

**ARCHAEOMETRICAL INVESTIGATION OF SOME MEDIEVAL GLASS
SAMPLES FROM ALANYA REGION**

**A THESIS SUBMITTED TO
THE GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES
OF
MIDDLE EAST TECHNICAL UNIVERSITY**

BY

ELİF BEŞER

**IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR
THE DEGREE OF MASTER OF SCIENCE
IN
ARCHAEOMETRY**

AUGUST 2009

Approval of the thesis:

**ARCHAEOMETRICAL INVESTIGATION OF SOME MEDIEVAL GLASS
SAMPLES FROM ALANYA REGION**

submitted by **ELİF BEŞER** in partial fulfillment of the requirements for the degree
of **Master of Science in Archaeometry, Middle East Technical University** by,

Prof. Dr. Canan Özgen
Dean, Graduate School of **Natural and Applied Sciences** _____

Prof. Dr. Asuman Türkmenoğlu
Head of Department, **Geological Engineering** _____

Prof. Dr. Ali Uzun
Supervisor, **Statistics Dept., METU** _____

Prof. Dr. Şahinde Demirci
Co-Supervisor, **Chemistry Dept., METU** _____

Examining Committee Members:

Prof. Dr. Ali Uzun
Statistics Dept., METU _____

Prof. Dr. Şahinde Demirci
Chemistry Dept., METU _____

Prof. Dr. Asuman Türkmenoğlu
Geological Engineering Dept., METU _____

Prof. Dr. Emine Caner Saltık
Architecture Dept., METU _____

Prof. Dr. Öztaş Ayhan
Statistics Dept., METU _____

Date: _____

I hereby declare that all information in this document has been obtained and presented in accordance with academic rules and ethical conduct. I also declare that, as required by these rules and conduct, I have fully cited and referenced all materials and results that are not original to this work.

Name, Last Name : Elif Beşer

Signature :

ABSTRACT

ARCHAEOMETRICAL INVESTIGATION OF SOME MEDIEVAL GLASS SAMPLES FROM ALANYA REGION

Beşer, Elif

M.S., Graduate Program of Archaeometry

Supervisor : Prof. Dr. Ali Uzun

Co-Supervisor: Prof. Dr. Şahinde Demirci

August 2009, 153 pages

The archaeological questions of historical glass have lead to remarkable research activities such as identification and sourcing the raw materials used in the glass production, investigations of the ways in which the colors of glass can be modified due to dissolved and/or colloidal coloring agents, the furnace conditions, and the time of fritting and melting.

Considering publications, it can be suggested that compositional studies of well-dated glass samples have supplied useful information concerning raw materials' characteristics and technology of glassmaking. Within this context, the aim of this study was to determine elemental compositions and production techniques of some 13th century Seljukian Period window glasses from Alanya excavation region. During the excavations at Alanya archaeological site involving Inner Castle and out of Inner Castle many glass pieces of varying colors have been found. In this study 25 samples from the area have been examined.

Elemental analyses have been carried out using X-Ray Fluorescence Spectroscopy (XRF) to determine major, minor, and trace elements. The data

obtained by XRF has revealed that all samples have typical soda-lime-silica composition with the average values of, 68.22 % (SiO_2); 11.3 % (Na_2O); and 6.7 % (CaO). Hierarchical Cluster analysis has been employed and the samples have been grouped depending on their potassium oxide (K_2O) and magnesium oxide (MgO) contents which indicate the probable alkali flux source.

The colors of the samples are honey-yellow, brown-yellow, navy blue, blue, turquoise, purple, and green. The coloring agents have been determined as Fe, Cu, Co, and Mn.

The data from Optical Microscopy has shown that most of the window glasses might have been produced by cylinder technique. Some other samples have revealed the signs of crown technique, and some might have been produced by casting.

Keywords: Seljukian Period, Islamic Glass, Window Glass, Alanya

ÖZ

ALANYA BÖLGESİNDEN ELDE EDİLEN BAZI ORTAÇAĞ CAMLARININ ARKEOMETRİK İNCELEMESİ

Beşer, Elif

Yüksek Lisans, Fen Bilimleri Enstitüsü Arkeometri Programı

Tez Yöneticisi : Prof Dr. Ali Uzun

Ortak Tez Yöneticisi : Prof. Dr. Şahinde Demirci

Ağustos 2009, 153 sayfa

Tarihi camlar hakkındaki arkeolojik sorular önemli bilimsel araştırmalara yol açmıştır. Bunlar, cam üretiminde kullanılan hammaddelerin tanımlanması, bunların kaynaklarının bulunması, çözülmüş ve/veya colloidal renk verici metallere, fırın atmosferine ve ön-eritme ve eritme süresine bağlı olarak cam renklerinin oluşumunun incelenmesi gibi alanlardır.

Doğru tarihlendirilmiş cam örneklerinin bileşimlerinin, hammadde özellikleri ve cam yapım teknolojisi hakkında yararlı bilgiler sağladığı söylenebilir. Bu kapsam içinde bu çalışmanın amacı İç Kale bölgesini ve İç Kale'nin dışını kapsayan Alanya kazı bölgesinde bulunmuş bazı 13. yüzyıl Selçuklu Dönemi pencere camlarının kimyasal bileşimlerini ve üretim tekniklerini saptamaktır. İç Kale'yi ve İç Kale'nin dışını kapsayan Alanya arkeolojik alanında yürütülen kazılar sırasında çeşitli renklerde cam buluntular elde edilmiştir. Bu çalışmada bunlardan 25 adet örnek incelenmiştir.

Örneklerin temel, az ve iz element içerikleri X-Isınları Floresans Spektrometrisi ile belirlenmiştir. Analiz sonuçları camların tipik soda-kireç-silis camı

olduğunu ve ağırlıkça % 68.22 (SiO₂); % 11.3 (Na₂O); ve % 6.7 (CaO) göstermiştir. Hiyerarşik Kümeleme istatistik yöntemi uygulanmış ve örnekler, alkali ergitici kaynağı hakkında bilgi verebilen potasyum ve magnezyum oksit içeriklerine göre gruplandırılmıştır.

Camlar bal sarısı, kahverengi-sarı, lacivert, mavi, turkuvaz, mor ve yeşil renklindedir. Renk veren metaller demir, bakır, kobalt ve manganez olarak saptanmıştır.

Optik Mikroskop ile inceleme camların çoğunun silindir tekniğiyle üretildiğini göstermiştir. Diğer camlardan bazıları “crown” tekniğinin izlerine sahipken bazıları da döküm tekniğiyle üretilmiş olabilir.

Anahtar Kelimeler: Selçuklu Dönemi, İslam Camı, Pencere Camı, Alanya

ACKNOWLEDGMENTS

I would like to express my gratitude to Prof. Dr. Ali Uzun, supervisor of the thesis, and Prof. Dr. Şahinde Demirci, co-supervisor of the thesis, and Prof. Dr. Ömür Bakırer for their valuable guidance beyond their knowledge and teaching skills.

I owe very special thanks to Prof. Dr. Asuman Türkmenoğlu and Prof. Dr. Ay Melek Özer for the valuable assistance given in the timely preparation of this thesis.

I really would like to express my gratefulness to AKMED (Research Institute of Mediterranean Civilizations) for founding scholarship for the expenditure of the thesis.

I am very grateful to Prof. Dr. M. Oluş Arık and Prof. Dr. Kenan Bilici for giving the samples.

I am extremely grateful to Prof. Dr. Yusuf Kağan Kadioğlu at the Department of Geological Engineering at Ankara University for XRF analysis and Dr. Ali Akın Akyol at Başkent Vocational Higher School, Program of Conservation at Ankara University for his support.

Very special thanks to everyone at Material Conservation Laboratory at the Faculty of Architecture in METU.

Finally, special thanks to my parents and my sister for their support and belief in this thesis.

TABLE OF CONTENTS

ABSTRACT	iv
ÖZ	vi
ACKNOWLEDGMENTS	viii
TABLE OF CONTENTS	ix
LIST OF TABLES	xi
LIST OF FIGURES	xii
CHAPTERS	
1. INTRODUCTION	1
1.1. Aim of the Study	2
2. GENERAL ASPECTS OF GLASS AND ITS HISTORY	4
2.1. Definition of Glass	4
2.2. Viscosity	6
2.3. Oxide Glasses	11
2.4. Soda-Lime-Silica Glass	14
2.5. The Components of Soda-Lime-Silica Glass	15
2.5.1. Silica	17
2.5.1.1. Natural Silica	18
2.5.1.2. Manufactured silica	19
2.5.2. Fluxes	24
2.5.3. Stabilizers	27
2.5.4. Intermediates	29
2.5.5. Fining and Opacifying Agents	32
2.5.6. Coloring Agents	33
2.6. Decay of Glass	41
2.7. Ancient Glassmaking	44
2.7.1. Fritting	45
2.7.2. Melting	48

2.7.3. Furnaces.....	50
2.7.4. Glass Forming	53
2.8. Brief History of Glass.....	56
2.8.1 The Origins of Glass.....	57
2.8.2 The Chemical Compositions of the Bronze Age Glasses (3300-1200 B.C.)	60
2.8.3. The Chemical Composition of Roman Glass	64
2.8.4. Post-Roman Period.....	65
2.8.4.1. Western Glass.....	66
2.8.4.2. Islamic Glass	69
2.8.5. Historical Window Glass.....	72
2.8.6. Window Glass from Anatolia.....	77
2.9 Alanya (Alaiye) Castle	81
3. MATERIALS AND METHODS	88
3.1. Glass Samples and Their Visual Discription.....	88
3.2. X-Ray Fluorescence (XRF) Analysis of the Samples	91
3.3. Statistical Analysis of the Sample Data.....	92
4. RESULTS AND DISCUSSION	93
4.1. Visual Examination	93
4.2. Examination with Optical Microscope (OM).....	95
4.3. Photographs of the Samples	97
4.4. Elemental Composition of the Samples	103
4.4.1. Sand.....	111
4.4.2. Alkalis and Alkaline Earths.....	121
4.4.3. Coloring Agents	128
5. CONCLUSION	134
REFERENCES.....	139
APPENDICES	
A. The Properties of PED-XRF.....	152
B. Statistical Analysis of Sample Data.....	153

LIST OF TABLES

Table 1 Functional classification of common oxides.....	14
Table 2 Some components used to make different types of glass.....	32
Table 3 Some coloring metal ions.....	34
Table 4 Chemical compositions of some ancient glasses.....	72
Table 5 Visual Colors and Munsell Codes of the samples studied	90
Table 6 Element compositions (%) of glass samples studied.....	104

LIST OF FIGURES

Figure 1 Commonly accepted reference points for soda-lime-silica glass.....	8
Figure 2 Three-dimensional Si-O tetrahedron.....	12
Figure 3 The schematic representation of silica in two-dimension.....	13
Figure 4 Two dimensional structure of soda-lime-silica glass.....	21
Figure 5 The map of the probable route of the ship found in Uluburun and likely sources of materials for the various artefacts found on the wreck	48
Figure 6 A beehive-shaped furnace illustrated by Agricola.....	52
Figure 7 Core-forming of glass	54
Figure 8 Casting methods of glass	55
Figure 9 Bronze Age sites in Egypt and Mesopotamia	62
Figure 10 The cylinder-blown technique	74
Figure 11 The crown technique.....	75
Figure 12 The reconstructed quarries from Jarrow Monastery	76
Figure 13 The grill designs used in Islamic architecture.....	77
Figure 14 Alanya Inner Castle excavation site.....	83
Figure 15 The Seljukian Palace in the south-eastern border of the Inner Castle in Alanya excavation site.....	84
Figure 16 The view from Watching Patio at the north side of Inner Castle.....	86
Figure 17 The plan showing the area between the south end of the Vaulted Ward and the north part of the apsis of the Church and the gate to the Inner Castle.....	87
Figure 18 A few glass cup pieces found at the site	87
Figure 19 Glass pieces studied	89
Figure 20 (a) 1:1 scaled and (b) OM photographs of the sample AL1.....	97
Figure 21 (a) 1:1 scaled and (b) OM photographs of the sample AL2.....	97
Figure 22 (a) 1:1 scaled and (b) OM photographs of the sample AL3.....	97
Figure 23 (a) 1:1 scaled and (b) OM photographs of the sample AL4.....	98
Figure 24 (a) 1:1 scaled and (b) OM photographs of the sample AL5.....	98
Figure 25 (a) 1:1 scaled and (b) OM photographs of the sample AL6.....	98

Figure 26 (a) 1:1 scaled and (b) OM photographs of the sample AL7.....	99
Figure 27 (a) 1:1 scaled and (b) OM photographs of the sample AL8.....	99
Figure 28 (a) 1:1 scaled and (b) OM photographs of the sample AL9.....	99
Figure 29 (a) 1:1 scaled and (b) OM photographs of the sample AL10.....	100
Figure 30 (a) 1:1 scaled and (b) OM photographs of the sample AL11.....	100
Figure 31 (a) 1:1 scaled and (b) OM photographs of the sample AL12.....	100
Figure 32 (a) 1:1 scaled and (b) OM photographs of the sample AL13.....	101
Figure 33 (a) 1:1 scaled and (b) OM photographs of the sample AL14.....	101
Figure 34 (a) 1:1 scaled and (b) OM photographs of the sample AL15.....	101
Figure 35 (a) 1:1 scaled and (b) OM photographs of the sample AL16.....	102
Figure 36 (a) 1:1 scaled and (b) OM photographs of the sample AL17.....	102
Figure 37 (a) 1:1 scaled and (b) OM photographs of the sample AL18.....	102
Figure 38 The scatterplot of K_2O versus MgO of 25 samples	110
Figure 39 Dendrogram with Ward Linkage and Euclidean Distance of 25 Alanya Samples	111
Figure 40 The scatterplot of TiO_2 versus Fe_2O_3 of 25 samples.....	113
Figure 41 The scatterplot of Fe_2O_3 versus Al_2O_3 of 25 samples	114
Figure 42 The scatterplot of TiO_2 versus Al_2O_3 of 25 samples.....	115
Figure 43 The scatterplot of Fe_2O_3 versus SiO_2 of 25 samples.....	116
Figure 44 The scatterplot of CaO versus Al_2O_3 of 25 samples.....	119
Figure 45 The scatterplot of CaO versus MgO of 25 samples	126
Figure 46 The scatterplot of CaO versus K_2O of 25 samples.....	127
Figure 47 The scatterplot of SnO versus CuO of 25 samples	132
Figure 48 The scatterplot of As_2O_3 versus CoO of 25 samples.....	133

CHAPTER 1

INTRODUCTION

Glass is classified as a ceramic and the pyrotechnology and the raw material processing in glass manufacture have similar features to the other high temperature industries involving pottery, metal, glaze, and faience production. On the other hand, the physical and chemical properties of glass are specific and different from the others. These differences determined the variety of functions of glass performed in the past societies. It was formed into jewellery, inlays in metal surfaces, perfume, water, and wine containers, plates, and window panes (Henderson, 1989).

There are three main areas of research determined by archaeological and technical questions about historical glass. The first is the identification and the sourcing of the raw materials used in glass production. The second is determining the ways in which glass colors can be modified. The third area of research is the chemical characterization of glass products. This characterization is crucial because the use of a specific combination of raw materials precedes a chemical “fingerprint” of the glass which is often specific to the time and sometimes to the place of its production. Once sufficient compositional data representative of a specific time and region has been determined, the relationship between a specific glass composition and the regional archaeology can be assembled (Henderson, 1989).

Considering archaeological and technical questions within the frame of this thesis, some Seljukian glass window pane and cup pieces dated to the 13th century from Alanya archaeological site were attempted to be investigated.

The study has been presented in five chapters. This first chapter includes general properties of glass and aim of the study. The second chapter includes general characteristics of glass components, history of glass production and description of

Alanya castle and excavation done in the area. In the third chapter materials analyzed and methods applied in the analysis of glasses samples excavated from Alanya region have been explained. The results have been discussed in detail in the fourth chapter. And, finally interpretation of the analytical results has been summarized in the fifth chapter.

1.1. Aim of the Study

Glassmaking has always been a complicated skill. The materials used to make glass, the batch, obtained by mixing them together, the furnace conditions, and all the treatments, applied in and out of the furnace affect the resulting object. One glass object produced in one place may be different from, or similar to another object produced in the neighbor, or remote place. Glass like all other goods was the subject of trade and was carried from one place to another in the form of either raw ingot, or cullet (pieces of broken glass from previous batches or glass waste) or as a finished product. Moreover, glass artisans moved from one region to the other to spread their style. They brought their materials with them or used the local materials they could achieve. Therefore, a work of glass-art, resembling another glass object for its design and decoration, may totally be different from this object in terms of its composition and/or manufacturing technique (Vandini *et al*, 2006). For this reason, an archaeologist or any related person who would like to investigate the secrets of ancient glassmakers, should bear in mind that visual examination alone would never be enough to understand historical glass, and any attempt to identify glasses according to only their appearances may bring incorrect conclusions.

Especially, when the glass of Medieval period in Anatolia is considered, nothing much can be said because, the findings are rare or sometimes are in very bad conditions that making analyses is not possible. In most cases, only very small fragments of an object can be found that it is not possible to suggest anything about its whole shape and design (Bakirer, 1986). In order to make satisfactory classifications and identifications of glass types, archaeometrical analyses are required. Chemical analyses give sufficient data about the glass compositions, and

hence make it possible to indicate chronological and geographical differentiations associated with the recipes and the production techniques (Ubaldi and Verità, 2003). Chemical studies on ancient glass can contribute to mainstream archaeology by generating implications of the raw materials, the manufacturing sites, and the probable trade routes.

However, successful accomplishments require large number of analyses with large number of findings. Unfortunately, it has been a problem to achieve the findings datable to the Medieval period of Turkey. It is not easy to indicate anything about provenance of glass artefacts belonging to the Medieval era, because archaeological studies in Turkey mostly focus on the pre-Roman and the Roman periods, and post-Roman studies are excluded from archaeological context. Seljuk art is thought as an interest of the art historians, who, although can postulate a general point of view about the aesthetics of ancient industries, cannot help much in experimental studies. Reconstruction of past can only be done by scientific approaches to artefacts, and by understanding the characteristics of materials used to produce them. For glass artefacts, chemistry can imply much more than art history because, the ingredients composing the glass are more useful to provide information about the logical development of technology than making comparisons based on figures on the pieces.

This study takes into account the data relative to the chemical analyses of glass pieces dating to the 13th century from Alanya region with the aim of contributing to the studies on Seljukian archaeology. This study can be considered as the more detailed and extended version of the introductory study carried out in 2006 by U. B. Aksoy, the archaeometry student at the Middle East Technical University. These two studies seem to be the only studies held according to the archaeometrical data. We hope that such archaeometrical studies on medieval glasses of Turkey increase in number to be able to constitute an efficient ancient glass characterization of our country.

CHAPTER 2

GENERAL ASPECTS OF GLASS AND ITS HISTORY

2.1. Definition of Glass

In traditional sense, glass is a substance made of silicon dioxide (sand) mixed with some other oxides which are heated together, and then cooled. However, today, the term “glass” cannot be limited to silicate systems produced by cooling from a melt only (Shelby, 1997). The necessity and the desire for understanding the fundamental principles of glass along with the investigations in chemistry and physics as well as in many other disciplines of science have led many extensive and thorough studies on the properties of all types of glass. After the recognition of the properties of glass forming materials through several observations and analyses, it has become possible to make glass from distinct substances, which, even, have no tendency to be transformed into a glass (Doremus, 1973; Amstock, 1997).

The improvements achieved until the present day, give us the opportunity to form glass from large numbers of substances under special conditions, such as organic polymers, resins, silica-free inorganic materials (e.g. chalcogenides of sulfur (S), selenium (Se), or tellurium (Te); phosphates, ionic salts (nitrates and sulfates), halide glasses based on fluorides (especially BeF_2 and ZrF_4) (Rawson, 1967), candies made of sucrose or glucose (McMillan, 1964), and even metallic alloys by splat cooling of metals (Doremus, 1973). The organic liquids that form glasses have relatively low melting temperatures and have asymmetric molecules which are not easy to be rearranged, thus nucleation and crystal growth are reduced when they are cooled, and therefore they do not crystallize upon cooling (Shand, 1958; Doremus, 1973). Chalco has been derived from a Greek word for copper, and chalcogenide is

used for the elements which form compounds with copper. Chalcogenide glasses are electronic semi-conductors and they also transmit infrared radiation well. Ionic salts form glasses only as binary or multicomponent mixtures. Metallic glasses as ribbons and foils can be produced from metallic alloys by cooling them very rapidly (Le Bourhis, 2007).

Moreover, cooling from a melt is not the only process needed for glass formation; glass can be formed by deposition from the vapor phase, by sol-gel processing of solutions, and by neutron irradiation of crystalline materials (Doremus, 1973). For example, an aqueous solution of sodium-silicate which involves water can be evaporated and the deposit can be baked to remove water. A fine sodium-silicate glass obtained by this process is not distinguishable from another sodium-silicate glass made by cooling from the liquid (Rawson, 1980). These glasses obtained by such techniques, have the same chemical composition of, and identical properties to, glasses produced by cooling from the melt. Usually the differences between some of those glasses may be so slight that intricate instruments are required to distinguish one from the other (Scholes, 1975). On the other hand, the purpose of the usage of one glass of a certain category is seldom the same of another one of a different category. Thus, the most excellent plate glass may not be satisfactory for optical purposes (Rawson, 1980, 1991).

As a result of all these developments in glass science and technology since the very first day of the discovery of the natural, and the invention of the artificial glass, it is not easy to state a comprehensive definition of glass, because; there is not any satisfactory definition which covers all types of glass and glassy materials, and moreover, it may bring new categorizing problems difficult to handle (Rawson, 1980). For example, the definition stated by ASTM (American Society for Testing and Materials) in 1945 is a limited one since it excludes organic glasses produced in a special way. However, as it seems meaningful and satisfactory for the glasses within the archaeological context, it can be quoted here: “Glass is an inorganic product of fusion which has cooled to a rigid condition without crystallizing” (Rawson, 1967).

Although many authors tend to consider glass as an additional state of matter (the fourth state of matter to be added to solid, liquid, and gas) (Scholes, 1975). Such a consideration does not clarify the contradictions of whether the glass is an amorphous solid (non-crystalline solid among other vitreous substances), or an under-cooled (super-cooled) liquid. Glass is in a condition which is analogous to, and continuous with the liquid state (Morey, 1954), but it attains a viscosity so high that it becomes rigid as the result of a change during cooling (Rawson, 1967; Shelby, 1997). It maintains the energy, volume, and atomic arrangement of a liquid, and at the same time, the changes in energy and volume with temperature and pressure are similar in magnitude to those of a crystalline solid (Morey, 1954). Glass structure is obtained when a liquid is cooled down in such a way that on passing the liquidus (melting) temperature, “freezing” happens instead of crystallization. The final temperature must be so low that molecules or atoms move too slowly to rearrange to the more stable crystalline form (Morey, 1954).

Today, all amorphous materials both inorganic and organic are accepted as glass in the scientific sense (Shelby, 1997). Amorphous material means that it has no long-range order; in other words, the same geometric arrangement of molecules within the chemical composition is not repeated over large distances throughout the material and angles between bonds, and distances between pairs are not constant (Baltă and Baltă, 1976). Crystalline solid materials have long range order but amorphous solids do not. For this reason, glass may not be regarded as a ceramic material. Ceramics present generally a long-range order (McMillan, 1964). The magnitude of viscosity is the main reason for a material for gaining its amorphous character. Therefore, it is necessary to briefly mention about viscosity before describing the oxide glass category in which the glass fragments within the scope of this study are included.

2.2. Viscosity

One of the most important properties of glass is viscosity which determines the melting conditions and the homogeneity of glass (Le Bourhis, 2007). Viscosity is

resistance to flow, in other words, a viscous liquid flows slowly. A liquid with a high viscosity such as molasses will flow at a very slow rate whereas water with a considerably lower viscosity will flow much more readily.

The relationship between the glassy state and the normal solid and liquid states can be understood on the basis of what happens during the cooling of melts. When a crystalline solid is heated to its melting point, it turns into a liquid; and on cooling the reverse phase change takes place. This time the liquid turns into solid, having a specific structure with rigid crystals below its freezing temperature. This is the process of crystallization which involves the rearrangement of the molecules into a definite pattern. However, the materials which are called glasses have a characteristic property that when melted and then cooled fast enough, they do not devitrify (crystallized) in most conditions (Shelby, 1997). Here, the molecules cannot assume definite positions required by crystal structure. For a substance which crystallizes it is observed that there is a closely defined temperature at which solidification occurs and at this temperature a discontinuous volume change occurs. Heat is evolved when solidification takes place. For a substance which can be cooled to glassy state on the other hand, no discontinuous change of volume, and hence, exothermic effect corresponding with the change from the liquid to the solid state are seen. Instead, the viscosity of the melt increases progressively as the temperature falls and eventually viscosity attains values which are so high that for all practical purposes the substance behaves as a rigid solid (Feltz, 1993). Thus, the glassy state is continuous with the liquid state and is distinguished from the normal liquid state by the high magnitude of viscosity. Recently, it has been recognized that virtually any material can form glass if it is cooled so rapidly that the required reorganization of molecules or atoms within its structure is not allowed since they move too slowly to rearrange to the stable crystalline form. Rapid cooling increases the viscosity (resistance to flow), and hence reduces the ability to form crystals (Morey, 1954; Rawson, 1980, 1991).

The relationship between viscosity and temperature for glasses is important in a number of respects. There are some reference points, or reference temperatures determined by the viscosity of molten glass. These viscosity and temperatures permit

the specification of values most favorable for each step of glass production. Figure 1 represents the typical curve for viscosity as a function of temperature.

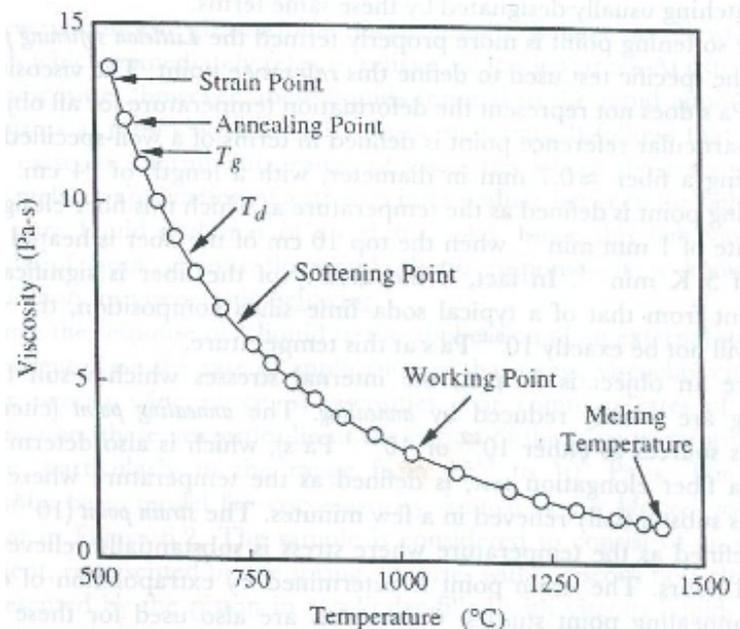


Figure 1 Commonly accepted reference points for soda-lime-silica glass (NIST Standard No. 710) (Shelby, 1997)

Certain temperature points determined by the viscosities at these points are in common use as a means of describing the characteristics of glasses. A glass is conventionally said to have melted when its viscosity is between 10^8 and 10^2 poises. Poise is the CGS unit of dynamic viscosity, which is identical to $\text{g cm}^{-1} \text{s}^{-1}$. SI equivalent is Pa-s (Pascal second with dimensions $\text{kg m}^{-1} \text{s}^{-1}$). For comparison, bear in mind that water has a viscosity of 10^{-2} poises at room temperature (Amstock, 1997). Poise which is the unit of viscosity is the force required to produce shear movement across a section of liquid at a unit rate. Glasses cannot be worked at viscosities much above 10^4 poises, and when the viscosity rises to 10^{15} poises, glass becomes essentially rigid (Shand, 1958).

One of the crucial differences between crystals and the glass is the absence of explicit melting or freezing point in glass. The exact melting point of a crystalline

material can be determined since the chemical bonds within the crystal are identical and they all break at the same temperature when they are heated. Glass has no real melting point; because; different chemical bonds within the glass structure are distorted at different temperatures meaning that each has its own melting point. When heated it loses the perfect elasticity it has when it is cold; and it gradually acquires mobility becoming softer and softer until it will actually flow as a viscous liquid. So, the glass, in fact, softens gradually into a liquid in the range of increasing temperatures rather than melting at a sharp temperature point (McMillan, 1964).

Increasing the temperature of the molten batch has an enormous effect in reducing the viscosity and to remove the bubbles which are caused by entrapped gasses. Chemical and physical changes at this high temperature result in the conversion of the heterogeneous mixture into a homogeneous one which has the properties of molten glass. The predictions of Roman glasses give a range of temperatures from 1000°C to 1200°C indicating that a period of many hours could have been required to homogenize and refine the glass to achieve the quality (Brill, 1988).

The temperature range between working and softening points (Figure 1) is known as the working range where the melt is fluid enough to allow flow under reasonable stresses and at the same time viscous enough to retain its shape after shaping processes such as cutting, pressing, or blowing. This range is generally between 700°C – 900°C for soda-lime-silica glasses (Henderson, 2000). The viscosity is generally between 10^8 and 10^2 poises. After some time (usually several hours), the temperature is lowered down resulting in the melt's becoming increasingly viscous, and suitable for glass forming operations. This is the period of time during which molten glass is within a working range of temperatures at which it has the viscosity appropriate for shaping. These shaping operations (e.g. blowing; casting) have to be completed in a relatively short period of time (from as little as a few seconds to as much as several minutes) depending on the actual composition of the melt and the working conditions (Goffer, 2007).

The softening point (Figure 1) is a temperature above the working point, and corresponds to a viscosity of approximately 10^8 poises (Phillips, 1960). At lower

viscosities the glass is too fluid to hold a shape and near to and below the softening point the glass no longer flows sufficiently and cannot be worked.

Two other reference temperatures are often quoted for glass forming melts. One is the glass transformation temperature, T_g , which can be determined from measurements of the temperature dependence of either the heat capacity or the thermal expansion coefficient during reheating of a glass. The viscosity corresponding to T_g for common glasses has an average value of $10^{11.3}$ Pa-s. Below T_g the melt becomes too viscous for molecular movement, and so the system is metastable with respect to the crystalline state, and has the structure of a frozen liquid. Glasses of the same composition exhibit a range of temperatures over which formation occurs, and the exact position of T_g depends on the rate of cooling of the melt. The other is the dilatometric softening temperature, T_d , which is usually defined as the temperature where the sample reaches a maximum in a length versus temperature curve during heating of a glass. The viscosity corresponding to T_d is in the range 10^8 - 10^9 Pa-s (Le Bourhis, 2007).

The annealing point in Figure 1 indicates the temperature for removal of internal stresses generated during the shaping operations. The glass at this step has a viscosity of approximately $10^{13.5}$ poises (Phillips, 1960). Annealing is the process of heating the glass to the annealing temperature and maintaining this temperature for a specified length of time, and then cooling it down at a controlled rate (Goffer, 2007). It depends upon heating the glass to a temperature where its viscosity is low enough to permit stress relief without resulting in distortion of the glass. The glassware should be annealed at a temperature close to the annealing point to avoid danger of deformation. It must then be cooled slowly to minimize temperature ingredients which create strain as they are dissipated in the material after it has become rigid.

The glass object should not be held too long below the temperature range of transformation in which the crystallization may readily take place. Once the temperature of cooling of the melt passes below the lower limit of the metastable region, the thermodynamic barrier will diminish with falling temperature, allowing nuclei to form, which then will cause the devitrification, and thereby the flaking and ruining of the glass.

The strain point in Figure 1 is the temperature at which further stress is substantially relieved. This relieving may take several hours. The viscosity is approximately 10^{15} poises and the temperature is usually 35°C to 45°C below the annealing point (Phillips, 1960). Strain point is the temperature where the glass is so rigid that internal movement has virtually ceased and internal strain can be relieved only after hours.

The temperature at which glass, when cooling, ceases to undergo configurational change is called the fictive temperature. For common glass it is 500°C at which the glass is thermodynamically stable. In principle, common glass is unstable at room temperature since it goes on shrinking because configurational change will continue until the fictive temperature reaches the actual temperature; however, this process goes forward so slowly that millions of years would be needed for a glass at room temperature. The viscosity exceeds 10^{20} poises at room temperature (Amstock, 1997).

The term plastic and viscous are often confused. Plastic means capable of being molded or receiving form while viscous means sticky. In this sense, hot glass is both plastic and viscous. However, the term plasticity is given the further connotation of being able to maintain form after shaping. Clay is plastic which retains its form without change in temperature after being shaped. Glass has this property only because it is cooled rapidly. Cold glass has little plasticity (McMillan, 1964).

2.3. Oxide Glasses

Despite of the probability and the possibility of transforming a large number of substances and mixtures into glasses by proper manipulation in several disciplines of science, only a comparatively few compositions are suitable for glass manufacture on a commercial scale. Commercial glasses are almost exclusively multicomponent glasses resulting from the mixing of other oxides with the main glass former oxides.

V. M. Goldschmidt observed many glasses and, in 1929, developed the earliest and the simplest theory of inorganic glass formation. According to his theory,

only melts that contain tetrahedrally coordinated cations form glasses during cooling. After a few years, W.H. Zachariasen extended Goldschmidt's hypothesis and attempted to explain the difference between the crystalline and the vitreous state. Indeed, what he did was the application of the rules of crystal chemistry to the silicate glasses (McMillan, 1964). According to his currently accepted theory, the oxides, SiO₂ (silicon dioxide, or silica); B₂O₃ (boric oxide); GeO₂ (germanium oxide); P₂O₅ (phosphorus oxide); and As₂O₅ (arsenous oxide) can form glass with rapid cooling.

Zachariasen proved that silica (SiO₂) itself can form glass. When silica is cooled rapidly enough from above the melting point, no appreciable amount of crystalline substance is formed, because, the rate of crystallization alone is slow enough to allow glass formation under most conditions. If nucleation and crystal growth rates are slow comparatively than the rate of temperature decrease, cooling of a silicate liquid will result in its transformation to a glass at a range of temperatures. At temperatures that are significantly below the calculated glass formation temperature, the rate at which the liquid-like glass structure can change to the regular arrangement of the crystalline solid is infinitely slow and the silica becomes a stable glass.



Figure 2 Three-dimensional Si-O tetrahedron (The solid dot represents silicon; the open circles are oxygen atoms around silicon (Le Bourhis, 1997). Each oxygen atom has the same distance to the silicon atom, and the distances between the oxygen atoms are also all the same) (source: www.quartzpage.de/gen_struct.html, last visited on August 2009)

In silicate crystals, the basic unit is a SiO₄ tetrahedron which exactly exists in silicate glasses (Figure 2). The difference is that in crystal, chemically bonded atoms

exhibit long range order whereas in vitreous silica, and thus in glass, the bond angles and bond distances vary (Figure 3a and b).

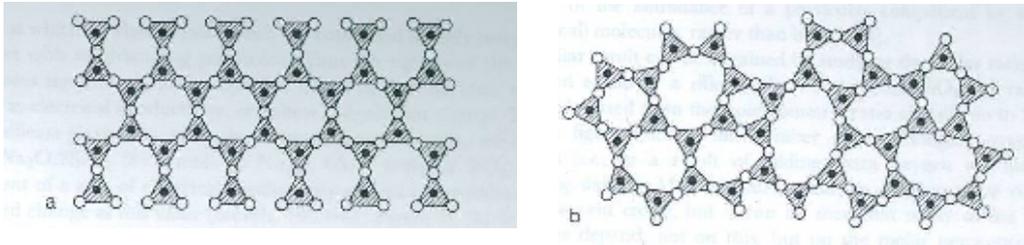


Figure 3 The schematic representation of silica in two-dimensions: (a) in the crystalline state as quartz; (b) in the vitreous state as glass (American Chemical Society, copyright 1932) (Pollard and Heron, 2008)

For other materials (and other glass forming oxides), which have the rate of crystallization not as slow as silica, a much more rapid cooling is needed to prevent crystallization. Pure silica which is very viscous even at high temperatures, is therefore, one of the most outstanding glass-formers. The cations of Ge (Germanium), As (Arsenic), P (Phosphorus), and B (Boron) substitute for Si (Silicon) in the network of glass if they act as network formers. If melts consisting of two or more components are considered, the range of glass-forming systems is enormously extended. By melting any of the oxides with a second (usually basic) oxide, many glass forming systems may be formed.

The identity of these components is the basis for the generic name used for the glass. For example, if B_2O_3 is present as the major glass former, the glass is called a borate, but if it is only present in a significant amount in addition to silica, the glass is called a silicate termed as borosilicate, which has the trade name Pyrex. Borosilicates have lower thermal expansion and thus better thermal shock resistance, and hence good for automobile headlamps, cookware, and laboratory apparatus (Le Bourhis, 2007). The functional classification of common oxides is given in Table 1.

Table 1 Functional classification of common oxides (Amstock, 1997)

Glass formers	Intermediates	Modifiers
B ₂ O ₃	Al ₂ O	MgO
SiO ₂	Sb ₂ O ₃	Li ₂ O
GeO ₂	ZrO ₂	BaO
P ₂ O ₅	TiO ₂	CaO
V ₂ O ₅	PbO	SnO
AsO ₃	BeO	Na ₂ O
	ZnO	K ₂ O

2.4. Soda-Lime-Silica Glass

Among all the glass forming oxides, silica (the oxide of silicon, in the form of quartz) is the most common and the most commercially important type of constituent that has been widely used for making glass everywhere in the world since the very first day of its discovery. Silica itself can form glass without any other component. On the other hand, the difficulty and the cost of manufacture make pure silica glass impossible to use for general commercial purposes, and other oxides must be added to flux the silica by reducing its viscosity, and the processing temperature to practical limits; and at the same time, to provide its chemical durability (Bloomfield, 1997).

Oxide glass network is an open structure and thus sufficient bonds linking the polyhedra (triangular or tetrahedral coordination of oxygen atoms surrounding the network cation) exist for the formation of a continuous network structure. This allows many other oxides act as network modifiers and network intermediates in glass formation. Thus glasses can be made over a wide range of compositions in all the alkali-alkaline earth-silicate systems (Newton and Davison, 1996). Therefore, alkali oxides as fluxes and alkaline earth oxides as stabilizers are necessary to be able to make glass for the daily objects we use, such as domestic ware, bottles, jars, crystal containers, plates, and window glasses. Soda ash (sodium carbonate, Na₂CO₃) which decomposes into soda (Na₂O) seems like the most favorable flux in commercial glasses since it is cheap, and relatively easy to obtain, and limestone (calcium carbonate, CaCO₃) which decomposes into lime (CaO) is a favorable

stabilizer in most glasses of this type which is called sodium-calcium-silicate (Bloomfield, 1997), or simply soda-lime-silica glass (SLS) ($\text{Na}_2\text{O}\cdot 3\text{CaO}\cdot 6\text{SiO}_2$) (Rawson, 1991).

Among silicate glasses, soda-lime-silica glass is the most commonly manufactured glass which can be transparent (colored or colorless), translucent, or opaque. Many studies on early glasses have proposed that typical archaeological glasses are soda-lime-silica glasses consisting of the principal network former which is silica, in combination with the alkalis (soda, Na_2O and potash, K_2O) and alkaline earths (lime, CaO and magnesia, MgO) as the network modifiers. The network modifiers (fluxes and stabilizers) disrupt the continuity of the network by changing the physical and chemical properties. Sometimes soda may be replaced by K_2O (potassium oxide). If dolomite is used to obtain CaO (calcium oxide), considerable amount of MgO (magnesia) is also present in the glass. Special purposes of production may affect the composition. In most cases, sodium-calcium-silicate (soda-lime-silica) glass roughly contains 70-75 mole % silica, 10-20 mole % soda, and 5-15 mole % lime. Especially for durability analysis, the weight-percentage figures from chemical analysis are converted to mole percentages by dividing each weight-percentage figure by the molecular weight of the oxide involved, and then normalizing the new figures to be added up to 100 % (El-Shamy, 1973). However, generally in chemical studies of glass, the amounts of the oxides within the glass structure are expressed in percentages by weight.

