

## STUDY OF CORROSION PATTERNS AND CONSERVATION PROCEDURES OF ROMAN GLASS VESSELS OF 1<sup>ST</sup> CENTURY AD FROM RHODES ISLAND - GREECE

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### ABSTRACT

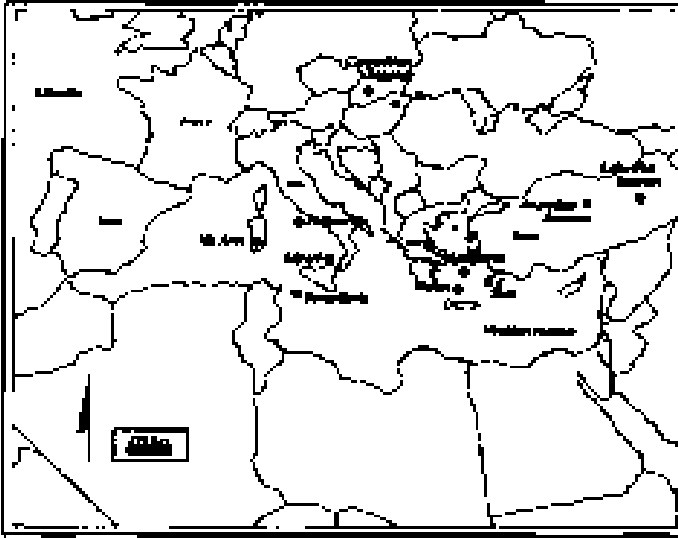
The study of the conservation and restoration of Roman blown glass cosmetic bottles from Rhodes, began with the gathering of historical - archaeological data and continued with the technological data of these archaeological objects. This important data about the ancient technology helps us to understand the corrosion forms that might have happened to these objects.

These forms of corrosion were confirmed macroscopically and microscopically. They included: dulling, crizzling, lamination, iridescences, pitting and crusting with biological deposits in almost all cases. The forms of corrosion were usually caused by the presence of humidity, temperature variations, the crystallization of soluble salts in the excavation area and also during the storage of these objects.

After these forms of corrosion were identified, the appropriate conservation and restoration methods were chosen to deal with the archaeological vessels. These include the analyses of the material's structure and deposits, the pre-consolidation of the corroded surfaces, the taking away of these deposits, consolidation of the corroded surfaces and finally the joining of the broken pieces. Lastly, the appropriate conditions for the storage and exhibition of these glass vessels were suggested.

### HISTORICAL DATA

Before the discovery of artificial glass, the objects of value and high art were manufactured from natural glass. Natural glasses were formed mainly by natural silicon casts that were mostly categorized geo-chemically within the acidic types that contain at least 65% of silicon oxides ( $\text{SiO}_2$ )<sup>10</sup>. Obsidian could be considered as the man's oldest contact with glass because of its macroscopic characteristics and structure that are similar to glass<sup>13</sup>.



*Map of Mediterranean Sea with presence of obsidian<sup>10</sup>.*



*Sample of obsidian<sup>10</sup>.*

The first glass objects were knives and peaks of arrows made from thin obsidian leaves and they date back to the beginning of the Paleolithic era<sup>6</sup>.

On the technological side, glass is an inorganic material that is classified in shapeless solids. It is hard, fragile with a "conical" rupture, usually transparent or semi-transparent, homogeneous and isotropic<sup>7</sup>. Oxides of silicon (Si), alkalis (Na, K), some alkaline earths (Ca, Mg) and aluminum (Al) are its main components. From the physiochemical prospective, it could be considered a "liquid" with exceptionally high viscosity and in usual conditions, of temperature and pressure, presents the attributes of a solid material<sup>1</sup>. The manufacture of glass is ineffably connected with magic and religion and has been considered as a material with magical attributes. The basic aim of the glass manufacturer was to imitate precious stones, mainly lapis lazuli and turquoise<sup>4</sup>.



*Imitation of lapis lazuli<sup>3</sup>.*



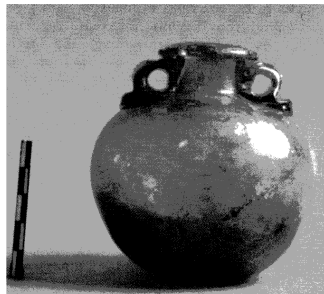
*Imitation of turquoise<sup>3</sup>.*

The precise chronology of the manufacturing and origins of hand-made glass is not apparent. However, it is almost certain that it was discovered in the eastern Mediterranean before 3.000 BC. It is reported by Pliny Senior that the traditional place for collecting sand suitable for the manufacture of glass was the estuary of the river Belus in Phoenicia. He also refers to another area for sand collection; this was the estuary of the river Volturnus, north of Naples that he connects with the “modern” way of glass manufacturing (blown glass) which appears to have been used during Roman times<sup>4</sup>. In Egypt, glass was first found in the kingdom of Touthmosis III and with basic stylistic and analytic studies; it appears that the first craftsmen were from Asia<sup>12</sup> and probably from Syria<sup>3</sup>. The Egyptian name for glass was “iner en wedeh” or “aat wed-het” which when translated means, “stone that flows”.

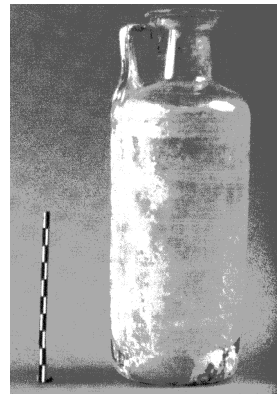
The techniques that were used for the production of glass objects were mainly by the core method and casting in open or closed molds<sup>6</sup>. During this period four types of vessels are thought to have been manufactured with the core method: the alabastron - cylindrical form with concave base, small amphora form - pear shaped, aryballos - spherical form and oinochoe - a vase with a handle and a flat base<sup>6</sup>. On the other hand casting in open or closed moulds was used for the production of open vessels - containers, such as bowls, dishes, bottles with wide neck and tiles<sup>6</sup>.



*Alabastron*<sup>3</sup>.



*Global aryballos*<sup>8</sup>.



*Oinochoe*<sup>8</sup>.



*Small amphora*<sup>3</sup>.



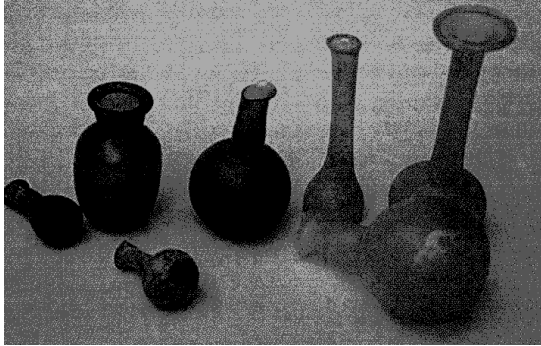
*Blown perfume unguentaria of candlestick type*<sup>8</sup>.

The revival of the glass manufacturing industry happened throughout western Asia, the near East and Mediterranean in the 9<sup>th</sup> BC<sup>3</sup>. The techniques that were used from the 7<sup>th</sup> through to the 9<sup>th</sup> century BC were similar to those of Egyptians, but the types of vessels were hemispherical bowls and drinking vessels, with various decorations<sup>3</sup>. Apart from the two previous techniques, the technique of mosaic glass was also used, but exclusively in western Asia and Mesopotamia. Important discoveries were: the perfume cruet (alabastron), known from Cyprus, Italy and Palestine as well as small amphora, oinochoe etc.

The core method, as a technique of manufacturing glass unguentaria (perfume vessels), was used widely by all the glass workshops in the Mediterranean from 550 to 50 BC<sup>3</sup>. These vessels were used to contain perfume oils and cosmetics. The forms of older Greek ceramic and metal vessels gave their name to them<sup>3</sup>. The last phase of Mediterranean workshops of glass manufacturing that used the core method was during the Hellenistic period between the second half of the 2<sup>nd</sup> century and the first half of the 1<sup>st</sup> century BC, while the most popular vessels of this period were still mainly types of alabastron and amphora, however they were smaller in size with a long neck<sup>3</sup>. At the same time as the core method, vessels were also frequently shaped by casting during the classic period (5<sup>th</sup> - 4<sup>th</sup> century BC), and just as frequently in the Hellenistic period from 3<sup>rd</sup> up to 1<sup>st</sup> century BC<sup>6</sup>. During the 3<sup>rd</sup> and 2<sup>nd</sup> century BC, the most characteristic technique is reported to be glass vessels with leaves of gold or silver enclaves between the two glasses layers<sup>6,3</sup>. These were manufactured in Rhodes and showed continuity of traditional Alexandrian products<sup>6</sup>. Finally, another technique that was developed in this period was the glass cameo that appeared from the end of the 1<sup>st</sup> century BC until the beginning of the 1<sup>st</sup> century AD<sup>6</sup>.

