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Procedia Chemistry 8 (2013) 11 – 19

Procedia Chemistry

Youth in Conservation of Cultural Heritage, YOCOCU 2012

Glasses & diamond: issues related to the archaeometric investigation of an archaeological bead

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Abstract

A glassy bead found during the archaeological excavation of the Palaeolithic rockshelter of Riparo Dalmeri has triggered the development of a broader research in the field of ancient glasses. The determination of the composition of the bead in a fully non-invasive way suggested an artificial origin of the glass. However, from the results of Raman spectroscopy a natural origin of the glass cannot be ruled out, as nanodiamonds were detected in the bead. A replica experiment was designed to shed light of this issue and provided new information on the material constituting the bead not measurable in a non-destructive way.

Selection and peer-review under responsibility of the IA-CS (Italian Association of Conservation Scientists) and University of Antwerp

Keywords: glass bead; lonsaleite; prehistoric glass; replica glass experiment

1. Introduction

Riparo Dalmeri is a Late Paleolithic rock shelter named after the first archaeologist (Giampaolo Dalmeri – Museo Tridentino di Scienze Naturali, Trento, Italy) who discovered and investigated the site since the early ’90s. This shelter is located in the Province of Trento (Italy) at 1200 m a.s.l. and is dated 13410-12900 BP cal. [1-3]. During the excavations of the site the archaeologists found a lopsided dark brown (Munsell colour charts: 2.5YR-10R 2.5/1) bead (Fig. 1). The bead was found in a perfectly sealed anthropic layer dated 13130 to 12900 y. BP cal. that, in the opinion of the archaeologists did not experience any contamination with materials from more

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Selection and peer-review under responsibility of the IA-CS (Italian Association of Conservation Scientists) and University of Antwerp
doi:10.1016/j.proche.2013.03.003

recent ages. Many interesting items were found at this site but only this one is a bead. Thus, from an archaeological point of view it is interesting knowing its provenance and manufacturing technique, as well as confirming the dating of the layer. In order to make hypothesis on the aforementioned archaeological issues, it was necessary to characterize the material constituting the bead. This article presents both the results of the non-invasive and non-destructive analysis made directly on the artefact and the information indirectly gained through the study of replica glasses imitating the original material. The production and characterization of model glasses is not uncommon in the field of archaeometry of glass and it has been used when there is a need for interpreting a very decayed artefact [4], study the deterioration process in soil [5-7] or in order to obtain information on the differences introduced in the final object by the use of different raw materials and manufacturing technologies [8]. In some cases, the experimental replications of glass allows the solution of the uncertainty about the identification of findings recovered from an archaeological excavation. For instance, Paynter and Dungworth [9] identified the frit found in the Post-Medieval site of Vauxhall (London, UK) through a replica experiment. The authors believe that this approach was suitable in the case of the study of the bead found in Riparo Dalmeri: the uniqueness of the item excluded to employ even the less invasive or destructive analytical techniques to obtain more information on the characteristics of the materials composing it. Moreover, it was already suggested by Matson [10] that preparing synthetic glasses based on the measured composition of an artefact may help to understand the working properties of the material which are useful to infer the manufacturing process from which it was obtained.

