Andrew Bearnot
UTRA Mid-Point Report

Archaeometry: Batting for Both Teams;
The Materials and Archeological Science of Glass Weathering

Introduction:

In my four week introduction to (field) archeology digging at Greene Farm I was introduced to the basic mechanics of archeological excavation and cataloging of a diverse selection of historical materials. This experience differed greatly from previous scientific laboratory theory and practice I have encountered. Renfrew and Bahn write that "Archaeology, in short, is a science as well as a humanity. That is one of its fascinations as a discipline: it reflects the ingenuity of the modern scientist as well as the modern historian."[1] As I reflect on what it means to approach the discipline of archaeology as a scientist I find myself noting many discrepancies as well as many parallels between the methodology and goals of these disciplines. Below is a brief enumeration of some observations and comparisons between my experience with archaeology and engineering (applied science) which have informed the direction of my current research and goals for future investigation:

1) *Archeology is a destructive process***.** In the biological sciences there is some concern surrounding tests which require harming living organism. However, the physical sciences rarely require irrevocably damaging those materials and systems which are being inspected (without the possibility of reproducing them – see 2).
2) *The "results" of an excavation are non-reproducible.* Science requires that experimental data be reproducible and objectively verifiable.
3) *It may take several years, even several decades, to process and cross-reference all the data being gathered from a site (compiling stratigraphic information, analyzing soil samples, compiling mean ceramic dates for each context, "conserving" corroded materials, etc). Experts in specific areas of material culture may be required to make sense of the artifacts collected. "It takes seven days in the lab for every one day in the field."*[2] In my experience, the process of decomposing and analyzing a complex system may also take a great deal of time. Experts in different fields may be brought together to work on a single problem, analyzing a particular aspect or feature.
4) *Once soil goes through the screen, it is no longer viable. Therefore, all information must be recovered prior to dumping the screen, any artifacts missed are irretrievable and irrevocably decontextualized.* We may always return to look again at the data collected during a specific test, or reproduce this data by repeating the experiment (see 2). Importantly, we can return to a

[1] Renfrew, C. and P. Bahn. 2001. *Archaeology: Theories Methods and Practice.* London: Thames and Hudson, 12.)
[2] Conversation with Krysta Ryzewski

system, or even a particular specimen after a long time to apply some new insight and/or analytical technique to it in order to gain further insight.[3]

5) *Contamination is a problem. Mixing contexts, and/or sloppy excavation affects the accuracy, and ultimately the usefulness of the data collected.* AMEN! Every scientific observation is associated with a margin of error. While care and diligence are essential, inaccuracy is ultimately unavoidable. However, science deals with this my establishing tolerances and ways to measure and compute the degree of inaccuracy. In this way, error becomes part of the vernacular of observation and is can be universalized and standardized. This is especially true of engineering, where safety considerations require that standards be enforced.[4]
6) *Most of the observations made in the field are qualitative. They are based on examination of macroscopic features and are limited by our unassisted human senses (i.e. sight and touch). Artifacts are analyzed primarily based on their extrinsic features: how does this artifact compare with other similar artifacts? What is its typology (form, style, decoration)?* Especially in the biological sciences, taxonomy is a predominant method of knowledge formulation. However, the sciences also make use of quantitative analysis to show trends and to compare systems with differing features but related formulation. By examining the intrinsic, microscopic nature of materials (structure, properties, and processing) we can gain insight into materials which are typologically undiagnostic.[5]

This final point is perhaps the most relevant to my present studies. The majority of the glass artifacts collected from Greene Farm have been deemed non-diagnostic. That is, there is not sufficient typological information to identify them conclusively.

-weathering is overlooked (i.e. scraped away to observe glass color – typology)

However, weathering captures information about the time the object has spend in the ground. We must learn to "read" the record preserved by the material.

