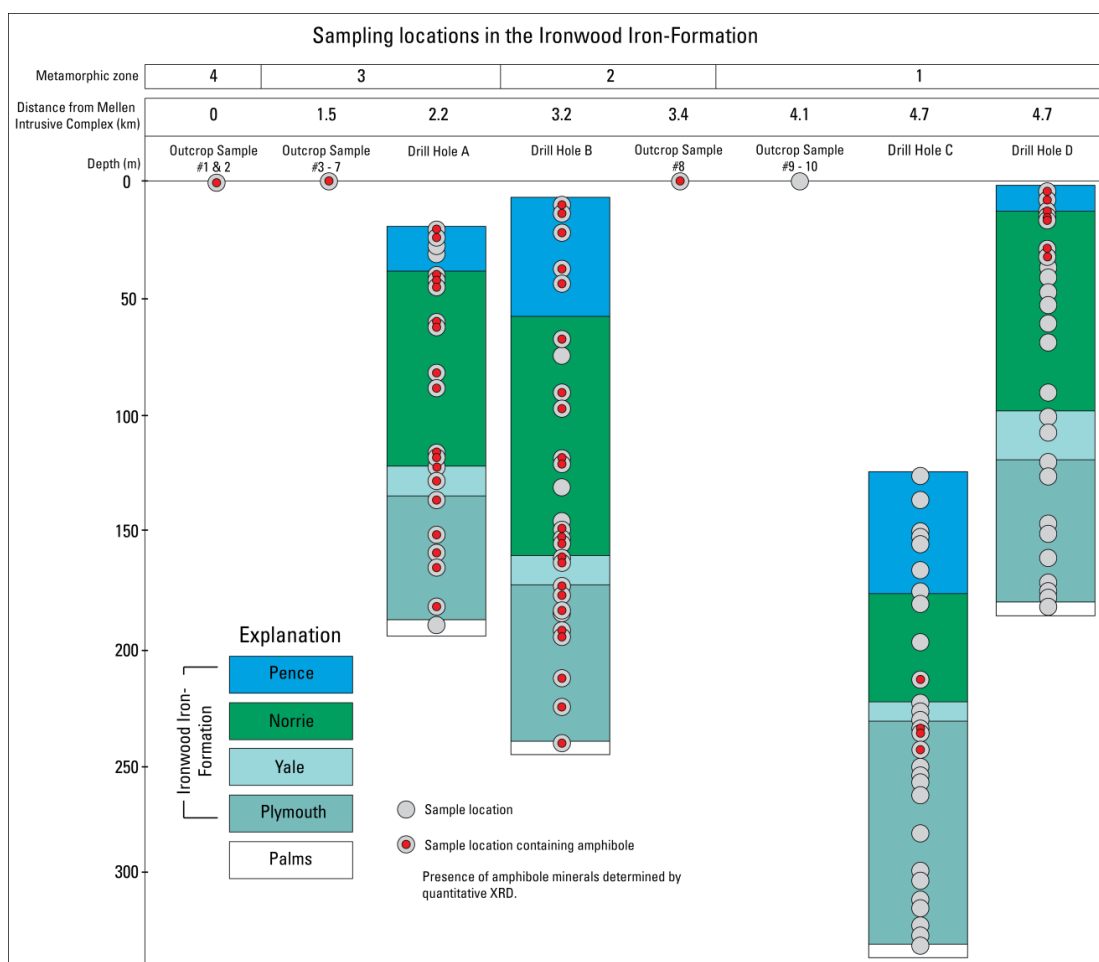
Figure 9. Location of samples containing amphibole minerals by drill-hole depth in the Ironwood Iron-Formation .

Thin sections from each drill-core and outcrop sample were comprehensively examined using a petrographic microscope to identify the location of fibrous amphiboles within the Ironwood Iron-Formation. Samples containing fibrous amphiboles are identified in Figure 10. Fibrous amphiboles are confined to the Pence, Norrie, and Plymouth members, which comprise the potential ore zones of the Ironwood Iron-Formation. No fibrous amphiboles were identified within the Yale member, which is considered to be waste rock (Mardsen, 1978).
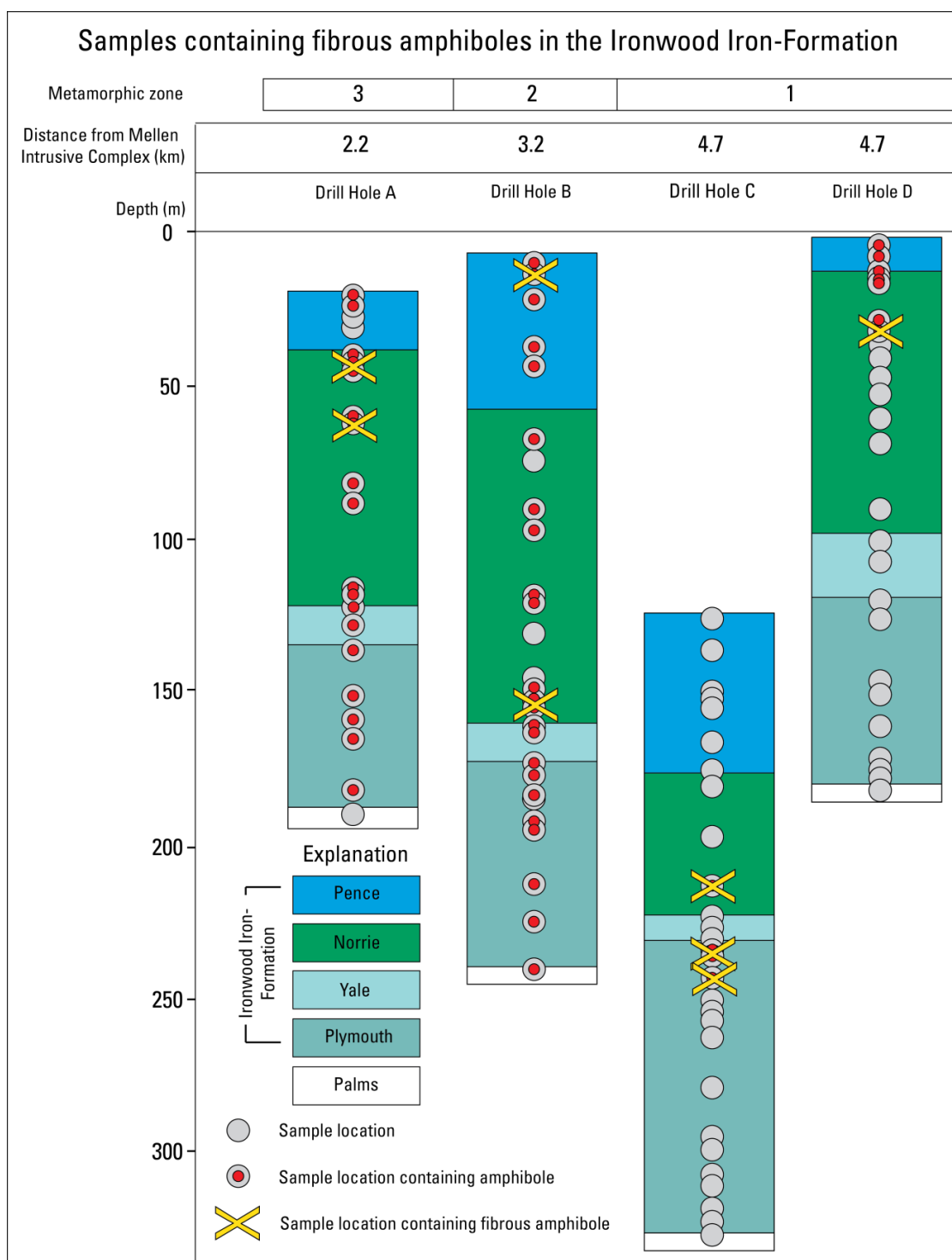
Figure 10. Location of samples containing fibrous amphiboles by drill-hole depth in the Ironwood Iron-Formation. No fibrous amphiboles were observed in outcrop samples.

