

Research Article

Chemical and Oxygen Isotopic Composition of Roman and Late Antique Glass from Northern Greece

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The present paper emphasizes the importance of measuring the oxygen isotopic and chemical compositions of ancient glass, in order to constrain some features such as age, raw materials, and production technologies and to identify the “fingerprint” of local productions. In this context, thirty-nine Roman and late Antique glass samples and eight chert samples from northern Greece were selected and analysed for their oxygen isotopic and chemical compositions. Results show that the majority of glass samples are produced using natron as flux and have $\delta^{18}\text{O}$ values of about 15.5‰, plus or minus a few tenths of one per mil, suggesting that raw materials probably come from Levantine area. Four samples are heavily enriched in ^{18}O , and their chemical composition clearly shows that they were made with soda plant ash as flux. Isotopic and chemical data of Greek chert samples support the hypothesis of local production of the above samples. About half of the glass samples have chemical compositions, which allow their age to be constrained to the late Antique period. For the remaining glass, similarities with literature compositional groups are reported and discussed.

1. Introduction

It is well-known that, at different periods of history, glass was produced by adding a flux, composed of natron (term here adopted with the meaning of usually complex, often polyphase evaporitic deposits rich in carbonates of sodium), or soda ash from the combustion of halophytic plants such as *Salsola* or *Salicornia*, or potash ash from the combustion of trees such as beech, birch, and oak, to quartz pebbles or quartz-limestone sand [1]. The use of these different raw materials influences not only final chemical compositions of the resulting glass [1], but also the oxygen isotopic compositions. The addition of natron during melting normally causes ^{18}O enrichment in final glass, at least when natron from the evaporitic lakes of Wadi Natrun in Egypt is used, as its oxygen isotopic composition is heavily enriched in ^{18}O [2, 3]. The

ash should not greatly affect oxygen isotopic composition of glass, which reflects that of the network former (normally SiO_2 , added to the batch in the form of quartz pebbles or quartz-limestone sand) [3], although Tite et al. [4] stated that ash, when relatively rich in carbonates, bicarbonates, and hydrates, may cause some isotopic changes in final product.

In this context, the existence in Greece of locally produced glass vessels [5], as well as the import and trade of raw glass and glass artefacts, probably produced in Near East or Middle East countries, draws attention to the importance of identifying the “fingerprint” of Roman and late Antique glass made in Greece, of distinguishing raw materials and fluxes used for glass melting, of defining production technologies, and, indirectly, of better constraining the age of analysed objects. Measurements of oxygen isotopic and chemical compositions of glass samples and possible raw materials seem

promising tools to advance in this direction. To the best of our knowledge, the present paper is the first contribution reporting chemical and oxygen isotopic analyses of Roman and late Antique glass from northern Greece and chemical, mineralogical, and oxygen isotopic analyses of Greek chert, which revealed particularly interesting to discriminate various raw materials and production technologies and to advance hypothesis on possible local products.

2. Materials and Methods

2.1. Materials. In the present study, thirty-nine glass samples were analysed from the isotopic and chemical points of view. Twenty-nine samples come from various archaeological excavations in Thessaloniki. In particular, ten samples come from the Agora area. The age of these samples is generally comprised within the Roman and late Antique periods (1st–6th centuries AD). Their colour varies from colourless to light green, light blue, green/brown, green-blue, and blue (Table 1). The other nineteen samples come from various archaeological excavations in Thessaloniki and their age is comparable with that of the samples from Agora. Their colour is mainly green or greenish, but blue, light yellow, brown, aquamarine, light green, or colourless samples are also selected (Table 1).

The fragmentary state of the Thessaloniki glass samples did not allow typological characterisation, except for those named 1-3, 2-3, 3-3, and 6-3, which were all identified as bottles, and sample 3-4, which is an oil lamp.

In addition to glass from Thessaloniki, a set of ten samples, all typologically identified as pane fragments, comes from the palaeo-Christian church of Maroneia located in the north-easternmost part of Greece. The age of the Maroneia samples ranges from the 4th to the 6th centuries AD, and the colours range from colourless to light yellow, light green, green, green-blue, and light blue (Table 1).

Finally, eight samples composed of chert from the quarry in Triadi of Thessaloniki (Central Macedonia, Greece) were selected for isotopic, chemical, and mineralogical analyses. Chert is a hard, dense, cryptocrystalline sedimentary rock, essentially composed of tiny quartz crystals, that is, less than about 30 μm in diameter, and may occur as nodular concretions and less commonly as layered formations (bedded chert). Chert is found in both western Greece and the Thessaloniki region (northern Greece) as layers in carbonate and/or magmatic rocks, and chert quarries, dated to prehistoric times, have been found near Thessaloniki. In particular, the above prehistoric chert quarries are located along a steep valley, 2 km north of the Triadi village, at the foothills of the Chortiatis Mountain (Central Macedonia). The rocks are part of a Mesozoic ophiolite complex and consist mainly of dunites and peridotites, partly serpentinized, as well as gabbros. Extended silicified rocks, comprising mostly chert, occur at the upper part of the dunites and peridotites and below the gabbros. In addition, rare milky-white microcrystalline quartz veins crosscut silicified rocks. The existence of chert formations in Greece would be in favour of their use for glass production and the present paper is also aimed at verifying this hypothesis.

2.2. Methods. Oxygen isotope measurements on glass and chert samples were carried out according to well-established techniques. In order to avoid contamination, glass samples were carefully cleaned prior to analysis. Fragments were crushed in a stainless steel mortar and then finely ground in an agate mortar. Aliquots of about 6–7 mg of the resulting powder were placed in the nickel vessels of a fluorination line. The samples were then degassed to better than 10^{-3} mm Hg for at least one hour and frozen to the temperature of liquid nitrogen; a fivefold stoichiometric amount of BrF_5 was introduced into each vessel and the samples were reacted at $600 \pm 10^\circ\text{C}$ for about 12 h. The oxygen produced by the reaction was converted to CO_2 by cycling over a hollow cylinder of spectrographically pure graphite and inductively heated to about 800°C in the presence of a platinum catalyst. CO_2 samples were measured for their oxygen isotope ratios in a Finnigan Delta S mass spectrometer versus a laboratory CO_2 standard. This standard was prepared by reacting a powdered very pure Carrara marble with 100% phosphoric acid at 25°C . Its isotopic values are the following: $+2.45\text{‰}$ ($\delta^{13}\text{C}$ versus VPDB) and -2.45‰ ($\delta^{18}\text{O}$ versus VPDB). Until now we have calibrated our working standard versus NBS-19, the isotopic values of which were taken as $+1.95\text{‰}$ ($\delta^{13}\text{C}$) and -2.20‰ ($\delta^{18}\text{O}$), and versus NBS-20 with isotopic values of -1.06‰ ($\delta^{13}\text{C}$) and -4.14‰ ($\delta^{18}\text{O}$) (the NBS-20 isotopic standard has not been available for many years. We had reasonable quantities of NBS-19 and NBS-20 standards inherited from three Italian universities and three foreign research centres, where A. Longinelli previously worked).

Isotopic results are reported in the usual delta terminology versus the VSMOW isotopic standard, delta being defined as follows:

$$\delta = \left[\frac{(R_{\text{sample}} - R_{\text{standard}})}{R_{\text{standard}}} \right] \times 1000, \quad (1)$$

where R is the ratio between the heavy and the light isotope, in this case $^{18}\text{O}/^{16}\text{O}$. The delta values were converted from VPDB to VSMOW standard according to the method of Friedman and O'Neil [6].

The reported values are the means of two or more consistent measurements of each sample. The standard deviation of the glass measurements is very good, ranging on average between ± 0.1 and $\pm 0.2\text{‰}$ (2σ).

The chemical compositions of glass samples were detected by electron microprobe analysis (EMPA). The instrument used for quantitative analysis of major and minor elements was a CAMECA SX50, equipped with four wavelength-dispersive spectrometers (WDS). The bulk composition of the analysed materials was identified by random point microanalyses (generally 10 per sample), and means and standard deviations were calculated. Standard deviations range from about 0.02% to about 0.5%, thus proving the homogeneity of the glass fragments; only mean values are reported in the tables. Analysed elements were Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, Mn, Fe, Sb, Co, Ni, Cu, Zn, Sn, and Pb. The following standards were employed: synthetic pure oxides for Mg, Al, Fe, and Sn, a synthetic MnTi oxide for Mn and Ti,

TABLE 1: List of analysed glasses from Greece. Colour, age and provenance also shown.

