THREE AND A HALF SKARNS

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INTRODUCTION

The Central Metasedimentary Belt (CMB) of the Precambrian Grenville series rocks of St. Lawrence, Jefferson and Lewis Counties, New York has been the source of a wide range of high-quality mineral specimens for over 150 years. Most of these localities occur in the Grenville Marble and associated calc-silicate rocks, as well as in skarns or skarn-like assemblages, with or without an obvious intrusive igneous source that supplied the heat, pressure and fluids required to make the skarn. Some of the latter have been called “vein-dikes,” and their origin is not well understood. Recent research suggests their calcite cores have both a mantle-derived carbonatitic component as well as a crustal derived marble component (Sinaei-Esfahani, 2013). This trip will visit sites hosting both types, and includes four stops:

Stop 1 – Bradley Farr property, Natural Bridge, Lewis Co.
Stop 2 – Gouverneur Minerals’ open pit wollastonite mine, Lake Bonaparte, Lewis Co.
Stop 3 – Rose Road Skarn (Purple Diopside Mound) adjacent to Rose Road skarn
Stop 4 – Rose Road Skarn (Mulvaney property) near Pitcairn, St. Lawrence Co.

Stops 1, 3 and 4 are best known to mineral collectors for having produced high-quality specimens of titanite, diopside, scapolite, zircon, albite, microcline, and other minerals. Wollastonite is present at three of the four sites, and is commercially mined at Stop 2. At stops 1 and 4 wollastonite occurs as euhedral crystals, some of which have been replaced by quartz, calcite and pyroxene, resulting in sharp pseudomorphs. Descriptions of these sites, their collecting histories, and major minerals of interest are summarized below and treated in greater detailed by Chamberlain et al. (1987, 1999, and 2013).

ROAD LOG AND STOP DESCRIPTIONS FOR TRIP A-6

Meet at 9:30 a.m. opposite the small church at the intersection of Route 3 and Richter Drive at the east end of the village of Natural Bridge. Allow at least an hour and 15 minutes to drive from Alexandria Bay to our rendezvous point.

NOTE 1. Stop 2 is at a working open pit mine and will require participants to sign a liability release waiver. Participants will also be required to provide their own hardhats, safety goggles and boots in order to gain access to the property.

NOTE 2. All stops are on private property and permission to visit them should be obtained in advance.

NOTE 3. Field Trip A-6 will end around 2:30 p.m., near the village of Pitcairn.

