What lies beneath: Analytical studies of bronze and glass artifacts from the prehistoric tumulus at Lofkënd

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• Excavated from 2004-2008
• 100 graves
  ▪ some with multiple burials
  ▪ 150 individuals
• Burials date from 14\textsuperscript{th} c. -6\textsuperscript{th} c. BC.
  ▪ Tumulus reused in 19\textsuperscript{th} c. AD
Techniques used:
- Portable X-ray fluorescence spectroscopy (pXRF)
- Metallographic examination
- X-ray diffraction (XRD)
 Majority are tin bronzes, many of which are leaded
 Traces of arsenic (As), silver (Ag), antimony (Sb) and nickel (Ni)
 Trace elements consistent with the use of copper sulfide ores for smelting (used in region starting in 2500BC)
Objects made mainly through cold working and annealing after initial casting-annealing the final stage for most.

Some objects made from hammered sheet.

A few cold worked but still retain some of the cast structure or show localized working in areas.
Corrosion Studies

- No cuprite on 3 samples
- Dark green corrosion overlying metal surface and extending into metal core
- Strange colored green corrosion on surface
- Conducted XRD analysis of corrosion
Copper sulfate corrosion brochantite \((\text{Cu}_4\text{SO}_4(\text{OH})_6)\) was found on 5 of the samples. Common on outdoor bronze in polluted environments due to sulfur dioxide. Few examples in burial context, but often in discussion with pollutants in the soil or in storage environment.
Need a sulfur source

- Not a pollutant in the soil at Lofkënd
- Decomposing organic material (skin, hair, textiles)
Microorganisms (bacteria) in the soil break down the proteins in the organic material releasing sulfur in the form of sulfides (i.e. hydrogen sulfide).

Sulfides then get oxidized to form sulfates, similar to formation of brochantite on outdoor sculpture.

Oxidation could occur through presence of oxygen in soil or from oxygen release as by-product of microbial metabolic activity.
Two conditions that may have existed during burial that led to lack of cuprite—high sulfur content and low pH (acidity)

In outdoor sculpture, cuprite can be transformed into brochantite under acidic conditions

Low pH influences the growth of cuprite and promotes its dissolution

Conversion of cuprite to brochantite observed on Statue of Liberty patina
How do we get acidic conditions underground?

- From bacteria and decomposing organic material-organic acids released
- Sulfur used in agriculture to lower pH of soils
Elemental analysis of 10 glass and 1 faience beads

Techniques used:

- Portable X-ray fluorescence spectroscopy (pXRF)
- X-ray diffraction (XRD)
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 or mixed alkali
  - Both used as this time period but can’t determine which one due to pXRF limitations
- Fe colorant for most beads, and Cu for a blue bead (top left)
4 beads had white decoration
- Presence of Sb
  - Used to make opaque white glass as lead oxide or calcium antimonate

- Verified presence of Sb in white using XRD
  - Calcium antimonate ($\text{CaSb}_2\text{O}_6$, $\text{Ca}_2\text{SbO}_7$)
  - Antimony oxide ($\text{Sb}_6\text{O}_{13}$)
Orange-brown or amber alteration?
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

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\begin{align*}
\text{Fe}^{2+} \text{ (blue)} & \quad + \quad \text{Fe}^{3+}, \text{S}^{2-} \text{ (amber)} \\
\text{dark green glass} & \quad = \quad \text{dark green glass}
\end{align*}
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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?
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 (12-11\textsuperscript{th} c. BC)
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