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Spontaneous glass fracture in archaeological artifact: The impact of fire

Teresa Palomar^{a,*}, Eva Peiteado^{a,b}, Nadine Schibille^c, Joaquín Barrio^d, Sebastián Celestino^e, Esther Rodríguez González^e

^a Instituto de Cerámica y Vidrio (ICV), CSIC, Campus de Cantoblanco, 28049 Madrid, Spain

^b Misión Biológica de Galicia (MBG), CSIC, Campus Vida, 15705 Santiago de Compostela, Spain

^c Institut de Recherche sur les Archéomatériaux (IRAMAT-CEB), UMR7065, Centre National de la Recherche Scientifique (CNRS)/Université d'Orléans, Orléans, France

^d Servicio de Conservación, Restauración y Estudios Científicos del Patrimonio Arqueológico (SECYR) - Universidad Autónoma de Madrid (UAM) and Departamento de Prehistoria y Arqueología, Facultad de Filosofía y Letras, Universidad Autónoma de Madrid, 28049 Madrid, Spain

^e Instituto de Arqueología de Mérida (IAM), CSIC - Junta de Extremadura, 06800 Mérida, Badajoz, Spain

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ABSTRACT

This study investigates the state of preservation of colorless glass bowls from the 5th century BCE found at the archaeological site Casas del Turuñuelo (Guareña, Spain). Despite having identical chemical compositions, the bowls are in varying states of preservation. Analytical techniques including SEM-EDS, Vickers hardness testing, polariscope examination, and hot-stage microscopy reveal that two bowls remain largely intact with common alteration layers, while another is shattered and has different mechanical properties. The results suggest that the exposure to ceremonial fires induced internal stresses that led to spontaneous fracturing. Subsequent burial conditions, including groundwater fluctuations and soil chemistry, favored fissure propagation and alteration.

1. Introduction

The alteration of glass during burial greatly varies depending on its chemical composition, the characteristics of the soil, and the duration of burial. Regarding the chemical composition, the most abundant archaeological material is soda-lime-silicate glasses and mixed silicate glasses with Na₂O, K₂O, CaO, PbO, and BaO. The greater chemical stability of the glasses containing sodium compared to other elements has enabled a larger number of samples to be preserved during burial [1,2]. The main alteration pathologies are degradation layers, pitting, and surface deposits. The alteration layer is formed by successive layers, which some authors have linked to annual climatic fluctuations [3,4]. This theory can no longer be upheld because it has been shown that the thickness of these layers depends, among other factors, on the composition of the glass, the characteristics of the soil and the adhesion, which is usually brittle and flakes off easily. The morphology of the lamellae depends on the surface of the original glass, inclusions, bubbles, etc. [5]. Chemical analysis of the dealcalization layer shows a high content of SiO₂ and Al₂O₃, due to the leaching reaction of alkali and alkaline earth ions from the glass [5–9]. Pitting is commonly found on the glass surface, beneath the dealcalization layer. It has a hemispherical or

elongated morphology and is often interconnected. The average pit depth ranges from 2 to 3 μm [10,11]. Deposits typically appear on the surface, in fractures, or between the dealcalization layers, and can be crystalline or amorphous. The most commonly identified compounds are carbonates, phosphates, and sulphates [12]. Dark deposits with manganese-rich deposits, Fe₂O₃ and amorphous iron hydroxides have been found in some glasses. These metal oxides tend to precipitate in cracks or between degraded layers because of a local increase in basicity [13–17].

In this study, the conservation problems of colourless glass bowls from the archaeological site Casas del Turuñuelo in Guareña (Badajoz, Spain) have been analysed [18]. The site consists of a building with adobe walls, lime mortar, and other materials, dated between the 7th to the 5th century BCE, the end of the Tartessian culture [19–21]. One of the factors that has favoured the preservation of the archaeological materials at the Casas del Turuñuelo site is the constant humidity of the site. This is due to the building's proximity to the Guadiana River, as well as the current agricultural use of the surrounding land, which is dedicated to irrigated farming. This circumstance has favoured the excellent preservation of organic materials, such as seeds, charcoal, and bones. In contrast, these microenvironmental conditions, with continuous rises of

* Corresponding author.

E-mail address: t.palomar@csic.es (T. Palomar).

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the groundwater level, have led to severe deterioration of metallic objects, especially pieces made of bronze and iron, which are in a very poor state of conservation.

