ARCHAEOMETRICAL INVESTIGATION ON SOME MEDIEVAL PERIOD GLASS BRACELETS

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

BY

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

SEPTEMBER 2006

Approval of the Graduate School of Natural and Applied Sciences

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ABSTRACT

ARCHAEOMETRICAL INVESTIGATION OF SOME MEDIEVAL GLASS BRACELETS

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September 2006, 68 pages

Glass has been used to make a variety of artifacts including bottles, drinking cups, vessels, window glasses, beads and bracelets.

Although occasional glass bracelets were dated back to 2000 BC, large scale manufacture of glass bracelets was encountered in Central Europe in the last centuries of 1000BC.

During the excavations of Mezraa Höyük (Birecik-Şanlıurfa) in 2000-20002, a number of glass bracelets were unearthed that belongs to 13th century AD.

On going excavations of Mersin Yumuktepe also give quite a lot of 11th-12th centuries Byzantine glass bracelets. In this study a group of those bracelets was started to be examined.

After technical drawings, color identification had been carried out by using Munsell color chart.

Thin sections of some samples of Mezraa Höyük have been prepared and then observed by an optical microscope in Mineral Research and Exploration (MTA).

Observation of thin sections showed the amorphous structure of glass with some impurities and gas bubbles.
On some samples deteriorated surface layers were present. XRD traces of those layers showed the typical amorphous background of glass in which no crystalline phase is present.
Elemental analysis of the samples has been done using ICP-OES method in METU Central Laboratory. In the analysis major (except SiO_2), minor and some trace elements were determined.
ICP-OES data showed that glass bracelet samples studied are of soda-lime-silica glass. But percentage of Na_2O is less than expected from typical composition of soda-lime-silica glass; being 10.5 wt % as average. This might be due to removal of Na ions from the glass network because of leaching under burial conditions. Concentration of Al_2O_3 in the samples of Mezraa Höyük is almost same. This may be due to the using one type of quartz sand in bracelet production. Color producing elements seem to be Fe, Mn and Cu.

Keywords: Şanlıurfa, Mersin, Medieval, Glass bracelets, ICP-OES

ÖZ

BAZI ORTAÇAĞ CAM BİLEZİKLERİNİN ARKEOMETRİK ANALİZİ

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Eylül 2006, 68 sayfa

Cam tarih boyunca şişeler, kaplar, kaseler, içki kadehleri, bardaklar, pencere camları, boncuklar ve bilezikler gibi eşyaların yapımında kullanılmıştır.
Büyük çapta cam bileziklere merkezi Avrupa'da M.Ö. 1000'in son yüzyılında rastlanmıştır, ancak yer yer cam bileziklere rastlanması M.Ö 2000'lere kadar uzanmaktadır.
Şanlıurfa'ya bağlı Birecik'te 2000-2002 yıllarında yapılan Mezraa Höyük kazılarında 13. yüzyıla ait cam bilezikler gün yüzüne çıkarılmıştır.
Ayrıca kazı çalışmaları halen devam etmekte olan Mersin'de Yumuktepe Höyüğünde ise çok fazla sayıda 11.-12.yüzyıl Bizans dönemine ait cam bilezikler bulunmaktadır.
Bu çalışmada gerek Mezraa Höyük'ten gerekse Yumuktepe Höyüğünden çıkan cam bileziklerden birer grup incelenmeye başlanmıştır.
Örneklerin teknik çizimlerinin yapılmasından sonra Munsell renk kataloğuna göre renkler belirlenmiştir. Mezraa Höyük örneklerinin bir kısmının ince kesitleri hazırlanıp optik mikroskopla gözlenmiştir.

Cam bileziklerin temel (SiO_2 dışında) az ve iz element içerikleri ODTÜ AR-GE Merkez Laboratuvarı'nda ICP-OES yöntemi kullanılarak bulunmuştur.
Mezraa Höyüğün bazı örneklerinde görülen bozulmuş yüzey tabakası XRD analizi yapılarak incelenmiş ve camın yapısına özgü tipik amorf yapıya sahip olduğu, herhangi bir kristal fazın bulunmadığı anlaşılmıştır.
İnce kesitlerin optic mikroskopla incelenmesinde camın amorf yapısı içerisinde safsızlıklar ve gaz kabarcıkları belirlenmiştir.
ICP-OES sonuçları, cam bileziklerin soda-kireç-silis camı olduğunu göstermiştir. Ancak Na_2O yüzdesi tipik soda-kireç-silis camı yapısından beklenen değerden küçük bulunmuştur (ortalama %10.5). Bu durum, toprak altı koşullarında çözünme ile Na iyonlarının cam yapıdan ayrılması şeklinde açıklanabilir.
Mezraa Höyük örneklerinin tümünde Al_2O_3 derişimi hemen hemen aynı bulunmuştur. Bu sonuç cam bilezik yapımında tek tür kuvars kumu kullanıldığı kanısını yaratmaktadır. Renk oluşturan elementler Fe, Mn ve Cu olarak belirlenmiştir.

Anahtar Kelimeler: Şanlıurfa, Mersin, Ortaçağ, Cam bilezikler, ICP-OES

To My Dear Parents and Sister

ACKNOWLEDGMENTS

I wish to express my deepest gratitude to my supervisor Prof. Dr. Şahinde Demirci and Prof. Dr. Ömür Bakırer for their guidance, advice, criticism, encouragement, patience and insight throughout the research.

I would also like to thank Assoc. Prof. Dr. V. Macit Tekinalp (Hacettepe University) and Assoc. Prof. Dr. Gülgün Köroğlu (Mimar Sinan University) for allowing me to study their excavation materials and for their suggestions and guidances.

I also wish to thank Prof. Dr. Ay Melek Özer for her support all the time no matter what, Talia Yaşar from Mineral Research and Exploration (MTA) and METU Central Laboratory for their invaluable support.

I am grateful to my parents and sister for everything.

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CHAPTER 1

INTRODUCTION

In this chapter general aspects of glass, history of glass and glass technology, properties of glass bracelets, aim of the study and archaeological areas related with glass bracelet samples studied have been explained.

1.1 Glass: General Aspects

Just as living organisms are based on carbon compounds, most rocks and minerals are based on silicon compounds. Quartz and much sand, for instance, are nearly pure silica, SiO_2, silicon and oxygen together make up nearly 75% of the mass of the earth's crust. Considering that silicon and carbon are both in groupIVA of the periodic table, we might expect SiO_2 to be similar in its properties to CO_2. In fact, though, CO_2 is a molecular substance and a gas at room temperature, whereas SiO_2 is a covalent network solid (Figure1a) with a melting point about 1700°C (Murray and Fay 2001).

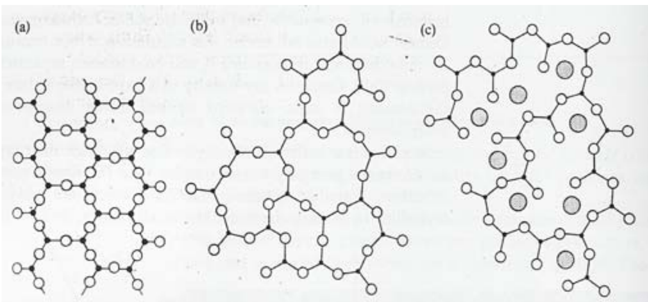


Figure 1. Crystalline structure of silica, (a) network of silica, SiO_2 ,
(b) network of glassy silica, (c) soda-silica glass.
Open circles indicate oxygen atoms, black dots silicon atoms, and shaded circles sodium atoms (Anderson et al. 1974).
●: Silicon atom, ○: Oxygen atom

When molten material is cooled down too quickly for a strict arrangement of atoms to align themselves as it sets, a random network forms instead. This gives the resulting glass with some fluid-like properties and an imprecise melting point (Figure1b). The melting point of pure silica, which is basic former of glass, is about 1700°C but if other elements, modifiers, are introduced into the glass, this point falls to less than 1000°C. Monovalent basic oxides (R_2O) such as Na_2O (soda) or K_2O (potash) modifiers behave as fluxes by interrupting some of the Si – O bonds and so breaking the continuous network. The unattached oxygen atoms become negatively charged and loosely hold monovalent cations in the spaces of the network (Figure 1c) (Cronyn 1990). This bonding is weak and the cations can migrate out of the network in the presence of water, making these glasses water soluble. To overcome this a second type of modifier, stabilizer, divalent oxides (RO) such as lime (CaO) or magnesia (MgO), must also be added. Being doubly charged they are more tightly held than the monovalent ions and so hold the fluxes within the network (Cronyn 1990).

The content and balance of silica: flux: stabilizer (SiO_2: R_2O: RO) in a glass is critical in determining its melting point and its character. An average soda-lime glass of 73% SiO_2: 22% R_2O: 5% RO has a melting point of about 725°C whilst a similar potash glass will harden at a higher temperature and more quickly. The former is more lustrous than the latter, whilst the substitution of some of the silicon by lead gives lead crystal which, being soft, is easily cut to show great brilliance. Lead is also used to make the fusible glass required for the manufacture of enamels (Cronyn 1990).

Types of materials used in glass are *Silica* (sand, quarts pebbles) silicon dioxide SiO_2 , *Soda* (soda ash (Na_2CO_3): natron, marine plant ashes, sodium oxide Na_2O , *Lime* (chalk, limestone ($CaCO_3$)), *Calcium oxide* CaO , *Potash* (ashes of inland plants (K_2 O)), *Potassium oxide* K_2O, *Lead* (oxidized lead metal) lead oxide PbO, *Boron* (modern mineral) boric oxide B_2O_3, *Magnesia* (impurity) MgO , *Alumina* (impurity) Al_2O_3, *Iron* (impurity) Fe_2O_3 (The Corning Museum of Glass 1998).

Color in glass is usually given by transition metal ions held in the network like the modifying ions. The final hue depends on the redox condition in the glass; the mixtures of ions present, and concentrations of ions. Color may be extinguished by additives. Thus, the blue-green hue of reduced iron is diminished by introduction of pink manganese ions; the iron is oxidized to give yellow color which, when viewed with pink from excess manganese, appears colorless. Some metal compounds can opacify glass but it may also appear opaque from large quantities of gas bubbles (Cronyn 1990). Some opacifying agents used in different periods are given in the Table 1 (Newton and Davison 1989)

Table 1. Opacifying agents and their using periods (Newton and Davison 1989).

Period	Type of glass	Opacifying agent
1450BC to fourth century AD	Opaque white and blue Opaque yellow Opaque red	$Ca_2Sb_2O_7$ (occasionally $CaSb_2O_6$) Cubic $Pb_2Sb_2O_7$ Cu_2O Cu_2O+Cu Or Cu
Fifth century AD to seventeenth century AD	Opaque white and blue Opaque yellow and green Opaque red	SnO_2 usually $3Ca_3(PO_4)_2.CaF_3$ occasionally Cubic Pb_5SnO_4 Cu Cu+Cu_2O rarely Cu+SnO_2 sometimes
Eighteenth century AD to Present day	Opaque white	$3Pb_2(AsO_4)_2.PbO$ (apatite type structure) CaF or CaF_3+NaF $(Na_2Ca)_2Sb_2O_6F$

Glass artifacts may be manufactured in one place and shaped in another.This latter activity is enormously varied from the chipping and grinding of solid blocks of glass to the bending of softened glass requiring temperatures of only 500°C but the blowing of molten glass which requires much more heat of about 1000°C (Cronyn 1990).

As mentioned before a typical glass contains formers, fluxes, and stabilizers. **Formers** make up the largest percentage of the mixture to be melted. In typical soda-lime-silica glass the former is silica (silicon dioxide) mainly in the form of sand. Melting sand by itself requires high temperatures of about 1850°C. **Flux** lowers the temperature at which the former will melt at 1300°C. Soda (sodium carbonate) and Potash (potassium carbonate), both alkalis, are common fluxes. Potash glass is slightly more dense than soda glass. But fluxes also make the glass chemically unstable, liable to dissolve in water or form unwanted crystals.So stabilizers are needed.

Stabilizers make the glass strong and water-resistant. Calcium carbonate, often called calcined limestone is a stabilizer.Without a stabilizer, water and humidity attack and dissolve glass. Stabilizers keep the finished glass from dissolving, crumbling or falling apart. Glass, lacking lime, is often celled “waterglass.” The addition of lime to the mixture renders the glass chemically more stable, and it is this soda-lime-silica glass that is the first known from the archaeological records. Stabilizers other than limestone are litharge (PbO), alumina (Al_2O_3), magnesia(MgO), barium carbonate ($BaCO_3$), strontium carbonate ($SrCO_3$), zinc oxide (ZnO) and zirconia ($ZrSiO_4$) (The Corning Museum of Glass 1998). Addition of B_2O_3 produces a high- melting borosilicate glass that is known with the trade name Pyrex. Borosilicate glass is particularly useful for cooking utensils and laboratory glassware because it expands very little when heated and is thus unlikely to crack (Murray and Fay 2001).

Thousands of different chemical compositions can be made into glass. So, there is no single chemical composition which characterizes all glasses.

Percent composition of some soda-lime types of ancient and modern glasses are given in Table 2 (The Corning Museum of Glass 1998; Forbes 1957).

Table 2. Main composions of Ancient and Modern Soda-lime Glasses (The Corning Museum of Glass 1998; Forbes 1957).

	Roman	Modern	Ancient	Modern	Ancient Egyptian	Modern
SiO_2	67.0%	73.6%	57-72	63-74	55-65	65-75
Na_2O	18.0	16.0	9-12	6-22	15-22	12-15
CaO	8.0	5.2	3-10	3-15	3-10	5-12
K_2O	1.0	0.6	0.2-3.0	0.4-3.0	1-3	ca. 1
MgO	1.0	3.6	0.2-5.0	0.3-5.0	3-5	>1
Al_2O_3	2.5	1.0	0.6-5.0	0-5.0	1-3	1-2
Fe_2O_3	0.5	-	0.2-3.0	0.2-2.0	1-2	>1

Another table (Table 3) which shows the compositions of some ancient glasses are obtained by the convention of Morey from Neumann (Kocabağ 2002). The compositions of glasses are represented by listing the weight percentages of their components as oxides.

Table 3. The percent compositions of some ancient glasses (Kocabağ 2002, 3).

