FRACTURE AND GEOCHEMCIAL CHARACTERITICS OF FLUID MIGRATION IN CAMBRO-ORDOVICIAN UNITS, NEW YORK STATE

DRAFT

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Submitted by:
Dr. Robert Jacobi
Norse Energy USA
3556 Lake Shore Road, Suite 700
Buffalo, New York 14219
(716) 218 4234
Email: Rjacobi@nornew.com

Submitted to:
Dr. John Martin, NYSERDA Senior Project Manager
NYS energy research and development Authority
17 Columbia Circle
Albany, NY 12203-6399

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ABSTRACT

The project objectives were to integrate studies of vein-filled fractures in the Cambro-Ordovician section in central New York State and in the Mohawk Valley with geochemical studies of the vein fills. Such integrative research would yield a picture of the fluid migration history recorded by the veins. The ultimate goal was to better describe the fluid migration history in these units. Fracture studies were carried out on an oriented horizontal core in central NYS and on an unoriented vertical core in the eastern Mohawk Valley region. Detailed field studies of fractures and faults in outcrops were accomplished along the Mohawk Valley from the Little Falls quadrangle in western Mohawk Valley through the valley to Hoffman's fault in the central Mohawk Valley. Geochemical studies on the veins included d^{13}C and d^{18}O isotopes, ^{87}Sr/^{86}Sr isotopes, REE, trace elements, transition and metals, and limited fluid inclusion studies. Evidence for at least periods of fluid migration (Cambrian-Ordovician boundary, Taconic, and Alleghanian) were documented, and each phase probably had several sources of mineralizing fluid, including seawater, seawater that leached basement along fault systems, fluid that severely leached volcanic ash layers in the Ordovician section (especially the Utica), and fluid from clay dewatering/dissolution in the accretionary prism and the local sediments.

KEY WORDS

Appalachian Basin, faults and fractures, fluid migration, Trenton/Black River, Utica

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LIST OF GRAPHICAL MATERIALS

SUMMARY

Fracture studies and geochemical analyses of veins (as a proxy for the fluids from which the vein precipitated) in central New York State and the Mohawk Valley in eastern New York State reveal a complex history of fluid migration in the Cambro-Ordovician section that involved at least three periods of fluid migration and several fluid sources. Geochemical analyses included d^{13}C and d^{18}O isotopes, ^{87}Sr/^{86}Sr isotopes, REE, trace elements, transition and metals.

The fluid circulation in the Cambro-Ordovician section in central and eastern NYS has several fluid sources and at least three periods of circulation. In the first phase, dolomitizing fluids circulated along the active faults and into the Little Falls dolomite. This fluid circulation was proposed by Jacobi et al (2006b) to be coeval with the faulting that accompanied the development of the unconformity at the Cambrian Ordovician boundary. The stable isotopes of C and O are consistent with hydrothermal circulation in the matrix of the Little Falls dolomite, but the age of the dolomitization in this analyzed sample is uncertain—it could represent this early event, or the later events.

The second phase of fluid circulation is the principal phase described in this report. It is probable that there were at least three fluid systems that mixed to form the veins observed in the Cambro-Ordovician sequence. In central NYS (the Finger Lakes region), isotopes suggest that Taconic aged seawater first circulated and promoted vein development very early in the history of the Trenton/Black River—before the Black River reached sub-seafloor depths sufficient to develop horizontal stylolites-- perhaps 100 m. Strike slip motion on reactivated ENE-striking Iapetan-opening faults were already active at this time, in response to Laurentia converging with the continental-based arc, and this strike slip motion was recorded in the early veins. As burial continued, horizontal stylolites developed, but since the faulting remained active during convergence, ENE-striking vein fills associated with left-lateral and then right-lateral slip developed as a result of the SH rotating about a vertical axis as Laurentia tightened in collision with the arc. Apparently the Finger Lakes region was sufficiently distant from the convergent zone that the mineralizing fluids were not derived from significant basement leaching or mineral dissolution, based on Sr isotope data. The d^{13}C values suggest precipitation at moderate depths below seafloor (on the order of 100 m) with a moderate fluid component associated with carbonate reduction with methanogenesis.

Another end member in terms of fluid circulation is the veins in the unoriented vertical core in the eastern Mohawk Valley. These veins fill fractures, normal faults and thrust faults (no strike slip/oblique slip indicators were found). Deformed zones in the upper units (Frankfort and Schenectady) show a progressive deformation from soft-sediment deformation to brittle faulting (including some thrusts). Based on the progression from soft to brittle deformation in these deformation zones, the zones developed in late Taconic, including the veins along the associated normal and thrust faults (Hanson et al., 2010). These veins, which are primarily in units above the Utica, suggest two fluid sources (either reflecting different times or migration paths). One fluid was derived from mineral dissolution during cleavage development (and/or, less likely, leached basement), based on both the strongly negative d^{18}O values and

the high Sr isotope ratios in the samples. Another fluid promoted precipitation of carbonate with heavy d^{13}C values (positive values); this precipitation probably occurred as a result of carbonate reduction with methanogenesis, which for similar heavy d^{13}C$_B$ values in the accretionary prism offshore Peru occurred between 100 m and 300 m depth. The single ^{87}Sr/^{86}Sr analysis conducted on samples with heavy d^{13}C values indicates that the fluid either leached basement and/or volcanic ash layers and/or had a strong component from clay dewatering/dissolution (^{87}Sr/^{86}Sr = 0.71422).

In the central Mohawk Valley, stable isotopes of C and O of both veins and vugs of the Little Falls and Tribes Hill carbonates indicate a hydrothermal origin, unlike the carbonate matrix values. The Tribes Hill quarry dolomite has high Sr isotope ratios that indicate fluid that leached basement or volcanic ash or was (partly) derived from clay dewatering/dissolution. No samples with heavy d^{13}C values indicate a lack of carbonate reduction with methanogenesis for these units low in the stratigraphic section. High abundances of Cu and Cd indicated basement leaching to Cross (2004). Distinctive REE patterns with Eu negative anomalies strongly suggest massive volcanic ash diagenesis by these fluids or Adirondack basement leaching or both. In general the units stratigraphically below the Utica display NNE/NE- and WNW- striking fractures and vein fills, but in the Utica WNW-striking fractures are dominant, and along the NNE-striking fault primarily WNW-striking fracture fills increase in density. This increase in WNW-striking veins adjacent to the fault is consistent with the model of Jacobi et al. (2003) that suggested that the originally normal faults (in early Taconic) became high angle reverse faults in the late Taconic when the convergence was “jammed”.

In western Mohawk Valley, the Utica carries both NNE-NE and WNW-striking vein fills, but the WNW-striking vein fills, like the region to the east, increase in fracture frequency toward the NNE/NE-striking faults. Geochemical considerations suggest several fluids precipitated vein material in this area. Stable isotopes of C and O of veins in the carbonates indicate a near-MVT hydrothermal origin, and the matrix of the Little Falls matches the MVT field for stable isotopes of C and O. Dolgeville and Indian Castle veins have heavy d^{13}C, consistent with precipitation during carbonate reduction with methanogenesis at sub-seafloor depths from about 150 m to greater than 300m (or consistent with later methanogenesis of carbon (bitumen) in the fracture systems). ^{87}Sr/^{86}Sr analysis indicate at least two mineralizing fluids: 1) Taconic-aged (or neoAcadian or Alleghanian aged) seawater for veins in the Trenton, Tribes Hill, Flat Creek units , 2) elevated ^{87}Sr/^{86}Sr water carrying dewatered clay diagenesis products (and, less likely, leached basement or volcanic ash products). The lack of generally relatively high Cu and Cd in the sedimentary section, and the lack of strongly negative Eu anomalies suggest that the fluids did not significantly leach either basement or the volcanic ash layers typical in the central Mohawk Valley region.

The only strong evidence for Alleghanian (or younger) vein development comes from the horizontal core in the Finger Lakes region. There, NE-striking vertical stylolites that are assumed to be related to Alleghanian tectonics are cut by later NNE-striking veins with left-lateral slip.

INTRODUCTION

That fluid migration has affected the Upper Ordovician Trenton/Black River (TBr)-Utica-Frankfort-Schenectady section in NYS has been well established (see reviews in Smith, 2006; and Jacobi, 2007). However, the history of fluid migration in the Upper Ordovician section has not been published in detail—which fracture systems carried the fluids, the source of the fluids, and the possibility of multiple phases. This final report integrates field, core, and geochemical work accomplished by the author (Dr. Jacobi) and his graduate students (Cross, Agle, and Hanson) from the mid-2000s to present.

The basic model for fluid migration for the TBr in the Finger Lakes region of New York State was first presented by Beardsley (1999, Figure 1). In this model fluids migrated along faults and associated fractures to relatively high porosity zones in the Black River, where the fluids spread laterally away from the faults. The fluids first dissolved the limestone, and then precipitated dolomite (along with other MVT precipitates). Based on fluid inclusion temperatures and cross plots of d^{13}C ($^{0}/_{00}$)$_{PDB}$ vs.d^{18}O ($^{0}/_{00}$)$_{PDB}$, Smith (2006) judged the fluids to be hydrothermal. The original model, based on well logs from the Glodes Corners Road Field in central New York State (NYS), showed that the graben associated with the faults and fluid migration had greater stratigraphic throw upsection (more throw on the Trenton than the underlying Black River, Figure 1). This upsection increase is consistent with a solution collapse graben. In contrast, Smith (2006) believed that all the grabens were releasing bend features (rhombochasms) or riedel shears, and not related to solution collapse (Figure 2). Smith (2006) suggested that the fluids were transported along the basal Potsdam sandstone, and then seismically pumped upsection along syndepositional faults. These faults were reactivated basement faults, as had been proposed earlier by Jacobi (2002). Jacobi et al. (2004), based on only 2D seismic data, found releasing bend geometries (negative flower structures) that would support the Smith (2006) model, but also found cases where the offset did increase upsection from the Black River to the Trenton.

The timing of the fluid migration was, and remains, equivocal. Early suggestions were that veins in the Ordovician section of the Mohawk Valley (a proxy for fluid migration) were of Alleghanian age (O'Reilly and Parnell, 1999). This proposal was based on evidence for extensive fluid–rock interactions resulting from the proposed subsurface fluid "flood" driven west out of the Alleghanian orogenic system into the Appalachian foreland Basin (e.g., Oliver, 1986), thought to be evidenced by Alleghanian-aged reset paleomagnetic poles in the mid-Paleozoic section along the Hudson River (e.g., Scotese et al., 1982) and in the southern Appalachians (Bachtadse et al.,1987), and on Alleghanian dated illitization/K feldspars in the central Appalachians and westward (Hearn et al. 1987, Elliot and Aronson 1987, 1993), on Rb-Sr dated sphalerite in Mississippi Valley Type (MVT) lead-zinc deposits (see the review of the Rb-Sr controversy in Bradley et al., 2004), and the presence of veins in the mid Paleozoic units. (It should be noted that some of the Alleghanian dates have since been discounted and suggested to be Acadian, see for example Nakai et al. [1993]). Smith (2006) suggested that the timing of fluid migration in the TBr was related to seismic pumping, and thus had to date from when the faults were active. Since the mapped faults that offset the TBr and overlying Utica section in the Mohawk Valley were thought to terminate upsection in the Utica, based on mapping (Fisher 1980), the faults could not have conducted significant fluids after Utica time. Thus, the fluid migration must have been Taconic (Ordovician) in age. Jacobi et al. (2003a, b, 2004) first presented seismic sections across the discovery TBr grabens in central NYS, and showed that the boundary faults on the grabens indeed did not extend into the Siluro-Devonian section; he also proposed therefore that the fluid migration must have been Taconic aged. Jacobi et al. (2006) added additional evidence for a Taconic aged major fluid migration accompanied by dolomitization by noting that the same upsection sequence of interlayered Cambro-Ordovician limestones and dolomites is found both in the autochthonous Mohawk Valley section and in the allochthonous Taconic thrust sheets. This similarity suggested to Jacobi et al. (2006) that the dolomitization had occurred early in the history of the carbonates, before the carbonates had been inserted into the Taconic orogen and involved in the Taconic thrusting.

HYDROTHERMAL FLUID MIGRATION EFFECTS

PHYSICAL CHARACTERISTICS

Mohawk Valley Region (Central and Western)

The fluid migration in the Cambro-Ordovician section in New York State is recorded by veins in pre-existing fractures (Figure 5), in vugs that in many cases are localized in certain facies (e.g., Marner et al., 2008, Figure 6), such as stromatolites (Figure 6b), and in breccias (Figure 7). Significant sulfide mineralization is not common along the vein-filled fractures, but relatively rare sulfide deposits are observed along the major faults in the Little Falls quadrangle. Such deposits occur in the Little Falls Formation along the Dolgeville fault (Figure 8) and along the Little Falls fault at an abandoned sulfide mine found by Jacobi that appears to have no published record. The relative timing of the different crystallization phases can be determined from the layers of different minerals in many of the vugs and veins. For example, in Figure 6b some anthraxolite deposition predates the dolomite crystallization. In general the sequence of mineralization in the Mohawk Valley Cambro-Ordovician section is as shown in Figure 8 and is in agreement with that proposed by Smith (2006) based on core data. The mineralization sequence is a typical hydrothermal precipitation series (see Smith, 2006, for details).

The distance of mineralization away from the major faults, which are presumed to be the primary fluid migration pathways, was generally thought to be fairly limited, based on graphs such as those shown in Figure 10a. In these graphs, it appears that mineralized localities drop of quite precipitously away from the faults, no matter which trend the faults have, and that mineralization (and presumed fluid flow) occurred primarily within a few hundred meters of the faults, on the order of < 200m. However, the field localities are also localized along, or near, the faults, so that the steep drop off in mineralized sites away from the faults is primarily apparent, not real. For example, with sufficient sites, and with the mineralized field locations normalized to the total number of field locations at the same distance from the fault, there is actually no significant drop off in mineralization sites within about 1000m of NNE-striking faults (1000 m is as distant as field locations commonly occur from NNE-striking faults; Figure 10b, Agle, 2008). Within that distance, about 30-60% of the sites have experienced mineralization, with a maximum of 100% at some distances (Figure 10b).

The vein-filled fractures in the Utica in the Little Falls graben strike primarily NNE and WNW; a relatively minor number of veins trend ENE and EW (Agle, 2008; Jacobi et al., 2008; Figure 10). The NNE-striking veins are parallel to the NNE-striking faults and presumed related to stress fields associated with motion on these faults. The WNW-striking veins are parallel to the WNW-striking cross-faults, but as discussed below, WNW-striking veins increase in frequency near NNE striking faults, consistent with a stress field associated with reverse-slip motion on the NNE-striking faults. The vein-filled fractures in the Trenton/Black River in the Little Falls graben strike primarily WNW; a small number of veins trend NNE and EW (Agle, 2008; Jacobi et al., 2008).

The spacing, orientation, and thickness of vein-filled fractures varies toward the NNE-striking faults, based on sub-orthogonal transects (recalculated to distances orthogonal to the faults) at the Manheim Fault (Figures 12 and 13) and the Little Falls Fault (Figure 14). At the Manheim Fault, vein-filled fractures that are parallel to the fault (set A) display an isolated fracture frequency increase about 70 m away from the fault, but distinctly do not increase in fracture frequency closer to the fault (Figure 12). In contrast the vein-filled fractures that are oriented orthogonal to the fault (sets C and D) increase in fracture frequency dramatically about 55 m away from the fault. (ENE-striking fractures are not present at these locales.). The thickness of veins (a proxy for the fracture aperture at the time of vein filling, Figure 13) orthogonal to the fault (set D) also increases toward the fault, with a general increase about 70 m away and a final sharp increase about 15 m away where the aperture reaches 8 mm. The veins parallel to the fault (set A) also increase in thickness near the fault. A less complete transect at the Little Falls Fault (Figure 14) shows a similar relationship: the orthogonal fractures increase in fracture frequency toward the fault, whereas those parallel to the fault do not. Further, on the Manheim Fault transect, no ENE-striking faults are observed within 200 m of the fault.

These two single transects present a consistent picture with the frequency of WNW-striking veins increasing toward the NNE-striking faults. Agle (2008) compiled fracture frequencies for all fracture sets and at distances up to 6 km from the NNE-striking faults, and found that at some localities both the NNE and WNW striking fractures increase in fracture frequency toward the NNE-striking faults within about 200 m for the NNE-striking fractures and within about 100 m for the WNW-striking fractures, distances that are comparable (but larger than) those from the individual transects. However, the bulk of the localities show no significant increase in fracture frequency of NNE and WNW-striking fractures toward the faults, and NNW-striking fractures actually decrease in the closest 150 m to the faults.

The increase of WNW-striking veins close to the NNE-striking faults was first predicted in 2003 from analyzing the horizontal stress fields associated with the evolving Taconic convergence (Figures 15, 16; Jacobi et al. 2003b). Jacobi et al. (2003) had predicted that the rotation of SH about a vertical axis should occur during the Taconic orogeny, with Sh directed EW during early convergence (Figure 15) and SH directed EW during subduction zone "jamming" (Figure 16), with the result that the NNE-striking formerly normal faults should become high angle reverse faults. This rotation in stress fields would result in more NNE-striking veins during the early convergence, and more WNW-striking veins during late convergence. Thus, the discovery of WNW-striking veins increasing in frequency close to the NNE-striking fault is entirely consistent with the stress rotation model. The WNW-striking veins are thus recording a stress field near the end of the Taconic convergence, during subduction jamming, which is consistent with the veins occurring high in the stratigraphic section. In fact Cross (2004) and Cross et al. (2004) documented a possible upsection rotation in the primary fracture trends—from NNE to WNW, consistent with this proposed stress rotation.

Eastern Mohawk Valley

Hanson and Jacobi (Hanson, 2008; Hanson et al., 2010) performed a detailed structural study on features observed in a 360 m unoriented vertical core (71-NY-2) that penetrated the Cambro-Ordovician section near Saratoga Springs, NY (for location of the core, see Figure 3). Four hundred and fifty-five vein-filled fractures and faults were described and measured in the core. The Utica displayed relatively little deformation, whereas the Schenectady and Frankfort formations are highly fractured and exhibit discrete deformed zones that include 94 slickensided/fiber calcite surfaces, many coated with anthraxolite. The upper three deformation zones include soft-sediment deformation and scaly cleavage. The sediments in the deformed intervals are mid Katian (late Caradocian) in age (~450-448Ma). The soft sediment deformation, scaly cleavage, and localization of brittle fractures in soft sediment deformation zones suggest these deformation zones were the sites of progressive deformation during dewatering in the late Taconic.

In order to determine relative timing of the structural features, and to determine relative slip vectors on the features, Hanson and Jacobi (Hanson, 2008; Hanson et al., 2008) used rhombochasms in the veins, vein offset, bedding offset, cut veins, slickensides and slickenfibers (for example, see Figure 17). The result was that both normal faults and thrust faulting are prevalent in the core, primarily in the Frankfort and Schenectady units, not the Utica. No strike slip (oblique slip) indicators were discovered. In a few cases, slip vectors inferred from rhombochasms were confirmed by either bedding or vein offsets.

Nineteen samples were collected from vein-fills for δ^{13}C and δ^{18}O stable isotopes, $^{87/86}$ Sr, and fluid inclusion analyses; the vein-filled fractures sampled were: normal faults, thrust faults (high angle and bedding parallel), horizontal fractures, shallowly dipping fractures, and four steeply dipping fractures. The results of these analyses are reviewed in the geochemical section of this report.

Central New York State

In 2006 a joint UB-DOE-Talisman-Norse Energy project retrieved the first oriented horizontal core from the Schwingel #2 horizontal well in the Black River carbonate in a Talisman TBr field in central NYS (Figure 18). The core is 11.18 m long. An FMI log was collected in the same hole, providing an independent verification of the core orientation and depth. The objectives of the core study were to determine the deformation, geochemical and geotechnical characteristics of the Trenton/Black River play in the Southern Tier of New York State. This gas play had the largest on-shore continental USA gas well two years in a row.

The results of detailed study of the structural aspects and geochemistry of the veins in the core were reported in Jacobi (2007), Agle (2008), Agle et al. (2008), Jacobi et al. (2008a), and Marner et al. (2008). A brief review of salient points is provided herein. Jacobi and Agle measured and described 233 structural features on the full diameter core (pre-slabbed), including 94 veins and 43 stylolites. On the slabbed core, 179 features were measured and described, including 93 veins and 42 stylolites. Many of the veins exhibited rhombochasms, from which a sense of incipient motion can be inferred (Figure 19). Kinematic indicators, cross-cutting and abutting relationships on over 200 veins and stylolites document a complex, multi-phase deformation history (for example, see Figures 20, 21; Jacobi et al. 2008a, Marner et al., 2008).

The earliest veins strike ENE, parallel to the reactivated Iapetan-opening faults in the area. These veins display rhombochasms which indicate left-lateral motion. These veins are developed before the generation of horizontal stylolites. Since horizontal stylolites form under shallow loading conditions (as shallow as 100m), these fractures are probably related to early tectonism before the Trenton/Black River had significantly subsided and been loaded. That fluids are migrating through these open fractures (and faults) at near surface conditions (possibly <100m), suggests 1) the Laurentian convergence faulting was coeval with the Trenton/Black River development, 2) the fractures and faults were open to the seafloor at that time, and 3) the source of fluid was therefore most likely seawater, which could provide the Mg necessary for dolomitization after the fluid had been heated in deeper reaches of the fault systems. In this model there is no need for a high-Mg igneous body at depth (e.g., ultramafic) to be leached as a source for the Mg, unlike early models proposed by Smith that included an ultramafic source rock for the Mg.