2.5. The Components of Soda-Lime-Silica Glass

Soda-lime-silica glass consists of these components: the former (silica, mostly in the form of sand); the modifiers (the fluxes and the stabilizers); the intermediates; the opacifying and/or fining agents; and the coloring agents.

As shortly mentioned above, soda and potash are the common fluxes and lime and magnesia are well-known stabilizers. Fluxes such as soda or potash and stabilizers such as lime are rarely available in nature. Thus other, easily available

compounds of these metals (their naturally occurring carbonates and/or hydroxides) are used instead.

Soda and potash has been obtained since early antiquity, by burning weeds until only their ash remains. Soda or potash in ancient glass usually is present in higher proportion than in modern glass. Although the relative amounts of these components may vary widely, the upper limit of their concentration is usually about 30 wt % of the total mass of glass. Other alkalis (Li_2O , Rb_2O , and Cs_2O) are not seen in historical glasses. Li_2O (lithium oxide) is mostly used in ceramic glasses. Rubidium and cesium oxides (Rb_2O , Cs_2O) are rarely used (Brill, 1988).

Lead oxide (PbO) which is not an alkali may take part as the flux. Lead lowers the softening point and increases the stability and fluidity. It is included in optical glass to increase the indices of refraction. Lead glass reflects light strongly and disperses its colors.

Stabilizers prevent the degradation caused by the addition of large amounts of alkali, and hence, make the glass durable. Small amounts of magnesia have a favorable effect in lowering the liquidus (melting) temperature.

Intermediates are oxides which can either enter the network as a former or occupy interstitial holes as a modifier, but are unable to form glasses themselves. Al_2O_3 (alumina), TiO_2 (titanium oxide), and ZrO_2 (zirconia) are in this category. For example, alumina may form silica-free aluminates or aluminosilicate glasses in which the content of silica is relatively lower. Aluminosilicates are resistant to devitrification and have greater strength in cookware, glass-ceramics, fibers, and seals (Shand, 1958). But it is considered as a modifier in soda-lime-silica glasses. Alumina (Al_2O_3) plays an important role in stabilizing the network and is the most important of the network intermediates. Small amounts of barium oxide, of boric oxide, and of fluoride frequently are added to diminish to tendency toward devitrification.

Pure soda-lime-silica glass is not possible; it always contains small amounts of other constituents, which are either introduced deliberately or incidentally by impurities in the batch ingredients, or by crucible or furnace corrosion. Addition of some minor and trace constituents that together usually make up less than 5 % by

weight of the total mass of glass has considerable effects for improving certain properties. They also act as coloring or in some cases as decolorizing agents.

Iron oxide has a proven effect in lowering the melting point, and it was present in amounts which would not be tolerated today, except when the color it gives is definitely wanted. Iron may occur in a wide range of concentrations varying from trace amounts to a maximum of about 10 %. It was not intentionally added to the glass mixture, but was probably introduced as an integral constituent of sand.

2.5.1. Silica

Silicon is one of the most widely distributed elements in the world. Silica is the compound of silicon which is found in both crystalline and amorphous forms. In all crystalline and amorphous silicates the coordination number of silicon-to-oxygen ions is four; therefore the silicon-oxygen tetrahedron with Si atom at the center is the basic building block for silicate structures. These tetrahedra can be attached to none, one, two, three, or four other tetrahedra by silicon-oxygen bonds at their corners, depending on the concentration of other oxides present.

Each silicon atom is bonded to four oxygen atoms and each oxygen atom is shared between two silicon atoms making covalent bond (Figure 2). The angle among the silicon-oxygen bond is fixed, but the angle between two bonds of each oxygen atom is not critical, so that oxygen atoms joining two tetrahedrons provide flexibility necessary for the amorphous structure. Oxygen atoms at four corners are replaced by oxygen triangles in the imaginary two-dimensional system.

The Figures 3a and b below show the slices through the two-dimensional networks of the silica in the crystalline state and in the vitreous state. It must be remembered that, in reality, silicon and oxygen atoms are not in the same plane, and thus, the slices should not be regarded as flat. The fourth oxygen atom is excluded in two-dimensional representations in order to make the drawing less complicated.

Silicon and oxygen in crystalline silica are arranged in a definite pattern (Figure 3a), the units of which are repeated at regular intervals forming a three dimensional network consisting of tetrahedra with a silicon atom at the center, two

oxygen atoms being shared by each of the adjacent tetrahedra. Thus the structure is said to be of long-range order.

In vitreous silica each tetrahedron is attached to four others, giving a three-dimensional network (Figure 3b), which lacks any symmetry or periodicity, and this random-network model is generally accepted as the best description of the structure of the fused silica. The structure of vitreous silica is quite uniform at a short range order (Newton and Davison, 1996).

2.5.1.1. Natural Silica

Natural silica (the basic ingredient of glass) is found in crystalline forms: quartz, tridymite, and cristobalite; and in amorphous forms: obsidian, pumice, and lechatelierite that are formed as a result of melting at very high temperatures. Amorphous natural glass represents molten rock masses which were extruded and cooled so quickly that they did not have time to become transformed into the usual crystalline materials (Le Bourhis, 2007).

At atmospheric pressure, pure silica crystallizes with decreasing temperature and forms its mineral structures (Scholes, 1975).

Quartz is the thermodynamically stable form found in natural deposits and is a major rock-forming mineral in many igneous, metamorphic, and sedimentary rocks.

Tridymite and cristobalite are metastable, in other words, they are in equilibrium under ambient conditions (prevailing and uncontrolled atmospheric and weather conditions in a place) and minor amounts are found in natural deposits.

Obsidian is a glassy volcanic rock. It is formed by highly siliceous lava, which is the result of sudden volcanic eruptions followed by rapid cooling. Obsidian may be considered as a mixture of alkali feldspar (soda feldspar which is known as albite) and silica. It has the composition of $\text{Na}_2\text{O}\cdot\text{Al}_2\text{O}_3\cdot 6\text{SiO}_2$, and if the composition would be $\text{Na}_2\text{O}\cdot\text{CaO}\cdot 6\text{SiO}_2$ which means that if alumina was replaced by lime, this would be the most favorable glass. But obsidian cannot be imitated by

glass manufacturer and the alkali feldspar glasses are not suitable for commercial purposes because of their enormous viscosity (Cann and Renfrew, 1964).

Pumice is foamed glass that is produced by gases being liberated from solution in the lava before and after rapid cooling.

Lechatelierite is a fused silica glass that is sometimes formed in deserts by lightning striking a large mass of quartz sand. It has also been discovered in association with meteorite craters (Newton and Davison, 1996).

2.5.1.2. Manufactured silica

Although silica in the vitreous state is a perfectly well-behaved glass, its value is limited as a usable substance because of its very high working temperatures. These temperatures are far too high to have been achieved regularly by the ancient glassmakers, and it was only by the discovery of the fluxing effect of the alkalis on these thermal properties that glassmaking became possible.

Glass made from silica itself possesses in the highest degree the necessary properties of freedom from devitrification and resistance to weathering due to attacks by water and by acids, and low coefficient of thermal expansion, and if it was not so difficult to melt it, to free it from bubbles and to work it, silica alone would be the most suitable material for most glasses. The melting point of silica is approximately 1713°C, and at its melting point it is so exceedingly viscous that special and expensive treatment is required to free it from bubbles to obtain a clear glass. The resulting cost of manufacture is prohibitive and other oxides must be added to lower the melting point and viscosity.

When an alkali oxide reacts with silica to form a glass, the silicon-oxygen network is broken up by the alkali ions; the connectivity of the structure is diminished due to the formation of non-bridging oxygen anions which must be associated with a nearby alkali ion to maintain local charge neutrality. This broken connectivity results in a significant decrease in softening temperature. When an alkaline earth oxide, i.e. calcium oxide, CaO is added along with the alkali, the

greater field strength of the divalent calcium ion (Ca^{2+}) strengthens the bond to neighboring oxygens, thus increases the stability of the network.

Figure 4 shows two-dimensional structure of soda-lime-silica glass. Black dots within shaded triangles represent silicon ions. Each is surrounded by three oxygen ions, which can be of two kinds (bridging and non-bridging). Here, as in Figure 3a and b, oxygen atoms at four corners are replaced by oxygen triangles in the imaginary two-dimensional system. The bridging oxygen ions (shown by open circles) are shared between two triangles. Non-bridging oxygen ions (shown by circles with a central dot) belong to only one triangle; each of these bears a negative charge which is neutralized by a positive charge on one of the cross-hatched circles (cations of the fluxes).

All triangles, except four triangles making a small amount of crystalline material at A in Figure 4, form irregular chains enclosing relatively large spaces (and hence the density of glass is less than that of crystalline form). The network modifiers (the cross-hatched circles) are responsible for the spaces in the network. These ions, which bear one or more positively electrical charges, are held more or less loosely in these enlarged spaces by those electrical charges. The monovalent cations which are the alkali metal ions such as Sodium (Na^+) or Potassium (K^+), bring with them one extra oxygen ion when they are added to the glass as soda (sodium oxide, Na_2O) or potash (potassium oxide, K_2O). Because these cations bear only a single positive charge they can move from one space to another in the network. Thus, when an electric field is applied to the glass they carry the electric current, or when the glass is placed in water they can move right out of the glass into the water (being replaced by hydrogen ions, H^+ , from the water). The divalent alkaline earth ions, on the other hand, which bring one extra oxygen ion when they are added to the glass as lime (calcium oxide, CaO) or magnesia (magnesium oxide, MgO) have double electrical charge; and hardly do they move from one space to the next one, and thus, they play little or no part in carrying an electric current through the glass under ordinary conditions. Similarly, they neutralize the negative charges on two non-bridging oxygen ions and thus tend to form a new link in the network (Newton and Davison, 1996).

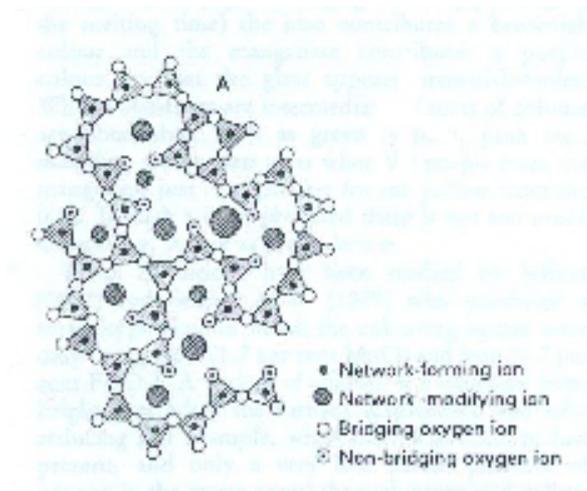


Figure 4 Two dimensional structure of soda-lime-silica glass (The monovalent cations are represented in Figure 3 by the smaller cross-hatched circles. The two larger cross-hatched circles are the divalent alkaline earth ions and they bear a double positive charge) (Newton and Davison, 1996)

Small amount of crystalline material seen at area A in Figure 4 where four triangles are joined together is the result of phase separation. In some glasses minute areas of $0.1 \mu\text{m}$ in diameter may occur due to inhomogeneous mixture of molten glass (Rawson, 1980). In some cases, when the glass cools down, a few components, mostly the polyvalent ions of magnesium, phosphorous, antimony, tin, and zinc, may crystallize and remain as separated phases in the continuous phase of glass. These separated areas might be more durable, or less durable than the rest parts of the glass. The relative amount of crystallites in a glass is important since this affects its appearance. When visible light falls on these regions, it is not transmitted, but scattered; and the glass may seem opaque, although it is transparent. The opacity of some ancient glasses derives from light scattered from internal crystals resulting either from incomplete melting or from crystals that grew in the glass as it cooled. Surface crystallization of glass can lead to serious problems in glass manufacture because of the resultant changes in glass properties such as viscosity and coefficient of thermal expansion. High stresses resulting from nonuniform contraction on cooling can cause fracture of the piece (Artioli *et al.*, 2008).

Sand is the commercial name of silica. Other commercial names are quartz and flint (Sinton, 2001). Sand which refers to natural accumulations of small particles separated from massive rocks by environmental effects is the main component of typical glasses. Sands can have a wide range of compositions depending on the local geology of their formation area and degree to which they are subjected to weathering and alteration (Henderson, 2000). Very mature sands are compositionally similar to quartzite pebbles which are very pure form of silica. The analyses of some Egyptian quartzite pebbles showed that they contain 19 ppm Ba (barium), 5 ppm Sr (strontium), and 6 ppm Ce (cerium) with no other elements above the detection limits (Turner, 1956; Wely 1992; Lilyquist and Brill 1993).

However, sands generally contain impurities: feldspars account for some of the alumina, calcium, sodium, or potassium in the final glass (Henderson, 2000); titanite ($\text{CaO}\cdot\text{TiO}_2\cdot\text{SiO}_2$) introduces impurities of titanium oxide and chromium oxide; chromite ($\text{FeO}\cdot\text{Cr}_2\text{O}_3$) introduces iron; and epidote ($\text{Ca}_2(\text{Al,Fe})_3(\text{SiO}_4)_3\text{OH}$) introduces alumina and iron (Goerk, 1977; Highley, 1977). Low levels of trace elements, in general, are a reflection of the use of mineralogically mature sand which was rich in quartz and poor in heavy minerals and clay minerals which are likely to host the rare earth elements (Freestone, 2002). The low contents of Al_2O_3 and CaO are indicative of the use of a pure sand rich in quartz and relatively poor in feldspars, calcite, and heavy minerals, as also shown by the low contents of Fe_2O_3 and trace elements (Freestone, 2002). Aluminum and iron are generally positively correlated in most glassmaking sands due to the minerals present in the raw material (Shortland, 2000; Freestone *et al.*, 2003). The presence of variable concentrations of both of these elements, in some cases, may indicate the use of untreated (unprocessed) sands importing variable chemical compositions in the batch. The presence of insoluble elements such as Zr makes it likely that they might be brought in accidentally or deliberately with sand, clay, or rock-powder. High TiO_2 (titanium oxide) content is related to the refractory heavy mineral content of the sand. Ti, Cs, Sc, Sb, Ba, and Br are introduced into the glass mainly with the sand and to a lesser extent with the alkali. Al, Ti, V, Fe, Zr, Nb, La, Md, Ce, Yb are the elements that provide important

information about the probable sources of the raw materials (Shortland and Tite, 2000).

The levels of these elements in the final glass are important in the provenance analyses to determine the source of sand, or in other words, to find out the probable place from where the sand came. In 1994, I. Freestone analyzed some Egyptian glasses and detected high levels of iron, manganese, and titanium. Many types of glass produced in Egypt between the fourth and the sixth centuries A.D. have been found to have high percentages of iron, manganese, and titanium with their distinctive olive-green colors, and hence, have been called “High Iron-Manganese-Titanium” glasses, or shortly HIMT (Freestone *et al.*, 2005) in literature. Further analyses on the fifth century glasses found throughout the Western Europe have shown the same character. Chunks of raw HIMT glass were found in the cargo of a shipwreck discovered at a port near the French/Spanish border. Other chunks of HIMT glass were excavated at Marseille and Toulouse (Freestone *et al.*, 2005). Vessels made of HIMT glass have been found in Rome, Cyprus, United Kingdom, and Belgium (Aerts *et al.*, 2003). From the fourth century A.D. onwards, a change in silica source might have occurred in glass manufacturing because of some social and economical changes that have not been fully interpreted yet (Freestone *et al.*, 2005).

First information about the sand sources used for ancient glassmaking came from Pliny the elder, the pope in Italy, who lived in the first century A.D. In his book *Naturalis Historia*, he emphasized two locations as the sources of sand. One is the mouth of Belus River, a small waterway flowing between Haifa and Aere (Israel); the other is a shore deposit near the mouth of the Volturno (Volturnus) River in Italy (Silvetri *et al.*, 2006). However, analysis taken by Turner (1956) has shown that Volturno River sand is not suitable for glassmaking. It is also confirmed that the probability of finding sands in the Western provinces similar to the Belus River sand is very low (Mirti *et al.*, 2001). On the other hand, excavations carried out so far in the region have confirmed the data given by Pliny that Levantine coast where the Belus River flowed into the sea was an important source for sand.

The renowned sand from the Belus delta in the Bay of Haifa or similar coastal sands containing calcareous fragments were used for the production of Levantine I

glass (Freestone *et al.*, 2003). Levantine I types dating to between the 4th and the 7th centuries A.D. are typical of the early Byzantine glasses (the 6th and the 7th centuries A.D.) which were made with calcareous sand of the Palestinian coasts. This type of glass has high lime and alumina contents and negligible content of manganese ($\text{MnO} < 0.1 \%$). Levantine II types dating to the 6th and the early 8th centuries A.D. are distinct from Levantine I and European Roman glasses for their higher silica and lower lime and sodium concentrations which indicates a different sand source (Freestone *et al.*, 2003; Vandini *et al.*, 2006). The Levantine II category is associated with the large-scale glass manufacture installations at Bet Eli'ezer, near Hadera in Israel, which seems to have been active between the sixth and the early eight centuries (Freestone and Gorin-Rosen, 1999).

2.5.2. Fluxes

Flux is a solid substance that when added in minimal amounts to another solid it promotes melting of the other solid (Goffer, 2007). Fluxes in the glass are the alkalis. They are obtained by burning coastal and desert plants or from an evaporate (for mainly soda) or woods (for mainly potash). The ashes of plants or woods are added to the glass batch. Alkalis lower the melting temperature or softening temperature of silica to a minimum liquidus temperature. For historical glasses with a composition of 18-20 % Na_2O , 6-9 % CaO , and 68-70 % SiO_2 , the softening point was around 700°C; the softening temperature was 1000°C; and the working temperature was 1000-1100°C (Brill, 1970; Henderson, 1982, 1985).

Soda;

Soda means both the raw material used in manufacture, sodium carbonate (Na_2CO_3), which may be introduced either in the hydrated form of washing soda or dehydrated soda ash; and sodium oxide (Na_2O), which is left in the glass after the reaction of the sodium carbonate with the silica during melting. Depending on its location, the glassmaker's source of soda could be seaweed, or other marine plants from dried lake deposits, or the ashes of burned salt-marsh plants. The sodium-rich

plants of the genus *salicornia* have been assumed by many researchers as the source of alkali for prehistoric European glasses (Henderson, 1985).

There was also another source for soda for the Roman, Islamic, and European glasses up to the tenth century A.D. It was natron, a natural mixture of sodium bicarbonate, sodium carbonate, lesser amounts of common salt, and sodium sulfate, and some organic matter. It occurs in a few places in the world, such as dry lakebeds in desert regions; at Wadi-el-Natron in Egypt, and in the Beheira region of Lower Egypt, for example. According to the analyses done by Turner (1956), natron from Egypt has the composition of 22.4-75 % sodium carbonate, 5-32.4 % sodium bicarbonate (NaHCO_3), 2.2-26.8 sodium chloride (NaCl), and 2.3-29.9 % sodium sulfate (Na_2SO_4). Natron used to make glass should be pure and rich in sodium carbonate and relatively free of chlorides and sulfates (Shortland, 2004). Actually, there is confusion in the terminology of the minerals in archaeology; the mineral name, “natron” is used in general sense meaning all polyphase evaporate deposits rich in sodium carbonate (Brill, 1999; Shortland, 2004). Indeed natron from Egypt has no “natron” in it; recent analyses have shown that what is known as natron at Wadi-el-Natron is trona, the evaporate sesquicarbonate mineral ($\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$) which is not exploited in the region even on a small scale today because of geological changes occurred in the region over time (Shortland, 2004).

The earliest glasses were not produced mainly with natron. It must have been widely used for mummification (David, 2000). The widespread use of natron began with the Roman period. It was traded and transported to many other places in the ancient world. It was the most effective flux for silica (Nicholson, 1995; Nicholson and Henderson, 2000; Costaglibla *et al.*, 2000; Dal Bianco *et al.*, 2005) used for glass production from around 800 B.C. to around 900-1000 A.D. Due to its composition natron brings very small amounts of potassium, magnesium, and aluminum oxide (Vandini *et al.*, 2006), and hence in archaeology, a soda-lime-glass with low potash and magnesia ($\text{K}_2\text{O} < 1\%$; $\text{MgO} < 1\%$) is generally considered to have been made with natron from Egypt and is called “natron glass” in literature. However, low MgO and K_2O contents may also imply seaweed or seasalt as the source of alkali (Brill,

1988; Henderson, 1985; Sayre and Smith, 1974), but plant ash glasses, in most incidents, have correspondingly more sodium and aluminum concentrations than natron-based glasses. Natron glasses were the dominant types of glass in the Mediterranean and Europe from the middle of the first millennium B.C. through to the 9th century A.D. (Bimson and Freestone, 1983; Freestone *et al.*, 2003).

In soda-lime-silica glass soda decomposes at around 728°C and forms an eutectic with quartz which means that it makes the mixture melt more easily, giving rise to a liquid phase that covers and consumes the quartz crystals, thus ion diffusion is easier and the reaction is faster than in the case of solid diffusion (Pagès-Camagna and Colinart, 2003). Soda lowers the softening temperature from 1710°C to around 728°C for a composition of 73 % silica, 22 % soda, and 5 % lime. At such a low temperature a long time would be required to obtain a homogeneous glass because of the high viscosity of the melt (Morey, 1954). The softening (or melting) temperature for a soda-lime-silica glass containing 74 % silica, 19 % soda, and 7 % lime is 867°C which rises to 1060°C for a glass containing 65 % silica, 18 % soda, and 15 % lime (Henderson, 2000).

Potash,

In forest regions, soda was substituted by potash derived from wood-ash. Beech-wood was a favorite material; in some places it was replaced by oak-wood. It was mainly used as a glass modifier. It was generally introduced into the glass melt in the form of either pearl ash (the hydrated carbonate of potash ($K_2CO_3 \cdot 1\frac{1}{2}H_2O$)), composed of potassium carbonate (K_2CO_3), vegetable ash, one of the main constituents of potassium carbonate, or saltpeter, a mineral composed of potassium nitrate. Lead glasses contain much more potash. Potash glass has proved to be significantly less resistance to weathering than soda glass (Brill, 1970).

The positive correlation between magnesia and potash is indicative of that magnesium was introduced to the glass with potassium as an impurity in alkali source rather than with calcium (Henderson, 1985). MgO and K_2O contents below 1 % suggests that glasses could have been obtained by use of an evaporate mineral such as natron as the flux. Natron glasses contain 0.1-0.2 % of potash, magnesia, and

phosphorus in a phase of 10 % of soda (Brill, 1999). High contents of these two suggest resource of plant-ash. Plant-ash glasses contain significant amounts of potash and magnesia (Potash, being up to 1-2 %; magnesia, being up to 2-3 %; and phosphorus being up to 1 %) (Brill, 1999). Different magnesia (MgO) and phosphorus (P₂O₅) contents allow us to separate samples of glass, pointing the use of different kinds of plant-ash (Hall and Yablonsky, 1997).

If quartzite pebbles are used as the silica source, the remaining elements other than silica should come from the plant-ash. The ratios of some of these elements might indicate the type of the plant-ash used. The composition of plant ash depends on the environment in which the plant grows, and the way in which it is burned (Brill, 1970). If two different plant ashes were mixed together, it would be extremely difficult to identify the glass as a two-plant-ash rather than one-plant-ash glass. Nevertheless, mixed-alkali glasses are frequent, because; glassmakers know that a glass melt containing a mixture of two or more different alkali oxides has a lower viscosity value than the melt containing the same total concentration of a single alkali oxide, and thus, it does not require high processing temperature (Henderson, 2000).

2.5.3. Stabilizers

Since alkali-silica glass is readily dissolved by water, some other oxide must be added to make the glass chemically durable and permanent.

Lime;

Lime may be incorporated deliberately or accidentally with another component. The lime-bearing components in glass are limestone in calcareous earths; shell, comprising a mineral polymorph of CaCO₃ (i.e., aragonite and/or calcite); or plant-ash which is usually lime-rich (Brill, 1970; Freestone *et al.*, 2003). If quartz pebbles were used as the silica source, then lime, if accidentally incorporated, must come from the plant-ash (Shortland and Eremin, 2006). If natron was the sole alkali source then the lime in the glass which would otherwise be derived from plant-ash, is

likely to have been derived from use of calcareous (limestone-bearing) sand; from crushed limestone; or from crushed marine shell (Freestone *et al.*, 2003).

The use of quartz sand can introduce significant amounts of other elements, in particular alumina. Typical sand from the Near East and Egypt contains some 2.18 % of lime and 1.4 % of alumina (Turner, 1956; Brill 1999). These concentrations are consistent with those observed for glasses assumed to have been produced in the region during the Roman and Byzantine periods (Sayre and Smith, 1961; Freestone *et al.*, 2000). Lime and alumina reflect the impurities (calcite, feldspar, and clay minerals) present in the sand. Their levels are particularly diagnostic of the sand source, in other words, aluminum and calcium contents are highly correlated and allow us to infer that some calcium entered the batch with sand (Freestone *et al.*, 2000).

Ancient glassmakers might have not known the usage of calcium as a separate batch material. Pliny the elder was the only one who made reference to shells which can be seen as fragments in the sand (Brill, 1970; Henderson, 1985). Shells (aragonite with calcite) in sand are potential sources for calcium. The content of strontium, which shows similar geochemical behavior to calcium (Wedepohl and Baumann, 2000), may indicate whether lime was added as shell (aragonite \pm calcite, high strontium) or limestone (calcite only, low strontium). Calcium substitution by strontium ions are easier in the structure of aragonite rather than calcite since the former characterizes the presence of calcium carbonate in marine shells; a higher strontium content should generally be featured by glass obtained using coastal sand rather than inland sand (Wedepohl and Baumann, 2000; Freestone *et al.*, 2003). The strontium content between 300 and 600 ppm are consistent with the use of coastal sand for low-magnesia samples since contents above 300 ppm would rule out the use of limestone-bearing sand together with an evaporate flux (Mirti *et al.*, 2001; Freestone *et al.*, 2003). In the case of high-magnesia samples, however, one could not exclude mixing inland sand with plant-ash depending on the Sr content of the latter. The majority of glasses in the second and the third centuries were produced using high-purity sands such as these with high levels of strontium which are beach sands, typically Mediterranean coastal sands (Mirti *et al.*, 1993). Contamination by

wood-ash in firing or melting might significantly increase the Sr concentration of natron-based glass (Henderson, 1995).

Magnesia;

MgO is usually present only as the result of corrosion of the clay container in which the glass is melted, but small amounts of magnesia have a favorable effect in lowering the liquidus (melting) temperature. It can be introduced by the use of dolomitic limestone. If there is a unity in the ratio of calcium and magnesium, in other words if there is a positive correlation between calcium and magnesium, a single ingredient, dolomitic sandstone, containing both stabilizers must be considered as the source of calcium (Matson, 1940; Marchesi *et al.*, 2005).

Lime and magnesia usually make up about 10 wt %, that is, similar to, or slightly higher than their concentrations in modern glasses; magnesia usually occurs below the range 2-5 wt %. Magnesia is used in glass in the absence of burnt lime formed by the complete calcinations of limestone in lime kilns.

2.5.4. Intermediates

Alumina;

Alumina (Al_2O_3) in small quantity is a frequent constituent of glass. It gives greater chemical durability, lower coefficient of expansion, and greater freedom from devitrification. Too much alumina, however, increases the viscosity of glass, making it difficult to melt and work. It was widely used in ancient glassmaking. It was probably not added deliberately in the pot. It was, however, often introduced as an impurity together with the other raw materials; usually it occurs in low concentrations, below the range 1-5 wt %. Feldspar is the most important source of alumina (Goffer, 2007). It is represented by the formula $\text{R}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$. R_2O is Na_2O in albite, or K_2O in orthoclase. The variability of SiO_2 and Al_2O_3 in glass indicates that each component was introduced separately (Basso *et al.*, 2007).

Phosphorus;

Phosphorus (P_2O_5) is present in bone-ash and is often inevitably present in glass accompanied by calcium and small amounts of magnesium. Negative correlation of calcium/phosphorus indicates that phosphorus in the glass is not introduced by bone-ash. The positive correlation between phosphorus and the alkalis indicates that phosphorus comes from plant ash (Marchesi *et al.*, 2005). It can appear in a special and in some way, intractable form, as apatite in certain types of sand. Apatite crystals are insoluble even in the melt at high temperatures, and cause opacity.

The presence of Al_2O_3 or P_2O_5 in the glass brings about a dramatic increase in durability, and it seems that these polyvalent ions have the power to immobilize the alkali ions so that they are no longer free to move through the silicate network. Zinc, titanium, and zirconium improve the durability, although zinc in addition to aluminum and phosphorus is likely to be present in appreciable amounts in ancient glasses.

Lead;

PbO (lead oxide) is especially useful in dissolving any refractory or other impurity particles which might otherwise result in flaws in the final glass. It reduces the softening point even more than lime. If CaO is replaced by PbO , lead glass is obtained. Low-lead soda-lime-silica compositions contain up to 8 % CaO ; and lead glasses usually contain 2-5 % Ca or less. It is generally introduced to the melt either as the mineral litharge which is a yellow polymorph of lead oxide produced as a by-product of cupellation or as one of the natural salts of lead such as white lead (composed of lead carbonate, $2PbCO_3 \cdot Pb(OH)_2$) and galena (composed of lead sulfide, PbS). Lead oxide (PbO) content in the glass may seem too much if it is calculated by weight. But lead is a very heavy element and when it is calculated on a molar basis, it can be seen that it, indeed, acts as a modifier in glass composition, and therefore lead glasses should be regarded as silicate glasses (Biek and Bayley, 1979). Lead-alkali-silicates or lead glasses are used for their high refractive index and

greater density as lamp envelopes, seals, flint optical glass, and crystal glass for art and tableware.

In cuneiform glass recipes which belong to 2nd millennium BC. lead was mentioned as one of the ingredients. The very first utilization of lead in silicate structures were lead-based glazes described with copper in Babylonian texts which belong to the second millennium B.C. (Oppenheim, 1973). Some contemporary examples of lead glaze were recorded at Alalakh (Antakya), Turkey, which is located in the area between Southeast Anatolia and Mesopotamia. Lead-containing glassy materials were known in Mesopotamia and Egypt, but it might have been added unintentionally until the Roman period (Vendrell *et al.*, 2000). Analysis of a red cake from Nimrud (Iraq) has shown the presence of 13.5 % Cu₂O and 22.8 % PbO (Turner, 1956). Sealing wax red glasses of 200-100 B.C. excavated at Tell el-Amarna (Egypt) have shown remarkable amounts of lead oxide. Lead antimonite (Pb₂Sb₂O₇) has been detected in yellow-green colored opaque Roman glasses which are rich in lead (33 wt % PbO) and poor in antimony (less than 4 wt % Sb₂O₃) (Mass *et al.*, 1998). It is suggested that such glasses were made from an antimony source different from the one used for making calcium antimonite opaque glasses. Lead antimonite glasses contain the impurities of litharge (PbO). Antimony in the smelted argentiferous galena is partially lost as fume and partially oxidized along with lead during cupellation process. Argentiferous galenas have high silver contents positively correlated with antimony contents and there is also a correlation between antimony and lead (Pernicka *et al.*, 1982). Opaque lead-rich glasses were also used as enamels because it was easier to soften them without distorting the substrate to be enameled (Bimson and Freestone, 1983). In the late 17th century A.D. lead crystal (flint glass) was invented. Flint glass was used for optical glasses which possess a higher refractive index and greater dispersive power than antecedent crown glass which had lime instead of lead. Lead oxide and borax which had been unknown as constituents and antimony as a fining agent were first seen in an ancient record on glass manufacture in the 17th century (Morey, 1954). The components of some types of glasses are briefly represented in Table 2.

Table 2 Some components used to make different types of glass (Brill, 1962)

Components	Modern Soda-Lime-Silica %	Typical Roman %	Typical Baking of Laboratory %	Optical High Lead %
SiO ₂	73.6	67.0	80.5	35.0
Na ₂ O	16.0	18.0	3.8	-
K ₂ O	0.60	1.0	0.4	7.2
CaO	5.2	8.0	-	-
MgO	3.6	1.0	-	-
Al ₂ O ₃	1.0	2.5	2.2	-
Fe ₂ O ₃	-	0.5	-	-
Sb ₂ O ₅	-	1.5	-	-
MnO ₂	-	0.5	-	-
B ₂ O ₃	-	-	12.9	-
PbO	-	0.01	-	-

2.5.5. Fining and Opacifying Agents

Fining means the removal of bubbles which is one of the hardest tasks in glass manufacture. Bubbles are caused by gases of particularly carbon dioxide and water vapor trapped in the early stages of melting or released during melting. Grain size of batch components and cullet as well could be effective on bubble formation. When the glass batch is composed of fine particles, escape of gases is inhibited since the channels between the particles are reduced in size (Artioli *et al.*, 2008). The presence of gas bubbles or foreign particles within the interior of the glass could lead to devitrification in the surrounding regions (McMillan, 1964). In order to get rid of bubbles, waiting for them to float to the surface and adding small quantities of extra compounds are essential. Arsenic and antimony are the most effective constituents that help the escape of bubbles. Potassium and sodium nitrates, and fluorides such as CaF₂, NaF, and Na₃AlF₆, and a number of sulfates can also act as the fining agents in glass. These materials are usually present in very small quantities (< 1 wt %).

Antimony (Sb) can be an opacifying agent as well. Especially in Mesopotamia, antimony oxide was added to molten glass as the mineral of stibnite (composed of antimony sulfide, Sb₂S₃) (Goffer, 2007). Stibnite reacts with other components of the melt to form metal antimonates. For example, calcium forms

colorless calcium antimoniate ($\text{Ca}_2\text{Sb}_2\text{O}_7$), which crystallizes on cooling and produces white opaque glass; if antimony reacts with lead, yellow lead antimoniate ($\text{Pb}_2\text{Sb}_2\text{O}_7$) is formed, and it produces yellow opaque glass. Antimony-based opacifiers (lead antimonite yellow and calcium antimonite white) were used from the beginning of glass production in the Near East and Egypt around 1500 B.C. through into the Roman period (Ubaldi and Verità, 2003; Fiori and Vandini, 2004). Antimony is most probably the relict of calcium antimonite which was commonly used as an opacifier until the late first millennium A.D. (Wolf *et al.*, 2005). Antimony was replaced by tin in Europe between the 2nd and the 4th centuries.

Tin-based opacifiers (lead stannate yellow and tin oxide white) were first used in glass production for a short period in Europe from the second to the first centuries B.C. and then again throughout the Roman and Byzantine Empires from the fourth century A.D. onwards. Tin oxide also was used in the production of Islamic opaque glazes from the ninth century A.D. and subsequently in enamels applied to Islamic and Venetian glasses from the 12th century A.D. onwards (Henderson *et al.*, 2004).

Colored opaque glasses are among the earliest glasses in the archaeological record (Newton and Davison, 1996). These materials have been found in the third and the fourth millennia B.C. contexts but they do not occur in significant quantities until the middle of the second millennium B.C. The white and blue glasses were predominantly opacified with white calcium antimonite crystallites ($\text{Ca}_2\text{Sb}_2\text{O}_7$ and CaSb_2O_6). The yellow and green glasses were predominantly opacified with yellow lead antimonite crystallites. A source of Cu^{2+} ions was added to the white and yellow glasses to create opaque blue and green glasses respectively. Red opaque glasses were colored and opacified with metallic copper particles or with cuprite (Cu_2O) or red copper (II) oxide (Shortland, 2002).

2.5.6. Coloring Agents

The color of glass is generally due to the presence of trace amounts of transition metal oxides. Most of the color in glass is produced by metal ions, or metal

atoms derived from minerals, usually in relatively very small amounts within glass composition. The coloring effects of the metal oxides are produced because they dissolve in the glass and, in fact; the colors are similar to those produced when soluble compounds of these metals are dissolved in water (Goffer, 2007). Table 3 represents some colorants used in soda-lime-silica glass.

Table 3 Some coloring metal ions (Goffer, 2007)

Glass Color	Coloring Metal		Glass furnace environment
	Metal	Ionic form	
Black	Manganese	Mn ²⁺	Reducing
	Copper	Cu ⁺	Reducing
Red	Copper	Cu ⁺	Reducing
	Gold	-	Reducing
Pink	Manganese	Mn ⁴⁺	Oxidizing
Yellow	Uranium	U ⁴⁺	Oxidizing
	Silver	-	Reducing
Green	Copper	Cu ²⁺	Oxidizing
	Iron	Fe ²⁺	Reducing
	Chromium	Cr ³⁺	Oxidizing
Blue	Copper	Cu ²⁺	Oxidizing
	Cobalt	Co ²⁺	Reducing
Violet	Manganese	Mn ³⁺	Reducing

The color produced by a metal ion depends not only on its oxidation or reduction state, but also on the position it occupies in the glass structure (Pollard and Heron, 1996). The position of substituting ions distributed in possible sites in the glass network can affect the color achieved. The color achieved when a metallic ion acts as modifier is different from the color when the same ion acts as network former. The oxygen coordination with metal ions may change from four to six (from tetrahedral to octahedral) in the network; and this affects the color of glass. The nature of other metallic ions present also must be considered. The color obtained by an ion with soda may be different from the color by the same ion in the same glass with potash, if potash is replaced by soda and acts as the only alkali in the composition (Weyl, 1992).

All the colors desired can be obtained by controlling the furnace conditions without any explicit addition of colorants. The production of colors in glass depends not only upon the inclusion of a specific metal oxide, but also upon the presence of other oxides in the batch, the temperature, and the state of oxidation (combining with oxygen to form an oxide) or reduction (losing oxygen) in the kiln, and the nature of the coordination sphere around the coloring ion (Bamford, 1977). For example, the same copper ion (Cu^{2+}) in the same oxidation level but in two different environments produces both the blue and the turquoise colors. In Egyptian blue, the divalent Cu ions are in square-planar environment (fourfold coordination with oxygen atoms) inside the cuprorivaite ($\text{CaCuSi}_4\text{O}_{10}$) which results in the characteristic blue hue. In contrast, in the Egyptian green, the copper ions in the octahedral environment (sixfold coordination with oxygen atoms) of a silica-rich glass result in a turquoise color which is affected when the temperature and CuO concentration increase, but not related to the flux concentration (Pagès-Camagna and Colinart, 2003). The Egyptian blue and the Egyptian green were two pigments discovered by Egyptians and used only by Egyptians in the third millennium B.C.

Other coloring effects can be produced when a metal does not dissolve, but when it is dispersed as minute particles. The coloring depends on the size of the colloidal dispersion. Colloidal particles are suspended in the glass. The effect is caused by the scattering of the light and the resulting color is determined by the size and concentration of these particles. Dispersed metal colors are conveniently silver stain yellow, and gold or copper rubies (Shand, 1958).

The coloring elements could either occur as impurities in the raw materials. The formation of aggregates or particles of colloidal or microcrystalline dimensions occurs under special conditions during the melt, causing varying colors and shades. The deliberate use of small quantities of coloring, clarifying, and opacifying elements clearly indicates that prehistoric glassmakers understood their materials and were able to control the amount of the effective coloring elements added. They probably used small quantities of colorant containing frit or cullet, and added it to a colorless or weakly-tinted glass so that the coloring effect could be controlled by diluting the additive (Weyl, 1992).

Iron;

If pure silica, and soda (or potash), and lime are heated together, heating yields a colorless glass. However, the raw materials never exist in pure forms, i.e. sand always contain varying amounts of iron particles. Iron oxide, the almost universal coloring agent of practically all ancient and modern ordinary glass, produces a characteristic, usually unintentional, greenish color. The greenish tint can be easily seen, even in so-called uncolored glass when it is viewed edgewise.

Iron can produce varying colors ranging from pale blue, brown, to yellowish-green and dark olive depending on the furnace conditions (Weyl, 1992).