No	SiO_2	Na_2O	K_2O	MgO	CaO	Al_2O_3	Fe_2O_3	Mn_2O_3	CuO	SO_3
1	61.70	17.63	1.58	5.14	10.05	2.45	0.72	0.47	0.32	-----
2	62.71	20.26	20.26	4.52	9.16	1.47	0.96	-----	-----	0.92
3	63.86	22.86	0.80	4.18	7.86	0.65	0.67	-----	-----	-----
4	65.95	20.30	0.96	1.37	6.89	2.49	0.28	0.97	-----	1.08
5	67.82	13.71	2.34	2.30	4.03	4.38	------	1.12	1.96	0.98
6	64.10	18.26	0.77	1.30	6.06	3.59	------	1.38	1.18	1.53
7	63.20	16.57	1.34	2.20	7.10	3.77	------	0.74	-----	1.10
8	68.48	14.95	2.83	5.28	5.71	0.70	------	------	-----	0.54
9	69.82	13.51	2.18	4.09	5.79	1.40	1.80	0.41	0.36	0.96
10	67.80	16.08	2.08	2.89	3.80	3.22	0.92	0.54	1.51	1.01
11	67.03	10.12	1.82	4.93	7.83	2.48	1.88	2.64	0.79	0.75
12	65.03	17.37	1.65	2.52	5.65	2.13	0.97	0.65	1.94	1.70
13	64.41	13.98	2.37	5.59	6.19	1.52	1.36	------	2.60	1.28
14	62.70	15.21	2.12	3.29	8.80	3.82	1.07	0.83	1.00	0.94

1. Dark blue, semi transparent piece dated to 1400 BC, from Tell-el-Amarna,
2. Light yellow, semi transparent piece dated to 1400 BC, from Tell-el-Amarna,
3. Transparent red, colorless,has bubbles, dated to 1400 BC, from Tell-el-Amarna,
4. Colorless glass, external surface highly deterioated, dated to 1st-2nd century Elephantine,
5. Dark blue, semi transparent piece, dated to 1500 BC from Tebes,
6. Dark blue, partly transparent piece,which also has 1.59 FeO, belongs to Roman period, 2nd century AD,
7. Dark green, semi transparent is dated 1500 BC, found in Tebes,

8. Window piece is dated to 9th century AD,it has 0,91 FeO and 0,95PbO,
9. It is found in Nippur and dated to 250BC,
10. Dark blue,transparent piece found in Egypt from Gorub Medined, dated to 1500BC,
11. Deep blue,transparent, found in Egypt from Gorub Medined, dated to 1500BC,and has 0.39 SnO_2 ,
12. It is found in Nippur, Babil-Asur, and dated to 1400 BC and also has 0.93 CaO and 0.19 PbO,
13. It is found in Nippur, Babil-Asur, and dated to 1400 BC and also has 0.32 SnO_2 ,
14. Dark blue,transparent piece is found in Eigypt from Gorub Medined, dated to 1500BC,and also has 0,41 SnO_2)

Eventhough nearly all commercial glasses can be categorized as six basic types based on their chemical compositions, in this study soda-lime glass is the one focused on and explained.

1.1.1 Soda-lime glass

This is the earliest, the simplest (Pearson 1987) and the most common commercial glass, 90% of glass made and least expensive form of glass. It usually contains 60-75% silica, 12-18% soda (sodium oxide) (from the raw material soda ash or sodium carbonate(Na_2CO_3)), and 5-12% lime (calcium oxide) (from the raw material limestone or calcium carbonate), and a low percentage of other materials for specific properties such as colouring. One of the major disadvantages of soda-lime glass is its relatively high thermal expansion. Pure silica glass does not expand greatly when heated, but the addition of soda has a dramatic effect in increasing the expansion rate. Therefore, the resistance of soda-lime glass to sudden temperature changes are not good and resistance to corrosive chemicals is only fair. The chemical and physical properties of soda-lime glass are the basis for its wide use. Soda-lime glass is primarily used for bottles, jars, everyday drinking glasses, and window glass. The most important property is its light transmission, which makes it suitable for use as flat glass in windows. In addition, its smooth, nonporous surface allows glass bottles and packaging glass to be easily cleaned.

Soda-lime glass containers are virtually inert, so they will not contaminate the contents inside or affect the taste. Their resistance to chemical attack from aqueous solutions is good enough to withstand repeated boiling (as in the case of preserving jars) without any significant changes in the glass surface.

1.2 Glaze, Enamel and Faience

There are four vitreous products known which are glass, glaze, enamel and faience. All consist of silica, alkali and small amounts of calcium. Glass, glaze and enamel always contain large quantities of soduim oxide, that is soda glass, or another alkali, usually potassium oxide, that is potash glass; whereas faience contains only very small amounts of alkali (Newton and Davison 1989).

Glaze is vitreous coating applied to a core or base of another material either to make it impermeable and/or for decorative effect, or in other words to give a sufficient opacity to mask the body of earthenware. The glaze was sometimes mixed with the body material before firing, but more often it was applied to the core after firing, after which the artefact was refired to form the glazed surface (Newton and Davison 1989).

Faience (glazed siliceous wares) is composed of fritted silica with about 2 percent calcium oxide and about 0.25 per cent sodium oxide lightly held together with a binding medium such as water. The resulting paste was shaped by hand or in an open mould, and then heated until the lime or soda had sufficiently reacted and fused to hold the silica particles firmly together. The body of the object thus formed could then be coated with a similarly produced glaze if required, usually coloured with copper and ranging in appearance from green to dark blue (Newton and Davison 1989). As early as 4700 BC, Egyptians produced this glass-like compound, faience, to simulate turquoise and lapis lazuli.

Enamel resembles glaze in that it is also fused to a body of a different material, in this case a metallic surface (Newton and Davison 1989). But the term of enamel is also used to describe vitreous paint used to decorate ceramics and glass. Enamel must be so formulated as to satisfy two conditions: (1)it must have coefficient of expansion roughly equivalent to that of the metallic backing; and (2) its melting point must be slightly lower than that of its backing to ensure fusion with it. Therefore, most enamels were lead-soda or lead-potash glass with or without colorants and opacifiers; the material being applied as a dried frit,powder, and fused in an enamelling oven. On cooling, the surface of the enamel was often polished flat with a fine abrasive (Newton and Davison 1989).

1.3 Colored Glass

Glass was made by heating together silica,lime(CaO) or limestone ($CaCO_3$), alkaline carbonates and some metal carbonates, such as $CuCO_3$, to impact color to the glass. Ancient Egyptian glass relics with a delicate blue color contain approximately 3 % $CuCO_3$ while those with 20 % $CuCO_3$ are deep purplish-blue (Abrash and Hardcastle 1981).

In fact, glass is colored by the presence of metal ions due to two reasons;

(1) as impurities in the batch ingredients, or

(2) by addition of colorants in three processes:

a. using a dissolved metallic oxide to impart a color throughout

b. forming a dispersion of some substance in a colloidal state, and

c. suspending particles of pigments to form opaque colors.

Some metals and their resultant colors can be summarized as follow;

iron - greens,

iron and sulfur - ambers and browns,

copper -light blues,

cobalt - very dark/deep blue,

manganese - shades of amethyst color and violet,
tin - white,
lead and antimony - yellow ,
chromium- green
uranium- yellow and
various metals produce reddish glasses (The Corning Museum of Glass 1998).

Decolorizer is a substance (such as manganese dioxide or cerium oxide) used to remove or offset the greenish or brownish color in glass that results from (1) iron impurities in the batch or (2) iron or other impurities in the pot or elsewhere in the production process (The Corning Museum of Glass 1998).

Beside fluxing ions coloring metal ions can also be leached from the glass network by water. Alternately, the ions may change color in situ by oxidation.

For example; from manganese ions, black MnO_2 may be deposited and red cuprite (Cu_2O) becomes green copper compounds.

Finally, coloring ions from the environment may be taken up, a colorless crust becoming blackened with iron or manganese or stained green with copper corrosion products. Lead glass can be blackened by lead sulphide (PbS) in a wet anaerobic deposit. It is possible that bacteria play a role in both decomposing and blackening this and other types of glass.

1.4 Natural Glasses

There are also naturally occurring glasses namely obsidian, tektites, pumice, fulgurites and lechatelierite, which are the results of melted natural silica, at very high temperatures, and rock crystal (quartz) (Newton-Davison 1989).

1.4.1 Obsidian

Obsidian is formed by volcanic action. Therefore it is also called as volcanic glass. It can be found in many parts of the world. Obsidian is formed when a felsic(highly siliceous) lava cools rapidly and freezes without sufficient time for crystal growth. It is commonly found within the margins of felsic lava flows, where cooling is more rapid.Because of natural impurities, it is usually shiny, black, and opaque, but it can also be very dark red or green; its splinters are often transparent or translucent.

Despite its dark color, obsidian consists mainly of SiO_2 between 63%-76% by weight; the rest comprises alumina (10 % to 18%) and several other oxides. Obsidian is mineral-like, but not a true mineral because it is not crystalline. Its composition is very similar to that of granite and rhyolite. It is sometimes classified as a mineraloid.

Obsidian is basically a mineral glass originated by quenching igneous rocks. But it also can contain -as minor or trace components- certain elements which, properly arranged in crystals, will form magnetic domains within the glass. As a consequence, the resulting magnetic properties will be characteristic for a given obsidian region and can be used in the provenance analysis of obsidian artifacts (Leute 1987).

Surface of obsidian attracks water from the surrounding atmosphere or soil, and this is done so effectively that even in the most arid environment, the surface of a piece of obsidian is covered by a thin layer of water a few molecules thick. The water absorbed migrates inwards. The diffusion front will cover the distance d during the time t. The relationship between d and t can be written as follow (Leute 1987).

$$d= \sqrt{D.t}$$

Where D is diffusion constant, t is time passed.

The diffusion front is visible under a microscope, especially if working with poalized light (Leute 1987). The specimen has to be a thin slice of obsidian prepared by grinding and perpendicular to the surface.

Under crossed polarizers the hydration layer becomes bright and its thickness can be measured with the accuracy of about 0.1µm. D varies with temperature. From arctic environments to the hot tropics the speed of the diffusion front ranges from about 0.2 to 4 µm per 1000 a. Thus, the thickness of hydration layers is used in dating studies.

While pure obsidian is always dark in appearance, the color varies depending on the presence of impurities. Iron and manganese typically give the obsidian a dark green to brown or to black color. The inclusion of small, white, radially clustered crystals of cristobalite (a kind of SiO_2) in the black glass produce a blotchy or snowflake pattern (snowflake obsidian). It may contain patterns of gas bubbles remaining from the lava flow, aligned along layers created as the molten rock was flowing before being cooled. These bubbles can produce interesting effects such as a golden (sheen obsidian) or rainbow sheen (rainbow obsidian). Obsidian is relatively soft with a typical hardness of 5 to 5.5. Its specific gravity is approximately 2.6.

Humans probably began to use this natural material to make tools as early as 75,000 B.C. Obsidian had been chipped and flaked to make arrows, spearheads, blades (knives), razors and mirrors (Figure 2). Obsidian is also used for producing ornamental and ceremonial objects, but it was usually fashioned into tools and weapons. It was highly valued and locations of sources were often closely guarded. Not only Ancient Egyptians imported obsidian from Anatolia and Iran, but also the other close settlements, such as Cyprus, (in Shillourokambos, a Neolithic site, large quantities of obsidian bladelets and flakes had been found and it is mentioned that they were brought from Cappodocia in finished form(Steel 2004) , most probably the source was Hasan Dağ), and that shows us the presence of knowledge of the surrounding environment at that ages and the ability of them to reach out and get the raw material and bring it back to their own lands. There are quite a lot of neolithic obsidian tools known from Çatalhöyük, Aşıklar, Musullar and many others in Anatolia which shows us that it was common in those periods.

Figure 2. Obsidian mirror found in Çatalhöyük, 6000BC (Uzuner 2004)

1.4.2 Tektites

Tektites (from Grek *tektos*,molten) are rounded, indefinitely shaped natural glass objects,up to a few centimeters in size. According to most scientists, these have been formed by the impact of large meteorites on Earth's surface, although a few researchers favor an origin from the Moon as volcanic ejection.The composition of tektites is similar to that of obsidian, but they have a higher proportion of iron and manganese (Newton and Davison 1989). Tektites are the driest known minerals, with an average water content of 0.005%. This is very unusual, as most if not all of the craters where tektites may have formed were underwater before impact. Also, partially melted zircons have been discovered inside a handful of tektites. This suggests that the tektites were formed under very high temperature and pressure,they have been heated by passage through the atmosphere while rotating (Newton and Davison 1989). Tektites are found in Czechoslovakia, Indonesia, Vietnam, Australia, the United States, etc.

Australites, Darwin Glass, Indochinites, Javanites, Libyan Desert Glass (which is found in the Sahara Desert in large sand dunes and these slightly yellowish lumps were probably created by meteoritic impact), Moldavites, Philippinites, Bediasites are some tektites (Figure 3) (Dictionary of Science and Technology, 1995).


(a)

(b)

Figure 3. Two types of tektite (a)Tektite (b) Tektite Moldovite (http://en.wikipedia.org/wiki/Tektite)

1.4.3 Pumice

Pumice is a natural foamed glass produced by gases being liberated from solution in the lava before and after rapid cooling (Newton and Davison 1989).

1.4.4 Fulgurites / Lechatelierite

Lightning (Latin: Fulgur) can create glassy formations when it strikes desert areas with the right combination of minerals,a large mass of quartz sand. The resulting crude, brittle, slender, irregular tubes are called fulgurites.There are two types;sand fulgarite and rock fulgarite (Newton and Davison 1989).

1.4.5 Rock Crystal (Quartz)

Rock Crystal (Quartz) has a hexagonal prism shape and generally used as knick-knack. It is especially used in a lot in Roman period and became an art material in Italy and in other countries as well. It is thick and can be sculptured with stone (Figure 4) (Küçükerman 1997).

(a)

(b)

Figure 4 (a) Rock crystal (Uzuner 2004)
(b) God figurine made from rock crystal, 14th-13rd century BC, Hittite, from Tarsus (Uzuner 2004)

1.5 Some Physical, Chemical and Mechanical Properties of Glass

Some physical, chemical and mechanical properties of glass can be summarized as follow.

Glass is strong as it has great inherent strength. It is weakened only by surface imperfections which give everyday glass its fragile reputation. Special tempering can minimize surface flaws.

It is hard as its surface resists scratches and abrasions.

It is elastic under stress up to a breaking point and rebounds exactly to its original shape.

It withstands intense heat or cold as well as sudden temperature changes.

It retains heat rather than conducts it and it absorbs heat better than metal. It reflects, bends, transmits, absorbs light with great accuracy. It strongly resists electric current and stores electricity very efficiently (The Corning Museum of Glass 1998).

Glass is much more resistant to corrosion than most materials, so much so that it is easy to think of it as corrosion-proof. It is affected by few chemicals; hydrofluoric acid, concentrated phosphoric acid (when hot, or when it contains fluorides), hot concentrated alkali solutions and superheated water. Hydrofluoric acid is the most powerful of this group; it attacks any type of silica glass decomposes SiO_2 structure and forms volatile substance SiF_4

$$SiO_2 + 4HF \rightarrow SiF_4 + 2H_2O$$

Other acids attack only slightly; such corrosion is rarely significant in service for acids other than hydrofluoric acid and phosphoric acid.

Acids and alkali solutions attack glass in different ways. Alkalis attack the silica directly while acids attack the alkali in the glass.

When an alkali solution attacks a glass surface, the surface simply dissolves according to the following reaction

$$SiO_2 + 2NaOH \rightarrow Na_2SiO_3 + H_2O$$

This process continuously exposes a fresh surface, which in turn is dissolved. As long as the supply of alkali is sufficient, this type of corrosion proceeds at a uniform rate.

Acid corrosion behaves quite differently. By dissolving the alkali in the glass composition, a porous surface is left that consists of the silica network with holes where the alkali has been removed by the acid. This porous surface slows the rate of attack since the acid must penetrate this surface layer to find alkali to dissolve.

Corrosion by water is similar to acid corrosion in that alkali is removed from the glass surface. Water corrosion acts at a much slower rate. At high temperatures, however, water corrosion can become significant. Many laboratory tests have been devised for testing corrosion resistance of glass (The Corning Museum of Glass 1998).

Glass resists most industrial and food acids such as formic acid, citric acid and tartaric acid.

Corrosion is important in historical glass artifacts. In this case we talk about deterioration of glass.