The history of pre-industrial glass manufacturing can be divided into two periods: the first, that extends from the 3<sup>rd</sup> millennium BC to roughly between 100 and 50 BC, where the craftsmen devised the process of transformation of natural primary materials in glass as well as the methods of manufacturing various vessels with the use of molds or with the configuration of glass melt around core, which afterwards was detached<sup>16</sup>. These time-consuming and particularly laborious techniques limited the production of glass to relatively small quantities and seldom allowed its wide distribution.

The most important innovation in the treatment of glass in antiquity was the discovery of blowing<sup>3</sup>. The technique of blown glass was a discovery that was likely to have emanated from the Syro-Palestinian region in the 1<sup>st</sup> century AD<sup>6,3</sup>. Blown glass dates back to the 1<sup>st</sup> century AD until 4<sup>th</sup> century AD and is mainly a Roman technique<sup>6</sup>. The method of blowing was believed to be the motive for mass production and use of glass that could be implemented without any particular technological requirements or changes in the figure of the furnace<sup>1</sup>.



*Blown perfume vessels<sup>8</sup>.*



*Mosaic glass<sup>3</sup>.*



*Core formed perfume vessels<sup>3</sup>.*

The earlier discoveries of blown glass emanate from Jerusalem. Although the archaeological discoveries are from the East, it is not evident if the real free blowing was first produced there or in Italy. It is there that earlier discoveries of blown unguentaria had been discovered, that dated back to the last fourth of the 1<sup>st</sup> century BC up to the first decade of the 1<sup>st</sup> century AD<sup>1</sup>. The small Italian unguentaria are similar to those from Syria, Palestine, Asia Minor and Cyprus<sup>1</sup> and they date back to the 1<sup>st</sup> century AD, whereas in Greece (Samothrake, Rhodes islands) were believed to be from the first half of the 1<sup>st</sup> century AD.

### **RHODES' GLASS INDUSTRY**

One of the most important and long lasting centers of the glass industry in the Mediterranean, according to the archaeological bibliography on glass artifacts, is the island of Rhodes<sup>15</sup>. The glass in Rhodes dates back to the 14<sup>th</sup> century BC<sup>15</sup>. The older finds were manufactured by the core method, but unfortunately today most of them have been lost.

With the fall of the Mycenaean civilization, the manufacture process of glass, from the end of the 12<sup>th</sup> century BC up to the 9<sup>th</sup> century BC in the Hellenic mainland, decreased. Apart from in Rhodes, which continued to possess an important place as a distribution center of new glass products from East to West. This was because of its geographic position, up to the first half of the 6<sup>th</sup> century BC<sup>13</sup>. However, from the end of the 6<sup>th</sup> century BC the wealth of glass utensils discovered, led researchers to identify Rhodes as one of the most important manufacturing areas of the archaic and classic years in Eastern Mediterranean<sup>15</sup>.

During the 3<sup>rd</sup> and 2<sup>nd</sup> century BC the manufacturing of glass objects presented outstanding results. The most characteristic technique of this period is reported to be

glass vessels with leaves of gold and silver enclosed between two layers of glass<sup>6</sup>. With the discovery of the blowing method during the second half the 1<sup>st</sup> century BC on the coast of Phoenicia, blown glass was propagated in all the centers of glass production and also in new Mediterranean centers. In the southeastern Aegean, glass produced both with the blown method or with casting, was used for the production of utilitarian as well as luxurious vessels that decorated Roman villas in Rhodes and Kos<sup>14</sup>. Colorless, painted bulb-type and spherical ampoules used for holding cosmetics were discovered in the necropolis of Rhodes dating back to the early productions of the 1<sup>st</sup> and 2<sup>nd</sup> century AD<sup>15</sup>.

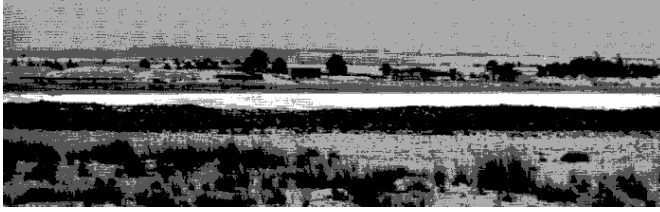
From the roman vessels that have been found in Rhodes we can conclude that locally produced products existed at the same time as imported ones. Although, the workshops from the early roman times have not yet been discovered. The archaeological finds though, imply that roman workshops existed during late antiquity. Samples of blown glass have been discovered and dated back to the late roman and early Christian years in the medieval city of Rhodes near the Ancient Agora<sup>15</sup>. However, at the same time with these indications many utensils have been excavated, such as; "prohous", "skyfous", plates and alabastron which cover all the typical groups of late antiquity up until Byzantine times. This shows that glass objects were also used at the Christian ceremonies<sup>13</sup>.

## TECHNOLOGY

The usual use of term "glass" coincides with the definition of Morey (1954): "glass is an inorganic material in the state of proportional liquids, but because of its high viscosity, it is considered for practical aims, solid". The glass is defined, as an inorganic material product of melting that has been frozen solid, without crystallization<sup>7</sup>. It is characterized as a shapeless solid<sup>6</sup> that in the past was considered to have magic attributes.

Raw materials for the production of ancient glass were silicon dioxide ( $\text{SiO}_2$ ), calcium oxide ( $\text{CaO}$ ) and alkalis oxides ( $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ )<sup>12</sup>. The main material for the production of glass is silicon dioxide that was mainly collected from sand. However, because the sand was mixed with many other materials they preferred to mine quartz or flint<sup>5,4</sup>.

Natural calcium can be found in the form of limestone, marble or chalk<sup>12</sup>, but limestone as a source of calcium was only used when the other two sources of raw material didn't contain a suitable quantity of calcium. It is most likely that the calcium was added indirectly<sup>4</sup>, rather than on purpose<sup>12</sup>, even if calcium is used today in the glass industry as a basic stabilizer of the sand and alkaline mixture<sup>15</sup>. Finally, the alkaline come from mines such as natron, known during antiquity in the Wadi Natrum in Egypt, Minor Asia, Macedonia, Thrace (near Philippous) and in Liti<sup>15</sup>, from the sediments of drained lakes or from vein<sup>12</sup>. Potassium comes from the ash of various plants that mainly grew in brackish grounds that belonged to the Salicornia plant family<sup>12</sup>. These plants include the Salsola Soda and Salsola Kali<sup>15</sup>. Potassium was used as a main component in the manufacturing of medieval glass artifacts<sup>15</sup>.

