

OBSIDIAN ANALYSIS WITH RAMAN SPECTROSCOPY

APPLICATION NOTE RAMAN-013 (US)

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Abstract

A portable TSI ChemLogix EZRaman-I instrument was used to perform obsidian composition analysis on archaeological samples.

Motivation and Background

Obsidian is volcanic glass, formed when lava with high silicon and aluminum content cools too quickly to form crystals. It incorporates other metals as they are present in the lava and crust near volcanic activity. It is generally black or gray in color. Being a glass, the atomic structure of obsidian is entirely disordered and amorphous, allowing flakes to be struck from it in any direction. It is an easily worked material that results in very sharp structures, making it ideal for cutting instruments. The material is formed in volcanic flow, therefore, obsidian sources are isolated and not very common.

For all these reasons, obsidian is a focus of archaeological studies because of its practical use to help trace the trade routes of prehistoric peoples. Obsidian is uniquely interesting for this purpose, because the composition of the material differs by site, and within a given site, the material is generally homogeneous. Because of its use by many cultures as a tool and as jewelry, combined with the discrete nature of its formation, it can therefore be used to track movement and trade of many cultures.¹

The composition of most obsidians ranges from about 66-75% SiO₂, 10-15% Al₂O₃, 3-5% Na₂O, 2-5% K₂O, and 1-5% total Fe₂O₃ + FeO. Peralkaline varieties of obsidian are typically higher in Fe composition than are rhyolitic obsidians. The color of the material is contingent on total metals composition, but in general is black or gray. In addition, the intrinsic water content of obsidian ranges from 0.1 to 0.5%.¹

Typically, the composition of obsidian artifacts is established by X-ray Fluorescence (XRF) and neutron-activation analysis (NAA). XRF tends to be used in the field, as portable instruments are available. The principal disadvantage of XRF is that only 8-10 elements are measured well. NAA is a more penetrating analysis and provides information on about 30 elements. Unfortunately, NAA is a destructive technique and also more expensive than XRF. Other laboratory instruments have also been used to determine obsidian composition; data from particle-induced X-ray emission and particle induced gamma ray emission (PIXE-PIGME), laser ablation ICP-MS and scanning electron microscopy energy dispersive spectroscopy (SEM-EDS) have all been discussed in open literature. Raman spectroscopy has been successfully utilized for structural analysis and characterization of silicate glasses. Obsidian itself tends to exhibit a luminescent or fluorescent background when

excited with a CW laser. The basic structure of glass is silicate tetrahedral $[\text{SiO}_4^-]$, which forms a covalently bonded Si-O network. When other ions replace the Si^{4+} (Ca^{2+} , Mg^{2+} , etc.), the three-dimensional structure is disordered. The altered structure contains non-bridging oxygen atoms, which are readily discovered with Raman spectroscopy. Obsidian shows two overlapping features centered at 1123 and 1021 cm^{-1} and another at 801 cm^{-1} . These are Si-O stretching modes and represent tetrahedral units with three, two and zero bridging oxygen atoms, respectively. Relative shifting between intensity of these features may be useful to indicate an increase in non-silica cations in the matrix. Low wavenumber bands originate in twisting and bending motions of the Si-O-Si that connect the tetrahedral units.²⁻⁴

Source discrimination with Raman has been done in literature examples by curve fitting the Si-O stretching region from 850 - 1400 cm^{-1} . Raman spectroscopy has also been used to determine the dissolved water content ($\text{H}_2\text{O}+\text{OH}$) using the 3455 cm^{-1} band. In addition, portable Raman instrumentation has been used in concert with principal component analysis (PCA) to perform source attribution on obsidian samples from islands near New Guinea.^{2,4,5}

Samples

Six small samples of flaked obsidian were borrowed from a local archaeologist, discovered during a trip to Armenia. They are thought to all have originated in volcanic domes near Hankavan, Armenia. The pieces are worked artifacts that have been dated at 2500-3500 years old. Some of the pieces have very clean surfaces; others have a tan crust over much of the surface. A photo of one of the samples is shown in Figure 1.



Figure 1. Photograph of one of the Armenian obsidian samples (3).

Spectra of the Armenian samples have been compared with spectra acquired from a polished sphere of obsidian with an unknown origin.

Measurements and Results

A TSI ChemLogix EZRaman-I with 532 nm excitation was used to acquire the spectra of all the samples. An XYZ translation stage was used to position the samples under the probe lens (working distance 3 mm). About 30 mW of laser excitation power was used for all samples. The Armenian samples required 8-80 seconds to acquire reasonable signals. All spectra were acquired with 10x averaging. The collected spectra were acquired on the cleanest portion of each individual sample. Spectra of all the Armenian samples are all very similar, as expected based upon the place they were found. The spectrum acquired on the recently produced sphere of obsidian is noticeably different.

