## Trip B -1

## DETRITAL ZIRCON GEOCHRONOLOGY OF THE ADIRONDACK LOWLANDS

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### ABSTRACT

During this day-long trip we will visit and discuss several sites in the Adirondack Lowlands for which detrital zircon geochronology is available. Stops will include quartz-rich protoliths from throughout the upper Amphibolite facies stratigraphic succession including the turbiditic sequence at Pyrites, NY, sandy and tourmaline-rich intervals in the Lower marble, sandy, calc-silicate interlayers within the Popple Hill gneiss, and base, middle, and top of the Upper Marble. The data collected to date has important implications for the age of metasedimentary rocks deposited before Grenville orogenesis, shifting provenance in response to tectonism, the events leading to the formation of the world-class Pb-Zn sedimentary exhalative deposits, the timing and intensity of metamorphism in the Lowlands, and potential basement rocks. Much of this information is summarized from Chiarenzelli et al. (2015a; 2017); some is a summary of on-going work.

# **GEOLOGICAL SETTING**

The contiguous Grenville Province forms an extensive part of the Canadian Shield added to the southern and eastern margin of Laurentia (present coordinates; Figure 1) during a sequence of orogenic events occurring during the Mesoproterozoic (ca. 1600-1000 Ma). McLelland et al., (1996) summarize the orogenic event effecting the Adirondack Region. As one of the last major continent building events during the Precambrian, associated tectonism reworked, and incorporates, rocks of significantly older parts of the Canadian Shield including the Archean Superior Province and Paleoproterozoic terranes (Dickin et al., 2016; Figure 1). In a global context, the end of the Mesoproterozoic was a time of world-wide orogenesis resulting in the formation of the supercontinent Rodinia; hence orogenic rocks of this age occur globally.

2022



**Figure 1.** Regional map of the southwest Grenville Province (from Dickin et al. 2016). Abbreviations are as follows. ABT – Allochthon Boundary Thrust; AH – Adirondack Highlands; AL – Adirondack Lowlands; CMBBZ – Central Metasedimentary Belt boundary zone; CLF – Clarendon–Linden fault; FT – Frontenac Terrane; G – Grimsthorpe domain.

The Adirondack Region is physically connected to the remainder of the Grenville Province via the Frontenac Axis or Arch (for summary of the geology see Chiarenzelli and Selleck, 2016). Several fundamental lithostructural and tectonic terranes occur in the Adirondacks including, from northwest to south: the Frontenac Terrane, the Adirondack Lowlands, the Adirondack Highlands, and the Southern Adirondack Terrane (Figure 2; Valentino et al., 2019). The metasedimentary sequence in the Adirondack Lowlands is dominated by calcitic and dolomitic marbles and calc-silicate gneisses, and includes meta-evaporitic units and metamorphosed clastic rocks consisting of quartzites, pelitic gneisses, meta-arkoses, meta-greywackes and meta-siltstones. As part of orogenic activity between 1250-1150 Ma (Elzevirian and Shawinigan orogenies) in the southern Grenville Province, these metasedimentary rocks are deformed and metamorphosed to mid-upper Amphibolite facies. They are part of a larger region of the southern Grenville Province, characterized by a thick, marble-rich supracrustal succession, named the Central Metasedimentary Belt (Wynne-Edwards, 1972). Similar metasedimentary rocks can be found in the Adirondack and New York-New Jersey Highlands (e.g. Peck et al., 2009) and adjacent areas. However, in contrast to most other areas in the Adirondacks and

elsewhere in the Grenville Province, the Lowlands stratigraphic succession, while deformed and intruded, is relatively intact and well described due to the world-class zinc deposits it hosts (Figure 3). The stratigraphy of the Upper Marble, in particular, is well documented from thousands of diamond drill cores obtained from the Sylvia Lake syncline and other nearby zinc deposits hosted in the Upper Marble (deLorraine, 2001; deLorraine and Sangster, 1997).



**Figure 2.** Simplified geological map of the Adirondack Region after Chiarenzelli and Selleck (2006). Abbreviations of lithologic units: AR/HG/HSG – Antwerp Rossie, Hermon Granite, Hyde School Gneiss; GSG – Grenville Supergroup; HWK – Hawkeye Suite; LMG – Lyon Mountain Granite; MCG – Mangerite, Charnockite, Granite Suite; PLG – Pisceo Lake Granite; SAT – Southern Adirondack Tonalites; mug – supracrustal rocks extensively intruded, migmatized, and disrupted. Abbreviations of Terranes and Terrane Boundaries: AH – Adirondack Highlands; AL – Adirondack Lowlands; BLSZ – Black Lake Shear Zone; CCsz – Carthage-Colton Shear Zone ; FT – Frontenac Terrane; PLSZ – Piseco Lake Shear Zone; SA – Southern Adirondacks.

With one likely caveat, to be discussed later, the oldest, known rocks in the Lowlands are metasedimentary rocks of what was known regionally as the Grenville Supergroup. In the Lowlands they are intruded by several metaigneous suites ranging in age from 1200-1150 Ma and thus must have been deposited before 1200 Ma (Peck et al; 2012); the time associated with the beginning of the Shawinigan Orogen (Corrigan, 1995; ca. 1200-1140 Ma). It is also possible that metasedimentary rocks in the Adirondack Lowlands where deformed during the Elzevirian Orogeny (ca. 1245-1220 Ma), as field relations in the Lowlands indicate

isoclinal folding occurred before intrusion of the oldest Shawinigan intrusive suite – the ca. 1200 Ma Antwerp-Rossie granitoids (Chiarenzelli et al., 2010b). If so, this would indicate the deformational effects and metamorphism associated with the Elzevirian Orogeny, defined in the Central Metasedimentary Belt of Ontario, may extend farther to the south than previously confirmed.