Following horizontal stylolite development (i.e., the Black River was buried by more than 100m of sediment, Phase 2 in Figure 23), apparently the same horizontal stress conditions existed at first, resulting in more ENE-striking veins with left-lateral motion (phase 4 in Figure 23), as well as WNW- and NW-striking veins with right-lateral slip. However, after those veins developed, the horizontal slip vector on the ENE-striking veins reversed, such that ENE-striking veins are now right lateral (phase 4 in Figure 23). Following these veins, unloading resulted in horizontal veins (Phase 5 in Figure 23) and is consistent with late Taconic time (or neoAcadian).The orientation of the later vertical stylolites is consistent with an Alleghanian NW-directed push (Phase 6 in Figure 23). NNE/NE-striking left-lateral veins that postdate the vertical stylolites could reflect late Alleghanian or younger fluid migration. In this model, based on key stylolite geometries (horizontal and vertical), the primary fluid migration and precipitation did not occur in the Alleghanian—rather it occurred before the onset of the primary Alleghanian motion, since it predates an unloading event that itself predates the Alleghanian NW-directed push.

GEOCHEMICAL CHARACTERISTICS OF THE FLUID(S)

Discrimination crossplot of d^{13}C ($^{0}/_{00}$)$_{PDB}$ against d^{18}O ($^{0}/_{00}$)$_{PDB}$ (Figure 24)

These and metal abundances clearly show a spatial variation from the central and eastern part of the Mohawk Valley to the western part at Little Falls quadrangle and into the Finger Lakes region where the horizontal core was taken. Structural differences that could account for these geochemical changes in the fluids include closer to the Taconic deformation front in the east, and larger throw faults in the east where basement is thrown against the lower Paleozoic section (although the same occurs along the Little Falls Fault in the western part of the Mohawk Valley).

Eastern Mohawk Valley (Figure 24a). In the eastern Mohawk Valley (vertical core 75-NY-2), samples of veins in primarily the Ordovician Frankfort and Schenectady formations constitute two groups based on d^{18}O values (Figure 24d). (These groups may merge with more analyses). One group has very low (negative) d^{18}O values, and overlaps d^{18}O values of samples (<13 $^{0}/_{00}$ PDB) from 1) mineral "beards" associated with metamorphic mineral dissolution during cleavage development in the Taconic allocthons and 2) veins associated with Taconic thrusts (Goldstein et al., 2005; Hilgers and Sindern, 2005; Lim et al., 2005), although the bulk of published metamorphic dissolution samples are more strongly negative in d^{18}O than the core samples. Based on salinity data, Selleck (2010) proposed a group (Selleck "A" in Figure 24a) with very negative d^{18}O values that he believes represent fluids that leached basement. This group has d^{18}O values of about < 12.5 $^{0}/_{00}$PDB, and overlaps more significantly the samples from the vertical core. However, from the d^{13}C-d^{18}O cross plot, it is obvious that basement leaching fluids vs. mineral dissolution fluids during cleavage develop cannot be easily discriminated (a situation that is not surprising considering the thermo-dynamics).

The other group of samples from the vertical core has less negative d^{18}O values (about -11 $^{0}/_{00}$PDB) but distinctly higher d^{13}C values of about +1 to +10 $^{0}/_{00}$PDB. This group significantly overlaps Selleck's (2010) Group B which has maximum d^{13}C values of about +16 $^{0}/_{00}$PDB (Selleck "B" in Figure 24a). Such high values of δ^{13}C have been found in cements 100-300 m below the seafloor in the accretionary complex on the Peru convergent margin (Thornburg and Suess, 1990). They observed that d^{13}C in the cements is enriched as methanogenesis proceeds. The d^{13}C values range from -20.1 $^{0}/_{00}$PDB near the surface where sulfate reduction occurs to +17.4 $^{0}/_{00}$PDB at subsurface depths of about 320 m where carbonate reduction with methanogenesis occurs. Thornburg and Suess (1990) suggested that high angle fault systems could rapidly deliver these fluids over relatively long distances with the result that the fluid chemistry would not evolve appreciably, thus providing δ^{13}C dolomitic fluids to other depths and regions. Very high d^{13}C ($^{0}/_{00}$)$_{PDB}$ values in carbonate in the Monterey Formation (up to +19 $^{0}/_{00}$PDB) have also been explained by experimental evidence from methane producing bacteria (Murata et al., 1967). Agle (2008) suggested that residual organic matter in the fracture or wall rock could have been attacked by these methane producing bacteria, resulting in carbonate veins with high $d^{13}C$ values. From this discussion, it is apparent that *in terms of* $d^{13}C$ it is not necessary to invoke basement leaching or mineral dissolution during cleavage development to arrive at Selleck's (2010) Group B values with heavy $d^{13}C$ $(^{0}/_{00})_{PDB}$ values. However, one of the samples with heavy $d^{13}C$ $(^{0}/_{00})_{PDB}$ values was analyzed for $^{87}Sr/^{86}Sr$ and found to have a very high ratio (0.71422). Thus, at least in this one case, the $d^{13}C$ $(^{0}/_{00})_{PDB}$ carbonate also was precipitated from a fluid that had leached basement or volcanic ash or was partly derive from clay dissolution. In conclusion, the two different fluids, one associated with mineral dissolution in the accretionary prism (and or with basement leaching) mixed in varying amounts with seawater-modified fluids associated with carbonate reduction and methanogenesis at depths of >100-300 m. These fluids also probably mixed with seawater. All the fluids may be Taconic or the heavy $d^{13}C$ $(^{0}/_{00})_{PDB}$ fluids could be Alleghanian. Based on $d^{13}C$ $(^{0}/_{00})_{PDB}$ values alone, the source of the heavy $d^{13}C$ $(^{0}/_{00})_{PDB}$ fluids could be seawater or include a component of mineral diagenesis from the fluid flow through the accretionary prism or basement.

Central Mohawk Valley (Figure 24b). In the central part of the Mohawk Valley (from Hoffman's Fault to the Little Falls quadrangle), the discrimination crossplot of $d^{13}C$ $(^{0}/_{00})_{PDB}$ against $d^{18}O$ $(^{0}/_{00})_{PDB}$ clearly shows that the vein compositions form a field that generally falls in the Mississippi Valley hydrothermal field (MVT; red Xs in Figure 24b; Cross, 2004 and Cross et al., 2004). Similarly, vug fills form a field that significantly overlaps the vein field and the MVT field (black Xs in Figure 24b). Significantly, matrix samples fall almost exclusively outside Mississippi Valley hydrothermal field (blue Xs in Figure 24b). In the central Mohawk Valley region, it is clear that the veins and vugs are similar to hydrothermal fluids found in MVT deposits. The veins and vugs with strongly negative $\delta^{18}O$ values ($< 13\ ^{0}/_{00}$PDB, near the left edge of the Mississippi Hydrothermal field) fall in the fields of fluids derived from mineral dissolution during cleavage development in the Taconic allocthons (see discussion above and compare Figure 24b to Figure 24a), and in the field of fluids that leached basement with $\delta^{18}O$ values of $<12.5^{0}/_{00}$PDB. Vug and vein samples in the black dashed field (Figure 24b) fall in the Selleck B group; the samples with heavier $d^{13}C$ $(^{0}/_{00})_{PDB}$ values in this group ($+\ 1^{0}/_{00}$PDB) may indicate a contribution from carbonate reduction with methanogenesis in fluids mixing from the accretionary prism.

Western Mohawk Valley (Little Falls quadrangle) (Figure 24c). Farther west in the Little Falls quadrangle the data are more variable (Figure 24c). Vein samples taken in Precambrian basement north of the Little Falls quadrangle along the continuation of the Little Falls Fault system at Indian Lake have a MVT signature (red triangles). However, the veins in the dashed field in Figure 24c, the Tribes Hill (pink triangle),Trenton (blue triangles), Flat Creek (yellow triangles), and some Indian Castle samples (brown triangles), have an equivocal origin—they are close to the MVT field, and so might be considered MVT.

None of the samples from veins in the Cambro-Ordovician section has $\delta^{18}O$ values as strongly negative ($< 13^{0}/_{00}$PDB) as those from mineral dissolution during cleavage development in the Taconics (see discussion above and Figure 24d), although the Trenton matrix (Figure 24b) has a d^{18}O value that approaches the basement leaching field (< 12.5 $^{0}/_{00}$PDB). The two veins in the Precambrian at Indian Lake have distinctly more negative d^{18}O values (<12 $^{0}/_{00}$PDB) than any of the other samples also do not fall in the fields of basement leaching and mineral dissolution during cleavage development. Both veins have a stronger negative δ^{13}C value than the basement leaching field and mineral dissolution during cleavage development field (compare Figure 24c to Figure 24a), and the WNW-striking vein is also more negative in δ^{18}O than the fields of basement leaching and mineral dissolution during cleavage development.

The Dolgeville (green triangle in Figure 24c) and Indian Castle (brown triangles) outliers with extremely heavy d^{13}C ($^{0}/_{00}$)$_{PDB}$ values at first appear to be analyses errors. However, duplicates of these samples are remarkably similar. The high d^{13}C ($^{0}/_{00}$)$_{PDB}$ values may indicate that carbonate reduction with methanogenesis at sub-seafloor depths from about 150 m to greater than 300m (see discussion above, and compare Figure 24c to Figure 24a), or could indicate later methanogenesis of carbon (bitumen) in the fracture systems.

Finger Lakes Region (Figure 24d). In the Finger Lakes region, the stable isotope values for both the matrix and the veins in the Schwingel #2 horizontal core (Figure 24d) have the same compositions as those that formed the dashed field in Figure 24c, except for one vein that clearly falls in the MVT field. These samples, and those from the Whiteman core (Smith, 2006) lie close to the MVT field, and so may be considered MVT, but only one sample actually falls in the MVT field. None of the samples has d^{18}O values as strongly negative as those from mineral dissolution during cleavage development in the Taconics (see previous discussion and Figure 24a), although the core matrix dolomites and a few veins (Figure 24d) have values that approach the basement leaching field (< 12.5 d^{18}O).

^{87}Sr/^{86}Sr Plot (Figure 25).

Finger Lakes. The ^{87}Sr/^{86}Sr ratios in both veins and matrix in the Schwingel #2 horizontal core and in the Whiteman core (Smith, 2006) are tightly constrained (narrow gray band across the plot in Figure 25a), and have values that match seawater values of Taconic age (where the gray band intersects the purple band of Taconic age in Figure 25). The values are distinctly too high for Alleghanian times, but are possible for Acadian times, but not the “neoAcadian times” that typify the Appalachian orogenic belt east of the Hudson River. Thus, it is probable that these veins and matrix represent precipitation from seawater in Taconic (TBr) times.

Central Mohawk Valley. The data from the Mohawk Valley have much more variance than the Finger Lakes samples. The Trenton matrix (Agle, 2008; Agle et al., 2008) and the Cambrian Tribes Hill calcite matrix (“quarry calcite” in Figure 25a) in central Mohawk Valley (Smith and Nyahay in Agle et al., 2006) have ratios that are consistent with precipitation from seawater of Taconic age. In central Mohawk Valley the dolomite at the Tribes Hill quarry and the Little Falls dolomite matrix both have similar significantly elevated ratios that suggest the fluids leached rocks with a feldspar component (felsic igneous/volcanic or arkose) or the fluid was a mixture of seawater with a contribution from clay dissolution in the Taconic accretionary prism.

Modern accretionary prisms also commonly contain carbonate precipitates with $^{87}Sr/^{86}Sr$ values distinct from seawater values of the carbonate age. For example, Sample et al. (1993) proposed that carbonate cements with high $^{87}Sr/^{86}Sr$ values of 0.70975 to 0.71279 were related to fluids with strontium derived from clay-rich parts of the Cascadia accretionary prism. They believed that the carbonate preferentially precipitated along channeled fluid flow in a zone of vertical faults at the deformation front of the wedge. Sample et al. (1993) observed that the pervasiveness of the carbonate precipitates and the isotope data imply that the vertical fault zones are efficient conduits for fluid dewatering from deep levels of the accretionary wedge. Similarly, in the Barbados accretionary prism carbonate with $^{87}Sr/^{86}Sr$ values distinct from present-day seawater (in this case, lower than present day) precipitated from fluid flow along fault zones, principally the decollement (e.g., Kastner et al., 1997); these $^{87}Sr/^{86}Sr$ values are thought to reflect clay dehydration effects. In the Costa Rica accretionary complex Silver et al. (2000) noted that Sr isotope ratios are 1) strongly affected by diagenetic reactions, 2) distinct from seawater values in calcareous sediments, and 3) the Sr isotopic values become more radiogenic in a volcanic-rich section, suggesting a volcanic ash diagenesis for the $^{87}Sr/^{86}Sr$ deviations from seawater.

Western Mohawk Valley. WNW- and NNE-striking veins in Tribes Hill, Trenton, and Flat Creek all have values that are consistent (or nearly so) with a seawater source in Taconic times (samples in the dashed ellipse in Figure 25a). These relatively low $^{87}Sr/^{86}Sr$ ratios are also consistent with seawater in the later neoAcadian and Alleghanian times. In contrast to these low $^{87}Sr/^{86}Sr$ ratios values, other veins in the Trenton (blue), as well as veins in the Dolgeville (green) and Little Falls (purple) have significantly elevated $^{87}Sr/^{86}Sr$ ratios, similar to those in the Little Falls and Tribes Hill farther east (all incorporated in the dashed box field in Figure 25a). The possible cause(s) of the high $^{87}Sr/^{86}Sr$ ratios in the *western* Mohawk Valley samples are the same as those proposed for the higher ratios in *central* Mohawk Valley. Agle (2008) argued that there is no evidence for a significant leaching of basement rocks in the Little Falls quadrangle, based on metal abundances and REE abundances, and the present report demonstrates that there is little effect from the volcanic ash layers (no strongly negative Eu anomaly). If basement and ash leaching are not prominent sources, then the high $^{87}Sr/^{86}Sr$ ratios in the veins from the Little Falls quadrangle may reflect sea water mixing with fluids from clay dissolution. The distinct group in the dashed ellipse (Figure 25a) versus those samples with elevated $^{87}Sr/^{86}Sr$ ratios indicates different fluid masses, either representing several periods of fluid migration, possibly Taconic, neoAcadian, and Alleghanian, or different fluids migrating during one orogeny. Both are possible alternatives. If both masses are Taconic, then the seawater signature samples represent early circulation, and the high $^{87}Sr/^{86}Sr$ ratio samples indicate seawater mixing with a later fluid drive from clay dissolution in the Taconic allocations. Conversely, the high $^{87}Sr/^{86}Sr$ ratio samples could indicate that the circulation cells reached basement to leach—either because more significantly open faulting developed over time, or that the throw on the faults became sufficiently large to juxtapose Precambrian basement against the Lower Paleozoic units, providing a local source for basement leaching by fluids along the faults and in the hanging wall section. Although this second alternative is plausible in terms of $^{87}Sr/^{86}Sr$, the REE do not support a highly significant influence from leached basement in most of the Cambro-Ordovician section veins in the Little Falls quad.

Eastern Mohawk Valley. Samples from core 75-NY-2 also displays two groups—one with $^{87}Sr/^{86}Sr$ ratios that are consistent with Taconic seawater values (and fall in the exact range of the Finger Lakes and Mohawk Valley quarry calcite values (the gray band in Figure 25a and 24b). These veins fill fractures that experienced normal fault slip. A second group of extremely high $^{87}Sr/^{86}Sr$ ratios indicates a fluid with a component of fluids from Taconic metamorphic clay dissolution or ash, or from basement leaching. A horizontal vein sample with high $^{87}Sr/^{86}Sr$ ratios is associated spatially with low angle thrust veins. Assuming this vein is structurally related to the thrusts, the high $^{87}Sr/^{86}Sr$ ratios are consistent with the tectonic model that suggested EW directed compression in late Taconic in the Mohawk Valley region, since the fluid flood from metamorphic clay dissolution in the Taconics would arrive at any site later that the early seawater circulation down the normal (open) faults in early Taconic times.

Base Metals and Trace Elements (Figure 26)

Central Mohawk Valley. Forty-one samples of secondary calcite/dolomite were analyzed for base metal and trace element abundances (Figure 26a; Cross, 2004; Cross et al., 2004). The samples were divided into two groups based on relative transition element abundances. Group A (28 samples) is characterized by higher transition metal abundances than Group B (13 samples). For example, Group B has negligible Cr abundances (.22-1.67 ppm) whereas group B samples vary from 3 to 42 ppm. The ratio between the average transition element abundances for group A and B varies from 2.70 to 34.39 (except for Fe). All Group A samples were collected within 350 m of faults, and all Group B samples more than 1 km from faults.

All samples are highly enriched in Cu and Cd relative to typical carbonates and to the abundances of other element measured such as Cr, Mn, Fe, and Ni (Figure 26a). The average enrichment of Cu in Group A samples is about 100 times and Cd is about 200 times (Figure 26a), and in Group B both Cu and Cd are enriched about 10 times. That the enrichment increases toward the faults provides strong evidence that the faults were the source of the fluids, and that bedrock at distances greater than 1 km (and perhaps 300 m) experienced more dilute fluids.

The enrichment of Cu also provides evidence that these fluids did not leach local sediment as a source for the Cu (Cross, 2004; Cross et al., 2004). In the Mohawk Valley samples Cu is enriched by a factor of 21 for Group A samples relative to the Trenton equivalent Glen Falls Formation (using Garver et al., 1996 trace element data) and by more than 10 times relative to the Utica, and about 5 times relative to the Schenectady (Cross, 2004). Cu in sediment is mobile under hydrothermal conditions (Rollinson, 1993), but Cross (2004) contends that comparable enrichment in similarly mobile elements such as Mn and Zn would be expected if these sediments were the source. Instead, Mn and Zn in the Mohawk Valley samples are depleted relative to the abundances in the sedimentary units (compared to the ratio of Cu abundance in veins to sediments, the Zn ratios are less by a factor of 10+). However, Cu sulfide hydrothermal deposits commonly exhibit preferential uptake and precipitation of Cu (e.g., Sweeney et al., 1991). Never-the-less, hydrothermal fluids leaching basement complexes have been proposed as a source of Cu in Cu sulfide deposits, especially where sediments rich in Cu (such as red beds) do not exist. For example MVT hydrothermal fluids leached Precambrian basement before precipitating Cu-rich MVT deposits in the Cambrian Boneterre Dolomite in Missouri (e.g., Shelton et al., 1995), low-temperature connate and groundwater leached basement in Zambia (e.g., Sweeney et al., 1991), and modern extreme hydrothermal marine systems leached basalt (e.g., Humphris et al., 1998). Thus, the observed Cu enrichment in the veins is consistent with leached basement units, and the high Cu abundances probably exclude the non-red bed Taconic and older sediments as the principal source for Cu in the mineralizing fluids. Rather, Cross (2004) proposed that the enrichment of Cu was the result of hydrothermal fluid circulation into, and leaching of, basement rocks along fault systems.

Western Mohawk Valley (Little Falls quadrangle). Samples from the western Mohawk Valley generally do not exhibit significant Cu and or Cd enrichment relative to Ni (< 10 times), and in fact several samples are slightly depleted in Cu compared to Ni (Figure 26b; Agle, 2008). The only samples that display Cd enrichment are veins collected in the Precambrian basement along the northern extension of the Little Falls Fault (samples with a 150 prefix) and three samples from veins in the Indian Castle—one a horizontal vein, one a NE-striking vein, and the third a WNW-striking vein. Similarly, the only vein (except those in the Precambrian) with modest Cu enrichment (7.2 ppm) is the WNW-striking vein in the Indian Castle that also has enriched Cd.

The generally minimal Cu enrichment compared to Group A farther east supports Agle's (2008) contention that most of the fluid at Little Falls quadrangle did not significantly leach the basement rocks. However, the few veins high in the section (Indian Castle) that display characteristics similar to (but with lower abundances than) Group B farther east do indicate that these Indian Castle fluids had some propensity for limited leaching. If these fluids are related to the same fluid migration phase as that farther east, then it is probable that these fluids arrived late in the Taconic sequence in the Little Falls area, may have been colder than the fluids farther east, and primarily affected units higher in the section. The horizontal vein supports the relatively late stage of the anomalous veins, in that the simplest scenario for the horizontal vein indicates vertical unloading and indicates the end of the Taconic orogenic cycle.

Rare Earth Element (REE) Abundances (Figure 27)

Central Mohawk Valley. The chondrite-normalized REE abundances for groups A and B (defined above) for central Mohawk Valley samples are shown in Figure 27a. Because calcite precipitation from a hydrothermal fluid does not fractionate REEs (Carignan et al., 1997; Subias and Fernandez-Nieto, 1995) the relative abundances (and therefore the REE pattern) of the calcite/dolomite accurately reflect the source (although the absolute REE abundances in the secondary carbonates may differ from mineralizing fluid and its source).

The most distinctive feature of both groups A and B is the pronounced negative Eu anomaly. No non-volcanic sediment type standard has such a pronounced negative Eu anomaly (for example, see the composite curves in Figure 27a).

The enrichment in the LREE also indicates that the central Mohawk Valley fluids did not leach mafic MORB rocks. Felsic suites are characterized by Eu anomalies (the Eu is taken up by feldspar crystallization). More specifically, silicic continental arc and anorogenic igneous rocks that have sustained feldspar fractionation display very similar REE patterns to the Mohawk Valley samples, such as 1) anorogenic leucogranite (Hess, 1989), 2) evolved, silicic rocks from the continental arc plutonic, 3) volcanic rocks from the Coastal Batholith of Peru (Winter, 2001), and 4) late-stage anorogenic rhyolitic Bishop Tuff (Hess, 1989). Although chondrite-normalized REE patterns for average granitic rocks display Eu anomalies, the negative anomaly is not nearly as strong as in the Mohawk Valley samples, and the HREE are generally relatively enriched compared to the Mohawk Valley samples (i.e., the granitic HREE patterns are generally slightly flatter than the Mohawk Valley samples). It appears, then, that the most likely source for the REEs in the mineralizing fluids, based on the REE patterns, is silicic continental arc and anorogenic volcanic or plutonic rocks or their metamorphic equivalents. Were such rocks available for leaching in Taconic times in the central Mohawk valley?

