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Veins, Fluid Migration and Hydrocarbon Generation in the Utica Shale, Northern Appalachian Basin, New York

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Abstract

The Upper Ordovician Utica Formation of the Appalachian Basin is a potential target for natural gas development. This black shale outcrops throughout the Mohawk Valley in Central New York State. The lower Flat Creek Member is characterized by E-W Mode 2 (strike-slip) fractures, bed-parallel thrusts, and N-S Mode 1 (tensile) fractures. E-W fractures and dilational jogs host the majority of calcite veins, some with hydrocarbon staining and methane-dominated low-salinity aqueous fluid inclusions. Mode 1 fractures host calcite veins and sand injectite dikes sourced from sand and dolomite sourced from underlying Paleozoic strata and Proterozoic basement. Volcanic ash beds from within the Utica are also a source of material for sand injectites. These features promote the hypothesis that faulting was active at the time of burial and seismic pumping may have allowed vertical migration of fluids from overlying and underlying units. Horizontal veins also promote this hypothesis, as low confining pressures and/or high fluid pressure would allow fracturing and vein precipitation.

The migration of multiple fluids is evidenced by stable isotope data for carbon and oxygen ($\delta^{13}C_{calcite}$ =-11 to +15 PDB; $\delta^{18}O_{calcite}$ = -6 to -12 PDB) and fluid inclusion data (T_h ≈105-185°C, T_{Mice} = -0.5 to -4.5 C), and indicate that vein generation occurred during hydrocarbon maturation, and that vein-forming fluids were mainly derived from within the Flat Creek Member. Multiple events and mixtures of fluids caused the variation in isotope values and suggest mixing of seismically pumped fluids in fault systems during the evolution of the Taconic foreland basin.

The upper Utica (Indian Castle Member) and overlying units show different fracture patterns than the Flat Creek Member and generally lack mineralization, suggesting relatively early burial likely caused the fracturing and fluid expulsion in the Flat Creek Member. Basement-derived hydrothermal fluids may have facilitated hydrocarbon maturation during the early burial and diagenesis in the Flat Creek Member. Later burial and fracturing events in the Utica occurred after deposition of Silurian sandstone strata and permitted up-migration of dry gas into sandstone reservoirs.

Introduction

The late Ordovician Utica Formation outcrops in central New York and extends into the subsurface through much of the Appalachian Basin (Figure 1). Deposition occurred during the downward flexure of the Appalachian Foreland during the onset of the Taconic Orogeny (Bradley and Kusky 1986). The Utica is a high total organic carbon (TOC) (>3.0%) black shale, making it a potential target for natural gas development (Martin, 2005). The potential zone of Utica production (fairway) includes portions of south-central New York. In the eastern and central Mohawk Valley region, the Utica Formation is separated into two members: the basal Flat Creek and upper Indian Castle (Figure 2). The Flat Creek Member overlies Trenton Group limestones. Overlying the Indian Castle Member is the Frankfort Formation, which is unconformably overlain by the Oneida Formation in the central Mohawk Valley (Brett and Baird, 1982). The Flat Creek Member is replaced westward by the Dolgeville Member, which in turn is replaced by platform limestones in the Tug Hill Region. The highest TOC intervals are found in the lower Flat Creek and basal Indian Castle (Nyahay and Martin, 2008). Successful well stimulation of gas shale reservoirs is enhanced by an understanding of the orientation of natural fractures in the shale (e.g. Engelder et al, 2009). The character of natural fractures, whether open or mineralized is also critical to successful gas shale development.

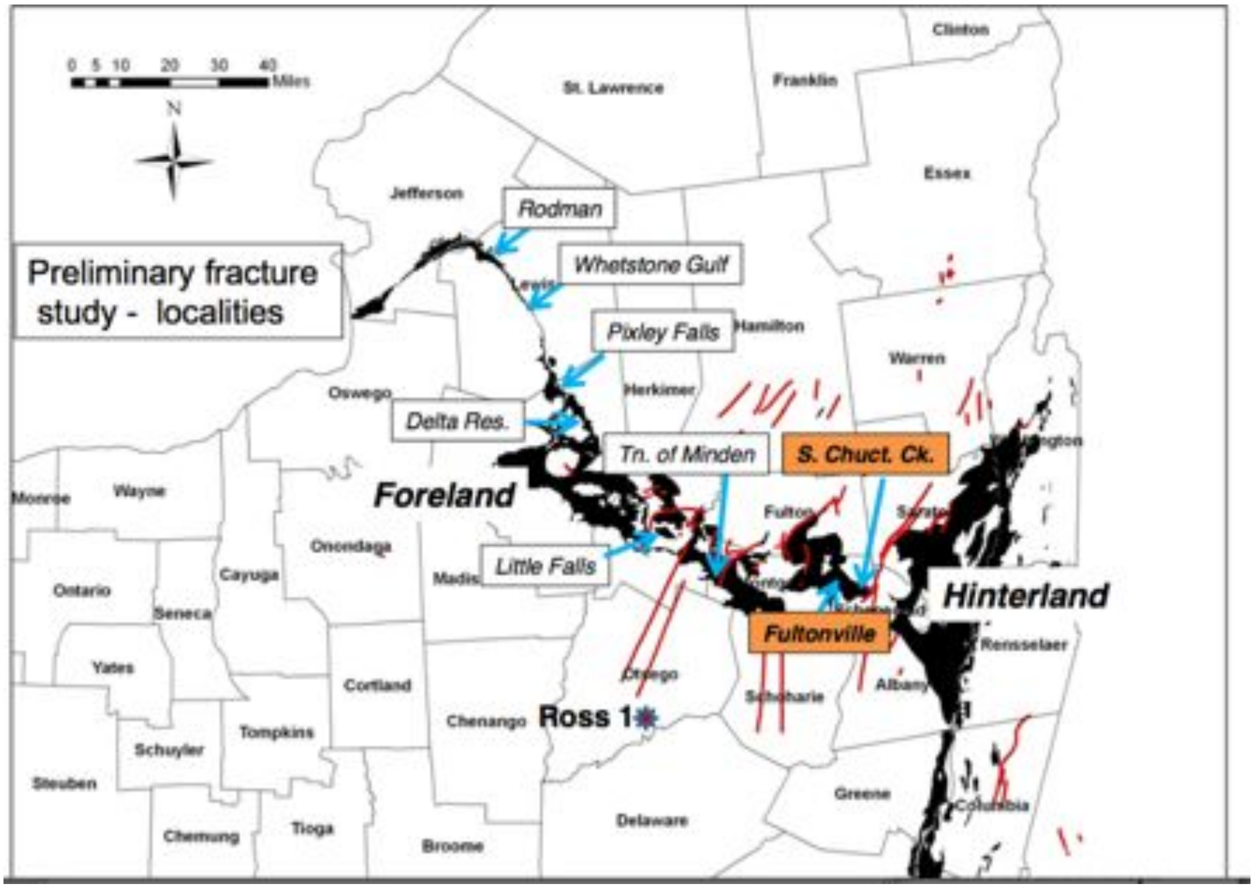

Figure 1: Map of Utica Formation outcrop in New York (Selleck, 2010)

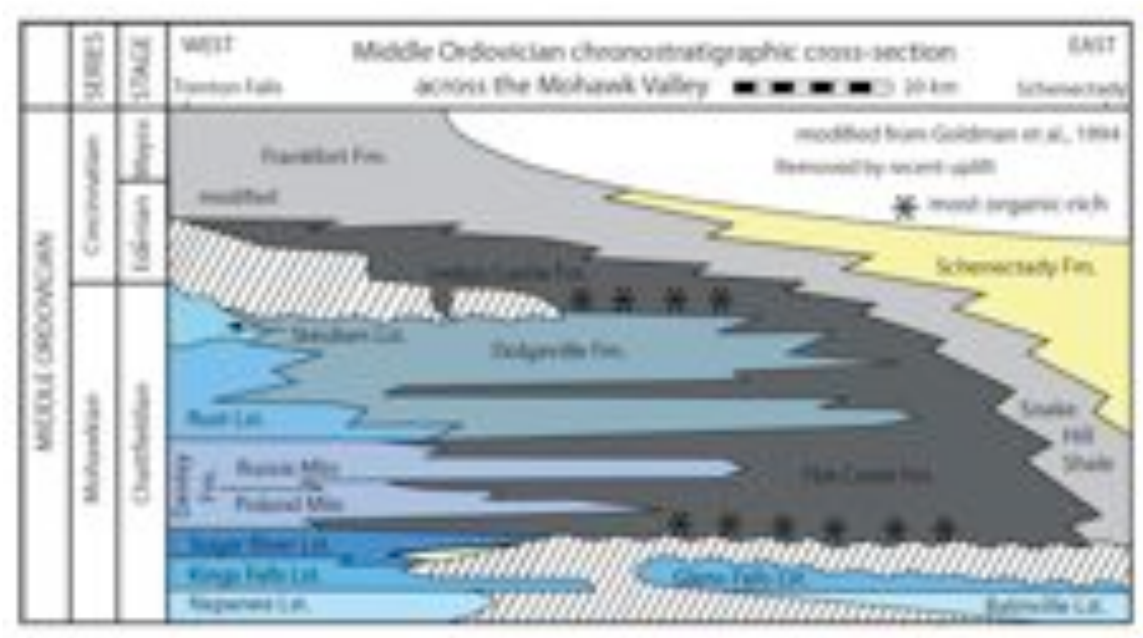

Figure 2: Stratigraphic column of central New York during the late Ordovician (Selleck, 2010)

Fractures and mineralized veins are present in the Utica Formation. These features record the stress history and fluid evolution, key factors in understanding the hydrocarbon potential of the Utica. The systematic patterns of both the fractures and veins are of importance to the petroleum industry, as fractures and faults often serve as conduits for hydrocarbon migration. Since these fractures offer access to hydrocarbons present in the Utica, drilling horizontally and at an angle perpendicular to the systematic fractures at depth could reduce or eliminate the need for high volume hydraulic fracturing, a practice not currently permitted in the New York. Analysis of regional fracture trends demonstrates that the Flat Creek underwent an early stress history different from the overlying units (Colborne, 2011). In this study, the orientation and compositional aspects of mineralized veins in the Flat Creek Member are used to define the relationship between fracturing, fluid sources, and hydrocarbon potential.