Sample Number	Colour	Age Century AD	Provenance
1-1	Light green	1st–6th	Agora-Thessaloniki
2-1	Green blue	1st–6th	Agora-Thessaloniki
3-1	Colourless	1st–6th	Agora-Thessaloniki
4-1	Blue	1st–6th	Agora-Thessaloniki
5-1	Light green	1st–6th	Agora-Thessaloniki
6-1	Colourless	1st–6th	Agora-Thessaloniki
7-1	Green/brown	1st–6th	Agora-Thessaloniki
8-1	Light green	1st–6th	Agora-Thessaloniki
9-1	Light blue	1st–6th	Agora-Thessaloniki
10-1	Colourless	1st–6th	Agora-Thessaloniki
1-2	Light green	4th–6th	Maroneia church
2-2	Green	4th–6th	Maroneia church
3-2	Light yellow	4th–6th	Maroneia church
4-2	Green-blue	4th–6th	Maroneia church
5-2	Light green	4th–6th	Maroneia church
6-2	Colourless	4th–6th	Maroneia church
7-2	Light yellow	4th–6th	Maroneia church
8-2	Very light brown	4th–6th	Maroneia church
9-2	Light blue	4th–6th	Maroneia church
10-2	Very light green	4th–6th	Maroneia church
1-3	Light green	1th–6th	Agora, cryptoporticus-Thessaloniki
2-3	Colourless	1th–6th	Agora, cryptoporticus-Thessaloniki
3-3	Light green	3th-4th	West cemetery, tomb-Thessaloniki
4-3	Green	1th–6th	School of religion-Thessaloniki
5-3	Greenish	1th–6th	School of religion-Thessaloniki
6-3	Colourless	6th	Administration building-Thessaloniki
7-3	Light yellow	1th–6th	Administration building-Thessaloniki
3-4	Light green	5th–6th	landscape of Nastos-Thessaloniki
4-4	Greenish	1st–6th	Socratous street-Thessaloniki
5-4	Greenish	1st–6th	Socratous street-Thessaloniki
6-4	Greenish	1st–6th	Socratous street-Thessaloniki
7-4	Aquamarine	1st–6th	Socratous street-Thessaloniki
8-4	Green	1st–6th	Thessaloniki
9-4	Colourless	1st–6th	Thessaloniki
10-4	Blue	1st–6th	Thessaloniki
11-4	Green	1st–6th	Thessaloniki
12-4	Brown	1st–6th	Thessaloniki
13-4	Greenish	1st–6th	Thessaloniki
14-4	Green	1st–6th	Thessaloniki

albite for Na, diopside for Si and Ca, apatite for P, sphalerite for Zn and S, vanadinite for Cl, orthoclase for K, Sb_2S for Sb, PbS for Pb, and pure elements for Co, Ni, and Cu. Operating conditions were 20 kV and 2 nA sample current, with beam defocused at not less than 10 μ m for Na, K, Si, and Al, in order to minimise the loss of alkali elements and better evaluate Si contents, and at 20 kV and 30 nA for other elements. X-ray counts were converted to oxide weight percentages with the PAP (CAMECA) correction program. The detailed analytical

conditions used and the precision, accuracy, and detection limits of EMPA are given in Silvestri and Marcante [7], as the present samples were subjected to the same analytical protocol. It is stressed here that the precision and accuracy of data were calculated by comparisons with measures on the international reference standard, Corning glass B, in the same analytical conditions as our Greek samples. The precision of EMPA data was generally between 0.5% and 10% for major and minor elements, respectively. Accuracy

TABLE 2: Isotopic and chemical composition of Roman and late Antique glasses from Thessaloniki Agora, 1st–6th century AD in age. Note that CoO and NiO contents are not reported because they are lower than EMPA detection limits for all samples (LOD of CoO and NiO = 0.03 wt%).

Sample Number	$\delta^{18}\text{O}$ (VSMOW)	SiO ₂ Wt%	Na ₂ O Wt%	CaO Wt%	Al ₂ O ₃ Wt%	K ₂ O Wt%	MgO Wt%	FeO Wt%	TiO ₂ Wt%	MnO Wt%	P ₂ O ₅ Wt%	SO ₃ Wt%	Cl Wt%	CuO Wt%	ZnO Wt%	SnO ₂ Wt%	Sb ₂ O ₃ Wt%	PbO Wt%	
1-1	15.5	66.17	16.90	8.60	2.68	0.65	1.46	1.22	0.18	1.64	0.13	0.35	0.68	<0.03	<0.04	<0.04	<0.04	<0.08	
2-1	15.6	64.65	14.96	6.14	3.16	0.94	1.49	1.11	0.20	1.48	0.65	0.16	0.65	0.67	0.04	0.89	<0.04	2.90	
3-1	15.5	71.48	15.40	7.42	2.44	0.37	0.59	0.58	0.09	0.55	0.02	0.24	0.96	<0.03	<0.04	<0.04	<0.04	<0.08	
4-1	15.6	64.24	9.88	5.74	1.59	11.47	3.48	0.30	0.03	<0.05	1.30	0.07	0.64	<0.03	<0.04	<0.04	0.09	<0.08	
5-1	15.4	67.68	16.94	7.08	2.73	0.57	0.96	1.59	0.28	1.09	0.07	0.23	1.09	<0.03	<0.04	<0.04	<0.04	<0.08	
6-1	15.5	72.98	17.00	4.98	2.09	0.56	0.51	0.29	0.09	<0.05	0.01	0.22	0.90	<0.03	<0.04	<0.04	0.25	<0.08	
7-1	15.6	65.43	19.76	6.54	2.38	0.40	1.08	1.14	0.26	1.12	0.02	0.27	1.60	0.14	<0.04	<0.04	<0.04	0.33	
8-1	15.5	67.14	16.83	7.86	2.92	0.91	1.29	1.65	0.20	1.45	0.26	0.25	0.54	<0.03	<0.04	<0.04	<0.04	<0.08	
9-1	15.6	65.53	17.33	7.84	2.95	0.85	1.41	1.39	0.19	1.67	0.26	0.30	0.53	<0.03	<0.04	<0.04	<0.04	<0.08	
10-1	15.5	76.51	9.67	8.11	0.25	3.78	1.03	0.06	<0.04	<0.05	0.06	0.40	0.19	<0.03	<0.04	<0.04	<0.04	<0.08	
<i>15.5 ± 0.07‰ mean isotopic composition</i>																			

was better than 1% for SiO₂, Na₂O, and FeO, better than 5% for CaO, K₂O, P₂O₅, and Sb₂O₃, and not worse than 12% for other major and minor elements.

The chemical and mineralogical compositions of chert samples were obtained by means of X-ray fluorescence (XRF) and X-ray powder diffraction (XRPD), respectively.

X-ray fluorescence (XRF) was carried out on a Philips PW 2400 instrument equipped with a Rh tube with a rated capacity of 3 kW (60 kV/125 mA max.). Three primary collimators (150, 300, and 700 μm spacing) and four analytical crystals (TlAp100, LiF200, Ge111, and PE002) were selected. The spectrometer was interfaced with a personal computer with SuperQ software (Philips). Instrumental parameters and analytical conditions are detailed in Alberta et al. [8]. Geological reference standards were used for calibration [9]. Precision was better than 0.6% for major and minor elements and about 3% for trace elements. XRF accuracy was checked by reference standards [9] and was within 0.5 wt% for Si, lower than 3% for other major and minor elements, and lower than 5% for traces. The lowest detection limits of XRF were within 0.02 wt% for Al₂O₃, MgO, and Na₂O, within 0.4 wt% for SiO₂, and within 0.005 wt% for TiO₂, Fe₂O₃, MnO, CaO, K₂O, and P₂O₅ and range from 3 to 10 ppm for trace elements. For this type of analysis, chert fragments were crushed in an agate mortar. The resulting powders were heated in an oven at 860°C for 20 min. and then at 980°C for 2 hours, and the loss on ignition (LOI) was determined. The powders were then mixed with Li₂B₄O₇ at a 1:10 ratio and beads were prepared.