The similarity between REE patterns of the central Mohawk Valley samples and Daly and McLelland's (1991) Adirondack meta-igneous suites 2 and 3 suggest that Adirondack basement rocks could be a source for the REEs in the Mohawk Valley mineralizing fluid (Figure 27b). Suite 2 is consists of meta-igneous gneisses of anorthositic, mangeritic, charnockitic and granitic composition. Suite 3 comprises granitic gneisses, and Suite 1, which does not have a negative Eu anomaly, is composed of tonalitic gneisses. The points of similarity include: 1) all samples in suites 2 and 3 exhibit negative Europium anomalies, 2) all three Adirondack meta-igneous suites show a strong HREE depletion, comparable to the Mohawk Valley samples, 3) the degree of LREE enrichment in the Adirondack meta-igneous suites (in particular Suite 1) is similar to the Mohawk Valley samples, 4) a few Suite 1 and Suite 2 samples display a slight La depletion, comparable to the depletion present in 19 Mohawk Valley samples, and 5) Chondrite-normalized abundances for Suite 1 samples are similar to the average Mohawk Valley sample; LREE abundances for suites 2 and 3 also are comparable to Mohawk Valley Group Asamples.

The similarity between REE patterns of the central Mohawk Valley samples and Daly and McLelland's (1991) Adirondack meta-igneous suites 2 and 3 suggest that Adirondack basement rocks could be a source for the REE in the Mohawk Valley mineralizing fluid. An additional source very likely could be the common meta K-bentonites in the Taconic section. Since these ash layers resulted from the Taconic silicic continental arc, REE patterns of these ash layers should have been similar to those observed in the vein samples before diagenesis. In fact REE analyses of an ash layer in the Utica (Figure 27c, Delano, et al., 1990) has a strong Eu negative anomaly, and exhibits extensive diagenesis of the REE out of the ash into the shale (in the "mixed layer", Figure 27c). Comparison of the ash REE pattern to the vein REE pattern shows marked similarities (Figure 27b), although the HREE are depleted in the veins compared to the ash sample. The ash diagenesis observed in the Utica could well be related to hydrothermal fluid circulation, as is commonly reported in accretionary prisms. For example, in the Barbados accretionary prism, volcanic ash was extensively altered by fluid flow from deep in the accretionary prism along fault zones (chiefly the decollement) and minor permeable layers (e.g., Gieskes et al. , 1990, Martin et al., 1996; Kastner et al., 1997).

In the central Mohawk Valley samples most transition and LIL elements, in particular Rb and Ba, are depleted in Rb relative to the standard sedimentary compositions (Cross, 2004). These elements are among the first elements to be mobilized and leached from sedimentary rocks under hydrothermal conditions (Rollinson, 1993). Thus, the central Mohawk Valley secondary calcite/dolomite samples should have higher concentrations relative to the sedimentary standards, rather than the much lower concentrations observed in the Mohawk Valley secondary carbonates. The low concentrations relative to the surrounding sediments of the highly mobile, soluble elements thus supports the proposal for a non-sedimentary source for these elements in the mineralizing fluids.

Western Mohawk Valley. The veins in western Mohawk Valley (Little Falls quadrangle) have a very different REE pattern (Figure 27d) from those in central Mohawk Valley. In general the primary differences are that the western Mohawk Valley samples do no exhibit a strong negative Eu anomaly, and some even exhibit a positive Eu anomaly (Figure 27d, Panel B). Furthermore, the LREE are significantly more enriched in the central Mohawk Valley samples, and the HREE have a flatter pattern in the Little Falls samples.

Inspection of the plots shows that in several cases the chondrite normalized pattern and abundances match fairly well with the enclosing wall rock, or nearby wall rock. A prominent example is the cluster of three of the four veins in the Precambrian north of the Little Falls quadrangle at Indian Lake. Veins 150B-A4, 150A-B8, and 150C have enriched chondrite normalized REE values compared to the remainder of the western Mohawk Valley samples, and are comparable to the enclosing Precambrian rocks (curve labeled pCB in Figure 27d, panel A) suggesting that the fluids leached the surrounding Precambrian units. The most prominent example of vein and matrix similarity is the vein in the Trenton (312A) that has a pattern extremely similar to that of the Little Falls Dolomite. Either the hydrothermal fluid leached the Little Falls dolomite or the fluid that dolomitized the Little Falls sample was the same as that in the Trenton vein. The depleted Tm values are especially distinctive, and are related to the dolomitization process (e.g., Qing and Mountjoy, 1995), although the depletion observed here is excessive.

The two Flat Creek samples (yellow, #7-A and #7-B in Panel B, Figure 27d) have flat HREE and moderately enriched LREE, similar to “average limestone” values and moderately similar to the Black River and Trenton samples in Panel A. These samples are distinctly depleted compared to the Utica sample in Panel A (Figure 27d) and the Utica samples in Figure 27c. The two samples with positive Eu anomalies may indicate leaching of rock rich in feldspar crystals; sample 150-A-4 is from the veins in the Precambrian at Indian Lake, and so the source may be Precambrian basement (see Suite 1 in Figure 27b). However, the REE pattern for this sample in general is distinctly not like the other veins at Indian Lake; rather it is very similar to the other veins in the Indian Castle, in which case, the positive Eu anomaly may have resulted from feldspar leaching in the Taconic crystal ash layers. If this vein represents fluid that leached the Ordovician section, then the distance of fluid migration was significant along the faults (a minimum of 35-40 km horizontal from present day Paleozoic cover), or the Ordovician sequence once covered this part of the Adirondacks. Slight positive Eu anomalies are common in carbonate veins, and in some case are associated with Au ore bearing veins that are derivation from SEDEX deposits and not from leaching of sediments (e.g., Rosenberg, 2009). The second positive Eu anomaly sample is from the horizontal vein in the Indian Castle (153-BP) that also is moderately enriched in Cd. This combination suggests leaching of basement (although ash layer diagenesis cannot be totally discarded).

The conclusion for the source of the leached element concentrations in the central Mohawk Valley veins is that the Taconic-aged sediments do not appear to have the necessary chemical abundances to provide the abundances observed in the veins. Hydrothermal circulation into basement and known diagenesis of the Taconic ash layers are two possible candidates for sourcing the leached element abundances. In the western Mohawk Valley, the REE abundances indicate leaching of surrounding, or nearby units. Particular conclusions are that some of the dolomitization in the Little Falls is exactly the same as a vein in the Trenton. Either the two are related to the same mineralization fluid, or the vein in the Trenton leached almost completely the Little Falls. Veins in the Precambrian at Indian Lake have two characteristic REE patterns suggesting two times of migration—one that leached the surrounding Precambrian and another that appears the same as the Indian castle veins. The Indian Castle type vein suggests that Ordovician (Utica) rocks did lie above the Adirondack dome, or that 35+ km of horizontal transport of the fluids took place.

MODEL

The fluid circulation in the Cambro-Ordovician section in central and eastern NYS has several fluid sources and at least three periods of circulation. In the first phase, dolomitizing fluids circulated along the active faults and into the Little Falls dolomite. This fluid circulation was proposed by Jacobi et al (2006b) to be coeval with the faulting that accompanied the development of the unconformity at the Cambrian Ordovician boundary. The stable isotopes of C and O are consistent with hydrothermal circulation in the matrix of the Little Falls dolomite, but the age of the dolomitization in this analyzed sample is uncertain—it could represent this early event, or the later events.

The second phase of fluid circulation is the principal phase described in this report. It is probable that there were at least three fluid systems that mixed to form the veins observed in the Cambro-Ordovician sequence. In central NYS (the Finger Lakes region), isotopes suggest that Taconic aged seawater first circulated and promoted vein development very early in the history of the Trenton/Black River—before the Black River reached sub-seafloor depths sufficient to develop horizontal stylolites-- perhaps 100 m). Strike slip motion on reactivated ENE-striking Iapetan-opening faults were already active at this time, in response to Laurentia converging with the continental-based arc, and this strike slip motion was recorded in the early veins. As burial continued, horizontal stylolites developed, but since the faulting remained active during convergence, ENE-striking vein fills associated with left-lateral and then right-lateral slip developed as a result of the SH rotating about a vertical axis as Laurentia tightened in collision with the arc. Jacobi et al. (2008) suggested that the close of the Taconic phase is documented by the horizontal veins in the core, which would reflect an unloading event. Apparently the Finger Lakes region was sufficiently distant from the convergent zone that the mineralizing fluids were not derived from significant basement leaching or mineral dissolution, based on Sr isotope data. Stable isotopes of C and O are consistent with hydrothermal, or nearly so, circulation. The $d^{13}C$ values suggest precipitation at moderate depths below seafloor (on the order of 100 m) with a moderate fluid component associated with carbonate reduction with methanogenesis. The $d^{18}O$ are also consistent with fluids without significant basement leaching or mineral dissolution.

Another end member in terms of fluid circulation is the veins in the unoriented vertical core in the eastern Mohawk Valley. These veins fill fractures, normal faults and thrust faults (no strike slip/oblique slip indicators were found). Deformed zones in the upper units (Frankfort and Schenectady) show a progressive deformation from soft-sediment deformation to brittle faulting (including some thrusts). Based on the progression from soft to brittle deformation in these deformation zones, the zones developed in late Taconic, including the veins along the associated normal and thrust faults (Hanson et al., 2010). These veins, which are primarily in units above the Utica, suggest two fluid sources (either reflecting different times or migration paths). One fluid was derived from mineral dissolution during cleavage development (and/or, less likely, leached basement), based on both the strongly negative $d^{18}O$ values and the high Sr isotope ratios in the samples. Another fluid promoted precipitation of carbonate with heavy $d^{13}C$ values (positive values); this precipitation probably occurred as a result of carbonate reduction with methanogenesis, which for similar heavy $d^{13}C$ values in the accretionary prism offshore Peru occurred between 100 m and 300 m depth. The single $^{87}Sr/^{86}Sr$ analysis conducted on samples with heavy $d^{13}C$ values indicates that the fluid either leached basement and/or volcanic ash layers and/or had a strong component from clay dewatering/dissolution ($^{87}Sr/^{86}Sr$ = 0.71422).

In the central Mohawk Valley, stable isotopes of C and O of both veins and vugs of the Little Falls and Tribes Hill carbonates indicate a hydrothermal origin, unlike the carbonate matrix values. The Tribes Hill quarry dolomite has high Sr isotope ratios that indicate fluid that leached basement or volcanic ash or was (partly) derived from clay dewatering/dissolution. No samples with heavy $d^{13}C$ values indicate a lack of carbonate reduction with methanogenesis for these units low in the stratigraphic section. High abundances of Cu and Cd indicated basement leaching to Cross (2004). Distinctive REE patterns with Eu negative anomalies strongly suggest massive volcanic ash diagenesis by these fluids or Adirondack basement leaching or both. (Other accretionary prisms also exhibit strong diagenesis of volcanic ash layers). In general the units stratigraphically below the Utica display NNE/NE- and WNW- striking fractures and vein fills, but in the Utica WNW-striking fractures are dominant, and along the NNE-striking fault primarily WNW-striking fracture fills increase in density. This increase in WNW-striking veins adjacent to the fault is consistent with the model of Jacobi et al. (2003) that suggested that the originally normal faults (in early Taconic) became high angle reverse faults in the late Taconic when the convergence was “jammed”.

In western Mohawk Valley, the Utica carries both NNE-NE and WNW-striking vein fills, but the WNW-striking vein fills, like the region to the east, increase in fracture frequency toward the NNE/NE-striking faults. Geochemical considerations suggest several fluids precipitated vein material in this area. Stable isotopes of C and O of veins in the carbonates indicate a near-MVT hydrothermal origin, and the matrix of the Little Falls matches the MVT field for stable isotopes of C and O. Dolgeville and Indian Castle veins have heavy d^{13}C, consistent with precipitation during carbonate reduction with methanogenesis at sub-seafloor depths from about 150 m to greater than 300m (or consistent with later methanogenesis of carbon (bitumen) in the fracture systems). ^{87}Sr/^{86}Sr analysis indicate at least two mineralizing fluids: 1) Taconic-aged (or neoAcadian or Alleghanian aged) seawater for veins in the Trenton, Tribes Hill, Flat Creek units , 2) elevated ^{87}Sr/^{86}Sr water carrying dewatered clay diagenesis products (and, less likely, leached basement or volcanic ash products). The lack of generally relatively high Cu and Cd in the sedimentary section, and the lack of strongly negative Eu anomalies suggest that the fluids did not significantly leach either basement or the volcanic ash layers typical in the central Mohawk Valley region (except for one sampled vein). Rather, the veins have chondrite normalized REE abundances that suggest an influence from the units associated with the veins.

The only strong evidence for Alleghanian (or younger) vein development comes from the horizontal core in the Finger Lakes region. There, NE-striking vertical stylolites that are assumed to be related to Alleghanian tectonics are cut by later NNE-striking veins with left-lateral slip. It is therefore likely that at least three phases of vein development are recorded in central and eastern NYS—the Cambrian/Ordovician unconformity event, the Taconic and the Alleghanian (neoAcadian is also probable, but we have no strong evidence for such a fluid migration event).

CONCLUSIONS

Fracture studies and geochemical analyses of veins (as a proxy for the fluids from which the vein precipitated) in central New York State and the Mohawk Valley in eastern New York State reveal a complex history of fluid migration in the Cambro-Ordovician section that involved at least three periods of fluid migration and several fluid sources. Geochemical analyses included d^{13}C and d^{18}O isotopes, ^{87}Sr/^{86}Sr isotopes, REE, trace elements, transition and metals. In the central Mohawk Valley there is evidence for a dolomitizing event associated with the Cambrian/Ordovician unconformity. The principal recognized fluid migration events were associated with the Taconic orogeny. In central NYS in the Finger Lakes region, the vein precipitates in the Trenton/Black River in an oriented horizontal core were from Taconic-aged seawater, and the veins in strike-slip faults developed very early in the history of the Black River subsidence, perhaps while the Black River was shallower than 100 m below seafloor. Such a shallow depth is consistent with the proposal that the strike slip faults related to convergence were already active at this time. Following horizontal stylolite generation from continued subsidence, additional vein filling of strike slip faulting occurred, and the motion on the faults reversed (consistent with the proposed horizontal stress field rotations in the Jacobi et al. (2003) model during Taconic convergence).

Unlike the Finger Lakes region, in the Mohawk Valley, closer to the Taconic Front, the seawater was mixed with, and was modified by, several sources. In a vertical core through the Cambro-Ordovician section in the eastern Mohawk Valley near Saratoga Springs, two vein geochemical compositions are recognized. One has C and O isotopes that are similar to precipitates from clay dissolution during cleavage development in the Taconic accretionary prism. The second is related to carbonate reduction with methanogenesis possibly at sub-seafloor depths of 100-300m that resulted in heavy $d^{13}C$ $(^{0}/_{00})_{PDB}$ values. Both of these vein types apparently had varying contributions from at least two fluids, based on Sr isotopes: a seawater source and a fluid that leached basement, and/or volcanic ash and/or had a clay dissolution source. The veins are primarily associated with deformation zones the clastic section of the Frankfort and Schenectady. The vein fills are judged to be Taconic because the deformation zones display a progressive deformation from soft sediment deformation to brittle normal and thrust faults, and the sediments are dated as Caradocian.

Farther west in the “central” Mohawk Valley, stable isotopes of C and O of both veins and vugs of the Little Falls and Tribes Hill carbonates indicate a hydrothermal origin, unlike the carbonate matrix values. The Tribes Hill quarry dolomite has high Sr isotope ratios that indicate a fluid that leached basement and/or volcanic ash or was (partly) derived from clay dewatering/dissolution. High abundances of Cu and Cd indicated basement leaching to Cross (2004). Distinctive REE patterns with Eu negative anomalies strongly suggest massive volcanic ash diagenesis by these fluids (or less likely Adirondack basement leaching). In general the units stratigraphically below the Utica display NNE/NE- and WNW- striking fractures and vein fills, but in the Utica WNW-striking fractures are dominant, especially near NNE-striking faults. This increase in WNW-striking vein fills upsection and adjacent to faults is consistent with the proposed stress field rotations in the Jacobi et al. (2003) model that suggests the originally normal faults (in early Taconic) became high angle reverse faults in the late Taconic when the convergence was “jammed”.

Still farther west in the Little Falls quadrangle, the Utica carries both NNE/NE- and WNW-striking vein fills, but the WNW-striking vein fills, like the region to the east, increases in fracture frequency toward the NNE/NE-striking faults. Geochemical considerations suggest several fluids precipitated vein material in this area, but the distinct fluids present in the central Mohawk Valley with volcanic ash/basement Eu anomaly signatures are not observed in the Little Falls quadrangle. Stable isotopes of C and O in the carbonate veins indicate a near-MVT hydrothermal origin, and the matrix of the Little Falls has isotopes of C and O that match the MVT field. Dolgeville and Indian Castle veins have heavy $d^{13}C$, consistent with precipitation during carbonate reduction with methanogenesis at sub-seafloor depths from about 150 m to greater than 300m., or with later methanogenesis of carbon (bitumen) in the fracture systems. $^{87}Sr/^{86}Sr$ analysis indicate at least two fluids: 1) precipitation from Taconic-aged (or neoAcadian or Alleghanian aged) seawater for veins in the Trenton, Tribes Hill, and Flat Creek units , 2) precipitation from elevated $^{87}Sr/^{86}Sr$ from water carrying dewatered clay diagenesis products (and less likely from basement or ash leaching).

Detailed analyses of stylolites and veins in the oriented horizontal core in the Finger Lakes revealed NE-striking vertical stylolites of presumed Alleghanian age. These stylolites postdate the Taconic vertical and later horizontal veins. The Alleghanian stylolites are cut by NE-striking veins, strongly indicating that Alleghanian fluid migration also occurred in the region, as far west (and north) as the Finger Lakes region.

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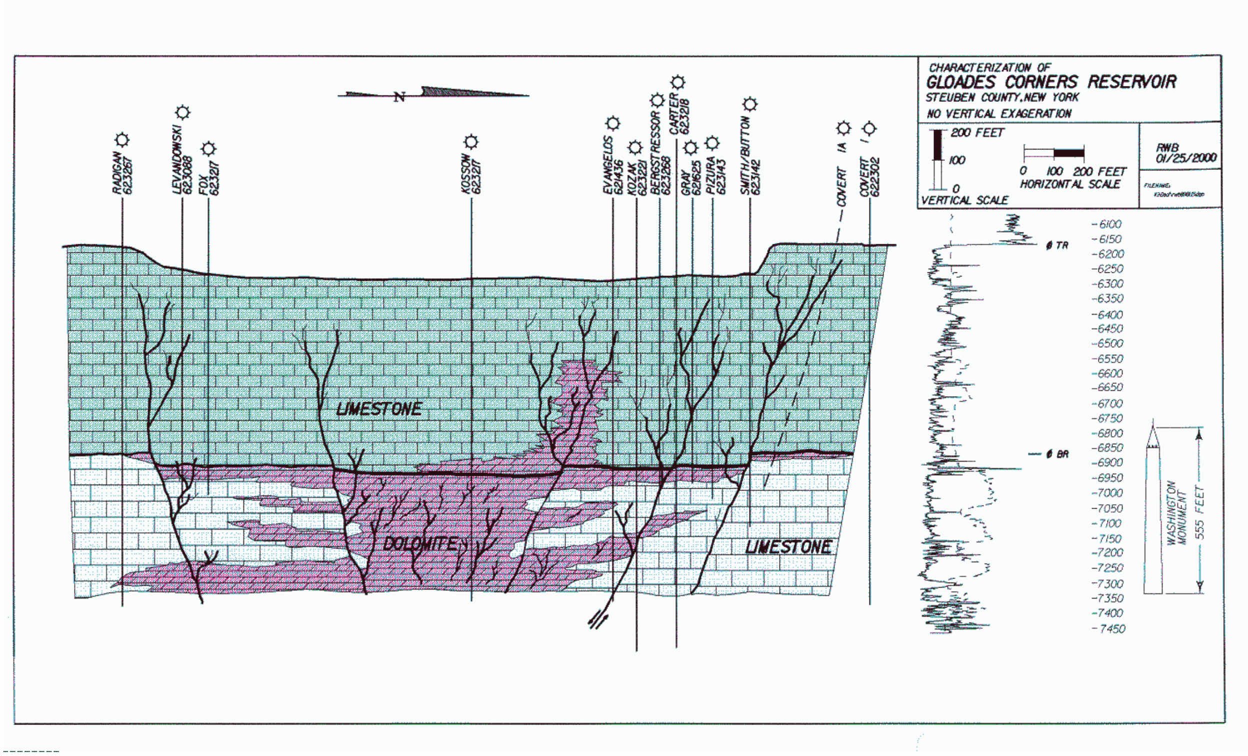


Figure 1. Model for Trenton-Black River gas fields. From Beardsley (1999).

