

Trip A-2

EXPLORING THE ROOT ZONE OF AN ANCIENT FAULT-DRIVEN HYDROTHERMAL SYSTEM IN THE ADIRONDACK LOWLANDS, NEW YORK

BRUCE SELLECK

Department of Geology, Colgate University, Hamilton, NY 13346 bselleck@mail.colgate.edu

ABSTRACT

This trip examines exposures in the Adirondack Lowlands that contain Paleozoic hydrothermal and fault-related features hosted by Mesoproterozoic ‘Grenville’ marbles and Cambrian Potsdam Sandstone. These features have been the source of some debate historically and are now explicable as resulting from hydrothermal activity within an ancient wrench fault system. This system is similar to the deep structures that give rise to economically important gas and oil fields in the Appalachian Basin and elsewhere. The trip will include localities where the direct effects of coupled fault-related deformation and hydrothermal alteration can be seen, and the results of recent petrographic, stable isotope and fluid inclusion work will be used to better explain outcrop-scale features. The trip concludes with a stop in Ordovician Black River Group carbonates that demonstrates on a small scale the effects of hydrothermal dolomitization related to brittle deformation that may be linked to basement faulting. The regional extent, timing and tectonic significance of the fault systems will also be considered.

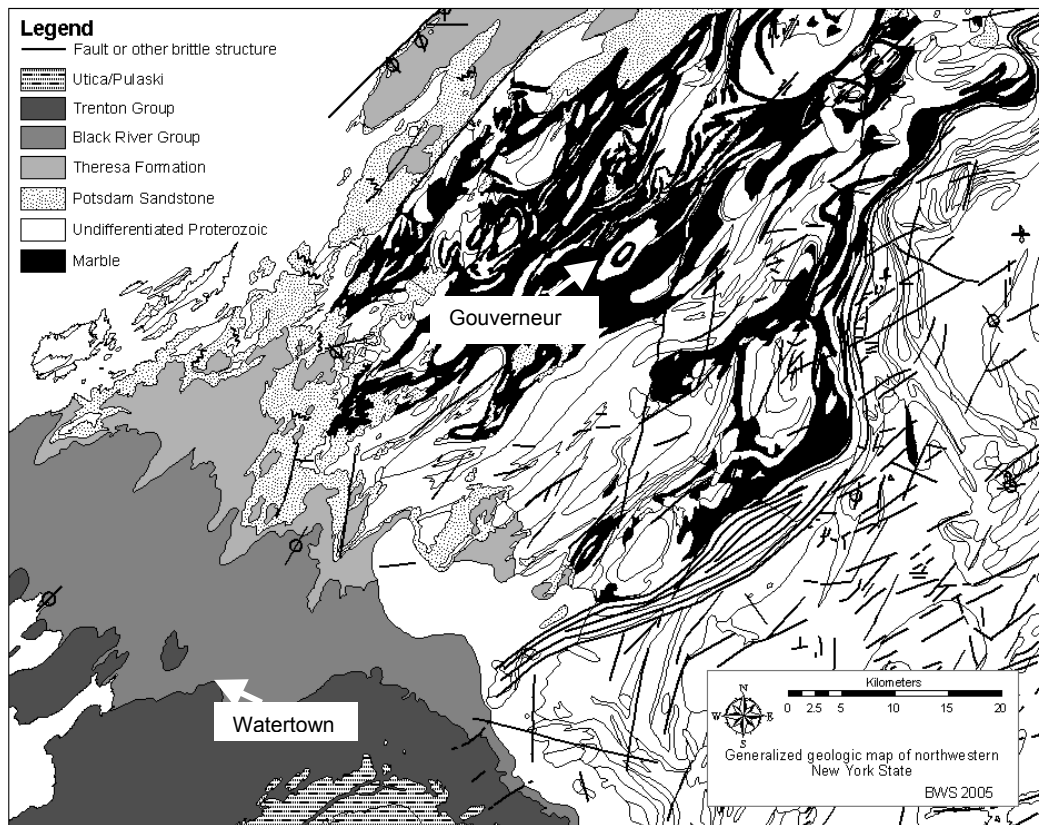


Figure 1 - Generalized geological map of northwestern New York.

INTRODUCTION

The southern Canadian Shield of Ontario and the Adirondack periphery in northern New York State offer numerous exposures of the contact between high-grade metamorphic Mesoproterozoic basement and Cambrian Potsdam Sandstone. In some outcrops in this region the pre-Potsdam erosional topographic surface of the 'Great Unconformity' is exposed at small scale (Tiller and Selleck 1992). Higher order topography, particularly in the Adirondack Lowlands and Frontenac axis region, locally reflects Pleistocene and Holocene erosional unroofing of basement that has been underneath Paleozoic cover for 500 million years. While this region has been in general tectonically inactive during that time interval, insofar as major deformation of the Paleozoic rocks is not regionally evident, it is not surprising given that long interval of time that minor structural deformation and hydrothermal alteration has occurred. Faulting and gentle folding involving the basement and Paleozoic cover have been recognized in the Adirondack Lowlands (Barber and Bursnell 1978) and modern earthquake activity is a reminder of the ongoing brittle deformation of the crust at depths of 10 to 18 km in the region (Daneshfar and Benn 2002; Mitronovas 1985).

Hydrothermal alteration caused by fluids derived from the Paleozoic sedimentary sequence interacting with basement rocks immediately underlying Paleozoic cover is well-documented in southern Ontario and northern New York (Ziegler and Longstaffe 2000). This alteration has a distinctive spatial distribution related to fluid flow from the basal sandstone aquifer and presence of reactive rocks in the underlying basement. The mineralogical signature of this hydrothermal interaction includes a range of low-temperature (<300°C) phases that occur as vein and vug fills in both the basement and cover rocks, as authigenic phases in the sedimentary cover, and as distributed retrograde alteration of basement rocks. Mineral systems associated with this alteration include carbonates (dolomite, calcite, siderite, ankerite), phosphates (apatite, monazite, xenotime), sulfides (pyrite, galena, sphalerite), oxides (magnetite, hematite, anatase), phyllosilicates (kaolinite, illite, chlorite), and framework silicates (quartz, K-feldspar). This field trip will focus on the hydrothermal mineralization and alteration found in the marble belt region of the Adirondack Lowlands province. In the exposures we visit on this trip widespread dolomitization associated with Potsdam Sandstone erosional outliers and fault structures is the dominant type of basement alteration. This zone is interpreted as the structural root of an ancient hydrothermal dolomite (HTD) reservoir system. The overlying Paleozoic strata which hosted the HTD reservoir have been eroded away, but the fault-related features and hydrothermal mineralization of basement rocks and basal Potsdam Sandstone provide a window into the processes which give rise to these economically important systems which are well-known in a number of hydrocarbon provinces (Berger and Davies 1999). The timing of the coupled fault-hydrothermal activity is not well-constrained, but available data suggest activity could have occurred in medial-late Ordovician time coeval with the Taconic Orogeny or later in late Devonian time during the Acadian Orogeny.

REGIONAL GEOLOGIC SETTING

Proterozoic Basement

The Adirondack Highlands Massif and adjacent Adirondack Lowlands are part of the Grenville Province, a Mesoproterozoic collisional tectonic belt extending from Labrador to Mexico that represents the addition of crustal material to the Laurentian craton during successive orogenic episodes, with intervening sediment deposition and anorogenic magmatic events. The oldest rocks of the Adirondack Highlands are a series of ca 1300 Ma arc-magmatic systems and intervening sedimentary basins. These rocks were metamorphosed during a collisional event ca. 1180-1170 Ma. A period of magmatism marked by intrusion of anorthosite, gabbro and coeval granitoid rocks at ca. 1160-1150 Ma emplaced large volumes of plutonic rock throughout the Adirondack Highlands and Lowlands. The Ottawan compressional orogenic episode marked the final assembly of the supercontinent of Rodinia at ca. 1070-1050 Ma (McLelland et al. 2001). This produced a Himalayan-scale mountain belt resulting in granulite facies metamorphism in the Adirondack Highlands. At that time the Adirondack Lowlands were likely at a higher crustal level, because peak metamorphic Ottawan ages are not for the most part recorded in the Lowlands, although certainly there was widespread deformation. The later phases of the Ottawan orogeny are marked by generation of

leucogranite melts that were often preferentially emplaced along zones of crustal extension. One of these zones, the Carthage-Colton Shear Zone, marks the boundary between the Highlands and Lowlands, and represents a northwest-dipping, top down to the northwest extensional structure within which ca. Ma 1045 leucogranite was emplaced synchronously with extension. The zone is marked by mylonite, ultramylonite and pseudotachylite.