XRPD data were obtained on a computer-controlled Philips X’Pert PRO, with Bragg-Brentano θ - θ geometry. The normal-focus Cu X-ray tube (Cu K α_1 λ = 0.154056 nm) operated at 40 KV and 20 mA. Data were recorded in the 2°–70° 2 θ range, in step-scan mode with step width increments of 0.02° and a step counting time of 10 s. Data were processed by the X’Pert HighScore (PANalytical copyright); 2 θ and d values were calculated with the second-derivative algorithm of Savitzky and Golay [10]. All XRPD diffraction profiles were carried out on about 500 mg of samples, finely ground into an agate mortar.

It should be stressed here that XRPD analyses were carried out on all the chert samples, while XRF analyses were carried out only on samples Trd 1-2 and Trd 1-5, which are representative of the two mineralogical compositions identified.

3. Results and Discussion

3.1. Results. The ten samples from the Thessaloniki Agora show an extremely homogeneous oxygen isotopic composition (15.4–15.6‰; Table 2). All the samples from the church of Maroneia, 4th–6th centuries AD in age, also have isotopic compositions ranging from 15.2 to 16.0‰, with mean value equal to 15.6±0.25‰ (Table 3). Their mean isotopic values are practically identical to those of the first set of samples from Thessaloniki, although the range of values from Maroneia is slightly larger. The isotopic results obtained on the remaining nineteen glasses from Thessaloniki indicate that only nine samples (4-3, 5-3, 7-3, 4-4, 5-4, 6-4, 7-4, 11-4, and 14-4) have values very close to those measured in samples from Thessaloniki Agora and Maroneia (Table 4).

In contrast with the remarkable isotopic homogeneity of the majority of Greek glass samples (29/39 samples), chemical compositions are rather heterogeneous (Tables 2, 3, and 4). In particular, samples 1-1, 5-1, 8-1, 9-1 (Table 2), 4-3, 6-4, 11-4, and 14-4 (Table 4) from Thessaloniki and all the samples from Maroneia (Table 3) show SiO₂ contents ranging from 64.48 to 67.68 wt%, Na₂O from 16.36 to 18.46 wt%, CaO from 7.02 to 9.07 wt%, and Al₂O₃ from 2.29 to 2.92 wt%. K₂O and MgO contents are both lower than 1.5 wt% in all the considered samples, although MgO is higher than K₂O (MgO = 1.25 ± 0.15 wt% versus K₂O = 0.70 ± 0.13 wt%). This group of samples also shows the highest iron, titanium, and manganese contents (FeO from 0.80 to 2.12 wt%; TiO₂ from 0.14 to 0.37 wt%; and MnO from 0.96 to 2.65 wt%) and nondetectable trace elements.

The other glass samples from Thessaloniki (2-1, 3-1, 6-1, 7-1, 5-3, 7-3, 4-4, 5-4, and 7-4), whose $\delta^{18}\text{O}$ is in the range 15.3–15.6‰ (Tables 2 and 4), also show comparable SiO₂,

TABLE 3: Isotopic and chemical composition of glasses from Maroneia, 4th–6th centuries AD in age. Note that CoO, NiO, CuO, ZnO, SnO₂, Sb₂O₃, and PbO contents are not reported because they are lower than EMPA detection limits for all samples (LOD of CoO, NiO and CuO = 0.03 wt%; LOD of ZnO, SnO₂, Sb₂O₃ = 0.04 wt%; LOD of PbO = 0.08 wt%).

Sample Number	$\delta^{18}\text{O}$ (VSMOW)	SiO ₂ Wt%	Na ₂ O Wt%	CaO Wt%	Al ₂ O ₃ Wt%	K ₂ O Wt%	MgO Wt%	FeO Wt%	TiO ₂ Wt%	MnO Wt%	P ₂ O ₅ Wt%	SO ₃ Wt%	Cl Wt%
1-2	15.4	67.11	17.39	7.84	2.29	0.61	1.10	1.06	0.15	1.54	0.07	0.30	1.02
2-2	15.5	66.23	17.80	7.83	2.70	0.76	1.23	1.33	0.17	1.23	0.15	0.31	0.92
3-2	15.6	64.62	17.70	8.98	2.40	0.72	1.47	1.04	0.16	1.82	0.12	0.34	0.92
4-2	15.9	65.64	18.46	7.95	2.70	0.82	1.21	1.38	0.16	0.96	0.13	0.32	0.91
5-2	15.6	65.70	17.38	8.25	2.38	0.59	1.21	0.88	0.15	1.69	0.09	0.34	0.95
6-2	15.6	66.79	17.17	7.50	2.53	0.60	1.25	0.98	0.16	1.84	0.08	0.30	1.00
7-2	15.7	64.63	17.96	9.07	2.57	0.71	1.50	1.10	0.18	1.72	0.13	0.33	0.92
8-2	15.2	65.56	17.56	7.52	2.50	0.65	1.25	0.93	0.17	2.34	0.09	0.29	1.01
9-2	16.0	66.13	18.14	7.83	2.73	0.84	1.22	1.28	0.15	0.99	0.16	0.34	0.90
10-2	15.3	66.59	16.36	8.59	2.40	0.69	1.11	0.88	0.17	1.60	0.11	0.36	0.87

15.6 ± 0.2‰ mean isotopic composition

TABLE 4: Isotopic and chemical composition of Roman and late Antique glasses from Thessaloniki, 1st–6th centuries AD in age. Samples with moderate and strong ¹⁸O enrichment are in italics and bold font, respectively. Note that NiO, ZnO, and SnO₂ contents are not reported because they are lower than EMPA detection limits for all samples (LOD of NiO = 0.03 wt%; LOD of ZnO and SnO₂ = 0.04 wt%).

Sample Number	$\delta^{18}\text{O}$ (VSMOW)	SiO ₂ Wt%	Na ₂ O Wt%	CaO Wt%	Al ₂ O ₃ Wt%	K ₂ O Wt%	MgO Wt%	FeO Wt%	TiO ₂ Wt%	MnO Wt%	P ₂ O ₅ Wt%	SO ₃ Wt%	Cl Wt%	CoO Wt%	CuO Wt%	Sb ₂ O ₃ Wt%	PbO Wt%
1-3	22.6	67.46	13.00	9.74	1.17	4.85	2.01	0.58	0.06	0.96	0.69	0.07	1.28	<0.03	<0.03	<0.04	<0.08
2-3	22.5	67.31	13.20	9.80	1.15	4.77	2.00	0.57	0.05	0.96	0.66	0.07	1.29	<0.03	<0.03	<0.04	<0.08
3-3	<i>18.6</i>	<i>66.95</i>	<i>19.46</i>	<i>6.71</i>	<i>2.21</i>	<i>0.43</i>	<i>0.96</i>	<i>0.63</i>	<i>0.10</i>	<i>1.27</i>	<i>0.10</i>	<i>0.25</i>	<i>1.43</i>	<i><0.03</i>	<i><0.03</i>	<i><0.04</i>	<i><0.08</i>
4-3	15.8	64.20	17.67	7.02	2.85	0.40	1.28	2.12	0.37	2.65	0.10	0.40	1.23	<0.03	<0.03	<0.04	<0.08
5-3	15.6	67.89	16.17	8.64	2.68	0.53	0.83	0.44	0.07	1.36	0.07	0.35	1.19	<0.03	<0.03	<0.04	<0.08
6-3	<i>17.3</i>	<i>64.92</i>	<i>19.19</i>	<i>8.21</i>	<i>2.32</i>	<i>0.59</i>	<i>1.06</i>	<i>0.94</i>	<i>0.14</i>	<i>1.58</i>	<i>0.07</i>	<i>0.45</i>	<i>0.87</i>	<i><0.03</i>	<i><0.03</i>	<i><0.04</i>	<i><0.08</i>
7-3	15.2	71.62	15.53	6.47	2.63	0.65	0.42	0.26	0.04	0.33	0.09	0.03	1.06	<0.03	<0.03	<0.04	<0.08
3-4	<i>16.1</i>	<i>64.78</i>	<i>18.62</i>	<i>7.75</i>	<i>2.37</i>	<i>0.59</i>	<i>1.19</i>	<i>1.15</i>	<i>0.15</i>	<i>1.52</i>	<i>0.05</i>	<i>0.44</i>	<i>0.93</i>	<i><0.03</i>	<i><0.03</i>	<i><0.04</i>	<i><0.08</i>
4-4	15.3	67.32	16.96	7.85	2.52	0.31	0.88	0.72	0.22	1.61	0.01	0.28	1.36	<0.03	<0.03	<0.04	<0.08
5-4	15.3	66.78	17.96	6.52	2.40	0.50	0.95	0.79	0.21	1.66	0.02	0.29	1.19	<0.03	<0.03	<0.04	<0.08
6-4	15.3	65.25	17.46	7.83	2.46	0.62	1.00	0.80	0.15	1.92	0.05	0.47	0.99	<0.03	<0.03	0.04	<0.08
7-4	15.3	65.80	18.76	6.30	1.89	0.54	0.87	0.67	0.10	0.77	0.04	0.31	1.46	<0.03	1.78	<0.04	<0.08
8-4	15.6	61.56	12.48	10.03	3.90	4.95	1.93	0.79	0.17	0.73	0.43	0.14	0.88	<0.03	<0.03	0.04	0.50
9-4	22.7	67.80	9.80	9.21	1.10	5.45	2.35	0.51	0.05	0.67	0.52	0.10	0.91	<0.03	<0.03	0.04	<0.08
10-4	<i>16.4</i>	<i>65.46</i>	<i>19.83</i>	<i>6.36</i>	<i>2.48</i>	<i>0.49</i>	<i>1.16</i>	<i>1.17</i>	<i>0.16</i>	<i>0.11</i>	<i>0.01</i>	<i>0.52</i>	<i>1.23</i>	<i>0.04</i>	<i>0.21</i>	<i><0.04</i>	<i>0.63</i>
11-4	15.4	64.51	17.91	8.64	2.65	0.76	1.18	1.43	0.14	0.66	0.11	0.45	0.98	<0.03	<0.03	<0.04	<0.08
12-4	20.5	62.72	11.79	9.45	1.34	4.40	2.04	0.92	0.06	4.38	0.39	0.13	1.05	<0.03	<0.03	0.06	<0.08
13-4	<i>17.3</i>	<i>64.44</i>	<i>12.68</i>	<i>9.64</i>	<i>2.34</i>	<i>4.23</i>	<i>2.07</i>	<i>0.76</i>	<i>0.12</i>	<i>1.21</i>	<i>0.42</i>	<i>0.16</i>	<i>1.01</i>	<i><0.03</i>	<i><0.03</i>	<i>0.04</i>	<i>0.14</i>
14-4	15.6	64.48	17.81	7.23	2.58	0.79	1.34	1.97	0.15	1.15	0.14	0.54	0.98	<0.03	<0.03	<0.04	<0.08