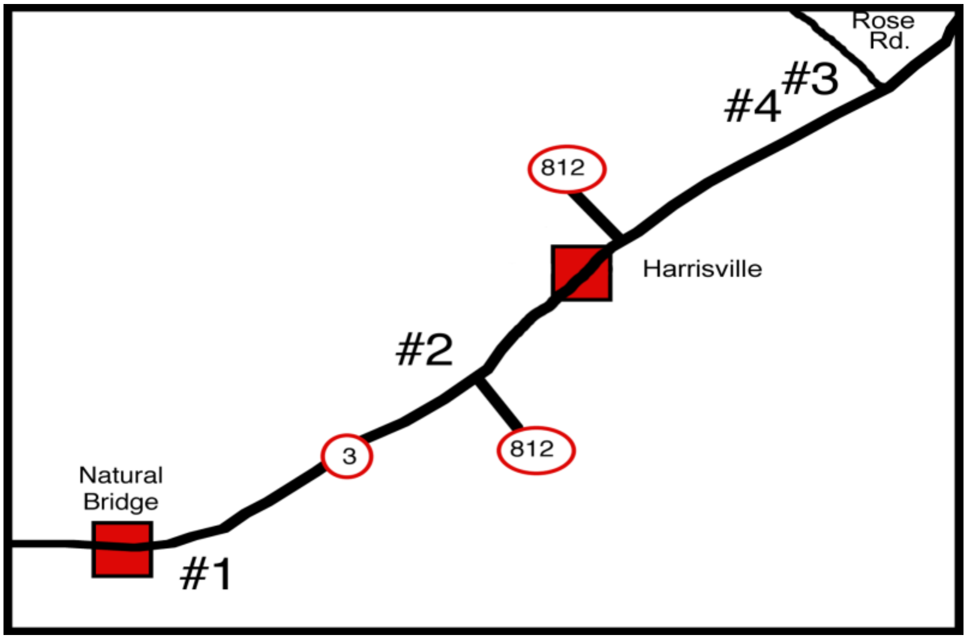

Figure 1. Field trip stop locations. See road log below for detailed directions.

Cumulative Mileage

0.0 From the church at Route 3 and Richter Dr. in Natural Bridge, take Route 3 east toward Harrisville for 1.1 miles. Just past the old K.O.A. Campground on the left (north) side of highway, you will come to a narrow, gated, gravel road on the right side of the highway. Park here. Walk south along the gravel road approximately 100 feet and enter the wooded area on the right (west). Walk approximately 75 -100 feet into the woods to the several old, hand-dug trenches that comprise the site.

1.1 **Stop 1**. Classic Dana mineral locality for wollastonite, titanite, scapolite, diopside, etc.

7.1 Continue east on Route 3 for 6.0 miles to Hermitage Road; turn left (north) onto Hermitage Road and proceed downhill ~ 0.1 mile to the mine entrance on your left.

7.2 **Stop 2**. Gouverneur Minerals No. 4 (Valentine) wollastonite mine.

17.7 Return to Route 3 and continue east 10.4 miles to Rose Road. Turn left (north) onto Rose Road.

17.9 At approximately 0.2 miles on Rose Road, you will come to a gravel road on your left. Take this road to the second house on the right, the LaPlatney residence, where permission to visit the site(s) should be obtained. (note: a small collecting fee is normally charged). Continue on the gravel road to mile 18.2. Stop 3 is approximately 50 feet into the wooded area to your left.

18.2 **Stop 3:** Purple Diopside Mound

Continue on the gravel road for approximately another 0.1 mile to Stop 4, which should be visible high on the hillside to your left about 100 feet into the woods.

18.3 **Stop 4:** classic Dana locality for wollastonite, diopside, titanite and albite at Pitcairn.

END of TRIP

STOP DESCRIPTIONS

Stop 1: Bradley Farr Property, Natural Bridge, NY

INTRODUCTION

This stop is famous for its well-formed crystals of wollastonite that occur in calcite-filled veins in syenite, associated with crystals of titanite, meionite, microcline, diopside and zircon. Known prior to 1840, it is among the earliest of American mineral localities, and has been referred to as the Cleveland, Ashmore, or Whitestone farm, depending on when reference is made. It is also commonly referred to as simply Natural Bridge, Diana, Lewis County, NY, and is the type locality for the two now discredited species *lederite* (= titanite) and *nuttallite* (= meionite).

GEOLOGY

The two principal rock types present at the locality are Grenville Marble and a gneissic pyroxene syenite of the Diana Complex. Previous investigators all conclude that the observed skarn assemblage formed when the syenite intruded the marble (Smyth and Buddington, 1926; Agar, 1923). However, what first appears to be a simple contact metamorphic skarn, upon closer examination also shows characteristics of calcite vein-dikes (Mills, 2014; Moyd, 1990). There can be little doubt that mineralogically, the observed assemblage is typical of a skarn, but if it formed by the syenite intruding the marble, then one should expect to see additional skarn development at the syenite – marble contacts in the immediate area, rather than being confined solely to the "veins." The syenite in contact with the skarn assemblage developed on the walls of the veins shows a marked cataclastic texture that would have provided a preferential pathway for the mineralizing fluids to enter and form the minerals observed. Similar skarn-like deposits occur throughout the CMB of the Grenville in Canada, and have recently been interpreted as having formed from a mixed crustal and mantle-derived fluid based on carbon and oxygen isotope studies (Sinaei-Esfahani, 2013). Preliminary carbon – oxygen isotope analyses of the calcite from the Natural Bridge locality yield similar results ($\delta^{13}C_{pdb}$ = -1.1 ‰, $\delta^{18}O_{smow}$ = +16‰), but additional isotopic and trace element analyses, as well as radiometric age determinations of both the skarn and syenite will be required to resolve which (if either) model is correct. Unfortunately, detailed mapping of the area is greatly hampered by copious glacial overburden and vegetation.