MORPHOLOGY AND GEOMETRY OF AMPHIBOLES IN THE IRONWOOD IRON-FORMATION

The various habits of amphibole in the Ironwood Iron-Formation are commonly intergrown or found in proximity to one another. The results of this part of the study are intended to provide a general representation of the frequency with which various amphibole habits occur in the Ironwood Iron-Formation. Of the 158 areas that contained amphiboles which were observed using the method described previously, 63 and 25 % of these areas contained massive and prismatic amphiboles, respectively. These are the most common habits assumed by amphiboles in the Ironwood Iron-Formation. Less common forms include equant and fibrous morphologies, which were each observed in 6 % of the areas examined.
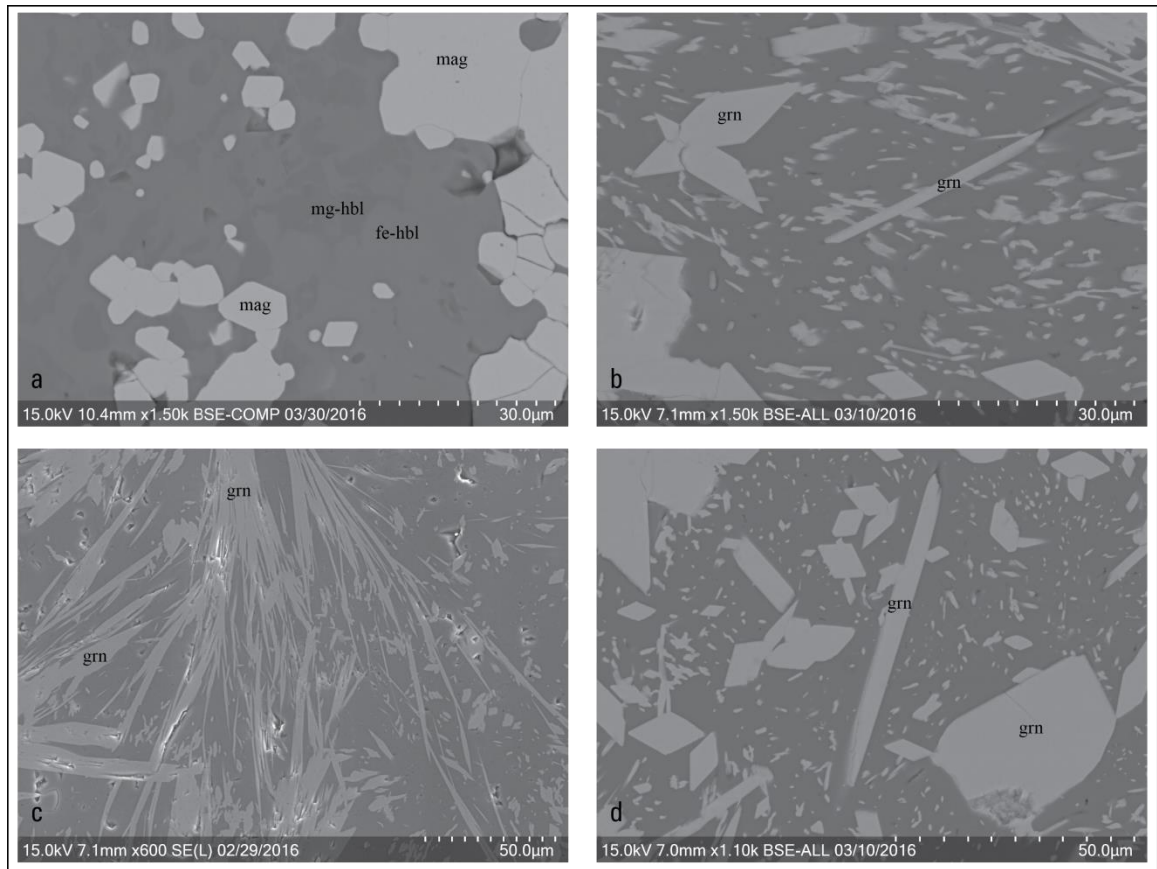
Figure 11. SEM images of examples of various amphibole morphologies in the Ironwood Iron-Formation. a. massive intergrowth of ferro- and magnesio-hornblende (light and dark grey) with magnetite (white), sample A-607.5. b. Interpenetrant prismatic grunerite crystals (upper left) and an elongate grunerite crystal (length = 37 µm, width = 1.9 µm), sample A-395.5. c. Sprays of fibrous grunerite crystals, sample B-512.5. d. Equant grunerite crystals and an elongate grunerite crystal (length = 67 µm, width = 4.7 µm), sample A-395.5.
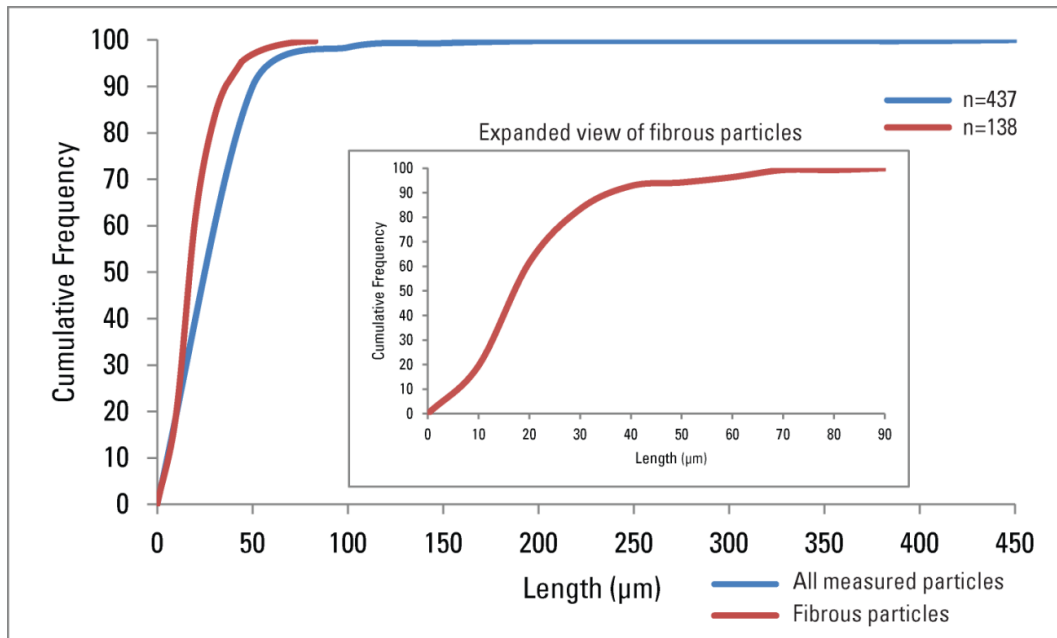
Figure 12. Cumulative frequency distribution of lengths for amphibole particles in the Ironwood Iron-Formation.
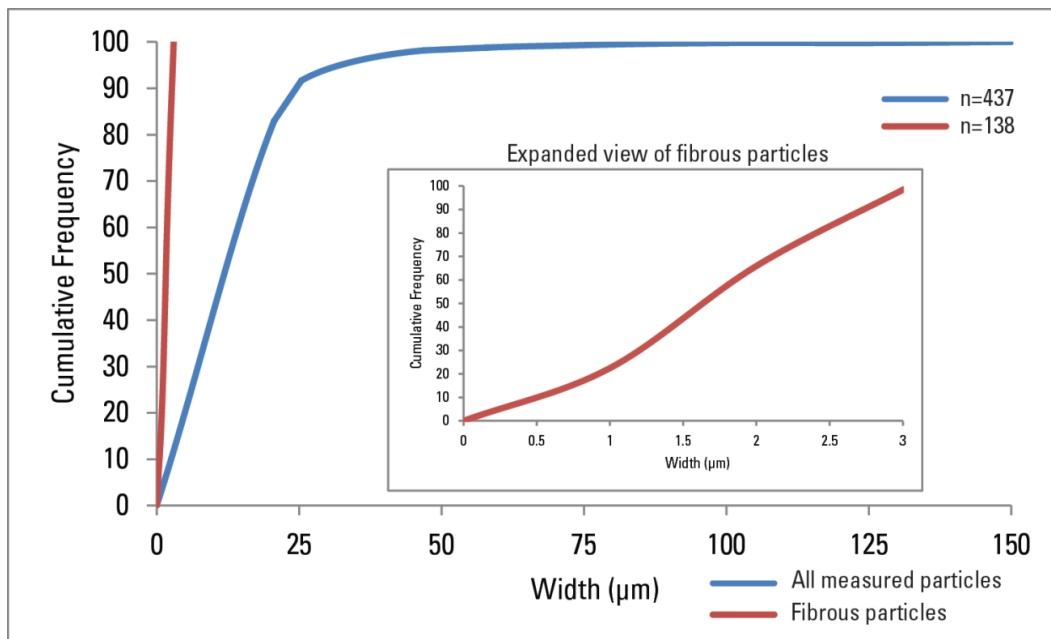
Figure 13. Cumulative frequency distribution of widths for amphibole particles in the Ironwood Iron-Formation.
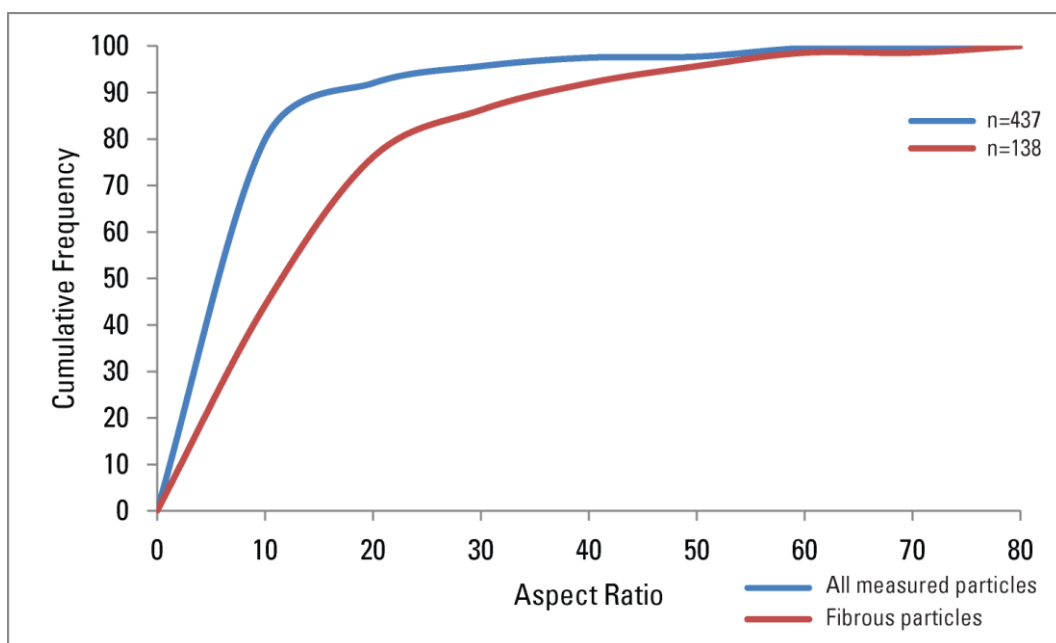
Figure 14. Cumulative frequency distribution of aspect ratios for amphibole particles in the Ironwood Iron-Formation.