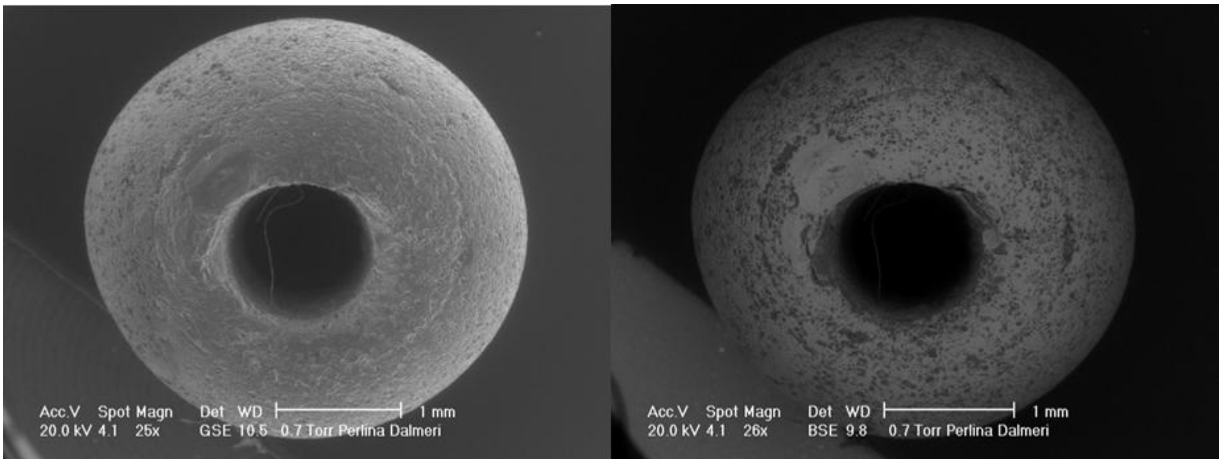

Fig. 1 LVSEM micrographs of the bead found at the Dalmeri rockshelter in a layer dated 13130 to 12900 y. BP cal.. acquired in secondary (left) and backscattered (right) electron modes respectively.

2. Experimental methods

X-ray diffraction (XRD) analyses were conducted with an image plate diffractometer with copper source (λ= 1.5418Å). The diffractograms obtained were analyzed with the MAUD software [11], which is based on a Rietveld approach.

Micro-Raman spectroscopic analyses were conducted with a Jobin-Yvon Horiba LabRAM Aramis instrument. The 632.8 nm He-Ne laser line was used as excitation source. Excitation power on the samples was kept below 5mW using a filter in order to avoid thermal effects. The diameter of the laser beam was about 2μm. Backscattered Raman light was collected with a confocal Olympus microscope with 50X objective for a total magnification of 70 times. A CCD (1024x256 pixels) cooled by Peltier effect was used to detect the signal. Two different gratings characterized by 1200 and 1800 lines/mm were used for the measurements. They allowed to obtain a spectral resolution of respectively about 4 and about 2 cm^{-1}. The measurements were acquired directly on the surfaces of the glass samples without any preliminary preparation.

Scanning electron microscope observations were carried out using an environmental scanning electron microscope (ESEM) operated in low-vacuum mode (LVSEM) at 20 KV and equipped with an energy dispersive X-ray spectroscopy (EDXS) system.

Density measurements were conducted using an Archimedes' balance with a sensitivity of 0.0001 g. The density of the glasses (ρ) was then calculated from the measurements of the weight in air (W_1) and in distilled water (W_2) according to (1):

$$\rho = \frac{W_1}{W_1 - W_2}\rho_{water} \quad (1)$$

(the density of water, ρ_{water}, at ambient temperature is 1 g/cm^3 ca).

The recipes for the production of the three replica glasses were developed to imitate that of the bead (Table 1). Considering that the silica present in ancient glasses may come from different sources (quartz contained in sand, fluvial pebbles, rocks and minerals or glass scraps) it was decided to attempt the reproduction of the original material (Table 1) powdering one of the rocks that may contain diamond [12] (the reason for this choice will be explained later) and adding to this grinded material the other components as pure chemical reagents in the form of carbonates ($CaCO_3$ and Na_2CO_3) or oxides (MnO_2 and Fe_2O_3) (glass II; Table 2). The chosen rock was granite, available in Trentino region mainly as Cima d'Asta granite and Predazzo pink granite [13]. These geological formations are not located exactly in the area of Riparo Dalmeri, which is characterized by the presence of sedimentary rocks but their distance from the site is not prohibitive for a use also at the shelter. In the production of the glass a granite of composition similar to the Cima d'Asta type [13], made available by the Monte Zaccon Company, was employed. Its composition was determined by inductively coupled plasma mass spectrometry (ICP/MS). Other two glasses (glass I and glass III; Table 2) were produced starting from chemical reagents only (no natural mineral precursor), in order to enhance possible differences in the properties of the archaeological glass with respect to those produced artificially. Each batch of reagents, in the form of a powder mixture was put into a crucible and then melted in an electric furnace by increasing the temperature up to 1300°C in five hours and then keeping it stable for one hour. After melting, glass I and III were quenched in water.