The iron impurities occur in glass as ferrous (Fe^{2+}) and ferric (Fe^{3+}) ions; the ferrous oxide imparts to the glass paler blues and greens in a fully reduced stage, while ferric oxide make it darker yellow or brown when fully oxidized. The reason for this indeed is the position of iron ions in the network. Ferric iron is likely to occupy the tetrahedral site of silicon whereas ferrous iron is likely to occupy the octahedral site emptied by sodium. The combined effect of the two is the bottle green of ordinary glass (Pollard and Heron, 1996).

Manganese;

Manganese dioxide (MnO_2) is mainly used in the production of purple glass resembling the color of potassium permanganate (KMnO_4) crystals. The purple color is achieved by the trivalent manganese (Mn^{3+}) however in its divalent state (Mn^{2+}) it only imparts a weak yellow or brown color which are responsible for the green and orange fluorescence of glass. The addition of manganese will oxidize the iron to the yellow ferric state, and if there is very slight excess of manganese the pale purple color which develops will tend to neutralize the yellow to produce grey. Manganese ions, which impart a deep violet color to the glass, optically mask the green imparted by the iron, modifying it to a less noticeable grey. Iron and manganese are present in uncolored glasses at approximately the same concentrations ranging from 0.5 % to 1.0 % suggesting a deliberate attempt to decolorize the glass. Manganese has its decolorizing effect only on the iron and not on the other coloring oxides in glass. There are also other oxidizing agents, such as the pentoxides of arsenic (As_2O_5) and

antimony (Sb_2O_5) which have an analogous effect on the iron, except that they do not neutralize the yellow color. Arsenic oxide which is a by-product of copper metallurgy acts as an oxidizing agent toward ferrous oxide.

During melting, iron and manganese atoms may lose (oxidation) or gain (reduction) electrons reversibly. Iron and manganese can mutually reduce and oxidize each other as in the equation below, corresponding to the furnace conditions, and the range of possible colors becomes enormous.



When the conditions during melting are fully reducing, iron contributes blue color, and manganese contributes none; whereas, iron makes a brownish color, and manganese makes purple when the conditions are fully oxidizing because of the addition of oxidizing agents, and the prolonged time of melting. When conditions are intermediate, the color may be green, yellow, or pink (Newton and Davison, 1996).

If concentrations of MnO and Fe_2O_3 are below 1 %, intentional addition cannot be considered; rather, sand or flux should be considered as the sources for these elements (Mirti *et al.*, 2001).

When the main alkali is potash, manganese produces a color of bluish violet; when the alkali is soda, manganese makes a reddish-violet color.

Sulfur;

Plant ashes and shells contain large amounts of sulfate (SO_4). When plant ash is used as the source of mostly sodium or potassium flux, or sand containing shell fragments is used for glassmaking, sulfur is introduced to the glass unintentionally and it is contaminated during melting (Brill, 1970). Under strong reducing conditions, some of the sulfate is reduced along with iron. The sulfide ion combines with some of the remaining trivalent iron (Fe^{3+}) to form a color which is also affected by divalent iron (Fe^{2+}). It may give green or amber color to the glass. If amber colored glass has low potassium, magnesium, manganese, and phosphorus, the possibility of the use of sodium-rich plant ash is excluded considering that the glass

has not been refined before inclusion to the melt. In such case sulfur might be derived from sand. Amber color can also be obtained by adding a strong reducing agent such as powdered charcoal.

Cobalt;

Cobalt as a colorant agent was first used in Egypt during the Eighteenth Dynasty (1550-1292 B.C.) (Shortland and Tite, 2000). Cobalt oxide is such a strong coloring oxide that very little amount (< 1 wt. %) is enough to produce a blue glass and only 0.025 wt. % will produce a light blue color. On the other hand it requires some 2-3 wt. % of the fully oxidized copper for a good copper-blue or copper-green color; whereas 0.5 to 1 wt. % of the fully oxidized iron can give a good iron-blue color. Where cobalt is absent, copper of 1 wt. % or less produces a paler blue even in 2-5 wt. % lead enamel, whilst 2 wt. % or more of copper makes a green material, at least when this also contains larger amounts of lead (4-35 wt. %) (Biek and Bayley, 1979).

Cobalt is found in ancient rock mineralizations in association with other minerals. By looking at the correlation between the cobalt, copper, iron, manganese, and zinc contents, the type of cobalt minerals used to color the glass can be determined (Garner, 1956; Henderson, 1985, 2000). Arsenical cobalt ores such as cobaltite or erganite are exceedingly low in manganese and usually contain significant traces of copper, iron, and zinc (Hall and Yablonsky, 1997). Cobalt was present in the majority of the Eighteenth Dynasty Egyptian blue glasses (Farnsworth and Ritchie, 1938). The sources of cobalt were cobalt-bearing alum minerals from the western oases of Egypt. Mycenaean blue glasses of around the same date show very similar characteristics, suggesting that Bronze Age Greece obtained its cobalt pigment, or perhaps its raw glass from Egypt (Freestone, 1991).

Significant cobalt (≥ 0.05 % CoO) content in glass which always contain elevated levels of alumina, manganese, nickel, and zinc is indicative that cobalt source is cobaltiferous alum (Shortland and Eremin, 2006). Other cobalt sources are cobaltite (CoAsS) containing cobalt in association with sulfur and arsenic and

sometimes a trace of zinc, and skutterudite ((Co, Ni, Fe)As₃) containing cobalt in association with nickel, iron, and arsenic (Henderson, 2000).

The ores of Cu and Co are commonly found associated with other metals which are often incorporated presumably accidentally into the vitreous materials. Copper is present in glasses with relatively low cobalt levels (0.05-0.19 % CoO) but absent from those with high levels (0.19-0.28 % CoO) (Shortland and Eremin, 2006). Either copper metal or ore was added to the cobalt-colored glass, perhaps to deepen the color, or cobalt-colored and copper-colored glasses are mixed. Copper commonly occurs at about 0.1 mol % levels in ancient glasses colored blue by the addition of cobalt and may, for example, have been deliberately added to enhance or dilute the effect introduced by this element or may have been present as an impurity in the cobalt ore (Cox and Gilles, 1986). Inclusions of metal-rich type which is presented by metal-containing phases derived from crystallization and reaction processes involving the chromophore elements, are usually found in the Cu-colored glasses that frequently in the blue and red glasses. The composition of the inclusions is often close to Cu, CuO, Cu₂O, and SnO₂. The Co-colored blue glasses do not generally show metal inclusions, though sometimes they contain unmixed droplets of metals, metal sulfides, or even arsenites.

Copper;

Copper is a very powerful and also a versatile coloring agent when used in coloring glass and its use can be marked back many years. The famous “Egyptian Blue” color of faience, which was so popular during the time of the Roman Empire, was made by heating the raw materials with some basic copper carbonates. It has been found that this blue color, due to oxidized copper in the crystalline copper calcium silicate (CuCaSi₄O₁₀) dispersed through a matrix of soda-lime-silica glass and developed at temperatures above 850°C (Pagès-Camagna and Colinart, 2003). The intensity of the color may vary depending on the Cu/Ca ratio.

Copper greens and blues are not difficult to produce, although the behavior of copper in a silicate melt can be complicated. Copper was used most profusely to produce green glass. Minor quantities of Cu²⁺ may be responsible for the green color

of glass together with iron, lead, and manganese (Henderson *et al.*, 2004). Brass alloys can be another alternative (Heck and Hoffmann, 2000). The art of using copper for ruby glass goes far back to ancient times but using copper oxide (CuO) to make ruby glass could be very difficult (Biek and Bailey, 1979). Ruby glasses were mainly produced by gold particles dissolved in the glass as an ion (Henderson, 2000).

The addition of highly oxidized copper, in the form of cupric ions (Cu²⁺), makes the glass appear bright blue, whereas mildly oxidized copper, in the form of cuprous ions (Cu⁺), colors it red. Traces of furnaces and cakes of sealing wax red glass were discovered at Nimrud (Iraq). The cakes had fragments of charcoal on them which is the evidence of reducing conditions (Mallowan, 1954).

Ancient red glass was generally made by using copper in a reducing furnace atmosphere. This resulted in a brilliant red opaque glass. A fine red glass from copper was made in Egypt from the time of the Eighteenth Dynasty (1550 – 1292 B.C.) (Henderson, 1985). Oxidized and corroded bronze scrap could be included in the molten glass to introduce copper as a colorant. Tin content of Cu-colored glass may suggest whether bronze was added or not (Sayre and Smith, 1974). If bronze was used as the source of copper then the glass has a high concentration of tin. Copper and tin ratio of about 1 to 10 indicates the use of bronze or bronze scrap (Turner, 1956; Kaczmarczyk and Hedges, 1983; Shortland, 2000). There were two kind of Mesopotamian glass. The one is the green and yellow opaque containing yellow lead antimonite (Pb₂Sb₂O₇). The other is the copper containing sealing wax red glass used in a special manner. It needs suitable reducing conditions; otherwise the Cu₂O will be oxidized to give a transparent blue glass (Brill, 1970).

Cullet or scrap glass having almost the same contaminants of the batch to be melted, is added to basic ingredients to reduce the viscosity, and thus to allow air bubbles to escape. The function of cullet is physical; it acts as a nucleus around which the new glass formed, and helps to eliminate unevenness (Freestone, 2002). For ancient glasses glass melt may not be well-defined if the cullet had been collected by itinerant glass-traders from a wide geographical area. On the other hand, a long continued reuse of cullet in one area could perpetuate a chemical characteristic of the glass long after one of the raw materials had ceased to be available (Baxter *et*

al., 2005). If the cullet is added, it is the first to soften and melt at a temperature lower than most of the other mixture ingredients; it provides a fluid through which the still solid grains of the other ingredients move around, mix with each other, and, as the temperature steadily increased, gradually melt.

2.6. Decay of Glass

Over time the composition of glass can deteriorate due to compositional and environmental factors. Archaeological glasses are all soda-lime-silica type and the ratios of silica, alkalis, and alkaline earth elements within the bulk glass affect the durability of glass artifact. In particular, buried glass usually exhibits pitting, dulling, strain cracking, frosting, and iridescence, milky, or enamel-like opaque and semi-opaque crusts of laminated structure (Griffiths and Feuerbach, 2001).

The high percentage of silica may prevent extraction in large amounts in case of exposure to weathering conditions. High alkali content, and hence the amount of highly mobile ions in unstable glass may cause crazes, flakes, cracks, and pits on the surface, if the glass interacts with aqueous solutions, or with water vapor. In such environment, ion exchange occurs between the mobile ions and the adsorbed water molecules. Inwardly diffused water molecules react with non-bridging oxygen atoms to produce hydroxyl ions which migrate out with the alkali cations. This is called alkali extraction (Newton and Davison, 1996). If the humidity surrounding the glass surface is somehow reduced, this leached layer bonded to the unaltered glass substrate, will be dehydrated and will cause the development of interface stresses. These stresses will then result in peeling of the layer from the substrate that is associated with volume shrinkage. Peeling causes craters in the surface; and these craters significantly degrade the transparency of the glass. Potash glasses that contain relatively more potassium oxide are more susceptible to aqueous attack than soda glasses of the same molar composition; potassium ions being larger, the center of positive charge being further away, and the corresponding non-bridging oxygens, thus being more polarizable than their sodium silicate counterparts (Weyl, 1992). If both soda and potash are present in a glass in proper ratios, the alkali mobility is

reduced, and hence, glass becomes more durable. This is known as “mixed alkali effect” (Doménech-Carbó *et al.*, 2006). Alumina and phosphorus are also very efficient to immobilize the alkali ions.

Calcium content affects the properties of glass such as viscosity and coefficient of thermal expansion. If too little lime is added, glass may have poor chemical durability. On the other hand, too much lime results in a glass hard to melt and with a tendency toward devitrification. If the calcium is leached out along with sodium, remaining silica may not be enough to maintain the bonds, so the glass may disintegrate. Lime content over 15 % by weight in the finished glass may lead to corrosion of glass (Brill, 1970).

As well as its chemical composition, thermal history and surface treatments are also intrinsic factors that influence degrading of glass. The temperature must be high during melting process of raw materials within glassmaking operations to provide a homogeneous melt in which no solid particles remain. If the melting process is incomplete, crystals may grow as the glass cools. Nonuniform contraction within the structure of glass may result in high stresses, and thus, may accelerate the deterioration of glass (Griffiths and Feuerbach, 2001). Microheterogeneities in the glass structure, such as those arising from phase separation during cooling of the glass melt or poor mixing of the components of a melt, are likely to influence the durability of glass. In the case of phase separation during cooling, one phase may be less durable than the corresponding homogeneous glass. The tendency of a glass melt to undergo phase separation during cooling is a function of composition and also depends on whether the rate of cooling is slow enough to allow time for phase separation to occur (Weyl and Marboe, 1962, 1967). If phase separation produces droplets much greater than 180 nm in diameter and the refractive indices of the two phases are significantly different, the glass will be cloudy or white like milk due to the scattering of light by the droplets of one phase suspended in another (Griffiths and Feuerbach, 2001). In surface crystallization impurities are the most important source of nucleation. Various transition metal ions such as iron, zinc, and vanadium at concentrations of a few per cent were found to increase crystallization rate whereas chromium ions decreases the rate of crystal growth (Artioli *et al.*, 2008).

If thin layers crack off the surface but remain in place, iridescence may be observed due to the constructive interference of light of certain wavelengths reflected from successive glass-air interfaces. Drying corroded glass reveals existing cracks because light is reflected from the air-glass interface to a far greater extent than from the previous water-glass interface. Drying cracks from shrinkage is associated with dehydration of a hydrated glass layer.

Crizzling and weeping are generally observed in glass with less than 5 mole % alkaline earth metal oxide, this being too low to stabilize the amount of alkali present (Brill, 1970). In such glasses a very thick hydrated layer forms which may crack into a crazy paving pattern (crizzle) in any case and may crack if stored at low ambient relative humidity. Where low alkaline earth glasses have a high potash content, potassium salts deposited on the glass surface as a result of ion exchange with water absorbed on the surface may deliquesce if the ambient relative humidity becomes too high (weeping).

Blackening is quite commonly found on the surface of glass particularly excavated glass and it may exhibit a dendritic invasion into the interior perhaps along microcracks. The staining might be due to lead sulfide, ferric ions, or manganese dioxide. Blackening may be the result of bacteria that use Mn in their metabolic processes and thereby concentrate it on and in the glass.

Pitting is another feature. The pits may contain crystalline deposits or be empty. Under the microscope, pits can often be seen to be comprised of concentric hemispheres of glass originating from a point on the surface, sometimes with those hemispheres nearest to the surface having disintegrated into a crystalline mass (Griffiths and Feuerbach, 2001).

Crusts on the surface of glass may range from off-white to black depending perhaps on pollution and organic growths. Crusts are primarily composed of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) that occur on glass which has too much lime and too little silica; the calcium leaches out and forms salts.

Removal of corrosion layer to restore glass to its original appearance exposes glass that had been below the surface and leaves the object thinner and more fragile (Doménech-Carbó *et al.*, 2006). Corrosion must be considered evidence of the

object's archaeological history and must be retained if consolidation is not really urgent and necessary (Newton and Davison, 1996).

Glass from Egypt tends to be exceptionally well-preserved without the leaching of mobile elements often found in glass from elsewhere, especially Mesopotamia and Greece where wetter burial environments mean that well-preserved glass is rare (Shortland and Eremin, 2006).

2.7. Ancient Glassmaking

The knowledge of glassmaking was empirical. People learned to make glass objects by some trial and error processes. For a very long time glassmakers were ignorant of controlling redox conditions when working with multivalent elements, and the raw materials could be variable of quality. However, glassmakers were well aware of common techniques used in pottery work, and also in metallurgy. They observed that small changes in ingredients can result in marked changes in the final product. In time they developed the rich possibilities offered by the nature. Glassmakers also noticed that glass could be made through two processes, instead of one single stage. The first one was the fritting which was producing the raw glass. Fritting can be associated with the primitive glass producing accomplished at a primitive, lower-temperature oven; or it can be dealt with a more sophisticated industry of raw-glass, carried out at huge tank furnaces (Freestone *et al.*, 2002). The second stage was the melting of the glass batch in the furnace until a homogeneous mixture was achieved for shaping and then annealing operations. The fritting and the melting processes can take place at different centers. Therefore, glassmaking and glassworking are different crafts that require distinct technical specialization (Diamond, 1953). Glassmaking includes the fritting, or the raw-glass producing process; glass-working includes remelting of raw glass and all the shaping activities which result in the final object.

The first records of glass industry were found in Mesopotamia. They were cuneiform tablets. One of them is the tablet found at Tell U'mar near River Tigris, which mentions a recipe of glaze of the 17th century B.C. There are many Assyrian

tablets (the copies of previous ones belonging to the second millennium B.C.), which give information concerning the manufacture of glazes and colored glasses of the 7th century B.C. These copies have the earlier Sumerian and the later Akkadian words and phrases. It may be proposed that the glassmakers stuck to the same tested recipes and kept on producing glass with known recipes (Oppenheim, 1973). However, translation of these early texts should be held with much care; it should be considered that their interpretations may be wrong on the part of the author, the translator, and the reader (McCray and Kingery, 1998).

2.7.1. Fritting

Frit is used liberally to describe any siliceous substance which possesses a sand-stone-like structure, i.e. small, equal-sized mineral grains coagulated by a small amount of glassy binder. It was used both for the body of faience and colored substances (Tite, 1987). It is also used for raw glass that is primarily fused in a low-temperature oven. Temperatures of 700-800°C were efficient for fritting (Turner, 1956). The raw glass is then remelted in a secondary furnace with efficient heat (Freestone *et al.*, 2002).

In this stage, the raw materials consisting of sand, lime, and alkali, are selected and/or collected from available sources and are mixed together in an open hearth or a hole in the ground with or without a pot. Before the raw batch preparation, the alkali plants are burned in a shallow pot and left to cool overnight (Freestone *et al.*, 2002). Ancient glassmakers tested the quality of the alkali by tasting the ash. Sodium salts taste much sharper on the tongue than potassium (Smedley *et al.*, 1998). If quartz pebbles are used, they are broken and ground, and then mixed with the alkali. The hearth or the hole is surrounded by a layer of sand in order to protect glass materials from any soil contamination. Further protection can be given by a layer of fuel ash obtained from the preheating of the hearth. In fact, fritting is required a separate, lower-temperature oven. When a pot is used, it is placed in a furnace of bricks in a circular form with an opening in the center of its dome through which the combustion products ascended (Henderson, 2000). There

may be interaction between the molten part of the contents and the material of which the fritting pot is made. Due to this interaction, alterations in chemical and mineralogical composition can be seen (Henderson, 2000). There is no need to add the coloring oxides. Low temperature is sufficient enough for this initial fusion. Complete fusion to a clear and homogeneous glass is not necessary. A slow chemical reaction between the alkali (i.e., sodium carbonate) and sand occurs below 600°C long before melting occurs. The solid compounds remain in a powdered state below 700°C and only assume a sintered condition above 750°C (Turner, 1956). Quartz disappears above 950°C and is slowly replaced by cristobalite and tridymite and silica phase exists at about 1100°C (Pagès-Camagna and Colinart, 2003). The grinding of raw materials is an important part of batch preparation.

By fritting the raw materials, the solid state reaction has been initiated which produces a denser material less prone to dusting. Fritting includes the initiation of the chemical reactions between the raw materials, thus helping speed up the final melting of the glass, the removal of the excess carbon in the ash, as evolved carbon dioxide and other volatiles. After final regrinding, an improvement of the homogeneity of the final glass can be achieved. Unfritted raw ash circulating in the furnace is able to react with the furnace refractory. The interaction of the ash and furnace structure would produce liquid glass phases which would then be free to drip from the roof of the furnace down onto the unprotected surface of the melt located below, contaminating the molten glass (Smedley *et al.*, 1998).

The fritted blocks of glass can be exported to other places where the raw materials needed for glass production does not exist. These imported raw glass blocks are then broken and mixed with coloring materials such as metal oxides and cullet. Therefore, it is possible to prepare varying batches of glass of varying colors and shapes from the same frit block.

The evidence of raw glass trade has come to light in 1982 when a Mycenaean shipwreck was discovered at Uluburun, an isolated coast about 6 kilometers east of Kaş, Turkey. The find made in 1982 is a treasure ship that sank at the height of the Bronze Age. A Turkish sponge-diver had seen some unknown objects on the seabed at Uluburun (the coast about 5,5 km east of the Kaş Port). He described them as

looking like “metal biscuits with ears”. What the diver has reported as ears were the carrying handles at the corners of each copper ingot. The principal cargo had been 350 copper ingots, ten tones of them along with a nearly a ton of tin and ingots of blue, turquoise, and lavender glass. The ship was carrying a royal cargo, since it resembles cargoes sent from Near Eastern rulers of the Egyptian pharaohs mentioned in the tablets from the site of Tell el-Amarna (the capital of Phaorah Akhenaten from 1373 – 1362 B.C.). Objects of the ship have been traced a dozen different areas at the Eastern Mediterranean (Bass, 1986). Dark-blue glass nuggets, the color of beads of the Mycenaean period made by the casting technique, were found in a sunken vessel off the Kaş peninsula. One reason of the rapid spread throughout the Aegean region of the glass manufacture that had begun in the eastern Mediterranean was the ease of transport by sea (Figure 5). It would appear that the art of glass manufacture arriving from the sea found a very great potential in the settlements it reached and an environment favorable for its expansion, development, and in a sense, the growth of its competitive power. There are several pieces of evidence suggesting significant exchange of raw glass ingots between the Late Bronze Age nations of Egypt, Mesopotamia, and Greece. (Bass, 1986; 1989). The diverse and valuable items on board the vessel suggest that it was engaged in a state-sponsored trade mission. Furthermore, when the ship sank, it appears to have been headed west toward the Mycenaean states in the Aegean Sea (Bachhuber, 2006). Out of the finds recovered from the ship, approximately 175 glass ingots colored blue, turquoise, purple, and amber were identified. In particular, the blue ingots colored with cobalt were found to match the exact discoid shape of molds excavated from the glassmaking factories at Amarna, Egypt (Bass, 1986; 1989; Nicholson et al., 1997).

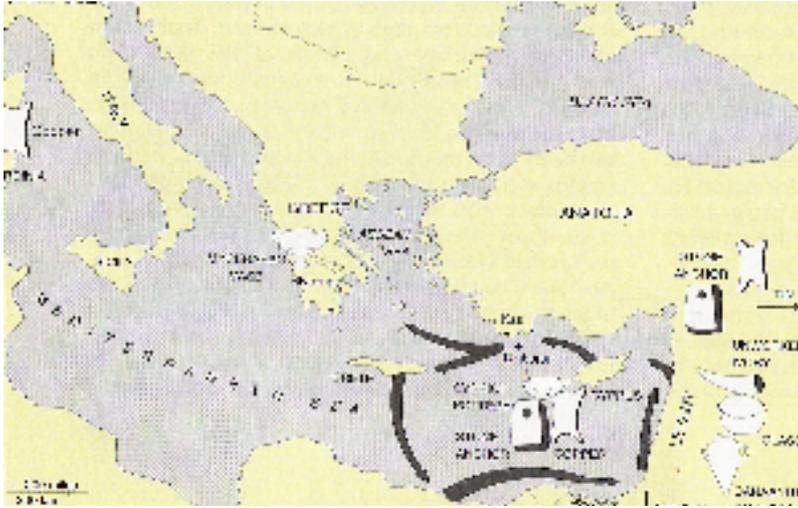


Figure 5 The map of the probable route of the ship found in Uluburun and likely sources of materials for the various artefacts found on the wreck (Renfrew-Bahn 1998)

Raw glasses based on Egyptian natron were produced at the primary installations settled mainly in the Levant and Syria-Palestinian coasts and were exported as chunks to remote areas where they were worked and shaped into varying finished objects at the secondary installations (Oppenheim, 1973). The Roman glasses, the early Medieval Mediterranean glasses and the Western European glasses from around 800 B.C. until the early Islamic period around 800 A.D. seem to have been based on traded natron from the East (Silvestri *et al.*, 2005).

2.7.2. Melting

Melting is the process where the fritted mixture is subjected to a high temperature to yield fully fused glass. Melt formation depends on temperature, specific batch components, grain size of batch components, and grain size and amount of cullet. Glass metal is the term used for the molten glass batch. The fritted blocks are broken and grinded up to get the batch powder. This powder is, then, gradually heated. Many ingredients, intentionally or accidentally, are added to the

batch as coloring, decolorizing, opacifying, or fining agents. For example, a lump of scrap copper is heated and the surface oxide is scraped off, and then added to the glass batch to provide color. Cu^{2+} is the first ion to diffuse into the liquid phase (Cable, 1991).

Grinding of components to a small size seems essential. Fine particles melt more rapidly than the larger ones. On the other hand, they may agglomerate to form porous particles which do not let the penetration of the viscous liquid. These particles may float on the surface of the melt because of their low bulk density (Stoch *et al.*, 1978). The crucial point is that the ingredients should be well-mixed for the homogeneity of the glass. Some of the devitrification in glass composition may be due to the contamination of the glass from the crucible walls during melting (Preston and Turner, 1940). Migration of sodium and calcium from the glass melt to the ceramic and of potassium, iron, and aluminum from the ceramic to the melt can occur during both the primary fritting and the melting processes. Open surface pores would promote infiltration of molten glass into the ceramic matrix or increase the surface area in contact with the glass and the resulting corrosion products (Preston and Turner, 1940).

Glassforming ability of the fritted batch is affected by time and temperature. In his text, *De Diversis Artibus* (Treatise on Divers Art, translated by J.G. Hawthorne and C. S. Smith in 1979), Theophilus, a metallurgist who lived in Germany in the 12th century (Smedley *et al.*, 1998) stated that twelve hours is needed to produce glass from the fritted raw materials. In order to investigate the accuracy of his statement, an experiment was carried out by a few scientists from University of Sheffield, UK. It was found that a very homogeneous glass could be produced only when the frit was melted at 1200°C for 24 hours (Smedley *et al.*, 1998).

A large number of components are quite volatile at elevated temperatures, in other words they are lost. These losses are particularly significant for alkali oxides, lead, boron, phosphorus, halides, and other components which have high vapor pressures at high temperatures. The loss of a component can be reduced by increasing the concentration of that component in the atmosphere in the melting furnace (Brey, 1995). Loss of volatile constituents from the glass surface during

melting could account for the composition difference and a further factor is that those constituents which lower the surface energy tend to be concentrated at the surface (Morey, 1954; McMillan, 1964).

2.7.3. Furnaces

The furnace is the essential piece of equipment for making good glass. For many hundreds of years glasses were melted in pot furnaces and the glass worked by hand. Both pot and the furnace often were made with the same refractory clay. Therefore the existence of clay deposits may be indicative of a glasshouse nearby (Nicholson and Jackson, 1997).

Ancient furnaces could only reach temperatures of about 1000-1100°C and as a result of this it was difficult to produce glass at one operation as it is in modern conditions (Brill, 1963). Making glass at low temperatures results in a viscous semi-glassy material full of air bubbles (seed) and unmelted batch materials which are called “stones” (Freestone *et al.*, 2002). True or common glass could not be manufactured until furnace technology developed to the extent where higher temperatures could be reached (Noble, 1969). The earliest vitreous materials produced in the Near East and in Egypt before 4000 B.C. were faience beads in imitation of colored semi-precious stones. For producing faience, a paste of ground quartz or sand was mixed with alkali and sintered in an open pot. The mixture was then covered with a blue or greenish copper glaze in a small furnace with low temperature after shaping (Henderson, 2000; Freestone *et al.*, 2002). These were opaque and crude beads as a result of low fusion temperature. Later, 2500 B.C. when furnaces were available to be maintained at temperatures high enough to soften glass, the same material was used in Egypt to make beads which were the first objects to be made entirely glass. Glass beads can be made by at least six methods: winding threads of glass around a rod; drawing from a gob of glass which has been worked into a hollow; folding glass around a core; pressing glass into a mold, perforating soft glass with a rod; and rarely blowing.

Allowing a furnace to cool down by more than 200-300°C could seriously damage the structure, thereby reducing its maximum operating temperature. The inevitably slow recovery of so large a thermal mass to maximum temperature could mean that several days of glassmaking might be lost. Inability to melt due to lack of sand or alkali for a few days would do much less long term harm than lack of wood to stoke the furnace. The Diderot Encyclopédie (1765) states that the furnace must be stoked with exact regularity, never putting in too much wood at each time, and it must be very well dried. All types of wood can be used. It is very important to keep the fuel wood dry enough to supply efficient heat (Tillman, 1978). If the furnace is charged with moist fuel, the temperature drops, even below the liquidus temperature of the melt, because; some of the heat is lost when it is used to get rid off gaseous combustion waste products including water and volatiles (Preston and Turner, 1940; Tillman, 1978). The fuel must be brought to the furnace in its original form but the wood used to provide alkali flux might often conveniently be burnt a considerable distance away. It must also be true that the wood best suited for heating the furnace may not be the same as that providing the best proportion of ash for alkali. Beech has been found to be the most suitable fuel. Poplar gives very light ashes which fall onto the melt and sticks to the ware being reheated. Oak crackles and spits if it is not very dry, and particles of its ash contaminate the melt. It produces too much ash and liable to contaminate with carbon particles.

The historical record indicates different types of furnaces in Mesopotamia. The mostly used one of these furnaces was the circular, “beehive” furnace or three-storey furnace which had one fire in the center of its floor of its middle storey with multiple holes giving opportunity to look inside and to take out the glass for working (Figure 6). It had also a vaulted upper storey (lehr) where the glass was annealed (Tillman, 1978). The monk named Agricola who lived in the 16th century in Italy illustrated this type of furnace in his text *De Re Metallica (On the Nature of Metals)* (Figure 6). In this type of furnace the activities of the worker who was responsible for carrying the fagots interfered with the glassblower.

Another later type of furnace operated especially in the Medieval Europe had a rectangular floor plan with the auxiliary furnaces at each corner of the rectangle

making the furnace look like a butterfly (Cable, 1991). This furnace had a fire at each end of the melting chamber with two pots standing on raised sieges along each side of the hearth. It was easier to reach high temperatures with two fires. The glassblower was less disturbed by the activities including furnace stoking and removal of the ashes (Crossley, 1990).



Figure 6 A beehive-shaped furnace illustrated by Agricola, the Italian monk, in his text *De Re Metallica* (1556, translated in English by H.C. Hoover and L.H. Hoover in 1912) (Cable, 1998)

The archaeological evidences of glass production at a site are moils as the evidences of glassblowing; glass rods; glass dribbles; glass drops; crucible fragments; and raw glass chunks. Stones, the defective aggregates which were accidentally discarded from the melting process are also one of the best findings for investigating glass manufacture at a site since they retain relics of raw materials (Basso *et al.*, 2007).

Many primary glass workshops have been excavated in the Near East, and in Egypt where it was easier to achieve the major deposits. In these primary glass houses large batches of raw glass were produced but no glassware were fabricated. These large masses were then broken up and distributed as chunks to secondary furnaces in remote regions where they were re-melted and worked into vessels (Freestone *et al.*, 2002). The Malkata complex is the earliest known site for the manufacture of glass artifacts in Egypt. The excavations at Lisht revealed evidence of glassmaking that included large amounts of glass waste and slag, glass cores,

ceramic crucible fragments with adhering glass layers, manufacturing accidents such as melted beads. The glass furnaces having huge melting tanks were discovered at Apollonia (Israel) in the 1950s. Excavations at Bet She'arim in Israel in the 1960s revealed a glass slab weighing about 9 tons. Many furnaces with big tanks were found at Bet Eli'ezer in 1992. The remains of several furnaces similar to others recognized in the region were uncovered at Tyre and Lebanon in 2001. The largest one of them is considered to have contained about 30 or 40 tons of slab (Nicholson, 1995; Shortland, 2000). All the results obtained through these excavations have supported the hypothesis that installations in Palestine produced large masses of glass which were widely distributed as chunks for remelting, working, and shaping at secondary manufacture centers. The export of raw glass from Palestine and Egypt to distant parts of the Roman Empire indicates a production on a large scale which went on from the late Roman times to the early Medieval times (Hartman, 1994; Jackson, 1996).

2.7.4. Glass Forming

There are varying types of glass-forming operations as given below:

Core-forming;

The earliest method of making glass vessels is known as core-forming. Core-formed glass vessels have been excavated over a wide area in the Near East from Anatolia, Mesopotamia, and Egypt (Newton and Davison, 1996). A core of clay or some other material was covered with glass either by dipping it into the glass melt or by winding trails of softened glass over it. When the glass gets hard the core is scraped out (Küçükerman, 1985). Small containers were produced by trailing molten glass over a shaped, clay core fashioned on the end of a metal rod. Upon completion, the rod was removed, the vessel annealed (gradually cooled), and the clay core scraped out (Figure 7) (Küçükerman, 1985).

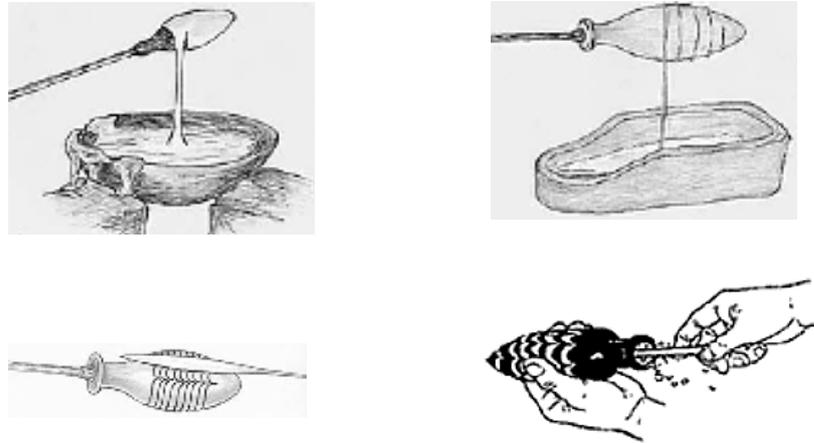


Figure 7 Core-forming of glass (The Corning Museum of Glass, 1998)

Mosaic/Millefiori Glass Technique;

The intriguing history of millefiori which has appeared, disappeared, and reappeared in different geographical areas began in Egypt, Mesopotamia, and Western Asia from the 15th and 14th centuries B.C. (Newton and Davison, 1996; Carboni 2001). It continued in Rome and Alexandria in the second century B.C., in Islamic Mesopotamia in the ninth century A.D., and in Venice in the 15th century (Carboni, 2001). The term millefiori is a combination of the Italian words "mille" (thousand) and "fiori" (flowers). A. Pellatt (in his book *Curiosities of Glass Making*) was the first to use the term "millefiori", which appeared in the Oxford Dictionary in 1849. The beads were called mosaic beads before that time. While the use of this technique long precedes the term millefiori, it is now frequently associated with Venetian glassware.

The millefiori technique involves the production of glass canes or rods, known as murrine, with multicolored patterns which are viewable only from the cut ends of the cane. Colored glass rods or mosaic tesserae (broken flat pieces of glass) were packed into clay mold in the required pattern. They are fused together with an adherent to prevent them from becoming misplaced during the actual molding. They were then held in position with another counter mold so that when molten glass

flows into the cavity between the molds; the heating process does not cause the mosaic pieces to distort.

Press molding;

This technique has also been widely employed throughout the history of glassmaking from its inception. Mold embossing or pattern molding in a press mold is actually the easiest and fastest way of shapen glass. The metal is poured into an open mold and a counter-mold is pressed onto it.

Casting;

It is the process generally used for small objects e.g. beads, inlays, and figurines. However, from the eight century onwards mold-casting was used for larger vessels, particularly bowls. This process involved the shaping of molten glass in a closed mold or over an open former. Closed vessels were probably cast using the lost-wax technique. A mold was made by creating a wax or wax-coated model of the object to be produced. The model was enveloped in clay or plaster and then baked, so that the wax melted, leaving a mold into which molten or, more probably, powdered glass could be poured. After casting, the vessels were allowed to cool, and then they were usually cut and ground into their final form (Figure 8).

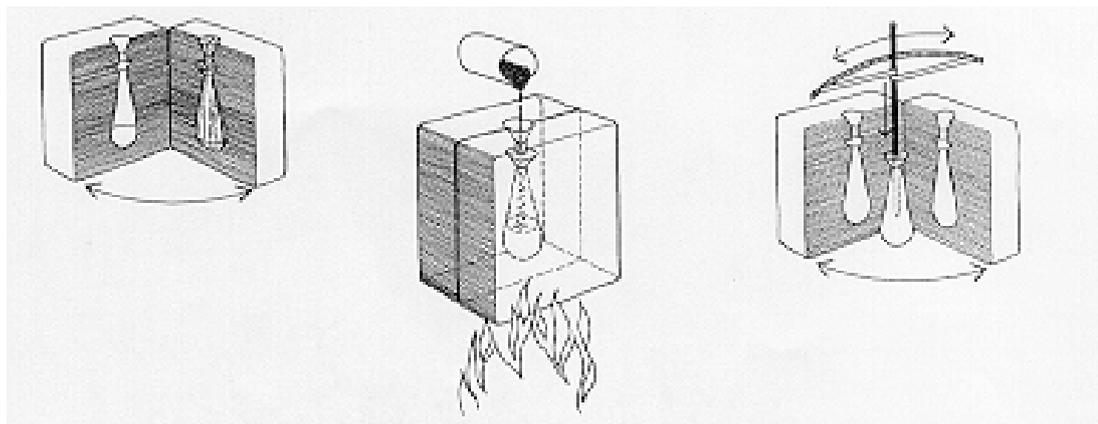


Figure 8 Casting methods of glass (Küçükerman, 1985)

Glassblowing Technique;

With the invention of glassblowing technique by Phoenicians around 40 B.C., the expectations from glass production changed, and the transparency of glass became a desired quality. The glassblowing technique has made possible the production in quantity of better and cheaper glasses. It led the rapid expansion of glass manufacture that gained commercial stability in the Roman Empire. Glass manufacture spread throughout the eastern and the western provinces of the Empire consisting of United Kingdom, France, Spain, Portugal, Germany, Belgium, the Netherlands, Switzerland, Eastern Europe, Turkey, the Middle East, and North Africa. However, the decline of the western Empire caused decadence in glass manufacture in Europe while it continued to flourish in the eastern centers.

Until the invention of glassblowing, many time-consuming and laborious processes had been applied for glass shaping. The invention of this innovative technique stimulated a transformation of the ways in which glass was made and used. This new process enabled the glassworker to produce limitless array of vessels in any shape and size in a short time with the same old basic equipment. Glass which had been produced only for the elite class as a luxury object became a daily house-hold material which was widely used by ordinary people. Blown glasses became the common articles of commerce in the Roman period.

Cylinder technique and crown technique used for window glass manufacture, developed after glassworkers gained sufficient experience in blowing glass. The techniques used to make window glass are summarized in Section 2.8.5.

2.8. Brief History of Glass

Here, the brief history of ancient glasses has been given chronologically on the basis of their chemical compositions. The production techniques of window panes and the sites where window fragments were excavated in Anatolia have been cited.

2.8.1 The Origins of Glass

The objects made of natural glass, obsidian, were the primary glass objects that have been found in many places in the world. Because it could easily be broken into elongated pieces, many useful tools such as spearheads, arrowheads, and knives could be made by obsidian. In advanced cultures it was valued for ceremonial purposes and for jewelry, and it was an article of commerce as early as the Bronze Age. Obsidian mirrors were of widespread use, and obsidian blades and razors were the most efficient tools until the Iron Age (Morey, 1964).

When the artificial glass is considered, it is not possible to mention one single origin, where the manufactured glass was first seen. But it is quite probable that glass was first appeared in Mesopotamia (Ur and Tel-Asmar, Iraq), in the late third millennium B.C. onwards. These earliest glass objects were very small, opaque, and crude beads and pendants used for ceremonial purposes only. Therefore it is not easy to regard them as true glass (Lilyquist and Brill, 1993). True or common glass objects did not appear until the 16th century B.C. when the industry flourished throughout the Eastern Mediterranean area, especially at Sidon, Thebes, Tyre, and Alexandria. Glass appeared in the Middle East during the Bronze Age. It is not known whether glass was first produced in Mesopotamia, in Syria, or in Egypt. A single origin is unlikely. Similar sequences or discoveries probably led to similar processes and products in different places in the Middle East.

