Geochemistry of Anatolian Obsidian: Implications for Sourcing and Dating of Artifacts

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Abstract

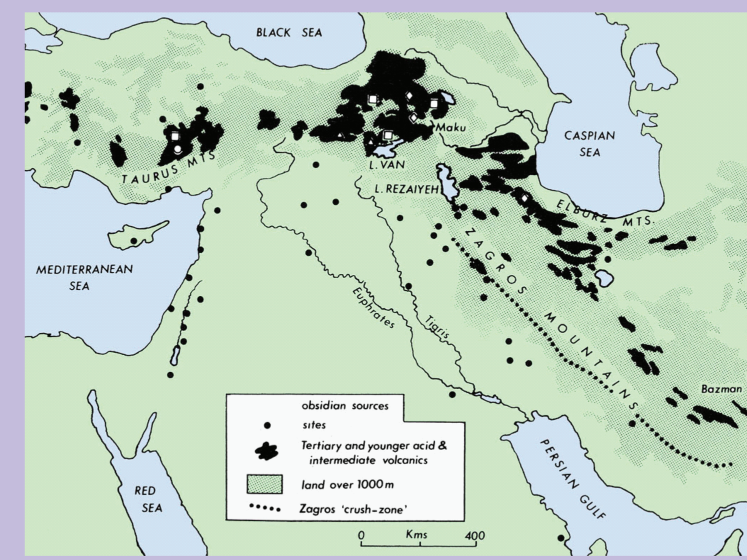
Abundant volcanism in southwest Asia provided early civilizations with obsidian, which was used to manufacture tools and other carved items. Because each obsidian flow has a unique chemical composition, ancient trade routes can be traced, and artifacts can be sourced to the volcanoes from which they originated. The presence of water in obsidian is also invaluable to both geologists and archaeologists. The relative abundance of the two hydrous species in obsidian (OH hydroxyl groups and molecular H2O) allows geologists to distinguish glasses that retain their initial magmatic water content from those that have experienced post-eruption hydration. In addition, the diffusion of water into exposed surfaces of glass artifacts has allowed archaeologists to develop a relative dating technique for the manufacture of obsidian artifacts.

Using the XRF at UWEC, we perform an analysis of major and trace element composition of obsidian samples from 30 different flows in southwest Asia. We then compare our results with microprobe measurements of the same suite of obsidians, taken by Ellery Frahm at the University of Minnesota. These measurements are compared with micro-FTIR measurements of hydrous species concentrations previously taken at UWEC. We find that samples that experienced low-temperature, post-eruption hydration also experienced depletions in SiO2, Na2O, and Fe2O3.

Motivation: Obsidian Artifacts from Early Civilizations

Obsidian outcrop in Anatolia, Turkey

Young Felsic Magmatism in the Near East

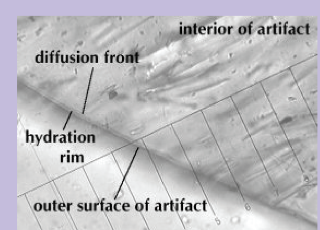


Obsidian artifacts can be used by archaeologists to:

I. Determine the specific lava flow from which it was derived:

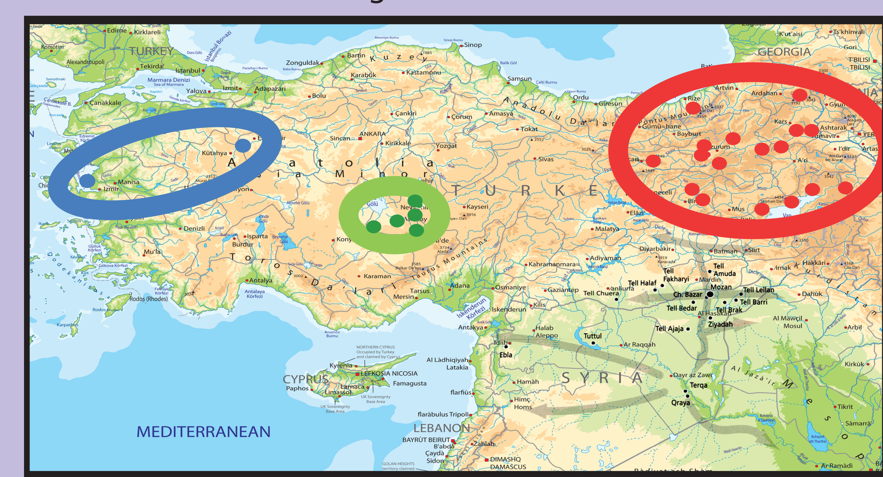
The trace element concentration of every obsidian flow is unique. As a result, every obsidian artifact can be sourced to an individual lava flow. This information allows archaeologists to establish the evolution of ancient trade routes (Griffin et al., 1969).

