PSVarimax-Rotated Visible Derivative Reflectance Spectroscopy of the Utica Shale / Point Pleasant Formation in Ohio*

Julie M. Bloxson¹, Beverly Z. Saylor², and Barbara M. Kemeh¹

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Abstract

The Ordovician Utica Shale is an extensive and significant portion of the Appalachian Basin subsurface, marking the transition from shallow water conditions to a deeper marine, tectonically active depositional environment. The Utica Shale Play consists of calcareous shale and siltstone interbedded with limestone, creating a heterogeneous, complicated mixed siliciclastic-carbonate system. Generally, there is not a quick, accurate method for determining lithology, especially in core. Here, we present an approach previously used on loose sediment cores and apply it to rock cores of the Utica Shale/Point Pleasant Formation, undifferentiated, to determine down-core mineralogy at a high-spatial resolution (1 cm). Three cores containing the Utica Shale, the overlying Kope Formation, and underlying Lexington Limestone were analyzed using visible derivative reflectance spectroscopy at 1 cm spatial resolution. The data were processed with principal component analysis to extract mineral components, which were then verified with quantitative x-ray diffraction. The visible derivative reflectance spectroscopy detected illite and chlorite varying inversely with carbonate content throughout the cores. Iron oxides (hematite and goethite) were detected in one core, with a high concentration at the boundary between the Kope Formation and Utica Shale, and various, lesser amounts throughout the rest of the core. The type and relative quantities of minerals detected via visible derivative reflectance spectroscopy of whole core were compared with mineral abundance determinations using quantitative X-ray diffraction analysis of ground samples. Calcite content was also quantitatively estimated using L*, the brightness of the core measured during reflectance spectroscopy. This estimated calcite content, along with two other previously measured cores, were then compared to the gamma ray core log to determine correlations between mineralogy and log signatures. Overall, the reflectance spectroscopy was able to provide quick, accurate, semi-quantitative information on the down-core mineralogy of these mixed siliciclastic-carbonate formations.

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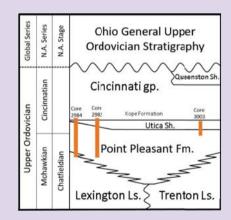
Varimax-Rotated Visible Derivative Reflectance Spectroscopy of the Utica Shale/ Point Pleasant Formation in Ohio

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Introduction

The Utica/Point Pleasant play consists of calcareous shale and siltstone interbedded with limestone, creating a heterogeneous mixed siliciclasticcarbonate system deposited across the Appalachian Basin. Generally, there is not a quick, non-destructive, and accurate method for determining lithology, especially in core.

Here, we present an approach previously used on loose sediment cores which uses visible light analyzed with statistical techniques, and apply it to three sets of rock cores consisting of the Utica shale/Point Pleasant Formation, undifferentiated, to determine down-core mineralogy at a high-spatial resolution (1 cm). These results were compared to well log data and previously measured mineralogy in two other cores to determine correlations.



Generalized stratigraphic column of Ordovician strata in Ohio, with the relative stratigraphic locations for the three cores marked in orange. The Utica Play is more correctly termed the Utica/Point Pleasant Play, and consists of the Trenton and Lexington Limestones, Point Pleasant Formation, and Utica shale (lower shaley portion of the overlying Kope Formation of the Cincinnati Series). Modified from Ohio Division of Geological Survey (1990) and Hickman et al. (2015b).

Core Information

Core No. 2982: API34017600040000, Izaak Walton League, Butler Co., OH Core No. 2984: API 34017600110000, Davis Mickey, Butler Co., OH Core No. 3003: API 34031228380000, Barth Fred T No. 3, Coshocton Co, OH All cores are archived at the Ohio Division of Geological Survey, Columbus,

Well No. 4:API 34005241600000, Well Name Eichelberger David, Measured by the New York State Museum (Smith, 2015)

Well No. 38: API No. 34169256690000, Well Name Hershberger, Measured by the New York State Museum (Smith, 2015)

Utica Shale extent — state boundary core location The Utica shale and Point Pleasant Formation expands throughout eastern North America. Three cores were used for visible derivative reflectance spectroscopy, in addition to two others used for comparison, all within the Appalachian Basin. Boundaries of the formation extents were created based upon data from Hickman et al (2015) and Hart Energy (2012).

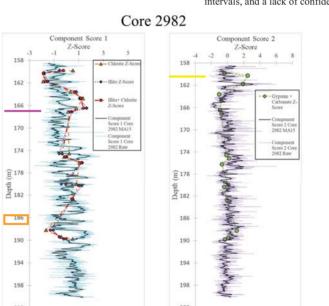
Methods

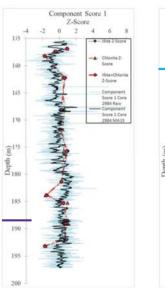
Three cores containing the Utica shale, Point Pleasant, and underlying Lexington Limestone were analyzed using visible derivative reflectance spectroscopy at 1 cm spatial resolution with a Konica-Minolta UV/VIS CM2600d. The data were processed with Varimax-rotated Principal Component Analysis (VPCA) to extract mineral assemblages (clays vs. carbonates), which were then verified with QXRD on 30 samples. QXRD calcite content was found to correlate with L* (brightness) of the samples, and a non-linear regression was used to determine the relationship. Calcite content was then estimated down-core at 1 cm resolution. This estimated calcite content, along with two other cores with previously measured mineralogy, were then compared to the gamma ray core logs to determine correlations between mineralogy and log signatures.