The only ancient record giving information about the discovery of glass is the *Naturalis Historia*, written by Pliny the Elder (23 – 79 A.D), in Italy. According to his text, glass was discovered by a few Phoenician traders who rested on the beach near the mouth of the Belus River whose present name is Naaman River, near Haifa, modern Israel (Freestone, 1991). While preparing their meal, they supported their cooking pots over the fire with cakes of soda. Soda reacted with sand to form “a strange translucent liquid that flamed forth in streams” (Book XXXVI, translated by Forbes, 1950) (Mass *et al.*, 1998). This liquid would have formed glass on cooling; nevertheless his explanations are doubtful because he wrote this text some thousand years after the earliest recorded human-made glass objects. In the Roman times when

Pliny lived, people already knew how to make glass, and hence his assumptions may not be regarded true. On the other hand, the Belus River has been determined by scientists as the source of sand in the Roman period (Henderson, 1985).

When glass was first made artificially is not known but it must have been early in the cultural history of human. The firing of crude pottery was the first step in the development of the arts based on fire and from this the development of glaze and hence of glass was a logical step. However, the discovery of glass was an independent occurrence (Henderson, 1985). It is suggested in literature that artificial glass was the consequent of two older technologies which are metal-working and related faience producing. Once fire was invented, ancient people, indispensably, began to develop various fire-based technologies including glassmaking which is thought to have been derived from or inspired by the antecedents, metal-smelting and related faience producing. Probably ancient people first observed the artificial, pale-grey glassy material, which is fuel-ash slag or vegetable slag as the initial artificial glassy material which attracted attention of the artisans and led them to make resembling objects. Fuel-ash slag which requires a moderate temperature up to 800°C occurs wherever silica fuses with alkaline plant ashes; it can be even seen when a wheat field is burnt (Folk and Hoops, 1982). In the kilns and furnaces which were constructed by bricks and heated by wood, the slag was easily formed as a waste product as a result of many activities such as firing of clay (Biek and Bailey, 1979). Another glassy slag formed in copper-smelting with the characteristic colors of green and red, would have attracted attention and promoted producing of such materials deliberately. The production of glassy (or vitreous) materials, mainly faience, began in the fifth millennium B.C. in Egypt and Mesopotamia by using the known processes of ceramic and metal-smelting technologies. The link between faience and metallurgical features (i.e., metal scraps, smelting stags) is so direct that faience which consists of a body or core of crushed quartz pebbles covered with an applied or self-formed colored glaze of varying thicknesses, contain metal (mostly copper) impurities as a coloring agent in its layer of glaze (Artioli *et al.*, 2008). Sintering was the technique for faience producing. Quartz was mixed with alkali and sintered in an open pan. While soft, the mixture was molded into shape and its glaze was then

fired on the surface. Several hypotheses suggest that the first colored opaque glasses were metallurgical in origin (Brill, 1963; Swann *et al.*, 1990). Previous researches have considered the metallurgical origins of copper-based ancient glass colorants and also addressed the direct formation of vitreous silicate objects from metallurgical slags (Sayre and Smith, 1974; Dayton, 1993; Stapleton *et al.*, 1999).

For a very long time glassmakers used raw materials of variable quality, and probably were ignorant of the importance of controlling furnace conditions when working with multivalent elements. Because their knowledge was strictly empirical, their operations were tricky and not necessarily reproducible. They believed in gods to ensure success. However, glassmakers were good observers (McCray and Kingery, 1998). In Mesopotamia, they were well aware of the deleterious effects of fumes and, thus kept recommending keeping a good and smokeless fire burning. They shared many points with metallurgists in their use of earthy materials and operation of their furnaces. They were familiar with sintering, grinding, and stirring to achieve a homogeneous melt. Slowly glassmaking had spread from the Middle East. Beads made during the late 2nd millennium B.C. have been found in many places from Italy to central Asia and China. Glass vessels reached in Greece toward 13th, in France toward 11th in Belgium toward 8th, and in Rhine valley toward 5th centuries B.C. Glass would remain unknown in America until the Spanish conquest (Morey, 1954).

The earliest glasses were produced by cold-working lapidary techniques which did not require very high temperatures. Those glasses were crude and had low refractive index. It seems that early glass workers did not mind transparency and brilliancy. Until the 16th century B.C. the production of glass in the form of beads was limited. Archaeologically recorded earliest glasses are scarce. After 1500 B.C., the late Bronze Age when better furnace conditions could be achieved, the earliest vessels made by core-forming technique appeared.

2.8.2 The Chemical Compositions of the Bronze Age Glasses (3300-1200 B.C.)

Analytical investigations carried out to date have shown that the Bronze Age glasses from the East and from the West were distinct from each other in terms of their chemical character on the basis of major elements (Artioli *et al.*, 2008). Therefore it is not possible to mention a standard manufacture of glass during this early period. Indeed glass industry was limited to local sources, native recipes and methods, especially in Europe because the mass-reproducible methods of glassmaking and the widely distribution and importation of raw materials or raw glasses had not been developed yet as in the Roman times (Newton and Davison, 1996). The early and middle Bronze Age glasses collected from Mesopotamia and Egypt show a character of high magnesia with varying potash content whereas European glasses belonging to same period are distinct with their low magnesia and high potash compositions (Sayre and Smith, 1961). This certainly indicates different alkali sources used for making glass.

Materials with a higher percentage of glass phases have been found in the Near East and the Mycenaean world, reaching what seems to be a significant production in the 2nd millennium B.C., as testified by the Egyptian evidences of production and by the Uluburun shipwreck which sank off the Turkish coast with a large number of glass ingots to be traded in the Mycenaean world and possibly the western Mediterranean. The principal cargo had been carrying copper ingots of blue and turquoise glass. Objects on the ship have been traced to a dozen different areas of the eastern Mediterranean (Bachhuber, 2006). The glass ingots found in the cargo have revealed high magnesia glass (HMG) character which was the dominant type of glass in the early and the middle Bronze Age in Egypt and the Near East. In 1954 Turner analyzed the Eighteenth Dynasty Egyptian glasses (1550 B.C. – 1307 B.C.) from Tel-el Amarna and detected high levels of magnesia (Turner, 1956). Brill's and Wypyski's analysis of Egyptian glasses dating to between the 16th and the 14th centuries B.C. gave the similar results (Brill, 1999). Sayre and Smith (1961, 1974) classified Egyptian glasses from 1500 BC to 800 BC as high magnesia glasses (HMG) as the result of their investigations in 1961 and 1967. I. Freestone studied

with his colleagues on early Eastern glasses from Deir 'Ain' Abul, Jordan, dating to between 1900 BC and 1550 BC; and from Tel Den, Israel dating to approximately the 19th or the 18th centuries BC and has come to the similar conclusions (Freestone, 2002). From 1600 to 800 B.C. in the Eastern Mediterranean, Egypt, and Mesopotamia glass was the HMK type (magnesia 3-7 %; potash 1-4 %) (Brill, 1970; Lillyquist and Brill, 1985; Henderson, 1989). Analytical investigations of early glasses dating to between 1900 and 1550 B.C. from Deir "Ain" Abuta, Jordan and 19th - 18th century B.C. Tell Den, Israel have shown that HMG was certainly in use of this very early time in the history of glassmaking. Turner (1956) has collected and summarized the early chemical analyses of the Eighteenth Dynasty glasses from Tell el'Amarna, dating to between the 16th and 14th centuries B.C. All these glasses have been found to have high magnesia contents. Glasses from Tell Brak, Syria have high levels of MgO, and most 14th century B.C. middle-eastern glasses are of the HMG composition (Jackson, 1996; Silvestri *et al.*, 2006).

On the other hand, some exclusions are present. For example, contemporary glasses found in other sites in Mesopotamia and cobalt-blue glasses from Egypt have lower levels of MgO and they are classified as LMG (Low Magnesia Glass); and Minoan Crete glasses are of LMG composition. They were certainly produced by a plant ash different from the one used to make most eastern Bronze Age glasses. However, LMG glasses of the East were still distinguishable from the Western contemporary glasses with their lower potassium contents (Henderson, 1989).

Glasses in this category have been readily discriminated on the basis of major element compositions from the Bronze Age European glassy materials, systematically carrying a distinct low-magnesia-high-potash (LMHK) signature. The compositional differences identified between the glasses from the East and from Western countries have proved that in the Bronze Age glass was produced with available local sources and in spite of the evidences of trade of glass in large quantities, distribution of glass was limited to neighboring regions due to the lack of efficient road network and communication between two parts of the world (Jackson, 2005; Shortland and Eremin, 2006; Artioli *et al.*, 2008) (Figure 9). Glasses found in Frattesina, a 11th – 9th century B.C. site near the mouth of the River Po, Italy,

revealed LMHK composition (Angelini *et al.*, 2004). Glasses found in different sites in Ireland and in Switzerland have been found to have similar compositions (Henderson, 1989).

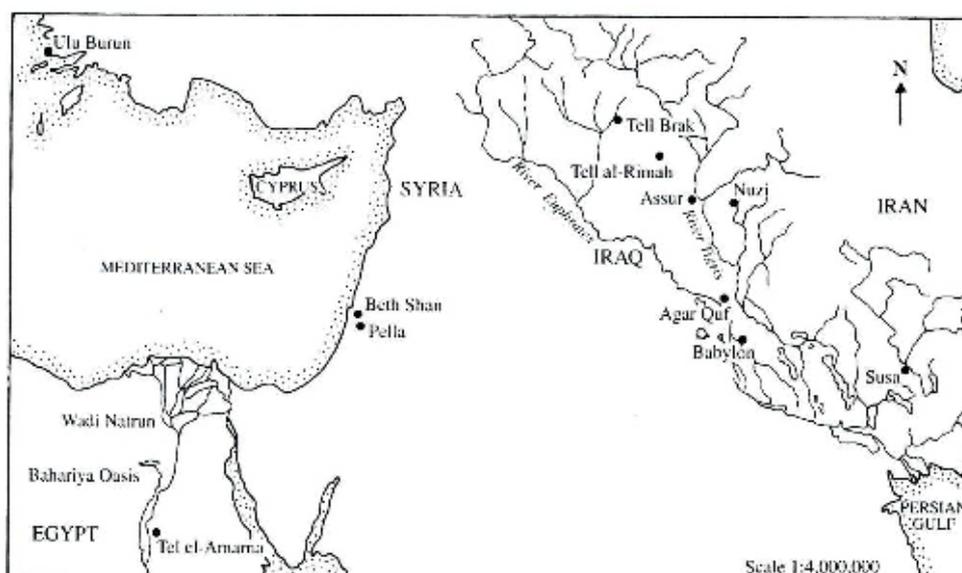


Figure 9 Bronze Age sites in Egypt and Mesopotamia (Henderson, 2000)

It has been established by Sayre and Smith (1967) in Mycenaean Greece, Anatolia, Egypt, Mesopotamia, and south-west Persia, a change occurred; high-magnesium glasses (HMG) persisted from 1500 B.C. until 800 B.C. were replaced by low-magnesia glasses (LMG) produced a very different type of alkali source which was predominantly used to make glass from around 800 B.C. to around 900-1000 A.D. (Henderson, 1989, Sayre and Smith 1974). Probably the new source of alkali which was rich in sodium with lower magnesium and potassium contents were found to be more efficient than the usual plant ashes used to produce glassy materials and previous glasses in the Bronze Age. Low Magnesia-Low Potash glasses produced with this sodium-rich alkali are called natron glasses in literature. Natron usually is retained as a general term for inorganic soda with no specific mineralogical or geographical connotations intended. Other soda sources, i.e. seaweeds containing little MgO and K₂O, or seasalts obtained in the Mediterranean area or in other coastal

regions are all called natron glasses. LMG or LMLK (Low Magnesia-Low Potash) glasses generally contain 0.5-1.5 % of magnesia; and 0.1-1.0 % potash (Shortland, 2000).

Natron glass is equivalent in composition to late Roman and Byzantine glasses in Egypt at Hermapolis (Bimson and Freestone, 1983) and small numbers of Fustat (Brill, 1999) and in the Levant region in Jalame (Brill, 1988), Caesaria (Brill, 1999) and Bet Eli'ezer, Dor, and Apollonia (Freestone *et al.*, 2000). Brill (1988) has established the possible raw ingredients: sand gathered from beside the Belus River in Israel seems to give rise to about 3-4 % alumina impurity and natron from Tell el'Amarna accounts for the low magnesia and potash impurities. Shell fragments in the Bellus River sand are thought to have provided the 8-10 wt % of lime in natron glasses (Freestone *et al.*, 2003).

Colorless natron glasses from the sixth to about the fourth centuries B.C. have been found to be decolorized by antimony. Sb contents of many colorless glasses have been detected as 0.53-1.93 wt % (Sayre and Smith, 1961).

Glass manufacturing had declined starting from the 13th century B.C. to the 9th century B.C. There was even an almost total absence of glass forming from the end of the second and the beginning of the first millennia B.C. in Mesopotamia and Egypt (Leslie *et al.*, 2006). Production was largely stopped for a few hundred years beginning about 1200 B.C., a time of wars, invasions, and disruption of trade and infrastructure (McCray and Kingery, 1998). The cultural and economical significance of this production gap has not been fully interpreted yet, and within this context there is still much debate on the relative importance of local production versus the reworking of imported raw glass. Mosaic glass and cameo glass were two new achievements of late Hellenistic world (c. 4th - 2nd B.C.). At the beginning of the first millennium B.C. there was gradual end of the dark age of stripe and infrastructure breakdown. More or less simultaneous with the conquest of Egypt in 30 B.C. and the establishment of Roman hegemony over the entire Mediterranean area new centers of power developed: Greeks in the Aegean, Phoenicians along the Palestine coast, and Syrians along the Euphrates. Extensive trade commercial

ventures and colonizing were accompanied by a revival of all aspects of the economy including glassmaking (Foster, 2009).

2.8.3. The Chemical Composition of Roman Glass

It was only when the Romans appeared in the history that glass became a mass-producible industrial object. Romans built new roads and systematically organized the distribution of products in all the provinces within the borders of the Imperial. All the technologies and the knowledge of the period provided the standardization of raw materials, recipes, and techniques to produce glass, and therefore Roman glass gained well-defined characteristics (Morey, 1954). Its composition was standard and it is generally constituted by soda-lime-silica glass with small presence of MgO and K₂O (0.5 – 1.0 wt %) which is called LMLK glass in literature (Costaglibla *et al.*, 2000; Dal Bianco *et al.*, 2005). Although the centralized / regional glass production of Roman is questionable to a few scientists who have raised some doubts on the accepted idea that glass in Roman territories (United Kingdom, France, Spain, Portugal, Germany, Belgium, parts of the Netherlands, Switzerland, Eastern Europe, Turkey, the Middle East, and North Africa) was extremely homogeneous (Baxter *et al.*, 2005), it is widely accepted in literature that from the first century B.C. to the sixth century A.D. the major composition of Roman glasses represent similar character in terms of alkali elements. Glasses made with natron usually have K₂O and MgO levels less than 1.5 % and Al₂O₃ levels around 2-3.5 % by weight (Brill, 1988).

During the height of the Roman Empire glassmaking had at least by 50 A.D. spread from Syria and Egypt to western areas and then northern Europe so that by about 100 A.D. glassmakers were operating in the Rhineland, Germany (Henderson, 1989). The glasses made in Europe at that time had low amounts of magnesia and potash and since there do not seem to have been any sources of soda with the same characteristics available in Europe, it seems reasonable to assume that the glasses were made with natron rather than the ashes of maritime plants which have significant contents of MgO and K₂O. Natron must have been exported from the East

to the West. It is possible that natron continued to be transported to the Rhineland even after the collapse of the Roman Empire in the West, because glassworkers were conservative about the use of tried and tested raw materials and insisted on using them traditionally (Newton and Davison, 1996). Some archaeologists suggest that the general homogeneity of Roman glass was due to the use of the same recipes through the centuries in different places. This involved the use of the same or at least similar raw materials.

Colorless glasses from the fourth century B.C. to the 9th Century A.D. seem to have been decolorized by manganese rather than antimony, which was the dominant decoloring agent of LMG glasses of the Late Bronze Age. Colorless Roman glasses have revealed low antimony contents being 0.018-0.089 wt % (Sayre and Smith, 1961).

2.8.4. Post-Roman Period

After the fall of Roman Empire, trade of glass did not stop but it became more expensive since the roads being active in the Roman times became unimportant. Natron was not systematically imported to remote western areas; it even seems to be disappeared in its original land. In the Middle East and southern Europe the alkali source became plant ash, growing on the shores of the Mediterranean and Atlantic. It was the source for sodium together with some quantities of potassium and magnesium of about 2-3 % for both. Glassmakers in the West and in the Islamic lands developed new technologies by using local raw materials. Glass composition began to differentiate (Dal Bianco *et al.*, 2005). However, soda-lime glass, the most common type produced in Roman Imperial times was still common in Europe many centuries after the fall of the Empire. Egyptian natron seems to have been used as the flux to produce soda-lime-silica glass as late as the ninth century in the Islamic world and it may have still reached in Europe in late antiquity. In fact recent studies on glass production between late Antiquity and the early Middle Ages suggest that glassmaking sites located in the Levant and Syria-Palestinian coast still produced and exported soda-lime raw glass in the eight and the

early ninth centuries and this may imply that this material continued to be imported in the West (Freestone and Gorin-Rosen, 1999). Every chemical analysis of a post-Roman glass object made in Western Europe, including the British isles before the late eighth century reveals the presence of natron; not a single object was come to light that was made with plant-ash (Oppenheim, 1973). On the other hand, mixed-alkali and early wood-ash glass types have begun to be produced in northern Europe from the eighth to the ninth centuries A.D. before potash and potash-lime glass spread in Medieval and late Medieval times (Mirti *et al.*, 2001).

Despite the fact that the alkali source as termed “natron” remained same for centuries in many parts of the world, radical changes occurred in the sand source in the 4th century, and hence glasses made with the same source of alkali began to differentiate according to their silica source (Freestone, 1994). Some different types of LMG glass have been identified. From the fourth century onwards HIMT glass type containing high iron, manganese, and titanium appeared in Egypt and Levant (Freestone, 1991). The sites excavated were briefly given in the paper. Natron glasses produced in the Palestinian coasts near the delta of Belus River from the fourth to the seventh centuries A.D. have been classified as Levantine I (Freestone, 1991) which have been found to be different from other Roman glasses with higher alumina and calcium and lower manganese contents. The glasses of Levantine II type mainly diffused in Israel (the 6th – 8th centuries A.D.) were again natron glasses with lower natron/silica ratios (Freestone *et al.*, 2003; Vandini *et al.*, 2006). Glasses from the Roman workshop at Jalame, near Israel have been found to be produced by mixing two components; natron and a shell-bearing coastal sand (Brill, 1988) whereas some fourth century Roman glasses from Germany have been found to be made with three components; natron, sand, and shell (Wedepohl and Baumann, 2000).

2.8.4.1. Western Glass

There is not much information concerning glass in the period from the fall of the Roman Empire to the 11th century. No written records of western European glass

manufacture during this period are known. Political and social affairs consequent to the overthrow of the Roman Empire caused decadence in glass industry in Europe; and the migration of the center of the industry to the eastern Empire. There is not much information concerning glass manufacture in Europe in the period from the 5th to the 11th centuries A.D. No written records of western European glass during this period are known. After the fall of the eastern Roman Empire glass manufacture regained its success in Venice in the beginning of the 11th century. Venice maintained a dominant position for at least four centuries. Murano, a separate borough of the city, became a very important center. The Venetian glass was, and still is associated with the tradition of excellence quality. The mirrors silvered by mercury reflected the high standard of technical competence. After this period the developments were rapid; glass factories multiplied in Europe. In the 17th century, coal became the source of fuel in England. It was replaced later by natural gas and oil (Morey, 1954).

Soda-lime-silica glass, the most common type produced in Roman Imperial times was still common in Europe many centuries after the fall of the Empire; however, mixed-alkali and early wood-ash glass types were produced in northern Europe from the eight to the ninth centuries before potash and potash-lime glass spread in medieval and late medieval times (Mirti *et al.*, 2001). Natron started to become exhausted and plant-ash came to be used. In the West between 800 and 1000 A.D. wood-ash had become the main alkali source for the manufacture of glass needed for the windows of cathedrals in northern Europe. The ash of inland plants, containing potash, was replaced by soda (Silvestri *et al.*, 2005). In the Middle East and southern Europe, on the other hand, the alkali source was ash from marsh plants which grow on the shores of the Mediterranean and Atlantic coasts. It introduced sodium in the batch, like natron-based glass, together with quantities of potassium and magnesium in the range up to 2.3 % of K₂O and MgO (Silvestri *et al.*, 2005). This new pattern of alkali use was set for hundreds of years to come; first being imported from the Middle East to Italy as early as the 14th century (Jacoby, 1993).

The Alps became an important barrier to trade and the technologies developed in different ways in north and south of the Alps. Glass compositions

started to differentiate according to the available raw materials. The use of fluxes changed according to the setting of the glass furnace. The glassmakers of the Mediterranean area continued to use their own typical fluxes while the glassmakers living in the Germanic territory developed new technologies with the aim of using cheaper raw materials coming from closer areas. The new flux used as ash was beech-wood ash or plant ash (*salicornia herbacea*, a type of plant ash that contain relatively less soda than coastal plants) and this gave the glass new characteristics. This new type of glass is called high-magnesia glass (HMG) and it is characterized by high contents of MgO and K₂O (4-5 wt % and 2.5 wt %) respectively (Costaglibla *et al.*, 2000). Once it was realized that the use of beech-wood ash would enable a variety of colors to be produced, glassmakers would have moved the areas where beech forests existed. The manganese content in beech-wood depends on the place where the tree has grown, the maturity of the wood, etc. and there must have been many difficulties and failures in trying to make the right colored glass. Glasses made of beech-wood ash also contain much lime, for this reason medieval window glass decays in dump atmosphere (Marchesi *et al.*, 2005). In northern Europe mixed-alkali and early wood-ash glasses were produced from the eight century to ninth century A.D. (Henderson, 1993), before the production of wood-ash and wood-ash-lime glass in medieval and late medieval times (Mirti *et al.*, 2001).

Forest glasses which have their origins in the medieval period were manufactured by using the ashes of forest plants and are characterized by low levels of soda, high levels of potash; and a wide range of minor components derived from the plant ashes such as alumina, magnesia, phosphorus oxide, manganese, and iron oxide (Fe₂O₃). It is the relatively high levels of iron oxide which gives the glass a distinct green color. High Lime-Low-Alkali (low soda) glasses seen in England in the late 16th century are characterized by low levels of alkalis (soda + potash < 10 wt %) but high levels of lime (CaO > 15 wt %) (Turner, 1956). Glasses of the same overall type have been identified among assemblages of post-medieval glass in Britain and continental Europe. HLLA glass was used in the production of both glass vessels and window panes. While forest and HLLA glasses were used in the manufacture of a wide range of artifacts, high status tableware made from soda glass

was often imported from Italy. The most prestigious example was the *cristallo* produced on the island of Murano, Venice (Dungsworth and Cromwell, 2006). It is characterized by high levels of soda and low levels of impurities. In the western Europe imitated *cristallo* (*façon de Venice*) often contained slightly lower proportions of soda and higher proportions of potash, probably due to the use of slightly inferior plant ashes (Dungsworth and Cromwell, 2006). In fact, many same four hundred western Europe stained glasses analyzed for the Corning Museum, no soda glasses at all were found dating even as late as the 15th to the 16th centuries. The Jarrow and Wearmouth glasses are excluded from this generalization. Also some mixed-alkali were made early in southern France. They might have been made with *barilla* (a coastal plant, rich in soda), considering their proximity to the Mediterranean coast (Brill, 2005). Moreover, although soda-lime glasses are found on the continent from the middle ages, some of them were natron-based glasses, in other word, not made from soda derived from plant ashes. Similarly most Byzantine mosaic tesserae analyzed proved to be natron-based. In the middle age and especially after the Gothic revolution glass was greatly demanded for churches and later for palaces.

2.8.4.2. Islamic Glass

Although progress has been made recently in the study of Islamic glass, it is nonetheless difficult to suggest precise attributions and to understand the historical development of glass in specific parts of the Islamic world. One reason is the scarcity of the Arabic and Persian inscriptions which can be efficiently found for other media such as metal-work. Another reason is that there was a wide circulation of Islamic glass both within its area of production and beyond from China and south-east Asia to Europe and north Africa as an item of exchanged gift (Carboni, 2003). Additional reason is that Islamic glass was often recycled as cullet and remelted as low-cost fuel for glassmaking process.

What definitely became apparent is that after the decline of Roman Empire, the development of a European and Islamic glassmaking technology went through

the use of independent recipes and alkali sources in different places, resulting in a variety of compositions and textures of the final products. Some of the materials are certainly unique in shape and composition, and they are certainly found nowhere else bearing on the hypothesis of local production and testing of new recipes (Artioli *et al.*, 2008).

After the fall of the Roman Empire, glass manufacture was carried on in the eastern part of the world. The dark ages in which glassmaking had no progress in Europe were the period of intellectual dynamism in Moslem lands. In its early stage, the influences of previous and surrounding civilizations were certain in Islamic art. The artistic activities of the nations making up the Islamic community had much in common, but differ in regional styles and motifs. In glass production they developed their own distinctive ways due to different geographies, and hence due to the social and political conditions which they had to embrace. Islamic art was at its height from the 10th to the 17th centuries and in an abstract sort of way fused various influences together with its own particular idiosyncrasies. In modern literature, Islamic art is generally classified into three main types: Arabian, Persian, and Turkish. Each of these main types has sub-types divided locally, and varying forms have been developed as a result of this (Bayramoğlu, 1974).

With the transfer of the seat to Constantinople in A.D. 305, the capital of the Empire was on the doorstep of the Syrian glass houses which were in Tyre and Sidon. During the Sassanian period (100 B.C. – A.D. 600) tradition of cut glass developed. Cutting is a type of decoration applied on the glass when the vessel is cold. Enameled and gilded glassmaking technique which started probably in Iraq in the 12th century was widespread in Moslem countries. Islamic enamels were prepared by cold mixing the standard pigments such as ferric oxide (ochre), calcined bone, and lapis lazuli with crushed glass. The mixture was painted on to the vessel, and then fired. Some other elements were prepared by pre-fritting to produce a colored opaque glass. In this case the colored glass was crushed and painted on as enamel (Freestone, 2002). In the Islamic world, tin oxide started to be used for white opaque glazes in Abbasid Iraq from the ninth century A.D. Tin-based opacifiers were used in the production of yellow and white enamels applied to Islamic glasses from about the

12th century A.D. (Henderson, 2000) and Venetian glasses from about the 13th century A.D. (Freestone, 2002; Ubaldi and Verità, 2003). Many colorless Islamic glasses have been found to be decolorized by manganese with high levels of potassium and magnesium (Vandini et al., 2006).

The greatest era of Islamic glass had its rise in the 12th century and reached its climax in the 13th and the 14th centuries under the Ayyubid and Mamluk rulers. By this time, the whole of the Middle East had settled under the rule of Islam and new styles in glass began to emerge to suit the tastes of a new society. Glass vessels were exported from Damascus to every part of the Islamic world, even as far as China. The Islamic wreck of Serçe Limanı which sank off the south-west coast of Turkey in 1025 A.D. has been excavated by Bass of the American Institute of Nautical Archaeology. The ship had a cargo that included approximately several tons of raw and scrap glass (Bass and Van Doorninck, 1978).

Because of the Mongolian invasion in 1258 in Aleppo (Syria), many craftsmen immigrated to Damascus (Syria) and Egypt where the industry reached remarkable stage of development in the 14th century. In the 15th century Tamerlane invaded Syria and brought craftsmen to Samarkand. Glass industry fell into decadence in this century. During Fatimid period, Alexandris and Fustat became important centers in Egypt. Chemical compositions of some ancient glasses are given in Table 4.

Table 4 Chemical compositions of some ancient glasses (Mysen and Richet, 2005)

	SiO ₂	Na ₂ O	Al ₂ O ₃	K ₂ O	CaO	MgO	Fe ₂ O ₃	PbO
Babylonian, 14 th cent. B.C.	61-71	9-14	1-3	1-3	5-8	3-6	1-2	
Egypt, 18 th dynasty, translucent	62-66	17-22	1-2	0-1	8-12	4-5	0-1	
India (3 rd - 5 th cent. B.C.)	58-71	13-19	2-6	2-5	5-9	1-5	1-2	
Alexandria	72.7	19.0	1.8	0.39	5.2	0.4	0.12	
Soda glass, Europe, 1 st - 9 th cent.	65-73	14-20	2-5	0-2	4-9	0-2	0-3	
Potash glass, Europe 9 th cent.	51-54	1-2	1-3	14-18	12-16	5-7	1-3	
Islamic glass, 13 th cent.	68	14	3	3	8	4		
English crystal	57-72	0-3	0-1	8-14	0-1			9-29
Bohemia	55			32	12			

2.8.5. Historical Window Glass

The earliest glass window panes were probably produced by the Romans in the 1st century A.D. (Wolf *et al.*, 2005). Mosaic and opus sectile glasses might have inspired to produce window panes. Opus sectile refers to an art technique where larger pieces of glass were inlaid into walls and floors to make a picture. It was popularized in Rome (Vandini *et al.*, 2006). One of the oldest glass windows was used in a public bath-house in Pompeii. It is a circular glass sheet with a diameter of about 13 cm and is mounted in a bronze frame. Window openings up to size of 200 x 200 cm were planned for the house being built just before Pompeii was destroyed in the eruption of Vesuvius in 79 A.D. Waxed paper, animal bladders, ground mica and

alabaster were also widely used in window openings of private houses in Europe even in the 19th century when there was no glass available for windows. It is more probable that the use of glass for windows spread slowly and continuously after its introduction. Indeed, the scarcity of historical records in the period from the third to the ninth centuries causes a gap in the chronology of the use of glass as window pane.

As far as it is known from the archaeological records, Roman glassmakers employed two different processes for producing window panes.

The earlier technique is known as cast glass produced by pouring the fully molten and viscous glass onto a flat surface made of polished rock, metal, or wood (Wolf *et al.*, 2005) that makes panes of uneven thickness that are fired polished or glossy on the lower side and a matt finish with irregular swirling patterns on the upper side (Wolf *et al.*, 2005). This one-side-only matt structure is the result of the flowing and viscous behavior of the molten glass which was poured and then flattened and spread with a tool (casting-roller, molding technique). Molten glass was poured into mold in much the same way metals are cast. Casting seems to have been the prevailing technique during the Roman period up to the third century (Schibille *et al.*, 2008).

The later technique is known as cylinder glass (Figure 10) making panes of even thickness which are glossy on both sides. The cylinder-blown window sheets seem to become more widespread from around 300 A.D. and initially existed alongside the older technique (Schibille *et al.*, 2008). This method is well-known, being first documented by Theophilus in the 12th century and still being employed on an industrial scale in the 19th century in glassmaking centers such as Charleroi in Belgium (Boon, 1966). It involves a glass blower who blows a bubble and let the bubble hang down to make the narrow and elongated shape of a cylinder. Its hemispherical ends are cut off by reheating and the round glass is flattened lengthwise with a tool or allowed to sink to a flat state to produce a sheet of glass (Diamond, 1953). The cylinder-blown technique is thought to produce two smooth surfaces but, in thicker samples the parallel grooves caused by the concomitant accumulation of excess glass can be observed. Such samples have elongated air

bubbles that can be seen under microscopy. One other reason of distorted upper surface is that the outer surface of the cylinder is inevitably larger than the inner one and the tool used to make the glass flat may cause wrinkle on the surface of the glass (Schibille *et al.*, 2008).

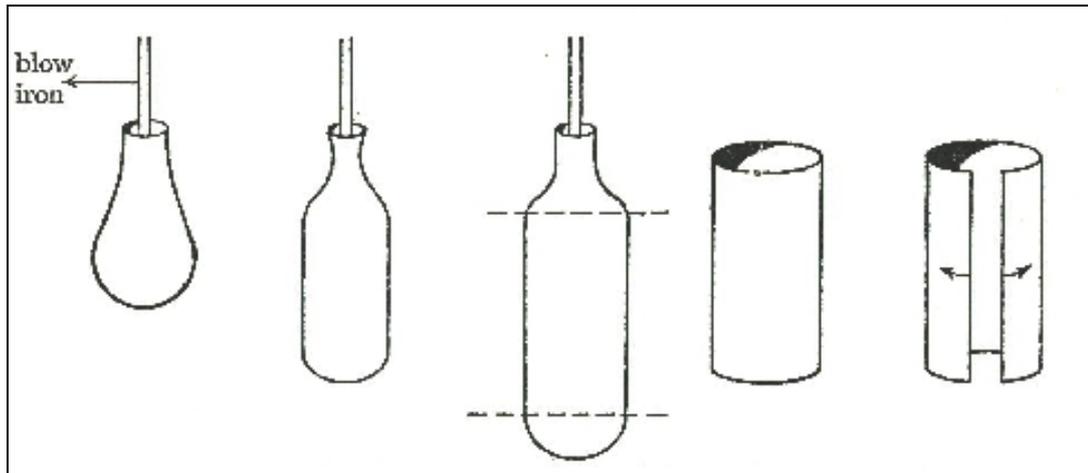


Figure 10 The cylinder-blown technique (Diamond, 1953)

In the eight century B.C. the technique of spinning window crowns was developed in Syria and spread (Figure 11). Crown glass technique is more complicated than that of cylinder glass and the glass produced in this way needs more polishing (Boon, 1966). To make crown glass a bubble of blown glass is transferred from the blowpipe to a pontil and is cut open and rotated until it has spread into a flat disk by centrifugal force. It is then annealed and cut into pieces of the desired shape, each piece being fairly thin but showing slight convexity and concentric wave lines caused by the rotation (Diamond, 1953). It can be recognized by the boss or the bullion (bull's eye) in the center where the pontil is attached, and then detached. The round pane is usually thick at its center and significantly thinner towards the edges. For the purpose of strengthening the rim, the edges of the glass disc are sometimes folded over (Harden, 1959; Meyer, 1988). Such glass has many air bubbles and a pattern of concentric circles, but it is transparent and effective in keeping out the wind.

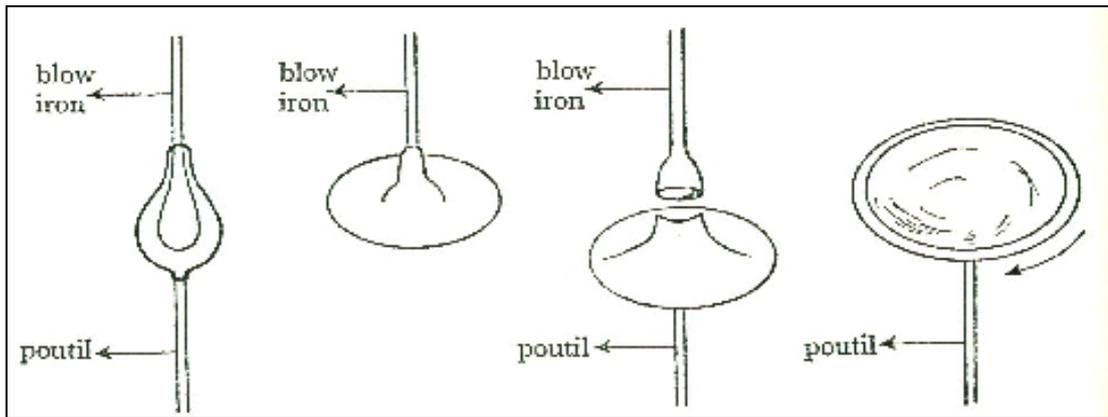


Figure 11 The crown technique (Diamond, 1953)

Glass produced by cylinder or crown technique can be cut into small pieces and trimmed into different geometrical shapes before being assembled into perforated grilles (Figure 12). Such grilles made of terracotta, stone, or marble were used in Italy, Spain, and in Syria in the 4th and the 5th centuries A.D. (Bakirer, 1995).

With the breakup of the western Empire, glass manufacture was carried on in the Byzantine Empire. The Byzantine workers were especially adept in making colored glass and mosaics. It has been suggested that the art of making stained glass owes its origin to Greek workers of the period. If so, it must have been introduced into France because Theophilus regarded it as French art; a century later glass was imported to England (Djingova and Kuleff, 1992). In Western architecture, the earliest examples of stained glass are dated to the 9th-10th centuries. Techniques and styles developed with the evolving Gothic architecture of the 12th century which lasted in the 16th century (Bakirer, 1995). Stained window glass of the 12th and 13th centuries in Western Europe appears to be almost invariably potash-lime-silica glass. The very special exceptions are some dark-blue soda glasses found together with potash glasses of other colors in certain windows (Brill, 2005).

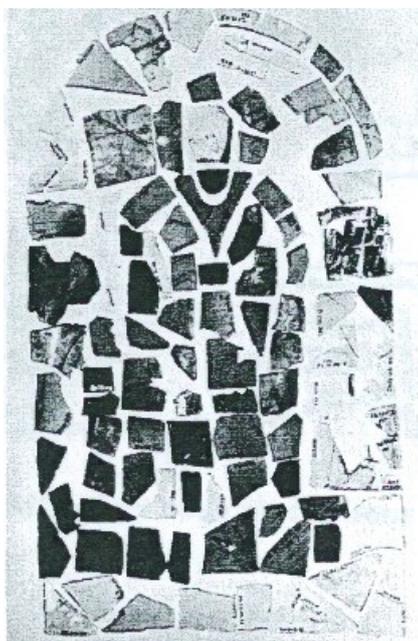


Figure 12 The reconstructed quarries from Jarrow Monastery (Britain) dated to the 7th-8th centuries A.D. (Cramp, 1976)

Window glass was frequently used in the Islamic world as well. At the beginnings glass was cut to size from sheets and set into stone grilles composed of geometric lattices. Later, stucco or marble was used instead of stone (Bakirer, 1986). A few marble grilles have been found *in situ* in the western vestibule and under the western riwaq of the Great Mosque of Damascus (Creswell, 1953). Lead-lined grilles or lead bars, which were popular in the West, were not preferred in the Islamic world (Eyice, 1990). In Islamic architecture windows in domes and walls were built with rounded and pointed arches with pediments decorated with Rumi (words from Koran) motifs. The tradition of windows ornamented with stained glass in Turkish architecture can be seen on walls overlooking the courtyards of mosques and palaces (Öney, 1988). Unlike Byzantine tradition, in Islamic, and hence Seljuk architecture windows in the outside of buildings consisted of two parts being exterior and interior in one opening. Two common styles of installation of the decorative window panes have been developed in Islamic architecture. One is called “umbrella” which is organizing vegetal motifs in rectangular arched openings (Figure 13a). The resulting

window would filter the sunlight in a pleasant manner by throwing colors inside the buildings. Another one is “qamariyya” with the circular frame (Figure 13b) (Bakırer, 1986). Rounded, relatively thicker and mostly colorless glass pieces inserted in perforated grids (Figure 13c) which are called “elephant eye” have been used in exterior windows. They were functional to protect the inner window from external factors, i.e., wind. Windows of this sort have been produced in large quantities throughout the centuries; on the other hand, the use of decorated glass as architectural wall ornament was not frequent in the Islamic world (Carboni, 2003). Nevertheless, lunette openings with semicircular arcades over the doors of the halls inside the buildings could allow ornamental glass use.

