1ST INTERNATIONAL CONFERENCE

H
V
G

HISTORY, TECHNOLOGY AND CONSERVATION OF GLASS AND VITREOUS MATERIALS IN THE HELLENIC WORLD

ATHENS 2002

"GLASNET" PUBLICATION

Organizing Committee

G. Kordas	Chairman
I. Bassiakos	Co-chairman
G. Moraitou	Secretary General
A. Kontogeorgakos	Treasurer
A. Giannikouri	Member

Scientific Committee

A. Antonaras
Prof. R. Aylon
Prof. J.M.A. Caen
S. Davison
D. Ignatiadou
S.P. Koob
Prof. I. Liritzis
Prof. A. Marangou
Dr. I. Papachristodoulou
Prof. J. Price
Dr. H. Römich
Prof. A. von Saldern
Prof. M. Schreiner
Dr. E.M. Stern
Prof. P. Themelis
Dr. P. Triantafyllidis
Dr. D.B. Whitehouse

Sponsors

Ministry of Development
Ministry of Culture
Ministry of Aegean
NCSR "DEMOKRITOS"
22nd Ephorate of Antiquities, Rhodes
Greek Glass Federation
EBO
Analytical Equipment A.E.
ACS
Τεχνοεκδοτική AEBE
University of Thessaly Publications
The Municipality of Rhodes
Prefecture of Dodekanissa

Active Members of GLASNET

G. Kordas	Physicist
Chr. Trapalis	Chemist
A. Kontogeorgakos	Chemist
I. Bassiakos	Geologist
E. Kossionides	Physicist
I. Chatzis	Chemist
N.I. Valavanis	Glass Scientist
P. Tschaoussoglou	Chemist
G. Priftis	Glass Scientist
N.S. Vlachos	Mechanical Engineer
N. Katsavos	Physicist
I. Lekakis	Mechanical Engineer
I. Sarris	Mechanical Engineer
Chr. Panagopoulos	Engineer
D. Ignatiadou	Archaeologist
A. Antonaras	Archaeologist
G. Moraitou	Conservation Scientist
P. Triantafyllidis	Archaeologist
B. Lampropoulos	Conservation Scientist
P. Chryssikopoulou	Physicist

Conference Secretariat
Chr. Nikolaou, NCSR DEMOKRITOS, 143 10 Aghia Paraskevi Attikis, Greece

Compositional and Technological Characteristics of Glass Tesserae from the Vault Mosaics of Dafni Monastery, Greece

C. Fiori[1], D. Chrysopoulos[2], I. Karatasios[2,3] and V. Lampropoulos[3]

[1]*Consiglio Nazionale Delle Ricerche, Istituto Di Ricerche Technologiche Per La Ceramica, Italy*
[2]*Ministry of Culture, Directorate for the Conservation of Antiquities, Greece*
[3]*T.E.I. of Athens, Dpt of Conservation of Antiquities and Works of Art, Greece*

Abstract

During the conservation study of the mosaics from the Dafni Monastery, a number of glass tesserae of different colours were collected and analyzed in order to determine their chemical composition.
The interpretation of the above results provides information concerning a) the type of the glass, b) the type and the sources of alkali used during the production processes and c) the colourants and opacifiers used.
Glass tesserae from Dafni are soda-lime-silica glasses of natron type, while they owe their colour to different concentrations of iron, copper and manganese oxide.
A comparison between the analytical results of Dafni glasses and those of Hosios Loukas Monastery is also attempted, based on data provided by Freestone et al. [1].
According to the data deriving from the comparison of the above two groups of glasses, it seems that they have similar composition, as shown in the two-phase diagrams (MgO versus K_2O and K_2O versus Al_2O_3). Those tesserae have quite different composition from other Byzantine glasses of the 5th and 6th centuries.
Finally, from the analysis of the Dafni tesserae it is hypothesized that some modern glasses have been used during previous conservation projects.

1. Introduction

This report concerns the analytical results that derived from the compositional analysis of some representative colours of glass tesserae from the Dafni Monastery in Athens, Greece. The Dafni Monastery was constructed in the 11th century and its decoration consists of some of the most famous vault mosaics in the Byzantine context (Fig. 1 and Fig. 2). The compositional analysis of the glass tesserae and other construction materials was carried out during the preliminary conservation study of the mosaics in order to plan their consolidation and restoration methodology.