This paper describes the characteristics of mineralized veins in the Flat Creek Member from east to west across the Mohawk Valley and the relationship between vein formation and hydrocarbon maturation. These results show that the Flat Creek member fracture and mineralized vein systems in the Mohawk Valley evolved during relatively shallow burial in response to a generally E-W directed shear stress field. Veins formed as fluids migrated from the dewatering of shale, as documented by fluid inclusion and stable isotope data. Fracture and vein systems also provided connections to fluids derived from underlying Cambrian and Ordovician strata, and faulted Proterozoic basement (Jacobi, 1981; Brett and Baird, 1982). These fluids mobilized and transported sand from the basement and underlying sedimentary units to form sand dikes that fill primarily N-S Mode 1 (extensional) fractures. Volcanic ash beds within the Flat Creek were also mobilized and mixed with transported detrital grains and precipitate within vein material to form carbonate cemented sand injectite dikes. Extensive hydrocarbon staining, hydrocarbon inclusions, and stable isotope patterns indicate that fracturing and vein development was co-incident with organic maturation.

Previous Studies

Why Study the Utica Formation?

The Utica Formation is of interest to the petroleum industry. There has been active exploration in Ohio and Ontario within the Utica. Wickstrom et al. (2011) notes that 44 wells have been drilled into the Utica Formation (and Point Pleasant Formation, a western Appalachian Basin equivalent) in the state of Ohio, and thus the Utica has proven to be a productive gas shale. Artificially fractured wells in Quebec target the Dolgeville Member of the Utica Formation, which is over 200 feet thick in some areas and has proven to be productive gas shale reservoirs (Marcil et al., 2011). There are potential plays in the southern tier of New York, in Otsego County (Oil and Gas Journal, -Ross 1 Well Test Report).

Regional Stratigraphy and Tectonics

The regional tectonic setting for Ordovician-age sedimentary units of New York State is key to understanding the depositional history of the Utica Formation. Bradley and Kidd (1991) describe the creation and deepening of the Appalachian Foreland Basin during the Taconic Orogeny. The Flat Creek Member was deposited in the foreland basin that developed in response to subsidence as Laurentia collided with, and was overridden by, a prism-arc complex in the late Middle Ordovician. As summarized by Joy et al. (2000), "The accretionary load flexed the eastern Laurentian margin, resulting in structural deepening in the Taconic foredeep and a rapid increase in the rate of accommodation space growth." The overriding arc-prism caused a flexural deepening of the basin in the eastern Mohawk Valley and accommodated sedimentation. "Locally dominating forces of differential subsidence created by collision tectonism, sediment loading, and resulting lithospheric flexure" created a progressive east to west deepening of the Taconic foreland basin (Joy et al 2000). The Taconic foreland basin received fine-grained, organic-rich mud relatively poor in terrigenous clastic material. Bradley and Kusky (1986) noted that downward flexure of the Taconic foreland was accomplished as, "former continental shelf was being cut by high-angle faults." This syndepositional faulting influenced sedimentary facies patterns, and continued through deposition of the Utica Formation. This tectonic influence is supported by Smith et al. (2011) as, "Deposition and preservation of sediments is strongly influenced by syndepositional active faulting." Normal faults allowed for extension of the basin and an increase in accommodation space, allowing fine-grained sediments to accumulate, resulting in deposition of the organic-rich Flat Creek Member. Even as the Utica was deposited in the calm-water setting which is necessary for black shale development, the uplift of the Taconic Orogen produced an increase in terrigenous clastic sediment supply. This terrigenous clastic sediment is the source of the units overlying the Utica, including the Frankfort and Schenectady Formations (Figure 2).

The Frankfort is a coarsening-upward sequence of cross-bedded, submarine-fan deposits that records the initiation of erosion of the Taconic allochthon (Bradley and Kidd 1991). "Late Ordovician Frankfort Formation mud, silt and sand represent rapid filling of the Taconic foreland basin" (Selleck 2010). The filling of the basin by clastic sediments occurred rapidly, as little organic material is found in the Frankfort Shale and shallow marine clastics of the Lorraine and Pulaski Formations overly the Frankfort to the west. It is likely that the Frankfort was deposited at higher sedimentation rates, and the coarsening-upward pattern is related to both sediment accumulation and local sea-level fall resulting from relaxation of compressive stresses and lithospheric flexure as the Taconic Orogeny drew to a close. The rapid burial of organic material allowed its preservation before oxidation may have occurred. The lack of oxidation may also be influenced by oxygen-depleted, or even anoxic, conditions in the bottom waters of the Appalachian Basin.

The Utica and Frankfort formations are cut by N-S trending normal faults that were active prior to deposition of the overlying Silurian and Devonian strata in the Mohawk Valley region. These east-dipping faults accommodate normal, dip-slip displacement (Bradley and Kusky 1986). Few dip-slip indicators were noted in this study apart from three faults at Flat Creek locality that exhibited small-scale (cm to dm-scale) displacement and at the Town of Minden locality that showed oblique slip down to the west. East-dipping faults are well documented in the region (Jacobi, 1981). These N-S normal faults may be related to the N-S fracture pattern of the Flat Creek in the eastern part of the Mohawk Valley. It has been hypothesized that basement faulting and post-Taconic orogenic events (Acadian and Alleghenian) may have caused the NW-SE and NE-SW trending fractures of Utica Formation in western New York (Smith et al, 2011; Colborne, 2011). These later orogenic events may have caused some of the N-S Mode 1 fractures in the Utica Formation in the eastern segment of the Flat Creek member (Colborne, 2011).

Fractures and Veins

Lim, et al (2005) summarized the origins, temperatures, structural, and fluid characteristics of veins hosted by deformed Utica Formation equivalents in the distal portions of the Taconic frontal thrust zone (Figure 4). Most veins described by Lim, et al (2005) are calcite-filled with some minor quartz, and are "planar with continuity of <1 m to several meters or more," and are a few millimeters to a few centimeters thick. Lim, et al (2005) cite homogenization temperatures for fluid inclusions in the Taconic vein samples between ~180-250° C, while $\delta^{18}O$ values ranged from -14.36 to -10.87 PDB ‰ and $\delta^{13}C$ values ranged from -6.4 to 0.7 PDB ‰. In the veins closer to the Taconic Orogen, Lim et al (2005) proposed metamorphic sources for the fluids present while vein precipitation occurred. These values give some insight into possible fluids present in the Utica Formation during burial, however a complicated mixing of fluids is likely a cause for variation in stable isotopes.

A preliminary analysis of fractures and veins in the Utica Formation by Selleck (2010a) proposed possible changes in fracture mode from east to west in the Mohawk Valley. Mode 2 (strike-slip) fractures, as well as filling of mineralized veins, are more common in eastern and central Mohawk Valley within the Flat Creek Member. The western portion of the outcrop belt displays a different overall fracture orientation with most fractures of Mode 1 origin. E-W oriented fractures in the eastern portion of the Flat Creek Member show slip indicators such as slickenlines, en echelon fracturing, dilational jogs, and step surfaces. N-S fractures are not often mineralized, are Mode 1 tensile fractures, and are associated with sand injectite dikes in a few rare cases (Selleck 2010a). Selleck's (2010b) descriptions of veins at Town of Minden point out that, "The most abundant fracture sets trend ~N70W and N15E and are often mineralized with hydrocarbon-stained calcite." This E-W fracture set is prevalent throughout much of the Flat Creek Member in the eastern and central Mohawk Valley and is described in detail in following sections and by Colborne (2011).

Selleck et al. (2009) suggests that elevated $\delta^{13}C$ values in some calcite vein samples, were due to microbial fermentation of bitumen in later mineralized veins. Many samples also have negative $\delta^{18}O_{PDB}$ values, interpreted as secondary precipitation of calcite from of fluids that were present in the sediments at the time of burial and were reaching oxygen isotopic equilibrium with the rock reservoir (Figure 3). This preliminary study included subsurface core data, which was not available for this project.

