ULTRAMAFIC/MAFIC ROCKS OF THE PYRITES COMPLEX

JEFFREY CHIARENZELLI Department of Geology, St. Lawrence University, Canton, New York 13676

MARIAN LUPULESCU Research and Collections, New York State Museum, Cultural Education Center, 222 Madison Avenue, Albany, NY 12230

DAVID BAILEY

Department of Geosciences, Hamilton College, 198 College Hill Road, Clinton, NY 13323

INTRODUCTION

General overviews of the geology of the Adirondack Lowlands incorporating new results can be found in Chiarenzelli et al. (2010a; 2010b; 2011a; 2012), Lupulescu et al. (2010), Peck et al. (2013), and Wong et al. (2011), among others. The purpose of this trip is to provide additional insight into the tectonics of the Adirondack Lowlands by highlighting mafic and the ultramafic rocks exposed in the region. The trip will leave from Alexandria Bay and end at Pyrites, where ultramafic rocks of the Pyrites Complex occur (Figure 1).



Figure 1. Route of trip B-2 showing location of roadways, field trip stop locations, larger lakes, villages, and other features.

The Adirondack Lowlands are a small part of the greater Grenville Province (Figure 2), a Mesoproterozoic orogenic belt of global proportions. The tectonic assembly and collisional orogenesis recorded here, and elsewhere, resulted in the formation of Rodinia, one of the Earth's Supercontinents. In fact, breakup of Rodinia set the stage for the deposition of the widespread blanket of Potsdam sandstone along the rifted margin of Laurentia, to our east in the Champlain Valley, and exposed nearby on the fringes of the Ottawa Embayment.

The Adirondack Lowlands are delineated from the Adirondack Highlands by a long-lived shear zone that displays evidence for both a ductile and brittle history (Figure 3). This structure, named the Carthage-Colton Shear Zone, marks a number of distinct geologic changes such as the proportion of metasedimentary to metaigneous lithologies, differences in metamorphic grade, variation in the timing of metamorphism, the orientation of structural grain, and a change in topographic relief and elevation. The Lowlands is composed mostly of metasedimentary rocks, predominantly marble, and was metamorphosed to Upper Amphibolite facies during the Shawinigan Orogeny (ca. 1150-1200 Ma), leading to widespread melting in some pelitic gneisses and the growth of metamorphic zircon at 1160-1180 Ma (Heumann et al., 2006). Its position higher in the crust has led to a lack of widespread (any?) effects of the Ottawan Orogeny (ca.1020-1090 Ma), in contrast to the Highlands where metamorphic zircon of this age and resetting of zircon is widespread (Chiarenzelli and McLelland, 1993; Chiarenzelli et al., 2011b).

The oldest known rocks in the Lowlands consist of metasedimentary rocks of Grenville Supergroup, first noted in the literature by Sir William Logan in 1863 to describe the sequence of metasedimentary rocks that occur across large areas of southern Ontario and adjacent parts of Quebec. In the Lowlands these rocks provide evidence of shallow water, marine deposition and include, among other lithologies, voluminous marbles, calc-silicate gneisses, tourmaline-rich quarztofeldspathic gneisses, the sedex sulfide exhalatives of the Balmat zinc mines, and metaevaporites. A tripartite stratigraphy and/or structural stratigraphy has been recognized and consists of the lower marble, Popple Hill Gneiss, and the upper marble, which has been further subdivided into 16 lithologic units (deLorraine, 2001; deLorraine and Sangster, 1997). In contrast to the proposed setting of the carbonate rocks, a deep water turbidite origin has been proposed for the Popple Hill pelitic and psammitic gneisses and equivalents (Chiarenzelli et al., 2012). However, all of these rocks may be allochthonous, as older basement rocks have yet to be identified. The maximum depositional age for the Grenville Supergroup in the Lowlands has recently been constrained between <1258 and <1284 Ma (Chiarenzelli et al., in review).

Recent investigation has revealed that ultramafic-mafic igneous rocks occur within northeast-trending linear belts (Figure 4) in the Lowlands and may be older or equivalent in age to the Grenville Supergroup. Named the Pyrites Complex for exposures along the Grasse River near Pyrites, New York, these rocks have required rethinking of the depositional environment of not only the Grenville Supergroup equivalents in the Adirondack Region but the origin of the Zn-Pb sedimentary exhalatives of the Balmat-West Pierrepont Belt. A model incorporating the discovery of ultramafic rocks suggests that the rocks of the Grenville Supergroup were deposited after 1300 Ma in a back-arc basin which closed at about 1240 Ma during the Elzevirian Orogeny (Chiarenzelli et al., 2011a; 2012). This back-arc basin has been named the Trans-Adirondack Back-arc Basin and is thought to be temporally equivalent to a similar basin in the Central Metasedimentary Belt of Ontario and Quebec (Dickin and McNutt, 2007). This implies that a broad region of the southeast margin of Laurentia underwent rifting and extension at this time.

During this trip we will see what is thought to be the remnants of a highly disrupted ophiolite complex and deep water sedimentary rocks including hydrothermal altered ultramafic rocks (Stops 4 and 5), amphibolite (Stop 1), and possible turbidites (Stop 4). We will observe a lamprophyre dike cutting the ultramafic rocks at Stop 5. In addition, two stops will be made to investigate candidates for inclusion in the the Pyrites Complex including a large block of serpentine (Stop 2) and a hornblendite unit (Stop 3), both which require further investigation. Isotopic and geochemical studies indicate widespread enrichment in incompatible elements suggests that the Pyrites ultramafic complex and associated rocks formed in a suprasubduction zone setting. Although the surface exposure of the ultramafic rocks is small, the largest gravity anomaly in the Lowlands extends from Pyrites to the southwest for over 10 km parallel to the trend of the Carthage-Colton Shear Zone, indicating substantial amounts of high density rocks at depth.



Figure 2. Figure showing the location of the Grenville Province within North America (upper left). Expanded polygon (upper right) shows the same region blown up to show surrounding provinces of the Canadian Shield. Abbreviations include: AH (Adirondack Highlands), AL (Adirondack Lowlands), FT (Frontenac Terrane), and GFTZ (Grenville Front Tectonic Zone). Lower figure shows the timing of recognized deformational events that make up the Grenville Orogenic Cycle (after Rivers, 2008). Additional abbreviations include: CAB (Central Arc Belt) and PSD (Parry Sound Domain). From Chiarenzelli et al. (2011a).