II. Determine the time elapsed since the artifact was manufactured:



Photomicrograph of edge of obsidian artifact showing hydration rim. The rate of advancement of the diffusion front is dependent on the time of exposure, the bulk composition of the glass, the climate (temperature and rainfall), the depth of burial, *and the initial water content of the glass* (Anovitz, 1999). Image from: www.obsidianlab.com/services.html

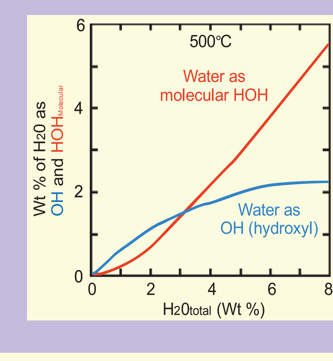
Geographic Distribution of Anatolian Rhyolites and Ancient Trading Routes in the Fertile Crescent



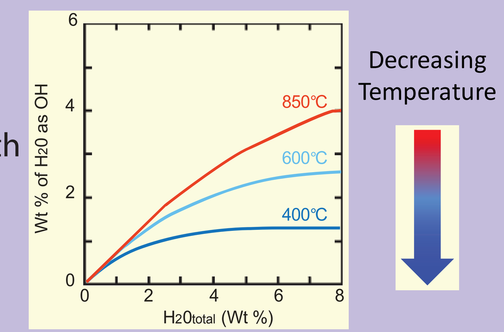
Anatolia and Upper Syro-Mesopotamia. Large colored dots represent obsidian lava flows. Small red dots are modern cities. Black dots are some of the important archaeological sites. Gray arrows represent principal trade routes around Urkesh (figure modified from Buccellati, 1997).

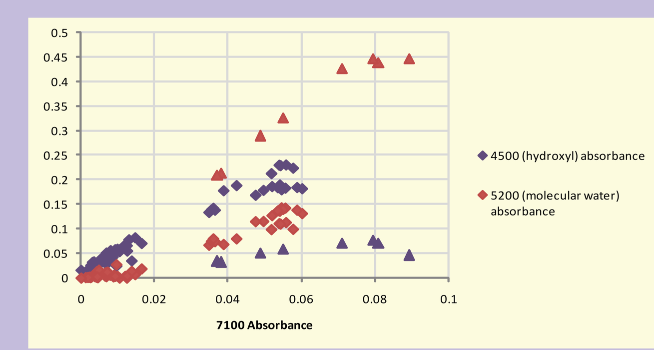
Our Previous Findings: Water Speciation as a Geothermometer

