PS Diagenetic Evolution of the Cherry Valley Member of the Oatka Creek Formation, Marcellus Subgroup, New York*

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Abstract

Textural and compositional heterogeneity within the Cherry Valley Member (CV) of the Oatka Creek Formation (Middle Devonian Marcellus subgroup) reveal a complex diagenetic history of the Appalachian Basin in New York. The CV represents laterally extensive, nodular offshore carbonates composed of pelagic fauna (e.g., goniatites), and it contrasts both lithologically and petrophysically with its bounding mudstones, regionally the East Berne Member of the Oatka Creek Formation (overlying) and Bakoven Member of the Union Springs Formation (underlying). The highly contrasting interfaces between carbonate and mudstone produce porosity- and permeability-controlled fluid flow that has influenced diagenesis. The CV is compositionally dominated by carbonates, all of which are diagenetic. Early diagenesis includes calcareous nodule formation prior to lithification, followed during burial by distinct generations inclusive of calcite, ferroan calcite, ankerite, siderite, barite, and other minerals likely representing distinct phases. The mudstones above and below have mixed matrices of illitic clays and a variable amount of calcite cement, with higher amounts coinciding with microfossil-rich laminae, and exhibit a divergent diagenetic history from the CV. Organic material is largely restricted to these mudstones and is characterized as highly dispersed, kerigenous residue that coats matrix components including pore walls hosted within clay crystallites and cements. Though the Marcellus subgroup is one of the most studied units in the United States, little work has been done to document the changes in lithology, composition, and texture from one portion of the basin to another as a function of diagenesis. The evolution of diagenesis has largely been studied within discrete zones of the basin, identifying compositional trends without specifying the diagenetic stage to which any mineral or chemical product corresponds. The CV provides a good opportunity to examine diagenetic changes to a basin-wide, contemporaneous unit that was subjected after deposition to a range of burial regimes during the Alleghanian orogeny. Qualitative petrographic descriptions and quantitative compositional analyses, including thin section petrography and scanning electron microscopy, are combined to describe the textural and compositional framework of the rocks at a range of scales. Compositional analyses include X-ray diffraction and energy dispersive X-ray spectroscopy.

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Core information/API: Tioga County Core (formally as “Strong #1”, 31-107-26466); EGSP NY-4 (also named “Valley Vista View 1”, 31-101-15268), Beaver Meadows Core (formally as “Beaver Meadows #1, 31-017-23006); Cargill Salt Core (formally as “Cargill Test #17”, 31-109-13173)

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ABSTRACT

Textural and compositional heterogeneity within the Cherry Valley Member of the Oatka Creek Formation (Middle Devonian Marcellus subgroup) reveal a complex diagenetic history within the Appalachian Basin in New York. The highly contrasting interfaces between the carbonate member and its encasing mudstones produced porosity- and permeability-controlled fluid flow that has influenced diagenesis. The Cherry Valley Member provides a very good opportunity to examine diagenetic changes to a basin-wide, contemporaneous unit that was subjected after deposition to a range of burial regimes during the Alleghanian orogeny and a range of subsequent exhumation and fluid flow regimes. Improved predictability of diagenetic minerals may lead to better models for reservoir risk assessment.

The Cherry Valley Member represents laterally extensive, nodular offshore carbonates composed of pelagic fauna (e.g., goniatites). It contrasts both lithologically and petrophysically with its bounding mudstones, regionally the East Berne Member of the Oatka Creek Formation (overlying) and Bakoven Member of the Union Springs Formation (underlying). Compositionally the Cherry Valley Member is dominated by carbonates, all of which are diagenetic. Early diagenesis includes calcareous nodule formation prior to lithification, followed during burial by distinct generations inclusive of calcite, ferroan calcite, ankerite, siderite, barite, and other minerals likely representing distinct phases. The mudstones above and below have mixed matrices of illitic clays and a variable amount of calcite cement, with higher amounts coinciding with microfossil-rich laminae, and exhibit a divergent diagenetic history from the Cherry Valley Member. Organic material is largely restricted to these mudstones and is characterized as highly dispersed, kerigenous residue that coats matrix components including pore walls hosted within clay crystallites and cements.

Though the Marcellus subgroup is one of the most studied units in the United States, little work has been done to document the changes in lithology, composition, and texture from one portion of the basin to another as a function of diagenesis. The evolution of diagenesis has largely been studied within discrete zones of the basin, identifying compositional trends without specifying the diagenetic stage to which any mineral or chemical product corresponds. This study reveals diagenetic features and paragenetic sequence in the Cherry Valley Member and adjacent mudstone across the Appalachian Basin, to be interpreted relative to burial, thermal, and fluid flow controls. This poster reports on four cores in New York State, to be followed soon by analysis of five cores from Pennsylvania and West Virginia.

GEOLOGIC SETTING AND BACKGROUND

Paleogeographic reconstructions place the eastern margin of North America at 30° S latitude during the time of Marcellus subgroup deposition in the Middle Devonian. The Acadian Orogen thickened the crust adjacent to the Appalachian Basin from present-day Canada to the southern Appalachians in the United States. Maximum burial of Paleozoic strata occurred at approximately 300 Ma, or concurrent with continued Alleghanian tectonism (Heizler and Harrison, 1998). Apatite-fission track analyses indicate that Upper Devonian to Upper Pennsylvanian strata near the Allegheny Mountain front cooled from greater than 110 °C during the early post-Alleghanian period (Roden and Miller, 1989), though Upper Devonian rocks at more distal positions in the basin cooled from lower temperatures (80-110 °C) (Miller and Duddy, 1989). Given assumptions about geothermal gradient, these results reveal a maximum burial depth of 3.4 km in Devonian to Pennsylvania strata in Pennsylvania (Roden and Miller, 1989), 3-4 km in the Catskill region of New York, 2-3 km for western New York (Miller and Duddy, 1989), and 3.1 km in Maryland, West Virginia, and Virginia (Roden, 1991). Rapid unroofing/cooling occurred during the Mesozoic and continues to present-day as the Marcellus subgroup is up to 1,500 m deep in New York.