Simultaneous thermogravimetry and differential thermal analysis were undertook with a TG-DTA/DSC Setaram apparatus to determine the glass transition temperatures of the replica glasses. About 20 mg of powder of each glass were put in a capsule and their behaviour during heating was compared to that of a reference alumina (Al_2O_3) sample. The heating program increased the temperature of 10°C/min from room temperature to 750°C. The flux of pure air in the oven was kept at 100 ml/min.

3. Results

The X-ray diffraction pattern of the bead (Fig. 2) revealed that this object is made of an amorphous material, as no coherent scattering diffraction peaks are observed. This was surprising, because Palaeolithic beads are typically made of shell, ivory, amber, stone and other natural materials and thereby it was expected to see diffraction peaks of crystalline phases in the relevant XRD pattern.

The amorphous nature of the material was confirmed by micro-Raman spectroscopy. The Raman spectrum, given in the inset of figure 3, shows the broad peak typical of an amorphous phase, upon a strong luminescence background. It also provide evidence of the presence of cubic (peak 1) and hexagonal diamond phases (Lonsdaleite , peak 2). From the peak broadening and shift in the spectrum, it can be estimated a crystallite size ranging from 100 nm down to 10 nm for the cubic diamond [14].

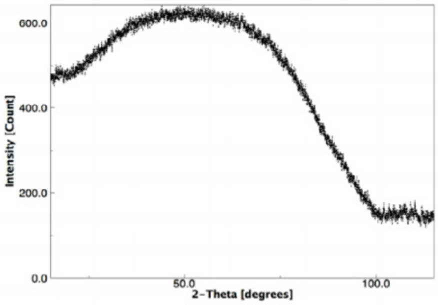

Fig. 2 X-ray diffraction pattern of the Dalmeri's bead which shows the amorphous nature of the material.

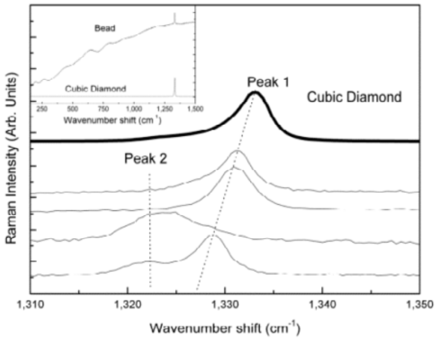

Fig. 3 Detail of the Raman spectrum of the Dalmeri bead, showing the presence in the glassy matrix of cubic (peak 1) and hexagonal Lonsdaleite (peak 2) diamond phases. In the inset the whole spectrum is provided where it is possible to observe the broad halo typical of an amorphous phase upon a strong luminescence background.

Scanning electron microscopy allowed to measure the diameter both of the bead and of its hole. The bead has a maximum diameter of 3.4 mm and a minimum diameter of 2.5 mm, while the hole 1.17 mm and 1.13 mm. A careful observation of the hole revealed that it is quite regular (Fig. 1). Instead the study of surface alteration (Fig. 4) confirms that the bead has been buried for a certain period. In fig. 4 the detachment of altered layers due to alkali (Na and K) migration characteristic of glass weathering [15]are shown.

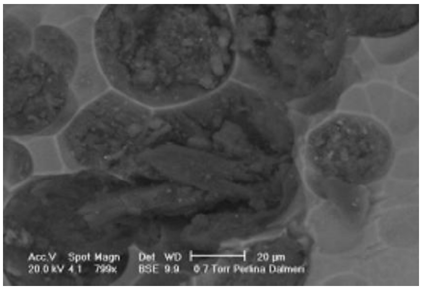

Fig. 4 LVSEM image of the surface of the bead characterized by craters with diameters of several tens of micrometers.