Background:

Glass weathering is a corrosion process in which water leaches out material from the glass, leaving behind a silicious, semi-crystalline and layered crust. The outermost layers of the crust have been observed to contain high quantities of certain ions uncharacteristic to the native glass, and it has

[3] Prof Sharvan Kumar of the Brown University Division of Engineering recounts an especially remarkable instance in which he was able to observe specimens he manufactured as part of his PhD thesis using new analytical techniques. After many years in storage, he was finally able to observe features in the specimens that were previously inaccessible (though he had theorized about their presence). This

[4] see American Society for Testing and Standards (ASTM): http://www.astm.org/

[5] "Introduction to Materials and Archeological Sciences," http://proteus.brown.edu/materialsscience/6162

been demonstrated that these materials come from the soil in which the artifact is deposited. This may allow provenance authentification, as well as aid in context determination.

Not yet fully characterized – especially stress effects!
In particular, question about layer formation process.[6]
Layer counting : Dating-as in dendrochronology.[7] Also, possibly cross-referencing this information between artifacts.
Weathering reveals minute compositional variation – may suggest manufacturing techniques. I.e. "Zig-zag Morphology".[8] In other words, weathering morphology could be used to diagnose glass type, manufacturing method(s), and/or soil conditions if the mechanistic relationship between the three can be deconvoluted.

Another reason why surface patinas on artifacts are of interest to the scientist is they demonstrate the result of corrosion processes over long periods of "real" time. In the laboratory, corrosion experiments are often designed to accelerate these processes to a more manageable time scale. These tests are notoriously inaccurate, as it is often impossible to observe the true mechanism. Thus, the deterioration of archeological materials may be of interest to the modern technologist as well as the archaeometrist since it allows the observation of materials which have undergone true durability simulations. This is particularly true of glass.

Prized for its relative chemical durability and flexible matrix (capable of accommodating large ions in a variety of oxidation states), glass is a good candidate for the immobilization of radioactive waste. Known as High Level Waste (HLW) Glass, this material has received a great deal of attention and concern in recent years. Though relatively stable, glass is very susceptible to attack by water, as discussed earlier. In addition to many accelerated weathering tests, scientists have also looked to ancient materials to better understand the mechanism of this decay, and to try and predict the rate at which nuclear material will leak out of these materials.[9] However, due to major differences in the glass chemistry, these comparisons have been largely inconclusive.[10]

An area that particularly required further study is stress effects.

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[6] Newton, R G. "The Enigma of the Layered Crusts on Some Weathered Glasses, a Chronological Account of the Investigations." Archaeometry 13 (1971): 1-9.
[7] Brill, R H., and H P. Hood. "A New Method for Dating Ancient Glass." Nature 189 (1961): 12-14.
[8] Cox, G A., and B A. Ford. "The Influence of Inhomogeneities in Glass on the Morphology of Weathering Layers." Glass Technology 30 (1989): 113-114.
[9] Romich, Hannelore. "Studies of Ancient Glass and Their Application to Nuclear-Waste Management." MRS Bulletin 28 (2003): 500-504.
[10] Unpublished correspondence, RH Brill, 7/14/2008

Data & Methods:

(Please see "Artifact Inventory" for complete artifact listing, as well as "Specimen Catalogue" to see the entire list of treatments which have been performed thus far). The following is am overview of some highlights and problems encountered thus far.

Sample Preparation (mounting and polishing):

Several of the weathered glass fragments from Greene Farm were selected for mounting and polishing. Due to the extreme friability of all the weathering products, the materials could not be cut on the diamond saw. Instead they were sectioned either by mechanical fracture, or by mounting the entire specimen and then sectioning with the diamond saw. The specimens were mounted in epoxy, and ground to an 800 grit finish. It was observed that the weathering product was being ground at a faster rate than the substrate material (and the unweathered glass). The problem was exacerbated when polishing was attempted on a felt wheel with diamond.

Cox and Ford (Journal of Materials Science, 1993) utilize a two step process to prepare their weathering crusts for microscopy. "Selected pieces of corroded glass were vacuum impregnated with a 5% solution of Acryloid B-72 (Rohm & Haas Co) in acetone to consolidate the crusts. They were then sectioned and embedded in epoxide resin (buehler) followed by polishing with diamond paste to a .25 m finish." This method would certainly solve the difficultly with sectioning the materials without disturbing the friable patina. However, this technique involves treating (irreversibly) the entire artifact before sectioning, and also requires vacuum impregnation.

