# **UTILIZATION OF MICRO X-RAY FLUORESCENCE SPECTROMETRY (µXRF) IN ANALYZING HEAVY MINERAL SORTING PATTERNS IN BIOTIC AND ABIOTIC DEPOSITIONAL ENVIRONMENTS**

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by

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## **ABSTRACT**

Utilization of Micro X-ray Fluorescent Spectrometry (µXRF) in Analyzing Heavy Mineral Sorting Patterns in Biotic and Abiotic Depositional Environments

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The field of evolutionary geobiology is focused largely on the presence of biosignatures in the geological record. Microbial mat communities have been shown to sort heavy element grains and produce patterns that differ from those seen in cross-laminated sandstones (Gerdes et al., 2000). The difference in spatial distribution patterns of heavy mineral grains may prove to be a viable biosignature. These patterns are studied using Micro X-ray Fluorescent Spectrometry to determine what significance or abundance, if any, exists between the patterns of distribution of heavy mineral grains contained within the two types of formations.

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### **SECTION I**

## **INTRODUCTION**

#### **Purpose**

Paleo-biosignatures make up the majority of our understanding of early life on earth. However, many of these biosignatures are difficult to interpret and understand. A new method is needed to properly quantify the differences in biosignatures observed in biotic and abiotic depositional environments. The aim of this research is to answer two questions: mainly, do biotic and abiotic sorting processes produce distinguishable deposition patterns, and if so, can spatial distribution of heavy mineral be used as a biosignature? This biosignature identification method could prove to be invaluable to NASA's 2020 Mars Rover mission and subsequent future research expeditions to find evidence of ancient life on Mars.

It is hypothesized that the distribution of heavy minerals will show a pattern that is distinct between microbial mat communities, a form of biotic forcing, and heavy minerals influenced solely by abiotic, physical processes such as alluvial and Aeolian erosion (Mange and Wright, 2007). Heavy minerals are commonly used in the understanding of depositional environments and the study of fall velocity; the three main forms of physical sorting are known in great detail (Mange and Wright, 2007).

#### **Background**

The method for analyzing the distribution patterns of the heavy minerals in question will rely on the HORIBA XGT-7000 µXRF machine, which produces elemental maps of sediment surfaces.

This instrument was chosen because it is similar in function to the NASA Planetary Instrument for X-Ray Lithochemistry, PIXL, apparatus that will be utilized on the 2020 Mars Rover mission. The major difference lies in the resolution of the PIXL camera which can deliver scans of accuracy on the order of 100µm versus the capable resolution of the HORIBA XGT-7000  $\mu$ XRF machine which can deliver scans up to 10 $\mu$ m in resolution. To resolve the majority of this difference, all scans obtained during the course of this project were set to a resolution of 100 $\mu$ m.

Rock samples from the Moodies Group ca 3.22 Ga of the Barberton Greenstone Belt in South Africa were analyzed using µXRF for establishing the patterns found in both the abiotic and biotic sediment formations. The Moodies Group was utilized in part because of the large amount of background research previously established by others, namely Donald Lowe and colleagues. The large body of research established around the Moodies Group of the Barbeton Greenstone Belt results primarily from the high quality of preservation seen in the sediments of the area during the Archaean time period (Heubeck et al., 2013).

## **SECTION II**

### **METHODS**

#### **Rationale**

The essential instrument utilized for data collection was the HORIBA XGT-7000 µXRF machine, commonly referred to as a  $\mu$ XRF machine. This instrument images the elemental content of any solid sample with an accuracy of up to ten microns. All scans completed were made at 100µm resolution because of the desire to have correlation with the PIXL apparatus of the 2020 Mars Rover mission.

Analysis of grain size distribution across different regions of the sedimentary structure relied on the grain size geometric mean that utilized the value of phi. Use of phi as an assessment of grain size is common practice in sedimentology to provide a more accurate and robust measurement. Formula for calculation of geometric mean can be found in any general use sedimentology text. Remaining calculations consist only of normal probability plots of each mineral across the two different depositional environments. These normal probability plots could offer more insight into the variance of grain size within the two depositional environments in more comprehendible manner.

