Geochemical Comparison of Cenomanian Post-Buda Rocks in South Texas and Big Bend Ranch State Park

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Abstract

The Eagle Ford Shale (EFS) is an interbedded marl and limestone unconventional Cretaceous play producing crude oil and gas extending from northeast Leon County to the Mexico-American border in Southwest Texas. This Cenomanian - Turonian formation records the drowning of the Texas carbonate shelf and transgression of the Western Interior Seaway (WIS) into North America. Regional depositional patterns were affected by a series of changes in tectonic activity and eustatic sea level. The formation recorded a distinct change in oceanography during the Oceanic Anoxic Event 2 (OAE2) between the lower and upper EFS sections. The Boquillas Formation, age equivalent to the EFS, is found west of the producing region in Big Bend State and National Park. Outcrops of the EFS can be found along the Ouachita orogen and in the Big Bend region due to tilting during the Laramide orogeny and intrusive igneous activity. The largest known EFS equivalent outcrops have been found within the state park, however, no data had been collected in these locations. Evaluation of the geochemical properties and redox indicators of the depositional environment is essential to understanding the potential for hydrocarbons. The main method to acquire this data has been through the X-Ray Fluorescence Spectrometer (XRF). For this study I have utilized two handheld analyzers, the XRF along with the Laser Induced Breakdown Spectroscopy (LIBS) for outcrop and core samples. Using both methods produces a more complete element suite including light elements not offered by XRF alone. Additionally, comparing LIBS data to the widely used XRF analyzer allows me to determine the practical usage of LIBS in petroleum geology

Methods

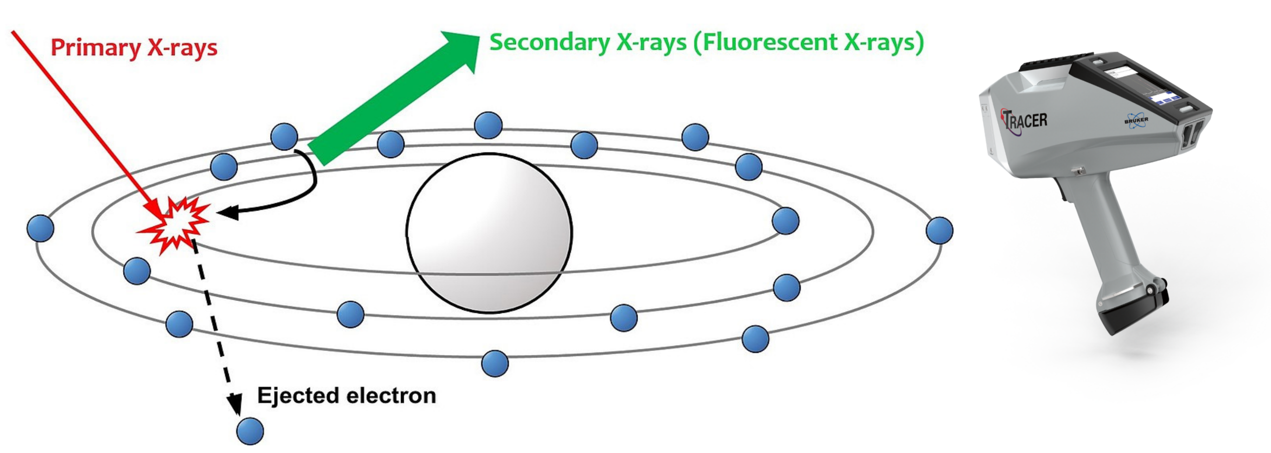

Figure 1: X-Ray Floresence process (Horiba)

Handheld energy-dispersive X-ray fluorescence (ED-XRF)

- The analyzer exposes the samples to radiation with high-energy photons from either an x-ray tube or a radio isotopic source that "excites" the electrons in the sample
- This causes secondary X-rays to be emitted, or fluoresce, as electrons return to their orbits
- Each element in the sample has a specific secondary X-ray energy and appears as spikes over a given energy spectrum with the concentration of the element correlating to the height of the peak (Shackley, 2018)