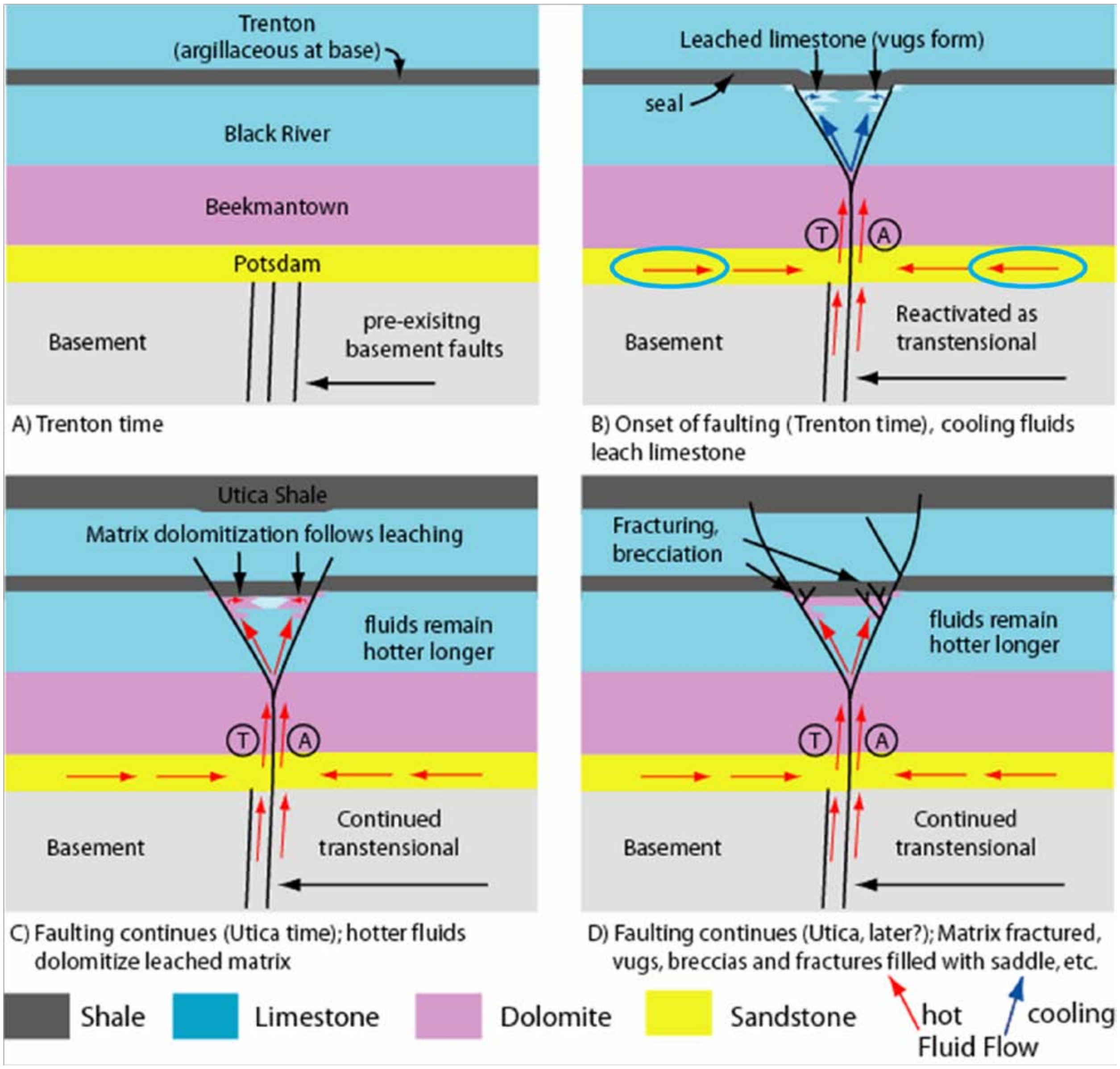


Figure 2.Smith's (2006) model for the Trenton-Black River gas field porosity development.

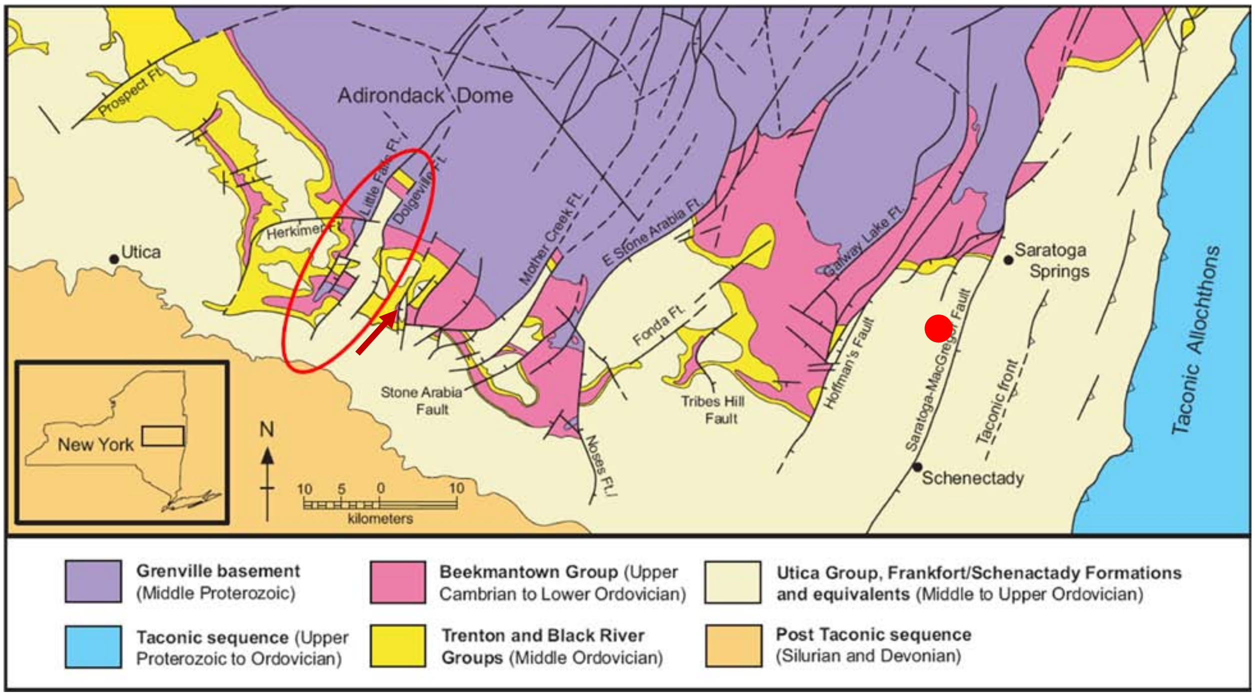


Figure 3. Fault systems in the Mohawk Valley region. Little Falls graben is circled in red. Manheim Fault indicated by red arrow. Location of vertical core 75-NY-2 indicated by red circle near Saratoga-MacGregor Fault. Map from Cross (2004), Cross et al. (2004), and Jacobi et al. (2004), map after Fisher (1980).

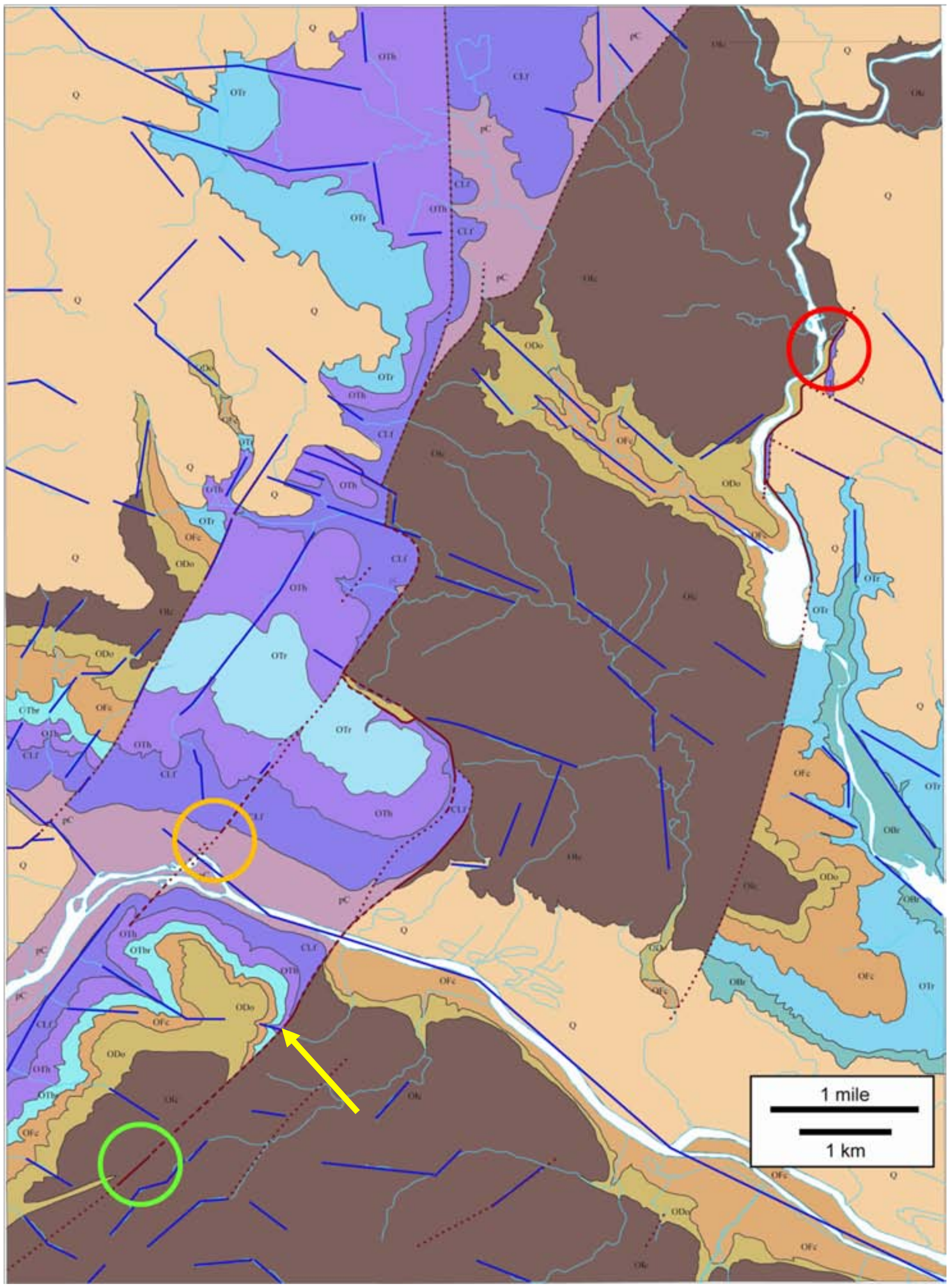


Figure 4a. Geological Map of the Little Falls 7.5’ topographic quadrangle (Jacobi et al., 2007). The Utica is shown by the dark brown color in the Little Falls graben. The Precambrian to Trenton passive margin complex is shown by the purple to light blue colors. pC = Precambrian, CLf = Cambrian Little Falls, OTh = Ordovician Tribes Hill, OTr = Ordovician Trenton, OTbr = Ordovician Trenton/Black River, OFc = Ordovician Flat Creek (lower Utica), ODo = Ordovician Dolgeville (middle Utica), OIc = Ordovician Indian castle (upper Utica). The border fault systems of the graben include: red circle = location of the Dolgeville Fault, orange circle = location of fault striations in the Precambrian, green circle shows location of the Little Falls fault exposure. Yellow arrow indicates approximate location of transect in Figure 13. The NNE-striking faults are reactivated Iapetan opening rift faults that were sequentially reactivated as the continent approached the subduction zone.

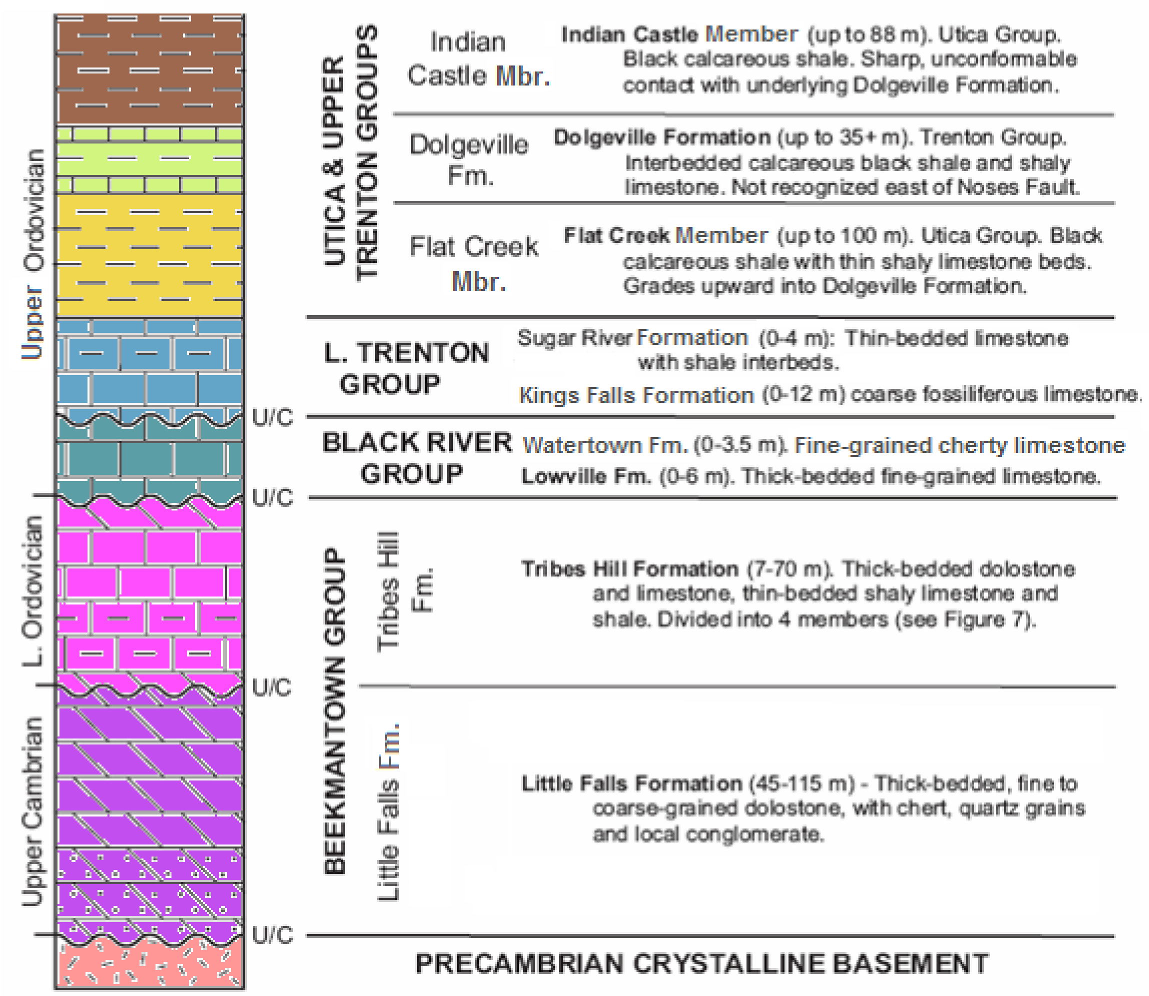


Figure 4b. Stratigraphic section of unites exposed in the Little Falls quadrangle (Figure 4a). Figure from Cross (2004) and Agle (2008).

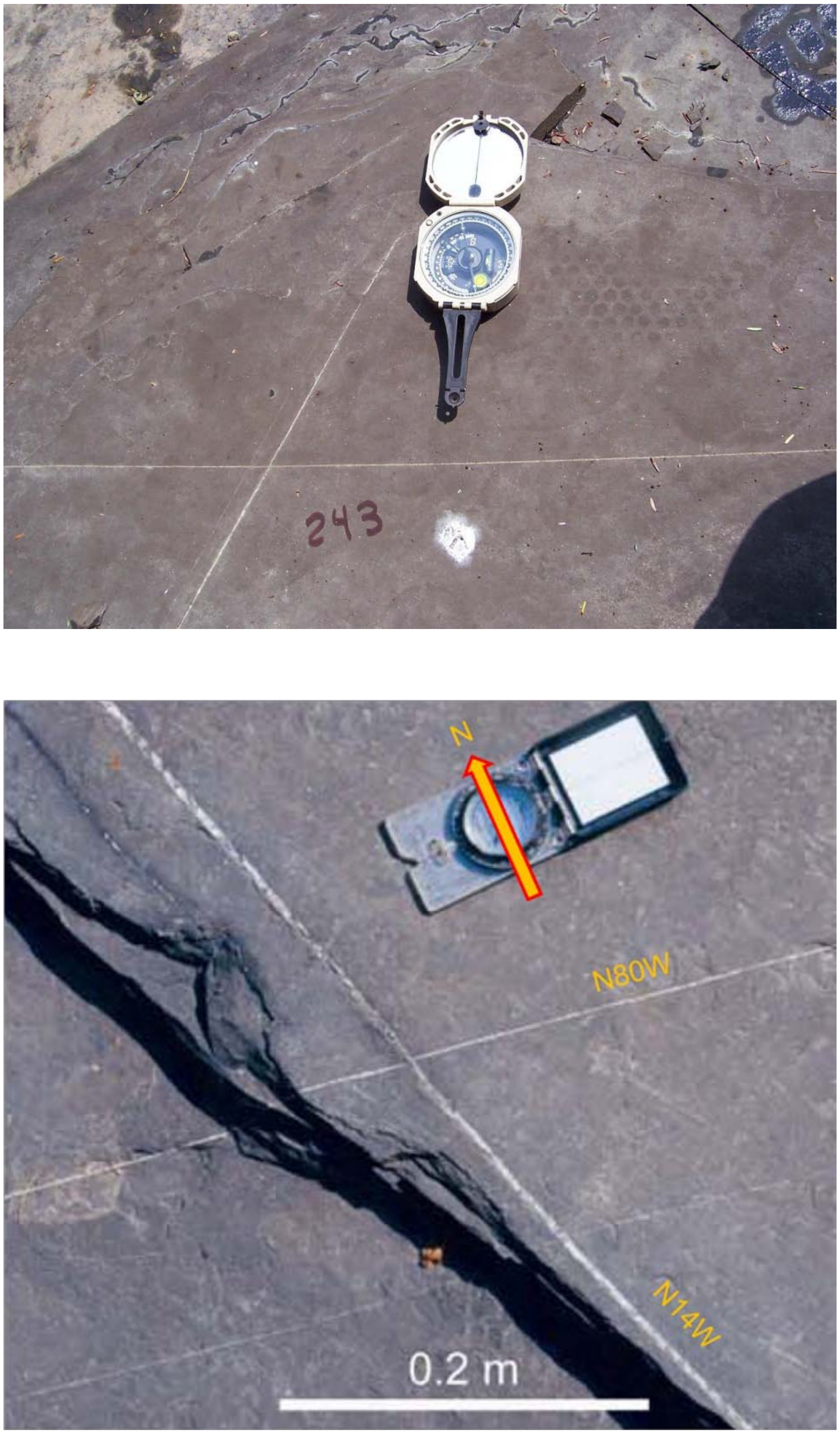


Figure 5. Typical veins in the Utica. Note in the lower panel that the NNW-striking vein crosscuts the WNW-striking vein (Upper panel from Jacobi et al. 2006a, and lower panel from Jacobi et al., 2008 and after Cross, 2004)

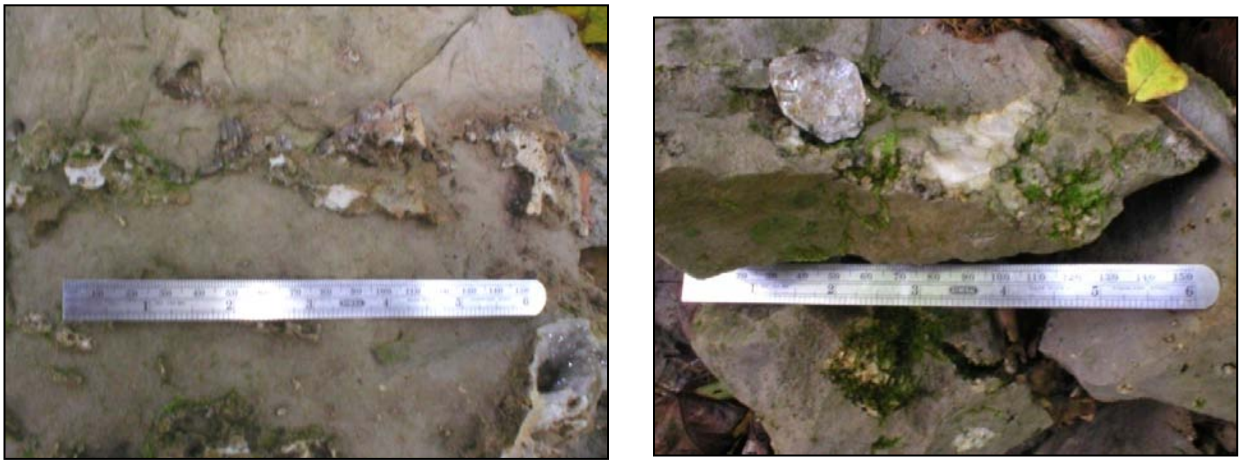


Figure 6a. Vugs with carbonate fill and a Herkimer “diamond” (quartz) in the right image (Agle, 2008)

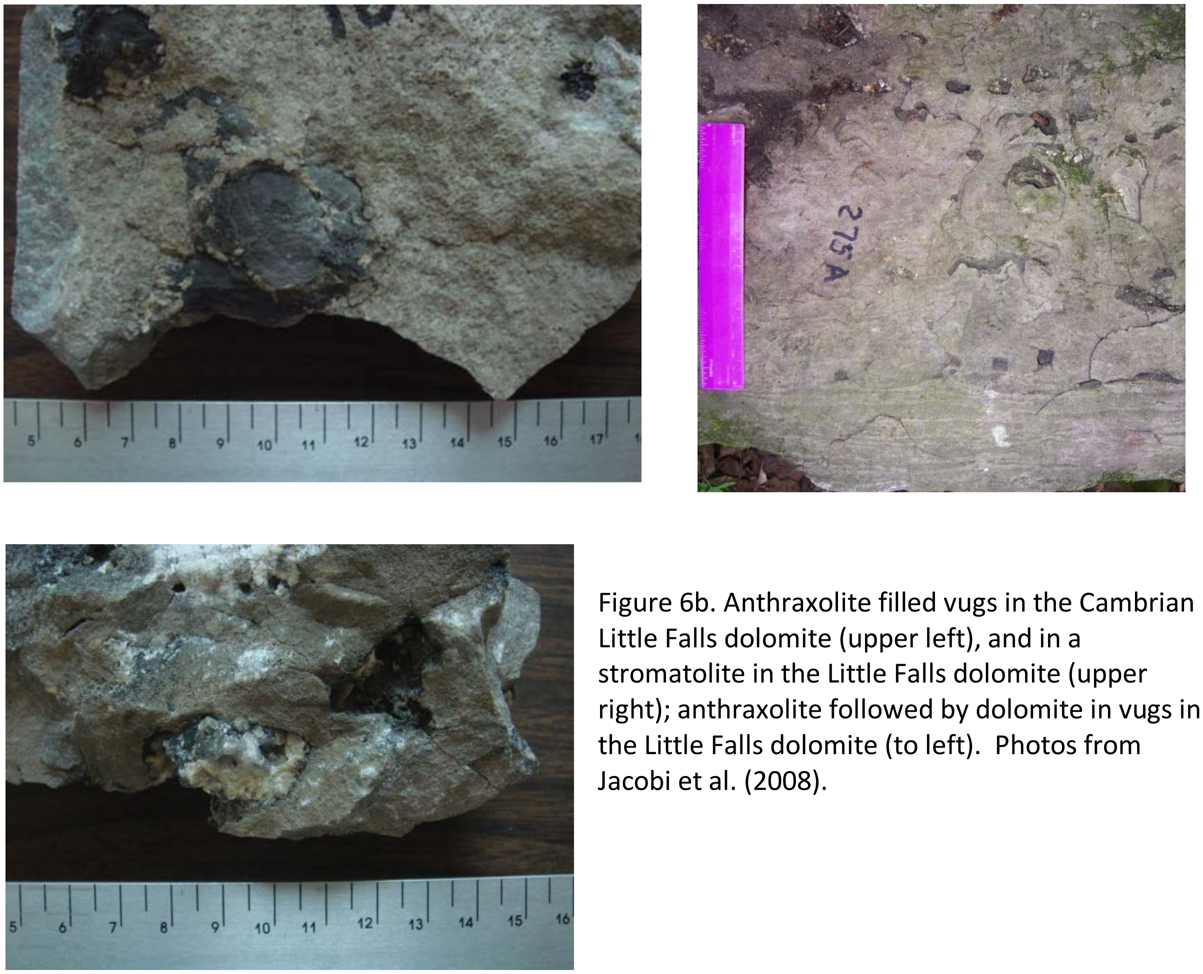


Figure 6b. Anthraxolite filled vugs in the Cambrian Little Falls dolomite (upper left), and in a stromatolite in the Little Falls dolomite (upper right); anthraxolite followed by dolomite in vugs in the Little Falls dolomite (to left). Photos from Jacobi et al. (2008).