Figure 3. Geology of the Adirondack Lowlands and surrounding terranes from Isachsen and Fisher (1970). The Black Lake (BLSZ) and Carthage-Colton (CCSZ) shear zones define the boundaries of the Adirondack Lowlands. Flat-lying Paleozoic rocks (orange) overlie Grenville basement rocks much of the St. Lawrence River Valley and Tug Hill plateau to the southwest. Note the predominance of marble (blue) in the Lowlands and general lack thereof in bounding Frontenac Terrane and Adirondack Highlands.

Stop 1 Amphibolite and Pyritic Gneisses near Antwerp <1 km southwest of Antwerp, along Rt. 11; Latitude 44°11'41.7", Longitude 75°37'28.8"

We have driven south from Alexandria Bay to the southern belt of pyritic gneisses, amphibolites, metagabbros, and ultramafic rocks exposed in the Lowlands. Here near Antwerp, New York we will see some of the amphibolites, associated pyrite-rich metasedimentary rocks, and igneous rocks which intrude them (Figure 4). This belt can be traced nearly 50 kilometers to Pyrites and beyond. The large outcrop in the foreground shows a sequence of rocks dipping shallowly to the northwest. The darker rocks are amphibolites with MORB-like geochemistry. Those with rusty staining are of metasedimentary origin and contain detrital zircons, in addition to pyrite. Unfortunately these zircons are metamict and discordant. However, similar rocks at Pyrites have yielded intriguing results that will be discussed later at Stop 4. Both of these rocks are cut by a variety of intrusive pegmatites which are correlative in age to the Antwerp-Rossie Suite (ca. 1200 Ma).

The intrusive age of the Antwerp-Rossie Suite provides a minimum age for rocks of the Grenville Supergroup and ultramafic mafic rocks of the Pyrites Complex. Further east along Route 11 large banded outcrops of marble, and isoclinal folds within it, are cut by rocks of the Antwerp-Rossie Suite (Figure 5) dated at ca. 1200 Ma. The Antwerp-Rossie Suite is calc-alkaline and the product of northward subduction which preceded the Shawinigan Orogeny.



Figure 4. Field photograph showing dark amphibolitic rocks along Route 11 in Antwerp, NY cut by lightcolored pegmatite veins related to the Antwerp-Rossie plutonic suite (ca. 1200 Ma). Note the strongly layered rusty gneisses on either side of the geologist.



Figure 5. Outcrop of Grenville Supergroup lower marble along Route 11 showing a large recumbent isoclinal fold (just above the geologist's hand) cut by rocks of the Antwerp-Rossie Suite (ca. 1200 Ma).



Figure 6. Generalized geologic map of the Adirondack Lowlands showing the locations of mafic and ultramafic rocks (in purple) analyzed for Nd isotopic systematics and corresponding Nd T_{DM} (red circles). The sample collected along Rt. 11 at Antwerp, which we will visit, yielded an unrealistically old model age of 1608 Ma). The red star denotes the cluster of samples collected at Pyrites where model ages varied between 1445-2618.

Orogeny (ca. 1150-1200 Ma). The deformation preserved in the marble must pre-date this subduction event and subsequent Shawinigan orogenesis (Figure 5). This implies that the Grenville Supergroup and Pyrites Complex where deformed during the Elzevirian Orogeny (ca. 1220-1245 Ma), consistent with the minimum age for the Grenville Supergroup in the region constrained by detrical zircons (Chiarenzelli et al., in review).

The amphibolite outcropping here has been characterized by geochemistry and Nd-systematics. The amphibolites and metagabbros of this belt yield unrealistically old NdT_{DM} ages of 1508-1624 Ma, as do

ultramafic rocks at Pyrites, which in some cases are even older (Figure 6). This suggests disturbance of the Sm-Nd isotopic system and the influence of a metasomatically altered mantle wedge in their origin. Elevated oxygen isotopic ratios have been found zircon in plutonic rocks extending across the Lowlands into the Frontenac Terrane by Peck et al. (2004). Peck et al. (2004) interpreted these elevated ratios as indicative of the influence of subducted hydrothermally altered oceanic crust and/or sedimentary material beneath the leading edge of Laurentia. As a group, rocks of the Pyrites Complex plot between the Nd isotopic arrays of Quebecia ca. 1570 Ma (Dickin and Higgins, 1992) and Ontario Juvenile Crust ca. 1277 Ma (Dickin and McNutt, 2007) indicating an age in excess of 1277 Ma (Figure 7) but younger than 1570 Ma.

An age greater than 1277 Ma for the Pyrites Complex is compatible with several lines of evidence. Barfod et al (2005) obtained a 1274±9 Ma Lu-Hf date on apatite from the lower marble and interpreted it as the time of diagenetic apatite growth in the marble. Sager-Kinsman and Parrish (1993) obtained a maximum depositional age of <1306±16 Ma from the youngest detrital zircon in a quartzite unit of the Grenville Supergroup on Wellesley Island. And as will be discussed below, Chiarenzelli et al. (in review) found a maximum age of 1284+/-7 on detrital zircons from turbiditic rocks overlying ultramafic rocks at Pyrites. A model for the generation of oceanic crust within a series of back-arc basins along the leading edge of Laurentia has been proposed by Chiarenzelli et al. (2011a). The opening of the Trans-Adirondack Back-arc Basin is believed to have been synchronous with the opening of a similar basin in the Central Metasedimentary Belt of Ontario and Quebec (Dickin and McNutt, 2007).



Figure 7. Neodymium evolution diagram showing the trend from mafic and ultramafic rocks of the Pyrites Complex and other Grenville rock suites from Dickin and McNutt (2007) and Dickin and Higgins (1992) used for comparative purposes.

