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CHEMICAL AND STATISTICAL ANALYSIS OF ROMAN GLASS FROM SEVERAL NORTHWESTERN IBERIAN ARCHAEOLOGICAL SITES

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ABSTRACT

A total 103 fragments of Roman glass tableware are studied, unearthed at 7 archaeological sites in the Northwest of the Iberian Peninsula, to establish both similarities and differences in their chemical composition. ICP Mass Spectrometry is used to characterize the chemical composition of: (i) major elements, so as to determine the type of glass; (ii) minor elements, added to improve the properties of the glass; and, (iii) trace elements, as indicators of the base raw material of the glass. Multivariate statistical studies are also used to establish links and significant differences between glass samples, shedding further light on knowledge of Roman glass manufacturing techniques in the Northwest of the Iberian Peninsula. Three main conclusions were achieved. (i) There are significant chemical differences between samples from Braga (*Bracara Augusta*, Portugal) and the other samples. (ii) These other samples may be sorted into three major groups according to their chemical constituents. (iii) Finally, the statistical analysis and the chemical composition of several glass fragments suggest they were found at some distance from their place of manufacture, requiring the reclassification of their archaeological site of provenance.

KEYWORDS: Roman Glass, Tableware fragments, Chemical analysis, Chemometric analysis, Iberian Peninsula.

1. INTRODUCTION

The first ancient glassware is widely held to be glass beads, while the manufacture of hollow vessels had to wait until 1500 B.C. in Egypt, where glassware was introduced by skilled artisans from Southern Asia. In the 9th century B.C., the principal centres of glass production were in Syria and Mesopotamia from where the craft spread throughout the Mediterranean area. The technique of glassblowing developed in Phoenician coastal cities around the 1st century B.C. and glassmaking then extended throughout the Roman Empire (Fleming, 1999).

While the study of the origin and trade in stone and ceramics is now highly advanced, it may not say the same of ancient glass, as the nature of the minerals used as raw materials and the geographical location of their transformation into finished artefacts remain largely unclear. The vast majority of ancient glassware was made with silica fluxed with either soda or potash (Sayre and Smith, 1961; Henderson, 2002; Degryse and Scheneider, 2008). In terms of its chemical composition, soda-based glass (soda-silica-lime glass) falls into two categories: (i) one involves natron, a mineral source of alkali that is a mixture of evaporitic minerals. Silica may be found in sand and lime extracted from carbonatic sand fractions and/or shells. The mixture produces low Mg and K types of soda-lime-glass. (ii) The second category uses plant ash as its main source of alkali. In the same way as natron-based glass, it introduces Na in the batch, together with quantities of K and Mg (Newton and Davison, 1996; Silvestri *et al,* 2005). Roman glass is a relatively homogeneous natron glass with little or no variation in the composition of its major elements (Freestone, 2006; Gliozzo *et al,* 2013).

However, elements such as Ca, Fe, Mg and Al may be related to concentrations of specific minerals (for example, feldspars or clays) in the glassmaking sand. Transition metal ions (Fe, Co and Cu among others) act as colouring agents, while Mn and Sb oxides are the principal decolorants used in ancient glass (Silvestri *et al,* 2005; La Delfa *et al,* 2008; Foster *et al,* 2009 and 2010). Rare earth element patterns are a promising tool for distinguishing between raw sandy materials that may have typical characteristics in certain geological environments, although these characterizations are largely unexplored (Freestone et al, 2002). Recent advances in the use of radiogenic isotopes (like Sr and Nd) have resulted in new approaches to determine the provenance of primary glass, even after its transformation or recycling in secondary workshops (Degryse and Schneider, 2008; Brems *et al,* 2013a and 2013b).

The expansion of our knowledge of Roman glasses has a serious limitation, insofar as glass fragments found at archaeological sites are the only source of original samples. Characterizations of Roman glasses in the Mediterranean area and in other archaeological settlements in Europe (mainly France, Great Britain and Italy) abound, while research in the Northwest of the Iberian Peninsula remains scarce. For example, most studies have been descriptive in nature: Sánchez de Prado (1984) and Fuentes *et al* (2001) for glasses from Spain or a description of glasses from *Conimbriga* (Portugal) by Alarcão and Alarcão (1967). However, over recent years some archaeometric studies in Roman Glass from the Iberian Peninsula have been conducted by Rincón (1984), Domínguez-Bella and Jurado-Fresnadillo (2004), Gómez-Tubío et al (2006), García Heras et al (2007), Carmona *et al* (2008), da Cruz (2009) and Petit-Domínguez *et al* (2013).

Our study concerns the chemical characterization of fragments of Roman glass tableware from the Northwest of the Iberian Peninsula produced throughout broad periods of Roman civilization. The primary purpose of the research is to determine the chemical composition of these glasses to contribute further knowledge of the types of glass produced by the Roman glassmakers over those time periods. A further objective is to classify samples as a function of the chemical composition of their major, minor and trace elements and to provide some insight into the technology developed to obtain the different colours and opacity of the glasses. Finally, the statistical analysis and the chemical composition of several glass fragments appear to suggest that they were discovered at some distance from their place of manufacture. These fragments were therefore reclassified as belonging to a different archaeological site.

2. EXPERIMENTAL

2.1 Sample description

Representative samples corresponding to 103 fragments of Roman glass tableware were selected on the basis of their morphology, colour, transparency and chronology (High and Low Roman Empire) (see Table 1).