Figure 2 shows the background corrected spectra of one of the Armenian pieces and the sphere. The two spectra have been overlapped at the feature near 480 cm^{-1} . It is clear from this data that the overlapping features centered at 1123 and 1021 cm^{-1} are present in different ratios in these samples. As previously discussed, these are Si-O stretching modes and represent tetrahedral units with three and two bridging oxygen atoms, respectively. The data seems to support an explanation involving more metal and alkali metal cations, and therefore relatively fewer bridging oxygen atoms in the Armenian samples.

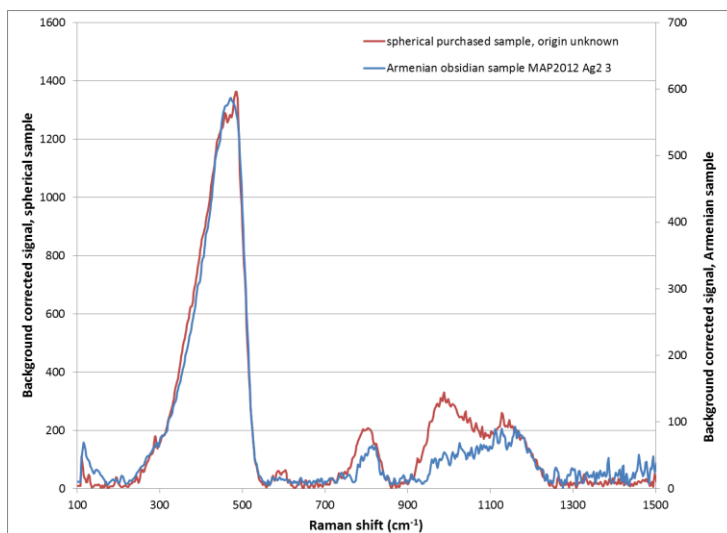


Figure 2. Raman spectra of Armenian sample of flaked obsidian and modern obsidian sphere.

The Armenian samples also display a different overall fluorescence/luminescence than the modern sphere. Figure 3 shows the difference in the raw signals of both pieces. The spectrum of the Armenian sample is similar to all the others, while the sphere has appreciably less broadband background. This observation is perhaps related to the overall coloring of the materials; the modern sphere is very dark with no hint of transparency, while several of the Armenian pieces are at least partially transparent to the excitation beam (Figure 4).

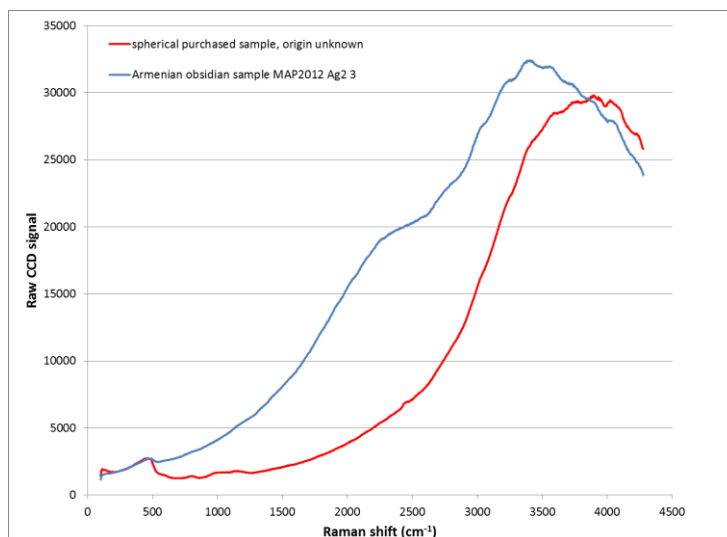


Figure 3. Raw Raman signals of prehistoric Armenian and modern obsidian.

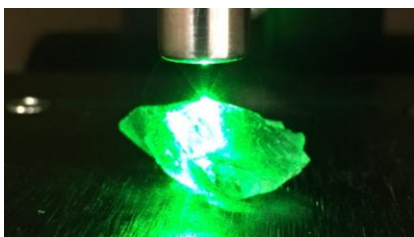


Figure 4. Armenian obsidian flake illuminated with green laser.

This preliminary data serves to show that different types of obsidian can be readily differentiated with a 532 nm TSI ChemLogix instrument. Further work with obsidian from the Western U.S. will be documented in a subsequent application note.

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