Energy dispersive X-ray spectroscopy provided the composition of the bead (Tab. 1). This composition suggests that the glass is viscous and difficult to be worked. The high content of alkali (13.5 wt%) which reduces the connectivity of the structure and thus should guarantee high workability is compensated by a similar content of alkaline earths (13.1 wt%) that have an opposite effect as the divalent cations Ca and Mg have a greater field strength and thus creates stronger bonds to neighbouring oxygen ions [16]. Moreover, the slightly higher amount of Fe_2O_3 is compensating for the lower amount of Al_2O_3 and allows the obtainment of a value of R_2O_3 (6.9 wt%) (sum of the two oxides) comparatively high, which again might suggest that the glass is durable but very viscous and thus difficult to be formed.

SiO_2 (wt%)	**Al_2O_3** (wt%)	**Na_2O** (wt%)	**K_2O** (wt%)	**CaO** (wt%)	**MgO** (wt%)	**MnO** (wt%)	**Fe_2O_3** (wt%)
60.5	2.3	11.1	2.5	9.8	3.3	5.9	4.6

Table 1. Composition of the bead as measured by EDXS (wt%), reported in oxide percentages.

The density of the bead is 1.7 g/cm^3. This quite low value can be explained only by the presence of air bubbles that again are another evidence of the fact that the artefact under investigation is not a stony but a glass bead [17].

From the analysis on the artefact it emerges that the bead has unique features: it is made of a glass matrix contemporarily very rich in iron and manganese that contains nano-sized diamonds and was found as an alone finding (only bead and only glass artefact) in a shelter dated at the Palaeolithic when, to our knowledge, glassmaking was unknown.

The appearance of the model glasses is shown in Figure 5. The composition (wt %) of each glass is provided in terms of concentrations of the main oxides, in Tables 2. The glass better reproducing the archaeological one is material n.3 (compare Table 1 and Table 2) with the exception of a small difference in the aluminium (3.0 wt% instead of 2.3 wt% in oxide) and in the alkali content (9.0 wt% Na_2O instead of 11.0 wt%) and an important difference in the iron content (6.5 wt% instead of 4.6 wt% in oxide). As can be observed by comparing the columns in the tables 2, referring to the batch and to the final composition of the glasses, the concentration of manganese oxide is the one that is changing most in the transformation from raw materials to glass.

The microstructures of the three glasses were similar and revealed unmelted residues of the raw materials. The densities of glass 1, glass 2 and glass 3 are respectively of 2.602 ± 0.004 g/cm^3, 2.668 ± 0.005 g/cm^3 and 2.692 ± 0.007 g/cm^3. The X-ray diffractograms did not show the presence of any crystalline phase but just “humps” characteristic of amorphous materials [18]. Another indication emerging from the diffraction results is that the residues of undissolved crystalline phases have concentrations certainly below 2 wt%, that is the estimated detectability limit of the experimental set up. The thermograms of the glasses showed an inflection at about 350°C, corresponding to the glass transition temperature (Tg).

Fig. 5 Crucible containing glass III. This glass was quenched in water.

	Glass I: from chemical reagents only		**Glass II**: granite (silica source) and chemical reagents		**Glass III**: : from chemical reagents only	
	batch (wt%)	final composition (wt%)	batch (wt%)	final composition (wt%)	batch (wt%)	final composition (wt%)
Al_2O_3	2.4	2.6	2.5	3.5	2.4	3.0
SiO_2	59.5	59.1	55.3	59.2	59.3	60.2
Na_2O	11.0	15.1	10.1	13.6	8.6	9.0
K_2O	3.3	2.3	2.9	2.3	3.3	2.5
MgO	2.7	3.7	2.5	3.9	2.7	3.6
Fe_2O_3	4.3	3.9	4.1	4.1	6.1	6.5
MnO	6.9	4.2	6.3	4.2	7.6	5.3
CaO	9.8	9.0	16.2	9.2	9.8	9.9

Table 2. The chemical composition (wt%) of the three model glasses, provided in terms of concentrations of the main oxides, was determined by EDXS and it is the average of at least five measurements carried out in different spots of each glass material.