Table 1. Samples studied: physical characteristics and dating

Site	Sample	Form	Colour	Date
Lugo	LU01	quadrilateral carafe with signal	colourless	1st -to- 3rd century
	LU02	bellical cup	bluish green	Reign of Augustus / Reign of Trajan
	LU03	glass in gross	yellowish green	Unknown
	LU04	bellical cup	yellowish green	Uncertain: mid-late 4th -to- 5th century
	LU05	chalice	colourless	Mid-late 2nd -to- early 3rd century
	LU06	quadrilateral carafe	bluish green	1st -to- 3rd century
	LU07	bellical cup-blown glass in mould	bluish green	Decade 40/60 1st century
	LU08	"modiolus"	bluish green	Decade 40/60 1st century
Veranes	VR01	bracelet	opaque black	Late Roman
	VR02	undifferentiated edge	yellowish green	Unknown
	VR03	fragment	colourless	Uncertain: late 1st -to- 3rd century
	VR04	bellical cup	yellowish green	Uncertain: mid-late 4th -to- 5th century
	VR05	quadrilateral carafe	bluish green	1st -to- 3rd century
	VR06	jug	dark green	Uncertain: 4th -to- 5th century
	VR07	silver cup reliefs	blue	Unknown
	VR08	plate	colourless	Uncertain: end 1st -to- 3rd century
Astorga	AS01	cup	colourless	Uncertain: 3rd -to- 4th century
	AS02	glass in gross	bluish green	Unknown
	AS03	grooved cup	bluish green	Reign of Augustus/Reign of Trajan
	AS04	smooth arcuate-shaped cup	yellowish green	Uncertain mid-late 4th -to- 5th century
	AS05	quadrilateral carafe	bluish green	1st -to- 3rd century
	AS06	bellical cup	dark green	Uncertain: mid-late 4th -to- 5th century
	AS07	window	colourless green	Uncertain: 1st -to- 4th century
	AS08	plate	colourless green	Uncertain: 1st -to- 3rd century
	AS09	jug	colourless green	Unknown
	AS10	plate	colourless green	Uncertain: 1st -to- 3rd century
	AS11	fragment	colourless	Uncertain: mid 2nd -to- 3rd century
	AS12	arched cup	colourless green	Uncertain: 4th century
	AS13	chalice	colourless green	Uncertain: 2nd -to- 3rd century
Castro de Viladonga	VL01	corrugated cup	bluish green	Reign of Augustus/Reign of Trajan
	VL02	quadrilateral carafe	bluish green	1st -to- 2nd century
	VL03	bellical cup	yellowish green	Uncertain: mid-late 4th -to- 5th century
	VL04	bellical cup	yellowish green	Uncertain: mid-late 4th -to- 5th century
	VL05	arched cup	greenish yellow	Uncertain: mid-late 4th -to- 5th century
	VL06	conical cup	colourless	End of 4th -to- 5th century
	VL07	tube cup edge	yellowish green	Uncertain: mid-late 4th -to- 5th century
	VL08	jug	yellowish green	Uncertain: 4th -to- 5th century

Site	Sample	Form	Colour	Date
Vigo	VG01	glass in gross	yellowish green	Unknown
	VG02	glass in gross	opaque green	Unknown
	VG03	glass in gross	yellowish green	Unknown
	VG04	bellical cup	yellowish green	Uncertain: mid-late 5th -to- 6th century
	VG05	bellical cup	yellowish green	Uncertain: mid-late 4th -to- 5th century
Chaves	CH01	bellical cup	bluish green	Reign of Augustus / Reign of Trajan
	CH02	quadrilateral carafe	bluish green	1st century to 3rd century
	CH03	bellical cup	yellowish green	Uncertain mid-late 4th -to- 5th century
Braga	BR01	glass in gross	colourless green	Unknown
	BR02	glass in gross	bluish green	Unknown
	BR03	window	colourless	Uncertain: 1st -to- 4th century
	BR04	glass in gross	brown	Unknown
	BR05	cup	yellowish green	Late 3rd -to- 4th century
	BR06	glass in gross	bluish green	Unknown
	BR07	hemispherical cup	brownish green	Reign of Augustus (1st century B.C.) / Reign of Nero (1st century A.D.)
	BR08	diatreta = cage cup	colourless	Early-mid 4th century
	BR09	Hellenistic cup	blue	Reign of Augustus (1st century B.C.)
	BR10	convex cup	yellow	Uncertain 1st -to- 3rd century
	BR11	ceramic profile cup	dark green	Uncertain 1st -to- 4th century
	BR12	ceramic profile cup	yellow	Reign of Augustus (1st century B.C.) / Reign of Nero (1st century A.D.)
	BR13	deep plate	colourless	Uncertain: 1st -to- 3rd century
	BR14	grooved cup	yellowish green	1st century
	BR15	Hofheim cup	bluish green	Reign of Augustus (1st century B.C.)
	BR16	quadrilateral carafe	bluish green	1st -to- 3rd century
	BR17	glass in gross	bluish green	Unknown
	BR18	glass in gross	yellowish brown	Unknown
	BR19	ball	white	Unknown
	BR20	ball	yellow	Unknown
	BR21	cup	colourless	Mid-late 1st -to- 2nd century
	BR22	pitcher edge	yellowish green	Uncertain: 4th century
	BR23	pitcher edge	yellowish green	Uncertain: 4th century
	BR24	container edge	bluish green	Uncertain: 4th century
	BR25	bellical cup	brownish green	5th -to- 6th century
	BR26	bellical cup	yellowish green	Uncertain: 5th century
	BR27	hoop	yellowish green	Unknown
	BR28	bottle	colourless	Uncertain: 4th -to- 5th century
	BR29	bottle	yellowish green	Uncertain: 4th -to- 5th century
	BR30	bottle	yellowish green	Uncertain: 4th -to- 5th century
	BR31	quadrilateral carafe	bluish green	1st -to- 3rd century
	BR32	jug	yellowish green	4th -to- 5th century
	BR33	jug	yellowish green	4th -to- 5th century
	BR34	rim of jug	blue	4th -to- 5th century
	BR35	salve bottle	bluish green	1st -to- 2nd century
	BR36	glass in gross	black	Unknown
	BR37	glass in gross	dark blue	Unknown
	BR38	glass in gross	brown	Unknown
	BR39	glass in gross	blue	Unknown
	BR40	tessera	green	Roman / Medieval
	BR41	glass in gross	yellowish green	Unknown
	BR42	grooved cup	bluish green	Late 3rd -to- 4th century
	BR43	plate	colourless	Uncertain: late 1st -to- 4th century
	BR44	blown glass	dark blue	Unknown
	BR45	fine walled glass and massive base	colourless	1st -to- 4th century
	BR46	fine walled glass	colourless	1st -to- 4th century
	BR47	conical trunk cup	yellowish green	Uncertain 4th century
	BR48	cabuchon cup, corp	colourless green	Late 4th -to- 5th century
	BR49	cabuchon cup, base of corp	blue	Late 4th -to- 5th century
	BR50	cabuchon cup, corp	yellowish green	Late 4th -to- 5th century
	BR51	cabuchon cup, base of corp	blue	Late 4th -to- 5th century
	BR52	hexagonal base	colourless green	Unknown
	BR53	hemispherical cup	colourless	1st -to- 3rd century
	BR54	arched cup	yellowish green	Uncertain: 4th -to- 5th century
	BR55	cylindrical cup	yellowish green	Uncertain: 4th -to- 5th century
	BR56	arched cup	colourless	Uncertain: 4th -to- 5th century
	BR57	bellical cup	brownish green	5th -to- 6th century
	BR58	bellical cup	brownish green	5th -to- 6th century

They were found at seven different archaeological sites in the Northwest of the Iberian Peninsula (Spain: 8 samples from Lugo (LU); 8 from Veranes (VR), Asturias; 13 from Astorga (AS), León; 8 from Castro de Viladonga (VL), Orense; 5 from Vigo (VG), Pontevedra and Portugal: 3 from Chaves (CH) and 58 from Braga (BR) (Fig. 1).

In all cases, minimal samples were taken to reduce any damage to archaeological objects. After cleaning in an ultrasonic bath with twice-distilled water and drying at 120ºC, external layers were cleaned off the fragments with a diamond-coated wheel and the samples were then cut from each fragment with a diamond-coated saw. Prior to analysis, each sample was ground with a pestle in an agate mortar, to ensure homogeneity and to reduce particle size. Due to the very small samples in most cases (sometimes less than 100 mg), not all analyses could always be replicated.