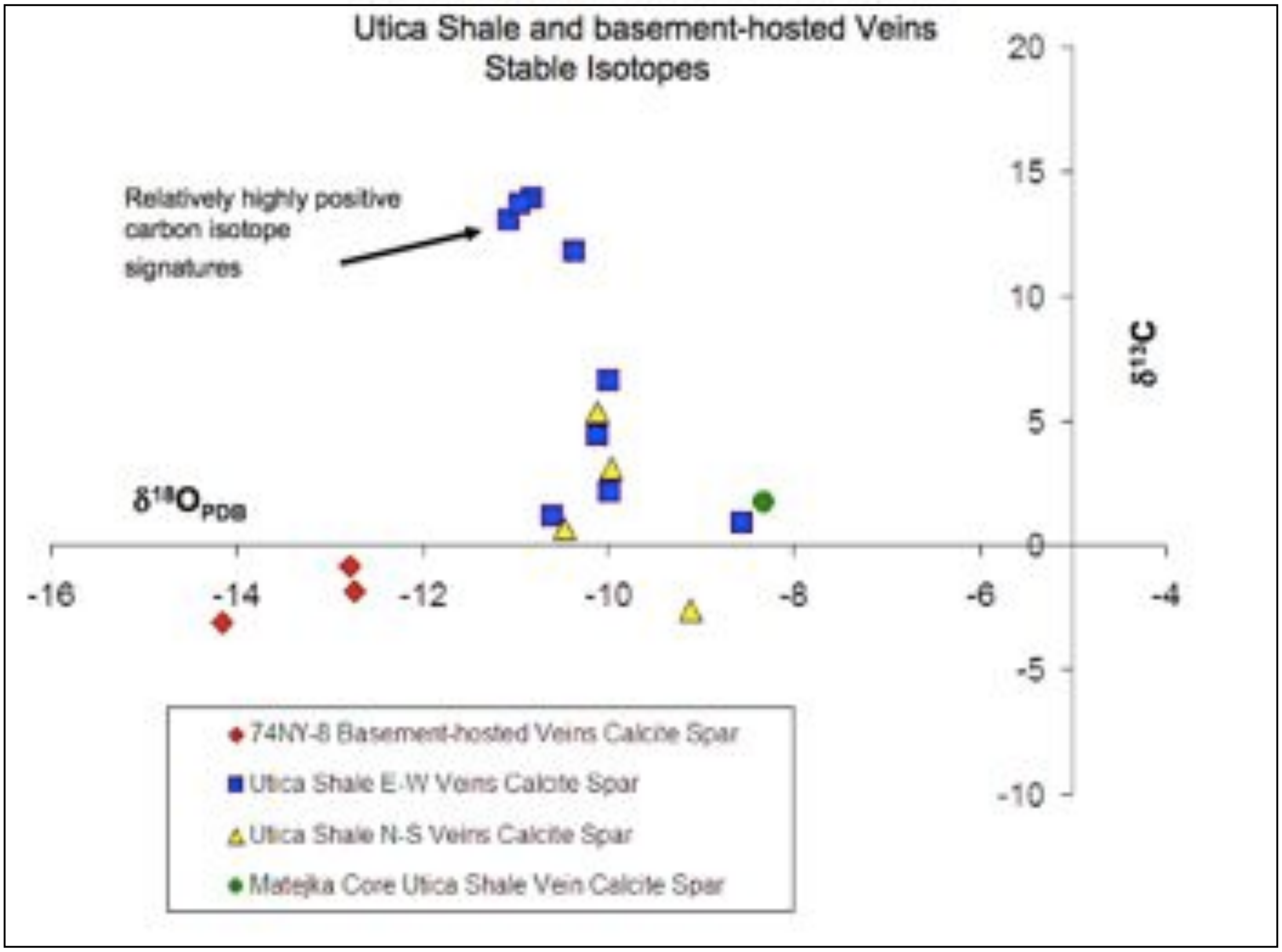

Figure 3: δ13C and δ18O plot samples from initial studies in the Utica Shale. Includes outcrop and core data (Selleck et al., 2009)

Methods

Field study of fracture and vein systems in the upper Ordovician Utica Formation and Frankfort Formation was accomplished in the summer of 2010. A total of eight localities in the Mohawk Valley were studied (Figure 4) to measure orientation of the veins and fractures and to characterize the fracture modes, as well as to assess crosscutting relationships of fractures and veins.

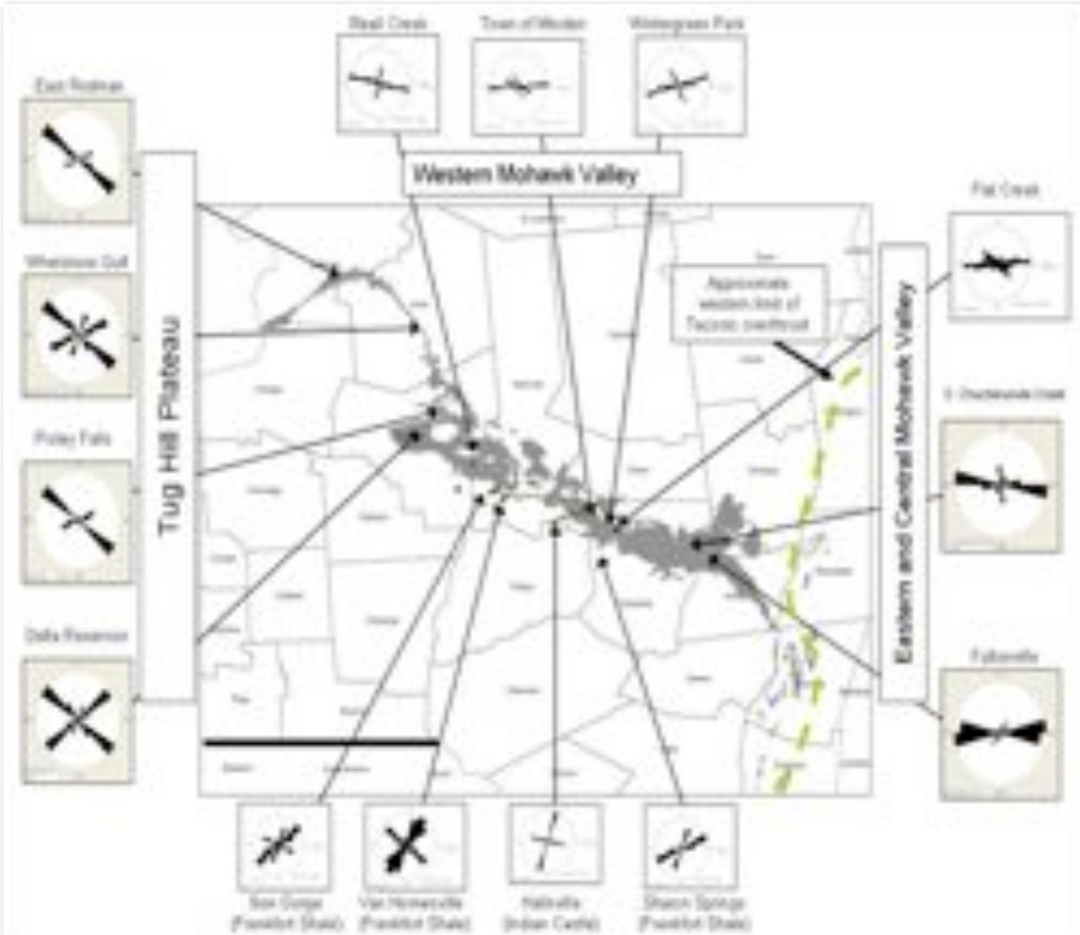

Figure 4: Map of Utica Formation outcrop in New York with generalized rose diagrams representing fracture patterns of near-vertical veins and fractures for localities of this study.

Outcrop locations were recorded using coordinates from a Magellan GPS unit. The number of measurements taken at each locality was dependent on the quality of the outcrop hence the number of observations varies considerably (Tables 1 and 2). Strike and dip measurements were made with a Silva compass were compiled to create rose diagrams (Figure 4) using the software program Stereo32. These rose diagrams allowed interpretation of strike of near-vertical fractures and veins.

Locality	**Number of Joint/Fracture Orientation Measurements**	**Stratigraphic Unit**
Frankfort Gorge	317	Frankfort
Flat Creek	412	Flat Creek
Town of Minden- Otsego Creek	94	Flat Creek
Ilion Gorge	230	Frankfort

Hallsville	62	Indian Castle
Wintergreen Park	36	Flat Creek
Reall Creek	170	Indian Castle
Total	**1321**	

Table 1: Number of fracture and vein measurements taken in this study

Locality	**Number of Joint/Fracture Orientation Measurements**	**Stratigraphic Unit**
Fultonville	21	Flat Creek
Delta Reservoir	32	Indian Castle
Whetstone Gulf	47	Indian Castle
South Chuctanunda Creek	42	Flat Creek
Pixley Falls	31	Indian Castle
Little Falls Exit	26	Flat Creek
Total	**211**	

Table 2: Number of fracture and vein measurements from Selleck (2010a)

Data from sites visited by Selleck (2010a) in the summers of 2009 and 2010 in the Tug Hill Plateau Region are included in this study, as shown in Figure 1. Different sites visited by Selleck in the summers of 2009 and 2010 in the Tug Hill Plateau Region also provide regional context for fracture differences and trends (2010a). Shale outcrop localities were recorded using the coordinates from a Magellan GPS unit. Location of field sites relative to regional stratigraphy was displayed using ArcMap, a Geographic Information Systems (GIS) mapping software program. Rose diagrams generated for each site were placed on the Figure 4 to assess regional changes in fracture orientation using a freeware program, Inkscape.