Na₂O, CaO, K₂O, and MgO contents with the previous glass samples, although they differ in contents of colouring/decolouring elements, for example, iron, copper, manganese, and antimony and minor elements, for example, tin and lead (Tables 2 and 4). In particular, samples 5-3, 4-4, and 5-4 show concentrations of manganese higher than 1 wt%, whereas sample 6-1 has no manganese but antimony (Table 2). Instead, samples 3-1 and 7-3 do not reveal any manganese or antimony (Tables 2 and 4). Sample 2-1 from Thessaloniki Agora has relatively high concentrations of CuO, SnO₂, PbO,

and P₂O₅ (Table 2). The chemical composition of sample 7-1 is comparable with that of sample 2-1, except for the lower copper and lead contents (Table 2). Lastly, samples 4-1 and 10-1 from Thessaloniki Agora, which have comparable $\delta^{18}\text{O}$ values, show chemical compositions different from each other, except for the similar (and relatively low) content of sodium (about 10 wt% Na₂O) and the absence of manganese and trace elements in both samples. In particular, sample 4-1 has lower SiO₂ and CaO and higher Al₂O₃, K₂O, MgO, FeO, P₂O₅, and Cl than sample 10-1 (Table 2).

TABLE 5: $\delta^{18}\text{O}_{(\text{VSMOW})}$ of chert samples from the quarries in Triadi of Thessaloniki (Central Macedonia, Greece).

Samples	$\delta^{18}\text{O}_{(\text{VSMOW})}$		Mean
Trd 1-1	25.0	25.1	25.0
Trd 1-2	23.4	23.5	23.4
Trd 1-4	23.6	23.8	23.7
Trd 1-5	26.0	26.1	26.0
Trd 2-1	24.2	24.4	24.3
Trd 3-1	26.1	26.0	26.0
Trd 3-2	25.8	26.0	25.9
Trd 5-2	22.5	22.3	22.4
<i>Mean value $24.6 \pm 1.4\text{‰}$</i>			

Lastly, sample 8-4 from Thessaloniki, with $\delta^{18}\text{O}$ equal to 15.6‰, is characterised by lower silicium and sodium contents and higher calcium, aluminium, potassium, magnesium, and phosphorous contents (Table 4) than other glasses with comparable isotopic composition.

In addition to samples with isotopic signatures ranging from 15.2 to 16.0‰, the isotopic data indicate that four samples from Thessaloniki are heavily enriched by about 7‰: sample 12-4 has $\delta^{18}\text{O}$ equal to 20.5‰, and samples 1-3, 2-3, and 9-4 have values from 22.5 to 22.7‰. Finally, other five samples from Thessaloniki (3-3, 6-3, 3-4, 10-4, and 13-4) show moderate ^{18}O enrichment, with values between 16.1 and 18.6‰ (Table 4).

The chemical analyses of the heavily enriched glass (Table 4) show that all samples are characterised by higher CaO, K_2O , MgO, and P_2O_5 and lower Na_2O and Al_2O_3 contents than other Greek samples with lower isotopic composition. In addition, sample 12-4 also has exceptionally high manganese ($\text{MnO} = 4.38 \text{ wt\%}$, Table 4).

The samples with moderate ^{18}O enrichment show quite variable chemical compositions but comparable to those of samples with lower and higher isotopic compositions. Samples 3-3 ($\delta^{18}\text{O} = 18.6\text{‰}$) and 10-4 ($\delta^{18}\text{O} = 16.4\text{‰}$) have chemical compositions comparable to those of samples 5-3, 4-4, and 5-4, although sample 10-4 has very little Mn and high Cu and Pb (Table 4). Sample 6-3 ($\delta^{18}\text{O} = 17.3\text{‰}$) is similar in chemical composition to samples 1-1, 5-1, 8-1, 9-1, 4-3, 6-4, 11-4, and 14-4 from Thessaloniki (Tables 2 and 4) and all the samples from Maroneia (Table 3). Finally, the chemical composition of sample 13-4 ($\delta^{18}\text{O} = 17.3\text{‰}$) is very similar to those of the heavily enriched glass, as deduced from its low Na_2O and Al_2O_3 and high CaO, K_2O , MgO, and P_2O_5 contents (Table 4).

The isotopic data obtained on the chert samples from the quarries in Triadi of Thessaloniki show that mean $\delta^{18}\text{O}$ value (equal to $24.6 \pm 1.4\text{‰}$, Table 5) is comparable to those of Greek glass samples heavily enriched (mean $\delta^{18}\text{O}$ value = $22.1 \pm 1.1\text{‰}$). Mineralogical data, obtained by means of XRPD, show chert samples are a mixture of quartz and goethite (semiquantitative contents of the two phases: 94% quartz and 6% goethite), except for sample Trd 1-5 composed of only quartz (Figure 1).

XRF data furtherly confirm the mineralogical compositions, sample Trd 1-2 being almost entirely composed of SiO_2 and Fe_2O_3 and Trd 1-5 of only SiO_2 (Table 6).

3.2. Discussion. The majority of the analysed samples from Thessaloniki and all the samples from Maroneia have a homogeneous oxygen isotopic composition ($\delta^{18}\text{O}$ value = $15.6 \pm 0.25\text{‰}$, Table 2 and Figure 2), 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 dated from the 1st to the 4th centuries AD, which show a relatively narrow range of $\delta^{18}\text{O}$ (from about 15.4‰ to 16.0‰) [2, 3]. Similar results (Figure 2) were also obtained for late Antique/early Medieval samples from Grado and Vicenza, two sites in Northern Italy [3] and for coeval glass from the Near East [11, 12].