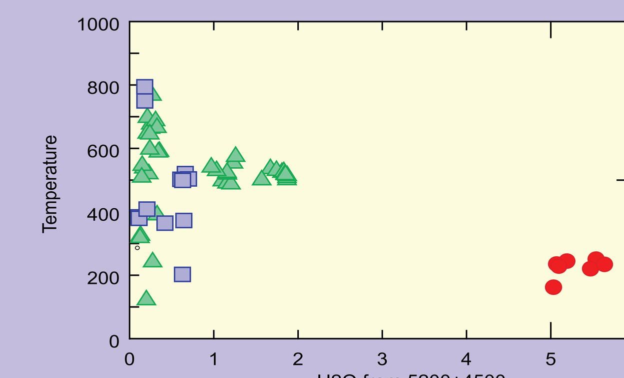
Two Hydrous Species in Rhyolite



Fraction of Dissolved Water as OH Changes with Temperature

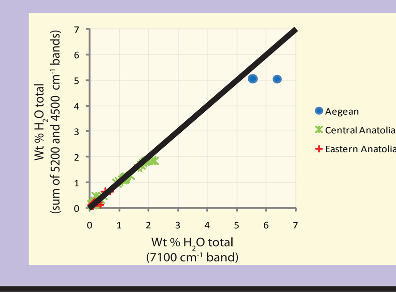




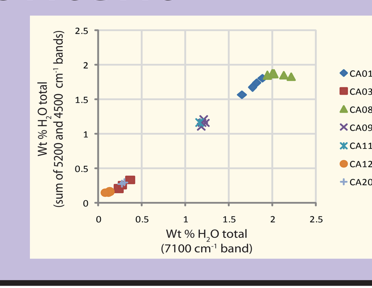


Equilibration of the two water species Si-OH (hydroxyl) and HOH (molecular water) is strongly temperature dependent and can serve as an effective measure of the temperature at which the glass was last at equilibrium.
Two trends of water speciation, one reflecting equilibration at high temperature (~500C--the glass transition temperature expected for magmatic water upon eruption) and another reflecting equilibration at low temperature (~200C--the temperature expected for post-eruption hydration via diffusion of surface water).

Water Content



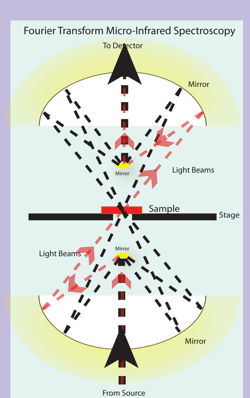
Some regional differences in total water content are apparent.

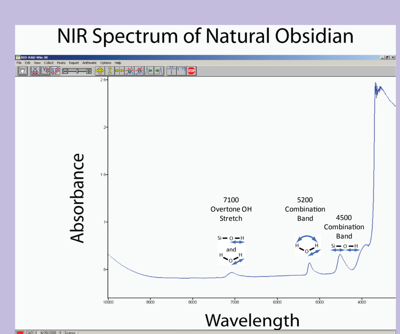


Observable variatons on the millimeter scale within individual polished wafers of Anatolian obsidian are apparent.

Methods

How the IR Microscope Works



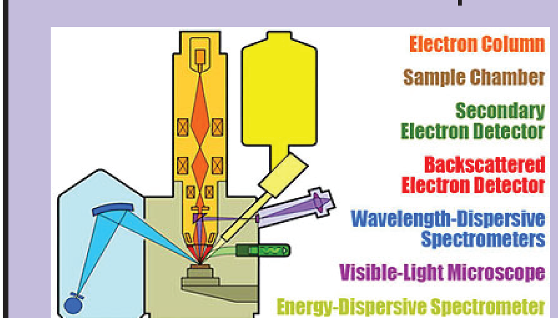


Schematic illustration of conoscopic focus in the FTIR microscope, enabling high spatial resolution

The XRF Facility at UW-Eau Claire

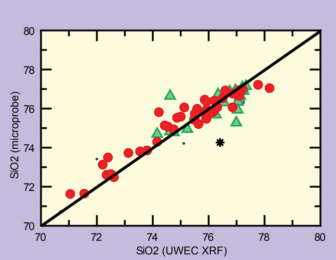
The X-ray fluorescence instrument emits intense X-rays which are directed at the sample. The X-rays hit the atoms in the sample and cause the inner shell electrons to be ejected. Outer shell electrons then fill in the occupied spaces in the inner shells. This exchange creates X-rays at varying frequencies which can be measured and correlated to specific elements, allowing the chemical composition of the sample to be determined.