2.2. *Optical microscopic analyses*

Samples were observed with a Minolta optical microscope to visualize possible physical defects. Several photographs were registered in digital format using two resolutions: x32 and x64 magnification.

2.3. *Chemical Analyses*

Samples were dissolved as follows (García Giménez *et al*, 2005): a minimum amount of sample was treated with hydrofluoric acid in an open vessel, heating it on a hot plate until dry. This treatment was followed by the addition of *aqua regia*, followed once again by heating until dry. The residue was dissolved with 1ml of concentrated hydrochloric acid and diluted with water to the mark in Teflon volumetric flasks. Care was taken to keep any possible contamination to a minimum. Ultrapure water was used at all times and all reagents were of analytical grade. Chemical analyses of major and minor elements were performed by Inductively Coupled Plasma–Mass Spectrometry (ICP–MS) in a Sciex Elan 6000 Perkin-Elmer spectrometer equipped with an AS91 autosampler. A total of 45 elements were determined: Al_2O_3, CaO, K_2O, Fe_2O_3, Na_2O, MgO, MnO_2, and TiO_2 as major elements; Ag, B, Ba, Be, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Ga, Gd, Ho, La, Li, Mo, Nd, Ni, Pb, Pr, Rb, Sb, Sc, Sm, Sn, Sr, Tb, Th, U, V, W, Y, Zn and Zr as minor and trace elements. SiO_2 content was estimated by difference. Blank samples and standard samples were simultaneously taken for quality control purposes. Several certified reference glass materials (soda-lime flat glass NIST SRM 620, soda-lime float glass NIST SRM 1830 and soft borosilicate glass NIST SRM 1411) were used to evaluate the accuracy of the analysis, with an error of up to 5% in all cases for the certified elements.

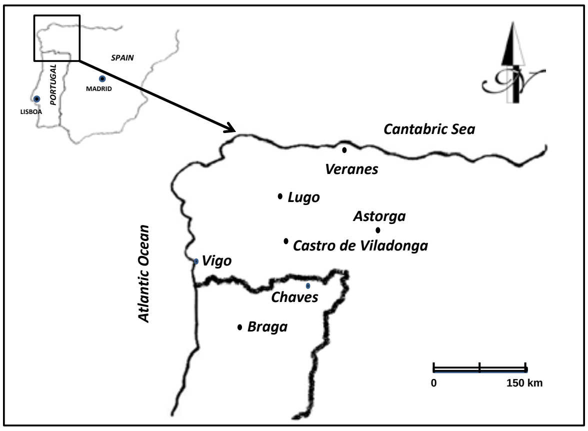

Figure 1 Location of Archaeological Sites

2.4. *Statistical analysis*

Statistical processing of the data was performed with the following programs: SPSS 18 Programme, STATGRAPHICS Plus 5.0 for Windows®, and Origin v. 75E. The first step was to obtain the main descriptive statistics for chemical concentrations (major and minor constituents) in the archaeological samples. The second step was to draw a ternary diagram as a function of their major elements (Marengo *et al*, 2005). The Box & Whisker plot, a histogram-like method, assisted interpretation of the data distribution and classification of the samples by archaeological sites. In this plot, each box encloses the middle 50% and the median is represented as a horizontal line inside the box. Vertical lines extending from each end of the box (called whiskers) enclose data within the 1.5 interquartile ranges. Values falling beyond the whiskers, but within three interquartile ranges, are plotted as individual points (suspect outliers) as well as points that are further away (outliers). Finally, in a third step, owing to the large matrix of chemical results (103 samples x 45 variables), several multivariate statistical studies were also performed to establish relations between glass samples with similar chemical compositions and to discern significant differences between them, so as to shed further light on existing knowledge of Roman glass manufacture in the Northwest of the Iberian Peninsula. This procedure is useful for classifying the dataset into groups. It generates a small number of functions of quantitative measurements, which are linear combinations of the standardized pattern variables with weighted coefficients. An assumption of this procedure is that the variables are drawn from populations with multivariate normal distributions and have equal variances.

3. RESULTS AND DISCUSSION

3.1 Chemical analysis

The content of such major elements as Al_2O_3, CaO, K_2O, Fe_2O_3, Na_2O, MgO, MnO_2, TiO_2 and SiO_2 were analyzed to characterize the type of glass (Table 2).

Fig. 2 shows a ternary diagram with alkaline (Na_2O + K_2O), structural (SiO_2 + TiO_2) and alkaline earth and other major constituents (MgO + CaO + Al_2O_3 + MnO_2 + Fe_2O_3). Most of the glass fragments are located in the right vertex of the triangle with five samples from Braga and one from Vigo outside this group.

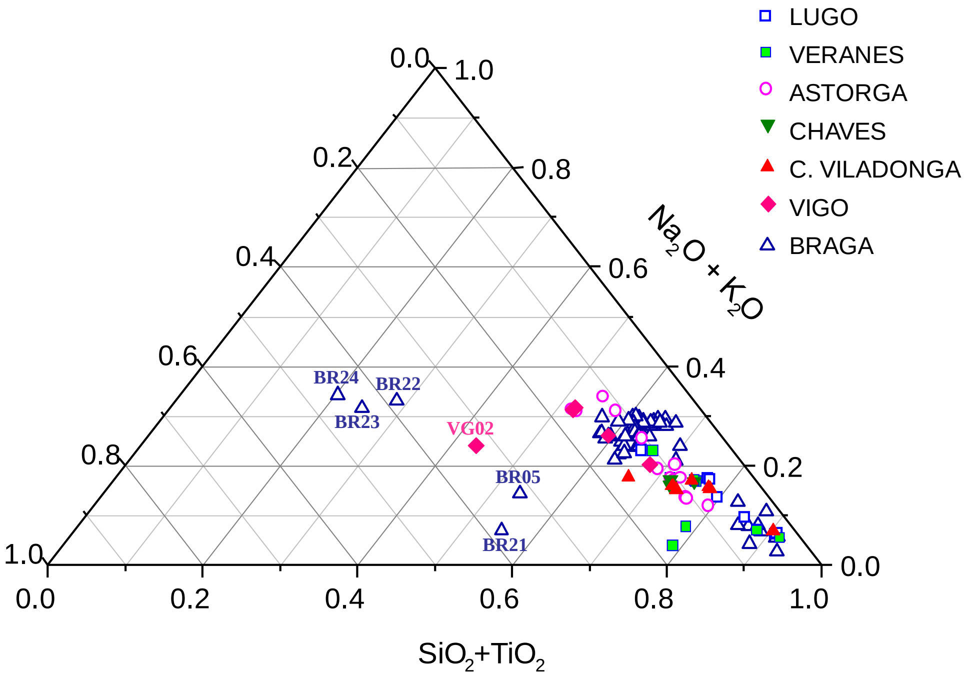

Figure 2. Ternary diagram of ($MgO+CaO+Al_2O_3+MnO_2+Fe_2O_3$) – ($Na_2O+K_2O$) – ($SiO_2+TiO_2$) for the glass samples.

