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THE ORIGIN OF A BASIN-SCALE THIN LIMESTONE: THE MIDDLE DEVONIAN CHERRY VALLEY MEMBER, MARCELLUS FORMATION

A Thesis in

Geosciences

by

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ABSTRACT

Petrology, geochemistry, stable isotopes and diagenetic signals were investigated to understand the origin and diagenetic process of the Cherry Valley member, a thin, basin-wide limestone interval within the Middle Devonian Marcellus Shale Formation. Three sub-members within the limestone interval were identified based on integrated petrological and geochemical analysis: 1) the lower facies is characterized by dark gray calcareous mudstone with pyritic lamiae parallel to bedding and abundant barite nodules; 2) the middle facies is marked with the massive black limestone section containing diverse fossil fragments; 3) the upper facies is characterized by grey calcareous mudstone or siltstone with pyritic lamination. Pyrite framboids size distribution, U-Mo covariance, and authigenic barite record the changing biogeochemistry dynamic and several diagenetic process, including barite concretion, methane oxidation, and barite to pyrite conversion. These diagenetic processes are controlled by redox dynamic and play an important role on the formation and alternation of this limestone interval. The depleted carbon isotopes, ranging from -10.2 to -2‰ VPDB, indicate a mixed signal between methane oxidation associated calcite and the seawater carbonate. The depletion of oxygen isotope spanning from -13.2 to -8.7‰ VPDB indicates a high temperature late diagenetic fluid overprint which is confirmed by low Sr/Ca ratios and properties of fluid inclusion in the veins. Petrological characteristics, geochemical proxies, isotopic compositions and fluid inclusion microthermometries are all consistent with the hypothesis that this carbonate member partially originated from methane oxidation and then underwent a high degree of high- temperature late diagenesis which altered the bulk isotopic composition. This integrated study demonstrated the depositional and diagenetic history of the Cherry Valley member from a geochemical point of view and illustrated that diagenetic process could contribute largely on the precipitation of carbonate within thick shale successions.

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"If you can't fly, then run; if you can't run, then walk, if you can't walk, then crawl, but whatever you do, you have to keep moving forward." – Martin Luther King Jr.

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INTRODUCTION

A decimeter-scale but basin-wide carbonate interval, the Cherry Valley Member, interbedded within the Marcellus Formation provides a unique opportunity to investigate the origin of carbonate layers within thick mudstone successions. This unit does not have typical characteristics of a normal shallow-water carbonate unit, but rather is dark-colored, pyritiferous, nodular muddy limestone. The Cherry Valley limestone is often regarded as a calibration layer for geosteering of horizontal wells or thought to be a "fracking barrier" during the energy development of the Marcellus Shale (personal communication with Rice Energy, Shell Co. and EQT Co.). As a result, investigation of the Cherry Valley Member holds not only scientific interest but also economic interest with development of ~500 trillion Marcellus shale gas play that has a huge impact on domestic energy supply and local economy (Engelder and Lash, 2008).

The occurrence of decimeter-to-meter-thick carbonate beds within a predominantly mudstone sequences has long intrigued geologists (Raiswell, 1988). Hypotheses concerning the origin of such carbonate-shale cycles have gravitated towards two views: environmental change versus diagenesis. The former concept related them to rhythmic climate or environmental change modulated by orbital cycles- (100ka eccentricity, 41ka obliquity and ~21ka precession) originally proposed by Milankovitch (Schwarzacher and Fischer, 1982; Cotillon, 1984; Arthur et al., 1984; Bottjer et al., 1986). Other researchers argued that diagenetic processes, especially the redistribution of calcite could play an important role (Munnecke and Samtleben, 1996).

This study integrates 891 well logs, and detailed petrological and geochemical data from two well cores (Figure 1) to: 1) provide a detailed description of the composite

characteristics of the Middle Devonian Cherry Valley Member; 2) elucidate the origin and inform a depositional model of this basin-wide spread carbonate interval; and 3) indicate the important role that diagenesis process played on the formation of thin interbedded carbonate layers. Although the Cherry Valley Member is thought to have been deposited during shallow-water regression (Brett and Baird, 1985; Kohl et al, 2014), we suggest this unit is not simply deposited under an oxygenated water body, but also represents dynamic variability in water depth and redox conditions; at the same time, the diagenetic processes had a major impact on the lithology and textures of this unit. We hope this study will not only lead to a better understanding of the depositional environment of the Marcellus Formation, but also could shed light on more efficient stimulation and development of the Marcellus and other shale plays.



Figure 1. Map of study area showing the Marcellus Formation outcrop belt and well locations.

GEOLOGICAL BACKGROUND

Tectonic and geological settings

Reconstructions of paleogeography reveal that the Eastern North America was located approximately 25-35° south of the equator, rotated clockwise on the order of 90° to the south during the Early to Middle Devonian (Figure 2; Scotese et al., 1999; Witzke 1990). A series of collisions of continental fragments, known as Taconic (Ordovician), Acadian (Devonian), and Alleghanian (Pennsylvanian-Permian) orogenies resulted in the formation of an elongate mountain belt that extended from Greenland and Maritime Canada to the southern Appalachians (Hatcher et al., 1989). The loading of the continental margin, and associated magmatism, metamorphism, uplift and deformation of the orogeny, led to subsidence and reorganization of the Appalachian foreland basin (Dennison and Hasson, 1976). The Acadian orogeny, which begins in the Middle Devonian and reaches the climax in the Late Devonian, was the major tectonic event during the Marcellus Formation deposition time (Bird and Dewey, 1970) and has been hypothesized as a cause of basin subsidence at that time. The unroofing and erosion led to progradation of synorogenic clastics into the basin, with eventual infilling onto the craton by the Late Devonian.



Figure 2. Paleogeopraphic map of North America in the Devonian time. Note the equator illustrated by the white line and the Appalachian basin marked by red rectangle (Modified from *NAU Gobal Palegeography Project*).



Figure 3. Stratigraphic column of the Middle Devonian Eifelian and Givetian stage in the Appalachian Basin (Modified after ver Straeten, 2007; Dennison and Hasson, 1976; Hasson and Dennison, 1988; Brett et al, 1990; Griffing and Ver Straeten, 1991).

Stratigraphy

The lower to upper Middle Devonian strata of the Appalachian basin, including Emsian, Eifelian and Givetian stages, comprise a vertical succession of marine siliclastics and carbonates representing approximately 25 million years of time, from around 407.5 to 382.5 Ma. (Kaufmann, 2006). Emsian-age mixed clastics and carbonates are overlain across much of the Appalachian Basin and eastern North America by a carbonate-dominated succession (Griffing and Ver Straeten, 1991; Lindemann and Feldman, 1987). This carbonate is variously termed as the Onondaga Formation (PA, NY), Columbus Formation (OH), Needmore Formation (VA, WV). This formation is relative well correlated by massive limestones and argillaceous intervals. We used the name Onondaga Formation in this report since we are primarily examining relations in central Pennsylvania. This widespread limestone deposition in the Lower Eifelian (Onondaga Formation) is succeeded by a major influx of clastic sediment in the upper Eifelian to Givetian stage, the Marcellus subgroup of the Eifelian-Givetian Hamilton Group (**Figure 3**; Dennison and Hasson, 1976; Hasson and Dennison, 1988).

The Marcellus Formation is the lowermost formation in the Hamilton group ranging in thickness from approximately 7.5m in western New York to 579m along the Catskill Front. The formation consists predominantly of marine black and gray shales, terrigenous siltstones and sandstones, and minor carbonates. Along the Catskill Front, these marine strata give way to nonmarine, fluvial siliciclastics of the partially equivalent Ashokan Formation. Ver Straeten and Brett (2006, 2007) have proposed to divide the Marcellus Formation into three units, elevating the Marcellus to Group status, a lower Union Spring Formation and higher, time-equivalent Oatka Creek or Mount Marion Formations.

We retained the trifold division of the Marcellus Formation, but revises a little based on lithology and sequence. 1) The basal organic carbon-rich unit of Marcellus Formation is called Shamokin Member (Kohl et al., 2014; same with the Union Spring Formation in Ver Straeten & Brett, 2006 2007). Marker beds in the Union Spring Member include the widespread Tioga "F" K-bentonite, found widely in eastern New York, Pennsylvania, Virginia, West Virginia and central Ohio. 2) The Union Spring Member is succeeded by a limestone grading to lime mudstone in the deeper basin and dolomitic siltstone to the Southeastern PA, for which we use the name Cherry Valley Member to describe the interval ranging from the previously discussed "limestone bed' to the lower contact with the Oatka Creek-Mount Marion Fms.. Ver Straeten (2006, 2007) argued the "Cabrieroceras bed", a nodular limestone bed that passes laterally from the upper Bakoven Member in east-central into the lower part of the Stony Hollow Member in eastern New York, is another marker bed in the Union Spring Formation. However, this bed is regarded here as a transitional unit of major base-level/ redox condition change. The calcareous to dolomitic, fine-to medium grained siliciclastic unit, Stony Hollow Member, in central and eastern New York, and the East Berne Member of New York and PA are also time-equivalent with the Cherry Valley Member (Brett et al, 1990; Griffing and Ver Straeten, 1991). In more proximal areas, the Cherry Valley Member grades into a clastic-dominated facies of calcareous shale, nodular limestone in shales, bioturbated sandstone, and dark gray mudstone or sandstone. 3) The Cherry Valley Member is overlaid by another shale-dominated Member which is called the Oatka Creek Member (the upper part of Oatka Creek and Mount Marion Formations in Ver Straeten 2006, 2007; Kohl et al., 2014).

Depositional sequences

The application of sequence stratigraphy provides a powerful tool to analyze the time-rock relationship. In the thesis, we apply the four subdivision of the depositional sequence system introduced by Catuneanu (2002; 2006), including lowstand, transgressive, highstand, and falling stage system tracts. In the Appalachian Basin, the Eifelian Stage strata have been divided into three depositional sequences (Ver Straeten 2006; Kohl et al., 2014, see Figure 4): Eif-1, Eif-2, and Eif-Giv. The Eif-2 and Eif-Giv sequences contribute most parts of the Marcellus Formation. The Onondaga limestone appears to represent lowstand deposits of Eif-2. Fining upward, the overlying Union Spring Member is associated with a rise in relative sea-level within the transgressive to highstand system tract. The carbonate-black shale contact of the Onondaga Formations and Union Spring Member and equivalents represents a major flooding surface. This contact is a locally prominent unconformity in some areas of the basin from central New York and eastern PA to the Albany area in eastern New York. However, across the central basin (PA, MD, northern areas of VA and WV), the Onondaga-Union Spring equivalent contact is relatively conformable, as sediment supply is presumed to have been more continuous in that area. Falling stage system tract deposits in sequence Eif-2 comprise silty black to grey shales, calcareous mudstones, siltstones and sandstones, and carbonates, whose equivalent strata includes the upper part of the Union Spring Member and the lower part of the Cherry Valley Member. In this thesis, based on well log characteristics and geochemistry proxies, I define the base of the Cherry Valley Member as the start of transgressive system tract or the beginning of the succeeding depositional sequences Eif-Giv, which appears conformable throughout much of the basin (Brett et al,

1990; Griffing and Ver Straeten, 1991). A drowning surface at the top of Cherry Valley Member marks a major stage of deepening and the shutting down of the carbonate production represents the continuous phase of the highstand system tract. Sequence Eif-Giv comprises the basinal facies of the Oatka Creek Member, and correlative proximal facies of the Mount Marion Formation in New York, and correlative strata across the basin, of which the middle to upper parts have not been a part of this study.



Figure 4 Gamma-ray correlation sections from the Onondaga Formation to the Cherry Valley Member of the Marcellus Formation showing the sequence changes during the Marcellus depositional duration (Modified from Kohl et al., 2014).

METHODS

The Appalachian Basin Black Shale group (ABBS) dataset includes 13 Marcellus shale cores and over 1000 wireline well logs throughout PA and adjacent portions of NY, WV and OH. The wireline logs were collected from publicly available PA, NY, WV and OH geological survey database and have been digitized and normalized for further correlation. The normalization method follows Shier (2004) and Kohl et al. (2014), which used baselines of minimum GR value of the Oriskany sandstone and a mid-high GR value of the mean GR value in the Mahantango Formation Although different types of well logs have been examined, gamma-ray, density log, and neutron porosity are primarily used for correlation (see **Figure 1** for well locations). 13 Marcellus cores have been described and photographed. Nine of cores were drilled from the thrust and fold belt of the Appalachian Basin. Some of the other cores were donated by industry, including the Snow Shoe core (Enerplus and Chevron) which we carefully examined in this study. The cherry Valley Member in cores is identified within the Marcellus Formation based on distinctive lithology and textures.

Figure 5 and **Figure 6** illustrate facies identified and a type log we further used for basin-wide correlation and mapping. The Cherry Valley limestone within thick shale formation is not only normal grey carbonates and the uppermost and lowermost parts of this interval are abnormal, dark-colored muddy lime with lots of nodules in them, regular well logs contributed onto the identification of it: low gamma ray, high density, and low neutron porosity.



Figure 5. Log suites (Gamma Ray, Bulk Density, Resistance, Neuron porosity) of the Bald Eagle core and their correlative lithofacies. All logs from borehole well logging operated by *ARM Geophysics*.



Figure 6. Log suites (Gamma Ray, Bulk Density, Neuron porosity) of the Snow Shoe core and their correlative lithofacies. All logs from borehole well logging operated by Schlumberger.

Detailed petrological and geochemical investigations in this study are based on two cores: Bald Eagle and Snow Shoe cores. The Bald Eagle coring Marcellus shale interval was collected in conjunction with the Pennsylvanian State Geologic and Topography Survey and is housed in the Appalachian Basin Black Shale Group core laboratory of Department of Geosciences, Penn State. It is a shallow core located in the thrust/fold belt of the Appalachian basin drilled by ABBS group and represents the proximal part of the basin. The core is 2.5 inch in diameter and the total depth is 1130 feet.

The Snow Shoe core (API Number: 3702721672; Well name: Enerplus Snow Shoe 4-8HG; data from PA DNCR core database) is from a production well and donated by Enerplus Resources (acquired by Chevron Co.). Although Snow Shoe core is also located in Centre County, it is further north, much deeper and is thought to provide some information about more distal part of basin. The Snow Shoe core is 4 inches in diameter and the total depth is 8906ft. After photographing and description, Snow Shoe and Bald Eagle cores were carefully half-cut for archiving and sampling.

For petrologic analysis, a suite of 12 typical Cherry Valley limestone facies was sent to *Texas Petrographic Services Inc.* for thin sections. Another 12 samples from the underlying Union Spring black shale through nodular intervals and muddy limestone were carefully cut and hand polished using 1µm and then 0.1µm diamond polisher in order to perform Scanning Electron Microscope (SEM) analysis. SEM provides much detailed petrologic information: The signals that derive from electron-sample interactions reveal information about the sample including external morphology, chemical compositions and crystalline structure of materials making up the sample. In this study, we mainly used backscattered electrons, which backscattered by beam electrons elastic scatter with specimen atoms, and focus more on chemical composition differentiation rather than specimen morphology. Each sample was mounted onto the stage allowing the viewing direction was normal to the bedding.

Every sample has been imaged for pyrite framboid distribution and detailed elemental mapping. As framboidal pyrite size distribution is most useful when secondary pyrite growth is limited, we only chose well-preserved samples and made sure >95% pyrite framboids are without infilling and overgrowth. After imaging, framboid diameters were then measured and recorded by use of an open-source software *Image-J*. The framboids distribution is likely skewed to a slightly lower value because of cutting and surface imaging, but the deviation from a true mean diameter is less than 10% (Wilkin et al. 1996). To identify the elements within the specimen, we relied on X-rays (EDS) mapping on the SEM. All SEM analyses were performed under *FEI Nova NanoSEM 630FESEM* system in Penn State Material Characterization Lab and the EDS mapping were processed under *AZtecTEM* software.

Isotope analyses were performed for the entire sequence of the Cherry Valley limestone. Core samples were cut into $1 \times 1 \times 0.2$ inch cubes and then crushed into 0.074 mm powders (Sieve No.200). Each quarter sample has been used for carbon and oxygen isotope measurement, disulfide sulfur extraction, TOC measurement, and archiving. All isotope measurements are taken by isotope ratio mass spectrometry.

Carbon and oxygen isotope in powdered bulk sediments were analyzed in Penn State Light Stable Isotope Lab using *Thermo Scientific Delta V Plus* isotope ratio mass spectrometer. Carbonate samples were reacted at 90°C with anhydrous phosphoric acid coupling to the mass spectrometer. Isotopic ratios were calibrated against NBS-18, NBS-19 and one internal standard and are reported in delta notation (δ^{13} C and δ^{18} O) to Vienna Peedee Belemnite (VPDB) standard. The internal precision (1 σ) of the mass spectrometer by continuous flow gas configuration is ±0.06‰ and ±0.08‰ for δ^{13} C and δ^{18} O respectively. Carbon and oxygen isotopic results were reproducible within ±0.13‰.

Sulfur isotope measurements were performed on *Finnigan MAT 252* massspectrometer in the Penn State Stable Isotope Lab. Each measurement has been repeated for at least three times to ensure the consistence. Barite nodules had been carefully microdrilled to collect the pure barite crystal. A modified separation method from Turchyn and Schrag (2006) has been performed to further purify the powder. Sulfur isotopic ratios were determined through replicate measurements of silver sulfide and barium sulfate. Isotopic ratios are corrected and reported in the standard delta (δ^{34} S) relative to Canyon Diablo Troillite (CDT). Analytical reproducibility, as determined through replicate measurements, was generally 0.3‰ for *FeS*₂ sulfur and 0.5‰ for *BaSO*₄ sulfur.

Similar to EDS, another technique used for elemental analysis in this thesis is Xray fluorescence (XRF). XRF is the emission of characteristic "secondary" X-rays from a material that has been excited by bombarding it with high-energy X-rays or gamma rays. The core scanning system located in Penn State ABBS Corelab equipped with the *Olympus Delta X* handheld spectrometer owning a 4W X-ray tube, 200uA current and calibration software has been used for in-situ core-base elemental analysis. Optimal exposure time was determined by analysis of certified powdered standards. Test exposure times ranged from 60-360s. All half cores had been cleaned and displayed onto the core scanning system. XRF measurements for Bald Eagle core were taken at 0.4inch (1 cm) intervals. The data quality was monitored by calibrating the instrument every 20 measurements were done and made sure those tests resulted in less than 5% variations. The limit of detection and range depends on each element and is provided in Appendix.

RESULTS

The Cherry Valley Member is a basin-wide fossiliferious limestone, nodular calcareous mudstone, or dolomitic siltstone interbedded with the overlying Oatka Creek Member and the underlying Union Spring Member. In the western Ohio-PA boundary region and the north Erie area the Cherry Valley Member sits unconformably on the Ononadaga Formation or is not present. On well logs, it is distinguished from overlying and underlying units by lower GR, higher density and lower neutron porosity (Dennison and Hasson, 1976; Lash and Engelder, 2011). The thickness of the Cherry Valley Member increases from less than 10ft thick in northwestern PA to more than 150ft in Wayne County, northeastern PA, and southeastern NY. The gamma-ray and bulk density logs suggest the lithology of the Cherry Valley becomes more and more arenaceous to the eastern PA and southeastern NY. The Mapleton outcrop and nearby Bilger core located in thrust/fold belt of central PA show a heavily bioturbated silty limestone containing occasional rounded quartz pebbles and barite nodules confirms that the limestone facies grade eastward into sandstone-dominated facies of the upper Turkey Ridge Member (See Figure 9 and Figure 27 for lithofacies distribution).