Stop 2 Yellow Lake Serpentinite

~8.5 km west of Gouverneur, off of Campbell Rd between Yellow Lake and the Oswegatchie River; Latitude 44°20'14.3", Longitude 75°34'47.8"

This stop is on private land and permission was obtained for this field trip to visit the area. Please respect the landowner's wishes and do not revisit this location without permission. Respecting land owners rights insures that future geologists will have access to key scientific sites. If in doubt, ask first.

While serpentine is a common mineral throughout much of the Lowlands, massive serpentinite, like that exposed here, is unusual. While this exposure may be a large serpentinized block of metasedimentary rock, the location of this body puts it within a linear trend of mafic and ultramafic rocks approximately 10 kilometers north and west of the Pyrites belt which we will visit again in the near future. These and other linear belts may represent separate thrust sheets, or perhaps, opposing limbs of a major nappe-like structure. In any event, the uniqueness of this exposure makes it an excellent place to visit regardless of its origin.

The Yellow Lake serpentinite is an unusually large body (~100 m) of massive serpentine hosted within marble of the Adirondack Lowlands metasedimentary sequence. The only detailed geologic map of the area shows a thin band of lower marble surrounded by the "Hermon granite-amphibolite" unit (Buddington, 1934). On the Adirondack Sheet this unit is denoted as amg and consists of highly disrupted and intruded amphibolite and metagabbro engulfed within the Hermon granitic gneiss. While localized areas of disseminated serpentine within the marble were noted in the report and are particularly common in the upper marble which is found to the south, this large mass of serpentine was apparently not recognized or described. Intriguingly about 10 kilometers to the southwest near Theresa a small stream is named Soapstone Creek, suggesting more massive serpentinite or talc is yet to be rediscovered.

It appears that the Yellow Lake serpentinite first came to the attention of geologists in the mid-1980s when it was discovered by George Robinson and Michel Picard while on a St. Lawrence County mineral collecting excursion (G. Robinson, pers. comm.). Since that time, local mineral collectors have explored the outcrop and found nice sky blue apatite crystals and a few nicely formed pseudomorphs of serpentine after forsterite (S. Chamberlain, pers. comm.).

The outcrop is extensively fractured and incoherent, and because of this property, has been used locally as a source of rock aggregate and fill. Most of the exposure is composed of a dull yellow-green massive serpentine with abundant radiating dendrites of an unknown black oxide /hydroxide mineral coating fracture surfaces and disseminated throughout the massive serpentine (Figure 8). Small (2-20 cm wide) irregular veins of coarsely crystalline calcite cut through the unit, and it is within these veins that the blue apatite crystals (up to 3 cm long) are found. Pseudomorphs after forsterite occur along the sides of the veins (S. Chamberlain, pers. comm.). Pyrite, talc, and an unidentified Ca-Mg-silicate (possibly harkerite?) have also been found within these veins (Chamberlain and Bailey, unpub. data). Table 1 gives the composition of select mineral phases in the serpentinite, including Mn-rich dendritic growths and serpentine.

The occurrence of a relatively large body of ultramafic rock within the metasedimentary sequence of the Adirondack Lowlands is enigmatic; possible explanations for its origin include a localized accumulation of komatiitic ash, or an unusual clay-rich evaporite horizon within the carbonate sequence. Alternatively it may prove to be another block of highly altered ultramafic metaigneous rock such as that exposed at Pyrites. Additional field, mineralogical, and geochemical studies at this location and along this belt are needed to better understand this unusual ultramafic body and place it in its proper geologic context.



Figure 8. Cut slab of Yellow Lake serpentinite body showing dull green color, calcite pockets and veins, and massive nature. Note the irregular network of carbonate veins and black dendritic growths. The area in the red square has been enlarged in the right hand photograph to show the region where pseudomorphs after euhedral crystals, perhaps olivine, can be seen in the calcite pocket in the upper left of the left-hand figure.



Figure 9. Scanning electron microscope back scatter image of the Yellow Lake serpentinite showing Mn-rich dendritic growths in a groundmass of serpentine.

Stop 3 Hornblendite near Elmdale

~1 mile north of Elmdale, right side of Rt. 58; Latitude 44°22'20", Longitude 75°33'14"

This outcrop consists largely of hornblendite whose age and origin is unknown. The rock falls along the general trend of serpentinite (last stop), and within a 40 kilometer linear, but highly disrupted, belt of amphibolite, pyritic gneisses, and metagabbro extending to the northeast from Yellow Lake to near Kendrew Corners, north of Dekalb. It is composed 1-2 centimeter blocky, equant black crystals of hornblende surrounded by k-feldspar, titanite, and apatite (Table 1 and Figures 10 and 11). The rock shows relatively little evidence of wholesale deformation but is cut by pegmatite, which is also undeformed.

Table 1. Composition (wt.	%) of select mineral	phases from Stor	ps 2 and 3 (Anal	vsis by David Bailey).
	, , , , , , , , , , , , , , , , , , , ,			<i>J</i> ~ - ~ <i>J</i> = • • · - • = • • - • <i>J J i</i>

Sample	Serpentinite	Serpentinite	Hornblendite	Hornblendite	Hornblendite
Mineral	Serpentine	Mn-dendrites /	Epidote	Hornblende	K-Fsp
		serpentine			
SiO2	51.93	39.17	38.32	42.73	64.95
TiO2				1.16	
Al2O3	0.08	0.52	20.12	13.57	19.84
FeO	1.64		12.46	17.50	
MnO		25.44			
MgO	46.35	30.27	0.80	10.10	
CaO		3.44	15.04	10.35	
BaO		1.15			1.56
Na2O				2.26	2.06
K2O				2.32	11.58
P2O5					
La2O3			4.21		
Ce2O3			8.15		
Sm2O3			0.91		
Total	100	100	100	100	100



Figure 10. Cut slab of the Elmdale hornblendite displaying large, equant hornblende crystals.



Figure 11. Scanning electron microscope back scatter image of the Elmdale hornblendite. Abbreviations: Ap-apatite; Biobiotite; CC-calcite; Hbld-hornblende; K-spar-potassium feldspar; Py-pyrite; Serp-serpentine; Tt-titanite.