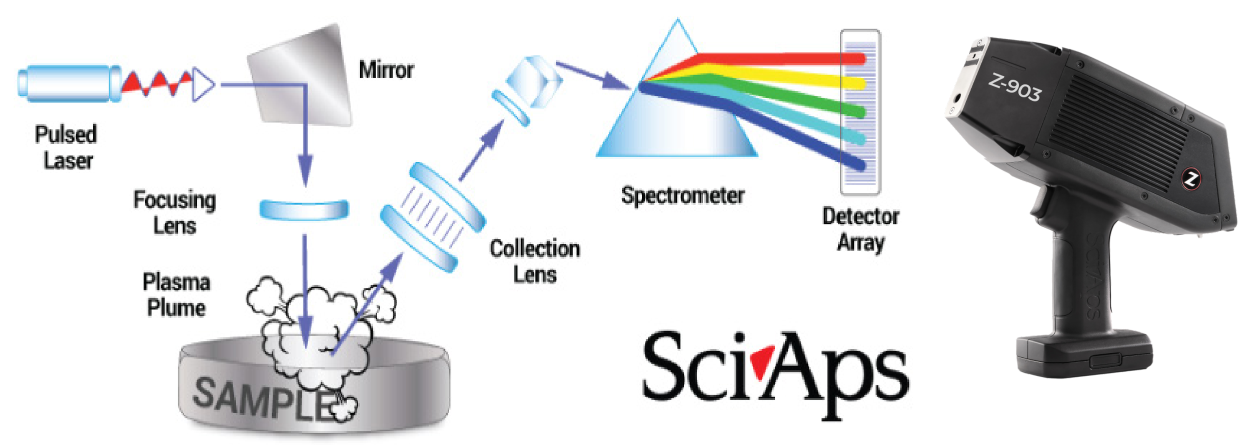

Figure 2: Geochemical analyzation process of the laser induced breakdown Spectroscopy (LIBS) (SciAps, 2023)

Laser Induced Breakdown Spectroscopy (LIBS)

- A high energy laser is directed at the sample, causing ablation of about 25 um of material in a plsma plume
- As "excited" atoms and ions return to their ground states, each atom will give off a specific light wave dependent on the element to be collected by the spectrometer
- The spectrometer separates all light emissions with high resolution optics to be detected by the charge-coupled device (CCD)
- To view the detected elements in the sample, the instrument creates a graph of light intensity as a function of wave length
- The quantitative chemical results are made by the on board processor that compares height of specific peaks.