CHEMISTRY OF AMPHIBOLES IN THE IRONWOOD IRON-FORMATION

The quantitative chemistry of 559 amphibole particles from drill-core and outcrop samples was determined using an electron microprobe analyzer (Figures 15 and 16). The amphiboles that occur in the Ironwood Iron-Formation are part of the monoclinic Mg-Fe-Mn-amphibole group and the Ca-amphibole group (Hawthorne et al., 2012). The predominant species are members of the cummingtonite - grunerite series and the actinolite - ferro-actinolite series. Minor amounts of other Ca-amphiboles include members of the magnesio-hornblende - ferro-hornblende series. Intergrowth of monoclinic Mg-Fe-Mn and Ca-group amphiboles is commonly observed at a small scale and most sampling areas contain members of both groups.

The range of molar $Mg/(Mg+Fe^{2+})$ values (referred to as Mg#) in massive and prismatic amphiboles is quite similar and spans from 0.06 to 0.87, representing both the most Fe- and Mg-rich compositions. In contrast, the Mg# of fibrous amphiboles, regardless of their location, is restricted to values of 0.14 to 0.35 (Figure 17). Analyses of fibrous grunerite reveal that among these restricted values, Mg# increases concomitant with distance from the Mellen Intrusive Complex (Figure 18).