The Adirondack Lowlands contain (by outcrop area) much more metasedimentary rock than the Highlands but belts of metaigneous granitoid gneiss and amphibolites are widespread. The Lowlands reached peak metamorphic conditions of the upper amphibolite facies (ca. 670°C, 6 kb) ca. 1170 Ma. The metamorphic expression of the ca. 1070-1050 Ma Ottawan orogeny is generally subdued in the Lowlands except in the vicinity of shear zones (Dahl et al. 2004). The Lowlands are characterized by a very strong northeast-southwest trending topographic grain that is related to the contrasts in erosional resistance of marbles, quartzites, metapelites, granitic gneisses, and amphibolites which form the majority of the rocks of the Lowlands. This erosional topography was present on the surface which was covered by the Cambrian Potsdam Sandstone and has been exhumed by Cenozoic stripping of Paleozoic cover rocks from the Mesoproterozoic basement of the Lowlands.

Paleozoic Sedimentary Strata

The Ottawan Orogeny ended in the Adirondack Highlands ca. 1040 Ma; extension and regional tilting brought the Adirondack Highlands and Lowlands into their current juxtaposition (Dahl et al. 2004). In late the Neoproterozoic (ca. 750 Ma) the breakup of Rhodinia gave rise to a rift-to-passive margin tectonic setting along the eastern margin of a new continent – Laurentia. The long period of post-Ottawan erosion removed ~ 20+ km of rock from the Highlands and by medial Cambrian time (ca. 520 Ma) northwestern New York was a low-lying coastal region with scattered aeolian dunes and braided streams which deposited quartz-rich sands of the basal Potsdam Sandstone. The region was flooded under shallow marine waters intermittently through the latest Cambrian and early Ordovician with carbonate-rich sandstones of the Theresa Formation and carbonates of the Ogdensburg Dolostone accumulating atop the Potsdam Sandstone. These younger units occasionally overlapped erosional monadnocks of Grenville basement such that no intervening Potsdam Sandstone was deposited. Early middle Ordovician Chazy Group limestones were deposited in the St. Lawrence Lowlands and Champlain Valley, and perhaps in northwestern New York State. Erosion of pre-middle Ordovician strata stripped these deposits from the western St. Lawrence Lowlands and interior of central and western New York (Robinson 1998). Widespread flooding of the continental interior in medial Ordovician time resulted in deposition of shallow marine and coastal lowland carbonate sediments of the Black River Group; these were succeeded by deeper subtidal and shelf carbonate facies of the Trenton Group. The development of the Taconic orogenic belt along the eastern margin of Laurentia in the medial Ordovician (ca. 440 Ma) produced a continental foreland basin that resulted in progressive flooding of the Trenton shelf and deposition of deeper water limestones and black organic-rich shales of the Utica and Canajoharie Formations. As the Taconic collisional event ended, late Ordovician and early Silurian deltaic and coastal plain facies infilled the relict foreland basin. These units are now found in the Tug Hill Plateau region and eastern St. Lawrence Lowlands. The Adirondack Lowlands region was likely covered by these and later Devonian, and perhaps Carboniferous, strata derived from erosion of the Acadian and Alleghanian orogens of the eastern margin of Laurentia as collision with magmatic arcs and assembly of the Pangean supercontinent closed the Paleozoic. The record of these events is based upon regional reconstructions and projections of stratal thickness patterns with little constraining data for area of this trip in northwestern New York. K-Ar and Ar-Ar dates on diagenetic illite in the Potsdam Sandstone in the Alexandria Bay area suggest elevated burial temperatures at ca. 350 Ma (Reynolds and Thomson 1993; Selleck 1995). Apatite fission track ages suggest regional unroofing was occurring in many areas of the Adirondack Highlands by ca. 120 Ma (Roden-Tice et al. 2000). All in all, as much as 4-5 km of Paleozoic strata may have covered the region by late Carboniferous time, but as little as 1-2 km is an equally likely total.

Mesozoic and Cenozoic Unroofing

Certainly dinosaurs once roamed the land which now makes up northwestern New York, but we have no record of their presence because no sedimentary deposits were laid down at the appropriate time. Based

upon regional patterns, the most likely scenario is that the region was subjected to minor uplift and extension related to late Triassic-Jurassic rifting of Pangea. Subsequent thermal relaxation of the continental margin coupled with regional erosion that began in earnest ca. 120 Ma lowered the region to a broad peneplain by Cretaceous time (ca. 90 Ma). In mid-Paleogene time (ca. 40 Ma) a regional uplift is suggested by changes in drainage patterns and warping of the Cretaceous peneplain. A regionally extensive dendritic drainage pattern that probably drained to the paleo-Mississippi River was in place over the region by ca. 15 Ma. The onset of Neogene glaciation ca. 1.2 Ma continued the erosional unroofing of the landscape and the modern erosional was exposed at the end of the last glacial advance retreat cycle which ended ca. 12,000 ya. The modern drainage was established by perhaps 7,000 ya, as isostatic rebound of the region allowed marine waters that had invaded the Ottawa-St. Lawrence Lowlands to recede. The modern topography expressed within the region is very much a relict of a long and complex history.

Modern Topography, Structural Control, Fault/Fracture Lineaments and DEM Imagery

The Adirondack Lowlands province is often set out as exemplar of structural/lithologic control on topography and drainage patterns. Indeed, any topographic, hydrographic, geologic, or even a road map of the region clearly displays the strong northeast to southwest ‘grain’ that is largely controlled by the

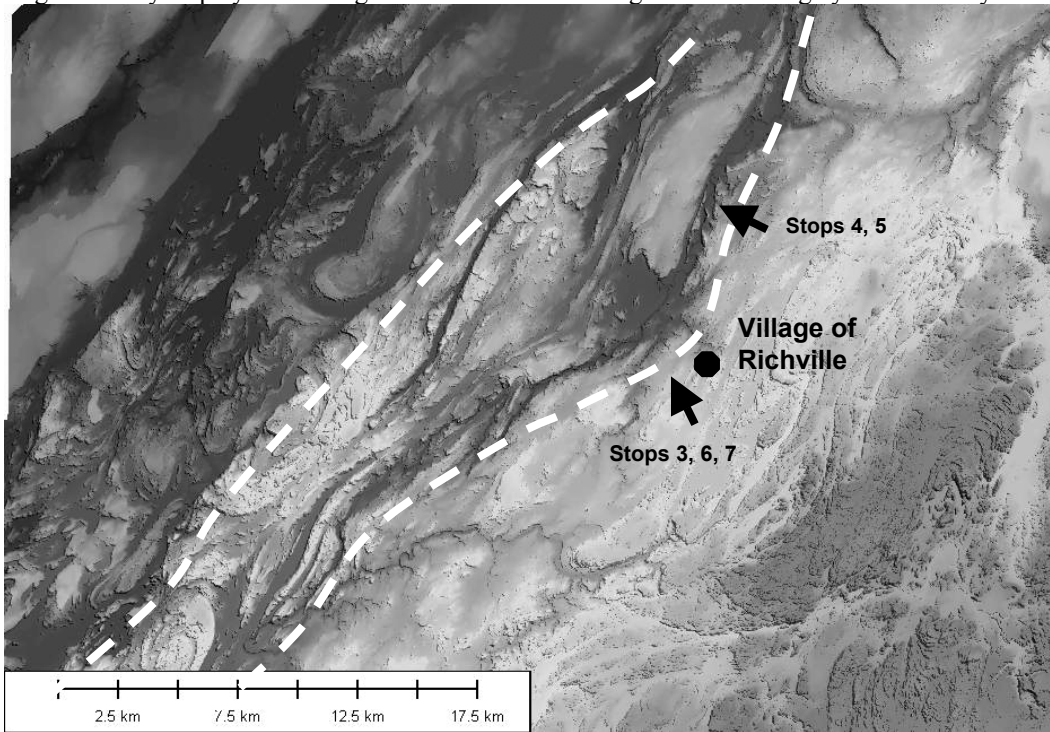


Figure 2 – Digital elevation model image of a portion of the Richville Shear Zone. White dashed lines indicate approximate boundary of zone with coupled fault/hydrothermal features.