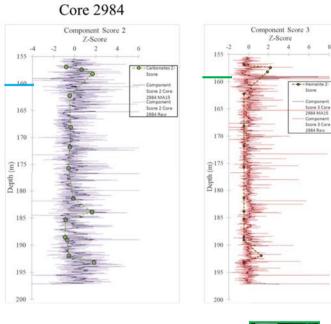
Core Visible Derivative Reflectance Spectroscopy Mineral Identification The center-weighted first derivatives for the intensity of reflected light at each wavelength from the down-core reflectance data were uploaded into SPSS for VPCA. The extracted loadings represent the influence of the wavelength for a core. These loadings were compared to a known database to determine the mineral/mineral assemblages. dom and in small percent ages, but the brightness of the mineral, especially com pared to the clay minerals. causes some influence in the Core 2982 Component 1 Loadings Core 2982 Component 2 Loadings compared to compared to Illite+Chlorite spectrum Dolomite+Calcite+Gypsum spectrum. Component Component 1 represents clay minerals. 2 represents carbonate minerals Core 2984 Component 1 Loadings Core 2984 Component 2 Loadings compared to Core 2984 Component 3 Loadings compared to Illite spectrum. Component 1 Dolomite+Calcite+Gypsum spectrum. Component compared to Goethite+Hematite spectrum represents clay minerals. 2 represents carbonate minerals Component 2 represents iron oxide minerals Core 3003 Component 2 Loadings Core 3003 Component 1 Loadings compared to compared to Illite spectrum. Component 2 Dolomite+Calcite+Gypsum spectrum. Component represents clay minerals 1 represents carbonate minerals - Sample 10 Mineralogy from reflectance spectroscopy was Spectrum verified using OXRD. Major clays include illite, Degree of fit chlorite and muscovite. Non-clays typical include quartz, pyrite, hematite, calcite and dolomite.

Down Core Mineralogy Variations Compared to OXRD and Core

Downcore component scores (colored lines) were calculated by SPSS, representing the amount of influence of each extracted component (mineral(s)) had on the reflectance at a specific measured depth. The downcore component scores were smoothed with a moving average of 15 cm (black lines) to make it easier to see larger-scale downcore trends, OXRD z-score values (dashed lines) were then plotted with the component scores to observed measured mineralogy changes in the core for comparison. Downcore trends are not shown for Core 3003 because of large missing intervals, and a lack of confidence in depths, although they provide useful comparison of extracted mineralogy.











Core 2982 Sample 7 corresponding to 167.2 m. While mostly siliciclastics, this sample has increased calcite as a whole, represented by the light laminations throughout. Pink line above.



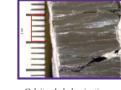
While much of the carbonate is in the form of storm deposits, some is

micrite mixed with clay minerals.

Core 2982 from 185.9 - 187.8 m.

Orange box above.

Limestone bed within the Point Pleasant Formation consisting of crinoid stem fragments. Ruler is in mm. Sample 2 from Core 2982 corresponding to 160.3 m. Yellow line above.



Calcite-shale laminations are commonly found throughout the Utica and Point Pleasant, Sample 11 from Core 2984 corresponding to 188.7 m depth. Purple line



Shell hah interval interpreted as a storm bed, and are commonly found throughout the cores. This represent a major influx of carbonate material into the basin. Core 2984 at 160.6 m depth. Ruler is in cm. Corresponds to blue line above.



Overall, the QXRD correlates with the component scores, although variations arise because the component scores have multiple influences on the spectra. Also, there appears to be a general inverse relationship between carbonate content and clay content.

Core 2984 at the boundary of the Kope Formation and Utica Shale showing iron oxide stain ing (orange color). Ruler is in cm. 159 m. Outlined in green

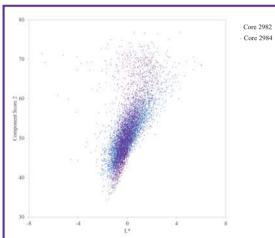


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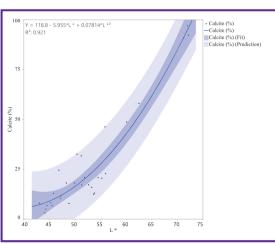
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Quantifying Calcite Content Within Core Using Visible Derivative Spectroscopy