Subsequent correspondence with Dr. Brill of CMOG has raised the possibility of impregnating the crust with a hard material before mounting in a softer material to facilitate polishing.

Optical Microscopy:

Observation under reflected light at 50x-1000x revealed a fine, layered structure in all specimens observed (AB-4, AB-5, AB-6, and AB-7). Figs 5-9 (Appendix II) show examples of the morphologies observed in AB-4 and AB-6.

SEM/EDS:

(Appendix III)

XRF:

Weathered and unweathered artifacts were non-invasively tested. This data must be normalized against Corning Standards (B, C, and D), which were also tested on the same instrument. I hope to compare bulk composition of weathering to composition of unweathered glass, and context soil.

XRD:

I am hoping to perform some XRD on the various weathering products to determine the extent of crystallinity, and the character of crystalline phase(s) present. Previous research has suggested that it is difficult to make conclusive assessment of this data[11]. I would like to compare the diffraction signature of the various weathering products to one another. I am particularly curious if this analysis can be used to probe the extent of weathering non-destructively.

Interpretations and Questions:

Imaging confirms that the weathering products are layered in structure. No two sherds seem to have weathered identically (even the two which appear to cross-mend), suggesting the importance of soil effects (moisture, pH, composition, temperature, etc...). Most of the weathering products recovered have not been well preserved, which makes observing the full progression of weathering layers impossible. However, AB-6 shows well preserved crust and may be characterized in further depth.

All quantitative and qualitative data (EDS, XRF, XRD) must be processed and normalized (against Corning reference standards) before any conclusions can be drawn. Compositional variation across the weathering crust must be probed, and compared against that of the unweathered glass core. These comparisons can then be evaluated against data reported in the literature.

[11] Cox, G A., and B A. Ford. "The Long-Term Corrosion of Glass by Ground-Water." Journal of Materials Science 28 (1993): 5637-5647.

Appendix I: Artifact Images

(See Artifact Catalogue for full listing, context info, and descriptions)

Fig 1, GF1731 13609 (AB-6)

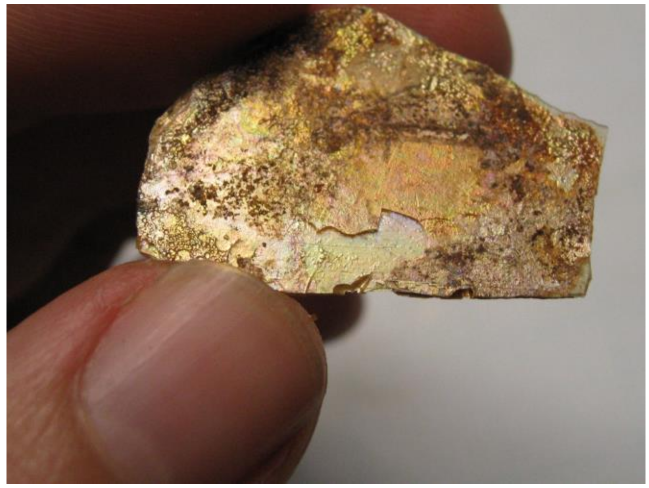


Fig 2, GF1716 13359 (AB-4)