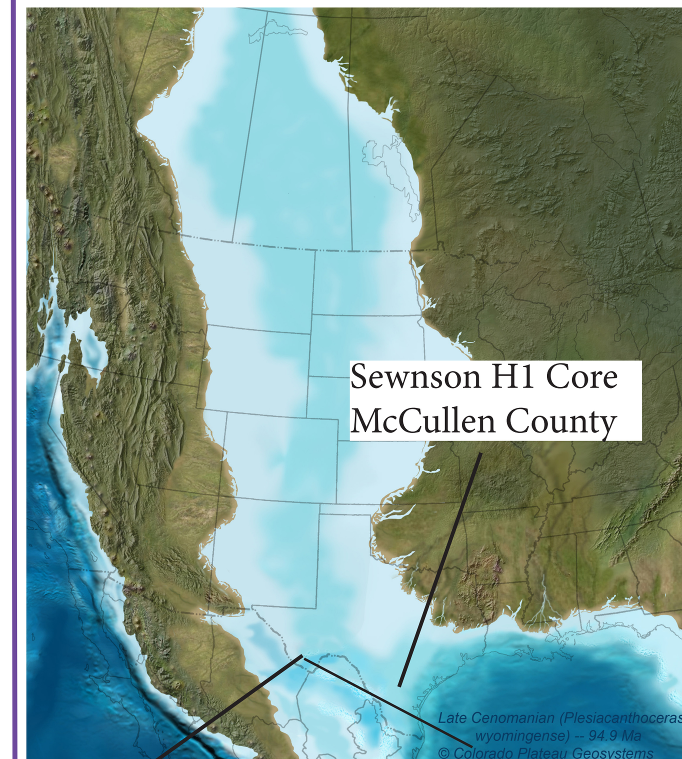

Figure 3: Modified R. Blakey map of the Late Cenomanian 94.9 Ma

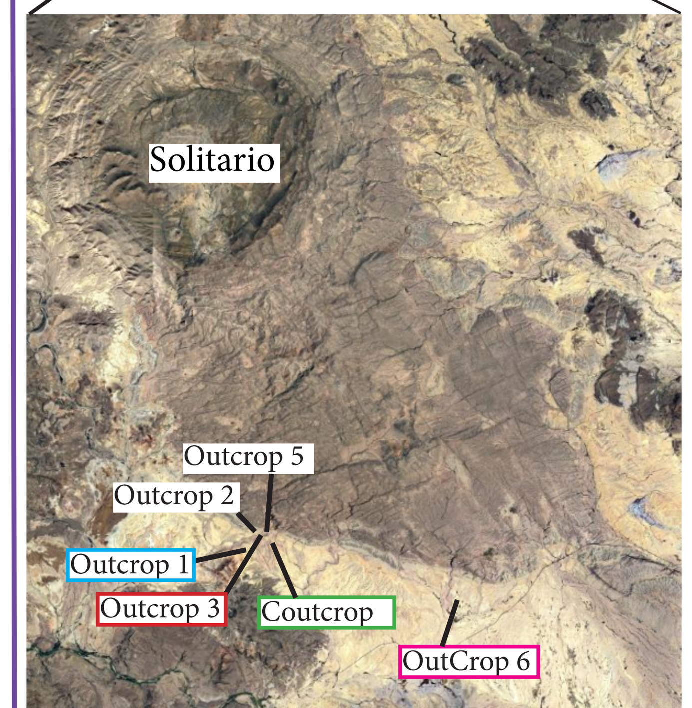

Figure 4: Big Bend Ranch State Park Solitario with the six outcrop sites of the study

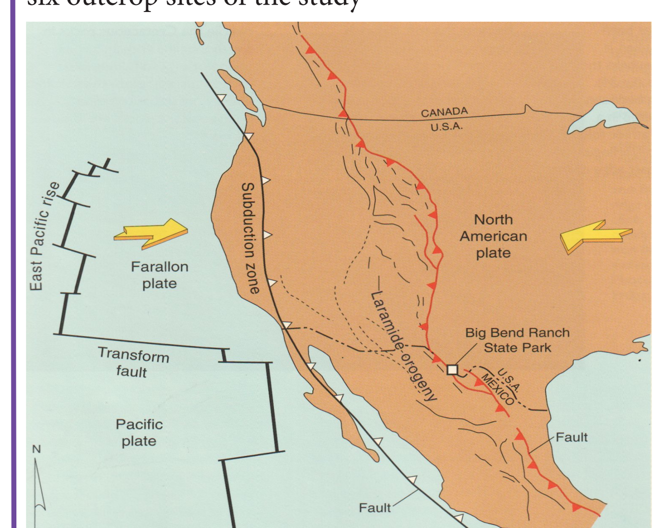

Figure 5: Map of Early Tertiary Laramide Orogeny fold front due to the subduction of the Farallon Plate

Figure 6-9: Outcrop in increasing age top to bottom (3, 4, 6, 1) in interpreted measured section positions