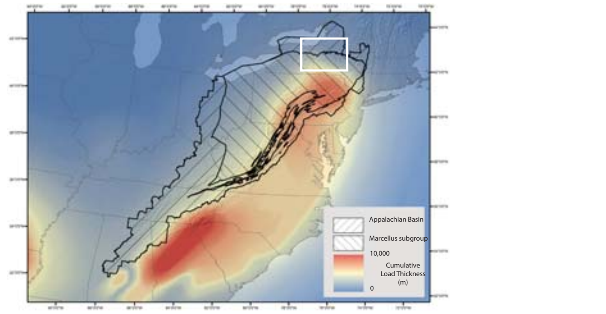

Fig. 1: Total Alleghanian orogeny isopach map with the extents of the Appalachian Basin and Marcellus subgroup in the United States (modified after Beaumont et al., 1987). White box defines area shown in Fig. 2.

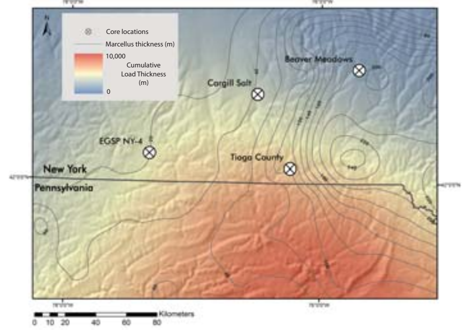

Fig. 2: Highlighted view of the total Alleghanian orogeny isopach map with total thickness contours (interval = 20 m) of the Marcellus subgroup in New York showing the locations of used cores in this study.

DEPOSITIONAL HISTORY

A vertical succession of marine siliciclastic and carbonate rocks composes the Middle Devonian strata. The Marcellus subgroup overlies the Onondaga Formation, typically a "clean" limestone. The Marcellus represents an influx of siliciclastic detritus. The Cherry Valley member divides the Union Springs Formation from the overlying Oatka Creek Formation (Figure 3, right; Figure 6, bottom-right). The Cherry Valley–Union Springs contact is unconformable. Organic-rich mudstones of the Marcellus subgroup are thought to have been deposited in anoxic to euxinic conditions (Lash and Blood, 2014; Mason, 2017). Precise depositional conditions for the Cherry Valley Member are largely unknown due to, in part, the destruction of depositional fabrics and fossil recrystallization during diagenesis. The macroscale properties of the Cherry Valley are taken as evidence of a drop in base level and influx of oxygenated conditions.

The Cherry Valley Member thins to the west and is generally less than 5 m thick in New York (Figure 4, right), compositionally dominated by carbonates, all of which are diagenetic, and lithologically made up of calcareous and dolomitic mudstones, wackestones, and packstones (by the Dunham classification system). Calcareous and baritic nodules are common. The fossil assemblage is extensive (Figure 5, bottom-left): dacryoconarids -- an extinct marine zooplankton -- trilobites, cephalopods, ostracodes, calcispheres, crinoids, phosphatic bone fragments, and nondescript fossil hash. The mudstones above and below have mixed matrices of illitic clays and a variable amount of calcite cement.

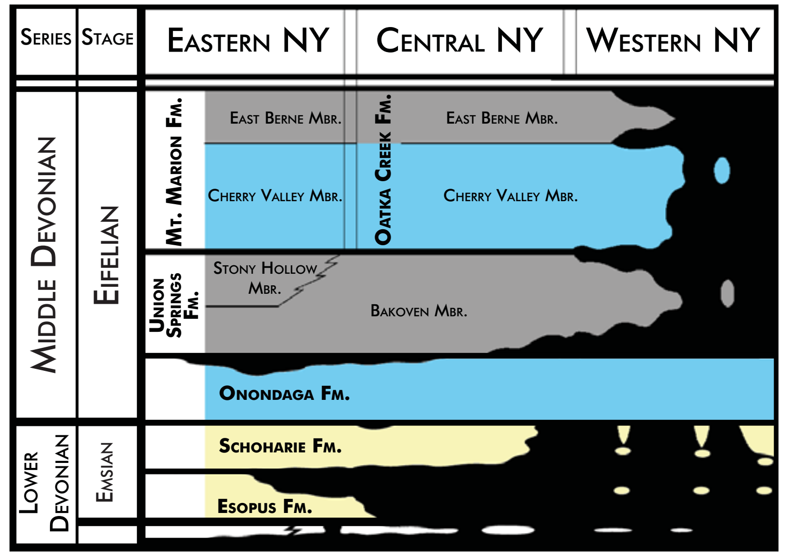

Fig. 3: From Ver Straeten (2007), Appalachian Basin stratigraphy across Lower and Middle Devonian units in New York. Mudstones are gray, carbonates are blue, and grain-supported strata are yellow.

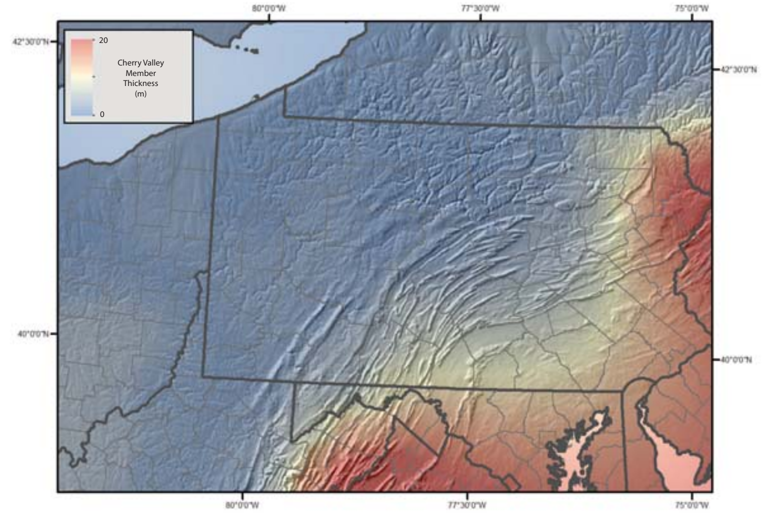

Fig. 4: Interpolated thickness map of the Cherry Valley Member across the Appalachian Basin (modified from Lash and Engelder, 2011).