Regarding the glass objects, three colourless bowls were found in the main courtyard of the building, at the foot of a staircase together with a fragment of a marble sculpture and the remains of an animal sacrifice [19,22]. The layer in which the bowls were found is composed of brown clay with a high proportion of ash and coal. This suggests that the entire structure was exposed to fire, as corroborated by the presence of vitrified walls and carbonized vegetable fibre mats, wood fragments, and skeletons of animals [23]. Two of the glass bowls, which were almost complete, were found on one side of the stairs, and the other one, which was shattered, approximately two meters away [24]. The main objective of this study is to understand the different states of preservation of the three glass bowls and the factors responsible for these differences.

2. Materials and methods

2.1. Samples

Three glass bowls were found in the archaeological site. All the glass fragments were heavily corroded. Two of the bowls, references 828 and 829, were reconstructed almost completely (Fig. 1a and b). The glass of

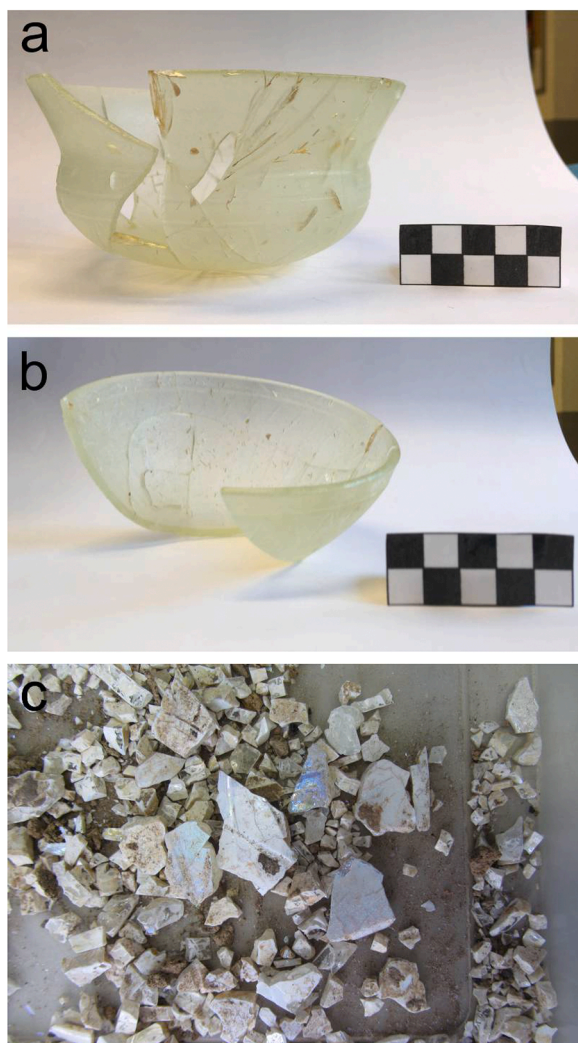


Fig. 1. Glass objects from Casas del Turruñuelo (Guareña, Spain): a) object 828 after reconstruction, b) object 829 after reconstruction, c) fragments from object 834.

both objects was slightly yellow, translucent, with 3–4 mm thick walls after cleaning and cut incised decorations [25]. It was possible to take one small sample not reintegrated from bowl 828. The third object (reference 834) was a series of fragments that has the same characteristics as the other two bowls in terms of colour, thickness, and surface decoration; however, their fragments are very brittle, making reconstruction impossible (Fig. 1c).

2.2. Analytical methods

The samples were characterized using stereomicroscopy, scanning electron microscopy with X-ray energy dispersive spectroscopy (SEM-EDS), Vickers hardness test, polariscope, hot-stage microscopy (HSM), and laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS).

The glass samples' surfaces and cross-sections were examined using reflected and transmitted light with a Nikon SMZ1000 stereomicroscope.

For SEM-EDS, small fragments were mounted as cross sections embedded in epoxy resin and polished, sputter-coated with carbon for conductivity, and examined and analysed with a Hitachi S-4700 instrument using high vacuum with a pressure of less than 1×10^{-3} Pa and an acceleration voltage of 15 kV at 12.0 mm of working distance. The analysis of the glass core was made in a surface of $\sim 320 \mu\text{m}^2$.

Vickers hardness of the glass samples was measured on the cross-sections using a Universal Indentation and Scratch Tester Model APEX-1 with a Model MH-1 indenter controller, using the CETR UMT Software 1.136.257.F05, build 1281. The areas without weathering layers or fissures were visually identified with a microscope for hardness testing. 36 indentations in the glass core were performed on each sample with a measurement time of 10 s and a force of 2 N.

Observations of internal stress were performed using a polariscope from Polarizing Instrument Co., Inc. Model Number 110.