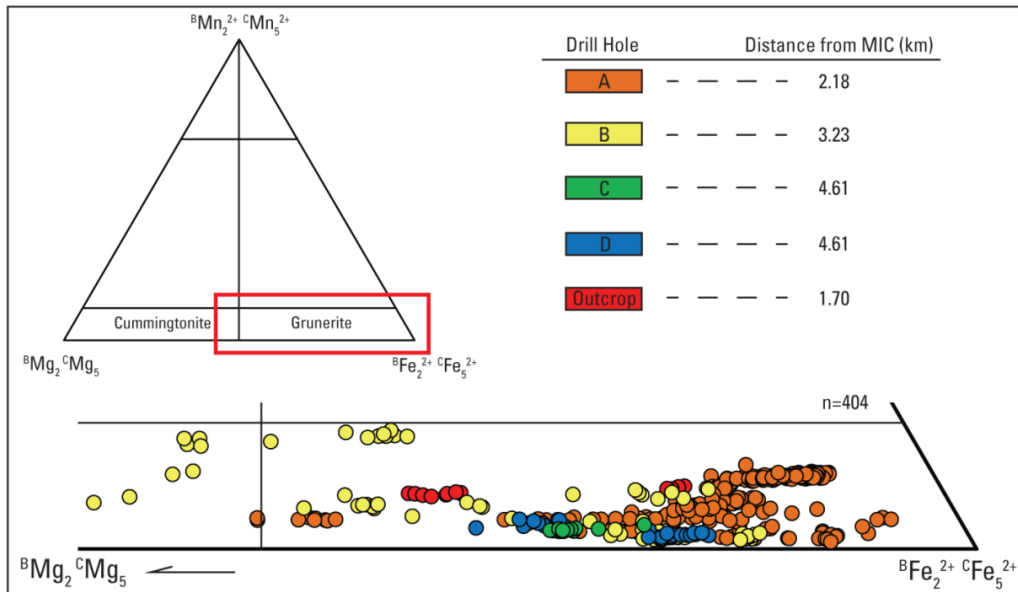
Figure 15. Monoclinic Mg-Fe-Mn-group amphiboles from the Ironwood Iron-Formation (after Hawthorne et al., 2012).
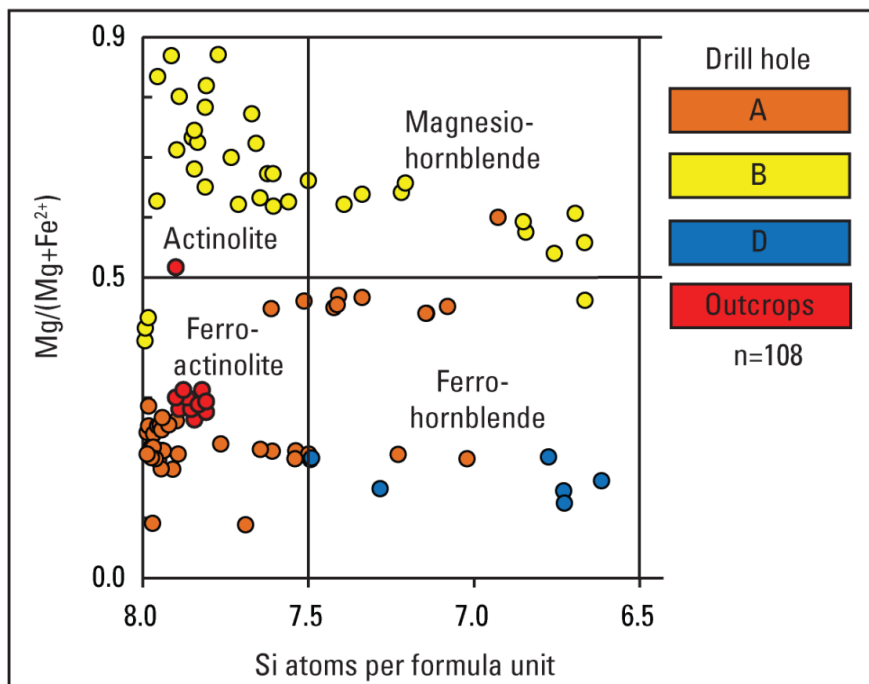
Figure 16. Ca-group amphiboles in the Ironwood Iron-Formation (after Leake et al., 1997). No Ca-group amphiboles were identified in drill-hole C.
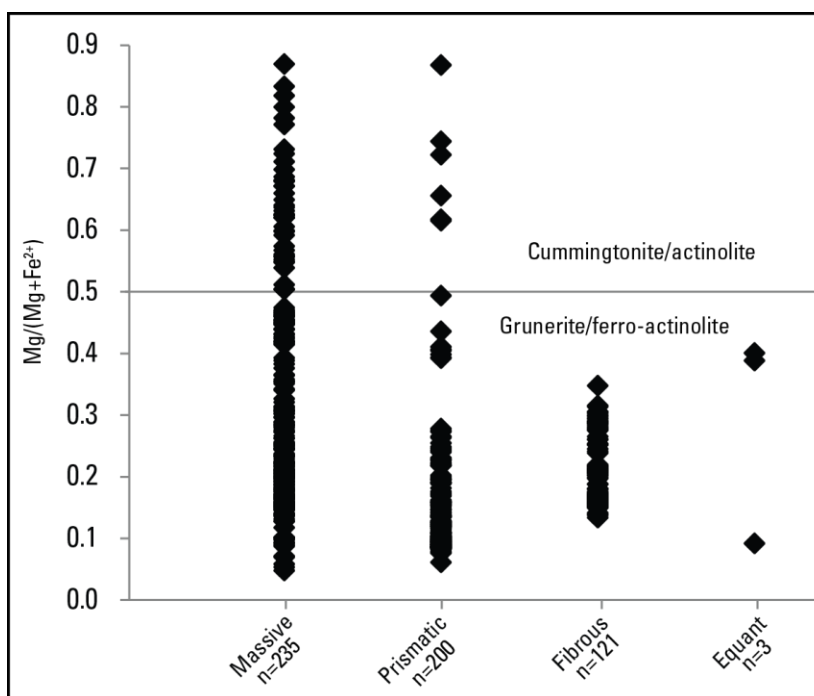
Figure 17. Mg# of Fe-Mg-Mn- and Ca-group amphiboles in the Ironwood Iron-Formation separated by morphology.
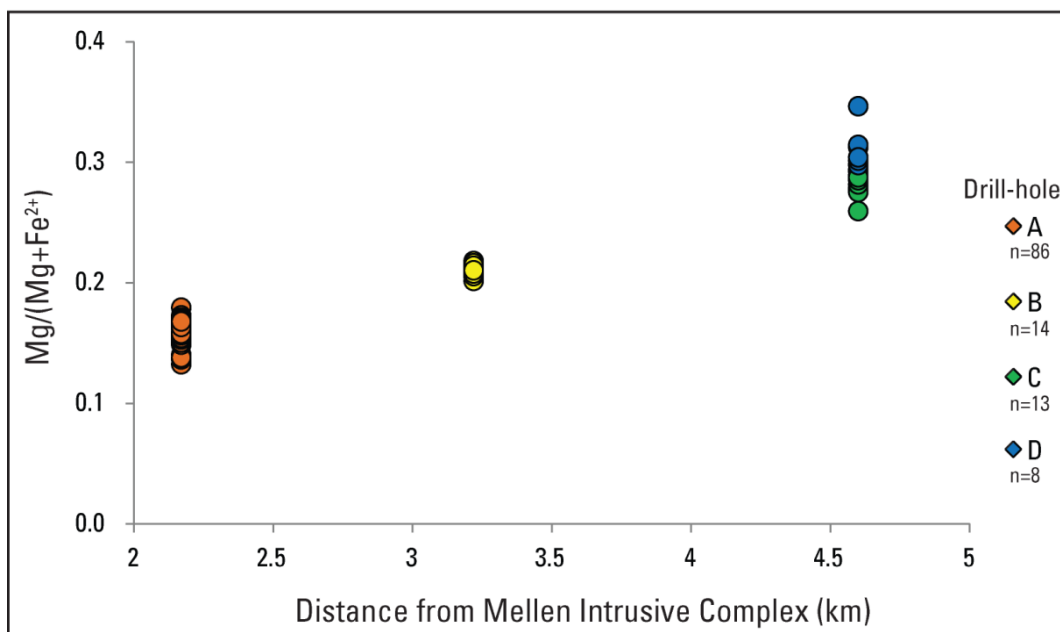
Figure 18. Variation of Mg# with true distance from the Mellen Intrusive Complex of fibrous grunerites in the Ironwood Iron-Formation.
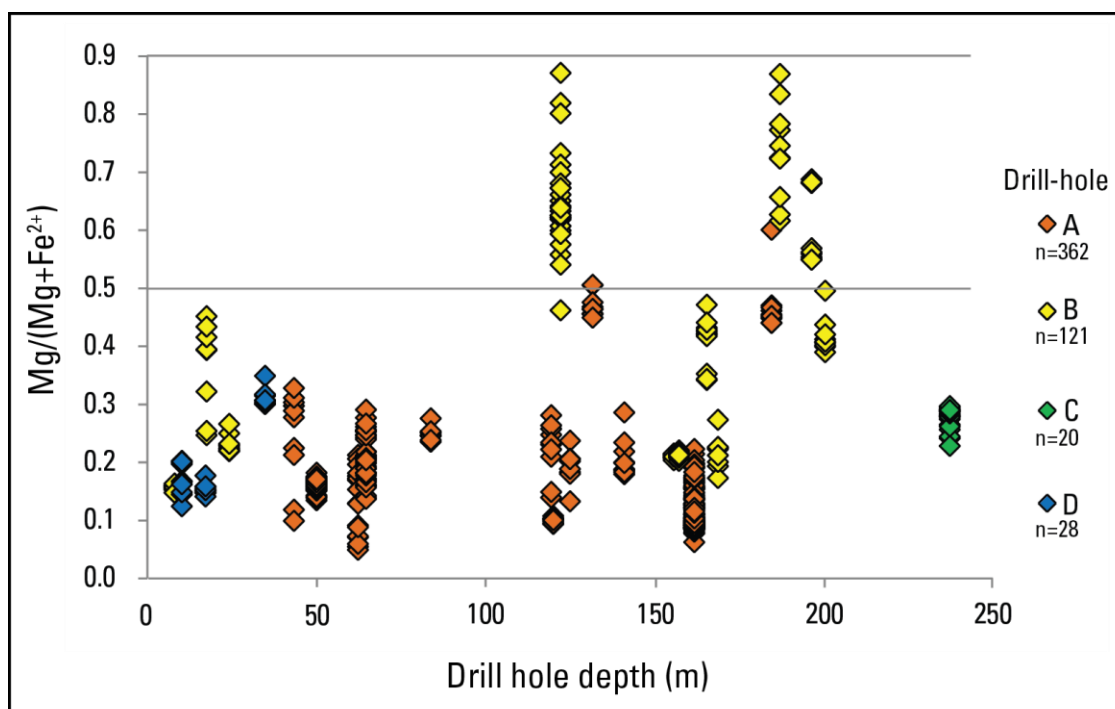
Figure 19. Variation in Mg# of Fe-Mg-Mn- and Ca-group amphiboles with drill-hole depth in the Ironwood Iron-Formation.

The amphiboles of drill-hole B exhibit the greatest range of Mg# values and the most magnesian compositions. This drill-hole lies within Zone 2, which is a medium-grade assemblage in which amphibole is the primary Fe-Mg silicate. In this zone, Fe-Mg-bearing carbonates have undergone decarbonation reactions to form amphiboles, and temperatures are not great enough to form pyroxenes.