#### **Execution**

Titanium, iron, sulfur, zircon, and chromite were the five elements used to distinguish the four heavy minerals used. The four heavy mineral types utilized were rutile, pyrite, zircon, and chromite, respectively. These four minerals were chosen based on their relative abundance in the

stratigraphic record as well as their stability. The software program equipped to run the  $\mu XRF$ machine requires wavelength absorbance values for each desired element; standard values were used as given by the manual provided. The data output from this machine comes in the form of tiff images, and these images were output to ImageJ for manipulation and data extraction. This process produced for each element a set of two or three images, one elemental image and one to two background images which needed to be subtracted from the single elemental image. ImageJ tools allows for subtraction of background images to produce one final corrected elemental map for each selected element.

Once the final image has been produced, it could then be analyzed in the program. Analyzing the grains in the elemental maps consisted of visually identifying bright portions, indicative of grains, which were drawn over using the line segment tool. A plot was generated using the density profile plot tool which depicted the relative pixel intensity across the line drawn. These plots help to see the parameters of the grain. By this method, two perpendicular axis could be established to find the outer relative dimensions of the grain. These data were then used to calculate a phi for each grain.

For the abiotic depositional environment sample, henceforth referred to as the tidal sandstone sample, four regions of interest were examined. These regions include the large lower facie which is evident of an erosional surface, also referred to as a cross-sub boundary. The other three regions selected constitute spatial regions of each cross-lamination band, including a high, middle, and low region. These regions were chosen based on the notion that larger grains would be found near the top and would decrease in size as one moves down to the lower region, an

assumption based on the concept of avalanching in dune sediments. Thus, a possible pattern may be visible and distinct within these three regions.

Three regions of interest were used for the biotic depositional environment, hereby referred to as the microbial mat sample. It is expected the scans will confirm the initial visual representation of small mounds in the sediment. These are presumed to be remnants of a microbial mat contained within the sediment layers based on previously known patterns of microbial influence on sedimentary structures and the principles of microbially induced sedimentary structures, MISS. The three regions selected were the top of mounds, the slope of mounds, and the valleys between mounds. These three regions are expected to differ in the grain size with larger grains at the top and down in the valleys with smaller grains on the slopes due to the relationship between fall velocity expected.

From each of the seven regions selected, twenty grains were counted in total containing the four minerals utilized. Counting the same number of total grains per region created more regular and comparable plots. In counting pyrite grains, only the sulfur scans were utilized for making phi calculations and the iron scans were used only to confirm that iron existed in the same space sulfur existed, providing evidence of a pyrite grain and not another mineral containing sulfur. For both depositional environments, one normal probability plot was created to compare the z-score of each of the four minerals found in both regions. This is helpful to see what correlation or difference may exist between the two depositional environments in terms of the range of each mineral size observed.

# **SECTION III**

## **RESULTS**

#### **Qualitative**

The result of the  $\mu$ XRF scans comprising the two depositional environments yielded some anticipated and some unanticipated results. Scan results for the tidal sandstone and microbial mat samples are contained within Figure 1. The major distinction between the two sediment depositional environments is observed in the accumulations of grains in differing regions. The majority of heavy mineral grains in the tidal sandstone sample can be seen around the erosional surface and the upper limit of the cross-lamination bands. This refers to the abundance of grains explicitly, not to grain size calculated. In the microbial mat sample, the greatest density of grains is observed in the valleys between mounds with few grains being observed on the slopes of mounds and slightly more grains being observed on the tops of mounds. The mound in question is observed in the upper portion of the sample and is noticeable by the small crested formation. The height is relatively small, and this is common



Figure 1: The upper row depicts the tidal sandstone and the lower row depicts the microbial mat. Titanium is shown in red; zircon in shown in blue; chromium is shown in green. Pyrite, iron and sulfur, is not shown due to the heavy iron saturation that distorts the image. The Facies Depiction shows a rendered visual of the major sedimentary structures evident, which are not easily visible in the µXRF scans.

#### **Quantitative**

Each of the seven regions selected yielded one plot that depicts each mineral grain sorted by size (Figure 2). One important note to mention is the limitation of the µXRF scanner to observe grains small than a geometric mean value of approximately 485µm; this is seen by the absence of grains observed below this value despite the apparent existence of these grains as seen in the

µXRF scans completed. Following the plots of distribution of grain size across different special regions are the normal probability score plots (Figure 3). Each z-score plot represents all of the grains counted for that respective sample and are mostly consistent between the two samples. This result is to be expected and allows one to make the assumption that both depositional environments originally contained similar grain size distributions for grains on this size order.