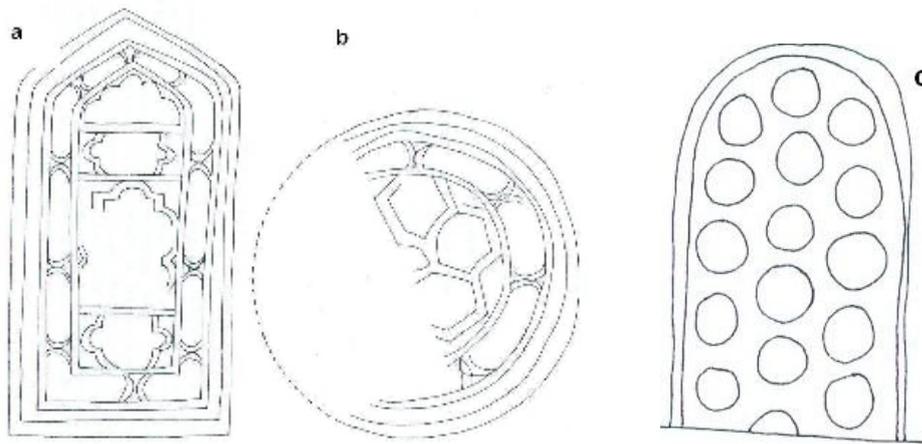


Figure 13 The grill designs used in Islamic architecture: (a) umbrella; (b) qamariyya; (c) elephant eye (Bakırer, 1986)

2.8.6. Window Glass from Anatolia

Unfortunately, we do not know much about the window glasses of Anatolia before the 6th century. Investigations of glass of the Paleolithic and Neolithic ages in Anatolia have barely begun and the domain of origins, dates and techniques is an extremely difficult one. Actually, when the archaeological evidences are considered, it can be stated that the window glass history of Anatolia begins with the early, even the middle Byzantine period. Here, it is necessary to note that the term “Byzantine”

covers badly-matched historical facts that scarcely contribute to the data about the glass used or produced in the lands under Byzantine domination between the 5th and the 15th centuries (Philippe, 1990). Byzantine art evolved through contacts with oriental, Western, Islamic and Slavic people. It is problematic to distinguish unambiguously between the late Roman, early Byzantine and Middle Byzantine glass finds. In this respect, the archaeological context is not entirely trustworthy, since few findings are securely dated. Identification depends in part on the nature of the glass finds. Archaeologists mostly rely on differences in shape, decoration, and technique to distinguish between groups of material.

There are a few places where window fragments or window grilles indicating the use of window glass are found in the ruins of ancient buildings or probable glasshouses. In Alişar (Yozgat); and in Anamur (Anemurium, Mersin) some pieces were found (Alexander, 1937). In Demre (Myra, Antalya) cylinder and crown glass pieces with folded rims were excavated along with the lattices with both round and square openings (Ötüken, 1992; Acara and Olcay, 1997). Some flat (broad or sheet), and a few crown glass pieces were found at the excavations of the ancient theatre in Iznik (Bursa). The flat pieces show both glossy/matt and glossy/glossy character, having parallels with Anamur, Demre, and Sardis glasses (Hayes, 1992; Özgümüş, 2000). The most important glass products of the Byzantine period consist of the early and middle Byzantine specimen found at Sardis (Manisa) where the glass furnaces in the vicinity indicate the existence at one time of an extensive local industry of the 6th and the 7th centuries. Some marble, wood, and clay frames were found with flat or concave-shaped, colored or green tinted glass fragments. As in Sardis, flat and green-colored fragments of 2 mm thicknesses were found at Side, dating to from the 5th to the 8th centuries (Eyice, 1990). These are, indicating that there might have been a glass atelier around. In Selçikler (Uşak) the icons of the marble iconostasis inlaid with colored glass discovered in the ruins of middle Byzantine period church (Fıratlı, 1970). The icons, resembling the colored stained-glass of the Western Europe, actually have parallels with the enameled icons of Constantinople, dating to the same period. The similar icons were found in Fenari Isa Camii (the church of the Lips Monastery) in Constantinople. The half of a marble grid with square openings and

some glass fragments, belonging to the 13th century were excavated here. Numerous fragments of painted window glass were found in Zeyrek Camii (Pantokrator Church; 1126, Istanbul) and in Kariye Camii (Chora Monastery; 1100-1110, Istanbul) (Eyice, 1990; Bakırer, 1990; Brill, 2005). Zeyrek Camii glasses vary in color-reddish, purple, dark, blue, green, and amber-and are heavily weathered; loose and, even, detached layers of paint have been detected (Brill, 2005). Although painted window pieces found in Zeyrek Mosque remind the initial examples of stained-glass seen in the Western architecture (Bakırer, 1990), it has been confirmed by archaeometrical analyses that Zeyrek glasses made in the 13th century during the Latin occupation of Istanbul (1204-1261) were locally produced as they were soda glasses made with plant ash whereas all the contemporary samples of stained-glass windows in the Western Europe were potash-based ones made with wood-ash (Brill, 2005). The similarities are in style but not in composition. The painted window glass fragments found in Kariye Camii have been found to be soda-lime-silica glasses as well. It is suggested that they may have been produced in the 13th century in a local atelier, however, the artist who painted them might have come from one of the western countries as the painting style reflects Western tradition of art of the period (Megaw, 1963, Eyice, 1990).some pieces of grids made of plaster of Paris were also found (Megaw, 1963). In St. Hagia Sophia (6th century, Istanbul) marble-lined colored glasses, belonging to the 9th century can be seen on the upper part of the apsis, which were used for the illumination of this part of building (Krautheimer, 1965). It is also interesting that in the 8th – 9th centuries, colored glasses inserted in the frames of stone or plaster of Paris could be seen in the civil buildings in Constantinople. Their designs reminded the vaulted windows (lunette) seen in Emevi palaces (Philippe, 1990). At Saraçhane, both flat and “elephant eye” glass fragments were excavated along with stone and marble grids (Harrison and Fıratlı, 1966; Philippe, 1990, Hayes, 1992). It is very probable that there were glass ateliers built in the 6th century in Tekfur Palace and in Eğrikapı district that supplied window glass for the churches and houses of the capital city (Eyice, 1990) where glasses, stone and marble frames were found. It is thought that there must have been ateliers in Tekfur palace and in Eğrikapı district. One of the examples of window glass outside

Constantinople was excavated in the ruins of a small church in Tuzla; a small fragment of window pane was found here (Eyice, 1990). Lead (western) and stone or plaster frames are indicative of the relation and communication between the artisans during Byzantine period. Eyice (1990) has supposed that no lead frames were found in Byzantine period. There were no interior windows in Byzantine buildings as in Turkish or Islamic buildings. Stained windows were common in the 10th and the 12th century Byzantine churches especially in big and important churches. They can be painted with figures and motifs or only colored ones.

It is an accepted truth that the art and the culture of every nation are affected by those of earlier and neighboring civilizations and the Seljukian art is no exception. The Seljuks, the newcomers of Anatolia from Central Asia created a civilization that was exemplified by the Hittites, Phrygians, Lydians, and Lycians, all of which contributed to pre-Hellenistic, Hellenistic, and Byzantine art of Anatolia. They adapted techniques and styles of surrounding civilizations to their Islamic structures together with Persian traditions and styles. Therefore, it is not easy to manifest the origins of different sorts of employment of glass as the window material (Bakırer, 1986). Moreover, written records are scarce and glass findings belonging the Seljukian period is very rare because of the fragility and heavy deterioration of the material in burial conditions. The Seljuk buildings have been repaired for many times, and hence some changes have occurred. But then again it is still possible to throw some light upon the use of glass in the Seljuk period in Anatolia. Scientific studies can help to find answers.

It is generally believed by many art-historians that window panes of glass were not used in public buildings such as mosques and medreses in the Anatolian Seljukian period (Bakırer, 1986). The openings on the upper walls could have been closed with onyx which is translucent enough to let the light come inside (Bayramođlu, 1974). The windows, especially base windows seen in these historical buildings have been added later in the Ottoman period (Bakırer, 1990). Restoration or renewal of these architectural units made it impossible to understand the original forms. The stone and tile frames found in window openings in İnce Minareli Medrese (Konya) could indicate the use of glass as window pane; even if so, it must

have been applied for its decorative beauty rather than the illumination of the buildings. Window panes produced for mostly decorative purposes had special designs such as “qamariyya” or “umbrella” mentioned before. Additional style for exterior windows was the “elephant-eye” or “fil-gözü” in Turkish (figure 13c). Grilles pierced in round or hexagonal openings were filled with mainly colorless glass pieces cut in the appropriate shape. Small stained-glass pieces were called “Gözenek” (Bakırer, 1990). A few pieces made in elephant eye style have been excavated together with a magnificent glass plate in the remains of the Kubad-Abad Palace which was built on the west bank of the Beyşehir Lake (Konya) by the Seljuk Sultan Alaeddin Keykubad I in 1221. These round glasses and other colored glass pieces embedded in stucco grille indicate the use of glass in both exterior and interior windows in private buildings. The window pieces found in the Palace had stucco remains attached to their corners. Unlike Byzantine pioneers, the Seljukian window openings consisted of two parts being exterior and interior (Önder, 1967).

2.9 Alanya (Alaiye) Castle

Alanya Castle (Alanya Kalesi) is a medieval castle in the southern Turkish city of Alanya. Most of the castle was built in the 13th century under the Seljuk reign following the city's conquest in 1220 by Alaeddin Keykubad I. The city was named as Alaiye to honor the Sultan. The castle was built on the remnants of earlier Byzantine era and Roman era fortifications. The castle is located 250 meters high on a rocky peninsula jutting into the Mediterranean Sea, which protects it from three sides. The Sultan strengthened the castle walls, built a harbor and a docyard, and to protect them a tower called Red Tower (Kızıl Kule). He finally built a palace for himself in the Inner Castle (İçkale). After the fall of Anatolian Seljukian Empire, the city was set under the control of Karamanogulları in 1293. In 1427 it was sold to Mamlukians. After the area was pacified under the Ottoman Empire, the castle ceased to be purely defensive, and numerous villas were built inside the walls during the 19th century.

Following the survey started at the Alanya Castle in 1985 by Prof. Dr. Oluş Arık, the excavation has been carried out in the year 1986 to uncover the ruins of the building located in north-western and south-eastern direction in the south-eastern part of the Inner Castle which is regarded as the Seljukian Palace (Arık, 1987). In the following excavation in 1987, the filling rubble has been removed, and the remains of a rectangular structure (XIV) with a size of approximately 2.45 x 3.15 m., and 6 m. height has been appeared (Arık, 1988). Here, glass fragments in dark blue, blue, yellow, and greenish colors have been found. The room XIII adjacent to the room XIV through an entrance which had been a window opening was built before XIV in north-east south-west direction (Figure 15). Here, some other glass pieces giving no clue about their shape or function have been found in the rubble.

During excavations in 1997 and in 1998 glass fragments have been found in the north section of Inner Castle at the corner where the Bayrak Bastion and the surrounding wall of the Inner Castle meet. Excavations went on at the north part of Inner castle in 1999 and the ruins of a structure with two rooms have been recovered in the area where the wall of Inner Castle meets with the city walls (Figure 14). In the room B heavily weathered glass pieces have been found (Arık, 2000). The structure called Vaulted Ward (Tonozlu Koğuş) located at the north part along the eastern wall of the Inner castle and forecourt between the gate of Inner Castle and the Palace respectively are other areas where glass fragments have been excavated (Figure 14). The forecourt extending out of the Inner Castle has been continuously used for farming by the local people since 1950s, and therefore has been seriously damaged (Arık, 2000). Findings dated to Hellenistic, Seljuk, and Ottoman period have been found together in this very same place. Window panes in various colors and glass cup pieces were among the findings.



Figure 14 Alanya Inner Castle excavation site (Arik, 2000). The sections where window pane fragments were found are marked with red dots

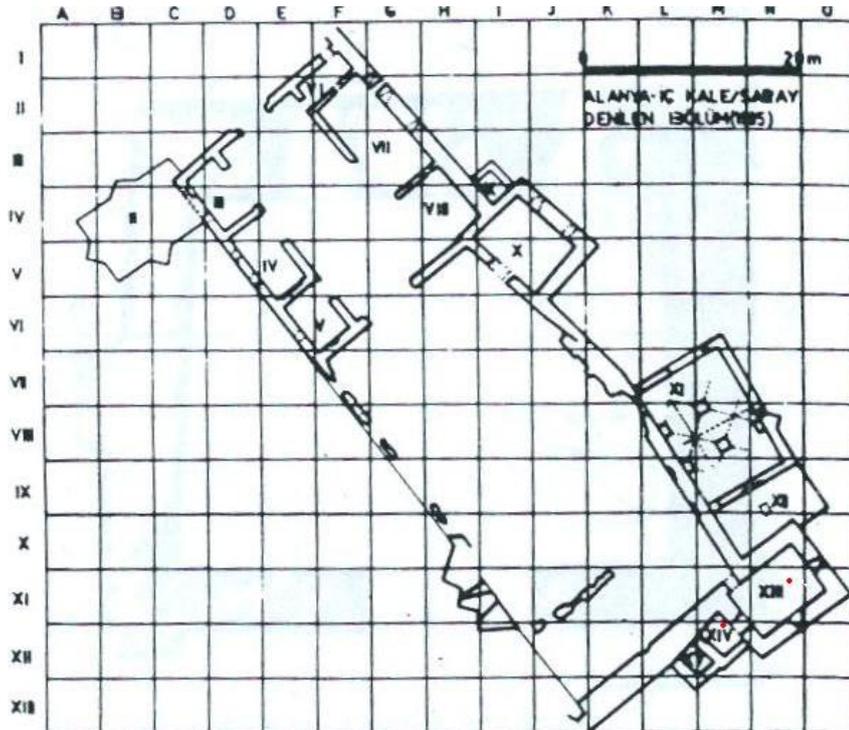


Figure 15 The Seljukian Palace in the south-eastern border of the Inner Castle in Alanya excavation site (Arık, 1987). The rooms XIII and XIV are marked with red dots

The Vaulted Ward with many sections was also very rich in glass findings. In Section III cobalt-blue window pane and a few honey-colored cup pieces have been found. In Section IV, again honey-colored pieces and purple window pane have been excavated. In Section V turquoise window pane and honey-colored cup fragments have been collected. In Section VI purple window pane has been found. In the north-west part of Section IX too many broken glass pieces have been excavated. Honey-colored cup pieces, cobalt-blue and turquoise window glass pieces were extensive. In Section X at Vaulted Ward at the Inner Castle pieces with honey-yellow color and the edge and body fragments of window glasses colored in navy-blue, cobalt-blue, and dark green have been found. At the west part of the Watching Patio (Seyir Terası) bordering the Inner Castle along the north margin the ruins of the structure called Court with Fresco (Freskli Avlu) have been uncovered in 2000. Here, cobalt-

blue, blue, green, and honey-yellow colored pieces of edges and bodies of glass panes, and also honey-colored cup pieces have been excavated. In the year 2000 excavations went on out of the Inner Castle. The Byzantine wall extending in north-west and south-east direction and bordering the area along the south margin, and two bastions (towers) located on the line of the wall were investigated (Arik, 2002). While removing the rubble in one of the towers, a structure attached to the wall from inside was discovered. Since the function of the structure was not understood, it was called "Undefined Structure". Excavation went on here during 2001 campaign. Here, many broken glass pieces in varying colors have been found.

During excavations in 2002 the structure called Vaulted Galeria (Tonozlu Galeri) has been appeared completely (Arik, 2003). It is a corridor-like structure located at the south-west part of the Palace. Here, window panes in varying colors have been found. It has been found that the panes with diameters changing between 14 cm. And 24 cm. had two different edge profiles with and without ribbon. All were horizontally flat and slightly concaved pieces with uneven thicknesses from the edge towards to center. It is interesting that when the iridescence layer on the honey-yellow panes has been removed, the pieces have become incredibly thin (Arik, 2003). In the same year, excavations went on around Cistern (Sarnıç) (Figure 16), and small glass pieces have been found.

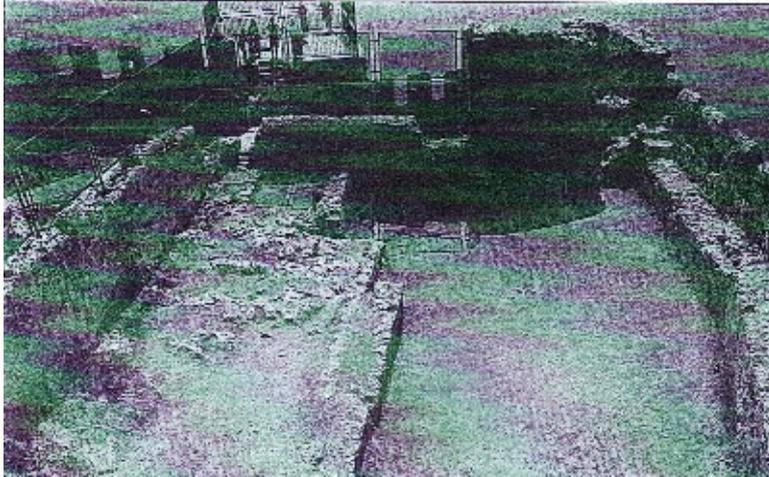


Figure 16 The view from Watching Patio at the north side of Inner Castle (Arık, 2002)

In 2003, the Church building (Şapel in Figure 14 and 17) located opposite to the entrance to Inner Castle gave glass findings, especially the rim and the bottom parts of glass cups (Figure 18). In 2003 and 2004, excavations continued at Vaulted Galeria; at the area between the eastern part of the Church and Vaulted Ward; inside the church building; and at the area between the Church and Cistern (Arık, 2005). In the deep hole discovered in the Church, many glass fragments which seemed to have been swept away for some reason with many ceramic pieces were found. No other glass findings were recorded at the following excavations outside the Inner Castle in the years 2005 and 2006 (Arık, 2007). Alanya site excavations ended in 2008.

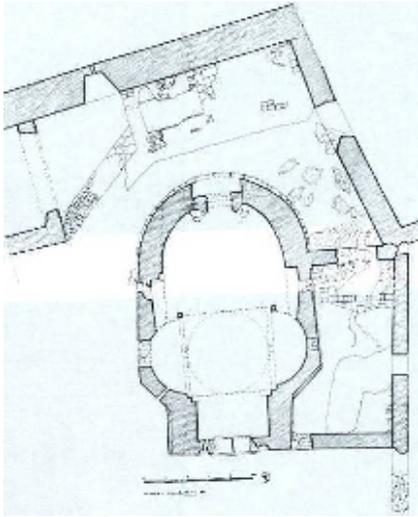


Figure 17 The plan showing the area between the south end of the Vaulted Ward and the north part of the apsis of the Church and the gate to the Inner Castle (*Arik, 2004*)



Figure 18 A few glass cup pieces found at the site (*Arik, 2004*)

CHAPTER 3

MATERIALS AND METHODS

In this study, a number of glass pieces recovered in the excavations at Alanya archaeological region have been examined with an archaeometrical point of view. Among these, the 7 samples (A19-A25) were studied before (Aksoy, 2006).

3.1. Glass Samples and Their Visual Discription

The 18 samples (A1-A18) were initially abraded with lens cleaning tissue and washed distilled water to remove accumulated dirt (if present). They were then photographed, and directly examined by an optical microscope. The glass pieces studied are given in Figure 19.



Figure 19 Glass pieces studied

Except AL1 and AL18, all samples were found to be the window panes (Bakırer, 2008). The surface structures, and the bubbles and their shape and orientation within the structures were determined by microscopic observation. The thicknesses of the pieces have been determined by vernier caliper. Their colors have been determined by Munsell Color Chart. The results are given in Table 5.

Table 5 Visual Colors and Munsell Codes of the samples studied

Sample	Visual color	Munsell code
AL1	honey-yellow	5Y 8/6
AL2	amber	5Y 6/10
AL3	navy-blue	5PB 3/8
AL4	turquoise	10BG 5/8
AL5	green	7.5GY 3/6
AL6	navy-blue	10B 2/6
AL7	purple	10RP 2/2
AL8	dark bue	10B 2/6
AL9	amber	5Y 6/8
AL10	purple	2.5R 2 / 4
AL11	amber	2.5Y 6/10
AL12	purple	10YR 5/2
AL13	navy-blue	2.5PB 3/10
AL14	blue	2.5PB 3/10
AL15	purple	2.5R 2/8
AL16	purple	2.5R 3/4
AL17	green	10GY 4/8
AL18	honey-yellow	5Y 8/6

The samples studied before (Aksoy 2006) have been included in this study in order to enrich the statistical analysis. The remainder 18 samples studied within the

scope of this study (AL1-AL18) were analyzed by XRF as well. The XRF results obtained from the previously studied seven samples and the other eighteenth samples have been interpreted together.

3.2. X-Ray Fluorescence (XRF) Analysis of the Samples

The elemental analysis of the samples has been carried out by polarized energy dispersive X-Ray Fluorescence spectrometer (PED-XRF) (see the properties of the instrument in Appendix A).

Samples were prepared by grinding the pieces into a fine powder in an agate mortar and pestle. The resulting powders were then mixed with a special wax in a 1:10 ratio. Then the pellets were prepared and put into the sample holder and XRF analysis was carried out. In the analysis major, minor and trace elements present in the glass samples have been determined. The results have been expressed as percentage concentrations of element oxides for major and minor elements and as parts per million (ppm) for trace elements. Precision was better than 0.6 % for major and minor elements and about 3 % for trace elements. The XRF analysis allowed determination of all the chemical components that characterize the glass fragments examined excluding boron, lithium, and fluorine which were lost on ignition (950 °C). The composition of the analyzed fragments as given by XRF is shown in Table 6. Trace elements given in ppm have been converted to percentage concentrations to investigate the correlations between variable components making together the bulk glass.

The results of XRF analyses of the previously analyzed samples (A19 – A25) and the ones examined within the scope of this study (A1 – A18) have been evaluated together in statistical analysis. XRF results have been used here as a data base for cluster analysis to give some insight into the similarities between the Alanya glasses involved.

XRF analyses have revealed that all the pieces are soda-lime-silica glass with silica as the glass former; Na₂O and K₂O as the alkali fluxes; and CaO and MgO as the alkaline earth stabilizers. Silica content varies 60.1 % and 77.2 % with the

average of 68.22 %; Na₂O content varies between 7.5 % and 15.0 % with the average of 11.3 %; K₂O content varies between 1.2 % and 3.8 % with the average of 1.8 %; CaO content ranges between 4.5 % and 13.6 % the average being 6.7 wt %; and MgO content ranges between 0.3 % and 3.2 % the average being 0.9 %.

3.3. Statistical Analysis of the Sample Data

Statistics and statistical methods has been widely used in archaeological research in recent years (Henderson, 1989; Sherdian, 1989) because, the verified statistical data allowing comparative examinations enhance the prospects for further understanding of the ancient glass industry, and hence generates a base for further studies on ancient glasses.

The results from the XRF determinations were subjected to cluster analysis. Hierarchical Cluster analysis (HC) was applied to the chemical data from the two components, K₂O (potash) and MgO (magnesia) of all 25 glass samples in order to verify the presence of compositional groups of glass fragments differentiated in their probable alkali sources. The measurement of distance used in the assignment rule was based on Ward's Linkage and Euclidean Distance algorithm. The results are presented in the form of a dendrogram (Figure 39 in Chapter IV) showing in the graphical form the distance between the glass samples on the basis of their K₂O and MgO concentrations. Bivariate scatter diagrams of K₂O versus MgO were performed using MINITAB statistical software. The scatter plot graph of 25 samples is presented in Figure 38 (Chapter IV).

In order to investigate the type of silica source used to produce these 25 glasses Al₂O₃ (alumina), Fe₂O₃ (iron), and TiO₂ (titania) contents of the samples have been compared. Scatter plot graphs are given in Figures 40, 41 and 42. The coloring metal oxides as impurities in the glass pieces have been studied to understand the color modification in the samples, and also to be able to indicate possible sources where the colorants were extracted from. For cobalt, CoO versus As₂O₃ scatter plot is given in Figure 48; and for copper, CuO versus SnO scatter plot is given in Figure 47.

CHAPTER 4

RESULTS AND DISCUSSION

Results of the experiments will be discussed in three headings: visual examination; microscopic examination; and elemental compositions of the samples.

4.1. Visual Examination

Visual observations of the 18 pieces revealed that all of the flat glass pieces were the broken parts of window panes which had been cut into pieces and trimmed into different geometrical shapes before being assembled within frames. Two pieces, AL1 and AL18 were broken cup pieces as they were not horizontally flat but concaved ones having even thicknesses at all points (Figure 20a and 37a). The length of the pieces changes between 2 cm. and 6.5 cm. The edge profiles showed that the pieces with ribbons (AL3, AL6, AL8, AL9, AL11, AL12, AL13, AL14, and AL15) were the borders of window sheets whose corners had been flame-rounded or had been folded over to make the glass pane stronger (Figures 22a, 25a, 27a, 28a, 30a, 31a, 32a, 33a, and 34a). The edges of other flat pieces (AL2, AL4, AL5, AL7, AL16, and AL17) represented no identifiable angular edges which could give some clues about the geometrical pattern of the whole pane of each piece (Figures 21a, 23a, 24a, 26a, 35a, and 36a). AL15 and especially AL10 had misshapen character; they were not as flat as a window pane should be. Probably they had been worked as window panes but they lost their shapes for some reason (Figures 34a and b).

The measured cross sections of the pieces revealed that the thicknesses of the pieces change between 0.01 cm. and 0.31 cm. Such thin pieces might have not been the parts of exterior window panes; they could only be the decorative pieces inserted

into the grids or grilles of interior windows; or installed at the upper parts of the architectural units, e.g. arched doors or vaulted corridors inside the building. The thinnest piece with an even thickness of 0.01 cm (AL2) was the most fragile one with layers of iridescence corrosion (Figure 21a). The thickest piece, AL7, had two thicknesses of 0.29 cm. at its left part and 0.32 cm. at its right with the average thickness of 0.31 cm (Figure 26a). For all the flat pieces the thicknesses were uneven at the body but did not reveal big differences. However, for some border pieces, the thicknesses differed in the ribboned edge and the body part being much thicker at the ribbons. It seemed that some pieces had been folded over twice at the edge, and some had been folded for almost four times to make the piece stronger during the shaping operations. For example, although it had a thickness of 0.09 cm. at its body, AL14 revealed a thickness of 0.30 cm at its ribbon. AL15 had a ribbon thickness of 0.31 cm. and a body thickness of 0.18 cm. Similarly, the thickness of AL2 was 0.27 cm. at the ribbon and 0.11 cm. at the body. The thickness of AL9 was 0.16 cm. at the body and 0.31 cm. at the ribboned edge. For the rest of border pieces with ribbons and with flame rounded edges (AL3, AL6, AL8, AL11, and AL13) thicknesses did not reveal such differences at either the edge or at the body parts. AL1 revealed an average thickness of 0.22 cm. at its middle part and of 0.10 cm. at the rim. Similarly for AL18, it gets thinner towards the rim indicating that the cup pieces of the period had been shaped in this way.

The samples generally appear to be well-preserved with no significant evidence of heavy weathering. AL1 and AL18 were slightly covered by a patina layer on surface due to accumulation of dirt caused by being remained in contact with soil for long periods of time. AL2, the thinnest piece had an iridescence layer on both surfaces accompanied with the aggregated brown stains giving partial opacity to the glass as it can clearly be seen in the photograph (Figure 21a). Similarly AL9 and to a lesser extent AL12 had iridescence weathering with aggregated inclusions filled with alteration materials that caused local dulling and laminated patterns on the surface (Figures 28a and 31a). All the other glass fragments had more or less hemispherical, longitudinal, and/or dendritic cracks and pits filled with dirt along the surface. AL11, which was the shiniest piece, had scratches on the upper side only.

Interestingly, the color was darker towards the middle part of the fragment (Figure 30a).

Such browning was probably the result of compositional or operational failure occurred at the production stage of the glass; and not related to the deterioration of the glass. The opacity of AL10 and AL15 seemed to be the result of the excess soil that coated on almost the whole surfaces of the pieces, however; soil which seemed to have been smeared over the surfaces was not responsible for the dark color of the pieces (Figures 29a and 34a). The dark color of AL10 was the result of the addition of large amounts (approximately 2.4 wt. %) of manganese (MnO) which makes the glass practically translucent to visible light and in lamplight.

4.2. Examination with Optical Microscope (OM)

The 18 pieces have been examined by optical microscope and it has been found that differing manufacturing techniques were employed to make window panes. Cylinder-blown technique seemed to be likely as a production technique for the majority of the pieces studied. This technique can produce thin panes with thicknesses less than 0.2 cm. (Harden, 1959). Microscopy observations revealed that AL2, AL3, AL6, AL8, AL9, AL12, AL13, AL14, and AL16 might have been produced by cylinder-blown technique (Figures 36-44). They all had elongated bubbles caused by hanging down the blown gob of glass while making the cylinder which then had been flattened. The bubbles had lengthened downwards in parallel alignment. The orientation of air bubbles is not the only indicator of cylinder-blown sheets; the existence of parallel grooves can also be the sign of flattening of a cylinder glass into a sheet (Wolf et al., 2005). AL6, AL8, AL9, AL13, AL14, and AL16 had groove layers associated with with the elongated bubbles.

The pieces with prominent grooves caused by gathering much glass onto the blowpipe before inflation tend to be slightly thicker than the ones with evidently smooth upper and lower sides (Wolf et al., 2005). AL8, the relatively thicker sample (with an average thickness of 0.25 cm.), had a structure with swirling lines that manipulation with a tool during flattening operation was probable. AL7 also had

swirls along with parallel grooving layers (Figure 26b). On the other hand, the curved ripples observed in AL6, AL8, AL13, and AL16 may be the indicators of crown technique. AL4 and AL10 had bubbles which kept their natural spherical shapes. The groovy structure of the pieces might have been the result of the accumulation of the excess molten glass which was poured onto a flat surface during shaping process of casting technique (Figures 23b and 29b). Crown technique could be likely for AL10 as the lines vertically cutting the groove patterns might have been the results swinging the disc of glass in one direction only. Nevertheless crown technique produces much thicker panes; therefore it is not easy to state anything definite about the production technique for AL10. The cup pieces AL1 and AL18 had glossy or fire-polished surfaces at both sides.

If the weathered surfaces are not considered, it can be stated that AL5 and AL17 had relatively smooth and bright surfaces. They had no elongated bubbles and/or grooves. After pouring or blowing, the panes might have been left to sink down without any interference with any tool, or addition of extra glass melt. AL11 had the most bubbles which had given them a knobby appearance. It seemed not possible to imply any production technique employed for it. However, insufficient melting temperature or any other interference during firing leading the entrapment of gases can be suggested for the piece (Figures 21b and 30b). AL15 did not give a clear appearance, and thus it is not possible to suggest anything about its production technique (Figure 34b).

4.3. Photographs of the Samples

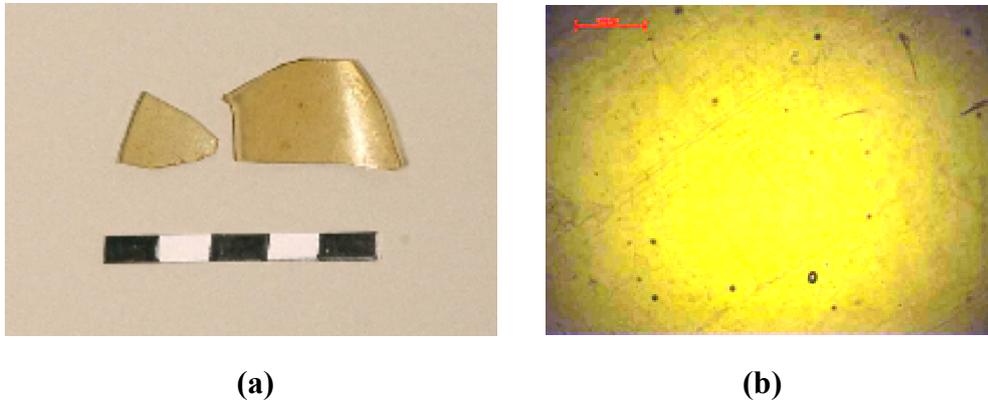


Figure 20 (a) 1:1 scaled and **(b)** OM photographs of the sample AL1

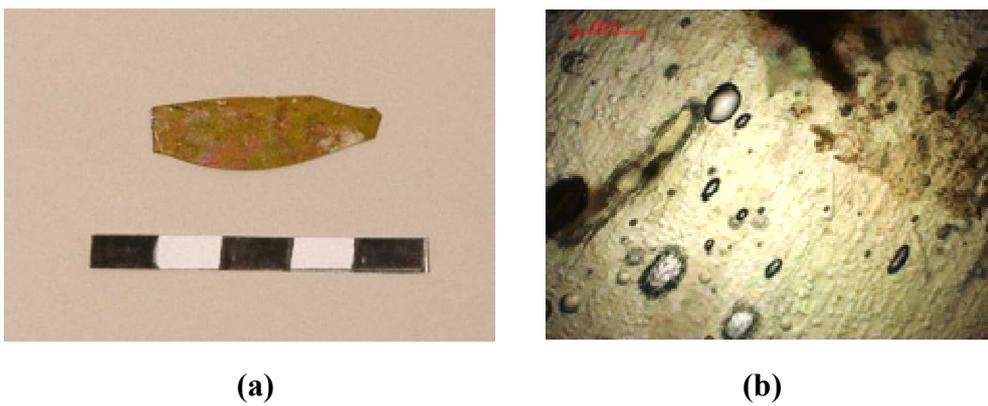


Figure 21 (a) 1:1 scaled and **(b)** OM photographs of the sample AL2

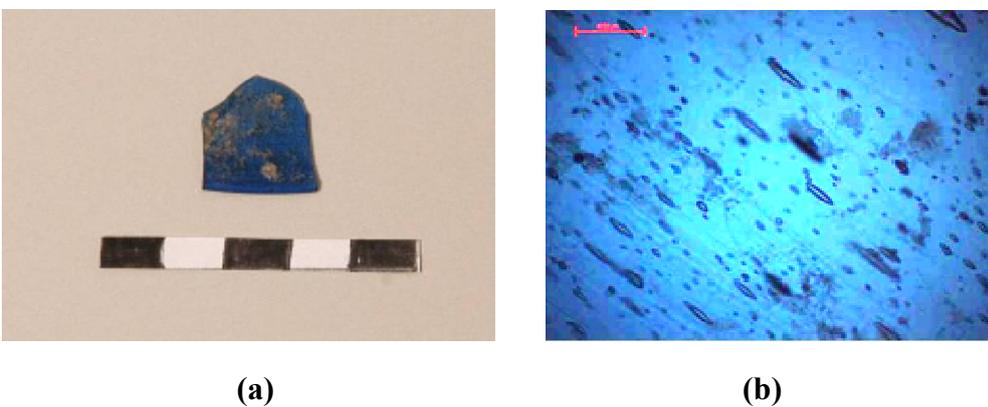
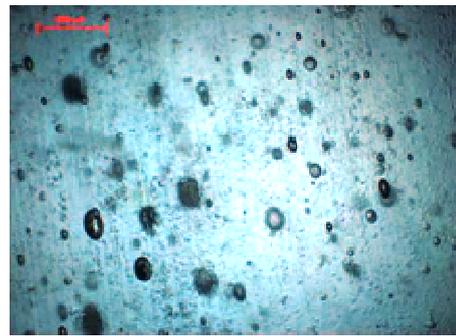


Figure 22 (a) 1:1 scaled and **(b)** OM photographs of the sample AL3



(a)



(b)

Figure 23 (a) 1:1 scaled and (b) OM photographs of the sample AL4



(a)

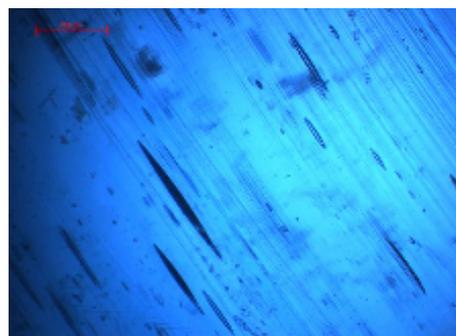


(b)

Figure 24 (a) 1:1 scaled and (b) OM photographs of the sample AL5



(a)

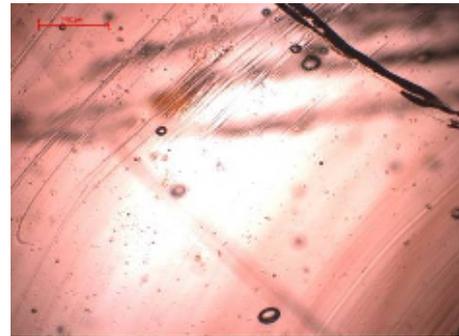


(b)

Figure 25 (a) 1:1 scaled and (b) OM photographs of the sample AL6



(a)

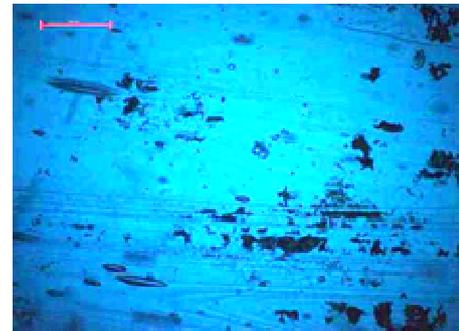


(b)

Figure 26 (a) 1:1 scaled and **(b)** OM photographs of the sample AL7



(a)



(b)

Figure 27 (a) 1:1 scaled and **(b)** OM photographs of the sample AL8



(a)

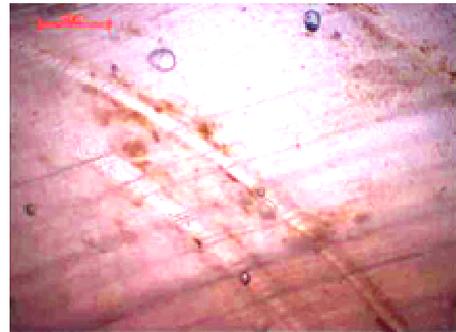


(b)

Figure 28 (a) 1:1 scaled and **(b)** OM photographs of the sample AL9



(a)



(b)

Figure 29 (a) 1:1 scaled and (b) OM photographs of the sample AL10



(a)

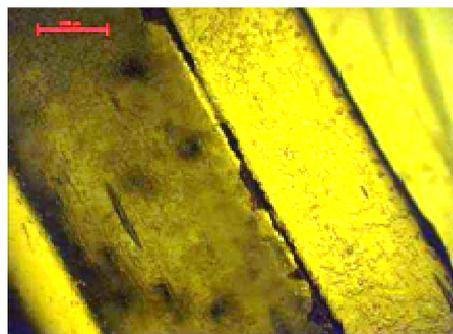


(b)

Figure 30 (a) 1:1 scaled and (b) OM photographs of the sample AL11



(a)

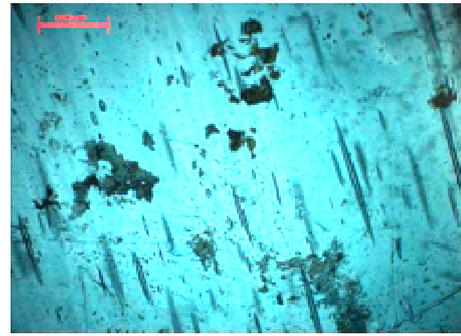


(b)

Figure 31 (a) 1:1 scaled and (b) OM photographs of the sample AL12



(a)

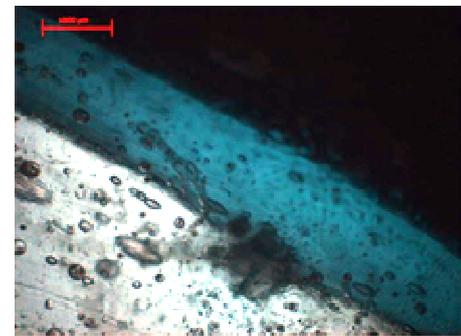


(b)

Figure 32 (a) 1:1 scaled and **(b)** OM photographs of the sample AL13



(a)

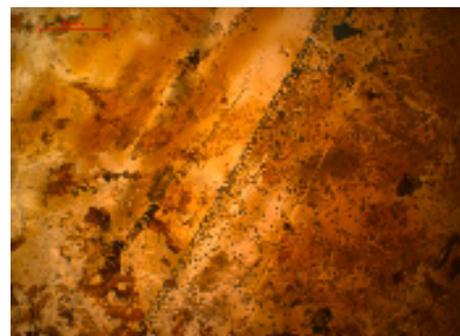


(b)

Figure 33 (a) 1:1 scaled and **(b)** OM photographs of the sample AL14



(a)



(b)

Figure 34 (a) 1:1 scaled and **(b)** OM photographs of the sample AL15

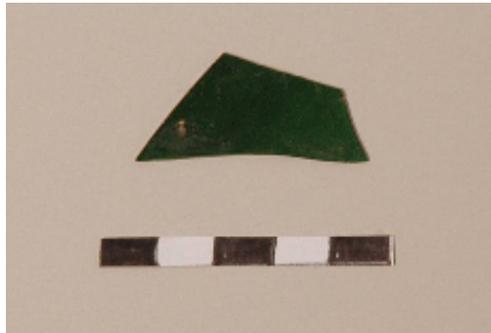


(a)



(b)

Figure 35 (a) 1:1 scaled and **(b)** OM photographs of the sample AL16



(a)

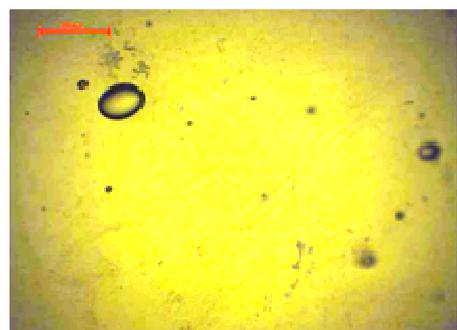


(b)

Figure 36 (a) 1:1 scaled and **(b)** OM photographs of the sample AL17



(a)



(b)

Figure 37 (a) 1:1 scaled and **(b)** OM photographs of the sample AL18

4.4. Elemental Composition of the Samples

Due to its network structure, glass can host a very large number of chemical elements. The analyzed elements include the major and minor elements which are Si, Ti, Al, Mn, Mg, Fe, Ca, Cl, S, Na, K, V, and Cr; and trace elements commonly investigated in the analyses of historical glasses: Nb, Zr, Y, Sr, Ce, Ba, La, Ni, Co, Cu, Sb, Zn, As, and Pb. XRF results of 25 samples from Alanya showed that the samples studied are all soda-lime-silica glasses. It is better to interpret the results of analyses with respect to glass components, namely the former (silica); fluxing agent (mainly Na₂O); stabilizer (mainly CaO); and the colorants. The results are given in Table 6. Silica content varies between 60.1 % and 77.2 % by weight with the average of 68.22 %. Fluxing agent Na₂O (soda) content varies between 7.5 % and 15.0 % by weight with the average of 11.3 %. Stabilizer CaO content varies between 6.76 % and 8.22 % with the average of 6.37 %. The other fluxing agent K₂O (potash) content varies between 1.2 % and 3.8 %, the average being 1.8 %. The other stabilizer MgO content is in the range 0.3-3.2 % with the average of 0.9 %.