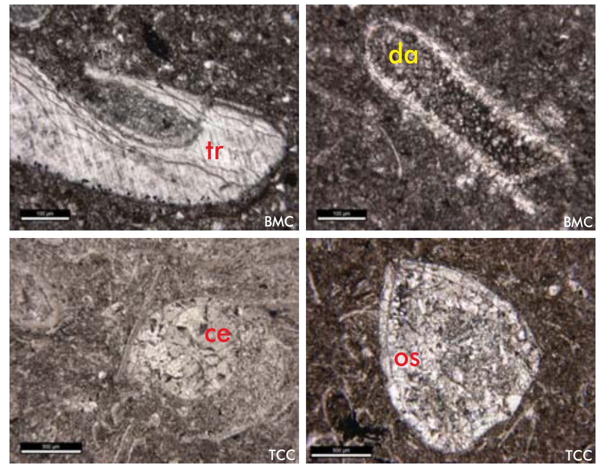

Fig. 5: Photomicrographs of common fossils observed in the Cherry Valley Member. tr = trilobite; da = dacryoconarid; ce = cephalopod; os = ostracode.

Fig. 6: Photo of the Cherry Valley Member exposed at the Chestnut Street outcrop east of Cherry Valley, NY, showing the overlying (East Berne Member of the Oatka Creek Formation) and underlying (Union Springs Formation) mudstones of the Marcellus subgroup.

METHODS

Reflectance Spectroscopy

Fig. 7: The reflectance spectroscope measures direct transmittance as a percent, representing the ratio of the incident light beam that is transmitted by the sample.

Reflectance spectroscopy is used on core to detect compositional changes among horizons and to narrow sample selection. This method uses resonance vibrations caused by activating chemical bonds by irradiating mineral crystals. An absorption spectrum is produced when the energy of these vibrations is reduced and its position in the visible- and near-infrared spectra indicates the type of bond. This spectrum is generally characteristic of a singular mineral.

A TerraSpec 4 Standard-Res Mineral Analyzer was used on the four available cores. The spectroscope analyzes at the visible near-infrared and shortwave infrared wavelength range of 350-2500 nm.

In carbonates, the cation present shifts the resultant spectrum to indicate the respective mineral. To collect a spectrum, core is first cleaned and dried to remove drilling mud or other material that may interfere with the analysis. Spacing of analyses is approximately 3-4 cm apart, with closer spacing within the Cherry Valley Member and wider in mudstones. A handheld contact probe fitted with a halogen bulb is white-balanced and then held against the surface of the core to collect for approximately 10 seconds before moving down the core to the next location. White balancing must be redone every 10 minutes to ensure consistent results. Mineralogy is matched to spectra using the Spectral Geologist Pro mineral analysis software to determine an on-the-spot, preliminary mineralogy and assist in thin section, X-ray diffraction, and scanning electron microscope sampling.

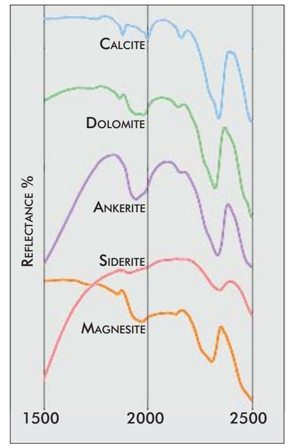

Figure 8: Stack plot of characteristic spectra of carbonate minerals from The Spectral Geologist® Reference Library. Reflectance values are relative to individual minerals.

X-ray Diffraction:

Leftover thin section material is ground using a mortar and pestle and loaded onto a glass holder. A Bruker D8 Advance ECO powder diffractor analyzes from 18-45° two-theta (2Θ) using Cu K-α radiation at 40kV and 25mA with a 0.2 second step time (1,389 total steps and 306.2 seconds total scan time). JADE software identifies mineralogy based on whole pattern fitting. This analysis yields data for the mineral phases that are present in the selected sample, though it does not quantify the proportions of minerals. Separate samples containing clay-sized particles are not prepared due to the low amount of clay present in the Cherry Valley Member.

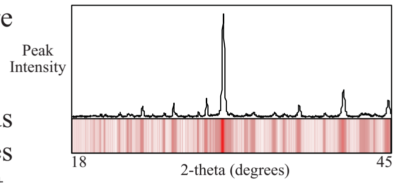

Fig. 9: X-ray diffraction spectrum of a dolomitic limestone. Spectra are converted to converted to one dimension for log view (center panel). Red represents peaks with increasing peak intensity being brighter and white representing noise.

Thin Sections:

Sampling from the Tioga County core was continuous throughout the Cherry Valley Member while sidewall plugs were chosen only at select horizons from the Beaver Meadows (8) and EGSP NY-4 (10) cores. Billets were mounted to standard glass slides and ground to a thickness of 30 microns. Thin sections are treated with a dual carbonate stain, including Alizarin Red and potassium ferricyanide, to highlight calcite (pink), ferroan calcite (purple), and ferroan dolomite or ankerite (blue). The prepared thin sections are observed under plane-polarized, cross-polarized, and reflected UV light at various magnifications on a Leitz Laborlux 12-POL petrographic microscope fitted with a Leica DFC 400 camera. Petrographic observations are intended to describe the relationship between texture and composition as they relate to diagenesis.

Fig. 10: Full thin-section photo of an ankeritic interval in the Tioga County core, displaying the effect of a dual carbonate stain as ankerite is stained blue.