Figure 3. General geologic map of the Adirondack Lowlands, St. Lawrence County, New York.

### STRATIGRAPHY OF THE ADIRONDACK LOWLANDS

Several previous versions of stratigraphy of the Adirondack Lowlands and, in some cases, Highlands, have been proposed in the literature and summarized in Wiener et al. (1984). Most are based on regional and local field studies completed before the widespread availability of geochronological data and constraints derived therefrom, modern structural interpretations, and information gleaned from recent zinc exploration. While many follow the general sequence noted below, some, such as that proposed by Wiener et al. (1984) have significant departures.

Modern analysis suggests that the Lowlands stratigraphic package is allochthonous as basement rocks are currently unknown or unrecognized. From bottom to top, the package includes the Lower Marble, Popple Hill Gneiss, and Upper Marble, which has a preserved thickness on the order of 2-3 kilometers (Figure 4). The Upper Marble, host to the Pb-Zn sedimentary exhalative deposits, has been subdivided into 16 units, largely from insight from the thousands of diamond drill cores penetrating the Sylvia Lake Synform near Balmat, New York in search of ore (deLorraine, 2001; deLorraine and Sangster, 1997).

The Upper Marble is the most spatially restricted of the three major stratigraphic units in the Lowlands, occurring in a discontinuous belt of rock extending from Balmat to Seven Springs, northeast of Colton. It also has the best preserved stratigraphic relations with earlier workers recognizing natural gas and evaporitic units similar to those found in much younger petroleum settings (Brown, 1932). Zinc mining in the Lowlands has occurred only in this unit and along most of the belt from Balmat to Edwards to West Pierrepont. It should be noted that zinc has not been mined in the Lower Marble or in marble units the Adirondack Highlands. The rocks within the Upper Marble consist primarily of dolomitic marble, siliceous marbles, and calc-silicate rocks with subordinate pelitic, evaporitic, and quartz-rich lithologies. Compilation of thousands of diamond drill cores in the Sylvia Lake synform, a ca. 10 km-scale over turned fold, has led to the recognition of 16 units and three evaporitic-ore cycles. Evaporites consist primarily of thick accumulations of anhydrite, presumably once gypsum, but halite is also found. A wide range of minerals with unique or different chemistry are found throughout the Balmat area making it a prime location for the identification of new or rare minerals, and mineral collection in general (Chamberlain et al., 2018).



**Figure 4.** Simplified diagram of the Lowlands stratigraphy after Chiarenzelli et al. (2017), deLorraine (2001), and deLorraine and Sangster (1997). Circles with red numbers/ letter correspond to field trip stops. Abbreviations: B – Bonus Stop (if time permits); BS – Balmat stromatolites; MG – Median gneiss; OB – O'Brien Road Popple Hill gneiss; PQ – Pyrites quartzite; RQ- Richville quartzite; UM – Upper Marble. Leucogranite of the Canton Body (STOP 6) shown schematically intruding Lower The Popple Hill Gneiss is primarily composed of medium-grained biotite-plagioclase-quartz gneisses (Chiarenzelli et al., 2012) occasionally containing garnet and/or sillimanite, particularly where highly strained. While various interpretations have been made regarding its ultimate protolith including volcanic rocks (e.g. Carl et al., 1988), the most likely scenario appears to be sandstones, siltstones, and mudstones deposited in a deep water basin. The base of the unit is often marked by regionally extensive pyritic gneisses once mined for sulfur. The bottom third or so of the unit is extensively intruded by amphibolite, gabbro, and mafic-ultramafic sills, while the upper portion generally lacks them. Towards the top of the unit, mm-cm-scale quartzite and dcm thick marble interlayers occur as the Upper Marble is approached. In contrast to the Lower Marble, intruded largely by the Antwerp-Rossie suite, the Upper Marble is extensive intruded by the coarse-grained Hermon Granite gneiss and has undergone extensive migmatization during the Shawinigan event (Heumann et al., 2006). It is uncertain if the Popple Hill gneiss is in sedimentary and/or structural contact with the Lower Marble but could have been, at least in part, synchronously deposited in a deeper parts of the same basin.

The Lower Marble consists of calcitic and dolomitic marbles, calc-silicate rocks dominated by tremolite or diopside, schists and gneisses (including talc-tremolite, tourmaline, and graphitic and schists and pyrite+/- graphite-rich pelitic gneisses), and minor quartzite and meta-arkosic interlayers. Zinc mineralization and evaporitic lithologies are generally absent, although minerals such as scapolite and tourmaline, likely associated with evaporitic conditions, are frequently found in specific stratigraphic intervals. Wiener et al (1984) suggested that a single marble unit (Gouverneur Marble) was present in the Lowlands and subdivided it into five units (A through E), but variable lithologies, regional variation, extensive ductile deformation and structural cutouts, disruption by later plutonic suites, and less detailed exploration / investigation has thus far limited stratigraphic resolution.

The contact between metasedimentary rocks of the Adirondack Lowlands and ultramafic rocks of the Pyrites Complex (Figure 5) are exposed along the Grasse River at Pyrites, New York (Chiarenzelli et al., 2010a; 2011). Here regionally extensive pyrite and graphite-rich gneisses overlie ultramafic rocks consisting of hydrothermally altered periodite, pyroxenite, and rare lamprophyre dikes. Lying immediately above the peridotite and below the pyrite and graphite-rich gneisses are inclined layers of metamorphosed turbiditic rocks with cm-scale sand-silt-mud packages, now quartzite to garnet-biotite-sillimanite gneiss folded about isoclinal hinges. The nature of their contact with the ultramafic rocks is ambiguous the supracrustal rocks becoming more mafic over several meters as the peridotite is approached, perhaps suggesting a structurally modified, depositional contact. The ultramafic rocks from Pyrites lie on a Sm-Nd isochron of 1442±120 Ma (Chiarenzelli et al., 2010a), indicating they are older than all other rocks thus far identified in the Lowlands.