Table 6 Element compositions (%) of glass samples studied

Element	Na₂O	MgO	Al₂O₃	SiO₂	P₂O₅	SO₃	Cl
AL1	13.210	1.115	3.562	63.780	0.092	0.086	0.503
AL2	10.860	0.589	1.626	62.290	0.074	0.077	0.824
AL3	14.990	0.703	0.788	72.490	0.017	0.101	0.881
AL4	9.560	1.400	0.362	71.360	0.203	0.168	0.852
AL5	11.800	0.738	1.816	69.890	0.068	0.131	0.696
AL6	10.600	0.495	0.612	65.650	0.067	0.095	0.889
AL7	7.670	0.271	0.609	68.940	0.003	0.027	0.622
AL8	11.640	0.613	0.736	68.960	0.072	0.082	0.844
AL9	12.570	1.126	2.584	64.230	0.130	0.146	0.697
AL10	11.700	1.306	1.326	64.070	0.362	0.126	0.781
AL11	11.270	2.145	1.475	65.070	0.260	0.258	0.773
AL12	11.600	0.577	0.886	67.060	0.079	0.051	0.796
AL13	8.060	0.360	0.587	69.370	0.055	0.041	0.737
AL14	7.450	1.297	1.355	68.440	0.248	0.124	0.613
AL15	13.380	0.629	0.943	69.430	0.085	0.051	0.843
AL16	11.700	0.799	1.377	61.860	0.083	0.097	0.516
AL17	9.450	0.620	1.489	66.040	0.060	0.130	0.634
AL18	13.860	0.892	4.057	60.120	0.081	0.125	0.625
AL19	12.780	0.611	0.995	74.770	0.085	0.080	0.826
AL20	11.740	0.704	1.682	70.990	0.062	0.144	0.671
AL21	14.240	1.155	3.767	67.270	0.111	0.079	0.615
AL22	10.180	0.435	0.540	77.160	0.044	0.025	0.728
AL23	11.660	1.151	0.681	69.550	0.430	0.129	1.016
AL24	8.4500	0.631	0.015	73.360	0.141	0.526	0.199
AL25	11.760	3.251	0.676	73.260	0.369	0.075	0.734

Table 6 (continued)

Element	K₂O	CaO	TiO₂	V₂O₅	Cr₂O₃	MnO	Fe₂O₃	LOI
AL1	1.885	6.593	0.389	0.007	0.005	0.742	2.090	6,560
AL2	1.851	8.215	0.231	0.004	0.004	0.295	1.861	11,860
AL3	1.992	5.002	0.217	0.012	0.006	0.436	2.906	0,420
AL4	2.317	6.829	0.160	0.019	0.002	0.825	1.514	2,780
AL5	1.491	7.414	0.194	0.004	0.007	1.015	2.279	0,740
AL6	1.239	6.567	0.163	0.009	0.002	1.047	1.225	9,560
AL7	1.436	7.023	0.136	0.003	0.002	1.356	1.339	10,640
AL8	1.223	4.755	0.158	0.010	0.007	1.077	1.292	6,960
AL9	1.770	7.898	0.264	0.005	0.006	0.511	1.634	6,370
AL10	3.010	9.100	0.197	0.005	0.004	2.380	1.671	3,640
AL11	1.623	6.094	0.154	0.009	0.002	0.553	1.073	9,260
AL12	1.393	5.119	0.127	0.007	0.003	1.236	1.158	9,387
AL13	1.379	5.118	0.176	0.010	0.003	1.259	1.575	9,670
AL14	1.664	5.557	0.146	0.008	0.006	0.504	1.276	9,960
AL15	1.409	5.082	0.131	0.005	0.002	1.300	1.151	5,480
AL16	1.432	5.953	0.203	0.005	0.006	1.331	1.512	12,750
AL17	1.493	7.166	0.194	0.008	0.005	1.054	2.387	2,370
AL18	1.971	5.255	0.446	0.009	0.004	0.582	2.100	9,620
AL19	1.405	5.299	0.137	0.006	0.006	1.288	1.196	
AL20	1.428	7.105	0.187	0.006	0.007	0.985	2.199	
AL21	2.024	6.790	0.432	0.007	0.005	0.811	2.175	
AL22	1.199	4.453	0.154	0.010	0.002	1.073	1.289	
AL23	3.782	8.177	0.203	0.006	0.005	1.014	1.359	
AL24	2.127	13.620	0.065	0.002	0.003	0.235	0.362	
AL25	2.004	6.108	0.110	0.002	0.004	0.113	0.845	

Table 6 (continued) (ppm)

Element	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br
AL1	32.8	20.8	270.5	34.3	8.3	8.1	15.9	0.4	15.6
AL2	13.5	23.4	76.8	28	7	16.7	17	0.6	24.4
AL3	734	18.9	655.7	10.7	3.7	13	626.7	0.7	23.5
AL4	182.4	12	18630	5	8.3	7.9	296	1.2	20.7
AL5	40.2	37	19980	4.6	2.5	12.1	77.2	0.9	15.3
AL6	202.2	38.3	14480	3.9	7.9	10.8	283.7	0.6	20.6
AL7	17.6	19.1	75.5	23.6	3.3	12.1	19.4	0.5	21.6
AL8	246.7	47.4	17010	4.2	5.3	10.3	353.7	0.6	18.7
AL9	14	17.9	243.8	25.6	5.1	8	9.6	0.5	20.8
AL10	20.7	19.8	117.2	47.6	4.2	1.2	12.6	0.6	24.8
AL11	12	12.1	92.3	17	4.1	1.2	12	1.2	23.1
AL12	18	15.6	83.9	23.7	4.3	11.1	16.1	0.4	19.7
AL13	221.7	55.7	17670	4.8	10.4	12.4	336.3	0.8	24.1
AL14	39.5	8.6	15290	3.8	3.8	5.4	91.3	0.7	17.9
AL15	17.6	12	109	23.2	3.4	10	16.4	0.4	19.3
AL16	27.4	17.5	497.7	8.7	4	10.6	28.4	0.4	15.1
AL17	36.7	39.6	20230	4.7	4.6	13.1	83.2	0.9	17
AL18	15	22.3	337.1	29.6	5.5	6.8	15.9	0.5	19.1
AL19	25.4	19.8	114	20.9	4.1	9.6	22.9	0.4	19.4
AL20	67.7	45.9	24100	5.5	2.9	11.2	98.6	0.8	14.7
AL21	27.1	24	317.3	46.6	6.6	7.5	20.4	0.4	15.7
AL22	305	57.9	19960	4.8	6.8	10.5	452.2	0.6	18.5
AL23	22.2	19.4	103.6	51.5	1.1	0.6	5.1	0.5	18.2
AL24	18.9	5.3	124.4	32.3	2.1	0.4	475.3	0.7	2.9
AL25	13	14.3	104.7	19.5	1.8	1.3	6.3	0.6	14.1

Table 6 (continued) (ppm)

Element	Rb	Sr	Y	Zr	Nb	Mo	Ag	Cd	In	Sn
AL1	85	537.5	16.6	166.3	9.3	5	< 0.1	0.8	0.9	37
AL2	94.3	822.8	6.8	64.1	6	5.8	< 0.1	2.1	2.4	5.6
AL3	95.9	603.9	6.7	67.4	4.7	4.7	< 0.1	1.7	1.8	21.3
AL4	36	648.2	1.8	44.9	5.7	5.3	< 0.1	2.1	2.1	93.4
AL5	80.5	664.7	7.2	85.6	3.3	10.7	14	1.3	1.6	664.7
AL6	65.9	556.1	5.4	64.6	6.6	4.5	10.4	1.3	1.3	49.3
AL7	75.8	589.5	6.6	45.4	3.8	11.5	< 0.1	1.4	1.4	4.9
AL8	66.1	547.2	5.9	77.4	7.7	16.7	13.4	0.9	0.9	53.4
AL9	72.8	678.5	10.7	111.5	10.8	3.2	< 0.1	1	1	26.5
AL10	19.6	1147	9.5	59.9	8.6	3.4	< 0.1	0.7	1.1	9
AL11	33.1	569.8	2.5	39.9	2.9	3.3	0.7	0.5	1.1	149.4
AL12	72.7	568.9	7.7	71.3	9	15.2	< 0.1	1	1.7	3.6
AL13	79.9	663.2	2.9	34.9	6.5	20.7	8.3	2.6	2.8	56.6
AL14	29.3	518.1	1.2	43.3	3.3	9.7	3.8	1.3	3.3	103.5
AL15	72.7	556.2	6.3	66.1	5.5	13.7	< 0.1	1.1	1.1	6.1
AL16	68.6	487.1	7.8	83.4	8.8	3.8	< 0.1	1	1	24.3
AL17	82.3	686.7	6.9	97.8	3.7	4.1	13.8	1.5	1.5	683.6
AL18	93.3	468.8	20.2	184.5	13	3.1	< 0.1	0.4	0.9	33
AL19	78.2	661.2	6.9	76	10.2	13.8	1	1.2	1	6.4
AL20	83.9	757.3	7.8	122.6	8.5	4	13.2	1.5	1.3	814.1
AL21	100	637.2	16.9	209.5	17.3	6.3	0.9	0.6	0.9	39.1
AL22	72.2	641.9	3.8	67.6	4.6	14.8	11	0.8	1.2	53.9
AL23	13	1354	3.6	65.9	4.3	6.8	0.9	0.9	0.9	9.1
AL24	26.7	209.7	2	88.1	4.2	2.8	1.1	1	1	103.2
AL25	19.1	834.9	0.9	28	3.8	3	1.1	1.1	1	37

Table 6 (continued) (ppm)

Element	Sb	Te	I	Cs	Ba	La	Ce	Hf
AL1	6.6	1.3	2.5	58.9	549.8	25.9	50.2	11
AL2	2.8	3.7	9.7	103.1	637	84	77	7.4
AL3	20.3	2.8	5.2	42.7	543	19	27	17
AL4	31.6	3.6	7.2	31.3	546	22	34	97
AL5	35.8	1.7	5.7	73.7	892.9	17.8	28.5	99
AL6	19.2	2	4.1	54	395.6	14	20	79
AL7	1.7	2.4	4.5	54	1603	33.3	38	8.4
AL8	23.4	1.3	2.6	57.8	440.3	7.9	60.4	87
AL9	3.7	1.6	3.1	51.3	565.2	14.6	15	13.7
AL10	2.2	1.6	3	5.3	710.6	13.3	16	8.2
AL11	81.5	1.5	3.5	11.6	477.8	9.9	30.9	9.5
AL12	1.3	1.7	3.2	70.5	1837	16.6	28.4	6.1
AL13	16.6	4.4	8.8	99.7	518	81	45	91
AL14	37.8	2.2	4.6	19.4	528.1	17.4	22	78
AL15	1.2	1.7	3.2	77.1	2003	26.4	15	7.4
AL16	1.7	1.7	3	58.1	369.7	16.1	26	14
AL17	39.7	1.9	6.3	72	964.7	22.1	17	99
AL18	5.2	1.5	2.8	50.4	561.9	21.9	52.7	12
AL19	0.9	1.5	3.1	68.6	1823	10	13	7.2
AL20	35.4	1.5	5.2	69.6	849	9.5	13	96
AL21	5.3	1.4	2.7	58.2	511.1	23.3	12	10
AL22	16.9	2.1	4.1	61.7	397.3	26.8	30	80
AL23	2.3	1.4	2.5	4.3	251.2	9.1	64.3	9
AL24	24.6	1.4	2.8	4	728.4	8.1	21.8	9.4
AL25	6.8	1.6	2.9	17.2	199.3	50.2	56.2	10.8

Table 6 (continued) (ppm)

Element	Ta	W	Au	Hg	Tl	Pb	Bi	Th	U
AL1	13	7.2	< 0.1	1.8	1.3	56.2	0.5	7,1	6,7
AL2	7.9	5.4	< 0.1	2.6	2	34.9	1.3	6,3	9,5
AL3	22	4.5	< 0.1	2.5	3.3	99.3	19.2	2,1	8,8
AL4	120	14	< 0.1	2.7	5.2	1470	6.3	2,2	15,4
AL5	120	12	< 0.1	2.4	3.8	1062	3.2	13,1	6,9
AL6	100	11	2.2	2.2	2.5	137.7	2.4	4,5	6,2
AL7	7.4	3.7	< 0.1	2.1	1	36.4	1.2	5,9	8,9
AL8	110	11	4.1	2.2	2.7	130.8	2.5	5,1	14,1
AL9	13	3.6	< 0.1	4.6	1.6	191.4	1.5	7,6	5,3
AL10	10	10.2	< 0.1	1.5	1.7	156.1	1.5	3,3	16,5
AL11	8.8	4.1	< 0.1	1.7	5.5	3083	4.7	22	7,1
AL12	7.7	3.1	< 0.1	1.8	0.7	37.6	1	5,1	6,5
AL13	120	14	4.1	2.8	3.1	159.6	2.9	5,2	11
AL14	100	11	< 0.1	1.8	2.6	524	4.1	4	7,3
AL15	9	3.3	< 0.1	2	0.5	37.3	0.4	5,5	6,9
AL16	17	3.4	< 0.1	1.8	0.7	90.7	1.3	5,6	6,3
AL17	130	13	< 0.1	2.6	3.7	1036	3.5	12,1	14,7
AL18	15	3.7	< 0.1	1.6	1.8	301.4	1.7	9,9	6,8
AL19	9.6	5.9		1.8	0.7	29.3	1	7	12,7
AL20	150	15		2.4	3.7	1084	3.1	11,1	12,2
AL21	16	9.2		1.7	0.7	65.4	1.1	8,9	5,4
AL22	120	14		2.1	2.6	131.9	2.3	4,9	6,5
AL23	10	4.3		0.9	1.9	365.8	1.8	4,7	5,8
AL24	10	3.8		0.9	3.5	886.6	2.8	5,8	6,2
AL25	9.2	3.8		1.2	2.1	592.2	2	4,8	5,8

Figure 38 displays the scatter plot diagram of K_2O versus MgO , and Figure 39 shows three clusters representing three distinct groups (Group 1, 2 and 3) of glass samples with different concentration levels of potash and magnesia. Since the correlation between the contents of these materials is diagnostic of the alkali source used as flux in the glass structure, it may help to search the probable sources of plants or other sodium-bearing ingredients used in sample glasses of Alanya region.

The association between the colors of samples and the impurities of Fe_2O_3 , Cu , Co and Mn they contain has been studied. An examination of these figures indicate that the element Fe (iron) exists in the form of Fe_2O_3 in all the samples of about 2 % and its existence is reflected in the samples with colors of navy blue, green, honey-yellow, and brownish yellow. Similarly, the existence of the element Cu (copper) in the samples is reflected as blue, navy blue, turquoise or green. It has also been found that all blue colored glasses contain significant amounts of Co (cobalt) as well. The existence of Mn (manganese) in glass can be related to only the purple color.

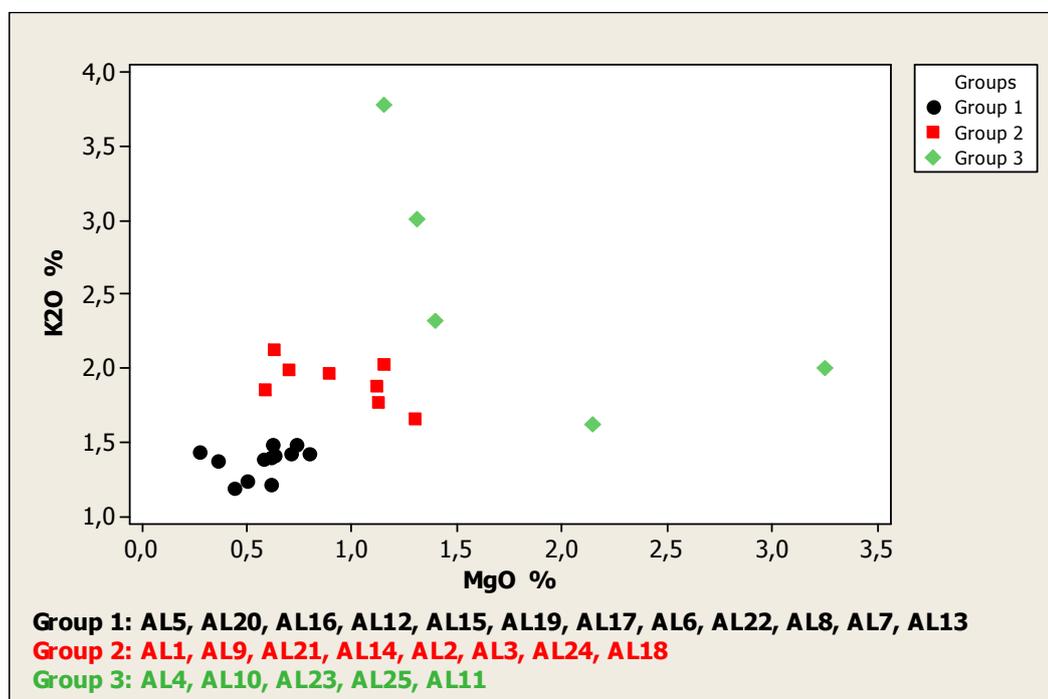


Figure 38 The scatterplot of K_2O versus MgO of 25 samples

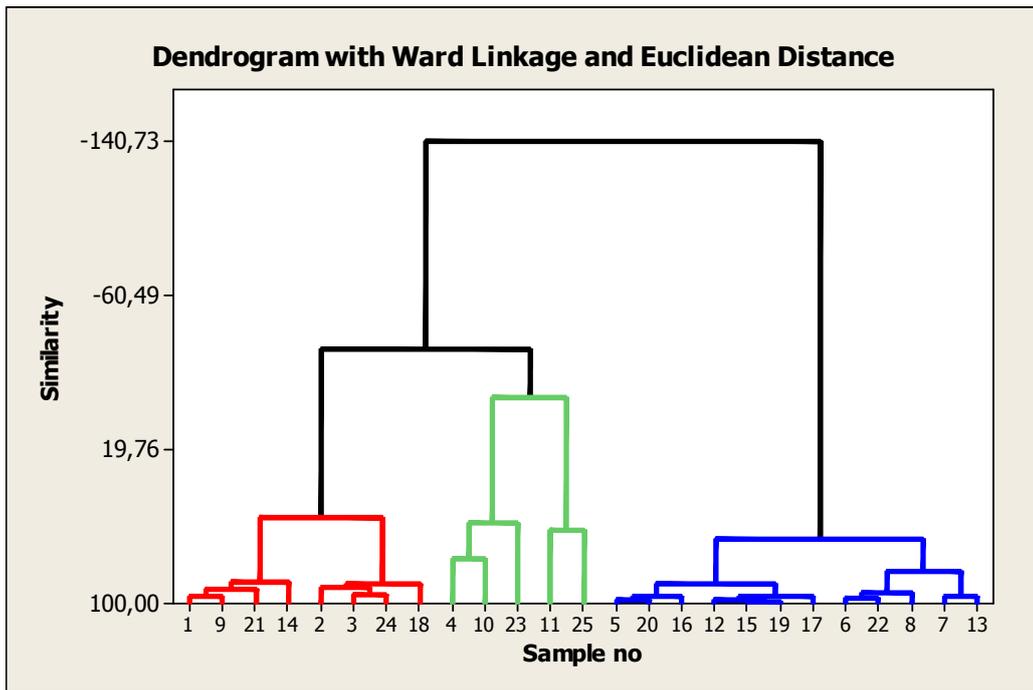


Figure 39 Dendrogram with Ward Linkage and Euclidean Distance of 25 Alanya Samples

4.4.1. Sand

Silica, the glass former of soda-lime-silica glasses was provided by sand or crushed quartz pebbles. Sands can be rich or poor in quartz. It is known that coastal sands have different contaminants than inland sands.

Quartz sands or mineralogically mature sands contain low level of trace elements; they are poor in heavy minerals and clay minerals which are likely to host elements such as thorium and zirconium (Sayre and Smith, 1974; Henderson, 1985). The low amounts of Al_2O_3 and CaO are the reflection of a pure sand, which is rich in quartz and poor in feldspars, calcite, and heavy minerals, and also has low amounts of Fe_2O_3 ($\leq 0.5\%$) (Freestone *et al.*, 2002). On the other hand impure sands or unprocessed sands import variable elements into the glass batch (Jackson *et al.*, 2005). Aluminum and iron are generally positively correlated and the presence of both in high and varying contents in the glass structure is generally indicative of sand

untreated before the batch preparation (Jackson *et al.*, 2005). Treatments such as combining, crushing, grinding, and washing of the sand before preparing the glass batch results in an improvement in the chemical composition of the sand. Such treatments help to decrease in Al_2O_3 and CaO due to carbonate and feldspar loss, and hence a relative increase in silica is observed (Silvestri *et al.*, 2008). The positive correlation between these components can also be related to crucible dissolution during melting process in the crucible. Some iron and alumina may contaminate from the crucible material to the melt depending on time and temperature (Jackson *et al.*, 2005). However, the existence of some correlation between iron and titanium indicates that both elements were introduced to the batch together as the contaminants of sand.

At first glance the elevated levels of iron in Alanya glasses studied indicate impure sand used for producing them. Iron was introduced to the batch incidentally as an impurity in the silica source. The increased iron concentrations could also be a result of a contamination from iron-containing crucible in which the raw materials were melted (Wedepohl and Baumann, 2000). The iron level of the pieces studied ranges from 0.3 % to 2.9 % by weight. Only two samples out of 25 samples (AL24 and AL25) have Fe_2O_3 less than 1 %; the former being 0.3 % and the latter being 0.8 % respectively (Table 6). Seven of the samples, which are AL3, AL17, AL5, AL20, AL21, AL18, and AL1 have very high amounts of iron, more than 2 %, that contamination from crucible or furnace refractory or accidental import of the element from other sources cannot be considered. The highest iron content (Fe_2O_3) which is approximately 3 % is seen in AL3, the navy-blue colored piece. The alumina content of AL3 is 0.7 % (Table 6). AL5, AL17, and AL20 have Al_2O_3 contents 1.8 %, 1.4 %, and 1.6 % respectively. The other pieces with high iron contents (AL1, AL18, and AL21) also have very high alumina contents being more than 3 % for each. The amount of Al_2O_3 is more than 1 % in the pieces (AL2, AL10, AL11, AL14, and AL16) having iron more than 1 %. AL9 with the amount of iron of 1.6 % has higher amount of alumina being about 2.6 %. AL24 has the lowest iron and alumina levels.

As can be seen in the scatter plot diagram of TiO_2 versus Fe_2O_3 in Figure 40, the iron and titanium amounts in most of the Alanya samples are correlated.

However, the four glasses, AL20, AL5, AL17, and AL3 with the highest levels of iron do not have much titanium and rule out the correlation. AL24 with the lowest iron has also the lowest titanium content. AL1, AL18, and AL21 with high iron more than 2 % have also significant levels of titanium.

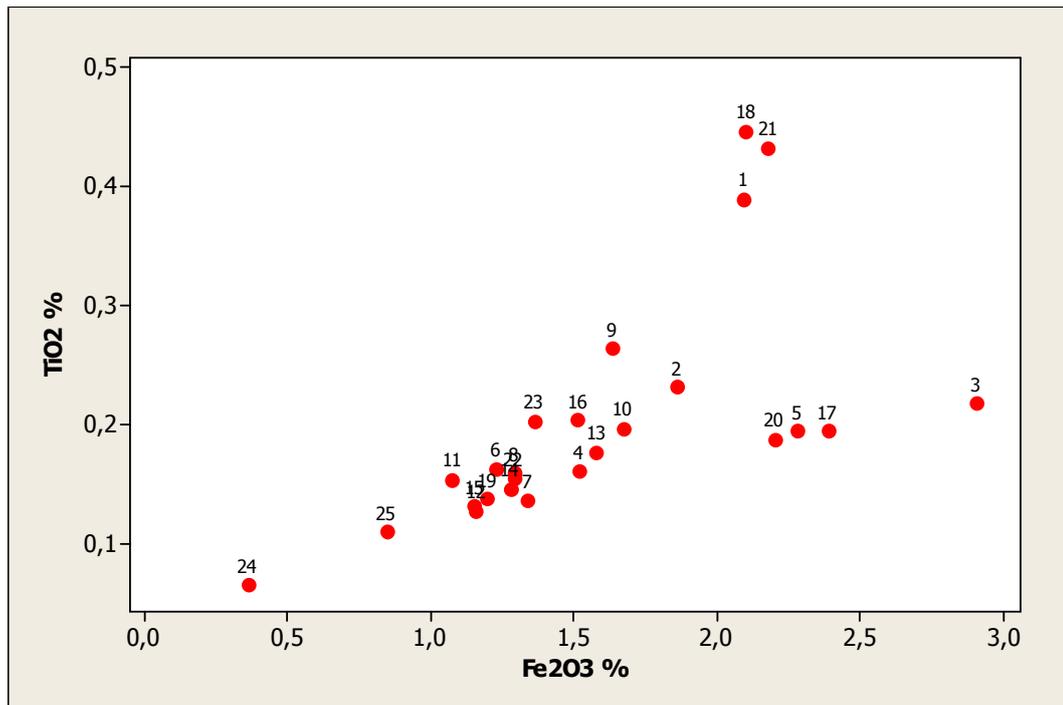


Figure 40 The scatterplot of TiO₂ versus Fe₂O₃ of 25 samples

The relationship between iron and alumina is given in the scatter plot diagram in Figure 41. Positive correlation between remarkable levels of iron and alumina may be related to crucible dissolution, in other words variable levels of both contaminate from the crucible into the glass melt depending on time and temperature of glassmaking process (Jackson *et al.*, 2003). For the glasses with alumina levels less than 1 %, the iron concentrations are varying. The sample AL3 has the highest iron concentration (2.9 %) but does not have much alumina (0.7 %). Special furnace conditions that increased the iron concentration in this glass seem quite possible when the blue color of the sample is considered. The glasses with the highest alumina levels (AL18 and AL21) have also significant amounts of iron.

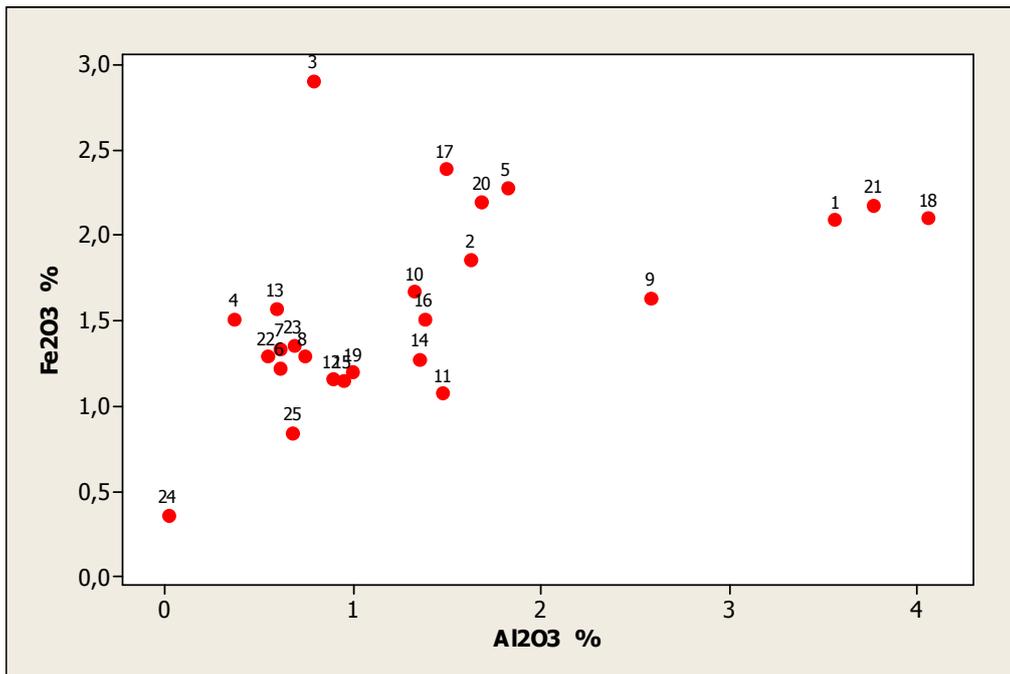


Figure 41 The scatterplot of Fe₂O₃ versus Al₂O₃ of 25 samples

It seems that for Alanya samples the relationship between alumina and titania (Figure 42) is stronger than the relation between alumina and iron. AL24 with lowest levels of alumina, iron and titanium might have been produced with purer sand whereas AL1, AL21, and AL18 seem to have been made with a silica source rich in heavy minerals. AL1 and AL21 have significantly higher levels of titanium as of aluminum and AL18 with the highest alumina content has the highest titania content as well. It can be suggested that the raw materials used to make glass cups were different from the ones used to produce window panes.

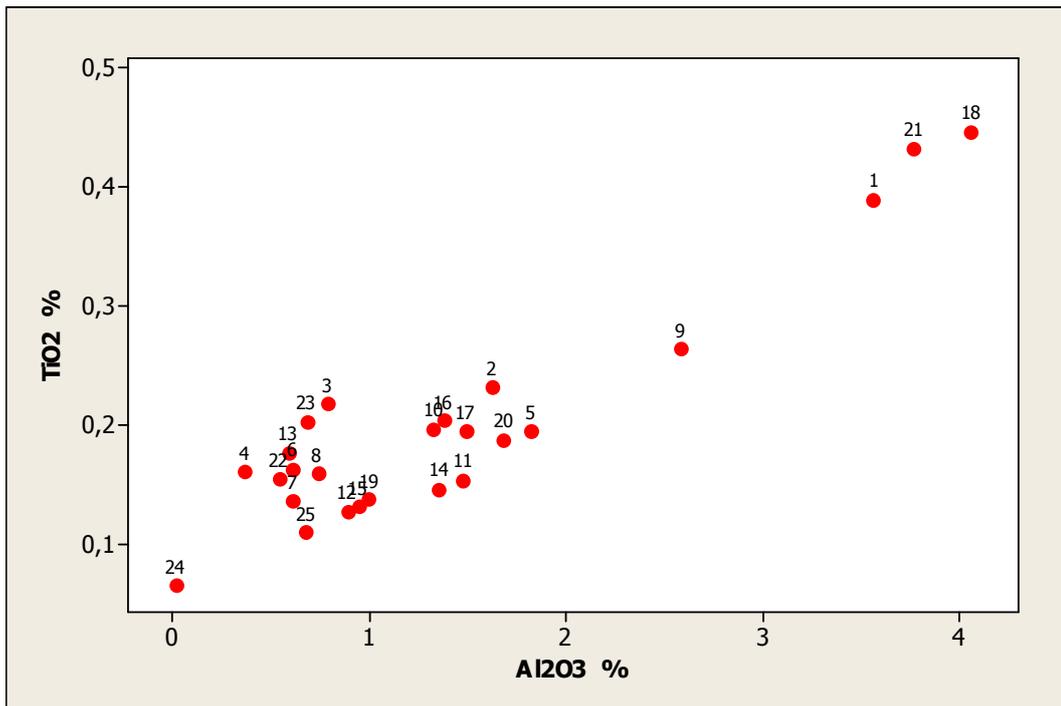


Figure 42 The scatterplot of TiO₂ versus Al₂O₃ of 25 samples

It is interesting to note that when alumina, iron, and titanium contents are compared to silica contents, the glasses are found to be highly scattered. It has been found that AL1, AL9, AL21 with high aluminum and titanium levels have relatively lower concentration of silica than the most of the glasses. AL18, which has the highest alumina and titania amounts has the lowest silica amount among 25 pieces. Apart from a few samples there is no positive correlation of aluminum and sand and of titanium and sand. The comparison of alumina to silica reveals that the contents are various and a clear strong relation is only seen in eight samples which are AL6, AL12, AL14, AL5, AL20, AL10, AL11, and AL17 on one hand; AL3, AL4, AL24, AL25, AL19, and AL22 constitute a separate group with their low titanium and aluminum and high silica levels on the other. When iron and silica contents are considered together, the samples may be classified into two main groups: one group including the glasses with low iron and high silica (AL19, AL22, AL24, and AL25); and the second one involving glasses (AL4, AL6, AL7, AL8, AL11, AL12, AL13, AL14, AL15, and AL23) whose iron amounts seem to be dependent on the silica

amounts they have (Figure 43). For the glasses of this group it can be suggested that iron had been introduced with sand into the glass batch. AL3, AL5, and AL20 with significant amounts of iron have also very high amounts of silica. AL1,AL2, AL9, AL10, and AL16 have lower amounts of silica being less than 65 %. Correlation existing between titanium and iron also depends on the fact that both elements had been mainly introduced to the glass as contaminants in the sand (Henderson *et al.*, 1985; Mirti *et al.*, 1993) although AL20, AL5, and AL3 seem to be exceptions with their high silica and iron but low titanium contents.

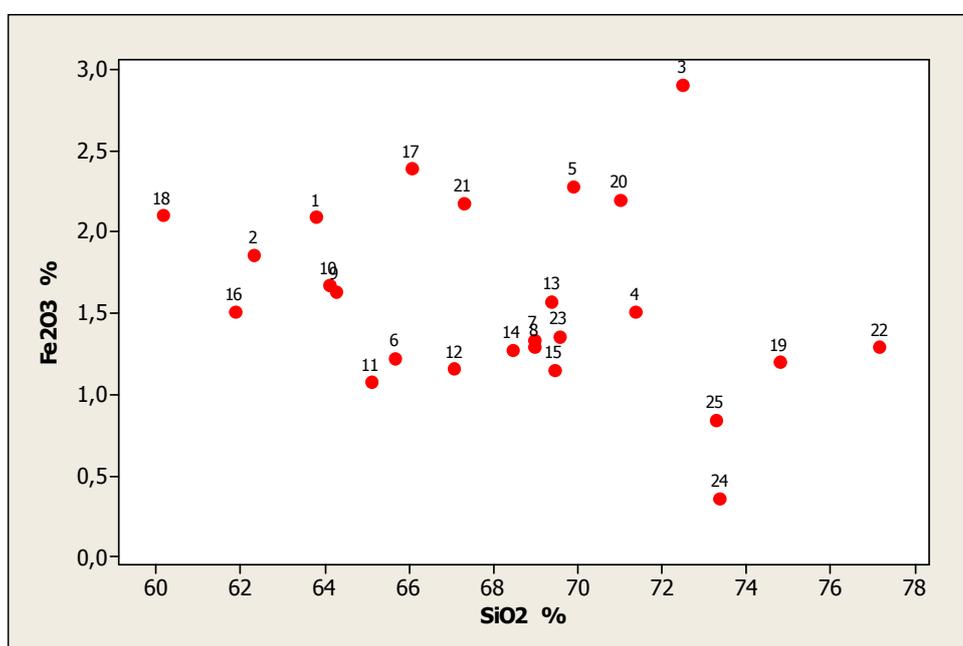


Figure 43 The scatterplot of Fe2O3 versus SiO2 of 25 samples

Scientists who investigate the historical glass from different parts of the world have classified the glasses they analyzed according to the comparisons based on the differing chemical compositions to be able to access clear identifications of ancient glasses. Despite the fact that the compositions of glasses have not been very closely defined yet, a type of glass having relatively higher levels of iron, titanium and manganese has been identified in Egypt and in the Near East of the 4th century A.D. Same type of glass dating to later periods has been found in Europe and in many

other places. It is called HIMT (High Iron Manganese Titanium) glass with the concentrations of iron more than 0.7 %; manganese at about 1-2 %; and titanium at or more than 0.1 % (Foster and Jackson, 2009). Any glass having these elements within the determined amounts with the correlation of iron and alumina can be regarded as HIMT glass. Thirteen Alanya samples analyzed (AL10, AL7, AL16, AL15, AL19, AL13, AL12, AL8, AL22, AL17, AL6, AL5, and AL23) have been found to be consistent with the HIMT glass criterion. Their MnO contents range between 1.0 % and 2.3 % with the average approximately 1.3 %; with an average level of iron at 1.49 %; and titania at 0.16 %.

It has also been stated that HIMT glasses contain elevated levels of trace elements such as vanadium, chromium (Arletti *et al.*, 2008), and barium (Henderson, 2000). Vr_2O_5 and Cr_2O_3 are minor elements detected at percentage concentrations in all Alanya glasses and barium levels are various ranging from 199.3 ppm to 1837 ppm. High levels of Ba accompanied by alumina and calcia levels in the glass are indicative of a sand rich in alkali feldspars (Silvestri, 2008). Among HIMT glasses studied, AL6, AL7, AL8, AL12, AL13, AL15, AL19, AL22, and AL23 have alumina content less than 1 % with varying amounts of calcium and barium. Among them AL8 and AL22 have less than 5 % CaO; and AL7 has very high content of calcia (7.0 %) suggesting that sands with differing amounts of alkali feldspars were used in their production. Another HIMT glass, AL10 has very high content of CaO (9.1 %). The amount of magnesia is moderate in AL10; excluding the probability of dolomite as the lime source, but it has very high content of strontium which could have been derived from deliberate shell use.