Hot-stage microscopy (HSM) of the glass powder from sample 834 was carried out to determine thermal properties. An EM-201 image analysis-heating microscope (Hesse Instruments) was used to measure the samples at a heating rate of $10 \text{ }^\circ\text{C}/\text{min}$ up to $1200 \text{ }^\circ\text{C}$. Glass powder with particle size $x < 63 \mu\text{m}$ was cold-pressed to form samples with 3 mm in both height and diameter. The variation of the sample area is recorded as a function of temperature.

To determine the chemical composition of the glass, laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) was performed using a Thermo Fischer Scientific ELEMENT XR mass spectrometer combined with a Resonetics M50E excimer 193 nm laser at IRAMAT-CEB, Orléans (France). Three individual measurements were carried out for object 828, and six for object 834 in single spot mode with a beam size of $100 \mu\text{m}$, an energy of 5 mJ and a repetition rate of 10 Hz. Following a pre-ablation time of 15 s, a 27 s acquisition resulted in 9 mass scans for each of the analysed isotopes. ^{28}Si served as an internal standard, while five reference glasses (NIST610, Corning B, C, D and APL1) were used to calculate the response coefficients for each element to convert the results into fully quantitative data [26,27]. Corning A and NIST612 were analysed at regular intervals and yielded accuracies of $< 5 \%$ for most major and minor elements, and $< 8 \%$ for trace elements. Reproducibility was within 5 % for most elements.

3. Results

3.1. Chemical composition

The LA-ICP-MS analyses proved that both bowls were made with practically identical glass (Table 1). It is a soda-lime-silica glass with low Mg and K contents that points to a natron glass.

The morphology of the pieces resembles Late Classical or Early Hellenistic bowls from Greece or the Eastern Mediterranean, in accordance with the marble sculpture fragment and three sand-core glass

Table 1

Average chemical compositions of the two bowls analysed by LA-ICP-MS. Data were reduced to the main oxides and Cl. n: number of analyses, SD: standard deviation.

	Chemical composition (wt. %)								
	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	Cl	K ₂ O	CaO	Fe ₂ O ₃	Sb ₂ O ₃
Bowl 828 (n = 3)	17.9	0.41	2.16	69.4	0.93	0.45	7.08	0.26	1.22
SD	0.02	0.002	0.009	0.03	0.01	0.002	0.05	0.001	0.02
Bowl 834 (n = 6)	17.8	0.41	2.19	69.5	0.92	0.46	7.00	0.26	1.27
SD	0.04	0.003	0.004	0.05	0.01	0.008	0.04	0.002	0.05

oinochoe also found in the archaeological site [28]. The chemical composition of the bowls was compared with contemporary pieces located in the Balkan peninsula and nearby. The analyses of the silica sources (Fig. 2a and b) showed they were made from Levantine glass similar to some Classical-Hellenistic beads and Hellenistic vessels from Thebes [29], 5th-century BCE aryballos from the Po Valley [30], and 5th-century BCE small containers and two 4th-century BCE bottles with stopper from Pydna [31], which is consistent with the chronology proposed for the archaeological site.

3.2. Glass alteration

Interestingly, although the two bowls have the same chemical composition (Table 1), their state of preservation is completely different. The well-preserved sample 828 showed the formation of alteration layers on its glass surface, as well as the presence of pits and plugs with some brown staining from iron ions from the burial environment (Fig. 3a). Moreover, a thick and homogenous layer (~50 μm) was visible on the surface (Fig. 3b). In areas where the layer was damaged (Fig. 3b) or removed (Fig. 3c), alteration advanced. This behaviour suggests that the layer protected the glass core. Analyses of these areas showed that lixiviation of sodium and calcium occurred in the decomposed multi-

layered structures (Table 2). A relative increase in SiO₂ and Al₂O₃, network formers of the glass matrix, as well as in K₂O and Fe₂O₃, elements presumably from the environment, was observed. The presence of ~5 wt. % K₂O in the alteration layers has previously been observed by Palomar in Roman glass fragments recovered from the seabed [34]. In the present case, this effect may be attributed to groundwater that periodically floods the archaeological site [35]. The protective layer shows a high-SiO₂ content, a loss of Na₂O and a relatively high CaO concentration (Table 2). The chemical composition corresponds to that of a leached layer; however, its morphology as a unique thick layer with protective property points to a dense rather than a hydrated layer and thus a different origin. A similar behaviour was observed in Roman glass from cremation deposits at Birdoswald Fort on Hadrian's Wall [36]. There, the greater sodium depletion in the molten glass fragments may be due to the evaporation of sodium during exposure to high temperatures as part of the cremation ritual.