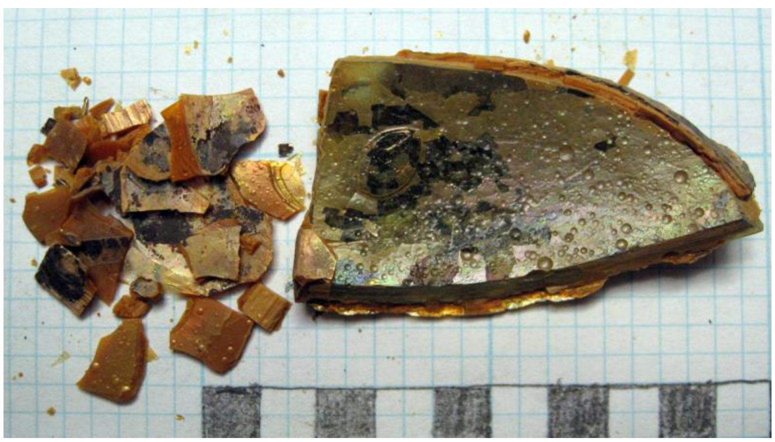


Fig 3, GF1710 13098

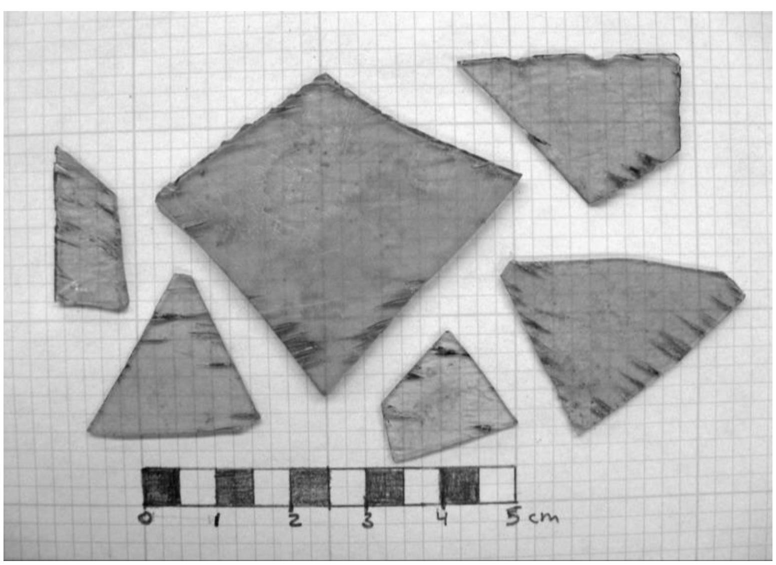


Fig 4, GF1710 13269 (selection)

Appendix II: Optical Microscope Images

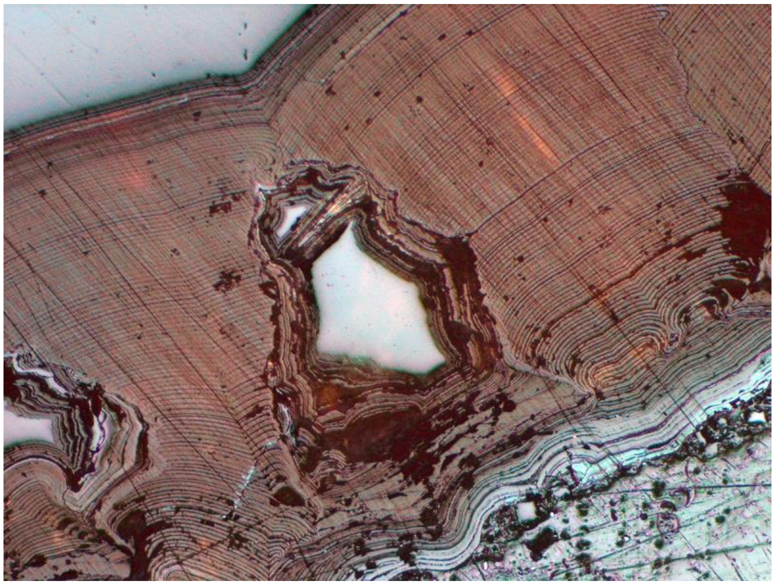


Fig 5, AB-6 (50x)

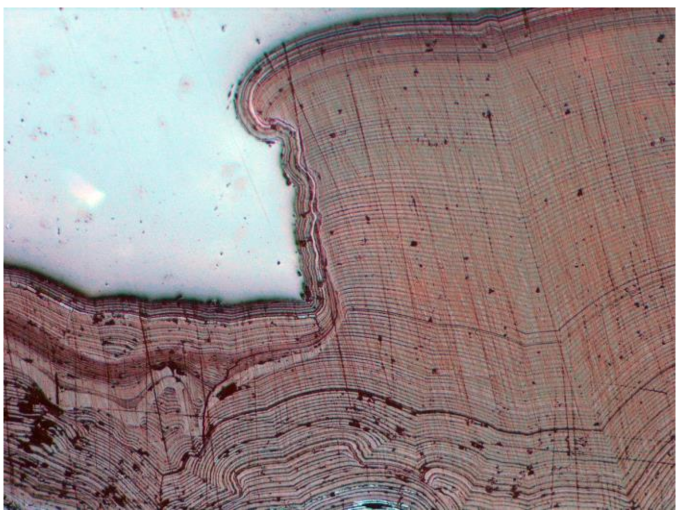


Fig 6, AB-6 (50x)

