What Can Microchemical Spot Testing Tell Us About the Composition of Archaeological Glass?

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Background

Research suggests that the chemical composition of glass directly relates to its long-term stability. Archaeological glass offers unique challenges for analysis because of its complex laminar structure, a degraded surface that is chemically distinct from the bulk glass.

In the absence of advanced analytical equipment, microchemical spot tests employ simple chemical reactions to identify the presence of specific elements or compounds, providing an accessible way to characterize materials. Their results are qualitative, and the tests are often destructive. Therefore, conservators rarely perform exploratory "spot tests" or investigate their limitations on complex materials.

This project explores the efficacy of a microchemical spot test for calcium in glass by comparing spot test results to elemental point analysis and mapping with X-ray fluorescence. "Testing the test" expands understanding of existing tools and their application

Above and Below: Archaeological Glass Goblet, 200-399 AD, Penn Museum (Object 86-35-30), Normal illumination

Degradation of Archaeological Glass

Moisture in the burial environment leaches the network modifiers (Na, K, Ca) from the glass body and redeposits them on the surface. Moisture levels, soil pH, and the components of the original glass body all affect the corrosion formation.

Chemical analysis of the corrosion may offer clues to the glass' original chemical composition or burial environment

A reliable microchemical spot test exists for **calcium** so this test serves as a case study.

Object

Archaeological Glass Goblet, Penn Museum (Object 86-35-30)

- University of Pennsylvania Museum of Archaeology and Anthropology dates to 200-399 AD.
- Possibly Roman glassware, potentially excavated in Damascus, Syria.
- **Provenance:** Donated to the Penn Museum in 1985. Provenance details originate from the dealer's information.
- **Condition:** Evidence of prior repairs, currently in six fragments. Varying degrees of darkening, laminar corrosion, pitting, and white deposits on all surfaces.

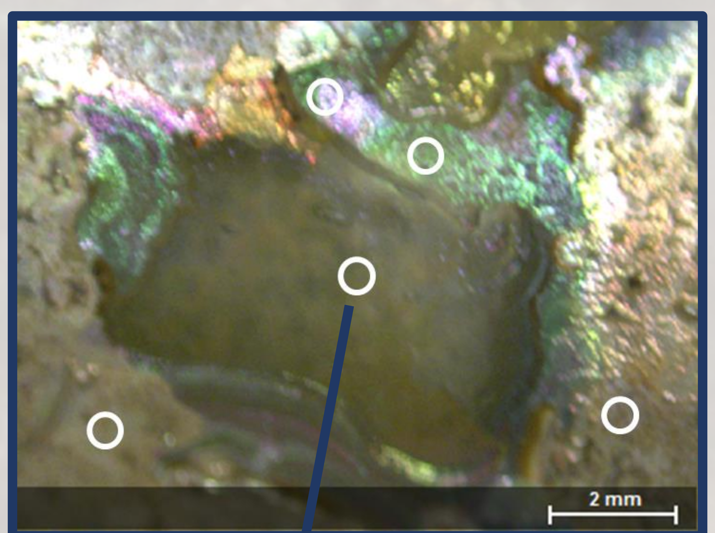
Methodology and Results

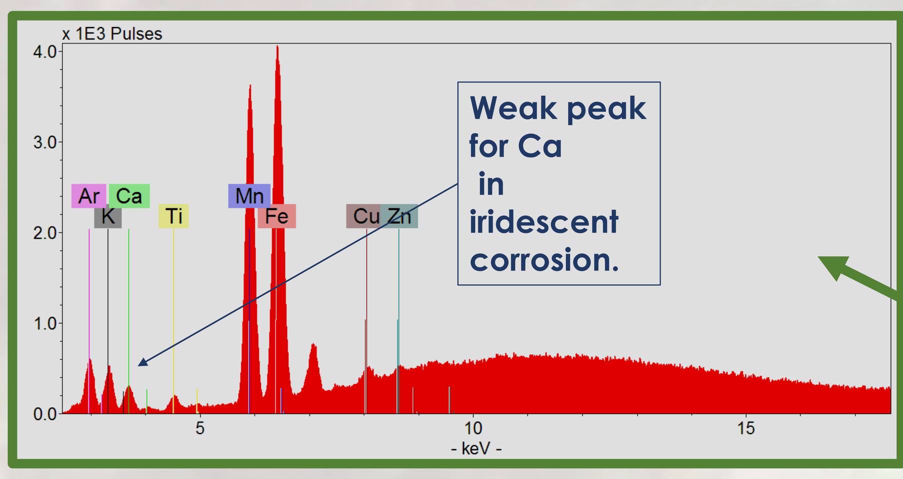
1. Pinpoint Analysis and Elemental Mapping with X-ray Fluorescence (XRF)*