Results

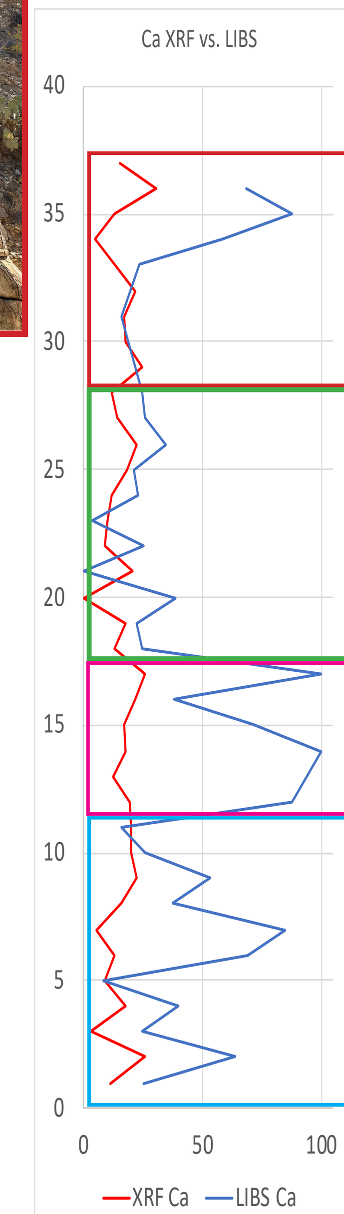

Figure 10: LIBS and XRF Calcium sample data from Big Bend Ranch State Park

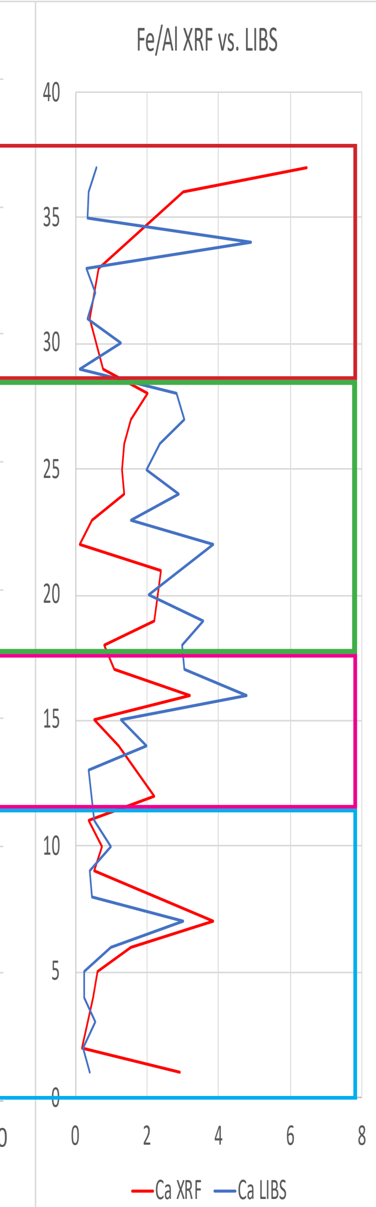

Figure 11: LIBS and XRF Fe/Al ratio sample data from Big Bend Ranch State Park

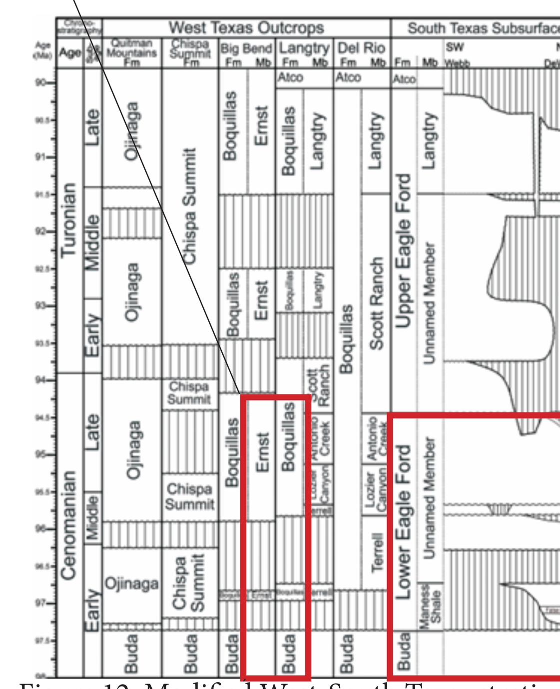

Figure 12: Modified West-South Texas stratigraphic column of Eagle Ford Age Equivilant rocks (Denne and Breyer, 2016)