Scanning Electron Microscopy:

The thin section billet is broken with a hydraulic splitter across bedding to expose a fresh surface for electron microscopy. The sample, matching the length of its corresponding thin section, is mounted on a standard aluminum SEM pin stub and sputter-coated with a conductive metal such as iridium, platinum/palladium alloy, or palladium/gold alloy. The samples are then imaged in a field emission scanning electron microscope, including a LEO 1550 FE-SEM or FEI Quanta 650 FEG, equipped with an energy dispersive X-ray spectrometer. Samples are viewed primarily with a secondary electron detector, with lesser use of a backscatter electron detector, to describe microtextural and compositional elements.

DIAGENETIC EVOLUTION OF THE CHERRY VALLEY MEMBER OF THE OATKA CREEK FORMATION, MARCELLUS SUBGROUP, NEW YORK

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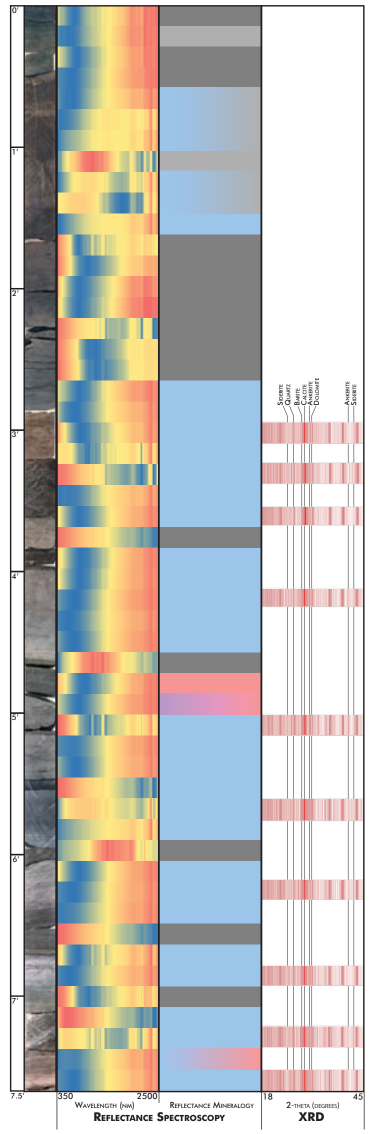
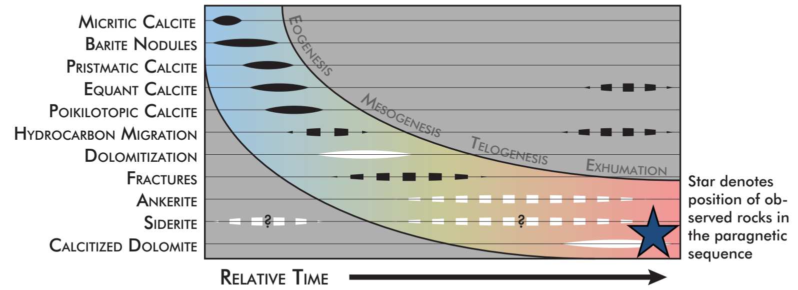
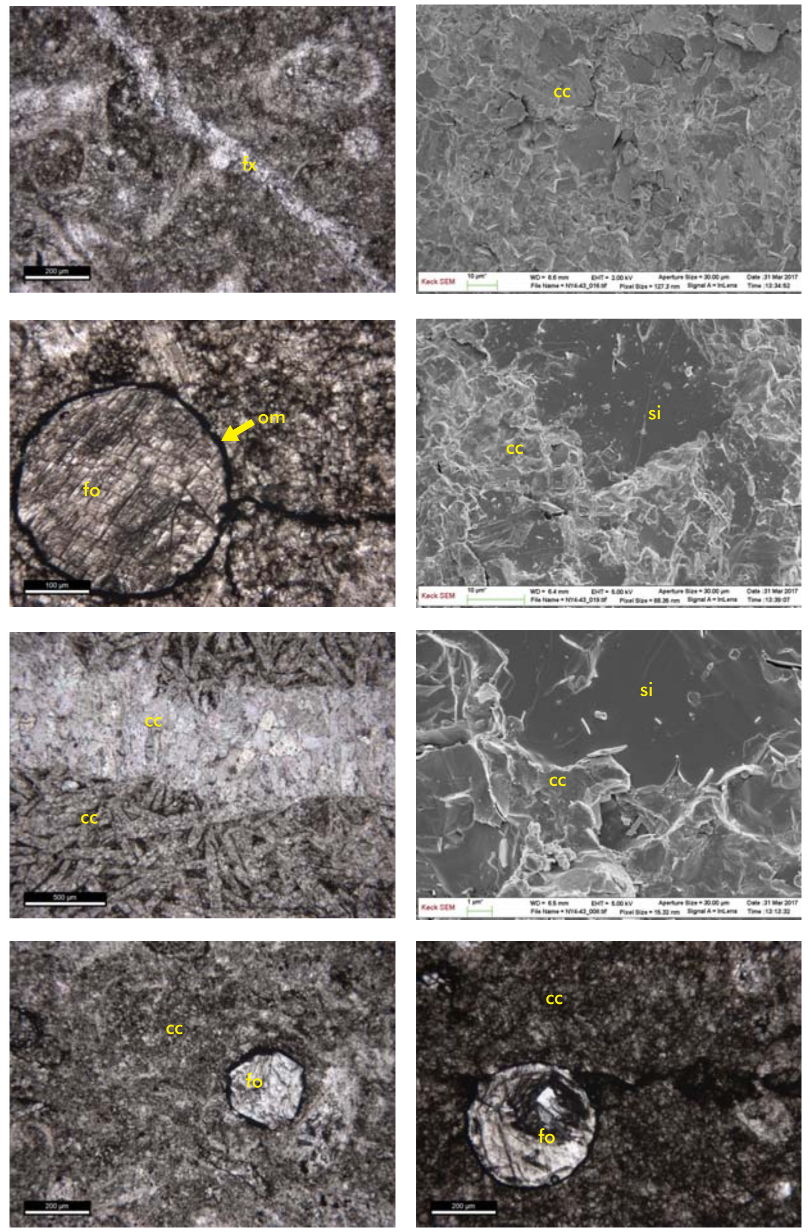
EGSP NY-4 Core