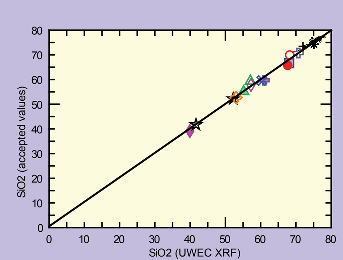
The Electron Microprobe at UM-Twin Cities



The electron microprobe emits electrons onto a 1-9 micron spot on the sample which excite atoms in the sample, causing them to produce characteristic X-rays. Because each element produces X-rays at specific frequencies, all elements except H, He, and Li can be detected and the chemical composition of the sample can be determined.

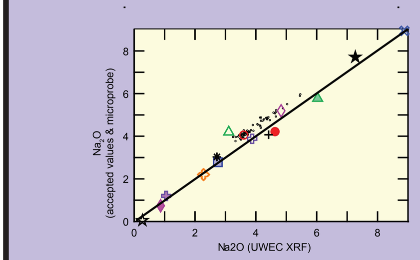
Calibrating Two Techniques: XRF vs Microprobe

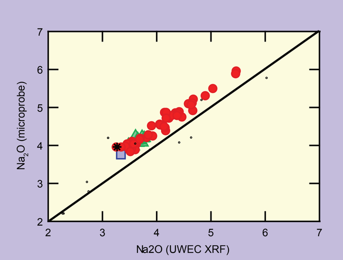




Silica values measured with the XRF and the microprobe are consistent with accepted standards. Line is drawn to show 1:1 correlation.

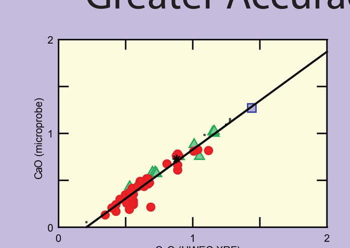
Alkalis
Greater Accuracy with XRF

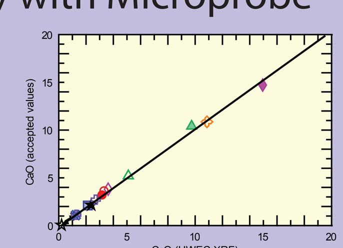


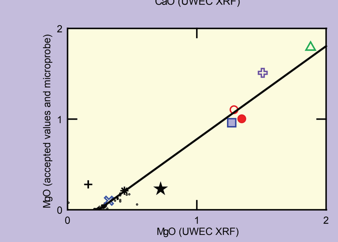


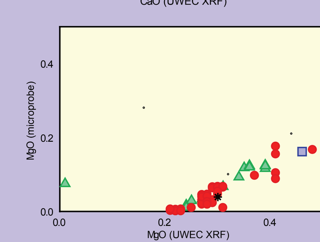
XRF measurements of alkaline elements appear to be slightly more accurate than microprobe measurements. Line is drawn to show 1:1 correlation.

