Mineralogy of the Point Pleasant Formation within the Sebree Trough, SW Ohio, using Visible Derivative Spectroscopy Spectroscopy and XRD

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Objective

➢ *Evaluate the feasibility of visible derivative spectroscopy for high-spatial resolution of mineralogical variations within rock core by using a case study of the Point Pleasant Formation in SW Ohio.*

➢ Visible derivative spectroscopy is a non-destructive method that can be used in combination with traditional techniques to give insight into mineral assemblages and how they vary with depth and amongst several sets of cores.

➢ Visible derivative spectroscopy has been proven effective on individual minerals [1,2,3], sediment cores [4,5,6], and remote sensing of surface materials [7,8]. Some rock core analysis has been completed with success [9,10]. We provide visible derivative spectroscopy data, its processing technique, and verification with qXRD for three cores of the Point Pleasant Formation. Here, the Point Pleasant Formation refers to both the Point Pleasant and Utica Shale.

Methods

➢ Visible derivative spectroscopy using a Minolta cm2600d was measured on three sets of cores at 1 cm resolution down core. Varimax Rotated Principal Component Analysis was performed using SPSS on each core dataset, extracting mineral assemblages and down core variations.

➢ Quantitative XRD was measured on 30 samples taken from two sets of cores (the third core was not able to be sampled). One gram of sample was mixed with 0.25 g of corundum and milled in a McCrone Micronizing mill with 4 ml ethanol and zirconia grinding elements.

➢ XRD was performed in side loading holders on a Scintag X-1. Results were then analyzed using USGS RockJock software. QXRD was used to validate the reflectance results by comparing the Component Scores to the Z-Scores of the qXRD ([%Value-%mean]/St.Dev).

Visible Derivative Spectroscopy

➢ Absorption patterns depend on the mineralogy because the varying elements in minerals have varying orbital configurations and bonds, exhibiting different reflectance derivative spectra in [11]. The Konica-Minolta UV/VIS CM2600d spectrophotometer measures from 360-740 nm at 10 nm intervals and a 3 mm measurement spot. The Minolta has its own independent light sources - 3 pulsed xenon lamps. This keeps the measurements independent of environmental effects (variable lighting sources).

➢ Center weighted first derivatives are typically used when interpreting visible spectroscopy data to emphasize the spectra shape [4] and to minimize matrix effects such as grain size and moisture content (**Figure 1**)[11]**.** This allows for easier interpretation and correlation amongst rock spectra and known mineral spectra.
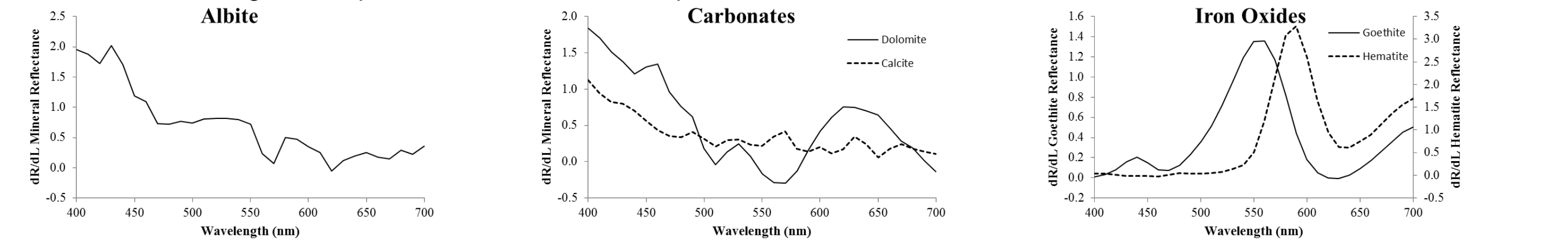

Figure 1.Examples of the first derivative of the visible spectra of Albite, Dolomite, Calcite, Goethite and Hematite (400-700 nm) to illustrate the differences in spectra. Pearson's Correlation Coefficient is used to calculate the correlation between sample spectrum and mineral spectra.

VPCA

➢ **Principal Component Analysis with Varimax-rotation (VPCA)**, similar to R-mode component analysis, was used on the visible derivative spectroscopy datasets.