4. Discussion

To produce a glass bead first it is necessary to make the glass or either to dispose of a natural glass. Glass technology was unknown in the Palaeolithic times [19], thus, the first hypothesis to be investigated is the opportunity to find a natural glass with composition, properties and possibly spherical shape already available for prehistoric people. Natural glasses can be divided, on the basis of formation process, microstructure and composition into four classes: volcanic glasses, biological glasses, folgorites and impact glasses. Volcanic glasses have an alkali content generally not higher than 10% and to our knowledge do not contain diamonds thus it can be excluded that the Dalmeri glass belongs to this group. Biological glasses as well should not contain diamond as they have a sedimentary origin and constitutes the skeleton of mollusks and shells. Folgurites have also a mainly siliceous composition and although present in the Italian Alps were not as interesting for this study as impact glasses, in particular microtektites. Microtektites exist in the form of spherules with diameters that reach 2 mm or ovoids reaching 5 mm in diameter [20] and moreover, they can contain diamond both in cubic and hexagonal phases. If Palaeolithic people dispose of such a spherical microtektite the production of the bead would only have required the manufacturing of the central hole. Although Palaeolithic people had good drilling skills [21-24], it is not likely that the hole of the Dalmeri bead was bored, as it would not look so regular. In particular, the two sides of the hole would have different dimensions as a result of beginning the perforation at the two sides of the bead until the two holes met [17].

Although the presence of nanosized diamonds may suggest the use of a glass of natural origin for the manufacturing of the bead [19], similar materials were obtained from different combinations of raw materials (table 2) suggesting that an artificial origin of the glass cannot be ruled out. In agreement with this hypothesis would be the peralcalinity ($Al_2O_3<Na_2O+K_2O+CaO$) of the chemistry of the glass is which is typical of artificial glasses [25]. The artificial hypothesis is also supported by the simultaneous high content of iron and manganese oxides, with a manganese content higher than 1% suggesting an intentional addition of this ingredient to the glass batch [26]. The fact that the concentration of manganese changes during the transformation from raw materials to glass allows to infer that in the glass batch used to produce the bead, in the hypothesis that the material was synthesized, there was even more manganese than the quantity that was measured on the final artefact. To support an artificial origin of the glass it would be of extreme usefulness to see traces indicating a particular manufacturing technology for the bead. The most common ancient technologies to produce beads were winding and drawing and it is possible distinguish the two by observing the shape of the air bubbles in the bead [17]. Unfortunately, due to the alteration of the surface of the bead it was not possible to observe the shape of the air bubbles and thus we are not able to state with certainty that one of the two technologies was employed. An alternative, less common, technique compatible with the artefact here studied is the "Indian" hand-perforation in which a drop of molten glass is quickly perforated with a hot iron nail on an earthenware dish [17]. Considering that the measured densities of the replica artificial glasses indicate their substantial full density, and indirectly confirm the conjecture of significant amount of gas inclusions in the archaeological bead, technologies leading to the obtainment of a low density bead should be considered plausible hypothesis. In recent (XX century) and present times, the Krobo of Ghana use baked clay mold to produce powder glass beads from glass scraps [27]. We are not aware of the existence of such a technique in prehistoric times, but starting from glass powder would lead to have a low density glass because of the space between the grains cannot be perfectly sealed by the melted material and still to obtain a quite good final material, like the Dalmeri glass, superior in aspect to the most ancient known (for example, Frattesina, Rovigo, Italy glass). While contemplating an artificial hypothesis, it cannot be forgotten that the object under investigation contains nano-diamonds. Lonsdaleite, the most common hexagonal form of diamond, can be found either in structures that form in association with meteoritic impact events, like impactites and meteorites, or in rocks of terrestrial origin, such as intrusive and metamorphic rocks [28]. The existence of diamonds in intrusive and metamorphic rocks may suggest their use as raw materials for the production of glass and open up a third intermediate hypothesis for which the glass is artificially made from raw materials naturally containing nano-diamonds. Diamonds are stable at the temperatures necessary for glassmaking unless they are exposed to oxidizing atmospheres. Useless to say that an artificial origin of the glass material would move its age to much more recent times. In the geographical area of the rock-shelter, glass production workshops are known only from the Late Roman period and they were all probably using glass scraps, as the town of Trento and surrounding areas were far from the sources of raw materials [29]. Apart from this, a Palaeolithic origin for the glass bead would be, of course, surprising also in other contexts, as the oldest evidences of glass beads, which were found in Egypt and in Mesopotamia, are dated to the Bronze Age, between the end of the third and the beginning of the second millennium B.C. [19]. Bronze Age glass beads have been also found in Europe: in British barrows [30] and in Germany, precisely in the surroundings of Göttingen and Kassel [31], but it is believed that they were imported from Frattesina (Rovigo, Italy), the only European Bronze Age glass manufacturing site [18], or from other Mediterranean or Near Eastern production sites, as it is known that in ancient times glass beads were traded [32].