Hornblende-rich ultramafic rocks are relatively rare and can have a variety of origins. Detailed petrographic, geochemical, and geochronological study will hopefully provide further constraints on the origin of this rock. However, it may represent the one of the magmatic products of subduction in the Lowlands. Previous work has identified a strong subduction signature in many of the plutonic rocks exposed in the Lowlands (Figure 12; Chiarenzelli et al., 2010b). In particular, the lamprophyre dike we will see later in the day is indicative of this enriched mantle signature prevalent in mafic and ultramafic rocks of the Pyrites Complex as well.

Shawinigan plutonic suites in the Lowlands crosscut the fabric and isoclinal folds (Figure 5) in metasedimentary rocks of the Grenville Supergroup (Chiarenzelli et al., 2010a; Peck et al., 2013). The geochemistry and Nd signature of these plutonic suites (Antwerp-Rossie Suite, Hermon Granitic Gneiss, and Hyde School Gneiss), intruded between 1170-1200 Ma, mark the evolution of arc magmatism to granitic

magmatism of the Anorthosite-Mangerite-Charnockite-Granite suite prevalent in the Adirondack Highlands but also found in isolated plutons in the Lowlands (Peck et al., 2013). These rocks track the tectonic evolution of the region and underlying mantle dynamics.



Figure 12. Incompatible element spidergram for the Antwerp-Rossie Suite. Note characteristic depletions in Nb, Ta, P, and Ti, typical of arc rocks. The hornblendite seen at this stop may be part of the suite.

Based on its state of deformation and geochemical affinities (alkali-rich), the hornblendite unit exposed here may be an ultramafic variant of the Antwerp-Rossie Suite. If this is verified, it would be the only ultramafic body yet recognized as part of the Antwerp-Rossie suite. Intrusive gabbros and diorites associated with the Antwerp-Rossie suite occur nearby at Pleasant Lake and Split Rock, and to the south near Balmat and Harrisville (see Carl, 2000; Chiarenzelli et al., 2011). If it is indeed part of the Antwerp-Rossie Suite, the hornblendite's occurrence along the linear trend of mafic and ultramafic rocks would be coincidental. However, like the serpentine body just investigated, the hornblendite occurs within a large belt of the Lower Marble. It may be an older tectonically emplaced block as will be demonstrated for the ultramafic rocks at Pyrites later in the trip. Regardless of its origin, this ultramafic rock is unique and has much to tell us about the geologic history of the Adirondack Highlands.

Stop 4 Contact between Pyritic gneiss and Ultramafic Rocks along the Grasse River Dirt trail on right just after crossing the Grasse River on County Route 21 when headed east ; Latitude 44°31'24.7", Longitude 75°11'28.5"

The rocks at Pyrites lie with the triangular core zone of a large winged structure defined by amphibolite and gabbroic rocks that extends northeast from Stellaville (former site of the largest pyrite mine in St. Lawrence County) nearly 15 km to Crary Mills (red star, Figure 6 and Figure 13). The general shape of the structure

indicates it is folded and most of the amphibolitic rocks have a strong foliation and are highly disrupted by later magmatism. The belt of mafic and ultramafic rocks lies within marble. Although the actual surface exposure of the ultramafic rocks is modest (~ 1 km²), the largest gravity anomaly in the region (Revetta and McDermott, 2003) extends from here southwest for about 10 kilometers (Figure 14). This suggests that it represents just a small part of the body and that a considerable mass of ultramafic rock, extending downward for some distance, lies parallel to the Carthage-Colton Shear Zone.

At this stop we will examine rocks associated with one of several pyrite mines that was in production between ca. 1880 to 1920 (Prucha, 1957) as a source of sulfur for industrial processes and sulfuric acid feedstock. Two adits can be seen on the side of the mustard-colored hill (Figure 15) as you approach the outcrop along the bank of the Grasse River. The adits intersect the steeply-dipping ore zone and the workings continued downward for as much as two hundred feet and extend underneath the river. On the bank, the rocks can be seen dipping steeply to the northwest and show differential weathering related to the variation in their mineral content and extent of weathering. Investigation at the top of the exposure shows the characteristic red coloration of pre-Potsdam weathering indicating that the unconformity was likely within a few feet of the current erosional level at the top of the hill.

The main ore zone consists of a ~2m thick planar layer of pyritic breccia. Examination of the rock at the outcrop, and in thin-section, indicates the ore is composed of rounded 1-2 cm fragments of breccia indicating enrichment of the ore during repeated fault movement. A black, rounded, 5 centimeter wide fragment composed of breccia within breccia can be seen at the foot of the hill within the primary ore zone. Carefully examination of the ore and surrounding rock reveals highly weathered lath-like crystals of sillimanite. Other minerals within the sequence include quartz, feldspar, mica, chlorite, sericite, garnet, graphite (Figures 16-18), and a host of trace minerals including pyrrhotite, rutile, sphalerite, chalcopyrite, molybdenite (Figure 17), and chromite (Tiedt and Kelson, 2008). Tiedt and Kelson (2008) suggest a possible biogenic origin for the pyrite on the basis of sulfur isotopes, in line with the presence of graphite. However, a hydrothermal volcanic influence is also possible based on the variety of metals found and association with mafic and ultramafic rocks.

In addition to a strong foliation and compositional layering, the sequence is cut by shallowly dipping veins which weather in positive relief. These veins are composed mostly of pyrite, minor pyrrhotite, and silica and represent a much later event in the history of the deposit. Early deformation is defined by compositional layering which is isoclinally folded. Thin seams of breccia less than a 1 cm wide can be seen cutting the foliation and/or folded layers in several areas in the exposure. Near the ore, within white feldspathic pods, relatively large, brown rutile crystals can be seen (Figure 18). Other non-sulfide minerals observed in the ore include chlorite, graphite, quartz, rutile, and monazite (Figure 18). Note the variation in resistance of the rocks to weathering, colors, and variation in layering as you walk upstream.

Towards the end of the accessible outcrop area along the river the rocks change in character and color to a massive, knobby weathering green ultramafic rock. The actual contact between the ultramafic rocks and metasedimentary sequence is well exposed in the wall of the river bank. Whether the contact is sedimentary or tectonic, or both, can be debated here. Regardless of the nature of the contact, the layered metasedimentary rocks become progressively greener in color and more Mg-rich towards the contact. Given the occurrence of chromite noted by Tiedt and Kelson (2008) in these rocks, proximity to ultramafic rocks during deposition is likely. Depositional along a transform fault is one possibility that could account for the juxtaposition of these two rock types and lend additional credibility to a deep water turbidity origin for the pyritic gneisses.



