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# **SURFACE AND INTERFACE INVESTIGATION OF ARCHAEOLOGICAL OBSIDIAN ARTEFACTS WITH TOF-SIMS: CASE STUDY**

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## **ABSTRACT**

The surface of six different archaeological obsidian tools are analyzed systematically with Time of Flight Secondary Ion Mass Spectrometry (ToF-SIMS) and Quad-SIMS for both the evaluation of the surface topography, as well as, the detection of remaining organic compounds via various amino acids, that may have been trapped in the surfaces. This initiates a new way to wear analysis and dating of prehistoric glass tools. The three basic criteria in surface topography and diffusion dating that has been investigated here for first time is the detection of organics, the elemental concentration mapping and 3D versus depth, and the simultaneous recording of several cations (C, F, Al, Mg). In any H<sup>+</sup> depth profile in obsidian hydration rim, C and Mg must also be included in measurement. A non-conformity of cation profiles between H<sup>+</sup> and these cations point an area with inclusions and the measurement has to be repeated in different spot.

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**KEYWORDS:** ToF-SIMS, surface spectroscopy, depth profiling, cations, ions, archaeological, prehistory, elemental mapping, wear analysis

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## 1. INTRODUCTION

Obsidian is a dense volcanic glass, formed when lava is rapidly cooled, often at the margins of flow and one of the most usable stones during prehistoric times for tool making. Its quasi-crystalline presence of minerals in micron range (quartz, feldspar, biotite etc), the diffused H<sub>2</sub>O through its microporous surface, the pristine water content, and the degree of surface smoothness and contamination are important parameters for the hydration dating by H<sup>+</sup> hydrogen profiling (SIMS-SS) (Liritzis 2015; Liritzis et al., 2008). The Secondary Ion Mass Spectrometry (SIMS) is an excellent tool for measuring the hydration layer of an obsidian tool for dating purposes (Liritzis and Laskaris, 2011). The technique is very useful due to high resolution for a wide variety of elements and molecular compounds along with almost non-destruction of the sample.

First report in using SIMS on obsidian artifacts is by Tsong et al (1981) in their paper Dating of obsidian artifacts by depth-profiling of artificially hydrated surface layers (Tsong et al., 1981). Since then, several studies have been published for the use of SIMS on obsidian artifacts for measuring the hydration profile, or low- temperature isotopic exchange and in general for dating the obsidian tool. (Tsong et al., 1981; Stevenson et al., 2001; Liritzis and Diakostama-

tiou, 2002; Riciputi et al., 2002; Anovitz et al., 1999, 2009).

Use of SIMS for dating of obsidians through nitrogen and other elements diffusion (but not hydrogen), for dating purposes has been reported (Patel et al., 1998). Even though Patel et al have not reported any pattern for dating by using the Nitrogen profile, their research is, until today, a useful source of information for the morphology of the obsidian surface and the presence of a variety of chemical compounds. A very important notice is that the concentration of carbon atoms (C) is reduced as a function of depth as a result of been diffused in the obsidian subsurface layers. Patel et al (1998) also stated that C is present in defects, such as pits and cracks, in the obsidian surface. These defects were formed near inclusion areas during crafting of obsidians and they are excellent environments for micro-bacterial activities best represented by changes in C and N profiles.

In this work, ToF-SIMS and quadrupole SIMS are used for studying the surface and interface of six archaeological obsidian samples. Our aim is to examine the potential of using SIMS for evaluation of the obsidian surface for wear analysis and to reinforce further criteria of reliability of the SIMS-SS dating method.

*Table 1: Sample Code and Provenance, type of SIMS and analysis*

Sample Code	Provenance	Type of SIMS	Analysis
1.RHD-1024	Prophet Elias Hill, Desfina (Delphi), Greece, Surface find	ToF-SIMS	Surface Composition, H profile up to 10µm, 16O & 18O profile, Cations profile, 3D analysis of first approx. 10µm
2.Rho-523	Moravany Site, Early Neolithic Settlement, East Slovakia	//	Surface Composition
3.Yr-3	Cyclops Cave ancient Settlement (late palaeolithic layer) Island of Youra, Alonissos, Greece (Sampson, 2011)	//	Surface Composition
4 & 5. Sar-7 Sar-8 Sar-9	Sarakinos Cave, Upper Paleolithic up to Neolithic Settlement, Boeotia Prefecture, Greece (Sampson, 2008)	Quadrupole SIMS	Profile of C, Mg, F, Al
6. Rho-892	Ikaria Mesolithic Settlement, Greece (Liritzis and Laskaris, 2012)	//	//

## 2. SAMPLES & INSTRUMENTATION

Table 1 shows the samples codes, along with their provenance, the type of SIMS (ToF or Quadrupole) and the type of analysis. ToF-SIMS measurements were carried out within the scope of an ION-TOF

ToF-SIMS.5 demonstration in the laboratories of Tascon in Germany. The applied instrument was a ToF-SIMS.5-200. 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 (Vickerman, 2001). For the Quadrupole SIMS measurements were carried out at the laboratories of Evans Analytical Group in USA (thanks to S. Novak). The analytical conditions are given in the inset below.

Quadrupole-SIMS experiments were performed at

the laboratories of Evans Analytical Group in USA with PHI 6300 and 6600 instruments. For analysis of negatively charged secondary ions a 5.0 keV Cs<sup>+</sup> primary ion beam with an impact angle of 60° and a raster area of 200 × 200 μm<sup>2</sup> was used. The depth accuracy is equal to 0.05 μm.

#### Technical details

*Surface Composition:* (Static SIMS spectra of positive and negative secondary ions). Analysis ion: 25keV Bi<sup>+</sup> in bunched (i.e. high mass resolution) mode; the maximum primary ion dose density of 4.37e+8 ions/cm<sup>2</sup> was well below the static limit.

*Depth Distribution of H:* Sputter ion: 2keV Cs<sup>+</sup>; target current: 101nA, sputtered area: 300x300μm<sup>2</sup>. Analysis ion: 25keV Bi<sup>+</sup>; target current: 3pA; raster area: 100x100μm<sup>2</sup>; bunched mode. Secondary ion polarity: negative.

*Depth Distribution of 16O & 18O and 3D Analysis:* Sputter ion: 2keV Cs<sup>+</sup>; target current: 125nA, sputtered area: 300x300μm<sup>2</sup>. Analysis ion: 25keV Bi<sup>+</sup>; target current: 0.2pA; raster area: approx. 100x100μm<sup>2</sup>; bunched mode.

*Secondary ion polarity:* negative.

*Depth Distribution of Cations:* Sputter ion: 2keV O<sup>+</sup>; target current: 555nA, sputtered area: 300x300μm<sup>2</sup>. Analysis ion: 25keV Bi<sup>+</sup>; target current: 1.18pA; raster area: 100x100μm<sup>2</sup>; bunched mode. Secondary ion polarity: positive.

### 3. SURFACE COMPOSITION

Several studies since 1996 report the presence of organic residues on the surface of ancient artifacts (Fiedel, 1996; Shanks et al., 2001; Hortola, 2002; Buonasera, 2005; Lowenstein et al., 2006; Mazel et al., 2007). These results along with Patel's (Patel et al., 1998) hypothesis for micro-biological activity in pits of the obsidian surface lead to the need for a further examination of the composition of such surfaces.