MINERALS

The brief descriptions that follow are for the more important species only. For more complete information on these as well as additional minerals present, see Chamberlain et al. (1987).

Diopside occurs as dark green to black prismatic crystals to 10 cm associated with white microcline, titanite, wollastonite and meionite. While sometimes referred to as "augite" microprobe analyses show the dark pyroxene crystals are a diopside – hedenbergite solid solution series with approximately $Di_{75\%}$ - $Hd_{25\%}$.

Meionite forms equant gray-white crystals to 5 cm associated with diopside and microcline. Sometimes the meionite has a distinctive gray-blue surface coating of a K-Al-silicate (probably microcline) that was originally described as the now discredited "species" *nuttallite*.

Microcline is perhaps the most abundant of the well-crystallized minerals in the skarn assemblage, and occurs as blocky, somewhat rounded, white crystals several cm across.

Titanite occurs in sharp, dark brown, wedge-shaped crystals to 7 cm, though most are much smaller. One of the crystal habits of titanite from this locality was originally described as the species *lederite* (Shepard, 1840), but has since been shown to be titanite.

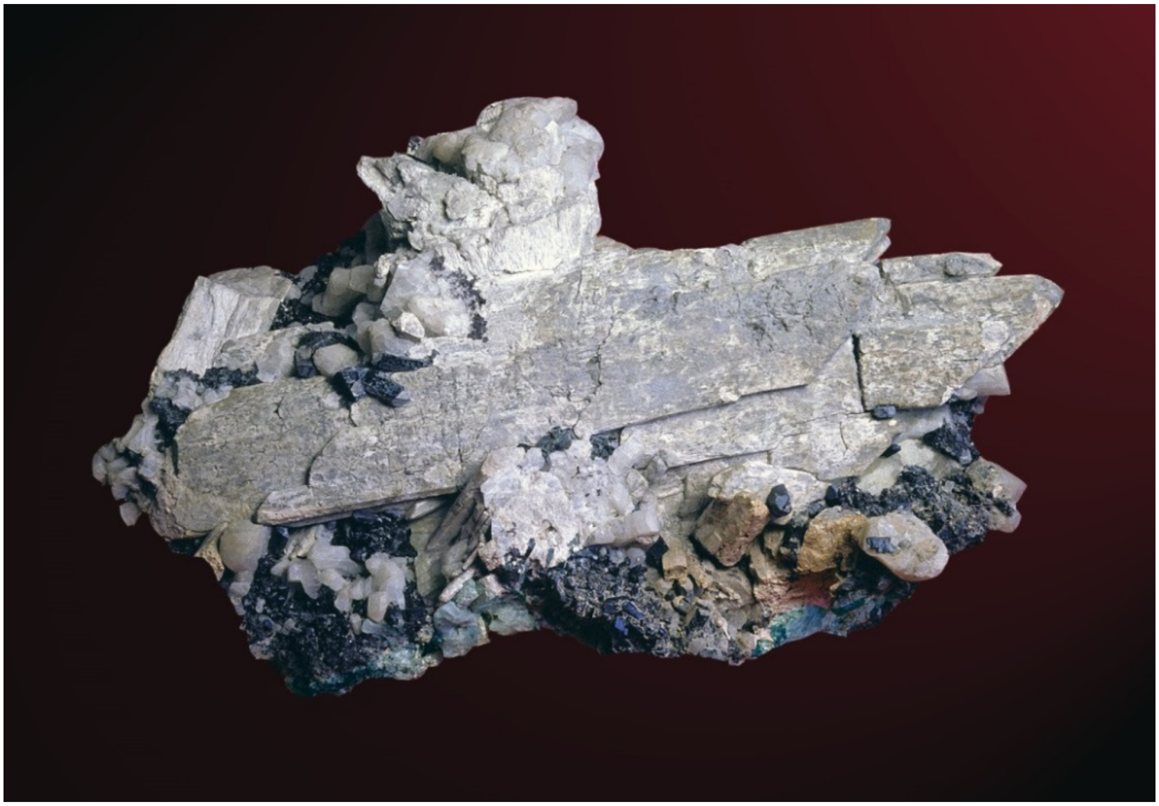

Figure 2. A 30-cm long wollastonite crystal with microcline and diopside from Natural Bridge, NY. Hamilton College collection, New York State Museum. S. Chamberlain photo.

Figure 3. Titanite, 7-cm crystal from Natural Bridge, NY. Harvard University specimen, S. Chamberlain photo.

Wollastonite forms elongated, pinacoidal, cream-white crystals to nearly 30 cm in length, making them among the largest and best examples of the species known.

Zircon forms small, pink, prismatic crystals seldom exceeding 2 cm in length. They are not common.

Retrograde minerals. Several of the species described above show evidence of partial to nearly complete replacement by other minerals, resulting in a variety of pseudomorphs. These are thought to have formed as a result of retrograde metamorphism, and include diopside coated by ferroactinolite, titanite by rutile and amorphous Ti-oxide, and wollastonite by quartz, calcite, diopside and hedenbergite.

Figure 4. Zircon, 3-cm crystal with calcite and meionite from Natural Bridge, NY. New York State Museum specimen and photo.