Lithofacies Description

From the investigation of the Bald Eagle and Snow Shoe cores, we document that "Cherry Valley limestone", as now defined in this study, is not simple grey carbonate beds that broadly cut across facies boundaries as shown in the type log (**Figure 5** and **Figure 6**) but are complex sedimentary packages comprising of dark-grey nodular calcareous mudstone and fossiliferious limestone, with gradually changing boundaries, recording varied depositional environments, especially redox conditions. In this case, based on a variety of textural features as well as lithology, we divided the Cherry Valley Member into three different lithofacies or submembers (see **Figure 7, Figure 8** for lithofacies images and descriptions):

1) The lower lithological unit characterizes by dark gray calcareous mudstone with pyritic lamiae parallel to bedding and abundant nodules. The matrix of this unit is dark-gray, calcareous mudstone or marlstone with thin plan-parallel pyritic or silty lamination. The carbonate concentration of matrix in this unit is about 28.7% to 65%. Nodules are oblate spheroids, subrounded forms that are from 2 to 7 cm in diameter elongated with bedding exhibiting differential compaction. Nodules are composed of clear barite crystals with surrounding pyritic rims or a pyrite grain assemblage with sparse barite. Some nodules have shrinkage frackures filled by calcite. The total organic matter becomes leaner from ~4.3% in the Union Spring Member to ~3.1% in the Cherry Valley Member of the Snow Shoe core and from ~5.8% in the Union Spring Member to \sim 3.9% in the Bald Eagle core. On the well log, this unit of the Cherry Valley Member is usually marked on well logs by gamma-ray low, density high and neutron porosity low. The low gamma-ray value could be due to the low organic matter compare to the Union Spring Member and the high carbonate concentration, and the density high and neutron porosity low is largely due to the lithology and abundances of barite nodules. The dark colored, highly calcareous, pyritic subfacies of the Cherry Valley Member is associated with deep water (Wendt and Aigner, 1985) and an early diagenesis resulting from changes in the accumulation rates of terrigenous sediments (Raiswell, 1988). Although large fractions of matrix are quartz grain and clays, recrystallized calcite in the pores and cemented micro-fractures are found as diagenetic signals in this facies.

2) With an upward decrease in pyrite barite nodules, the facies gradually grades into a fossiliferious carbonate facies, which we termed "the middle facies". The main lithology of the middle facies is gray to dark gray wackstone and micrite with abundance of fossil fragments. The carbonate content increases to 85% from lower facies. And the organic matter content becomes even leaner in comparison with the lower facies to ~1.0%. Poorly sorted, complete (rare) and incomplete *brachiopod, styliolinid, gastropod,* as well as indiscriminate skeletal debris most commonly occur in this unit, which could because of the transportation of gravity debris. The plane-paralleling laminations contain fine-grained *tentaculites, brachiopod* and bivalves fragments, which indicates a frequent reworking by strong currents. Although this unit is bioturbated, it preserves some primary sedimentary structures. Slump structures and venting structures at the boundary between this facies and the lower one are found in this unit (**Figure 8**). Lots of fossils are all recrystallized and cemented by late precipitated calcite. The depositional environment of this unit could be storm-swept, sediment-starved marine slopes with strong bottom water currents.

3) This facies is then overlain by grey calcareous mudstone or siltstone with pyritic lamination and sparse coquinoid laminae. The carbonate content decreases to $20\sim35\%$. Under thin sections, this facies is $50\sim70\%$ silts-sized grains, dominated by quartz. A strong diagenetic signal is found in this facies as all grains seem to "float" on the carbonate matrix. The organic matter content increases slightly to $\sim1.5\%$. The absence of barite nodules is the main difference between this topmost Cherry Valley facies and the lowest facies. In this unit, the bottom water deepens again and gradually transits into the overlying euxinic conditions in the Oatka Creek interval (Werne et al., 2002; see Figures 4.1.1 for description of different facies in the Cherry Valley Member).



Figure 7 Core photos of the Cherry Valley Member in the Bald Eagle core and the Snow Shoe core. 1- the Bald Eagle core; 2-the Snow Shoe core.

Core Photoes	Lithofacies description	Thin Section Images
1 1 inch	Upper facies: gray to dark gray calcareous mudstone or siltstone with pyritic lamination and sparse coquinoid laminae. Carbonate concentration is 20~35% and the silts abundance is about 50~65% dominated by quartz.	А
2 <u>1 inch</u>	Middle facies: Gray to dark gray wackstone and micrite with abundant fossil fragments including poorly storted brachiopod, styliolinid, gastropod fragments. Plane- paralleling laminations contain fine-grained fossil fragments. Carbonate concentration is 70~85% with sparse silt grains. Slump and venting structures are found in this facies.	B 100µm
1 inch 1 inch	Lower facies: Matrix is dark-gray, calcareous mudstone or marlstone, composing of 40-50% silt- sized grains. Plane-parallel laminations are generally pyritic or silty. Nodules are composed of clear barite crystals with surrounding pyritic rims. Lack of fossil in this facies. Carbonate concentration is about 30~60%.	<u>του</u> μπ

Figure 8. Core photos, thin section images and lithofacies description of the Cherry Valley limestone. 1- Upper facies of the Snow Shoe core, 8630'2''; 2- Middle facies of the Bilger core, 401'; 3- Middle facies of the Bald Eagle core, 782'2''; 4- Lower facies of the Bald Eagle core, 788'5''. A- Upper facies of the Bald Eagle core 775'4''; B-Middle facies of the Bald Eagle core 780'6''; C- Barite nodule in the Bald Eagle core, 785'; D- Lower facies of the Bald Eagle core, 790'3''.



Figure 9. Isocore map of mean gamma-ray values of the Cherry Valley Member. High Gamma values in the central portion of the basin suggest the Cherry Valley limestone is thin, especially the middle facies is missing.



Figure 10 Isopach map of the Cherry Valley Member based on the lithology showing the thickness changes of this member across the basin.

Sediment flux

On average, the Si/Al ratio in the Bald Eagle core ranges from 3.3 to 4.4 and is higher than those of the Snow Shoe core, which varies from 2 to 3.5 shown in Figure 11 and **Figure 12**. The difference could be explained by quartz proportion variation between these two cores, which could be due to distance from the sediment source, as the Bald Eagle core is more proximal than the Snow Shoe core. In both cores, the overlying Oatka Creek Member and the underlying Union Spring Member set a good baseline for mudstone. In the Bald Eagle core, the Si/Al ratio in the Union Spring Member ranges from 3.6-4 and varies not significantly upwards into the lower facies of the Cherry Valley Member. A significant decrease of Si/Al, from 4 to ~ 3.3, marks the boundary between the middle carbonate facies of the Cherry Valley Member and the lower facies (below \sim 787ft). Si/Al ratio is highly variable from 3.5 to 4 within the middle facies, followed by a gradual up-section decrease to stable low value in the upper facies. An increase to 3.6 marks the boundary between the overlying Oatka Creek Member. In the Snow Shoe core, the trend is much clearer: High Si/Al ratio characterizes the underlying Union Spring Member background line. A sharp increase at the value of 3.5 ends the Union Spring Member followed by a gradual decrease to 2.2 in the lower facies of the Cherry Valley Member A decrease to 2 (the lowest value) marks the boundary between lower facies and middle facies, which could correlate to the similar decrease in the Bald Eagle core. Si/Al then catches up to about 2.3 in the upper facies. The ratio increases up to about 2.8 in the overlying Oatka Creek Member.

Ti/Al ratio trend in the Bald Eagle core generally divides into two phases: the first phase is from the Union Spring Member to the lower facies of the Cherry Valley Member characterized by high Ti/Al ratios between 0.1 to up to 0.5 and the second phase starts from the sharp decrease of Ti/Al ratio in the beginning of the Middle facies and the Ti/Al ratio stays stable and low (0.05 to 0.075) till the overlying Oatka Creek Member. This trend is partially consistent with the other core as the ratio showing less variability in the Snow Shoe core. But the ratio is still relatively high ranging from 0.025 to 0.03 from the underlying Union Spring Member to the lower facies of the Cherry Valley Member and a sharp decrease marks the beginning of the middle facies and keeps relatively low ratios till the end of the Cherry Valley Member. The Ti/Al ratio in Oatka Creek Member is higher ranging from 0.025 to 0.04.



Figure 11. Stratigraphic plots of the sediment flux proxies (all in ppm) of the Bald Eagle core.



Figure 12. Stratigraphic plots of the sediment flux proxies (all in ppm) of the Snow Shoe core

Pyrite framboid distribution

Three different textural forms of pyrite shown in have been distinguished in the Cherry Valley limestone, including framboids, euhedral crystals, and anhedral grains associated with organic matter (**Figure 13**). The abundance of pyrite differs significantly from base to top: the middle facies has much lower abundance, whereas the proportion of pyrite is much greater in the upper and lower facies. The dominant texture of pyrite is framboidal pyrite. Over 80% percent of pyrite particles observed had framboidal morphology in these two facies. Less abundance is anhedral grains associated with clots organic matter. The euhedral crystal pyrite is much larger in size (10-20 microns) but can be found only within the nodule indicating a different origin of the pyrite.

The pyrite size distributions in each facies are shown in the box-and-whisker plots of **Figure 14.** The largest framboids observed were around 15 microns in diameter in the middle facies, about 11 microns in the upper facies and 11.5 microns in the lower facies respectively. Generally, the framboid size distribution are broad in the upper and lower facies but relatively narrow in the middle facies. In the upper facies, the average framboid size is about 7 microns, and the large proportion of size ranges from 5.5 to 8.2 microns. In the middle facies, around 75 percent of framboids are larger than 9micron. The lower facies is similar to the upper facies in that it has a relatively large distribution range but relatively small size. Half of its pyrites are less than 6 microns in diameter.


Figure 13. Different texture forms found in the Cherry Valley Member. A. Framboidal pyrite in the lower facies of Bald Eagle core, 790'2''. B. Euhedral pyrite within barite nodules in the lower facies of Bald Eagle core, 788'6''. C. Anhedral pyrite associated with organic matter in the upper facies of Bald Eagle core, 777'9''. D. Crystal pyrite and framboidal pyrite association in the rim of nodule, Bald Eagle core 795'. Images are all backscatter mode taken under SEM.



Figure 14. SEM images of pyrite framboids size and whisker plots of size distribution .Images are all in backscattered mode taken under SEM. Sample A is from Bald Eagle 777.95 ft; B is from Bald Eagle 782.5 ft; and C is from Bald Eagle 795.5ft.

Isotopes

The carbon and oxygen isotope values (∞ , VPDB) for bulk carbonate in the Bald Eagle core and the Snow Shoe core are listed in **Table 1**. In the shallow Bald Eagle core, carbon and oxygen isotopes ranges from -8.54‰ to -1.10‰, and -11.39‰ to -6.14‰ respectively. The carbon isotope values decrease upward in the Cherry Valley Member, but the values are variable depleted in upper (from -6.16‰ to -3.0‰, n=6) and lower facies (from-3.33‰ to -1.97‰, n=5) but relatively enriched within the middle facies (from -3.6‰ to -1.1‰, n=6). The oxygen isotopes follow the same pattern with the exception of one outlier point. Carbon and oxygen isotopes are slightly more depleted than those in the Snow Show core, ranging from -10.13% to -1.92%, and -13.21% to -10.44%. However, the carbon isotope distribution is broader in contrast to a relatively narrower range for oxygen isotope in this well. The carbon isotopes show a relatively depleted trend with depth, ranging from -4.67% to -2.88% in the upper facies, -5.08% to -1.92% (with a -10.11% outliner) in the middle facies, and -10.13% to -3.6% in the lower facies. Carbon and oxygen isotopes in veins with the Cherry Valley Member are also listed in the **Table 1**. Although the oxygen isotope values range widely from -6.0% to -12.6%, carbon isotope values range only from -2.6% to -1.5%.

Barite sulfur isotopic values (‰, CDT) are listed in **Table 2**. In general, barite sulfur isotope signatures range from 42‰ to 55‰ for pyritic-barite nodules in the Bald Eagle core, and 28‰ to 45‰ for nodules in the Snow Shoe core. In additions, the sulfur isotope signatures increase from the rim to the center within nodules. And the differences are from 5‰ and can be up to 11‰. The barite sulfur isotopic values are consistent with the measurements reported by Nuelle and Shelton (1986).

Bald Eagle Core				Snow Shoe Core				
Depth	$\delta^{13}C$	$\delta^{18}O$	Depth	$\delta^{13}C$	$\delta^{18}O$			
8627.9	-2.88	-11.333	762	-4.32	-9.83			
8628.98	-3.36	-10.982	763	-8.54	-10.91			
8629.31	-4.67	-11.06	764.25	-5.98	-10.40			
8630.64	-4.63	-11.314	766	-5.39	-9.92			
8630.82	-2.45	-10.844	767.25	-7.22	-11.01			
8630.98	-1.92	-10.667	768	-5.17	-10.62			
8631.3	-10.11	-10.935	769.1	-6.77	-11.19			
8631.91	-5.37	-10.449	770.2	-5.20	-10.77			
8632.14	-3.44	-10.502	771.1	-6.16	-10.85			
8632.97	-4.56	-11.039	772.25	-4.46	-10.75			
8633.98	-5.07	-10.931	773.2	-4.03	-9.80			
8634.98	-6.79	-11.305	774.2	-3.04	-10.20			
8635.56	-10.13	-10.855	775.6	-3.00	-10.17			
8635.88	-5.37	-13.215	776.1	-2.58	-9.74			
8636.07	-7.05	-11.165	777.25	-5.05	-9.19			
8636.98	-4.93	-10.721	778	-1.18	-6.14			
8637.98	-4.60	-10.925	779.2	-1.32	-10.12			
8638.98	-5.42	-12.222	780	-3.60	-8.95			
8639.55	-7.20	-11.11	781	-1.10	-8.96			
8639.97	-5.27	-11.122	783	-2.21	-10.49			
8640.64	-3.60	-10.61	784	-1.97	-9.96			
8641.9	-5.48	-10.835	785.75	-2.54	-9.26			
8642.9	-5.44	-10.435	787	-3.33	-8.74			
8643.9	-5.60	-11.336	789	-2.90	-11.39			

Table 1 Bulk carbon and oxygen isotopes of the Cherry Valley Member in the Bald Eagle core

 and the Snow Shoe core

Table 2 Sulfur isotopic compositions of barite in nodules. Microdrill location is shown in Figure29

	BE 777'		BE 792'			
Location	Average	Standard Deviation	Location	Average	Standard Deviation	
1	55.09	-	1	45.82	3.2	
2	54.56	-	2	47.69	0.92	
3	39.52	0.14	3	50.02	0.16	
4	24.92	0.06	4	50.48	0.10	
			5	54.06	0.20	
			6	52.70	0.61	

	BE 793'4'	,		SS 8635'10''			
Location	Average	Standard Deviation	Location Averag		Standard Deviation		
1	42.5	0.87	1	42.45	0.15		
2	44.88	0.83	2	42.36	1.35		
3	44.89	0.49	3	44.33	0.44		
4	43.17	0.57	4	45.25	0.75		
5	42.22	0.78	5	42.82	0.32		
			6	43.62	1.36		
			7	39.01	1.56		

	SS 8637'		SS 8638'11'			
Location	Average	Standard Deviation	Location	Average	Standard Deviation	
1	36.01	0.74	1	40.67	0.91	
2	40.75	0.32	2	38.75	0.15	
3	41.21	0.45	3	39.17	1.42	
4	40.00	0.59	4	35.06	0.52	
5	40.34	1.39	5	32.02	0.63	
			6	30.60	1.18	

U and **Mo** enrichment

Samples of the Marcellus Formation in the Snow Shoe Core exhibit a welldefined pattern of U-Mo covariation (Table 3). To diminish the impact of detrital flux and better compare the respective enrichments of Mo-auth (concentration of authgenic Molybdenum) and U-auth (concentration of authgenic Uranium) in the studied cores, we adopted the calculations of "enrichment factors" (EF, Algeo and Tribovillaro, 2009), which are given in the form of $X_{EF} = \frac{(X/Al)_{sample}}{(X/Al)_{PAAS}}$, and X and Al stand for the weight concentration of element X and Al, respectively. Samples are normalized using Al concentration and the post-Archean average shale (PAAS) compositions of Taylor and McLennan (1985). Mo-auth is substantially more enriched than U-auth, typically by a factor of 10 times, where Mo-ef is larger than 10. Samples from the underlying Union Spring Member yield similar enrichment of U and Mo; those from the overlying Oatka Creek Member overlaid in the range of those of Cherry Valley Member but the U-ef and Mo-ef covariance clusters tighter in the area where U-ef is about 8-20, Mo-ef is about 50 to 100. However, the U and Mo concentrations in the Cherry Valley Member vary over a much larger range than other two members. A finer division based on different facies shows the upper and middle facies of the Cherry Valley Member have the largest variation in U and Mo enrichments falling across the 0.3 times of seawater line and the seawater line on the covariance plot (U-ef ~8-80, Mo-ef ~8-100), whereas the middle facies shows the modest enrichment (U-ef ~4-20, and Mo-ef ~30 -40).

Location	Al	Мо	U	Mo-ef	U-ef	Location	Al	Мо	U	Mo-ef	U-ef
The Oakta Creek Member					The Cherry Valley Member						
8621.50	102553	73.92	14.98	60.55	13.48	8641.5	117184	40.82	13.64	29.26	10.74
8622.00	120810	156.64	19.44	108.91	14.85	8642	113972	60.86	8.73	44.86	7.07
8622.50	124122	76.45	15.28	51.74	11.36	8642	122235	62.61	12.6	43.03	9.52
8623.00	130784	115.11	11.70	73.93	8.26	8642.5	70406	87.71	13.61	104.65	17.84
8623.50	129276	61.56	13.45	40.00	9.60	8643	119294	50.39	12.33	35.48	9.54
8624.00	113313	87.02	21.75	64.51	17.72	8644	106761	55.58	19.16	43.73	16.57
8625.00	120251	114.05	17.69	79.67	13.58	8644.5	118671	46.78	13.61	33.11	10.59
8625.50	136726	73.04	16.99	44.87	11.47	8645	105058	44.81	15.04	35.83	13.21
8626.00	128689	164.64	19.52	107.47	14.00	8645.5	123884	49.18	17.03	33.35	12.69
8626.00	136664	166.07	18.47	102.07	12.48		The	Union Spi	ing Memb	er	1
	The Cl	herry Valle	ey Memb	er	1	8730.50	117301	250.55	95.80	179.42	75.39
8626.5	92653	12.46	6.48	11.30	6.46	8731.00	118948	249.57	95.78	176.24	74.33
8627	96574	22.19	13.55	19.30	12.95	8731.50	88131	232.34	55.42	221.45	58.05
8627.5	142088	49.71	13.11	29.39	8.52	8732.00	58725	77.78	29.81	111.26	46.86
8628	122727	46.45	20.29	31.79	15.26	8732.50	109278	316.33	64.51	243.16	54.49
8628.5	81470	43.38	16.74	44.73	18.97	8733.00	162245	13.04	18.23	6.75	10.37
8629	111605	55.56	21.47	41.82	17.76	8733.50	79776	228.28	71.78	240.37	83.06
8629.5	98693	107.9	15.95	91.84	14.92	8734.00	24334	52.91	36.55	182.64	138.7
8630	113756	14.95	10.53	11.04	8.54	8735.00	39522	35.16	17.67	74.73	41.27
8630.5	94414	23.22	11.14	20.66	10.89	8735.50	34835	33.29	22.96	80.27	60.84
8631	92890	13.09	12.26	11.84	12.18	8736.00	8885	21.92	15.52	207.23	161.2
8631.5	103960	8.43	7.97	6.81	7.08	8736.50	23478	198.06	34.05	708.63	133.9
8632	140895	9.2	9	5.48	5.90	8737.00	52674	183.94	27.87	293.33	48.84
8633	153164	66.87	19.38	36.67	11.68	8737.50	26989	83.25	24.82	259.10	84.89
8633.5	15407	10.02	5.54	54.63	33.19	8738.00	74205	191.26	36.92	216.51	45.93
8634	19572	12.49	9.63	53.61	45.42	8738.50	13102	18.89	9.38	121.11	66.09
8634.5	128622	48.82	20.97	31.88	15.05	8739.00	48943	19.36	12.10	33.23	22.82
8635	114861	76.32	29.27	55.81	23.52	8740.00	37490	46.62	19.85	104.46	48.87
8635.5	126190	64.61	25.02	43.01	18.30	8740.40	36870	184.14	31.03	419.53	77.69
8636	146967	52.32	19.04	29.90	11.96						
8636.5	101902	68.3	36.22	56.30	32.81						
8637	134192	43.78	21.04	27.41	14.47						
8637.5	133327	42.57	20.35	26.82	14.09						
8638	119089	50.97	18.79	35.95	14.56						
8638.5	125282	61.25	20.59	41.07	15.17						
8639	126357	54.06	20.82	35.94	15.21						
8639.5	117468	51.64	23.09	36.93	18.14						
8640	115313	51.29	16.38	37.36	13.11						
8640.5	132417	64.46	17.17	40.89	11.97						
8641	106296	47.42	17.08	37.47	14.83						

Table 3 Al, Mo, U concentrations and enrichment factors of three members in Marcellus Shale.