➢ Component analysis is a statistical sorting technique used on large, multivariate datasets to identify a much smaller number of dimensions (components or components) that explain the majority of the variance/characteristics within a dataset [12].

➢ VPCA seeks to decompose a data matrix into independent (orthogonal) components by finding the largest variances within a dataset (**Figure 2**). It is the same as solving a system of linear equations for eigenvalues and eigenvectors. For each extracted component, the eigenvectors are the direction of maximum variance in a dataset, and the eigenvalue indicates how much variance there is in that direction. The eigenvectors are also called **component loadings**, and describes the weight a variable has on the extracted component. Component loadings can be thought of as "data-adaptive filters". Component loadings are then projected back onto the dataset to obtain **component scores**, which represent the weight of the extracted component on a particular data point. Many datasets are then rotated because it puts emphasize on fewer variables for each extracted component, and each variable preferably only correlates to one component, thus making the model easier to interpret (**Figure 3**). **Varimax** is commonly used because it minimizes the number of variables that have high loadings within a component, enhancing the interpretability of the extracted loadings [6,11,12,13].
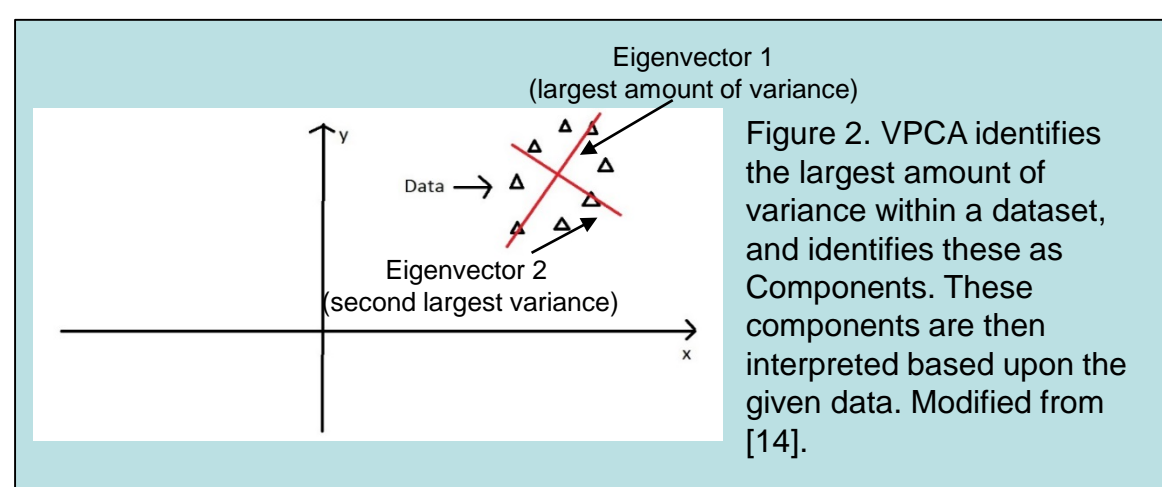

Figure 2. VPCA identifies the largest amount of variance within a dataset, and identifies these as Components. These components are then interpreted based upon the given data. Modified from [14].
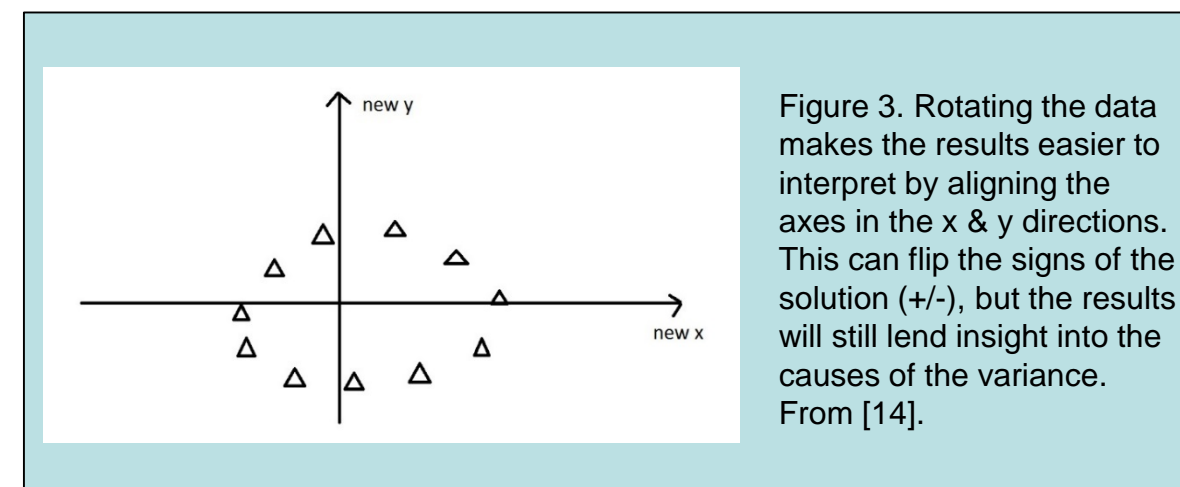
Figure 3. Rotating the data makes the results easier to interpret by aligning the axes in the x & y directions. This can flip the signs of the solution (+/-), but the results will still lend insight into the causes of the variance. From [14].