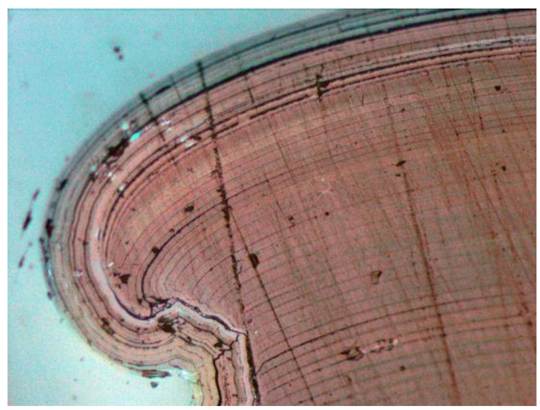


Fig 7, AB-6 (200x)

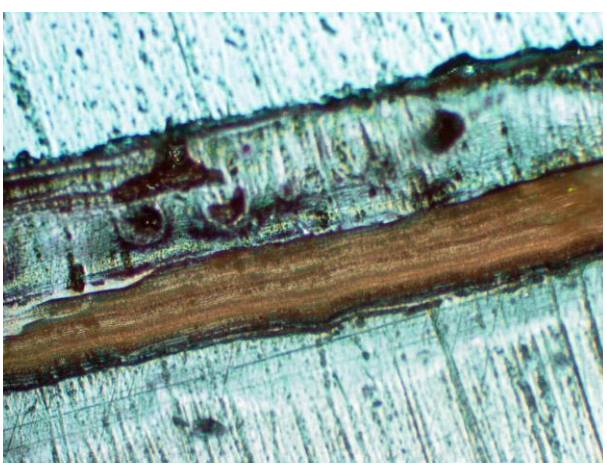


Fig 8, AB-4 (50x)

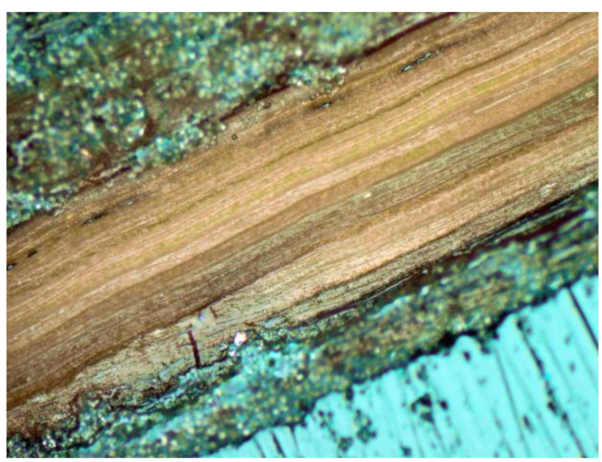


Fig 9, AB-4 (200x)