These similarities may be explained by assuming that the Greek glass samples were produced with raw materials with equal or very similar oxygen isotopic composition. Sand from the rivers Belus in Palestine and Volturno in Italy, mentioned by Pliny the Elder in *Naturalis Historia* as materials for making glass, is suitable for glass production and has the same oxygen isotopic composition, when the Volturno sand undergoes selective grinding [3]. It follows that glass produced with either Belus or Volturno sand as network former and natron as flux is practically indistinguishable from the oxygen isotopic point of view. Consequently, the isotopic composition of most of the Greek samples in Tables 2, 3, and 4 cannot help to distinguish among glass samples imported from Italy or the Near East or glass samples produced in Greek secondary glass workshops by melting raw glass: from the geographic point of view, a Levantine origin for the Greek glass samples is quite reasonable. This origin is reinforced by data reported in Brill [13] on five culettes from an ancient glass workshop at Jalame in western Galilee (3rd-4th centuries AD). The author suggests that the silica used for these culettes came from sand taken from the mouth of the Belus and that the oxygen isotopic composition of quartz was enriched in ^{18}O by the calcium carbonate contained in the sand in the form of sea shells, with natron as flux. The $\delta^{18}\text{O}$ values of the Jalame glass are slightly lower than those of Greek samples and range from about 14 to 15‰ (Figure 2). Although the use of various other raw materials cannot be completely excluded, this small difference may be explained by amounts of natron used for melting which are slightly smaller in Jalame than in Greek glass samples. The oxygen isotopic study carried out by Silvestri et al. [3] on Roman natron glass demonstrated the “positive natron effect”; that is, it is presumed that flux, which has very positive $\delta^{18}\text{O}$ values, caused ^{18}O enrichment in the final glass, as confirmed by the plot of Na_2O versus $\delta^{18}\text{O}$, which clearly shows a positive correlation. Other glass samples from the Near East have $\delta^{18}\text{O}$ values close to those of our samples, showing “Roman” values (Figure 2). These samples, measured by Leslie et al. [12], came from different locations: three from the Beth She’an in Israel (6th-7th centuries AD), mean value 14.6‰; three from Tel el-Ashmunein in Egypt (8th-9th centuries), mean value 14.8‰; and three from Carthage in Tunisia

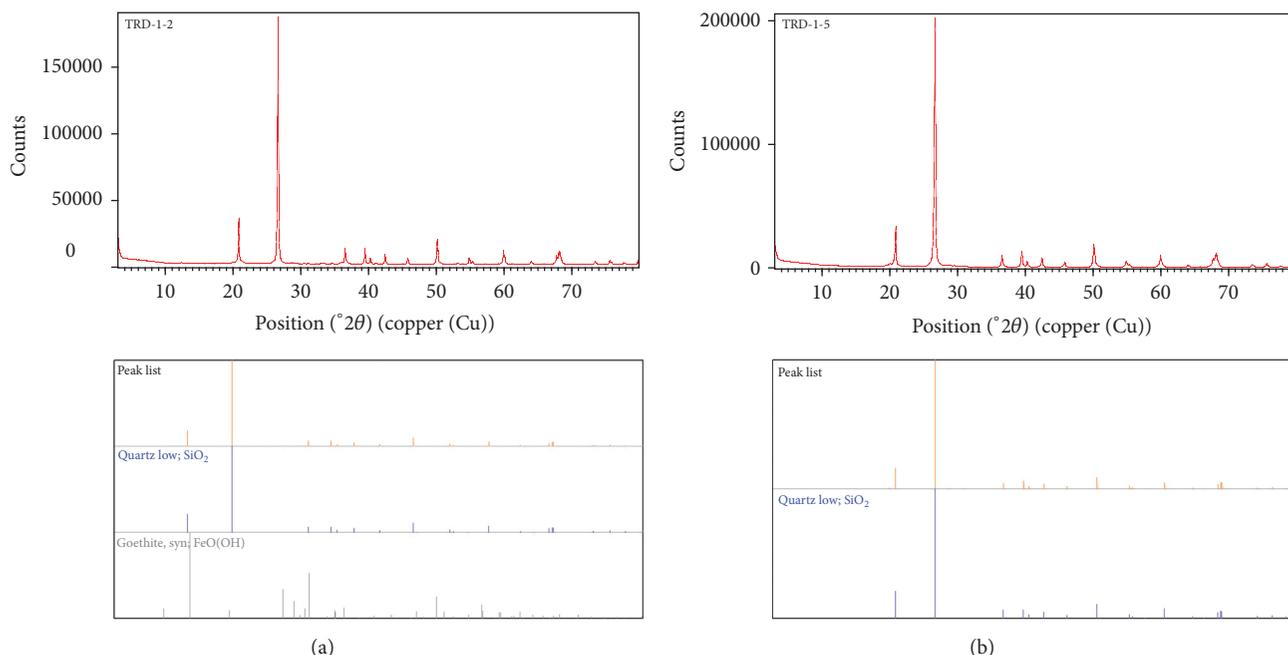


FIGURE 1: XRPD patterns of chert samples, named Trd 1-2 (a) and Trd 1-5 (b), representative of the two mineralogical compositions identified.

(4th–6th centuries), mean value 15.0‰. All these samples are obtained using natron from the evaporitic lakes of Wadi Natron in Egypt. The provenance of sand from a relatively short stretch of the eastern Mediterranean coast is suggested for the Beth She'an samples, and the similarity between the delta values of the Tel el-Ashmunein and Carthage samples is explained by their production with the same Egyptian sand. The isotopic similarity among these three groups of samples can be explained taking into account a common provenance for natron and that Levantine sand comes from Egypt and is transported up to the eastern Mediterranean coast by sea currents [14, 15]; therefore the use of sand and flux with similar provenance yields glass samples with similar isotopic compositions. The same source may thus be hypothesised for the Greek glass samples analysed here. However, it should be stressed that natural natron deposits in the region of Macedonia in northern Greece were well-known in the time of Plato (5th century BC) and were also described by Pliny the Elder in his *Naturalis Historiae*. Hatzopoulos and Loukopoulou [16] identified Lake Chalastra (so-called in antiquity, that is, the place where the “Chalastraion nitron” formed and dissolved over a period of a few days) as the modern lake of Picrolimni, located about 20 km NW of Thessaloniki. The geochemical conditions responsible for the formation of “Chalastraion nitron” have recently been studied and discussed by Dotsika et al. [17]. The salts deposited by the lake brine were mineralogically identified by XRD analysis and include not only calcite and dolomite, but also trona ($\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$), burkeite ($\text{Na}_2\text{CO}_3 \cdot 2\text{Na}_2\text{SO}_4$), and halite (NaCl), thus confirming the mineralogical similarity between these deposits and those from Wadi Natron in Egypt. However, the oxygen isotopic compositions determined on the Picrolimni salt deposits

range from about 11 to 25‰ (VSMOW), much lower than the values for Wadi Natron (about 34 to 40‰ [2, 3]). Therefore, in the case of our samples, use of “Chalastraion nitron” as flux can hardly be considered.

In contrast with the remarkable isotopic homogeneity of the majority of Greek samples (29/39 samples), the chemical composition is rather heterogeneous (Tables 2, 3, and 4), although they are all obtained with natron as flux, having both K_2O and MgO contents lower than 1.5 wt%. In particular, samples 1-1, 5-1, 8-1, 9-1, 4-3, 6-4, 11-4, and 14-4 from Thessaloniki (Tables 2 and 4) and all the samples from Maroneia (Table 3) show the HIMT (High Iron, Magnesium, and Titanium) signature. This reference group is defined by high levels of iron (≥ 0.7 wt%), manganese (usually ~ 1 –2 wt%), magnesium (usually ≥ 0.8 wt%), and titanium (≥ 0.1 wt%), and its yellow-green colour is due to the amount of iron, suggestive of a relatively impure sand source [18]. These also are the key characteristics of Greek glass samples, which have high FeO (1.20 ± 0.31 wt%), MnO (1.54 ± 0.35 wt%), MgO (1.24 ± 0.16 wt%), and TiO_2 (0.18 ± 0.05 wt%) contents. The acronym HIMT was first applied by Freestone [19] to raw glass from Carthage and glass vessels from Cyprus [20], although glass with high contents of iron, manganese, and titanium was already identified by Sanderson et al. [21]. However, all the Greek samples (except 4-3), containing about 50–60% of the amount of iron, titanium, and manganese oxides measured in “typical” HIMT glass, such as Group 1 of Foy et al. [22] (about 1.21 ± 0.31 wt% as FeO, 0.17 ± 0.03 wt% as TiO_2 , and 1.51 ± 0.37 wt% as MnO versus 2 ± 0.8 wt% as FeO, 0.5 ± 0.1 wt% as TiO_2 , and 2.2 ± 0.4 wt% as MnO for Greek samples and Group 1, resp.), show a better fit with “Group 2” of Foy et al. [22], which may be considered as a “weak” HIMT glass [18], due to lower contents of the key oxides of HIMT

TABLE 6: Chemical compositions of chert samples, named Trd 1-2 and Trd 1-5, representative of the two mineralogical compositions identified (XRF data; LOI: loss on ignition). Note that Ga, Y, Nb, La, Ce, and U contents are not reported because they are lower than XRF detection limits for all samples (LOD of Ga = 5 ppm; LOD of Y, Nb and U = 3 ppm; LOD of La and Ce = 10 ppm).