➢ Here, our matrix consists of visible derivative spectroscopy spectra (columns) with depth (rows) taken on rock cores. The component loadings represent the weight of a variable (particular wavelength) on an extracted component. The component loadings can be used to help identify mineral spectra by comparison to known mineral standards obtained by lab measurements or the USGS Spectroscopy library. The component scores represent the down core variability of an interpreted mineral (assemblage).

Core 2984

➢ Core 2984 consists of ~140 ft (~43 m) of core, encompassing the boundary between the overlying Kope Formation and the Point Pleasant Formation. Three components were extracted, explaining 91.4% of the variance within the dataset. Component 1 Loadings correlate with Illite (R=-0.972) (**Figure 4**). Component 2 Loadings explain the bright, highly reflective minerals within the cores: calcite, dolomite and gypsum (R=0.897) (**Figure 5**). Component 2 Scores also highly correlate with L*, which is the lightness of the surface (R=0.796). Component 3 Loadings correlate with the iron oxides within the core, a mixture of goethite+hematite (R=0.950) (**Figure 6**).

➢ Z-Scores of the qXRD values were then plotted against the Component Scores 1 and 2 (**Figures 7 and 8**) and values generally correlate with the Component Scores.

➢ The down core variation for Component Score 3 (**Figure 9**) has little variation down core (the iron oxides generally comprise of just a few wt percent or trace amounts within a sample), but the boundary between the Kope Formation and Point Pleasant has previously been documented as an unconformity with hematite coatings. This is represented as the large spike in Component Score 3 at 522 ft depth.
