Energy Dispersive Spectroscopy for Mapping Surface Chemistry of Foraminifera

(Honors Option Report)

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Contents

Background 2
Methodology 2
Results and Discussion 3
Sample 1: Cupulorid bryozoans from offshore Pensicola, FL 3
Sample 2: Mollusc from Sarasota, FL 4
Sample 3: Cyclammina (foraminifera) 5
Conclusion 5

Figure 1: SEM image of Cupulorid bryozoan test 3
Figure 2: (a) EDS mapping results with percentage composition by region and (b) SEM Image of Cupulorid bryozoan sample 3
Figure 3: SEM of mollusc test 4
Figure 4: (a) EDS mapping and percentage composition by region of the mollusc surface (b) SEM image of mapped surface 4
Figure 5: SEM of cyclammina test 5
Figure 6: (a) EDS mapping and percentage composition of the cyclammina surface (b) SEM image of mapped surface 5

Background

Foraminifera are often used as determinants of geological strata age, as different species are specific to the various archeological ages. While some Foraminifera species' shells, known as tests, are composed of only calcium carbonate others are composed on agglutinated material from the surrounding sediments. This means that the composition of the shell can be used to match a specimen to a geographical location as well as a time-period. Therefore, high-resolution 3D x-ray interferometry can be a useful technique to examine Foraminifera specimens. Since we are constructing a micro-resolution x-ray interferometer beamline on the Center for Advanced Microstructures and Devices (CAMD) a sample such as the foraminifera is useful in determining the limits of the resolution of the instrument. Energy dispersive spectroscopy (EDS) will act as a good standard to which we can compare the results from our instrument.

Methodology

The goal of doing EDS analysis is to determine the dispersion of chemicals on the surface of the foraminifera's tests. Because composition location was the desired result, the best technique to use was elemental mapping. However, foraminifera are biological samples which presents some challenges for analysis with the SEM. While there were no tissues present in the sample that were particularly sensitive to the electron beam, the organic materials are very resistive. An AuPd coating was applied for one minute in a vapor deposition chamber as opposed to the standard four minutes due to worries about the layer absorbing the lower energy x-rays emitted by the low Z elements present in biological samples.

While using the EDAX system the following parameters were used for analysis with the idea of having multiple low-resolution scans as opposed to a single high resolution scan:

- Hang time: 200μs
- Scans: 16
- Resolution: 512x512

In addition, the counts were consistently above 20,000; however, the filament burned out after looking at the first sample so the other two samples were obtained with a different filament.