1.6 Deterioration of Glass

The deterioration of glass is a function of its composition, its firing history, and the burial environment and duration. Glass can appear in extremely varied states of decay, and, since so many factors are involved it is sometimes dangerous to assume the composition of a glass from its condition. In general, glass with too little silica in it is not stable to moisture, and if there is less than or more than the optimum of 10% lime (RO) there is also instability.

Soda glass is almost twice as durable as potash glass, possibly because the potassium ion being larger than sodium ion, (r_{Na+} = 0.98 A° r_{K+} = 1.33A°) its loss during burial causes greater damage. A small percentage of alumina (Al_2O_3) increases stability. Because of higher charge of aluminum ions (Al^{3+}), they are held in the glass network more strongly.

If the composition of glass is exact for stability or even if it is unbalanced, with water absent from the environment glass can be in perfect condition after even thousands of years of burial. It is more usual that these conditions are not met with and, whilst the glass seems to be in good condition, it has in fact deteriorated minutely. This is because the surface has dissolved, but weathering products have been lost and so the glass appears glassy.

Iridescence/Dulling: When glass is in contact with moisture, the alkali metal ions (R^+) are slowly leached out to be replaced by protons (H^+) from the water.The surface layer loses its glassy nature and characteristic refractive index (1.4588) and so appears dull or iridescent. Just as a thin skin of oil on water appears iridescent, so can the translucent decayed surface of glass when it is less than 0.9mμ thick.

However, if a liquid such as water is introduced into this weathered layer, the inconsistency of refractive index are obliterated and the decay is not visible. Thus, on examination ,such damp glass may appear in better condition than it actually is.

An iridescent surface may in fact be composed of a large number of very thin weathered layers. It is not yet clear exactly what causes glass to decay in layers; it could be that as large sodium or even larger potassium ions are replaced by protons the physical stress on the structure causes the leached surface layer to split. Water can now seep through to attack fresh glass underneath, repeating the process again and again.

Total loss of glassy nature: Badly decayed glass may survive only as a chalky mass of silica gel and be somewhat difficult to identify as glass.

1.7 A Brief history of glass and glass technologies

It is known that glass was first produced in West Asia. The earliest pieces obtained are a faded, blue-green, translucent glass rod from Babil's Eşnunna (Tel-elEsmer in Iraq) approximately dated to 2600 BC (Rona 1997) or mentioned as it had been found together with other artifacts dated to Sargon period 2340-2284 BC (Özgümüş 2000), glass beads found in Egypt approximately dated to 2500BC (Rona 1997) and an opaque blue glass lump which has a lot of bubble found in Eridu, Iraq dated to 2100 BC (Özgümüş 2000). During Egypt's 18th dynasty (1600 BC ~ 1700 BC) real glassmaking began, with goblets and bottles as the main glass products. Core molding was the earliest method of glass production. The oldest glass vessel piece was recorded in Alalakh which is produced in core molding technique, a sherd of the neck of a bottle and dated approximately 1550 BC. Glass objects of Alalakh are dated to late 16^{th} century B.C to 13^{th} century B.C, the levels show no interruption. It is also known that from the excavations in the North Mesopotamia in Assur, Nuzi, Ninive, Tell al-Fakar, Tell al-Rimah and Çağar Bazar (Iraq), Tell Brak (Syria) which were all Hurri countries, that core-molding was used after 1550 BC (Özgümüş 2000).

The core was modeled in clay and manure, fixed to a metal rod, given the shape of the desired vessel and then dipped into molten glass. When cool, the clay core was picked out leaving a small hollow glass object. Simple casting and pressing methods such as pouring molten glass into molds and cutting were also used as earliest methods as well (Figure 5). Casting method was widely in use in the Hurrian-Mitannian, Mycenaean, Utarian, Phrygian, Greek and Roman periods.

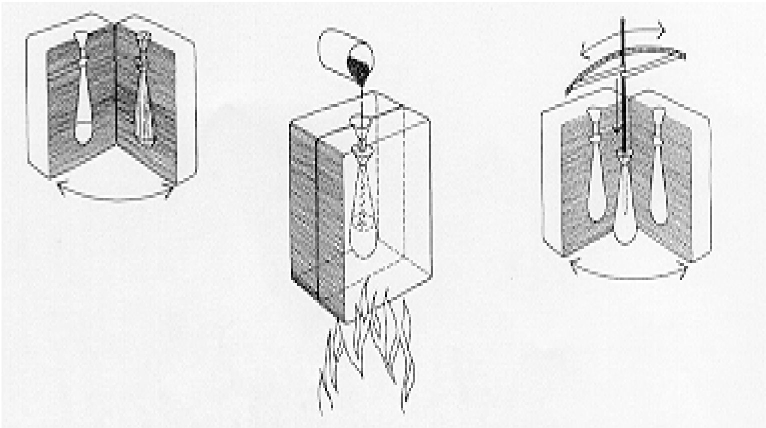
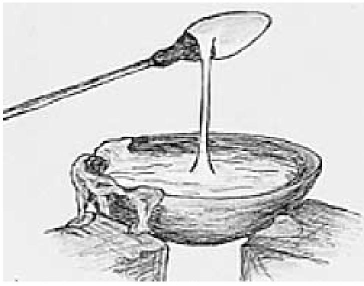


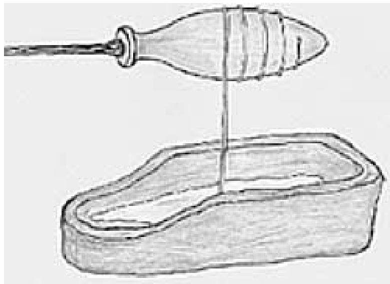
Figure 5. Casting Method of glass making

These techniques were good for the production of flat and deep bowls only, and mass production was still impossible (The Corning Museum of Glass 1998).

The core forming is the method of producing small vessels. Steps of this process start with a shaped clay and it was formed at the end of a metal rod. After getting the clay dried, the core was covered with molten glass drawn from a small crucible (a pot used for melting which is usually made of fired pottery material in ancient times) taken from a furnace. Then the dried clay was coated (Figure 6a) and a contrast color was drawning around the first color (Figure 6b). The hot, soft bands of glass were pulled to gain a wave-like pattern (Figure 6c). When the core cooled, clay was scraped out (Figure 6d) (The Corning Museum of Glass 1998).



a



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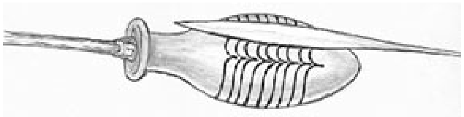

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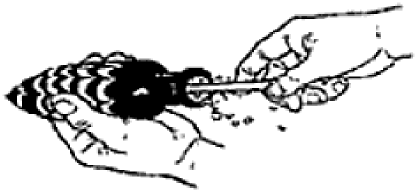


d

Figure 6. Core forming process (The Corning Museum of Glass 1998)

In 1400’s BC, North Mesopotamian glass makers were producing mosaic glasses and grainy glasses. In 1400’s BC developments in Hurri countries had effected other regions as well.

Kaş-Uluburun Shipwreck is dated to the late of 14th century BC; within its cargo, over 175 cobalt-blue, turquoise and purple disk ingots and beads have been found (Renfrew and Bahn 1998). The map of the probable route of the ship found in Uluburun is given in Figure 7.

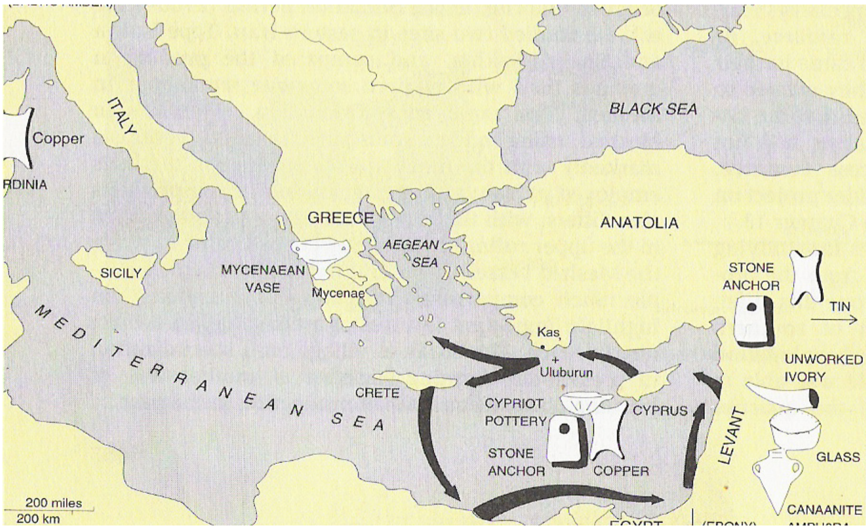


Figure 7 The map of the probable route of the ship found in Uluburun and likely sources of materials for the various artefacts found on the wreck (Renfrew-Bahn 1998).

Many casted beads are found in Necropolis of Müsgebi near Bodrum and the necklace found here is associated with Uluburun shipwreck's glass ingot as well, that is considered as made from the same ingots. In Aegean, casted beads and jewelleries are recognized in Late Helladic II period (1500BC) and became very common in Late Helladic III period 1300-1400 BC. But the first records of these are West Asian.

At the end of Bronze Age around 1200 BC, regression was observed in glass making. In West Asia, renaissance in glass making was observed backdate to 800 BC(Özgümüş 2000). As early as 800 BC, the glassmakers were probably based in Gordion (Yassıhöyük-Turkey) and in Nimrud (Mesopotamia) (Newton and Davison 1989). The oldest group that dated to 1000 BC was from Hasanlı, Iran.While core molding was going on at the end of 700 BC and at the beginning of 600 BC, glassmakers began to casting. The most important example for this is the plate found in Gordion, dated to the end of 700 BC. Another active glass making center, but not known well is in North Italy where coarse but interesting core molding cups were produced (Özgümüş 2000).

After the invention of glass blowing, in the mid of 100 BC, producing became easier and was speed up. Romans, probably Phoenicia (Lebanon), discovered that an object could be formed by gathering molten glass on the end of a hollow blowing pipe, and inflating it like a bubble. It could be blown into a hollow mold to form it or freely shaped with simple tools on the end of the blow pipe. For the first time, a worker could mass-produce dozens of objects a day with glassblowing technique. Most, but not all of these products became common and inexpensive. Around 200 BC, Syrian craftsmen in the area between Sidon and Babylon made a breakthrough with the discovery of the glassblowing pipe. The glassblowing pipe is made from a hollow metal pipe with a mouthpiece at one end. The glassmaker places a gob of molten glass on the other end and blows through the mouthpiece to inflate it into a hollow body. The blown glass, with its large surface contact with the air, cools quickly. Small objects harden in 2-3 minutes and larger ones in about 10 minutes, making glass vessels easy to produce in mass quantities. The blowing of glass with a pipe enabled thin-walled, fine glasses in a large variety of shapes to be made. In addition, using a mold with this technique allowed the standardization and duplication of objects.

Ateliers of glass were mainly in Syria and Palastine. After Syrian glasssmakers brought that technique to Italy, a big development occurs and this industry spread to Asia, Europe and Africa. Glass manufacture began in China around 300 BC, and glass accessories with distinctive Chinese characteristics were created. Glass did not seem to be of much interest in China except as an imitation of jade and other natural materials. Transparent qualities were largely overlooked. About the time of the Hellenistic Greek and Roman periods in the West, Chinese glassmakers made small, jade-like carved glass figures and Pi disks, (symbolized heaven). Glass was introduced to Korea through China, and Korean glassmakers created various types of beads, such as small beads and tubular beads. Korean glass objects and glassmaking technology in turn, were spread to Japan (The Corning Museum of Glass 1998). In Japan, early imports of Chinese glass stimulated the development of glass making paralleling that of China. Later characteristic Japanese styles were produced. Archeological finds of Western glasses, and some remains of local manufacture, have been uncovered in Korea, throughout Southeast Asia, and in India (The Corning Museum of Glass 1998). Beads, bangles, and other small glass objects were made in India in pre-Roman times, and the production of blown utilitarian wares had been firmly established there by the Middle Ages. Beads made in India were widely distributed throughout Southeast Asia.

It is thought that the ability to make glass developed over a long period of time from experiments with a mixture of silica-sand (ground quartz pebbles) and an alkali binder fused on the surface. The material called faience had been used for well over a thousand years to make small decorative objects such as beads and amulets.

Glass beads were also found in China. They are most likely the product of technological interchange between China with Mesopotamia and Egypt. Later in Egypt, the glassmakers painted colourful feather or zigzag patterns on the surface of glass vessels.

The real origins of modern glass lay in Alexandria during the Ptolemaic Dynasty (323-30 B.C). The glassmakers in Alexandria developed a new technique called Mosaic glass. Glass canes of different colors were cut crossways to make decorative patterns. Millefiori glass, with colourful flower patterns, is a type of mosaic glass.

The Romans perfected cameo glass, in which the design was produced by cutting away a layer of glass to leave the design in relief. The glass objects of that period are generally named Roman Glass, and they are characterized by filigree, mosaic, and engraved decors. In Roman architecture translucent sheets of alabaster or mica were commonly used as the window material, but it is also during this time that glass was first used to enclose wall openings. Two small 230 mm x 540 mm flat panes of glass were used in the ceiling window of the bathhouse in the plaza of Pompeii. It is believed that the expertise and technology of glass manufacture of Roman Empire was spread throughout Europe, and as far east as China.

Manufactured glass contains far fewer impurities. Glass in ancient times was mostly colored, but with the development of glassmaking technology, production of thin and clear glass became possible.

After the West Roman Empire was ruined in 500 AD, regression in glassmaking was observed in Europe and the developments went on in Byzantine.

Later types can be mentioned as Sassanian glasses (early Islamic glasses) and in Abbasi Period (750-1258) in Iran, Iraq, Syria and Egypt Islamic glasses. Many glasses had found in Halep, Hama and Damascus in Syria, Rakka and Samarra in Iraq, Nishapur in Iran and Fustat in Egypt (Özgümüş 2000).

In Medieval Period the most important ones in Near East glasses belonged to Memluks. Crusaders had taken these away to Europe. After the invasion of Timur in 1400's, Islam glassmakers were taken away to Semerkand.Therefore Syrian glasses were regressed, while Venetian were progressed (Özgümüş 2000) and influence spread throughout Europe, all the way to Asia. The foundation for modern glass making is set.. The flat sheets of glass were succeeded in Medieval Period. Palace of Termiz (in Uzbekistan) colorfull glass alabasters and glass medallions indicate glass products of Karahanlılar Period.

In the period of Eyyubis glass products such as jars, lamps and other glass wares were produced in Halep.

In the 13th and 14th centuries Turk Memluks as well developed glass works and the most successful ones from this period were hallmarked lamps.

The evidences of the use of colorful glass in the Anatolian Seljucks came from the Palace of Kubadabad in Beyşehir (Ödekan 2000).

Other than the previuosly mentioned artifacts, many glass artifacts found in Anatolia unearthed from many sites such as Alişar, Boğazköy, Yanarlar (a Hittite necropolice near Afyon), Toprak Kale, Gordion, Çandarlı (Pitane), Ephesos, Kaunos, Myrina, Sardes, Xanthos, Cilician finding centers Kadirli (Flaviopolis), Anavarza (Anazarbus), Kozan (Sisum), Osmaniye, Yumurtalık (Aigaia) and Misis (Mopsuestia), Anemurium, Antioch, Stratonikeia (in Bodrum), Edirne, Eskişehir, Gaziantep, Nicaea(İznik), Herakleia Pontica (Karadeniz Ereğlisi), Kaunos, Köşker Baba (near Fırat), Maşattepe, Priene, Reyhanlı-Esentepe, Sardes, Troya, Aphrodisias, Alahan, Amorium, Mezra Höyük, Yumuktepe Höyük, Derme (Myra), İmikuşağı, İstanbul, Kudab-Abad, Samsat, Diyarbakır (Özgümüş 2000).