Hand samples were taken at most sites, with the majority of these retrieved from the Town of Minden-Otsego Creek, Chuctanunda Creek and Flat Creek localities. Hand samples taken from these sites are of interest because they include mineralized calcite veins, some stained with hydrocarbon bitumen. Other features include sand dike intrusions, veins containing sphalerite and pyrite, volcanic ash beds (bentonite), horizontal mineralized veins (Image 3) and en echelon mineralized veins.

Carbon and oxygen stable isotope data analysis was done on samples of vein calcite from various localities. Samples collected in this study include vein calcite from Town of Minden, Flat Creek, Reall Creek, and Wintergreen Park. Other calcite analyzed in this study are from South Chuctanunda Creek, Route 5S Roadcut, Majteka Core, and Mohawk Valley Core (Selleck et al., 2009). Prepared samples were analyzed for carbon and oxygen SIRA at the Stable Isotope laboratory at New York State University at Albany. The samples were placed in septum vials and loaded into a heated rack with temperature controlled to ± 0.1°C. 100% phosphoric acid was sequentially needle injected producing CO_2 which was then passed to a Micromass Optimagas-source triplecollector mass spectrometer for determination of stable isotope ratios. Regular standardization with NBS-7 and replicate analysis of samples indicate precision of better than 0.1% for both $\delta^{13}C$ and $\delta^{18}O$. All isotopic data are reported relative to PDB. Gas chromatography analysis was conducted on a number of bitumen and hydrocarbon samples found in vein calcite from localities of Town of Minden and Flat Creek by Exploration Technologies, Inc. in Houston, TX using a flame ionization detector.

Thin sections were prepared from many of the samples collected. Thin sections were examined under petrographic microscope and Scanning Electron Microscope (SEM), in combination with Energy Dispersive X-ray Spectrometer (EDS). These processes allowed for individual mineral analysis, imaging, and identification of individual mineral grains in features such as sand dike intrusions.

The $\delta^{13}C$ of organic carbon in shale samples was also analyzed. Dissolution of carbonate from samples in hydrochloric acid eliminated the influence of carbonate-derived carbon from calcite and dolomite, which are 60+% of most analyzed host-rock samples. After rinsing and decanting with distilled water, the samples were washed once more through filter paper and collected. Each sample was measured, weighed, sealed in foil packets, and combusted following the method established by Peck et al. (2005), "Using a Costech ECS 4010 elemental analyzer (EA) online with the Delta Plus Advantage mass spectrometer at Colgate University in continuous-flow mode." This data was plotted in Microsoft Excel and analyzed against $\delta^{13}C$ of carbonate veins at the same localities.

Results

Field Study

Field study was conducted for this project in the central Mohawk Valley region of New York. The primary goal of field analysis was to characterize the Utica Formation and overlying units, primarily the fractures and veins associated with the shale. Strike and dip measurements were taken on fractures and mineralized veins. The most notable feature in outcrop is the significant change in orientation of fractures across the outcrop belt. Table 3 indicates the orientation of major and secondary joint sets at different localities across the Mohawk Valley and Tug Hill Plateau. The eastern Mohawk Valley, including the farthest east Chuctanunda Creek locality, and central Mohawk Valley, including the western Reall Creek locality, show a dominant E-W fracture set with lesser N-S set. The E-W fracture set hosts many of the mineralized veins and many display Mode 2 strike-slip indicators. Colborne (2011) presents a more thorough discussion of fracture characterization. An attempt was made to characterize the differences between intensity of fractures in different parts of the Flat Creek Member, however the mineralogical data did not help to elucidate any trends in fracture intensity. Further research was beyond the scope of this study.

Locality (East to West)	Dominant Joint Set	Secondary Joint Set
Frankfort Shale		
Sharon Springs	N60-75E	N15-30E
Van Hornesville	N30-45E	N45-60W
Ilion Gorge	N45-60E	N30-45W
Indian Castle Member		
Hallsville	N15-30E	N75-90W
Pixley Falls	N30-45E	N15-30W
Whetstone Gulf	N30-45E	15-30W
Delta Reservoir	N30-45E	N30-45W
East Rodman	N15-30W	N40-45E
Reall Creek	N60-75W	N15-30E
Flat Creek Member		
Fultonville	N75-90E	N30-45E
S. Chuctanunda Creek	N75-90W	N0-15W
Flat Creek	N75-90 E	N45-60W
Wintergreen Park	N75-90 E	N15-30W
Town of Minden	N75-90E	N15-30W

Table 3: General strike of the two fractures set at each locality in this study.

Mineralized vein samples were collected at many localities. Large, cm-scale veins were collected at localities between Reall Creek and Chuctanunda Creek. Collection of Reall Creek samples was significantly more difficult, as only two mm-scale veins were present in a 500+ meter section of outcrop. Localities such as Chuctanunda Creek in the east, showed some impressive ~0.5m thick veins (Figure 5), while veins of 2-5 cm veins were common in many localities. The spacing of veins varies between outcrops and there is a lack of systematic spacing in most cases. There is a close association between vein mineralization and faulting, where veins were prevalent within a few meters of small faults within the Utica; however, vein mineralization is in no way limited to areas near faults. Vein mineralization was observed in the Frankfort Formation or Oneida Sandstone. Figure 6 shows the orientation of the mineralized veins at the Flat Creek locality. Figure 7 shows the orientation of unmineralized fractures at the same locality. Examples of vertical veins from the Flat Creek locality are in Figure 5. Vein mineralization in the most common in E-W trending fractures. Some minor vein filling occurred at orientations other than E-W, however it is clear that E-W fractures host vein mineralization to the greatest extent. Fractures act as conduits for fluid flow and most veins show multiple vein growth events, sometimes with hydrocarbon stained terminated calcite crystals. Most veins have margin to center mineralization patterns.

A)

B)

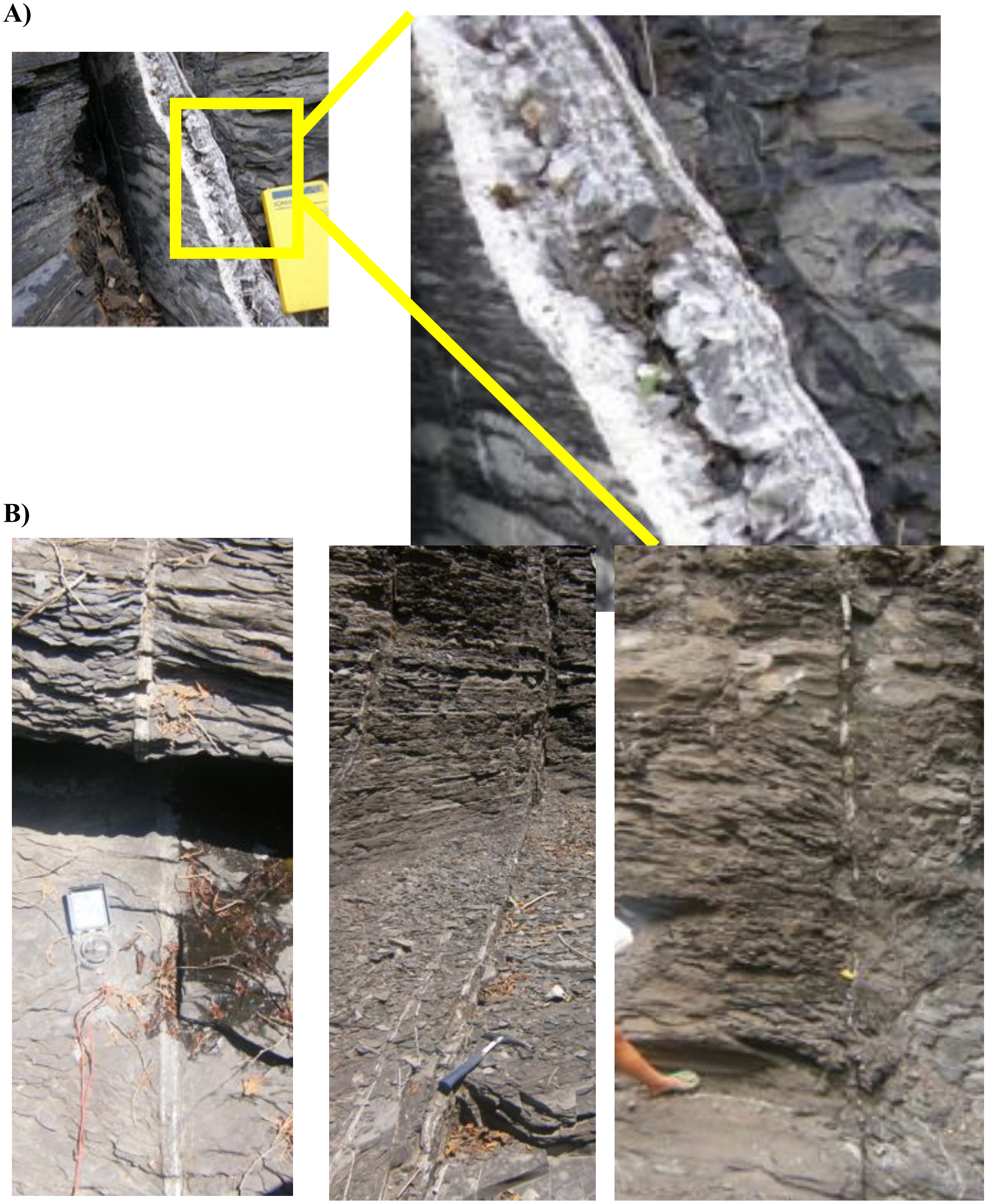

Figure 5 A: ~10cm thick vertical calcite vein with hydrocarbon staining showing multiple generations of calcite precipitation at Chuctanunda Creek locality. **Figure 5 B**: Various ~2 to 5 cm vertical calcite veins at Flat Creek locality