Results and Discussion

Sample 1: Cupulorid bryozoans from offshore Pensicola, FL

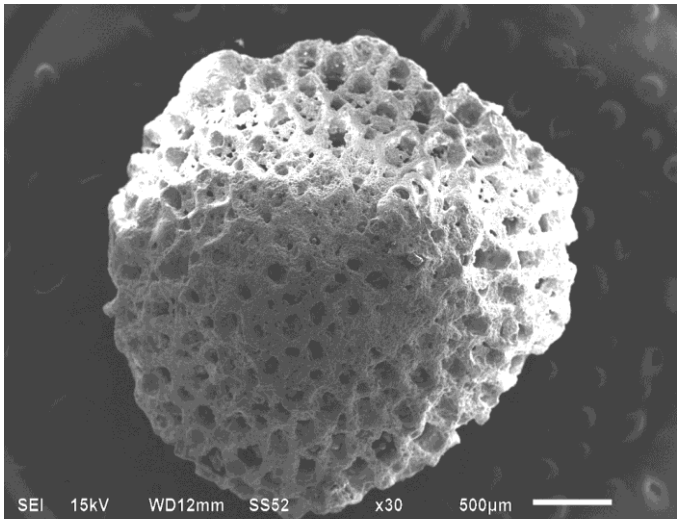


Figure 1: SEM image of Cupulorid bryozoan test

The low-magnification image of the sample seen in Figure 1 makes it apparent that this test has a porous surface, and the higher resolution image in Figure 2b shows that appears to have non-uniform surface. The spectral mapping in Figure 2a shows a varied chemical composition across the surface. The yellow regions (PoM/AsL/S K/MgK/BaL) mostly appear around the edges of the pores, and the dark red region (SrL/CaK) can also be seen in clustered areas in the bottom half of the image. There is a relatively uniform background composition that appears across the whole surface, which is identified by the blue and red regions which were observed to be composed of BaL/AsL and BaL/AsL/MgK/PoM respectively. It was expected to see this uniform region since the test should be mostly composed of a single compound, though it is interesting to note the spectra did not indicate Ca or Si in this region which two main components of known shell structures.

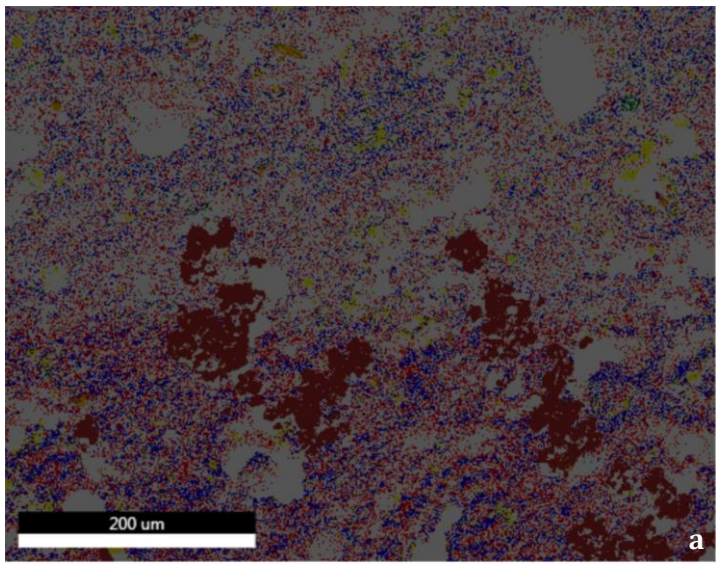


Figure 2: (a) EDS mapping results with percentage composition by region and (b) SEM Image of Cupulorid bryozoan sample

Sample 2: Mollusc from Sarasota, FL

This mollusc has a relatively non-porous surface when looked at with a low-magnification, as seen in Figure 3. The EDS mapping spectra seen in Figure 4a also show that it has a uniform composition across its surface with the presence of Ca across the entire area. This is an expected result as $CaCo_3$ is a common mineral in the composition of marine shell structures.

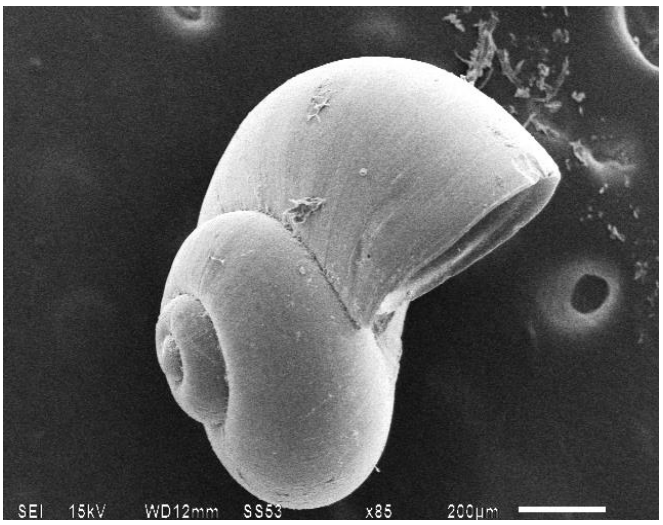
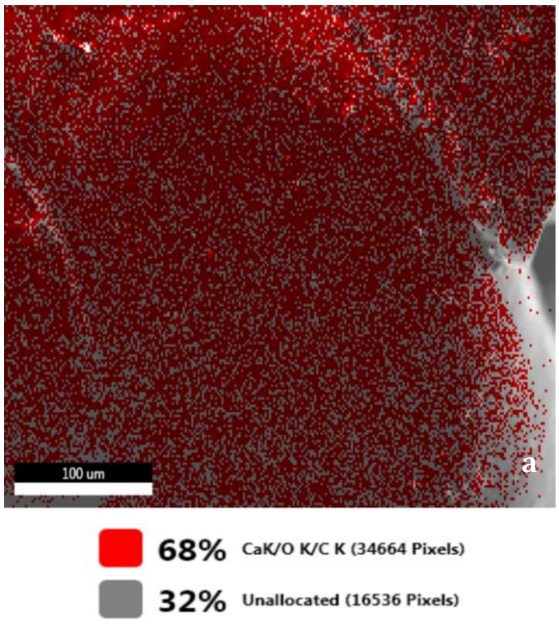


