The Eurasia Proceedings of Science, Technology, Engineering & Mathematics (EPSTEM)
ISSN: 2602-3199

The Eurasia Proceedings of Science, Technology, Engineering & Mathematics (EPSTEM), 2023

Volume 24, Pages 63-70

IConTech 2023: International Conference on Technology

Origin of Raw Materials of Ancient Glass (B.C.) from Kythnos Island, Greece

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Abstract: Glass samples (B.C.) from the ancient town of Kythnos in the Cyclades were selected and analyzed for their oxygen isotopic and chemical compositions. Results show that the majority of glass samples are produced using natron as flux, suggesting that raw materials probably came from Wadi Natron and the Levantine area. The majority of the analyzed samples from Kythnos have a homogeneous oxygen isotopic composition, which is equal or very close to the mean value of "B.C." glass, as deduced from a set of isotopic measurements on glass from Europe dated from the 8^{th} to the 4^{th} centuries B.C., showing a relatively narrow range of $\delta^{18}O$ values. Similar results were also obtained from Ancient Pydna in Northern Greece.

Keywords: Oxygen isotopes, Compositional analysis, Ancient glass, Kythnos

Introduction

Natron was the dominant type of glass from the 10th century BC until almost the 9th century AD. For all these centuries the natron they used mainly came from the natural natron deposits found in the evaporating lakes of Wadi Natron (Beni Salama, Bir Hooker and Zakikin the oases of the Western Desert of Egypt) (Nenna, et al., 2005). During different times, glass was produced by a silica sand source mixed with a soda-rich mineral matter (i.e. natron) acting as the flux and a lime-source was added as shells or limestone sand components (Henderson, 1985). Other potential facilities for glass production from the 6th to the 9th century AD were found at Apollonia (Tal, et al., 2004), at Bet Eli‟ezer (Gorin-Rosen & Hadera, 1995; Gorin-Rosen, 2000; Freestone, et al., 2000) and at Bet She‟arim (Brill, 1967; Freestone, 2005; Gorin-Rosen, 1999). In Greek area, the main natron source that has been known and proven in international literature since 2003, is Lake Pikrolimni in Macedonia (Dotsika et al., 2004(a), 2004(b), 2008(a), 2008(b), 2009, 2014, 2015, 2018; Ignatiadou et al., 2003).

Archaeological Information

Kythnos belongs to the complex of northwestern Cyclades, located between Kea and Serifos. It is an island with a long history and special archaeological interest. The most important site of the historical era was Vryokastro, the ancient capital of Kythnos. The fortified polis is situated on the northwest coast of the island and has been continuously inhabited from the beginning of the first millennium B.C. until the 6th – 7th century A.D (Fig 1). The remains of the ancient city occupy an area of approximately 28,5 hectares, including the small islet of Vryokastraki, which was connected to the shore in antiquity by a narrow isthmus.

During the systematic investigations that have been in progress since 1990 (survey and subsequent excavations) several ancient structures, such as temples, public buildings, houses, port facilities, burial monuments, etc., and numerous finds from a wide range of materials and possibly of different origins, have been brought to light. These discoveries have provided valuable insights into the urban planning of the city and the sociopolitical and economic development of the ancient community. The determination of the origin and construction technology of the movable finds will be crucial to understanding and interpreting the production and circulation of artifacts on the island, as well as the role of Kythnos in the trade network of these objects in the wider Aegean area.

For this reason, samples were selected from the Archaic sanctuary dedicated to Artemis and Apollo (Mazarakis Ainian, 2017, 2019), dating from the 6th to 5th century BC. They encompass 8 fragments of vessels such as amforiskoi (perfume bottles) from translucent turquoise blue, deep blue to yellow color glass, pendants and beads of glass paste (for instance triangular and rock-cut pendant types) (Fig 2.).

Figure 1. Aerial photograph of Vryokastro

During the excavation, a wide range of glass vessels and glass beads were discovered, dating back to the 5th to 6th century BC. The purpose of the current study is to investigate the composition of the glass and the origin of the material during this time period. The study's primary objective was to expand the archaeometric database of B.C. aged glass discovered in Greece. Additionally, we aimed to compare the chemical composition of these glass samples with other Greek glass samples based on similar external features and functions.

Henderson, J., Evans, J., Sloane, H., Leng, M., & Doherty, C.(2005). The use of oxygen, strontium and lead isotopes to provenance ancient glasses in the Middle East. *Journal of Archaeological Science, 32*(5), 665–673.