The results indicated that the samples are typical silica-soda-lime glasses (García Heras *et al*, 2005; da Cruz, 2009; Mirti *et al*, 2009), with low concentrations of MgO, CaO, Al_2O_3, MnO_2 and Fe_2O_3. The main component of the samples was SiO_2 with values of between 43 and 93% (with exception of three samples with lower contents) and with a concentration range of 0.2-30% for Na_2O and of 0.3-9% for CaO. Although this representation appears to indicate some similarity between the samples, a detailed Box & Whisker plot, classified by archaeological sites, revealed important differences (Fig. 3). Accordingly, glass from Lugo and Veranes glasses showed the lowest content of Na_2O, while glass from Astorga, Braga and Vigo showed the highest content. Important amounts of CaO and MgO were found in the Vigo samples, while dispersed and elevated K_2O concentrations were found in the Braga samples.

According to Liritzis *et al* (1997) the ratio $(Na_2O+K_2O):(CaO+MgO)$ can be used to evaluate the recipe used by the several *glassmaking Schools*. In this way, ratio value ranges for most samples from Lugo (3.1-3.6), Chaves (2.9-3.2), Castro de Villadonga and Vigo (2.8-3.2) indicate that they can be assigned to the *Metropolitan Roman School*; while most samples from Astorga (2.0-2.5) could be assigned to the *Provincial Roman School*.

Table 2. Concentrations of major elements (expressed as percentages of their respective oxides).

Sample	Na_2O	MgO	Al_2O_3	K_2O	CaO	TiO_2	MnO_2	Fe_2O_3	SiO_2
LU01	17.1	0.35	1.63	0.41	3.35	0.05	0.25	0.45	76.5
LU02	5.95	0.15	0.80	0.20	1.60	0.02	0.11	0.19	91.0
LU03	22.4	0.77	3.39	0.67	5.64	0.13	0.61	1.37	65.0
LU04	6.81	0.54	1.33	0.22	1.60	0.13	0.52	0.79	88.0
LU05	16.8	0.39	1.61	0.38	3.16	0.05	0.23	0.42	77.0
LU06	9.23	0.32	1.55	0.26	2.72	0.03	0.13	0.43	85.3
LU07	13.1	0.32	2.02	0.52	3.72	0.04	0.12	0.50	79.7
LU08	6.22	0.13	0.73	0.19	1.46	0.02	0.11	0.19	91.0
VR01	5.34	0.37	nd	0.21	2.09	nd	0.01	0.18	91.8
VR02	3.09	1.13	4.53	0.92	9.13	0.15	1.03	1.48	78.5
VR03	16.2	0.30	1.91	0.64	4.89	0.07	0.01	0.75	75.2
VR04	6.81	0.30	1.39	0.22	1.82	0.13	0.53	0.79	88.0
VR05	16.6	0.27	3.07	0.98	6.49	0.07	0.32	0.67	71.5
VR06	7.14	0.67	3.49	0.56	4.97	0.54	1.58	2.99	78.1
VR07	22.2	0.96	3.08	0.98	2.97	0.21	0.62	2.71	66.3
VR08	16.5	0.32	1.95	0.67	4.89	0.07	0.01	0.75	74.8
AS01	19.7	0.55	2.42	0.45	4.79	0.07	0.02	1.02	71.0
AS02	16.4	0.27	3.03	0.98	6.64	0.07	0.24	0.67	71.7
AS03	16.1	0.25	2.97	0.92	6.54	0.05	0.23	0.62	72.3
AS04	13.3	0.66	2.69	0.32	4.76	0.26	0.85	1.78	75.4
AS05	11.7	0.27	2.36	0.27	5.68	0.03	0.07	0.25	79.4
AS06	13.1	0.65	2.72	0.31	4.87	0.22	0.80	1.71	75.6
AS07	18.6	0.28	3.26	0.79	6.32	0.07	0.93	0.66	69.1
AS08	30.3	6.14	2.82	0.80	6.04	0.09	0.02	1.14	52.7
AS09	33.2	0.60	2.97	0.76	6.47	0.09	0.03	1.17	54.7
AS10	17.1	3.52	1.60	0.41	3.63	0.05	0.27	0.51	73.0
AS11	24.9	0.38	2.96	0.67	6.04	0.09	0.02	1.01	64.0
AS12	30.5	6.27	2.86	0.83	6.19	0.10	0.02	1.20	52.0
AS13	30.2	0.63	2.95	0.74	6.33	0.09	0.03	1.19	57.8
VL01	16.5	0.30	2.06	0.64	5.14	0.07	0.03	0.72	74.6
VL02	6.75	0.11	0.76	0.19	1.64	0.02	0.11	0.19	90.2
VL03	15.1	0.44	2.49	0.77	4.96	0.30	1.20	2.17	72.5
VL04	15.0	0.45	2.54	0.82	5.12	0.29	1.21	2.08	72.5
VL05	14.4	0.48	2.53	0.80	4.96	0.27	1.20	2.00	73.3
VL06	14.6	0.46	2.49	0.78	0.53	0.27	1.19	2.09	77.6
VL07	14.9	0.48	2.51	0.82	0.54	0.28	1.17	2.07	77.2
VL08	17.1	0.75	3.73	0.68	5.62	0.49	2.02	4.00	65.6
VG01	30.7	1.07	3.77	0.91	8.86	0.15	0.94	1.43	52.1
VG02	23.2	0.99	2.01	0.89	6.49	0.06	0.82	22.3	43.3
VG03	30.4	1.13	3.90	0.92	9.01	0.15	1.02	1.48	52.0
VG04	19.4	0.28	3.37	0.79	6.83	0.07	0.96	0.69	67.6
VG05	25.5	0.87	3.09	0.61	8.00	0.15	1.03	1.55	59.2
CH01	16.3	0.27	3.03	0.98	6.64	0.07	0.32	0.67	71.7
CH02	16.2	0.30	1.95	0.64	5.01	0.07	0.03	0.75	75.0
CH03	15.3	0.45	2.60	0.88	5.12	0.32	1.21	2.11	72.0
BR01	22.7	0.67	6.85	2.64	4.81	0.34	0.33	2.64	59.0
BR02	19.2	0.63	8.12	1.98	5.16	0.19	0.48	1.76	62.5
BR03	25.3	0.30	4.00	0.51	4.28	nd	0.73	0.03	64.9