Crushed quartz pebbles contain very few impurities, and thus make a negligible contribution to the overall composition of glass (Brill, 1999). Conversely, the use of less mature sand can introduce significant amounts of alumina and lime. It is known that lime and alumina concentrations are particularly diagnostic of the sand source for soda-lime-silica glass (Freestone *et al.*, 2000). Mature sands, or in other words, pure silica sources generally contain alumina at about 1 %. The amounts of alumina ranging between 1.86 % and 3.04 % are associated with sand having feldspars (Freestone *et al.*, 2002; Henderson *et al.*, 2004). Low contents of Al_2O_3 and

CaO indicate the use of pure sand poor in feldspars and calcite (Freestone *et al.*, 2000, Freestone, 2002) while high contents of these elements indicate a sand rich in feldspars. On the other hand, calcium may derive from both sand and plant ash in varying amounts and it may also be introduced as a separate constituent, e.g. shells. Therefore, calcium alone is not diagnostic of sand source. Typical sands from the Near East and Egypt have been found to contain 2-18 wt % CaO and 1-4 wt % Al₂O₃ (Turner, 1956). The glasses assumed to have been made in Mesopotamia and Egypt during Roman and Byzantine periods have amounts of lime and alumina (2-12 % for CaO; 1.5-4.5 % for alumina) consistent with the previous glasses produced in these regions (Brill, 1999; Freestone *et al.*, 2002).

CaO versus Al₂O₃ amounts for all the analyzed glasses are plotted in Figure 44. AL1 and AL21 have moderate levels of calcium (6.5 wt % for AL1 and 6.8 wt % for AL21) which are close to the average value (6.65 %) of all 25 samples. AL18 with the highest level of aluminum has a lower content of calcium (5.2 %) than these two glasses. With the exception of AL24 and these three glasses, Al₂O₃ and CaO seem to be related to in the other pieces. It is interesting that AL24 with the lowest alumina content (0.01 %) has the highest calcium content (13.62 %). When AL24 is considered to have been produced with mature sand, its high calcium content may be the result of a separate lime source such as marine shell introduced to the glass with pure sand. It is quite interesting that all glasses from Alanya have significant amounts of Sr (strontium) although, as explained above, most of them were not produced with pure sand. Shells could have been separately used to import calcium to the glass batch, or sands from different sources were mixed, but generally this issue is unlikely for ancient glasses. AL23 which is a HIMT glass has the highest content of SrO (1354 ppm) and very high content of CaO being 8.17 %. Feldspars in the sand influence the Sr content in glass (Wedepohl and Baumann, 2000) and cause an increase in strontium levels.

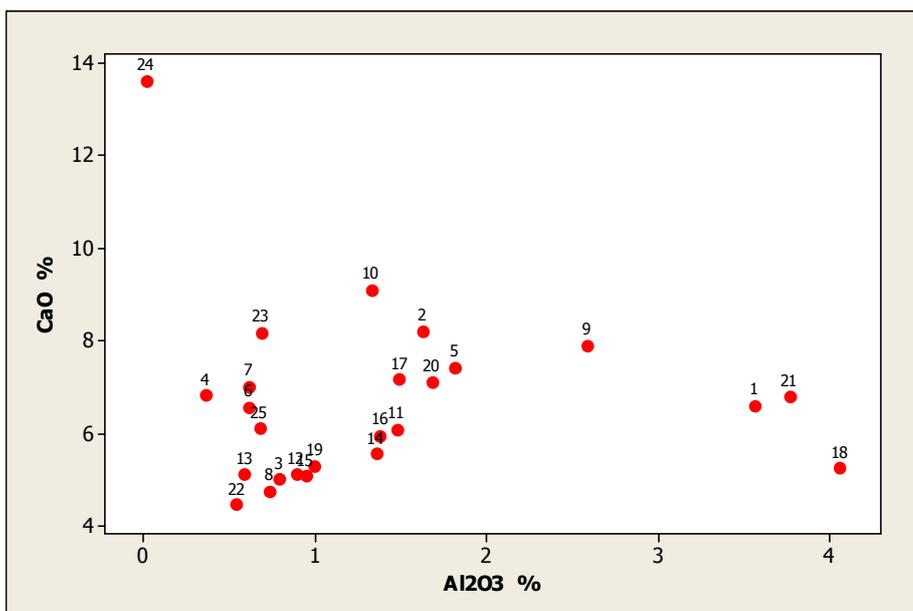


Figure 44 The scatterplot of CaO versus Al₂O₃ of 25 samples

In the glass pieces studied aluminum (Al₂O₃) ranges from 0.01 % to 4.06 %. AL9, AL1, AL21, and AL18 are distinguishable with their very high aluminum contents, which are 2.6 % for AL9; 3.5 % for AL1; 3.7 % for AL21; and 4.0 for AL18 respectively. AL1 and AL18 were the cup pieces with honey-yellow colors. The addition of alumina is known to aid glass in its resistance to aqueous attack in weathering conditions (Morey, 1964) by increasing the mechanical strength of glass. AL1 and AL18 were in good condition having less deterioration than other pieces, however; it would be assertive to claim that their bright and clear appearance depended directly on the elevated levels of alumina in these glass pieces. Among these four glasses, AL9 with the highest CaO content (7.8 %) has the lowest alumina content. However, when alumina and calcia levels of all glasses are compared the values of AL9 remain in the zone of correlation like most of the glasses.

Trace elements do not only give information about the selection of raw materials but also do they indicate the extent of recycling. Generally high levels of trace elements in the 100-1000 ppm range may suggest that earlier glasses, cullets, and frits produced in the primary centers were recycled in the secondary workshops to make new glass objects (Freestone *et al.*, 2002).

Strontium, which is geochemically similar to calcium, is mainly incorporated with the lime-bearing materials such as shell, limestone, or plant ash. High levels of strontium at about 400 ppm have been suggested by some scientists as the indicator of coastal sand used for glassmaking. Coastal sands contain large amounts of shell which incorporates strontium. Glass made with inland sand containing limestone, on the other hand, has less strontium (~ 150 ppm) but more zirconium (~ 160 ppm) (Freestone *et al.*, 2000; Silvestri *et al.*, 2008). Alanya glasses studied have elevated levels of strontium ranging from 209.7 ppm to 1354 ppm with the average of 656.4 ppm. High strontium (413 ± 32 ppm) and low zirconium (51 ± 8 ppm) may indicate coastal sand used for glassmaking (Sayre and Smith, 1974). For Alanya glasses, zirconium contents are variable differing between 28 ppm in AL25 and 209.5 ppm in AL21. AL10, AL11, AL13, AL14, AL4, and AL7 have low amounts of ZrO₂. AL4, AL11, AL14, and AL25 have not been determined as HIMT glasses. Moreover, a definite negative correlation between SrO and ZrO₂ has not been detected for the samples studied. Only considerably AL25 and AL11 which have high Sr contents have been found to be low in Zr. The samples, AL1, AL18, and AL21 have very high zirconium concentrations while their strontium levels are moderate (Table 6).

Barium and rubidium together can be diagnostic of alkali feldspars in the sand (Silvestri *et al.*, 2006). They are introduced to the batch with the sand. AL4, AL11, AL14, AL10, AL24, AL23, and AL25 have lower BaO and Rb₂O contents, and AL7, AL12, AL15, and AL19 have remarkable barium levels associated with high rubidium levels. For other glasses no correlation has been detected between BaO and Rb₂O.

Lead contents of the glasses with high alumina contents are not high. Thirteen glass samples, AL19, AL15, AL12, AL3, AL8, AL23, AL25, AL6, AL7, AL13, AL22, AL4, and AL24 have alumina less than 1 %; eight samples, AL20, AL2, AL17, AL11, AL16, AL14, AL5 and AL10 contain alumina more than 1 %. It has been stated by some scientists that pure sources of silica, i.e. chert, accounts for low levels of aluminum varying between 1 % and 1.4 wt % as an impurity. AL10, AL14, and AL16 have amount of alumina less than 1.4 %. The remainder samples, AL3, AL4, AL6, AL7, AL8, AL12, AL13, AL15, AL19, AL22, AL23, AL24, and AL25

have low amounts of alumina less than 1 %. A silica source poor in feldspars, therefore, may be suggested for these glasses.

4.4.2. Alkalis and Alkaline Earths

As mentioned before, the hierarchical cluster analysis was carried out to verify the presence of distanced compositions of glasses based on their potash and magnesia concentrations. The amounts of K_2O and MgO within a glass composition may be related to each other and when these amounts are taken into account together, it may be possible to imply the probable source of the alkali flux used to make glass. Potash and magnesia are in most cases diagnostic with the alkali source which introduces both of them together in various proportions into the glass. The dendrogram in Figure 39 displays the similarity relations between 25 sample glasses based on the K_2O and MgO concentrations of each glass.

Results of hierarchical cluster analysis confirm the clear distinction between three large compositional groups related to the contents of potash and magnesia of the samples, hereafter called Group 1, Group 2, and Group 3. Cluster analysis allowed us to subdivide Groups 1 and 3 into numerous subgroups which indeed slightly differ. The differences can be observed in the K_2O vs. MgO diagram in Figure 38 as well.

Group 1 consisting of the samples AL7, AL13, AL22, AL6, AL8, AL12, AL17, AL20, AL5, AL16, AL19, and AL15 can be classified as LMG (Low Magnesia Glass) as the samples in the group have very low amounts of magnesia which is less than 1 % and also low amounts of potash up to only 1.5 %. Group I glasses can be divided in two main groups and these two groups can again be divided in two small groups, but no need to take each small group separately as the differences between the glasses in terms of their potash and magnesia contents are too small to be considered. LMG glasses are known to be found in a broad band geography stretching from the central Mediterranean to eastern Siberia (Henderson, 2000).

AL2, AL3, AL24, AL18, AL21, AL1, AL14, and AL9 make Group 2 with their low magnesia and slightly higher potash contents. AL4, AL10, AL23, AL11, and AL25 are distinct glasses constructing Group 3 with their uncorrelated amounts of both elements. It seems possible to subdivide Group 3 in two distinct groups, Group 3a and Group 3b, based on the inverse ratios of potash and magnesia contents. AL4, AL10, and AL23 can be grouped as Low Magnesia-High Potash (LMHK) glasses. However, they are different from earlier LMHK or mixed-alkali glasses produced in Egypt by the 11th century B.C. (Brill, 1999) with their significantly high lime contents. AL11 and AL25 on the other hand exhibit High Magnesia-Low Potash (HMLK) character with magnesia content higher than 2 % and potash content lower than 2 %.

The glasses of the first group (LMG) might have been produced by using natron. Natron, in fact is the term used in literature to refer evaporate sodium sources that contain too little potash and magnesia. The deposits in the lakes change over time. It has been recently found out that the sodium carbonate mineral present in the lakes at Wadi el-Natron, which is thought to be the primary source for natron in Egypt, is almost always trona ($\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$) with remarkable amounts of chlorides and sulfates rather than any other form (Shortland, 2004; Silvestri *et al.*, 2006). However, in ancient glass literature, LMG glasses are in most cases called natron glasses. In the period including Roman Imperial period from the first millennium B.C. to the first millennium A.D. LMG glass was produced in large quantities in the primary ateliers in Egypt and was imported to many close and remote areas in the world (Henderson, 2000, 2004). Many glass findings in the Mediterranean countries dating to between 700 B.C. and 400 A.D. have revealed a soda-lime-silica composition containing 15-20 % Na_2O , and 0.5 % K_2O and MgO (Henderson, 1988).

The potash and magnesia contents of the glass pieces studied are higher than the levels found in typical natron glasses which are ought to be less than 1 % for both and about 0.1-0.2 % for P_2O_5 (phosphorus) in a 10 % soda glass phase (Brill, 1999). There might have been plant ashes used to obtain sodium which produce glasses with similar compositional ratios to those produced by natron (Brill, 1970). Coastal plants

usually contain high levels of sodium and low levels of potassium. Inland plants, especially wood ash generally introduce high levels of K_2O , CaO , and P_2O_5 to the glass (Turner, 1965; Stern and Gerber, 2004). Inland plants cannot be thought for Group I glasses. Another possibility is that a small amount of plant ash could have been deliberately added or could be introduced to the glass as a result of contamination from the fuel (wood) during firing (Tite and Shortland, 2003). For LMG glasses seaweeds or seasalts can also be considered as sodium sources (Sayre and Smith, 1974; Henderson, 1985).

Natron which contains sodium salts such as $NaCl$ (sodium chloride) and $NaSO_4$ (sodium sulfate) introduce high amounts of Cl^- (chloride) and SO_4^{2-} (sulfate) to the glass, Cl^- being about 1.4 % and sulfur (as SO_3) being about 0.26 % (Colinart *et al.*, 1999; Shortland, 2004). This is not the case for Alanya glasses. LMG glass pieces from Alanya have Cl concentrations ranging from 0.5 % to 0.8 %; and SO_3 concentrations from 0.05 % to 0.1 %. In fact, only small amounts of chlorides and sulfates can be incorporated into the glass since they are non-reactive without decomposition or react only slowly prior to decomposition unless reduced to sulfites or sulfides as a result of the presence of carbonaceous patterns. 1-2 % for Cl and similarly 1-2 for SO_3 are typical amounts for glass composition (Tite *et al.*, 2006).

In LMG samples zirconium levels are various differing between 34.9 ppm for AL13 and 122.6 ppm for AL20; and hafnium levels are differing between 99 ppm AL5 and 6.1 ppm for AL12. Alumina and calcia levels of Group 1 glasses are various. AL19, AL15, AL12, AL8, AL6, AL7, AL13, and AL22 have less than 1 % of alumina. The others, AL5, AL20, AL17, and AL16 have relatively higher contents of Al_2O_3 ; calcium levels range from 4.4 % for AL22 to 7.4 % for AL5. Al_2O_3 and SiO_2 are also variable that Group 1 glasses make three subgroups according to the correlation between their alumina and silica levels. AL5, AL20, AL17, and AL16 are the most positively correlated ones. Alumina in these samples increases with the silica increase. AL12, AL15, AL6, AL8, AL7, and AL13 make the second group with similar alumina and silica ratios. It is interesting that AL22 in the third group has the highest level of silica and the lowest alumina content (0.5 % Al_2O_3 and 77.1 % SiO_2). The samples, AL8, AL7, AL16, AL15, AL13, AL12, AL22, AL5, AL17,

AL19, and AL6, which have been categorized as HIMT glasses due to their sand source also take place in the group of LMG glasses based on alkali source. Burial conditions, alkali leaching due to aqueous attack, and other weathering factors might have affected the contents of oxides within the glasses. Even if these factors are excluded, it is still questionable to suggest that these eleven glasses have been made with the same or very similar raw materials. They might have been produced with trona mineral or any other sodium-rich plant which is poor in potassium as the alkali; and with sand rich in impurities and rare earth elements.

The second group consisting of AL2, AL3, AL24, AL18, AL21, AL1, AL14, and AL9 (Figure 38) can not be regarded as LMG (Low Magnesia Glass). Considering their high levels of potash and slightly higher levels of magnesia, it may be suggested that Group 2 samples are mixed-alkali glasses produced with the plant ashes low in magnesia and rich in potassium. Plant ash glasses usually contain magnesia up to 2-3 % and phosphorus up to 1 % by weight (Brill, 1999) but there are many types of plant ashes with distinctive compositions. As much as the plant species, the growing season, the components of the plants such as leaves or body parts, the composition of the soil and the ground water in which the plants grow, and the way the plants are ashed are also very important factors that determine the composition of plant ash (Tite *et al.*, 2006). Contamination from the ceramics during firing could also increase the magnesia and potash contents in the final glass (Tite and Shortland, 2003). The concentrations in the final glass may not reflect the original composition of the plant ash used; treatments during glassmaking may affect the levels of many elements in the final product (Tite and Shortland, 2003). Many specific processing factors of raw materials influence on oxide ratios resulting in minor and trace element partitioning that the oxide ratios in the glass analyzed may not be representative of the original plant ash composition (Rehren, 2008). AL1, AL18, AL9, and AL21 of Group 2 have the highest alumina contents among all the 25 glasses. AL2 and AL14 have more than 1 % of alumina. The calcium contents of Group 2 glasses range between 5.2 % (AL18) and 13.6 % (AL24). None of the Group 2 glasses are found to be HIMT glasses since they do not contain high levels of manganese.

Calcium derives from limestone if shells in beach sands in the polymorph aragonite were not used as the lime source. The type of limestone can be determined by investigating the CaO/MgO ratios in the glasses analyzed. Positive correlation between the bulk lime and magnesia concentrations indicates the use of dolomitic limestone which introduces some magnesia to the glass. However, this task can only be considered if there is no correlation between potash and magnesia in the glasses examined. Apart from Group 3a and Group 3b, which should be evaluated separately, Alanya glasses are correlated in their potash and magnesia contents. Excluding AL24, AL2, and AL8, calcium levels of Alanya glasses studied are neither low insufficiently making the glass less durable nor are they high enormously causing devitrification, and hence a different type of deterioration of the samples.

AL24 which has the highest calcium content (13.6 wt %) has magnesia less than 1 %. Its strontium level is the lowest one (209.7 ppm) of all the other glasses. Besides, the sodium content of AL24 is relatively lower being 8.4 %. Since we do not have the photograph of the sample it is not possible to say anything about the depth and degree of corrosion or other factors which might have affected its final composition. AL11 and AL25 are distinctive with their magnesia contents being more than 2 %, 3.2 % for AL25 and 2.1 % for AL11. The other glasses make four small groups, all of which have to some extent, correlation between calcium and magnesium (Figure 45).

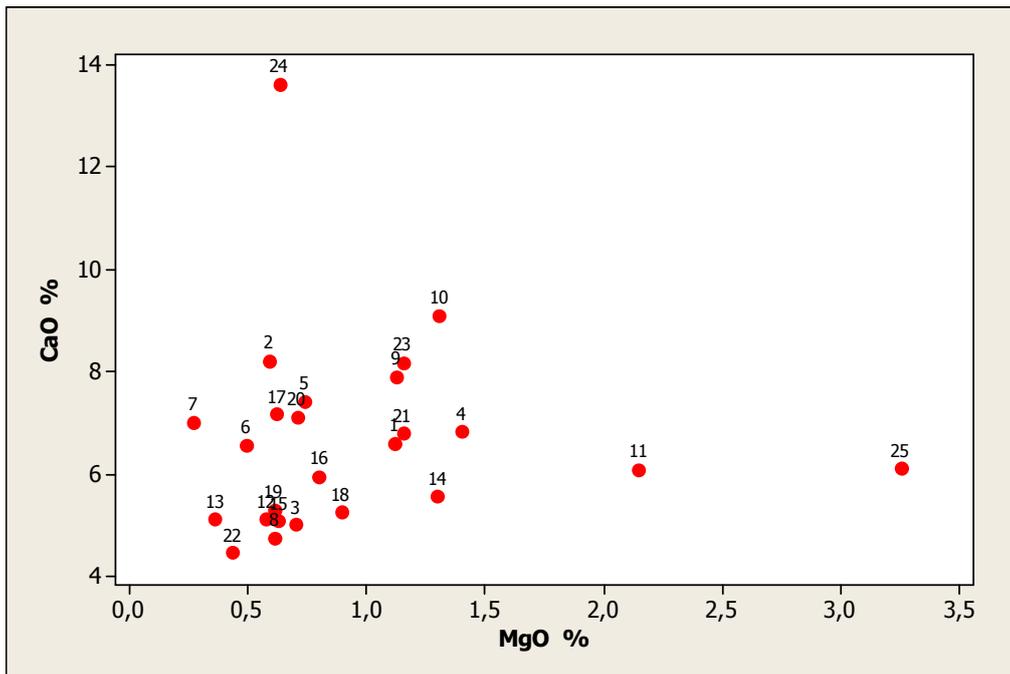


Figure 45 The scatterplot of CaO versus MgO of 25 samples

The relationship between potash and calcium seems to be stronger than the relation between magnesia and calcia. AL10 and AL23 have high potash contents (3.01 % for AL10; 3.7 % for AL23). Apart from AL24, they also have elevated levels of calcium higher than all the other glasses being 9.1 % for AL10 and 8.1 % for AL23. The other glasses seem to have a constant K_2O/CaO ratio at 0.26 ± 0.07 . AL8 and AL22 have very similar potash and calcium levels. The correlation can be seen in the Figure 46 below.

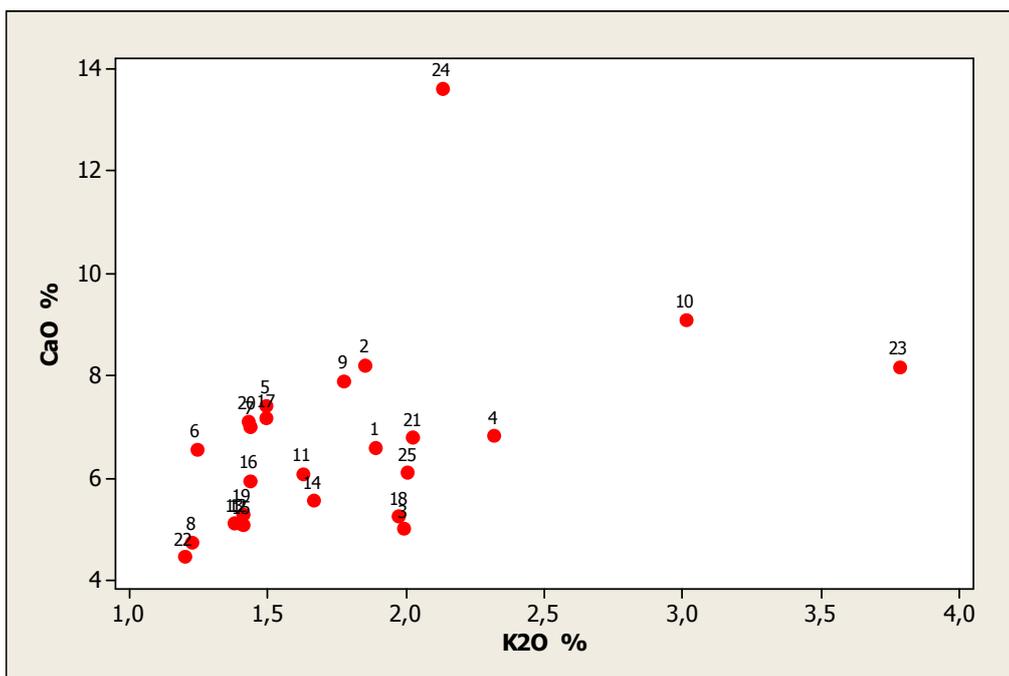


Figure 46 The scatterplot of CaO versus K₂O of 25 samples

Plant ashes or other sodium source used to produce Group I glasses must be responsible for very little concentration of calcium. The remainder must have come from other sources. Shells in beach sands are probable, but mature sands are out of our consideration since sands used to produce the glasses are not mature. It is well-known that the interaction of the glass melt with the melting crucible or pot directly affects the alkali earth concentrations of the glass. Such interaction may contribute additional calcium to the glass melt depending on the furnace temperature (Rehren, 2008). The possibility of chance contamination of the glass from clay crucibles or metal tools, the possible deliberate addition of lime as a separate component, and the possibility of intermediate stages in the glass production make it difficult to investigate its provenance.

CaO and P₂O₅, on the other hand, are not correlated, and thus bone-ash which introduces phosphorus to the glass is not the case for Alanya glasses studied. Phosphorus derived from the alkali source in small amounts (lower than 1 %), and hence lower than the levels expected for inland plants (Marchesi *et al.*, 2005).

4.4.3. Coloring Agents

The choice of several possible forms of chemical colorants would not be the only factor in achieving the final glass color; the colorant material mixed in the batch and the furnace conditions employed in the melt are the other determining factors for the color of the glass (Henderson, 1985).

The color of the pieces under study varies from green to yellow and blue to purple. The elements as the coloring agents have been detected mainly as manganese for the purple; iron for honey-yellow and brown-yellow, and to some extent for blue; copper for the green and blue; and cobalt for the blue pieces.

Manganese content of glasses ranges between 2.38 % and 0.11 % with the average of 0.9 % by weight. As it can be seen in Table 6, manganese is relatively higher in purple-colored glass panes. AL10, one of the darkest pieces, has a significant level of MnO (2.38 %). AL7, AL12, AL15, and AL16 had been colored by MnO as well. AL12 and AL16 were thinner than the other ones, and hence the color of them looks lighter. MnO seemed to be introduced to these glasses intentionally to obtain purple color. A manganese-rich mineral such as pyrolusite (Mn_2O), can be suggested as the source of manganese in AL10 and other purple glasses. The purple color is due to the equilibrium between Mn^{2+} and Mn^{3+} ions in the glass. The trivalent ion (Mn^{3+}) which is much more stable in glass than it is in an aqueous solution is thought to be mainly responsible for the deep purple color of the glass (Weyl, 1992). However, it should be borne in mind that the color is modified by the presence of other ions in the glass rich in manganese content.

Barium in glass may be brought with manganese. Pyrolusite and smaller quantities of psilomelane [$(Ba(H_2O)_2Mn_5O_{10})$] contain appreciable amounts of barium (Peacor and Wedepohl, 1969). The presence of barium in psilomelane is due to its structure with complex chains of MnO_6 octahedra and large channels between adjoining chains which are occupied by large cations of barium. However, there must be positive correlation between Mn and Ba to be able to suggest the manganese source as the source of barium as well. There is not a correlation between these two in the glasses studied; concentrations are various. Therefore, it is more realistic to

suppose that barium was introduced with the sand. The differing Ba contents in groups indicate the use of different sands containing varying amounts of alkali feldspars.

Iron can produce many different colors from green to blue when Fe(II) ions are present and yellow to brown with Fe(III) ions depending on mainly the furnace atmosphere. The common blue-green glass is produced by a mixture of ferrous [Fe(II)] and ferric [Fe(III)] ions in the glass melt (Pollard and Heron, 1995) but in some cases it is possible that frits or cullets of blue glass were also added to melt (Mirti *et al.*, 1993). The green and blue glasses contain mainly Fe(II) because under fairly strongly reducing conditions a large fraction of the iron is reduced to Fe²⁺ giving the glass a blue appearance while yellow glasses are richer in iron predominated by Fe(III) (Weyl, 1992)..

Iron, as given above, differs between 0.3 % and 2.9 % in 25 samples (Table 6). AL24 and AL25 have low iron contents being 0.36 % for AL24, and 0.54 % for AL25. The glasses with visual appearances having iron more than 2 % are AL1, AL3, AL5, AL17, and AL18. Two pieces in this group, AL1 and AL18 are honey-yellow-colored glasses with Fe₂O₃ levels 2.09 % for AL1 and 2.1 % for AL18. The other pieces which have yellow or brownish yellow colors are thought to be colored by iron as well. AL2 has 1.86 % of iron and AL9 has 1.63 % which are higher than the levels of other pieces which have iron concentrations less than 2 % and more than 1 %. On the other hand, AL11 with its yellow-brown color (Figure 30a) interestingly has the lowest iron content of all glass pieces studied (1.07 %). It has also relatively lower levels of manganese, cobalt, and copper. However, it has the highest amount of sulfur (as SO₃) which seems to be responsible for the brownish yellow or amber color of the piece. Sulfur is not added as an ingredient but is brought to the glass as a contaminant with one or more of the batch materials. Plant ashes are generally rich in sulfur (Brill, 1970), and inorganic sodium-rich sources such as natron is also found in association with sodium sulfate (Na₂SO₄). Under strong reducing conditions some of the sulfate is reduced and forms the sulfide ion which combines with some of the remaining Fe³⁺ ion to form a chromophore. Brown-yellow or amber may have been originated as a result of the formation of (Fe³⁺ - S²⁻) (ferri-sulfide) chromophore

(Weyl, 1992). The magnesium content of AL11 is also very high being 2.1 % by weight. MgO and SO₃ seem to be positively correlated in this glass. Sulfur might have been brought with magnesia with the plant ash. But, the potash content of AL11 is low. A type of plant rich in magnesium and sulfur, and poor in potash may be considered; or another factor leading to contamination of magnesium and sulfur must be taken into account. AL10 with the highest MnO content has more iron than the other purple glasses.

Two green-colored pieces have very high levels of iron being higher than the yellow glasses, but the main coloring agent used to color these two pieces seems to be copper which has been found 2.4 % for AL5 and 2.5 % for AL17. Green color is due to divalent Cu²⁺ ions and not to Fe²⁺ nor to a change of oxidation number of the copper during the firing process. Furthermore the Fe²⁺ concentrations found in archaeological glasses are higher in blue than in green (Pagès-Camagna and Colinart, 2003).

The highest iron level (2.9 %) has been determined in AL3, the navy-blue or dark blue piece. In fact blue colors are not exceptional in the chemistry of iron compounds. For example, the oxidation of precipitated white ferrous hydroxide (Fe(OH)₂) to the brown Fe(OH)₃ passes through blue intermediate products (Weyl, 1992). However, considering that AL3 has also the highest level of cobalt rather than iron; and cobalt seemed to be the main coloring agent used in this glass. It seems more likely that excess iron in the glass derived from the cobalt ore which was rich in iron.

Copper ranges from 0.009 % to 2.5 % by weight in the samples studied. The green pieces, AL5 and AL17 have the highest copper contents being 2.4 % and 2.5 % respectively. The turquoise-colored piece AL4 and the other blue pieces are also rich in copper. The presence of lead produces green instead of blue (Weyl, 1992). Lead oxide contents of green-colored glasses are higher than the other pieces. For AL20, the piece without the visual appearance, copper, tin, and lead are strongly correlated. It has the highest values for copper and tin, and excluding AL11, the highest content of lead as well. The glass was most probably colored in green. In the green pieces and the turquoise-colored glass, AL4, PbO concentrations are over than 1000 ppm.

AL4 has also higher potassium content than the blue-colored glasses. It has been stated that copper concentration of 327 ± 238 ppm indicates the use of recycled glass (Tite and Shortland, 2003). Almost all Alanya glass pieces have copper levels more than the levels stated. Lead content at 211 ± 121 indicates the recycling as well (Tite and Shortland, 2003). AL11, AL4, AL20, AL5, AL17, AL24, AL25, AL14, AL23, and AL18 have significant levels of PbO indicating the intentional addition of lead oxide. AL11 and AL4 were the pieces with remarkable shiny surfaces. Lead is known to be added to impart brilliance to the glass. Glasses having bright appearance could have been recycled to produce new bright glass panes.

It is very well-known that when bronze is used as the source of copper elevated levels of tin is introduced to the glass. Copper and tin ratio at about 1 to 10 is the evidence for bronze use (Kaczmarczyk and Hedges, 1983). To investigate whether bronze was used or not, the copper and tin contents of copper-colored glasses have been compared (Figure 47). As it is seen in the figure for green pieces a perfect correlation has been detected. The Sn/Cu ratio for the pieces is in unity being 3.3 for both. Bronze scrap was used to color these glasses in green. For blue pieces it is not easy to state such a correlation. Copper concentration of these glasses results from any cobalt-bearing ore which almost always contain some amount of copper, or any cobalt-rich copper ore (Weyl, 1992).

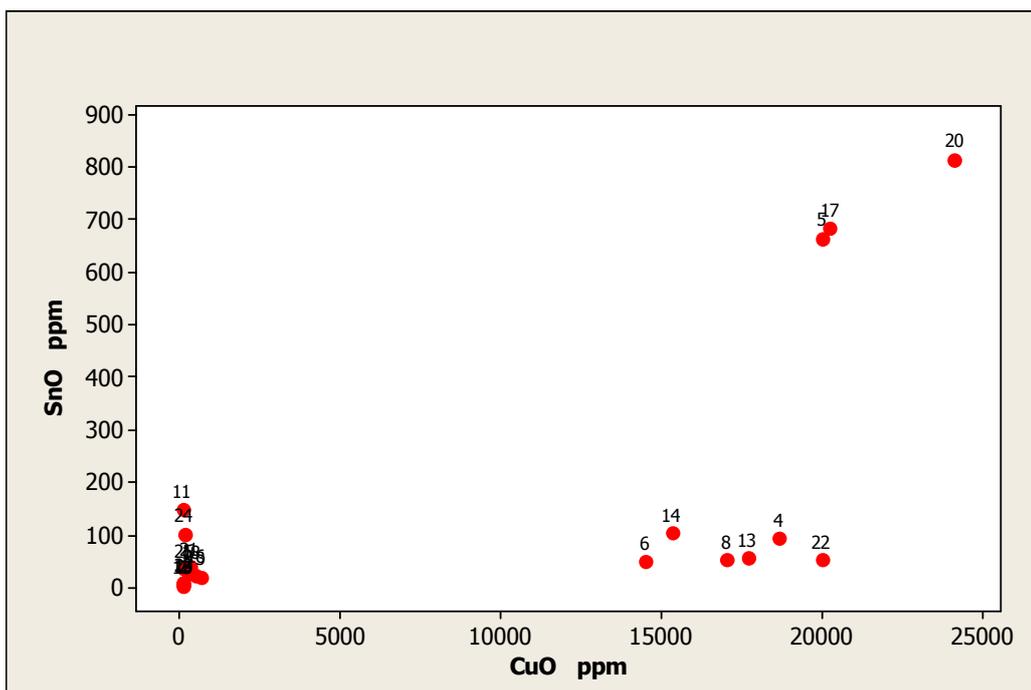


Figure 47 The scatterplot of SnO versus CuO of 25 samples

Cobalt is such a strong coloring oxide that only about 0.1 % is enough to produce a blue glass and 0.025 % will produce a light blue color. All blue-colored samples examined have been found to contain elevated levels of cobalt ranging between 0.008 % (AL20) and 0.09 % (AL3). The levels of copper in the blue samples are also high ranging from 3.01 % (AL20) and 0.08 % (AL3). AL20 and AL22 are the pieces without photographs. AL4 is the turquoise-colored glass with the cobalt level at 0.02 % and the copper level at 2.3 % (Table 6). AL8 has 0.03 % cobalt and 2.1 % copper by weight; AL6 has 0.02 % cobalt and 1.81 % copper; AL13 has 0.028 % CoO and 2.2 % CuO; AL14 has 0.005 wt % CoO and 1.9 % CuO. It has been detected that copper present in the blue glasses having cobalt contents between 0.19 and 0.28 % (Shortland, 2004). In most cases, in order to obtain navy-blue or dark blue colors 2-3 % of copper is required. There are two possible ways in which copper could have been incorporated into the blue-colored glasses. One possibility is that copper metal or ore was added to the cobalt-colored glasses to deepen the color (Shortland and Eremin, 2006). Cobalt is commonly found in ancient rock

mineralizations in association with other minerals. Trianite ($2\text{Co}_2\text{O}\cdot\text{CuO}\cdot 6\text{H}_2\text{O}$) is a copper-bearing cobalt ore (Henderson, 2000). The other possibility is that cobalt-colored and copper-colored glasses were mixed and added to the batch prepared to make blue glass.

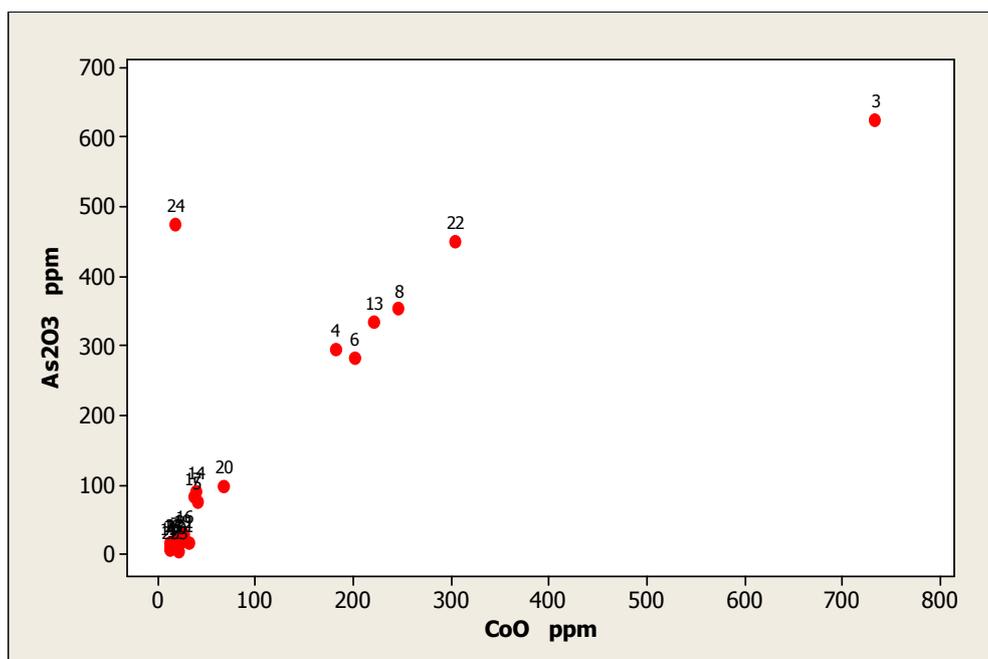


Figure 48 The scatterplot of As₂O₃ versus CoO of 25 samples

Many elements along with cobalt are indicative of the cobalt ore from where the colorant is obtained. The presence of cobalt in glasses is associated with raised levels of other elements, principally alumina, magnesia, manganese, and nickel if cobalt-bearing alum as the source of cobalt was used (Henderson, 2000). For the glass pieces studied no correlation has been detected between cobalt and these elements. Al₂O₃, MnO, MgO, and NiO levels are varying in the blue samples, and hence they cannot be related to alum as the cobalt source. On the other hand, cobaltite, or erythrite are arsenical cobalt ores that introduce arsenic with cobalt to the glass (Garner, 1956). In all blue samples a very strong correlation has been found between cobalt and arsenic (Figure 48). As an example AL3 which has the highest level of cobalt has the highest level of arsenic.

CHAPTER 5

CONCLUSION

In this study 25 glass pieces obtained from the excavations of Alanya archaeological region have been investigated. Visual and microscopic examinations have been carried out and chemical composition of the samples has been determined by PE-XRF. Cluster analysis on the basis of K_2O and MgO amounts of the 25 samples has been applied to categorize the glass pieces according to the alkali flux sources used in their manufacture.

All samples have been found to be soda-lime-silica glasses containing silica as the former; soda as the fluxing agent; and calcia as the stabilizer.

The cross section analysis has revealed that the thicknesses of the eighteen pieces range from 0.01 cm. to 0.31 cm. Two of the samples were cup pieces; the other 18 samples were flat window pane fragments. The thicknesses of each sample vary in the middle part and at the edges. AL3, AL6, AL9, ALAL11, AL12, AL13, AL14, and AL15 are thought to be the broken pieces of the corner panes as they were rounded at the edge. AL9, AL11, AL12, and AL14 had been folded over at the edge; the other corner fragments are thought to have been polished by fire as they revealed smooth round edges. The other pieces had sharp edges that it is not possible to suggest what part of the whole pane they occupied.

Two samples (AL2 and AL9) had iridescence layers and small or large dulling areas throughout the surfaces; AL13 had the same dulling pattern. Except AL1, AL11, and AL18, and the fragments showing iridescence weathering, the remainders were stained by soil accumulation on the surfaces. The soil layers were impossible to be removed. No treatment, except from cleaning the pieces with distilled water was employed because the fragments were not big or thin enough to allow any chemical cleaning; and some were extremely fragile that any treatment

could cause breakage, and hence total loss of the samples. On the other hand soil accumulation or weathered parts did not affect their transparency, and did not affect the XRF results as there was not serious damage caused by external solid materials which may otherwise interfere with the bulk composition of the glasses.

The heterogeneous distribution of minor elements being potash, magnesia, alumina, iron, sulfur, chloride, manganese, titanium, chromium, vanadium, and phosphorus have revealed that the glasses differ from each other in terms of chemical structure. This difference can be explained in many ways. The production techniques and furnace conditions might have affected the final glass composition and caused differences between glasses although the batch prepared before firing was the same. However, this is not a strong possibility; generally different compositions are the result of different batch sources.