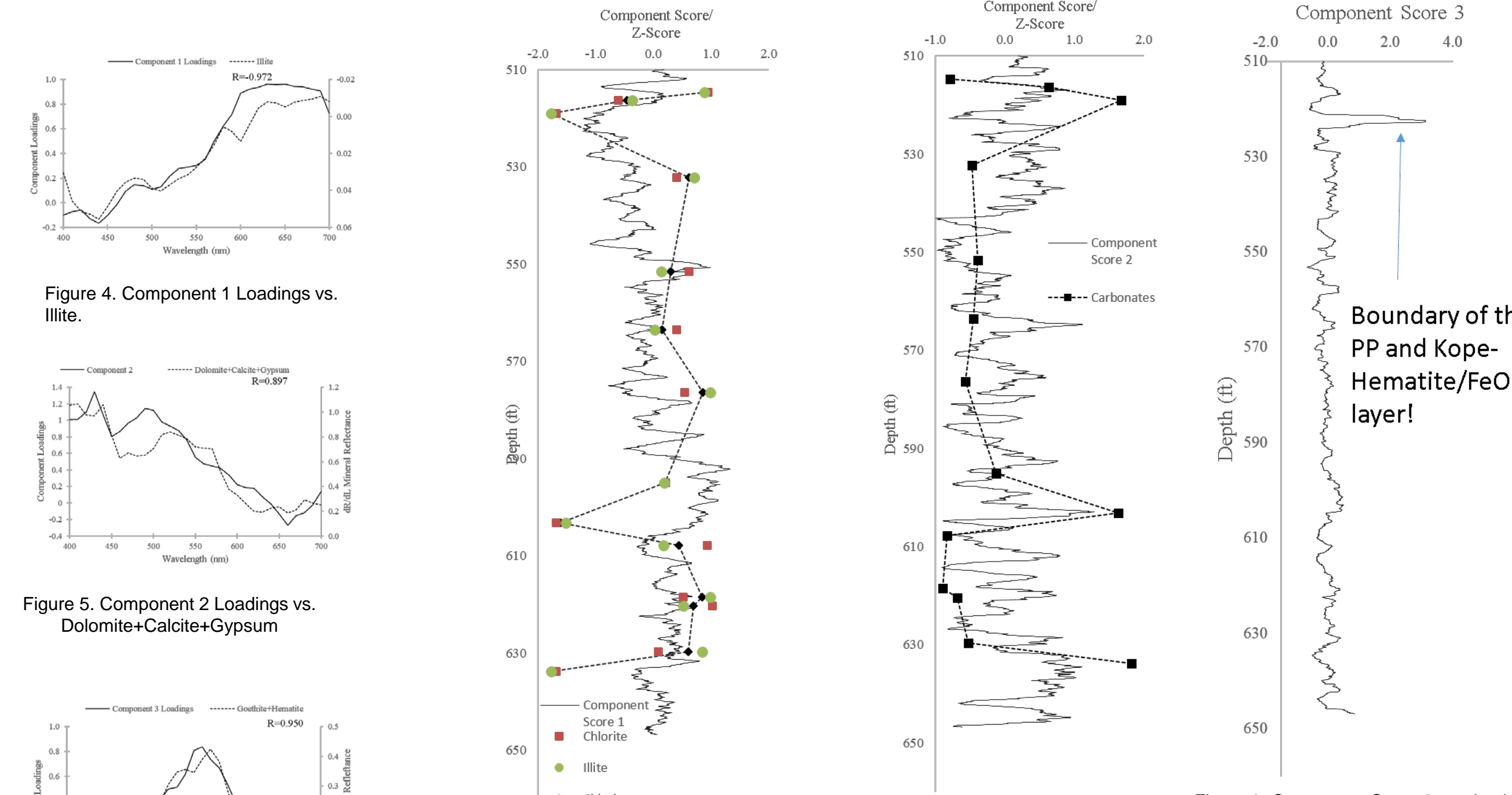

Figure 4. Component 1 Loadings vs. Illite.

Figure 5. Component 2 Loadings vs. Dolomite+Calcite+Gypsum

Figure 6. Component 3 Loadings vs. Goethite+Hematite.

Figure 7. Component Score 1 vs. depth compared to corresponding mineral Z-Scores calculated from qXRD results. The qXRD values generally correspond with the Component Scores, but a perfect correlation is not expected because the reflectance spectra do not have 100% correlation. Some minerals are able to be estimated from reflectance (see [4,15,16]) with additional information and calibration

Figure 8. Component Score 2 vs. depth compared to corresponding mineral Z-Scores calculated from qXRD results.

Figure 9. Component Score 3 vs. depth compared to corresponding mineral Z-Scores calculated from qXRD results. At ~522 ft, a high component score is present, indicating a large influence from the mineral assemblage (here, goethite+hematite). This locations roughly corresponds to the boundary between the Kope and PP, and has been noted previously to have localized iron rich layer at the boundary [17].

Boundary of the PP and Kope-Hematite/FeO layer!

Core 3003

➢ Core 3003 is located in Eastern Ohio, within the "sweet spot" for hydrocarbon production. Two components were extracted that again matches the other two studied cores. Component 1 Loadings correspond Calcite+Dolomite (R=0.925) (**Figure 9**), and Component 2 Loadings correspond to the clay content (Illite; R=0.977) (**Figure 10**).

➢ Down core variations are not presented because of large missing sections of core and previously inconsistent handling practices.