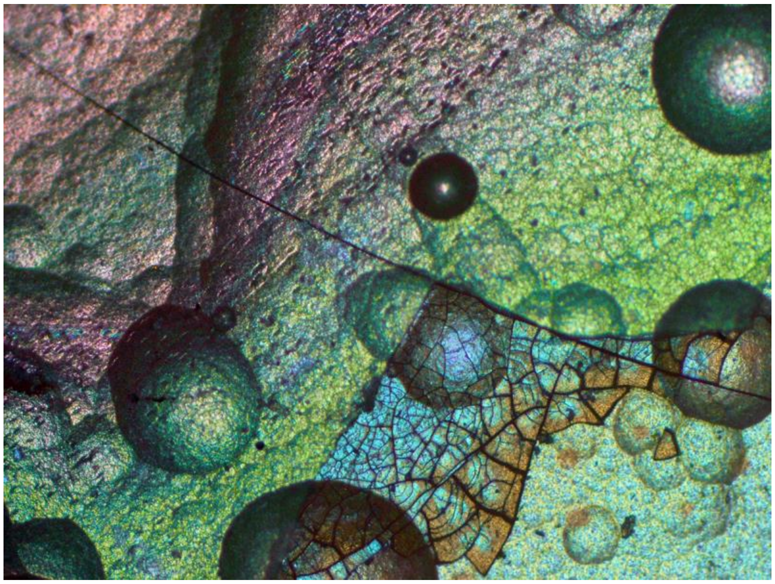


Fig 10, 13098 (50x)

Fig 11, 13098 (200x)

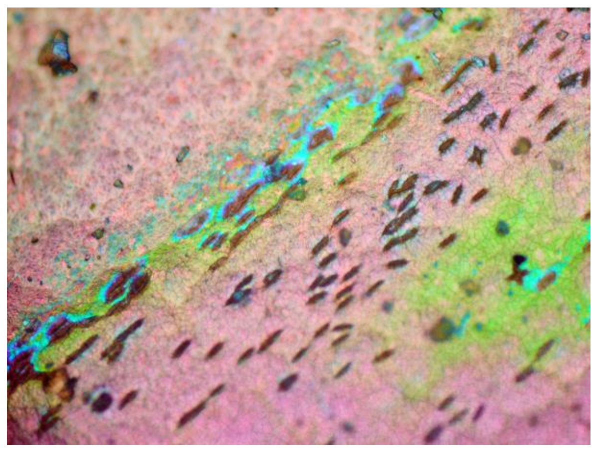


Fig 12, 13098 (200x)

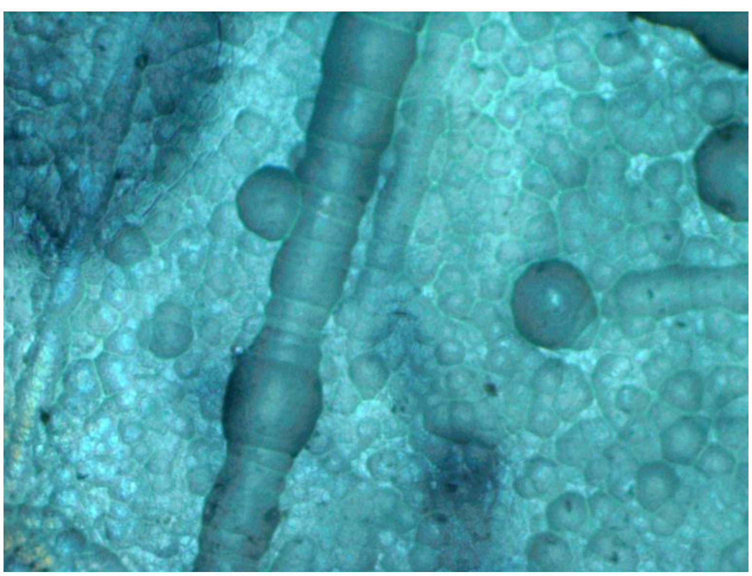
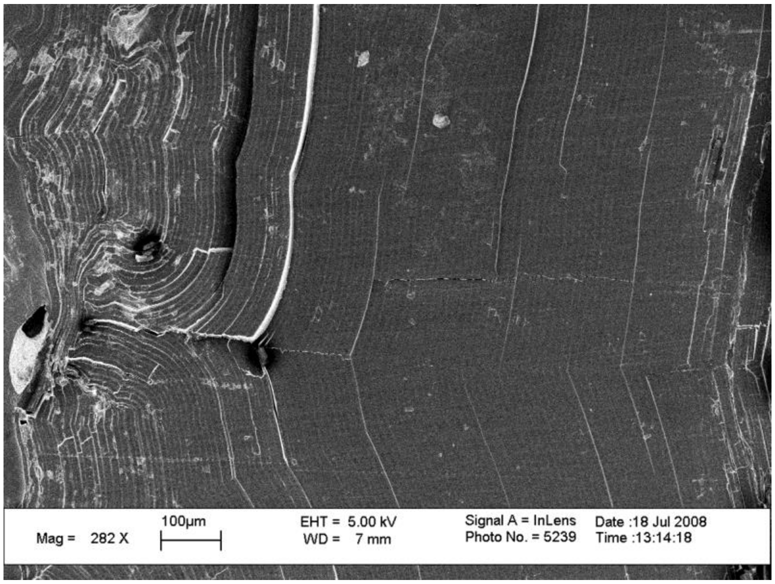
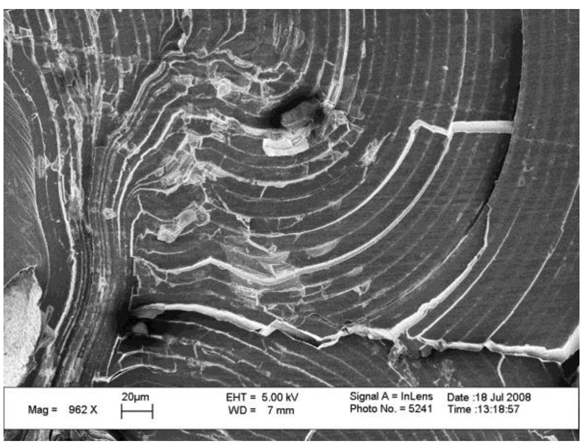