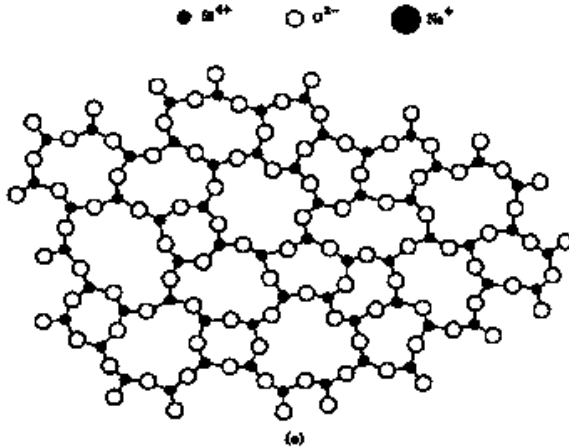


*Wadi Natrum area in Egypt<sup>15</sup>.*

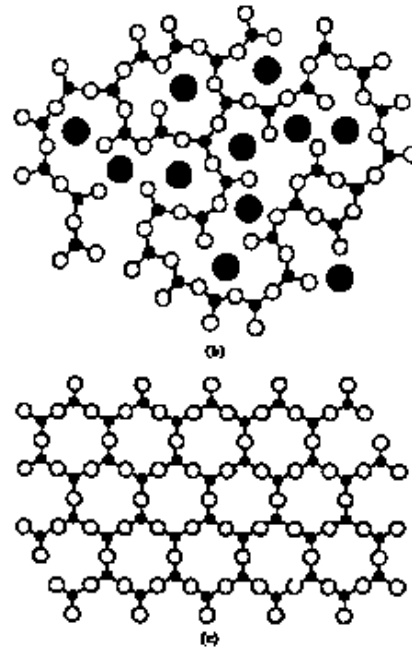


*The plant Salsola Soda (left) and the plant Salsola Kali (right)<sup>15</sup>.*

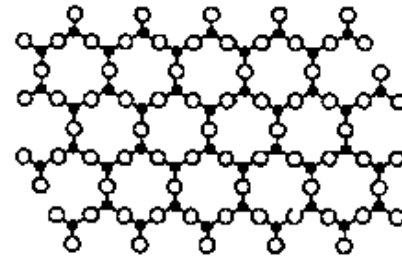
It has been mentioned before that the solidifying of a melted solid, without crystallization, creates glass. If glass is compared with various other crystalloid materials, its structure is deprived of a regular geometric placement of various elements atoms within the network of shaping an atom<sup>6</sup>. This differentiation is observed in the case of silicon dioxide ( $\text{SiO}_2$ ), which is found in crystalloid and in glazed forms<sup>6</sup>. The differences between the structure of crystalloid  $\text{SiO}_2$  (c), the glazed  $\text{SiO}_2$  (a) and glass  $\text{SiO}_2$  - NaO (b) are distinguished in the next diagram:



*Glass net of silicon - oxygen (a)<sup>6</sup>.*



*Glass net of silicon -sodium - oxygen (b).  
Crystal of mineral quartz (c)<sup>6</sup>.*



The knowledge of the chemical structure and natural attributes of glass are basically in order to understand the process of deterioration, conservation and manufacturing technology. The manufacturing and the glassmaking of glass during antiquity, constituted two separate processes of production that up until recently were confused by researchers<sup>15</sup>. Pliny Senior, in his work *Natural History XXXVI* (p. 193, 194) reports about the manufacturing of glass: "They start a fire with light and dry timber add copper and soda, preferably Egyptian. (The glass), as well as the copper, melting in a line of furnaces and takes dark-colored shapes... After it has crumbled, melt it again in the workshop and decorate it... This was the ancient method of manufacturing glass"<sup>4</sup>.

Glass manufacturing, with the fusion of raw material, was done in two stages that are also clarified by the sources:

1. Good mixture of raw materials, sand containing calcium and natron, and heat it slowly at 750 - 850 °C in simple ceramic crucibles or small containers. The result of this process was sand nitro, an intermediary product<sup>4</sup>.
2. Crumbling and reheating of sand-nitrum at 1100 °C and add colorings and opacifiers.

The second phase is completed with annealing, that is the progressive refrigeration of glass in the crucibles or containers<sup>4</sup>. Apart from these two stages an important role was also possessed by the process of coloration of glass metal that was applied by specialized craftsmen<sup>15</sup>.

The pigmentation of glass was applied in three ways:

a. With the presence of small quantities of metal oxides of precession, as cobalt (Co), copper (Cu), iron (Fe), nickel (Ni), manganese (Mn) etc., which were imported to the mixture of the silicon network.

b. With the growth of colloid dissemination of soluble particles, as in the glasses of silver, copper and red-gold.



c. With the import of coloring materials in the glaze<sup>6</sup>.

It is important to note that the manufacture of glass and its formation into an object are two different processes. As Pliny Senior reports in his book "Natural History XXXVI" "One is formed by blowing, another is formed on a wheel and another is turned like silver"<sup>4</sup>.

Before the invention of the technique of blowing, glass production was dependant on the characteristic of glass to return from solid to its liquid form, this characteristic influences the configuration and the technique of the formation of ancient objects. Viscosity of glass depends on the composition of its components, as well as from the temperature. For example, at high temperatures ( $\approx 1050$  °C), viscosity is low and allows the manufacture of glass<sup>4</sup>. The ancient glassmakers calculated the temperature of glass from its behavior on the tools, and also from its color. The manufacture temperatures of ancient soda type glass can be grouped as follows:

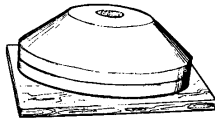
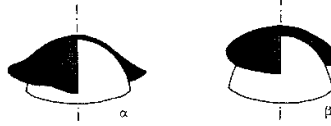
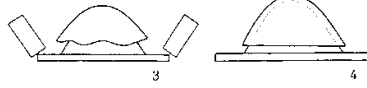
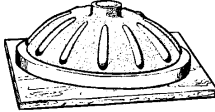
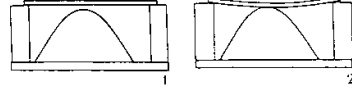
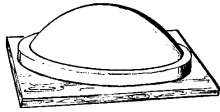
a. 505 - 590 °C: Warm-up of glass items that will be treated<sup>4</sup>. At the temperature of 573 °C we have the transformation of a-quartz with hexagonal crystalloid system, in b-quartz with triangular system, which is followed by an increase in the volume of the material 0,82 - 1,3%<sup>6</sup>.

b. 625 - 970 °C: Manufacture of glass with various techniques, such as bending, casting with cullet, the spiral and rotation pressure<sup>4</sup>. In between these two temperatures and more precisely at 870 °C, one more transformation takes place, that of a-tridimite with a hexagonal crystal system that comes along with an important increase of volume, 14,4 - 16%<sup>6</sup>.

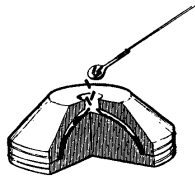
c. 970 - 1150 °C: Manufacture of glass with the technique of blowing and the possibility of gathering thick glass from crucible<sup>4</sup>. At 1025 °C, when the a-quartz has high purity it changes into a-cristobalite with a cubic crystalloid system. This transformation happens slowly and is accompanied by an increase in volume 15,4 - 17,4%<sup>6</sup>.

d. At higher temperatures, such as 1470 °C, the a-tridimite is changed into a-cristobalite with an increase of volume 1 - 1,4%, while at 1726 °C the a-cristobalite is changed in the cast in a slow process<sup>6</sup>. The changes from one form to another of SiO<sub>2</sub> have been discovered by studies with derivative thermal analysis (D.T.A.)<sup>6</sup>.

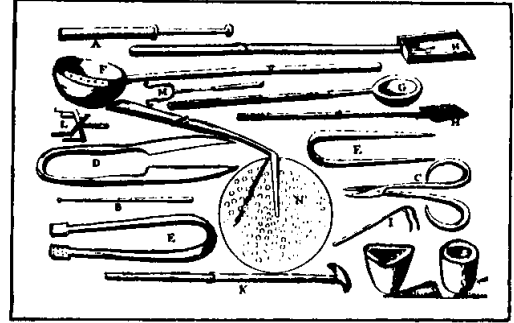
The technique of casting was used to describe the manufacturing method of transparent and semi-transparent glass objects from the early roman years. A variation of casting is the technique of lost wax<sup>15</sup>, which is based on the manufacturing of an original wax object<sup>4</sup>. The prototype is molded with plaster or clay and is heated. With this technique the heated double closed mould (of plaster or clay) and intermediary wax wall was filled with cullet glass or fragments that were poured through a crucible that were melted by heating at lower temperatures (850 - 970 °C)<sup>15</sup>. The melted wax was removed by passages at the base of the mould<sup>11</sup> and the melted glass was forming the shape of vessel inside mould<sup>15</sup>. Afterwards the annealing, the mold was also removed<sup>4</sup>. The treatment of vessel was completed with cool abrasion.