Figure 2.1: This plot depicts the grain size distribution of the tidal sandstone erosional surface.



Figure 2.2: This plot depicts the grain size distribution of the upper cross-lamination region of the tidal sandstone.



Figure 2.3: This plot depicts the grain size distribution of the middle cross-lamination region of the tidal sandstone.



Figure 2.4: This plot depicts the grain size distribution of the lower cross-lamination region of the tidal sandstone.



Figure 2.5: This plot depicts the grain size distribution of the upper mound region of the microbial mat.



Figure 2.6: This plot depicts the grain size distribution of the mound slope region of the microbial mat.



Figure 2.7: This plot depicts the grain size distribution of the valley mound region of the microbial mat.



Figure 3.1: This plot depicts the normal probability of all grains considered in the tidal sandstone sample.



Figure 3.2: This plot depicts the normal probability of all grains considered in the microbial mat sample.

## **SECTION IV CONCLUSION**

#### **Findings**

The original search for a distinct pattern in the grain size distribution between the two depositional environments proved to yield unfavorable results. The Figures 2.5-7 plots show that there is not a discernable pattern for the grain size distribution of the microbial mat across the three selected special regions. Figures 2.1-2.4 depict no substantial evidence for a pattern in the tidal sandstone sample analyzed. The normal probability plots, Figure 3.1 and Figure 3.2, show similar z-scores for each mineral across the two depositional environments. This can conclude that both depositional environments contained similar distributions of heavy minerals as a whole, which is an important assumption that would be necessary to verify any pattern seen between the two depositional environments.

One major contribution made by this work is the observed abundance of heavy mineral accumulation between microbial mat mounds that is distinct when compared with the observed abundance seen in the tidal sandstone erosional surface and cross-lamination bands. This pattern may likely be the result of biological action sorting grains out of growth areas, in essence pushing heavy minerals to either side as the microbes continue to build up and accumulate (Noffke et al., 2013). From this data the sorting mechanism cannot be determined; only the result of a biological sorting mechanism has been observed. The observation of this sorting pattern is a form of biosignature that may be useful for future evolutionary geobiology research efforts, possibly even application to future astrobiology research endeavors.

#### **Future Prospects**

The most promising aspect of this project is the vast capacity for using the  $\mu XRF$  scanner in data acquisition of sedimentology structures. This technique has been growing in use and popularity over the last decade and will likely prove to be an essential method of baseline research prior to the 2020 Mars Rover mission. While the exact mechanism by which biological activity sorts the four heavy minerals studied is unable to be interpreted by the data methods used here, understanding that mechanism is one major area of research currently being conducted (Gerdes et al., 2000). Future research utilizing µXRF possesses vast possibilities in the fields of geobiology and astrobiology in the coming years.

One major area of research understudied as of yet is the quantification the density of abundance of heavy minerals to determine their compositional patterns across special regions of sediment structures from differing rock formations. A more comprehensive study is required to establish credible existence of a biosignature. This may likely revolve around multiple rock groups, quantification described previously, and the development of distribution models capable of predicting based on grain abundance alone how the sedimentary structure differ from biotic and abiotic depositional environments.

## **REFERENCES**

Gerdes, G., Klenke, T., Noffke, N., 2000, Microbial signatures in peritidal siliciclastic sediments: a catalogue: Sedimentology, v. 47, p. 279-308. doi: 10. 1046/j.1365-3091.2000.00284.x

Heubeck, C., Engelhardt, J., Byerly, G. R., Zeh, A., Sell, B., Luber, T., Lowe, T., 2013, Timing of deposition and deformation of the Moodies Group (Barberton Greenstone Belt, South Africa): Very-high-resolution of Archaean surface processes: Precambrian Research, v. 231, p. 236-262

Mange, M.A., Wright, D.T., 2007, Heavy Minerals in Use: Amsterdam, The Netherlands, Elsevier, 1283 p.

Noffke, N., Christian, D., Wacey, D., Hazen, R. M., 2013, Microbially Induced Sedimentary Structures Recording an Ancient Ecosystem in the ca. 3.48 Billion-Year-Old Dresser Formation, Pilbara, Western Australia: Astrobiology, v. 13, p. 1103-1124.