Major Elements
Greater Accuracy with Microprobe





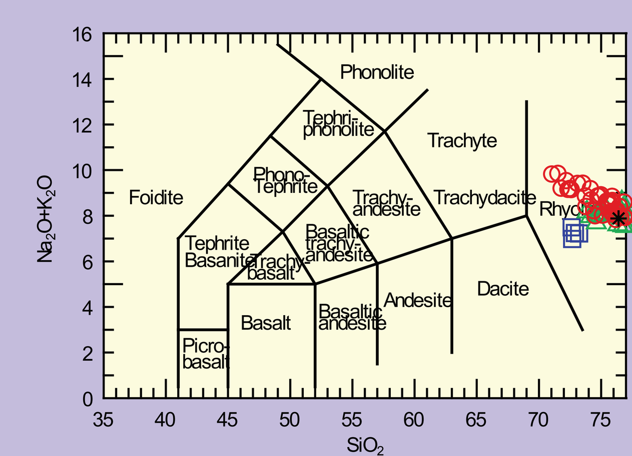


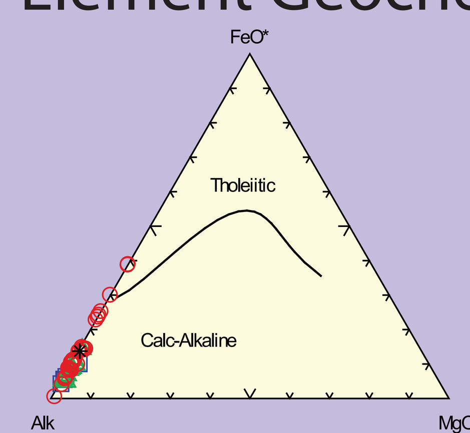


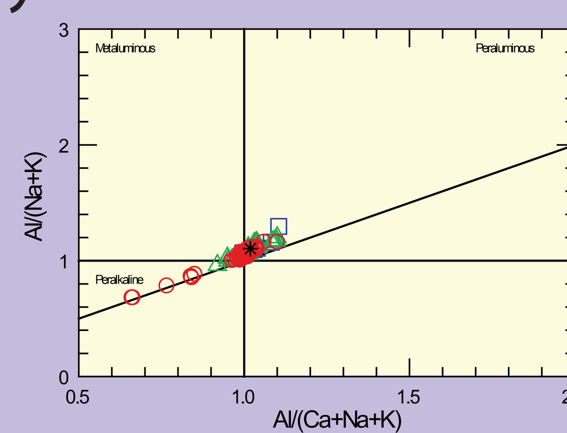
The XRF measurements exhibit a slight offset, which most likely is accounted for by an imprecise calibration. However, the advantage of the microprobe is that it is able to extract major element variations that help to constrain the source locality of a particular sample, with minimal destruction of artifacts. XRF sample preparation involves crushing samples into a fine powder, whereas microprobe measurements can be taken from a spot directly on a given artifact with a spacial resolution of 10 nanometers.

Geochemistry of Anatolian Obsidian

Major Element Geochemistry

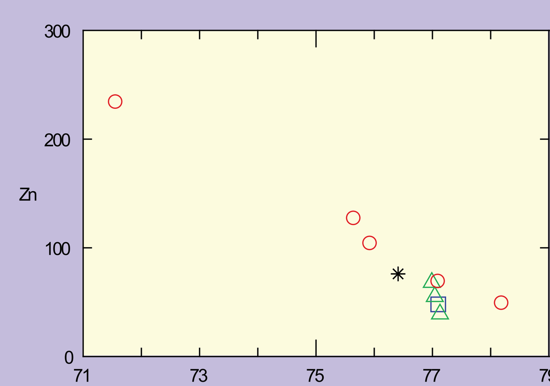


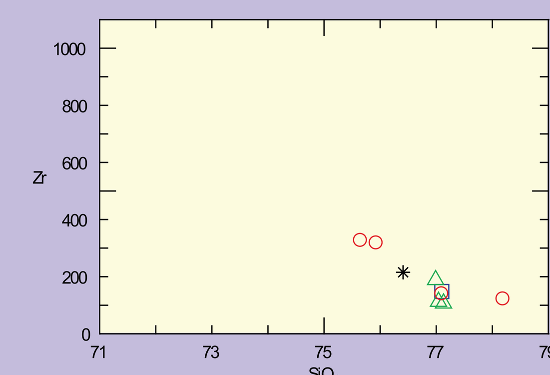


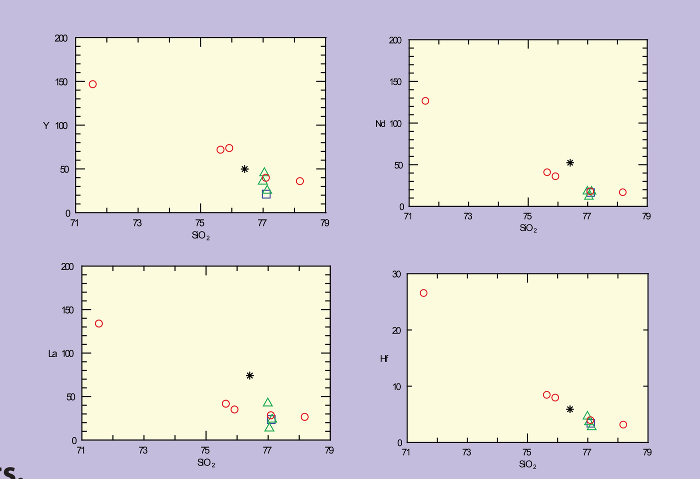


Major element compositions of eastern Anatolian obsidians show them to be peralkaline rhyolites.
Magmas from central and western Anatolia are more felsic and metaluminous in character.