Fig. 1. *Detail from Dafni wall mosaic, made by polychrome glass tesserae.*

Fig. 2. *Detail from Dafni wall mosaic, made by polychrome glass tesserae.*

The aim of the project is to identify the compositional and technological characteristics of the glass tesserae and to relate them chronically to the development of Byzantine glass technology as a whole. Moreover, we were interested to determine if there were any technological relationships between the glass tesserae from the Dafni Monastery, Athens- Greece, and those from the Monastery of Hossios Loukas (10th century), Central Greece.

2. Description of the samples

Glass samples were selected during the preliminary conservation study of the vault mosaics. They were chosen from representative colours (both opaque and transparent) of all the glass tesserae used in the construction of Dafni mosaics'. The tesserae display a wide variety of colours and shades. Under the stereomicroscope transparent tesserae show many bubbles and some of them whitish grains. Opaque glasses contain small pieces of mineral fragments used as colorants. Moreover, it is observed that glasses of different colours have been melted together in order to produce new ones.

Finally, the surfaces of most tesserae are heavily pitted with a very thin weathering layer.

3. Analytical Results

Analytical data were determined using X-ray fluorescence analysis (XRF) at the "Istituto di Ricerche Technologiche per la Ceramica", Italy.

The results of the compositional analysis of each different colour of tesserae are presented in Table 1 for main and trace constituents. Glass tesserae from the Dafni Monastery are typical soda-lime-silicate glasses with a relatively high content of magnesia (MgO) [2]. PbO, which sometimes was added as network former [3] is present in very low quantities, with the exception of the three samples, where it is present in concentrations of 4.05/ 5.46 and 7.70% w/w.

Samples analysed contain also manganese oxide (MnO) in a range from 0.3 up to 2.5% w/w as well as very low amounts of potash (K_2O). In diagram 1 and 2 glass compositions are presented in terms of MgO versus K_2O and of K_2O versus Al_2O_3, in comparison with those from Hosios Loukas. Glass tesserae of different composition form distinct groups according to their provenance.