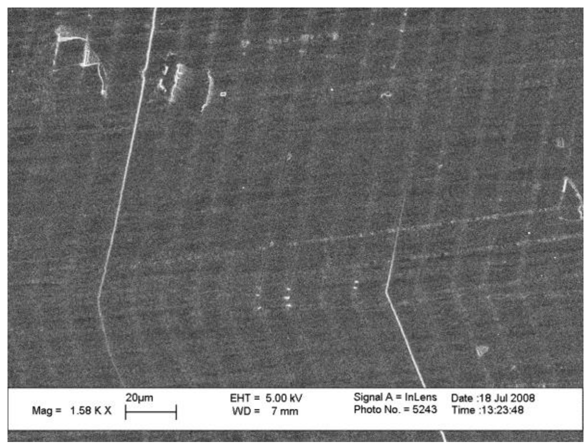
Fig 13, 13098 (50x)

Appendix III: SEM Images



AB-6 (In Lens)
Fig 14 (Left)
Fig 15(below, left)
Fig 16(below, right)





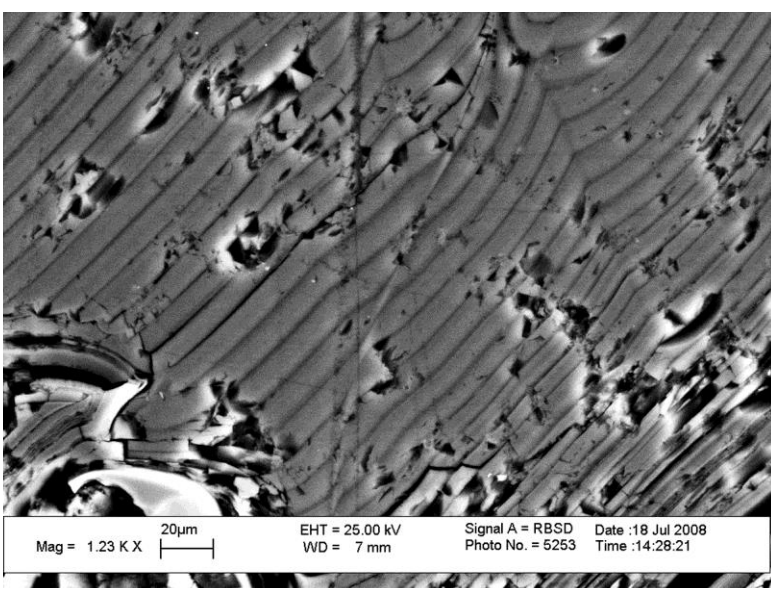


Fig 17, AB-6 (Backscatter)

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