differential erosional resistance of ductilely deformed basement rocks. In particular, the so-called marble belts often define (or at least have been mapped as such) linear valleys with intervening ridges of resistant metaigneous and metasedimentary gneiss. The well-defined linear outcrop patterns also define second-order fold structures, particularly in the vicinity of deformed plutons of ca. 1200 Ma alaskites which intrude older metasedimentary and metaigneous rocks. This topographic arrangement is a central feature of the lowlands terrain, and where the structures are masked by Paleozoic or Quaternary cover, the contrast is striking. Post-folding fault structures are evident as offsets of the linear topography or as truncations of arcuate fold ridges. Figure 2 illustrates digital elevation model (DEM) data for the region of this field trip. This imaging method has clear advantages over traditional contour maps, satellite or aerial photographs at

this scale in that the image generated is based upon pure topography without the distraction of vegetation cover, roads or other anthropogenic features. The relationship between brittle structures, linear valleys and offsets in the Proterozoic structural topography are obvious and indeed a number of the mapped brittle structures are based on the existence of the lineaments without, in some cases, known geologic offset. Where these structures encounter Paleozoic or younger cover, the pattern of faulting is less clear, although fold and fault structures mapped in the Theresa, NY area by (Barber and Bursnall 1978) may be directly related to the basement features described here. One striking aspect of the terrain depicted in figure 2 is the set of lozenge-shaped structural domains outlined by shear zones, faults and lineaments. These domains are the manifestation of a 10-km broad sinistral strike-slip wrench fault system, with later minor dextral motion. The system is termed the Richville Shear Zone (RSZ) for exposures in the vicinity of Richville, NY, some of which we will visit on this trip. The along-strike extent of the RSZ is some 60 km and its continuation beneath Paleozoic cover to the northeast and southwest is not well-constrained.

FAULTING AND HYDROTHERMAL MINERALIZATION

One of the goals of this trip is to examine outcrop-scale features produced by faulting and hydrothermal activity along the Richville Shear Zone. The spatial arrangement of these features within the RSZ system and other similar fault systems in the area suggests a close linkage between faulting and hydrothermal activity. However, evidence of hydrothermal alteration can be found along the Potsdam Sandstone basal unconformity where no evidence of post-Potsdam faulting exists. These examples reflect passive fluid alteration and mineralization of the basement rocks, and these phenomena have been recognized widely in the St. Lawrence Lowlands and adjacent areas in the southern Canadian Shield and in the eastern Adirondack Highlands (Selleck 2004).

Rock and mineral assemblages

Marble. The majority of the outcrops we will examine contain calcite marble as the dominant lithology. Unaltered marble of the Adirondack Lowlands is typically coarsely crystalline (cm-scale calcite crystals are typical) white, bluish gray or gray in color with cm- to dm-scale metamorphic banding marked by segregations of calcsilicate minerals and graphite. A variety of calcsilicate lithologies (diopsidite; talc-tremolite quartzite; amphibolite; quartz-tremolite schist, etc) are found within marble and these rocks may form boudins, clots and dismembered fold hinges scattered in ductilely deformed marble.

Dolomitized marble. The outcrops we visit also contain dolomitized marble that resulted from Paleozoic alteration of Grenville calcite marble by Mg-bearing hydrothermal fluids. Dolomite may be difficult to distinguish from calcite on freshly broken surfaces, but modest weathering will usually clearly define the dolomite by its tan, buff, or yellow-gray color. The yellowish cast is due to the formation of hydrous Fe-oxides on the weathering surface produced when the dolomite dissolves slightly and releases ferrous iron from the dolomite crystal structure. Although there are dolomite marble layers that were part of the original depositional sequence deformed to produce the marble belts of the Lowlands, the Paleozoic dolomitized zones are clearly distinguished by calcite-dolomite boundaries that cut across compositional banding produced by metamorphic segregation that accompanied Proterozoic deformation. The Paleozoic dolomite is also characterized by numerous mm- to micron-scale voids that are often partly filled by crystals of dolomite, calcite quartz and sulfides. These voids are produced during the calcite to dolomite conversion process which results in a solid volume reduction. The void space could not have survived Grenville metamorphism so must be related to the Paleozoic dolomitization event. Areas of undolomitized marble adjacent to dolomite/calcite marble boundaries are often marked by a red or pink cast due to disseminated micron-scale hematite crystals in the undolomitized marble. Dolomite in the vicinity of fault zones may form lineations marked by arrays of dolomite crystals aligned parallel to slickenlines on weak cleavage or fracture surfaces.

Potsdam Sandstone. The Potsdam Sandstone in the outcrops we will visit is generally easy to identify as a coarse to medium yellow-white to red-orange sandstone with cm to dm thick pebble conglomerate and pebbly sandstone beds. Although most Potsdam Sandstone outcrops are clearly stratified, primary sedimentary structures are not easily discerned due to minor structural disruption or mineralization. Sand from the Potsdam is also found within open fractures and filling hydrothermal karst tunnels and pipes.

These fillings are often deeply colored red or maroon by abundant hematite cement, and the sand is usually tightly cemented by quartz and carbonate minerals, but rounded sand grains can usually be seen with a hand lens. Some of the conglomerates within the Potsdam contain chert clasts that are the result of silicification of marble clasts. Pebbles of jasper and clasts of laminated sandstone that had been silica-cemented, reworked and re-deposited are also present in the conglomerate and pebbly sandstone beds. A sandstone fracture-fill in granitic gneiss at Popple Hill (Rt. 58 south of Gouverneur and not visited on this trip) contains fragments of the inarticulate brachiopod *Lingulepis accuminata*. This species is a widespread form found in the Lower Ordovician Theresa Formation of the St. Lawrence Lowlands. Its presence in the fracture-fill in the Gouverneur area demonstrates that the Theresa Formation once extended over the region, and that unconsolidated sand with brachiopod fragments was sluiced downward into the fracture as it was opened during a faulting event.

Deformed Potsdam Sandstone. Within fault zones proper, the Potsdam Sandstone is extensively recrystallized and locally forms discrete fault knockers or tectonic clasts which may have an internal fabric of highly strained quartz ribbons. Clasts of Grenville quartzite may be similarly entrained within fault gouge rock and are also internally deformed and difficult to distinguish from recrystallized Potsdam Sandstone clasts. Fault gouge rock more generally consists of a mélange bearing cm-to m-scale clasts of the strongest rock types, quartzite and cemented Potsdam Sandstone, typically. The matrix of the mélange is typically a fine-grained mixture of quartz, hematite, illite and chlorite. Fabric development in the mélange is variable, but alignment of clasts with intervening weakly cleaved matrix is typical.

Hydrothermal Features. Fractures and hydrothermal leaching voids, and relict void space from partially filled tunnels, pipes and veins often contain coarsely crystalline dolomite and calcite which precipitated directly from hydrothermal fluids to form vuggy crystal void fills. Floors of voids may be filled with internal sediment derived from crystal precipitates from the contained fluid; these crystals then settled through the fluid to accumulate as sediment on the bottom of the void with a surface defined by the gravitational horizontal at the time of internal sediment accumulation. Voids that are partly filled this way are termed geopedal and record the horizontal as the flat boundary between finely crystalline internal sediment and overlying coarsely crystalline minerals precipitated *in situ* or as overlying void space. Some large individual voids at outcrop scale may record a number of internal sediment-crystalline precipitate episodes, each apparently the result of a fluid flow – fluid stagnation event. The termination of each successive episode of void-filling may be marked by thin rinds of quartz and sulfide minerals, which appear to have formed as the fluid composition or temperature changed as each mineralization/fluid flow event ended. At stop 7 near Richville we will examine multiple geopedal void-fills were tilted out of the horizontal as they formed within a fault block that was undergoing active tilting during hydrothermal mineralization. Void space not filled with mineral material is common within dolomitized marble, as well as in partially filled fractures and solution openings. This space was filled with fluid when the hydrothermal system was active. These spaces are of interest because the liquid or gas which fills them at depth can be petroleum or natural gas of economic value. Tiny voids that formed at defects on crystal surfaces as the crystals grew via precipitation from the hydrothermal fluid may trap bits of the fluid as further mineral growth occurs. These bits of trapped fluid are primary fluid inclusions and may be accompanied by inclusions that form when a crystal later fractures; the fracture fills with fluid and is healed by mineral solids that precipitate in the crack, thus forming secondary fluid inclusions. The fluid inclusions in the Richville shear zone hydrothermal system are discussed below.

Limestones and Dolostones of the Black River Group. We will make one stop at an exposure of the Pamela Formation of the Black River Group which consists of blue-gray weathering calcite limestones and buff-brown weathering dolostones. The color distinction is very similar to that seen in dolomitized versus undolomitized marbles noted above. The Pamela Formation outcrop also contains thin (mm to cm thick) mineralized veins that host coarse calcite and dolomite spar, pyrite and barite. These veins provide evidence for movement of hydrothermal fluids into the Ordovician carbonate sequence and reflect on a small scale the effects of structural deformation coeval with fluid migration. A key question for explorationists is the set of geological parameters that led to large-scale development of HTD in Black River and Trenton Group carbonates in the subsurface during hydrocarbon migration.