Although small in aerial extent (1-2 km<sup>2</sup>), a gravity survey indicates significant subsurface extension of the Pyrites Complex to the southwest (Revetta and McDermott, 2003). The exposure of the ultramafic rocks occurs within the core of a folded layer of amphibolite aligned parallel with the regional northeastern lithological and structural trend. This is one of many elongate linear, discontinuous amphibolite-dominated lithologic bands associated with pyritic gneisses throughout the Lowlands (Prucha, 1957), extending more than 50 km within close proximity, and parallel to the Carthage-Colton shear zone. The association of metamorphosed mafic, hydrothermally altered ultramafic, and chemogenic metasedimentary rocks with shallow water metasedimentary rocks of the Lowlands sequence, including vast volumes of marble, suggests tectonic interleaving of a suprasubduction or back-arc ophiolite complex during obduction associated with the Shawinigan Orogeny (Chiarenzelli et al., 2010a; 2011).



**Figure 5.** Left. Peridotite (above) in contact with knobby weathering pyroxenite, exposed along the Grasse River at Pyrites. Hammer spans the contact. Right. Tectonic blocks of dark green ultramafic blocks within mustard yellow pyrite-rich gneisses along the Grasse River in Pyrites, New York. Two poorly balanced geologists for scale.

### DETRITAL ZIRCON GEOCHRONOLOGY

Our study of detrital zircons targeted quartz-rich units in each of the major metasedimentary units in the Lowlands. Previous work by Heumann et al. (2006) revealed that migmatitic rocks of the Popple Hill gneiss contain a bimodal population of zircons, with one population, derived primarily from leucosomal portions of the rock, yielding ages of ca. 1160-1180 Ma. This age overlaps with numerous metaigneous rock suites in the Lowlands and Highlands and falls within the recognized time frame of the peak metamorphic conditions associated with the Shawinigan Orogeny. Thus, these zircons were interpreted as anatectic in origin, in contrast to those yielding older ages, ca. 1300-1400 Ma, interpreted as detrital in origin. A similar distribution of zircon ages was found by Bickford et al. (2008) in the eastern Adirondack, but there, 1050 Ma anatectic zircons dominate the histogram (Figure 6).

In our samples, many detrital zircons showed thin rims (ca. 10-20 microns) or outer areas of recrystallization. Most of these were of limited width and volume precluding direct analysis; however, they may have likely played a role in some of the "hybrid" ages found, adding some uncertainty to the results and conclusions reached. However, in comparison to zircons from quartzites subjected to granulite facies in the southern Adirondacks (Peck et al., 2010), recrystallization appears to be relatively minimal (Figure 7).



*Figure 6.* Relative probability histogram utilizing the data of Heumann et al. (2006) and Bickford et al. (2008) for the Popple Hill Gneiss and inferred Highlands equivalents (from Chiarenzelli et al., 2012).



**Figure 7.** Scanning electron microscope images of zircons from Adirondacks quartzites. Top row: Granulite facies zircons imaged by CL from the southern Adirondack Irving Pond quartzites (from Peck et al., 2010). Bottom row: Upper Amphibolite facies zircons images by BSE from Lowlands quartzites (from Chiarenzelli et al., 2017). Note the difference in outer rim development, presumed to be related to recrystallization during metamorphism. Thickest rims highlighted in white rectangular outlines.



Figure 8 summarizes the results of the detrital zircon study. Our findings suggest:

- 1) The metasedimentary rocks in the Adirondack Lowlands were deposited in a relatively short interval of time between about 1260-1280 Ma.
- 2) The age of metamorphic overgrowths indicate both Elzeviran (ca. 1225-1235 Ma) and Shawinigan effects (ca. 1170-1185 Ma), with little to no secondary growth / recrystallization of zircon in the most quartz-rich units. Later Grenville events appear to have little to any impact on zircons in the Lowlands.
- 3) Several drastic changes in provenance occur throughout the sequence, with samples from the Lower and Upper marble containing detrital zircons of a wide age range and as old as ca. 3300 Ma; while those of the Popple Hill gneiss were derived predominantly from a terrane composed of rocks whose age is between ca. 1300-1400 Ma.
- 4) Detrital zircons from turbiditic metasedimentary rocks overlying the Pyrites Ultramafic Complex are largely restricted to a unimodal source ranging in age from ca. 1280-1300 Ma, likely derived from rift volcanism during birth of the Trans-Adirondack Back-arc Basin (Chiarenzelli et al., 2013).

# IMPLICATIONS FOR THE TRANS-ADIRONDACK BACK-ARC BASIN

From their study of Nd T<sub>DM</sub> model ages in the Central Metasedimentary Belt of Ontario and Quebec, Dickin and McNutt (2007) proposed a back-arc failed rift environment for supracrustal rocks of the Central Metasedimentary Belt (labeled Elzevirian rift zone in Figure 1). In concert with their work, Chiarenzelli et al. (2010b) used the term Trans-Adirondack Basin (TAB) to describe the depositional setting of metasedimentary rocks of the Adirondack Region and suggested that a series of back-arc basins developed along the southeastern margin of Laurentia prior to the Elzevirian Orogeny (ca. 1220-1245 Ma). Ultramafic rocks, occur in both the Central Metasedimentary Belt and Adirondack Region, indicating sufficient spreading occurred to generate oceanic crust (Chiarenzelli et al., 2010; Smith and Harris, 1996). The presence of both shallow and deeper water sedimentary protoliths in the Lowlands represent deposition in various depositional environments and during various stages of basin evolution (Figure 8).