*Technique of glass formation with bent in open mould<sup>15</sup>.*



*Mould glass formation<sup>14</sup>.*



*Tools of glass formation<sup>11</sup>.*

Another technique of manufacturing glass objects was bending. With the method of bending, the glass-maker produces simple semi-spherical forms of vessels, mainly narrow, late-Hellenistic bottles or skyfous of Syro-Palestinian and Rhodian groups<sup>15</sup> with the heating of glass disks in a concave or a convex mold<sup>4</sup> or bending it or bending with the help of a ceramic wheel, while its further treatment was done with the help of blastings<sup>15</sup>.

For the manufacture of transparent and non-transparent luxury vessels with the core technique, the latest research indicates the widespread use of open glow instead of using a glass-kiln, which provides progressive heating and achieves the necessary bending and plasticity of glass, basic characteristics for its successful treatment<sup>15</sup>. Also, pressure technique was often used in combination with casting for the fast filling of the mold and the almost direct imprinting of decorative elements on the glass surface. The configuration of the object with pressure of thick glass, takes place in an open or bilateral mold. The method is used for the manufacture of beads and vessels<sup>4</sup>.

The method of fusion is the technique of melting by heating two or more fragments of glass that are placed on a flat heat proofed surface. Fusion can be achieved when the glass remains either for a relatively long time in the furnace at a steady temperature, in order for its surface to remain sticky. Alternatively, the glass can remain in a furnace for a short period at a high temperature<sup>16</sup>. If the desirable form is flat, the glass is removed from the fireproofed surface as soon as the process of fusion is completed and it is placed in a furnace to cool down gradually. On the contrary, if a curved surface is required, the process of casting is applied immediately. The casting technique is used for the transformation of flat fragments of glass into

curved ones. Usually, the product of casting is a shallow mug or porringer. The first role here is gravity. A flat item of glass is placed onto fireproofed metal or ceramic form. As the temperature increases, the glass melts and flows to cover the surface of the form. When it reaches its final form, it is removed from the mold and is placed in a furnace to cool down slowly.

So that the fluid glass does not stick in the form, the last one is covered before its use with a thin coating of baked clay<sup>16</sup>.

The technique of blowing was probably not yet discovered in the years of Pliny<sup>7</sup>. The invention of blowing glass, during the second half of the first century BC, on the coast of Phoenicia helped promote widespread use of glass in the markets and transit centers of the Mediterranean. Rhodes has an important collection of early earless shallow vessels, bulb-type or overall ampoules of 1<sup>st</sup> half of the 1<sup>st</sup> century AD and blown skyfous that imitate Rhodian type ones. In the Rhodes' productions are included cosmetic bottles of candlestick type, many from which they are deformed by manual laboratorial construction<sup>13</sup>.

The glass production process includes two or three stages. First is the constructional or heavy work stage, at this point the glassmakers change the raw material in melted, clean limp glass. In the second stage, the craftsmen or the artists shape the melted glass into an object. Sometimes, it follows the third stage of the object decoration with the use of various techniques<sup>16</sup>.

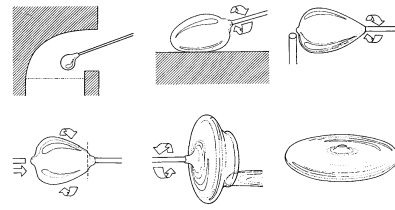
The blown glass can be carried out independently from the manufacturing process of melt glass because of the use of smashed glass or imported crude glass fragments or bars as source of raw material<sup>16</sup>. During the 1<sup>st</sup> century BC the blowpipe was invented, either in the roman province of Syria or in the Palestinian region. The basic tools for the treatment of glass, such as the blowpipe and the stick, were used centuries before and they haven't changed much from the ones that are used today<sup>16</sup>.

One end of the blowpipe is submerged into the melted glass, which is kept in the blast furnace where it collects a small amount of the glass mass. The glass sticks to the iron after being heated to 500 - 600 °C. With the blowing of air from the other end of pipe, a thin walled glass "bubble" is formed. Wooden tools and pincers can shape this glass ball. During the whole process, the object is spun with a circular motion, in order to prevent it from "drooping" downwards and it is heated again in a furnace when its needed<sup>5</sup>.

In order to maintain the required temperature for the treatment of glass, the "bubble" is placed from time to time onto an iron bar, which exists inside the kiln and is kept warm constantly<sup>2</sup>. The configuration of glass requires it to be in melted form so that it appears red or white in color. During the manufacturing process it is not possible for anyone to handle the glass with their bare hands and shape it as he wishes, but you can do that only by using instruments made of metal, stone or wood that have been previously placed in water<sup>2</sup>. Blowing, stretch, spinning, pressure, stinging, fission, engraving or cutting undertakes the treatment of glass. The finished glass objects should remain in a heated furnace for several days in order to cool down gradually<sup>2</sup>.



*Blowing process<sup>11</sup>.*



*Blowing process<sup>11</sup>.*



*Blown Perfume vessels<sup>8</sup>.*

Generally, there are three types of blown glass:

- The "free blowing".
- Blown in an open mould.
- Blown in closed mould.

The free blown glass, it has the ability to be reheated and to take a new form with a lot of methods. The submerging of a glass mass into an open mold is one of the initial stages in the process of blowing, before the glass bubble maintains its bigger dimensions. This technique, allows the heating and further configuration of the object<sup>16</sup>. The most important metal tools required for the manufacture and treatment of glass objects, apart from the pin of kiln and the ladle, are the following:

- The blowpipe.
- A pair of tongs.
- The shear.
- A type of "pinsetas".
- The circular scissors.
- The conjunctive iron tool for melting glass belts.
- A board in form small shovel<sup>2</sup>.

Therefore, with the technique of blowing glass, we have been able to create thinner and clearer glasses. It has contributed to a big increase in the variety, form and number of small concave objects and for first time they could produce bigger windows<sup>11</sup>. In general, the first century after the invention of free blowing is characterized by the great decoration and stylish nature of the objects. They are usually made from simple transparent, light blue or greenish glass<sup>1</sup>. The roman glass meant for daily use, is green up to azure and sometimes yellow. Intensely colored glass also existed. Colorless glass has been known to exist since the first half of the first century AD and is considered more precious than colored glass objects. It should be noted, that the colors of ancient glass depend on the chemical composition of the raw materials and on the production process<sup>8</sup>.