Prograde and retrograde grunerite, distinguished previously on the basis of textural evidence, can also be identified by chemical composition. Analyses show that prograde grunerites are relatively enriched in Mn, but fall within the range of Mg# values exhibited by retrograde grunerite (Figure 20).
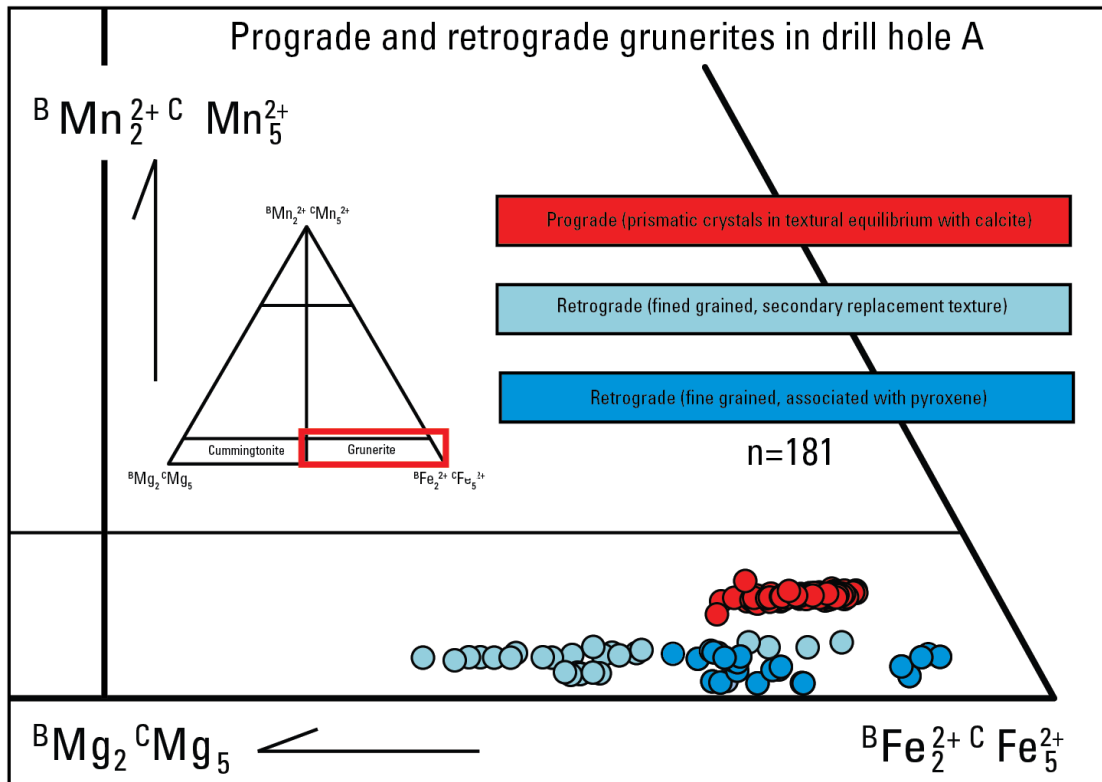
Figure 20. Chemical variations between prograde and retrograde grunerites in drill-hole A.

DISCUSSION

The amphibole-bearing zone that developed as a result of regionally extensive contact metamorphism in the Ironwood Iron-Formation is comparatively smaller than that of the Biwabik Iron Formation. Along strike, the amphibole-bearing zone of the Ironwood Iron-Formation is approximately 7 km less extensive than that of the Biwabik Iron Formation. Additionally, the true distance between the amphibole-bearing zone of these iron formations and their intrusive counterparts is approximately 0.7 km smaller in the Ironwood Iron-Formation than in the Biwabik Iron Formation. This is a consequence of the relatively smaller size of the Mellen Intrusive Complex compared to the Duluth Complex, which resulted in a decreased rate of heat flow (French, 1968; Laybourn, 1979).

The mineralogical information gathered from drill-core samples throughout the Ironwood Iron-Formation is invaluable in describing the nature and extent of amphibole development. Previous investigations have been limited by access to outcrop exposure, which, while good in some areas, is lacking in the eastern portion of the study area (Laybourn, 1979). Drill-core sampling in this area (drill-holes C and D) revealed the presence of amphiboles at depths of approximately 200-250 and 10-30 meters, respectively. With the exception of localized amphibole development, the mineralogical character of these drill holes is that of a low-grade metamorphic assemblage. The occurrence of amphiboles within these drill-holes may indicate another mechanism by which localized areas within the iron-formation may be brought to temperatures permitting amphibole development. If the influence of the contact metamorphic

aureole that developed as a result of the emplacement of the Mellen Intrusive Complex was great

enough to produce grunerite at approximately 200-250 meters of depth within drill-hole C,

additional amphibole development at shallower depths should also be expected. The conspicuous

lack of amphibole elsewhere in drill-holes C and D, along with the restricted nature of grunerite

development, may be a result of localized metamorphism associated with diabase and gabbro

dikes and sills of Paleoproterozoic and/or Mesoproterozoic age. These mafic intrusions were

commonly exposed in mine workings in the formerly active portions of the central Gogebic iron

range, where they played an important role in controlling the location and distribution of iron ore

bodies (Cannon et al., 2007). The presence of several diabase dikes is noted in the drill logs of

Zone 1 and observed in drill-core samples (Figure 21).

Figure 21. Photomicrographs of a diabase dike in sample C-485.0 that cuts across relict

granules (left image) at a high angle relative to bedding (right image, oriented horizontally).

Based on this evidence, the presence of amphibole in the Ironwood Iron-Formation cannot be

constrained solely to areas affected by the regionally extensive contact metamorphism resulting

from the emplacement of the Mellen Intrusive Complex, but may also result from localized contact metamorphism by dikes and sills which may be difficult to recognize.

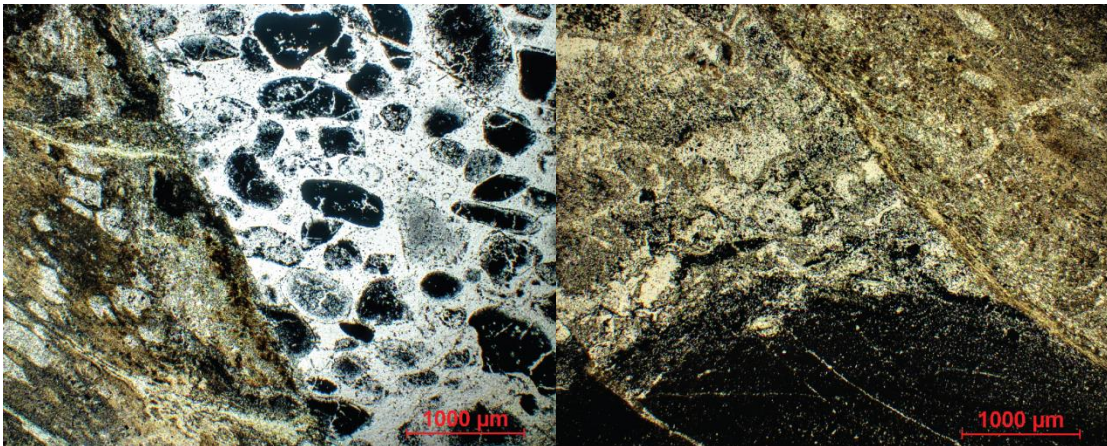Amphiboles in the Ironwood Iron-Formation are chemically simple and consistent with published values of amphiboles from worldwide BIF occurrences (Table 1).

Table 1. Amphibole EPMA data from the Ironwood Iron-Formation compared to other BIF-hosted amphiboles.