The fragmented sample 834 shows a higher density of fissures that criss-cross the fragment, making it prone to breaking under very low pressure (Fig. 3d). Most of them showed multilayers of alteration in parallel to the crack and, even pits inside the cracks (Fig. 3e and f). This behaviour agrees with the presence of reiterative groundwater flooding of the archaeological site. The water can filter through the fissures and cracks, inducing the alteration inside them [37,38]. Apart from the presence of a higher concentration of fissures, there are no observable differences compared with the well-preserved sample 828. Moreover, the chemical analyses showed similar results on the glass core, the degradation layers and the protective layer (Table 2), probing the similar conditions of alteration. This suggests that the fractures might have formed before or during burial and refutes the hypothesis of a different alteration mechanism.

3.3. Mechanical properties

The hardness of the glass core was measured with the Vickers microindentation technique. Sample 828 exhibited homogenous behaviour, meaning that all analysed areas had similar hardness (Fig. 4a, Table 3). In contrast, the hardness of sample 834 showed a higher scatter of the results, indicating that the analysed areas are not homogeneous. Additionally, several cracks appeared during the experiment, suggesting the presence of internal stresses. This different behaviour in the unaltered glass core is unusual for historical glass. A well-made piece of glass has a homogeneous glass core, with a uniform chemical composition and, therefore, a homogeneous glass structure [39]. Since the chemical composition of both fragments is identical, the higher variability of hardness in fragment 834 is not related to the chemical composition, but to its distribution in the glass matrix [40]. Minor changes in material properties can lead to failure processes beneath an indenter [41].

Young's modulus produced a similar behaviour (Fig. 4b, Table 3). Sample 834 showed a similar mean Young's modulus, but a higher scatter in the data. This confirms that the measured areas have different elasticity, which is also related to the structure distribution. The question that arises is how this non-altered material modifies the glass structure during use or burial.

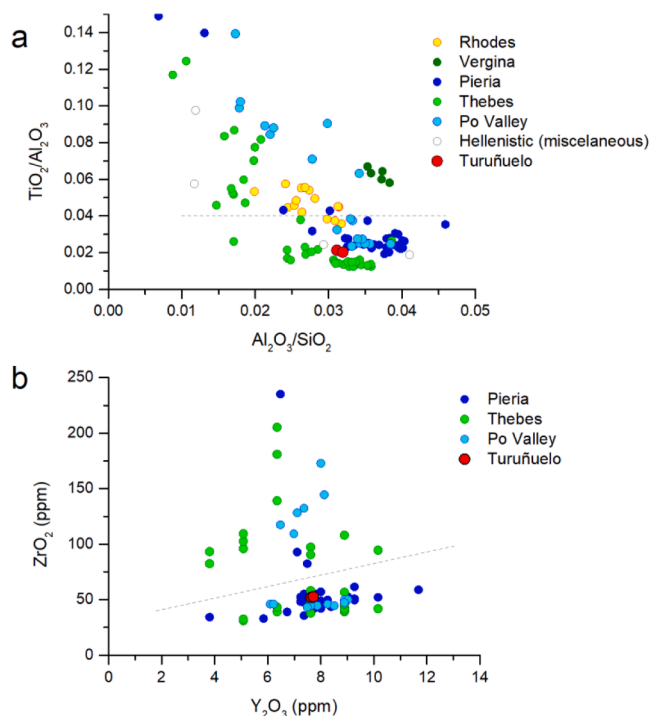


Fig. 2. Glasses from the 1st Millennium BCE located in the Balkan Peninsula and nearby in comparison with the bowls from Casas del Turruñuelo. a) TiO₂/Al₂O₃ versus Al₂O₃/SiO₂, dashed line from [32]; b) Y₂O₃ versus ZrO₂, dashed line from [26]. Natron glass is compared to samples from Rhodes, Vergina and Hellenistic (miscellaneous) [33]; Thebes [29]; Po valley [30].