The documentation of shifting provenance from detrital zircon study of rocks of the Lowlands metasedimentary sequence is thought to reflect drastic changes in the sediment supply in response to tectonic events (Figure 8). Initially, a deep basin formed in which turbiditic rocks, rich in organic material (graphite) and chemogenic components (pyrite) was derived from a restricted source yielding ages between ca. 1280-1300 Ma, likely a thin veneer of rift related volcanic rocks. Quartz-rich units in the carbonate-dominated Lower Marble, in this case, a biotite and tourmaline-bearing quartzite in the Lower Marble sequence, yielded a much wider range of ages compatible with derivation from a vast area within the interior of Laurentian, including zircons as old as 3300 Ma.

Rapid deepening of the Trans-Adirondack Basin, perhaps related the initial impingement of the Southern Adirondack Terrane during the Elzevirian Orogeny, resulted in a shift of provenance as the basin received detritus from the south, largely restricted in age to ca. 1300-1400 Ma. A foredeep, similar to the one developed during the Taconic Orogeny in eastern New York, is envisioned. Filling of the basin after deposition of the Popple Hill Gneiss led to shallow water deposition of the Upper Marble. Cessation or relaxation of tectonic forces and erosion led to rearrangement of drainages and shifting provenance. A broader, shallower basin, perhaps yoked to the Central Metasedimentary Belt. incorporated a source region once again incorporating eastern and central Laurentia. Figure 8 provides a schematic of the proposed sequence of events.

#### IMPLICATIONS FOR ZN-PB ORES

The metasedimentary sequence in the Adirondack Lowlands has long been of interest for numerous reasons, especially the occurrence of Zn-Pb ore within the stratigraphic sequence of Upper Marble. Dominated by sphalerite (Figure 9), these ores have been interpreted as sedimentary exhalative deposits related to the venting of basinal brines similar to younger unmetamorphosed and undeformed examples (deLorraine, 2001; deLorraine and Sangster, 1997). A key observation, made by former principal mine geologist William deLorraine, is that the ore horizons are restricted to three distinct stratigraphic intervals and each is underlain by evaporitic intervals, largely composed of anhydrite (deLorraine, 2001). Subsequent metamorphism and ductile deformation has resulted in the remobilization of the ore along fault planes cutting across the stratigraphy of the Sylvia Lake synform (Matt et al., 2019; 2020) thus explaining the occurrence of ore throughout much of the sequence and its occurrence within later cross-cutting faults.

The association of Zn-Pb sedex deposits with underlying evaporitic horizons is intriguing. Chiarenzelli et al. (2015) suggested that the stratigraphic positioning of the ores may be related compression from the approach of Southern Adirondack Terrane resulting in the beginning phases of closure of the Trans-Adirondack Back-Arc Basin. In such a scenario, communication with the open ocean may have been temporarily shut off due to compression allowing evaporative processes to dominate in a hot, dry climatic setting. Renewed subsidence upon relaxation of episodic compression allowed carbonate sedimentation to resume, punctuated by the ejection of basinal fluids along faults driven by far-field compression to the southeast. The uppermost unit of the entire sequence, the Median gneiss (Unit 16), is a fine-grained feldspathic unit, clastic in origin, with a multi-aged provenance, indicative of the Laurentian interior. It documents renewed clastic sedimentation, likely as the fringe of molassoid rocks encroaching on, cannibalizing, and covering the earlier carbonate-evaporite sequence.



*Figure 9.* Coarsely crystalline sphalerite ore displaying interlocking twinned crystals, pyrite, and barite. Note the lack of brecciation and marble clasts typically found in ore associated with cross-cutting fault zones.

## **BASEMENT ROCKS?**

The Adirondack Lowlands has the hallmarks of a thin-skinned fold and thrust belt and also lacks recognizable basement involvement. Nonetheless, significant horizontal translation is implied due to the juxtaposing of shallow and deep water metasedimentary units and the incorporation of oceanic crust and upper mantle rocks. Evidence from Nd T<sub>DM</sub> studies of various Shawinigan plutonic suites (Chiarenzelli et al., 2010b), oxygen isotopes in zircon (Peck et al., 2004; Figure 10), geographic changes in the nature of metasedimentary rocks, and structural studies, suggests the Black Lake shear zone (Wong et al., 2011), the boundary between the Frontenac and Lowlands terranes, represents a significant tectonic boundary, perhaps the reactivated northwest rifted margin of the TABB. Thus it is reasonable to expect that the basement to the Lowlands stratigraphic sequence is related to basement rocks of the Frontenac Terrane, itself rifted southwestward (present coordinates) during formation of the Central Metasedimentary Basin back arc-failed rift (Dickin and McNutt, 2007; Moretton and Dickin, 2013). On the northwest margin of the CMB boundary zone ca. 1300-1350 Ma arc plutonic rocks of the Dysart-Mt. Holly suite occur (Agustsson et al., 2013), while the Frontenanc Terrane consists of a variety of plutonic gneisses with Nd T<sub>DM</sub> ages ranging from 1350-1640 Ma (Dickin and Strong, 2021) indicative of a segment of older crust reworked along the margin of Laurentia.