Figure 2. Glass samples

Materials and Methods

Colorful and colorless samples of ancient glass objects, with Roman ages, were selected and characterized. The collection represents different typologies of glass objects, such as vases, flasks, incense holders, plates, lamps, and bottles. These artifacts show a variety of colors (yellow, green, blue, purple, honey, to opaque) caused by the addition of various colors and opacifying agents. Elemental analysis is usually applied to determine the raw materials of glass-made artifacts. Compositional variations in major and trace elements are an indication of the use of different raw material mixtures or different manufacturing procedures. The relation between certain elements detected in glass and the original mineral resources offers the potential to use them as indicators of glass origin (Degryse & Shortland, 2009).

Chemical analysis was performed by Scanning Electron Microscopy (SEM) with Energy – Dispersive X-ray microanalysis (EDX). Energy Dispersive X-Ray Spectroscopy (EDS or EDX) is calculating element concentrations based on energy measurement of X-Rays. The X-Rays are produced after an electron beam from SEM strikes the given point or area. Electrons from inner shells are released and outer shell electrons cover their positions. The X-Ray has a specific energy that is equal to the energy difference between the two shells and is characteristic of each element. The spectrum is taken at the same time for all energies. All the peaks are being evaluated and those that have a value above the detection limit are presented in the results. The detection limit is not strictly dictated, it depends on the area or the element, commonly is somewhere between 0.1-0.2% but it could be more or less than these values. Samples were measured through a Jeol JEE-4X, with an attached Rontec EDX microanalysis system equipped with a windowless Si (Li) detector, using acceleration voltage 15 kV and 20 kV. Before the measurement small parts of each glass were mounted in epoxy resin blocks, then polished with a 1 μm diamond paste and, last, to ensure conductivity, samples were coated with a thick carbon layer. Conductivity is necessary for observation, photography, and analysis in a SEM-EDS. Standardization for the EDS analysis is achieved by a daily Co analysis. The EDS spectrum is taken at the same time for all elements. And the same peaks (K, L, or M) are placed linearly. Each peak has on its right the next heavier element's same peak and on its left the previous lighter element's same peak (Kα, Lβ, whatever). By analyzing Co we have a standard point for our spectra and all other peaks are positioned accordingly. For each glass sample, we measured 5 different areas/angles and we present the mean value as a result.

The isotopic analyses took place in the Stable Isotope Unit of the Institute of Materials Science (NCSR Demokritos) on a Thermo Delta V Plus IRMS. $^{18}O/^{16}O$ ratio was determined and expressed as $\delta^{18}O$ relative to the international VSMOW standard. Isotopic results are reported in the usual delta termi- nology versus the VSMOW isotopic standard, delta being defined as follows:

δ=[(Rsample-Rstandard)/Rstandard]*1000

where R is the ratio between the heavy and the light isotope, in this case $^{18}O/^{16}O$.

Chemical Analysis

34 colorful and colorless samples of ancient glass objects were selected and characterized, with ages ranging from the origin of the first millennium B.C. From the data, it appears that the chemical analyses of almost all the samples are quite homogenous and the major element compositions of all samples are consistent with typical natron glasses produced between 8th and 4th c. BC (Shortland & Schroeder, 2009; Arletti et al., 2010; Arletti et al., 2012; Panighello et al., 2012). In Fig. 3, the levels of K_2O and MgO show that almost all the glass samples analyzed, regardless of the typology (vessels, beads) and site of provenance, were produced starting from a sodic inorganic source of alkalis, as confirmed by the high levels of Na_2O found in the chemical analyses. In fact, the glasses show K_2O and MgO contents below 1.5 wt% and high levels of Na_2O, between 17.3 and 20.1 wt%, confirming that the analyzed glass samples were made on a soda-lime-silicate basis and produced using mineral natron as a source alkaline flux (Fig. 3). This hypothesis is also consistent with the low levels of SO_3, Cl, and P_2O_5 in these glasses (Shortland et al., 2007). The values of SO_3, Cl and P_2O_5, ranging between 0.1 and 0.3% wt., 0.8 -1.45% wt. and 0.02 and 0.1 wt% respectively, show which is typical of glasses made with natron as a fluxing agent. In fact, natron is a relatively pure mineral source of soda containing low levels of magnesium and potash, indicating that all measured soda lime silicate glasses were produced in the Roman glassmaking tradition using natron as a flux.

In the same image, Fig 3., data of glasses from Pydna and Methoni are given. Compared to the B.C period (8th - 4th BC) natron glasses (which utilize a pure soda alkali as a flux) from Greece (Blomme et al., 2017; Karalis, 2023), these glasses present similar compositions (Figs 3 and 4). All the glasses are colored by either or both Co and Cu metals.