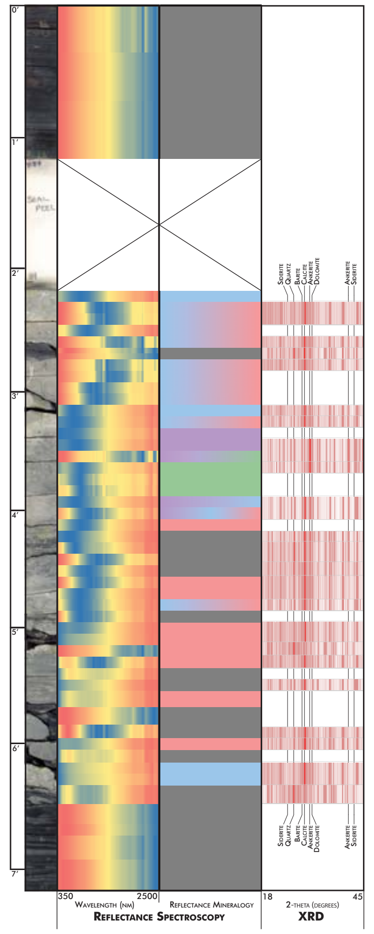


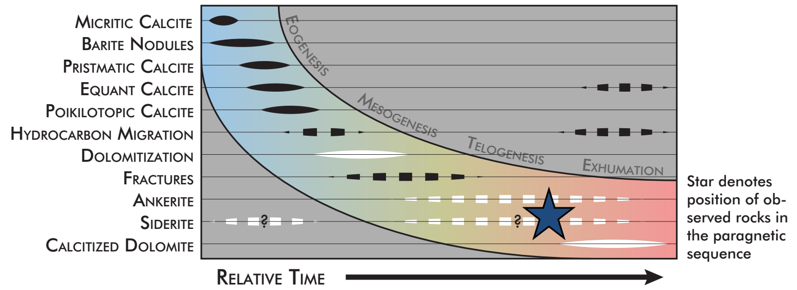


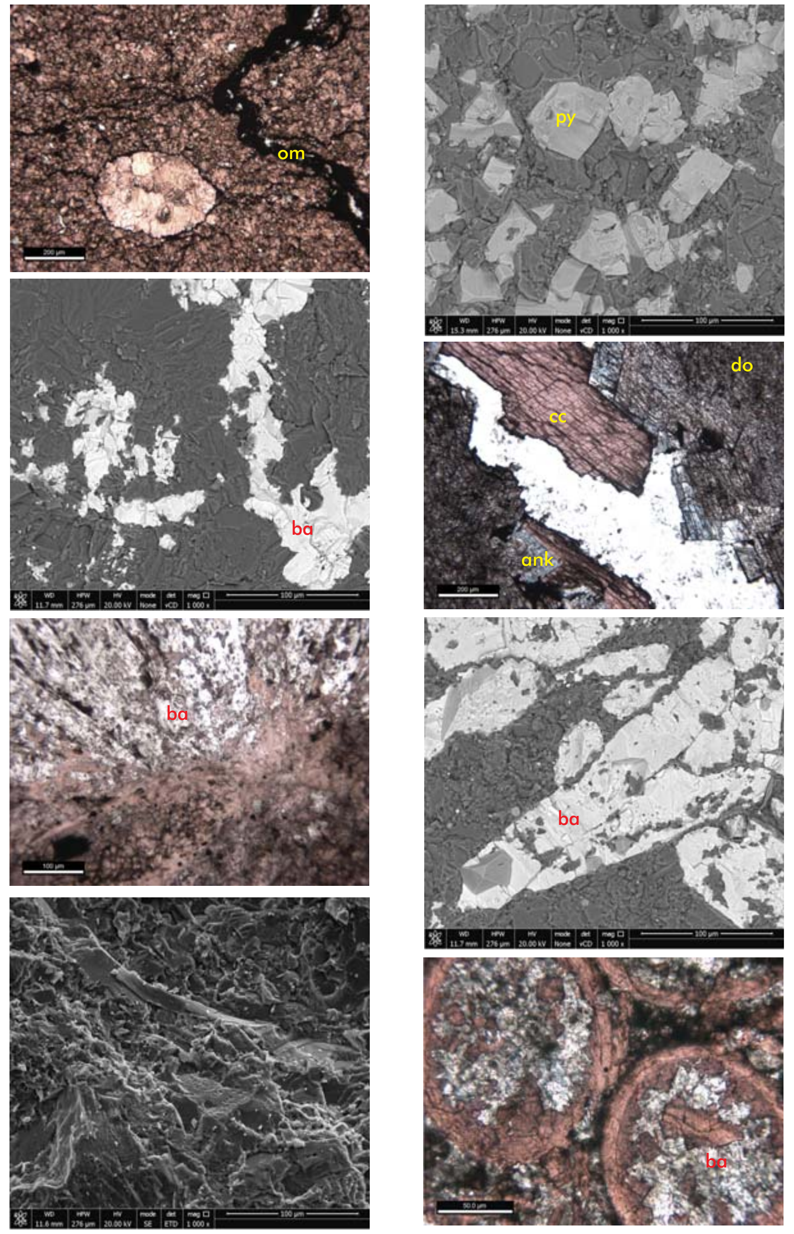
Thin Section / SEM Annotations:

- **ank** - ankerite
- **ba** - barite
- **cc** - calcite
- **ch** - chlorite
- **do** - dolomite
- **fo** - fossil
- **fx** - fracture
- **om** - organic material
- **py** - pyrite
- **si** - silica