Figure 13. Geological map of the greater Pyrites area of the Adirondack Lowlands (geology modified from the Adirondack Sheet). Inset shows sample locations of ultramafic rocks plotted on a Google Earth image.

Several meters above the contact a large isoclinal fold can be seen. About the hinge of the fold, one can see both recessive and resistant cm-scale layering (Figure 19). The recessive layers consist of quartzofeldspathic gneiss with both sillimanite and garnet, whereas the more resistant layers consist of up to 85% or more quartz. This exposure provides insight into both the original nature of the layered metasedimentary rock and its metamorphic grade. Couplets of mud and sand are suggestive of a turbiditic sequence deposited in a relatively deep water setting. At some point, likely associated with the Shawinigan Orogeny (1150-1200 Ma), these rocks were intensely deformed and metamorphosed to Upper Amphibolite facies (garnet-sillimanite).



Figure 14. Gravity anomaly map of St. Lawrence County and surrounding environs. Inset shows the gravity anomaly associated with the exposure of ultramafic rocks at Pyrites and its extension to the southwest (after Revetta and McDermott, 2003).



Figure 15. Field photograph showing the contact between the underlying mustard colored pyritic gneisses and underlying dark green ultramafic rocks along the Grasse River at Pyrites. The photograph was taken looking upstream from the Enel Hydropower Station.



characteristic of the ore.



Figure 17. Scanning electron microscope back scatter image of pyrite ore showing pyrite, chlorite (Chl), quartz (Qtz), and molybdenite (Moly) characteristic of the ore.



Figure 18 Scanning electron microscope back scatter image of pyrite ore showing pyrite, chlorite, quartz (Qtz), rutile, biotite,(Bio) and monazite.



Figure 19. Nose of isoclinal fold showing resistant quartzite layers (Qtz) and recessive weathering garnetsillimanite gneiss layers (Sil-Grt). Note gradual gradation in metamorphic mineral grain-size, indicative of original composition. Several of the thicker resistant layers were sampled for detrital zircon geochronology.

The thin, resistant, quartz-rich layers were sampled for detrital zircon geochronology and yield a sparse, but very homogeneous, population of detrital zircons. The zircons are between 25-100 microns in length, fairly euhedral, and zoned (inset Figure 20). Limited evidence of metamorphic rims or xenocrystic cores was found, despite BSE and CL imaging of cross-sectioned grains. The zircon yielded a near unimodal population of grains with a maximum depositional age of 1284+/-7 Ma (Figure 20). This result is compatible with a restricted source consisting of igneous zircon, perhaps derived from a sheet of rift-related volcanic rocks.

The massive green rock at the end of the outcrop is composed of a mass of hydrous secondary minerals including Mg-rich phases such as talc, tremolite, chlorite, serpentine, and phlogopite. While the vast majority of primary minerals are replaced, isolated core fragments of augite survive in addition to chromite. Consisting of ~40% SiO₂ and nearly 33% MgO, it also contains substantial amounts of Cr and Ni (Chiarenzelli et al., 2011). Its knobby texture likely represents the pseudomorphic replacement of large okiocrysts. Further upriver the ultramafic rock varies from peridotite to pyroxenite to layered ultramafic rocks (Figure 21) all highly altered and nearly completely pseudomorphically replaced (Figure 22). Nonetheless, original layering is frequently preserved and no indication of ductile deformation is found in stark contrast to the adjacent metasedimentary lithologies, which are isoclinally folded. Classification based on normative mineralogy determined by the CIPW method indicates that most ultramafic rocks are peridotites and a few pyroxenites, consistent with field observations (Figure 23).

The lower grade assemblage and undeformed nature of the ultramafic rocks appears to be at odds with the intensely folded garnet-sillimanite gneisses they are in contact with. This can be explained either juxtaposition of the rocks after peak metamorphic conditions or the competent and hydrous nature of the ultramafic rocks which contain as much as 10% H₂O.



Figure 20. Analysis of ~100 detrital zircon grains yielded an essentially unimodal population with a peak at 1288 Ma. Statistical analysis indicates the rock was deposited at some point after 1284±7 Ma. Note the small size, zoning in BSE, and homogeneity in the zircon population shown in the insert.



Figure 21. Contact between knobby weathering pyroxenite (below) and overlying layered ultramafic rock (above).



Figure 22. Photomicrograph showing pseudomorphic replacement of pyroxenite by a variety of hydrous secondary minerals including talc, chlorite, serpentine, and tremolite. The field of view is 4 mm and the photograph was taken with crossed polarizers.



Figure 23. CIPW normative mineralogy classification of Pyrites ultramafic rocks.

Several attempts were made to directly determine the age of the ultramafic rocks. A range of rock types were analyzed for both Rb-Sr and Sm-Nd isotopes but unfortunately both systems appear to have undergone strong disturbance and provide isochron ages with large errors. Small zircons (~50-200 microns) were observed within thin mm-scale, calcite-rich veins in samples of both periodite and pyroxenite (Figure 24). Attempts to recover them were successful and isotopic analysis by laser ablation – inductively coupled plasma mass spectrometry (LA-ICP-MS) and Sensitive High Resolution Ion Microprobe (SHRIMP) were conducted.

Zircons from the peridotite were dated by SHRIMP in Perth, Australia and yielded an age of 1140 ± 7 Ma with a few older grains yielding an age of 1202 ± 20 Ma (Figure 25). Zircon from the pyroxenite were dated by LA-ICP-MS at the Arizona Laserchron Center and yielded and age of 1197 ± 5 Ma (Figure 25). Given the unlikely occurrence of zircon as a magmatic product in silica-undersaturated rocks, these ages are thought to represent the timing of zircon growth during metamorphic events and thus provide only a minimum age for the ultramafic rocks. The ages correspond to the known effects of the Shawinigan Orogeny in the Lowlands from previous studies (Heumann et al., 2006).