In Figs 1- 6 surface composition analyses are presented for the first 3 samples of Table 2. Identification of compounds was based on the internal database of the ToF-SIMS instrument and data sets in literature (Mazel et al., 2007; Silverstein et al., 2005; Sanni et al., 2002). Horizontal axis is the mass to charge ratio (m/z) and in vertical axis the intensity in arbitrary units.

Tabl 2. ToF-SIMS identification of organic compounds (vw=very weak at 74.06.03u, dl=detection limit)

Sample / organics	Ala- nin	Pro- lin	Va- lin	Leu- cine	Threo- nine	Oleami- de	Dial- kylam- moni- um	Ser- ine	Histi- dine	Phenylala- nin
RHO-1024, Desfina					+			+dl	+dl	+dl
RHO-523,	+	+	+	+	+			+	+	
YR3, Youra Cave	+	+	+	+	+vw	+	+			

NOTE: Alanine: It is one of the non-essential amino acids as it can be synthesized by birds and mammals from sugar metabolism and does not require immediate dietary intake. However, the following foods are a good source of alanine: meat, seafood, dairy, eggs, gelatin, beans, nuts, seeds, rice, corn, wheat, etc. Alanine is found in a wide variety of foods, but is particularly concentrated in meats

#### Sample YR-3

Surface composition of YR-3 reveal that it is difficult or even impossible to separate between fragments of contaminants and 'real' amino acid signals. At the masses of Alanin, Prolin, Valin, Leucine and Threonine (very weak signal at 74.06.03u) are SI detectable. The high intensities of Oleamide and Dialkylammonium might be also an explanation for the

detected "amino acids" (e.g. a signal at mass 60u with the assignment C<sub>2</sub>H<sub>6</sub>NO (= Serine) can also be detected as a fragment of Oleamide; small C<sub>x</sub>H<sub>y</sub>N signals are also observable in spectra of dimethyldialkyl ammonium. It is also very likely that the other detected molecules are contaminations / residues from a former cleaning of the glass and or storage in polymer/plastic bags or boxes. Oleamide (slip agent

in polymers); Dodecylbenzene sulfonate (tenside), Dimethyldialkyl ammonium (antibacterial, antimicrobial; defoaming agent and antistatics in polymers, plasticizer, Tenside), Polysiloxane (used nearly everywhere, Sodiumlauryl sulfate (tenside) (see also Liritzis & Laskaris, 2011).

### Sample RHO-523

In sample RHO-523, surface composition reveals the presence of Alanin, Prolin, Threonine, Serine, Valin, Histidine (weak), Leucine, Phenylalanin.