DISCUSSION

Statistical evaluations of lithofacies

X-ray fluorescence provides a dataset of geochemical elements (All bulk chemical data can be found in Appendix) for a quantitative exploration of core description. Mathematical methods including R-mode hierarchical cluster analysis and principal component analysis (PCA) is the method used to evaluate multivariate geochemical dataset quantitatively. (Note that Cluster analysis was applied to all elements detected by XRF, but only selected elements are used in principal component analysis).

Cluster analysis

The Hierarchical methods provide a purely statistic way to classify groups and present them in the form of dendrogram. The basic idea behind this method is to firstly calculate the distance matrix, merge two groups determined by minimum distance, combine the attributes of the entities in the two groups that were fused and then merge the next two groups. After attempting several different methods, we adopted Euclidean distance and Ward's method as our dissimilarity and clustering methods (See Appendix for mathematics).

The clustering of bulk elements confirms our qualitative classification based on lithology and textures. Generalizing for all samples, three major groups can be distinguished. Overlaid with our colored lithological division, we can clearly see that the carbonate middle facies (colored by blue) is highly clustered by itself; however, the lower facies (colored by brown) and upper facies (colored by grey) differ from one other but some samples share similarities. The dendrograms suggest that these three different facies have quite different chemical compositions and may have been deposited in different environment at, or at least redox conditions. Nevertheless the upper and lower facies experienced somewhat similar process which explains their similarities with each other.

Principle Component Analysis

In order to dig into which components are best characteristic for each group, we adopt another statistical method called principal component analysis (PCA), which is a method to express multivariate dataset in a visualable dimension (See Appendix for mathematics). PCA seeks the strongest correlation structure among variables so that it can express many variables in a smaller number of composite variables. With the help of PCA, we can better observe the clustering and which element is driving it. Before applying PCA, we diminished our dataset into 10 variables by selecting most representative elements in two groups: Al, Si, and negatively correlated Ca, as indicators of detrital fluxes and Fe, Cr, V, Cu, Mo, U, Ni as redox proxies.

Coded by clustering groups, **Figure 17** and **Figure 18** illustrate the driving factors of each group. Both in the Bald Eagle core and Snow Shoe core, the first component is characterized by high loadings for elements bound to minerals of clastic origin, for instance, Al and Si, and high but opposite loading for the carbonate component, Ca. As shown in the figure, this principle component differentiates the blue coded group that represents middle facies with brown and grey coded groups representing upper and lower facies. The brown and grey coded groups, mainly upper and lower facies respectively, however, are more characterized by the second principle component. In the Bald Eagle core, the grey group of the lower facies is characterized by some redox proxies, including V, Ni, Mo, and pyrite indicator, Fe, suggesting a reducing condition. The brown group is driven more by detrital fluxes, Al and Si. Cr could be transported to the sediment with

land-derived clastic fraction (for example, chromite, clay minerals, ferromagnesian minerals, Brumsack, 1986; Hild and Brumsack, 1998). This complexity of Cr transport and enrichment limits its application for paleoenvironment and is reflected on Figure 17 showing the brown group is characterized by high Al and Si as well as high Cr concentration. In the Snow Shoe core, the grey and brown groups are clustered together indicating a similar depositional environment or some diagenetic processes altered its original signatures. The brown group of the lower facies clusters more in the center and the grey group of upper facies spreads more widely. The lower facies in the Snow Shoe core enriches in Silica, but not in Aluminum arguing that this enrichment of silica may come from biogenic rather than terrigenous sources.

The philosophy of employing bulk geochemical data to constrain the deopositional environment are based on the assumption that the properties of sediments deposited from different depositional environment should be reflected by their bulk chemical element. And the clustering analysis and the principle component analysis provided a quantitative way to examine them. The results shown in **Figure 15**, **Figure 16**, **Figure 17**, and **Figure 18** confirmed our lithological division in a statistic way and enable us to use this division to interpret the changing depositional environment in the duration of the Cherry Valley Member.



Figure 15. Dendrogram of clusters of the Bald Eagle core bulk chemical suites. Note sample numbers in the lower facies are coded by brown, sample numbers in the middle facies are coded by blue and sample numbers in the upper facies are coded by grey.



Figure 16. Dendrogram of clusters of the Snow Shoe core bulk chemical suites. Note sample numbers in the lower facies are coded by brown, sample numbers in the middle facies are coded by blue and sample numbers in the upper facies are coded by grey.



Figure 17. Biplot of samples and chemical elements of the Cherry Valley limestone in the Bald Eagle Core. Note samples in the lower facies are coded by brown, samples in the middle facies are coded by blue and samples in the upper facies are coded by grey.



Figure 18. Biplot of samples and chemical elements of the Cherry Valley limestone in the Snow Shoe Core. Note samples in the lower facies are coded by brown, samples in the middle facies are coded by blue and samples in the upper facies are coded by grey.

Redox conditions

Paleo-redox reconstruction using pyrite framboid size dirstribution

Framboidal pyrite size distribution in ancient sediments provides an independent way for paleo-redox condition reconstruction (Wilkin et al 1996; 1997). The term "framboid" was adopted by Rust (1935) to describe the raspberry-like pyrite morphology. Pyrite framboids are actually a spherical aggregate of small equigranular pyrite microcrystals, are the dominant form of pyrite in modern euxinic marine basins and are well preserved in ancient sediments (Vallentyne, 1963; Berner, 1984; Love and Amstutz, 1966). According to the aggregation model proposed by Wilkin and Barnes (1997), four consecutive processes may happen during pyrite framboid formation, including: 1) nucleation and growth of the initial iron monosulfide microcrystals, 2) conversion of microcrystals to greigite, 3) aggregation of greigite microcrystals, and 4) conversion of greigite framboid to pyrite framboid. Greigite formation requiring dissolved sulfide and ferrous ion, and oxidant limit the most productive pyrite framboid region in nature to those redox interfaces which transition downward from an oxygen-bearing to a hydrogensulfide-bearing water column (Berner, 1969). Many studies of modern and ancient sedimentary pyrite-bearing sediments suggest that pyrite framboid size distributions could serve as a redox indicator by showing that framboids formed in euxinic basin are constantly smaller and less variable in size than those formed in sediments underlying oxic or dysoxic water columns (Wilkin et al., 1996; Wilkin and Arthur, 2001; Wignall and Newton, 1998; Bond and Wignall, 2010; Tian et al., 2014). In euxinic to anoxic environments, where the oxic-anoxic boundary within the water column, the framboid formation has a relatively short average growth time due to hydrodynmic instability (e.g. the growing framboids become too dense to be supported in the water column by

buoyancy force) and therefore has smaller size. In dysoxic environments, the bottom water is weakly oxygenated and the redox boundary is in the sediments allowing a longer duration of the mixing of reactants and resulting in larger size and variability of framboids (Wilkin et al., 1996; Bond and Wignall, 2010).

Modern euxinic basins typically exhibit relatively small mean value of framboids diameter, around 4.3 - 7 microns and a standard deviation less than 2 micron, whereas dysoxic and oxic environments (conditions at the sediment/water interface) exhibit a mean value about 5.7 to 11.9 microns and a standard deviation around 2.5-7.9 microns (Wilkin et al., 1996). Wignall and Newton (1998) argued the mean size of pyrite framboids separating dysoxic and euxinic facies follows the line *Mean size* = -3.7 Standard Deviation + 14 in the study of ancient mudrocks, and Bond and Wignall (2010) revised the line to Mean size = -3.3 Standard Deviation + 14. We interpreted redox facies in the Cherry Valley Member based on the criteria of (Bond and Wignall, 2010) Figure 19. Bald Eagle samples from the lower facies fall in the euxinic area, indicating persistently oxygen-free conditions in the water column. This inference is also confirmed and supported by the absence of bioturbation and abundance of pyrite in these samples. Two samples that in the dysoxic region are from the middle facies, where carbonate concentration increases and pyrite abundance decreases significantly, indicating an increase of diagenetic pyrite and a possibly oxygenated to dysoxic bottom water conditions. The pyrite framboids in the upper facies fall in the transition area between euxinic and dysoxic. Although the utilization of pyrite framboid size is limited to separating anoxic and dysoxic, the increased clay content and pyrite, and absence of bioturbation and fossils observed under SEM reveal a quick change into anoxic conditions of the Oatka Creek Member near the top of the Cherry Valley Member.



Figure 19. Plot of mean diameter versus standard deviation of framboid sizes. The dotted line separating euxinic/anoxic from dysoxic facies is from Bond and Wignall (2010). And histograms of distribution in five samples. Note sample codes are correlating to codes showing on the plot.

Thus, redox conditions within the Cherry Valley interval were not as consistently oxygenated as thought (Brett and Baird, 1985); degree of oxygenation evolved as follows: 1) continual but gradual lessening of the intensity of euxinic conditions, the Union Spring Member; 2) an oxygen-poor water mass in the lower facies marking the gradually boundary of Eif-2 to Eif-Giv to dysoxic conditions in the middle facies of the Cherry Valley Member; 3) finally, the bottom-water layer apparently thickens and becomes anoxic in the upper facies but never as reducing as the first stage; 4) the bottom-water continues to be anoxic moving into the Oatka Creek Member deposition during the transgressive system tract of Eif-Giv sequence and becomes euxinic in the highstand

system tract known as the "a type euxinic" in Oatka Creek time (Werne and Sageman, 2002).

Mo-U covariance

Low sediment accumulation rate and strong-reducing conditions allow U and Mo to be employed as redox proxies to reconstruct redox paleoenvironments (Rimmer, 2003; Tribovillard et al., 2006; Algeo and Tribovillard, 2009). Under oxic conditions, Mo enrichment is limited and Mo is stable represented in oxic seawater by the unreactive molybdate oxyanion (MnO_4^{2-}) ; modern continent-margin sediments typically contain only 1-5 ppm Mo in total (Zheng et al., 2000). Under anoxic to exunic conditions, Mo becomes reactive when sulfide species, including hydrogen sulfide, facilitates the conversion of molybdate to thiomolybdate and the accumulation of Mo in sediments (e.g. adsorbs onto growing framboids and co-precipitates in sediments). Similar to Mo, U is present as soluble U (VI) form in the form of uranyl-carbonate complexes under oxicsuboxic conditions; modern continental margin sediments typically contain only 1-5 ppm U (Morford, et al. 2009). But under anoxic conditions, U (VI) is reduced to U (IV), forming the highly soluble uranyl ion UO^{2+} or less soluble uranous-fluoride complexes (Zheng et al., 2000; Morford et al., 2001). The uptake of U by sediments could happen through the formation of organic-metal ligands in humic acids or the precipitation of crystalline uraninite (UO_2) or a metastable precursor to it (Anderson et al. 1989; McManus et al., 2005). U flux to sediments enhanced by precipitation of organic-metal ligands and slow sediment accumulation allows the enrichment of U (Zheng et al., 2000; Klinkhammer and Palmer, 1991; Morford et al., 2001). Mn-Fe redox cyclying represents an additional mechanism of authigenic Mo enrichment but not known by U in some

marine systems.

Some researchers have reported that under certain conditions the authigenic enrichment mechanisms of U and Mo appear to differ from each other in terms of concentrations in the sediments (**Figure 20** and **Figure 21**, Algeo and Tribovillard 2009; Tribovillard et al. 2012). The benthic redox conditions supposed to be a dominant one: little or no enrichments of Mo and U under oxic environment; suboxic conditions exhibit modest enrichment with Mo/U ratios distinctly lower than the seawater ratios; under anoxic conditions, the redox boundary rises close to sediment/water interface, formation of thiomolybdates most likely converts aqueous Mo to a practical-reactive form and enhances the uptake of authigenic Mo by the sediment. Such conditions result in rates of uptake of Mo that substantially exceed those of U, resulting in a progressive increase in sediment (Mo/U) ratios. Furthur, they demonstrated that covariance patterns of Mo and U enrichments of marine deposits yield information regarding water mass conditions during sedimentation.



Figure 20. Mechanism of Mo and U authigenic enrichment in response to the changes of redox conditions (Modified from Algeo and Tribovillaro, 2009).



Figure 21. Model of enrichment patterns and changes in (Mo/U)auth ratios. The diagonal dotted lines represent the seawater (SW) Mo/U molar ratio of ~7.5-7.9 and fractions of SW (Modified from Algeo and Tribovillaro, 2009).

Uranium and Mo enrichment data of the whole Marcellus Formation collected by XRF in the Snow Shoe core illustrates two general trends (**Figure 22**): 1) at low U and Mo enrichment, the data population from the Cherry Valley Member evolves from a reference line of 0.3 times molar value of modern seawater to normal seawater reference line, indicating an increase of Mo uptake; 2) at relatively high enrichment, data points from the Union Spring Member fall along the normal seawater reference line and the concentrations of Mo and U appear to differ little from each other. Samples from the Oatka Creek Member fall in between and along the normal seawater reference line.



Figure 22. Enrichment factors relationship of Mo and U in the whole Marcellus section. XRF Data of the Oatka Creek Member and the Union Spring Member from ABBS group database.



Figure 23. Enrichment factors relationship of Mo and U in the Cherry Valley Member, separating into upper, middle and lower facies according to the lithofacies.

Such trends are suggestive of a change from intense anoxia condition, even euxinic conditions, to dysoxic conditions and then anoxic conditions. In an intense anoxic condition, the redox boundary rises close to sediment/water interface. The formation of thiomolybdates most likely converts aqueous Mo to a practical-reactive form and enhances the uptake of authigenic Mo by the sediment. Such conditions as shown in the Union Spring samples result in rates of uptake of Mo that substantially exceed those of U-auth, and a progressive increase in sediment (Mo/U) ratios as EFs increase parallel to the seawater reference line. Mo and U exhibit modest enrichments higher in the Cherry Valley as the uptake of authigenic Mo and U are both limited under dysoxic condition. Meanwhile, the a higher reduction potential of U and the less reducing conditions needed for the onset of uptake of U could account for the observation that the Mo/U ratios are distinctly lower than the seawater ratios. From the Cherry Valley Member to the Oatka Creek Member, the enrichments of U and Mo increase but less than those of the Union Spring Member indicating that the bottom-water evolved to anoxic but levels not as reducing as that of the Union Spring Member.

Samples from the Cherry Valley shows the highest variance. **Figure 23** shows samples separating from the Cherry Valley Member and coded colors are based on different facies discussed above. In fact, only the middle facies and the underlying lower facies extend from the dysoxic/ low enrichment area indicating a rapid establishment of dysoxic bottom water from the previous anoxic condition, and a consequent upward displacement of the sulfide chemocline to the sediment-water interface.

Sources of carbonates

The changing paleo-redox conditions which the three individual lithofacies units of the Cherry Valley limestone raise the question: where does the carbonate come from? Carbon and oxygen are two major element of carbonate and, therefore, their stable isotopic values contain fingerprints of its origin. Carbon and oxygen isotopic compositions have long used as an indicator to trace the origin of the carbonate (Arthur et al., 1984; Morse and Mackenzie, 1990).

Here 46 analyses of carbon and oxygen isotopes have been performed on the Cherry Valley interval. The results are shown in **Figure 25**: for carbonate carbon isotope values, the lowest values are exhibited in the upper facies (range from -10‰ to -5‰) and the most enriched values occur in the middle facies (range from -1‰ to -2‰); for oxygen isotope values, the isotopic values are more constant, with a slight enrichment within the middle Cherry Valley facies. Whereas the carbon and oxygen isotopic compositions of normal Devonian marine carbonate range from -1 to 2‰ δ^{13} C and -3.5 to 2‰ δ^{18} O VPDB (records from brachiopods and foraminifers, Joachimski, et al., 2004; Brand, 2004; Veizer et al., 1986) respectively, the carbon and oxygen isotopes in Bald Eagle and Snow Shoe cores are significantly more depleted than normal seawater values.

Generally, four possible carbonate sources may account for the depleted carbon values: 1) lacustrine carbonates for relatively depleted ¹³C of CO₂ is derived from the decay of plant material in soil; 2) carbonates formed within shallow ground water because of acidic weathering and/or biogenic soil CO₂ dissolution and precipitation; 3) carbonate precipitated from CO₂ enriched pore waters in organic matter-rich marine sediment (e.g. during sulfate reduction) bearing ¹³C-depleted signals; 4) carbonates

formed by oxidation of CH_4 by sulfate-reducing bacteria which is depleted in ${}^{13}C$ (Faure, 1986; Clark and Fritz, 1997). Since the Appalachian Basin is foreland marine basin and there is no evidence of post-depositional sub-aerial exposure, the first two sources are not likely an origin of the Cherry Valley limestone. For pore water carbonate precipitation, enhanced organic matter productivity and decomposition rate are needed to generate enough CO₂ and precipitate carbonate (Morse and Mackenzie, 1990). Although there is no clue of increases of organic matter productivity in this time, we cannot exclude this mechanism as CO₂ and bicarbonate ions could diffuse through porous sediment during early diagenesis. Since the Cherry Valley unit is a basin-scale limestone, a basin-wide mechanism is needed to build this unique layer. Abundance of methane bearing fluid inclusions found in the veins of the Cherry Valley interval favors the hypothesis that basin-scale advection of methane bearing fluid may have promoted the precipitation of the Cherry Valley limestone. As a characteristic of methane oxidation-derived carbonate, the depletion in ¹³C should be expected in the range of -20 to -50‰ VPDB (Suess et al., 1989; Aharon and Fu, 2000). This origin could partially explain the ¹³C-depleted carbonate, however values of the Cherry Valley bulk carbonates are not as depleted as typical methane oxidation-derived carbonate.

For the depleted carbon isotopic values, one possible explanation of is that the limestone has undergone diagenesis which altered the original signal. Oxygen isotopic compositions, on the other hand, are more complex and can be effected by the formation temperature, the isotopic composition of the source water and the respective fractionation of the carbonate phases (Friedman and O'Neil, 1977). Depleted oxygen isotopic values of the Cherry Valley limestone and lack of correlation between δ^{18} O and δ^{13} C suggest a

diagenetic signal of alteration (Figure 26; Irwin et al., 1977). Strontium has received attention stemming from its potential importance for studying carbonate diagenesis (Kinsman and Holland, 1969; Banner, 1995). In carbonate, the variation of Sr concentration may be a function of precipitation rate, mineral stoichiometry, crystal growth mechanism, fluid composition and temperature. Experimental and empirical results have shown that the substitution of Sr is an exothermic reaction, thus the Sr/Ca ratio is expected to decrease with increasing temperature (Villiers et al., 1995; Banner, 1995; Rosenthal et al., 1997; Hart and Cohen, 1996; Cohen et al., 2001). For primary carbonate, relatively high Sr/Ca ratio is expected as it precipitate in a relatively mild environment (e.g. surface water) and bears the normal seawater value. And for diagenesis, the recrystallization, fluid composition and temperature are most important. Low Sr concentrations in diagenetic carbonate that would be expected from trace element distribution coefficient values or fluid composition (Banner, 1995). The average Sr/Ca value of the Devonian seawater is around 6-8 mmol/mol (Steubur and Viezer, 2002) As shown in the Figure 24, the average Sr/Ca ratio in the Cherry Valley limestone is around 4 mmol/mol,: in the upper facies and middle facies of the Cherry Valley limestone, it is around 2 to 3 mmol/mol, lower than the overlying Oatka Creek Member (10~15 mmol/mol); the lower facies of the Sr/Ca is relatively higher (around 5 mmol/mol) but still lower than 10 mmol/mol in the Oatka Creek Member. One explanation of these low values is that during diagenesis, the diagenetic fluid, especially hot fluids, leaches the carbonate and cause the recrystallization and strontium element redistribution resulting in low strontium contents of most ancient limestones (Banner, 1995). Moreover, petrographic evidence, as discussed above (e.g. the matrix of recrystallized calcite,

abundance of veins) also supports the diagenetic alternation of carbonate. Now the main question is whether the methane oxidation-associated values are the primary signal being altered or it is the entire signal due to a diagenetic process that altered a primary isotopically enriched matrix?