Figure 24. Left-hand side. Scanning electron microscope photograph in the back-scattered electron mode showing 80 micron long zircon (zrn) within secondary minerals including serpentine (srp). Augite (cpx) occurs as remnant cores which have undergone partial replacement. Right-hand side scanning electron microscope photograph in the cathodoluminscence mode showing zoning in zircons separated from pyroxenite.



Figure 25. Left-hand side - Concordia diagram for zircons separated from peridotite and analyzed by SHRIMP at Curtin Technical University in Perth, Australia. Right-hand side - Concordia diagram from zircon separated from pyroxenite and analyzed by LA-MC-ICP-MS at the Arizona Laserchron Center.

Stop 5 Enel Hydropower Station on Grasse River at Pyrites Entrance to Hydrostation is sharp right turn on to a dirt road which follows the penstock when headed south towards Pyrites on Churchill Street; Latitude 44°31'18.5", Longitude 75°11'17.1"

Our final stop will be just a few hundred meters upriver from the last stop at the Pyrites Enel Hydropower Station. This area is privately owned and off-limits to the public. Special arrangements have been made to bring our group here and the owners require prior submission of a liability waiver. If you wish to visit this site in the future please respect private property laws and get permission beforehand.

Along the back wall of the parking lot of the Enel Hydrostation a layered sequence of ultramafic rocks occurs. Here the layers dip steeply to the right. Obvious and widespread alteration can be seen and the rocks are composed of a variety of Mg-rich secondary minerals and are discolored by hematitic veins. Secondary minerals included substantial amounts of serpentine and few, if any, primary phases survive (Figure 26).

A number of layer perpendicular fractures occurs here (Figure 27) and appear to define columnar jointing, a typical cooling-related phenomena in some volcanic sequences. Preservation of columnar jointing seems unlikely, but the general appearance and alteration of these rocks is distinctly different than the mostly massive periodite and pyroxenite downriver. Here layering on the decimeter to meter scale is well developed. It is conceivable that the rocks are metamorphosed lavas, but, if so, they are ultramafic in composition!

Proceed carefully down from the parking lot to river. Here near the discharge from the Hydrostation, you can again see the contact between the pyritic gneisses and ultramafic rocks exposed in the far wall of the river bank. However, of special interest is a meter-wide lamprophyre dike consisting of large, cm-scale, phlogopite phenocrysts with a black serpentine-rich groundmass cutting the other ultramafic rocks (Figure 28). Again small areas of augite are preserved but little else. Large, euhedral apatite crystals, several millimeters in size are also abundant and likely a primary phase.



Figure 26. Strongly altered ultramafic rock composed almost exclusively of secondary hydrous magnesium silicates.



Figure 27 Dipping ultramafic rocks in parking lot of Enel Hydropower Station in Pyrites, New York. Note meter to decimeter-scale layering and set of fractures perpendicular to the layers. Field book for scale.



Figure 28. Field photograph of the lamprophyre dike (foreground) cross-cutting ultramafic rocks (background) at Pyrites, New York. Insert shows cut and polished slab of lamprophyre showing its texture and coarse grainsize. Dashed line shows approximately contact of dike with altered peridotite.

The geochemistry of this rock indicates substantial enrichment in incompatible elements and suggests derivation from metasomatized mantle. Despite having just 33% SiO₂ a population of zircons was separated from this rock. The zircons, nearly all concordant, gave an age of 1183 ± 6 Ma with individual grains as old as 1213 ± 16 Ma (Figure 29), again indicative of growth during Shawinigan metamorphism or conversely, intrusion at that time. If the zircons do indeed mark the time of intrusion they are likely related to arc magmatism associated the Antwerp-Rossie suite (ca. 1200 Ma).

Further upriver these rocks are in structural contact with a sequence of gabbroic rocks cut by finer-grained dikes. The gabbros appear exceptionally coarse-grained, baseball-sized (Figure 30), however, this appears to be the consequence of anastomosing, closely-spaced shear zones and the widespread growth of coarse phlogopite rather than the original grain-size. Some low strain domains between the sheared areas show a typical gabbroic texture. Samples of gabbro and a fine-grained dike rock cutting the gabbro share similar geochemical and isotope trends with the ultramafic rocks and are likely part of the same sequence. Given the occurrence of ultramafic rocks, gabbros, amphibolites, and sulfide deposits Chiarenzelli et al. (2011b) interpreted the Pyrites Complex as a highly dismembered and intruded ophiolitic complex. If so, it must be in thrust contact with shallow water metasedimentary marbles of the Grenville Supergroup it is often enveloped by.



Figure 29. Left-hand side - Concordia diagram for zircon from the Pyrites lamprophyre dike showing spread of concordant data point. Right-hand side - Weighted mean age calculation for zircon separated from the pyrites lamprophyre. Note that concordant analyses yield a range of ages from ~1150-1210 Ma.



Figure 30. Gabbroic gneiss upriver of the Pyrites Enel Hydrostation. Note interesting fabric created by anastomosing shear zones of phlogopite.

ACKNOWLEDGMENTS

We would like to acknowledge the financial support of the James S. Street Fund at St. Lawrence University. Drs. Eric Thern (Curtin Technical University), Brian Cousins and Lyndsey Coffin (Carleton University), George Gehrels (Arizona Laserchron Center), and Sean Regan (UMass) are thanked for their help with geochronology and isotopic analysis. St. Lawrence students Peter Christoffersen, Ashley Durham, Hillary Hagen-Peter, and Thomas Lockwood participated in data collection. The authors have benefited from discussion with many of our colleagues including Larry Aspler, William deLorraine, J. Allan Donaldson, Yngvar Isachsen, James McLelland, William Peck, Bruce Selleck, Phil Whitney, and David Valentino. Chiarenzelli would like to thank his undergraduate mentors at St. Lawrence University, Drs. William Elberty, William Romey, and Char Mehrtens, for imparting a sense of wonder and insatiable curiosity for the study of the geology.

REFERENCES CITED

Barford, G. H., Krogstad, E. J., Frei, R., and Albarède, F., 2005, Lu-Hf and PbSL geochronology of apatites from Proterozoic terranes: A first look at Lu-Hf isotopic closure in metamorphic apatite: Geochimica et Cosmochimica Acta, v. 69, p. 1847-1859.