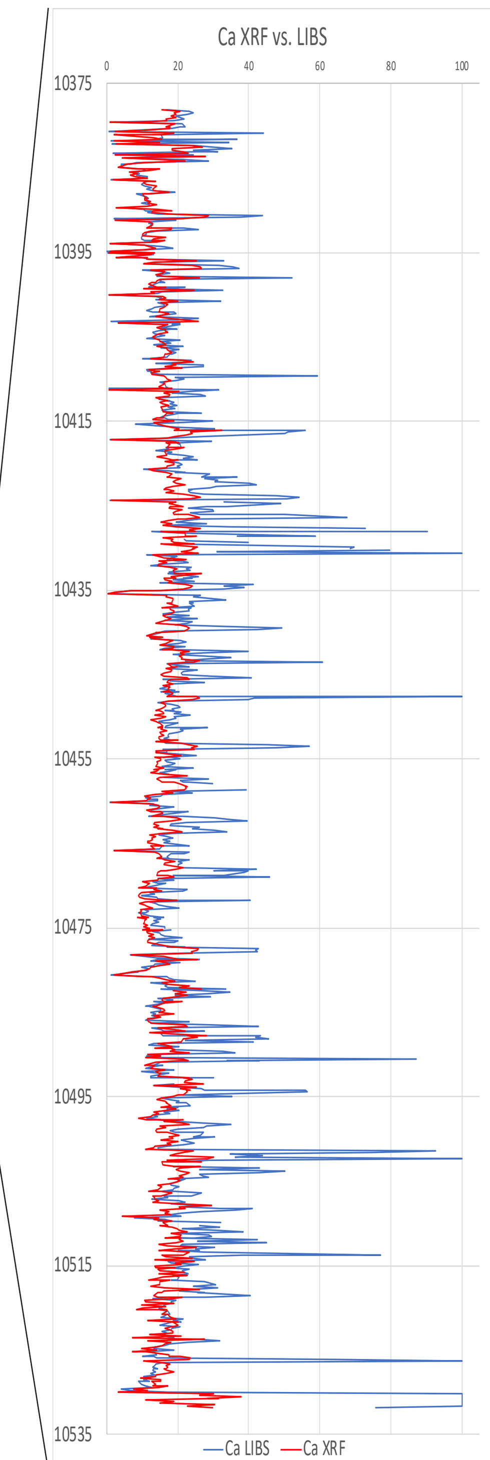

Figure 13: LIBS and XRF Calcium data in weight percentages from the Swenson H1 core

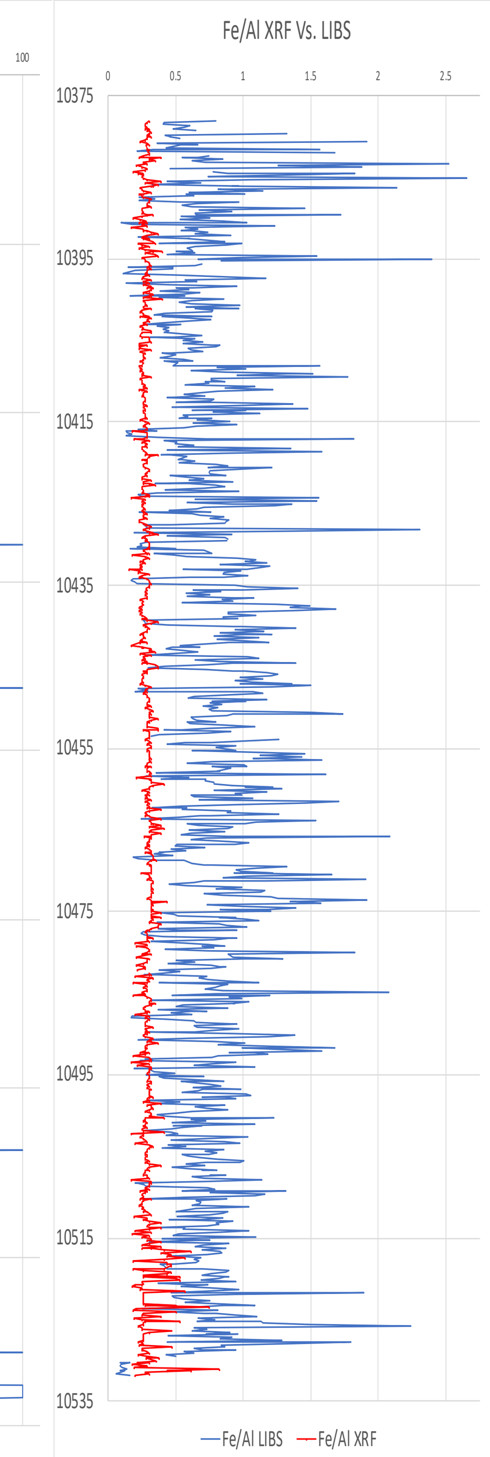

Figure 14: LIBS and XRF Fe/Al data in weight percentages from the Swenson H1 core