Mineral systems and geochemistry of the mineralizing fluids

Characterization of the fluid chemistry of the mineralizing system that operated in the vicinity of the Richville Shear Zone must take into account the range of minerals and the various dissolution/reprecipitation processes. The fluid must have varied at least subtly in composition and temperature through the mineralization history because some minerals are at times dissolved and at other times precipitated (e.g. calcite). The system must also have been cyclically variable in that void fills show sequences of alternating internal sediment and passive crystal growth, and chemically precipitated grains within hydrothermal pipe fill breccias show alternating oxidized iron phases (hematite) and reduced iron phases (siderite).

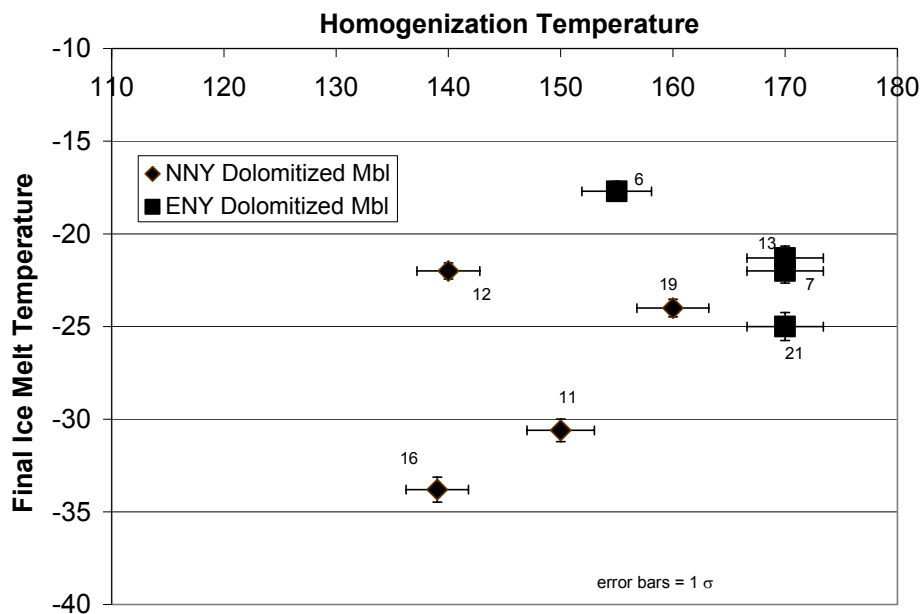


Figure 3 – Fluid inclusion data. NNY Dolomitized Mbl data include analyses of dolomite spar from stops 6 and 7. ENY Dolomitized Mbl data is from dolomite spar near Putnam Center and Fort Ann, New York. The eastern New York dolomitized marbles are similar in origin to the St. Lawrence Lowlands examples seen on this trip and the modern outcrops are near normal faults with adjacent Potsdam Sandstone. The homogenization temperatures provide an estimate of the minimum temperature of mineral crystallization. The final ice melt temperature is controlled by the salinity of the aqueous fluid in the inclusion. The numbers above each point indicate the number of individual inclusions analyzed.

Fluid inclusions. Fluid inclusion analyses were carried out on dolomite spar from void and fracture fill in marbles. As shown in figure 3, fluid inclusion homogenization temperatures range from 135°C to 175°C, with the eastern New York samples recording modestly higher temperatures. The final ice melt temperatures range from ~ -17 to -37 °C indicating a range of salinities from ~12 % to ~27% NaCl equivalent. These salinities are 3 to 9 times higher than the dissolved solids content of modern seawater (3.5%) and reflect derivation of the fluid from an evaporite brine, seawater or meteoric water that had received significant solute input. The salinity of the fluids in the Adirondack Lowlands marble belt dolomite is slightly higher, on average, than the Eastern Adirondack Highlands samples.

The fluid inclusion homogenization temperatures in the Richville Shear Zone hydrothermal system are beyond the typical range of the liquid petroleum window (80-120°C) and suggest that any hydrocarbons would have been present as methane or as high-molecular weight solids. Methane gas inclusions are common in quartz crystals from quartz + calcite veins that crosscut some earlier hydrothermal mineralization features. The methane-bearing inclusions are apparently primary and suggest that methane was being generated within the hydrothermal fluid system. Overall, these temperature and salinity determinations are consistent with results from other hydrothermal dolomite systems (e.g. Hulen et al. 1990; Luczaj 2001; Nesbitt et al. 1996; Qing and Mountjoy 1994; Smith et al. 2003).

Stable Isotope Data. $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ stable isotope data from unaltered Proterozoic marble, dolomitized marble, dolomite spar and calcite spar presented in figure 4. The unaltered Proterozoic marble samples are interpreted as originally sedimentary limestones whose stable isotope values are inherited from their deposition as marine carbonate sediments, and by equilibration with organic carbon as graphite during metamorphism. In general, the fields defined by the hydrothermal products such as dolomitized marble, dolomite spar and calcite spar

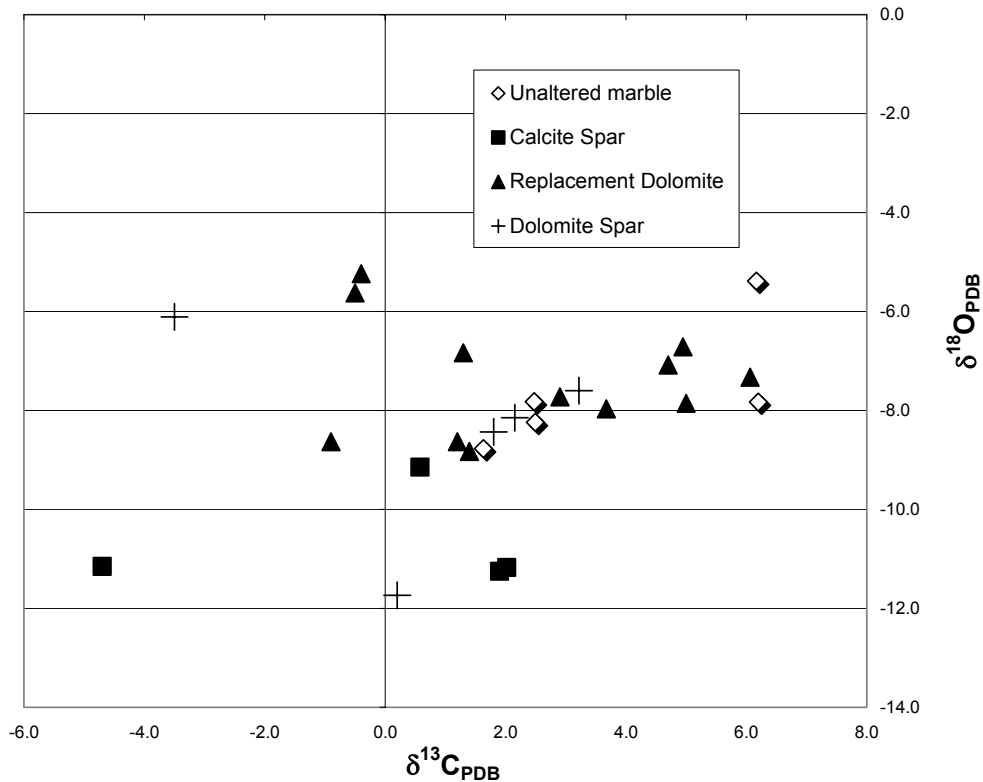


Figure 4 - Isotopic data from the Richville Shear Zone dolomitized marbles. Data from stops 1, 4 and 6 is shown.

overlap with unaltered marble. The most straightforward interpretation of this data is that the stable isotopes of the hydrothermal system are buffered by the marble. When waters interact with rock, isotopic exchange between the water and rock occurs as minerals dissolve into and precipitate from the fluid. Given time the system will reach isotopic equilibrium determined by temperature and fractionation factors of the mineral/fluid combinations. If the mass of water is much greater than the mass of minerals (a high water-rock ratio), such as in the case of carbonate minerals precipitating in the open ocean, the minerals isotope composition will reflect that of the water and the temperature at which the minerals precipitate. If the amount of rock is much greater than the amount of water (a low water-rock ratio) the stable isotope value

of the water will be dominated by input from the rock, and the stable isotope signature of minerals which precipitate from that water will be controlled by rock system.