Buddington, A. F., 1934. Geology and mineral resources of the Hammond, Antwerp, and Lowville quadrangles. New York State Museum Bulletin No. 296, University of the State of New York, 251p.

Carl, J. D., 2000, A geochemical study of amphibolites layers and other mafic rocks in the NW Adirondack Lowlands, New York: Northeastern Geology and Environmental Sciences, v. 22, p. 142-166.

Chiarenzelli, J. and McLelland, J., 1993, Granulite facies metamorphism, paleoisotherms, and disturbance of the U-Pb systematics of zircon in anorogenic plutonic rocks from the Adirondack Highlands. Journal of Metamorphic Geology, v. 11, p. 59-70.

Chiarenzelli , J., Kratzman, D., Selleck B., and deLorraine, W., in review, Opening, spreading, and closing of a Mesoproterozoic back-arc basin: tectonic evolution tracked by detrital zircons in upper amphibolite facies rocks: Submitted to Geology, July 29th, 2014.

Chiarenzelli, J.R., Hudson, M.R., Dahl, P.S., and deLorraine, W.D., 2012, Constraints on deposition in the Trans-Adirondack Basin, northern New York; composition and origin of the Popple Hill Gneiss: Precambrian Research, v. 214-215, p. 154-171.

Chiarenzelli, J., Lupulescu, M., Thern, E., and Cousens, B., 2011a. Tectonic implications of the discovery of a Shawinigan ophiolite (Pyrites Complex) in the Adirondack Lowlands: Geosphere, v. 7, no. 2; 2, p. 333-356.

Chiarenzelli, J., Valentino, D., Lupulescu, M., Thern, E., and Johnston, S., 2011b, Differentiating Shawinigan and Ottawan Orogenesis in the Central Adirondacks: Geosphere, v. 7, p. 2-22.

Chiarenzelli, J., Regan, S., Peck, W.H., Selleck, B.W., Cousens, B., Baird, G.B., and Shrady, C.H., 2010a, Shawinigan arc magmatism in the Adirondack Lowlands as a consequence of closure of the Trans-Adirondack backarc basin: Geosphere, v. 6, no. 6; 6, p. 900-916.

Chiarenzelli, J., Lupulescu, M., Cousens, B., Thern, E., Coffin, L., and Regan, S., 2010b, Enriched Grenvillian lithospheric mantle as a consequence of long-lived subduction beneath Laurentia: Geology, v. 38, p. 151-154.

deLorraine, W.F., 2001, Metamorphism, polydeformation, and extensive remobilization of the Balmat zinc orebodies, northwest Adirondacks, New York: Guidebook Series [Society of Economic Geologists [U.S.], v. 35, p. 25-54.

de Lorraine, W. F. and Sangster, A. L., 1997, Geology of the Balmat Mine, New York: Field Trip A5, Geological Association of Canada/Mineralogical Association of Canada Joint Annual Meeting, Ottawa, 43p.

Dickin, A.P., and McNutt, R.H., 2007, The Central Metasedimentary Belt (Grenville Province) as a failed backarc rift zone; Nd isotope evidence: Earth and Planetary Science Letters, v. 259, no. 1-2; 1-2, p. 97-106.

Dickin, A. P. and Higgins, M. D., 1992. Sm/Nd evidence for a major 1.5 Ga crust-forming event in the central Grenville province: Geology, v. 20, p. 137-140.

Heumann, M.J., Bickford, M.E., Hill, B.M., McLelland, J.M., Selleck, B.W., and Jercinovic, M.J., 2006, Timing of anatexis in metapelites from the Adirondack lowlands and southern highlands; a manifestation of the Shawinigan Orogeny and subsequent anorthosite-mangerite-charnockite-granite magmatism: Geological Society of America Bulletin, v. 118, no. 11-12, p. 1283-1298.

Isachsen, Y.W., and Fisher, D.W., 1970, Geologic map of New York: Adirondack sheet: New York State Museum, Map and Chart Series 15, scale 1:250000.

Logan, W. E., 1863, Geology of Canada, Geol. Survey of Canada, Report of Progress from Commencement to 1863.

Lupulescu, M., Chiarenzelli, J., Pullen, A., and Price, J., 2011, Using pegmatite geochronology to constrain temporal events in the Adirondack Mountains: Geosphere, v.7, p. 23-39.

Peck, W., Selleck, B., Wong, M., Chiarenzelli, J., Harpp, K., Hollocher, K., Lackey, J., Catalano, J., Regan, S., and Stocker, A., 2013, Orogenic to postorogenic (1.20–1.15 Ga) magmatism in the Adirondack Lowlands and Frontenac terrane, southern Grenville Province, USA and Canada: Geosphere, v. 9, p. 1637-1663.

Peck, W.H., Valley, J.W., Corriveau, L., Davidson, A., McLelland, J., and Farber, D.A., 2004, Oxygen-isotope constraints on terrane boundaries and origin of 1.18–1.13 Ga granitoids in the southern Grenville Province: in: Tollo, RP, Corriveau, L, McLelland, J, and Bartholomew, MJ, (Eds.), Proterozoic tectonic evolution of the Grenville orogen in North America: Boulder, Colorado, Geological Society of America Memoir 197, p. 163-182.

Prucha, J., 1957. Pyrite deposits of St. Lawrence and Jefferson Counties, New York: New York State Museum Bulletin No. 357, The University of the State of New York, 87 p.

Revetta, F.A., and McDermott, A. M., 2003, The compilation and preparation of high resolution gravity data for petroleum exploration in New York State and adjoining regions: New York State Energy Research Development Authority (NYSERDA) PON #715-02

Rivers, T., 2008. Assembly and preservation of lower, mid, and upper orogenic crust in the Grenville Province – Implications for the evolution of large hot long-duration orogens: Precambrian Research, v. 167, p. 237-259.

Sager-Kinsman, A. E. and Parrish, R. R., 1993, Geochronology of detrital zircons from the Elzevir and Frontenac terranes, Central Metasedimentary Belt, Grenville Province, Ontario, Can. J. Earth Sci., v. 30, p. 465–473.