A common observation in the Cherry Valley interval is abundant fractures cemented by calcite along the depth, which could have provided conduits for fluid that promote the interaction of sediment matrix with these fluids. In order to determine the origin of these fluids, carbon and oxygen isotopes and fluid inclusions in the veins of the Cherry Valley interval were examined. The carbon isotope values of vein calcite are more enriched than those of carbonate matrix of the Cherry Valley (from -2 to 2‰), except one set of data from a vein in the Snow Shoe core that seems to have been generated by dewatering exhibiting depleted δ^{13} C. Most values would support the hypothesis that deep burial fluid bearing enriched $\delta^{13}C$ interacted with the $\delta^{13}C$ -depleted matrix carbonate generated by methane oxidation and reset their isotopic composition to a relatively enriched value. Oxygen isotope values for vein carbonate spanning -6.5 to -13‰ provide furthur evidence for this hypothesis. As oxygen isotopes can be affected by the ambient temperature (e.g. an increase of 1°C in temperature results in a depletion of 0.2‰ in δ^{18} O in precipitated carbonate, O'Neil et al, 1969), an estimate of temperature of alteration can be made. Assuming Devonian seawater as the source of fluids (-2‰ VPDB) and the surface temperature is 15°C, the estimated paleo-temperature of alternation as about 56-58°C. If the sources of alternation is deep burial fluid with δ^{18} O of veins and Devonian brine value (-3~2‰ VPDB, Dorobek, 1987), the estimated temperature is about 92-105°C. This temperature range is corroborated by the primary fluid inclusions examined in calcite veins of the Cherry Valley interval. The homogenization temperatures are measured from primary aqueous inclusion ranging from 90-98°C. Because of the reequilibriation of aqueous fluid inclusions during the burial overheating, the homogenization temperature of primary aqueous fluid inclusions in calcite record a temperature close to the maximum reached by the rock (Prezbindowski and Larese, 1987; Barker and Goldstein, 1990). This constraint further supports the hypothesis that diagenetic alteration resulted from hot burial fluid with enriched carbon isotopic values and depleted oxygen values. To summarize, the plausible explanation for the abnormal Cherry Valley Member (as shown in **Figure 26**) is that early diagensis process, primarily methane oxidation, generated isotopic depleted carbonate, but leached and altered by hot fluid characterized by enriched carbon and depleted oxygen isotopic signatures. This diagenetic alternation is confirmed by petrologic analysis, low Sr/Ca ratio, and fluid inclusions within cemented fractures.



Figure 24. Stratigraphic plot of Sr/Ca ratio in the Snow Shoe core.



Figure 25. Stratigraphic plots of Carbon and oxygen isotopic compositions of the Cherry Valley limestone in the Bald Eagle core (left) and Snow Shoe core (right).



Figure 26.Correlation plots of carbon and oxygen isotopes in the Bald Eagle core and Snow Shoe core as well as veins. Note the carbon and oxygen isotopic value of the Devonian seawater is - 1~2 and -3.5~2‰ respectively (Joachimski, et al., 2004; Keith and Weber, 1964).

Sediment flux and hiatus

In hemipelagic facies, the Silica-Aluminum ratio (Si/Al) can provide useful information about detrital versus biogenic sedimentation (Arthur and Dean, 1998). In general, Al in mudrock packages is primarily associated with aluminosilicates derived from fluvial or volcanogenic inputs (Arthur et al., 1985; Arthur and Dean, 1998). For Si, the main source is silicates (dominated by quartz) derived from continental. The sediment flux could also be a useful indicator for sea-level changes (Arthur and Sageman, 2003). In the Bald Eagle core, the ratio is relatively high in both the overlying Oatka Creek Member and the underlying Union Spring Member (Figure 11). As the Bald Eagle core is located in marginal part of the basin, large variations in sediment flux can be expected and shown in the Cherry Valley Member. But the stratigraphic trend of Si/Al ratio is shown much clearer in the proximal Snow Shoe core (Figure 12) with less variation and noise in the Cherry Valley interval. A baseline of Si/Al ratio for the shale is around 2.8 in both underlying Union Spring Member and the overlying Oatka Creek Member. An obvious decrease to around 1.8 happens in the Cherry Valley Member and marks the decrease in sediment flux. Based on these, the lowstand system tract characterized by highest sediment flux rate should be identified in the upper Union Spring Member, while the sedimentation starvation as noticed in the boundary of lower facies and the middle facies should be marked as the beginning of transgressive system tract. High variability of the Si/Al ratio occurs in the Cherry Valley Member in the Bald Eagle core. One of the explanations for the variability of the Si/Al is the shoreline transgression-derived eolian process in a sedimentation starvation time. Eolian processes could transport quartz and other silt-sized particles and account for large variations in Si/Al under these depositional conditions (Lever and McCave, 1983). As the Bald Eagle core is more proximal, it is

closer to the shoreline and more vulnerable to this process.

In order to better constrain the sedimentation process, we employed another proxy: Ti/Al. Ti derives partly from aluminosilicates and quartz, and partly from silt-size heavy mineral grains (e.g. sphene, ilmenite). Bertrand et al. (1996) have shown that the ratio Ti/Al is a reliable proxy for siliciclastic grain size. For a foreland basin like the Appalachian Basin, the rapidly subsiding depocenter acts as a proximal clastic catchment. The change of grain size could, to some extent, represent sedimentation rate (Bertrand et al. 1996; Murphy et al., 2000; Sageman et al., 2003). In both cores, the Ti/Al ratio is higher in the Union Spring Member and the lower facies of the Cherry Valley Member, and Ti/Al remains stable within the middle and upper facies towards the Oatka Creek Member. The distance to the sediment source also reflects on the Ti/Al plots, but similar trends indicate that sediment input diminished in the Cherry Valley Member and then recovered in the Oatka Creek Member.

Despite the variations and difference of baseline in the Bald Eagle and Snow Shoe core, the Ti/Al ratio as well as Si/Al decreases dramatically at the lower contact of the middle facies or the upper boundary of the lower facies indicating a major event associated with sediment flux happened at this time. A layer of distorted cemented carbonate or so-called "hardground" has been found and examined by detailed petrologic analysis shown in **Figure 7.** The hardground is surface of synsedimentary cemented carbonate layers hosting unique fauna and flora on the hard surface (Wilson and Palmer, 1992). It is an evidence of exposure to seawater on the seafloor and more importantly, the evidence of sedimentation hiatus. This sedimentation hiatus could account for the dramatic changes of Si/Al and Ti/Al in the boundary of the middle facies and the lower

facies. Abundant fossils and heavily bioturbated layers are supplemental evidences. The pause of sedimentation could be an important mechanism for the formation of barite nodules commonly found in the lower facies, which we will talk about in the following section.

The Barite puzzle

One of the most characteristic textures in the lower facies of the Cherry Valley Member is the barite nodular facies. Investigators have reported these sediment-hosted barite exposures in outcrops extending from central PA through eastern WV and southern VA (Chen, 1977; Nuelle and Shelton, 1986; Clark and Mosier, 1989) and nodules from well cores are observed throughout the basin (**Figure 27**, Zhang et al., 2013; unpublished data, Core Lab). These barite nodules are so abundant and spatially extended in the Cherry Valley limestone that some researchers even evaluated the barite deposits as a favorable economic resource (Nuelle and Shelton, 1986). These barite nodules raised industrial interests because of the high barium concentration in the flowback water from the Marcellus stimulation and production operations (Fortsen, 2011; Gregory et al., 2011; Haluszczak, et al., 2013). In this thesis, we studied these nodules from petrological and isotopic points of view, and expected to reveal the origin and mechanism of these barite accumulations, and further shed light on the reconstruction of paleo-environments.

The origin of barite

Barite, whose constituents are Ba^{2+} and SO_4^{2-} , is well studied as a major carrier of barium in water column and sediment (Bishop, 1988; Dymond et al., 1992). The extremely low solubility of barite (ca 10^{-10} at 25 °C, 1 atm; Church and Wolgemuth,

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1972) enables natural conditions to maintain high concentration of either dissolved barium or sulfate, but not both. Sulfate is abundant in today's ocean, however under anoxic conditions promoted by abundant organic matter, sulfate reduction consumes sulfate within the sediment. With the depletion of sulfate, high concentration of barium are found in marine sediments, such as the Black Sea at water depth below 100m (Moore and Falkner, 1999). Because of the dynamic interaction between barium and sulfate ions, the mineral barite carries information about the solution where it precipitates and the redox conditions where it undergoes.

Four different mechanism of barite precipitation have been distinguished: (1) marine or pelagic barite, (2) biogenic precipitation, (3) hydrothermal barite, and (4) diagenetic barite (Griffith and Paytan, 2012; Torres et al, 2003; Paytan et al, 2002). Each mechanism has its own particular depositional environment and generates different types of barite. Nodules observed in the lower facies of the Cherry Valley Member are oblate spheroids, subrounded, irregular forms that are from 1 to 5 cm in diameter. The deformation of laminae in the surrounding shales forms stress shadows and indicates the growth of nodules started before compaction in unconsolidated sediments. Some nodules contain septarian structures filled by pyrite and calcite suggesting that the nodules formed in highly porous, water-rich sediment and that fissures developed in the nodules formed during early diagenesis in response to fluctuations in bottom water conditions that existed when the surrounding sediments were still unlithified.

The morphology and size of barite crystals controlled by the chemical and physical environment of precipitation are the most direct indicators of precipitation environment (**Figure 28**; Griffith and Paytan, 2012). Authigenic marine barites are small sized (usually < 5 microns), sub-spherical to elliptical crystals, whereas hydrothermal braites are well-formed polyhedral to euhedral lathlike crystals ranging from tens of microns to hundreds of microns. The barite crystals under SEM shown in **Figure 28** are flat, tabular-shaped crystal, smaller than hydrothermal barite crystals but generally larger than 10 micron, which is consistent with a diagenetic origin (Dean and Schreiber, 1978).

Isotopic signatures of major elements in barite are also indicative of the sources of the fluids from which it precipitates. Table 2 illustrates characteristics of barites from different origins and their isotopic signals (modified from Griffith and Paytan, 2012). In a bacteria-mediated sulfate reduction sediment column, 32-sulfur is preferentially consumed by bacteria. This leaves the residual sulfate relatively enriched in 34-sulfur with up to ~60‰ fractionation (Harrison and Thode, 1958). There is little fractionation between barium sulfate and the original sulfate from which it precipitated (less than 0.4 ‰, Kusakabe and Robinson, 1977). If barium reacts with residual sulfate in an early diagenetic environment experiencing sulfate reduction, barite should retain the original enriched- δ^{34} S signature from residue sulfate of pore water. The sulfur isotope of barite in nodules of the lower Cherry Valley facies varies, but all are enriched in δ^{34} S. The data, presented in Table 3, also include sulfate isotope values available in the literature for the Cherry Valley barites. The δ^{34} S enriched signatures of barite are consistent across the basin from central PA, WV and KY (Nuelle and Shelton, 1986). These signals indicate a basin-wide event during the deposition of the lower Cherry Valley facies--- the beginning of the transgressive system tract.



Figure 27. Isocore map of average bulk density of the Cherry Valley Member in the study area. Stars marked the location where barite nodules are found in both cores and outcrops (Modified from Zhang et al. 2013 and Nuelle and Shelton, 1986). Density increases to the eastern PA and southeastern NY indicates the lithology of the Cherry Valley becomes more and more arenaceous as closer to the sediment source.



Figure 28. SEM images of barite cyrstals from different origins. A. Sub-spherical to elliptical marine barite, size <5 um from Paytan et al. (2002); B. Rosette structures of hydrothermal barite, Mid-Atlantic Ridge, Griffith et al. (2012). C. Platy tabular diagenetic barite, Baja California, Paytan et al. (2002); D. Tabular diagenetic barite from the lower facies of the Cherry Valley Member

Origin	Size	Crystal Morphology	Sulfur Isotope Signature
Marine Barite	< 5 um	Sub-spherical, elliptical	20-25 ‰
Hydrothermal Barite	10 um ~ > 500 um	Rosette, ployhedra, vug- filling	15-25‰
Cold Seep Barite	10 um ~ > 100 um	Chimney, rosette, euhedral	20-35‰
Diagenetic Barite	5~20 um	Tabular, rounded, flat	>25 ~ 80‰

Table 4 Crystal properties and sulfur isotopic compositions of barite from different source

Mechanism for barite accumulation

Authigenic barite is partially dissolved at depth intervals where interstitial sulfate in sediments in depleted because of high rates of anoxic reduction. Below this zone, barites are dissolving according to the solubility product (Church and Wolgemuth, 1972). Barium ions are released from barite crystal and accumulate in the pore water. If near the sediment/water interface, sulfate will diffuse downward and barium will diffuse upward from the zone of barite dissolution. Theoretically, barite may reprecipitate at the lower end of the sulfate reduction zone, which is termed "barite front" (Brumsack, 1986; Torres et al, 1996). This barium-enriched interval provides abundant material source of diagenetic barite. However, Torres et al (1996) extended Fick's diffusion model into diagenetic barite precipitation, and argued that under steady-state conditions, with constant sedimentation rate, diffusion of diagenetic redistribution of barium cannot account for the formation of barite nodular deposits. Two other mechanisms have been suggested that would enhance the accumulations of barite in diagenetic environments: 1) sedimentation pauses, and 2) the advection of fluid from deeper within the sediment sequences (Dean and Schreiber, 1977; Torres et al, 1996; Torres et al, 2002).

High sedimentation rates generate a relative closed pore-water system. In this system, the sulfate pool in the pore-water system becomes exhausted at relatively shallow depth and a barite front would form at the lower end of this interval (Berner, 1980; Torres et al, 1996). When the sedimentation rate decreases or during a hiatus, sulfate diffusion continues from overlying waters, but the rate of reduction consumption slows. However, the accumulation of barite front would remain at a fixed depth relative to the sediment-

water interface, the amount of sulfate from diffusion will allow for the formation of larger deposits or concretions (Breheret and Brumsack, 2000).

The advection of fluids from deep within the sediment sequences is another mechanism of barite formation. Sulfate bearing fluids or barium bearing flux are common occurrences in convergent margin settings (Torres et al., 1996; Torres et al, 2003). In some settings, e.g. along major faults, submarine discharge of barium by hydrologic or tectonic processes causes the barite reprecipitation at sites on the seafloor (Torres et al., 1996). This mechanism is similar to the hydrothermal origin of barite, except the barium comes from diagenetic dissolution of authigenic barite. We exclude this scenario because of the occurrence site and the sulfur isotopic composition of barite (e.g. in this scenario, the barite will bear the seawater sulfur value rather than diagenetic signals). In other settings, diagenetic barium within the sediment meeting with the advecting sulfate from deep demonstrates an "in-situ" formation of barite (barite precipitates within sediments, Torres et al, 2003).

Then the question is how we can distinguish between the sediment starvation scenario and a formation process based on the addition of sulfate-enriched fluids from deep. Barite distributions of both modern seep and Paleozoic deposits are limited to stratigraphically defined areas and are often associated with faults or are adjacent to steep slopes, similar to that of modern sites of fluid seepage along subduction zones, e.g. Nevada (Dube, 1988; Poole et al., 1991; Torres et al., 2002). In these settings, the accumulations of barite are usually episodic and the sulfur isotopic compositions usually tend to be uniform within a narrow sediment profile (**Table 2** showing the variance of sulfate sulfur). However, **Figure 29** illustrates the sulfur isotopic compositions of barite

nodules encountered in sediments showing a large variance (~20‰) ranging from close to Devonian seawater values 17~22‰ (Claypool, 1980; Strauss, 1999; Kampschulte and Strauss, 2004) upwards to extremely heavy values of more than 50‰. This fluctuation is less likely due to a sulfate source change in fluid discharge system, but rather because of different phases or rates of sulfate reduction, or in other words, the availability of sulfate.

As discussed in redox condition section, the bottom water continues to be anoxic during the deposition of the lower facies of the Cherry Valley Member, the sulfate reduction zone is up in the water column or near the sediment-water boundary. In this case, the "barite front" formed at the lower end of the sulfate reduction zone is up in the sediment column. A pause of sedimentation rate at the beginning of the middle facies, indicated by sediment flux proxies (Si/Al, Ti/Al, see previous section for explanation), turns the sediment column into a more open system: The seawater sulfate diffusing downwards, the sulfate reduction zone diminished while barite front stay fixed, generates interbedded barite nodules that carry relatively depleted isotopic signatures close to seawater sulfate. This is similar with the lowest values of sulfate-sulfur isotopic composition record in the anoxic events in lower Albian, in Niveau Paquier (Breheret and Brumsack, 2000). With the water column changed to more oxygenated conditions, the sulfate depletion zone enlarged and the barite front was pushed deeper into the sediment. In this case, the generated barite carried more enriched values as the sulfate is less available than from seawater at the beginning of the sediment pause.


Figure 29. Sulfur isotopic composition of barium sulfate and mineral proportion of nodules in the Bald Eagle core (left) and the Snow Shoe core (right). Note the microdrill location is marked and correlated to the sample number.

The relationship of pyrite and barite

The interpretation of the formation mechanism of barite nodules confirms the sedimentation pause and a dynamic change of seawater redox. Another post-early diagenesis process may be recorded by these nodules as well, especially by the bariteassociated pyrite in these nodules. The pyritic rim in barite nodule is one of the most obvious characteristics on the nodules of the Cherry Valley interval (Figure 29). Under the SEM, the crystal of barite-associated pyrite is euhedral and shown as pyritohedrons, while the morphology of pyrite in matrix is framboid, indicating two different mechanisms of formation (Figure 13): as mentioned above, the framboidal pyrite in the matrix formed in the water column or during very early stage of diagenesis in the sediment column; the enhedral pyrite crystals could form in veins, hydrothermal vent, metamorphic rock or during diagenesis process (Berner, 1980; Berner, 1984; Raiswell 1988; Raiswell and Canfield, 1998; Wilkin and Barnes, 1996). Petrologic description both in the thin section and under SEM has shown the pyrite crystals only associated with the barite, which indicate that barite may have some association with crystal pyrite formation. A detailed mapping of nodules using EDS under SEM shows that although enriched in the rim of the nodules, crystal pyrite is also found in the rim of existing barite assemblages in the middle of the nodule. The qualitative ratio of barite and pyrite in the rim and the center of the nodule are also provided by this technique (Figure 30 and Figure 32). These features indicate these euhedral pyrite crystals are formed during diagenesis briefly after the barite formation.



Figure 30. Mineral proportions in the nodule from EDS under SEM, Bald Eagle 790'2".



Figure 31. Photo of polished sample, Bald Eagle 790'2'. The nodule is parallel to the bedding. Note no specific location is determined under SEM but the EDS mapping moved to the center across the nodule shown in the red arrow.

Table 5 EDS mapping locations and mineral proportion data of Bald Eagle 790'2''

No.	Location	Pyrite	Matrix	Barite	No.	Location	Pyrite	Matrix	Barite
1	Edge	32.46	35.9	31.64	10	To Center	16.27	18.85	64.88
2	To Center	18.64	24.171	57.189	11	To Center	16.85	22.98	60.17
3	To Center	18.09	18.83	63.08	12	To Center	14.59	21.58	63.83
4	To Center	15.85	22.52	61.63	13	Center	13.25	21.6	65.15
5	To Center	16.83	17.3	65.87	14	Center	14.92	19.54	65.54
6	To Center	16.31	13.88	69.81	15	Center	13.77	19.57	66.66
7	To Center	16.27	21.84	61.89	16	Center	12.67	19.19	68.14
8	To Center	15.19	19.31	65.5	17	Center	11.73	22.56	65.71
9	To Center	13.99	14.21	71.8		To Center	16.27	18.85	64.88



Figure 32. Mineral proportions in the nodule from EDS under SEM, Bald Eagle 795'5'



Figure 33. Photo of polished sample Bald Eagle 795'5'. The nodule is parallel to the bedding. Note no specific location is determined under SEM but the EDS mapping moved to the center across the nodule shown in the red arrow.

Table 6 EDS mapping locations and mineral proportion data of Bald Eagle 795'5''

No.	Location	Pyrite	Matrix	Barite	No.	Location	Pyrite	Matrix	Barite
1	edge	28.71	44.56	26.73	7	to center	21.11	43.8	35.0
2	edge	20.47	66.6	12.93	8	to center	22.19	44.8	32.9
3	edge	35.82	45.43	18.75	9	Center	20.11	42.35	37.54
4	to center	25.5	41	33.5	10	Center	22.86	47.	29.94
5	to center	22.65	55.9	21.45	11	edge	26.2	62.	11.4
6	to center	25.1	53.3	21.6	12	Edge	26.29	63.0	10.69

Vertically, XRF mapping (**Table 5, Table 6**) shows a rapid change of pyritebarite proportion in the nodules within a relatively narrow interval. In the most nodular interval of the lower facies in the Cherry Valley Member, the Barite to Pyrite ratio: $\frac{Barite\ Mole\ fraction}{Pyrite\ Mole\ fraction} = \frac{Ba\ Mass\ Percentage/Ba\ Atomic\ Mass}{Fe\ Mass\ Percentage/Fe\ Atomic\ Mass}$ (assuming all Fe is in form of

pyrite) increases from 0.21 in the lowest sample from Bald Eagle 795 ft, to 0.55, 2.87 and 2.74 in the samples from Bald Eagle 793'ft, 792'ft, 790'ft respectively. With sediment burial and depth increases, diagenetic pyrite could form below the sulfate reduction zone (Berner, 1980; Wilkin and Barnes, 1996), and this reductive process could potentially dissolve the barite and replace them by pyrite if iron is available. This dissolution and replacement could support by the enrichment of sulfur isotopic compositions from center to the rim within the nodule shown in **Figure 29** because of the preference of 34-sulfur in the sulfate reduction (Goldhaber and Kaplan, 1980; Habicht and Canfield, 1997). However, it could not explain entirely about the rapid change of Barite to Pyrite ratio within a relatively narrow interval. One of interpretations is that an advection of reducing fluid reductively dissolves barite and replaces them by pyrite starting from the lowest; with the advection continues, the reducing potential diminishes and less barite is reacted and replaced towards the top. Niu et al., (2013) measured in-situ sulfur isotope analyses of barite and pyrite in the nodules and suggested that an advection of depleted 34-sulfur bearing fluid is necessary to balance the isotopic composition detected by Secondary Ion Mass Spectrometer. And we believe this post-early diagenesis happen briefly after the formation of the barite before the late diagenesis of compaction.