Tioga County Core







Normalized Spectra Reflectance

Low — Hi

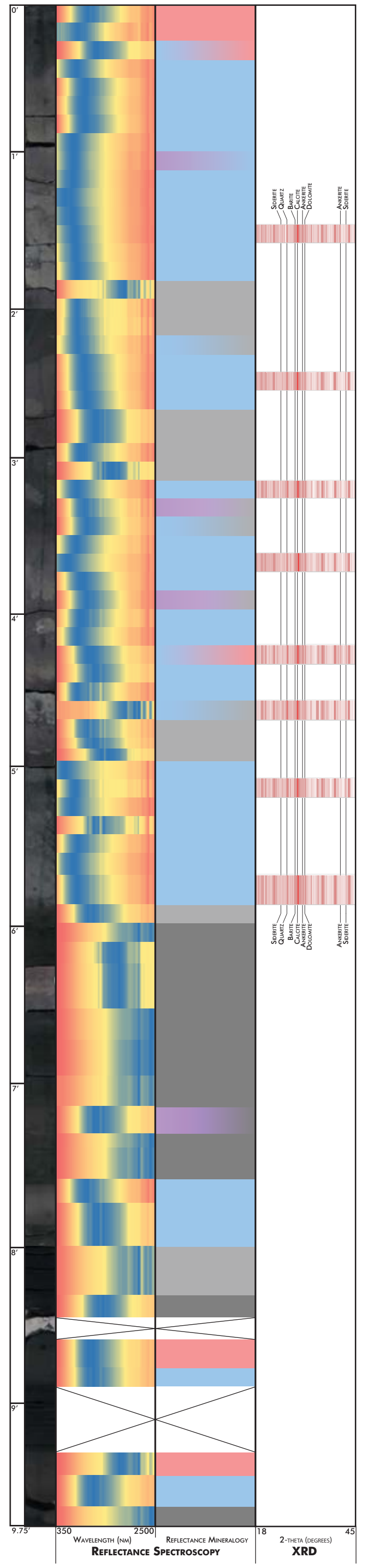
Reflectance Mineralogy Key

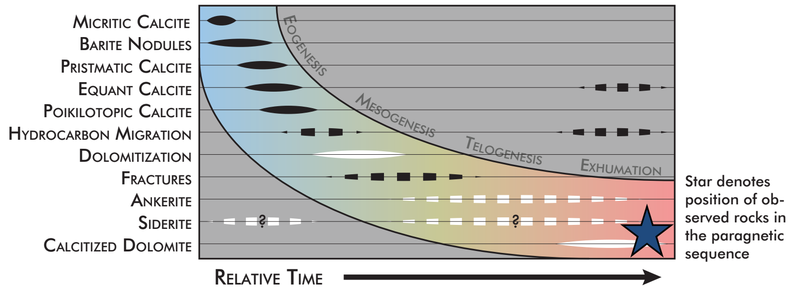
Ankerite $Ca(Fe,Mg)(CO_3)_2$
Aspectral
Calcite $CaCO_3$
Dolomite $CaMg(CO_3)_2$
Illite/mica $KAl_2[(Si,Al)_4O_{10}](OH)_2$
Siderite $FeCO_3$