## **ANALYSES OF STRUCTURAL MATERIAL**

### **Sample 1 (Y932)**

External



1mm

x500 C



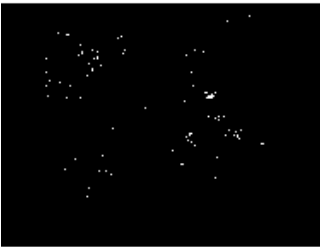
1mm

x500 Al



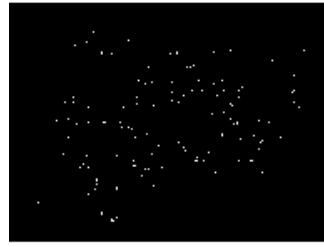
1mm

x500 Ca



1mm

x500 Mg



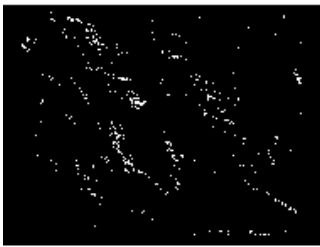
1mm

x500 Fe



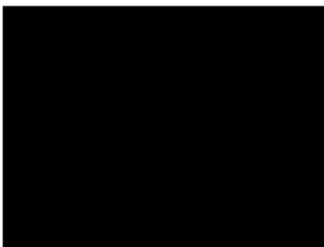
1mm

x500 Mn



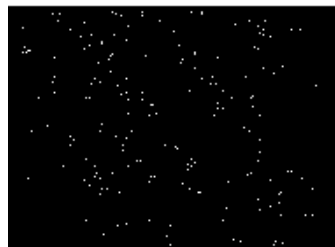
1mm

x500 O



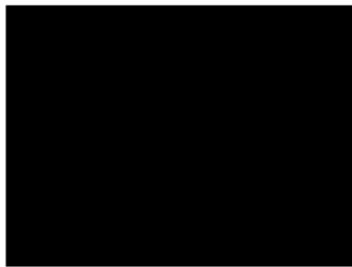
1mm

x500 Ni



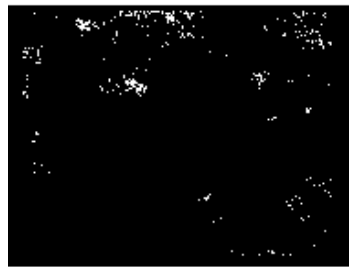
1mm

x500 S



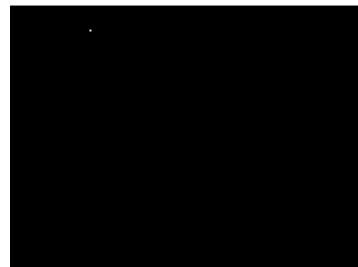
1mm

x500 Ti



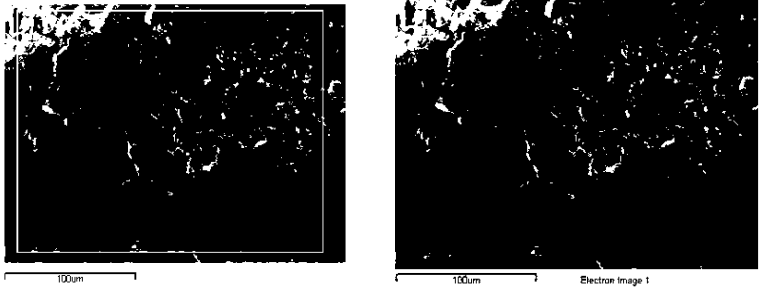
1mm

x500 Si



1mm

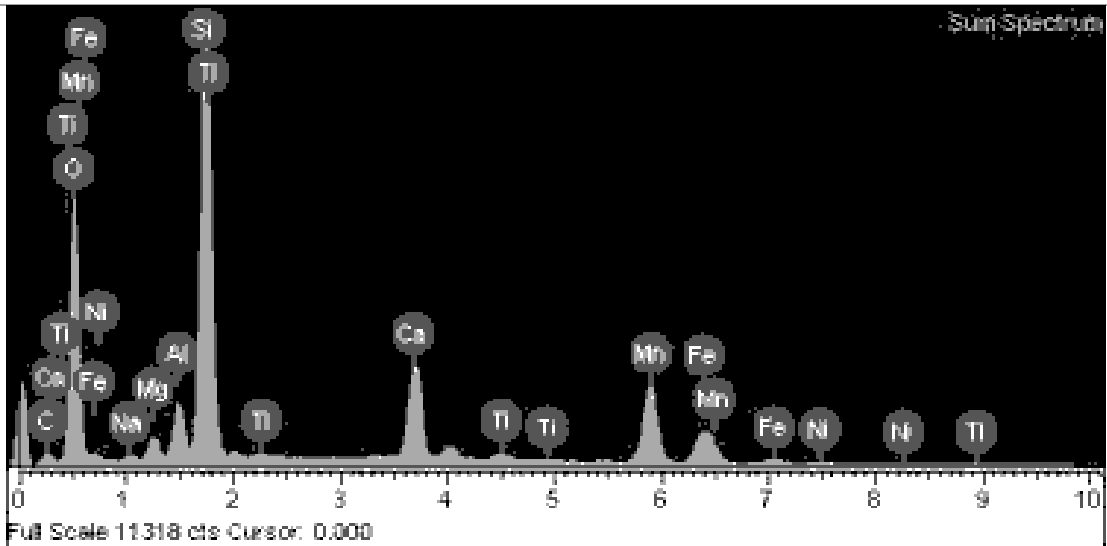
x500 Tl



x500 Area

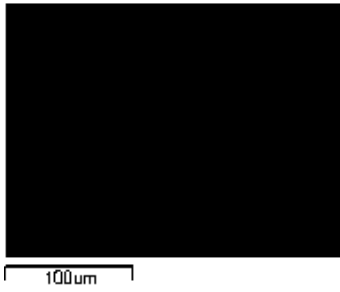
x500 Quantitative

Element	App	Intensity	Weight%	Weight%	Atomic %	Compd%	Formula	Number
	Conc.	Corrn.		Sigma				of ions
Si K	28.74	0.7974	18.52	0.22	13.47	39.62	SiO <sub>2</sub>	1.71
C K	4.58	0.3366	7.00	0.55	11.91	25.64	CO <sub>2</sub>	1.51
Mn K	15.90	0.8196	9.97	0.15	3.71	12.87	MnO	0.47
Ca K	10.36	0.9854	5.40	0.08	2.76	7.56	CaO	0.35
Al K	3.03	0.7122	2.19	0.04	1.66	4.13	Al <sub>2</sub> O <sub>3</sub>	0.21
Fe K	7.14	0.8378	4.38	0.10	1.60	5.63	FeO	0.20
Mg K	1.36	0.5965	1.17	0.03	0.98	1.94	MgO	0.12
Na K	0.46	0.6009	0.40	0.04	0.35	0.53	Na <sub>2</sub> O	0.04
Ti K	0.88	0.8304	0.55	0.03	0.23	0.91	TiO <sub>2</sub>	0.03
Ni K	0.72	0.8305	0.45	0.07	0.16	0.57	NiO	0.02
Tl M	0.77	0.6952	0.57	0.06	0.06	0.59	Tl <sub>2</sub> O	0.01
O			49.42	0.58	63.12			8.00
Totals			100.00					
x500 Quantitative							Cation sum	4.67