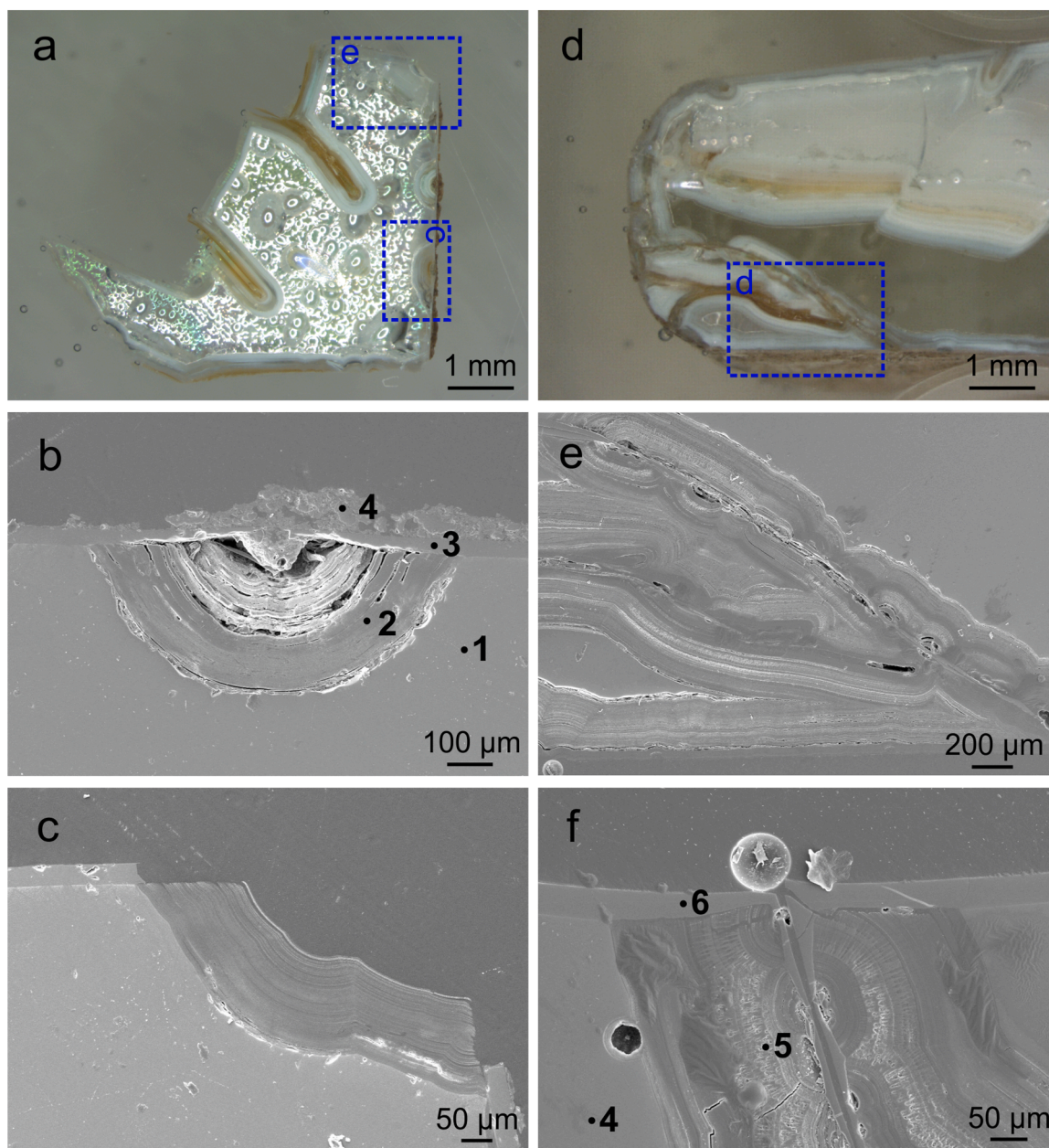


Fig. 3. Images of stereomicroscope and SEM-EDS of the samples analysed. a) Overview of the cross-section of sample 828, b) magnification of a surface pit, c) magnification of alteration layers on the surface. d) Overview of the cross-section of sample 834, e) zoom of the alteration layers in the fissures, f) magnification of the protective layer on the surface. The numbers represent the areas analysed by SEM-EDS (Table 2).

Table 2

Chemical composition by SEM-EDS (wt. %) of the areas indicated in Fig. 3, <d.l. = below detection limit (0.1 wt %).

Glass sample	Analyses	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	SO ₂	Cl	K ₂ O	CaO	TiO ₂	Fe ₂ O ₃
828 (well-preserved)	Glass core	18.7	<d.l.	1.4	70.2	0.7	1.2	0.4	7.4	<d.l.	<d.l.
	Degradation layer	<d.l.	0.1	7.9	84.0	<d.l.	0.8	5.0	1.2	<d.l.	0.8
	Protective layer	1.3	<d.l.	1.4	85.8	<d.l.	1.7	0.6	9.4	<d.l.	<d.l.
	Surface deposits	1.5	0.9	11.0	77.1	<d.l.	<d.l.	2.3	<d.l.	0.5	6.8
834 (smashed)	Glass core	17.3	0.2	1.4	71.7	<d.l.	1.3	0.5	7.6	<d.l.	<d.l.
	Degradation layer	0.6	<d.l.	4.4	86.3	<d.l.	1.4	4.0	3.4	<d.l.	<d.l.
	Protective layer	<d.l.	0.4	1.4	83.9	<d.l.	2.1	0.7	11.6	<d.l.	<d.l.

