Analyzing deteriorated glass using pXRF: A preliminary study of vitreous beads from the Late Bronze Age/Early Iron Age tumulus of Lofkënd in Albania

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Excavated from 2004-2008
- 100 graves
  - some with multiple burials
  - 150 individuals
- Burials date from 14th c. - 6th c. BC.
  - Most 9th-early 8th c. BC.
  - Tumulus reused in 19th c. AD
Factors influencing analytical methodology:

- Elements present unknown
- Heterogeneity of matrix
- Deterioration/condition
- Limitations of the instrument-no Na
- Size of beads
- Spot size of instrument (≈5mm)
- Surface geometry-curved
Bruker Tracer III-V pXRF excitation conditions:
- no filter, 40 kV, 1.6 µA, vacuum, 180 seconds
- Ti-Al filter, 40 kV, 1.6 µA, 180 seconds
- Cu filter, 15 kV, 15 µA, vacuum, 180 seconds
Spectrum overlay used to compare areas because of heterogeneity/decoration
- Blue-green glaze over a quartz core
- Barrel bead with a raised grid pattern
- Glaze contains Cu, Pb and Sn
  - possible reuse of bronze scrap as copper/color source?
Similar elements found regardless of color (blue-green, white, yellow, amber, dark green)

- Contained Al, Si, S, K, Ca, Ti, Mn, Fe, Cu, Zn, Pb, Sr, Zr
- K is from alkali flux-plant ash
  - mixed alkali with Na and K, used in this time period
- Fe colorant for most beads, and Cu for a blue bead (top left)
Glass Beads

- Differences noted in beads with white decoration
  - More intense Pb peak
  - Presence of Sb
    - Both used to make opaque white glass as lead oxide or calcium antimonate

- Verified presence of Sb in white using XRD
  - Calcium antimonate (CaSb\textsubscript{2}O\textsubscript{6}, Ca\textsubscript{2}SbO\textsubscript{7})
  - Antimony oxide (Sb\textsubscript{6}O\textsubscript{13})
Black or brown alteration/staining on glass
Dark green glass can be formed by:

- Presence of Fe$^{2+}$ and Fe$^{3+}$
- Presence of a ferri-sulfide complex (Fe$^{3+}$, S$^{2-}$)
  - Combines with Fe$^{2+}$ to make olive green, dark olive amber, amber glass
  - Occurs under strong reducing conditions
  - Only small amount of S needed—could be introduced in alkali

Fe$^{2+}$ (blue) + Fe$^{3+}$, S$^{2-}$ (amber) = dark green glass
Tend to see this alteration on glass with K as alkali
Alkali leaches out Si-rich layer with Fe from original glass
- gives it an orange or brown color
These glasses have thicker weathering crusts and break into chunks
Beginning of the orange-brown alteration?
Current Research Questions

- What were the original colorants of the glass?
- What elements were present in the corrosion layers?
- What role do the colorants and raw materials play in the alteration or level of deterioration observed?
- What role does the burial environment play in the alteration and deterioration of these beads?
Why is there such a difference in the condition of beads excavated from the same grave?

How does the alteration/deterioration affect the long term preservation of the beads?

Beads from Grave 77 (12-11th c. BC)
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And all of you for your attention!