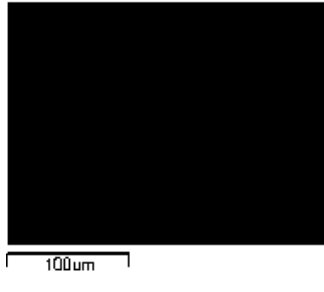


Quantitative x500

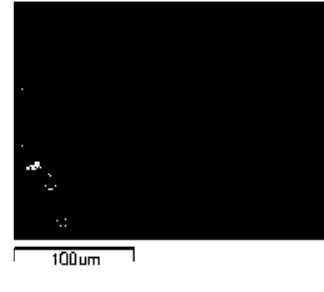
Internal



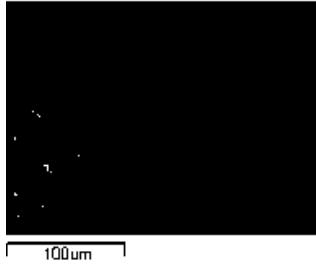
x500 C



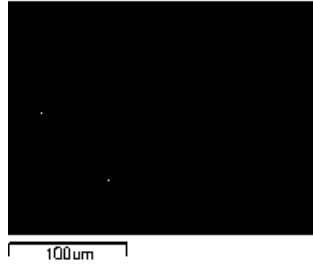
x500 Al



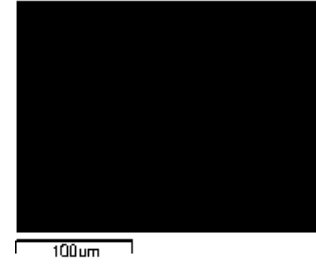
x500 Ca



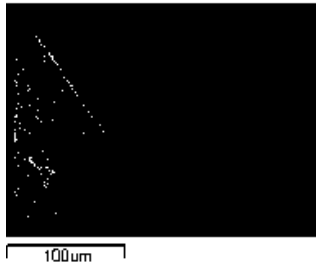
x500 Mg



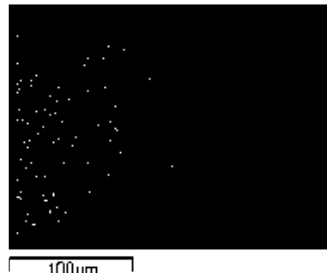
x500 Fe



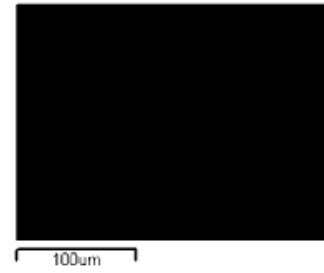
x500 Mn



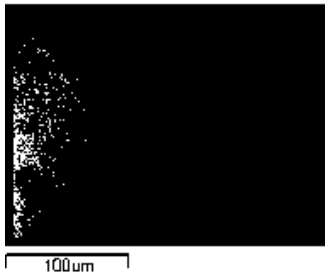
x500 O



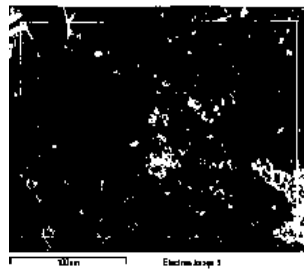
x500 Na



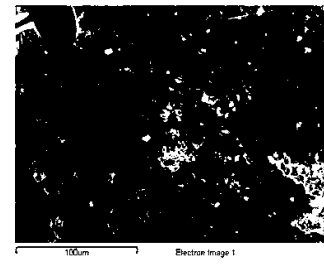
x500 S



x500 Si



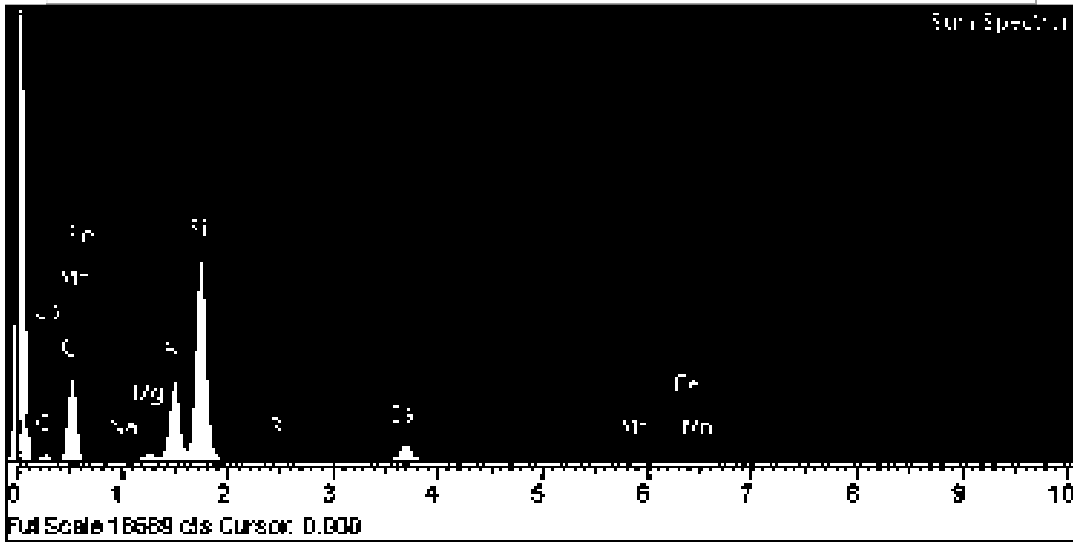
Quantitative x500



Area x500

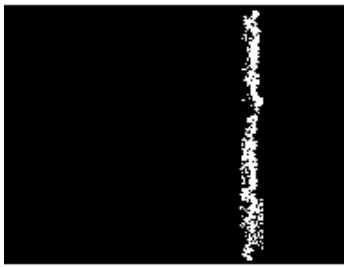
Element	App Conc.	Intensity Corn.	Weight%	Weight% Sigma	Atomic %	Compd%	Formula
Si K	39.58	0.7985	27.73	0.39	19.21	59.32	SiO <sub>2</sub>
Al K	14.45	0.8395	9.63	0.15	6.94	18.20	Al <sub>2</sub> O <sub>3</sub>
C K	1.72	0.2421	3.98	0.68	6.45	14.59	CO <sub>2</sub>
Ca K	5.21	0.9359	3.11	0.07	1.51	4.36	CaO
Mg K	0.77	0.7298	0.59	0.05	0.47	0.98	MgO
Fe K	1.44	0.8189	0.98	0.09	0.34	1.26	FeO

Na K	0.36	0.7624	0.26	0.05	0.22	0.36	Na <sub>2</sub> O
Mn K	0.58	0.8016	0.41	0.07	0.14	0.52	MnO
S K	0.21	0.7106	0.17	0.03	0.10	0.42	SO <sub>3</sub>
O			53.14	0.67	64.61		
Totals			100.00				
Quantitative x500							



Quantitative x500

## Section - Edge



x1500 Al



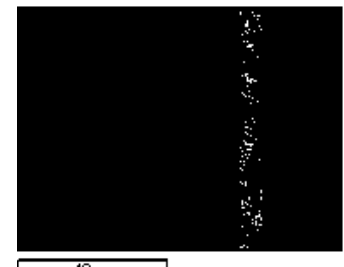
x1500 Ca



x1500 C



x1500 Cl



x1500 K



x1500 Fe





x1500 Mg



x1500 Na



x1500 Mn



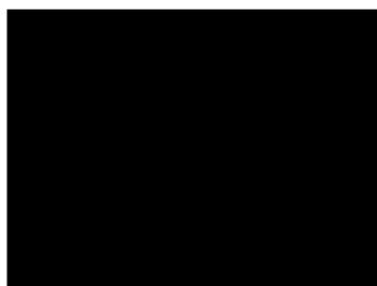
x1500 O



x1500 P



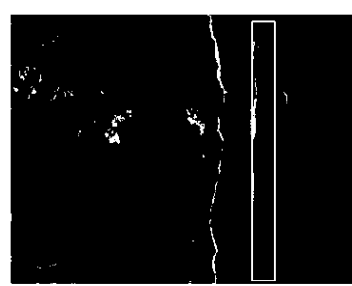
x1500 Si



x1500 Te

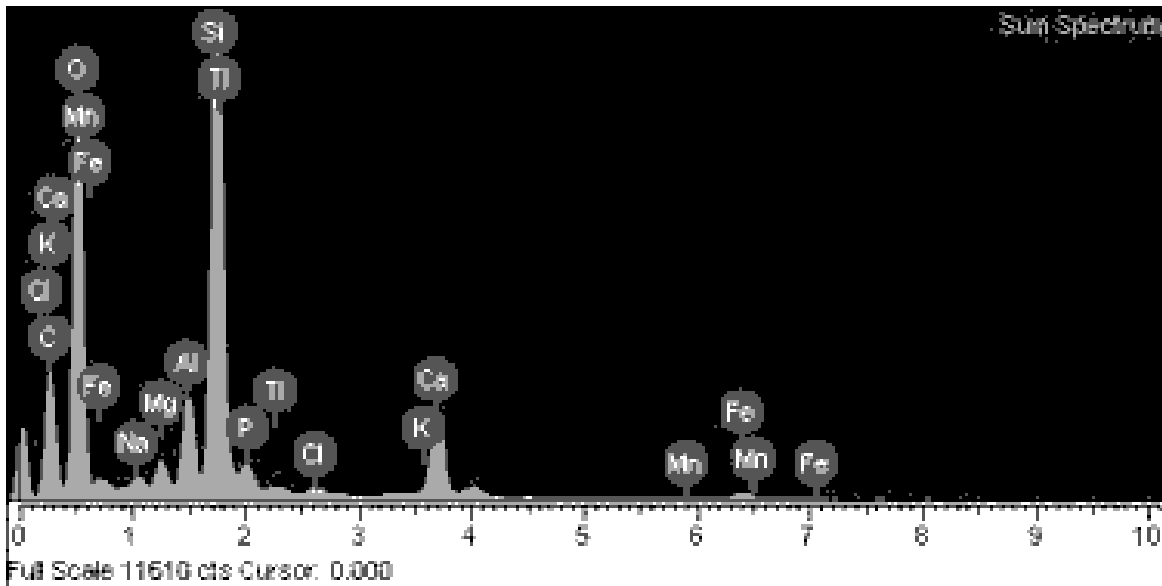


Quantitative x1500



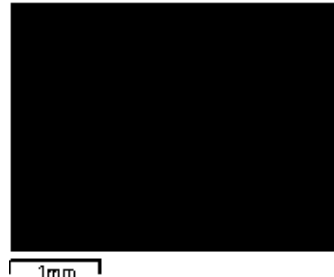
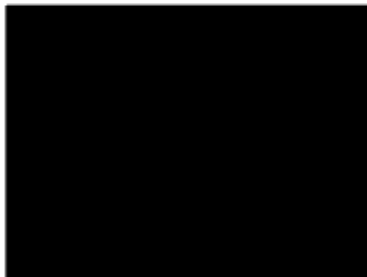
Area x1500