1.8 GLASS BRACELETS

Glass has been used to make a variety of artifacts including bottles, drinking cups, vessels, beakers, bowls,vases, jars, pendants, lamps, goblets, window glasses, beads and bracelets. Occasional glass bracelets were dated back to 2000 BC. Large scale manufacture of glass bracelets was encountered in central Europe dated to the last centuries of 1000 BC. These were made in seemless method and many of them are quite elaborate,decorated both by tooling and applied colored glass. Some multicolored bracelets were made in British Isles in 1st and 2nd centuries AD. Early bracelets were found in India and Vietnam as well. In Levant, glass bracelets were common in 3rd century (Spaer 2001).

Few amount of bracelets were also found in Sardis that were assigned to the Early Byzantine Period (Spaer 1988). Closed ring glass bracelets were common in Paletsine from late Roman to recent times. They were inexpensive ornaments, neither artistically nor technically outstanding, but not without charm, and in time they became more prevalent type of glass jewellery in all of the Levant and further field (Spaer 1988).

There are two major techniques of bracelet manufacturing; seamed and seamless. Seamed ones were made from drawn-out glass canes which were bent and closed with a seam. Seamless ones were made by picking up glass on a rod and with or without the aid of additional tools centrifugally rotating it untill the desired ring form was obtained. The inner surfaces of such bracelets are always flat and usually show longitudinal streaks. Bracelets which has round cross section are invariably seamed. Seamed bracelets are in a variety of shapes (Spaer 2001).

Twisted bracelets were made from glass canes which were constantly turned during the drawingout process and then closed with a seam. The application of coloured trails to twisted bracelets was achieved either by adding the trails to the gob of glass about to be drawn and turned, or by adding the trails along a turning pre-drawn cane. The former method was presumably the common one. The latter method is likely to have been used when the basic ring shows few traces of spiral turning (Spaer 2001).

Four major types of glass bracelets from the Near East were distinguished(Spaer 2001).

- Type I: Plain bracelets which are monochrome and have either circular (always seamed), semicircular (mainly seamless), flat (with very few exceptions seamless) or pointed(with very few exceptions seamless) cross sections.Pointed or quite flat profiles largely belonged to Islamic period.
- Type II: Bracelets with tooled or molded decoration which are monochrome as well but divided as their patterns: sparse vertical ribbing; vertical ribbing;diagonal ribbing;horizontal ribbing,seamed; prunts and other protuberances;stamped symbolic motifs. Tooled or molded decoration, although occasional examples are known from other times, primarily encountered in 3rd-7th centuries AD.
- Type III: Spirally twisted bracelets are all seamed but divided according to the types of decoration: monochrome without further decoration; monochrome with stamped motif on seam; added single trails; added symmetrically fused trails; added asymmetrically fused trails and inside trails.

Twisted bracelets are unlikely to have appeared before the 4th century AD. Monochrome twisted ones were popular throughout most periods and at most places but may be especially in Syria and Anatolia. Added colored trails were common throughout the Islamic period. Inside trails were in use only in late Ottoman contexts.

- Type IV: Bracelets with applied colored decoration are divided according to both their cross sections and the type of decoration: semicircular: flat; evenly pointed and obliquely pointed (Spaer 2001).

1.9 Aim of the study

Glass bracelets are one of the important glass artifacts to be studied to get the raw material characteristics and production technologies. Glass bracelets as archaeological artifacts are not well studied same as glass in general. Almost all studies made on glass bracelets in Anatolia are mainly typological. Fortunately, in two archaeological sites Mezraa Höyük and Yumuktepe, a number of glass bracelets of Medieval Period had been found. Aim of this study is to start the investigation of glass bracelets obtained from these two sites, sixteen samples from Mezraa Höyük and fiftyseven samples from Mersin Yumuktepe.

1.10 Mezraa Höyük and Yumuktepe Höyük

Mezraa Höyük is in the south of Mezraa region of Birecik in Şanlıurfa in Southeastern Anatolia. It is located at the east of the River of Euphrates and in the effected region of Carchamish Dam. The excavations were held under the TAÇDAM (Centre for Research and Assessment of the Historic Environment) Ilısu and Carchamish Dam Project, on behalf of Archaeology Museum of Şanlıurfa and conducted by Assistant Prof. Dr. Derya Yalçıklı and Assistant Prof. Dr. Vahit Macit Tekinalp from Hacettepe University during the 2000, 2001 and 2002 excavation seasons (Figure 8).

Mezraa Höyük has settlement levels from Late Chalcolithic end of 4000 BC till AD 11th -13th century. According to the existence of 3 levels on the three sides of the Höyük, in southeastern, eastern and northwestern parts, the site had a wide settlement in the Medieval period (Figure 8).

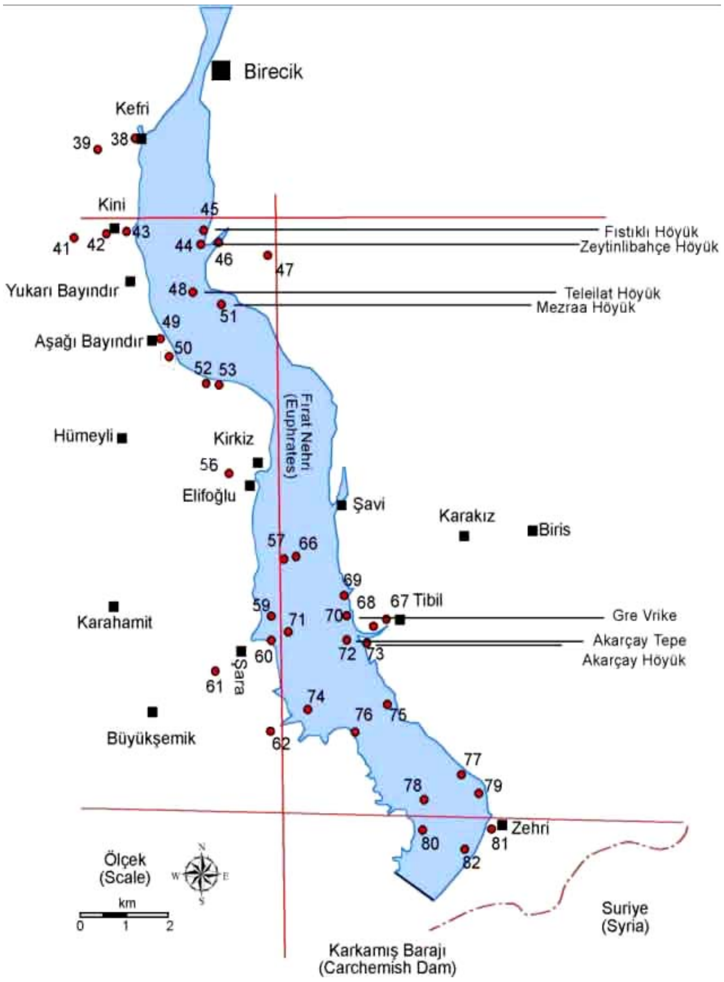
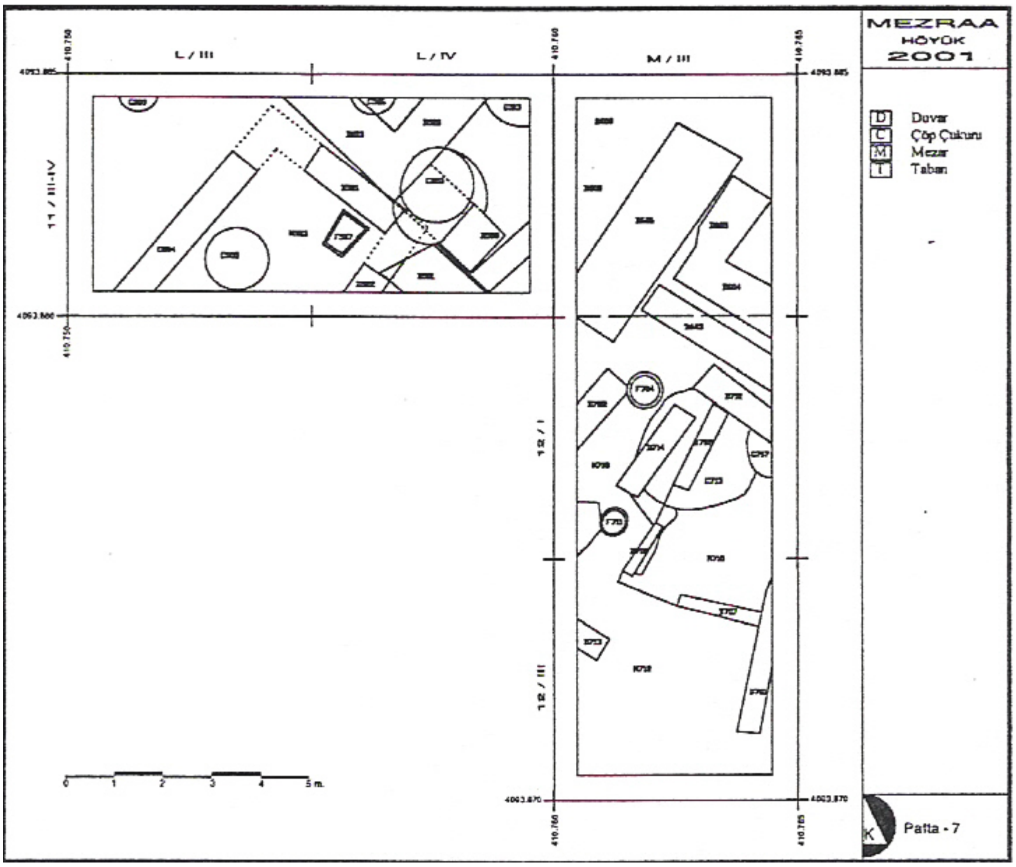


Figure 8. Mezraa Höyük and neighbourhood sites located near Euphrates (Yalçıklı and Tekinalp, 2002).

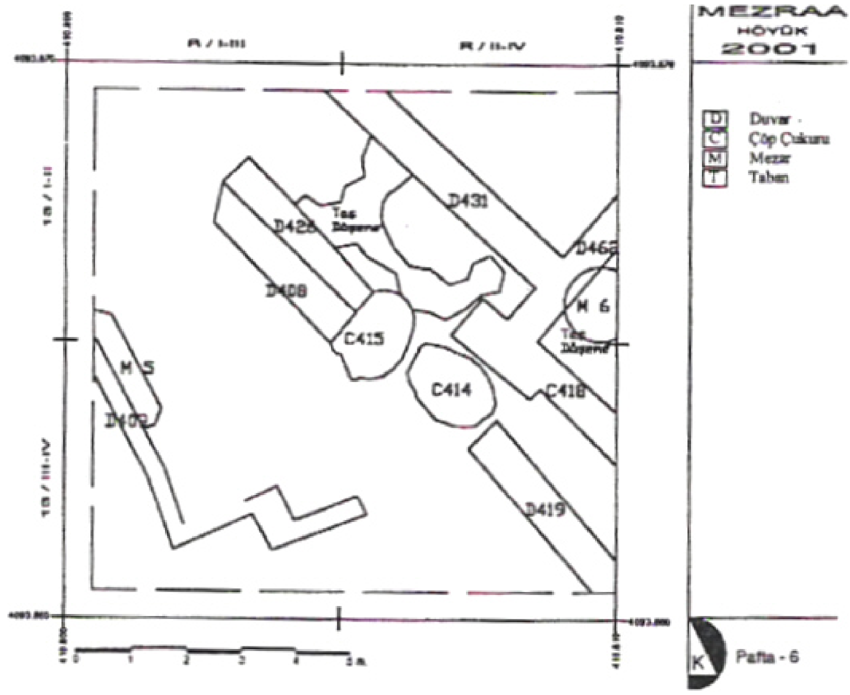
Figure 9. General view and plans of Mezraa Höyük

(a) A view from northwest trench of Mezraa Höyük

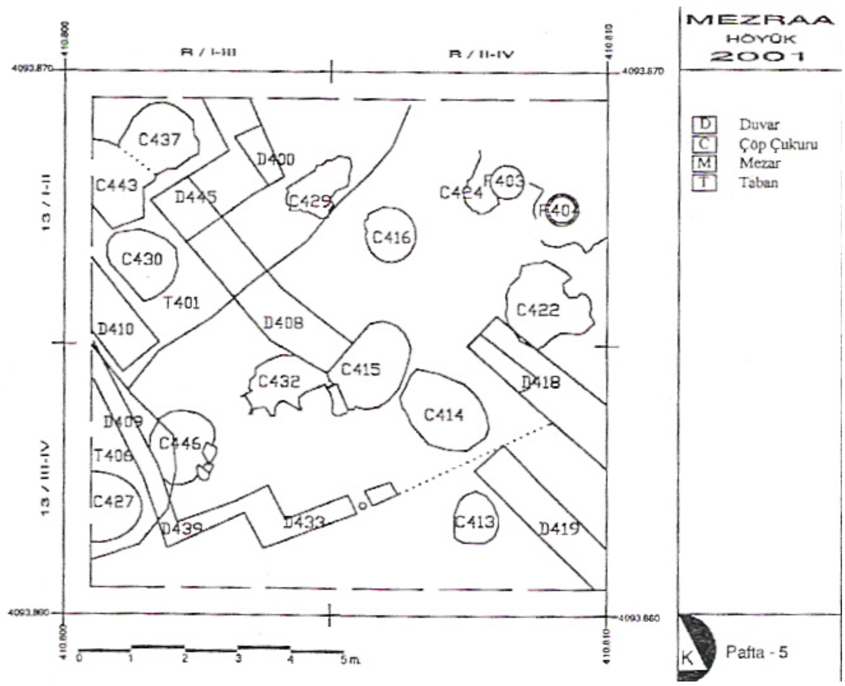


(b) Plan of Northwest slope trenches of Mezraa Höyük

(c) A view from east slope

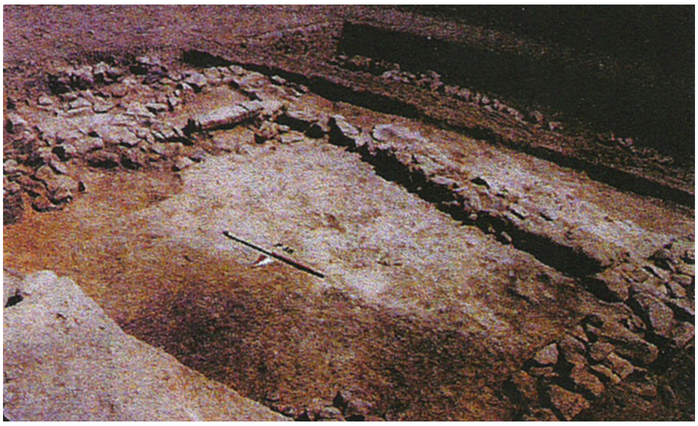


(d)