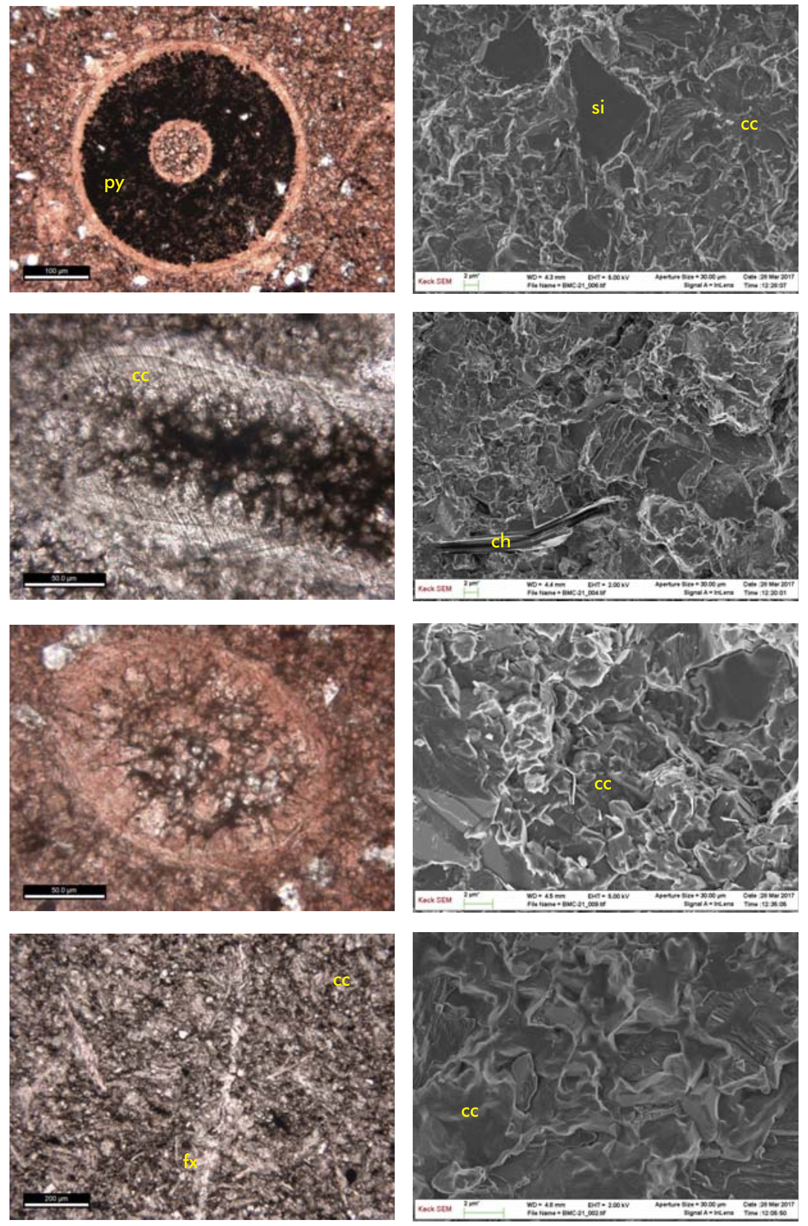
Normalized XRD Peak Intensity

Low — Hi

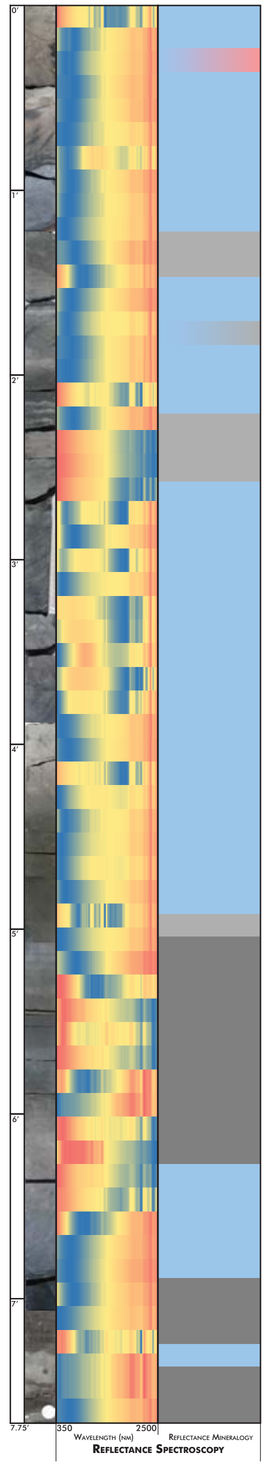
Beaver Meadows Core







Cargill Salt Core



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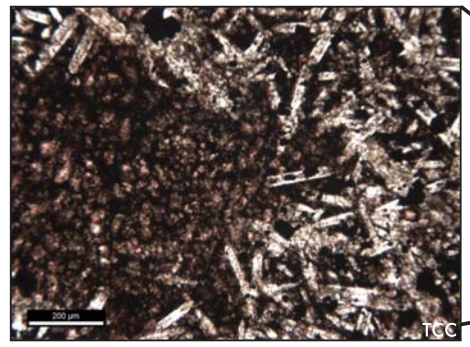
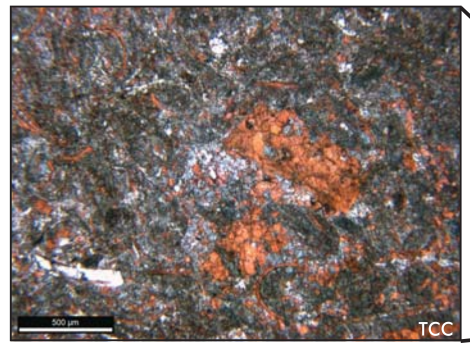
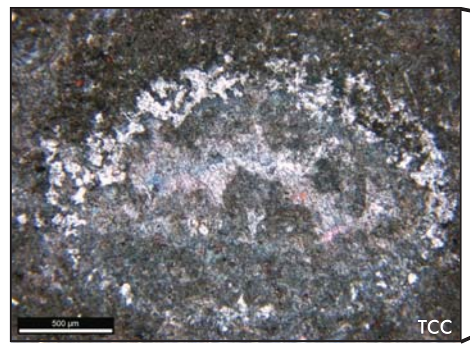
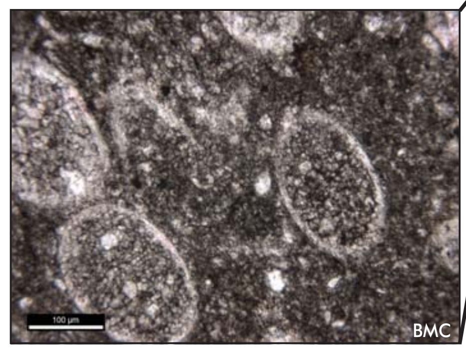
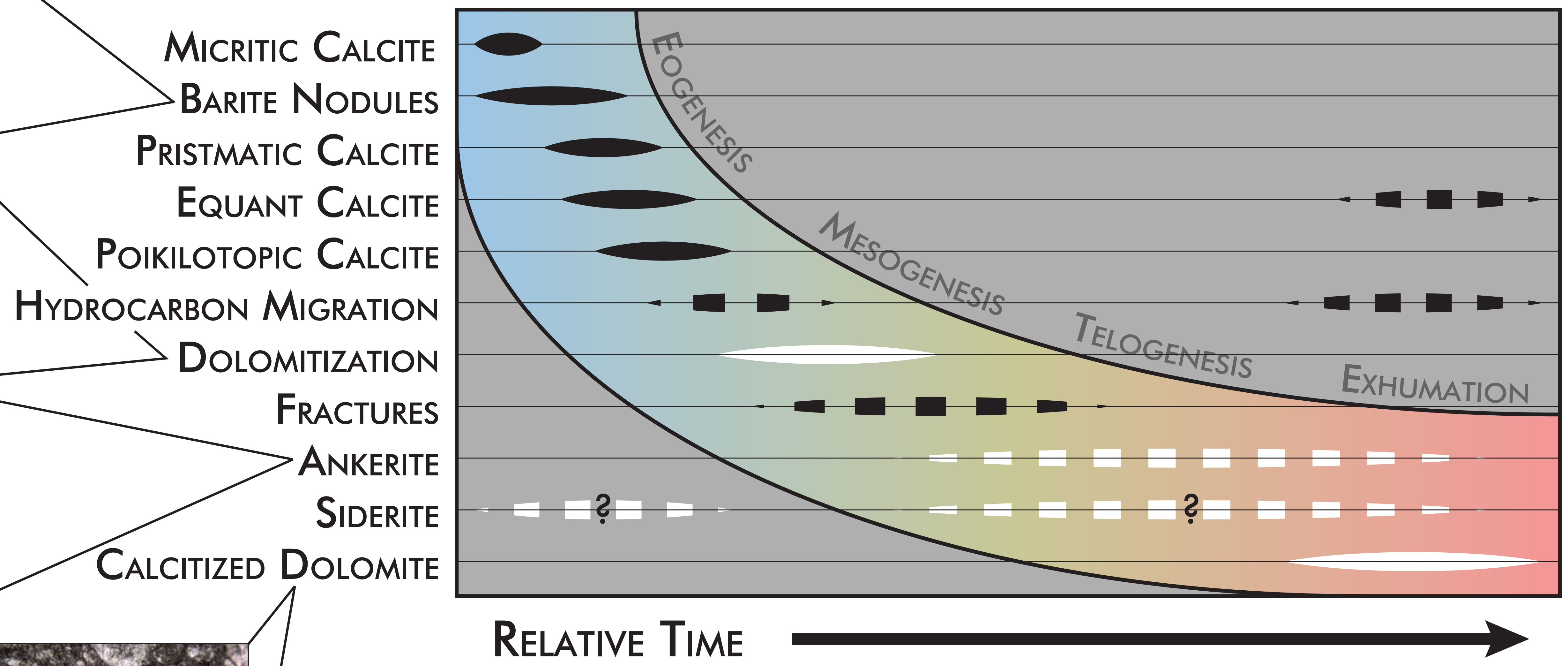
CONCLUSIONS