Stop 2: Gouverneur Minerals No. 4 Wollastonite Mine

INTRODUCTION

Originally known as the Valentine property, this active wollastonite mine commenced operations in 1977, and is today operated by the Gouverneur Minerals Division of Vanderbilt Minerals, LLC, producing commercial grade wollastonite which is used primarily in the ceramics and plastics industries. In addition to the wollastonite, other minerals of interest include abundant blue calcite, graphite, prehnite, quartz, and the rare species orientite and brewsterite-Ba, the latter for which it is the type locality.

GEOLOGY

The main orebody at the mine consists of a wollastonite skarn developed along the contact of Grenville Marble with a metasyenite of the Diana complex. The wollastonite occurs as coarse interlocking creamy white crystals 1- 6 inches long, locally cut by veinlets of fine-grained, fibrous wollastonite and veins or pods of massive, pale yellow prehnite. It is thought that the skarn resulted from silica-rich hyrothermal solutions reacting with the silica-poor marble under relatively low pressure, forming wollastonite ($CaSiO_3$). Subsequent retrograde alteration is responsible for epidote and quartz replacing the metasyenite and wollastonite, the prehnite and secondary wollastonite veins noted above, and calcite veins cutting the metasyenite and marble. Open cavities in some of the prehnite and quartz veins host a variety of crystallized minerals, the more interesting of which are described below. For an in-depth discussion of the geology of this deposit, as well as a more detailed coverage of the 30 some mineral species that have been found here, the reader is referred to Chamberlain et al. (1999), Gerdes (1991), Petersen and Totten (1993) and Gerdes and Valley (1994).

MINERALS FOUND IN THE MARBLE

Calcite. Ton quantities of pale-to-dark blue intergrown cleavages of calcite constitute much of the marble, particularly along the eastern edge of the skarn. The blue color is thought to be due to the development of radiation-induced lattice defects in sheared calcite.

Graphite is found throughout the marble units, where it occurs in a variety of habits varying from small euhedral hexagonal plates to unusual spherical aggregates several millimeters across. The hexagonal crystal plates occasionally show remarkable spiral growth features on their {0001} pinacoids.