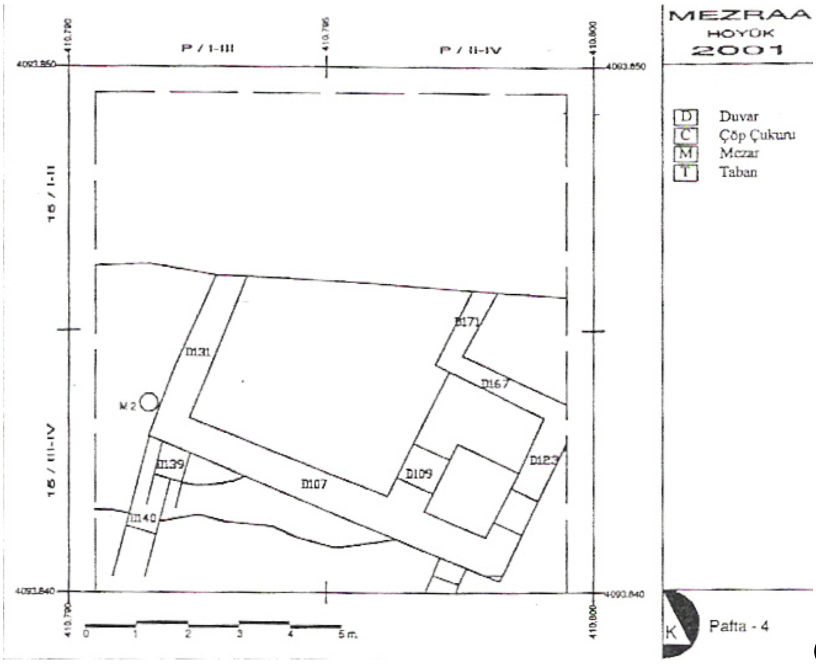


(e)

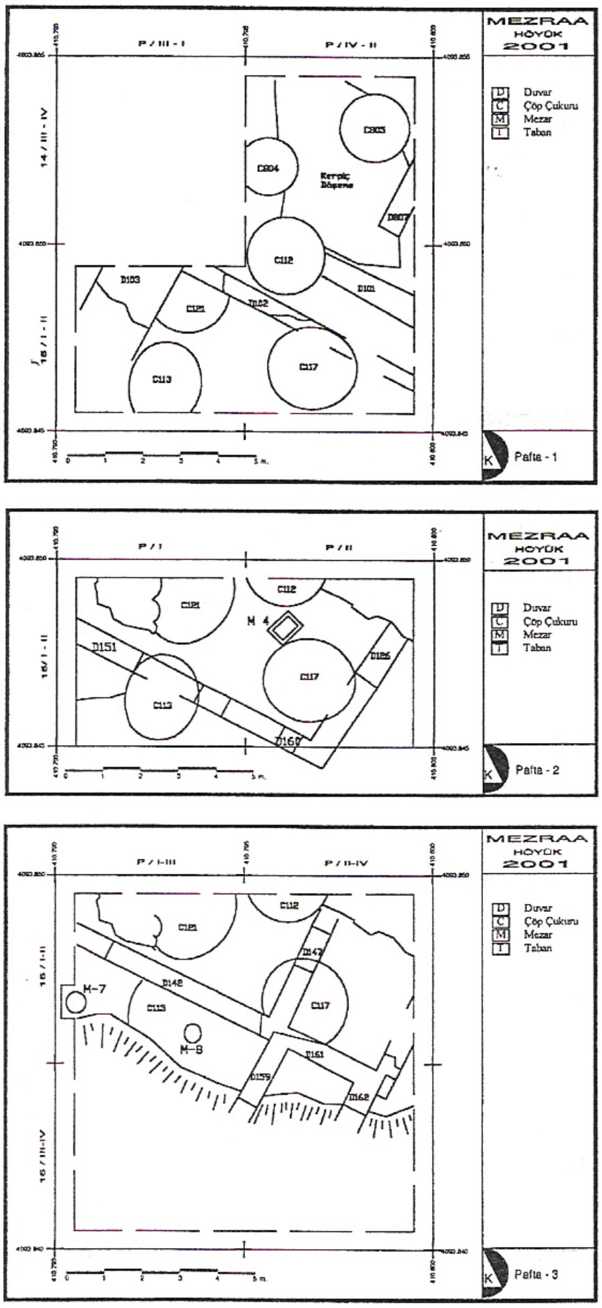
(d) and (e) Plans of East slope trenches



(f) Trench from southeast



(g)



(h)

(g) and (h) Plans of Southeast slope trenches

Figure 9. General view and plans of Mezraa Höyük (Yalçıklı and Tekinalp)

(a) A view from northwest trench

(b) Plan of Northwest slope trenches

(c) A view from east slope

(d) and (e) Plans of East slope trenches

(f) Trench from southeast

(g) and (h) Plans of Southeast slope trenches

Mezraa Höyük has sgraffito and luster ceramics in general and casted cups had found which is known from Raqqa (Tekinalp 2004). Raqqa was one of the centers of this type of ceramic manufacturing and these are dated to 12th-13th century. A coin dated to AD 1238-1242 had found also, therefore the site relatively dated into 11th-13th century (Tekinalp 2003).

Edessa, the ancient name of Urfa, was under the rule of Byzantines in 1031 but retaken by the Arabs. Later, it governed by Greeks, Armenians and the Seljuk Turks (in 1087). In 1099, the Crusaders established County of Edessa and ruled the city untill 1144(http://en.wikipedia.org/wiki/Edessa%2C_Mesopotamia).

Figure 10 shows the map of Edessa about 1140.
(http://en.wikipedia.org/wiki/County_of_Edessa)

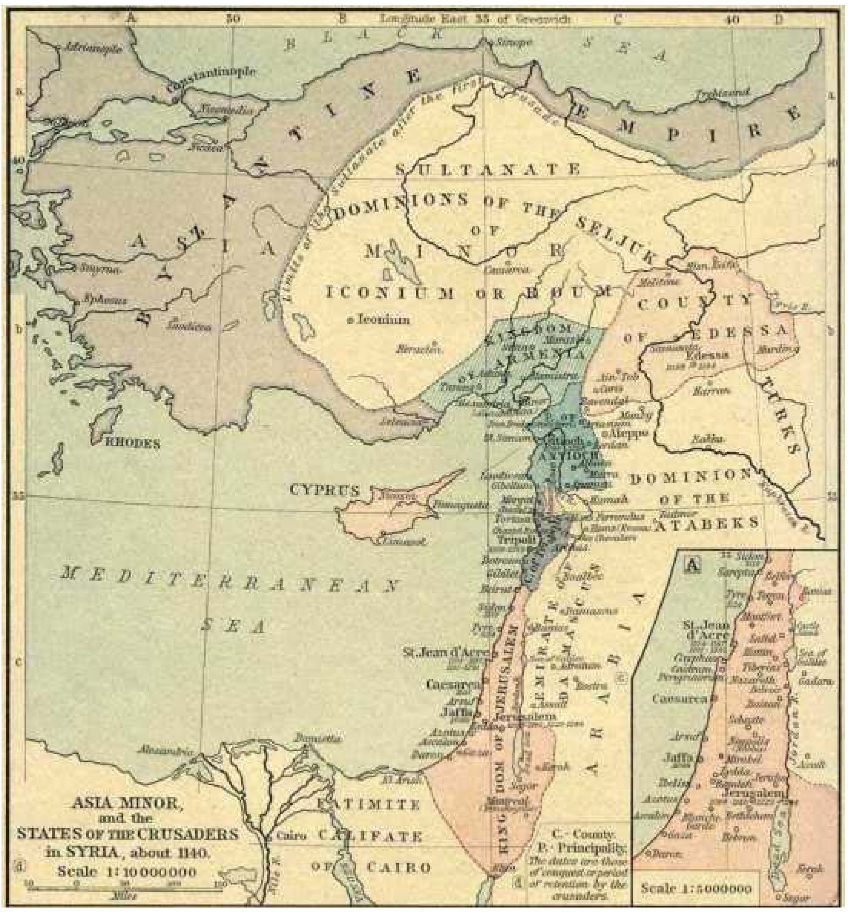


Figure 10 Map of the Edessa about 1140
(http://en.wikipedia.org/wiki/County_ of_Edessa).

City was taken by Turk Zengui after 1144 and has belonged to the Sultans of Aleppo, the Mongols, the Mameluks and later to Ottoman Empire in 1517.

Yumuktepe is in Mersin (İçel) in Southern Anatolia. It is located on the left site of the Müftü (Soğuksu) Beck. The site is excavated in two terms in general; first excavations were made under the supervision of British John Garstang and by a team in which Gordon Child, Seton Lloyd, Richard Barnett and Oliver Gurney was joint (Köroğlu 2002). That term excavations were made before and after the Second World War, in 1936-1939 and in 1947-48. In 1993 the second term excavations had been started. The site excavation went on in 1993-1999 and 2002-2006. Second term excavations are still going on under the supervision of Isabella Caneva. Figure 11 shows one of the peak trenches Ib dated to mid of 12th century.

Figure 11. Plan of Ib level of Medieval Yumuktepe Peak Trenches dated to the mid of 12th century (Köroğlu 2002).

The site had been a continual settlement for 7000BC to the second half of AD 1300 (Caneva-Köroğlu 2003).

Unfortunately, peak of the site, which was the Medieval Period of the settlement had been destroyed in 1963 by the Municipality of Mersin to make the Höyük a park. During this interference site became terraced and trees planted. Peak of the Höyük flattened by taken off 1-1.5 m depth. Some parts of Islamic and Byzantine levels that Garstang mentioned in his book are destroyed in these years (Köroğlu 2002). Therefore, the structure level of the late period structure with few surface findings and Marsilya tile and also the structure level of Islamic Period, 14th century with the findings of glass spoon, glass lamp, body sherd made in luster technique, some glazed and non-glazed ceramics and coins that Garstang mentioned had removed in 1963.

In the 2004 excavation season, glass drinking cup had found in grave together with other glazed plate, ware, bead, earring and som Crosses. Glass bracelet pieces and a glass ring had found in a long pit, which was opened to take the wall stones in either in the second half of 13th century or later(Köroğlu 2004). According to coins found in the site, the latest one was made by Armenian King I.Levon in Sis (Kozan), the capital city of Armenian Kingdom of Cilicia, and it is dated to the first mid of 12th century (Köroğlu 2004).

In the second term excavations, the excavation started from Ia structure level, and for not to change the stratigrafy completely which mentioned by Garstang the removed structural levels called as “O”. Ia is the partially destroyed level that starts right after the surface and no coins had found there. So the dating for this level is made according the comparison of the ceramics found in Byzantine centers. Similars are dated to mid of 12th century and to the beginning of 13th century. Ib is the next and older structural level and it is the best preserved and highest architectural Medieval level of the site.Ib is dated to the last quart of 10th century to 11th century according to the coins and other artifacts (Köroğlu 2004).

The history of Cilicia region during 10th and 14th century was highly related with the Byzantine settlement of Yumuktepe Höyük. After Arab incursions and invasions, the region was under the rule of Byzantine Emperor Nicephorus II Phocas in 963 or around 965 and the region ruled by Byzantines till 1085. Armenian Kingdom, a province of Byzantine, ruled the region from 1085 to Mameluks dominance in 1375 (Köroğlu 2004). Figure 12 shows the map of the region in the year of 1265.

(http://en.wikipedia.org/wiki/Armenian_Kingdom_of_Cilicia)

Figue 12. The map of the region in 1265

(*The Historical Atlas,* William R. Shepherd, 1911)

(http://en.wikipedia.org/wiki/Armenian_Kingdom_of_Cilicia).

Therefore, “I” structure level of the site was under the rule of Byzantine during 11th and 12th century and the later Islamic level that mentioned by Garstang is considered as it belongs to Mameluks, dominated the region in 14th century (Köroğlu 2002).

CHAPTER 2

MATERIALS AND METHOD

2.1 Sampling

In this study a number of glass bracelets obtained from two sites Mezra Höyük and Yumuktepe Höyük have been started to be examined.
Photographs of the samples are given in Figure 13 is from Mezraa Höyük and in Figure 14 is from Yumuktepe Höyük.


(a)


(b)

(c)

Figure 13 Glass artifacts obtained from Mezraa Höyük
(a) and (b) are bracelets and (c) half of a ring and two vessel pieces are shown.