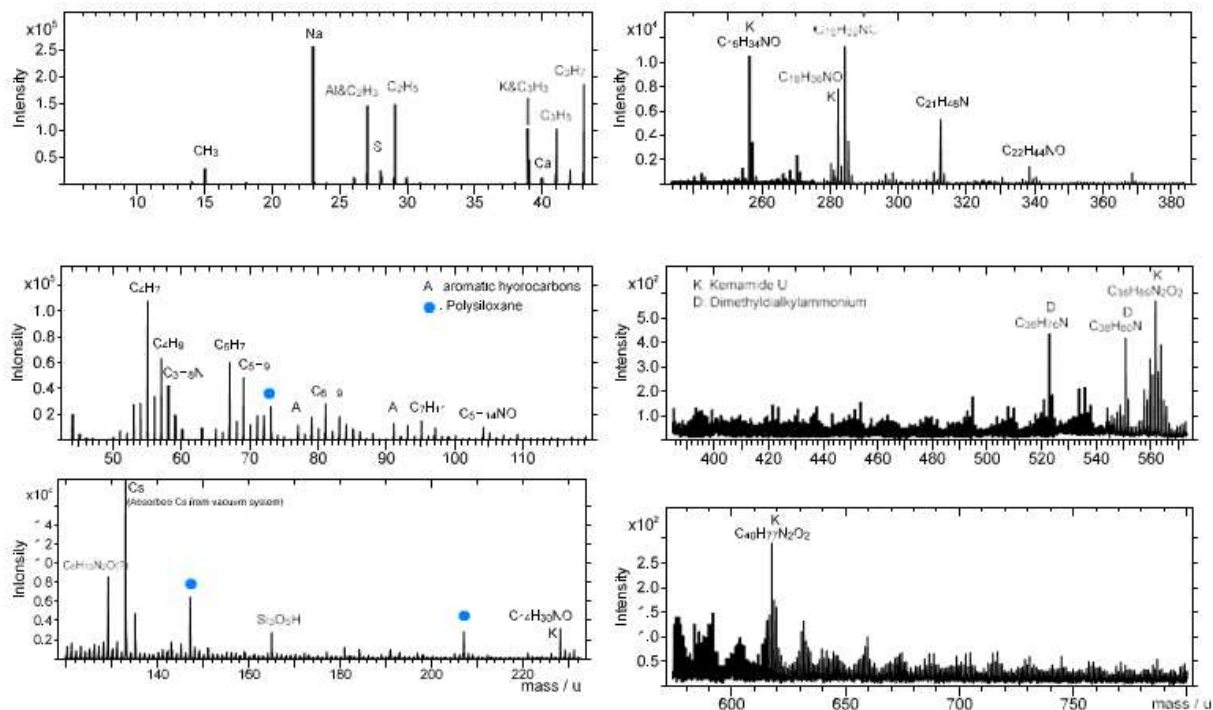


Figure 1: Surface Composition of sample YR-3. Positive Secondary Ion Polarity

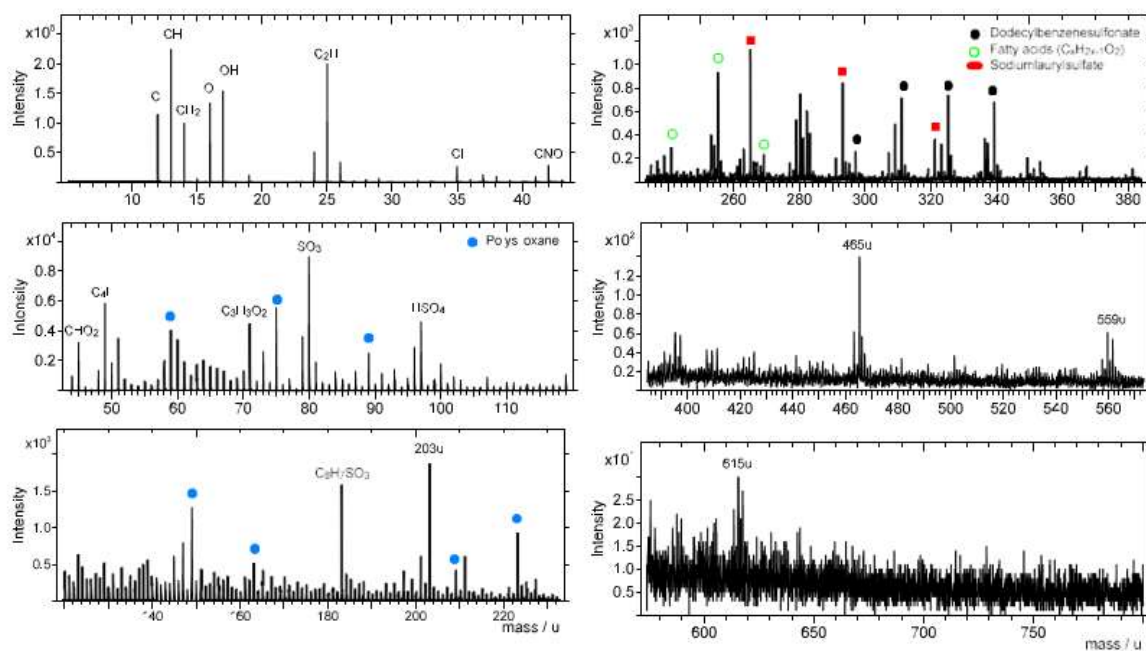


Figure 2: Surface Composition of sample YR-3. Negative Secondary Ion Polarity

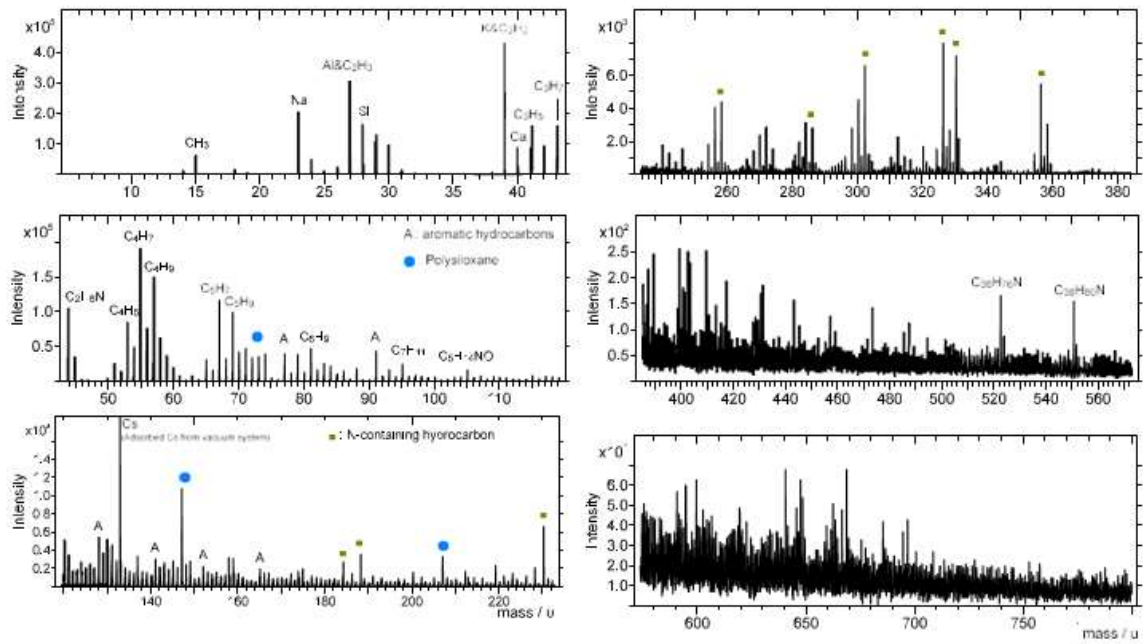


Figure 3: Surface Composition of sample RHO-523. Positive Secondary Ion Polarity

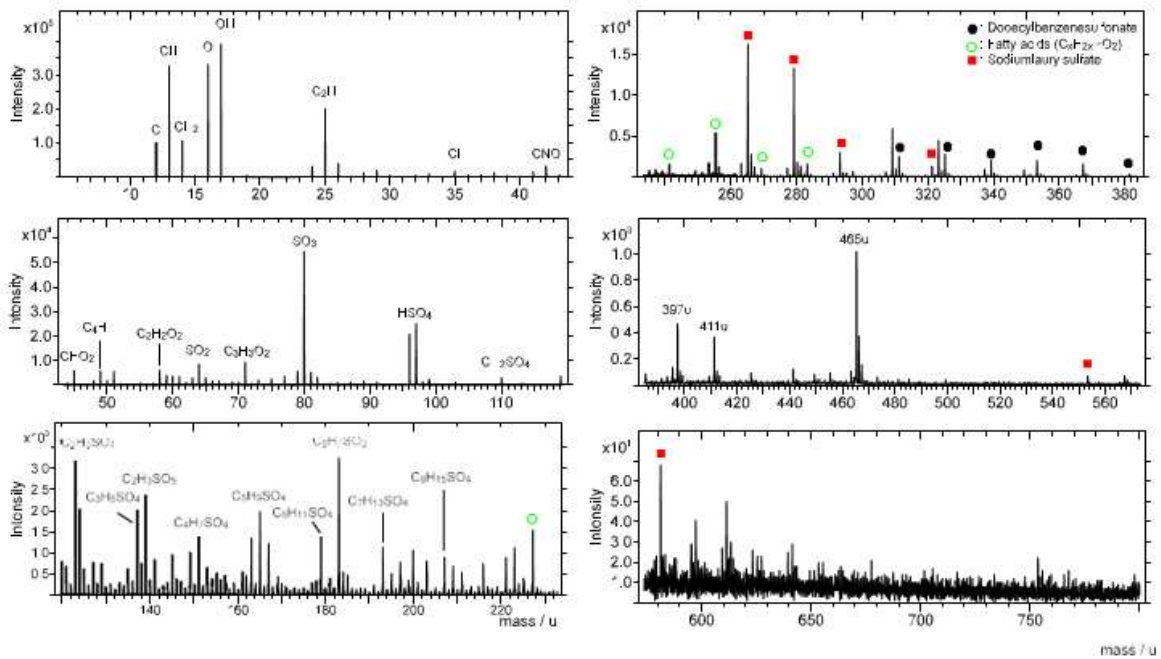


Figure 4: Surface Composition of sample RHO-523. Negative Secondary Ion Polarity



The existence of organic residuals on the obsidian surface is an undisputed fact. ToF-SIMS provides just some signal at a certain mass, but it provides no information about the origin of the mass. This means that a signal might be an amino acid or a fragment of a nitrogen containing polymer additive.

Nevertheless, it is yet unclear if these residuals are from micro-biological activity, human use (e.g. hunting) or from other contamination (e.g. plastic bags). Though the use of obsidian arrow heads for hunting is well known and similar one was found in one of the sites (Desfina, Phokis, Central Greece).

#### 4. DEPTH PROFILE WITH QUAD-SIMS

The reported presence of carbon and nitrogen in obsidian surface (Patel et al., 1998) has been investigated if it has any impact on hydration measurement

and/or the hydration itself. Further investigation of this hypothesis was done by examining obsidian surfaces with Quad-SIMS. Depth profiles of Carbon (C), along with Fluorine (F), Aluminum (Al) and Magnesium (Mg). Figures 7 - 10 show the depth profiles of the aforementioned elements for samples Sar-7, Sar-8, Rho-892. As it is shown, profiles of C are correlated to that of Mg more than that of Fluorine or Aluminum. Also, C profile is the same to that reported by Patel et al., (1998).

In all cases the disturbance of the smooth drop or straight line of C-Mg was in the initial layers of the surface (approx. 1-2 $\mu$ m) but in sample Sar-8 (Fig. 9) the disturbance is in depth of approx. 3.5  $\mu$ m. Such a disturbance in this depth is clearly an evidence of a carbonate mineral microlithic inclusion.