➢ The results indicate that the three cores, although very different in appearance, contain similar mineralogy. The differences in the detected mineralogy can give insight into the different processes that occurred within different locations of the Sebree Trough.
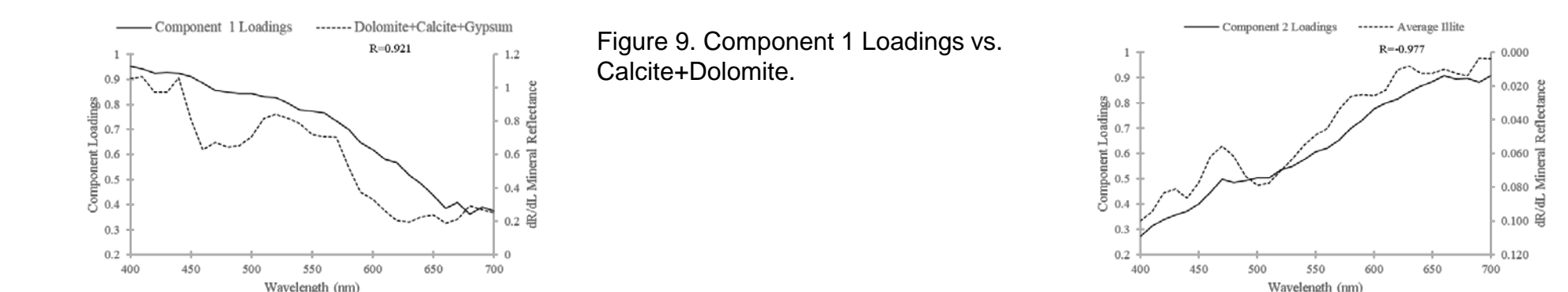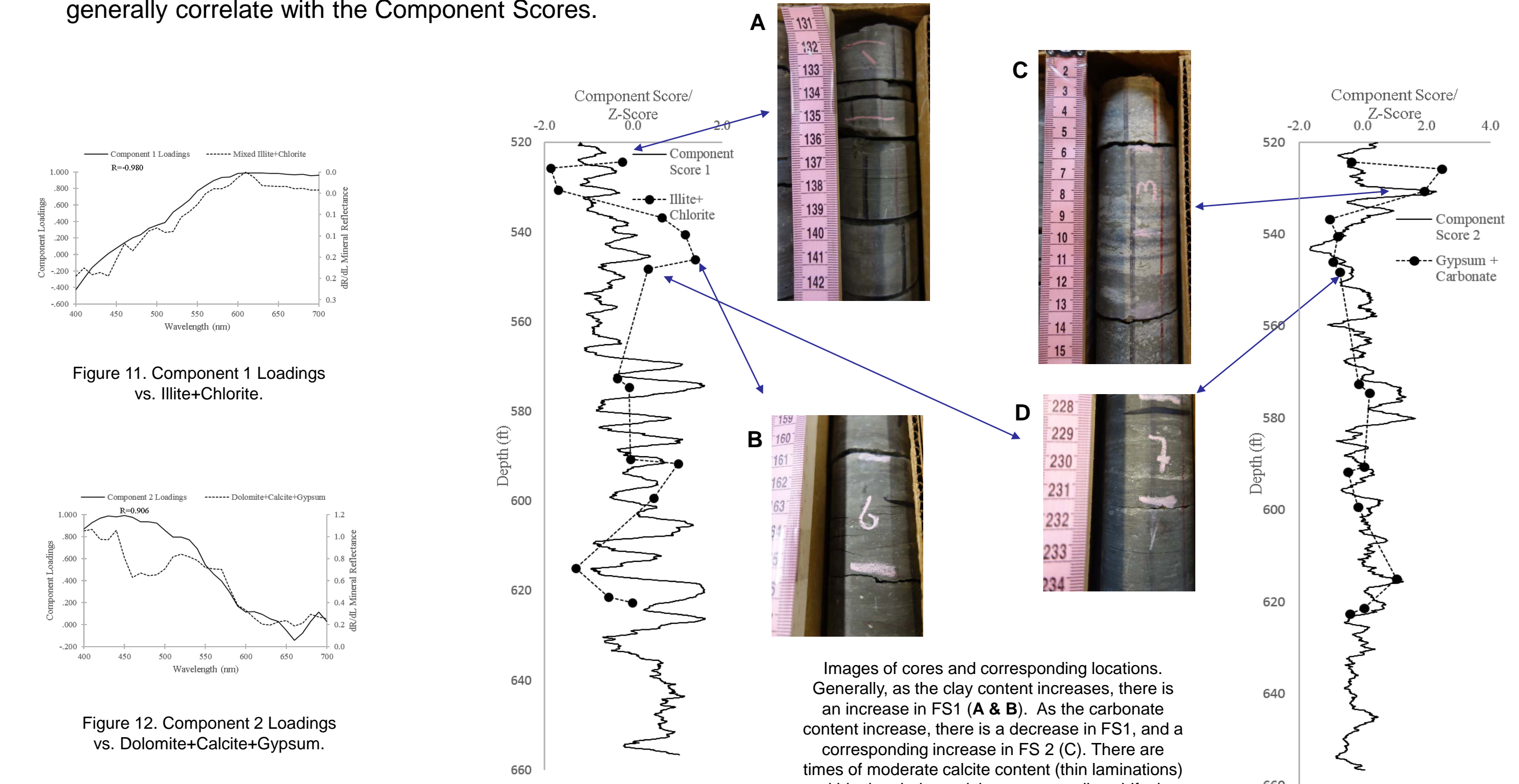