One way to assess the degree of rock-water interaction is to calculate the isotopic composition of water that was in equilibrium with the precipitating minerals at the temperature of mineral precipitation. In this case we can use the fluid inclusion homogenization temperatures in dolomite, recognizing that these represent minimum temperatures of mineral precipitation since the true trapping temperature may be somewhat higher than the homogenization temperature. As shown in figure 5 the water in equilibrium with hydrothermal dolomite spar in the Richville Shear Zone and eastern Adirondack Highlands marble

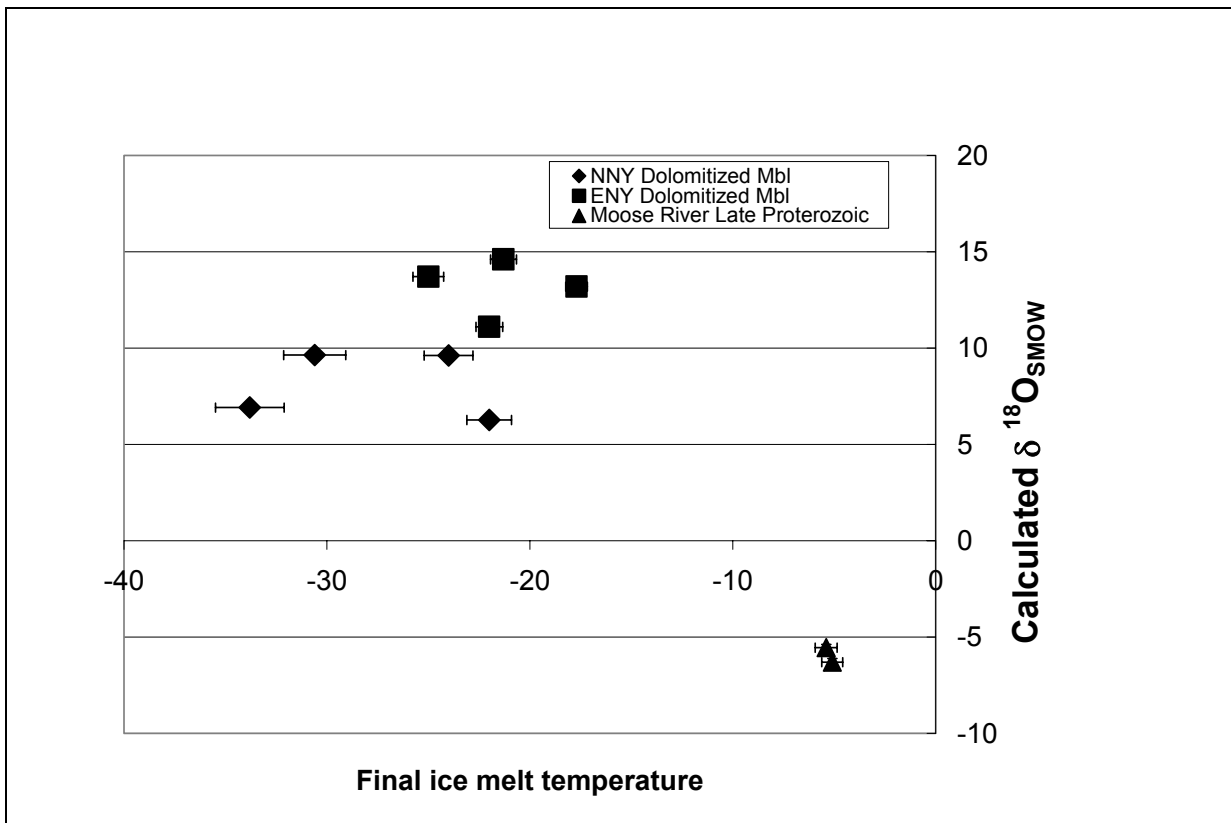


Figure 5 - Calculated oxygen isotope signature of water in equilibrium with dolomite and calcite. Final ice melt temperature is a proxy for salinity; less saline fluid from Moose River vein is much lighter isotopically and is interpreted as meteoric (freshwater). Fluids in equilibrium with dolomitized Proterozoic marble were much heavier isotopically.

had $\delta^{18}\text{O}_{\text{VSMOW}}$ (VSMOW is the standard used for water isotopic composition) values in the +8 to +12 range. This water is enriched in heavy oxygen relative to seawater, which has a $\delta^{18}\text{O}_{\text{VSMOW}}$ of around 0. The hydrothermal waters are also enriched relative to meteoric waters, which have negative $\delta^{18}\text{O}$ values since they contain relatively more light isotopic oxygen than seawater. An example of a meteoric hydrothermal fluid is plotted on Figure 5. Moose River calcite+quartz vein data from Selleck et al. (2004) and shows $\delta^{18}\text{O}$ water values calculated from quartz and calcite stable isotope systems. The positive or enriched values of calculated hydrothermal waters seen in the RSV are interpreted as resulting from a low water-rock ratio because as a little water reacts with lots of hot rock, the oxygen isotope values of the water become more positive. We use the term 'evolved' to refer to water whose isotopic composition has been changed by interaction with rock. Another interpretation consistent with this data is that the hydrothermal waters were derived from evaporite brine that made its way downward into the basement rock. Evaporation of seawater in an enclosed basin can produce water with a heavy isotopic signature as the isotopically light

water evaporates to vapor preferentially. Many samples of water from deep wells in the Canadian Shield have this heavy isotopic signature and are very salty, like the fluids in the RSZ system, and some workers interpret this water as evaporite brine that descended from saline basins that once overlaid the Shield. Equally plausible is that this brine results from long periods of water-rock interaction during which the water picks up high levels of solute and is progressively modified isotopically to its 'heavy' state. In the RSZ hydrothermal system it is not difficult to visualize the extent of rock-water interaction as small amounts of water were squeezed through finely crushed rock within fault gouge and filtered through tiny intergranular cracks and fissures in marble. The pattern of dolomitization of marble in the vicinity of fractures illustrates that significant rock-water interaction occurred. Along those flow paths the water would have had time to exchange isotopically to produce heavier signatures, and pick up high concentrations of dissolved constituents. The high chloride content could have been derived from evaporite brine or from minerals in the enclosing rocks, including halite, that contain chloride. The widespread shield brines discussed above similarly have high salinity with chloride the dominant anion.

A model for petroleum and gas exploration

Lithological, mineralogical, structural and geochemical aspects of Richville Shear Zone system are best explained as resulting from coeval faulting, hydrothermal karsting and hydrothermal mineralization. As discussed below, the system is an example of a fault zone that could have generated hydrothermal dolomite reservoirs resembling those that are important in the Appalachian Basin (Lavoie and Chi 2003; Martel and Durling 2003; Smith et al. 2003), the western Canada Basin (Berger and Davies 1999; Nadjiwon et al. 2000; Qing and Mountjoy 1994) and elsewhere (Waddell 1996; Westphal et al. 2004). Because it is now unroofed and at the surface, the RSZ hydrothermal system affords an unusual opportunity to examine the scale and style of deformation and hydrothermal alteration and mineralization at the interface between basement and sedimentary cover. The physical dimensions of the zone and its structural features provide a model of the subsurface character of hydrothermal dolomite reservoirs and potential keys to identification of these from seismic and subsurface geological data. The following section outlines elements of the system that are critical for development of km-scale hydrothermal alteration coupled with transcurrent, wrench-fault tectonics.

Fault/seismic pump dynamics. The occurrence of vigorous hydrothermal mineralization within a shear zone, the variation in hydrothermal fluid chemistry from oxidizing to reducing, the precipitation of layered void fills adjacent to fault zones, and evidence of high and/or fluctuating fluid pressures all point to a system evocative of the seismic pumping mechanisms described by (Sibson et al. 1975). In this scenario, motion along an irregular fault zone produces regions of extension/dilation that locally induce dramatically lowered fluid pressures causing surrounding fluids to flow into potential void space. These fluids are then expressed from the extensional zones as fault irregularities close to form compressional domains. The expressed fluids have interacted with crushed rock within the fault zones and thus contain solutes obtained from mineral alteration reactions. Fluids exiting from compressional zones move upward and laterally under high fluid pressure to alter and mineralize surrounding rock. Expressed fluids might also carry heat from the deeper part of the fault system, and conceivably could find permeable conduits that would permit outflow at the surface as hot mineral waters, as seen in many modern fault zones. The seismic pumping model is particularly attractive for the Richville Shear Zone system in that most of its critical features are explicable within this framework. The seismic pumping model may also apply to many hydrothermal dolomite reservoir systems, and indeed more widely to a number of diagenetic phenomena including color-banding of iron oxide cements in the Potsdam Sandstone (Selleck 1978).