To better understand the possible basement rocks to the Lowlands stratigraphic sequence two samples of the Hyde School gneiss were sampled and analyzed to examine zircon xenocrysts. Dominated by xenocrystic zircon, the Hyde School gneiss, originally thought to be the basal stratigraphic unit in the Lowlands, was selected due to its ferroan leucogranitic composition compatible (Peck et al., 2013) with the preservation of considerable quantities of inherited zircon. Its age was reported as 1172 Ma (Wasteneys et al. 1999). Previously unreported, a sample of the Canton Body yielded xenocrysts of a single age (1322.5 ±2.1 Ma) and a sample from the Gouverneur Body yielded a range of xenocrysts and zircon cores from (1227-1363 Ma). Finally, xenocrystic cores from a diopside-kspar pegmatite cross-cutting breccia in the Raquette River associated with the Carthage-Colton shear zone in Colton gave an age of 1328.5 ±8.3 Ma (Chiarenzelli et al., 2019). Thus it appears likely that the basement rocks upon which the Lowlands metasedimentary sequence were deposited on are similar to those found in Dysart-Mt. Holly Suite, including those exposed in the Southern Adirondack Terrane, Green Mountains of Vermont, and the NY-NJ Highlands (Agustsson et al., 2013; McLelland and Chiarenzelli, 1990; McLelland et al., 2010).



**Figure 10.** Left. Oxygen isotope in zircon cross-section from the Frontenac Terrane (NW) extending across the Adirondack Highlands (SE). Note the jump in values at the Black Lake Fault (BLF). Right. Neodymium time of depleted mantle ages ( $T_{DM}$ ) in the Adirondack Lowlands. Note the difference between felsic (pink) and mafic (green) igneous precursors and the older ages obtained from felsic plutons as the Black Lake Shear Zone (BLSZ) and Frontenac Terrane are approached.



*Figure 11.* Location of stops to be made during this field trip arranged in sequence. Note that the trip starts at the USPS in the village of Richville (Main Street, near Stop 1) and ends at STOP 6 west of the village of

Canton, New York on Highway 11. Stop 5 is at Brown Hall on the campus of St. Lawrence University in Canton, NY, where we will stop to see core from the Sylvia Lake Synform and the quartzite from the Popple Hill Gneiss/Upper Marble transition.

# FIELD GUIDE

Meeting Point: USPS parking lot, Main Street, Richville, New York

Meeting Point Coordinates: lat. N 44.417641° long. W -75. 391066°

Meeting Time: 9:00 AM, Sunday, September 25, 2022



Figure 12. Starting point of field trip, USPS, Main Street, Richville, NY.

**STOP #1** – Lower Marble, Richville, Tourmaline-bearing gneisses (Figure 13)

The Lower Marble includes a number of detrital metasedimentary rocks in addition to the marble and subordinate calc-silicate gneiss (Wiener et al., 1984). Of particular interest is an extensive (50 km) belt of black to reddish-brown tourmaline-rich rocks that are interlayered with dolomitic marble near the top of the sequence (Brown and Ayuso, 1985; deLorraine and Carl, 1986). Along Rt. 11, just outside of Richville, a meter-thick layer of feldspathic quartzite (arkose) within biotite, tourmaline and pyrite-rich gneiss was sampled for U-Pb zircon geochronology.

A meter-wide, shallowly inclined quartz-rich layer, whitish in color, on the north side of Rt. 11 was sampled (Figure 14). A small population (n = 300-400) of zircon grains and a large number of pyrite and tourmaline grains were separated from approximately 1 kg of sample. The zircons ranged in size from 50 to 300  $\mu$ m and were predominantly rounded to oval in shape, although some are euhedral (Figure 15). Truncated oscillatory

zoning and a few, thin 1-5  $\mu$ m, partial, euhedral metamorphic overgrowths were observed. Uranium concentrations in zircon range from 12 to 742 ppm and average 163 ± 135 ppm. Ratios of uranium to thorium range from 0.4 to 12.4 and average 2.0 ± 1.9. The vast majority of analyses are concordant.



Figure 13. Sampling location of tourmaline-rich quartzose unit along Rt. 11, near Richville, New York.



**Figure 14.** Outcrop of the tourmaline-rich unit exposed near Richville, New York. The sample was collected just to the left of Ms. Roselyne Laboso, within the whitish layer of glassy quartzite, speckled with black tourmaline grains (outlined in purple). Note abundant pyrite staining.

One hundred and one grains are near concordant and show a wide range of ages from 1241.6 Ma to 3082.9 Ma. The youngest grain analyzed is 1241.6  $\pm$  41.9 Ma. A cohort of the 20 youngest grains, all within analytical error of one another, gave a weighted mean of 1263.9  $\pm$  4.3 Ma (MSWD = 1.4; PROB= 0.11), and are interpreted as the age of the youngest detrital population. Two large peaks, one at 1260.2  $\pm$  4.7 Ma and the other at 1841  $\pm$  2.1 Ma, are clearly defined on the probability density histogram (Figure 16) and represent the dominant ages found in this sample.



**Figure 15.** Left. View of RT-11 zircon mount in backscattered electron mode of the scanning electron microscope (BSE-SEM) Right. Detail of inset outlined in white on the left side. Note the various shapes and internal features of the zircons, including zoning, truncated zoning, inclusions, and thin, discontinuous, bright rims.



*Figure 16. Probability histogram of detrital zircon U-Pb ages from the Richville quartzite sample of the Lower Marble.* 



Stop #2 – Upper Marble, Unit 4, Balmat, Stromatolites (Figure 17)

*Figure 17.* Location of the Upper Marble Unit 4 (stromatolite-bearing) sampling site. The Empire State Mine is currently owned by the Titan Mining Corporation (formerly Zinc Corporation of America).