Analysis (wt %)	Ironwood Iron-Formation Wisconsin, USA		Kushaka belt BIF Nigeria	Penge Mine South Africa	Bell Lake BIF Slave craton, Canada	
	Grunerite Avg (n=20)	Actinolite Avg (n=20)	Grunerite Avg (n=2)	Grunerite Avg (n=10)	Grunerite Avg (n=14)	Actinolite Avg (n=11)
SiO_2	50.32	51.72	49.06	50.51	51.70	53.22
TiO_2	0.03	0.07	-	0.02	0.00	0.01
Al_2O_3	0.37	1.04	0.19	0.20	0.23	0.54
Cr_2O_3	0.01	0.02	-	0.02	0.00	0.00
MnO	1.13	0.91	2.51	0.63	0.73	0.30
FeO	38.04	23.42	40.68	38.78	35.83	23.04
Fe_2O_3	0.42	1.26	0.46	-	-	-
MgO	6.48	8.63	4.69	6.65	8.72	9.45
CaO	0.85	10.75	0.37	0.12	0.73	11.70
Na_2O	0.15	0.16	-	0.07	0.03	0.07
K_2O	0.03	0.05	-	0.04	0.00	0.00
F	0.00	0.00	-	0.04	-	-
Cl	0.07	0.17	-	0.02	-	-
H_2O	1.89	1.95	1.86	2.91	-	-
Total	99.70	99.92	99.80	97.09	97.98	98.34

Forumula assignments

Ironwood Iron-Formation — based on - 24 (OH, F, Cl, O):

	Grunerite	Actinolite
Si	7.97	7.85
Al	0.04	0.17
Ti	0.00	0.01
Fe3+	0.06	0.09
Ti	0.01	0.01
Al	0.06	0.07
Cr	0.00	0.00
Fe3+	0.07	0.21
Mn2+	0.00	0.15
Fe2+	3.41	2.92
Mg	1.52	1.89
Mn2+	0.15	0.10
Fe2+	1.64	0.14
Ca	0.14	1.75
Na	0.04	0.03
Na	0.02	0.03
K	0.01	0.01
O	22.00	22.00
OH	1.99	1.97
F	0.00	0.00
Cl	0.02	0.05
Sum	15.01	15.01

Kushaka belt BIF — 24 (OH, F, Cl, O):

	Grunerite
Si	7.91
Al	0.04
Fe3+	0.06
Fe2+	5.51
Mg	1.10
Mn	0.34
Ca	0.06
O	22.00
OH	2.00
Sum	15.02

Penge Mine — 23 O:

	Grunerite
Si	8.03
Fe^{2+}	5.16
Mg	1.58
Mn	0.08
Al	0.04
Ca	0.02
Na	0.02
Sum	14.92

Bell Lake BIF — 23 O:

	Grunerite	Actinolite
Si	8.05	7.95
Ti	0.00	0.00
Al	0.04	0.10
Cr	0.00	0.00
Fe^{3+}	0.00	0.17
Fe^{2+}	4.67	2.71
Mn	0.10	0.04
Ni	0.00	0.00
Mg	2.02	2.10
Ca	0.12	1.87
Na	0.01	0.02
K	0.00	0.00
Sum	15.01	14.96

Mücke and Annor, 1993 | Lafuente et al., 2015 | Katsuta et al., 2012

The most salient difference among them is the incorporation of Ca or Al, which is a result of the presence of minerals like dolomite-ankerite or stilpnomelane, respectively, in the protolith. Among amphiboles of all groups, variations in their chemistry are observed primarily as changes in the Mg#. Several factors may influence amphibole chemistry, such as the presence of coexisting minerals that can incorporate or buffer Fe and Mg, bulk chemistry of the iron-formation, temperature of formation, amphibole morphology, and variations in prograde and retrograde metamorphic reactions.

The wide range of Mg# values in drill-hole B (Zone 2) may be explained by the lack of coexisting minerals that can incorporate Mg. Mineral assemblages of Zone 1 contain abundant dolomite, whereas Zones 3 and 4 contain pyroxenes, both of which incorporate Mg (Table 2).

Table 2. EPMA data for Mg-bearing pyroxenes and carbonates.

Analysis (wt %)	Pyroxenes Avg (n=43)		Carbonates (Zone 1) Avg (n=114)
SiO_2	50.31	CaO	34.73
TiO_2	0.12	MnO	2.61
Al_2O_3	0.29	FeO	7.14
Cr_2O_3	0.00	MgO	10.00
MnO	1.23	SrO	0.05
FeO	31.29	O	0.00
MgO	8.09	CO_2	44.91
NiO	0.01	Total	99.46
CaO	8.37		
Na_2O	0.04		
K_2O	0.01		
Total	99.76		

Assuming a constant bulk chemical composition, isochemical metamorphism of the iron-formation would result in an increase in the Mg content of amphiboles in Zone 2 where

amphiboles are the most common Fe-Mg-bearing silicate. Changes in Mg content may also be influenced by temperature of formation. Due to the relationship between the Ironwood Iron-Formation and the Mellen Intrusive Complex, an increase in drill-hole depth results in greater distance from the intrusive body. In drill-holes where amphiboles are present at varying depths, an increase in drill-hole depth results in an increase in the range of Mg# values (Figure 19). Decreasing temperature of formation is also correlated with an increase in Mg content in fibrous grunerite (Figure 18), which are shown to be restricted in composition compared to common forms such as massive and prismatic (Figure 17).

The occurrence of fibrous amphiboles and their Fe content is of particular importance because they are known carcinogens in particulate form through an inhalation exposure pathway. Exposure to fibrous amphiboles can result in asbestosis; lung, ovarian, and larynx cancer; mesothelioma; pleural fibrosis; and possibly other health effects including depressed immune function, cardiovascular disease, and gastrointestinal cancer (Agency for Toxic Substances and Disease Registry, 2001; Camargo et al., 2011; International Agency for Research on Cancer, 2012; Shannahan et al., 2012; Buck et al., 2013). The Fe content of fibrous amphiboles has human-health implications as the mobilization of Fe from the surface of mineral particles by chelation may produce deleterious reactive oxygen species that damage biomolecules. The relative toxicity of amphibole fibers is dependent on factors such as width, length, aspect ratio, surface area, and surface chemical composition of the mineral fiber (Aust et al., 2011). Separable fibers longer than 5 μm with aspect ratios greater than 3:1 and those that contain Fe are considered to be more toxic; however, criteria for the regulation of commercial asbestiform minerals may not adequately address these factors in what are known as naturally occurring asbestos, which is found as a natural component of rocks and soils but may not meet the

regulatory definition of asbestos (Lowers and Meeker, 2002; Harper, 2008; Meeker, 2009; Aust et al., 2011; Case et al., 2011, Buck et al., 2013).

A difficulty inherent to classifying the morphology and geometry of amphiboles in thin section is the random orientation of mineral particles, which obscures their maximum dimensions. As a result, it is possible for a prismatic particle, cut perpendicular to its c-axis, to be misidentified as an equant particle. Due to the randomly-oriented nature of amphibole particles, geometric data should be interpreted as minimum values. Another drawback of observing amphibole particles in thin section is the inability to determine whether particles possess the properties of flexibility or high tensile strength. Both of these properties are inherent to asbestiform minerals, which are a subset of fibrous minerals that may not otherwise exhibit these features. Having no means of demonstrating the properties of flexibility or high tensile strength, it is inappropriate to describe the amphiboles identified in this study as asbestiform based on the information currently available.

The process of taconite production includes several stages in which amphibole particles, should they be present in the iron-formation, may be released to the environment. The first step in the taconite production process involves drilling and blasting rock at the mine site. It is then loaded and hauled to a processing plant, where it is dry-crushed and ground to a sufficiently small size to allow the liberation of iron ore minerals from the surrounding gangue (Kohn and Specht, 1958; Nielsen and Lownds, 1997). These processes occur prior to the generation of taconite tailings and may allow for the introduction of amphibole particles to the air at both the mine site and the processing plant. Following magnetic separation, the remaining material, which is highly siliceous, is typically separated into coarse and fine tailings. Coarse tailings are one of

the largest components of taconite mining by-products. They are generally less than 10

mm in size, and contain less than 10% fine material, which is defined as material which

passes through at 200 mesh sieve (approximately 75 µm or less) (Figure 22). It is

important to note that not all taconite operations separate their tailings into these two categories,