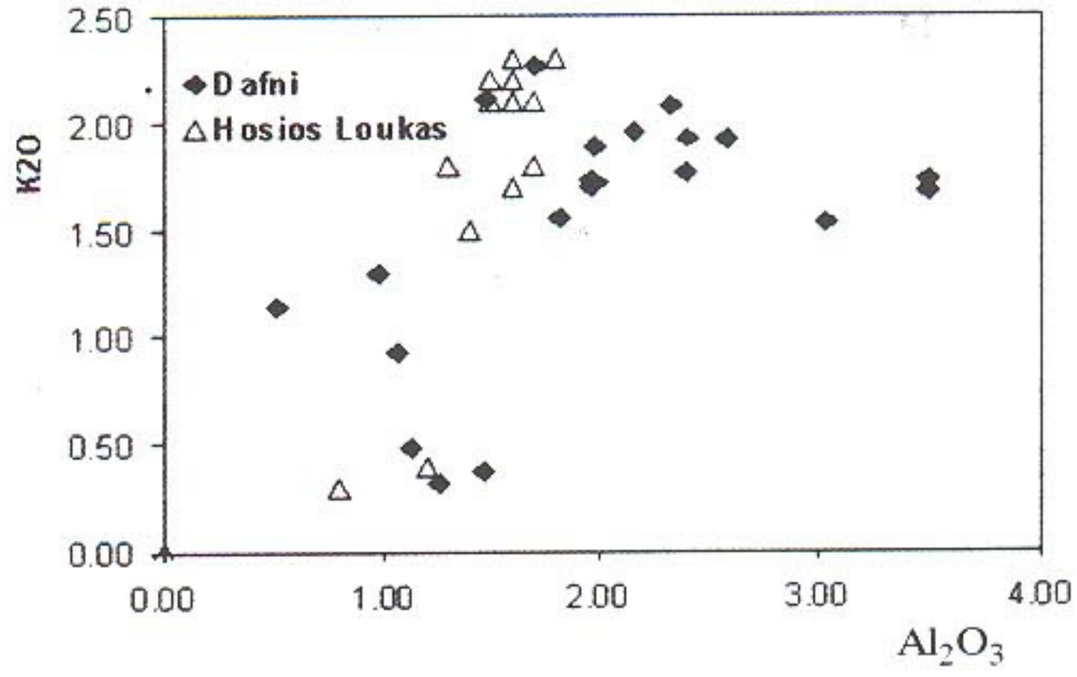

Diagram 1. *K_2O versus Al_2O_3 for the Dafni glass tesserae. Only some of the samples have compositions similar to those of the H.Loukas glasses.*

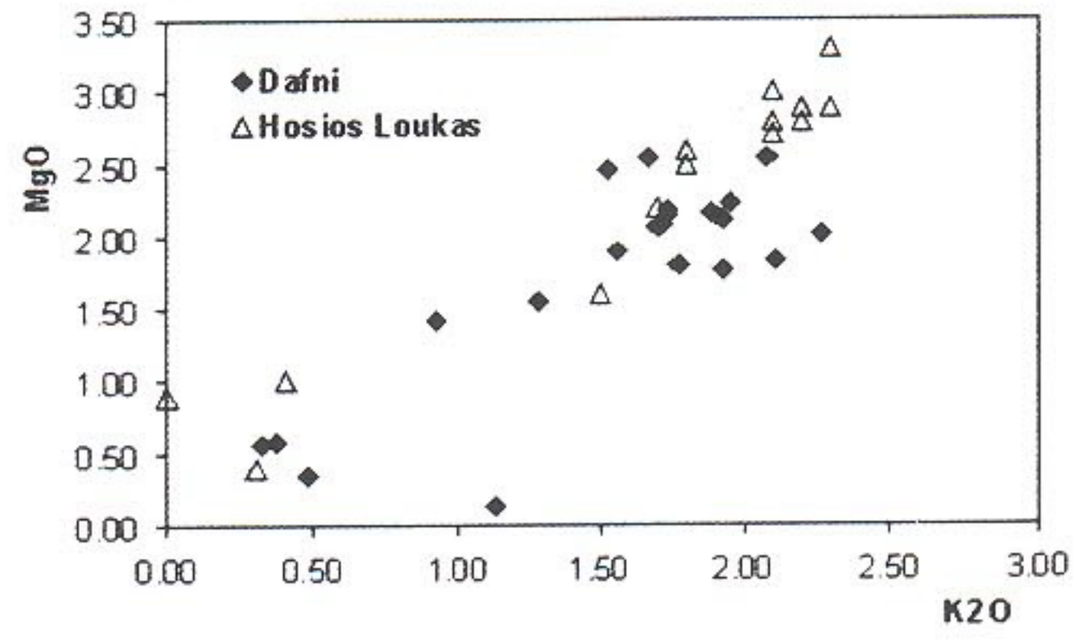

Diagram 2. *MgO versus K_2O for the Dafni glass tesserae.*

4. Colorants and Opacifiers

The main elements used as colorants in glasses from Dafni Monastery are iron oxide (Fe_2O_3), copper oxide (CuO) and manganese oxide (MnO). Lead oxide (PbO) has also been detected in high concentrations in the case of two opaque tesserae, green (7.70%) and blue (4.73%).

Antimony (Sb) and zinc (Zn) have been used in different concentrations as main opacifiers in green glasses, while antimony and tin (Sn) were used in blue and red glasses [6].

The composition of different green glass tesserae varies and the different colour shades are related to the high concentrations of copper oxide (CuO) (in the ratio 0.64 to 5.21) and to elevated concentrations of manganese oxide (MnO) (up to 2.59%). Opaque green glasses (Fig. 3a) owe their colour to the high concentrations of lead and antimony oxides (PbO 7.7% and Sb_2O_3 3.12%).

Opaque red tesserae (Fig. 3b.) contain a great concentration of iron oxide (Fe_2O_3 3,87%) and have similar composition with those of Hosios Loukas.

The colour of the single black glass sample analysed is due to the combined effects of the manganese and iron oxides (MnO 2,11% and Fe_2O_3 0,92%).