Interaction of fluids with labile Mg-bearing minerals. The widespread dolomitization of marble in the Richville Shear Zone and indeed the dolomitization of overlying carbonate strata of the Theresa Formation and Ogdensburg Dolomite of the Ottawa-St. Lawrence Lowlands require significant importation of dissolved magnesium in the circulating pore fluids. While seawater itself can be a source of Mg for dolomitization, hydrothermal fluids not immediately connected to the seafloor may require another source of Mg. In the Richville Shear Zone system the interaction of hot salty fluids with Mg-bearing silicate minerals (e.g. biotite, hornblende, diopside, garnet, etc) in the Grenville metamorphic rocks commonly resulted in the conversion of these minerals to low-temperature phyllosilicates such as illite, kaolinite and Fe-chlorite which are Mg-poor (Tiller and Selleck 1992). The Mg liberated from this alteration process,

likely taking place most effectively within the crushed rock of the fault zone as fluid was emplaced during dilational events, would then be transported into adjacent and overlying rock. Where this Mg-rich fluid interacted with calcite marble, dolomitization resulted. This fluid was also capable of directly precipitating dolomite spar and dolomite internal sediment, perhaps as fluids injected upward from below were cooled during ascent into cooler rocks. The presence labile Mg-bearing minerals interacting with circulating fluids may be a key factor in the development of hydrothermal dolomite reservoirs in deep-seated basement-cover settings.

Availability of basal sand aquifer. The Potsdam Sandstone and other basal Paleozoic equivalents served as a regional fluid aquifer throughout the Paleozoic and later history of the Appalachian Basin. In the Richville Shear Zone system, this sand served locally as part of the fluid transport network and its presence was likely critical in maintaining a fluid supply to the system. In New York State Potsdam outcrop and subcrop is absent over a region extending from the western Adirondack margin west to the Lake Ontario basin and south into the northern Finger Lakes region. This ‘Potsdam absent’ region is well-known in gas and oil exploration when deeper targets are explored. The link between the Potsdam basal aquifer and dolomitization in the Richville Shear Zone suggests that hydrothermal dolomite reservoirs might be not be as prevalent in regions where the basal sandstone is absent.

Appropriate burial temperatures. The dolomitization and related mineralization in the RSZ occurred at temperatures generally in the range of 140-170°C. The depth of mineralization is not well-constrained because of the possibility that hot fluids from depth were rapidly expressed upward into cooler rock in a seismically pumped hydrothermal system. These temperatures lie beyond the normal range of liquid hydrocarbon generation, but were within the range of methanogenesis. The shallower, now eroded portions of the section overlying the RSZ may have contained petroleum liquids at one time. A critical feature of the RSV system was the deep circulation of fluids at temperatures sufficient to rapidly alter Mg-bearing minerals and then transport solutes and heat into adjacent rock.

Evolving hydrocarbon system. The evidence for active hydrocarbon generation in the RSZ fluid system is limited to the occurrence of methane fluid inclusions in quartz and solid organic matter inclusions in dolomite and calcite spar. The dissolution of calcite marble that preceded mineralization events was likely due to CO₂ and organic acids produced during decarboxylation of organics as kerogen compounds were converted to saturated hydrocarbons. These acidic components would then be available to promote calcite dissolution and alteration of labile silicate minerals. This process is widely recognized as a mechanism for evolution of secondary porosity in deeper carbonate and siliciclastic reservoirs, and its inferred presence in the RSZ suggests that hydrocarbons were generated in the immediately overlying strata and that fluids from these penetrated downward into the RSV during dilational seismic events. The interrelationship between hydrocarbon maturation and hydrothermal fluid movement to produce HTD reservoirs is a key factor for explorationists to consider.

Timing and regional tectonic perspective. The timing of hydrothermal activity in the Richville Shear Zone system is important because it may be tied to the development of HTD reservoirs elsewhere in the northern Appalachian Basin including a number of current exploration targets. In addition, the understanding of regional patterns and evolution of fault and fracture systems in the basement of eastern North America has implications for the tectonic evolution of the continent. Based upon a number of studies of dolomitization and fluid alteration of the Cambrian and Ordovician strata of and eastern New York and adjacent Ontario we know that the fluid systems of the RSZ type are found in other areas, and may signal widespread development of similar basement fault/hydrothermal alteration systems during the Paleozoic history of the region. The timing of these fluid alteration events is not well understood and few radiometric dates have been determined within the RSZ proper; however some studies of minerals in the region that can be radiometrically dated provide constraints. One source of potentially useful dates derive from Ar-Ar analyses of authigenic K-feldspar in altered basement and overlying Paleozoic cover from northern New York and southeastern Ontario. In general, these dates suggest a fluid alteration system linked to the medial-late Ordovician Taconic Orogeny (Ziegler and Longstaffe 2000b). If the RSV system was active during medial to late Ordovician, it would suggest that the fault system developed after the otherwise N-NE trending normal faults that were related to foreland basin subsidence elsewhere in northern New York. If

the RSV system developed in response to late Taconian compressional tectonism, the burial depth of the system may have been no more than one km, based on regional isopach patterns. It is easier to explain the co-occurrence of oxidizing fluid signatures with higher-temperature features if the system was recharged from near-surface oxidizing fluids that were heated at depth and then injected into the shallower parts of the regime.

Relatively younger ages of burial mineralization are indicated by K-Ar (Tiller and Selleck 1992) and Rb-Sr (Reynolds and Thomson 1993) geochronological studies of illite in the Potsdam Sandstone in the western St. Lawrence Lowlands. These dates indicate a fluid alteration event in late Devonian-early Carboniferous time (ca. 365-355 Ma). This likely represented a time of maximum burial beneath sedimentary cover and was co-incident with compressional tectonism along the eastern margin of North America. Deeper burial alteration is consistent with the temperatures determined from fluid inclusion work as temperatures of 170°C would imply a burial depth of 4 km if a geothermal gradient of 40°C/km existed at that time. However, as noted above, the temperatures recorded by fluid inclusions may reflect transient conditions related to upward seismic pumping of hot brines into shallower, cooler rock and thus temperatures in this system may be a wholly unreliable guide to burial depth. Alleghanian faulting during the late Carboniferous/Permian is also possible but no mineral ages of latest Paleozoic age have been determined in the region.

Related phenomena

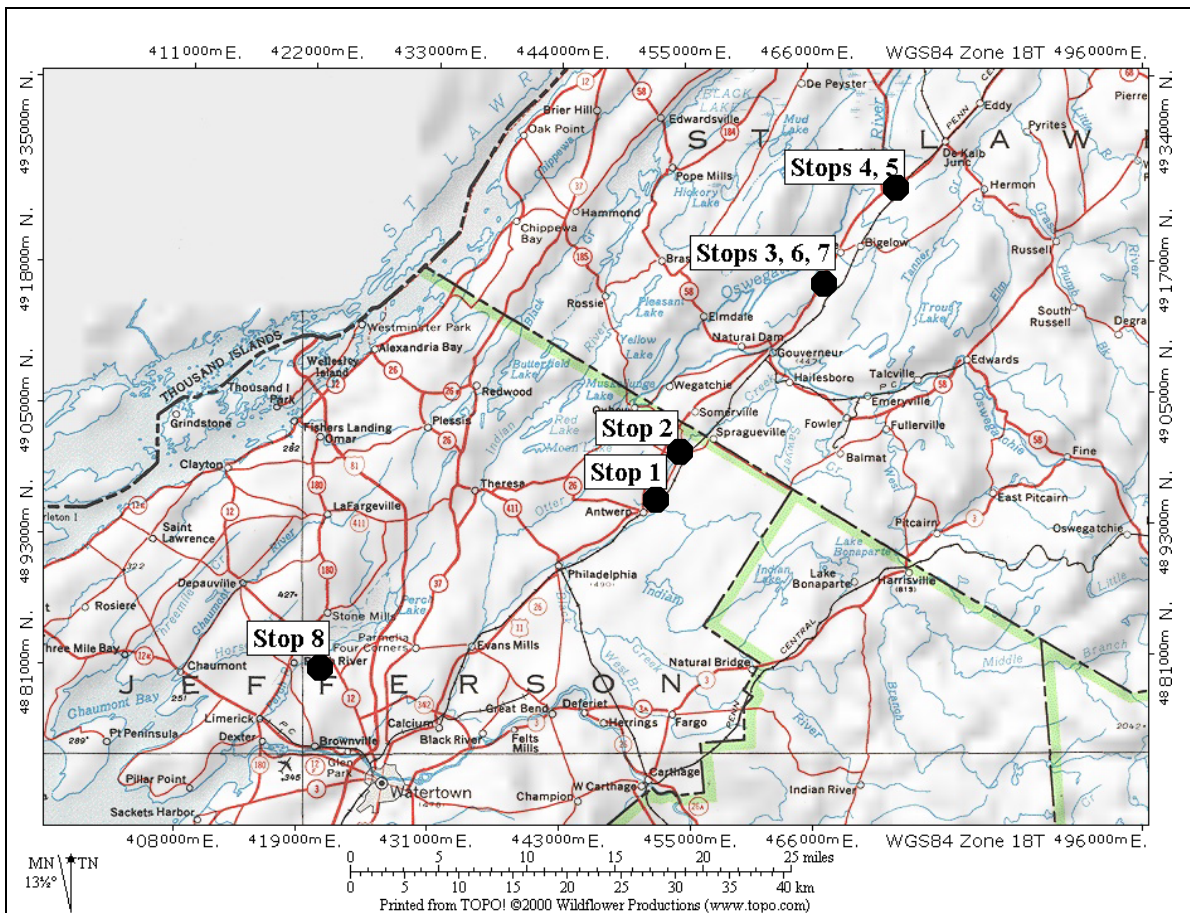
Rossie-type galena-calcite veins. The well-known Rossie-type galena-sphalerite-calcite veins, exposed 15-20 km WNW of the Richville area, were emplaced after the Potsdam Sandstone had been tightly cemented, based on the sharp wall-rock vein contacts and the absence of infiltration of vein material into the adjacent sandstone. Fluid inclusion data indicate homogenization temperatures of 120-140°C (Foley et al. 1985). These veins have a NW-SE orientation and appear unrelated to the stress system of the RSZ, although further study is needed.