Figure 15-17: Photos of Swenson H1 Core top, middle and base buda contact

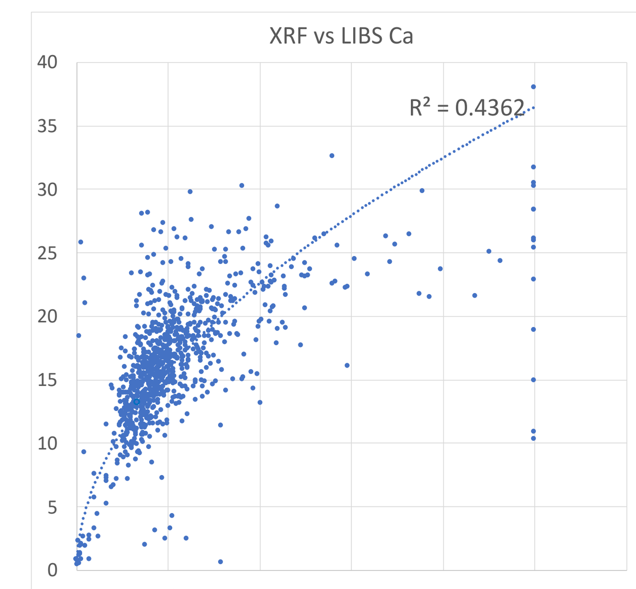

Figure 18: Calcium plot of XRF vs. LIBS core data

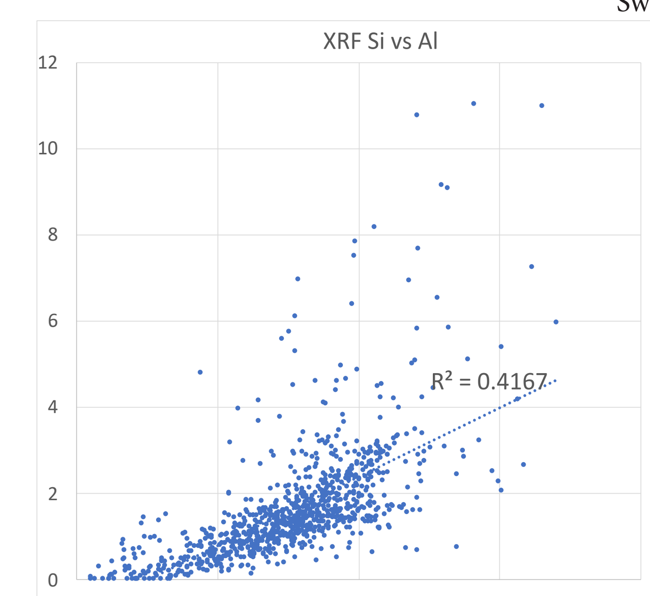

Figure 19: Silica vs. Aluminum plot of XRF core data

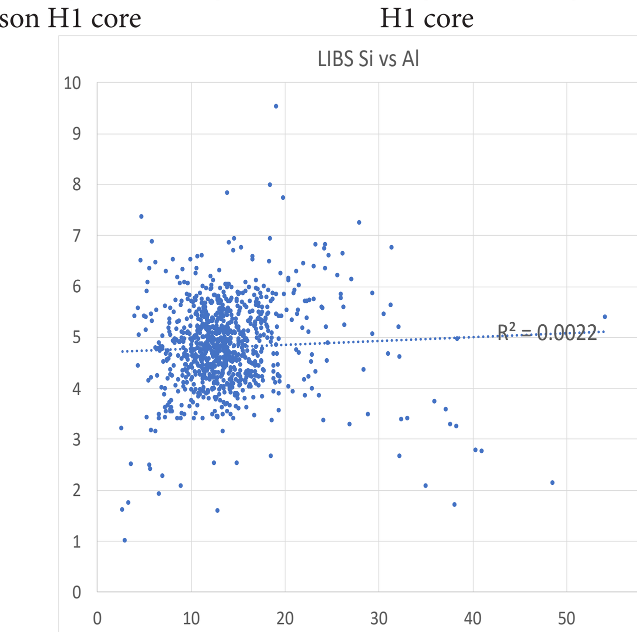

Figure 20: Silica vs. Aluminum plot of LIBS core data revealing possible inaccuacies of one or both elements