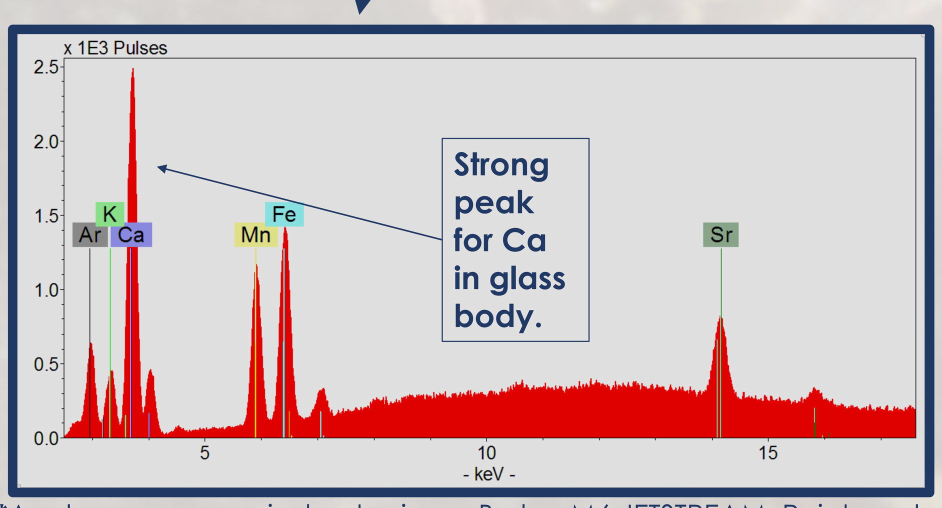
37 Locations were analyzed on all areas of the goblet and corrosion flakes to generally characterize calcium levels.

RESULTS: Strong peaks for Ca in the glass body and weak peaks for Ca in the corrosion for all testing locations

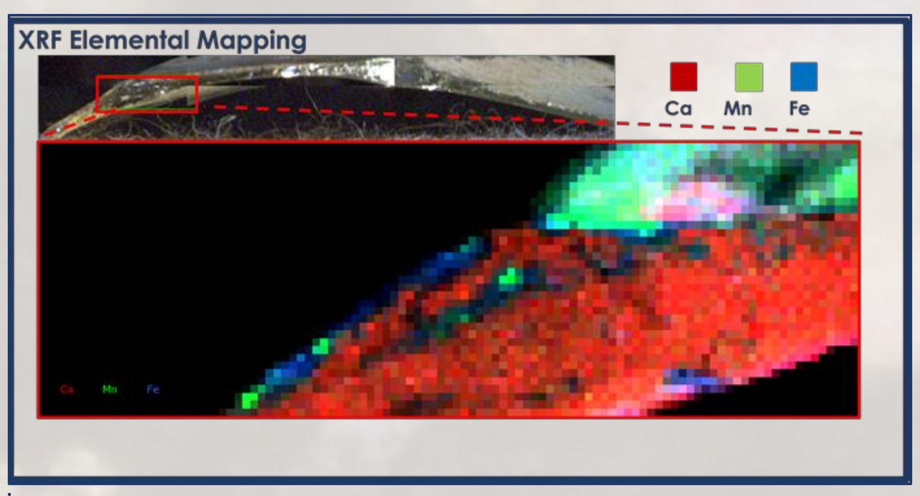
Glass Body







*Analyses were carried out using a Bruker M6 JETSTREAM. Point analysis mode: 40 kv, 700 µA at a 30 second live time. Elemental mapping: 40 kv 699 µA, 50 ms/pixel, Polycapillary lens (100 µm spot size) air, no filter



False-color elemental mapping of a cross-sectional break edge of a fragment shows high Ca in the glass body.