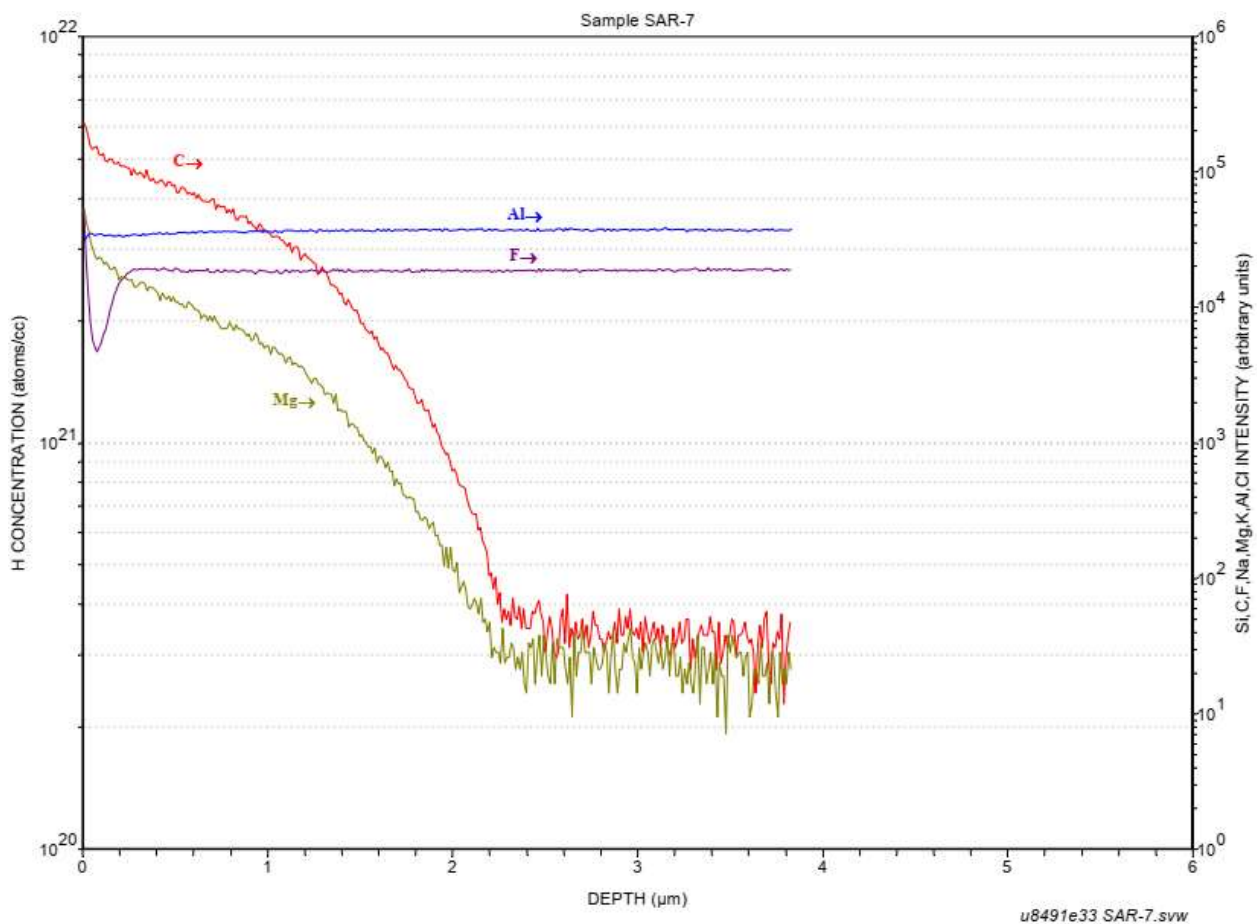


Figure 7: Depth profile of C, Al, F, Mg of sample Sar-7

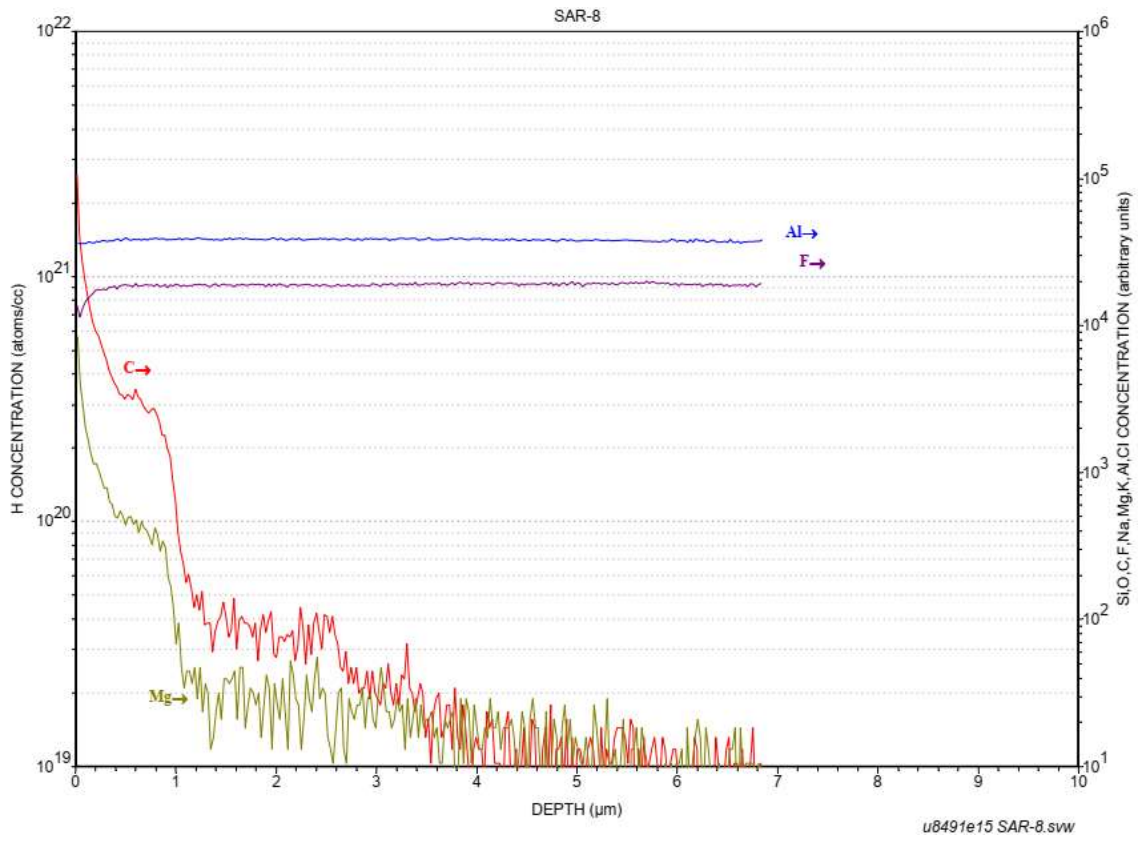


Figure 8: Depth profile of C, Al, F, Mg of sample Sar-8

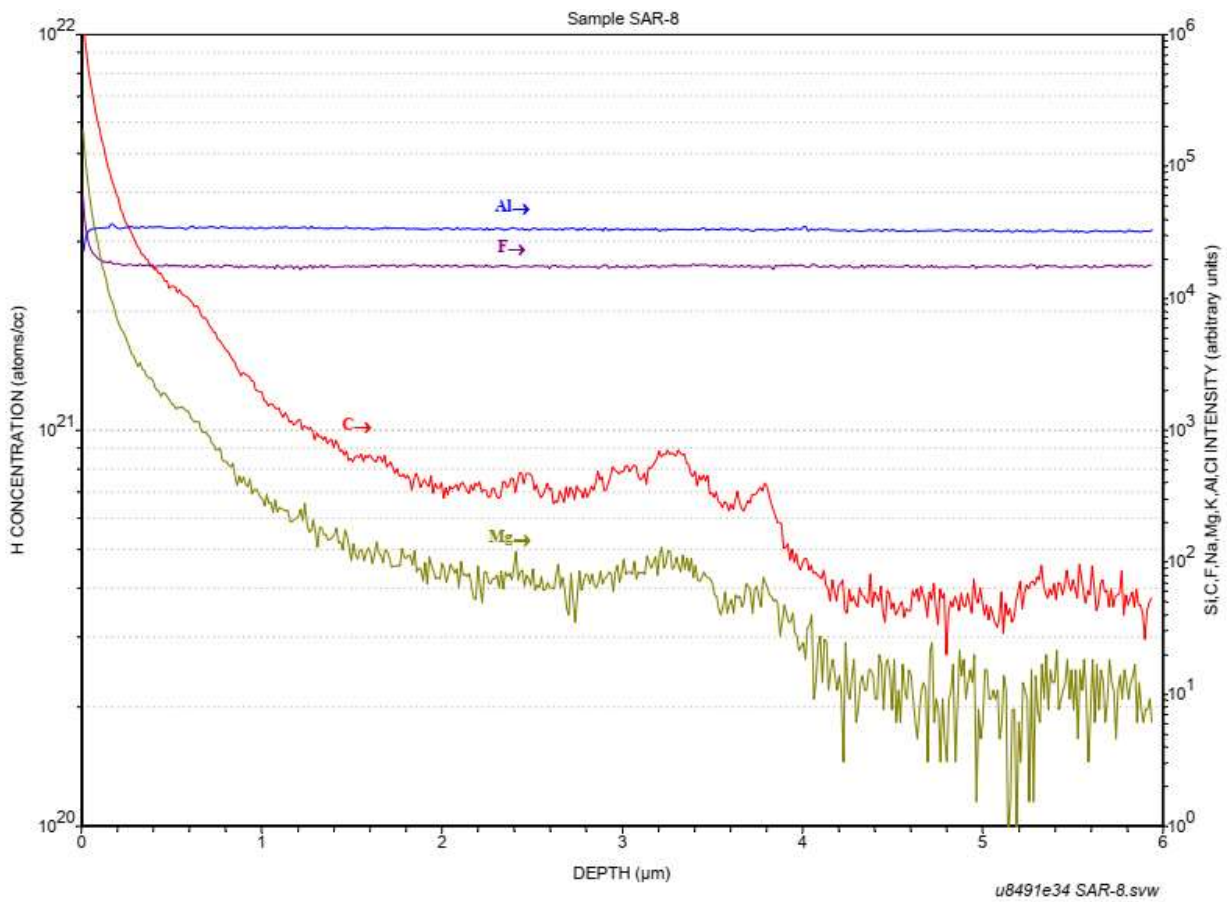


Figure 9: Depth profile of C, Al, F, Mg of sample Sar-8 (different spot than Fig. 8)