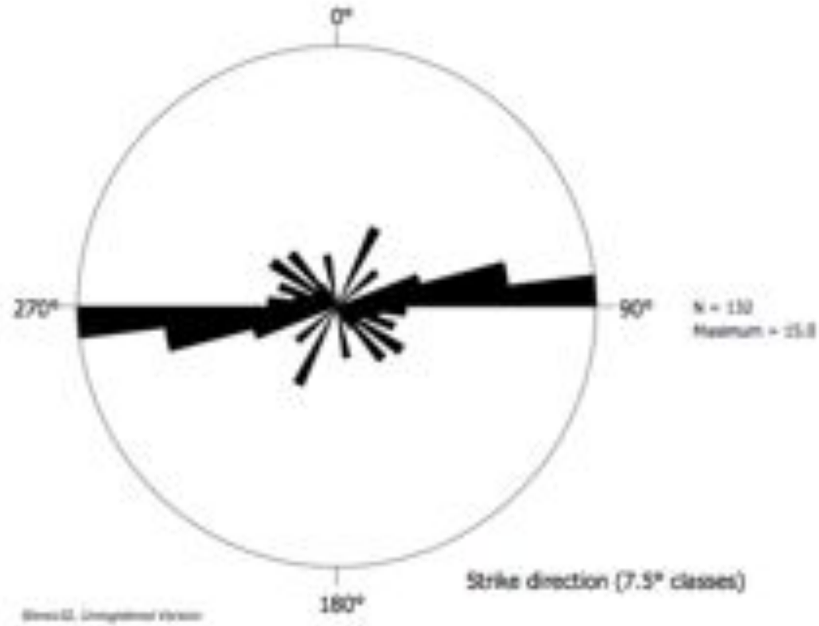

Figure 6: Rose diagram for mineralized veins showing orientation of primary set (E-W) in the Flat Creek locality, type section for the Flat Creek Member.

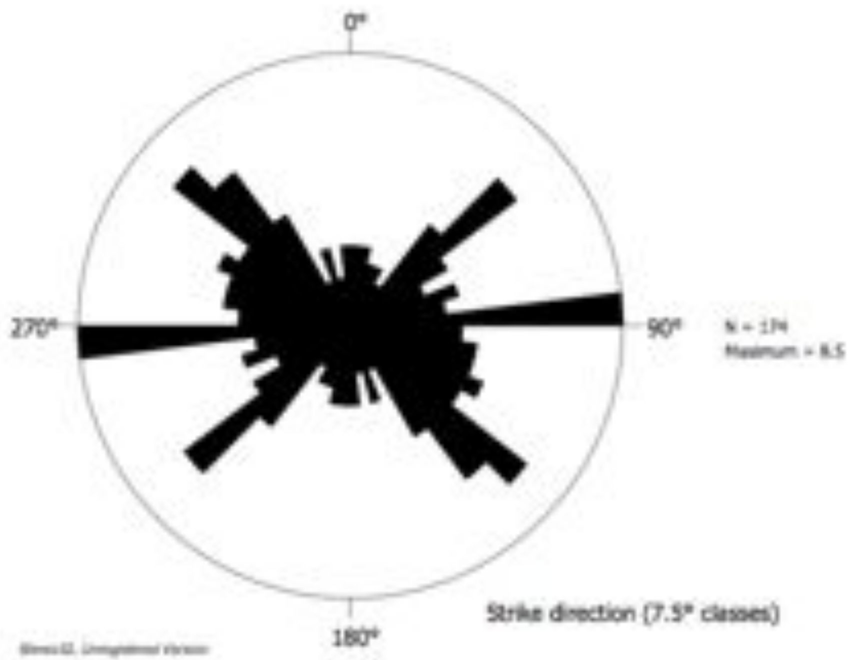

Figure 7: Rose Diagram for fractures without mineralized veins showing orientation of primary (E-W) and secondary (NE-SW and NW-SE) sets in the Flat Creek locality, type section for the Flat Creek Member.

Figure 8: Horizontal calcite veins at Town of Minden and Flat Creek localities. Town of Minden vein has hydrocarbon staining and aromatic hydrocarbons

Influences on Fracture and Vein Intensity

The vertical fractures in the upper and lower members of the Utica Formation show different strike orientation. Two distinct orientations were present in the lower Flat Creek member. Using notation presented in Engelder and Lash (2008), the J1 set of joints is an E-W oriented set of fractures that dominates outcrops from the Taconic overthrust front to the west at the Reall Creek locality (Figure 4). Near the Reall Creek locality, the Flat Creek member pinches out (Figure 2), and the Indian Castle and Dolgeville members make up the Utica. This E-W joint set hosted a large number of mineralized calcite veins at various localities in the eastern Mohawk Valley. Vein mineralization was most intense, in amount of vein filling, vein frequency, and amount of displacement between joint surfaces in the form of large spar calcite in localities eastern Mohawk Valley sites such as Chuctanunda Creek. Many of the differences in mineralization seem to depend on the distance from the Taconic thrust front. For example, Reall Creek contained two mm-scale veins within an extensive stream cut while a small length of Chuctanunda Creek outcrop contained numerous 10+ cm thick veins at close intervals (<10 m). The Flat Creek Member contained a thinner and fewer veins with increasing distance from the Taconic Orogenic front. The overlying Indian Castle member in the western Mohawk Valley and Tug Hill Plateau show a different orientation of J1 and J2 fractures in NW-SE orientation and only one mineralized vein at the Delta Reservoir outcro

Laboratory Results

The carbon and oxygen stable isotope ratios help to constrain fluid sources and temperatures of vein mineralization. The $\delta^{18}O$ in samples ranged from ~ -12.8 to -6.3 PDB ‰. The δ13C values range from ~ -11.3 to 13.9 PDB ‰. Figure 9 shows that many localities exhibited a variety of values while other localities showed grouping of values. Indian Castle Member showed a wide range of $\delta^{18}O$ values while remaining negative in $\delta^{13}C$ space. The majority of Flat Creek Member points were generally widely distributed for $\delta^{18}O$ while most $\delta^{13}C$ values are either near zero or quite positive.

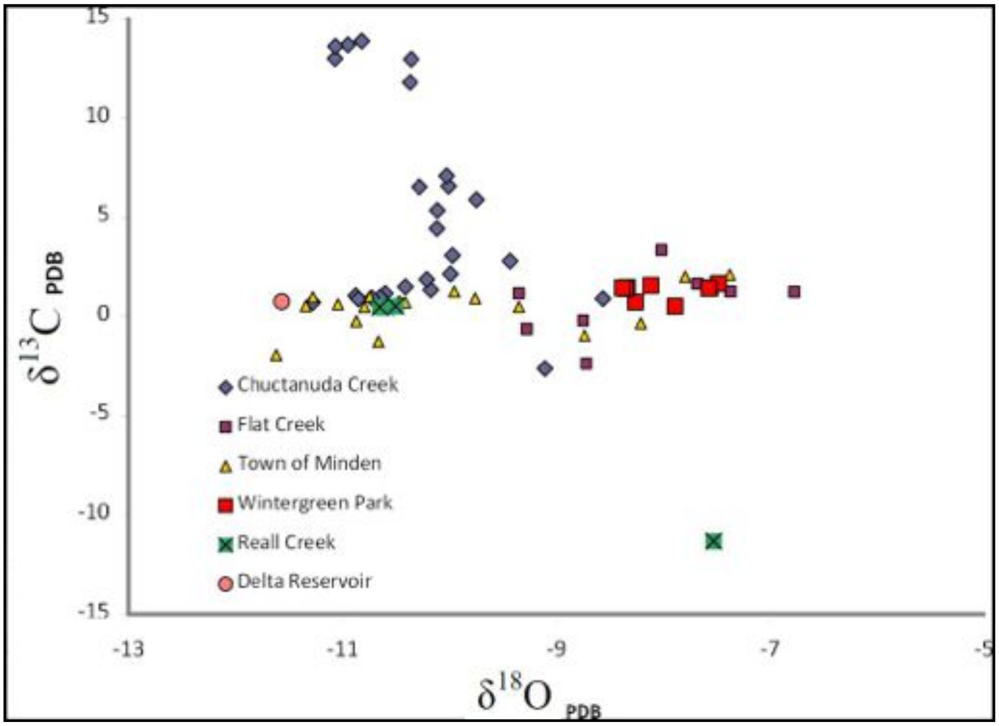

Figure 9: Stable isotope plot of calcite from various localities in the Mohawk Valley; Flat Creek Member: Chuctanunda Creek, Flat Creek, Town of Minden, Wintergreen Park; Indian Castle Member: Reall Creek, Delta Reservoir

Traverses were done across one large calcite vein from the Chuctanunda locality by Selleck et al. (2009). These traverses started at the vein margin and proceeded to the center of the vein, or to the opposite margin. Calcite was collected at 0.5 cm intervals. Figure 10 shows the $\delta^{13}C$ values associated for each incremental move toward the center of the vein. Enrichment of $\delta^{13}C$ values occurs at the center of the vein in both traverses.