Wollastonite is uncommon as a “secondary” mineral, yet it has been found here clearly as a late-stage species in dense, fine-grained fibrous veinlets in the earlier-formed wollastonite and marble skarn. This material may resemble a fine-grained quartzite in hand specimens, and fluoresces a powder blue color with an intense, and long-lived phosphorescence (afterglow) in longwave UV light.

Figure 5. Blue calcite from the Grenville Marble, Gouverneur Minerals No. 4 mine, 6 cm, G. Robinson photo.

Figure 6. Typical wollastonite ore. Gouverneur Minerals No. 4 mine, 10 x 12 cm, G. Robinson photo

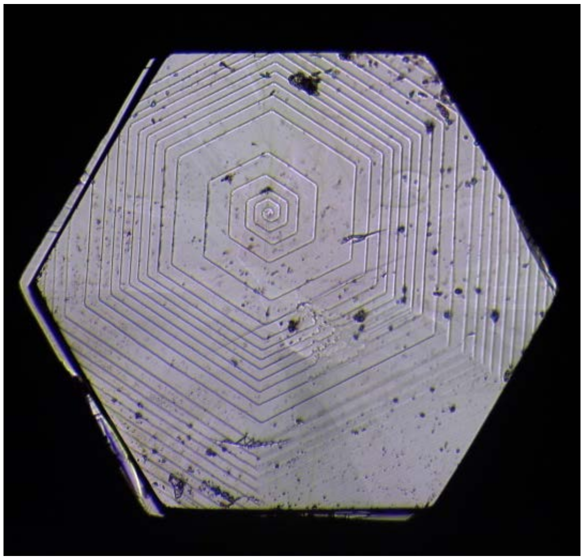

Figure 7. A 1-mm crystal of graphite showing well-developed spiral growth features. John Jaszczak specimen and photo.

Figure 8. A 4-mm rosette of graphite in calcite. A. E. Seaman Mineral Museum specimen, John Jaszczak photo .

MINERALS FOUND IN CAVITIES IN MASSIVE PREHNITE

Apophyllite group minerals occur as chalky white tapered pyramidal crystals generally less than 2 mm in length. Electron microprobe scans show they are compositionally zoned with respect to fluorine, and both fluorapophyllite and hydroxyapophylite may be present within a single small crystal. Rarely fluorapophyllite cleavages up to 2 cm across have been found.

Brewsterite-Ba is a rare member of the zeolite group that was first noted here in the late 1980s, but not formally described until 1993 (Robinson and Grice, 1993). At the same time the mineral was also found and described from Italy (Cabella, et al. 1993). Both occurrences have been referred to as “type localities.” At the No. 4 mine it occurs sparingly in some cavities in the massive prehnite as aggregates of colorless, tabular crystals 1-3 mm across. It is easily found using a shortwave UV lamp, since it fluoresces yellow-green.

Datolite is an uncommon mineral in some of the prehnite veins, but has been found in glassy, yellow-green crystals to 1 cm.

Hedenbergite is relatively common in some of the prehnite veins, where it forms elongated dark green prismatic crystals1-2 mm long. Diopside is also present, but tends to be much paler in color.

Microcline is a common accessory mineral in the prehnite cavities. It’s most common habit is small, white, adularia-habit crystals, often with serrated edges.

Orientite is a rare species, and is included here solely because of that fact. It is known from only six other localities, worldwide. At the No. 4 quarry it forms brush-like aggregates of acicular brown crystals to 1 mm as well as smaller, granular, rounded red-brown coating prehnite and babingtonite. To date, only two specimens are known (see Chamberlain et al., (1999) for a more complete description).

Pectolite occurs as micro tufts of white acicular crystals, which are practically indistinguishable from the more common wollastonite without X-ray or chemical data.

Prehnite crystals 1-5 mm across occur as pseudo-octahedral, dipyramidal, pale yellow-green crystals lining cavities in the massive prehnite.