Figure 7. Incipient breccia with dolomite (Agle, 2008)

Figure 8. Sulfide mineralization along the Dolgeville Fault in the Little Falls Formation. In the left photo complex sub horizontal faults are observed; the right photo displays fault/carbonate-sulfide mineralization breccia. This locality is indicated by the red circle in Figure 4a. Dr. Cortes and quarter for scales. Photos by Jacobi.

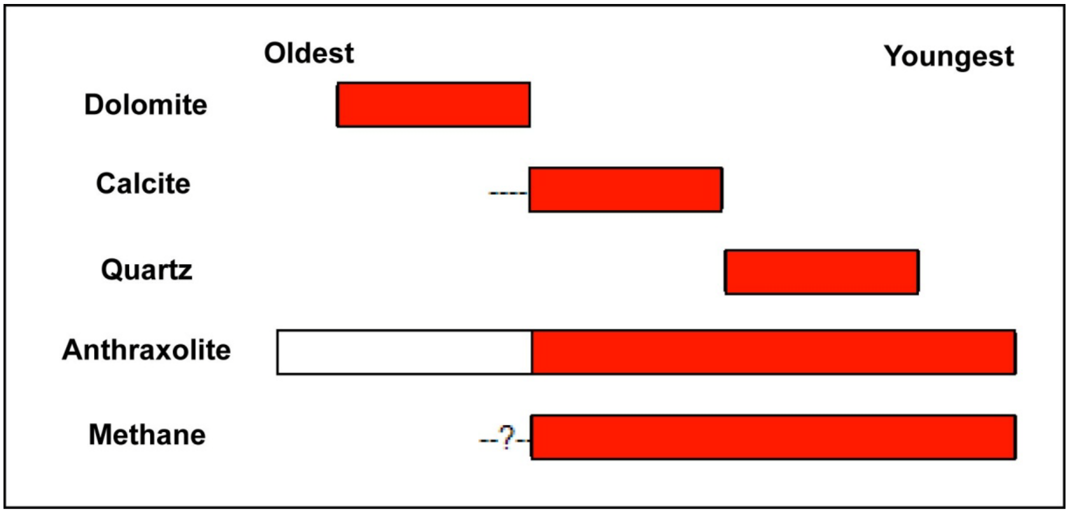


Figure 9. Sequence of mineralization in the Mohawk Valley, based on veins and vugs. The white box for anthraxolite indicates that in some localities, the anthraxolite is oldest. From Agle (2008)

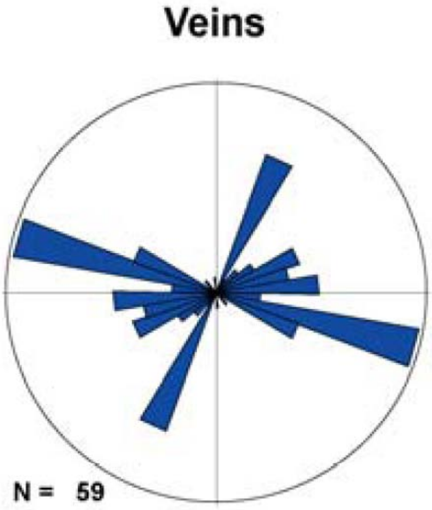


Figure 10. Rose diagram of veins measured in the Utica in the Little Falls graben. (From Agle, 2008; Jacobi et al., 2008)

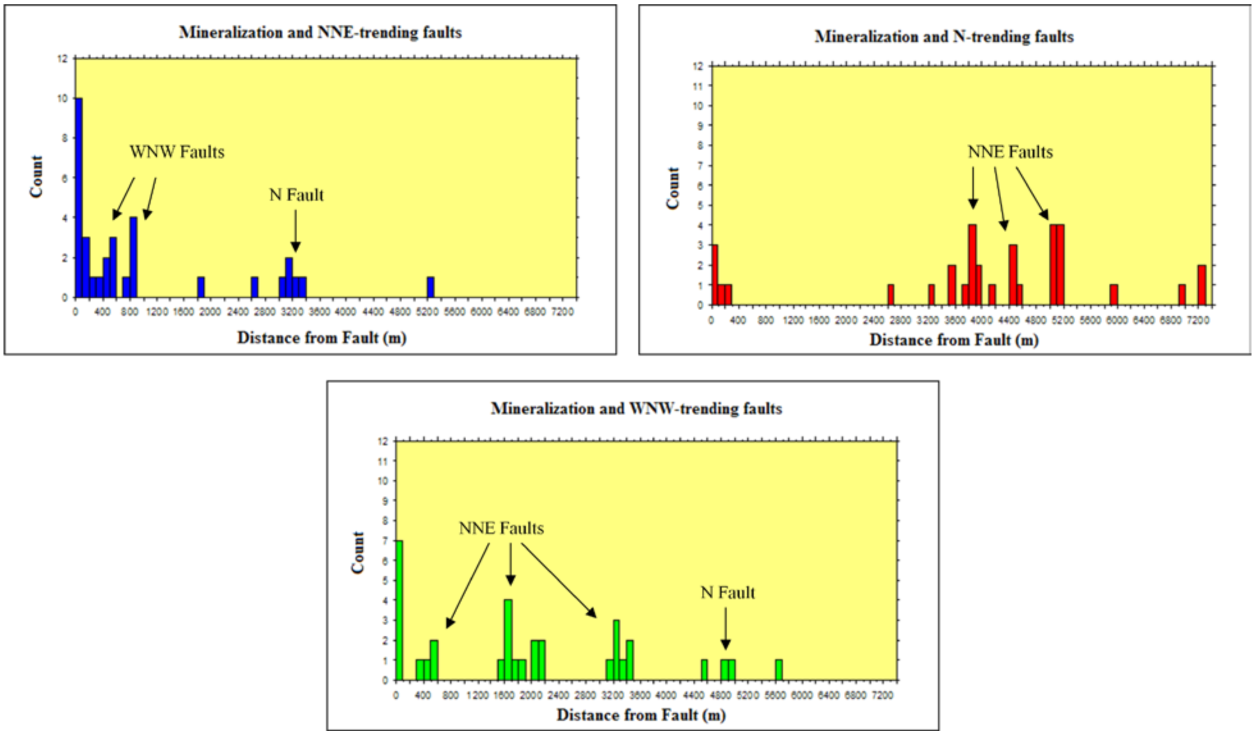


Figure 11a. Distance from faults to mineralization. From Agle et al. (2006, 2008); Jacobi et al. (2007, 2008)

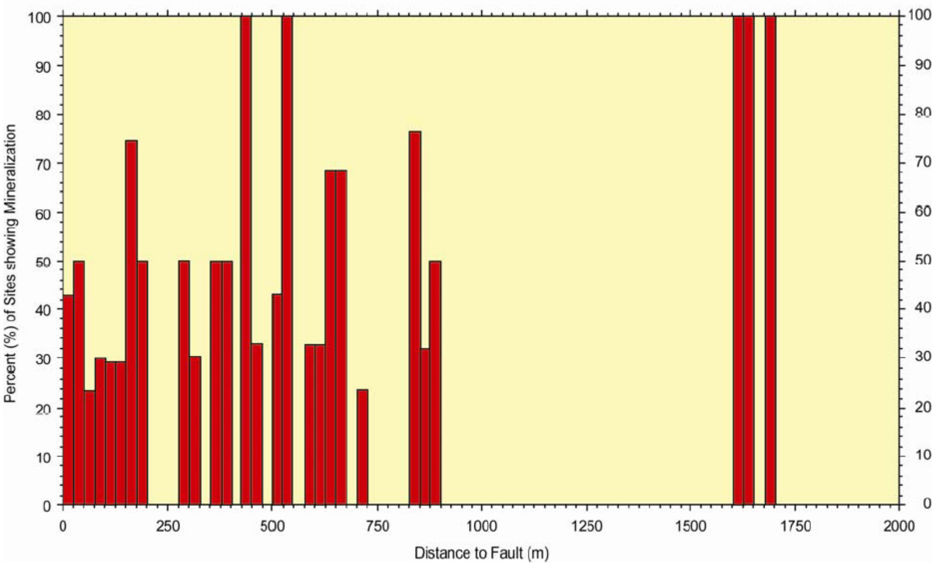


Figure 11b. Percentage of outcrops with mineralization at various distances from NNE-striking faults. From Agle (2008)

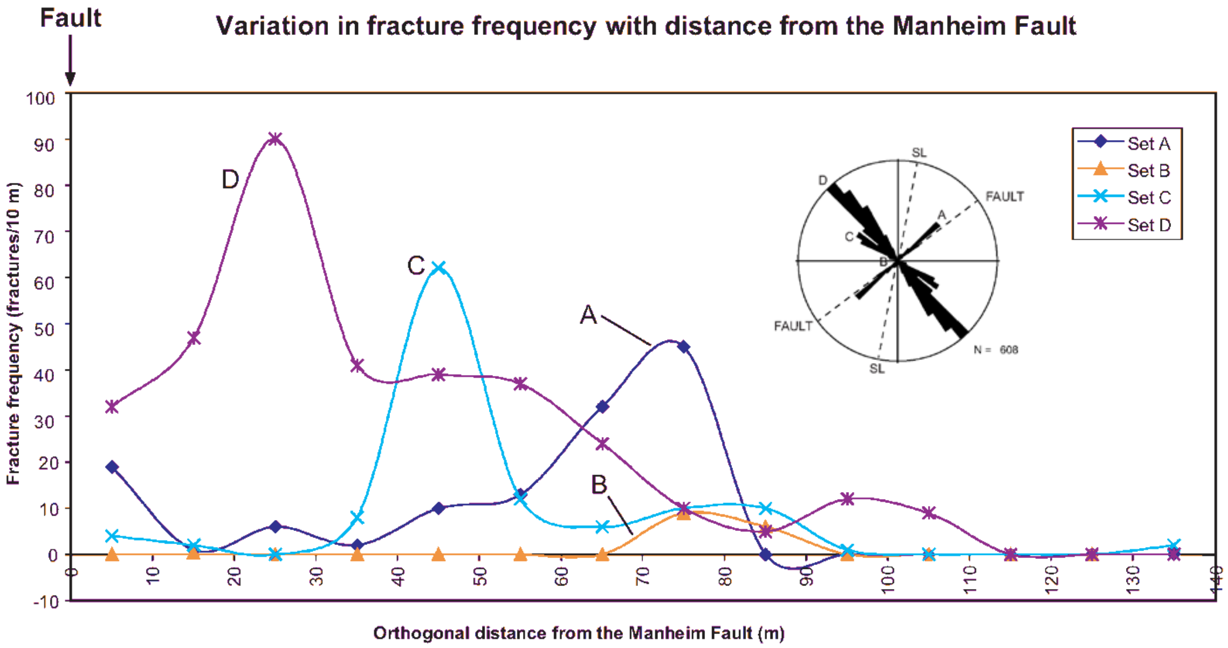


Figure 12. Vein-filled fracture frequency variation orthogonal to the Manheim fault along a single transect in the Utica. Location of the Manheim fault is shown by red arrow in Figure 3. Curves indicate variation in fracture frequency for various fracture sets (keyed to the rose diagram inset). Inset rose diagram indicates the orientation of the fault (NE at this locality) and keys the various fracture sets to the fracture frequency curves. Note that the fractures oriented orthogonal to the fault (in this case WNW-striking fractures, C and D) display an increase in fracture frequency toward the fault. Also—no ENE striking fractures were observed in the transect, which extends 140 m away from the fault. From Cross (2004), Jacobi et al. (2008).

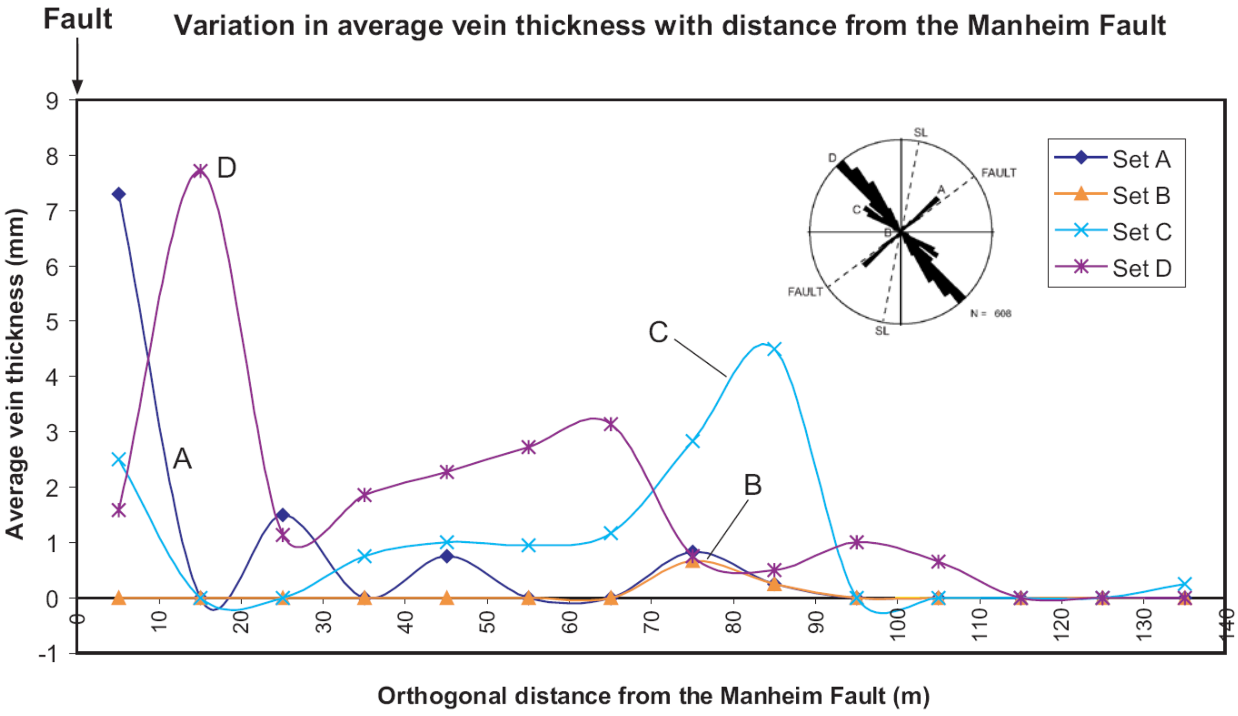


Figure 13. Fracture aperture (vein thickness) variation orthogonal to the Manheim fault along a single transect in the Utica. The WNW-striking set (D) increases in aperture toward the fault. From Cross (2004); Jacobi et al. (2008).

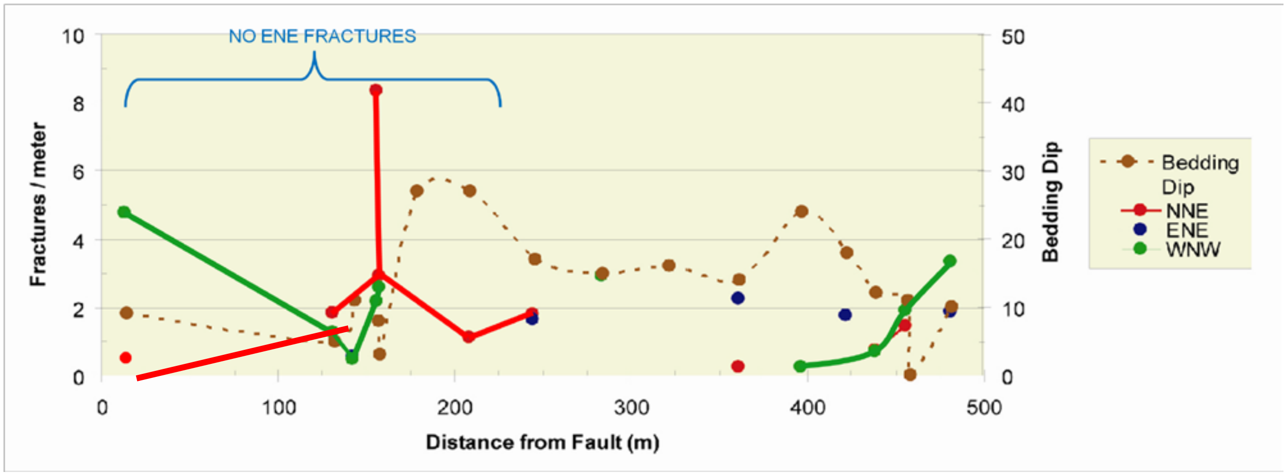


Figure 14. Fracture frequency variation orthogonal to the Little Falls Fault along a single transect in the Utica. Location of the transect is shown by yellow arrow in Figure 4a. Curves indicate variation in fracture frequency for various fracture sets (keyed to the rose diagram inset). Orientation of the fault is NNE at this locality. Note that the fractures oriented orthogonal to the fault (in this case WNW-striking fractures, green) display an increase in fracture frequency toward the fault. Also—no ENE striking fractures were observed near the fault. After Agle et al. (2006, 2008) and from Jacobi et al. (2008, 2009).

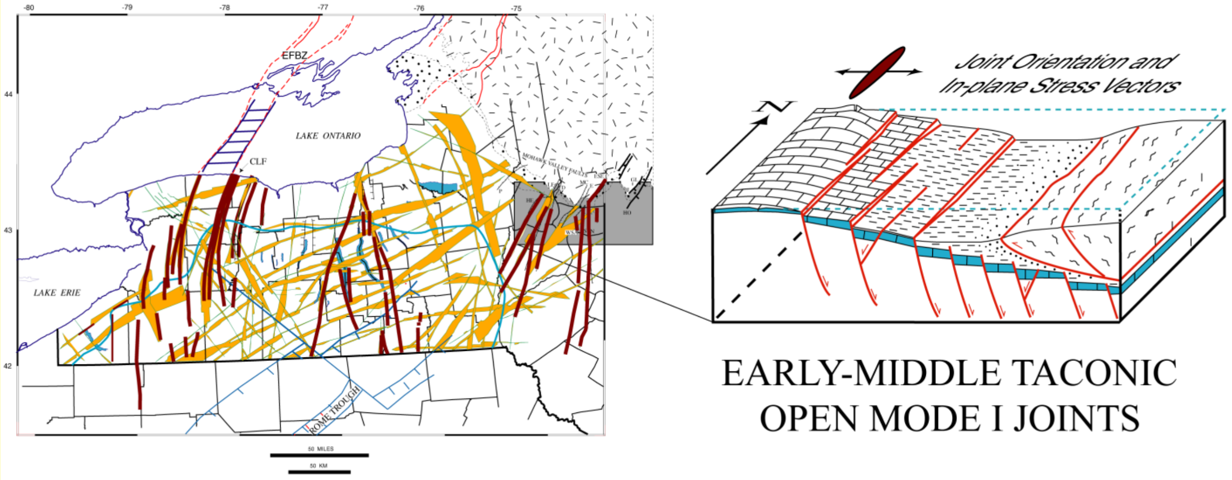


Figure 15. Taconic convergence model for the NNE-striking faults in "Early" Taconic convergence. At this time Sh is oriented EW (present day coordinates). Fault map after Jacobi (2002), and model after Bradley and Kidd (1991); figure from Jacobi et al. (2003).

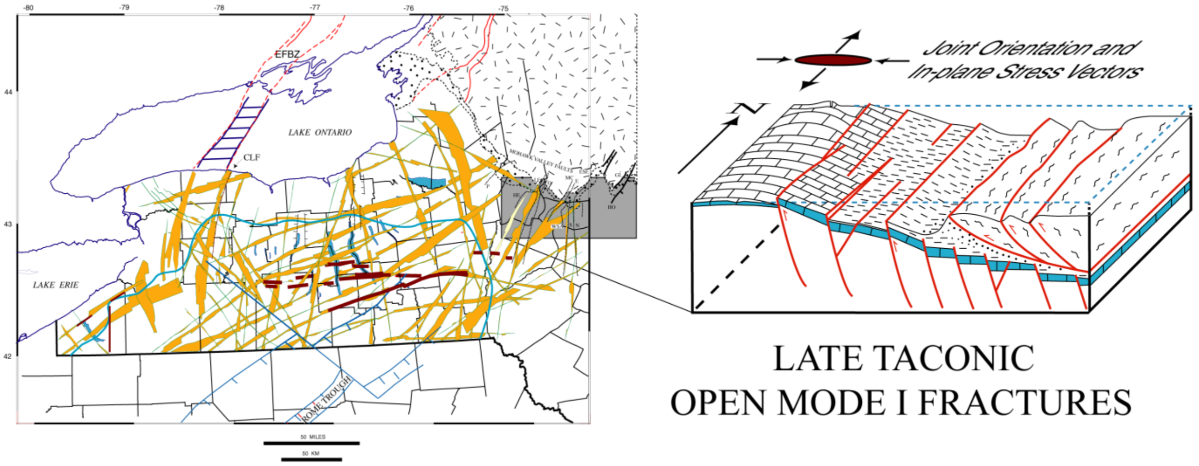


Figure 16. Taconic convergence model for the NNE-striking faults in “Late” Taconic convergence with a “jammed” subduction zone. At this time SH is oriented EW (present day coordinates). Fault map after Jacobi (2002), and model after Bradley and Kidd (1991); figure from Jacobi et al. (2003).