Samples of Mezraa Höyük

Sample 1

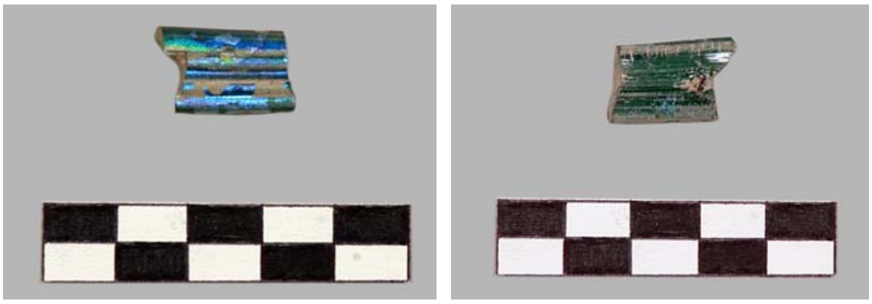
Sample 2

Sample 3

Sample 4

Sample 5

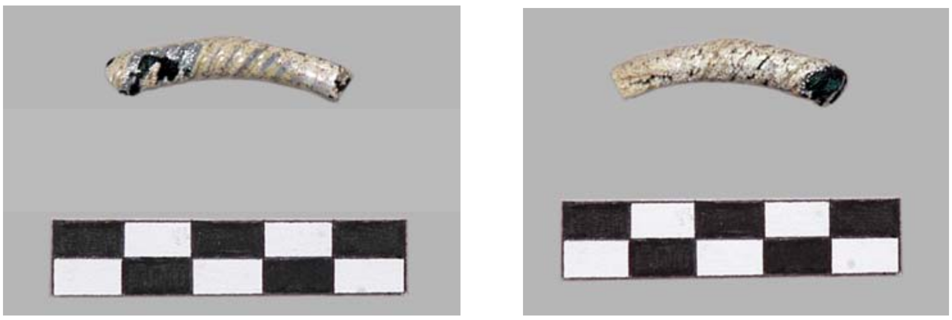
Sample 6



Sample 7

Sample 8

Sample 9



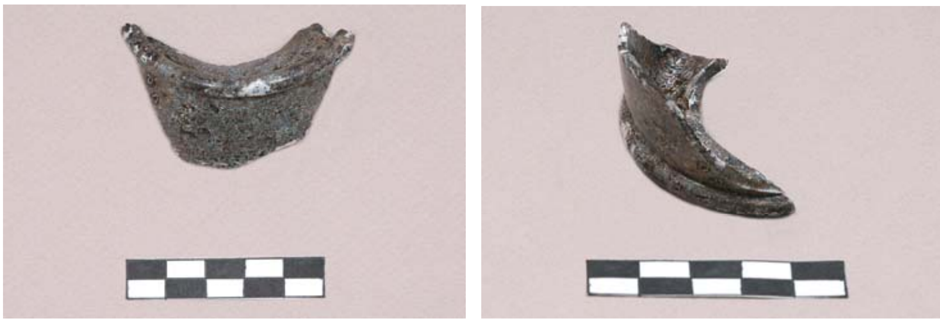
Sample 10

Sample 11

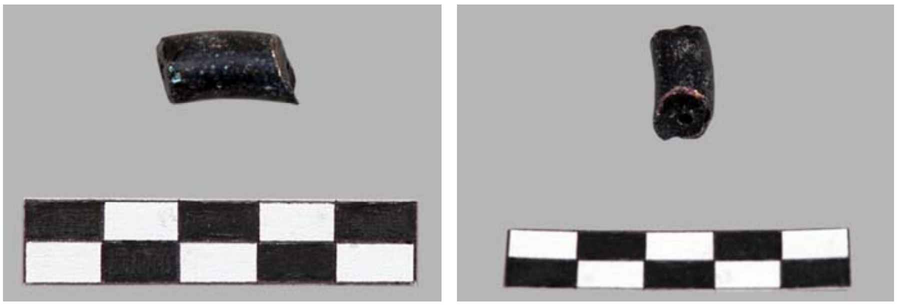
Sample 12

Sample 13

Sample 14



Sample 15



Sample 16

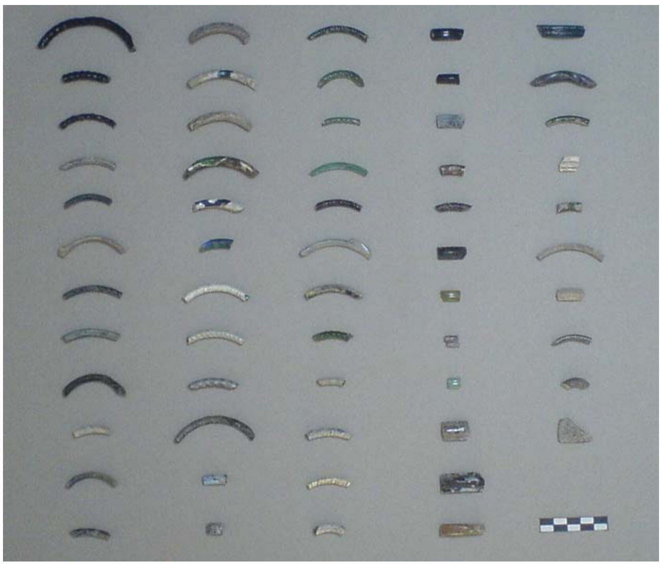
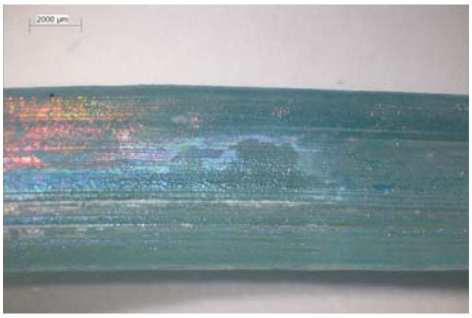


Figure 14 A group of glass bracelets of Yumuktepe Höyük

The technical drawings of the samples have been carried out and given in Appendix A, as Figure 18 a,b.
The colors of the samples were determined by using Munsell Color Chart and shown in Table 5.

2.2 Visual Classification

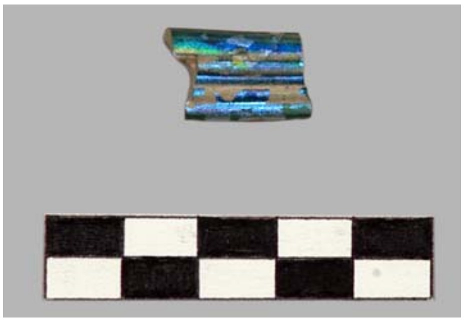
After a first naked eye inspection , it was determined that some samples; such as samples 1,2,7,10 and 15 showed altered surface (iridescence)(Figure 15) and other samples seemed to be undeteriorated. But under the microscopy photographs, they had also seen somewhat deteriorated such as samples 3,11 and 14.



Sample 1

Sample 2

Sample 3



Sample 7 Front Back

Sample 10

Sample 11

Sample 14

Sample 15 A vessel piece

Figure 15 Samples that show iridescence and deterioration.

Deteriorated surface layers of all samples were scratched out and XRD analysis had been done for four samples. XRD trace of one of the samples is given in Figure 16.

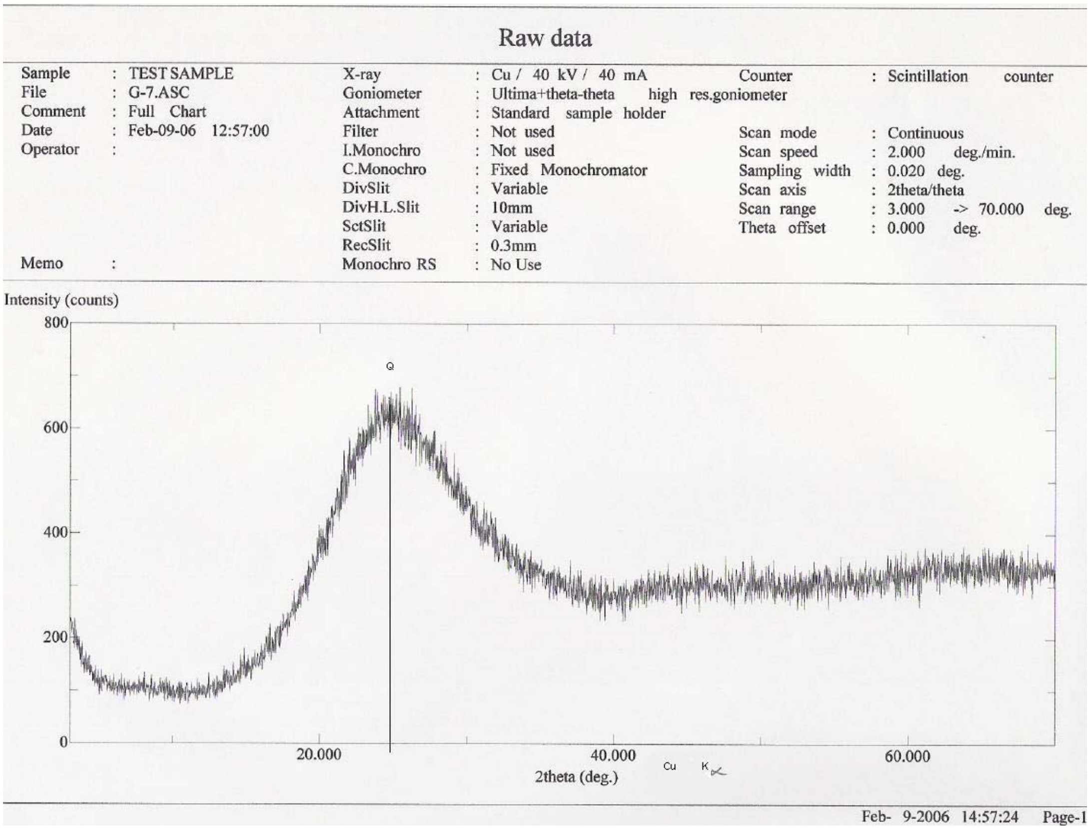


Figure 16 XRD traces of the deteriorated surface layer of Sample 10 of Mezra Höyük.

2.3 Thin Section Analysis

Thin sections have been prepared from 7 samples of Mezra Höyük in Mineral Research and Exploration Laboratory (MTA) and examined by using a convenient optical microscope.

2.4 Elemental Analysis

Elemental analysis of the samples had been done by using Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-OES) in METU Central Laboratory. The high temperature of plasma (9000-10000 K) normally reduces or eliminates chemical and spectral interferences, common to lower temperature flames such as those used in atomic absorbtion methods (Lambert et al. 1996). Therefore ICP-OES method was used to analyze elemental composition of the bracelet samples.In the analysis major (except Si), minor and some trace elements have been determined. Before analysis, surface layers of the samples had been scratched out, the remaing part of each sample was powdered by using agate mortar and pestle. Results of the analysis are given in Chapter 3, in Table 6.

CHAPTER 3

RESULTS AND DISCUSSION

3.1 Sample Description

All the bracelet samples were broken. This is mostly the case for glass artifacts. Visual examination showed that bracelets from Mezraa Höyük have three main characteristics; twisted monocrom, plain and cylindrical ribbing.

Similar glass bracelets of Mezraa Höyük were found in the neighbourhood sites in the region; in the child tomb in Zeytinlibahçe (Figure 17a) and also in Akarçay Höyük. The similar glass bracelets are known from the north of the Euphrates region such as İmikuşağı (Figure 17b) in Elazığ and Pirot in Malatya (unfortunately these two archaeological sites are lost below of Karakaya Dam) and also from Samsat in Adıyaman which was the capital city of Commagene Kingdom (that is also lost below of another dam, Karababa Dam), and also known from some other sites in the South Anatolia such as Kinet, Mersin Yumuktepe and Demre-Myra Aziz Nikolaos Kilisesi (Church of Demre-Myra Saint Nicholaos).

(a) (b)

Figure 17 Glass bracelets (a) Zeytinlibahçe, (b) İmikuşağı

Yumuktepe has quite a lot of glass bracelet collection, it was over 500 in the year 2002 (Köroğlu 2002). Some samples of Yumuktepe Höyük were also started to be examined. The collection is mainly characterized as plain monochrome and twisted bracelets and it also has typical Byzantine bracelets which are color decorated and made in enamelled technique. Similar glass bracelets of Yumuktepe Höyük were found in Hama, Sardes, Korint, Amorium and in many Byzantine settlements in Balkans. On the other hand, the studied materials of this site are in the same type as Mezraa's; twisted monocrom, plain and cylindrical- ribbing.

By the result of XRD analysis (Figure 16) the patina of the samples of Mezraa Höyük, it is understood that they have the typical amorphous structure and has no crystalline phase (Garcia-Heras et al. 2005). Due to amorphous structure of the surface XRD trace gave a hump instead of peak at around 3,34 A° (2θ=26.6°) which corresponds to quartz mineral.

Table 4. Description of the samples: M=Mezraa Höyük YT=Yumuktepe

Sample No	Archaeological Inventory Number	Inner diameters (cm)	Description
1	M-L11 3501 U 06	6	Plain
2	M-L11 3501 U 08	6	Plain
3	M-L11 3502 U 08	5	Cylindirical
4	M-L11 III-IV 3503 U 08	4	Cylindirical
5	M-L11 3503 U 11	1	Ring (half)
6	M-L11 3506 U 07	6	Plain with the band
7	M-M12 4003 U 06	6	Plain
8	M-M12 I-III 4501 U 04	6	Plain
9	M-M12 4501 U 11	7	Cylindirical
10	M-P14 IV 5003 U 08	7	Twisted monochrom
11	M-P14 IV 5008 U 05	5/6	Twisted
12	M-R13 3001/03 U 07	-	Unidentified piece
13	M-R13 3004/02 U 01	6	Twisted monochrom
14	M-R13 3023 U 01	4	Cylindirical, twisted
15	M-R13 3032 U 01	Outer 6.5	Bottom of a vessel (?)
16	M-R13 3057 U 03	6	Cylindirical with a hole inside
17	YT-2004 SURFACE-a	6	Cylindirical
18	YT-2004 SURFACE-b	7	Cylindirical
19	YT-2004 SURFACE-c	6	Twisted
20	YT104 13/09 2/05 4003 -a	-	Sherd
21	YT104 13/09 2/05 4003 -b	8	Plain D cross-section
22	YT104 13/09 4003 2/05	7	Cylindirical
23	YT104 4003 Z-105	7	Cylindirical
24	YT 104 N-18 4055-a	8	Plain D cross-section
25	YT 104 N-18 4055-b	6	Plain
26	YT 104 N-18 4055-c	6	Twisted
27	YT 104 N-18 4055-d	8	Twisted
28	YT 104 N-18 4055-e	7	Twisted
29	YT 104 N-18 4055-f	7	Cylindirical
30	YT104 N-18	4	Twisted
31	YT104 N-18 Z-106	6	Cylindirical
32	YT1006 M-21	7	Twisted
33	YT1047 M-22-a	6	Twisted
34	YT1047 M-22-b	7	Cylindirical
35	YT1055 M-22-a	7	Twisted
36	YT1055 M-22-b	6	Plain
37	YT4006 L-17 Z-100	7	Twisted
38	YT4020 N-18 Z-106-a	6	Plain
39	YT4020 N-18 Z-106-b	6	Plain B cross-section
40	YT4020 N-18 Z-106-c	8	Plain
41	YT4020 N-18 Z-106-d	5	Plain D cross-section
42	YT4020 N-18 Z-106-e	6	Cylindirical
43	YT4036 N-18 Z-106-a	7	Twisted
44	YT4036 N-18 Z-106-b	6	Twisted
45	YT4036 N-18 Z-106-c	6	Twisted

Table 4 (cont'd)

Sample No	Archaeological Inventory Number	Inner diameters (cm)	Description
46	YT 4036 N-18 Z-106-d	8	Twisted
47	YT4041 L-17 Z-101	5	Plain D cross-section
48	YT4042 O-16 Z-108	6	Twisted
49	YT4059 O-16/O-17-a	4	Twisted
50	YT4059 O-16/O-17-b	2	Cylindirical
51	YT4059 O-16/O-17-c	7	Twisted
52	YT4061 Z-108	7	Plain
53	YT4075 L-17 Z-100	5	Cylindirical
54	YT4077 L-17 Z-101	6	Cylindirical
55	YT4083 L-17 Z-103-a	7	Cylindirical
56	YT4083 L-17 Z-103-b	5	Cylindirical
57	YT4083 L-17 Z-103-c	6	Plain D cross-section
58	YT4087 O-16/O-17 P-16/P-17 Z-108 -a	6	Twisted
59	YT4087 O-16/O-17 P-16/P-17 Z-108 -b	6	Plain D cross-section
60	YT4087 O-16/O-17 P-16/P-17 Z-108 -c	7	Plain
61	YT4087 O-16/O-17 P-16/P-17 Z-108 -d	4	Cylindirical
62	YT 4119 O-17 Z-120	7	Twisted
63	YT4120 M-18/N-18 Z-121-a	6.5	Cylindirical
64	YT4120 M-18/N-18 Z-121-b	7	Cylindirical
65	YT4125 M-18 Z-125-a	6	Plain D cross-section
66	YT4125 M-18 Z-125-b	4	Cylindirical
67	YT4125 M-18 Z-125-c	8	Twisted
68	YT4125 M-18 Z-125-d	8	Plain B cross-section
69	YT4125 M-18 Z-125-e	8	Cylindirical
70	YT4125 M-18 Z-125-f	6	Twisted
71	YT 4146 N-18 Z-128-a	6.5	Twisted
72	YT 4146 N-18 Z-128-b	6	Plain
73	YT 4146 N-18 Z-128-c	6	Plain
74	YT4155 M-18/N-18 Z-127	6	Plain

Glass finger rings were popular and were made either by shaping molten glass around a metal rod of the right diameter or by placing a blob of molten glass on the point of an iron cone, which was then spun causing the glass to roll evenly down the cone until the desired size of ring was reached.

3.2 Color Examination

Color examination of the samples is made by using Munsell Color Catalogue (Table 5). For some of the samples it is tried to be examined by spectrocolorimetry (CIELAB) for detailed results, but unfortunately as neither of the surface of the diameters or the surface's flatness were sufficient for the measurement and therefore could not give a reliable evaluation. On the other hand, this may be used in the examination of color for flat glasses (windows) or flat surfaces of glass.