Element	App	Intensity	Weight%	Weight%	Atomic %	Compd%	Formula	Number
	Conc.	Corn.		Sigma				of ions
C K	37.54	0.4943	19.22	0.16	25.83	70.42	CO <sub>2</sub>	3.14
Si K	29.05	0.8247	8.91	0.04	5.12	19.07	SiO <sub>2</sub>	0.62
Al K	5.24	0.7473	1.78	0.02	1.06	3.35	Al <sub>2</sub> O <sub>3</sub>	0.13
Ca K	8.55	0.9673	2.24	0.02	0.90	3.13	CaO	0.11
Mg K	1.59	0.6326	0.63	0.02	0.42	1.05	MgO	0.05
Na K	1.27	0.6457	0.50	0.02	0.35	0.67	Na <sub>2</sub> O	0.04
P K	2.10	1.0973	0.48	0.02	0.25	1.11	P <sub>2</sub> O <sub>5</sub>	0.03
Fe K	1.28	0.8022	0.40	0.02	0.12	0.52	FeO	0.01
Cl K	0.37	0.7593	0.12	0.01	0.06	0.00		0.01
Mn K	0.30	0.7889	0.10	0.02	0.03	0.12	MnO	0.00
Tl M	1.07	0.7510	0.36	0.03	0.03	0.37	Tl <sub>2</sub> O	0.00
K K	0.20	1.0193	0.05	0.01	0.02	0.06	K <sub>2</sub> O	0.00
O			65.21	0.16	65.81			7.99
Totals			100.00					
Quantitative x1500							Cation sum	4.15

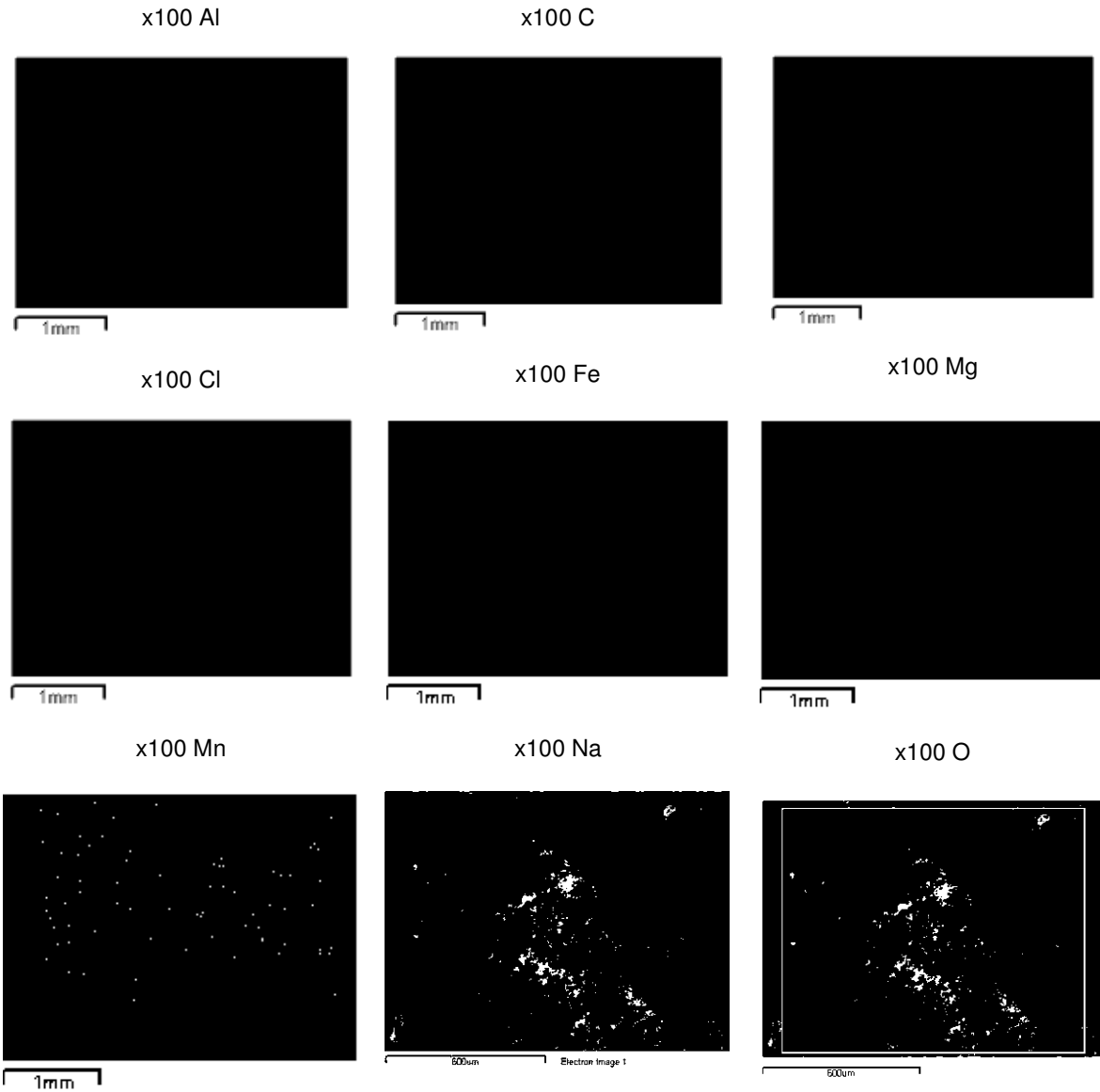


Quantitative x1500

Meddle

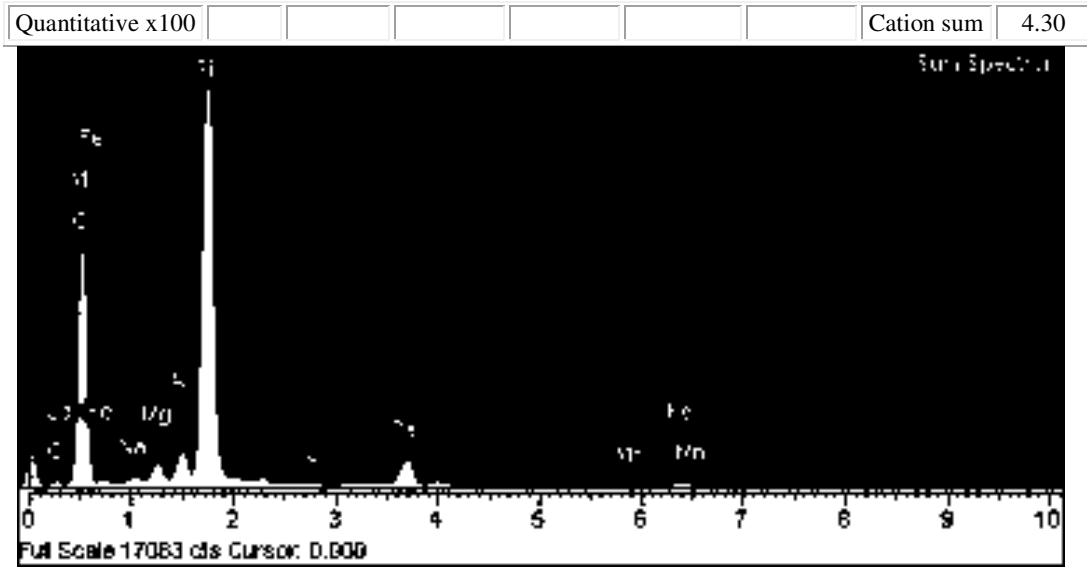


x100 Ca



Quantitative x100

Element	App Conc.	Intensity Corm.	Weight%	Weight% Sigma	Atomic %	Compd%	Formula	Number of ions
Si K	45.45	0.8747	34.25	0.31	23.85	73.28	SiO <sub>2</sub>	2.94
C K	1.21	0.2329	3.43	0.43	5.59	12.58	CO <sub>2</sub>	0.69
Al K	2.68	0.8180	2.16	0.05	1.57	4.08	Al <sub>2</sub> O <sub>3</sub>	0.19
Ca K	4.26	0.9307	3.01	0.05	1.47	4.22	CaO	0.18
Mg K	1.92	0.7222	1.76	0.04	1.41	2.91	MgO	0.17
Na K	0.81	0.7609	0.70	0.05	0.60	0.94	Na <sub>2</sub> O	0.07
Fe K	1.38	0.8175	1.11	0.06	0.39	1.43	FeO	0.05
Cl K	0.18	0.6655	0.18	0.03	0.10	0.00		0.01
Mn K	0.36	0.8000	0.29	0.05	0.10	0.38	MnO	0.01
O			53.10	0.43	64.92			7.99
Totals			100.00					



