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Original article

AFM and SIMS surface and cation profile investigation of archaeological obsidians: New data

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ABSTRACT

Obsidian surface roughness and rind structure both play a major influence on the Obsidian Hydration Dating (OHD). AFM (Atomic Force Microscopy) investigation coupled with quadrupole SIMS hydrogen data profiles establish a validation criterion of quantitative evaluation of roughness for OHD dating purposes. More evidence of the importance of the surface morphology at the nanoscale is given for five obsidian tools of different origin. The latter relates to the dynamic ion influx diffusion kinetics between surface and surrounded sediment media, and the obsidian structure, thus, 2D and 3D surface mapping, as well as, cation profiling (H, C, Mg, Al, F, S, Cl, CN, O isotopes) were made by TOF-SIMS and quad-SIMS. It was found that the C and Mg are considered as imposed criteria for accepting suitability of H^+ profiles for further processing by SIMS-Surface Saturation dating method. The effect of roughness to dating is discussed.

1. Introduction

Obsidian is a natural glass that undergoes hydration because of environmental humidity and forms a hydration rim in its interface layer (few microns below the surface). It is known that the hydration of obsidian is a complicated, diffusion-limited phenomenon, which is strongly affected mainly by environmental factors of temperature, water concentration on the glass surface, as well as, pristine water (glass structural water) [1–4].

In the last decade, novel approaches to the investigation of the obsidian surfaces by means of Scanning Electron Microscopy (SEM) and Secondary Ion Mass Spectroscopy (SIMS) have revealed the influence of microlithic inclusions on the hydration process [5–7]. Furthermore, preliminary results from investigation of the surface with Atomic Force Microscopy (AFM) have shown that the surface roughness has a significant impact on SIMS measurement [6–9]. Roughness derives from various causes, the weathering (burial conditions), cleavage during carving of the tool, usage.

Here, new measurements of AFM along with quadrupole SIMS and ToF-SIMS mapping and cation profiling on obsidians had lead to further assessment and evaluation of the criterion for choosing and accepting suitable obsidian surface areas for SIMS, and cation profiles. Investigations on surface roughness and profile data scatter and dispersion prior to any H^+ SIMS profile for SIMS-SS dating purposes [5] has been instrumentally and statistically documented.

2. AFM on archaeological materials and obsidians

Since its discovery [10], thanks to its versatility, the AFM technique has been widely used in many different fields, such as biology and micro/nano-electronics. Although there are studies reporting its use in modern glasses (especially for the study of optical fibers), there are very few reports describing its use in archeological glasses.

Considering the most relevant studies reporting the use of AFM in ancient obsidians and manufactured glasses these are by:

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Schmitz et al. in 1995 [11]; Schreiner et al. in 1999 [12] showing the characterization of the surface of mediaeval vitro (stained glass) exposed to natural environmental conditions; Carmona et al. in 2010 [13], comparing the surface micro-structures in ancient and modern glasses degraded by chemicals, Zacharias et al., 2010 [14] on the authenticity of glazed pottery; Melcher et al. in 2010 [15] studying the degradation of glass artifacts. AFM has been previously used in the investigation of obsidians by Liritzis et al. in 2008 [8,9] and by Novak and Stevenson in 2012 [16]. These results pointed out that the surface roughness can potentially influence the sputtering of ions, the diffusion profiles of cations into the glass and especially distorts the concentration of water (as H^+) versus depth.

3. SIMS on surfaces: the effect of roughness

The SIMS method is based on the sputtering of secondary ions from the surface of a material that is bombarded by a primary ion beam [17]. The type and the quantity of the sputtered secondary ions from the surface provide useful information on the chemical composition of the surface under examination. By using a profilometer to measure the total depth of the crater formed by the bombardment, information on the concentration distribution of the elements versus depth can be inferred. Several studies on materials, mainly in the research field of micro-/nano-electronics (e.g. thin films of silicon or germanium), show that the measurement of a surface by SIMS is subjected to the influence of the roughness of the surface [18].

Irrespective to the material's composition and the nature of the ion beam, the influence of the roughness on the experimental output (chemical composition versus depth profile) is twofold: the first one is connected to the intrinsic roughness of the material; the second one concerns the additional roughness induced by the ion bombardment [16–20]. In fact, the two types of impact in processed surfaces of silica was found for primer ion beam of oxygen (O) [19,21], and in the same surface but for primer ion beam of cesium (Cs) [20].