Table 5. The color examination of samples

Sample No	Inventory Number	Color of cross section	Munsell Color Code (1966)
1	M-L11 3501 U 06	Green	2.5BG 8/4, 10B 9/1
2	M-L11 3501 U 08	Black	5G 8/6, 10YR 8/2,10Y 9/2
3	M-L11 3502 U 08	Grey	5PB 9/2
4	M-L11 III-IV 3503 U 08	Dark brown, black	10R 2/1, 10BG 5/8, 7.5P 4/10
5	M-L11 3503 U 11	Blue	2.5B 7/4
6	M-L11 3506 U 07	Black with a red band	5P 2/1, 7.5R 4/8,2, 5B 7/6
7	M-M12 4003 U 06	Green	7.5G 8/6, 2.5PB 4/8,10B 4/10,10P4/6, 5Y8.5/2
8	M-M12 I-III 4501 U 04	Green	5Y 2/1, 10YR9/1
9	M-M12 4501 U 11	Green	2.5 GY 7/6
10	M-P14 IV 5003 U 08	Black	7.5G 3/8, 7.5G 2/6, 5Y 9/4, 10B 7/1
11	M-P14 IV 5008 U 05	Grey	7.5 Y 2/2, 7.5Y 9/4, 5PB 9/2
12	M-R13 3001/03 U 07	Grey-blue	5PB 2/1,10B 7/2,10B 6/2
13	M-R13 3004/02 U 01	Brown	5B 9/2,10Y 9/1
14	M-R13 30023 U 01	Light brown	5Y 2/2, 2.5Y 8.5/2, 5Y 9/1
15	M-R13 30032 U 01	Blue,brown,grey	2.5B 7/2,10R 4/2
16	M-R13 3057 U 03	Black	5PB 2/1, 2.5B 6/8, 2.5P 5/8, 7.5YR 8/8

Sample No	Inventory Number	Color of cross section
17	YT-2004 SURFACE-a	Green
18	YT-2004 SURFACE-b	Cobalt blue
19	YT-2004 SURFACE-c	Blackish brown
20	YT104 13/09 2/05 4003 a	White
21	YT104 13/09 2/05 4003 - b	Orange brown
22	YT104 13/09 4003 2/05	Green
23	YT104 4003 Z-105	Cobalt blue
24	YT 104 N-18 4055-a	Yellowish-orange brown

Table 5 (cont'd)

Sample No	Inventory Number	Color of cross section
25	YT 104 N-18 4055-b	Light green
26	YT 104 N-18 4055-c	Black
27	YT 104 N-18 4055-d	Shiny black
28	YT 104 N-18 4055-e	Green
29	YT 104 N-18 4055-f	Blue-green
30	YT104 N-18	Green
31	YT104 N-18 Z-106	Brown
32	YT1006 M-21	Black
33	YT1047 M-22-a	Olive green
34	YT1047 M-22-b	Light yellowish brown
35	YT1055 M-22-a	Light green
36	YT1055 M-22-b	Shiny black,brown
37	YT4006 L-17 Z-100	Yellow orange brown
38	YT4020 N-18 Z-106-a	light blue
39	YT4020 N-18 Z-106-b	Dark blue
40	YT4020 N-18 Z-106-c	Dark brown
41	YT4020 N-18 Z-106-d	Light (cobalt?) blue
42	YT4020 N-18 Z-106-e	Dark brown
43	YT4036 N-18 Z-106-a	Black with red band
44	YT4036 N-18 Z-106-b	Green
45	YT4036 N-18 Z-106-c	Black
46	YT 4038 N-18 Z-106	Shiny black
47	YT4041 L-17 Z-101	Black
48	YT4042 O-16 Z-108	Brown
49	YT4059 O-16/O-17-a	Light yellowish brown
50	YT4059 O-16/O-17-b	Dark brown
51	YT4059 O-16/O-17-c	Black
52	YT4061 Z-108	Black
53	YT4075 L-17 Z-100	Olive green
54	YT4077 L-17 Z-101	Light yellowish brown
55	YT4083 L-17 Z-103-a	Light grey
56	YT4083 L-17 Z-103-b	Green
57	YT4083 L-17 Z-103-c	
58	YT4087 O-16/O-17 P-16/P-17 Z-108 -a	Brown
59	YT4087 O-16/O-17 P-16/P-17 Z-108 -b	Black
60	YT4087 O-16/O-17 P-16/P-17 Z-108 -c	Green
61	YT4087 O-16/O-17 P-16/P-17 Z-108 -d	Cobalt blue
62	YT 4119 O-17 Z-120	Light green
63	YT4120 M-18/N-18 Z-121-a	Black
64	YT4120 M-18/N-18 Z-121-b	Grey
65	YT4125 M-18 Z-125-a	Shiny black

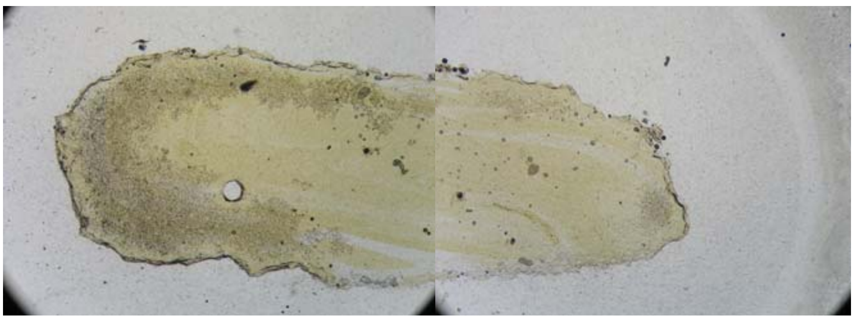
Table 5 (cont'd)

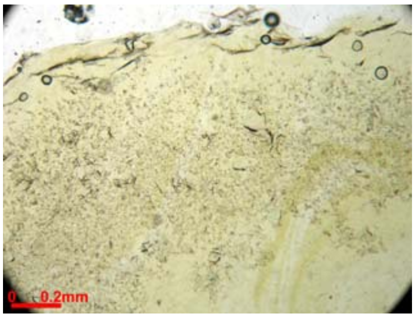
Sample No	Inventory Number	Color of cross section
66	YT4125 M-18 Z-125-b	Dark brown
67	YT4125 M-18 Z-125-c	Light green
68	YT4125 M-18 Z-125-d	Cobalt blue,red lines
69	YT4125 M-18 Z-125-e	Cobalt blue
70	YT4125 M-18 Z-125-f	Olive brown
71	YT 4146 N-18 Z-128-a	Black
72	YT 4146 N-18 Z-128-b	Cobalt blue
73	YT 4146 N-18 Z-128-c	Brown-dec.with white
74	YT4155 M-18/N-18 Z-127	Cobalt blue

3.3 Results of Thin Section Analysis

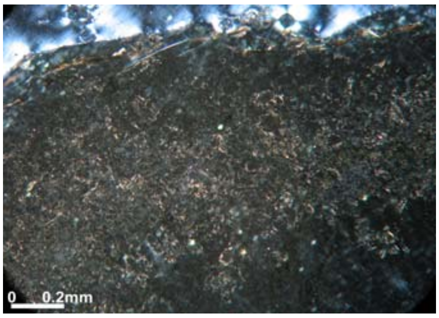
Observations of thin sections with an optical microscope showed the amorphous structures, as expected, with some impurities. In some samples gas bubbles were observed. Besides, some regions of the thin sections were darker (Figure 18). This might be due to the formation of different structures and the occurrance of devitrification. It can also be considered that the bracelets have heterogenous structure in general. This event needs to further studies.

(a) Sample 2



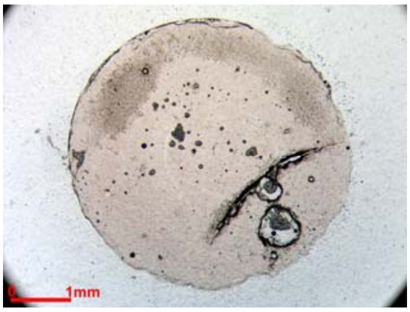


thin section - In

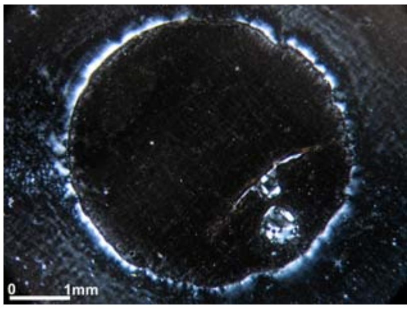


thin section - In

(b) Sample 4

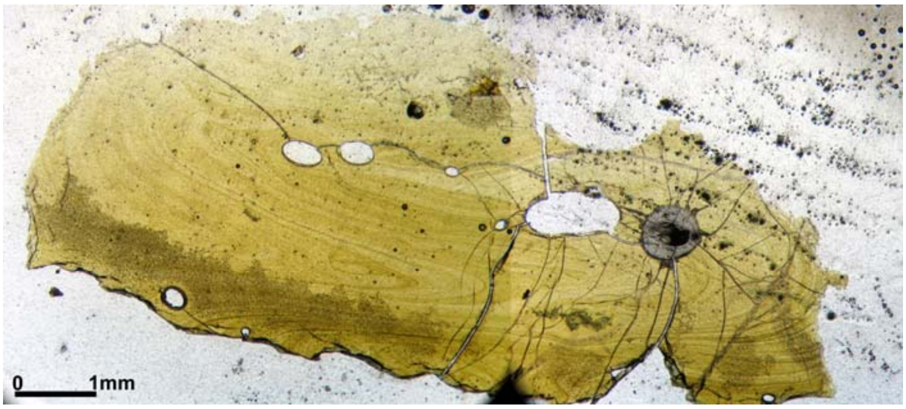


thin section - In



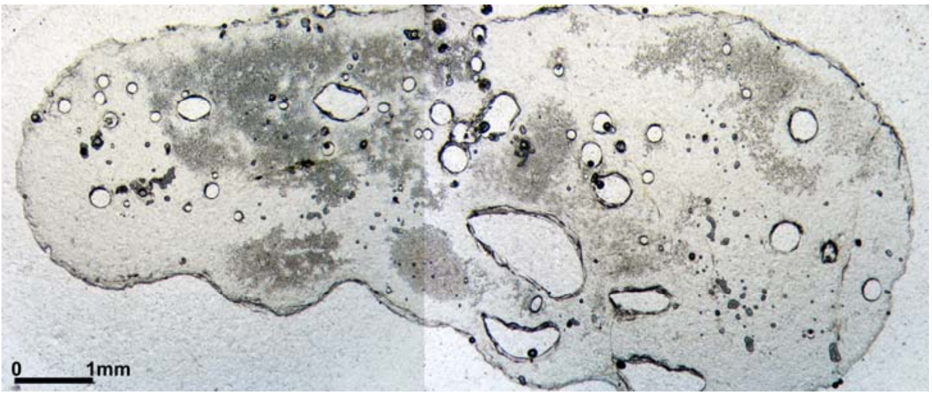
thin section - IIn

(c) Sample 6



thin section-In

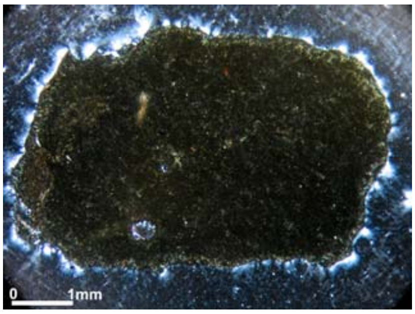
(d) Sample 7

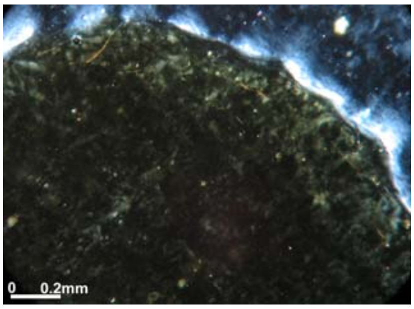


thin section – In

(e) Sample 10

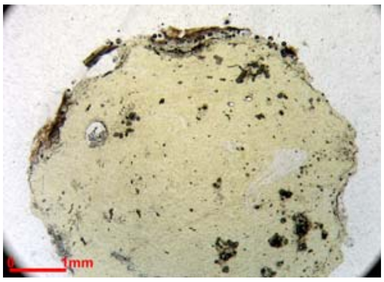
thin section – In

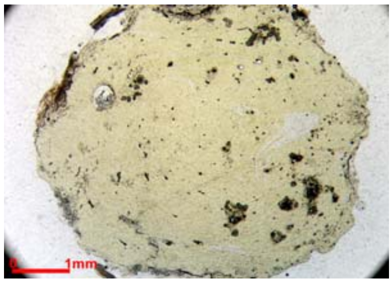


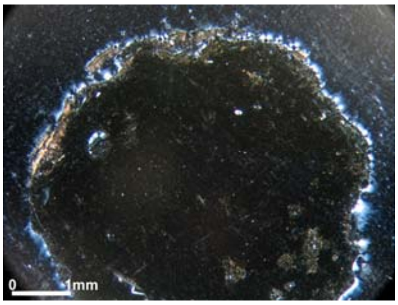


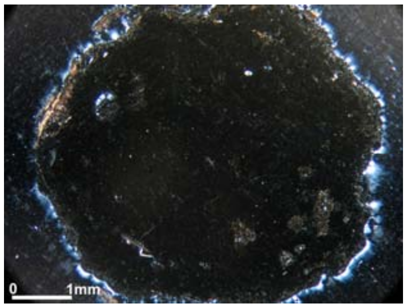
thin section - IIn

(f) Sample 13

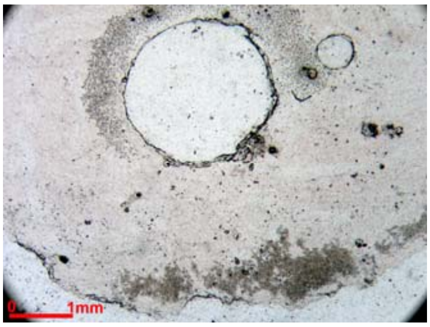

thin section - In


thin section – In


thin section - IIn


thin section – Iın

(g) Sample 16


thin section – In

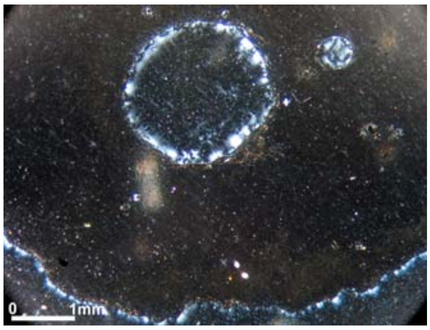

thin section – IIn

Figure 18 Optical microscopic images of the thin sections of some selected samples of Mezra Höyük. (a) sample 2, (b) sample 4, (c) sample 6, (d) sample 7, (e) sample 10, (f) sample 13, (g) sample 16.

3.4 Results of ICP-OES Element Analysis

ICP-OES data showed that glass bracelets samples studied are soda-lime-silica glass. Values and results of the elemental analysis of seven samples of Mezraa Höyük are as follow (Table 6). Errors in the analysis is not considerable and less than 3%.