DEPOSITIONAL MODELS

Base-level, which is the surface of balance between erosion and sedimentation, and water depth both define the depositional environment of the sedimentary system. Since the Appalachian Basin is a foreland basin, various workers have proposed that thrust-induced subsidence or uplift, migration of bulge, and tectonic rebound drive the development of depositional system (e.g. Ettensohn, 1985; ver Straeten and Brett, 2000). Comparing with coeval sequences in other North American intracratonic basin (Michigan, Illinois), Brett et al. (2011) revised the middle Devonian sea level curve and suggested that eustasy and climate are the primary causes of the Middle Devonian sequences. This work is further supported by Kohl et al., 2014. Here, we infer that the eustasy and climate change is primary control on the depositional environment, and the tectonic event could also possible function during the deposition of the Cherry Valley (e.g. the cause for fluid advection). The depositional model that we propose as the best explanation for the origin of the basin-scale Cherry Valley limestone has three different stages (see **Figure 34**):

Stage 1: Deposition of the lower facies of the Cherry Valley Member

The lower facies of the Cherry Valley Member overlies the Union Springs Member and is characterized by dark gray calcareous mudstone with pyritic lamiae parallel to bedding and abundant nodules. This nodular facies widely spread across the basin marks the continuous deposition of the Cherry Valley limestone (**Figure 27**). Sediments in this interval consist of silty quartz and clay from terrigenous as well as authigenic calcite matrix showing diagenetic signals. Sediment proxies in this interval, e.g. Si/Al and Ti/Al, vary but decrease upward in this facies document a diminishing sediment supply into the overlying middle facies, the transgressive system tract. The decreasing sediment flux indicates a possible transgression happened in this interval rather than lowstand as proposed before. The depth of water mass in this interval is still questionable. Investigators (e.g. Tucker, 1974; Franke and Walliser, 1983; Wendt and Aigner, 1985) argued pelagic-rich limestone of the Cherry Valley may deposit in deepwater or open ocean environment. The tectonic subsidence of the foreland basin could be active and still create enough accommodation space to generate a relative deep water column under the lowstand and the transgressive system tract. High enrichments of uranium and molybdenum and framboidal pyrite with relatively small size also suggest an anoxic to euxinic bottom water condition during this interval.

The high organic matter content in the underlying Union Spring Member and the continuous anoxia of the water column facilitate the sulfate reduction processes and narrow the sulfate reduction zone. The biogenic barite and marine barite dissolved and the accumulation of barium formed the barite front at the bottom of the sulfate reduction zone. Following the sulfate reduction zone, the methanogensis process which is promoted by abundant organic matter took apart. These generated methane could diffuse or advect upward to promote the methane oxidation and associated carbonate precipitation.

Stage 2: Deposition of the middle facies of the Cherry Valley Member

The main lithology of the middle facies is gray to dark gray wackstone and micrite with abundance of fossil fragments. This middle facies of the Cherry Valley limestone depositing above the fine-grained calcareous mudstone forms a coarseningupward succession. This facies contains the most diverse fossil assemblage including brachiopod, tentaculites as well as indiscriminate skeletal debris. Most fossils found in the Bald Eagle core and Snow Shoe core are incomplete and poorly sorted with no benthic fauna, which may suggest transported source. Lacks of framboids pyrite (with relatively large size framboids), low uranium and molybdenum enrichments and abundant bioturbation suggest the bottom water become probably midly dysoxic to oxic during this time. The middle facies is relatively thick up to 100ft in the northeastern PA and thin (or even missing) in southwestern to north PA indicating highly variable depositional environment during this time, from marginal shallow platform to basinal settings. This interval represents the main body of the transgressive system tract as sea level recovers from the lowstand system tract. Values of proxies of sediment flux keep low during this interval indicating a low sediment flux, but increase upwards. The lowest values of Si/Al and Ti/Al values of the middle facies are recording a possible sedimentation pause at the beginning of the transgressive system tract. This sedimentation hiatus could account for the formation of barite nodules in the lower facies, as the significant change of sediment supply could vary the sulfate reduction zone and facilitate the precipitation of barite nodules in the barite front within the unlithified sediment of the lower facies (Berner et al., 1988; see Section 5.4 for explanation). Biogenic carbonate (skeletal carbonate or fossil fragments) bearing the Middle Devonian seawater isotopic signatures also contribute to the body of carbonate in this interval. However, venting structures and associated pyrite assemblage found near the boundary between lower and middle facies suggest that the oxidation of methane bearing fluid may continue to be an important source of carbonate.

Stage 3: Deposition of the upper facies of the Cherry Valley Member

The upper facies of the Cherry Valley Member is characterized by grey calcareous mudstone or siltstone with pyritic lamination and sparse coquinoid laminae. Sediments in this facies are dominated by quartz silt. Si/Al and Ti/Al both increase suggesting that the sediment supply recovers at the end of the transgressive system tract. A strong diagenetic signal is found in this facies as all grains seem to "float" on the carbonate matrix. The variation in uranium and molybdenum from the underlying middle facies to this facies indicate a rapid change of bottom water redox condition. Framboidal pyrites formed at this time also confirmed a change to anoxic in the bottom water. This may be due to vertical expansion of water mass because of sea-level rise and possibly continued advection of reducing fluids.

With the burial continues, this interval get buried and deformed. Recorded by fluid inclusion in calcite veins, those fractures generated in the deformation within the Cherry Valley limestone may act as conduits for hot fluids bearing CO_2 and promote the interaction of sediment matrix with these fluids.









Figure 34. Depositional models of the Cherry Valley limestones

CONCLUSIONS

The Cherry Valley Member of the Marcellus Formation is an abnormal basinscale limestone interbedded in underlying Union Spring (Shamokin) Member and the overlying Oatka Creek Member, two thick shale sections. It composes three different facies: the lower facies is characterized by dark gray calcareous mudstone with pyritic lamiae parallel to bedding and abundant barite nodules; the middle facies is the "Cherry Valley limestone" in general sense, which is the massive carbonate section containing diverse fossil assemblage including brachiopod, styliolinid, gastropod, tentaculites as well as indiscriminate skeletal debris; the upper facies is characterized by grey calcareous mudstone or siltstone with pyritic lamination and sparse coquinoid laminae.

Pyrite framboids size distribution and covariance of authengic uranium and molybdenum enrichments establish the changing redox condition during the deposition time. In addition to the sequence stratigraphy studies (Brett, et al., 2011; Kohl et al., 2014) and the lithofacies investigations, depositional model of the Cherry Valley Member has been proposed. The lower facies of the Cherry Valley Member deposits in the end of the lowstand system tract and the onset of the transgressive system tract. However, the bottom water remains anoxic to euxinic due to the fast consumption of organic matter and the associated sulfate reduction and methane oxidation. This middle facies deposits above the fine-grained calcareous mudstone and forms a coarsening-upward succession marking the main duration of the transgressive system tract. The bottom water is more dysoxic or oxygenated in this time because of the decreased sediment flux and inhibited sulfate reduction, which confirmed by increased diagenetic flux of pyrite and lower U and Mo concentration. The deposition of the upper facies happens during the transitional time from the transgressive system tract to the following highstand system tract. The bottom water mass expands and the redox recovers from oxygenated to anoxia as sulfate reduction and methanogensis recover.

Besides the base-level and basin depth variation, the origin of the limestone of the Cherry Valley Member, as a whole, results from depositional and diagenetic events including clastic sediment starvation, advection of methane bearing fluid and the alternation of late diagenesis. Besides the biogenic carbonate (fossil debris and skeletal carbonate) in the middle facies, the most plausible origin of carbonate in the Cherry Valley Member is an interaction between an early methane oxidation process and late diagenesis alteration at depth by hot fluids bearing CO₂.

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APPENDIX A Mathematics of Clustering Analysis

1. Standardization

As our data have different unit and dispersion, it is useful to put all variables in different units on an equal footing, which is here called standardization. Here, we use adjustment to standard deviation t to standardize our data.

Adjustment to standard deviate: $b_{ij} = x_{ij} - \bar{x}_j / S_j$

Where S_j is the standard deviation within column j. Each transformed value represents the number of standard deviations that it differs from the mean. It will results in all variables having mean=0 and variance=1. Note that this transformation will produce both positive and negative numbers. So when conducting similarity analysis, it is not compatible with proportion-based distance measures.

After standardization, the next step of multivariate analyses is to calculate a matrix of distances or similarities among a set of items in a multidimensional space. The data matrix has q rows, which are sample units and p columns, which are selected elements. Each elements of the matrix, $a_{i,j}$, is the abundance of selected elements j in sample unit i.

2. Calculate the distance matrix

After standardization, the next step of multivariate analyses is to calculate a matrix of distances or similarities among a set of items in a multidimensional space. Here, we conduct Euclidean distance measures. The data matrix has q rows, which are sample units and p columns, which are selected elements. Each elements of the matrix, $a_{i,j}$, is the abundance of selected elements j in sample unit i.

Euclidean distance:
$$ED_{i,h} = \sqrt{\sum_{j=1}^{p} (a_{i,j} - a_{h,j})^2}$$

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This distance measures the direct distance between two points, which is the shortest distance or is expressed as "ordinary" distance.

3. Data clustering

With the measurement of points' dissimilarities, it is natural to place elements into groups using quantitative criteria. Here we propose the Hierarchical methods to present subgroups in dendrogram. The basic idea is firstly calculate distance matrix, merge two groups determined by minimum distance, combine the attributes of the entities in the two groups that were fused and then merge the next two groups.

Ward's method

Ward's method is based on minimizing increases in the error sum of squares, which is defined as the sum of the squares of distances from each individual to the centroid of its group. The fusion of groups yields the least increase in the error sum of squares. The initial cluster distances in Ward's minimum variance method are defined to be the squared Euclidean distance between points or Euclidean distance.

$$d_{ij} = d(\{X_i\}, \{X_j\}) = \sum_{j=1}^{p} (x_{i,j} - x_{h,j})^2$$

For our purpose, Euclidean distance is required in order to use the "ward" method provided by hclust (cluster package in R).

4. Method justification

In standardization procedure, we actually tried three different standardization methods, standardization by maximum, standardization by total and adjustment to standard deviation. All of those three methods have their advantages, but we finally choose the standardization by standard deviation as our method for clustering analysis. As our dataset display each element by column and samples by row, it is meaningful only standardize by column. Relativiation by maximum tends to equalize the difference between the highest and lowest value sample for each elements. However, it is too powerful to decrease the difference between each other. Adjustment to standard deviate results in all variables having mean=0 and variance=1, which put all data into the same foot.

For the distance measurement, we tried three different methods, Euclidean distance, Manhattan distance, and Bray-Curtis dissimilarity. As we can see the distance data, with standardization of data before application of the distance measure, many distance data become mathematically equivalent to each other. The Sorensen distance is basically the same as Jaccard distance. Euclidean distances are special because they conform to our physical concept of distance. However, in our dataset, it seems that the Bray-Curtis dissimilarity works better. The distance is bound between 0 and 1, where 0 means the two sites have the same composition (that is they share all the species), and 1 means the two sites do not share any species. At sites with where BC is intermediate (e.g. BC = 0.5) this index differs from other commonly used indices. In our study, we chose the Bray-Curtis dissimilarity as our method. The clustering method we use is ward's method. We also tried UPGMA, but it cannot divide the data into a smaller number of groups, which can be called chaining.

APPENDIX B Mathematics of Principle Component Analysis

Principle components analysis is a way of expressing covariance in many variables in a smaller number of composite variables. The philosophy is to seek the strongest linear correlation structure among variables, which are explained by eigenvalues, and eigenvectors combined the original variables. This section will go through the steps one needed to perform PCA on our trace elements data set.

1) Data transformation

As each variable owns different unit in our trace elements data set, it is useful to transform all variables in different units on an equal footing. The selection of transformation needs to justify different methods, including adjustment to standard deviate ($b_{ij} = (x_{ij} - \bar{x}_j)/S_j$) and standardization by maximum ($b_{ij} = x_{ij}/xmax_j$). Adjustment to standard deviate will result in all variables having mean=0 and variance=1, and produce both positive and negative numbers. As variance matrix is the basis of the PCA, we cannot use a transformed matrix whose variances are all equal to one. So we give up the adjustment to standard deviate method. Other method standardization by maximum equalizes the heights of peaks of different variables, which means it artificially changes the variance of each element and is also not the ideal way. Here, we use the method of standardization by column total:

Equations:
$$b_{ij} = x_{ij} / (\sum_{j=1}^{q} x_{ij})$$

Where rows (i) are samples and columns (j) are variables, standardization by column totals for a matrix of \mathbf{n} rows and \mathbf{q} columns. Standardization by total equalizes the areas under the curves of elements response, meanwhile keeps the variations of each elements. So we chose the method of standardization by total as our transformation method.

2) Calculate the cross-products matrix

Covariance is a measure of how much two random variables change together. It is always measured between 2 dimensions. For example, if you calculate the covariance between one dimension and itself, you get the variance. If you had a 3-dimensional data set (x, y, z), then you could measure 6 covariances. The formula for covariance is given as below:

$$cov(\mathbf{X}, \mathbf{Y}) = \frac{\sum_{i=1}^{n} (\mathbf{X}_{i} - \overline{\mathbf{X}}) (\mathbf{Y}_{i} - \overline{\mathbf{Y}})}{(n-1)}$$

Where **X**, **Y** represent different dimensions, $\overline{\mathbf{X}}$, $\overline{\mathbf{Y}}$ indicates the mean of the set **X** and **Y** separately. From a data matrix **A** as our original dataset containing **n** samples units by **p** variables, calculate a cross-products matrix:

$$\mathbf{S} = \mathbf{B'B}$$
 where $\mathbf{b}_{ij} = \mathbf{a}_{ij} - \mathbf{a}_{ij}$.

The dimensions of **S** are **p** rows and **p** columns. Down the main diagonal, it contains the variance value and besides, it has covariance values.

3) Calculate eigenvectors of the covariance matrix

Each eigenvalue represents a portion of the original total variance, that portion corresponding to a particular principal component. The largest eigenvalue goes with the axis explaining the most variance. The size of each eigenvalue tells us how much variance is represented by each axis. Eigenvalue is a lambda (λ) that solves:

$$|\mathbf{S} - \lambda \mathbf{I}| = 0,$$

where **I** is characteristic equation having **1**s in the diagonal and **0**s for others. Eigenvalues are roots of the polynomial.

$$a\lambda^{p} + b\lambda^{p-1} + c\lambda^{p-2} + \dots + constant = 0$$

4) Find eigenvalues of the covariance matrix

For every eigenvalue λ_i , there is a vector **y** of length **p**, known as the eigenvector. Each eigenvector contains the coefficients of the linear equation for a given component. To find the eigenvectors, we solve **p** equations with **p** unknowns:

$$[\mathbf{S} - \lambda \mathbf{I}]\mathbf{y} = 0$$

All eigenvectors are perpendicular to each other. Graphically, the eigenvector is showing us how data sets are related along the line shown by the eigenvector. Then the first eigenvector, ideally, goes through the middle of all the points showing, importantly, the primary line of our data. The second eigenvector gives us the other, less important, pattern in the data, that all the points follow the main line, but are off the side of the main line by some amount, whose meaning is the same for the third and following eigenvectors. So by the process of taking the eigenvectors of the covariance matrix, we have been able to extract lines that characterize the data. The first principal component is the linear combination of x-variables that has maximum variance (among all linear combinations), so it accounts for as much variation in the data as possible.

5) Find the scores for each object on each axis

Scores are the original data matrix postmultiplied by the matrix of eigenvectors:

$\mathbf{X} = \mathbf{A} \mathbf{Y}$

where **Y** is a matrix of eigenvectors, **A** is the original matrix and **X** is the matrix of scores on each axis.

6) Deriving the new loading data set

Now we altered our original variables into principle components dimensions, and the

value on each component is called loadings. The correlation matrix between each variable and each component is often called the principal components loading matrix. These correlations can be derived by rescaling the eigenvectors or be calculated as correlation coefficients between each variable and scores on the components.

Now, we have transformed our data so that is expressed in terms of the patterns between them, where the patterns are the lines that most closely describe the relationships between the data. Graphically speaking, if we initially have the simple x and y axis, it cannot tell us how that point relates to the rest of the data. However, after PCA, the values of the data points tell us exactly where the trend lines the data point sits. After the transformation using eigenvectors, we have altered the data so that it is in terms of those eigenvectors instead of the usual axes.