Tiedt, K. and Kelson, C., 2008, Geochemical and mineralogical characterization of ore from the Pyrites and Stella pyrite deposits, St. Lawrence County, NY.: Geol. Soc. Am., Abstr. Program v. 40, p. 6.

Wong, M.S., Peck, W.H., Selleck, B.W., Catalano, J.P., Hochman, S.D., and Maurer, J.T., 2011. The Black Lake Shear Zone: A boundary between terranes in the Adirondack Lowlands, Grenville Province: Precambrian Research, v. 188, p. 57-72.

Trip B-2 N	lileage and R	oad Log			
Distance	Cumulative		Latitude	Longitude	
0.0	0.0	Big M Parking lot Alexandria Bay, SH 12	N 44° 19' 38"	W 75° 55' 09"	
0.4	0.4	Turn right on to Church Street/SH 26	N 44 [°] 19' 55"	W 75° 54' 52"	0.41
3.7	4.1	Turn right at Browns Corners and stay on SH 26 pass	N 44° 17' 56"	W 75° 51' 23"	3.66
		through Plessis			5100
4.7	8.7	Right hand turn on to SH 37	N 44° 14' 47"	W 75° 48' 59"	4.66
1.7	10.4	Left hand turn on to CR 193/SH 26 at Coopers Corners	N 44° 13' 22"	W 75° 49' 18"	1.68
0.8	11.2	Turn left on to Main Street/SH26	N 44° 13' 01"	W 75° 48' 28"	0.78
0.6	11 7	Turn left on to Commerical Street/SH 26 downtown Theresa	N 44° 12' 55"	W 75° 47' 51"	0.55
0.5	12.2	Turn right on to Miller Street /SH 26	N 44° 12' 01"	W 75° 47' 18"	0.50
5.8	18.0	Turn left at traffic light in Philadelphia on to SH 11	N 44° 00' 32"	W 75° 47' 10	5.80
1.0	22.0	Park on right, outgrop on loft hand (north) side of SH 11	N 44 03 32	W 75 42 25	1.00
4.9	22.9	iust west of Antwern	N 44 11 42	VV 73 37 28	4.50
Stop 1: Ar	twerp Amph	ibolite (Please exercise extreme caution crossing SH 11)			
0.4	23.4	Continue on SH 11 then turn left on to CR 24	N 44° 12' 46"	W 75° 36' 54"	0.44
5.9	29.3	Turn left on to CR 25 pass through Oxbow	N 44° 17' 13"	W 75° 36' 43"	5.89
1.7	31.0	Bear right and continue on CR 10	N 44° 18' 01"	W 75° 37' 43"	1.72
3.2	34.2	Turn right on to Liscom/Hall/Yellow Lake Road	N 44° 20' 29"	W 75° 36' 07"	3.20
3.1	37.3	Turn right on to Campbell Road	N 44° 21' 37"	W 75° 33' 22"	3.10
1.9	39.2	Park, outcrop on left hand (south) side of Campbell Road	N 44° 20' 19"	W 75° 34' 46"	1.94
Stop 2: Ye	llow Lake Se	rpentinite (Private property, permission required)			
1.9	41.2	Reverse direction and return on Campbell Road,	N 44° 21' 37"	W 75° 33' 22"	1.94
		turn right on Yellow Lake Road			
1.0	42.2	Turn left on to SH 58, travel 1 mile north	N 44° 21' 41"	W 75° 32' 52"	1.00
0.9	43.1	Park, outcrop on right (east side) of road	N 44° 22' 20"	W 75° 33' 14"	0.88
Stop 3: Ye	llow Lake Ho	rnblendite (Please exercise extreme caution crossing SH 58)			
2.4	45.5	Carefully reverse direction onto SH 58 head south until	N 44°20'34"	W 75° 32'7.5"	2.44
		Gravel-Beaman-Seavey-Welsh Road turn left towards			
		Richville, pass dolomite quarry on right			
12.5	57.9	Continue on SH 58, through Dekalb Jct. and turn right on	N 44° 32' 16"	W 75° 13' 58"	12.45
		Eddy-Pyrites Road, cross Harrision Creek			
2.4	60.3	Turn left on to CR 21	N 44° 31' 20"	W 75° 11' 41"	2.40
0.2	60.5	Cross Bridge over Grass River, park on right and follow	N 44° 31' 25"	W 75° 11' 32"	0.17
		dirt path to outcrop along east bank of the river			
Stop 4: Py	rites Comple	x and overlying Metasedimentary Rocks			
0.2	60.7	Continue on CR 21 turn right on Churchill Street towards	N 44° 31' 33"	W 75° 11' 21"	0.19
		Pyrites Village			
0.4	61.0	Sharp right hand turn on to dirt road following pensotck	N 44° 31' 13"	W 75° 11' 12"	0.38
		(big green pipe) to Enel Hydropower Station			
Stop 5: Py	rites Comple	x and Lamprophyre Dike (Private property permission required)			
	1	· · · · · · · · · · · · · · · · · · ·			
End of Tri	p (Return fro	m whence you came)			

Stop 1 Amphibolite and Pyritic Gneisses near Antwerp <1 km southwest of Antwerp, along Rt. 11; Latitude 44°11'41.7", Longitude 75°37'28.8"



Stop 2 Yellow Lake Serpentinite ~8.5 km west of Gouverneur, off of Campbell Rd between Yellow Lake and the Oswegatchie River; Latitude 44°20'14.3", Longitude 75°34'47.8



Stop 3 Hornblendite near Elmdale

~1 km north of Elmdale, along Rt. 58; Latitude 44°22'19.5", Longitude 75°33'14.02"



Stop 4 Contact between Pyritic gneiss and Ultramafic Rocks along the Grasse River

Dirt trail on right just after crossing the Grasse River on County Route 21 when headed east ; Latitude 44°31'24.7", Longitude 75°11'28.5"

Stop 5 Enel Hydropower Station on Grasse River at Pyrites

Entrance to Hydrostation is sharp right turn on to a dirt road which follows the penstock when headed south towards Pyrites on Churchill Street; Latitude 44°31'18.5", Longitude 75°11'17.1"