This classic outcrop contains putative stromatolites originally noted by Yngvar Isachsen (Isachsen and Landing, 1983). Located directly across from the Titan Corporation Mine, here the contact between Units 4 and 5 of the Upper Marble can be seen. Structurally we are located on the overturned limb of Sylvia Lake Synform, which is consistent with the downward concave shape of the stromatolites.

The outcrop directly across from the entrance to the former Zinc Corporation of America headquarters near Sylvia Lake was sampled for detrital zircon geochronology (Figure 18). The rock sampled is from Unit 4 and comprised mostly of dolomite and diopside. It exhibits silicified layering interpreted as remnant stromatolites (Isachsen and Landing, 1983). Here the matrix between the sparse, upside-down stromatolite domes (located on the overturned limb of the Sylvia Lake Synform) was sampled and consisted of quartz, dolomite, serpentine, titanite, and gray diopside (no stromatolites were harmed or disfigured during the procurement of this sample). A sparse yield of approximately 200 silt-sized (20-100 µm) zircons of rounded to angular shape was obtained (Figure 19).

The U-content of zircons ranges from 95 to 2331 ppm and averages 947  $\pm$  431 ppm, consid-erably higher than all other samples. Ratios of U /Th range from 1 to 113 and averages 12  $\pm$  18. Because of the small size of the zircon and high U-content, little in the way of internal features can be discerned as the BSE signal is very homogeneous (Figure 19). Every grain in the mount larger than the 30  $\mu$ m analytical spot size was analyzed, yielding 92 data points. Nearly all grains are within $\pm$  3% of Concordia.

The youngest zircon grain analyzed gave an age of 994.7  $\pm$  29.1 Ma, which falls within the time frame noted for the Rigolet pulse of the Grenvillian Orogeny. A cohort of 66 grains yielded an age of 1172.7  $\pm$  3.0 Ma (MSWD = 1.09; PROB = 0.30). Thirteen grains yield ages ranging from 1214.5 to 2607.5 Ma (Figure 20). Two

grains gave a weighted mean of  $1224 \pm 13$  Ma (MSWD = 0.34; PROB = 0.80), interpreted as the timing of Elzevirian metamorphism or analysis ablation pits that sample across age domain boundaries.



*Figure 18.* Field photograph of the Balmat stromatolites, Unit 4, opposite to the entrance to the zinc mine. *Lens cap for scale.* 



**Figure 19.** Left. Population of zircons from sample of Unit 4, stromatolitic-bearing Upper Marble. Right. Blow up of inset on left showing the relatively bright SEM-BSE response of zircon (z) compared to accessory minerals including titanite.



*Figure 20. Relative probability histogram for the Balmat stromatolite matrix sample. Note the vast majority of the analyses give ages of ca. 1175 Ma and are interpreted as metamorphic in origin.* 



STOP #3 – Upper Marble, Unit 16, Talcville, Median Gneiss (uppermost unit; Figure 21)

Figure 21. Location of Median Gneiss sample near Talcville, west of Edwards, New York.

The Median Gneiss (Unit 16 of the Upper Marble) is the youngest member of the stratigraphic succession of the Grenville Supergroup in the Lowlands. It is primarily a pink, strongly layered, quartzofeldspathic rock with a small percentage of other minerals such as diopside, micas, tourmaline, hornblende, and scapolite. Foliation-parallel layers of leucosome and feldspar porphyroclasts attest to the unit's metamorphic grade and deformation (Figure 22). The protolith of the Median Gneiss is not known, although its composition is granitic or arkosic. A 1 kg-sized sample was collected from a small outcrop exposed near Talcville, New York and it yielded thousands of zircon grains.

The zircon grains range in size from 30 to 100  $\mu$ m in diameter; most grains are about 50  $\mu$ m and rounded, but small populations of angular and elongate grains were also noted (Figure 23). The average U-content is 842 ± 548 ppm and ranges from 52 to 2892 ppm. Ratios of U /Th range from 0.63 to 27.78 and average 3.28 ± 3.23.



**Figure 22.** Photograph of the sawn surface of the Median Gneiss sample from Talcville. Note the compositional layering, deformed leucosomal layers, and pink, feldspar porphyroclasts. Black crystals are tourmaline.



*Figure 23.* Left. Zircon population recovered from the Median Gneiss, the uppermost unit of the Upper Marble. Right. Blow up of inset on left showing the SEM-BSE response of zircon (here bright) and tourmaline (dark).

Zircon U-Pb analyses yielded ages from 1185.4 to 3303.3 Ma. Over 300 grains were analyzed; however, those falling outside the range of 95-105% concordant were filtered out of the data set leaving 158 analyses to be plotted (Figure 24). Of these, the largest peak on the probability density histogram is 1524.8 Ma. Two grains yield an age of 1234  $\pm$  12 (MSWD = 0.29; PROB = 0.59), falling within the range of timing of Elzevirian orogenesis. The next five oldest grains form a coherent group with an age of 1253  $\pm$  17 (MSWD = 3.7; PROB = 0.005).



**Figure 24**. Relative probability histogram from U-Pb analyses of zircons from the Median gneiss. **STOP #4** –Pyrites Complex, Pyrites, Turbiditic Basal Unit, (Figure 25)



*Figure 25.* Location of the Pyrites turbidite sampling site. Note gossaneous weathering cap at sampling site along the Grasse River.