Figure 9. Component 1 Loadings vs. Calcite+Dolomite.

Figure 10. Component 2 Loadings vs Illite. Although down core variations are unreliable, the Visible derivative spectroscopy gives similar mineralogy compared to the other two sets of cores.

Core 2982

➢ Core 2982 consists of ~140 ft (~43 m) of core, encompassing the boundary between the overlying Kope Formation and the Point Pleasant Formation. Two components were extracted, explaining 93.9% of the variance. Component 1 Loadings correspond to Illite+Chlorite (R=-0.980) (**Figure 11**). Component 2 Loadings correspond to the bright, highly reflective minerals within the core (Dolomite+Calcite+Gypsum; R=0.906) (**Figure 12**). Component 2 Scores for Component 2 also highly correspond to the L* (brightness) values (R=0.827).

➢ Z-Scores of the qXRD values were then plotted against the Component Scores 1 and 2 (**Figures 13 and 14**) and values generally correlate with the Component Scores.

Figure 11. Component 1 Loadings vs. Illite+Chlorite.

Figure 12. Component 2 Loadings vs. Dolomite+Calcite+Gypsum.

Images of cores and corresponding locations. Generally, as the clay content increases, there is an increase in FS1 (**A & B**). As the carbonate content increase, there is a decrease in FS1, and a corresponding increase in FS 2 (**C**). There are times of moderate calcite content (thin laminations) within the shale, and the corresponding shifts in FS1 and FS 2 are observed (**D**).

Figure 13. Down core Component Score 1 with corresponding Illite+Chlorite Z-Scores from qXRD analysis.

Figure 14. Down core Component Score 2 with corresponding Carbonate Z-Scores from qXRD anlaysis.

Geologic History and Visible derivative spectroscopy Implications

➢ The Sebree Trough is a bathymetric low filled with interbedded shales and carbonates (Utica Shale, Point Pleasant formation in Ohio) during the Middle-Upper Ordovician that extends from Tennessee, Kentucky, Illinois, through SW Ohio (**Figure 15**)[17]**.**

➢ During this time, Laurentia was located at the equator and an epeiric sea covered the North American continent from the highlands of the Taconic Orogen to the east and Transcontinental Arch and Canadian Shield islands towards the west[17,18].

➢ Shallow water carbonates were deposited on the Lexington and Trenton Carbonate Platforms while the trough filled with siliciclastics from the Taconic Highlands. Biostratigraphy and K-Bentonite deposits place the deposition of the siliciclastics that fill the trough coeval with the platforms [17,18].

➢ Results from the Visible derivative spectroscopy indicate that Core 2984 has a greater influence from carbonate, and appears to have generally thicker carbonate beds compared to Core 2982. Core 2982 has more interbedding of clays and carbonates.

