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

Vanessa Muros
Conservator, UCLA/Getty Program

SAA Annual Meeting, April 6, 2013


Montenegro
Kosovo
Lake Scodra
Scodra
Drin
Lissus
Mat
Drin
FYROM
Ishëm
Epidamnos
Adriatic Sea
Albania
Tirana
Lake Ohrid
Lake Prespa
Shkumbin
Seman
Apollonia
Dimal
Devoll
Lofkënd
Aulon
Byllis
Amantia
Orikon
Shushica
Vjosë
Vjosë
Chimaira
Panormos
Antigoneia
Drinos
Phoinike
Bouthroton
Korkyra

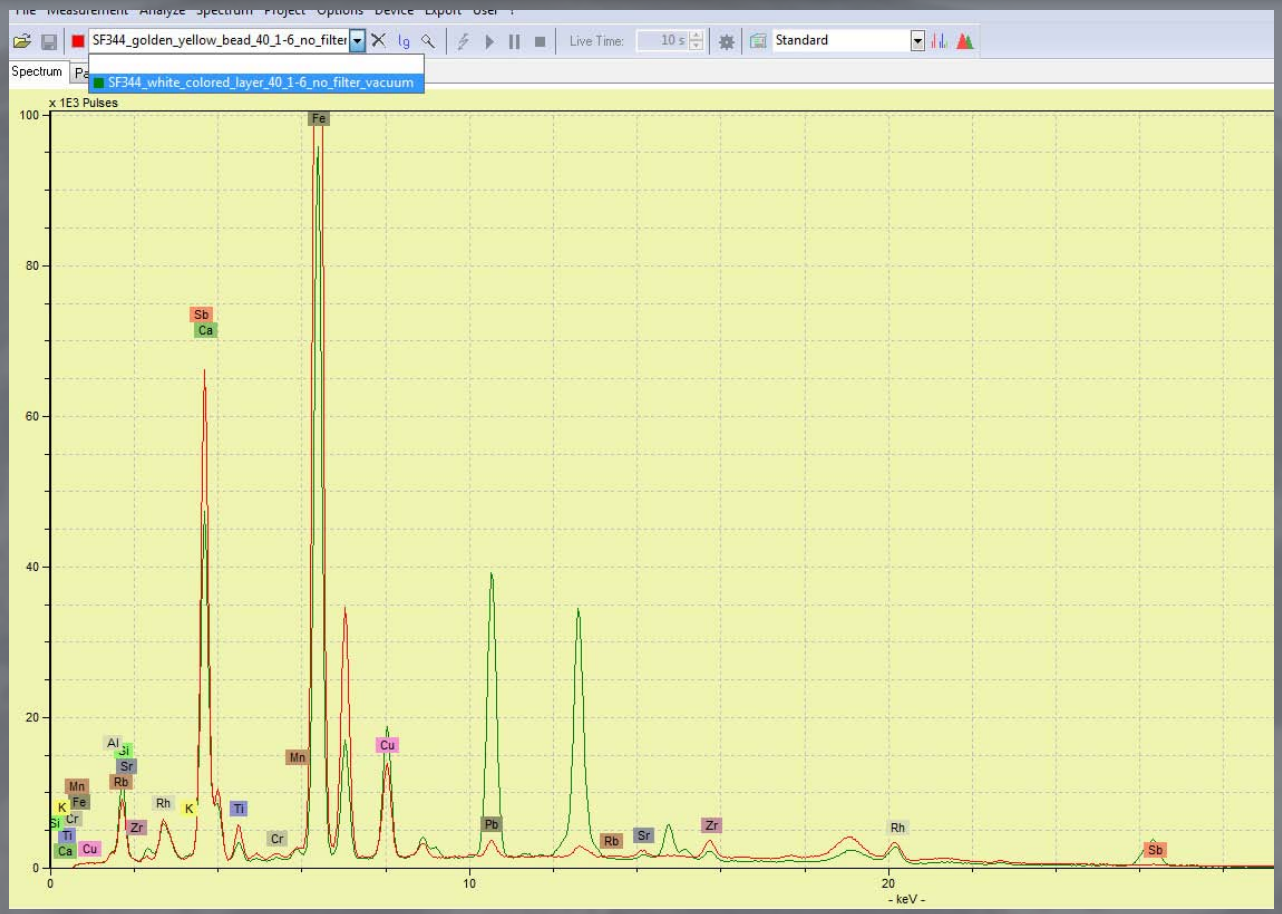
- Excavated from 2004-2008
- 100 graves
  - some with multiple burials
  - 150 individuals
- Burials date from 14th c. -6th c. BC.
  - Most 9th-early 8th c. BC.
  - Tumulus reused in 19th c. AD