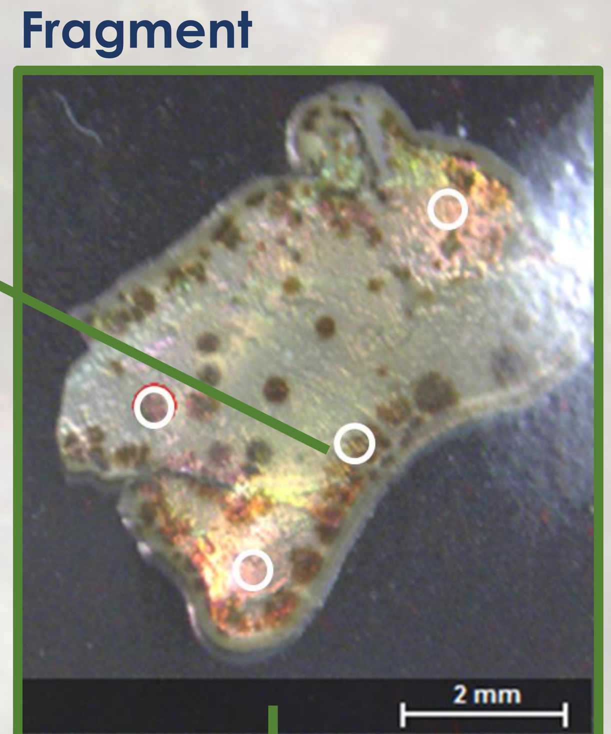
2. Microchemical Spot Test for Calcium

This test qualitatively assesses the presence of calcium in a solid sample.

The corrosion flake previously analyzed by XRF (pictured below) was divided into three samples, and each was dissolved using 0.5M nitric acid. A drop of each solution was treated with 2M sulfuric acid.

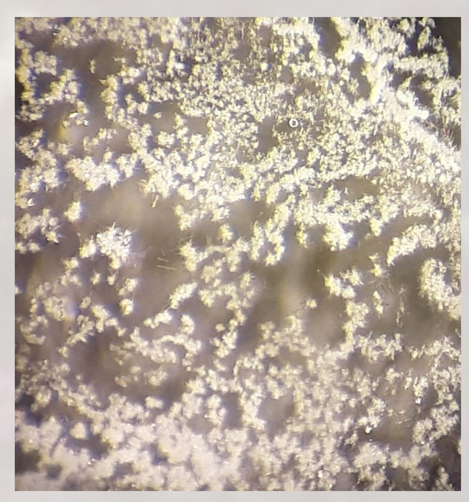
A positive reaction would be indicated by the formation of calcium sulfate ($CaSO_4 \cdot 2H_2O$), or gypsum, observable by characteristic white "needle" crystals.

Corrosion Fragment



$$Ca^{2+}(aq) + SO_4^{2-}(aq) \rightarrow CaSO_4 \cdot 2H_2O(s)$$

RESULTS: No crystals of calcium sulfate were observed in any sample.



Right: known positive (calcium carbonate) test result. Gypsum crystals are clearly visible. 20X magnification.

Left: *glass corrosion sample 2 of 3, negative test result. 20x magnification*

Conclusions

Weak peaks suggest trace amounts of calcium in the corrosion layers, while the bulk glass showed strong peaks. This implies calcium did not leach from the bulk glass and another degradation mechanism may have occurred.

The spot test results were negative for calcium in the corrosion. Given the trace levels of calcium detected by XRF, this result was not unexpected. This study suggests that this microchemical spot test cannot detect trace amounts of Ca, and spot tests do not work on all forms of glass corrosion as not all corrosion contains enough detectable Ca.

Further Questions/Future Work

- Is the calcium detected by XRF from the bulk glass, or burial conditions?
- What degradation pathways led to Mn and Fe in the corrosion?
- Can spot tests be effective on a wider range of corrosion products, for example, Iron?

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