➢ This is consistent with the general locations of the core compared to the Sebree Trough. Core 2984 is supposed to be on the SE side of the trough, intertounging the Lexington Platform, with a greater influence from the platform, while Core 2982 is located directly within the trough, with periodic carbonate deposits but most influence from the shedding of siliciclastics from the Taconic Orogeny.
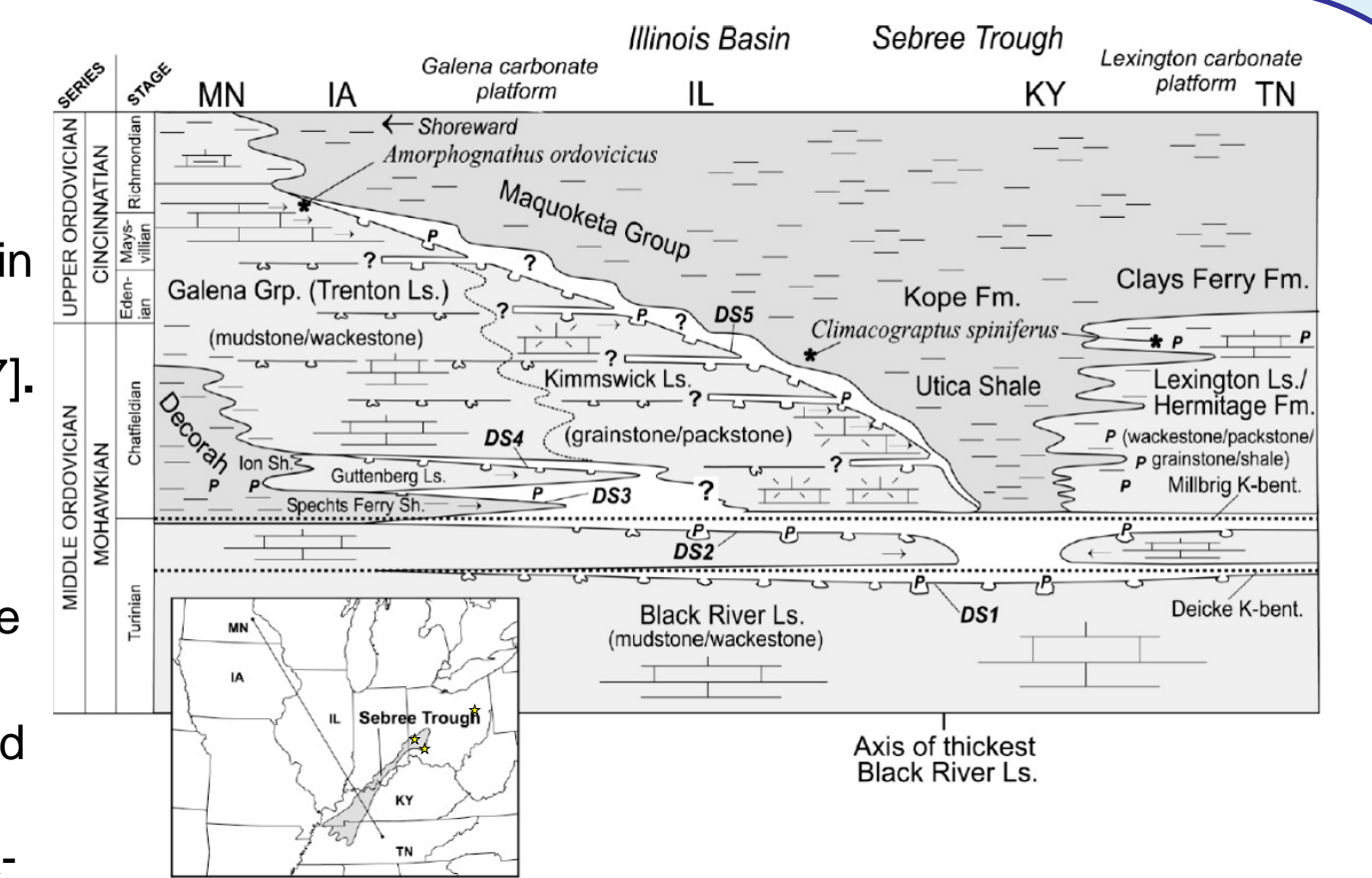

Figure 15. Generalized cross section showing the relationship of the Galena (Trenton) Platform, Utica Shale filled Sebree Trough (also the Point Pleasant Fmt below in Ohio) and the Lexington Platform. The Utica Trough Fill intertongues the Lexington Platform, while there is little interbedding between the Trenton Platform and Sebree Trough Fill. P indicates localized phosphors and iron mineral surfaces. Stars are the locations of the cores. Image from [17].

[References list]