APPENDIX C Dataset of Bulk Chemistry of Bald Eagle and Snow Shoe cores

Depth	Ti	V	Cr	Mn	Fe	Ni	Cu
770.26	4544.75	866.17	168.41	302.83	44705.17	96.80	75.87
770.35	4847.98	930.94	143.02	329.54	45479.31	108.95	74.62
770.44	4743.12	988.66	151.59	329.84	45525.07	100.42	76.95
770.54	4758.03	888.14	193.92	296.61	45203.83	101.43	73.11
770.64	4612.30	869.21	143.24	323.11	44724.87	103.28	76.23
770.74	4472.49	845.77	152.59	290.42	46671.52	98.51	72.78
770.84	4777.59	961.43	127.67	290.15	55102.77	107.21	84.34
770.94	4759.86	838.72	129.59	313.08	55636.68	99.88	73.66
771.04	5007.14	912.47	154.45	291.91	50451.98	90.76	65.88
771.10	4841.48	865.33	181.02	329.77	46721.97	109.82	61.06
771.34	5897.72	1531.32	176.05	352.51	46218.35	91.80	68.25
771.43	5560.45	1621.01	153.22	377.85	45543.71	89.88	65.63
771.52	4894.58	1079.53	188.08	317.24	48363.65	106.43	75.69
771.68	4792.85	994. 51	186.18	318.23	45424.82	84.53	68.71
771.76	5071.00	960.13	161.40	304.30	45639.34	98.44	76.59
771.86	7422.60	2755.97	191.38	504.16	47066.97	104.32	70.48
771.96	5578.45	1229.67	165.67	349.55	48513.90	99.76	64.47
772.03	4860.83	995.11	112.12	251.22	47946.65	96.13	65.30
772.36	4938.16	873.14	197.73	305.29	46737.76	86.46	73.63
772.46	4775.64	799.67	176.65	331.14	51055.67	97.82	66.91
772.56	4509.35	876.26	158.57	322.20	50124.09	93.59	66.98
772.66	4667.82	701.90	174.91	272.72	43875.33	96.89	76.95
772.75	4844.49	1013.08	108.75	278.31	44637.18	117.14	67.15
772.85	5280.10	1117.69	168.66	321.44	46884.29	111.99	77.69
772.95	4728.84	907.85	99.85	334.94	45816.13	91.26	64.33
773.05	4758.16	846.36	105.21	332.71	46996.61	82.07	65.33
773.35	4540.92	684.53	164.19	337.81	45202.24	91.52	62.12
773.45	4536.57	880.47	150.15	316.75	46172.81	106.36	80.14
773.55	4728.83	745.97	160.74	359.05	46726.17	108.54	78.82
773.63	4721.11	829.48	57.46	324.83	46756.32	114.36	74.66
773.94	4488.97	819.84	194.80	306.83	47301.16	118.10	80.45
774.16	4713.52	825.22	173.73	290.78	41652.08	95.59	73.57
774.24	4717.05	770.17	180.08	264.69	42981.61	104.13	65.11
774.55	4196.13	925.69	171.42	322.50	44602.00	113.09	89.06

Table Bulk chemical of the Bald Eagle core detected by XRF

774.62	4338.32	736.06	198.45	276.40	43524.84	101.92	86.91
774.97	3427.40	534.12	95.77	486.02	40355.48	88.27	77.98
775.06	3488.02	664.95	135.99	489.88	41406.64	100.46	88.86
775.16	3676.38	739.49	41.92	657.12	44450.25	71.34	102.87
775.26	3533.78	896.30	160.74	882.42	38730.62	53.26	68.56
775.36	3534.32	669.85	134.16	673.52	39095.93	28.27	67.47
775.46	4071.97	526.50	122.22	643.47	48049.58	52.37	71.57
775.54	3418.13	529.03	70.93	659.74	61505.73	61.68	114.85
775.79	1295.02	405.22	144.90	2105.44	30534.03	5.00	43.89
775.89	1379.26	385.35	5.00	2185.43	22272.75	52.34	35.22
775.95	1262.92	345.24	43.86	2225.23	22756.56	23.94	16.15
776.37	4182.36	553.85	81.45	570.86	61271.28	90.45	81.07
776.45	4781.72	613.19	177.67	399.08	52479.67	85.43	77.37
776.55	4751.64	644.11	166.18	280.37	48673.38	94.59	88.48
776.85	4594.47	669.72	142.55	275.74	44838.86	118.85	84.58
776.94	4379.27	707.82	181.75	278.25	47295.28	127.55	85.12
777.04	4690.97	788.63	121.29	303.46	48295.57	115.56	82.66
777.14	4573.29	913.63	169.75	295.93	45063.08	131.46	93.67
777.46	4107.22	579.66	179.84	312.81	39177.37	104.65	79.25
777.54	4835.84	807.65	183.01	377.33	45253.02	116.34	88.75
777.62	4468.08	702.05	166.46	344.97	42759.44	97.03	67.06
777.74	3053.58	693.55	69.56	723.93	38309.72	70.37	62.12
777.84	3331.58	711.83	131.06	658.76	37218.98	84.33	69.21
777.93	4379.92	830.47	176.02	464.51	46569.91	130.31	92.21
778.02	4388.47	779.65	167.20	449.83	44428.35	123.25	88.34
778.26	3824.86	852.05	189.25	410.82	43443.21	182.66	190.09
778.36	3940.91	9 14. 52	200.03	411.82	44933.22	184.42	201.87
778.46	4205.04	994.01	192.88	396.91	39948.73	174.72	176.65
778.76	3468.17	633.28	196.86	499.71	31448.60	120.71	113.37
778.86	3711.90	810.69	160.16	555.82	36354.28	121.21	119.81
778.96	3682.33	833.66	42.27	541.50	33071.48	115.88	105.12
779.06	2871.64	536.43	222.31	450.33	26496.92	97.90	92.71
779.16	3084.82	589.97	184.26	444.41	27757.88	116.88	324.75
779.45	4204.81	760.97	195.38	460.84	32429.10	133.49	117.52
779.54	3534.96	646.73	207.24	375.59	25763.08	95.67	65.49
779.65	3160.66	596.50	146.15	375.08	25898.41	81.13	83.32
779.94	3415.53	743.40	173.97	639.29	30448.31	131.92	135.49
780.04	3399.76	748.67	181.24	650.88	31470.27	115.31	102.27
780.14	3990.83	818.38	153.20	418.27	43464.25	82.23	101.07
780.24	3433.02	821.33	118.98	484.74	29976.26	90.93	86.83

780.32	3156.63	758.72	140.62	490.32	27208.41	78.51	76.83
780.48	3826.93	616.64	181.12	342.56	23529.62	85.40	74.51
780.57	3825.23	529.28	153.24	320.42	21455.69	72.29	72.56
780.66	3848.58	675.68	65.90	458.10	27337.33	114.14	98.49
780.76	4159.13	679.40	156.70	397.50	28028.99	101.78	71.63
780.86	4572.94	705.02	187.49	479.46	29014.17	98.26	78.91
780.96	4207.93	642.33	199.73	520.88	31247.81	78.39	87.88
781.06	3909.17	532.52	118.97	619.49	30461.85	82.10	99. 94
781.16	3646.46	521.80	168.87	536.48	26430.87	87.57	82.92
781.26	4179.07	746.66	140.71	519.51	28251.90	93.80	97.95
781.36	3853.96	615.04	163.38	442.32	27238.44	82.45	91.22
781.47	4635.71	736.05	178.20	414.67	25993.10	78.35	87.83
781.56	4183.42	743.05	167.34	503.68	25255.50	76.64	64.10
781.65	3747.05	827.35	65.19	679.11	29732.25	68.31	74.97
781.97	2865.68	700.23	79.81	722.40	41790.27	45.46	43.46
782.05	3383.72	1020.78	57.24	657.57	39132.96	60.05	47.48
782.15	3785.23	646.35	130.87	536.90	42141.62	57.63	65.92
782.25	4672.85	766.57	183.03	453.20	27784.86	59.92	77.15
782.35	5115.10	795.96	102.92	367.93	30960.71	64.95	67.31
782.45	4235.94	810.22	203.11	410.50	27134.46	62.04	93.53
782.55	3996.83	638.95	148.31	502.60	25227.01	70.62	65.61
782.64	3621.98	631.29	107.72	534.01	29144.29	70.75	67.36
782.74	2319.99	563.49	45.87	629.25	16167.92	24.15	54.11
782.84	1665.35	464.24	5.00	714.68	8163.74	29.14	0.00
783.14	4157.79	738.00	59.62	435.40	26435.24	70.09	87.51
783.24	4486.24	895.97	131.73	435.62	27918.67	85.24	74.23
783.34	4561.34	837.19	187.38	406.64	26175.29	89.98	95.75
783.44	4730.53	802.36	108.14	401.62	25300.22	76.34	76.09
783.54	4124.71	746.56	184.83	574.70	28374.58	68.30	69. 94
783.63	4858.93	937.17	133.08	561.61	38203.50	80.55	49.66
783.75	5309.69	1569.60	101.49	557.12	35880.94	61.21	53.44
783.85	4180.47	590.97	154.88	407.43	33273.98	58.73	16.34
783.96	1281.86	468.07	57.46	646.22	22516.82	49.96	11.23
784.47	3826.78	740.74	203.71	622.99	32321.25	104.11	118.67
784.56	3675.32	797.71	169.48	588.71	29844.15	120.27	132.36
784.66	3683.23	830.45	208.30	608.38	35332.87	116.05	91.13
784.76	4457.36	892.21	161.78	426.49	47820.00	93.97	103.19
784.86	3611.34	766.22	153.24	473.02	28152.33	81.16	88.89
784.96	3727.10	838.19	180.74	541.30	30856.69	106.06	90.39
785.06	4068.18	627.93	164.41	396.95	26110.53	85.63	90.54

785.16	3887.57	628.97	158.98	324.62	22254.23	60.53	64.94
785.26	4034.65	669. 34	107.25	437.55	27689.58	102.38	106.89
785.36	4117.71	720.49	179.45	378.13	28913.56	97.09	85.88
785.46	4359.11	803.77	154.29	461.87	29272.28	73.72	80.33
785.55	4305.58	713.99	129.06	541.93	31658.76	95.69	86.29
785.65	3563.07	593.47	106.40	622.84	30513.48	80.05	102.97
785.75	3712.56	586.49	175.21	571.63	27265.56	91.13	91.26
785.85	4488.84	691.33	112.37	518.26	29291.33	108.47	102.97
785.95	3949.07	522.09	208.54	495.91	28102.12	97.74	102.16
786.05	4253.27	860.64	192.90	433.04	25715.00	66.45	92.03
786.15	4651.21	701.22	151.71	469.48	26198.78	76.02	59. 62
786.23	3636.08	816.34	160.85	644.24	29154.32	65.86	65.04
786.54	2762.64	626.48	49.78	692.40	36709.67	21.02	30.65
786.64	3220.78	659.10	143.89	628.41	36092.99	46.15	46.76
786.74	4047.39	736.37	154.88	557.91	33825.12	59.89	48.35
786.84	4752.66	772.63	222.88	427.88	29537.15	64.79	64.44
786.94	5019.12	934.70	114.44	401.84	31845.75	75.72	67.50
787.04	4467.41	878.09	146.01	437.46	27800.29	75.68	118.29
787.14	3851.15	607.03	172.55	497.59	25512.22	62.68	70.12
787.24	3821.80	673.07	154.06	484.09	28108.87	74.29	73.44
787.34	1809.06	512.22	48.90	707.40	15553.28	20.04	39.70
787.44	1367.19	504.72	62.07	776.45	8202.29	18.70	0.00
787.67	4195.81	629.92	180.10	483.21	26951.10	63.01	64.24
787.77	4633.14	793.18	115.70	475.98	28654.11	75.85	72.44
787.86	4774.86	866.54	143.54	411.65	28430.87	80.97	79.71
787.96	4563.44	790.53	190.83	371.37	26431.84	88.97	108.95
788.06	4644.39	663.38	209.16	419.23	26196.44	81.45	77.87
788.16	4263.19	778.18	153.91	570.54	32709.69	73.08	59.74
788.26	5053.89	880.54	167.11	456.72	35419.48	74.34	61.01
788.36	5503.28	1685.68	68.74	590.13	37233.07	65.17	39.31
788.46	4615.31	807.63	108.57	442.85	35859.99	47.30	42.70
788.56	1007.83	540.65	42.01	655.19	27761.46	50.10	20.37
788.64	2242.55	1376.87	5.00	769.60	28046.78	64.91	33.90
788.87	4501.29	1216.73	172.52	319.23	44340.62	154.70	120.27
788.95	48633.09	33615.02	114.76	3010.80	50832.85	209.05	125.21
789.35	6310.82	2241.67	66.60	393.18	44237.81	132.55	113.60
789.45	24032.47	12798.79	5.00	1093.25	43823.96	154.34	100.22
789.55	20216.76	1552.69	80.86	497.16	36972.12	141.60	106.13
789.63	6748.46	2289.82	102.44	445.54	47051.61	148.06	108.12
789.70	8444.20	1341.46	126.72	423.40	42933.12	136.51	112.70

789.80	41800.83	16618.20	82.48	1534.15	43420.48	148.79	127.34
789.89	5153.76	2206.27	5.00	394.33	36344.66	150.87	87.95
789.99	10045.06	4692.15	5.00	595.13	46212.53	148.01	105.97
790.17	35405.32	20273.23	5.00	1703.22	53446.14	209.97	118.82
790.70	6788.98	2331.49	192.43	441.87	48841.55	161.37	96.31
790.79	4323.10	1205.52	108.34	351.10	42029.12	151.75	91.78
790.88	4653.90	1342.42	227.05	341.55	42117.15	165.40	91.33
790.95	8204.69	1593.90	96.30	423.81	45296.78	130.63	94.66
791.10	5378.13	1880.57	178.05	414.78	43027.53	151.49	101.87
791.20	7245.37	1494.86	119.28	383.13	45071.55	171.44	97.84
791.31	5248.07	1498.61	122.37	370.13	45970.69	169.71	83.17
791.61	8089.26	3533.68	99.75	537.64	45613.37	187.53	84.88
791.89	8408.80	1763.93	45.35	349.97	45756.22	134.50	87.68
792.11	4700.61	1233.86	157.21	345.51	40645.86	97.25	71.25
792.32	4812.96	1284.90	165.21	290.12	43198.55	92.60	70.91
792.40	5067.19	1266.55	173.05	388.38	48004.63	93.29	76.23
792.48	7180.93	1357.23	101.65	393.50	44107.84	122.51	82.80
792.70	5345.18	1321.01	201.56	366.87	47561.76	166.17	83.12
792.91	88485.34	61877.60	61.09	5344.13	60756.46	150.12	90.67
793.00	4407.38	1278.39	125.45	299.83	44012.35	128.28	81.49
793.10	4396.81	1198.87	136.17	341.08	44789.67	119.10	64.80
793.19	13101.90	4882.63	103.05	641.64	50941.07	132.15	82.47
793.29	4671.90	1240.23	47.27	479.79	59084.41	110.12	68.77
793.39	4255.30	1165.88	62.73	641.86	43709.17	126.57	65.54
793.47	10242.83	937. 29	233.88	384.84	41841.05	136.68	83.34
793.71	5943.7 6	1349.74	105.50	483.82	43450.03	137.93	73.66
793.79	5129.15	1307.54	123.49	356.62	47403.30	134.70	82.77

Depth	Zn	Zr	Mo	Ag	Cd	Sn	Sb	Pb
770.26	254.45	159.79	92.18	197.96	265.88	275.53	413.66	21.54
770.35	197.28	165.16	87.42	177.60	236.33	262.32	387.93	26.31
770.44	197.73	162.01	87.96	188.80	247.71	267.92	374.05	21.46
770.54	143.14	162.30	87.18	176.93	245.09	258.08	373.97	21.75
770.64	168.89	163.08	88.73	181.31	259.08	269.20	362.17	23.10
770.74	95.12	165.17	95.25	187.80	243.42	264.36	381.38	22.31
770.84	45.75	163.13	91.12	191.20	247.91	267.07	380.50	23.36
770.94	46.35	162.66	76.52	181.33	248.09	252.51	383.17	25.43
771.04	52.46	163.99	78.59	187.08	251.67	266.23	379.75	21.66
771.10	37.37	158.02	75.57	194.56	236.97	265.74	403.91	25.13
771.34	101.74	168.34	71.13	189.56	253.50	271.34	410.72	22.71
771.43	88.62	170.70	71.37	185.63	244.87	253.37	383.75	24.49
771.52	153.83	168.12	79.33	189.61	260.47	263.35	378.63	21.67
771.68	112.28	165.82	85.57	181.74	253.07	271.74	366.45	21.20
771.76	89.14	160.91	81.75	188.21	240.54	262.64	378.44	20.62
771.86	82.03	173.79	71.09	183.04	251.01	264.54	395.54	25.67
771.96	56.50	160.42	63.97	182.42	251.73	254.58	379.26	22.18
772.03	53.55	163.77	77.12	193.44	259.66	269.68	402.72	27.21
772.36	52.92	164.84	65.39	182.44	231.33	251.81	372.44	24.69
772.46	46.97	158.10	61.27	182.36	240.37	270.84	391.16	21.80
772.56	115.42	157.02	62.77	192.28	258.08	271.16	402.89	22.98
772.66	166.00	160.35	72.15	183.84	250.34	267.66	390.22	21.54
772.75	177.23	162.34	73.17	175.71	244.01	261.46	367.46	25.59
772.85	135.58	171.61	71.62	180.22	254.30	262.57	371.21	24.26
772.95	65.63	161.66	57.58	180.17	244.48	269.22	385.87	23.86
773.05	47.36	162.58	49.14	184.66	232.31	250.18	375.94	25.00
773.35	126.87	157.76	68.46	182.27	245.29	265.97	381.12	24.13
773.45	88.56	162.52	81.69	182.77	235.78	251.38	384.36	24.55
773.55	90.80	162.15	85.94	183.19	239.61	250.93	378.13	21.51
773.63	55.59	162.20	88.42	190.12	239.60	262.54	399.22	26.27
773.94	40.13	178.62	82.93	201.83	286.83	326.41	445.10	31.48
774.16	48.04	170.47	73.19	183.14	244.67	257.43	379.56	26.20
774.24	52.49	168.86	71.99	179.49	239.61	267.54	375.41	24.14
774.55	50.19	168.42	95.84	187.41	255.39	268.15	392.21	27.72
774.62	49.33	161.38	77.81	192.16	246.48	282.33	417.82	27.32
774.97	37.85	128. 52	49.99	182.75	243. 44	273.67	367.46	19.91
775.06	38.54	134.29	46.51	177.20	244.54	250.11	371.31	23.29
775.16	41.56	145.90	13.49	181.03	251.07	258.35	364.51	22.67
775.26	22.43	140.02	1.00	199.08	265.72	283.57	377.03	11.56
775.36	21.95	144.17	1.00	190.55	255.43	267.47	380.65	12.62
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775.46	37.77	150.91	1.00	196.04	259.78	260.61	382.07	16.79
775.54	39.39	137.32	7.97	193.18	253.10	259.36	389.70	25.89
775.79	5.00	68.85	15.97	223.75	301.52	276.39	395.93	1.00
775.89	5.00	63.69	1.00	211.30	295.68	265.85	400.15	1.00
775.95	5.00	62.9 4	1.00	210.12	276.32	271.35	376.12	6.93
776.37	49.76	150.26	45.82	199.13	252.42	266.06	394.14	26.06
776.45	49.77	162.12	55.04	184.26	263.01	281.80	402.47	29.64
776.55	43.20	166.94	52.71	182.00	241.24	280.57	382.26	29.05
776.85	62.57	166.17	66.40	194.23	264.74	302.91	404.97	28.71
776.94	47.26	164.14	68.31	193.02	244.55	275.71	371.53	32.08
777.04	52.86	166.43	56.00	182.51	240.28	254.15	378.13	30.06
777.14	40.82	162.40	66.53	169.99	235.14	265.26	370.70	27.40
777.46	47.72	159.14	51.27	189.12	260.16	283.96	411.57	19.60
777.54	64.96	162.81	45.78	189.42	244.58	253.95	368.51	28.34
777.62	42.33	165.08	44.00	187.10	228.01	246.05	366.54	29.01
777.74	45.18	140.14	31.13	196.95	246.06	268.60	383.88	18.14
777.84	38.65	136.67	34.96	191.70	252.85	258.39	379.14	16.32
777.93	44.64	155.94	46.15	190.55	252.76	262.09	385.07	26.09
778.02	62.07	158.12	48.50	196.67	244.30	271.93	373.19	26.71
778.26	2515.65	170.76	77.79	183.72	266.77	258.49	382.61	28.46
778.36	753.87	157.05	72.17	163.69	251.03	253.67	370.18	21.96
778.46	2096.69	172.98	79.75	199.90	286.68	259.87	384.92	21.60
778.76	114.31	167.86	20.08	176.92	229.31	257.65	365.27	11.40
778.86	340.84	164.01	26.67	173.53	243.83	235.44	355.59	17.12
778.96	367.24	160.51	22.47	190.71	258.15	272.62	374.37	14.04
779.06	113.20	153.26	25.76	212.62	283.84	309.83	440.36	4.47
779.16	2313.09	160.07	32.25	211.98	310.80	328.99	450.93	10.70
779.45	311.51	166.94	27.20	201.71	263.79	273.56	384.84	15.03
779.54	217.24	157.42	9.40	204.86	300.52	289.95	436.68	13.92
779.65	369.15	137.74	5.27	143.19	185.63	201.37	286.07	10.63
779.94	1221.47	163.63	24.11	204.95	260.40	273.98	381.47	9.78
780.04	84.24	162.73	11.82	185.98	261.83	268.91	404.30	9.50
780.14	137.74	145.15	13.95	163.46	212.69	217.86	323.85	14.76
780.24	80.42	139.60	12.39	160.16	211.28	235.97	325.39	11.44
780.32	53.21	127.34	13.62	149.63	185.56	205.12	288. 15	7.37
780.48	62.68	158.77	1.00	154.92	210.08	218.71	325.50	8.93
780.57	61.00	137.16	1.00	135.02	172.93	179.89	262.61	4.36
780.66	201.01	157.43	14.63	200.65	261.42	290.32	427.62	13.83
780.76	111.64	160.88	1.00	203.03	273.86	278.74	408.33	1.00