Finally, in the blue glasses (Fig. 3c) a very low amount of cobalt (Co) is detected and a high concentration of lead oxide was detected in one sample.

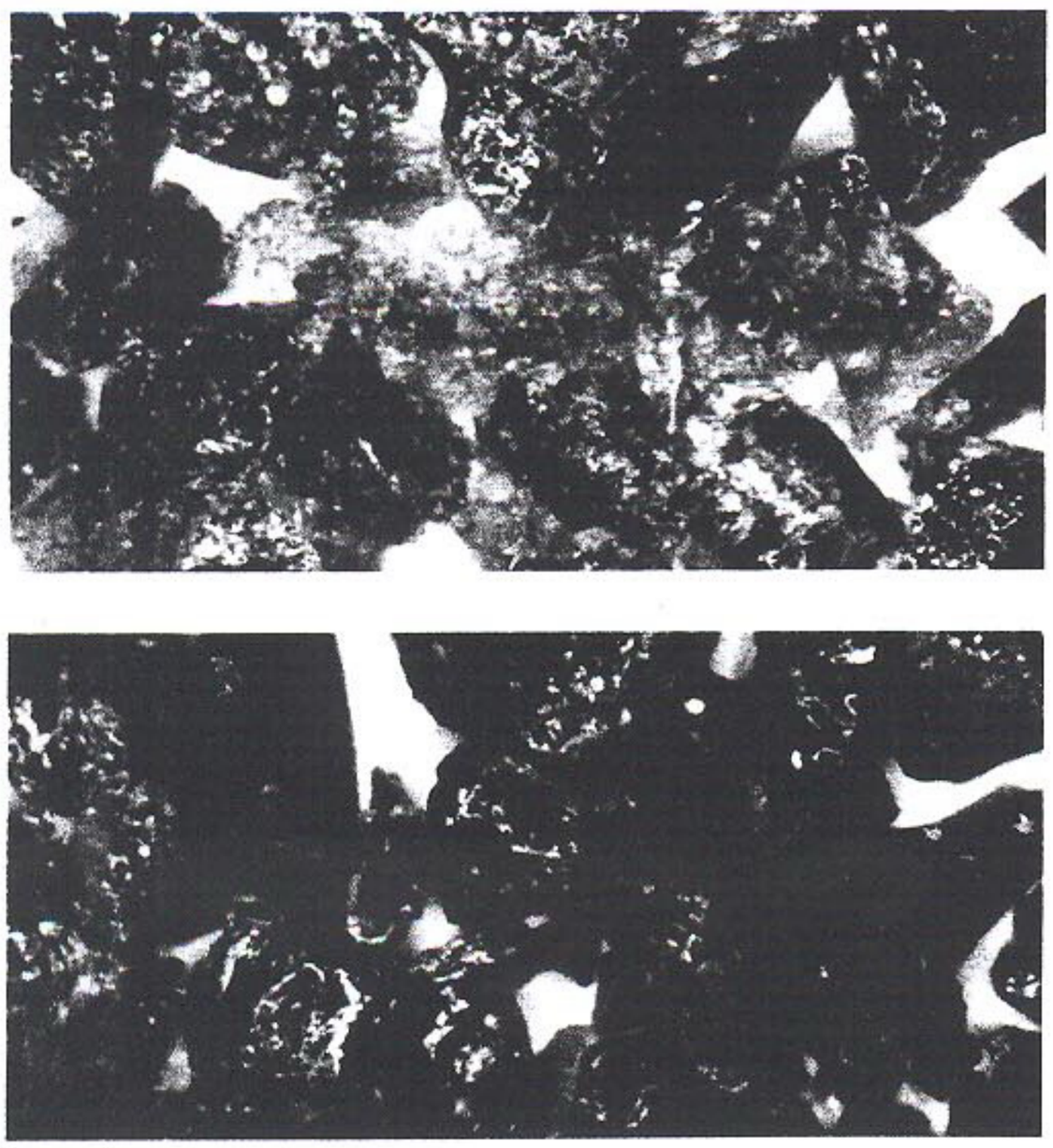

Fig. 3. *Original glass colour of Dafni glass tesserae, a) blue, b) green, c) red.*

5. Discussion

As observed from the tables and diagrams presented, the chemical data from the Dafni glasses are a bit dispersed showing that some of them have very different compositions, probably because of their different origins. Some of the glasses appear to have more modern compositions and may have been inserted during previous restoration works, while some other glasses have more ancient compositions and it seems that they have been re-used in the Byzantine mosaics [4]. This was also obvious during the current conservation study of the mosaics, where different type of mortars and different styles of glass mosaics are observed.