Sample Number	SiO ₂ Wt%	TiO ₂ Wt%	Al ₂ O ₃ Wt%	Fe ₂ O ₃ Wt%	MnO Wt%	MgO Wt%	CaO Wt%	Na ₂ O Wt%	K ₂ O Wt%	P ₂ O ₅ Wt%	LOI Wt%	Sc ppm	V ppm	Cr ppm	Co ppm	Ni ppm	Cu ppm	Zn ppm	Rb ppm	Sr ppm	Zr ppm	Ba ppm	Nd ppm	Pb ppm	Th ppm
Trd 1-2	90.68	0.01	0.21	7.13	0.15	0.37	0.12	0.05	0.01	0.02	2.18	9	314	507	124	146	18	46	7	8	9	20	19	12	7
Trd 1-5	99.98	<0.005	<0.02	<0.005	<0.005	<0.02	<0.005	<0.02	<0.005	<0.005	0.00	<3	<3	<3	<3	<3	<3	<3	<3	<3	<3	<10	<10	<10	<3

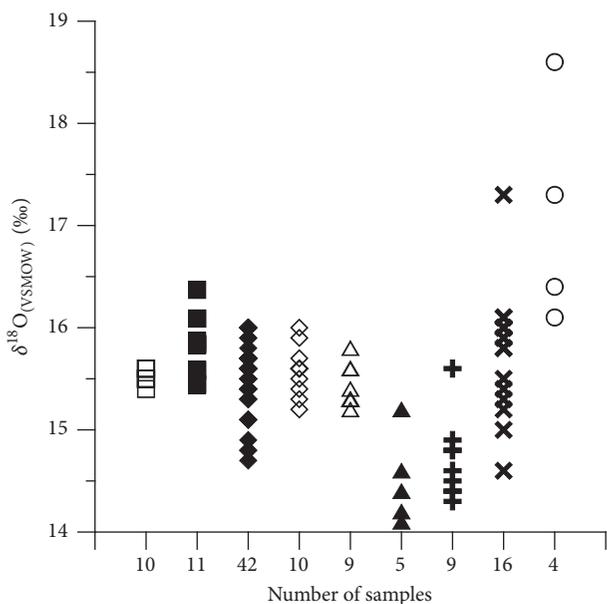


FIGURE 2: Comparisons among $\delta^{18}\text{O}_{(\text{VSMOW})}$ values of natron glass samples [open symbols: Thessaloniki Agora (\square); Maroneia (\diamond); Thessaloniki, various sites (Δ); Thessaloniki glass with moderate ^{18}O enrichment (\circ)] and those already reported in the literature [full symbols: Roman glass from Europe (\blacksquare) [2]; Roman glass from *Iulia Felix* (\blacklozenge) [3]; 4th century AD glass from Jalame (\blacktriangle) [2]; HIMT glass from Carthage and Levantine natron glass (bold plus sign) [12]; late Antique-early Medieval glass from Grado ad Vicenza (bold multiplication sign) [3]]. Number of analysed samples is also shown.

glass (Figure 3). Instead, sample 4-3 has FeO, TiO_2 , and MnO contents (Table 4) perfectly comparable with “typical” HIMT glass [18, 22]. In general, HIMT glass has also been identified in Britain [18], Egypt [23], France [22], Italy [24–29], Cyprus [20, 30], Carthage [31], Bulgaria [32], and Albania [33]. The chemical and isotopic signatures of HIMT glass are suggestive of continental sand sources of high maturity, rich in heavy minerals and located in the Near East, probably in Egypt [12, 31, 34]. As regards the dating of the reference groups, in general terms the HIMT group is probably more characteristic of the period from the mid-4th century AD onwards, although according to current research its composition seems to have continued after the 5th century [18]. In addition, according to Schibille et al. [31], “Group 2” is dated to the 5th–6th centuries and is thus coeval with the glass from Maroneia. Consequently, the age of Thessaloniki glass samples, similar in composition to those of “Group 2,” is constrained to the late Antique period.

The other glass samples from Thessaloniki (2-1, 3-1, 6-1, 7-1, 5-3, 7-3, 4-4, 5-4, and 7-4), whose $\delta^{18}\text{O}$ is in the range of “Roman” values, also show the chemical composition typical of Roman glass [35], although they differ in contents of manganese and antimony (Figure 3) and trace elements. In particular, samples 3-1, 5-3, 4-4, and 5-4 show $\text{MnO} > 0.5 \text{ wt}\%$, which suggests its intentional addition as a decolouriser [36], whereas sample 6-1 has no manganese but antimony (Table 2). As these two elements, the principal

decolourisers used between the 1st and 4th centuries AD, were both predominant from the late 1st to the 3rd centuries and as the use of manganese increased from the end of the 3rd to the 4th century [36–38], the age of these samples is constrained accordingly. Instead, samples 3-1 and 7-3 do not reveal any intentional addition of decolouriser, having no antimony and $\text{MnO} < 0.5 \text{ wt}\%$ (Tables 2 and 4). Sample 2-1 from Thessaloniki Agora has relatively high concentrations of CuO, SnO_2 , PbO, and P_2O_5 (Table 2), suggesting the inclusion of cullet, perhaps coloured and opaque mosaic tesserae containing high quantities of one or more of these elements, in the glass batch. The chemical composition of sample 7-1 is not far from that of sample 2-1, although the concentrations of copper and lead are much lower than those in sample 2-1 (Table 2). This indicates that the presence of the above elements is due to recycling of earlier coloured glass, because they occur in concentrations higher than those attributable to impurities in the raw materials but too low to have any technological significance [39]. Conversely, the high Cu in sample 7-4, not associated with high Sn, Co, Pb, Sb, and Zn (Table 4), suggests that this element was intentionally added to produce the aquamarine colour.

Lastly, chemical similarities between samples 4-1 and 10-1 from Thessaloniki Agora and data reported in the literature are difficult to establish. Sample 4-1 seems quite comparable with some soda-potash-lime glass from the 14th-century workshop at Saint-Chély (France). Two different hypotheses, both equally valid from an analytical point of view, are proposed to explain the peculiar chemical composition of these Late Medieval French samples [40]: both soda and potash ash were used by the glass-workers, soda ash remaining the main component; recycled glass from the surrounding areas, with both potash and soda ash compositions, was used as raw materials. Sample 10-1 also approaches, although not perfectly, the composition of “mixed soda-potash glass” dated to Late Bronze age [40] and the oxygen isotopic data obtained by Brill et al. [2] on some Late Bronze age objects are also quite comparable with that of sample 10-1. On the contrary, oxygen isotope data on samples with chemical composition similar to sample 4-1 are unfortunately still lacking, although data on Medieval soda ash and late Medieval and modern potash ash glass are systematically lower and range from about 12 to 14.5‰ [2, 3]. In any case, both isotopic and chemical data suggest that the age proposed for samples 4-1 and 10-1 from Thessaloniki Agora should be revised.