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780.86	164.20	179.50	1.00	189.92	252.74	261.08	375.22	7.59
780.96	89.83	182.89	1.00	184.83	253.62	272.49	398.82	2.79
781.06	68.17	171.00	1.00	189.38	259.42	260.37	378.54	2.83
781.16	77.60	166.73	1.00	190.16	256.68	252.48	373.23	11.18
781.26	166.43	168.95	1.00	184.89	250.52	265.37	380.34	9.94
781.36	142.34	168.22	4.17	177.76	250.36	262.77	389.77	1.00
781.47	165.55	193.23	1.00	193.64	249.62	260.17	411.68	11.87
781.56	212.55	192.73	1.00	178.39	247.28	247.11	372.99	7.86
781.65	256.75	187.38	1.00	190.12	267.40	276.31	381.75	4.47
781.97	19.23	172.38	1.00	198.54	291.66	305.75	409.85	5.70
782.05	9.58	180.41	1.00	218.92	286.48	290.13	434.72	3.97
782.15	49.88	208.37	1.00	193.14	266.42	260.80	377.60	3.35
782.25	46.08	214.02	1.00	199.66	248.03	261.41	356.21	7.43
782.35	56.17	205.29	1.00	181.58	247.63	250.16	380.35	8.16
782.45	83.76	207.38	1.00	189.95	252.32	267.24	386.50	8.19
782.55	60.40	198.21	1.00	184.46	258.01	257.28	371.83	1.00
782.64	91.92	198.33	1.00	198.16	258.73	267.75	387.61	1.00
782.74	19.85	124.82	1.00	190.93	267.67	271.50	359.75	3.63
782.84	10.56	77.08	1.00	223.15	285.76	286.65	403.69	1.00
783.14	146.49	189.11	1.00	211.88	272.77	291.37	405.93	1.00
783.24	148.15	180.59	1.00	172.86	229.73	250.51	355.72	6.75
783.34	155.15	194.39	1.00	186.98	256.50	266.92	394.66	1.00
783.44	52.21	192.27	1.00	183.87	256.45	258.83	380.06	6.87
783.54	97.64	198.48	1.00	199.60	261.46	265.61	356.73	5.66
783.63	96.06	196.53	1.00	193.88	260.89	262.68	378.05	1.00
783.75	109.89	209.39	1.00	185.95	254.08	265.55	365.71	2.02
783.85	71.27	244.13	1.00	172.74	249.73	274.21	392.62	6.30
783.96	269.51	59.26	23.95	206.00	279.62	273.28	383.43	3.97
784.47	1452.57	164.52	18.87	186.98	249.05	267.12	377.73	16.96
784.56	1031.29	167.12	15.69	185.90	250.27	271.16	374.17	10.02
784.66	87.94	166.32	1.00	193.05	262.62	284.15	389.23	15.49
784.76	154.67	158.62	15.43	177.15	236.14	241.71	356.33	16.05
784.86	67.13	129.15	15.54	155.21	209.43	205.05	299.77	7.62
784.96	272.26	154.42	11.40	174.55	233.54	244.16	369.66	17.15
785.06	137.01	171.87	1.00	177.85	226.36	261.22	353.53	10.57
785.16	56.37	138.73	1.00	135.48	173.37	187.04	257.86	5.29
785.26	220.70	162.34	14.14	187.17	250.50	277.77	410.98	10.09
785.36	110.36	161.46	10.48	201.93	258.67	29 <mark>0.</mark> 77	418.05	15.41
785.46	137.60	181.51	1.00	197.56	254.20	253.71	379.42	8.13
785.55	82.93	187.24	1.00	196.77	255.80	267.75	386.14	3.98

785.65	67.31	173.22	1.00	188.21	253.94	255.72	367.82	5.77
785.75	74.64	170.22	1.00	193.75	243.62	260.78	356.28	9.19
785.85	158.23	176.51	1.00	190.68	249.26	267.94	386.76	7.03
785.95	121.92	171.95	1.00	179.28	249.25	268.07	395.16	11.76
786.05	178.03	191.36	1.00	189.20	253.99	275.64	381.67	10.96
786.15	206.75	193.59	1.00	192.48	252.27	276.91	378.16	3.04
786.23	219.32	188.03	1.00	186.41	254.93	272.28	382.36	1.00
786.54	14.30	170.68	1.00	208.01	259.10	276.46	406.95	1.00
786.64	19.37	182.60	1.00	202.05	251.29	261.69	375.02	3.89
786.74	40.10	209.90	1.00	192.38	246.47	268.97	382.32	7.77
786.84	61.11	216.30	1.00	191.46	245.27	260.19	370.73	9.80
786.94	90.35	205.23	1.00	197.69	245.93	266.96	376.55	13.01
787.04	74.53	207.42	1.00	185.81	243.49	262.61	379.15	6.70
787.14	50.12	205.63	1.00	195.27	255.51	267.71	375.74	3.91
787.24	56.99	199.74	1.00	186.10	256.86	251.65	374.60	5.84
787.34	35.66	107.85	1.00	217.29	276.73	271.89	386.51	1.00
787.44	5.00	81.86	1.00	197.62	260.64	261.55	402.89	1.00
787.67	226.54	188.29	1.00	199.51	247.06	270.63	383.94	6.39
787.77	105.37	191.42	1.00	202.49	252.43	262.99	387.02	11.68
787.86	122.91	185.26	1.00	186.34	249.36	275.05	387.62	1.00
787.96	61.72	205.91	1.00	191.09	248.17	261.74	360.85	6.72
788.06	59.61	195.94	1.00	192.93	248.93	255.54	365.64	6.81
788.16	96.66	197.68	1.00	185.91	247.49	253.71	373.74	1.00
788.26	95.32	195.05	1.00	180.58	245.79	271.07	373.87	1.00
788.36	59.86	214.89	1.00	189.26	255.32	269.21	377.95	1.00
788.46	136.77	223.68	1.00	191.19	258.98	269.76	379.70	11.51
788.56	214.04	61.02	22.19	208.36	265.89	264.19	378.29	4.40
788.64	66.90	79.16	11.62	211.57	269.88	282.13	421.36	7.02
788.87	266.51	154.62	57.64	191.36	246.51	273.37	406.03	34.07
788.95	39.90	244.63	67.59	240.67	341.54	288.90	352.05	37.48
789.35	41.01	145.64	52.13	200.39	266.52	283.28	416.19	30.58
789.45	44.20	160.89	54.78	201.94	266.25	265.07	390.32	24.79
789.55	43.28	133.25	66.19	171.29	253.12	267.90	398.16	24.61
789.63	43.58	153.78	51.72	200.61	259.94	276.20	393.50	29.40
789.70	39.86	143.42	51.73	184.91	256.40	270.67	385.80	26.06
789.80	49.16	180.19	62.66	209.55	296.26	290.42	398.06	26.00
789.89	14.73	145.94	76.41	201.44	281.01	309.67	453.32	23.56
789.99	45.65	172.39	61.25	216.24	283.53	298.17	433.93	27.97
790.17	59.72	214. 52	75.32	224.96	311. 53	297.04	372.14	31.37
790.70	45.05	156.14	69.60	187.77	240.31	256.15	379.61	30.29

790.79	78.14	146.48	76.04	212.91	289.24	317.04	426.57	24.88
790.88	160.29	148.57	74.10	194.59	296.72	293.15	439.29	23.07
790.95	121.18	152.60	63.50	219.32	290.63	305.16	440.92	21.74
791.10	110.98	148.68	76.77	214.67	263.82	288.08	424.09	22.07
791.20	173.31	151.41	80.72	179.29	246.74	273.10	402.91	24.48
791.31	69.91	160.08	66.29	187.83	265.74	291.26	433.30	25.49
791.61	67.51	178.63	72.49	194.89	257.91	284.06	396.80	30.35
791.89	48.92	168.88	61.77	178.47	245.56	266.56	393.40	26.63
792.11	42.50	154.00	33.79	180.48	263.06	285.42	449.05	20.22
792.32	39.07	157.92	32.40	196.07	253.48	293.89	408.06	26.13
792.40	40.74	155.43	34.10	181.97	233.96	256.66	394.44	25.11
792.48	56.86	157.84	53.32	190.16	260.42	288.90	435.27	23.99
792.70	53.69	165.37	54.75	185.82	251.82	250.16	368.55	24.82
792.91	35.68	264.91	39.65	317.71	420.99	332.48	378.33	32.75
793.00	41.71	148.00	48.89	197.62	271.03	291.79	419.37	22.07
793.10	41.92	150.85	47.42	178.90	253.88	273.69	390.68	22.26
793.19	39.73	158.48	50.45	192.43	259.27	264.98	372.37	26.51
793.29	45.49	141.81	44.30	201.92	263.75	279.77	393.21	22.88
793.39	35.12	141.35	46.32	193.13	261.67	266.64	387.79	20.76
793.47	43.29	153.41	63.34	197.92	256.54	266.43	406.69	21.76
793.71	54.03	160.44	54.86	194.67	250.52	266.01	395.04	23.01
793.79	245.13	159.78	51.44	178.42	242.48	242.18	368.64	25.57
794.0685								

Depth	Mg	A1	Si	S	К	Ca
770.26	100.00	88824.35	327158.03	19749.60	32475.77	4056.69
770.35	100.00	83619.21	315963.73	20639.97	32647.62	4140.54
770.44	2591.60	89652.98	332891.40	20965.75	35256.53	100.00
770.54	2671.00	87119.22	327885.36	20426.85	34248.91	100.00
770.64	100.00	84926.56	320764.76	19732.30	34075.68	100.00
770.74	100.00	85476.20	323687.54	21541.81	34625.81	100.00
770.84	100.00	86950.18	332086.46	29677.01	35062.48	100.00
770.94	100.00	88363.91	329499.03	29188.06	34387.09	100.00
771.04	100.00	82066.13	308951.01	24461.10	32704.97	100.00
771.10	100.00	86248.93	315757.22	20552.77	32485.87	1986.74
771.34	100.00	86882.38	331786.93	21363.72	34904.75	2418.27
771.43	2616.08	82180.11	320126.65	21575.71	33886.15	3018.90
771.52	100.00	84711.84	326633.08	21963.37	33937.41	9478.59
771.68	100.00	77955.77	298370.58	21486.83	32247.04	2401.37
771.76	100.00	75757.59	300173.81	20809.34	32804.19	100.00
771.86	100.00	80928.63	311291.19	22455.23	33954.20	511.94
771.96	4939.26	87219.42	330028.62	22453.31	34701.71	100.00
772.03	100.00	88713.71	336971.32	22619.11	35781.05	100.00
772.36	100.00	86338.11	323917.61	20180.36	33850.83	1240.09
772.46	100.00	89570.48	335121.03	22244.58	35064.37	100.00
772.56	3455.53	82826.25	317598.65	20307.59	33810.38	1697.26
772.66	3001.25	78642.00	305055.60	18763.75	33881.88	842.50
772.75	100.00	82364.46	314035.57	19844.63	34351.99	100.00
772.85	100.00	89774.03	336092.80	21896.05	34678.44	100.00
772.95	2739.43	86096.61	328061.28	19991.99	33983.14	100.00
773.05	2343.15	87048.34	332534.49	20784.87	34695.20	1131.02
773.35	100.00	82282.70	310813.78	19005.53	33755.46	1342.07
773.45	100.00	86806.75	323460.57	20722.95	34205.62	972.86
773.55	100.00	88189.86	327338.56	21227.40	33818.89	3278.08
773.63	100.00	86502.42	324122.22	20426.43	33648.12	100.00
773.94	100.00	81237.95	314476.54	25542.13	32849.72	4236.73
774.16	3799.81	82022.63	318272.37	19460.87	33551.45	2636.73
774.24	100.00	83975.49	329790.79	20363.96	34507.20	100.00
774.55	100.00	80517.84	291037.64	19675.55	31262.45	4420.26
774.62	100.00	82512.26	304302.17	19383.61	33424.11	5858.04
774.97	100.00	57998.97	212426.61	14910.65	23696.63	79277.35
775.06	100.00	61937.79	217167.47	15775.49	22087.71	94374.02
775.16	100.00	68796.22	232545.85	13858.26	20122.73	142634.06
775.26	4111.70	60762.53	207548.51	9682.35	16413.74	193298.98

775.36	5168.19	65777.98	230041.29	9903. 52	20390.56	150422.12
775.46	6322.77	75245.85	269678.54	15648.13	24886.51	89590.46
775.54	10308.32	73711.64	253845.27	25307.63	24399.49	77933.57
775.79	12151.46	24760.99	89832.86	69 24.34	5715.04	321568.62
775.89	100.00	20018.34	70937.27	5571.22	4478.78	341923.22
775.95	100.00	19014.22	69863.82	5588.18	4432.53	341738.63
776.37	9911.28	81643.46	282622.03	30435.13	25639.94	64126.89
776.45	100.00	90102.09	306859.21	28333.19	32012.51	11333.33
776.55	100.00	87336.02	313903.00	26054.03	34911.82	7001.25
776.85	100.00	68167.08	254374.28	22158.44	30799.86	18721.31
776.94	100.00	74894.84	277101.40	25211.02	32536.15	8114.52
777.04	100.00	90949.64	322815.19	25607.16	35319.48	100.00
777.14	100.00	85140.04	302284.85	23864.56	33085.11	16884.38
777.46	100.00	58428.57	223155.40	15544.19	27373.63	48767.23
777.54	100.00	93851.61	331006.76	22101.11	35741.00	12754.36
777.62	100.00	84109.48	292789.21	19707.91	31221.61	46541.95
777.74	100.00	55165.44	193242.09	12000.96	18168.94	171788.17
777.84	3416.77	60803.31	209981.06	11715.38	20176.32	155302.86
777.93	100.00	87171.04	299164.03	19999.90	31683.23	48998.11
778.02	100.00	86189.16	294723.84	19317.54	31738.31	47579.25
778.26	2934.28	72615.00	260712.07	21494.46	26162.89	68828.20
778.36	6277.09	79951.41	273530.02	23957.70	25973.74	66640.92
778.46	100.00	72931.56	266281.25	17025.40	26382.36	50579.82
778.76	2924.69	60266.55	221391.94	7476.64	21519.24	109927.49
778.86	11387.48	80873.62	282228.76	12117.73	26597.21	86667.07
778.96	3834.27	72563.01	262749.20	10176.74	24349.87	101939.10
779.06	100.00	34963.68	149335.45	5666.63	17733.87	106960.87
779.16	6440.59	35002.59	157047.43	7383.62	19062.56	92085.37
779.45	100.00	73811.39	263327.31	10693.47	28101.18	67430.63
779.54	100.00	43300.59	171354.10	5393.43	22967.16	71088.34
779.65	1460.47	46685.39	167203.58	5418.02	20904.65	66761.35
779.94	2914.43	65919.73	236881.24	9582. 44	20092.45	134844.57
780.04	100.00	64396.89	224870.44	7619.37	19759.50	119767.37
780.14	100.00	61559.54	209170.65	16514.93	26004.79	63723.57
780.24	2735.66	51670.18	175291.31	7582.32	21838.49	82745.72
780.32	100.00	43473.38	150650.77	5891.99	21189.47	80635.86
780.48	100.00	58241.32	202589.53	4646.03	25721.89	55210.24
780.57	100.00	47349.07	158917.66	3661.54	24318.05	26484.68
780.66	5590.08	53766.80	205036.66	7125.00	26707.36	56545.24
780.76	100.00	58193.23	227191.43	7623.72	29028.53	46180.07

780.86	100.00	74287.40	289361.15	7446.18	30050.53	59264.85
780.96	2643.30	71130.30	271888.92	7243.48	24493.99	95335.08
781.06	2806.54	58916.07	227699.40	6240.24	18418.51	141398.40
781.16	3811.13	61569.09	224869.25	5927.45	20540.47	143293.40
781.26	4167.17	70614.12	257390.47	7859.22	24912.26	100862.88
781.36	100.00	63605.25	240803.69	7758.31	24884.47	95239.46
781.47	100.00	79266.86	269627.32	6755.10	26845.00	114283.35
781.56	100.00	70804.62	252795.89	6586.58	23048.55	137690.01
781.65	100.00	50974.25	190320.43	6632.10	14117.57	201864.61
781.97	6821.83	36086.71	144489.48	13192.07	11502.19	197517.81
782.05	5202.32	42248.57	173131.18	11686.92	11589.71	217861.03
782.15	7640.00	61375.53	238543.72	15286.02	17459.61	158543.10
782.25	3419.20	73185.00	269215.61	8268.44	23977.66	105519.97
782.35	100.00	78041.82	278219.02	11384.74	27625.73	64719.64
782.45	2792.84	72936.30	260742.56	8652.37	24465.53	111274.96
782.55	100.00	60489.76	222820.49	6442.25	19102.69	153906.43
782.64	100.00	52582.90	205892.05	8722.58	16541.39	168935.77
782.74	100.00	31615.90	122043.00	5011.15	8215.20	271538.81
782.84	100.00	18437.53	71836.57	1611.20	3984.91	353865.51
783.14	100.00	57792.57	228996.99	7062.73	23191.16	102578.80
783.24	4099.77	66021.68	245251.04	8621.61	26796.60	57990.37
783.34	100.00	66952.06	257926.12	7995.06	24973.47	89739.75
783.44	2686.94	75269.48	276637.28	7290.70	27241.39	86099.26
783.54	100.00	67705.47	258587.67	6419.87	20862.15	132873.27
783.63	7376.50	75058.29	297560.50	14255.72	25430.14	74337.49
783.75	6362.52	65600.09	262353.31	10698.14	23665.84	82917.03
783.85	100.00	51409.35	218797.09	10519.83	17507.48	110485.85
783.96	7140.09	23290.09	77151.43	8014.94	4500.02	339621.58
784.47	100.00	69757.51	261913.32	11237.04	24242.75	112087.72
784.56	4421.87	66240.41	235841.24	8836.18	20865.43	127220.16
784.66	100.00	64021.49	223644.29	10791.08	21180.72	120047.19
784.76	100.00	74519.35	258336.17	20228.83	29014.00	51055.04
784.86	100.00	44656.61	157971.33	5679.14	22195.02	71080.59
784.96	100.00	58079.99	203149.67	8764.40	23544.50	97945.04
785.06	3121.63	69387.11	244107.73	6612.98	25698.61	68012.40
785.16	100.00	46098.17	159598.87	3612.85	24786.40	26661.56
785.26	100.00	55125.83	212091.01	7396.36	26665.95	55358.02
785.36	100.00	59109.12	224333.86	7411.55	29136.62	45618.31
785.46	3444.46	74462.82	288640.39	7346.80	29727.33	58922.59
785.55	3209.28	72458.92	274156.79	7230.84	24833.77	94022.91

785.65	3414.15	58737.26	230126.27	6343.41	18929.65	138302.32
785.75	100.00	63328.16	226838.91	5914.07	20842.34	143663.14
785.85	2882.72	73849.45	267241.19	8125.79	26509.31	100562.84
785.95	100.00	62926.35	240426.37	7761.13	25503.77	93825.19
786.05	100.00	77836.69	266053.26	6562.70	27407.64	113044.59
786.15	100.00	72804.67	259891.51	6852.39	24121.71	131608.35
786.23	4585.09	47033.08	183990.84	6235.22	13360.10	208216.66
786.54	5294.07	30577.51	135393.07	9075.46	11478.56	193516.87
786.64	3686.33	46984.69	185546.96	12061.47	12730.66	186418.76
786.74	4320.98	64585.86	245447.83	11675.82	19558.57	146884.44
786.84	100.00	73905.88	275985.95	8789.66	25143.29	95133.04
786.94	100.00	77891.66	283081.44	11612.50	28635.10	74026.19
787.04	100.00	71110.88	253498.74	8656.70	23894.19	114941.03
787.14	100.00	56487.12	211056.69	6229.18	18032.82	163241.76
787.24	100.00	53974.90	213896.02	8580.19	17808.91	155979.53
787.34	100.00	25980.20	100270.60	4427.01	6595.31	305413.44
787.44	100.00	16563.94	71049.07	1438.66	3944.96	337907.38
787.67	3924.50	56422.82	225293.31	6779.95	21701.73	114765.06
787.77	5486.03	66682.61	253690.90	8351.27	25352.68	85772.66
787.86	100.00	68059.10	259951.95	9257.29	26424.56	74585.66
787.96	100.00	70643.25	268920.24	7969.44	25780.06	87697.25
788.06	100.00	75587.91	286627.31	7430.97	28004.33	80467.29
788.16	3545.73	68336.13	267462.85	9458.67	21829.91	114131.01
788.26	3353.51	77396.50	303537.40	12333.59	28596.63	53389.40
788.36	100.00	57810.66	240293.84	11204.77	19327.76	107790.82
788.46	6077.02	57380.77	217859.79	10822.38	18728.82	98467.88
788.56	100.00	17850.17	61875.36	9497.90	3280.70	341729.76
788.64	100.00	23561.21	83485.89	7181.36	6240 . 64	304638.95
788.87	100.00	82767.75	278651.10	22264.14	31463.54	19578.87
788.95	100.00	83148.12	285989.58	60540.73	32391.69	24773.31
789.35	100.00	63040.44	228996.09	22297.39	29866.92	28716.40
789.45	100.00	60274.50	212684.08	30150.00	27594.20	46514.16
789.55	100.00	59371.89	203366.05	18109.25	21548.58	85228.01
789.63	100.00	83337.84	286826.24	26873.88	33125.87	27050.42
789.70	100.00	70427.59	238070.45	21953.64	29187.94	50611.77
789.80	100.00	58924.88	201702.78	30269.78	21634.91	64724.53
789.89	100.00	49953.20	201961.22	17509.80	23873.66	36355.71
789.99	100.00	56637.16	226508.57	25447.85	30880.05	23482.31
790.17	100.00	79702.03	281394.67	42958.37	29574.08	28588.23
790.70	100.00	83992.41	292236.42	36540.62	32194.39	19505.07