Based on potash and magnesia correlation three types of glass have been determined. The first group consisting of glasses with very low potash and magnesia contents can be categorized as LMG (Low Magnesia) or LMLK (Low Potash Low Magnesia) glasses produced by an inorganic sodium source rather than plant ash (Table 6). Some of the Group 1 glasses have also been categorized HMT glasses due to the silica source. The elevated levels of trace elements detected for these glasses might have resulted from recycling. The variability of alumina and calcia rules out the possibility of calcareous sand as the source of silica. On the other hand, high levels of barium detected in the glasses may indicate alkali feldspars in the silica source. But alumina and barium levels are again variable and do not indicate the same source of sand used for all these glasses.

Group 2 glasses have relatively higher levels of potassium than the Group 1 glasses, and for this reason can be categorized as mixed-alkali glasses. In some cases, different soda sources, e.g., different plant ashes are mixed and the resulting glass contains high levels of potash. In this group, all the glasses have lower levels of manganese less than 1 %. AL24 has also very low levels of iron, titanium, and aluminum. It has lower sodium content when compared to other glasses. When high silica content of the glass is considered, sand which is rich in quartz and poor in impurities can be suggested for this glass. Very high calcium content in this glass

indicates sandstone as the source for calcium, or shells might have added to make the glass stable. In this case coastal sand and coastal plants may be the raw materials used to produce AL24. The alumina amounts in the Group 2 glasses are variable as in the Group 1 glasses. AL3 has alumina less than 1 %. AL1, AL9, AL18, and AL21, on the other hand, have very high alumina contents. Their calcium levels are in the range between 5 % and 8 %, and silica levels change from 60 % to 68 %. The high alumina contents are correlated with iron and titanium levels. These four glasses might have been produced with impure sand. AL1, AL9 and AL18 are honey-yellow pieces colored by iron. Probably AL21 had a similar color. Earlier glasses produced with impure sand can also be suggested as the colorant materials used to color these four glasses. This seems to be the best explanation for the high levels of heavy minerals in these glass pieces. Considering that AL1 and AL18 were the cup pieces, it can be suggested that the raw materials selected to produce cups were different from ingredients used to make window panes; or honey-colored and brownish yellow glass batches were prepared in a specific way with specific sand and plant ashes.

Group 3 including the samples different from other groups can be divided into two distinct groups. One subgroup consisting of AL11 and AL25 has been called LKHM because of relatively lower potash and higher magnesia amounts. Both have very high magnesium and moderate calcium levels. Dolomitic limestone seems unlikely. AL25 has considerably higher silica content; on the other hand, sodium contents of both glasses seem close to each other. AL11 was full of air bubbles. Insufficient melting temperature can be suggested. This glass has been found to be different from all pieces studied with the considerable lead and sulfur contents it has. The other subgroup involving AL4, AL10, and AL23 have more potash and more magnesia than Group 1 and 2 glasses. Plant ash which introduced both MgO and K₂O can be confidently suggested as the alkali source for these three glasses. AL4 is the second glass which has remarkable lead content. AL4 and AL11 have been found to be much brighter than the other glass pieces examined.

Purple glasses were colored by manganese. With the exception of AL11 (Figure 30a), all of the honey-yellow and yellow-brown glasses were colored by iron. All blue glasses and one turquoise glass (AL4) were colored by cobalt and copper.

Cullets of cobalt-blue and copper-blue glasses had been mixed and used together in the batch prepared to produce blue colored glasses. AL3, the dark blue piece with high levels of iron, cobalt, and copper might have been colored by fully reduced iron which could give a good iron-blue color. The green pieces were colored by copper. The positive correlation between copper and tin in the green glasses strongly indicates that bronze scrap had been used to obtain copper-green color. To obtain cobalt-blue an arsenical cobalt ore seems to be the source since it has been found that cobalt and arsenic are correlated in all blue pieces whereas there is no correlation between cobalt and alumina, and/or magnesia, and nickel which are thought to be introduced into the glass when the cobalt ore, alum is the source for cobalt.

The results given by PED-XRF and the interpretation of the results by HC analysis have revealed that there is no homogeneity in glasses from Alanya region studied in this thesis in terms of the raw materials, batch recipes, fritting and melting conditions, and shaping operations. Recycled glasses collected from different places might be the reason for compositional variability. Glass samples vary in their sand, alkali, and alkaline earth sources. Even within a group given glass pieces differ in elemental compositions, and hence the members of the same group are distinguished from each other on the basis of their chemical components. The differences determined by visual examination and scientific analyses of the samples have raised some doubts that glasses excavated from Alanya region may not be produced in the same center in one region. Some might have been traded from neighborhood or any distanced provinces. Recycled glass used especially as colorant makes it difficult to plot the sources of raw materials. Within the limits of this study, it can be stated that at least two different types of sand, one being rich in quartz; and one being rich in impurities; and different alkali fluxes from varying sources might have been used to produce the glass samples from medieval Alanya site. Identification of the probable sources requires much more detailed chemical and statistical analyses with more samples. Moreover, additional scientific disciplines such as botany may help in complementary research.

It could be possible to postulate a pattern of supply of raw materials to a particular manufacturing site, if this could be identified; similarly, if glass at the

manufacturing site is characterized, it may allow plot the probable trade routes of raw glass or finished glass objects found on distant sites. However, to successfully accomplish this task, it is necessary to have a large number of analyses to reveal compositional patterns. This has always been a problem since the glass is archaeologically rare, especially glass dated to medieval period of Turkey is almost impossible to be achieved for scientific analyses.

On the other hand, the usefulness of the typology proposed seems obvious since it is based on visual rather than technological characteristics of glass. Categories based on production technique, microstructure, and chemical composition should be used instead to be able to come to reliable and confidential conclusions. We hope that archaeometrical studies on the Medieval glass found in Anatolia will increase in quantity and the characterization of the Anatolian glasses within the identification of provenance in terms of raw materials will be possible. Further scientific investigations carried out by using archaeometrical methods will certainly contribute to mainstream archaeology to clarify and interpret efficiently the historical technology of glass in Turkey.

REFERENCES

Acara, M. and Olcay, Y., 1997, Bizans Döneminde Aydınlatma Düzeni ve Demre Aziz Nikolaos Kilisesinde Kullanılan Aydınlatma Gereçleri, *Adalya* (II), 249-266

Aerts, A., Velde, B., Janssens, K., and Dijkman, W., 2003, Change in silica sources in Roman and post-Roman glass, *Spectrochimica Acta*, Part B: Atomic Spectroscopy, Vol. 58, No.4, 659-667

Aksoy, U.B., 2006, Archaeometric analysis on the selected samples of glass artifacts recovered in the excavation of Alanya Castle, Unpublished M.S. Thesis, Middle East Technical University

Alexander, C., 1937, Glass, Hans Henning von der Osten, *AlisharHüyük 1930-32*, III, Chicago, 340-344

Amstock, J.S., 1997, *Handbook of Glass in Constraction*, McGraw – Hills Inc., 34-38

Arık, M.O., 1987, Alanya Kalesi 1986 yılı kazı çalışmaları, *IX. Kazı Sonuçları Toplantısı*, Cilt II, T.C. Kültür Bakanlığı Kültür ve Tabiat Varlıklarını Koruma Başkanlığı, Ankara, 365-368

Arık, M.O., 1988, Alanya Kalesi 1987 yılı kazı çalışmaları, *X. Kazı Sonuçları Toplantısı*, Cilt II, T.C. Kültür Bakanlığı Kültür ve Tabiat Varlıklarını Koruma Başkanlığı, Ankara, 421-430

Arık, M.O., 2000, Alanya 1999 çalışmaları, *22. Kazı Sonuçları Toplantısı*, 2. Cilt, T.C. Kültür Bakanlığı Anıtlar ve Müzeler Genel Müd., İzmir, 421-422

Arık, M.O., 2002, Alanya Kalesi 2001 yılı çalışmaları, *24. Kazı Sonuçları Toplantısı*, 2. Cilt, T.C. Kültür Bakanlığı Anıtlar ve Müzeler Genel Müd., Ankara, 519-530

Arık, M.O., 2003, 24. Kazı Sonuçları Toplantısı, Ankara, 123-125

Arık, M.O., 2004, 25. Kazı Sonuçları Toplantısı, Ankara, 37-43

Arık, M.O., 2005, 26. Kazı Sonuçları Toplantısı , Ankara, 213-217

Arık, M.O., 2007, 29. Kazı Sonuçları Toplantısı, Ankara, 91-99

- Arletti, R., Vezzalini, G., Biaggio Simona, S. and Maselli Scotti, F., 2008, Archaeometrical Studies of Roman Imperial Age Glass From Canton Ticino, *Archaeometry*, Vol. 50, No. 4, 606-626
- Artioli, G., Angelini, I. and Polla, A., 2008, Crystals and Phase Transitions in Prehistoric Glassy Materials, *Phase Transitions*, Vol. 81, Nos. 2-3, 233-252
- Bachhuber, C., 2006, Aegean interest on the Uluburun ship, *American Journal of Archaeology*, 110, 3, 345-263
- Baltă, P. and Baltă, E., 1976, *Introduction to the Physical Chemistry of the Vitreous State*, Abacus Press, 17-29
- Bakırer, 1986, Onaltıncı Yüzyıl Osmanlı Mimarisinde Pencerele İlişkin Biçim ve Malzeme Özellikleri, *II. Uluslararası Türk-İslam Bilim ve Teknoloji Tarihi Kongresi*, İ.T.Ü. 28 Haziran – 2 Mayıs, 113-125
- Bakırer, Ö., 1990, Anadolu Mimarisinde Pencere Camı Kullanımına Kısa Bir Bakış, *I. Uluslararası Anadolu Cam Sanatı Sempozyumu*, İstanbul, 70-80
- Bamford, C.R., 1977, *Colour Generation and Control in Glass*, Elsevier Scientific Publishing Co., Amsterdam
- Bass, G.F. and Van Doornick, Jr., F.H., 1978, An 11th century shipwreck at Serçe Liman, Turkey, *International Journal of nautical Archaeology*, 7, 119-132
- Bass, G.F., 1986. A Bronze Age shipwreck at Ulu Burun (Kas): 1984 campaign. *American Journal of Archaeology*, 90, 3, 269-296
- Bass, G.F., 1989, The Bronze Age Shipwreck at Ulu Burun: 1986 Campaign, *American Journal of Archaeology*, 93/1, 1-29
- Basso, E., Messiga, B. and Riccardi, M.P., 2007, Stones From Medieval Glassmaking: A Suitable Waste Product For Reconstructing An Early Stage Of The Melting Process, in: *The MT Lecco Glass Factory*, *Archaeometry*, 2-12
- Baxter, M.J. and Cool, H.E.M.; Jackson, C.M., 2005, Further Studies in the Compositional Variability of Colourless Romano-British Vessel Glass, *Archaeometry*, 47, 47-68
- Bayramoğlu, F., 1974, *Türk Cam Sanatı ve Beykoz İşleri*, Türkiye İş Bankası, Ankara, 17-56
- Biek, L.; Bayley, J., 1979, Glass and Other Vitreous Materials, *World Archaeology*, Vol. 11, No. 1, 1-25

- Bimson, M. and Freestone, I.C., 1983, An Analytical Study of the Relationship Between the Portland Vase and Other Roman Cameo Glasses, *Journal of Glass Studies*, 25, 35-65
- Bimson, M., and Freestone, I.C., 1985, The discovery of an Islamic glassmaking site in Egypt, *Annales du 10e Congrès de l'Association Internationale pour l'Histoire du Verre*, 237-43
- Bingham, P.A. and Jackson, C.M., 2008, Roman Blue-Green Bottle Glass: Chemical-Optical Analysis and High Temperature Viscosity Modelling, *Journal of Archaeological Science*, 35, 302-309
- Brill, R.H., 1962, A Note on the Scientist's definition of Glass, *Journal of Glass Studies*, 4, 127-138
- Brill, R.H., 1963, Ancient Glass, *Scientific American*, 209 (5), 120-131
- Brill, R.H., 1970, Scientific studies of stained glass, *Journal of Glass Studies*, 12
- Brill, R.H., 1970, Lead and oxygen isotopes in ancient objects, *Philosophical Transactions of the Royal Society of London*, A269, 143-64
- Brill, R.H., 1970, The chemical interpretation of the texts, in *Glass and glassmaking in ancient Mesopotamia* (eds. A. L. Oppenheim, R. H. Brill, D. Barag and A. von Saldern), Corning Museum of Glass, New York, 105-28
- Brill, R.H., 1988. Scientific investigations of the Jalame glass and related finds, in: Weinberg, G.D. (Ed.), *Excavations at Jalame, Site of a Glass Factory in Late Roman Palestine*. Univ. Missouri Press, Columbia, USA, 257-294
- Brill, R.H., 1999, *Chemical analyses of early glasses*, vols I and II, Corning Museum of Glass, New York
- Brill, R.H., 2005, Chemical Analyses of the Zeyrek Camii and Kariye Camii Glasses, *Dumbarton Oak Papers*, Vol. 59, 213-230
- Boon, G.C., 1966, Roman Window glass from Wales, *Journal of Glass Studies*, 8, 41-45
- Cable, M., 1991, Classical Glass Technology, in: Glasses and Amorphous Materials, Chapter I Vol. 9 (ed. J. Zarzycki) of *Materials Science and Technology*, VCH Verlag, Weinheim, 1-89
- Cann, J.R. and Renfrew, C., 1964, The characterization of Obsidian and its application to the Mediterranean region, *Proceedings of the Prehistoric Society*, 30, 111-133

Carboni, S., 2001, *Glass from Islamic Lands*, London and New York: Thames and Hudson, 272-279, cat. no. 73, 272-279

Carboni, S., 2003, The Painted Glass Decoration of the Mausoleum of Ahmad ibn Sulayman al-Rifa'i in Cairo, *Muqarnas*, Vol. 20, 61-83

Costagliola, P., Baldi, G., Secchioni, E. and Buccianti, A., 2000, Mineralogical and Chemical Characterization of the Medieval Glass Mosaic Tesserae and Mortars of the Grotta del Buontalenti, Florence, Italy, *Journal of Cultural Heritage*, Vol. 1, No. 3, 287-299

Cox, G.A. and Gillies, K.I.S., 1986, The X-ray fluorescence analysis of medieval durable blue soda glass from York Minster, *Archaeometry*, Vol. 28, No. 1, 57-68

Cramp, R., 1976, Window Glass from the Monastic Site of Jarrow, *Journal of Glass Studies*, 17, 88-96

Creswell, K.A.C., 1953, Problems in Islamic Architecture, *The Art Bulletin*, Vol. 35, No. 1, 1-7

Crossley, D., 1990, *Post-medieval archaeology in Britain*, Leicester University Press, London, 226-239

Dal Bianco, B., Bertocelli, R., Milanese, L. and Barison, S., 2005, Glass Corrosion Across the Alps: A Surface Study of Chemical Corrosion of Glasses Found in Marine and Ground Environments, *Archaeometry*, Vol. 47, No. 2, 351-360

Dayton, J.E., 1993, The Discovery of Glass: Experiments in the Smelting of Rich, Dry Silver Ores, and the Reproduction of Bronze Age-type Cobalt Blue Glass as a Slag, *Bulletin (American School of Prehistoric Research)*, 41, Peabody Museum of Archaeology and Ethnology, Cambridge, Massachusetts

Diamond, F., 1953, *The Story of Glass*, New York, Harcourt, Brace & World Inc., New York, USA., 1-57

Djingova, R. and Kuleff, I., 1992, An Archaeometric Study of Medieval Glass From The First Bulgarian Capital, Pliska, *Archaeometry*, Vol. 34, No. 1, 53-61

Doménech-Carbó, M-T; Doménech-Carbó, A; Osete-Cortina, L; Saurí-Peris, M-C, 2006, A Study on Corrosion Processes of Archaeological Glass from the Valencian Region (Spain) and its Consolidation Treatment, *Microchim Acta*, Vol. 154, 123-142

Doremus, R.,H., 1973, *Glass Science*, John Wiley & Sons Inc., New York, 1-120

Dungworth, D.; Cromwell, T., 2006, Glass and Pottery Manufacture of Silkstone Yorkshire, *Post-medieval Archaeology*, Vol. 40, No. 1, 160-190

- El-Shamy, T.M.M., 1973, The Chemical Durability of $K_2O.CaO.MgO.SiO_2$ Glasses, *Physics and Chemistry of Glasses*, 14, 1-5
- Ertuğrul, M., Şimşek, Ö., Dogan, O., Öz, E., Söğüt, Ö. and Turgut, Ü., 2001, Nuclear Instruments and Methods, *Physics Research B*, 179, 465–468.
- Eyice, S., 1990, Bizans'ta ve Osmanlı Devri Türk Sanatında Aydınlatmada Cam, *I. Uluslararası Anadolu Cam Sanatı Sempozyumu*, İstanbul, 51-57
- Farnsworth, M. and Ritchie, P.D., 1938, Spectrographic Studies on Ancient Glass, Egyptian Glass Mainly of the 18th Dynasty with Special Reference to Its Cobalt Content, *Technical Studies in the Field of the Fine Arts*, 6 (3), 155-173
- Fiori, C. and Vandini, M., 2004, Chemical Composition of Glass and Its Raw Materials: ChronologicL AND Geographical Development in the First Millennium A.D., in: *When Glass Matters* (ed. M. Beretta), Firenze, 107-150
- Fıratlı, N., 1970, Uşak-Selçukler Kazısı ve Çevre Araştırmaları 1966-1970, *TAD* (XIX/II)
- Foster, H.E. and Jackson, C.M., 2009, The Composition of 'Naturally Coloured' Late Roman Vessel Glass from Britain and The Implications for Models of Glass Production and Supply, *Journal of Glass Archaeological Science*, Vol. 39, 189-204
- Freestone, I.C., 1991, Looking into Glass, in: *Science and The Past*, (ed. Sheridan Bowman), British Museum Press, Toronto, 37-56
- Freestone, I.C. and Gorin-Rosen, Y., 1999, The great glass slab at Bet She'Arım, Israel: an early Islamic glassmaking experiment? *Journal of Glass Studies*, 41, 105-116
- Freestone, I.C., Gorin-Rosen, Y. and Hughes, M.J., 2000, Primary Glass from Israel and the Production of Glass in Late Antiquity and the Early Islamic Period, in: *La route du verre: Ateliers primaires et secondaires du second millénaire av. J.-C. Au Moyen Âge* (ed. M.-D. Nenna), Maison de l'Orient Méditerranéen, no. 3, Lyon, 65-85
- Freestone, I.C., 2002, The Relationship Between Enamelling On Ceramics and On Glass In The Islamic World, *Archaeometry*, Vol. 44, No. 2, 251-255
- Freestone, I.C., Ponting, M., and Hughes, M. J., 2002, The origin of Byzantine glass from Maroni Petrera, Cyprus, *Archaeometry*, Vol 44, No. 2, 257-272
- Freestone, I.C., Leslie, K. A., Thirlwall, M., and Gorin-Rosen, Y., 2003, Strontium isotopes in the investigation of early glass production: Byzantine and early Islamic glass from the Near East, *Archaeometry*, Vol. 45, No. 1, 19-32

Freestone, I.C., Wolf, S., and Thirlwall, M., 2005, The production of HIMT glass: elemental and isotopic evidence, in: *Annales du 16e Congrès de l'Association Internationale pour l'Histoire du Verre*, 153–157, AIHV, London, 153–157

Freestone, I.C., 2006. Glass Production in Late Antiquity and the Early Islamic Period: A Geochemical Perspective, In: *Geomaterials in Cultural Heritage, Geological Society of London Special Publication* (eds. Maggetti, M., Messiga, B.), 201-216.

Garner, H., 1956, The Use of Imported and Native Cobalt in Chinese Blue and White, *Oriental Art*, 2(3), 48-50

Goerk, I.H., 1977, Glass Raw Materials and Batch Preparation, Proceedings of the 9th International Congress on Glass, Prague, 4-8 July, Vol. 2, 38-111

Goffer, Z., 2007, *Archaeological Chemistry*, Second Edition, John Wiley & Sons, Inc., 111-134

Griffiths, D.R. and Feuerbach, A.M., 2001, The Conservation of Wet Medieval Window Glass: A Test Using an Ethanol and Acetone Mixed Solvent System, *Journal of the American Institute for Conservation*, Vol. 40, No. 2, 125-136

Hall, M. and Yablonsky, L., 1997, Chemical Analyses of Glass Beads Found in Two Sarmatian Burials, *Archaeometry*, Vol. 39, No. 2, 369-377

Harden, D.B., 1959, New Light on Roman and Early Medieval Window Glass, *Glastechnische Berichte*, Vol. VIII, 9-16

Harrison, M. and Fıratlı, N., 1966, 1964-1965 Saraçhane Araştırmaları, *Istanbul Arkeoloji Müzeleri Yıllığı*, Istanbul, 57-59

Hartman, G., 1994, Late-medieval Glass Manufacture in the Eichsfeld Region, *Chemie der Erde*, 54, 103-128

Hayes, J.W., 1992, Excavations at Saraçhane in Istanbul, c. II, Princeton

Henderson, J., 1985, The Raw Materials of Early Glass Production, *Oxford Journal of Archaeology*, Vol. 4, No. 3, 267-291

Henderson, J., 1987, Glass and Glass-Working, in: *Hemgistbury Head, Dorset, Volume I: The prehistoric and Roman Settlement 3500 B.C.-A.D. 500* (ed. B. Cunliffe), OUCA Monograph no. 13, 180-186

Henderson, J., 1988, Electron Probe Microanalysis of Mixed-Alkali Glasses, *Archaeometry*, Vol. 30, No. 1, 77-91

Henderson, J., 1989, The scientific analysis of ancient glass and its archaeological interpretation, in *Scientific analysis in archaeology and its interpretation* (ed. J. Henderson), Oxford University Committee for Archaeology, Monograph 19 and UCLA Institute of Archaeological Research Tools 5, Oxford University Committee for Archaeology, Oxford, 30-62

Henderson, J., 1993, Aspects of early medieval glass production in Britain, in: *Proceedings of the 12th Congress of the International Association of the History of Glass*, Amsterdam, 26-31

Henderson, J., 1995, An Investigation of Early Islamic Glass Production in Raqqa, Syria, in: *Materials Issues in Art and Archaeology IV* (eds. P.V. Vandiver), 433-444, *Materials Research Society Symposia Proceedings*, 352, Pittsburgh, 433-444

Henderson, J., 2000, *The Science and Archaeology of Materials: An Investigation of Inorganic Materials*, Routledge, Taylor and Francis Group, 24-90

Henderson, J., McLoughlin, S. D., and McPhail, D. S., 2004, Radical changes in Islamic glass technology: evidence for conservatism and experimentation with new glass recipes from early and middle Islamic Raqqa, Syria, *Archaeometry*, 46, 439-468

Higley, D.E., 1977, Silica, Mineral Dossier No. 18, H.M.S.O.

Jackson, C.M., 1996, From Roman to Early Medieval Glasses, Many happy returns or A New Birth? In: *Annales du 13^e congrès de l'Association Internationale pour l'Histoire du Verre*, Lochem, 289-301, AIHV, Lochem, Netherlands, 289-301

Jackson, J.W. and Joyner, L.; Booth, C.A.; Day, P.M.; Wager, E.C.W; Kilikoglou, V., 2003, Roman Glass-Making At Coppergate, York? Analytical Evidence For The Nature Of Production, *Archaeometry*, Vol. 45, No. 3, 435-456

Jackson, C.M., 2005, Making Colourless Glass In The Roman Period, *Archaeometry*, Vol. 47, No. 4, 763-780

Jackson, C.M. and Booth, C.A.; Smedley, J.W., 2005, Glass By Design? Raw materials, Recipes and Compositional Data, *Archaeometry*, Vol. 47, No. 4, 781-795

Jacoby, D., 1993, Raw materials for the glass industries of Venice and the Terraferma about 1370–about 1460, *Journal of Glass Studies*, 35, 65–90.

Kaczmarczyk, A., 1986. The source of cobalt in ancient Egyptian pigments. In: *Proceedings of the 24th International Archaeometry Symposium*, Olin, J.S., Blackman, M.(Eds.) Smithsonian Institute, Washington D.C., 369–376

Krautheimer, R., 1965, *Early Christian and Byzantine Architecture*, Baltimore, 158

- Küçükerman, Ö., 1985, *Cam Sanatı ve Geleneksel Türk Camcılığında Örnekler*, Türkiye İş Bankası Kültür Yayınları, 20-117
- Le Bourhis, E., 2007, *Glass: Mechanics and Technology*, John Wiley & Sons Inc., 1-39, 53-71, 83-86
- Leslie, K.A. and Freestone, I.C.; Lowry, D.; Thirlwall, M., 2006, The Provenance and Technology of Near eastern Glass: Oxygen Isotopes by Laser Fluorination as a Complement to Strontium, *Archaeometry*, Vol. 48, No. 2, 253-270
- Lilyquist, C., and Brill, R. H., 1993, *Studies in early Egyptian glass*, The Metropolitan Museum of Art, New York.
- Mallowan, M.E.L., 1954, The excavations at Nimrud (Kalhu), 1953, *Iraq*, 16, 59-163.
- Marhesi, V., Messiga, B. and Riccardi, M.P., 2005, Window Panes of the Certosa di Pavia: Chemical Composition, Microstructure and Alteration, *Surface Engineering*, Vol. 21, Nos. 5-6, 397-400
- Mass, J.L., Stone, R. E. and Wypyski, M. T., 1998, The Mineralogical and Metallurgical Origins of Roman Opaque Colored Glasses, in: *The Prehistory and History of Glassmaking* McMillan, P.W., 1964, Glass-Ceramics, Academic Press Inc., New York, 7-41
- Matson Jr., F.R., 1940, Technological Study of the Glass from the Corinth Factory, *American Journal of Archaeology*, Vol. 44, No. 3, 325-327
- McCray, P. and Kingery, W.D., 1998, *The Prehistory & History of Glassmaking Technology*, Volume VIII (eds. P. McCary and W.D. Kingery), The American Ceramic Society, 1-17
- Meyer, C., 1988, Glass from the North Theater Byzantine Church and soundings at Jerash, Jordan, 1982-1983, in: *Preliminary reports of ASOR-sponsored excavation 1982-1985: Bulletin of the American School of Oriental Research, Supplement, No. 25*, The John Hopkins University Press, Baltimore, 175-222
- Megaw, A., H.S., 1963, Notes on Recent Work of the Byzantine Institute in Istanbul, *DOP (Dumbarton Oak Papers)*, V.XVII, 349-362
- Mirti, P., Casoli, A. and Appolonia, L., 1993, Scientific Analysis of Roman Glass From Augusta Praetoris, *Archaeometry*, Vol. 35, No. 2, 225-240
- Mirti, P., Davit, P., Gulmini, M., and Saguì, L., 2001, Glass fragments from the Crypta Balbi in Rome: The Composition of Eighth Century Fragments, *Archaeometry*, Vol. 43, No. 4, 491-502

Morey, G.W., 1954, *The Properties of Glass*, Second Edition, New York, Reinhold, 1-97

Mysen, B.O. and Richet, P., 2005, *Silicate Glasses and Melts: properties and structure*, Elsevier, Amsterdam, 1-50

Newton, R. and Davison, S., 1996, *Conservation of Glass*, London: Butterworths, 1-98

Nicholson, P.T., 1995, Recent excavations at an ancient Egyptian glassworks: Tell el-Amarna 1993, *Glass Technology*, Vol. 36, No. 4, 125-128

Nicholson, P.T., Jackson, C.M., Trott, K.M., 1997. The Ulu Burun glass ingots, cylindrical vessels and Egyptian glass. *Journal of Egyptian Archaeology*, 83, 143-153

Nicholson, P.T. and Henderson, J., 2000, *Glass in Ancient Egyptian materials and technology* (eds. P.T. Nicholson and I. Shaw), Cambridge University Press, Cambridge, 195-226

Noble, J.V., 1969, The Techniques of Egyptian Faience, *American Journal of Archaeology*, Vol. 73, No. 4, 435-439

Oppenheim, A.,L., 1973, Towards A History of Glass in the Ancient Near East, *Journal of the American Oriental Society*, Vol. 93, No. 3, 259-266

Önder, M., 1967, Kubadabad Kazıları 1965 yılı ön raporu, *Türk Arkeoloji Dergisi*, 14

Ötüken, S.Y., 1992, 1990 Yılında Antalya'nın Demre İlçesindeki Aziz Nikolaos Kilisesinde Yapılan Çalışmalar, *XIII. Kazı Sonuçları Toplantısı*, Çanakkale, 291-303

Özgümüş, Ü., 2000, *Anadolu Camcılığı*, Pera Yayıncılık ve Kitapçılık A.Ş., İstanbul, 126-144

Peacor, D.R. and Wedepohl, K.H., 1969, Manganese, In: *Handbook of Geochemistry: Elements Cr(24) to Br(35)*, (ed. Wedepohl, K.H.), Springer, Berlin, 25A1-25O2

Pagès-Camagna, S. and Colinart, S. 2003, The Egyptian Blue Pigment: Its Manufacturing Process and Links to Egyptian Blue, *Archaeometry*, Vol. 45, No. 4, 637-658

Pernicka, E., Wagner, G.A., Assimenos, K., Dounas, C., Begemann, F., and Todt, W., 1982, An Analytical Study of Prehistoric Lead and Silver Objects from the Aegean, *Proceedings of the 22nd Symposium on Archaeometry*, University of Bradford

Philippe, J., 1990, Reflections on Byzantine Glass, *I. Uluslararası Anadolu Cam Sanatı Sempozyumu*, Istanbul, 40-46

Phillips, C.J., 1960, *Glass: Its Industrial Applications*, Reinhold Publishing Corporation, New York, 63-87

Pollard, A.M. and Heron, C., 1996, *Archaeological chemistry*, Royal Society of Chemistry, London, 149–195.

Preston, E. and Turner, W.E.S., 1940. Fundamental studies of the glass melting process. The effect of particle size and temperature on the rate of glassformation of a pure soda-lime-silica glass. *J. Soc. Glass Technol.* 24,124-138.

Rawson, H., 1967, *Inorganic Glass-Forming Systems*, Academic Press Inc. (London) Ltd., 1-115

Rawson, H., 1980, *Properties and Applications of Glass*, Amsterdam; New York: Elsevier Scientific Pub. Co.; New York: distributor for the U.S. and Canada, Elsevier, North-Holland, 1-67

Rawson, H., 1991, *Glasses and Their Applications*, London; Brookfield, VT: Institute of Metals, 3-84

Rehren, Th., 2008, A review of factors affecting the composition of early Egyptian glasses and faience: alkali and alkali earth oxides, *Journal of Archaeological Science*, Vol. 35, 1345-1354

Renfrew, C. and Bahn, P., 1998, *Archaeology Theories Methods and Practice*, 2nd edition, Thames and Hudson Ltd, London, UK, 358-359

Sayre, E.V., and Smith, R. W., 1961, Compositional Categories of Ancient Glass, *Science*, New Series, Vol. 133, No. 3467, 1824-1826

Sayre, E.V. and Smith, R.W., 1974, Analytical studies of ancient Egyptian glass. In: *Recent Advances in Science and Technology of Materials* (ed. Bishay, A.), Vol. 3, Plenum Press, New York, 47–70

Scholes, S.R., 1975, *Modern Glass Practice*, Cahners Publishing Company Inc., Massachusetts, 1-116

Schibille, N. and Marii, F.; Rehren, Th., 2008, Characterization and provenance of Late Antique window glass from the Petra Church in Jordan, *Archaeometry*, Vol. 50, No. 4, 627-642

Schreurs, J.W.H., Brill, R.H., 1984. Iron and Sulphur Related Colours in Ancient Glass, *Archaeometry*, 26, 199-209

Shand, E.B., 1958, *Glass Engineering Handbook*, Second Edition, McGraw-Hill Book Company, Inc. London, 3-13

Shelby, J.E., 1997, *Introduction to Glass Science and Technology*, Cambridge, England: The Royal Society of Chemistry, 1-198

Sherdian, A., 1989, Pottery Production In Neolithic Ireland Petrological and Chemical Study, In: *Scientific Analysis in Archaeology and Its Interpretation* (ed. Julian Henderson), 112-135

Shortland, A.J., 2000, Vitreous Materials at Amarna: The Production of Glass and Faience in 18th Dynasty Egypt, *British Archaeological Reports International Series*, S827, Archaeopress, Oxford.

Shortland, A. J., and Tite, M. S., 2000, Raw Materials of Glass From Amarna and Implications for the Origins of Egyptian Glass, *Archaeometry*, Vol. 42, No. 1, 141-151

Shortland, A.J., 2002, The Use And Origin Of Antimonate Colorants In Early Egyptian Glass, *Archaeometry*, Vol. 44, No. 4, 517-530

Shortland, A.J., 2004, Evaporites of the Wadi-Natrun: Seasonal and Annual Variation and Its implication for Ancient Exploitation, *Archaeometry*, Vol. 46, No. 4, 497–516.

Shortland, A.J., Eremin, K., 2006. The analysis of second millennium glass from Egypt and Mesopotamia, part 1: new WDS analyses. *Archaeometry*, Vol. 48, No. 4, 581-603

Shortland, A.J., 2007, Who Were The Glassmakers? Status, Theory and Method in Mid-Second Millenium Glass Production, *Oxford Journal of Archaeology*, Vol. 26, No. 3, 261-274

Silvestri, A., Molin, G., Salviulo, G., 2005, Roman and Medieval Glass from the Italian Area: Bulk Characterization and Relationship with Production Techniques, *Archaeometry*, Vol. 47, No. 4, 797-816

Silvestri, A., Molin, G., Salviulo, G., and Schievenin, R., 2006, Sand For Roman Glass Production: An Experimental And Philological Study On Source Of Supply, *Archaeometry*, Vol.48, No. 3, 415-432

Silvestri, A., 2008, The Coloured Glass of Iulia Felix, *Journal of Archaeological Science*, Vol. 35, 1489-1501

Silvestri, A., Molin, G., and Salviulo, G., 2008, The Colourless Glass of Lulia Felix, *Journal of Archaeological Science*, Vol. 35, 331-341

Sinton, C.W. and LaCourse, W.C., 2001, Experimental survey of the chemical durability of commercial soda–lime–silicate glasses, *Materials Research Bulletin*, 36, 2471–2479.

Smedley, J.W., Jackson, C.M. and Booth, C.A., 1998, Back to the Roots: The Raw Materials, Glass, Recipes, and Glassmaking Practices of Theophilus, in: *The Prehistory and History of Glassmaking Technology*, (ed. Patrick McCray, series ed. W. D. Kingery), The American Ceramic Society, Volume VIII, 145-165

Stapleton, C.P.; Freestone, I.C. and Bowman, S.G.E., 1999, Composition and Origin of Early Mediaeval Opaque Red Enamel from Britain and Ireland, *Journal of Archaeological Science*, 26, 913-921

Stern, W.B. and Gerber, Y., 2004, Potassium-Calcium Glass: New Data and Experiments, *Archaeometry*, Vol. 46, No. 1, 137-156

Swann, C.P., McGovern, P.E. and Fleming, S.J., 1990, Colorants used in ancient Egyptian glassmaking: specialized studies using PIXE spectrometry, *Nuclear Instruments and Methods in Physics Research*, B45, 311-314

The Corning Museum of Glass, 1998, *A Resource for Glass*, The Corning Museum of Glass Education Department, New York, USA

Tillman, D.A., 1978, *Wood As An Energy: The Value of Wood As Fuel*, Academic Press, New York

Tite, M.S., 1987, Characterisation of early vitreous materials, *Archaeometry*, Vol. 29, No. 1, 21-34

Tite, M.S., and Shortland, A.J., 2003, Production technology for copper- and cobalt-blue vitreous materials from the New Kingdom site of Amarna—a reappraisal, *Archaeometry*, Vol.45, No. 2, 285-312

Tite, M.S., Shortland, A.J., Maniatis, Y., Kavoussanaki, D. and Harris, S.A., 2006, The composition of the soda-rich and mixed alkali plant ashes used in the production of glass, *Journal of Archaeological Science*, Vol. 36, 1284-1292

Turner, W.E.S., 1956, Studies in ancient glasses and glassmaking processes. Part V. Raw materials and melting processes, *Journal of the Society for Glass Technology*, 40, 277T-300T

Uboldi, M., and Verità, M., 2003, Scientific analyses of glasses from Late Antique and Early Medieval archaeological sites in northern Italy, *Journal of Glass Studies*, 45, 115-137

Vandini, M., Fiori, C., and Cametti, R., 2006, Classification and Technology of Byzantine Mosaic Glass, *Annali di Chimica*, Vol. 96, 587-598, Società Chimica Italiana Vol. 96, 587-598

Vendrell, M., Molera, J., and Tite, M.S., 2000, Optical Properties Of Tin-Opacified Glazes, *Archaeometry*, Vol. 42, No. 2, 325-340

Wedepohl, K.H. and Baumann, A., 2000, The use of marine molluscan shells in the Roman glass and local raw glass production in the Eifel area (Western Germany), *Naturwissenschaften*, 87, 129-132.

Weyl, W.A., and E.C. Marboe. 1962-67. *The constitution of glasses: A dynamic interpretation*, Vols. 1-2 pt. I, and 2 pt. II. New York: Interscience

Weyl, W.A., 1992, *Colored Glasses*, Society of Glass Technology, H. Charlesworth & Co. Ltd., Sheffield, England, 57-235

Wolf, S., Stos, S., Mason, R. and Tite, M.S., 2003, Lead Isotope Analyses of Islamic Pottery Glazes From Fustat, Egypt, *Archaeometry*, Vol. 45, No. 3, 405-420

Wolf, S., Kessler, C.M., Stern, W.B. and Gerber, Y., 2005, The Composition and Manufacture of Early Medieval Coloured Window Glass From Sion (Valais, Switzerland)-A Roman Glassmaking Tradition or Innovative Craftsmanship?, *Archaeometry*, Vol. 47, No. 2, 361-380

APPENDIX A. The Properties of PED-XRF

Multi-element concentration was determined by using polarized energy dispersive XRF (PED-XRF). The spectrometer used in this study was Spectro-XLAB 2000 PED-XRF spectrometer which was equipped with a Rh anode X-ray tube, 0.5mm Be side window. The detector of spectrometer is Si(Li) by liquid N₂ cooled with resolution of < 150eV at Mn Ka, 5000 cps. Total analysis time for each addition element was 30 min. The main difference of polarized X-Ray fluorescence from the unpolarized X-Ray Florescence is to clarify the background reduction by excitation with polarized X-Ray radiation based on the anisotropy of the atomic scattering cross section for polarized X-Ray radiation. On the other hand, normal or unpolarized X-rays emitted from an X-Ray tube, on undergoing 90° scatter by a low-Z target, become highly plane polarized. The scattered polarized beam excites fluorescent X-Rays in the measurement sample but cannot rescatter at an angle of 90°. Consequently the result becomes the optimum position for placing a detector to receive the minimum amount of tube line scatter. As a result, if the sample to be analyzed is excited with linear polarized X-Ray radiation, only the fluorescence radiation excited in the measurement sample, and ideally none of the primary radiation scattered by the sample, reaches a suitably positioned detector (Ertuğrul *et al.*, 2001).

APPENDIX B. Statistical Analysis of Sample Data

A brief review of Hierarchical Clustering (HC) is given below.

Given a set of items (set of data) HC starts with all the items separate and then build up groups from these, starting by grouping the most similar items together, then grouping the groups at lower levels of similarity until finally all the items are linked together in one large group at very low level of similarity. For a cluster analysis it is necessary to have some measure which expresses the relationships between the individuals in the analysis. The measure most commonly used with interval or ratio scale data is the Euclidean distance.

Given two points on a plane with coordinates (x_1, y_1) and (x_2, y_2) the Euclidean distance between them is simply

$$d = \sqrt{(x_2 - x_1)^2 + (y_2 - y_1)^2}$$

There is a variety of hierarchical clustering methods but the Ward's method is widely used in case of archaeological data measured on interval or ratio scale. Results of a bivariate cluster analysis are always displayed by dendrograms with a similarity scale on the vertical axis and the items on the horizontal axis.