► The Cherry Valley Member acts as a conduit for fluid flow between its bounding mudstones and has recorded its diagenetic history in distinct stages of authigenic carbonates (Fig. 11, left).

► Diagenetic processes and authigenic mineralization (above) are paragenetically related in the Tioga County (TCC), Beaver Meadows (BMC), and EGSP NY-4 (NY4) cores. High-resolution reflectance data accurately identifies zones of authigenic mineralization whereas petrography shows that additional phases exist.

► Textural and compositional heterogeneity is a function of burial history in the Cherry Valley Member.

► Compositional results show iron-rich carbonates preferentially crystallize closer to the Appalachian orogenic front in New York (e.g., Tioga County rather than EGSP NY-4).

► Unroofing and interaction with deep meteoric waters may trigger dedolomitization, producing calcitized dolomite, where the Cherry Valley Member is shallowest (EGSP NY-4, Beaver Meadows, and Cargill)

This study will expand its research area to include core material of the Cherry Valley Member from central and southwestern Pennsylvania and northeastern West Virginia. An identical suite of analyses is currently in process for these additional rocks. Stable isotope analyses of carbonate cements, fossils, and/or void-fills are planned to better constrain timing and extent of diagenetic processes and authigenic mineralization.

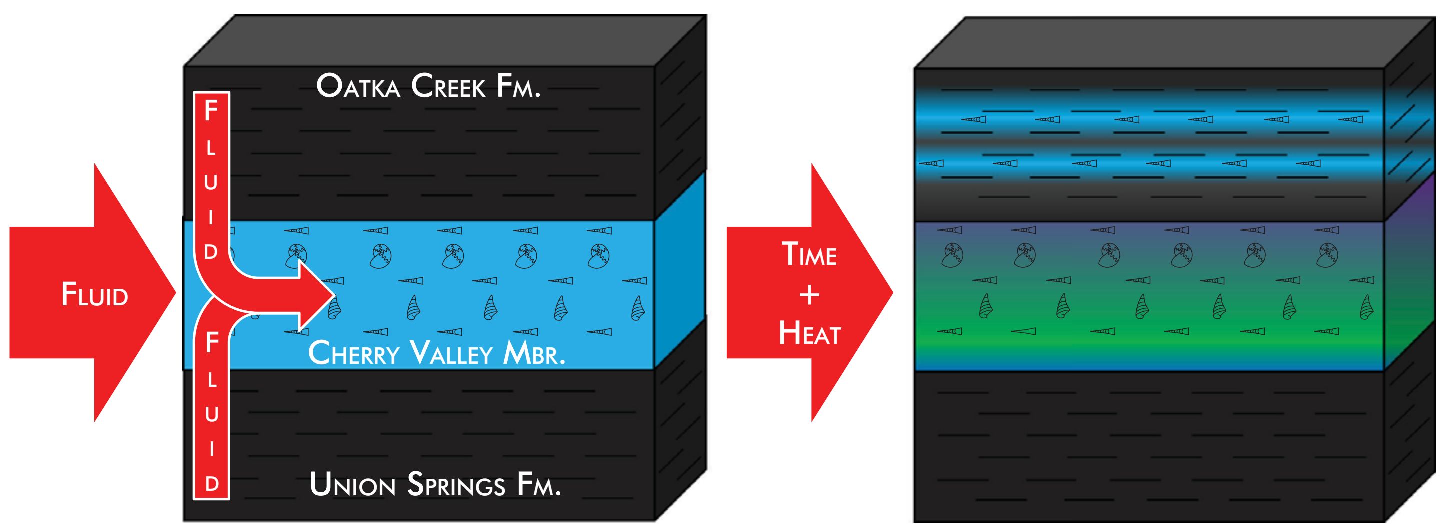


Fig.11: Theorized model of diagenesis in the Cherry Valley Member as it acts as a conduit of fluid flow between the mudstones of the Marcellus subgroup.

ACKNOWLEDGMENTS

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Core information/API: Tioga County Core (formally as "Strong #1", 31-107-26466); EGSP NY-4 (also named "Valley Vista View 1", 31-101-15268), Beaver Meadows Core (formally as "Beaver Meadows #1, 31-017-23006); Cargill Salt Core (formally as "Cargill Test #17", 31-109-13173)