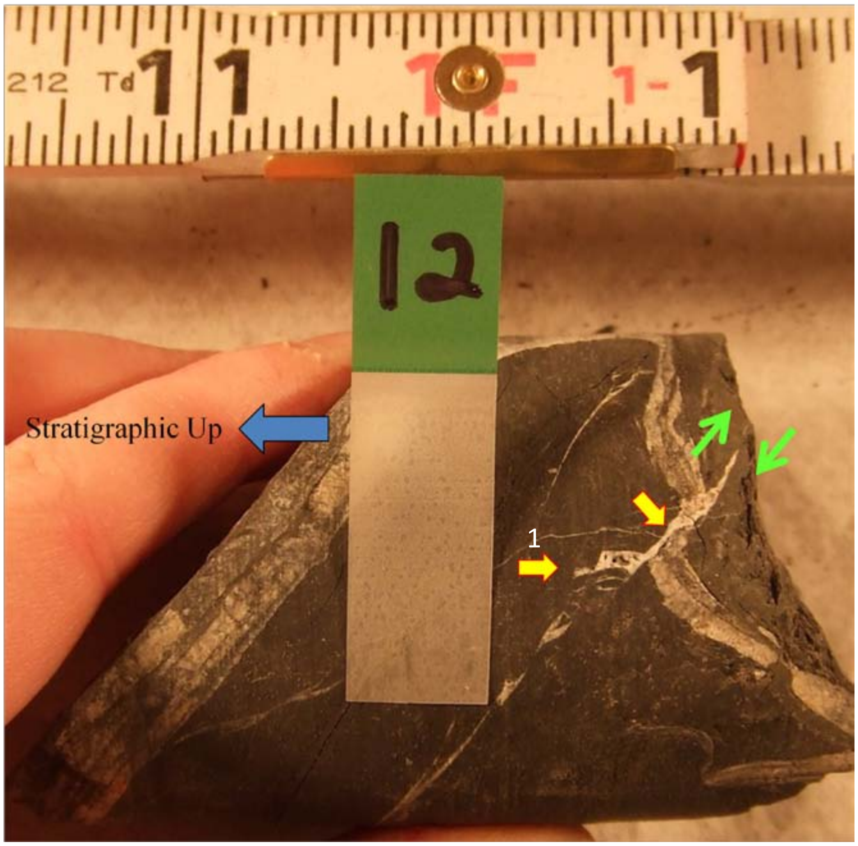


Figure 17. Example of kinematic indicators in core 75-NY-2. The yellow arrow labeled “1” points to rhombochasms from which a down-dip (stratigraphic up is to the left) sense of motion can be inferred, and this slip direction is consistent with the offset at the other yellow arrow.

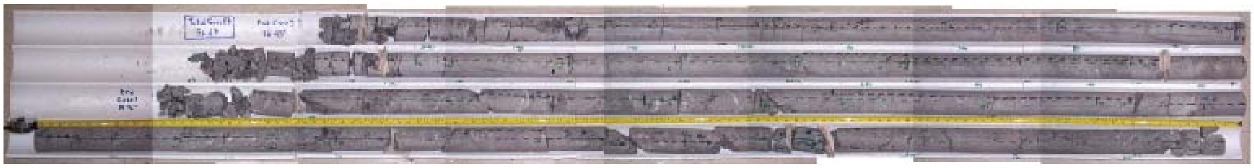


Figure 18. Core recovered from the Schwingel #2 horizontal well as part of a joint DOE/Talisman/Norse Energy project (Dr. Jacobi, PI, and PhD student Paul Agle). This core is the first oriented horizontal core ever taken in the northern Appalachian Basin. The goal was to determine the deformation, geochemical and geotechnical characteristics of the Trenton/Black River play in the Southern Tier of New York State. This play had the largest on-shore continental USA gas well two years in a row. Kinematic indicators, cross-cutting and abutting relationships on over 200 veins and stylolites document a complex, multi-phase deformation history. From Agle (2008).

(But core upside down, so right-lateral if core restored)

Figure 19. Example of rhombochasm (releasing bend) geometries that indicate sense of incipient motion from the Schwingel #2 horizontal core. From Jacobi et al. (2007).

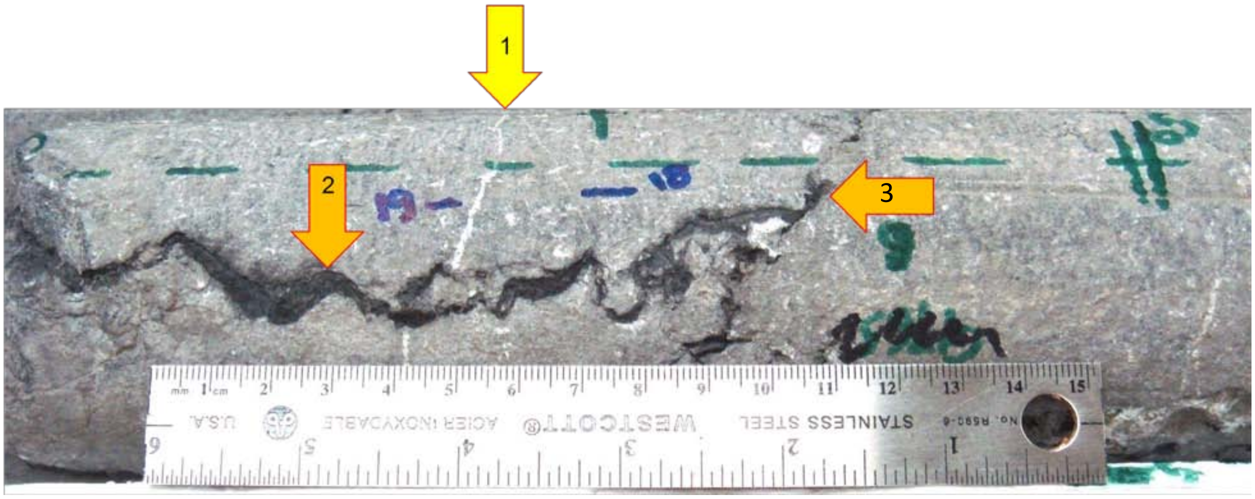


Figure 20. Example of the structural element sequences that can be constructed based on observable cross-cutting relationships in the core from the Schwingel #2 horizontal well. In this case an early vein filled fracture (1) is cut by a horizontal stylolite (2) which is in turn cut by a vertical stylolite (3). From Jacobi et al. (2007). The vein trends parallel to the Iapetan opening faults (ENE in this area) and the vertical stylolite trends ENE/NE, orthogonal to Alleghanian compression. From Jacobi et al. (2007, 2008; Agle, et al., 2008).

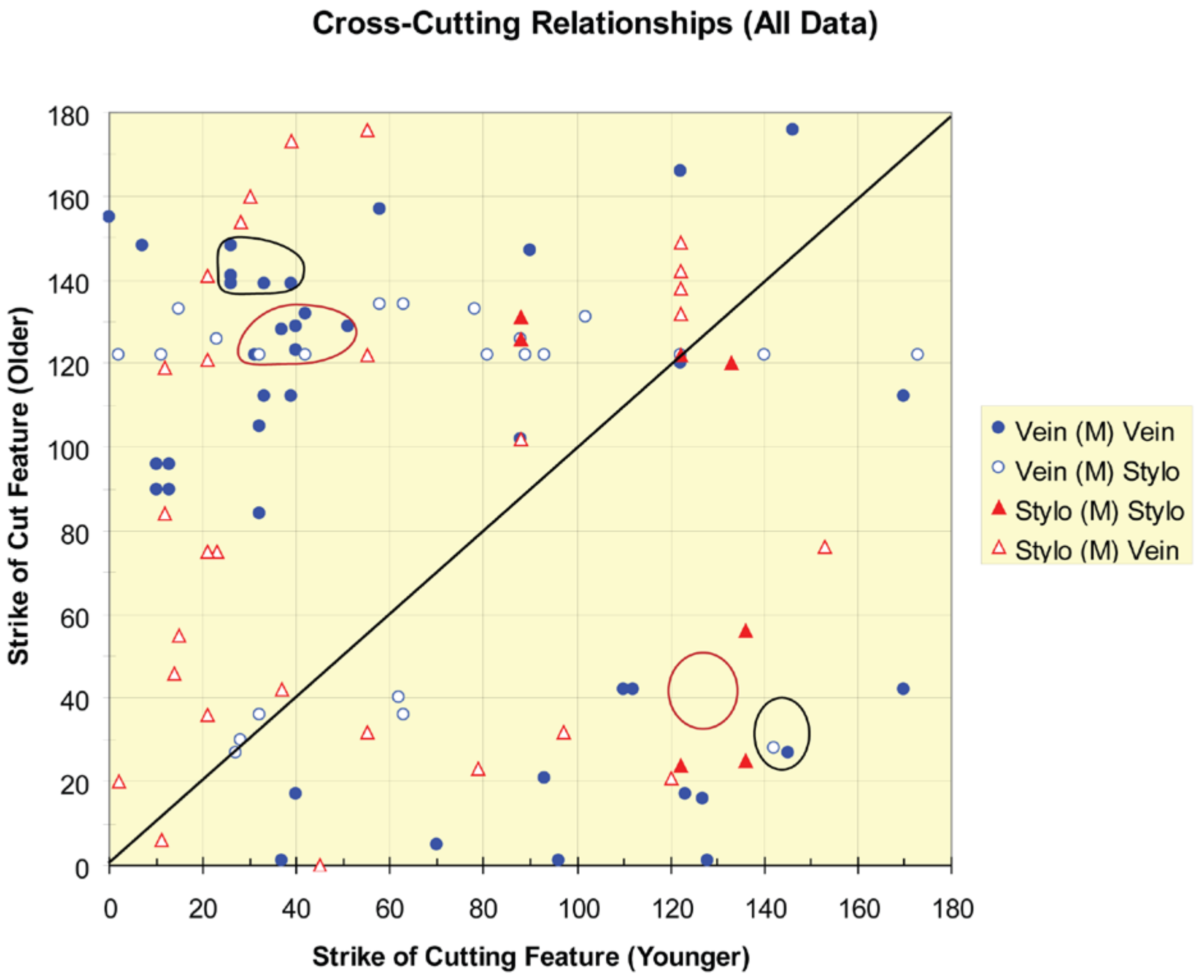
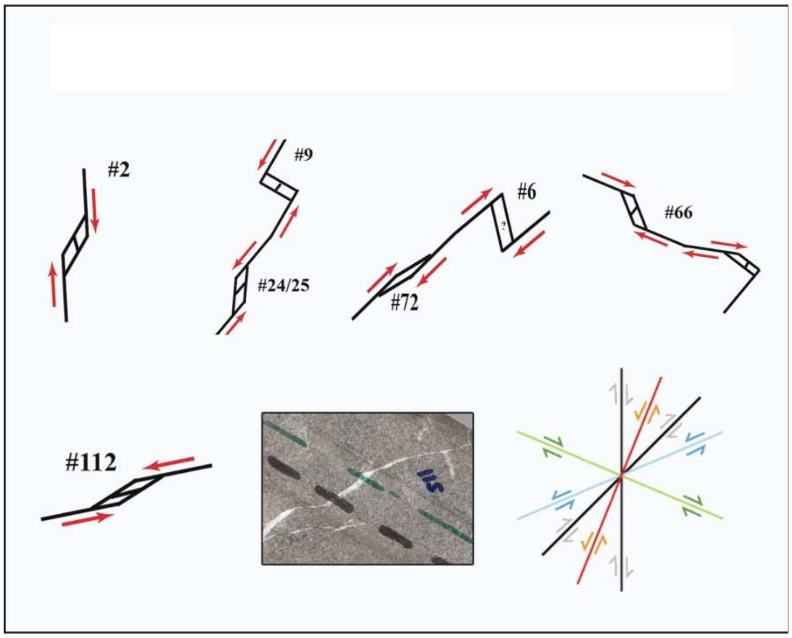


Figure 21. A cross plot of cutting and cut veins and stylolites from the Schwingel #2 horizontal core. In this example, 6 WNW veins are cut by NE-striking veins, but no NE-striking veins are cut by the WNW-striking veins (empty red circle in lower right, versus filled red circle in the upper left). From Jacobi et al. (2007, 2008), Agle (2008), Agle et al. (2008).



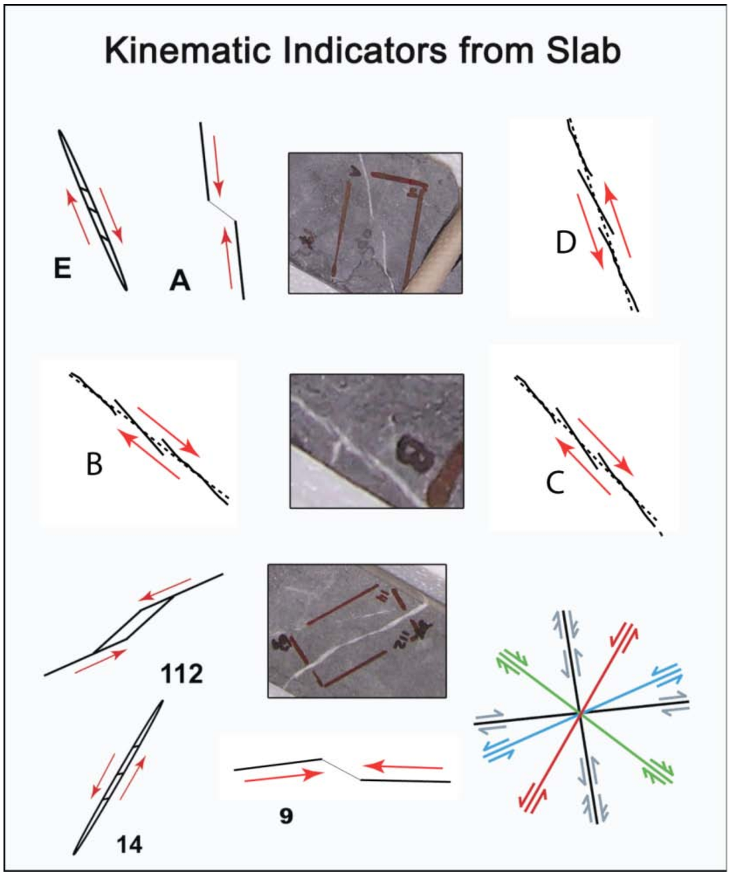

Kinematic Indicators from Slab

Figure 22. Sketches and photos of kinematic indicators for vein filled fractures from the the Schwingel #2 horizontal (full) core (upper panel) and the slabbed core (lower panel). Potential slip can be inferred along the fracture from the rhombochasms. Note that some of the vein orientations are consistent with riedal shears on other vein trends (e.g., the NE veins in the lower panel could be riedal shears on the ENE vein). These riedal shears and ENE left lateral sense of motion are consistent with the “Early to Middle” Taconic phase. From Agle (2008), Agle et al. (2008), Jacobi et al. (2008).

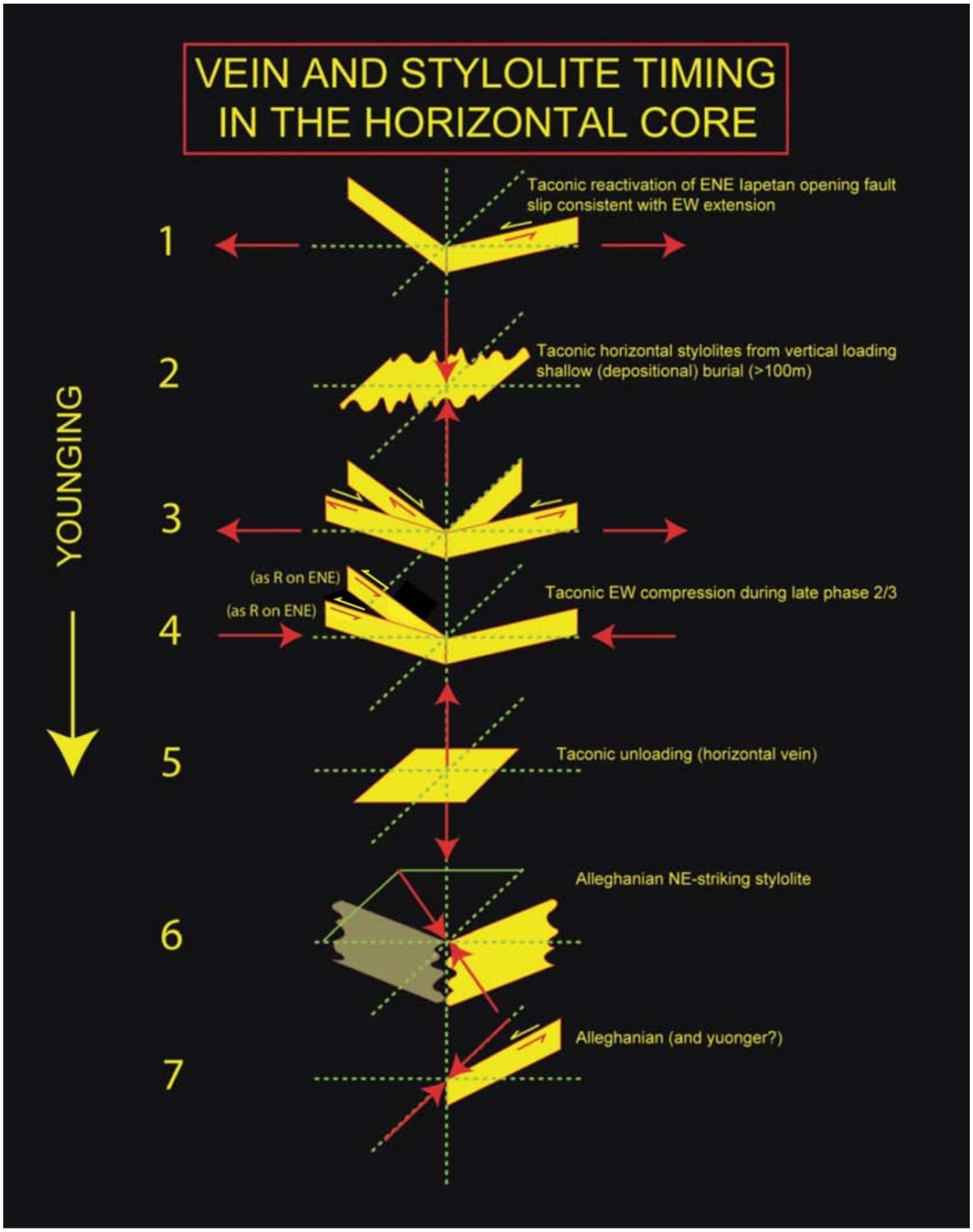


Figure 23. Sequence of events constructed from the veins and stylolites in the Schwingel #2 core. Key points are the early ENE-striking, left lateral fracturing that occurred before the development of horizontal stylolites. Since horizontal stylolites form under shallow loading conditions (as shallow as 100m), we assume these fractures are related to early tectonism before the Trenton/Black River had significantly subsided and been loaded. NE-striking vertical stylolites cut horizontal stylolites; the orientation of the vertical stylolites is consistent with an Alleghanian NW-directed push. A reversal in strike slip motion occurred before the vertical stylolites, and could be either related to “late” collisional stresses of the Taconic, or to the Acadian orogeny. The horizontal veins represent unloading of either late Taconic or Acadian orogenies. From Jacobi et al. (2008) and Marner et al. (2008)

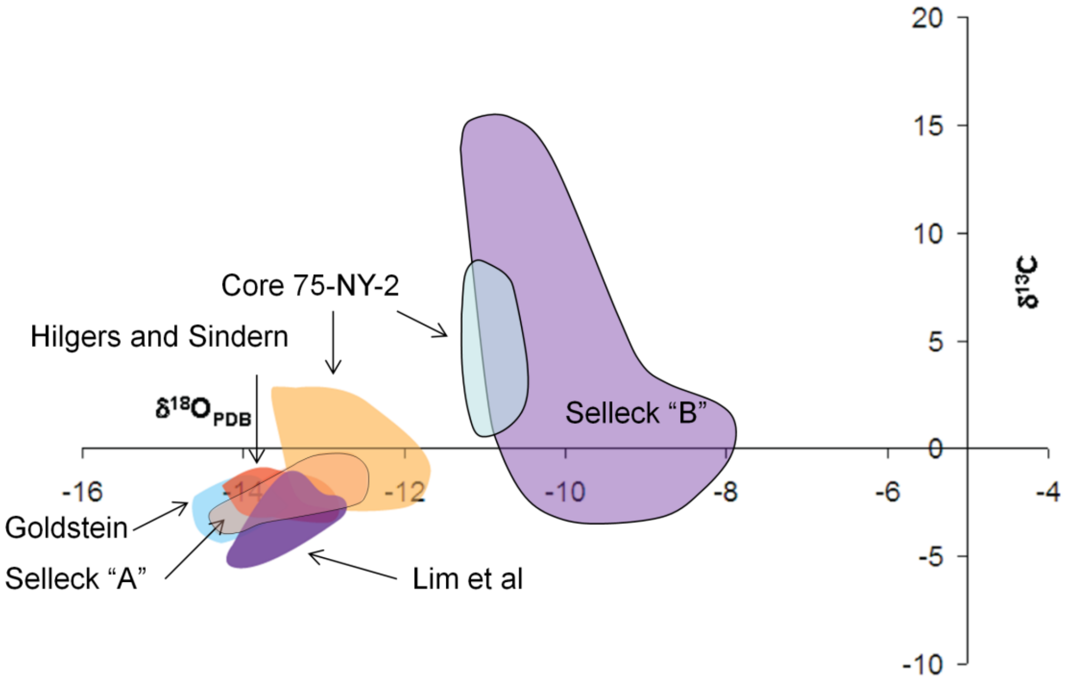


Figure 24a. Crossplot of $d^{13}C$ $(^0/_{00})_{PDB}$ against $d^{18}O$ $(^0/_{00})_{PDB}$ for samples from vertical core 75-NY-2 and various other reports. Goldstein = samples from Goldstein et al. (2005); Hilgers and Sindern = samples from Hilgers and Sindern (2005); Lim = samples from Lim et al. (2005). Selleck = samples from Selleck (2010). Figure after Hanson et al. (2010).