Along the Grasse River near the adits to the old pyrite mine at Pyrites, New York, small samples of quartz-rich (~ 85% SiO<sub>2</sub>), cm-scale interlayers within a gamet-sillimanite pelitic gneiss were removed utilizing a chisel and processed for zircon. The rock shows isoclinal folding of interbedded quartzite and metapelitic layers (Figure 26). Centimeter-scale layers are interpreted as the alternation of sand, silt, and mud formed within a turbidite sequence (Chiarenzelli et al., 2015). Three meters structurally below the sample site, a coarse-grained, green, hydrothermally altered peridotite is exposed. These rocks, along with more extensive gabbroic and amphibolitic units, have been named the Pyrites Complex and interpreted as a highly disrupted ophiolite suite (Chiarenzelli et al., 2011a). Continuous exposure, gradation in the composition of the metasedimentary rocks, and the occurrence of chromite (Tiedt and Kelson, 2008) in the pelitic gneiss near the contact suggests the metasedimentary sequence overlies the ultramafic in apparent depositional contact.



**Figure 26.** (A) Hinge area of isoclinal fold at Pyrites showing putative sand-silt-mud turbidites, now quartzite and pelitic gneiss. Note iron staining from abundant pyrite. Geological pick for scale. (B) Expanded view of same photograph showing extent of folding. Note the cross-cutting set of mineralized fractures, mostly quartz and pyrite, dipping shallowly upstream (to the right).

A small separate (n = several hundred grains) of zircon was obtained from a kilogram of sample quartzose, sand to silt-sized portions of the aforementioned outcrop. Zircons recovered are relatively small (<100  $\mu$ m), oscillatory zoned, and have shapes ranging from stubby dipyramids to grains with slightly rounded boundaries (Figure 27), thought modified by erosion. The zircons from this sample are noteworthy for their homogeneity. The U-content of the zircons analyzed in this sample averaged 243 ± 93 ppm and their U /Th ratio is 1.6 ± 0.4. Most grains are concordant with a range of 104.0-94.7%.

Ninety-seven near-concordant grains are plotted (Figure 28) and a group of 86 yielded a weighted average of 1289.7  $\pm$  1.1 Ma. One grain, of smaller size and lacking visible zoning, gave an age of 1176.2  $\pm$  24.1 Ma, in excellent agreement with the timing of Shawinigan orogenesis, and is considered to be metamorphic. Another grain yields an age of 1237.5  $\pm$  24.1 Ma, the timing of Elzevirian orogenesis in the Grenville Province and is also interpreted to be of metamorphic origin. A group of five analyses that are statistically indistinguishable, gave a weighted mean age of 1258.3  $\pm$  7.7 Ma (Mean Square Weighted Distribution (MSWD) = 1.4; Probability (PROB) = 0.22) and are interpreted to be the age of the youngest detrital population. Six other detrital grains range in age between 1372.9  $\pm$  21.2 Ma and 2294.9  $\pm$  21.7 Ma.



**Figure 27.** SEM – BSE image of zircon population from the Pyrite quartzite layers. Scale bar is 100 microns. Zircons from this sampling site were remarkably homogeneous in size, shape, and appearance and unimodal in their age, suggesting a restricted source.



*Figure 28. Relative probability histogram from U-Pb analyses of zircons from the Pyrites quartzite.* 

<u>Stop #5 – Contact of Upper Marble and Popple Hill Gneiss, Sylvia Lake Synform, Glassy quartzite intervals</u> (Figure 29)

Good time for a break. Core will be set out in the Department of Geology, 141-142 Brown Hall, St. Lawrence University



**Figure 29.** Location of Brown Hall on the St. Lawrence University campus. Here we will have a look at the glassy quartzite recovered from a drill hole penetrating the Popple Hill gneiss/Upper Marble contact within the Sylvia Lake synform. Park in the lot directly south of the red star and proceed to Rm. 141-142 Brown Hall.

A section of drill core from an overturned limb of the Sylvia Lake Syncline near Balmat, New York (Figure 30) penetrated the upper portion of the Popple Hill Gneiss and the lower portions of the Upper Marble (Chiarenzelli et al., 2012). The transition is considered to be conformable as the percentage of quartz in Popple Hill Gneiss gradually increases upward into ~ 30 m of glassy quartzite (Figure 31), then transitions into schist, before the first marble interval is penetrated. Portions of split drill core from several meters of section composed of the glassy quartzite were sampled, crushed, and zircon grains separated.

An excellent yield of several thousand grains was obtained from 1 kg of sample. Grains range from highly rounded to angular (Figure 32). Their average size is about 100  $\mu$ m, with large rounded grains up to 300  $\mu$ m. Smaller angular and euhedral grains are also present. Many zircon grains show truncation of oscillatory zoning, but distinct overgrowths are few, thin, and incomplete. The average uranium content of zircons from the sample was 106 ± 75 ppm and U /Th range from 0.4 to 13.6 and average 1.5 ± 1.5.



*Figure 30.* Sample location for the drill core sample (red star), just north of the square labeled Balmat, with the Sylvia Lake Synform.



*Figure 31. Glassy quartzite interval recovered from the contact between the Upper Marble just above the Popple Hill Gneiss.* 

One hundred and seven near-concordant grains were plotted and showed a wide range of ages from 1270.8 Ma to 3388.3 Ma. The youngest grain analyzed gave an age of 1270.8  $\pm$  113 Ma (note the large error). A cohort of 5 youngest grains, all within analytical error of one another, gave a weighted mean of 1277.9  $\pm$  13 Ma (MSWD = 0.09; PROB = 0.994) and are interpreted as the age of the youngest detrital population. Two large populations, one at 1446  $\pm$  7.8 Ma and 1650.3  $\pm$  6.2 Ma, occur on the probability density histogram (Figure 33).