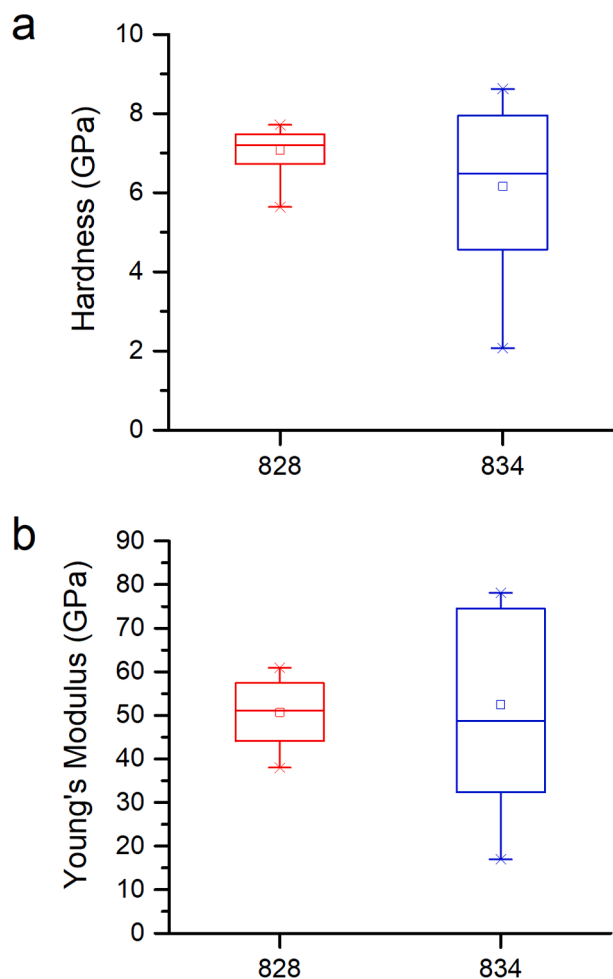


Fig. 4. Results of the vickers measurements: a) hardness, b) Young's modulus.

Table 3

Statistical results from Vickers measurements (Fig. 4). n: number of indentations, SD: standard deviation.

	Hardness (GPa)		Young's modulus (GPa)	
	828	834	828	834
n	35.00	39.00	35.00	39.00
Maximum	7.72	8.62	60.89	78.14
Minimum	5.64	2.07	38.02	16.98
Mean	7.08	6.16	50.65	52.46
Median	7.20	6.49	51.14	48.68
SD	0.47	2.00	6.84	21.60

3.4. Thermal properties

The bowl 828 is complete except for the small fragment that was embedded for SEM-EDS (Section 3.2). For this reason, it was not possible to analyse its thermal properties. Only one broken fragment of object 834 was pulverised and examined using hot-stage microscopy, which records the behaviour of glass powder with increasing temperature. The glass is stable up to 574 °C (Fig. 5, Table 4). At this temperature, the glass powder undergoes structural shrinkage. After reaching maximum shrinkage at approximately 680 °C, the glass powder begins to melt and sequentially forms the following structures: deformation, sphere, half ball and, finally, flow [42]. This behaviour is consistent with that of Roman soda-lime-silicate glasses of similar chemical composition [43], showing no significant difference in this property.

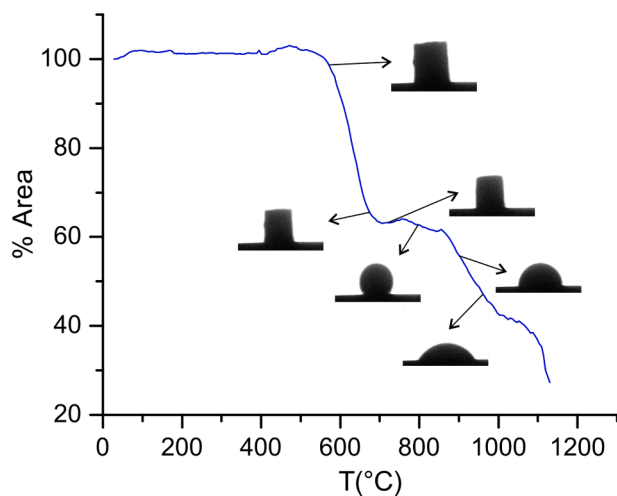


Fig. 5. HSM result of the glass fragment 834.