Trace Element Variations: **Useful Indicators of Obsidian Sources**

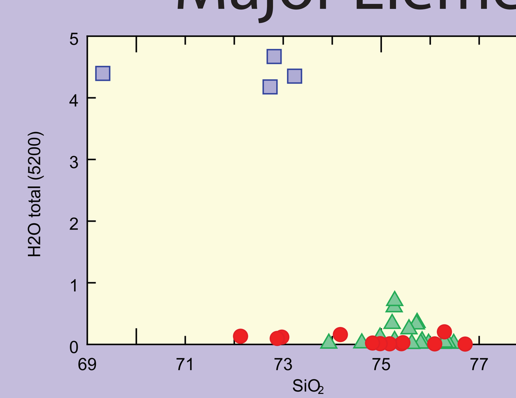


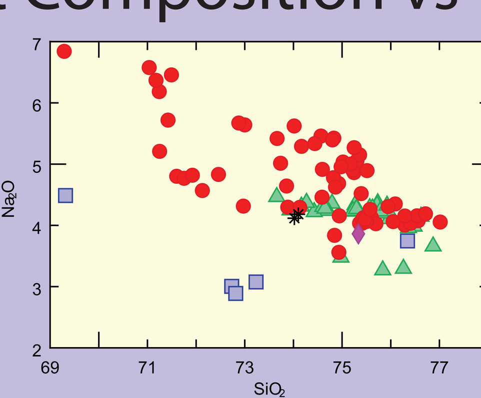


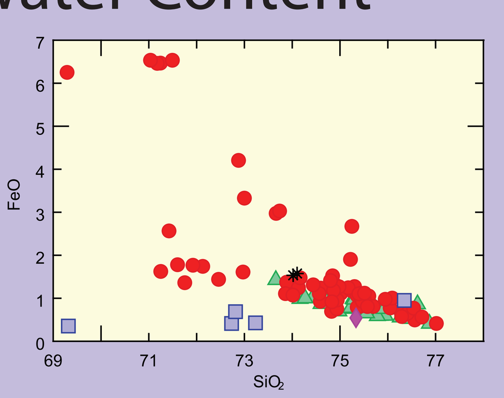


There are order-of-magnitude changes in zinc and zirconium concentrations between samples, illustrating that geochemistry can be used to accurately source obsidian artifacts.

Major Element Composition vs Water Content







In general, there is no correlation between major element composition and total water in Anatolian obsidians.
However, samples with elevated water contents have significantly lower Na_2O and FeO contents.

Conclusions

- The wide variations in trace element compositions between different samples, especially in zinc and zirconium, allow the source locality of an obsidian sample to be determined.
- XRF and electron microprobe measurements are generally consistent with standard accepted values. However, some elements are better measured with one technique rather than the other.
- Obsidian samples from the Middle East have a wide range of water contents. Regional differences in total water content may be real, but more data is required to verify this observation.
- The obsidian samples from the Aegean have unusually high water contents. The concentration of hydrous species within the glasses preserves the temperature of equilibration and reflects that some Anatolian glasses have experienced low temperature hydration of meteoric water.
- The observed variability of total water content in single, mm-sized wafers requires caution in interpreting obsidian hydration dates of individual artifacts. In order to extract reliable hydration ages on artifacts manufactured from Anatolian obsidian, care should be taken to characterize the water content adjacent to each spot where hydration rim measurements are performed.

What's Next

In the future, we will continue to look forcorrelations between water content and other aspects of rhyolite geochemistry, including major and trace element, and Sr, Nd, & Pb isotope composition. We hope to obtain obsidian artifacts from a representative suite of archaeological sites in space and time in order to expand our knowledge of trade routes during the development of early civilization.

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Acknowledgments

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