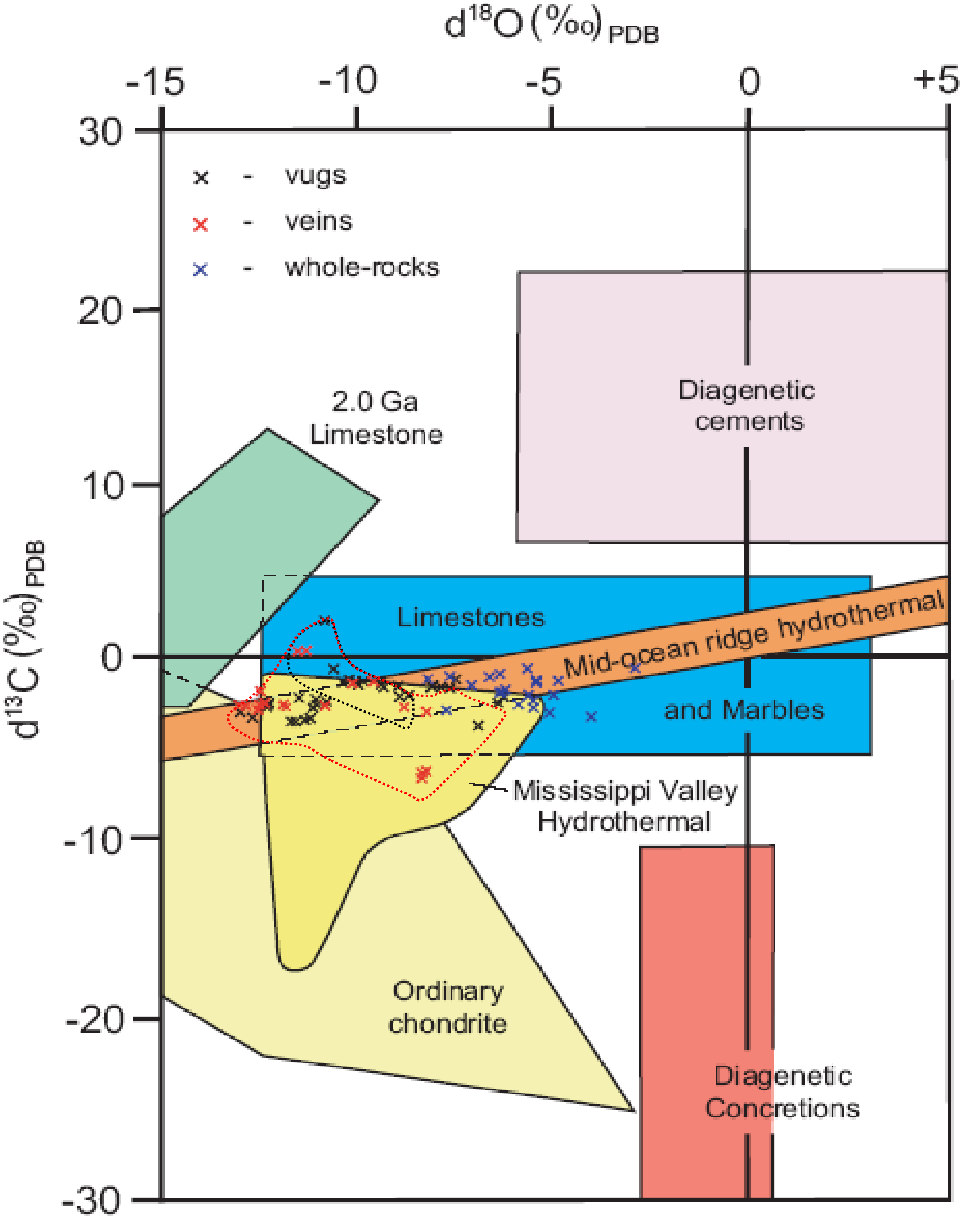


Figure 24b.Discrimination crossplot of d^{13}C ($^{0}/_{00}$)$_{PDB}$ against d^{18}O ($^{0}/_{00}$)$_{PDB}$ for the central Mohawk Valley. Red dashed encloses both vug and vein compositions. Black dashed smaller field discriminates vugs and veins that fall in Selleck's Group B. Note that the vein samples fall primarily in the Mississippi Valley hydrothermal field, as opposed to the whole rock samples, which fall in the limestone field. The samples were collected from the Cambro-Ordovician outcrops east of Little Falls Fault and west of the Hoffman's Fault (see Figure 3 for location of faults). After Cross (2004) and Cross et al. (2004). Fields from Rollinson (1993).

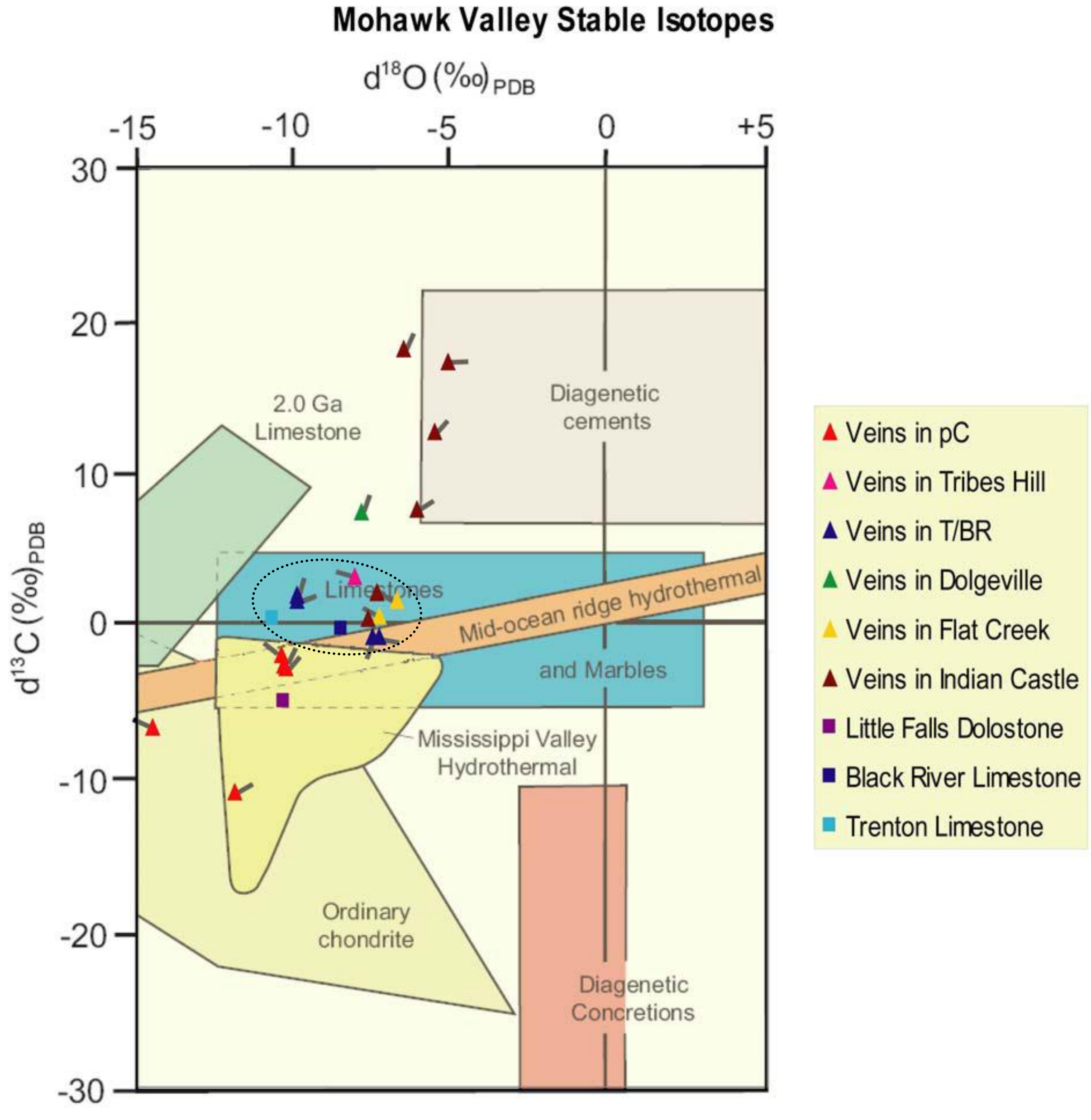


Figure 24c. Crossplot of d^{13}C ($^{0}/_{00}$)$_{PDB}$ against d^{18}O ($^{0}/_{00}$)$_{PDB}$ for samples in the Little Falls quadrangle (see Figures 3 and 4a for location). Squares indicate whole rock samples from visibly unaltered locales, whereas triangles indicate vein samples. The tail on the vein sample icon indicates the orientation of the vein. Dashed field discussed in text. From Agle (2008) and Jacobi et al. (2008). Fields from Rollinson (1993).

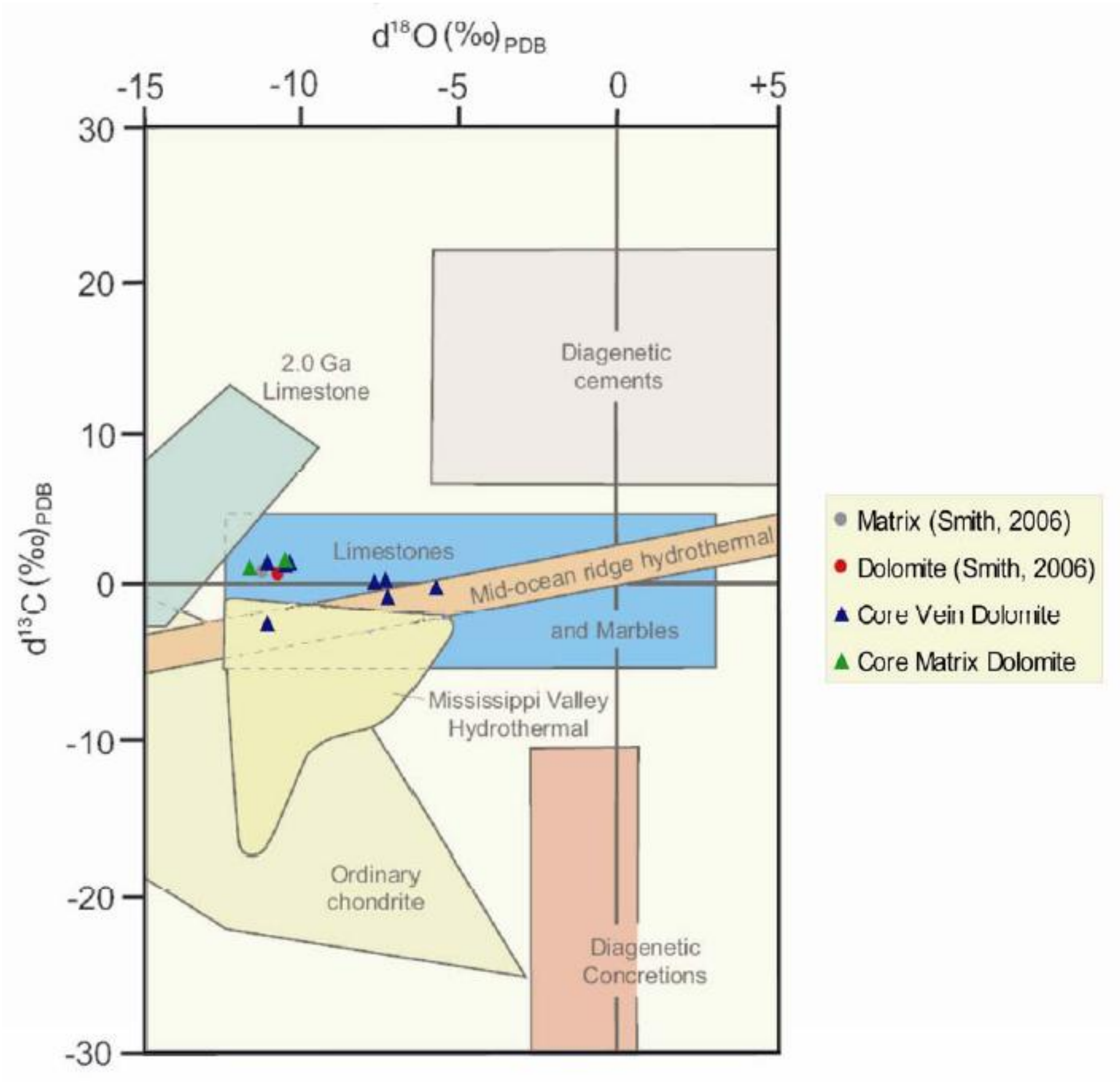


Figure 24d. Crossplot of $d^{13}C$ ($^{0}/_{00}$)$_{PDB}$ against $d^{18}O$ ($^{0}/_{00}$)$_{PDB}$ for samples from the Schwingel #2 horizontal core. Triangles indicate samples from the core and circles indicate reference samples from Smith (2006). Fields from Rollinson (1993). Figure from Agle (2008) and Jacobi et al. (2008).

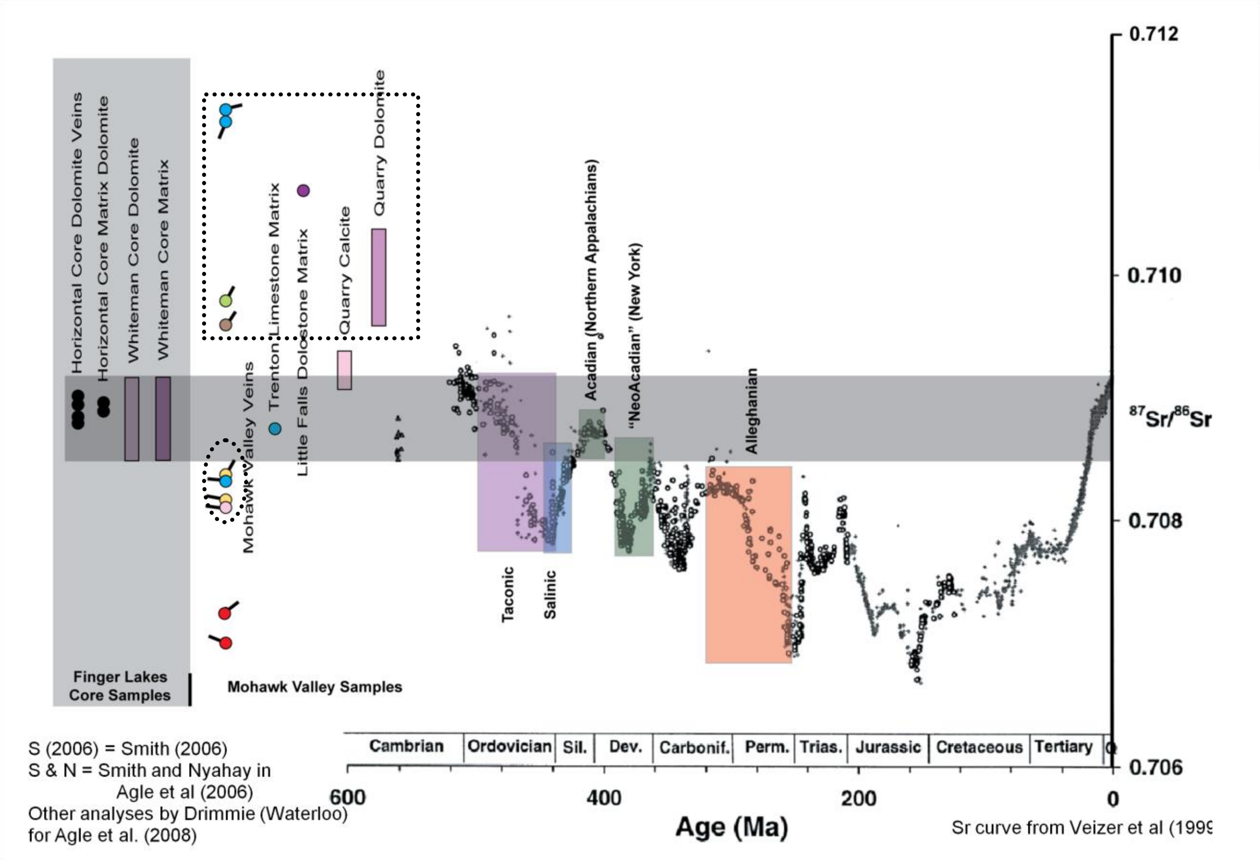


Figure 25a. Sr isotope data from Smith (2006), Agle (2007), and Agle et al. (2008) plotted on the Sr seawater curve from Veizer et al (1995). The horizontal core samples (Jacobi, 2007) and the Whiteman core samples (also from the Finger Lakes, Smith, 2006) confirm that the dolomite matrix and dolomitic veins in Finger Lakes region have values consistent with seawater in Taconic (and to a lesser extent, Acadian) times (the shaded values), and not with seawater in Alleghanian times. Circles with tails indicate samples from the Little Falls quadrangle; tail indicates the orientation of the vein. Red circle = vein in basement, purple circle = vein in Little Falls, pink circle = vein in Tribes Hill, purple circle = vein in the Little Falls, blue circle = vein in Trenton, yellow circle = vein in the Flat Creek Member of the Utica, green circle = vein in the Dolgeville, brown circle = vein in the Indian Castle Member of the Utica. Dashed ellipse and box fields discussed in text. Quarry samples from Smith and Nyahay (in Agle et al., 2006), and Whiteman core samples from Smith (2006). Figure after Agle 2008, from Jacobi et al. (2008).

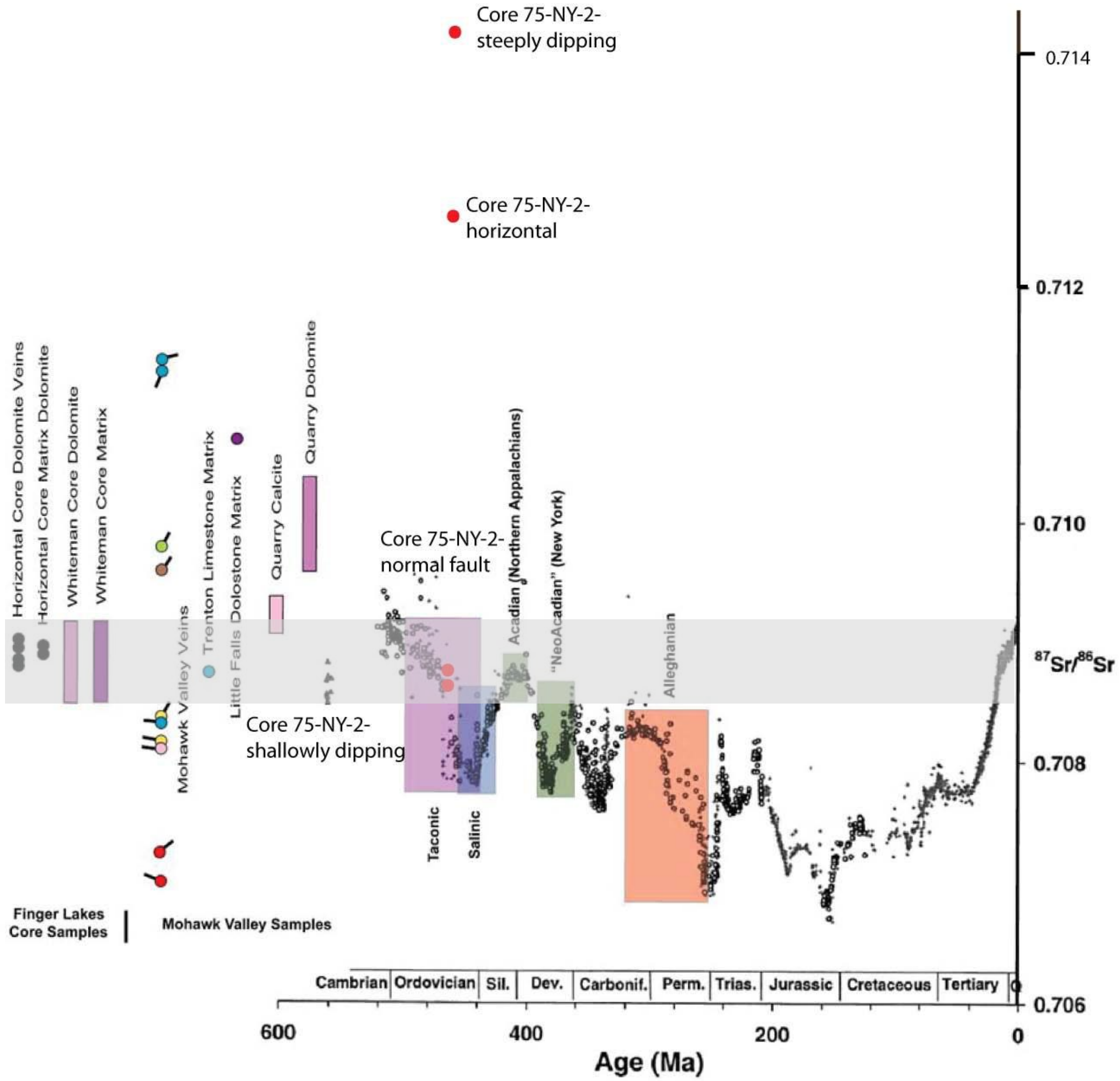


Figure 25b. Sr isotope data from core 75-NY-2 (red annotated circles; Hanson, 2010, and Hanson et al., 2010) added to Figure 25a (Figure 25a from Smith, 2006; Agle, 2007; Agle et al., 2008). Sr seawater curve from Veizer et al (1995).