SF294

- 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

SF339

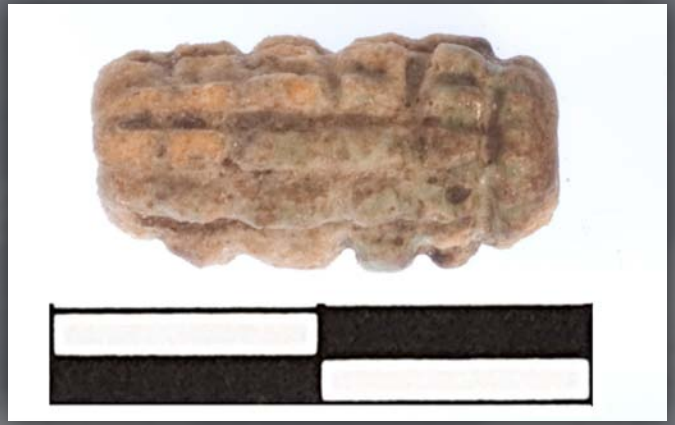
SF295

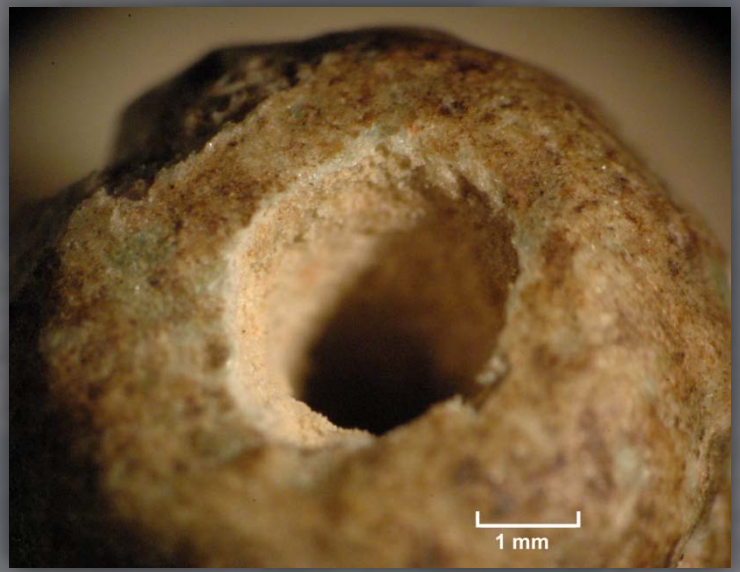


- Bruker Tracer III-V pXRF excitation conditions:
  - no filter, 40 kV, 1.6 µA, vacuum, 180 seconds
  - Ti-Al filter, 40 kV, 1.6 µA, 180 seconds
  - Cu filter, 15 kV, 15 µA, vacuum, 180 seconds
- Spectrum overlay used to compare areas because of heterogeneity/decoration

Faience bead

- 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?