Sample	Na_2O	MgO	Al_2O_3	K_2O	CaO	TiO_2	MnO_2	Fe_2O_3	SiO_2
BR04	21.1	0.72	7.66	2.09	5.09	0.24	0.53	1.52	62.4
BR05	12.0	0.18	22.4	2.34	1.43	0.39	0.23	7.53	53.5
BR06	20.4	0.44	7.63	2.10	4.17	0.14	0.60	1.34	63.2
BR07	24.5	0.25	2.21	1.43	3.65	nd	2.26	4.02	61.7
BR08	24.4	0.71	3.87	1.47	3.77	0.52	0.03	2.22	63.0
BR09	20.2	0.23	2.88	0.83	3.98	nd	0.19	1.00	70.7
BR10	22.4	0.25	2.41	1.41	3.37	nd	0.01	0.29	69.9
BR11	3.72	0.07	6.43	0.45	0.50	nd	0.05	0.14	88.6
BR12	2.12	0.01	3.56	0.42	0.70	nd	0.01	0.11	93.1
BR13	11.5	0.16	1.32	1.09	2.78	nd	0.03	0.24	82.9
BR14	6.39	1.05	2.33	0.28	0.78	nd	0.04	0.23	88.9
BR15	7.43	0.05	4.31	0.26	0.84	nd	0.21	0.10	86.8
BR16	7.72	0.04	5.77	0.19	0.91	nd	0.14	nd	85.2
BR17	5.36	2.22	0.17	0.22	0.25	nd	0.01	0.15	91.6
BR18	7.42	0.22	0.95	0.56	1.27	0.04	0.46	1.23	87.9
BR19	10.4	0.11	1.21	0.27	0.27	nd	0.01	0.18	87.6
BR20	3.44	0.09	1.64	1.95	0.97	nd	0.01	0.38	91.5
BR21	0.200	0.38	25.3	6.61	0.59	0.65	0.01	11.69	54.6
BR22	3.19	3.19	26.8	29.8	4.04	0.29	0.03	4.26	28.3
BR23	4.21	3.54	32.4	27.3	3.78	0.46	0.03	3.87	24.4
BR24	5.65	3.78	33.7	28.5	4.56	0.54	0.10	3.21	19.9
BR25	21.8	0.38	2.43	2.00	3.16	nd	2.53	3.48	64.2
BR26	27.6	0.12	3.52	0.90	3.21	nd	0.57	1.35	62.7
BR27	29.1	0.06	3.57	0.80	3.41	nd	0.55	1.38	61.1
BR28	25.3	0.24	3.07	0.64	5.84	nd	0.87	0.02	64.1
BR29	27.6	0.14	2.89	0.94	3.88	0.16	0.52	2.56	61.3
BR30	24.6	0.58	3.87	1.85	2.99	nd	2.87	5.01	58.2
BR31	22.3	0.67	6.28	3.54	4.85	0.34	0.68	1.86	59.4
BR32	26.9	0.54	3.08	0.91	3.12	0.52	0.36	3.12	61.5
BR33	28.5	0.31	2.94	0.61	4.52	0.21	0.23	2.37	60.3
BR34	28.3	0.68	2.83	0.59	4.87	nd	0.97	2.43	59.3
BR35	24.5	0.82	6.21	1.52	4.32	0.27	0.64	2.51	59.2
BR36	26.1	0.46	2.54	0.61	4.36	nd	0.84	2.53	62.6
BR37	25.4	0.35	3.11	0.86	4.00	nd	0.62	2.31	63.4
BR38	22.4	0.40	2.50	1.50	3.02	nd	2.10	3.62	64.5
BR39	20.1	0.71	7.26	2.09	5.08	0.24	0.53	1.52	62.4
BR40	23.4	0.52	3.15	3.26	2.99	0.12	2.64	5.77	58.1
BR41	21.5	0.67	2.87	2.47	3.59	nd	2.84	3.51	62.5
BR42	28.4	0.08	4.60	1.37	4.02	nd	0.65	0.05	60.8
BR43	27.2	0.22	2.15	0.70	5.36	nd	0.41	0.01	64.0
BR44	29.2	nd	2.89	0.51	8.03	nd	0.39	2.14	56.8
BR45	28.5	nd	2.70	0.37	4.27	nd	0.16	0.12	63.9
BR46	29.0	0.03	1.44	0.41	3.94	nd	0.01	nd	65.2
BR47	27.1	0.05	3.25	0.95	3.70	nd	0.53	0.20	64.2
BR48	28.3	nd	2.31	1.13	4.00	nd	0.03	0.09	64.2
BR49	26.3	0.09	1.70	1.70	3.82	nd	0.72	0.12	65.5
BR50	28.5	nd	2.86	1.21	5.27	0.17	0.51	0.08	61.5
BR51	27.2	nd	2.40	1.15	4.30	0.12	0.46	0.06	64.4
BR52	27.7	nd	2.51	0.25	3.41	nd	0.18	0.04	66.0
BR53	28.0	nd	1.28	0.53	3.20	nd	0.02	nd	66.9
BR54	27.9	0.09	3.60	0.80	3.46	nd	0.40	0.16	63.6
BR55	28.2	nd	3.32	0.42	3.14	nd	0.08	nd	64.8
BR56	27.5	0.31	2.30	0.63	4.80	nd	0.27	1.96	62.2
BR57	23.2	0.36	2.76	1.60	3.79	nd	2.48	4.16	61.7
BR58	28.0	0.09	3.31	0.82	3.56	nd	0.48	1.12	62.6

nd= no detected (under quantification limit)

Iron can produce many different colours (from green or blue when Fe(II) ions are present to brownish-yellow with Fe(III) ions), mainly depending on the kiln atmosphere (Silvestri et al., 2005). Besides, additions of minor elements that improve the properties of the glass were also found. Thus, some elements such as Cu, Se, Co, Pb, Mn, Sb and Cr may have been used as chromophoric agents in glasses (Costagliola et al., 2000; Garcia-Heras et al., 2005; Carmona et al., 2008 and 2009). Elements such as Mn, Sb or Pb were often added as decolouring agents in the preparation of the final glass product and the most common opacifier was SnO_2 (Costagliola et al., 2000). On the other hand, trace elements are usually good indicators of the base raw material. The results of the minor and trace elements (expressed as mean ± standard deviation) are summarized in Table 3, distributed by archaeological sites. Among the Spanish glass fragments, the samples from Lugo had remarkable concentrations of Mo and U, those from Veranes of Co, V and Zn. Samples from Astorga were characterized by high contents of Ce, Cr and Zn, those from Castro de Villadonga of Ba and Zr. Samples from Vigo had elevated concentrations of Sr, having one of the fragments (VG02) the highest content of an opacifier element such as Sn. Among the Portuguese glass fragments, the Chaves glass samples showed notable concentrations of Ba, La, Zn and Zr and those from Braga had high concentrations of Ce, Co, Cu, Li, Ni, Rb and Th and low concentrations of V.