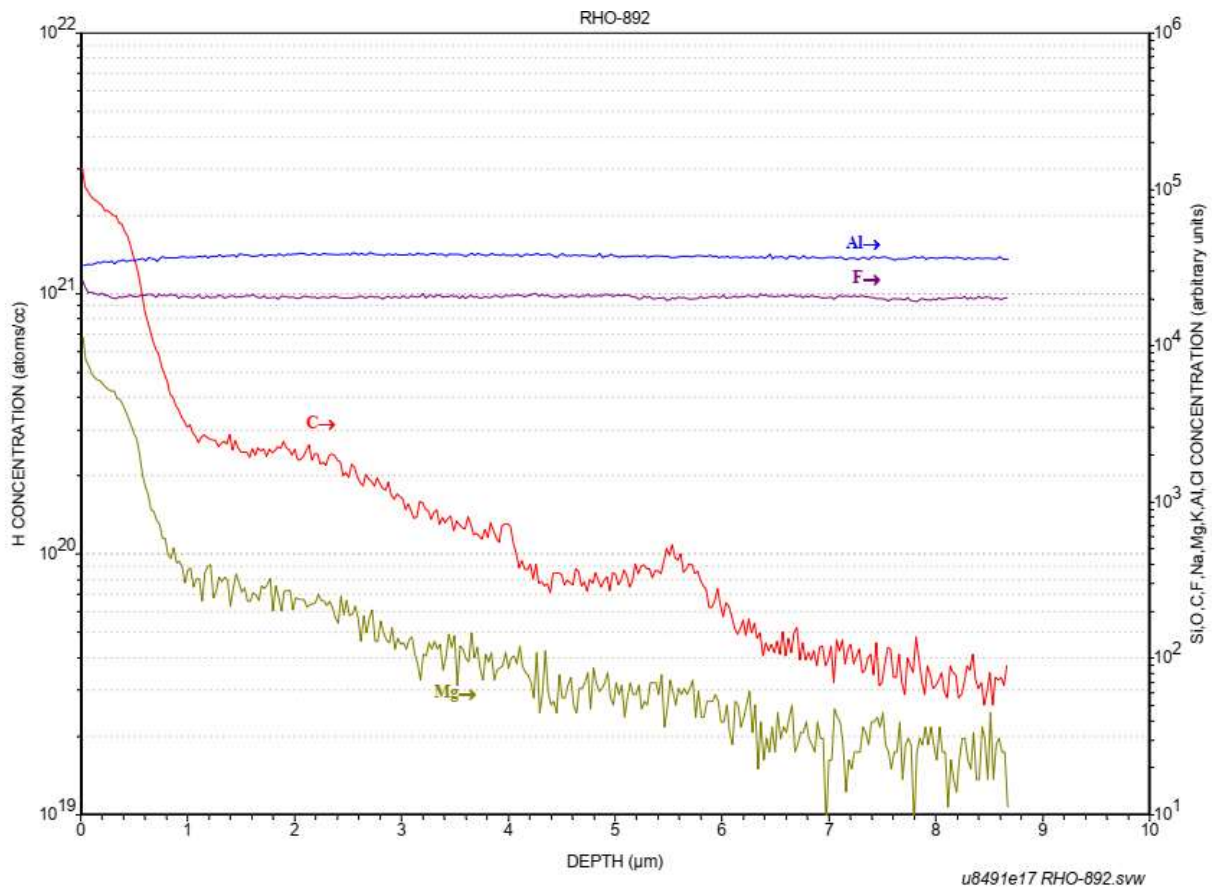


Figure 10: Depth profile of C, Al, F, Mg of sample Rho-892

Microlithic inclusions in obsidians are dispersed in the amorphous body since its formation from lava. Such inclusions have an impact on the difference in the hardness of the material.