and that some allow them to flow as slurry to the same location (Zanko et al., 2008).
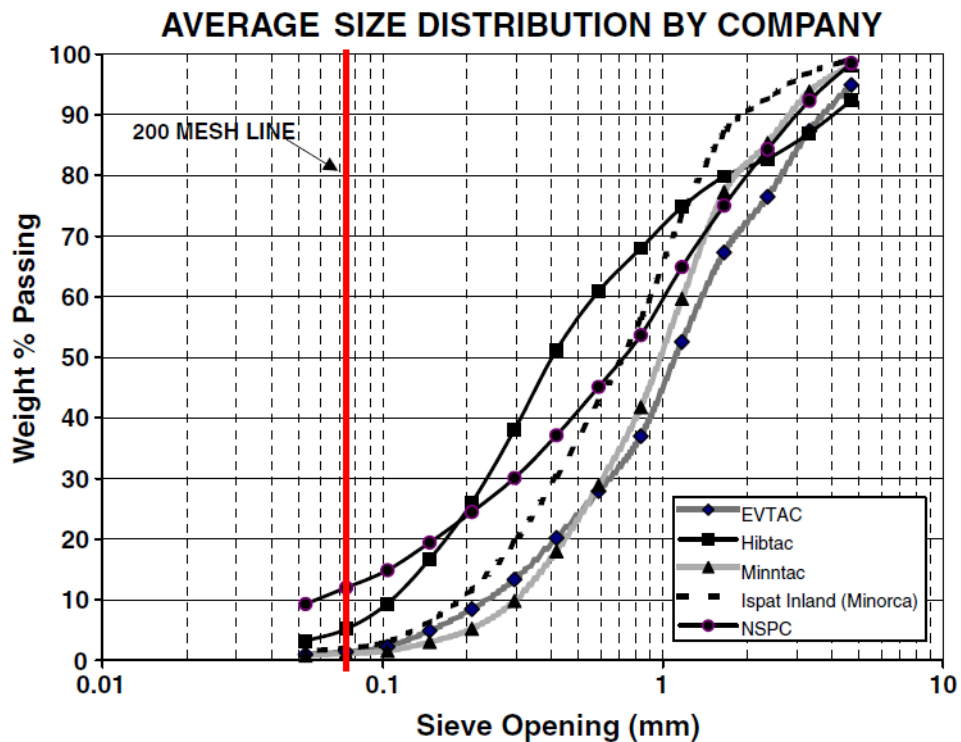
Figure 22. Average coarse tailings size distribution, by company (Zanko et al., 2008).

Measurements of amphibole particles in this study indicate that nearly all elongate amphibole

particles (prismatic and fibrous morphologies) in the Ironwood Iron-Formation would pass

through a 200 mesh sieve. It must therefore be assumed that if amphibole minerals are present in

the rocks being mined, fine-grained amphibole particles will be liberated during the dry stages of

taconite processing and that tailings will contain an amount of fine-grained particles proportional to the amount of amphibole present in the iron-formation (Stevenson, 1983).

Potential human-health risks associated with taconite production in the Ironwood Iron-Formation are dependent on the strategies a mining company may employ regarding ore processing and waste management. In the absence of a proposed mine plan, it is possible only to speculate about these strategies. In the wake of issues caused by tailings disposal in Lake Superior, which ended in 1975, it seems likely that waste disposal would be exclusively land-based. The primary human-health concern related to the mining of fibrous amphibole-bearing rocks and land-based disposal of tailings is environmental exposure to windblown amphibole particles. As a result, dust management is an important issue to be addressed by any potential mine plan.

The samples collected in this study encompass approximately 30 kilometers of strike length, approximately 10 to 300 meters of depth, and a wide range of metamorphic conditions. Despite the broad extent of sampling, and a representative sampling of each lithologic sub-unit, the 115 samples collected are only a small portion of the Ironwood Iron-Formation. They provide a large amount of information from which to draw conclusions, but the portions of the iron-formation that remain undescribed are greater still.

CONCLUSIONS

Amphibole minerals occurring in the Ironwood Iron-Formation have been examined using polarized light microscopy, XRD, SEM/EDS, and EPMA-WDS in order to determine their origin, distribution, morphology, and quantitative chemistry. Amphiboles of the cummingtonite – grunerite, actinolite – ferro-actinolite, and magnesio-hornblende – ferro-hornblende series developed through prograde metamorphism from decarbonation reactions involving siderite, ankerite, and dolomite, and dehydration reactions involving minnesotaite and stilpnomelane at temperatures in excess of approximately 300-340º C. Grunerite also developed through retrograde metamorphism from orthopyroxene at high metamorphic grades.

The emplacement of the Mellen Intrusive Complex and the resulting formation of a contact metamorphic aureole were sufficient to produce amphiboles in all members of the Ironwood Iron-Formation in areas where the iron formation is 3.5 km or less from the intrusive body. Additionally, this study identifies the presence of amphiboles in areas outside of the direct influence of contact metamorphism by the Mellen Intrusive Complex, which may be a result of localized contact metamorphism by Paleoproterozoic or Mesoproterozoic diabase and gabbro dikes and/or sills.

Examination of amphibole particles in thin section shows the development of four morphologies: massive, equant, prismatic, and fibrous. The vast majority of amphiboles in the Ironwood Iron-Formation assumed a massive or prismatic habit, whereas equant and fibrous forms are relatively uncommon. Despite their relative paucity, fibrous amphiboles are shown to occur locally in each of the four drill-cores examined in this study, and in each member of the

Ironwood Iron-Formation, with the exception of the Yale member. They exhibit high degrees of elongation, lengths up to 90 μm and widths between 0.25 and 3 μm.

Several chemical trends have been identified in the amphiboles of the Ironwood Iron-Formation. The compositional range of massive and prismatic amphiboles is highly variable and nearly identical; however fibrous amphiboles are restricted to a relatively narrow range of Mg# values. Among fibrous grunerites, an increase in Mg content is observed concomitant with distance from the Mellen Intrusive Complex. Regardless of morphology, the range of Mg# values increases with drill-hole depth. As a result, amphiboles with an Mg# of greater than 0.5 are not found in drill-cores at depths of less than approximately 120 meters, and amphiboles at shallower depths are generally more Fe-rich. Other factors that influence chemical variation in amphiboles are the presence of coexisting minerals that accommodate Fe and Mg in their structures. This is evident in Zones 1, 3, and 4, where compositional variability in amphiboles is relatively restricted compared to Zone 2, in which amphiboles do not coexist with either pyroxenes or Fe-Mg-bearing carbonates.

Although the Ironwood Iron-Formation represents a substantial taconite resource that may potentially be developed, there exists no current proposed mine plan. The details of strategies that may be employed by mining companies regarding ore processing and waste management are currently unknown. In order to mitigate potential human-health risks resulting from amphibole particle exposure, the issue of wind-blown dust will need to be adequately managed by any potential mine plan.

REFERENCES

Agency for Toxic Substances and Disease Registry, 2001. Toxicological profile for asbestos. ATSDR, Atlanta, GA. http://www.atsdr.cdc.gov/toxprofiles/tp61.pdf

Aust, A., Cook, P., and Dodson, R., 2011. Morphological and chemical mechanisms of elongated particle toxicities. Journal of Toxicology and Environmental Health Part B, vol. 14, p.40–75.

Berndt, M.E., and Brice, W.C., 2008. The origins of public concern with taconite and human health: Reserve Mining and the asbestos case. Regulatory Toxicology and Pharmacology, vol. 58, S31-S39.

Bonnichsen, B., 1969. Metamorphic pyroxenes and amphiboles in the Biwabik Iron-Formation, Dunka River Area, Minnesota. Mineralogical Society of America Special Papers, vol. 2, p. 217-239.

Bonnichsen, B., 1975. Geology of the Biwabik Formation, Dunka River Area, Minnesota. Economic Geology, vol. 70, p. 319-340.

Buck, B.J., Goossens, D., Metcalf, R.V., McLaurin, B., and Freudenberger, M.R.F., 2013. Naturally Occurring Asbestos: Potential for Human Exposure, Southern Nevada, USA. Soil Science Society of America Journal, vol. 77, p. 2192-2204.

Camargo, M., Stayner, L., Straif, K., Reina, M., Al-Alem, U., Demers, P., and Landrigan, P., 2011. Occupational exposure to asbestos and ovarian cancer. Environmental Health Perspectives, vol. 119, p.1211-1217.