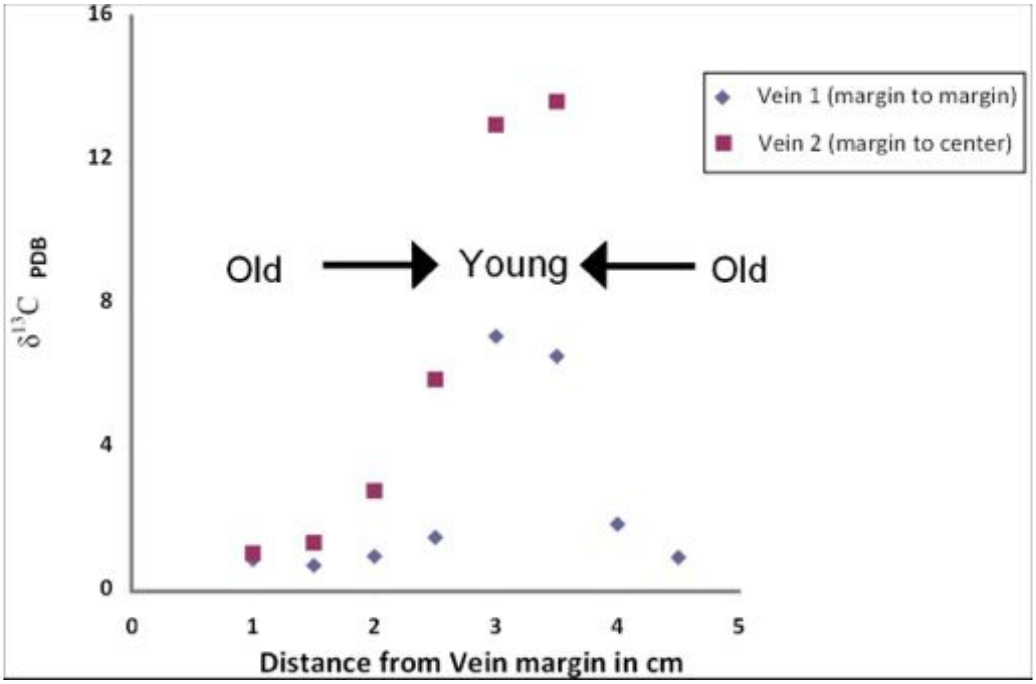

Figure 10: Calcite vein margin to center and margin-to-margin profiles of $\delta^{13}C$ showing enrichment in center of vein

Gas chromatography analyses provide data for hydrocarbons present in the calcite veins from the Flat Creek locality. 2-MP, 22, 4TMP, Toluene, and Xylene are compounds found in typical crude oil (Reuter et al. 1994), and document calcite vein formation and generation of liquid hydrocarbons in the Utica petroleum system (Figure 11 & 12).

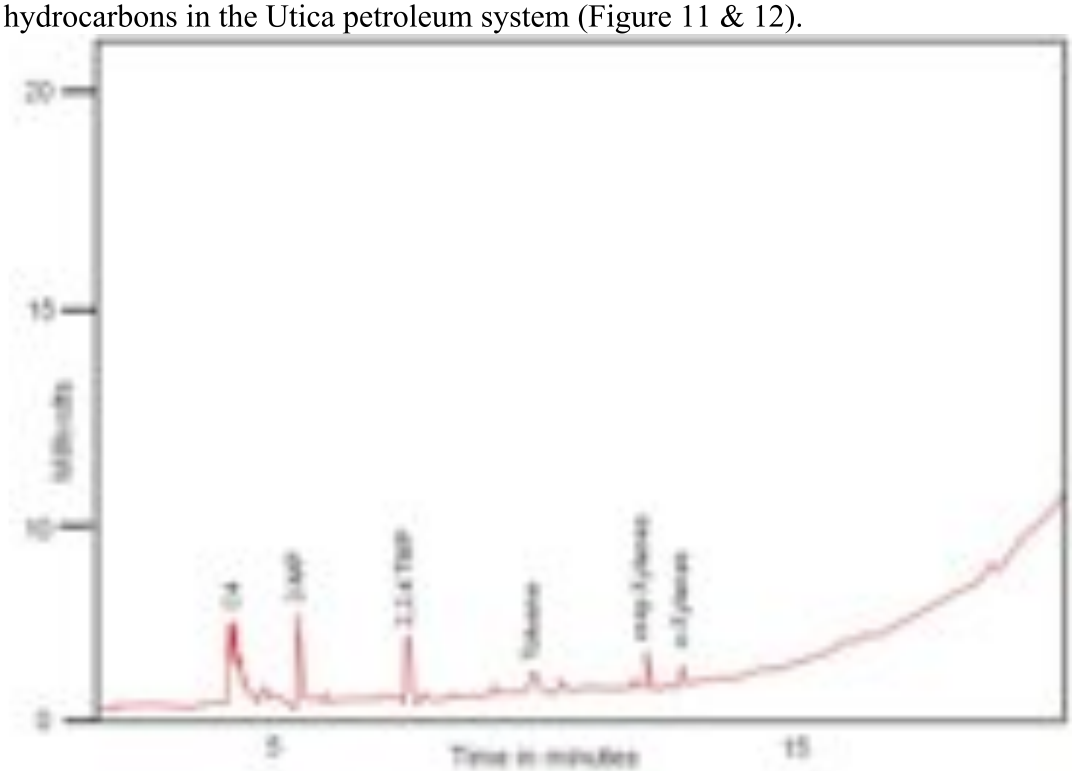

Figure 11: Gas chromatograph of heavy aromatic hydrocarbons

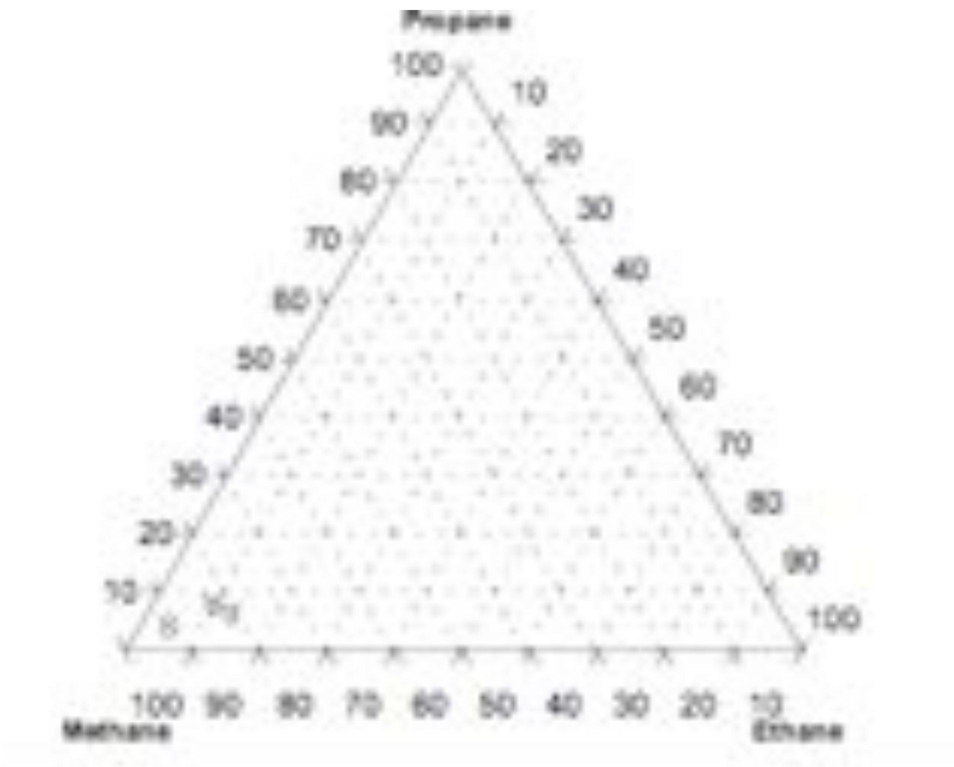

Figure 12: Ternary diagram showing C_1, C_2, C_3 hydrocarbons

Figure 13 indicates the range of temperatures for fluids involved in calcite precipitation. These values have been corrected using the equation:

$$\text{Calculated } \delta^{18}O_{Water} = \delta^{18}O_{Carbonate} - (-3.24 + 3.06*(10\text{^}6/(T_h+273)^2)$$

These calculated values indicate (at middle range temperatures and calcite values) that the initial $\delta^{18}O_{Water}$ values were slightly more enriched than normal marine seawater.

Calculated $\delta^{13}C$ values of organic carbon in the Flat Creek Member range from -29.2 to -28.4 ‰ PDB and one sample of overlying Frankfort Shale had a value of -29.4 ‰ PDB. Localities were separated and grouped for comparison (Figure 14).