Presence of Mg in crystalline materials makes them more fragile and therefore at the time of cleaving, pits or cavities are prone to form in areas rich with Mg inclusions. The matching (same depth, width) between C and Mg disturbances in depth profiles point that that cavities or pits have depth same as the width of the layer rich in Mg inclusions.

Summing up, obsidian surface has organic residuals in cavities or pits mostly in areas rich in Mg inclusions. Disturbances in C and Mg depth profiles point this existence and also the existence of carbonate mineral inclusions. Also, the agreement in disturbances between C and Mg lead to a new criterion in cases of measuring a depth profile with SIMS. This criterion is: *In cases of measuring a depth profile of an element or a hydration rim in obsidian, C, and Mg should also be included in the measurement. Any disturbance in these two elements, point to an area with inclusions, which naturally affect H<sup>+</sup> profile, and the measurement has to be repeated in different spot.*

## 5. SURFACE MAPPING & 3D ANALYSIS

A surface mapping of an area of  $103 \times 103 \mu\text{m}$  for several elements and figure 13 a XY slice with 3 color overlays of 3 compounds is given in Fig. 11. Color scale is normalized to the brightest pixel. From the examination of Figs 11, 12 the following remarks are drawn:

a) Hydrogen has uneven distribution over the surface with a maximum concentration in cracks and pits, b) Carbon and Cyanide (CN<sup>-</sup>) have the same distribution with Hydrogen, which reveals the presence of micro-bacterial activity, c) the main obsidian matrix contains <sup>16</sup>O with the distribution of <sup>18</sup>O to be much lesser, d) Fluorine is distributed over surface with maxima in cracks and pits, e) Sulfur and Chlorine have increased concentration in spots of bacterial activity, f) Magnesium has decreased concentration in inclusions which have increased amounts of Fluorine and g) the concentration of Iron in spots with a shortage of Silicon point the existence of Iron inclusions.

Fig. 13 shows the 3D distribution of H, <sup>16</sup>O, <sup>18</sup>O, Cl, MgO, SiO<sub>x</sub> for the same area as Fig.11.

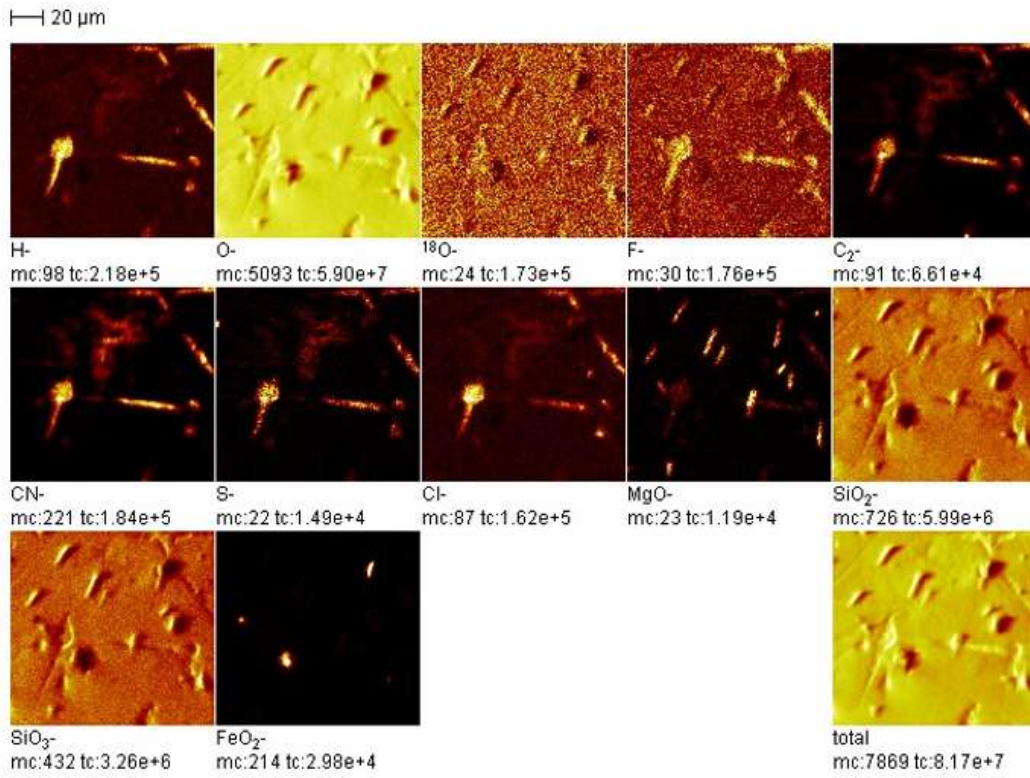


Figure 11: Surface mapping of Sample RHD-1024. mc: counts in the brightest pixel, tc: total number of counts in the image

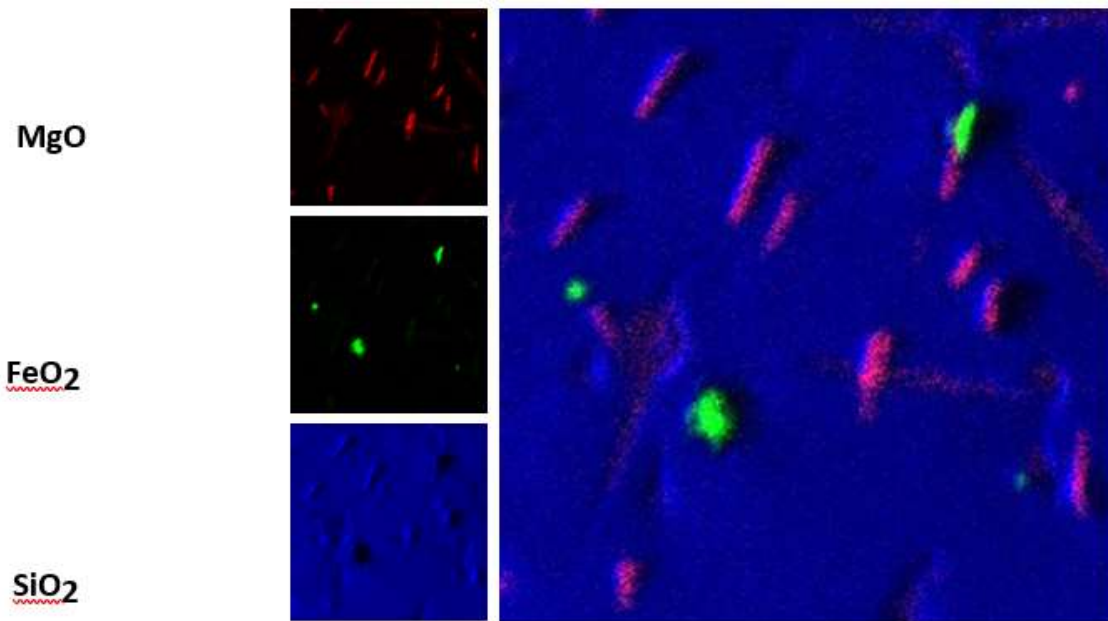
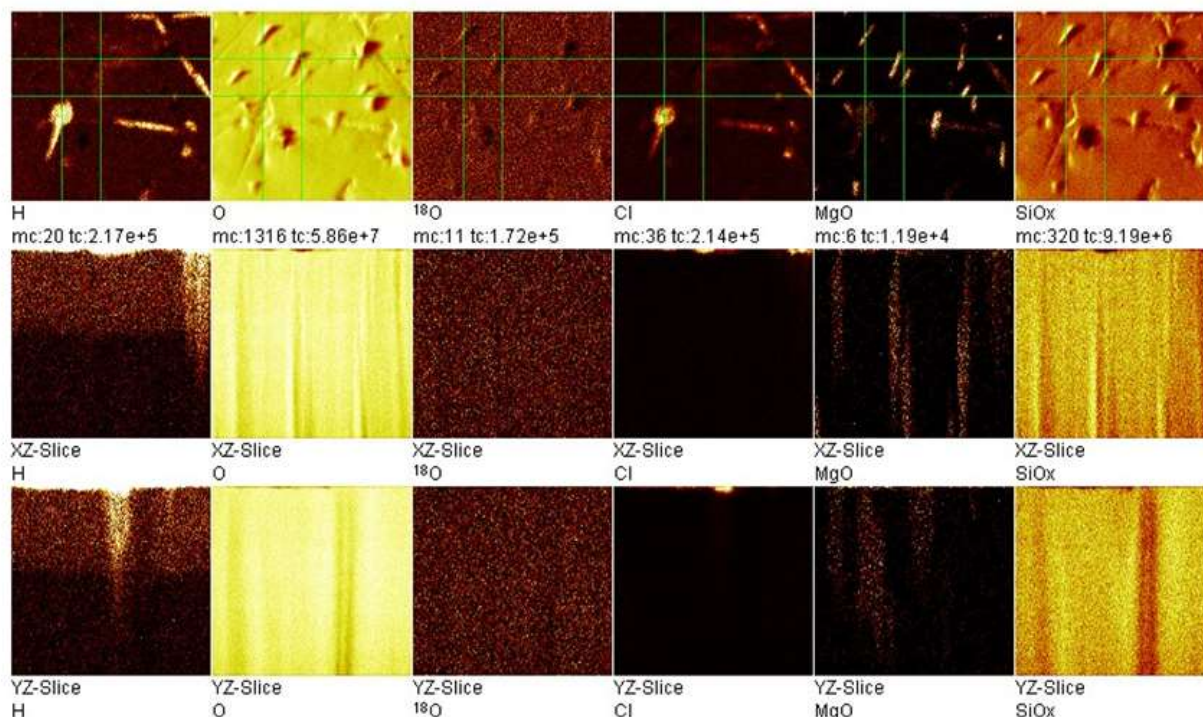