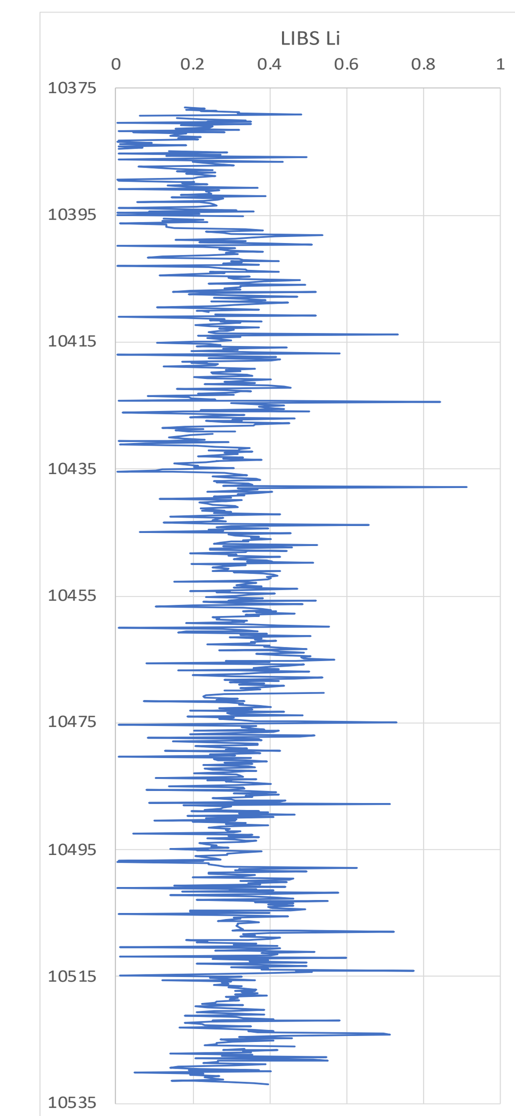

Figure 21: LIBS lithium Data from 2 inch intervals of the Swenson H1 core

Instrument	Sample Preparation	Light Elements	Trace Elements	Field Use	Data
X-Ray Florescence (XRF)	Clean Face	No	Yes	Too Fragile	Standardized by extensive testing
Laser Induced Breakdown Spectroscopy (LIBS)	Pelletization needed for quantitative results	Yes	Yes, if pelletized	Yes	Standardization and more data needed

Geologic Background

- The South Texas Eagle Ford depositional environment differs from Big Bend due to major tectonic and volcanic influences
- The Ouachita Orogeny elevated basement rock along its collisional folding front resulting in a Cretaceous rock outcrop belt extending from Big Bend and throughout Northeast Texas
- Salt deformation deepened the Maverick basin in South Texas leading to a silled basin environment not found in the Big Bend region.
- Additional Early Tertiary tectonic folding and volcanic influence in Big Bend cause by the subduction of the Farallon Plate
- These differences allowed for deposition and preservation of organic matter in South Texas but not in West Texas

Discussion and Future Work

- Without a standardized method to analyze LIBS values, this study uses trends presented by both analyzers to determine if the same patterns are recognizable in the LIBS data as XRF.
- Trends of the XRF and LIBS throughout the core share several similar tendencies
- Some isolated elemental data from the LIBS appears to have errors without clear trends
- Although outside the scope of this project, future suggested work would be to determine a standardized mudrock calibration for the LIBS Analyzer

Conclusion

- XRF and LIBS data share similar trends within the core and sample data
- Standardizing a reference material for the LIBS will lead to significantly better data interpretations
- To utilize this tool for petroleum geology much more testing and data is needed

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