The replica experiment shows that to produce a glass with that composition it is necessary at least to reach 1000°C, which would not be possible in Palaeolithic times since even Late Bronze Age glass production reached maximum estimated temperatures of 1100°C [33]. The glass materials in this study were produced at 1300°C and still unmelted residual of the components of the glass batch were visible in the micrographies acquired by SEM (not shown in this paper), proving that even with modern furnaces long melting times are required. This is in agreement with some experimental archaeology trials [34] that observed that to obtain complete melting of a batch made of sand and plant ash it is necessary to stay at 1390°C for 24 hours. This long time is required because first a liquid phase has to be formed and needs to percolate around the other grains of the solid material to guarantee a homogeneous melt through the good contact of the components of the batch [34]. On the other hand, the fact that the archaeological bead has a much lower density than the replica glasses suggests a low temperature of the ancient glass making furnace, as gaseous inclusions are more likely to be retained if the temperature of the furnace is low and viscosity stays high. The presence of air bubbles is not surprising as it was already highlighted from the composition data that the glass of the bead was viscous and difficult to be worked. Indeed, it has been observed that in a standard melt, composed of 54% sand, 24% $NaCO_3$, 16% $CaCO_3$ and 2% of mixed metal oxides, it takes one minute for a bubble with a diameter of 1 mm to move a distance in the material of 1 μm at 1330°C [24]. Therefore, in the glasses produced in the present work and in the bead, processed at lower temperatures and with a more viscous material the removal of the bubbles, once they formed, turned out to be very difficult. Moreover, with ancient furnaces the control of the temperature ramp was not possible and the fast heating rate involved the rapid formation of the liquid, which entrapped some air, contained among the space between the particles of raw materials forced to remain spherical in shape because of the surface forces of the liquid [16].

If a quite high temperature is required to make the glass, the comparatively low Tg, would allow correspondingly low working temperatures in principle accessible by a prehistoric fire camp or furnace.

5. Conclusions and perspectives

The regularity of the hole of the bead allows the Authors to exclude that the bead was bored. As a consequence, a natural origin of the glass composing the bead, such as the finding by Palaeolithic people of a tektite microspherule containing nano-sized diamonds, is unlikely.

Micro-Raman spectroscopy reliably indicated the presence of nano-diamonds of the cubic and hexagonal polymorphs [35-36]. The fact that in the literature no artefacts similar to the Dalmeri bead made of a glass matrix containing nano-diamonds are described may be due to the lack of a micro-Raman study of the other glassy spherules, and this study would foster further research in this field.

Replica experiments are useful to measure some material properties (Tg, etc.) not measurable on the unique archaeological artefact. With the limitations of the nature itself of a replication experiment, suggested by Henderson [25], that never guarantees that the choice of the raw materials for the experiment are matching those of the item to be mimicked, nonetheless the Authors believe that valuable reflections and questions raised by the experiment may direct future research on the artefact found at Riparo Dalmeri and on prehistoric glass-making in general.

The hypothesis that the Dalmeri's bead glass is artificial is possible, but, as was shown by the replica experiment, a temperature higher than 1000°C is required for its production and thus a technology more recent than that available in Palaeolithic times.

In the future, a better understanding of the weathering mechanisms, through the study of soil composition and bead alteration surface layers, would provide additional information on the actual duration of the burial and, indirectly, on the age of the bead.

Acknowledgements

The authors wish to thank Giampaolo Dalmeri for allowing the analysis of the bead, Romina Belli for the archaeological interpretations, Luca Lutterotti for the X-ray diffraction measurements and Wilma Vaona for the TG-DTA/DSC analysis.

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