The elements Pb and Sb were intentionally added to samples as decolouring agents: there are 2 samples from Veranes, 6 from Astorga, 1 from Chaves and 1 from Castro de Viladonga with very high concentrations of Sb (>1000 ppm) and Pb (between 100 and 300 ppm), the results for both elements being more disperse in the Braga samples.

Cu is used as a chromophore element in glass. It had been added to several samples from Braga (some samples with a Cu content of over 1000 ppm), Veranes, Castro de Viladonga and Chaves.

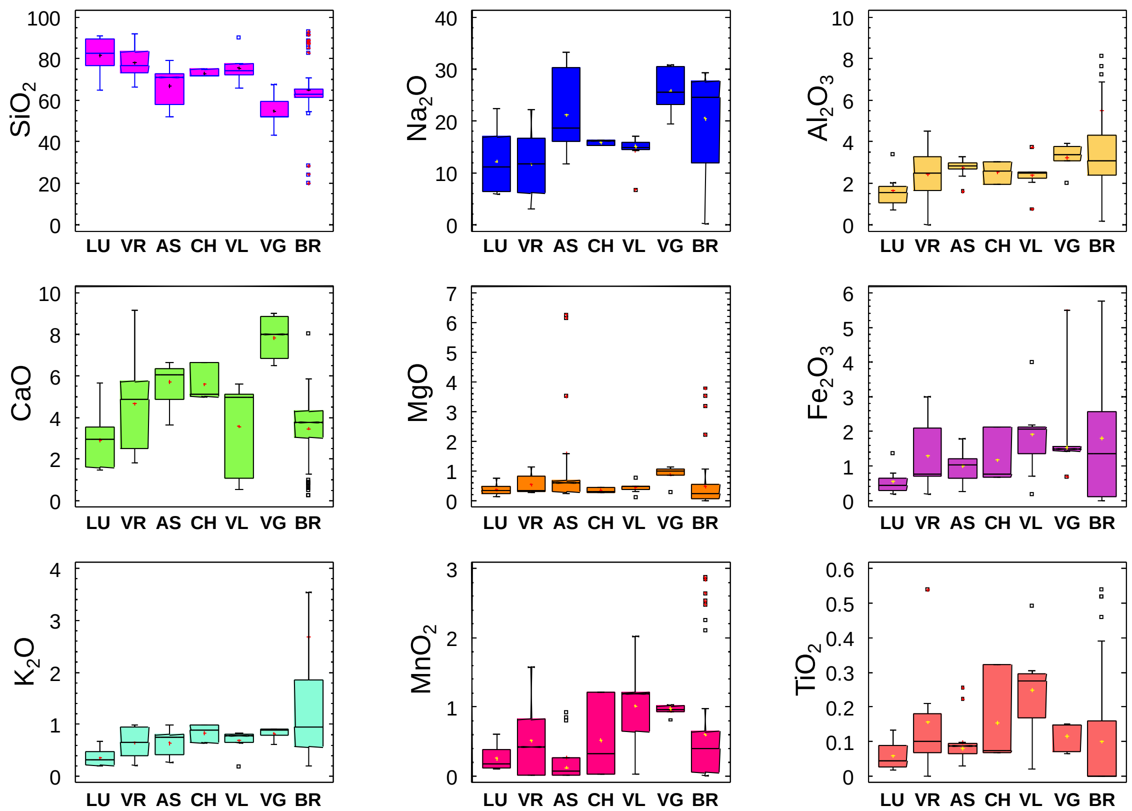

Figure 3. Box and Whiskers graph of the major elements in the glass samples as a function of sample origin.

Table 3. Minor and trace element concentrations (expressed in ppm).

	SPAIN					PORTUGAL	
	Lugo	Veranes	Astorga	C. Viladonga	Vigo	Chaves	Braga
Element	mean ± σ	mean ± σ	mean ± σ	mean ± σ	mean ± σ	mean ± σ	mean ± σ
Ag	0.4 ± 1.1	0.5 ± 0.9	0.3 ± 0.5	0.7 ± 0.7	nd	1.0 ± 1.0	1.4 ± 3.2
B	121 ± 86	195 ± 121	209 ± 108	236 ± 77	135 ± 80	276 ± 51	74 ± 112
Ba	94 ± 88	184 ± 147	137 ± 45	300 ± 106	175 ± 101	284 ± 84	232 ± 139
Be	0.90 ± 0.60	0.41 ± 0.52	0.55 ± 0.51	0.93 ± 0.32	0.20 ± 0.42	0.74 ± 0.62	0.62 ± 0.99
Ce	5.9 ± 3.3	9.0 ± 4.6	15 ± 13	11.6 ± 4.7	11.6 ± 2.0	11.0 ± 3.5	14 ± 17
Co	2.7 ± 1.4	137 ± 374	3.0 ± 1.5	7.0 ± 7.2	9.2 ± 6.2	5.7 ± 4.0	78 ± 203
Cr	19.2 ± 9.2	50 ± 26	212 ± 297	55 ± 15	45 ± 23	52 ± 29	31 ± 87
Cs	0.1 ±3.5	nd	nd	nd	nd	nd	1.7 ± 4.9
Cu	55 ± 72	204 ± 412	32 ± 17	197 ± 106	78 ± 51	120 ± 138	601 ± 1613
Dy	0.51 ± 0.50	0.54 ± 0.52	1.1 ± 0.3	0.92 ± 0.62	1.2 ± 0.7	1.0 ± 0.3	0.51 ± 0.93
Er	0.10 ± 0.32	nd	0.44 ± 0.51	0.62 ± 0.54	0.83 ± 0.42	0.75 ± 0.64	0.31 ± 0.62
Eu	nd	0.11 ± 0.34	nd	0.12 ± 0.35	nd	nd	0.32 ± 0.30
Ga	2.2 ± 1.2	4.2 ± 1.2	2.7 ± 1.0	3.9 ± 1.6	3.6 ± 1.5	4.0 ± 1.0	1.9 ± 4.0
Gd	0.4 ± 0.5	1.0 ± 0.7	1.0 ± 0.9	1.0 ± 0.5	1.2 ± 0.4	1.0 ± 0.0	1.2 ± 1.9
Ho	nd	nd	nd	nd	nd	nd	0.10 ± 0.10
La	2.6 ± 1.6	4.9 ± 2.5	5.3 ± 1.3	4.6 ± 2.4	6.0 ± 1.0	284 ± 54	7.1 ± 9.5
Li	6.2 ± 7.9	2.5 ± 2.7	2.1 ± 1.5	5.9 ± 2.9	0.8 ± 1.3	6.7 ± 2.1	11 ± 25
Mo	6.2 ± 7.5	1.7 ± 1.7	0.6 ± 1.2	2.5 ± 1.2	0.8 ± 1.8	2.0 ± 1.0	0.5 ± 1.3
Nd	2.7 ± 1.6	4.2 ± 2.2	4.8 ± 0.9	4.2 ± 2.3	4.6 ± 1.1	4.3 ± 0.6	7.2 ± 8.1
Ni	8.8 ± 9.5	16 ± 13	14.5 ± 5.2	13.2 ± 4.9	11.0 ± 1.9	16.0 ± 5.3	58 ± 148
Pb	63 ± 119	67 ± 85	67 ± 59	115 ± 66	760 ± 1592	125 ± 99	871 ± 4950
Pr	0.92 ± 0.64	1.1 ± 0.6	1.5 ± 0.5	2.0 ± 1.1	1.4 ± 0.5	1.3 ± 0.6	1.8 ± 2.1
Rb	4.1 ± 3.7	4.7 ± 4.1	4.6 ± 1.5	4.4 ± 1.8	9.2 ± 4.0	5.0 ± 1.7	28 ± 71
Sb	105 ± 100	750 ± 1289	1645 ± 1775	367 ± 575	92 ± 60	728 ± 947	298 ± 517
Sc	7.4 ± 4.0	13.2 ± 5.6	14.5 ± 7.6	16.0 ± 5.6	12.2 ± 8.4	19.0 ± 7.2	3.3 ± 5.3
Sm	0.62 ± 0.51	1.0 ± 0.5	1.0 ± 0.9	1.0 ± 0.5	1.0 ± 0.8	1.0 ± 0.9	1.2 ± 1.5
Sn	nd	nd	13 ± 26	nd	1167 ± 2609	nd	16 ± 48
Sr	181 ± 80	344 ± 146	430 ± 104	348 ± 108	636 ± 171	385 ± 18	272 ± 111
Tb	nd	nd	nd	nd	nd	nd	0.13 ± 0.20
Th	1.0 ± 1.3	0.64 ± 0.53	0.72 ± 0.55	1.0 ± 0.5	0.2 ± 0.4	0.70 ± 0.62	3.9 ± 6.5
U	89 ± 134	51 ± 29	47 ± 19	48 ± 22	47 ± 11	56 ± 12	2.0 ± 3.9
V	147 ± 85	467 ± 349	269 ± 241	384 ± 144	353 ± 360	405 ± 282	47 ± 87
W	0.14 ± 0.31	nd	0.15 ± 0.32	nd	nd	nd	0.33 ± 0.91
Y	3.0 ± 1.3	4.7 ± 2.5	5.3 ± 0.9	5.5 ± 2.3	6.8 ± 0.8	5.7 ± 0.6	4.6 ± 6.6
Zn	49 ± 24	96 ± 123	98 ± 104	84 ± 52	31 ± 59	91 ± 87	37 ± 104
Zr	26 ± 18	72 ± 70	49 ± 27	123 ± 80	1.8 ± 0.8	72 ± 55	35 ± 46