Based on the analytical data and diagrams provided by Freestone et all [1], the majority of glass tesserae from Dafni are of the same type as those of Hossios Loukas, central Greece. Based on the above-mentioned data and diagrams, it seems that the composition of these glasses is quite different from the Byzantine glasses of the 5th and 6th centuries. Only some of the samples have compositions similar to typical Byzantine glasses. In addition, the majority of glass tesserae analyzed have higher silica content than Byzantine glass of the 5th and 6th centuries.

Conclusions

The main difference between the glass tesserae used in Dafni and those used in Hosios Loukas is the use of lead-tin opacifiers in the first. The absence of tin from the Hosios Loukas (10th century) assemblage suggests that tin-based opacfiers

were not available, or too costly at that time [1].

The use of the above opacifiers in Dafni is probably a result of the development of glassmaking in the area (11th century) and of the availability of the proper raw materials. Concerning the quality of the tesserae it seems that the glass manufacturing techniques hadn't developed to the same standard as compared to the quality of the mosaics and mosaic patterns [7].

As far as concerns the glass tesserae, their range of colours is limited by the ability of mosaicist to obtain certain colours. The differences in the glass composition have also to do with the fact that wherever possible, mosaicists salvaged and recycled material from other mosaics or other glass artefacts [5].

Finally, in order to establish an all encompassing database concerning the glassmaking technology and compositional trends of mosaic tesserae in the Byzantine era (Diagram 3), it is necessary to analyse and compare the full range of coloured glasses from the majority of known monuments from this period.