Also, the majority of the glass present also lime contents that are similar to the glass artefacts of the first millennium AD, (e.g. Silvestri et al., 2017; Foster & Jackson, 2009; Conte et al., 2014; Freestone, 1994; Foy et al., 2003; Karalis, 2023). The samples show very similar ratios of the two components, CaO and Al_2O_3, indicating the use of same silica sources (Fig 4).

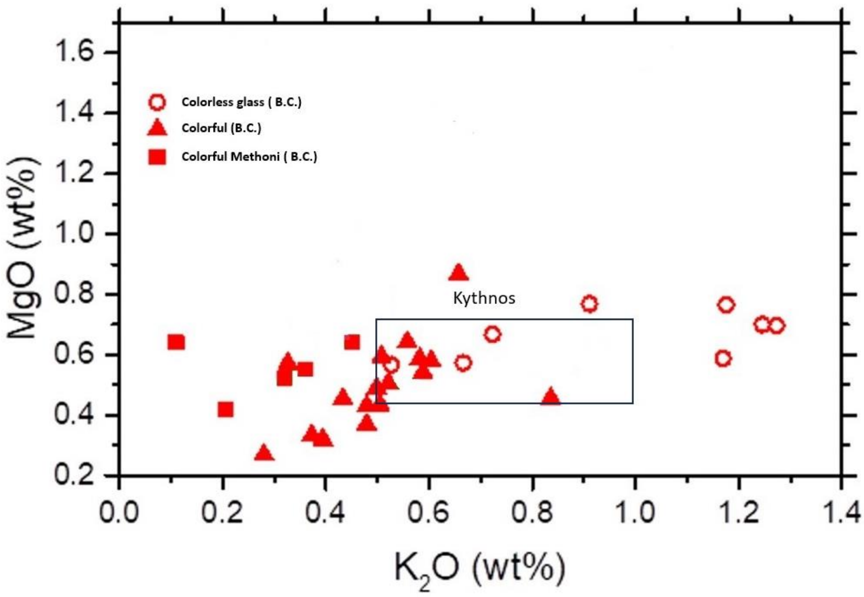

Figure 3. Elemental analysis of glass, K_2O vs MgO

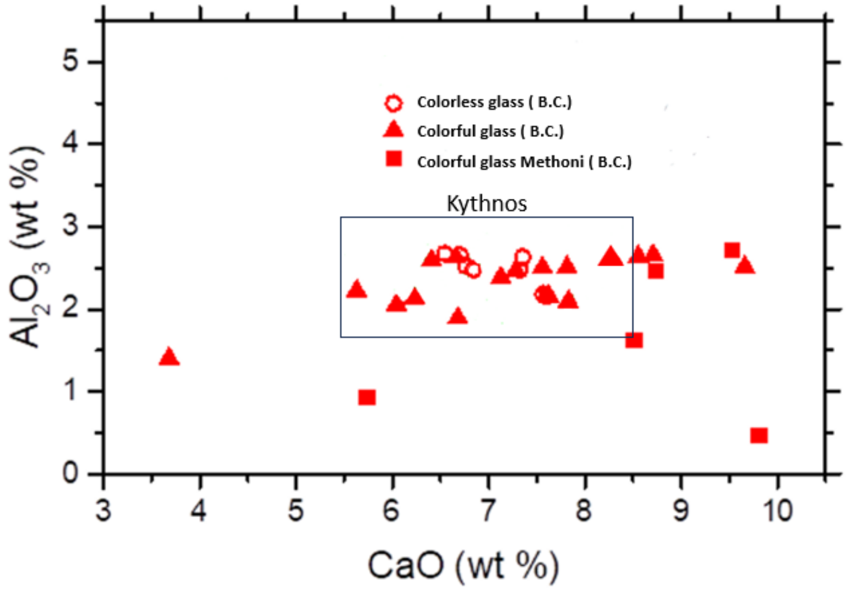

Figure 4. Depicts the Al_2O_3 (lower than 3%) and CaO (lower than 6%) contents of the analyzed glass, further emphasizing the chemical homogeneity of the sample sets.

The plot of Al_2O_3 versus CaO (Fig. 4) further shows the chemical homogeneity of the glass group. Therefore, based on soda ash, alumina and lime content, the glass samples were produced with soda ash and calcareous sand as a source of alkaline flux and vitrifying component respectively. Finally, based on the soda, alumina, and lime contents, the Kythnos glass samples were produced with natron and calcareous sand, as the source of alkali flux and vitrifying components respectively. Colored and colorless natron glass (BC) samples were analyzed for $\delta^{18}O$. The colored glass samples show fairly homogeneous $\delta^{18}O$ values, ranging from 15‰ (VSMOW) to 16.6‰, with an average value of 15.3‰, which is equal or very close to the mean value of “Roman” glass, as deduced from a set of isotopic measurements on glass from Europe, which show a relatively narrow range of $\delta^{18}O$ (from about 15.4‰ to 16.0‰) (Fig. 5). These Roman glasses were produced with Syro-Palestinian coast sand as raw material and Wadi natron as flux.