The chemical analyses of the heavily enriched glass (Table 4) show that all samples were melted with soda ash as flux, their K_2O , MgO, and P_2O_5 contents being higher than those of the other samples (Figure 3). The low Al_2O_3 content suggests that, as well as flux, a different silica source was used to produce these samples. Leslie et al. [12] report some highly variable isotopic results from glass samples, 10th–13th centuries in age, from Ra’s al-Hadd (Oman), one of which is close to 20‰ (Figure 4). Heavily enriched $\delta^{18}\text{O}$ values which range from 21.6 to 22.6‰ have already been measured by Brill et al. [2] on glass samples from Nimrud (Iraq) dated to the 7th century BC; the author obviously concluded that “these glasses must represent a glassmaking

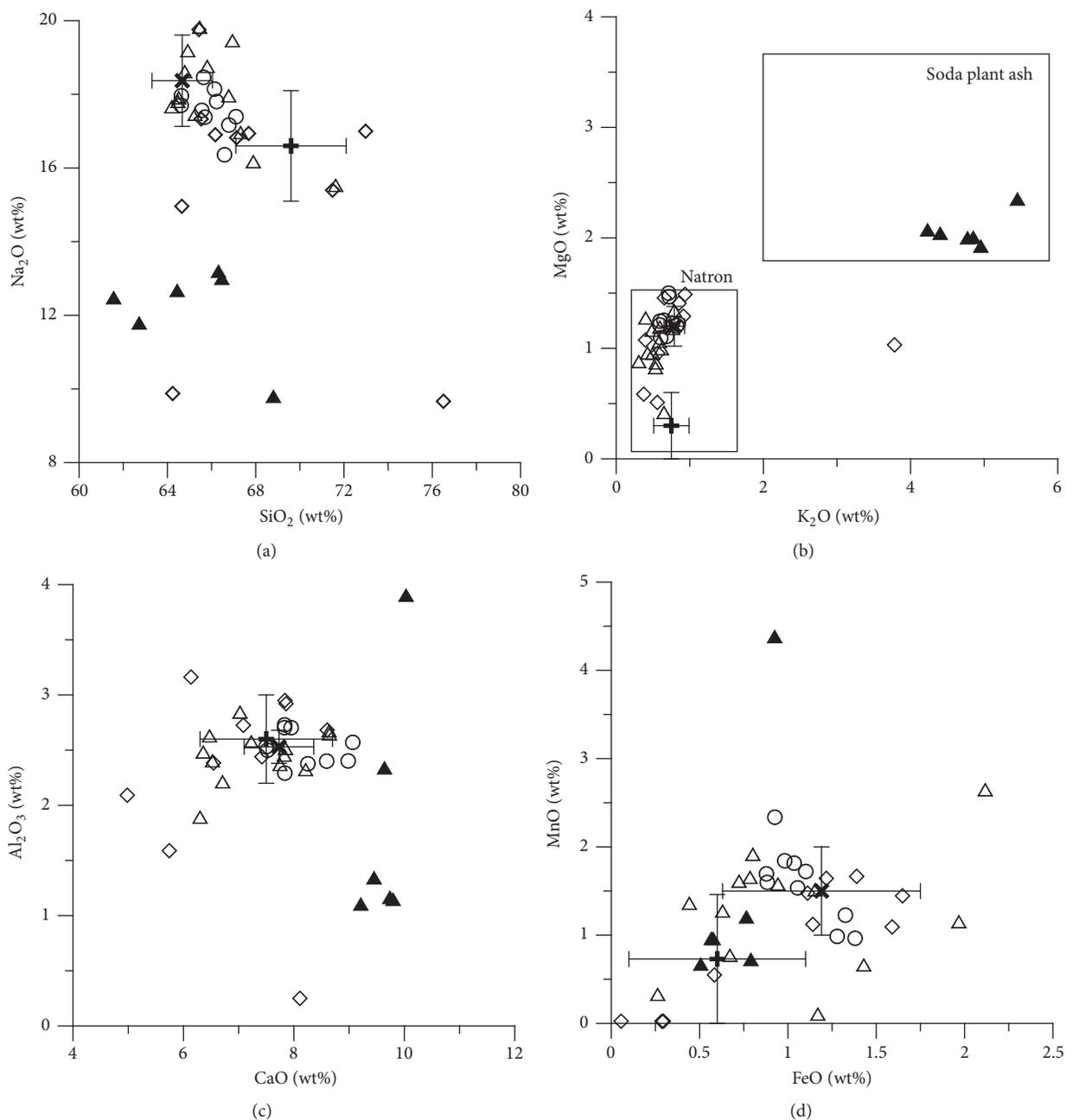


FIGURE 3: Na_2O versus SiO_2 (a), MgO versus K_2O (b), Al_2O_3 versus CaO (c), and MnO versus FeO (d) contents of Greek glass samples, subdivided by provenance: Thessaloniki Agora (\diamond), Maroneia (\circ), Thessaloniki, various sites (\triangle : natron glass; \blacktriangle : soda ash glass). Mean chemical compositions and standard deviations of main compositional natron groups, identified in literature and comparable with Greek samples, are also shown: "Roman" glass (bold plus sign), Group 2 (bold multiplication sign) [22, 35].

tradition that made use of some particular raw material." Two samples from Aphrodisias (Turkey), 6th-7th centuries AD in age, also yielded $\delta^{18}\text{O}$ values of about 23.4‰ (Figure 4). All the samples reported in the literature with very positive $\delta^{18}\text{O}$ values were obtained with soda ash as flux, although they show lower $\text{K}_2\text{O}/\text{MgO}$ and higher $\text{Na}_2\text{O}/\text{K}_2\text{O}$ ratios than Greek samples, suggesting the use of different kinds of plant ash.

In Europe and Mediterranean area soda ash glass dates from the 9th century AD onwards [4, 41]. This would exclude a Roman age for Greek soda ash samples, unless they were produced with raw glass imported from areas, such as Mesopotamia and Iran, where plant ash continued to be used as flux in glass production throughout the period of natron dominance in the West [4]. However, so far, chemical comparisons with 3rd-7th-century soda ash glass from Iraq

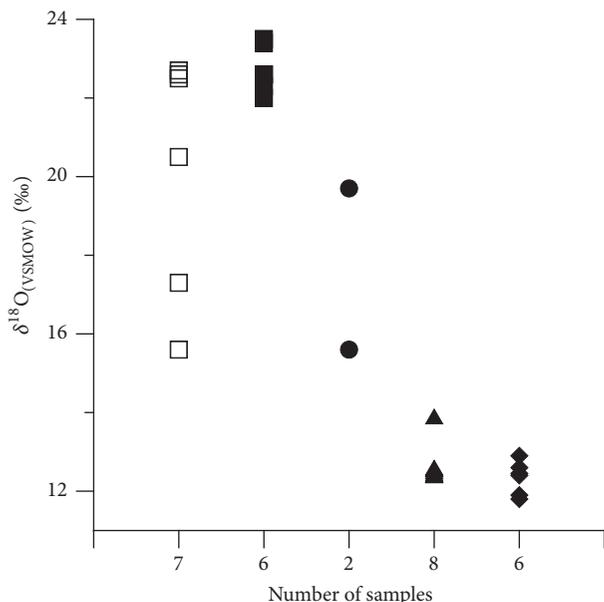


FIGURE 4: Comparisons among $\delta^{18}\text{O}_{\text{(VSMOW)}}$ values of plant ash glass samples [open symbols: Thessaloniki, various sites (\square)] and those already reported in the literature [full symbols: glass from Nimrud and Aphrodisias (\blacksquare) [2]; glass from Ra's al-Hadd (\bullet) and Levantine soda ash glass (\blacklozenge) [12]; Medieval soda ash glass from Italy (\blacktriangle) [3]]. Number of analysed samples is also shown.

[42, 43] have not shown any consistency with Greek samples. In addition, the heavily enriched $\delta^{18}\text{O}$ values do indicate that their raw materials differed from those normally used in Roman and Medieval glass production, and this would match the possibility of the different origin of these materials. The use of ash as flux may cause some ^{18}O enrichment when the ash is particularly rich in carbonate, bicarbonate, and hydrate [4] but hardly to this extent. Previous oxygen isotopic data, obtained on Medieval soda ash glass from the Western and Eastern Mediterranean (Figure 4), indicate that the addition of ash did not contribute to isotopically heavy oxygen and the $\delta^{18}\text{O}$ values essentially reflect the silica source (e.g., [2, 3, 12]). In the case of Greek heavily enriched glass the silica source is difficult to identify, taking into account the fact that quartz, with anomalously heavy isotopic composition, is uncommon in magmatic, sedimentary, or metamorphic rocks. Due to the large oxygen isotopic fractionation between SiO_2 and water at low temperatures, biogenic silica and chert have the highest $^{18}\text{O}/^{16}\text{O}$ ratios observed in rocks [44]. Therefore, the Greek samples with high isotopic values may be the product of local glass workshops which used raw materials, composed of chert, with the addition of ash, probably obtained from various plant species other than those considered by Tite et al. [4] or differently pretreated. The isotopic, chemical, and mineralogical data obtained on a selection of chert samples from the quarries in Triadi of Thessaloniki (Central Macedonia, Greece) further support the hypothesis of local production, at least if we consider sample Trd 1-5 composed of only quartz.