Figure 3: SEM of mollusc test



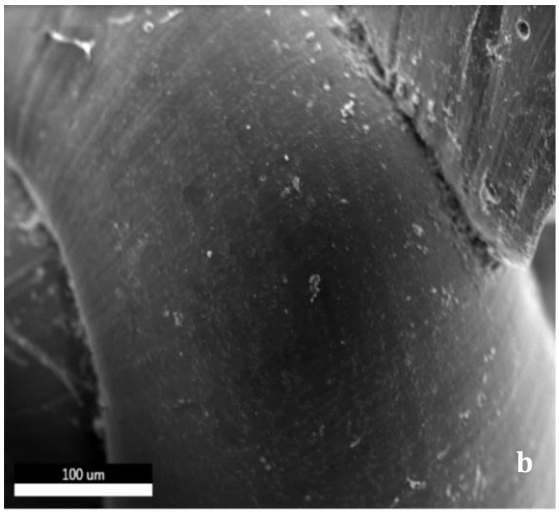


Figure 4: (a) EDS mapping and percentage composition by region of the mollusc surface (b) SEM image of mapped surface

Sample 3: Cyclammina (foraminifera)

From the SEM image in Figure 5 the cyclammina test is not very porous, though it appears to have a rougher surface than that of the mollusc. The mapping results show that it has a uniform composition across the surface with a Si compound. Silica compounds while rarer than $CaCO_3$ are also known to be main components of various marine shells.

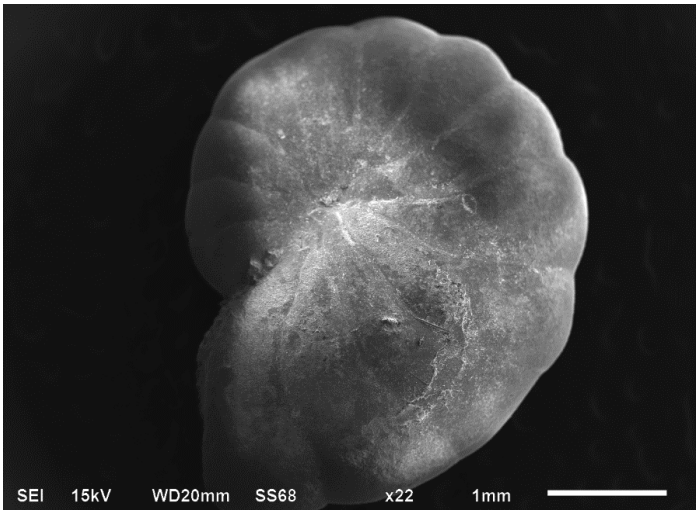
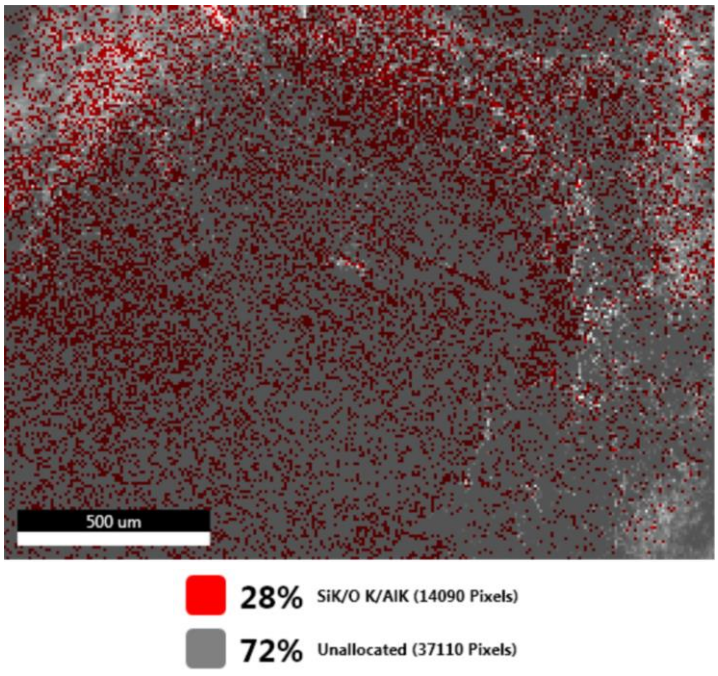