Hematite deposits of the Adirondack Lowlands. A discontinuous belt of hematite deposits extends from WSW to ENE across the Adirondack Lowlands from the vicinity of Antwerp to Russell, NY. A small number of these deposits were worked as open pit mines for locally consumed hematite ore for small forges and paint pigment in the 19th century, and were investigated in the 1920's and 1930's for possible development. The complex mineralogy of the Sterling deposit has been described by Robinson and Chamberlain (Chamberlain 1984; Robinson and Chamberlain 1984). In general, these deposits lie along the same trend as a suite of sulfide ore (largely pyrite) deposits that are part of the metasedimentary sequences of the St. Lawrence Lowlands. The trend of the hematite deposits is also generally parallel to the Richville Shear zone system although most of the hematite deposits lie somewhat to the southeast of the zone. The hematite deposits also share the common presence of nearby or directly overlying inliers of Potsdam Sandstone (Chamberlain 1984). The paragenesis of the hematite deposits is generally interpreted as multi-stage with pre-Potsdam surface weathering of Proterozoic iron sulfide leading to accumulation of locally thick gossans of limonite/hematite prior to Potsdam Sandstone deposition (Chamberlain 1984). Post-Potsdam reconstitution of the iron oxides involved hydrothermal fluids that dissolved and re-deposited hematite within Potsdam Sandstone as thick botryoidal masses, specular crystalline aggregates, veins and disseminated cements in sandstone and highly altered Proterozoic basement gneiss. In addition, a wide variety of oxide, sulfide, sulfate, phosphate and carbonate minerals were deposited, leading to a rich assemblage of hydrothermal origin (Chamberlain 1984; Robinson 1998; Robinson and Chamberlain 1984). Fluid inclusion temperatures from calcite indicate a minimum temperature of 140°C for some of the mineralizing fluids (Robinson and Chamberlain 1984), and the paragenetic sequence of the complex mineralogy suggests that geochemical conditions varied from oxidizing to reducing during active mineralization. The mineral systems at Sterling mine include sparry dolomite and coarse calcite spar as major void-filling phases, and outcrops of marble and Proterozoic granitoid rocks immediately adjacent to the mine contain fracture-related dolomitization and sandstone injection 'dikes'. The similarity in between the Sterling-type mineralizing system and the hydrothermal mineralization in the Richville Shear zone is striking, and suggests that the fluids involved were similar. Further study of fluid inclusions and stable isotopes in the hematite deposit mineral system and dating of mineral assemblages are needed to resolve the relationships.

Sandstone, quartzite and 'enigmatic enclaves'. Many geologists who have worked in the Adirondack Lowlands have called attention to quartzite and sandstone outcrops that are separated from the main mass of Potsdam Sandstone and lie within areas mapped as marble. One interpretation suggested that some sandstone occurrences are the result of 'protection' of sandstone from penetrative deformation during Grenvillian tectonism by the presence of ductile marble (Bloomer 1965), thus making the sandstones part of the original Mesoproterozoic sedimentary sequence. This interpretation has been vigorously challenged (Brown 1967) and a more viable interpretation suggests emplacement of Potsdam sands into karst caverns along the pre-Potsdam unconformity with later diagenetic burial alteration. However, the occurrence of strained quartzite clasts within breccias, and authigenic minerals that have been interpreted as metamorphic in origin have caused some workers to call upon a more complex origin and have left some aspects of these occurrences unresolved (Bursnall and Elberty 1993). The coupled hydrothermal/fault system paradigm provides a reasonable explanation for these unusual features and is consistent with both field and laboratory data.

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ROOT ZONE OF AN ANCIENT FAULT SYSTEM – ROAD LOG

This road log begins at the traffic light on Route 11 in Antwerp, NY. To reach Antwerp from Oswego, NY, take Route 104 east to Route 181; 181 north to the Route 11 Exit north of Watertown; Route 11 East/North toward Gouverneur. This drive will take approximately 90 minutes from Oswego. Mileage begins at the traffic light intersection in Antwerp. Note that the total round trip from Oswego is approximately 200 miles.

Cum Mi.	Road Log (UTM coordinate datum NAD83)
0.0	Traffic light at intersection on US Route 11, Village of Antwerp, New York; continue northeast on Route 11
3.1	<p>Stop 1 (18 452455E, 4898768N) – Outcrop on S side of Route 11 exposes “Antwerp” granite syenite intruding marble, which was followed by dynamothermal metamorphism producing upper amphibolite facies calcisilicate mineral assemblages, reaction boundaries between granitoid and marble, and deformation including boudinage, folding and fabric development. The high ductility contrast between the granitoid and marble results in disruption of original depositional and intrusive relationships. Paleozoic dolomitization of marble is evident along near vertical fractures and as diffuse zones extending away from fractures. An open fracture filled with dolomite-cemented sandstone is found on the top surface of the E end of outcrop. The old workings of the abandoned Sterling Mine, part of belt of hematite deposits found in this region (see text) are located on private property approximately 1 km SW of Stop 1. (20 minutes)</p> <p>The exposures on the N side of Route 11 contain brecciated and dolomitized marble, coarse dolomite and calcite spar and minor sulfide and quartz mineralization. Some calcite spar crystals are cored by deep brown or black calcite that contains abundant organic (petroleum) inclusions. The arrangement of dolomitized marble and void-filling minerals suggests multiple episodes of collapse brecciation and mineralization. Depending on the size of the group, we may visit the locality on the N side of the road when we return via same route.</p>
4.7	<p>Stop 2 (18 453868E, 4900891N) Low roadcuts on the SE side of Rt. 11 expose Proterozoic marble with cm- to dm-scale compositional bands defined by variations in abundance of graphite and calcisilicate minerals such as phlogopite and diopside. The banding dips gently to the SE. Vertical dolomitized zones are associated with joints that served, apparently, as conduits for dolomitizing fluids. The dolomitized zones are accentuated by minor weathering which imparts a brownish-tan or buff color to the dolomite in contrast to the white-blue-gray of the calcite marble. The contact between dolomitized and undolomitized marble represents a fluid alteration ‘front’ and minor hematite staining of partially dolomitized marble is present along this front. Note also the development of minor, millimeter-scale porosity in the dolomitized marble. The porosity is caused by the net reduction in solid volume during the $2\text{CaCO}_3 + \text{Mg}^{2+} > \text{Ca}_2\text{Mg}(\text{CO}_3)_2 + \text{Ca}^{2+}$ reaction. Why are dolomitized limestones often good hydrocarbon reservoirs? Could a dolomitized marble like this serve as a reservoir rock?</p> <p>Continue NE on Rt. 11 through the village of Gouverneur</p>
18.8	<p>Stop 3 (18 468148E, 4917434N) Roadcut on NYS Rt. 11 immediately NE of intersection with Richville Road exposes a fault contact between red-orange Potsdam Sandstone and Proterozoic basement. The Potsdam Sandstone here contains pebbles and small cobbles of quartzite, jasperite and cemented sandstone. Slickenlines on the E-W trending fault surface indicate reverse motion with Proterozoic marble moving up to the west over Cambrian Potsdam Sandstone. Note the dolomitization of calcite marble adjacent to fractures in basement rocks adjacent to the fault. The marble and calcisilicate rocks near the fault give way to the east along the roadcut to coarsely crystalline quartz-albite pegmatite. The exposures on the NW side of Rt. 11 will be examined as Stop 6 when we return via this route. Continue NE on Rt. 11</p>
24.4	<p>Stop 4 (18 473726E, 4923995N) The exposure on the SE side of Rt. 11 consists of near-horizontal beds of Potsdam Sandstone. Depending on the condition of the road ditch at the NE end of the outcrop, a contact with Proterozoic marble is exposed. The basal Potsdam is locally a conglomerate,</p>