Campbell, W.J., Blake, R.L., Brown, L.L., Cather, E.E., and Sjoberj, J.J., 1977. Selected silicate minerals and their asbestiform varieties: Mineralogical definitions and identification-characterization. U.S. Bureau of Mines, Information Circular 8751, 55 p.

Cannon, W.F., Peterman, Z.E., and Sims, P.K., 1993. Crustal-scale thrusting and origin of the Montreal River Monocline, a 35-km-thick cross section of the Midcontinent Rift in northern Wisconsin and Michigan: Tectonics, v. 12, no. 3, p. 728–744.

Cannon, W.F., Woodruff, L.G., Nicholson, S.W., and Hedgman, C.A., 1996. Bedrock geologic map of the Ashland and the northern part of the Ironwood 30' x 60' quadrangles, Wisconsin, and Michigan. U.S. Geological Survey, Miscellaneous Geologic Investigations Map I-2566.

Cannon, W.F., LaBerge, G.L., Klasner, J.S., and Schulz, K.J., 2007, The Gogebic iron range—a sample of the northern margin of the Penokean fold and thrust belt: U.S. Geological Survey Professional Paper 1730, 44p.

Case, B., Abraham, J., Meeker, G., Pooley, F., and Pinkerton, K., 2011. Applying definitions of "asbestos" to environmental and "low-dose" exposure levels and health effects, particularly malignant mesothelioma. Journal of Toxicology and Environmental Health, Part B, vol. 14, p. 3–39.

Ecology and Environment, Inc. 2005, El Dorado Hills naturally occurring asbestos multimedia exposure assessment, El Dorado Hills, California: Preliminary assessment and site inspection report, Interim final, Contract No. 68-W-01-012; TDD No. 09-04-01-0011; Job No. 001275.0440.01CP.

French, B.M., 1968. Bulletin No. 45. Progressive contact metamorphism of the Biwabik Iron-Formation, Mesabi Range, Minnesota. Minnesota Geological Survey Bulletin, vol. 45, 103 p.

French, B.M., 1973. Mineral assemblages in diagenetic and low-grade metamorphic iron-formation. Economic Geology, vol. 68, p. 1063-1075.

Frost, B.R., 1979. Metamorphism of Iron-Formation: Parageneses in the system Fe-Si-C-O-H. Economic Geology, vol. 74, p. 775-785.

Frost, C.D., von Blanckenburg, F., Schoenberg, R., Frost, B.R., and Swapp, S.M., 2007. Preservation of Fe isotope heterogeneities during diagenesis and metamorphism of banded iron formation. Contributions to Mineralogy and Petrology, vol. 153, p. 211-235.

Harper, M., 2008. 10th Anniversary critical review: Naturally occurring asbestos. Journal of Environmental Monitoring, vol. 10, p. 1394–1408.

Hawthorne, F.C., Oberti, R., Harlow, G.E., Maresch, W.V., Martin, R.F., Schumacher, J.C., and Welch, M.D., 2012. IMA report, nomenclature of the amphibole supergroup. American Mineralogist, vol. 97, p. 2031–2048.

Hotchkiss, W.O., 1919. Geology of the Gogebic range and its relation to recent mining developments: Engineering and Mining Journal, v. 108, p. 443–452, 501–507, 537–541, and 577–582.

International Agency for Research on Cancer, 2012. Asbestos. In: A review of human carcinogens. IARC Monograph. Evaluation of Carcinogenic Risks to Humans 100C. WHO Press, Lyon, France, p. 219-294.

James, H.L., 1955. Zones of regional metamorphism in the Precambrian of northern Michigan. Geological Society of America Bulletin, vol. 66, p. 1455-1488.

Katsuta, N., Shimizu, I., Helmstaedt, H., Takano, M., Kawakami, S., Kumazawa, M., and Brown, M., 2012. Major element distribution in Archean banded iron formation (BIF); influence of metamorphic differentiation. Journal of Metamorphic Geology, vol. 30, p. 457-472.

Kohn, C.F., and Specht, R.E., 1958. The Mining of Taconite, Lake Superior Iron Mining District. Geographical Review, vol. 48, p.528-539.

Lafuente, B., Downs, R. T., Yang, H., and Stone, N., 2015. The power of databases: the RRUFF project. In: Highlights in Mineralogical Crystallography, T. Armbruster and R. M. Danisi, eds. Berlin, Germany, W. De Gruyter, p. 1-30.

Laybourn, D.P., 1979. The geology and metamorphism of the Ironwood Iron-Formation, Gogebic Range, Wisconsin. [MSc thesis]: Minneapolis, University of Minnesota, 223 p.

Leake, B.E.,Woolley, A.R., Arps, C.E.S., Birch, W.D., Gilbert, M.C., Grice, J.D., Hawthorne, F.C., Kato, A., Kisch, H.J., Krivovichev, V.G., Linthout, K., Laird, J., Mandarino, J.A., Maresch, W.V., Nickel, E.H., Rock, N.M.S., Schumacher, J.C., Smith, D.C., Stephenson, N.C.N., Ungaretti, L., Whittaker, E.J.W., Guo, Y., 1997. Nomenclature of amphiboles: report of the subcommittee on amphiboles of the International Mineralogical Association, Commission on New Minerals and Mineral Names. Canadian Mineralogist, vol. 35, p. 219–246.

Locock, A.J., 2014. An Excel spreadsheet to classify chemical analyses of amphiboles following the IMA 2012 recommendations. Computers & Geosciences, vol. 62, p. 1-11.

Lowers, H., and G. Meeker., 2002. Tabulation of asbestos-related terminology. USGS Open-File Rep. 02-458. USGS, Reston, VA. http://pubs.usgs.gov/of/2002/ofr-02-458/index.html.

Marsden, R.W., 1978. Iron ore reserves of Wisconsin—A minerals availability system report, in Proceedings, American Institute of Mining Engineers, 51st annual meeting, Minnesota Section, Duluth, Minn. Jan. 11–13, 1978: Duluth, Minn., University of Minnesota, American Institute of Mining Engineers, no. 39, p. 24-1 to 24-28.

Meeker, G., 2009. Asbestos sans mineralogy? A view from a different hilltop. Elements, vol. 5, 269 p.

Mücke, A., and Annor, A., 1993. Examples and genetic significance of the formation of iron oxides in the Nigerian banded iron-formations. Mineralium Deposita, vol. 28, p. 136-145.

Nielsen, K., and Lownds, C.M., 1997. Enhancement of taconite crushing and grinding through primary blasting. International Journal of Rock Mechanics and Mining Sciences, vol. 34, paper No. 226.

Ojakangas, R.W., 1983. Tidal deposits in the early Proterozoic basin of the Lake Superior region; the Palms and the Pokegama Formations; evidence of subtidal-deposition of the superior-type banded iron-formation, in Medaris, L.G., Jr., ed., Early Proterozoic geology of the Great Lakes region: Geological Society of America Memoir 160, p. 49–56.

Schulz, K.J., and Cannon, W.F., 2007. The Penokean orogeny in the Lake Superior region. Precambrian Research, vol. 157, p. 4-25.

Shannahan, J., Schladweiler, M., Thomas, R., Ward, W., Ghio, A., Gavett, S., and Kodavanti, U., 2012. Vascular and thrombogenic effects of pulmonary exposure to Libby amphibole. Journal of Toxicology and Environmental Health Part A, vol. 75, p. 213–231.

Stevenson, R.J., 1983. Amphiboles at the base of the Duluth Complex, Minnesota: Unpublished Ph.D. Thesis, University of Minnesota, 162 p.

Zanko, L.M., Niles, H.N., and Oreskovich, J.A., 2008. Mineralogical and microscopic evaluation of coarse taconite tailings from Minnesota taconite operations. Regulatory Toxicology and Pharmacology, vol. 52, S51–S65.

BIOGRAPHY

Carlin Green graduated from George Mason University with a Bachelor of Science in Earth Science in 2015. He received the Dean's award for undergraduate research for his senior thesis entitled: 3-D strain analysis and structural development of the Chilhowee group in the western Blue Ridge province near Front Royal, Virginia. He is currently a graduate teaching assistant for geology laboratory courses.