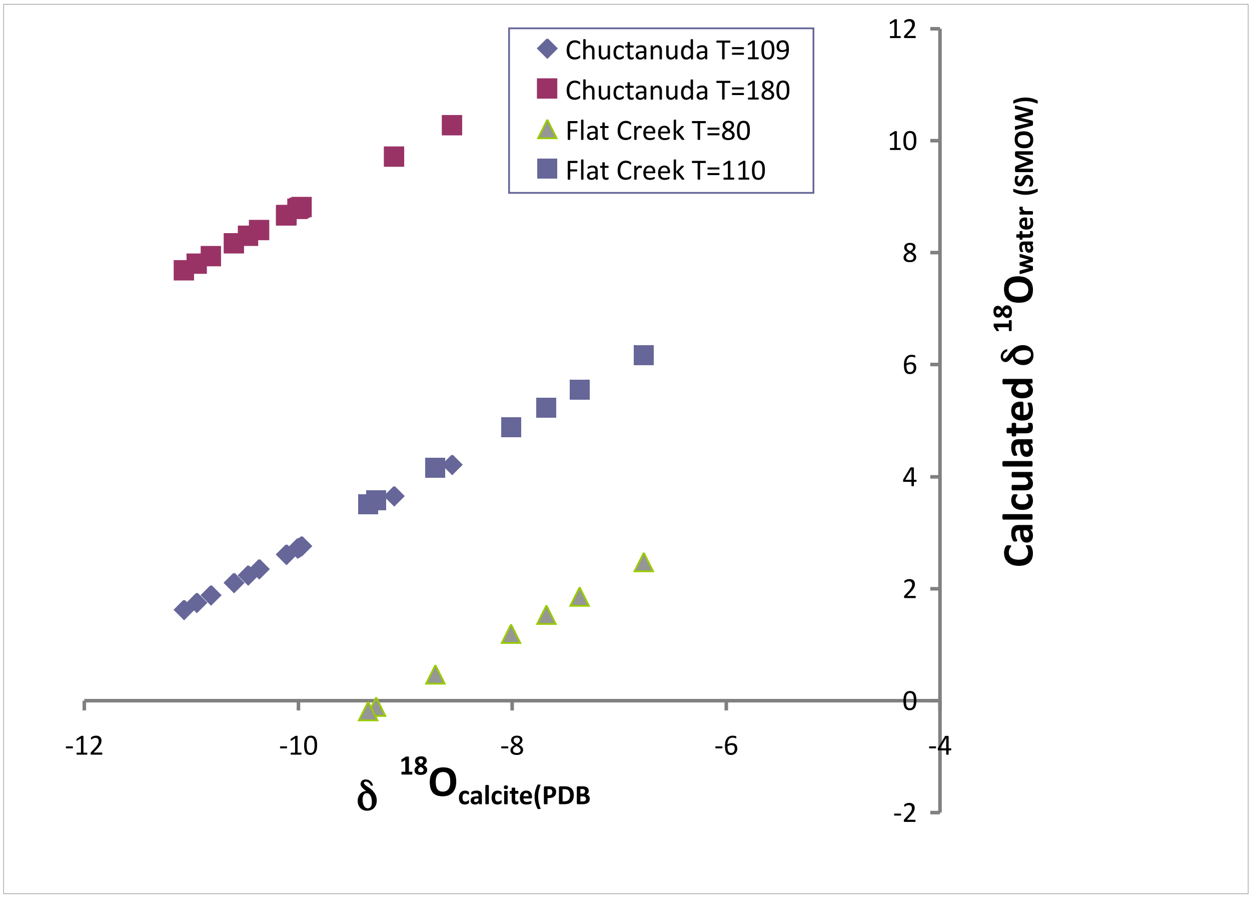

Figure 13: Calculated $\delta^{18}O$ water (SMOW) against $\delta^{18}O$ calcite (PDB) at range of temperatures displays evolved values for fluids at time of vein (calcite) precipitation.

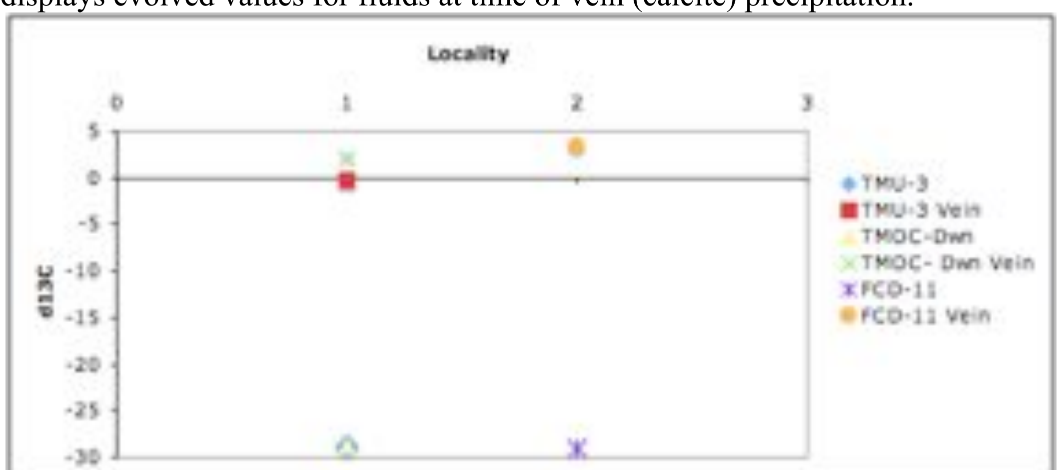

Figure 14: $\delta^{13}C$ of organic material in shale at various localities: 1-Town of Minden, 2- Flat Creek, 3- Frankfort Shale (from overlying Frankfort Shale)

Discussion

Fracture & Vein Intensity and Stratigraphic Distribution

The difference in orientation of vertical fractures between the two members in the Utica Formation may result from the influence of the Taconic Orogeny in fracturing of the Flat Creek Member. Fractures in the Flat Creek Member are primarily E-W Mode 2 (strike-slip) with less prevalent N-S Mode 1 (tensile) fractures. The overlying Indian Castle Member and Frankfort Shale show NW-SE Mode 1 fractures. The difference in orientation of fractures in the Flat Creek and Indian Castle indicate differing stress conditions causing the differing fracture orientation. The Mode 2 (strike-slip) fractures and related Mode 1 (extension) fractures in the Flat Creek Member may be an early feature in the burial history. Later extensional fracturing occurred in the post-Taconic relaxation of the Appalachian Basin (Colborne, 2011).

East-west trending Mode 2 (strike-slip) veins are dominant in the Flat Creek Member. A N-S Mode 1 (tensile) set of fractures also exists in the Flat Creek Member. Veins are ideal surfaces for recording and indicating strike-slip motion, as most fracture surfaces do not present clean surfaces for identification of motion and strike slip is often indistinguishable from bedding surfaces. Calcite veins are more resistant to weathering than the host shale. The majority of veins are filled in E-W oriented fractures and are believed to have precipitated nearly synchronously with fracturing. As evidenced by multiple generations of growth, multiple fluid events may have caused the vertically layered nature of veins. The intensity of vein mineralization is highly variable and changes between different parts of all visited outcrops. Fracturing and vein mineralization are most intense near small faults in the Flat Creek Member. Most small faults had intense fracturing, sometimes 10 or more fractures per horizontal meter of outcro The Indian Castle Member rarely hosted veins. Only two very thin (1-2 mm) veins were found at the Reall Creek locality and only one was found at the Delta Reservoir locality.

The Indian Castle Member likely does not contain vein mineralization because it may have been an unlithified sediment while the underlying Flat Creek Member underwent fracturing and sli Fluids that contributed to the mineralization of the Flat Creek Member may have migrated through the unlithified sediment to interact with seawater. This may be evidenced in stable isotope data. Sand dikes are evidence of the vertical migration of fluids and sediments in the Flat Creek Member. The N-S Mode 1 fractures, which parallel sand dikes, are possibly synchronous with vein precipitation in the Flat Creek Member. The majority of veins are seen in the eastern Mohawk Valley, imply that orogenic fluid sources may have played a part in the precipitation of veins and their intensity.

Timing of Vein Formation

The associated veins with E-W directed shear strain at many of the localities in the Flat Creek Member may support mineralization during the Taconic orogenic event. Many E-W mineralized veins contain strike-slip motion indicators not evident in veins with other orientations. The E-W component of slip is attributed to tectonically driven wrench faulting caused by the Taconic orogeny in eastern New York (Colborne, 2011). This reasoning also points to vein development shortly after deposition, prior to deep burial. This is consistent with the common occurrence of horizontal veins in the Flat Creek Member. Since one of the reasons for horizontal vein precipitation is low confining pressure, this could indicate that overlying lithostatic load was minimal and therefore early in burial history. N-S fractures are also mineralized and are parallel to sand dikes; however the timing of different vein sets is poorly constrained.

It is possible that the N-S fracture set in the Flat Creek Member was in response to the stresses of the Taconic Orogeny or as previously stated, may have been related to Post-Taconic relaxation and extension (Evans, 1995). The Utica Formation was later buried to depths > 1km, so fractures outside the E-W Mode 2 set may have been caused by a number of later stresses. The N-S Mode 1 fractures may have occurred as extension fractures at high angles to the shear fractures to accommodate the motion associated with the Mode 2 fractures and faults. The orthogonal nature of the two fracture sets in the Flat Creek Member favor this hypothesis.