Figure 9 (above). A 0.2-mm crystal of Brewsterite-Ba. New York State Museum specimen, S. Chamberlain photo.

Figure 10 (below). A 6-cm group of hematite-stained quartz crystals. S. Chamberlain collection and photo.

Figure 11. A 9-cm group of hematite-stained quartz crystals. S. Chamberlain collection and photo.

MINERALS OF THE NORTHWEST ALTERATION ZONE

Albite. In June, 1995, a large brecciated quartz vein was encountered while building a ramp along the northwest boundary of the skarn. While quartz was the predominant mineral present (q.v.), there were others worthy of mention, among them albite, which occurred as twinned, white, crystals to 1 cm associated with acicular microcline and reddish brown, botryoidal andradite on quartz.

Andradite occurs as coatings of red-brown microcrystals on quartz.

Calcite occurs as gray scalenohedral crystals up to 2 inches long, frequently with red and black inclusions of hematite and goethite, making interesting and attractive specimens.

Epidote crystals form aggregates up to a foot across in some of the larger pockets encountered.

Quartz is the mineral of primary interest in the northwest alteration zone, where it forms colorless to milky prismatic crystals several inches in length, and crystal groups several times that size. Some of the crystals have a dusting of hematite, giving them a pinkish hue, while others have a wide variety of hematite and goethite inclusions, resulting in an equally wide variety of appearance. Amethyst is also present, but less common.

Stop 3: Rose Road - Purple Diopside Mound near Pitcairn, NY.

INTRODUCTION

Although the mineralization at this stop was only recently discovered, an interesting variety of specimens has been recovered in the past two years. Despite being a few hundred yards from the classic wollastonite skarn, the purple diopside mound has a very distinctive suite of minerals of different age and origin from the skarn. Large quantities of well-crystallized scapolite, fine-grained masses and crystals of purple diopside, black titanite, and transparent phlogopite are noteworthy. The discovery of lesser amounts of pink corundum and pink spinel, secondary natrolite and prehnite, and still unidentified “gieseckite” pseudomorphs, have all added interest.

GEOLOGY

Excavations have revealed an occurrence of calcite-filled “vein dikes” typical of regional metamorphism in the Grenville Central Metasedimentary Belt. The zircon age of the vein-dike mineralization is 1170 Ma (Chamberlain et al., 2014), making it slightly older than the nearby wollastonite skarn. The principal veins are lined with scapolite crystals facing into a coarse calcite center. At places black titanite is an accessory mineral. Locally significant masses of acicular natrolite crystals coat the scapolite. Other parts of the mound have silicate-marble contacts with purple diopside crystals and “gieseckite” crystals developed at the contact. Phlogopite crystals are developed in the marble near the silicate-marble contacts. Spinel occurs as a rare accessory with the phlogopite in marble. Pink corundum occurs as anhedral masses in scapolite several centimeters away from the scapolite crystals developed facing into the vein. The association of corundum with fluorescent scapolite is noteworthy and appears paragenetically similar to the recently discovered gem sapphire occurrences in the Kimmirut area, Baffin Island, Nunavut, Canada (Cade et al., 2005; Lepage and Rohtert, 2006).

MINERALS

Since no detailed description of the minerals identified from this occurrence has yet been published, a summary of the complete list follows.

Albite occurs as white euhedral crystals to 1 cm and as white masses in purple diopside.

Corundum occurs as bright purplish-pink, anhedral masses to 25 mm in meionite on the margins of the scapolite vein dike.

Diopside occurs as grayish purple prismatic crystals to several cm and as fine-grained masses. The composition includes about 1 wt % FeO and 1 wt % TiO_2, which may account for its unusual color. The dark green diopside crystals, the yellow acicular diopside formed as an alteration of wollastonite, and the dark blue-green actinolite overgrowths at the adjacent wollastonite skarn all contain significantly more iron and no detectable titanium (by SEM/EDS).