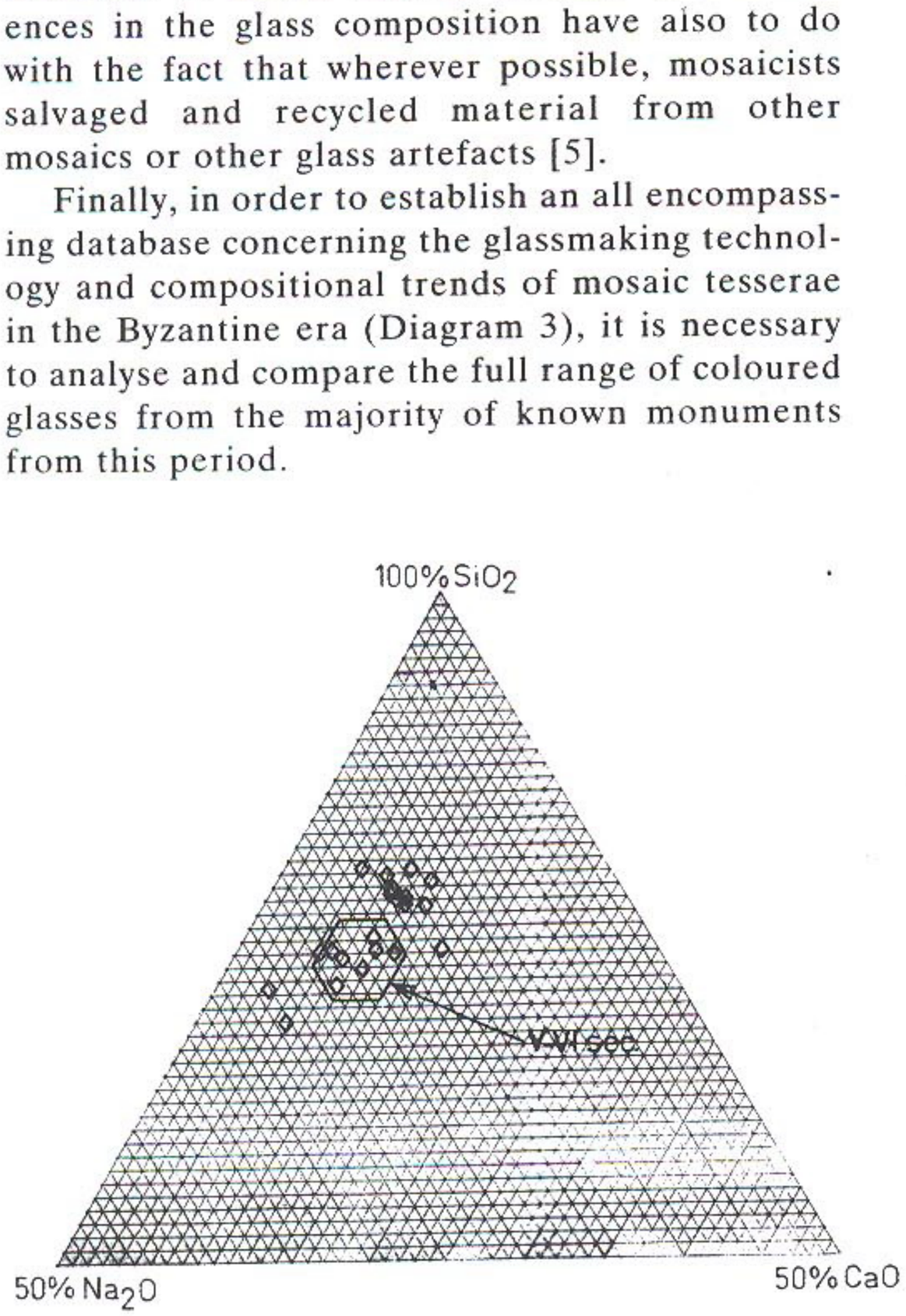

Diagram 3. *Three-phase diagram of the Dafni and other Byzantine glasses. Dafni glasses are quite different from the Byzantine glasses of the 5th and 6th centuries.*

References

1. I.C. Freestone, M. Bimson, D. Buckton, Compositional categories of Byzantine glass tesserae, Annales du 11e Congrès, (1988).
2. E.V. Sayer, R.W. Smith, Compositional categories of ancient glass, Science 133 (1961) 1824-1826.
3. R. Newton, S. Davison, Conservation of Glass, Butterworth-Heinemann, Oxford, 1989.
4. E. Kontou, D. Kotzamani, V. Lampropoulos, (1995), Gyali, Texnologia Diavrosi kai Syntirisi, Athens-Greece, pp. 71-156.
5. Ling R., 1998, Ancient mosaics, British Museum press, pp. 6-18.
6. O. Costagliola, G. Baldi, C. Cipriani, E. Pecchioni, A. Buccianti, Mineralogical and chemical characterisation of the Medicean glass mosaic tesserae and mortars of the Grotta del Buontalenti, Giardino di Boboli, Florence, Italy, Journal of Cultural Heritage, 1 (2000) 287-299.
7. R.H. Brill, The chemical interpretation of the texts, Glass and glassmaking in ancient Mesopotamia, ed. A. L. Oppenheim et al, Corning, (1970) 105-128.