The impact of surface morphology on SIMS results has been comprehensively discussed [18,22], assessing that natural cracks, pinholes or swellings could lead to unreliable results. The surface roughness has an influence on the spread of secondary ions during the bombardment and, as a result, distorted data for the composition of the surface are recorded as they reach the mass spectrometer. In addition, the roughness induced by the ion beam further influences the distribution of the secondary ions. In a recent report, Novak and Stevenson [16] have investigated modern and archaeological obsidian surfaces by means of SIMS and AFM, concluding that the roughness measured by SIMS is larger than its real value. It is not yet clear at which depth this induced roughness starts to be generated, while this information would be important to give a correct interpretation of the hydrogen profiles. In 2008 the first results from the AFM measurements were published [8,9] and they reveal that there seems a correlation between the spread of the profile concentration values found by SIMS and the value of the roughness obtained by AFM. This correlation could be related to the effect of the surface roughness on the dispersion of the secondary ions and the collection of disturbed data from the mass spectrometer.

This paper aims at confirming and expanding the validity of this approach, evaluating the importance of the structural characterization at the micro- and nanoscale, by complimentary quad-SIMS and ToF-SIMS mapping and cation profiling of rinds on obsidians of different archaeological origin.

4. Experimental details

All samples were investigated by means of a Park XE-100 AFM in contact mode (NSC36 probes, radius of curvature < 10 nm). To avoid microscopic cracks and inhomogeneities, the regions to be scanned by AFM were chosen with the aid of an optical microscope [8].

Secondary ion mass spectrometry (SIMS) analyses were conducted at the commercial laboratory of Evans Analytical Group, East Windsor, NJ, USA, and the profiles were collected using PHI Model 6300 and 6600 quadrupole-based secondary ion mass spectrometers. A 5.0 KeV Cs^+ primary ion beam with an impact angle of 60° with respect to surface normal was used and negative secondary ions were detected. The measurements were performed using a 300×300 micron ion beam raster, which results in very little visual disruption to the sample surface. Generally, the SIMS depth scale accuracy for archaeological samples is within 5–10%. This translates into an estimated error of ± 0.05 μm. This value is not equivalent to the ± 0.01–0.03 μm standard deviation usually associated with SIMS because of the irregular surface topography present on naturally cleaved samples. For polished test samples crater depths are measured using a Dektak 6 M stylus profilometer which is reproducible to within 1% on flat, well-controlled samples [8].

ToF-SIMS measurements were carried out within the scope of an ION-TOF ToF-SIMS.5-200 demonstration in the laboratories of Tascon in Germany. The chosen analytical conditions were adapted to the respective analytical needs. General information about ToF-SIMS instrumentation, modes of operation and typical applications can be found elsewhere [23].

A representative image displaying one of the AFM experiments is reported for each sample, showing the positioning of the tip over the surface. Table 1 reports the analyzed samples together with their place of origin. These together with some more measured by TOF-SIMS were chosen to investigate surface differences under different environments (Aegean, Carpathian, Asia Minor, Continental Greece), some of them have had stereo microscopic images with differences in surface appearance, while others are compared to samples from same stratigraphy and age of earlier made SIMS profiles.

5. Measurements by AFM and SIMS

5.1. AFM

5.1.1. Sample RHO-4 (ULUCAK)

Optical microscopy results show that the sample is not flat and that it is not homogeneous in the micrometric scale. The sample features cracks, voids and inhomogeneities typically in the range of few microns. The percentage of the area covered by such features is lower than 10%. The vast majority of the surface consists of regions similar to the one shown in the micrograph in Table 1. In these regions the surface mainly consists of sub-micrometric spheroidal structures. The size and shape of these objects are quite homogeneous. Typically, particle diameter is in the range between 20 nm and 100 nm, while the height is typically below 10 nm (Fig. 1).

5.1.2. Sample RHO-8 (ULUCAK)

Optical microscopy investigation (see Table 1) reveals a microscopic structure partly similar that of RHO-4, while AFM results display significant differences. Rod-like crystallites are present on top of spheroidal structures similar to those observed in RHO-4 (see Fig. 2). The dimensions of rod-like particles are typically around 100 nm in cross-section and few hundreds of nm in length.

5.1.3. Sample RHO-363 (MORAVANY-3)

By naked eye this sample looks very different from the others; in fact, the sample is not as black colored as the others, and is partly translucent. The surface is extremely flat, except for some linear scratches, clearly visible in the optical micrograph (see Table 1).

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