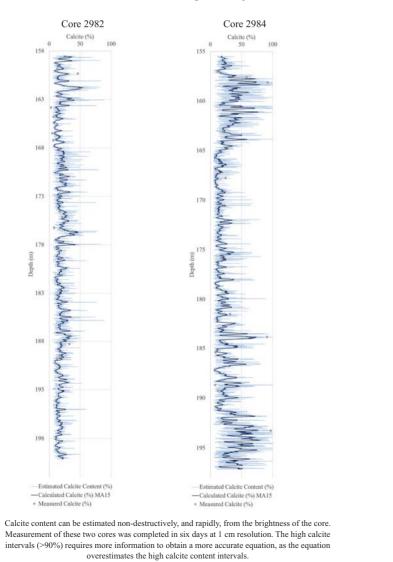
After establishing that the downcore component scores can qualitatively reflect carbonate content, and noticing that clay content inversely vary with carbonate content, calcite content was estimated throughout the cores based upon correlations between L* (brightness, or total amount of light reflected back) measured with the spectrometer and calcite percent measured by QXRD. Dolomite is present in low amounts, consistently ~5%. L* was used because it has the best correlation with the QXRD data, and also correlates well with Component Score 2 (carbonates+gypsum), suggesting that it is highly affected by carbonate minerals. A non-linear regression was used to best represent the calcite vs. I* data, and estimated calcite content was then calculated for Core 2982 and Core 2984 using the line equation.



Component 2 scores compared to L* (brightness) of both cores, indicating that component 2 is the light, bright, highly reflective minerals.



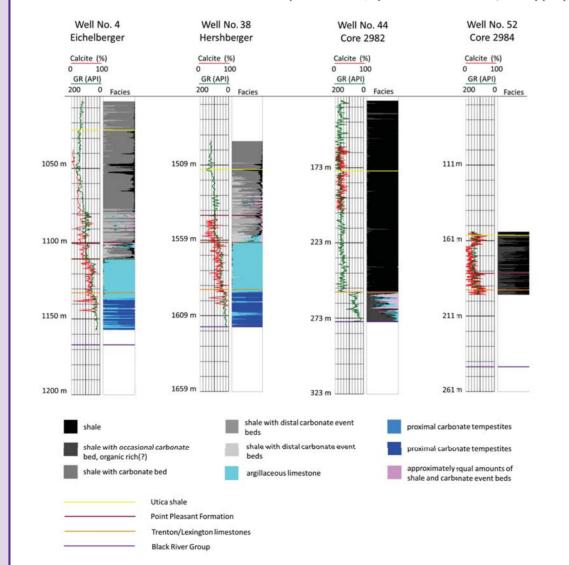
Calcite percent from qXRD for cores 2982 and 2984 compared to L* (brightness) from the reflectance measurements, indicating that L* correlates with aXRD values of calcite content.

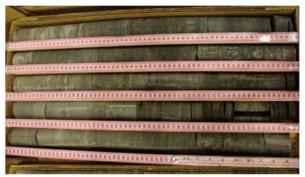


Comparison of Calcite Content and Gamma Ray Log

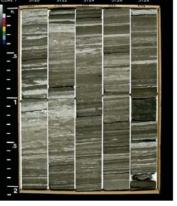
Estimated calcite content was then compared to the log gamma ray values, and an inverse relationship is present. Also, the two cores in this study (Core 2982, Well No. 44; Core 2984 Well No. 52) were compared to two other cores with previously measured calcite contents from Smith (2015) by dissolution (Eichelberger, Well No. 38). Overall, the calcite contents from the newly estimated cores presented here behave in a similar manner as the previously, traditionally measured calcite content.

Although we can estimate calcite content, how the carbonates are present in the cores is difficult to distinguish without hand samples. Some carbonate intervals are present as micrite mixed with clay minerals, creating a light grey mudstone. Other carbonate intervals are present as discrete, crystalline calcite laminations (secondary precipitation along natural fractures or bedding planes), or as storm deposits (tempestites).





Shale with very few carbonate beds from Well No. 44 (Core 2982) from 164.6-167.5 m.



Primarily argillaceous limestone with some shale beds and laminations. Core image from well no. 38, 1560-1563 m from Smith (2015).



Shale with carbonate beds from Well No. 52 (Core 2984) 161-164 m. The individual carbonate beds are not well represented on the well log because of typical resolution of a gamma ray log.

Conclusions

- The Utica/Point Pleasant interval are a mixed siliciclastic-carbonate system, where carbonates can occur as secondary in fractures, or primary in storm beds or micrite mixed with clay minerals.
- Calcite can be estimated semi-quantitatively within the Utica/Point Pleasant interval using brightness of the core. This can be done rapidly and non-destructively.
- Estimated calcite content behaves in a similar manner as previously measured calcite content when compared to the gamma ray values.
- Calcite inversely varies with gamma ray measurements, which also indicates an inverse relationship with clay minerals within the system, and log gamma ray values can generally be used to infer calcite vs. clay content.

Acknowledgment

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This research will be submitted for publication in the coming months.

The full dissertation manuscript can be found at etd.ohiolink.edu . Note there have been some changes in the processing of calcite vs. L* data (regression method).

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