Figure 12: 3 color overlay for Sample RHD-1024. Detail of Fig. 11



**Figure 13: 3D cross Sections. Sample RHD-1024. Detail of Fig. 11. First row: XY distribution integrated over total sputtered depth. Second Row: XZ slices along green line, viewing direction from the bottom. Third row: YZ slices along green line, viewing direction from the left. Total crater depth  $4.2\mu\text{m}$**

Inspection of Fig. 13 reveals that the formation of the hydration layer is uniform along X and Z axes. If the crater depth is  $\sim 4.2\mu\text{m}$ , the hydration depth is  $1.8\text{-}2\mu\text{m}$ . The depth scale was calculated based on sputter rates determined on a suited reference sampled. Moreover, we observe the increased concentration of H (due to biological activity) inside cracks which may disturb the hydration measurement by giving higher values of Hydrogen concentration. From the comparison of the second and the sixth image of Fig. 13 and figure 12 we conclude that  $^{16}\text{O}$  and Silica decrease in areas rich in Iron. It is ob-

served that  $^{18}\text{O}$  have uniform distribution along depth and it was found that areas rich in Mg are in deeper layers while spots rich in Chlorine are limited only in surface.

## 6. DEPTH PROFILING

Figs 14 - 16 demonstrate the depth profiles for sample RHD-1024. Depth profiling was performed under different analytical conditions as mentioned in section 2.