nd= no detected (under quantification limit)

3.2. *Optical microscopic analysis*

Different faults were observed by optical microscopy in the glass samples. These were mainly mass irregularities due to the fusion process, solid material and stone inclusions, bubbles and differences in coloration and fractures. A few of these imperfections were subsequently chosen and can be seen in Fig. 4: a yellowish green colour glass corresponding to sample CH03 (Fig. 4a) shows elongated bubbles in the direction of the mass of molten glass. Fig. 4b (VR01) corresponds to an opaque black glass that shows small and tiny bubbles and a conchoidal fracture. The photograph of a blue-coloured sample fragment with few bubbles is included in Fig. 4c (VR07), Sample 4d is a yellowish-green piece from a bellical cup (LU04) with many typical glass bubbles with a dark-black profile. Fig. 4e shows a colourless piece of a cup (AS01) with bubbles set around a fracture. Fig. 4f (BR40) shows a green glass fragment with bubbles and oxides on different planes, while Fig 4g (AS13) shows a fragment of a colourless green chalice with iron oxides around a fracture. Finally, a fragment of a colourless conical cup can be seen in Fig 4h (VL06) with fractures filled with oxides and some bubbles.

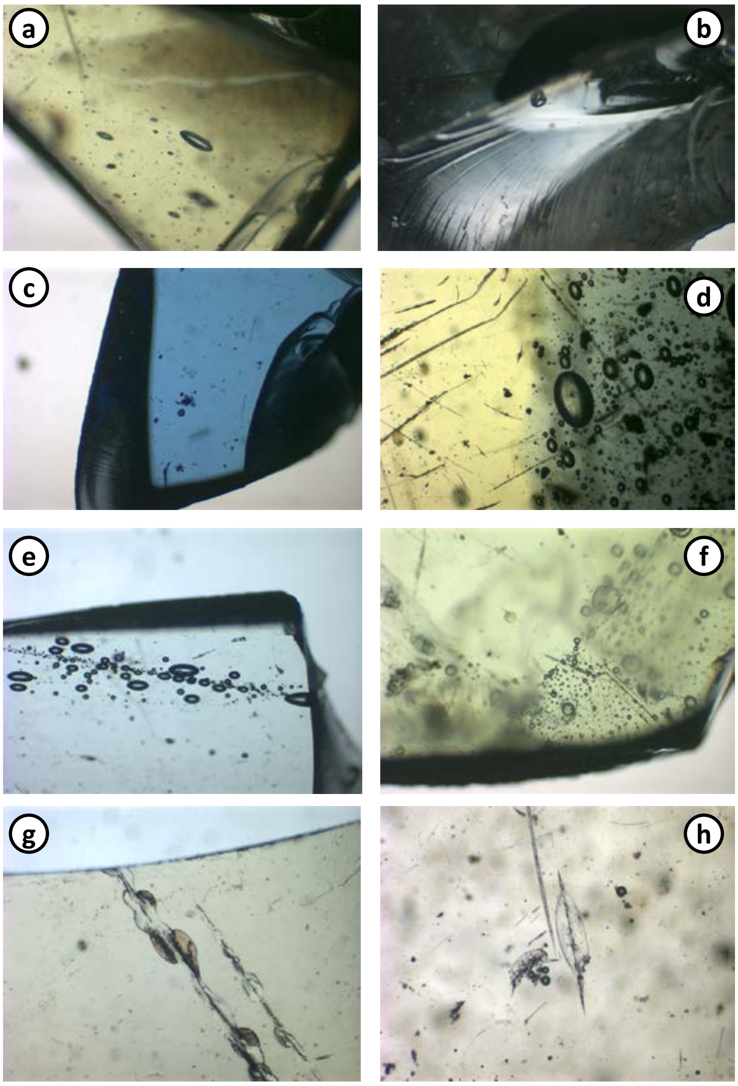

Figure 4. Photographs of glass samples with different faults observed under optical microscopy, a) CH03 b) VR01 c) VR07 d) LU04 e) AS01 f) BR40 g) AS13 h) VL06.