790.79	100.00	61229.25	236802.55	20678.66	30881.75	12799.10
790.88	100.00	47373.21	192835.06	18633.77	28561.62	17459.06
790.95	100.00	65911.88	246581.83	22687.54	31263.00	23844.56
791.10	100.00	55350.31	216671.26	19626.27	28675.61	24725.82
791.20	100.00	66541.02	243421.81	21211.44	28079.26	28366.28
791.31	100.00	89776.39	309859.31	25693.18	32925.67	20822.65
791.61	100.00	88397.86	318680.02	28575.07	36260.08	7321.64
791.89	100.00	74144.60	271566.47	24942.32	30430.80	10874.25
792.11	100.00	69601.95	264210.83	20073.39	29543.66	11491.65
792.32	100.00	77457.87	282188.21	20822.85	35655.17	3657.22
792.40	100.00	90785.48	334320.74	26368.08	37125.50	4445.64
792.48	3821.13	80684.55	279944.32	23660.63	29740.69	22106.30
792.70	100.00	89501.69	323865.96	27188.73	35289.41	17337.62
792.91	100.00	68028.30	231427.42	97389.91	23958.11	10773.32
793.00	100.00	64445.82	252808.23	22499.83	31238.05	19257.72
793.10	100.00	65992.13	256133.60	22879.57	30804.99	28380.35
793.19	100.00	73372.92	274038.66	30461.93	29743.50	31080.45
793.29	100.00	78464.04	273919.93	33478.97	27623.37	66719.99
793.39	100.00	70858.80	252347.26	18415.44	22935.65	129459.87
793.47	100.00	64231.04	236558.59	19629.18	26928.04	40014.90
793.71	100.00	78353.91	287006.55	22783.68	30974.20	37087.67
793.79	100.00	82511.33	331389.69	27672.15	34325.93	16032.75

Depth	Mo	Zr	Sr	U	Rb	Th	Pb
8615.0	57.21	146.55	266.36	23.79	69.59	8.91	23.37
8615.5	87.06	129.92	317.53	25.56	63.16	8.53	11.20
8616.0	36.90	144.65	578.96	12.61	62.30	7.34	22.68
8616.5	57.58	167.56	246.98	11.72	78.93	12.69	13.81
8617.0	34.13	147.44	237.48	7.34	67.66	8.54	13.14
8617.5	49.12	153.89	250.81	16.07	71.25	7.46	16.01
8618.0	46.49	163.05	222.21	8.83	71.75	10.93	22.87
8618.5	80.11	153.85	201.46	19.63	71.28	9.37	20.56
8619.0	72.93	156.93	219.99	19.70	69.44	7.37	19.79
8620.0	36.51	146.43	179.07	11.75	65.48	7.77	17.78
8620.5	59.29	150.92	221.34	7.58	66.35	7.52	18.50
8620.5	53.21	145.81	288.60	10.59	64.60	8.62	13.30
8621.0	61.41	162.89	265.40	11.65	70.78	7.88	17.18
8621.5	73.92	163.07	219.32	14.98	69.02	8.36	13.56
8622.0	156.64	160.15	225.89	19.44	72.09	7.52	15.18
8622.5	76.45	168.23	227.42	15.28	70.11	9.55	15.80
8623.0	115.11	155.41	200.95	11.70	73.79	8.27	18.57
8623.5	61.56	163.29	192.96	13.45	73.10	8.07	22.06
8624.0	87.02	166.23	187.13	21.75	69.50	7.53	15.70
8625.0	114.05	180.43	214.13	17.69	72.59	9.40	17.19
8625.5	73.04	173.70	193.51	16.99	73.20	9.37	22.20
8626.0	164.64	170.84	188.72	19.52	67.68	5.88	28.04
8626.0	166.07	161.05	193.83	18.47	66.77	6.85	29.42
8626.5	12.46	87.23	473.43	6.48	35.69	< LOD	12.90
8627.0	22.19	98.59	377.27	13.55	39.41	5.57	18.08
8627.5	49.71	160.58	190.03	13.11	72.75	10.00	28.16
8628.0	46.45	152.29	356.60	20.29	64.19	10.88	16.48
8628.5	43.38	97.08	370.68	16.74	38.22	6.59	14.92
8629.0	55.56	164.48	264.26	21.47	49.55	8.20	14.56
8629.5	107.90	180.27	326.91	15.95	51.73	9.68	8.97
8630.0	14.95	170.38	337.04	10.53	55.76	8.14	7.68
8630.5	23.22	137.79	367.37	11.14	41.56	7.14	9.32
8631.0	13.09	152.02	277.49	12.26	52.78	9.40	< LOD
8631.5	8.43	175.54	329.46	7.97	49.81	11.96	< LOD
8631.5	9.73	176.40	334.54	11.46	49.71	9.51	< LOD
8632.0	9.20	185.23	325.66	9.00	59.79	12.45	< LOD
8633.0	66.87	159.90	260.31	19.38	79.27	13.64	28.73
8633.5	10.02	22.56	164.44	5.54	20.18	3.12	< LOD

8634.0	12.49	25.77	210.59	9.63	20.76	3.57	< LOD
8634.5	48.82	155.30	458.23	20.97	70.30	13.91	26.03
8635.0	76.32	173.77	249.08	29.27	75.25	11.46	23.18
8635.5	64.61	166.93	264.04	25.02	74.30	9.92	20.96
8636.0	52.32	167.16	209.88	19.04	73.36	10.62	18.62
8636.5	68.30	141.44	258.02	36.22	63.26	11.38	14.38
8637.0	43.78	151.02	205.28	21.04	50.53	6.83	20.68
8637.0	45.00	150.65	217.12	19.44	49.59	5.91	22.36
8637.5	42.57	147.49	280.76	20.35	74.29	10.24	22.05
8638.0	50.97	136.01	272.88	18.79	61.43	8.82	13.10
8638.5	61.25	160.03	250.84	20.59	69.87	10.52	19.04
8639.0	54.06	151.91	273.45	20.82	76.06	9.23	23.50
8639.5	51.64	139.86	253.88	23.09	64.14	7.63	15.00
8640.0	51.29	158.77	209.37	16.38	69.61	7.65	20.01
8640.5	64.46	158.45	221.68	17.17	65.37	10.11	24.19
8641.0	47.42	134.75	238.94	17.08	59.96	8.08	20.27
8641.5	40.82	135.71	232.06	13.64	55.34	9.43	19.16
8642.0	60.86	158.80	248.90	8.73	64.75	10.80	16.42
8642.0	62.61	156.57	266.95	12.60	66.30	8.79	22.18
8642.5	87.71	139.38	211.35	13.61	59.97	10.61	16.23
8643.0	50.39	133.74	240.75	12.33	63.50	9.55	17.98
8644.0	55.58	134.38	262.25	19.16	57.94	9.51	16.83
8644.5	46.78	145.82	248.19	13.61	62.86	9.24	21.01
8645.0	44.81	143.98	270.65	15.04	56.99	7.36	14.96
8645.5	49.18	150.96	260.09	17.03	65.41	10.47	19.16
8646.0	43.69	133.15	304.61	19.15	62.99	11.26	17.12
8646.5	57.16	157.92	260.94	21.08	62.91	9.50	12.07
8647.0	51.90	153.83	268.38	19.14	62.57	10.98	17.38
8647.5	64.69	143.33	140.74	16.35	64.27	9.80	16.22
8647.5	65.22	146.50	154.98	17.47	64.83	6.42	21.57
8648.0	50.98	145.54	258.19	18.51	58.64	10.26	15.71
8648.5	32.48	137.02	176.63	14.40	62.51	9.14	14.33
8649.0	35.13	132.71	346.20	18.97	54.91	7.56	14.17
8649.5	33.95	170.28	255.88	16.67	59.08	10.25	13.47
8650.0	32.16	135.54	213.06	15.53	60.76	9.21	17.91
8650.5	30.44	152.35	200.69	14.32	63.55	8.51	15.34

Depth	As	Zn	Cu	Ni	Fe	Mn	Ba
8615.0	38.48	41.73	96.84	136.38	53234.77	151.46	1289.95
8615.5	19.49	62.46	80.95	142.37	37688.32	208.19	1370.79
8616.0	33.86	142.44	92.04	133.90	47207.41	441.92	1503.72
8616.5	22.33	109.42	73.56	141.20	38014.71	142.11	1480.24
8617.0	23.12	51.84	79.19	90.60	43630.52	241.98	1325.44
8617.5	19.71	115.17	65.85	115.85	38163.37	92.98	1245.72
8618.0	21.58	265.71	70.28	126.58	40245.41	138.03	1416.28
8618.5	22.56	210.72	80.18	143.30	44055.88	92.66	1432.21
8619.0	30.83	36.33	90.36	135.20	50930.65	89.62	1470.57
8620.0	19.98	37.62	66.94	130.73	41152.02	137.37	1279.71
8620.5	26.51	37.37	73.73	102.46	47760.07	148.96	1224.16
8620.5	22.33	34.59	67.91	99.88	43085.72	118.00	1312.18
8621.0	20.81	60.34	78.87	123.40	36870.91	123.45	1401.40
8621.5	22.10	32.87	82.24	121.41	40566.40	149.67	1344.53
8622.0	25.82	43.09	78.67	130.41	41422.08	155.67	1447.42
8622.5	25.63	42.97	76.41	134.44	42630.28	152.71	1519.94
8623.0	16.08	39.29	85.69	133.85	41737.68	135.93	1455.42
8623.5	24.91	40.51	74.42	130.58	48354.66	124.76	1331.47
8624.0	23.20	39.35	92.46	136.72	41646.27	120.51	1321.18
8625.0	26.03	77.78	90.42	122.30	37838.75	82.34	1284.41
8625.5	25.29	427.93	87.27	131.54	38178.02	103.69	1436.66
8626.0	30.85	45.93	121.98	175.69	49037.08	153.19	1464.88
8626.0	31.26	45.98	115.66	189.61	47682.18	137.84	1479.81
8626.5	12.10	31.91	86.36	116.19	34396.01	440.86	1015.41
8627.0	23.34	43.12	93.60	110.35	43840.79	429.12	1070.03
8627.5	25.97	38.54	94.16	149.47	40870.61	188.58	1457.48
8628.0	23.33	44.29	87.95	153.15	34507.55	229.60	1456.65
8628.5	21.92	116.04	103.66	108.71	32045.10	431.71	1016.67
8629.0	22.82	314.56	129.50	187.61	31845.42	291.19	1269.84
8629.5	18.28	1043.76	128.52	175.82	28816.98	220.73	1227.40
8630.0	14.98	66.59	107.77	140.26	26698.39	316.27	1257.78
8630.5	14.33	6912.71	181.77	160.10	28183.96	393.74	1200.12
8631.0	7.86	58.76	74.19	120.44	23045.98	268.43	1190.91
8631.5	5.89	95.70	68.70	113.79	22856.83	288.97	1073.31
8631.5	6.33	50.94	69.53	102.61	23256.29	282.00	992.15
8632.0	12.81	127.43	122.26	145.30	28460.59	276.85	1304.88
8633.0	38.45	49.74	133.88	212.03	45687.79	223.46	1998.86
8633.5	< LOD	18.04	24.09	74.03	4726.21	988.30	588.89

8634.0	< LOD	19.36	29.62	72.60	14978.76	1637.39	1159.34
8634.5	24.03	54.13	89.52	225.13	37453.49	505.42	8644.54
8635.0	30.39	46.90	104.33	187.22	39464.21	174.84	3267.11
8635.5	22.83	163.74	97.00	181.15	38779.23	239.19	1454.62
8636.0	27.00	99.37	80.23	162.87	38295.85	177.56	1533.84
8636.5	19.13	33.78	84.67	166.23	33173.20	240.99	1418.11
8637.0	32.40	70.81	112.79	170.68	73723.13	163.57	1825.64
8637.0	29.56	52.70	89.48	170.30	79768.21	208.37	1757.36
8637.5	28.49	36.83	82.19	151.85	41588.59	228.05	1544.42
8638.0	22.83	42.36	74.98	149.97	37923.22	349.59	1457.10
8638.5	26.76	269.61	80.50	164.58	40282.31	224.98	1552.47
8639.0	22.30	38.98	88.67	142.48	37335.91	167.46	1625.04
8639.5	23.77	56.27	61.71	157.63	36383.50	322.14	1447.71
8640.0	27.49	87.01	94.21	124.51	39102.56	152.65	1309.32
8640.5	24.16	147.24	84.26	172.51	36521.00	149.02	1567.25
8641.0	29.52	160.87	82.20	174.71	36756.55	229.71	5208.43
8641.5	21.53	153.12	68.37	145.75	35718.00	287.52	1470.83
8642.0	28.64	172.42	77.04	144.80	38621.32	191.49	1373.18
8642.0	26.83	196.00	81.29	167.63	38245.51	152.91	1496.65
8642.5	27.38	365.53	75.54	130.29	39620.07	134.64	1513.51
8643.0	26.94	291.47	84.94	151.37	38836.82	161.57	1473.36
8644.0	22.84	92.38	70.32	132.14	33778.01	230.16	1343.65
8644.5	25.23	183.41	75.73	134.45	39844.85	196.11	1375.62
8645.0	23.01	139.05	64.06	149.07	38779.86	247.73	1300.05
8645.5	25.36	251.18	74.65	169.27	40937.18	210.71	1458.39
8646.0	24.08	151.77	78.05	151.58	37719.20	169.07	1468.96
8646.5	30.62	317.37	78.01	147.70	42686.93	141.51	1341.05
8647.0	23.64	232.38	80.54	154.83	37154.31	264.43	1509.83
8647.5	24.27	136.27	61.82	122.59	41622.16	196.43	1362.14
8647.5	20.11	131.14	66.43	115.48	41497.56	189.85	1425.42
8648.0	22.73	113.78	72.04	167.30	35565.75	242.48	1549.92
8648.5	24.07	100.24	69.21	135.26	38971.64	277.73	1401.53
8649.0	16.80	174.40	70.09	146.71	37877.04	255.96	1365.84
8649.5	19.13	175.04	51.03	131.75	37359.73	204.09	1349.08
8650.0	18.14	98.63	59.87	116.31	40131.47	222.13	1384.46
8650.5	19.58	76.87	62.03	130.83	36633.14	239.59	1417.69

Depth	Cr	Ti	Ca	К	A1	Si
8615.0	185.36	4085.78	20834.17	24186.14	127699.24	306692.69
8615.5	201.34	2980.19	89355.95	18278.73	103984.45	273287.19
8616.0	205.78	3977.00	24078.99	20290.55	106862.14	281091.84
8616.5	150.00	4350.81	6643.40	25546.32	135169.56	352329.13
8617.0	197.27	3796.03	17660.70	22726.69	102955.05	303794.69
8617.5	242.59	4099.27	7527.04	23483.11	104146.34	318577.81
8618.0	178.43	4322.65	9402.08	23600.56	127208.52	345626.00
8618.5	161.45	3995.17	11174.23	23363.79	119673.41	329754.44
8619.0	257.09	3946.41	11617.13	23351.76	127006.17	339118.97
8620.0	169.54	3625.43	15460.81	20891.47	122458.68	368044.84
8620.5	194.42	2152.85	11361.03	21245.49	99414.14	322733.97
8620.5	197.09	2419.75	14640.45	21225.83	104632.55	329855.13
8621.0	155.61	2588.17	15467.22	22521.40	112305.00	328482.22
8621.5	191.76	2497.70	11743.44	21617.27	102553.41	299692.66
8622.0	212.91	2934.03	10661.26	23682.90	120809.87	322942.88
8622.5	193.25	2904.34	13706.84	23791.17	124122.30	332452.59
8623.0	217.60	2842.69	11972.55	23827.81	130784.06	335087.41
8623.5	216.88	2903.12	6816.55	24671.92	129276.47	326832.19
8624.0	194.04	2782.14	15668.28	23214.96	113312.94	312531.78
8625.0	189.41	2879.50	13882.71	24033.06	120251.20	328751.91
8625.5	201.54	3091.25	11657.31	24647.63	136725.80	344858.56
8626.0	222.21	3187.06	16784.03	23392.30	128689.13	310703.53
8626.0	214.63	2957.09	16133.63	22559.98	136664.09	315809.31
8626.5	167.03	1427.20	168980.34	15625.19	92653.19	223340.44
8627.0	219.23	1414.14	165831.28	15674.70	96574.20	218431.02
8627.5	220.04	3051.27	16662.33	24004.46	142087.75	325169.63
8628.0	171.76	2654.95	78759.84	20671.82	122726.98	282261.19
8628.5	136.75	1253.46	162296.81	14756.72	81469.74	191162.97
8629.0	186.69	1910.67	111859.09	17318.35	111604.58	254791.78
8629.5	163.95	1889.06	113152.21	17066.15	98692.71	238113.36
8630.0	159.28	1971.93	85726.58	19243.26	113755.61	291292.13
8630.5	171.54	2092.64	160869.42	14471.51	94413.54	227351.91
8631.0	179.02	2497.48	88562.33	18913.61	92890.18	245568.08
8631.5	179.06	2805.66	107664.72	18938.34	103959.53	260982.81
8631.5	171.91	2870.55	106186.99	19068.61	109401.92	263978.19
8632.0	187.84	3051.55	51398.88	24563.85	140895.14	287816.69
8633.0	236.31	3606.19	22841.00	26181.82	153163.52	299208.16
8633.5	< LOD	200.00	373931.31	2968.62	15407.08	42979.01

8634.0	98.67	314.14	341815.78	3566.75	19571.61	52783.11
8634.5	206.76	3572.53	13505.43	22760.65	128621.84	290624.38
8635.0	199.32	3486.72	95436.04	21390.79	114861.45	268612.19
8635.5	203.64	3942.30	61371.28	23405.63	126189.73	302557.78
8636.0	204.27	4256.92	46269.06	24919.09	146966.75	336778.50
8636.5	160.42	3418.42	93936.58	20680.53	101901.58	284724.09
8637.0	232.97	4466.83	73612.88	24131.15	134191.52	300945.47
8637.0	263.21	4165.19	68966.27	23247.13	140993.05	304918.19
8637.5	190.50	3957.64	61896.37	24634.98	133326.81	320933.69
8638.0	198.60	3465.00	105105.80	21054.54	119088.98	292418.25
8638.5	177.67	4254.39	57318.86	23195.35	125282.47	324292.59
8639.0	122.42	3903.25	53138.08	23987.37	126356.62	323275.50
8639.5	162.57	3520.71	95030.62	21172.56	117467.90	312379.75
8640.0	175.20	3967.99	49547.62	22921.03	115313.07	334860.22
8640.5	189.32	3657.39	53687.19	21934.02	132417.47	352435.13
8641.0	158.09	3456.99	89823.46	18525.90	106295.51	301974.69
8641.5	155.91	3590.44	85160.31	20333.34	117183.74	332782.38
8642.0	189.37	4023.70	54027.22	22312.49	113971.69	332547.06
8642.0	164.38	4146.03	55104.63	22370.02	122234.91	352724.75
8642.5	197.90	4137.42	57298.17	22947.62	70405.59	247679.52
8643.0	206.71	3721.11	46961.35	21599.72	119294.47	351284.91
8644.0	141.53	3301.82	46594.67	19280.35	106760.65	334290.31
8644.5	167.42	3577.80	27520.34	21219.04	118670.63	351477.94
8645.0	132.59	3622.91	50440.14	20150.59	105057.98	319019.59
8645.5	164.87	3842.23	28830.04	21339.70	123884.22	341869.47
8646.0	176.23	3543.93	39264.28	20596.88	111146.78	322963.09
8646.5	138.92	3634.88	21934.01	19802.23	102410.40	314557.81
8647.0	135.03	3655.46	34055.76	20930.15	121773.13	326505.06
8647.5	132.30	4012.79	14823.30	22375.89	100238.82	304570.28
8647.5	168.55	3936.81	15986.08	21654.20	94505.83	291433.09
8648.0	215.54	3854.75	44550.90	21508.79	110169.52	307609.66
8648.5	146.90	3766.42	47830.41	21037.87	112502.06	315858.38
8649.0	112.89	3494.07	55244.75	18345.57	104477.21	305872.56
8649.5	136.83	3929.38	33436.60	19243.95	99338.82	298666.91
8650.0	166.62	3704.45	41763.24	20405.51	114490.08	327608.72
8650.5	147.71	3984.41	17592.05	21122.81	112416.96	325952.72