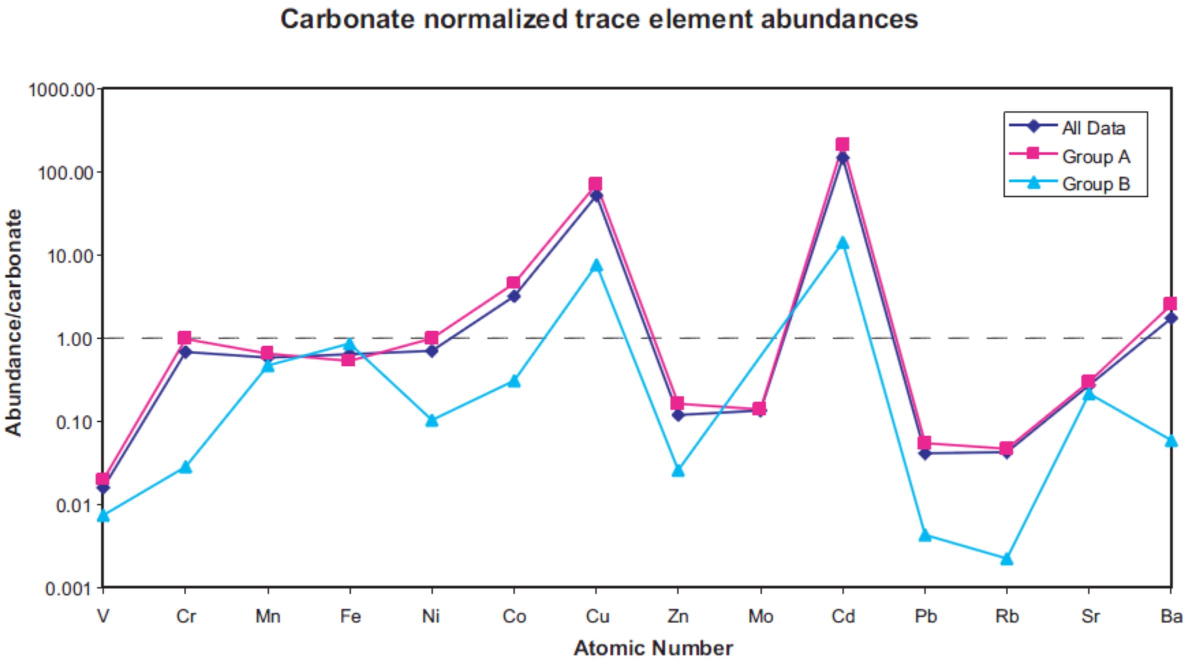


Figure 26a. Trace element abundances for central Mohawk Valley secondary carbonates normalized to typical sedimentary values from Turekian and Wedepohl (1971). See text for definition of groups. Figure from Cross (2004) and Cross et al. (2004).

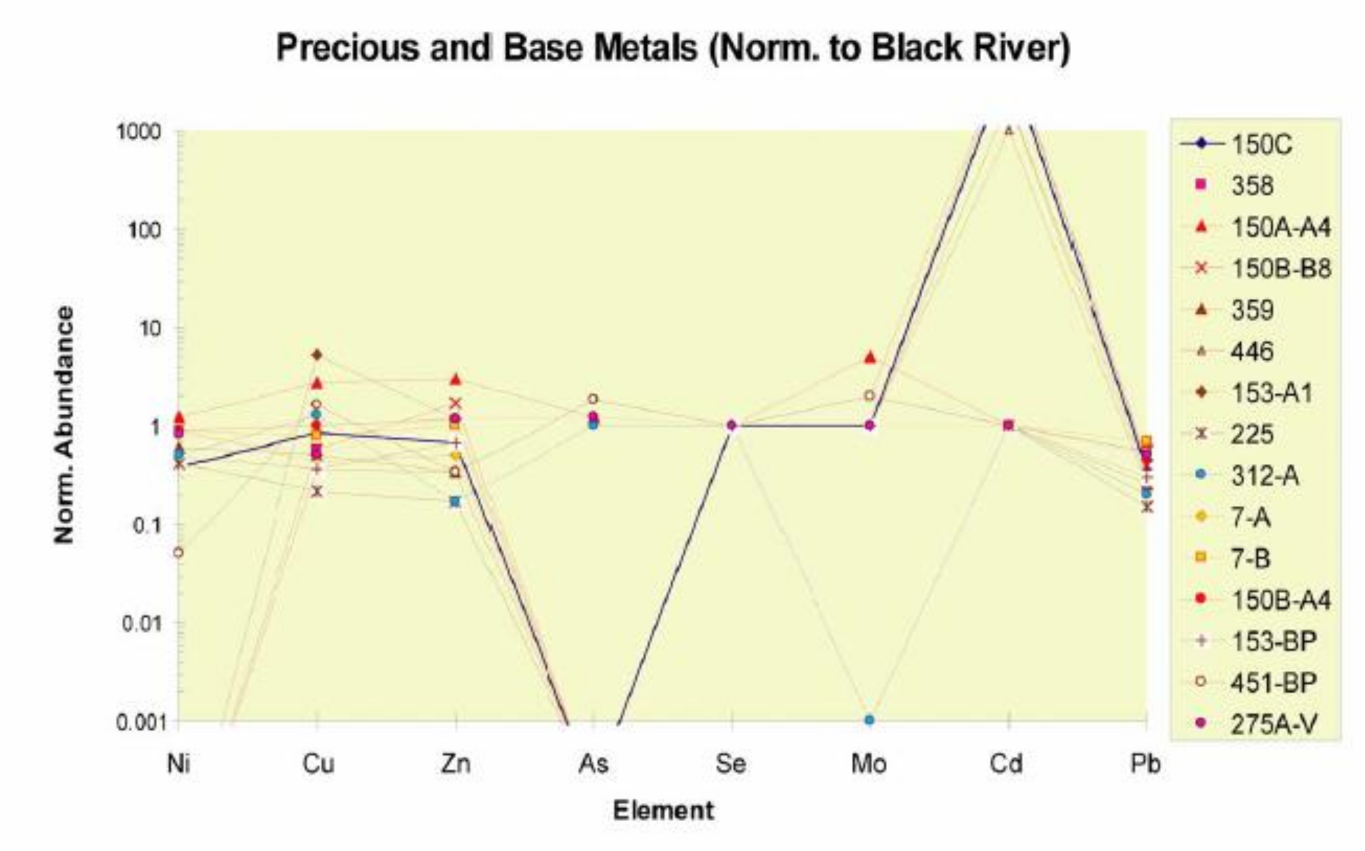


Figure 26b. Precious and base metals normalized to Black River values**.** Color-coding same as in Figure 25. From Agle (2008).

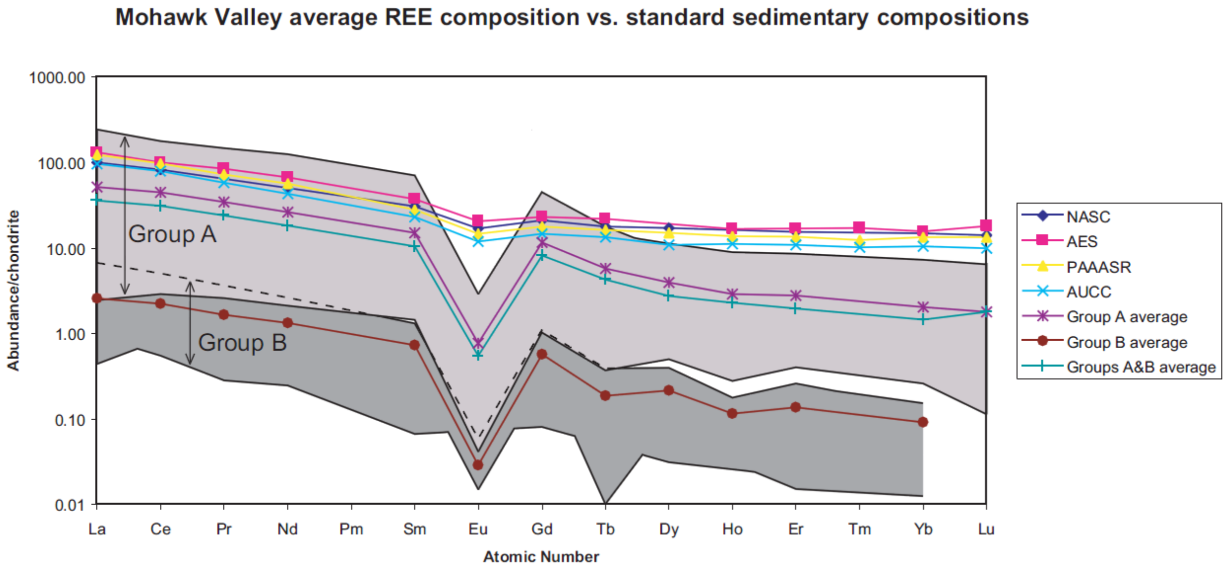


Figure 27a. Chondrite-normalized REE spider diagram for central Mohawk Valley secondary carbonate samples and standard sedimentary rocks. Fields and average values for groups A and B are shown (same groups as in Figure 26a, see text for definition of groups).
NASC = North American shale composite;
AES = Average European shale;
PAAASR = Post-Archean average Australia sedimentary rock;
AUCC = Average upper continental crust.
Data for standard comparison curves from Rollinson (1993). Figure from Cross (2004) and Cross et al. (2004).

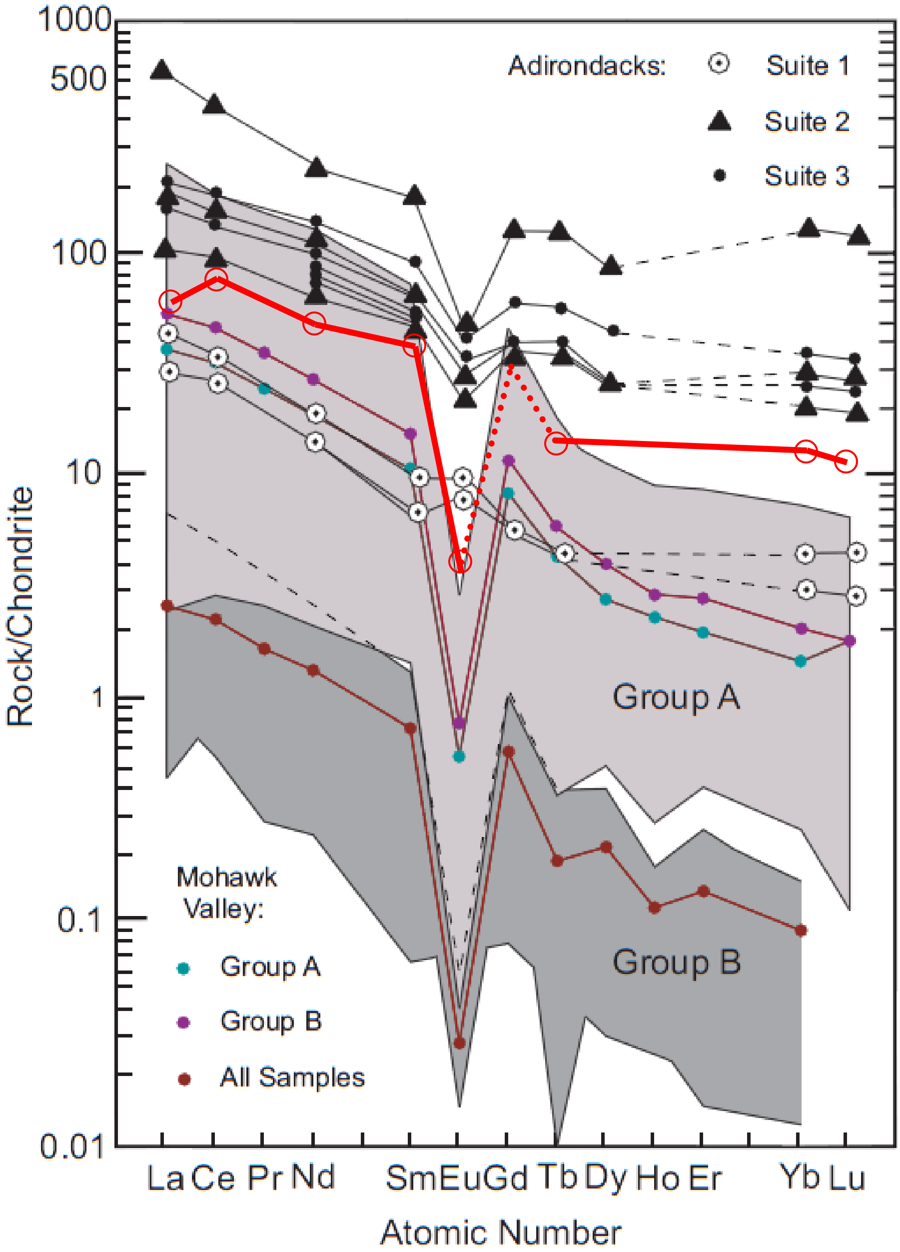


Figure 27b. Chondrite-normalized REE spider diagram displaying central Mohawk Valley secondary carbonates and REE patterns from Adirondack meta-igneous rock suites. Fields and average values for groups A and B are shown (same groups as in Figure 27a, see text for definition of groups). Adirondack suites from Daly and McLelland (1991). Thick red line with open circles is a REE pattern from a Taconic meta-K bentonite in the Utica shale (as displayed in Figure 27c, from Delano et al., 1990). Figure after Cross (2008)

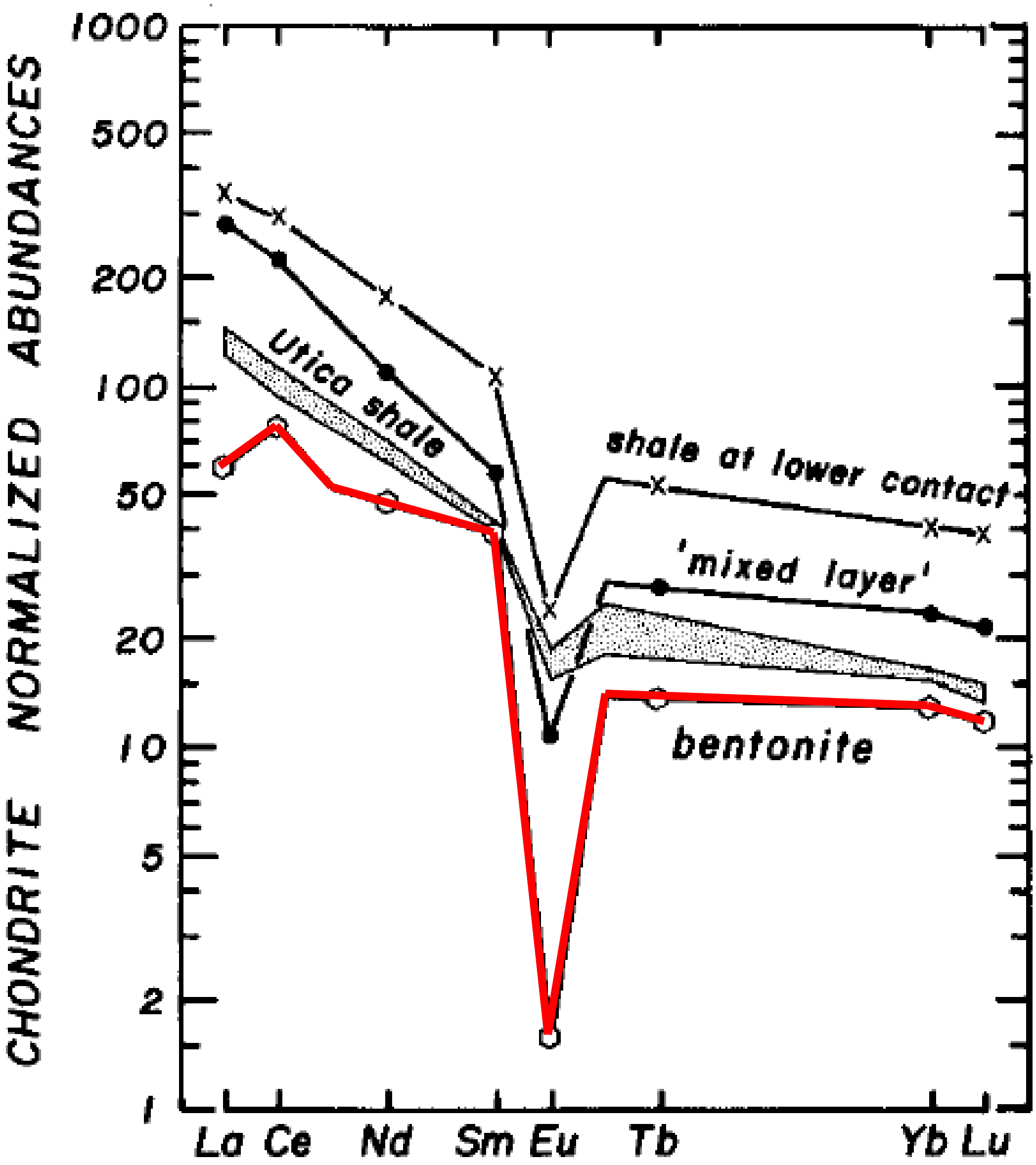


Figure 27c. Chondrite normalized REE spider diagram for meta bentonite samples in the Utica shale. The "mixed layer" refers to a mixture of shale and ash, but the composition indicates complicated pattern of diagenetic mobility of REE out of the bentonite (red line) into the "mixed layer" and the shale. (After Delano et al. 1990).

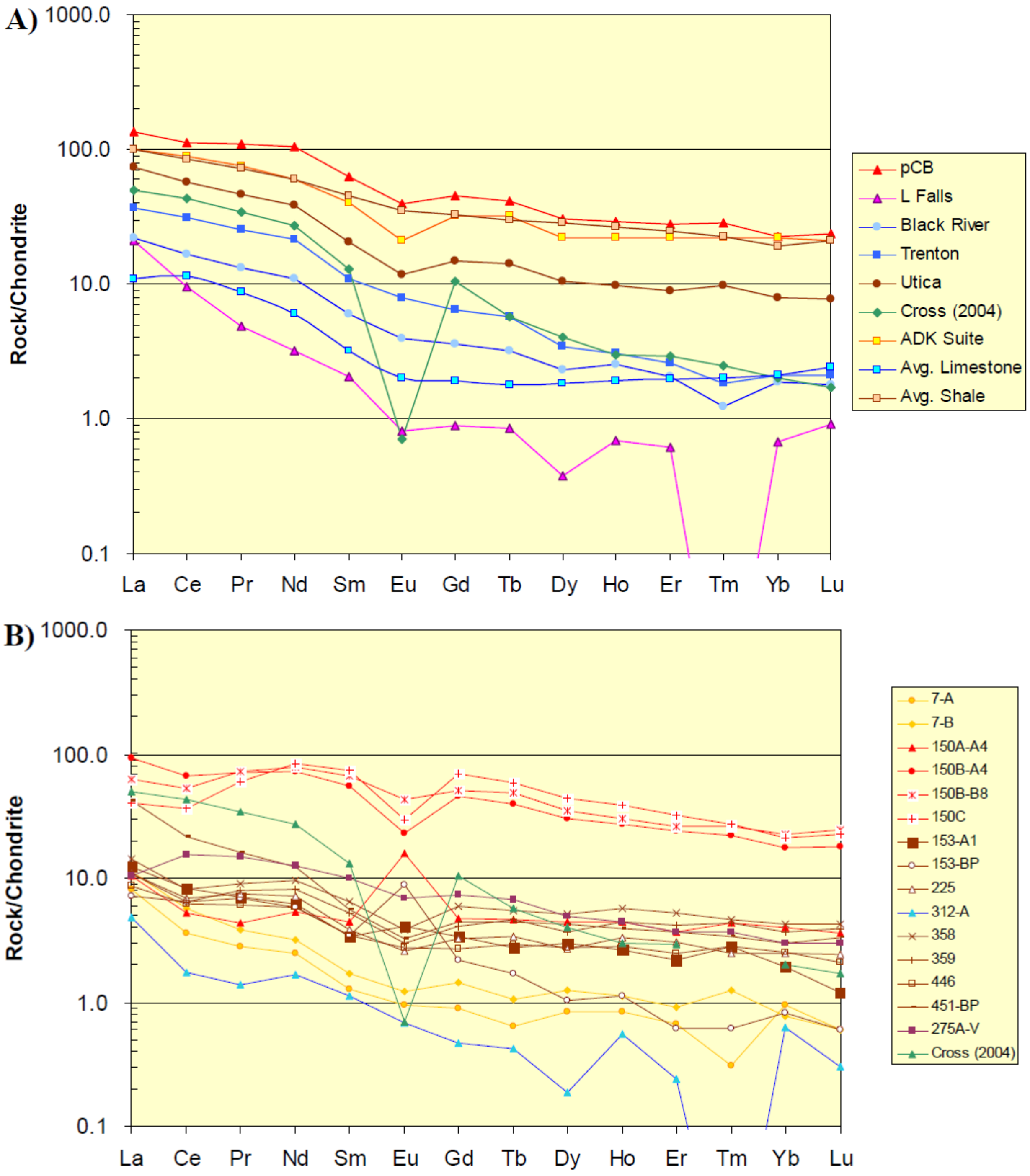


Figure 27d. Chondrite-normalized REE spider diagrams displaying standards from the literature (Panel A), from Cambro-Ordovician units in the Little Falls quadrangle (Panel A), and calcite veins in the Little Falls quadrangle (Panel B). Pattern labeled Cross (2004) is the average from secondary carbonates in central Mohawk valley (Figure 27a). ADK Suite is the Adirondack metamorphic basement from McLelland (1986). Avg. Limestone is from Haskin et al. (1966). In Panel B calcite vein samples are color-coded according to stratigraphic unit, as detailed in Figure 25. Figure from Agle (2008) and Jacobi et al. (2008).