	<p>and near the base of the exposure cobbles of quartzite and jasperite are common. The upper portion of the exposure is medium sandstone. Note the irregular, disrupted lamination and cross-cutting color banding in the Potsdam. We will examine the exposures on the NW side of Rt. 11 as Stop 5.</p>
26.0	<p>Continue NE on Route 11 to parking area opposite Hermon-DeKalb Central School. This is our turn-around.</p> <p>Head SW on Rt. 11</p>
27.6	<p>Stop 5 (18 473726E, 4923995N) A series of outcrops on the NW side of Rt. 11 expose complex fault and hydrothermal solution collapse contacts between marble and Potsdam Sandstone. Proceeding from the NE end of the exposures, the first outcrop is comprised of intricately folded gray marble with a low-angle lineation marked by thin dolomite segregations. The folding of the marble is most likely the result of Proterozoic dynamothermal metamorphism but the dolomitic fabric may have resulting from strain during Paleozoic wrench faulting. Diffuse dolomitization of the marble, localized dolomitic halos around veins and dolomite + calcite void fills are also present. Continuing to the SW along the road, a fault contact between marble and a hydrothermal/fault breccia is poorly exposed near the end of the main marble outcrop. The breccia and adjacent deep red-brown sandstone here contains Potsdam sand grains and clasts of cemented sandstone, clasts of apatite-dolomite-quartz that represent rinds detached from hydrothermal pipe walls, spheroidal grains consisting of concentrically alternating hematite and siderite, and fragments of calcsilicate minerals including 'bleached' phlogopite; xenotime, tourmaline and monazite grains in the breccia have authigenic overgrowths. Complexly slumped or faulted sandstone adjacent to the contact is cemented by barite, pyrite and quartz. Mm to cm-scale arborescent masses of the Fe-sulfate jarosite (found by Opportunity on Mars) are present on rain-protected surfaces where pyrite is weathering. The outcrop on the SW end of the series of exposures consists of less disturbed and altered Potsdam Sandstone, resembling the lithology exposed across Rt.11 visited as stop 4. Continue SW on Rt. 11.</p>
33.2	<p>Stop 6 (18 468148E, 4917434N) (Opposite stop 3). The lower portion of the NE outcrop at this stop consists of a hematite-stained fault gouge that grades progressively upward into more strongly layered and folded quartzite. The fault gouge consists of cm to meter scale blocks of quartz cemented sandstone and quartzite and deformed clasts of hematite-chlorite quartzite. The cleaved matrix consists of hematite-chlorite-illite quartz. Near the top of the exposure, the quartzite contains relatively unstrained layers of quartz-cemented sandstone with rounded grains. This outcrop is a relatively thick fault gouge zone associated with the Richville Shear Zone. The relatively resistant capping quartzite has prevented erosion and thus the weak fault gouge rock is exposed at the surface. Note the flattened, boudinaged quartzite fragments and the intense hematite staining. When the fault zone was active, material of this sort was flushed by reactive hydrothermal fluids.</p> <p>The second major outcrop at this stop is directly opposite the fault exposure seen at Stop 3 across Rt. 11. The outcrop is somewhat unstable so use caution. Note the diffuse dolomitization of marble, large voids with dolomite, calcite and minor quartz and pyrite. Barite occurs in some void fills. Sparry dolomite and calcite alternate in some void fills, and tilted void floors apparently represent progressive rotation of voids as faulting and hydrothermal dissolution and mineralization occurred. Note the veins that crosscut former calcsilicate pods in altered marble and the residue of illite/chlorite and kaolinite which is left as a soft material on the void floors. Hematite staining and dolomitization is localized along fractures and become more pervasive as the fault surface is approached at the SW end of the exposure. The next stop is located on Rt. 11 approximately 0.2 mi SW.</p>
33.4	<p>Stop 7 (18 468003E, 4916963N) These exposures offer an excellent opportunity to examine marble penetrated by hydrothermal pipes and tunnels, the material filling these voids, and patterns of dolomitization and hematite staining of the marble altered by hydrothermal fluids. Note that some pipes (near-vertical orientation) represent solution-enlarged fractures, indicated by the lack of 'fit' of opposing walls. The pipe filling is typically Potsdam sand tightly cemented by hematite and quartz, with minor apatite. Barite, leucoxene, siderite and pyrite also occur as cements. Note that some pipes are filled with red-brown sandstone at the base but the upper portion of the pipe contains sparry</p>

dolomite, calcite and quartz as mineral precipitates. Tunnels (horizontal orientation) show a similar pattern of fill, and some show multiple sandstone-dolomite-quartz-calcite internal layering, representing multiple episodes of sluicing of unconsolidated sand followed by mineral precipitation. Some larger pipes and tunnels contain fragments of cemented sandstone and quartz-apatite-dolomite clasts interpreted as mineralized rinds spalled from the walls pipes and tunnels elsewhere in the hydrothermal system and carried by rapidly flowing hydrothermal fluids. The outcrop also displays a range of dolomitization patterns associated with the pipe and tunnel network and fractures. Note the 'islands' of undolomitized marble, and relict calcite 'eyes' in otherwise dolomitized rock. How can we reconcile the presence of hematite associated with reduced iron minerals, sometimes as concentrically alternating spheroidal grains? What is the origin of the pervasive hematite staining associated with the dolomitization of marble?

End of road log for Stops 1-7

Continue on Rt. 11 SW through Gouverneur, Antwerp and Philadelphia to intersection of Rt. 342 and Rt. 11. Turn NW (right) onto Rt. 342, continue west to Rt. 12, crossing over I81. Turn right (NW) onto Route 12. Proceed NW to Stop 8, located 4.0 miles from the Rt. 12/Rt. 342 intersection.

Stop 8 (18 422107E, 4881242N) The outcrop on the NE side of Rt. 12 is in the upper portion of the Pamela Formation of the Black River Group. The lithologies here include dolostone, dolomitic shale, lime mudstone, and wackestone. In general, these sedimentary facies represent deposition on a broad, relatively low-energy carbonate platform of Medial Ordovician age. This platform covered much of the interior of eastern Laurentia (North America) prior to the onset of subsidence and foreland basin development in later Medial Ordovician time. Key sedimentary features to observe are cryptalgal/microbial laminations, bentonite (volcanic ash) beds, mudcracks, evaporite (gypsum/anhydrite) mineral casts, and storm event beds represented by mud rip-ups clasts, intraclast breccias, stylolites and solution voids. The SE end of the outcrop is capped by a massive, tan-weathering laminated dolostone. Immediately beneath the dolostone, beds of grey limestone are arrayed in a series of low, irregular folds with axes that trend N80W, approximately parallel to the highway. Thin (mm-cm thick) dolomite+calcite+pyrite+barite veins trending N70E are common in the limestone, and cm-scale calcite spar filled voids are present in the dolostone and some limestone beds. The mineralized fractures here are small-scale hydrothermal features that may be related to the dolomitization and related mineralization seen in the earlier stops on the trip. Note that the void fill minerals in the limestone beds are the same as those in the mineralized fractures. Examine the limestone - dolostone contact and see if you can trace mineralized fractures into the dolostone. Is the dolomitization here 'early' (preburial - related to Mg-rich brines derived from seawater that had precipitated gypsum) or is the dolomitization related to the later mineralized fractures? Why is some rock dolomitized whereas other rock remains nearly pure calcite limestone? Was there significant porosity in this rock at any time during its diagenetic history? Is the folding related to the minor mineralization or a later phenomenon?

Continue NW on Rt. 12 to the Perch River Refuge parking area (visible from Stop 7), turn back onto Rt. 12 heading SE. Continue on Rt. 12 to I81 south (3.4 miles); take I81 south through Watertown to Rt. 104 exit. Take Rt. 104 west to Oswego.

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