3.3. *Discriminant statistical analysis*

Supervised Pattern Recognition involving discriminant analysis was applied to all of the chemical results (Fig. 5). The glass fragments are represented as a function of two most outstanding canonical discriminant functions, which explain 79% of the total variance (66% for F1 and 13% for F2), thereby establishing a classification of the samples by their seven archaeological sites and their minor and trace element chemical compositions. These functions with *P*-values less than 0.05 are statistically significant at the 95% confidence level. Function 1 is a linear combination of the different variables and the elements with the most significant standardized coefficients are Cu, Ni, Rb, Ag and some rare earth elements in the positive axis and Sc in the negative one. In case of function 2, these are Sc, Ba and Nb in the positive axis and Cr and V in the negative one. The samples found in each group are framed within an enclosure and are characterized by a centroid, represented by a non-solid black square symbol of a bigger size. This symbol represents the average for each group (unique values in the classification factor field) that uses the discriminant functions. Linear Discriminant Analysis means that we can clearly differentiate the Braga samples from the other samples, due mainly to their higher Cu content, as well as their notable contents of Ni, Rb, Ag and some rare earth elements. Considering the rest of the samples, those from Veranes were also characterized by their content of V. On the other hand, samples from Castro de Viladonga (Spain) and Chaves (Portugal) presented similarities and were characterized by their content of B, Ba and Sc. In the same way, samples from Vigo, Astorga and Lugo were similar, but Sc concentrations were higher in the first two. In conclusion, we may say that: (i) there were significant differences between samples from Braga (*Bracara Augusta*, Portugal) and all of the other samples; (ii) these other samples may be sorted into three major groups: one formed by glass from Veranes; a second that includes samples from Vigo, Astorga and Lugo; and, a third that includes samples from Chaves and Castro de Viladonga; (iii) the statistical study led to the reclassification of six samples which were assigned to new groups, probably due to trade between different peoples: 2 samples from Castro de Viladonga (VL01 reassigned to Chaves and VL02 to Lugo), 2 from Veranes (VR04 reassigned to Lugo and VR05 to Astorga), 1 from Chaves (CH01 reassigned to Astorga) and 1 from Astorga (AS10 reassigned to Lugo).

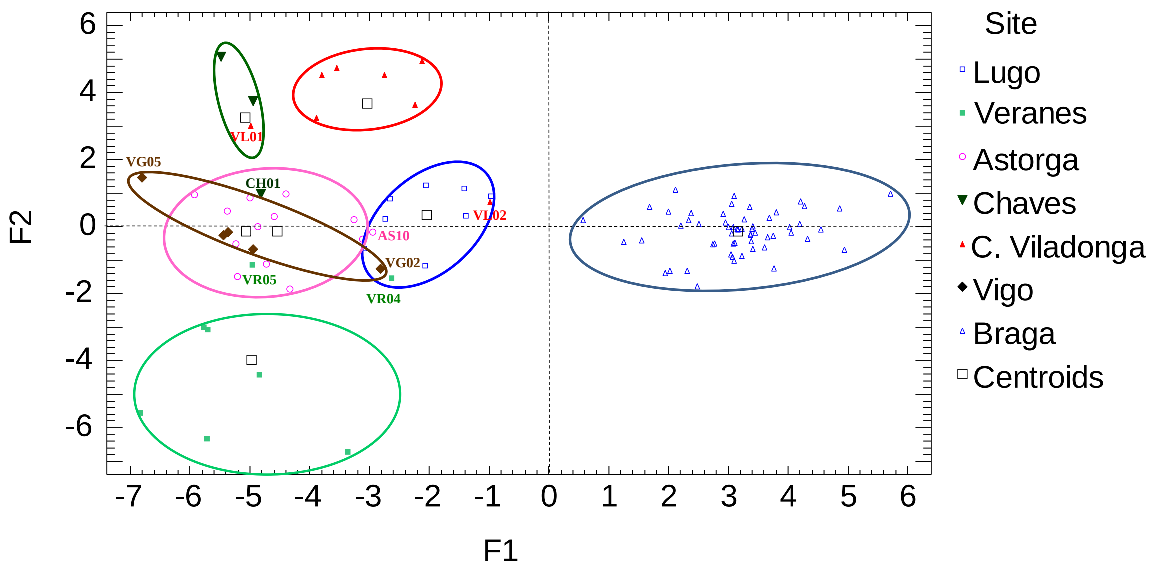

Figure 5. Graphical representation of the samples as a function of two canonical discriminant functions according to the sample origin.

In this step, the discriminant functions were examined to determine the importance of each independent variable (chemical composition) in the inter-group discrimination. Subsequently, the group averages were examined for each important variable, to highlight the differences between the groups. The criterion with which to assign each individual score is therefore determined by constructing the classification matrices and interpreting the discriminant functions, in order to establish their classification accuracy. Reclassification of cases based on the new canonical variables was highly successful: 92.2% of cases (95 glass fragments) were correctly reclassified into their original categories. The incorrectly classified samples were reclassified according to the probability of their belonging to one group or another. In statistical terms, samples VG02 and VG05 were well classified, in spite of their differences with the other samples from the Vigo group. One of them (VG02) was rich in Pb (about 3600 ppm) and Sn (5800 ppm). The other (VG05) had a higher content in B, Zn and Sr than the rest of the group samples; however, they were statistically similar and formed part of the same group.

4. CONCLUSIONS

Chemical characterization of selected glass samples has been performed to shed further light on existing knowledge of the manufacture of Roman glass in the Northwest of the Iberian Peninsula. Certain significant differences in major and minor constituents were observed among the seven archaeological sites under consideration. Major elements that determined the type of glass (typical soda-silica-lime glasses) and relative low concentrations of Mg, Ca, Al, Mn and Fe oxides were found with the exception of six samples. It is important to notice that there is a high dispersion in the major constituent compositions as a consequence of the evolution of the manufacturing processes of samples during a broad chronological range even if they are made in the same place. Minor elements intentionally added to improve the properties of the glass were detected, such as Sn as opacifier, Sb and Pb as decolouring agents, and Cu, Cr and Ni as chromophores. Trace elements, such as rare earth elements and associated elements, are indicators of the base raw material used to make the glass. The samples from Chaves had high contents of La, some glasses from Astorga and Braga had high contents of Ce, and others from Lugo had high contents of U.

Statistical analyses helped us to distinguish important peculiarities of each archaeological site as a function of its chemical composition. In this sense, (i) there were significant differences between the samples from Braga (*Bracara Augusta*, Portugal) and the other samples; (ii) These other samples may be sorted into three major groups: one formed by glass from Veranes; a second that includes samples from Vigo, Astorga and Lugo; and, a third that includes samples from Chaves and Castro de Viladonga; (iii) The statistical analysis and the chemical composition of six glass fragments (2 from Castro de Viladonga, 1 from Chaves, 2 from Veranes and 1 from Astorga) required the reclassification of their source to a different archaeological site. In all probability, they were discovered at some distance from their place of manufacture, probably due to local trade routes between different groups.

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