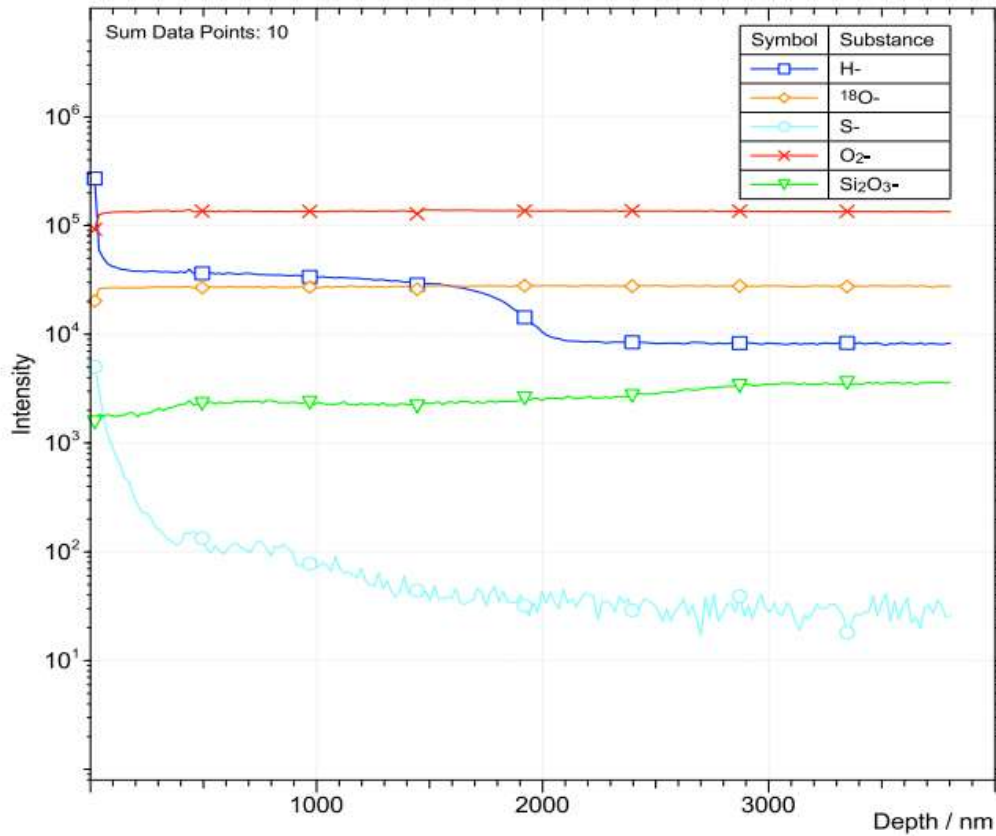


Figure 14: Depth Distribution of H

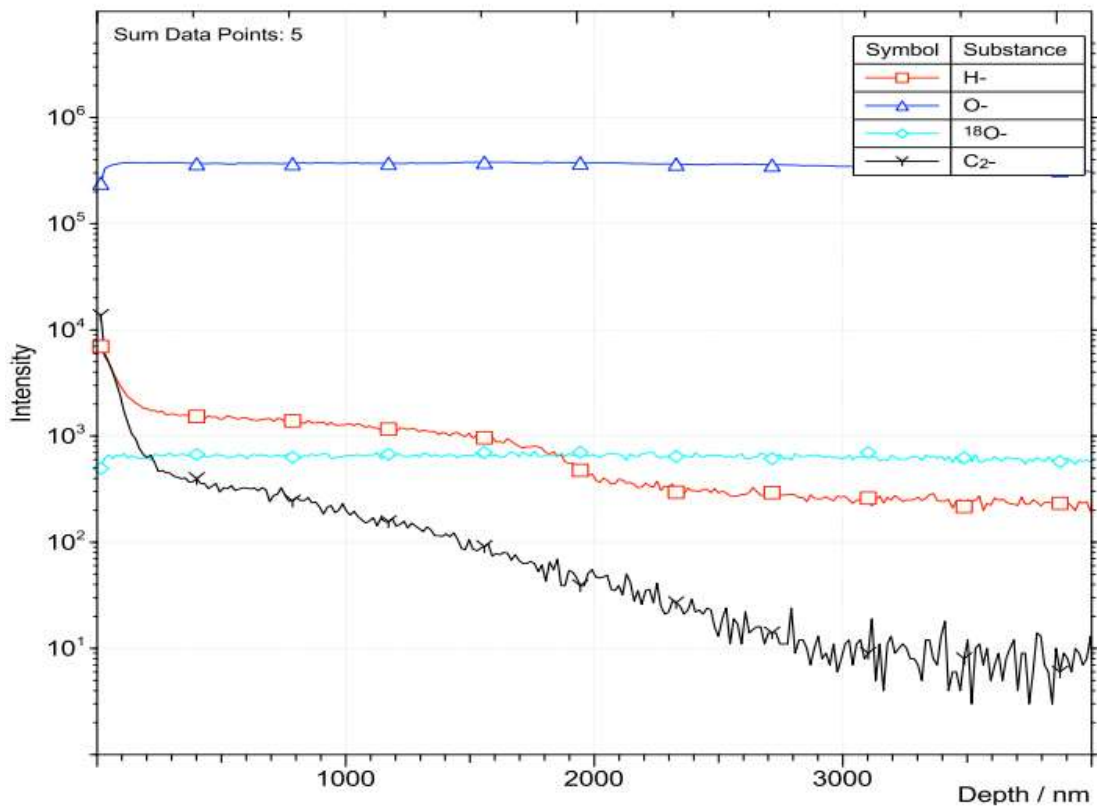


Figure 15: Depth Distribution of <sup>16</sup>O and <sup>18</sup>O

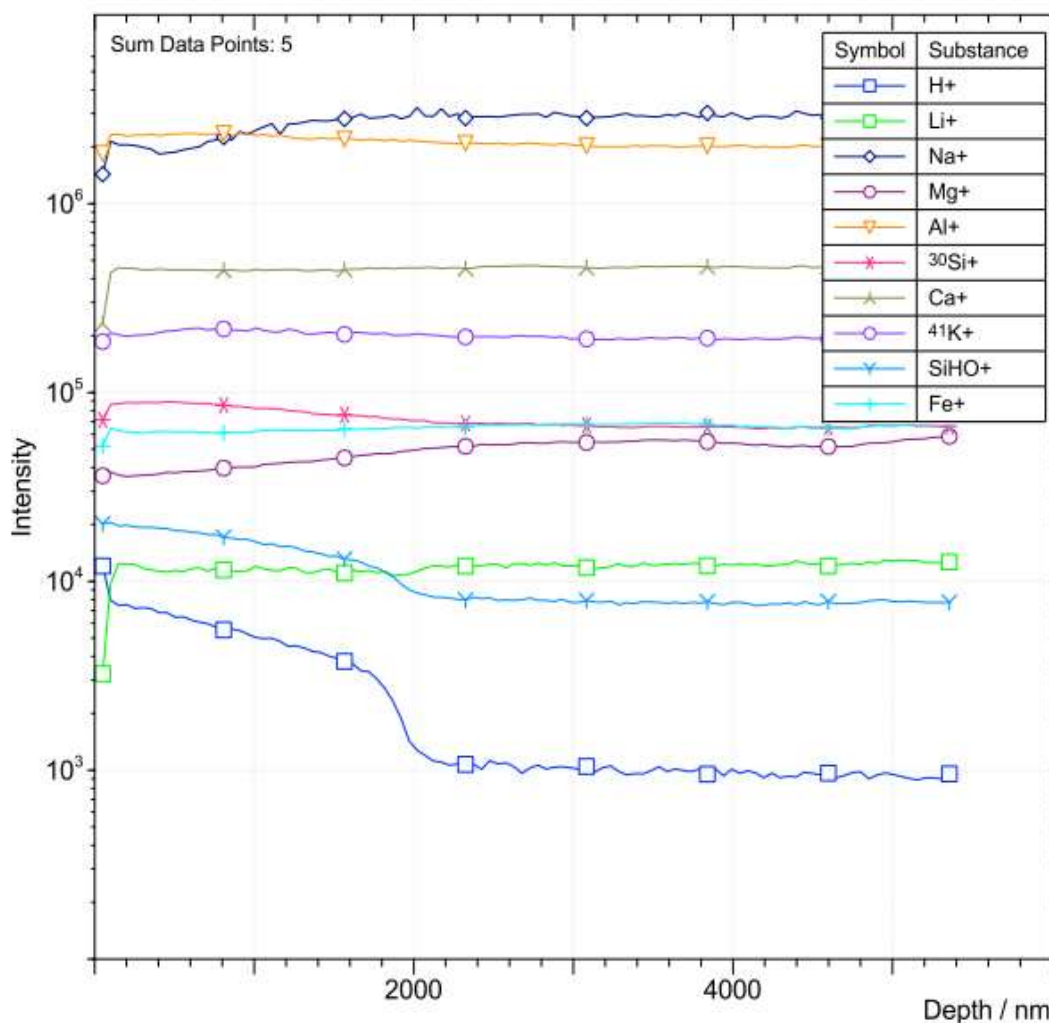


Figure 16: Depth Distribution of Cations

A depth scale was established by measuring the total crater depth of a suitable profile on RHD-1024 with a mechanical profiler and assuming linear sputter rates. The depth of the point of inflection of the H-profile was defined and was used to establish depth scales for all other profiles acquired on RHD-1024. The accuracy of the depth scale is limited due to the strong surface roughness of the obsidian. The impact of surface roughness on SIMS measurements is examined in details elsewhere (Laskaris et al., 2008).

We conclude that the sigmoid shape of the hydrogen (hydration layer) is also found for the Silicon Hydroxyl (Si-OH) or silanol. This is very important as it verifies the diffusion-reaction model suggested by Doremus (2000). Also, it was found that none of the other elements or compounds has any significant change except Sodium. The near surface leaching of Sodium is due to trace element exchange with the burial environment.

## 7. CONCLUSIONS

The obsidian surface is investigated with SIMS (ToF and Quad) in new aspects beyond but related to the hydration dating. First remark is the finding of organic residuals on the surface in concentrations that can affect the hydration measurement. Secondly, the mapping of the surface with ToF-SIMS prior to depth profile can be used in order to locate an area free of cracks, pits, troughs, shoulders or inclusions ensuring a depth profile of high accuracy. Thirdly, measuring of hydration profile along with other elements (Fluorine, Magnesium, Carbon) can give useful information for the reliability of the SIMS H profile measurement. Moreover, the diffusion-reaction model (Doremus, 2000) was verified, and the initial results of micro-bacterial activity on the surface (Patel et al., 1998) are reinforced.

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