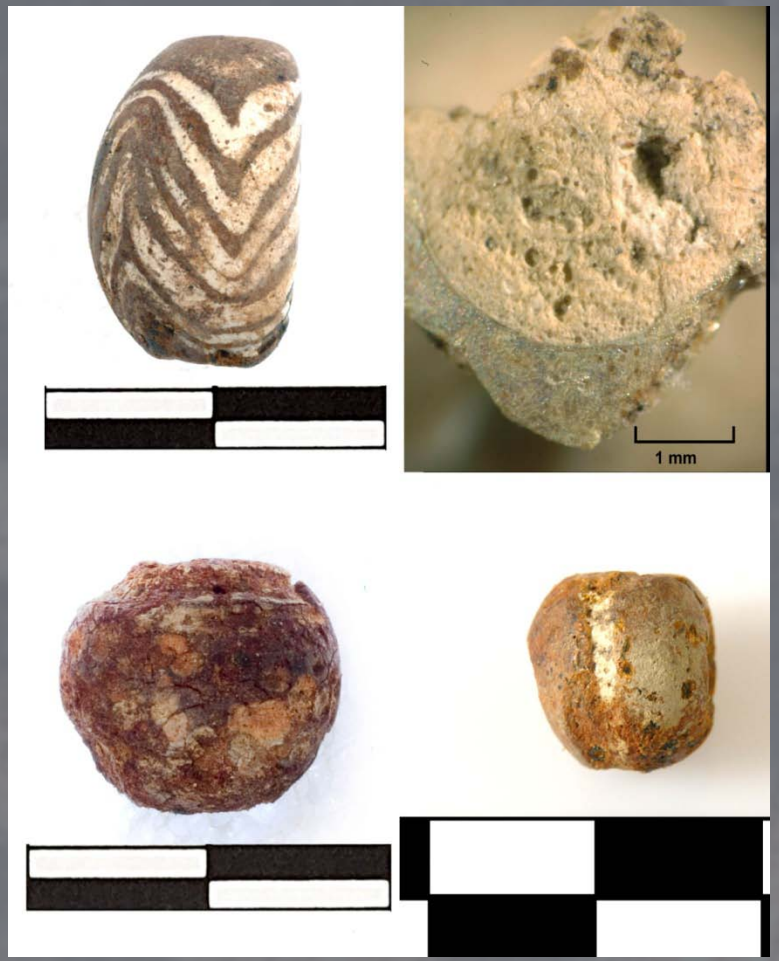


Glass Beads

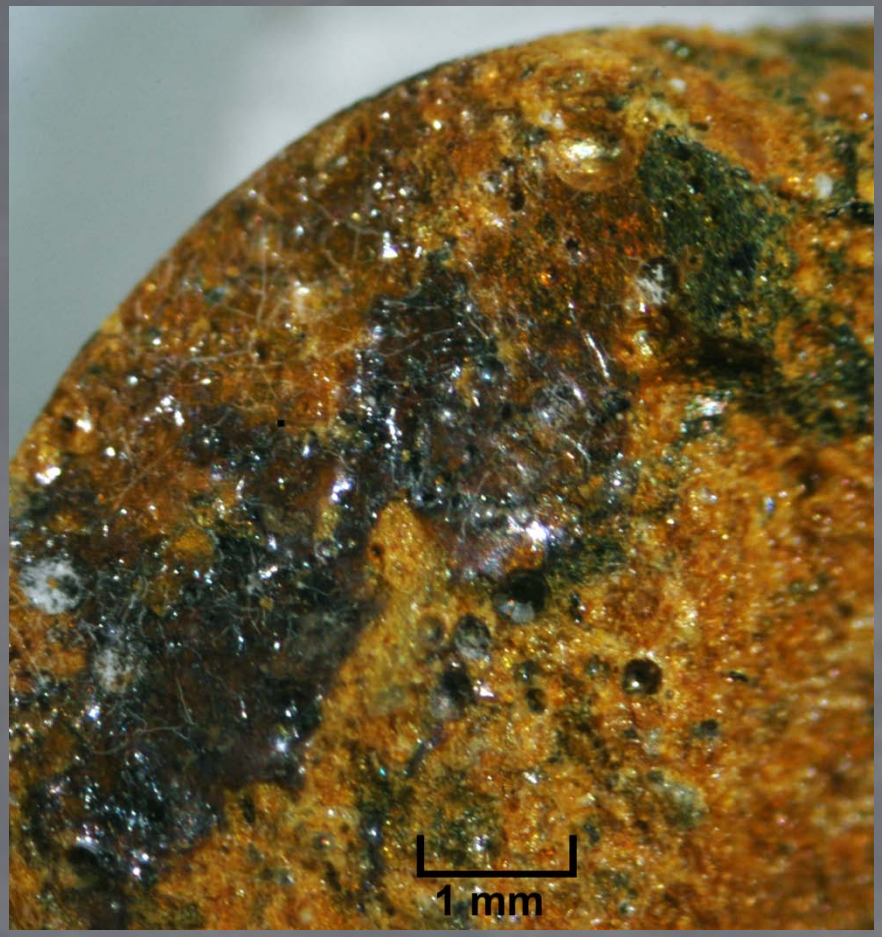
- Similar elements found regardless of color (blue-green, white, yellow, amber, dark green)
  - Contained Al, Si, S, K, Ca, Ti, Mn, Fe, Cu, Zn, Pb, Sr, Zr
  - K is from alkali flux-plant ash
    - mixed alkali with Na and K, used in this time period
  - Fe colorant for most beads, and Cu for a blue bead (top left)