Stable Isotope Analysis

Samples from the Flat Creek Member of the Utica Formation show little variability in $\delta^{13}C$ signatures for organic carbon (Figure 1). Agreement was found between this and other studies of organic carbon in the Utica Formation by Patzkowsky et al. (1997; Figure 15). When plotted against the vein carbonates most samples appear to be very similar across localities (Figure 14). This may be due to similar processes occurring at both localities in formation of vein carbonate. Sharp writes, "Inorganic thermal breakdown of the macromolecular carbon skeleton of kerogens favors the breaking of slightly weaker ^{12}C-^{12}C bonds, thereby liberating ^{13}C-depleted smaller molecules (e.g. methane and CO_2), such that ^{13}C is slightly concentrated in the residual kerogen" (2007). The more negative $\delta^{13}C$ values left over in the shale are essentially the ^{13}C molecules that have been left behind by thermal maturation. The CO_2 liberated through the thermal maturation that has occurred in the Utica is likely a significant factor in the more positive vein carbonate values, as well as the fractionation effect between organic carbon and carbonate.

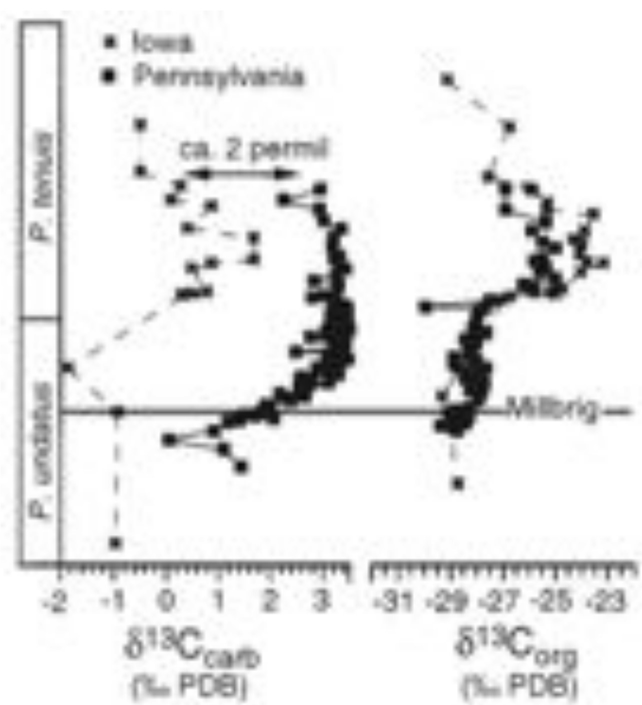

Figure 15: Data from Patzkowsky et al. (1997) indicates that $\delta^{13}C$ of organic carbon in agreement with that of this study. The Millbrig is a bentonite identifier in the section of Trenton-

Black River Formation, and the values around -28 to -29 ‰ PDB are equivalent to the Utica Formation.

$\delta^{18}O$ values of carbonate indicate a complicated temperature and source history of fluids that were present at the time of vein mineralization in the Utica Formation. $\delta^{18}O$ of water involved in the precipitation of calcite was found to be slightly enriched compared to normal marine seawater (Figure 13). The waters present at Chuctanunda Creek and Flat Creek localities may be considered to be evolved, as they underwent equilibration with the host carbonates to some extent. This fluid influenced the stable isotope signatures of veins precipitating in the Utica Formation. These slightly more positive fluids may have contributed to the spread nature of the $\delta^{18}O$ data. More careful sampling is necessary to constrain which event of fluid migration, and subsequent vein precipitation, is analyzed in future studies. This is exhibited by the varying nature of veins of $\delta^{13}C$ values in Figure 10. The values at the margin and center are affected by the source and temperature of fluids. Many sources of fluid may were been present during vein precipitation, from connate waters derived from the adjacent shale, to seawater, to basement-derived fluids. The large spread of $\delta^{18}O$ values indicates that no singular fluid sourced the precipitated veins in the Utica Formation, especially at the scale of individual localities.

One key point for upward migration comes from fluid dynamics and the permeability of shale. In many cases, any tectonic fluid sources present, even during 2-3 km burial, would have to travel from the Taconic thrust for (up to 160 km to the West) through relatively impermeable shale. The vertical fracture and fault network likely allowed for upward migration of fluids from basement sources, however did little to allow horizontal flow from the Taconic orogeny. Dix et al. (2010) suggest the possibility of such faulting that might have allowed for ocean-bottom exhalation of fluids rich in carbonate and basement material. This model is supported by the sand dike injectites found in the Flat Creek Member and possibly by an anomalous homogenous carbonate bed at the Hallsville locality in the Indian Castle Member. This evidence points to vertical fluid flow through the Utica Formation.

Temperature of Formation

Homogenization temperatures from fluid inclusions in calcite from Chuctanunda Creek indicate minimum homogenization temperatures of vein formation of ~140º C (Selleck et al., 2009). These temperatures represent syn-fracturing temperatures, possibly influenced by tectonically driven fluids of the Taconic orogen that had cooled away from the thrust front. Lim et al. (2005) found a range of temperatures in fluid inclusions from Taconic vein samples ranging from 133° to 297° C, with the majority of the samples between 190° to 260° C. These higher homogenization temperatures are from a study area significantly closer to the Taconic Thrust Front where temperatures would likely be higher. This is consistent with the theory that precipitation from tectonically-derived fluids show a cooling trend away from the orogenic areas and that tectonism played a role in the fracturing and vein mineralization in the Utica Formation. Hydrothermal influence from basement sources may have also influenced the heating around the time of fracturing and vein mineralization. The fluid inclusion data indicate moderate temperature which might be caused by a mixture of basement and fluid source from within the Utica Formation. Stable isotope data suggest that fluids present during vein mineralization were sourced from dewatering of the Utica during lithification and from hydrothermal sources, indicating slightly evolved oxygen values that have undergone slight heating.

The Chuctanunda Creek locality is less than 50 km west of the Taconic thrust front. Many veins at Chuctanunda Creek have bitumen staining, that of overheated hydrocarbon which forms small deposits of anthraxolite. Bitumen staining occurs at a number of localities in the eastern region of outcrop, indicating that burial, hydrothermal maturation, and orogenic heating may have provided temperatures necessary for converting fluid petroleum hydrocarbon to bitumen. Fluid inclusions temperatures are beyond those of liquid petroleum maturation. Hydrocarbon staining on calcite surfaces may represent heating beyond oil maturity.

Similar findings were presented by O'Reilly and Parnell (1999) for fluid inclusion temperatures in the underlying Little Falls Formation of ~68 to 130° C. These values are closer to those of this study and may have been the source of the fluids which precipitated the veins in the Flat Creek Member. The moderate temperatures of Selleck et al. (2009) indicate those above oil maturity. Presuming the model of fracturing and vein mineralization during early burial is correct, geothermal gradients are not sufficient for such temperatures found in the Utica Formation.

Relationship to Hydrocarbon Generation

The $\delta^{13}C$ values of serially sampled veins show that PDB values are elevated (more positive) that normal marine carbonate (0‰). The positive excursions are possibly due to the biodegradation of hydrocarbons or thermogenic degradation. Aerobic degradation of petroleum generates ^{13}C-enriched CO_2 (Dimitrakopoulos and Muehlenbachs, 1987), which could have been incorporated into the precipitated vein calcite. This degradation helps to explain the highly positive values associated with many of the localities shown in Figure 9. Dimitrakopoulos and Muehlenbachs (1987) note that the ^{13}C enrichment is mainly due to fractionation of CO_2 during the initial fermentation processes that lead to mineralization of ^{13}C- enriched calcite. These findings support the hypothesis that fluids become more enriched as the isotopically lighter CO_2 in the fluids is incorporated into mineralization of vein calcite.

The study of calcite veins from Chuctanunda Creek show isotopically heavy mineralized calcite vein material at the center of the vein, suggesting that the last fluids in each fracture were enriched in heavy ^{13}C (Figure 10). The fluids, especially at Chuctanunda Creek, indicate texturally and isotopically that multiple episodes of vein generation have occurred, and the growth of calcite with increased $\delta^{13}C$ values occurred toward the end of vein mineralization. It may be hypothesized that different fluids were present during the different crystallization events; however, the smooth curve of $\delta^{13}C$ values and the bell-shaped nature of the curve (Figure 10) help to indicate an enrichment of ^{13}C throughout the history of vein filling. This may be attributed to preferential fractionation of lighter ^{13}C in early stages of growth and is a sort of enrichment of the existing fluids to heavier $\delta^{13}C$ values.

One vein from Reall Creek showed extremely negative δ13C values (-11.3‰) while other veins show values closer to normal marine carbonate values (0.5‰), similar to those of the host shale. The very negative value may represent the influence of the oxidation of methane (Whiticar, 1999). Only one point indicates this effect, however methane was likely generated during early burial of the Utica.

Conclusions

1. Vein mineralization in the Utica Formation is most prevalent in the Flat Creek Member and is more intense near the Taconic Thrust Front in the eastern region of the Mohawk Valley.

2. The early precipitation of veins and maturation of hydrocarbons is an indication that fracturing, vein mineralization, and hydrocarbon generation were occurring almost synchronously, during early burial.

3. Horizontal veins represent low confining pressure and/or high fluid pressure and are evidence of early burial phenomena.

4. Original fluid composition is slightly positive in $\delta^{18}O$, indicating evolved waters in equilibrium with host shale carbonate.

5. $\delta^{18}O$ values indicate mixing of seismically pumped fluids in fault systems with connate fluids, and/or seawater.

6. Microbial degradation and thermodegradation of hydrocarbon has taken place in the Flat Creek Member and precipitated positive $\delta^{13}C$ calcite.

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