Colour	Green	Green	Green	Green	Green	Green	Green	Greenish Blue	Green	Red	Violet	Black	Blue	Blue	Azure	Red	Brown	Amber	Light Violet
SiO_2	66.19	60.20	67.53	57.28	68.20	72.79	66.71	69.36	68.12	72.72	63.82	66.65	65.09	61.49	75.35	62.10	62.61	64.28	70.25
TiO_2	0.07	0.04	0.10	0.02	0.10	0.05	0.09	0.15	0.11	0.08	0.16	0.10	0.10	0.06	0.06	0.12	0.27	0.12	0.09
ZrO_2	0.03	0.01	0.03	tr.	0.03	0.03	0.02	0.03	0.04	0.04	0.03	0.04	0.03	0.01	0.04	0.02	0.02	0.03	0.04
SnO_2	tr.	0.02	0.03	0.03	0.01	0.01	0.01	0.02	0.04	tr.	0.02	0.01	0.01	0.02	tr.	0.20	0.01	0.02	tr.
Al_2O_3	1.26	1.13	1.96	0.51	1.98	1.06	1.71	3.04	2.59	1.82	3.51	2.16	1.99	1.48	1.47	2.41	3.51	2.40	1.96
Cr_2O_3	tr.	0.31	ass.	0.95	tr.	ass.	ass.	ass.	ass.	ass.	ass.	ass.	ass.	ass.	ass.	ass.	ass.	tr.	ass.
Fe_2O_3	0.65	0.38	1.04	0.25	0.88	1.07	0.64	1.47	0.97	0.73	1.54	0.92	1.70	0.96	1.61	3.87	7.56	2.26	0.80
As_2O_3	0.06	0.25	0.01	0.12	0.03	0.04	0.02	0.02	0.04	0.06	0.01	0.05	0.04	0.15	0.09	0.03	ass.	0.02	0.06
Sb_2O_3	ass.	0.58	ass.	3.12	0.01	ass.	ass.	ass.	ass.	ass.	0.06	ass.	ass.	0.09	ass.	0.11	ass.	0.08	ass.
MgO	0.56	0.35	2.15	0.15	2.17	1.42	2.01	2.45	2.12	1.90	2.55	2.23	2.08	1.84	0.57	1.78	2.18	1.80	2.06
CaO	5.45	3.02	7.28	4.95	7.75	6.13	7.82	8.83	7.65	7.10	11.51	7.06	7.95	6.41	4.72	7.73	8.64	8.88	6.99
CoO	ass.	ass.	ass.	ass.	ass.	ass.	ass.	ass.	ass.	ass.	ass.	ass.	0.03	0.02	0.04	tr.	0.01	ass.	ass.
MnO	0.37	0.32	1.01	0.14	1.49	0.91	2.59	0.78	1.38	1.38	0.97	2.11	0.81	0.54	0.07	0.84	1.47	0.70	1.62
CuO	5.21	2.66	3.23	0.64	2.05	1.66	2.39	1.61	0.93	0.05	1.22	0.07	0.14	0.36	0.19	1.19	0.77	2.29	0.06
ZnO	0.04	1.96	0.02	0.15	0.02	0.02	0.02	0.02	0.01	0.01	0.02	0.01	0.19	0.08	0.19	0.04	0.05	0.05	0.01
SrO	0.02	0.01	0.09	tr.	0.09	0.06	0.09	0.07	0.09	0.11	0.08	0.14	0.09	0.03	0.04	0.05	0.05	0.05	0.12
BaO	ass.	0.02	0.03	ass.	0.06	0.01	0.13	0.02	0.06	0.05	0.05	0.10	0.03	0.01	ass.	0.05	0.06	0.03	0.05
PbO	0.04	5.46	ass.	7.70	tr.	0.15	ass.	0.04	ass.	ass.	tr.	ass.	0.02	4.73	ass.	1.98	0.05	0.94	ass.
Na_2O	18.78	22.56	12.95	22.55	12.35	13.29	12.45	9.98	13.04	11.74	11.99	15.50	16.96	19.07	14.64	14.71	10.23	14.51	13.45
K_2O	0.32	0.48	1.73	1.14	1.89	0.93	2.27	1.53	1.92	1.56	1.67	1.95	1.72	2.11	0.37	1.93	1.73	1.77	1.70
P_2O_5	0.09	0.03	0.21	0.02	0.22	0.11	0.24	0.19	0.26	0.20	0.22	0.24	0.21	0.11	0.07	0.21	0.27	0.16	0.22
V_2O_5	tr.	ass.	tr.	ass.	tr.	ass.	0.01	tr.	tr.	tr.	tr.	0.01	tr.	tr.	ass.	tr.	0.01	tr.	tr.
S	0.03	0.03	0.04	0.17	0.04	0.04	0.03	0.03	0.04	0.04	0.04	0.06	0.04	0.06	0.02	0.06	0.03	0.04	0.05
Cl	1.02	0.17	0.60	0.11	0.59	0.37	0.76	0.40	0.62	0.52	0.50	0.66	0.80	0.39	0.73	0.56	0.48	0.42	0.58

Table 1. *Compositional data from the analysis by XRF of glass tesserae from Dafni Monastery, Greece. All values are expresed as % wt.*