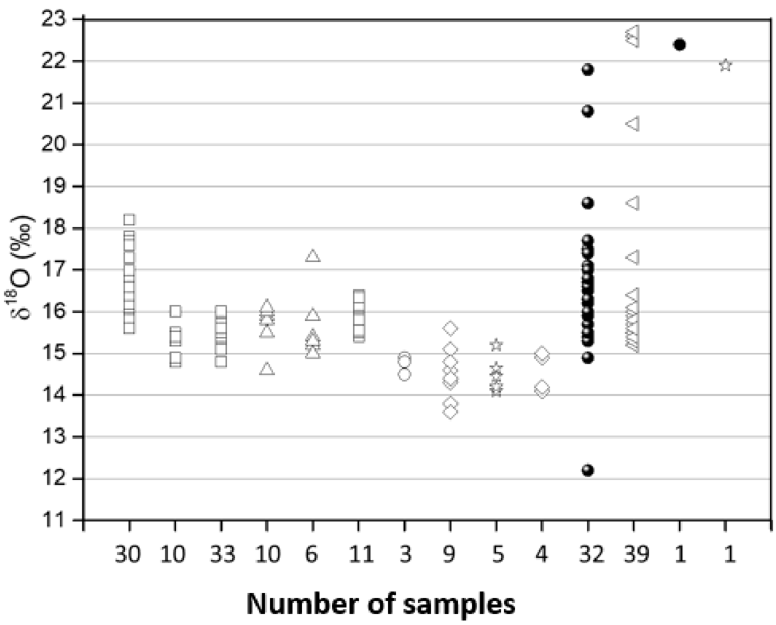

Figure 5. Comparisons among $\delta^{18}O_{(VSMOW)}$ values of natron glass samples, [open symbols: Doman glass (□) (Silvestri et al., 2010; Brill et al., 1999) - 4ου AD. (○)(Brill et al., 1999; Dotsika et al., 2018) – 4ου to 6ου AD (☆) (Leslie et al., 2006) – 6ου to 9ου AD (◇) (Leslie et al., 2006; Henderson et al., 2005) – 1ου to 6ου AD- (◁) (Silvestri et al., 2017) –. (●) (1ου to 4ου AD, Silvestri et al., 2017; Dotsika et al., 2018; Karalis, 2023). (△) (present work)].

Conclusions

The possible origin of 6th to 5th century BC glass artifacts recovered at Kythnos island was discussed from chemical and isotopic data. All glass samples could be classified as natron glass, made from a mixture of silica sand, and natron. The assemblage exhibits similar chemical characteristics with contemporary artifacts from archaeological sites on the Italian peninsula, and on the Ancient Pydna, Greece (Shortland & Schroeder, 2009; Arletti et al., 2010; Arletti et al., 2012; Panighello et al., 2012; Blomme et al., 2017; Karalis, 2023), suggesting that raw materials probably came from Wadi Natron and the Levantine area.

Recommendations

In the continuation of this study, the residual stress effect together with the geometry effect can be evaluated. This experiment would be more appropriate because HFMI does not only perform geometry improving. The relationship between residual stress and geometry can be direct or inverse. A test bench for residual stress measurement will make the results more realistic and consistent. In addition, outputs in terms of life can be obtained with a fatigue test bench.

Scientific Ethics Declaration

The authors declare that the scientific ethical and legal responsibility of this article published in EPSTEM journal belongs to the authors.

Acknowledgments

This research has been co-financed by the European Regional Development Fund of the European Union and Greek national funds through the Operational Program Competitiveness, Entrepreneurship and Innovation, under the call RESEARCH – CREATE – INNOVATE (project code: T1EDK-12500)

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To cite this article:

Karalis, P., Dotsika E., Mazarakis-Ainian, A., Kolofotia, E., Rizou, F., Poutouki, A.E., Poutoukis, P.L., Drosou, A., & Tzovaras, D. (2023). Origin of raw materials of ancient glass (B.C.) from Kythnos Island, Greece. *The Eurasia Proceedings of Science, Technology, Engineering & Mathematics (EPSTEM), 24,* 63-70.