Table 4

Results of the HSM technique on the glass fragment 834.

Viscosity points	log η (P)	T (°C)
Initial shrinkage	9.1	574
Maximum shrinkage	7.8	679
Deformation	6.3	714
Sphere	5.4	796
Half ball	4.1	899
Flow	3.4	963

3.5. Thermo-optical properties

The last method used was polarising microscopy to visualise non-visible internal stresses through the dispersion of the light that produce rainbow-like interference colours. The fragment from bowl 828 could not be examined with the polarising microscopy due to its small size (approximately 6 mm).

The examination of the 834 fragments revealed interference colours in the non-altered glass near the fissures (Fig. 6), indicating internal stresses. The internal stresses can be relieved through crack formation and are therefore likely the cause of the high number of fractures in the glass object.

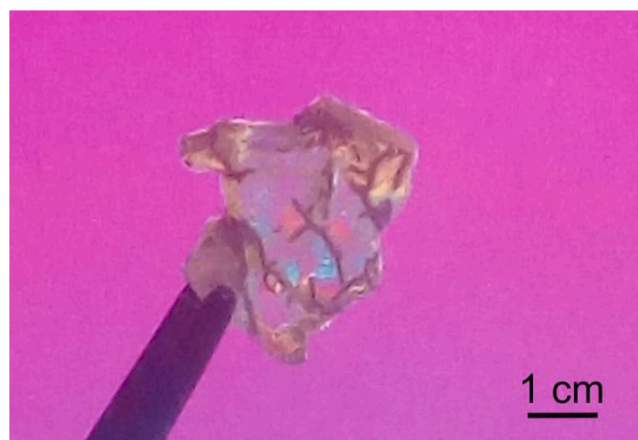


Fig. 6. Interference colours on the glass fragment 834 observed in a polariscope.

4. Discussion

The fragment from bowl 828 appears to have a homogeneous glass core with consistent hardness and typical surface alterations, including pits and weathering layers. The fragments from object 834 have the same chemical composition but different mechanical properties, including varying hardness of the glass core, internal stresses, and alteration characteristics, such as weathering along interior fractures.

The alteration pathology called “sugaring” or “sugared glass” leads to the fragmentation of objects into pieces that measure < 0.1 cm [8]. Sugared glass was found in a group of glass objects from the Roman Bocholtz burial. In this glass, fractures in the gel layers were caused by the natural wetting and drying cycles of the soil. More extensive disintegration correlates with a lower CaO content in the altered objects. Furthermore, the soil of the burial is slightly basic, which could accelerate the leaching rate [8,44]. This phenomenon has also been reported in archaeological 16th-century window glasses from the Cistercian Abbey of the Dunes - Koksijde (Belgium), where unaltered bulk glass remains in the core of the fragments and the alteration layers have a sugary appearance [45]. This sugaring effect seems to occur in glasses with low chemical stability as a result of a rapid and intense leaching. Nevertheless, the alteration observed in Casas del Turuñuelo’s bowls do not correspond to this sugary appearance of the alteration layers because homogeneous and consistent alteration layers were formed instead of the fragmented layers characteristic of sugared glasses. The fragments of bowl 834 shatter even under very gentle pressure during examination or handling because altered fissures run through the piece, but the cracks are long and continuous, rather than the short, interconnected structures that gives rise to the sugary appearance in glass [45].

The fact that both bowls (objects 828 and 834) were made with the same glass (Table 1) indicates that the different stability of the sample 834 cannot be attributed to the glass composition. The polariscope proved that the smashed glass had internal stresses that could be relieved by the formation of fissures. These stresses are probably the origin of the high number of fractures in the glass object.

Different hypotheses arise to the formation of these stresses:

1. During manufacture i.e., when a glass has not been sufficiently annealed. The chemical composition confirms that the glass bowls were produced in the Eastern Mediterranean (Section 3.1) and reached Casas del Turuñuelo with the other Levantine objects by boat and cart through trade [25]. If the stresses arose during production, the bowl must have broken during the long transportation.
2. During use. The fracture of the bowl during its use by a shock or an explosion could shatter the piece, such as the glasses from the Archaeological Museum of Beirut (Lebanon) [46], but this does not create internal stresses that are prone to the fractures.
3. During firing. The spontaneous-shattered bowl was found in the area most affected by fire, close to the horse skeletons, which exhibited severe heat-induced alteration. The other two bowls were located near the stairs, in a more protected area. The three bowls were not directly exposed to the fire as the fragments had not melted and the incised decoration remain perfectly visible. However, exposure to high temperatures, such as those generated by fire, can modify the internal structure of glass [47].
4. During burial. While the interaction of glass with the soil and the groundwater can cause a chemical reaction, it does not induce internal stresses. However, the presence of similar protective layers on both fragments (Fig. 3, Table 2) suggests that the fractures may have formed before or during burial.