Fluorapatite forms bright blue-green transparent prisms to 8 cm in the marble.

"***Gieseckite***" occurs as sharp euhedral pseudomorphs to several cm associated with graphite rosettes. These pseudomorphs have a complex internal replacement texture and variable composition. Some have zones of fine-grained plagioclase (labradorite). The original mineral has not been found nor inferred.

Graphite occurs as sharply developed crystals and rosettes to several mm, most often associated with "gieseckite".

Natrolite is present as radial aggregates of coarse, white, crystals to 5 cm and also as masses of acicular crystals in localized portions of the scapolite vein. This is a sodium zeolite with little detectable calcium that appears to have formed from the breakdown of scapolite, similar to other zeolite minerals found in similar "skarn" assemblages in the Grenville CMB (VanVelthuizen, et al., 2006).

Phlogopite occurs as honey-brown, transparent crystals to 1 cm and as masses of 20 cm or more in marble. Rarely, pseudomorphs of phlogopite after scapolite occur in the scapolite vein.

Prehnite occurs sparingly as brown botryoidal masses to 4 cm on a matrix of calcite, graphite, and pyrite. Like natrolite, it probably formed from the breakdown of scapolite.

Pyrite occurs as modified cubes to 5 mm, and as minute crystals often altered to goethite in "gieseckite", prehnite and scapolite. It also forms oriented arrays of acicular crystals embedded in meionite.

Scapolite occurs as sharp crystals to 20 cm on the walls of the scapolite vein. These crystals have intermediate compositions close to the middle of the meionite (calcium-rich)-marialite (sodium-rich) isomorphous series. Generally glassy gray scapolite is slightly enriched in calcium and is meionite. Sometimes a rind of white, translucent scapolite coats the crystals and is slightly enriched in sodium (marialite). Most of the volume of scapolite is meionite.

Spinel occurs as pink octahedral crystals to 1 mm in marble associated with phlogopite.

Titanite occurs as tabular, almost black crystals to 5 cm associated with scapolite and also as minute crystals of complex morphology embedded in albite.

Zircon occurs as minute euhedral crystals embedded in meionite.

Figure 12a. A 5 cm gray meionite crystal in calcite, in ordinary white light. G. Robinson photo.

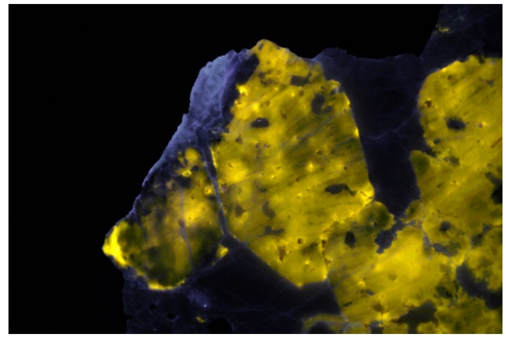

Figure 12b. Same specimen at left illuminated by LW ultraviolet light. G. Robinson photo.

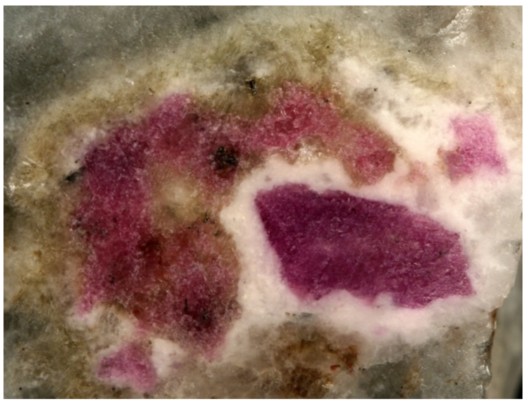

Figure 13. Pink corundum from the purple diopside mound; 3 cm field of view. St. Lawrence Univ. specimen, G. Robinson photo.