Figure 5: SEM of cyclammina test



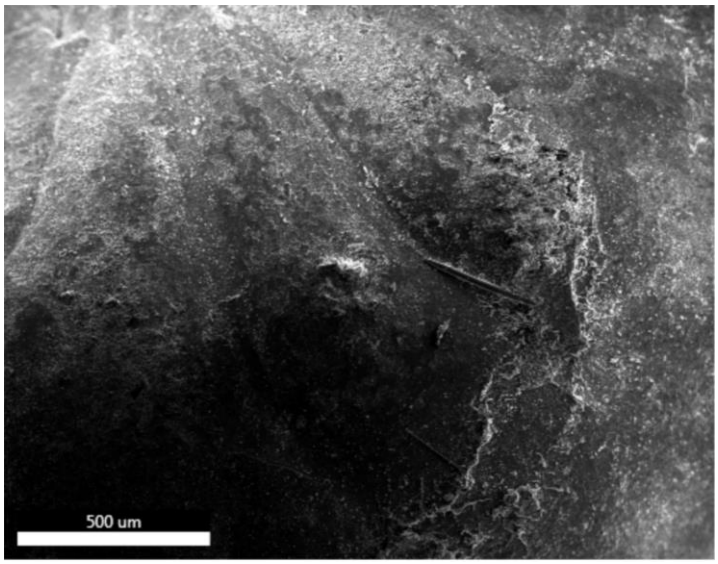


Figure 6: (a) EDS mapping and percentage composition of the cyclammina surface (b) SEM image of mapped surface

Conclusion

The non-porous samples 2 and 3 appeared to have a similar type of uniform chemical composition across the surface of the tests. The porous sample 1 appears to have a much more complex composition with multiple regions of chemical compositions. It is important to note the non-uniform composition, however the actual chemical composition was not well revealed by this experiment. Due to the low Z elements that I was expecting to find such as C, Ca, Mn, O, N, and S the errors were higher than if I were analyzing a heavier sample. The percentage error for the sample 1 mapping displayed anywhere from 4% to 60% error in the elemental composition readings, so further experiments with different scanning settings need to be carried out in order to get an accurate chemical composition. This could be done by increasing either the scanning resolution, the number of scans or both. It also may help to observe smaller areas at high magnifications.

It is also interesting to note that the 1 minute Au-Pd coating seemed to work well to prevent charging and did not noticeably interfere with the EDS imaging. There was no recognition of significant Au or Pd in the mapping spectra, which indicates it allowed for the lower energy x-ray dispersions from the low Z elements to escape.

Overall, these results give a good indication of the type of results as far as the distribution of composition that we should expect from our x-ray interferometer at CAMD, though further studies past this initial experiment may be carried out in order to get more accurate data on which chemicals compose each region, especially for sample 1.