Glass Beads

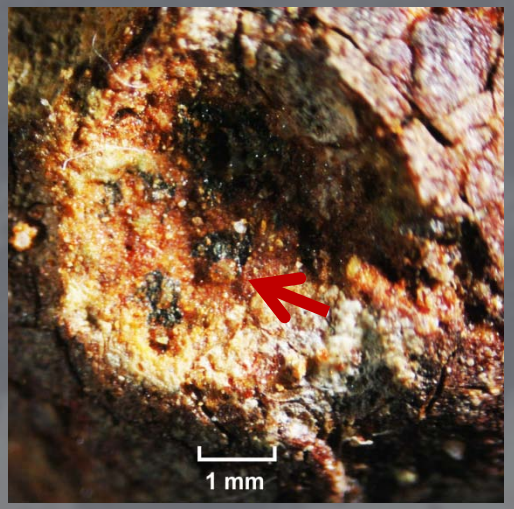
- Differences noted in beads with white decoration
  - More intense Pb peak
  - Presence of Sb
    - Both used to make opaque white glass as lead oxide or calcium antimonate
- Verified presence of Sb in white using XRD
  - Calcium antimonate ($CaSb_2O_6$, Ca_2SbO_7)
  - Antimony oxide (Sb_6O_{13})



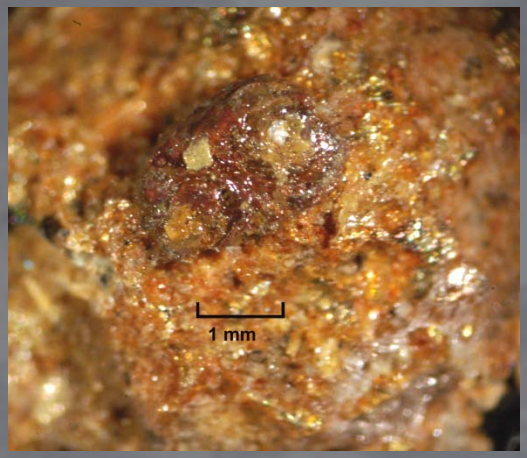
Black or brown alteration/staining on glass