In the case of samples with moderate ^{18}O enrichment, several causes must be considered to explain their values. Sample 3-3 ($\delta^{18}\text{O} = 18.6\text{‰}$) has a chemical composition quite close to that of Roman glass decolourised by the addition of Mn [45]; sample 6-3 ($\delta^{18}\text{O} = 17.3\text{‰}$) is chemically comparable to "Group 2" of Foy et al. [22], and its suggested age (6th century AD) matches the chronological diffusion of the reference group. However, both samples have $\delta^{18}\text{O}$ higher than the average "Roman" or "HIMT" values.

In view of the high Na_2O content of samples 3-3 and 6-3 (Table 4), ^{18}O enrichment may be explained by remelting of previous glass with addition of further amounts of natron as flux, which causes an increase in Na_2O concentration and in the ^{18}O content of the final products.

Apart from their slightly higher $\delta^{18}\text{O}$ values (16.1 and 16.4‰, resp.), samples 3-4 and 10-4 show quite different chemical compositions. Sample 3-4 is chemically comparable with "Group 2" [22], the chronological diffusion of which also matches the age proposed (5th-6th centuries AD), whereas sample 10-4 is similar to Roman glass, 1st-3rd centuries AD in age, although the presence of Cu and Pb may also indicate recycling of coloured and opaque glass, as in the case of sample 7-1. Both samples may be produced in local secondary workshops, by recycling previous glass (perhaps from the Levantine area), with the addition of further amounts of natron as flux, as suggested by their high Na_2O content (Table 4), thus increasing the ^{18}O content of the final product.

According to its chemical composition, sample 13-4 (Table 4; $\delta^{18}\text{O} = 17.3\text{‰}$) was obtained with soda ash as flux, as deduced from its high K_2O , MgO , and P_2O_5 contents. We suggest a different starting material for this sample, as in the case of other soda plant ash glass identified in the Greek assemblage.

Lastly, sample 8-4 from Thessaloniki has $\delta^{18}\text{O}$ of 15.6‰, that is, within the average Roman values, suggesting the use of Belus or Volturno sand and Egyptian natron as raw materials, but its chemical composition is comparable to that of glass produced with soda plant ash as flux. The chronological diffusion of soda ash glass in Europe and Mediterranean area [4, 41] excludes a Roman age for this sample and chemical comparisons with 3rd-7th-century soda ash glass from Iraq [42, 43], where plant ash continued to be used as flux throughout the period of natron dominance in the West [4], have not shown any consistency with the present sample. Therefore, great uncertainty remains in the case of sample 8-4, as regards both its age and provenance, also in view of the heavily enriched oxygen signatures of other soda ash samples identified here (Table 4). However, sample 8-4 differs from the others due to its lower SiO_2 (61.6 wt%) and higher Al_2O_3 (3.90 wt%), which suggest a different silica source, probably a silica sand rich in feldspars. This source may be characterised by a less positive oxygen signature, probably related to the feldspars content of the sand, which influences the ^{18}O content of the final product. This hypothesis is also supported by the isotopic and chemical signatures of sample 13-4. Obtained again with soda plant ash as flux, this sample has Al_2O_3 content intermediate between that of sample 8-4 and all other Greek soda ash samples and consequently shows an intermediate $\delta^{18}\text{O}$ value.

4. Conclusions

The results of the present study emphasize the importance of measuring the oxygen isotopic and chemical compositions of glass samples in order to constrain some features such as age, raw materials, and production technology. Comparisons of our isotopic and chemical data with those reported in the literature, particularly in the case of glass from the Levantine area, are of particular interest as regards the trading of raw glass to secondary workshops in Greece, although for some samples, obtained with soda ash as flux and heavily enriched in ^{18}O , production from local raw materials cannot be completely excluded.

In summary, the thirty-nine glass samples from northern Greece studied here have oxygen isotopic compositions which allow them to be subdivided into three groups.

The first is composed of twenty-nine samples (several from Thessaloniki and all those from Maroneia) with $\delta^{18}\text{O}$ values equal or very close to the mean value of Roman glasses from European and Middle Eastern areas. These similarities imply their production with raw materials with equal or very close oxygen isotopic composition, such as sand from the rivers Belus in Palestine and Volturno in Italy, as suggested by Pliny the Elder. In contrast with the remarkable isotopic homogeneity, heterogeneous chemical compositions allow the subdivision of these samples into several subgroups, which are compared with major compositional groups identified in the Western Mediterranean during the first millennium AD.

Seven samples from Thessaloniki and all the samples from Maroneia show chemical similarity with “Group 2” of Foy et al. [22], while one sample shows chemical similarity with HIMT glass. Accordingly, their age should be constrained to the late Antique period for the Thessaloniki glass and confirmed for the Maroneia samples (i.e., 4th–6th centuries AD). Nine samples from Thessaloniki are chemically comparable with Roman glass, although they differ in colouring/decolouring elements and recycling indicators. In particular, in some samples the identification of manganese, intentionally added as a decolourant, allows us to constrain their age according to the chronological diffusion reported in the literature of this decolourant, that is, from the 3rd to 4th centuries AD. Lastly, three samples from Thessaloniki (1st–6th centuries AD) with $\delta^{18}\text{O}$ values comparable with “Roman” values have chemical compositions very different from “typical” Roman glass, suggesting different production technologies.

The second isotopic group is composed of four samples from Thessaloniki, showing heavily enriched $\delta^{18}\text{O}$ values (20.5 to 22.7‰); their chemical analyses indicate that they were obtained using soda ash as flux, which has little effect on the final oxygen isotopic composition of glass. These high $\delta^{18}\text{O}$ values may be explained by the use of silica raw materials with heavy ^{18}O enrichment such as chert, which is also found in the Thessaloniki region. Therefore, these samples may be the product of local glass factories.

The third group is composed of five samples from Thessaloniki, showing moderate ^{18}O enrichment (16.1 to 18.6‰).

From the chemical point of view, four samples are natron glass with compositions similar to Roman or “weak” HIMT groups, and one is a soda ash glass. In the case of natron glass, the moderate ^{18}O enrichment may be obtained by recycling glass (perhaps from the Levantine area) in local secondary workshops, with the addition of further amounts of natron as flux, as suggested by their high Na_2O contents. In the case of soda ash, the moderate ^{18}O enrichment, with respect to other Greek soda ash glass, may be due to the use of less positive silica source.

In conclusion, these interesting results, the first obtained on glass samples from northern Greece, support trades and commercial exchanges between the Near East and Greece and suggest, although further data are required to confirm it, that the “fingerprint” of Greek glass production could be related to the use of local chert and soda ash, as possible raw materials.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

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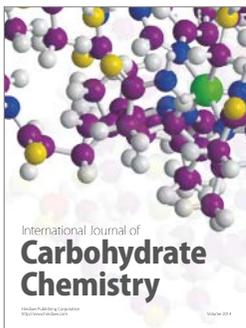
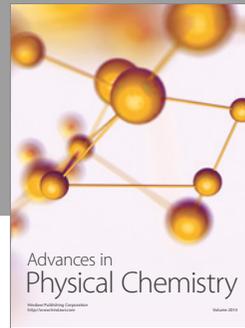
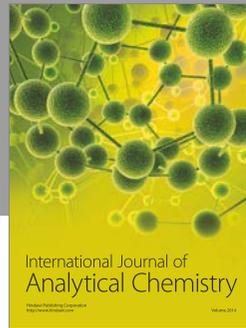
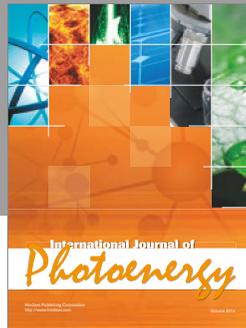
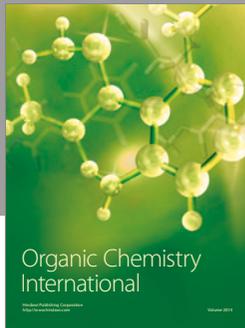
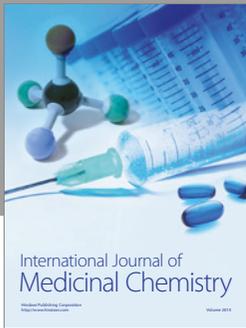
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