*Figure 32. Zircons recovered from the glassy quartzite drill core interval, Sylvia Lake Synform. Note rounded shapes.* 



*Figure 33. Relative probability histogram from U-Pb analyses of zircon separated from the glassy quartzite core interval between the top of the Popple Hill Gneiss and base of the Upper Marble.* 



**Stop #7** – Canton Alaskite Body, Canton, Leucogranite and amphibolite (Figure 34)

*Figure 34.* Location of the sample collected from the Canton leucogranite body just southwest of the Canton railroad overpass of State Highway 11. The Grasse River is visible to the right.

About a dozen, kilometer-scale, domical leucogranite bodies, known as alaskites occur throughout the Adirondack Lowlands. Originally interpreted as volcanic rocks at the base of the stratigraphic sequence (Carl and van Diver, 1975; Carl et al., 1990; deLorraine and Carl, 1986), subsequent work (McLelland et al. 1992; Peck et al., 2013; Wasteneys et al., 1999) has reinterpreted the suite as of intrusive origin. Known as the Hyde School gneiss these bodies range in composition, contain supracrustal xenolithic screens, and are often intruded by dismembered mafic dikes/sills or layers (now amphibolite). A large portion of these bodies consist of medium-grained interlocking crystals of alkali feldspar, plagioclase, and quartz. Nearly all mafic minerals are magnetite. Foliation is often difficult to see, however, the rock is gneissic in nature particularly near the margins of the bodies. A kilogram sized sample was collected from the pink leucogranite layer above the mafic enclaves in Figure 35.

Zircons from the leucogranite bodies investigated thus far are dominated by large crystals yielding core ages of ca. 1325 Ma. Some show dissolution, presumably from interaction with magma, during the formation of their igneous precursors. Many zircons have thin, clear, rims which yields an U-Pb age of ca. 1170 Ma. A small population of euhedral, smaller crystals lacking cores, are often observed. Earlier attempts (1985) to date the zircons using multi-grain samples yielded hybrid ages (ca. 1230 Ma; McLelland et al., 1992). Subsequent attempts at dating using refined techniques (single grain analyses of coreless crystals) yielded an age of 1172 Ma (Wasteneys et al., 1999). This data indicates substantial inheritance from the source terrane(s).



**Figure 35.** Photograph of sampling site of the Canton leucogranite body west of Canton along Rt. 11. Three main lithologies occur, leucogranite, boudinaged amphibolite layers, and pegmatite. Here the leucogranite layer was sampled. Hammer for scale.



*Figure 36.* Back scattered electron SEM image of zircons separated from the Canton leucogranite body. Note the shapes, internal features, and core-rim relationships.



*Figure 37.* Left. Concordia diagram of cores analyzed from zircon separated from the Canton leucogranite body. Right. Relative probability frequency diagram from the Hyde School Gneiss, Gouverneur Body, showing a bimodal distribution of 1175 and 1315 Ma (Unpublished data from Erkan Toraman).



Bonus Stop – Popple Hill Gneiss, Pierrepont, Calc-silicate interlayer (Figure 38)

Figure 38. Location of the sampling site of a calc-silicate interlayer in the Popple Hill gneiss.

A stop on private property at O'Brien Rd. in Canton, New York will be made if time and interest permits.

A rusty, granular, calc-silicate gneiss was sampled from a 10 cm thick interval in garnet-bearing pelitic portion of the Popple Hill Gneiss near O'Brien Road, near West Pierrepont, New York (Figure 39). The gneiss is interlayered and cut by numerous concordant to discordant leucogranitic gneissic sheets. The Popple Hill Gneiss consists of a thick (several kilometers?) sequence of metamorphosed mud, silt, and sand, that is, at least in part, turbiditic (Chiarenzelli et al., 2012). Samples from partially melted pelitic to psammitic portions of similar gneisses have been investigated for U-Pb zircon geochronology by Heumann et al. (2006) and Bickford et al. (2008) in the Adirondack Lowlands and Highlands and have been shown to have zircons of both detrital and igneous-anatectic origin.

A small population (~500 grains) of zircons was separated from a kilogram-sized sample of rusty calc-silicate gneiss (Figure 40). Zircons range in size from 20 to 80  $\mu$ m and display a wide range of shapes from nearly rounded and oval to subhedral and faceted. A number of angular grains also occur.



**Figure 39.** Ten cm-thick interlayer of calc-silicate in the Popple Hill Gneiss, sampled for zircon U-Pb analysis. Wallet for scale. Dashed purple line shows contact between leucogranite and pelitic gneiss. Note calc-silicate unit pinches out towards the right side of the photograph and forms boudins up to a meter or more in width in other nearby localities.

Seventy-nine grains are near concordant and yielded a range of ages between 1127.0 Ma and 1667.4 Ma (Figure 41). A population of 61 grains yielded an age of 1170.6  $\pm$  4.0 Ma (MSWD = 1.5; PROB = 0.010), which falls in between the range of 1180-1160 Ma interpreted by Heumann et al. (2006) as the time of anataxis in nearby samples of this unit. Two grains, interpreted as the youngest detrital population, give an average age of 1260  $\pm$  23 Ma (MWSD = 0.024; PROB = 0.88). Four grains gave an age of 1223  $\pm$  8 Ma and are interpreted as metamorphic (Elzevirian) or hybrid in origin (MSWD = 0.57; PROB = 0.64).



**Figure 40.** View of the entire mount prepared for the O'Brien road calc-silicate sample, showing zircons recovered and mounted standards. Zircons from the sample are rounded and mid-grey in BSE, similar to the larger zircon standards surrounding the sample population. Darker and brighter grains are other accessory minerals.



*Figure 41.* Relative probability histogram from U-Pb analyses of zircon separated from calc-silicate layers in the Popple Hill Gneiss. Note the major peak occurs about 1170 Ma; peak timing of Shawinigan metamorphism in the Adirondack Lowlands.

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