Table 6. Results of the elemental analysis of seven samples of Mezraa Höyük (%)

Element	Sample13	Sample16	Sample2	Sample4	Sample6	Sample7	Sample10
Na_2O	13.0	7.60	11.2	7.5	11.8	9.90	12.5
CaO	2.3	2.47	2.55	2.46	2.42	2.50	2.00
K_2O	1.6	1.365	1.365	0.96	1.26	1.15	1.17
MgO	1.64	1.95	2.13	1.48	1.48	1.22	1.94
Fe_2O_3	0.89	0.60	0.86	0.69	0.68	0.99	0.77
Al_2O_3	0.33	0.50	0.28	0.27	0.32	0.3029	0.154
MnO	0.067	1.04	0.02	1.11	0.0184	0.020	0.0168
Cr_2O_3	0.003	0.0028	0.0063	0.0049	0.0039	0.0048	0.0004
NiO	0.002	0.0052	0.0027	0.0035	0.0021	0.0029	0.0027
CuO	0.002	0.015	0.0027	0.030	0.0189	0.0027	0.0011
PbO	0.0070	0.05	0.00117	0.00258	0.00189	0.00247	0.00118
TiO_2	0.11	0.087	0.097	0.10	0.098	0.13	0.10
CoO	0.00043	0.0011	0.00017	0.00317	0.00019	0.00022	0.00019
V_2O_5	0.00251	0.0046	0.00259	0.00397	0.00186	0.00242	0.00186
CdO	0.00019	0.00019	0.00021	0.00017	0.00018	0.00019	0.00019
SiO_2	<80.0	<84.16	< 81.5	<85	<82	<85	<81

Although, the samples are soda-lime-silica glass, the percentages of alkali oxides, especially Na_2O is less than expected from typical composition of soda-lime-silica glass.Its amount varies from 7.5 % to 13.0 % , average being 10.5 % by weight. This might be due to the removal of Na^+ ions from the glass network due to leaching.

The leaching of alkaline ions is a well known weathering pattern of archaeological glasses (Cox and Pollard 1977; Freestone 2001). Such patterns are produced by the interaction of both ground water and its dissolved chemical compounds with the glass surface. In addition, water acidity or basicity also plays an important role in the corrosion process of glass (Pollard and Heron 1996).

The first stage in the corrosion of glass involves an ion exchange of alkaline ions (Na^+, K^+) from the glass surface by H ions from the water, which promotes the formation of a silica gel layer. The second stage is produced by the attack of hydroxyl ions(OH^-), which are getting free in the increasingly alkaline aqueous medium, to the siloxane bonds (Si-O-Si) of the glass network. These bonds then breakdown and produce silanol groups (Si-OH) and non-bridging oxygen groups   (Si-O) which implies gradual destruction of the glass network (Garcia-Heras et al. 2005). It seems that weathering pattern of the samples under study is in the first stage, ion exchange has been occurred and some alkaline ions such as Na^+ have replaced by H^+ ions from the environment under burial condition.

Weathering conditions and environmental effect should be investigated in the futher study.

Concentration of glass network stabilizer, alkaline earth oxide CaO were almost same in all samples being about 2.4 %. Concentration of other network modifiers K_2O and MgO varied from 0.96 % to 1.6 % and from 1.22 % to 2.13 %, respectively (Table 6).

Potasium oxide as an alkaline oxide acts as fluxing agent while MgO stabilizes considerably the structure of silicate glasses, avoiding devitrification and formation of crystalline nuclei (Garcia-Heras et al. 2005).

Concentration of Al_2O_3 were found to be rather low being about 0.31 % as average (Table6).

The Al_2O_3 can be either network-forming or network modifiying of the glass structure depending on its concentration. As it enters into the glass network, a progressive closing of bridging oxygens is produced, thereby enhancing the glass resistance against hydrolytic attack and alkaline media (Garcias-Heras et al. 2005). Since the concentration of Al_2O_3 is rather low, its effect in the glass structure is expected to be not so significant. Similar concentration of Al_2O_3 in all of the samples except two samples (samples 10, sample 16) may show using one type of quartz sand in bracelet production. Exceptinal two samples may be imported or produced in different workshops.

Considering the summation of percentages of all oxides to become 100, SiO_2 percent concentration were calculated by subtracting the percentages of oxides given in Table 6 from 100. As it is seen concentration of SiO_2 is about 80 %. The network former SiO_2 could have been obtained from quartz sand, containing some impurities such as MgO, TiO_2 and Fe_2O_3 . Ideally total percentage of oxides is expected to be 100. But owing to the large numbers of gas bubbles in the glass structure, analytical total fall short of 100 percent (Freestone and Stapleton 1998). This might be true for our bracelet samples. Because significant number of gas bubbles were observed in thin sections under the microscope. Thus, percentage of SiO_2 could be less than 80 %, like 75-78 %.

Amount of Fe_2O_3 and TiO_2 varied in the range of 0.60-0.99 wt % and 0.087-0.13 wt % respectively.

The sodium oxide could be obtained from natron (or trona), a naturally occuring mineral containing high percentages of Na_2CO_3 . The use of this material is also indicated by the presence of minor amounts of MgO and K_2O. The use of plant ashes has less possibility. However to be sure about this fact, determination of P and Cl should be necessary, since in the plant ash beside Na, Ca, K and Mg, P and Cl are also present.

Network stabilizer calcium oxide could be provided from some calcium rich materials such as limestone or calcite.

The majority of the main components of glass are colorless. Therefore, to produce a colored glass some coloring agents (chromophores) are needed. Ancient glasses were commonly colored by ionic coloring agents using transition metal ions (Pollard and Heron 1996). Color producing elements seem to be Fe, Mn and Cu being in relatively higher concentrations among the transition elements studied (Table 6)

Amount of iron as Fe_2O_3 varied in the range of 0.60-0.99 wt %. It should be noted that the presence of Fe^2 ions gives blue color to the glasses because of their absorption bands at around 1100nm. Such a color moves to green when the ratio Fe^{2+} / Fe^{3+} diminishes, since the Fe^{3+} ions are responsible for yellow color due to their absorption bands at around 380, 420 and 440 nm. (Bamford 1962).

Copper gives green color to the glass together with iron. Copper alone gives turquoise blue. Copper is also coloring agent in red glass.

Manganese gives violet (purple) color to the glass beside its decolorizing effect to the color of iron (Morey 1960).

Colors of the samples were found to be consistent with the above explanations. Various combinations of chromophores Fe, Mn and Cu altogether with smaller amounts of other chromophores such as Cr and Ni result in the colors of the glass bracelets studied.

CHAPTER 4

CONCLUSION

In this study some glass bracelets obtained from 13th cetury cultural level of Mezra Höyük (Şanlıurfa,Turkey) have been examined. As far as we know, this is the first study related with raw material characteristic and production technology of glass bracelets obtained from archaeological site in Anatolia for Medieval Period. Major (except Si), minor and some trace elements of the bracelet samples were analyzed by using ICP-OES method which was found to be the most suitable method in the analysis of major, minor and trace elements at the same time.

Analytical data showed that they are of soda-lime-silica glass. But the percentages of Na_2O is less than expected from typical composition of soda-lime-silica glass; being 10.5 wt % as average. The expected value is about 15% or more. This might be due to the removal of Na ions from the glass network because of leaching under burial conditions.

Similar concentration of Al_2O_3 (0.3% as average) in all of the samples except two samples (sample10 and sample 16) indicate that one type of quartz sand was used in bracelet production. Exceptional two samples may be imported or may be produced in different workshops.

Natron mineral may be used as source of Na_2O . This result is also approved by the presence of minor amounts of MgO and K_2O. In addition, trona which is similar to natron mineral, is present in Anatolia (Beypazarı, Ankara) in great amounts. Concentration of glass network stabilizer, alkaline earth oxide CaO was almost same in all samples being about 2.4 %. Concentration of thek modifiers K_2O and MgO varied from 0.96 % to 1.6 % and from 1.22 % to 2.13 % respectively. Presence of K_2O and MgO in minor amounts indicate that the use of plant ashes has less possibility. However, to be sure about this fact, determination of P and Cl should be necessary which is planned to do in the further study.

Color producing elements are Fe, Mn and Cu, being in relatively higher concentrations than the other transition elements analyzed. Amounts of iron, manganese and copper varie in the range of their oxides, respectively. It should be noted that the presence of Fe^{2+} ions gives blue color to the glass. Such color moves to green when the ratio of Fe^{2+} / Fe^{3+}diminishes.

Manganese gives violet (purple) color to the glass besides its decolorizing effect to the color of iron.

Copper gives both turquoise blue and red color to the glass. Copper also gives green color to the glass together with iron. Various combinations of chromophores, Fe, Mn and Cu altogether with other chromophores present in smaller amounts such as Cr and Ni result in the colors of the glass bracelets studied. This subject also requires further study.

In the future studies, other glass bracelets obtained from other sites in Anatolia will be examined and their elemental compositions will be determined. This way, all the data will be collected and bracelet technology of Anatolia will be understood.

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APPENDIX A

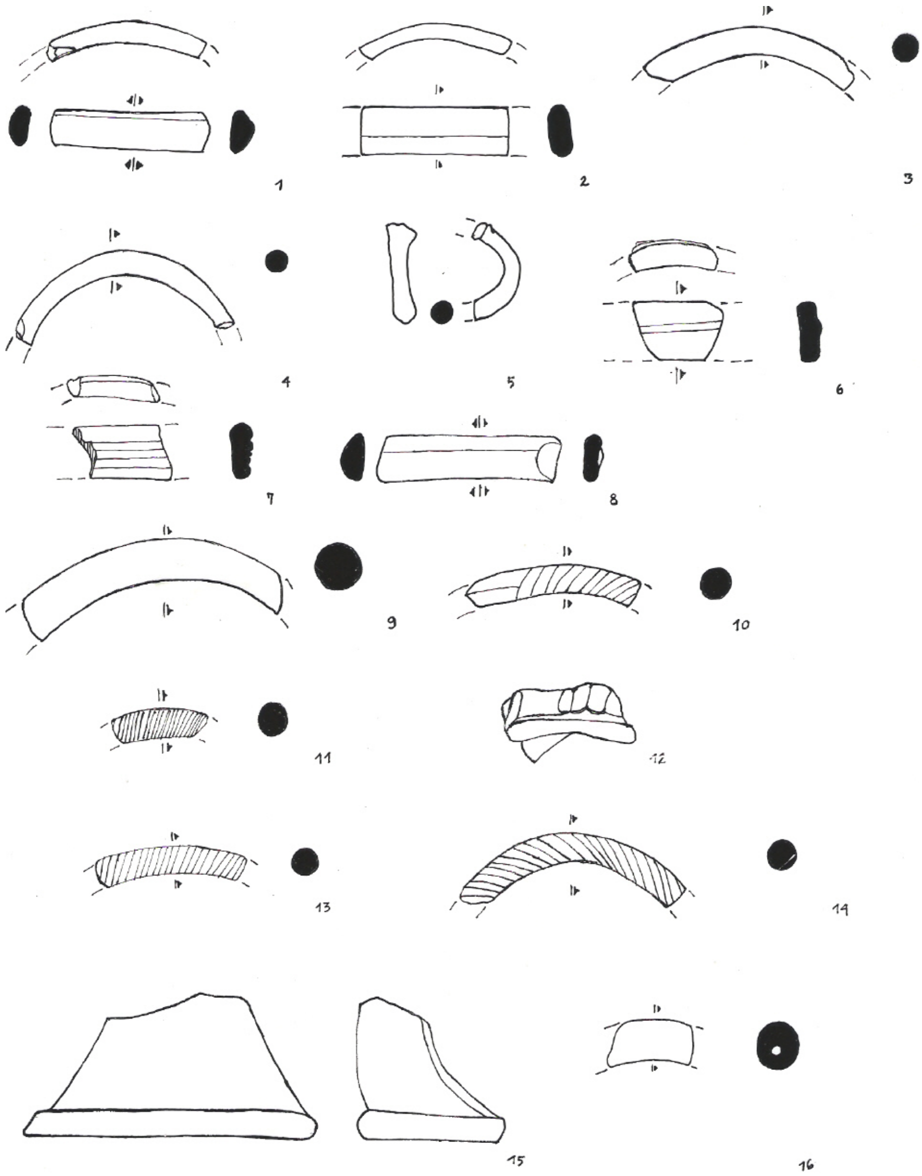

Figure 18 (a) Drawings of Mezraa Höyük samples

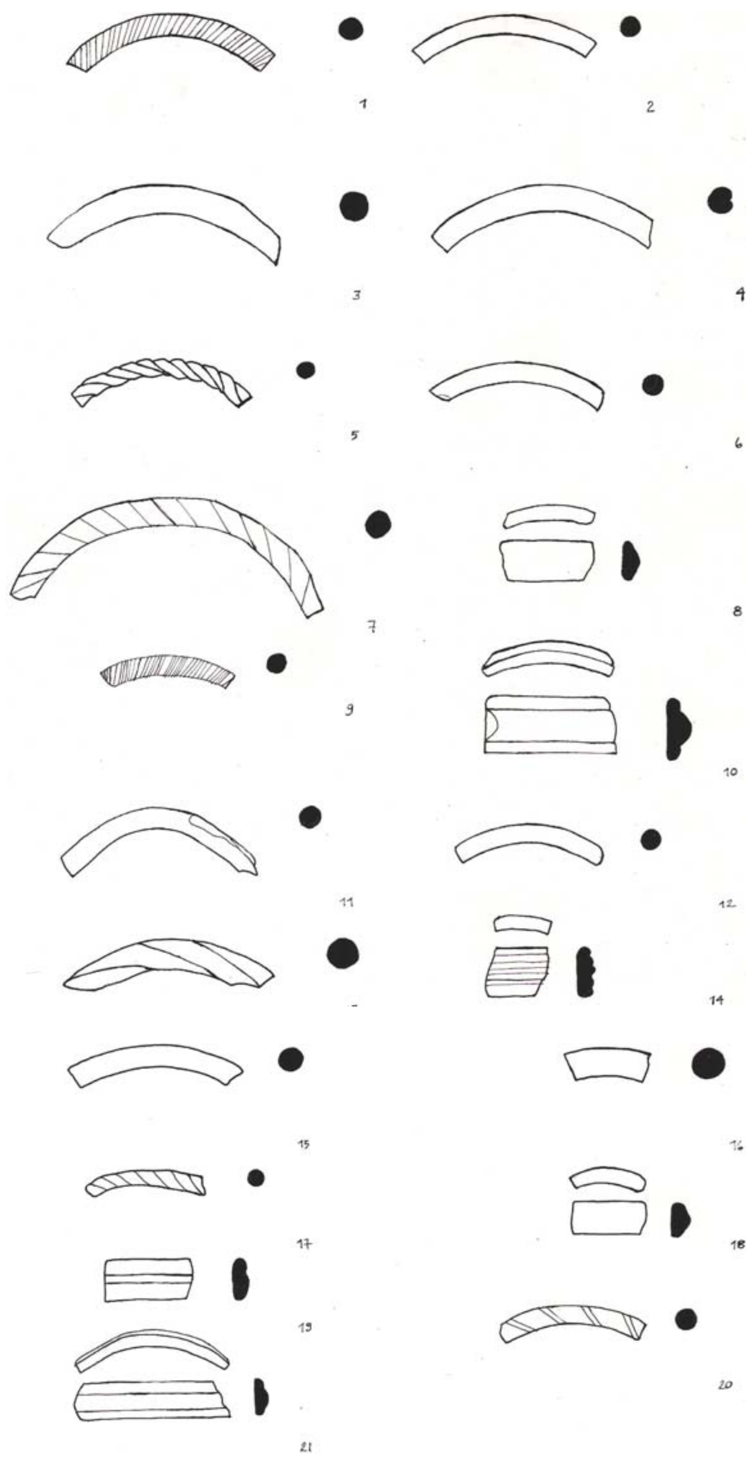

Figure 18 (b) Drawings of a group of Yumuktepe Höyük samples