Figure 14. Purple diopside with calcite, 5 x 5 cm. S. Chamberlain collection and photo.

Figure 15. A 2.5 cm "gieseckite" crystal from the purple diopside mound. M. Walter specimen and photo.

Figure 16. A 16.5 cm group of scapolite crystals from the purple diopside mound. M, Walter specimen and photo.

Stop 4: Rose Road - Wollastonite Skarn near Pitcairn, NY.

INTRODUCTION

This classic locality (also known as the Mulvaney sugar bush) has been a source for well-formed crystals of wollastonite, titanite, diopside and albite for about 125 years. Williams (1885), Luquer (1893), and Ries (1893-94, 1895) all published reports on various aspects of the mineralogy of this site. All of the various species reported from this site (Chamberlain and Robinson, 2013) are still collectible today

GEOLOGY

The locality is a wollastonite skarn formed by the emplacement of the Diana Complex (estimated at ~ 1164 +/- 11 Ma (Hamilton et al. 2001)). It is a secondary skarn in the sense that it was apparently formed by solutions from the Diana Complex invading fractures along a contact between the Grenville Marble and a metamorphic albite-diopside rock. The age relationships between the skarn formation and the regional metamorphism of the Adirondack Lowlands are somewhat confusing, given the zircon age we report for the nearby vein dikes at Stop 3. Significant alteration of the wollastonite and minor uralitization of the diopside have occurred subsequent to the original mineralization.

Minerals

A summary description of the minerals is provided below. For more details see Walter et al. (2009) and Chamberlain and Robinson (2013).

Actinolite occurs relatively rarely as a blue-green coating on diopside crystals. It contains 7.5 wt % FeO which is significantly more iron than is found in the diopside.

Albite occurs as equant or elongated white blocky crystals to 8 cm. Both Carlsbad and Manebach twins have been found (Chamberlain, 1985; Walter, 2009; Chamberlain and Robinson, 2013). The perthitic texture is due to minor exsolution lamellae of microcline making this an antiperthite.

Diopside is perhaps the best known species from this locality, and forms lustrous dark green prismatic crystals to 20 cm. It contains about 2.5 wt % FeO. Diopside also occurs as a granular replacement of wollastonite.

Fluorapatite occurs as prismatic crystals to 8 cm in colors ranging from dark blue to bright blue to blue-green.

Goethite usually replaces pyrite, forms brown stains on the adjacent albite and occasionally forms small clusters of microscopic needles.

Graphite rarely forms small tabular crystals to 2 mm. It is more common as gray inclusions in albite.

Pyrite occurs as microscopic crystals on albite. Most have completely altered to goethite.

Quartz occurs as granular masses and white to colorless rounded crystals to 1 cm replacing wollastonite.

Titanite occurs as tabular, clove-brown crystals to 12 cm. Some of the finest titanite crystals found in New York have come from this skarn. Most of the larger crystals have somewhat rounded faces and prominent parting.

Wollastonite occurs as white well-developed, euhedral crystals to 35 cm. These are almost always altered, at least on the surface. Pale brown alteration consists of acicular yellow diopside crystals containing 5 wt % FeO intermixed with calcite formed from the breakdown of wollastonite. Greenish, granular alteration is mostly diopside. White granular alteration is quartz. Green and white patchy altered wollastonite crystals are typical (Chamberlain et al. 2009).

Figure 17. A 4.5-cm titanite crystal in calcite-wollastonite from the Rose Road wollastonite skarn. S. Chamberlain specimen and photo.

Figure 18: A 7-cm specimen of wollastonite from the Rose Road wollastonite skarn. S. Chamberlain specimen and photo.

Figure 19. An 8-cm specimen of fluorapatite in calcite from the Rose Road wollastonite skarn. S. Chamberlain specimen and photo.

Figure 20. A 7-cm specimen of diopside and titanite on albite from the Rose Road wollastonite skarn. S. Chamberlain specimen and photo.

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