SF341



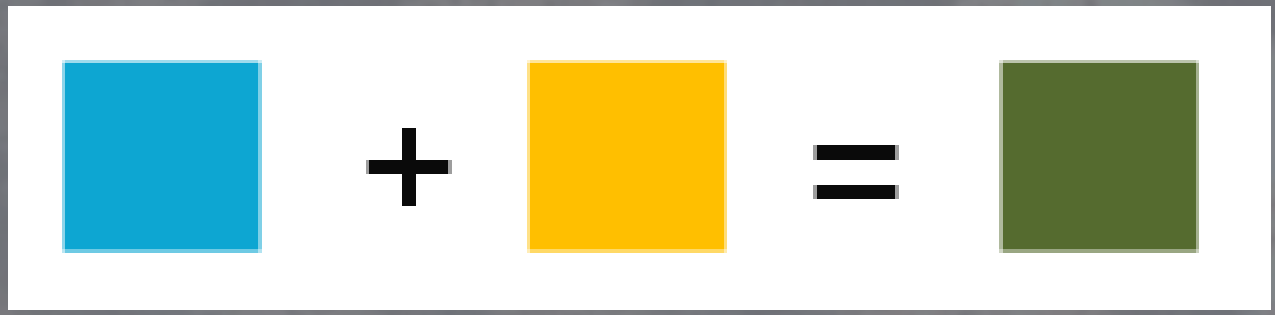
SF294



SF342

Ferri-sulfide compounds

- 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

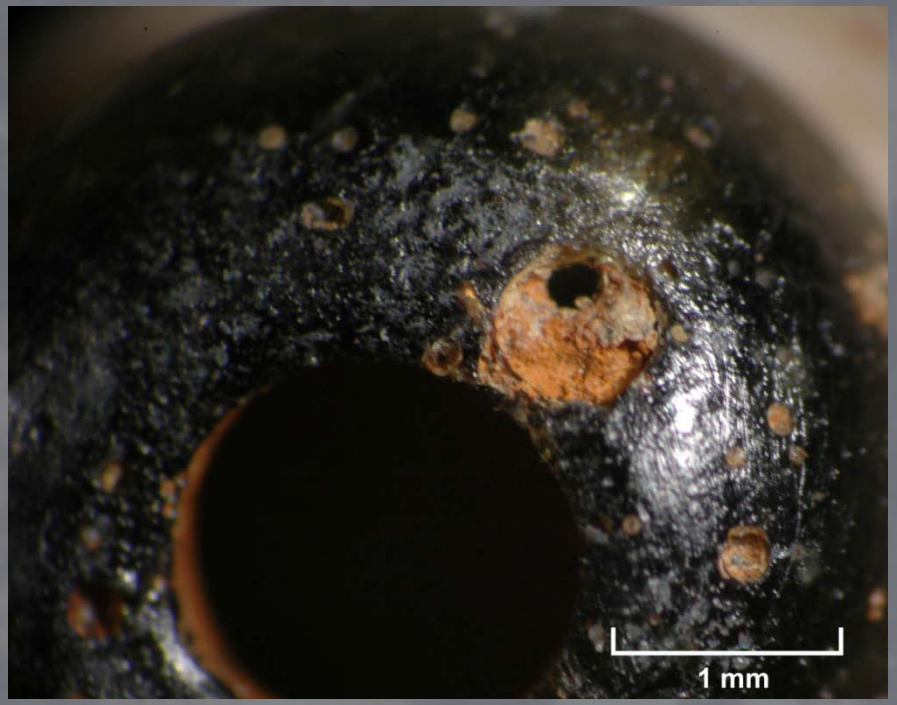
- Tend to see this alteration on glass with K as alkali
- Alkali leaches out Si-rich layer with Fe from original glass
  - gives it an orange or brown color
- These glasses have thicker weathering crusts and break into chunks

SF341

SF295

Beginning of the orange-brown alteration?

SF339



SF283

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)

Acknowledgements

- Lofkënd Archaeological Project
- Institute of Archaeology, Tirana
- UCLA/Getty Conservation Program
- Dr. Robert Brill
- Dr. David Scott
- Dr. Ioanna Kakoulli
- And all of you for your attention!