Smedskjaer et al. (2010) studied the effect of thermal history on hardness of silicate glasses and observed that longer annealing times increase the glass hardness, as they allow configurational rearrangements [48]. However, archaeological glasses exposed to uncontrolled fire, such as cremations, may not show this effect because temperature

fluctuations above and below the T_g prevent stable structural rearrangements. Additionally, when the fire is extinguished, the glass may undergo rapid quenching [49]. If the temperature is not too high, gel layer channels can be formed running from the surface to the glass core. As the damage progress, the gel layer channels widen. At a certain stage, the gel layer begins to crack forming fissures [49].

The altered glass n. 834 was located near animal bones with signs of severe damage consistent with exposure to intense fire [23]; therefore, it may have been subjected to higher temperatures than the other bowls. The direct effect of fire on the glasses was also confirmed by the formation of a protective layer, formed predominantly of $\text{SiO}_2\text{-CaO}$, which prevented alteration of the glass core (Fig. 2c and f). A similar behaviour was produced by thermal treatment on commercial glasses with flow of air, N_2 or NH_3 , which promotes cationic depletion in soda-lime-silicate glasses, thereby enhancing the resistance of the glass to the initiation and the propagation of radial cracks [50]. The presence of unconsumed animals near the bowls [23] may have favoured the emission of gaseous nitrogen compounds, such as NH_3 , HCN and HNCO , during the decomposition of the animal meat and bones by fire [51], potentially inducing this protective effect.

Environmental water has an important role in the crack propagation in glasses [52–54]. The periodic rise of the Guadiana River, which moistens the archaeological site, leached out the modifying ions, causing an increase in hydrogen bonding of hydrous species within the glass surface layer. This exchange promoted the crack-initiation and growth, and therefore, the internal alteration (Fig. 3b-d). Additionally, the high temperature of the fire can also accelerate crack growth [52], as can the presence of basic compounds in the object’s surroundings, such as ammonia (NH_3) released during the decomposition of unconsumed animals, which can be converted to ammonium (NH_4^+) under soil conditions [55]. These basic species have a very strong influence on the position of the fatigue limit [53].

Based on the different facts, the most plausible hypothesis for the spontaneous fracture of the glass is that the ceremonial fire induced a change in the glass structure, generating internal stresses within the object 834. These stresses propagated throughout the glass in the form of fissures, which were subsequently altered during burial. This network of fissures and fractures likely generated extremely fragile fragments that can shatter easily, even under slight pressures.

5. Conclusions

This study analysed the various changes to three glass bowls of Casas del Turuñuelo resulting from different ceremonial offerings. Despite identical chemical compositions, the colourless glass bowls exhibit different states of preservation. Two of the bowls appeared almost complete and display specific mechanical properties; the third bowl was completely shattered, with variable mechanical properties in its glass core as a result of internal stresses. The results strongly support the hypothesis that exposure to ceremonial fire induced internal stresses within the shattered bowl that led to spontaneous fractures. Subsequent burial conditions in the soil promoted the propagation of the fissures and further alterations. Additionally, the analysed fragments exhibited a surface layer that may have formed as a result of exposure to high temperatures, which protect the glass core from further changes.

This case study illustrates how environmental factors affect glass stability, highlighting the complex relationship between historical production, use, and burial conditions in archaeological glass preservation. Understanding these mechanisms is crucial for developing improved conservation strategies for similar glass artifacts.

CRediT authorship contribution statement

Teresa Palomar: Writing – review & editing, Writing – original draft, Supervision, Methodology, Formal analysis, Conceptualization.
Eva Peiteado: Writing – review & editing, Writing – original draft,

Formal analysis. **Nadine Schibille**: Writing – review & editing, Writing – original draft, Formal analysis. **Joaquín Barrio**: Writing – review & editing, Writing – original draft, Investigation, Formal analysis. **Sebastián Celestino**: Writing – review & editing, Writing – original draft, Investigation, Funding acquisition. **Esther Rodríguez González**: Writing – review & editing, Writing – original draft, Investigation, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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