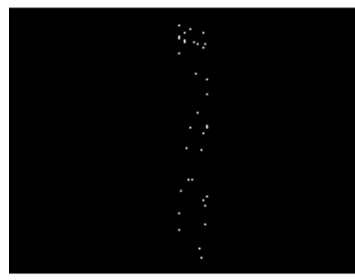
Quantitative x100

Before the edge



600um

x100 Al



600um

x100 C



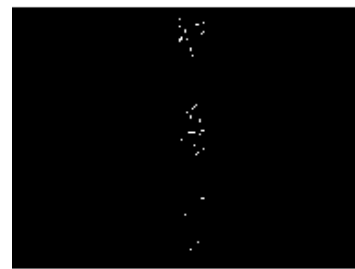
600um

x100 Ca



600um

x100 Cl



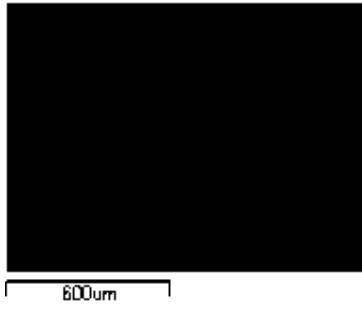
600um

x100 Fe

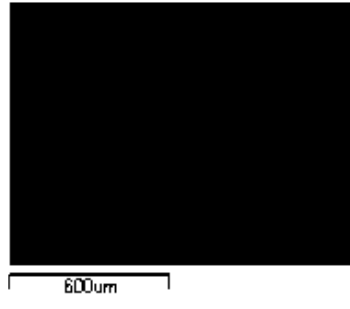


600um

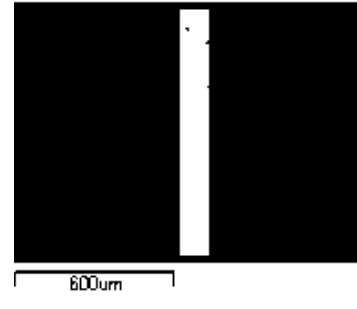
x100 Mg



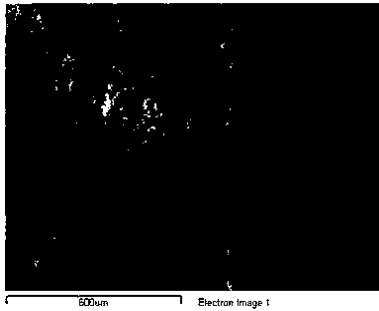
x100 Mn



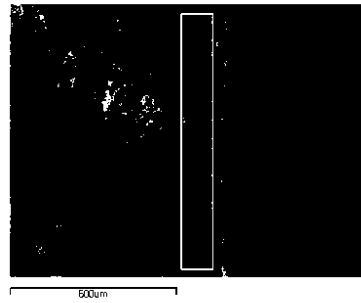
x100 Na



x100 O



Electron Image 1

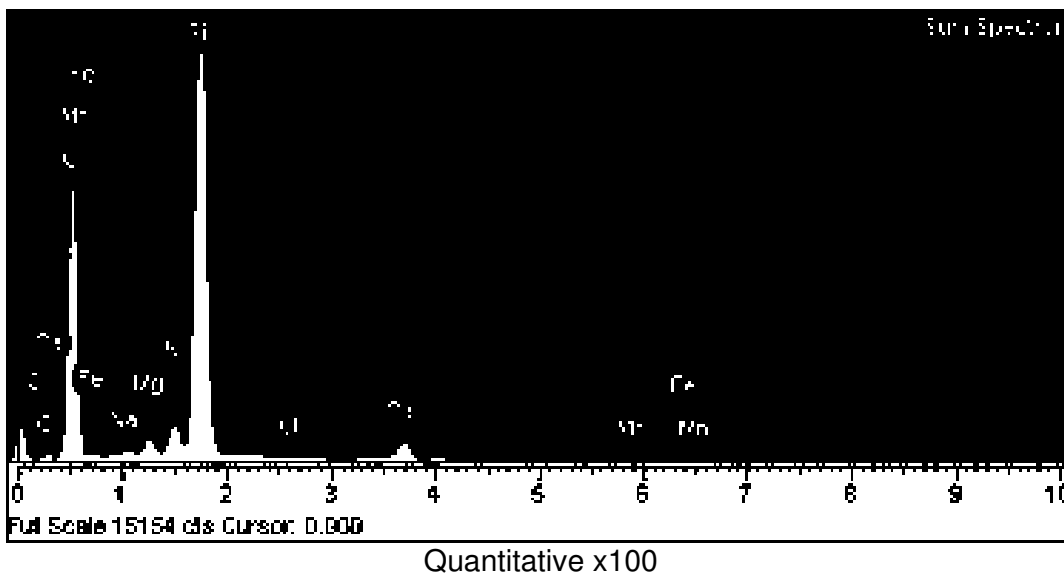


Electron Image 1

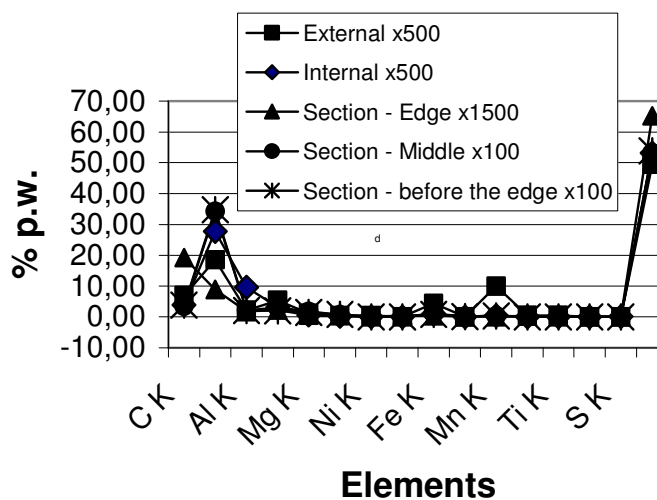
Quantitative x100

Area x100

Element	App Conc.	Intensity Corrn.	Weight% Sigma	Weight% Sigma	Atomic %	Compd%	Formula	Number of ions
Si K	45.65	0.8790	34.68	0.35	23.90	74.18	SiO <sub>2</sub>	2.93
C K	1.31	0.2313	3.79	0.49	6.10	13.87	CO <sub>2</sub>	0.75
Al K	2.61	0.8235	2.12	0.05	1.52	4.00	Al <sub>2</sub> O <sub>3</sub>	0.19
Mg K	1.61	0.7240	1.48	0.04	1.18	2.46	MgO	0.14
Ca K	2.79	0.9286	2.01	0.05	0.97	2.81	CaO	0.12
Na K	0.92	0.7652	0.80	0.05	0.68	1.08	Na <sub>2</sub> O	0.08
Fe K	1.01	0.8171	0.82	0.06	0.28	1.06	FeO	0.03
Mn K	0.36	0.7999	0.30	0.05	0.11	0.39	MnO	0.01
Cl K	0.16	0.6634	0.16	0.03	0.09	0.00		0.01
O			53.85	0.48	65.17			7.99
Totals			100.00					
Quantitative x100							Cation sum	4.26



### Elementary p.w. % - Sample 1



### CONCLUSIONS

The following conclusions have been drawn from the previous element analysis:

1. The Si is generally low (<35%), very low (<10%) on the edge of section, very low in exterior and internal surface and low (<35%) in the middle of section and before the end of sample. This is because the material has been leached away by the intense humidity present.

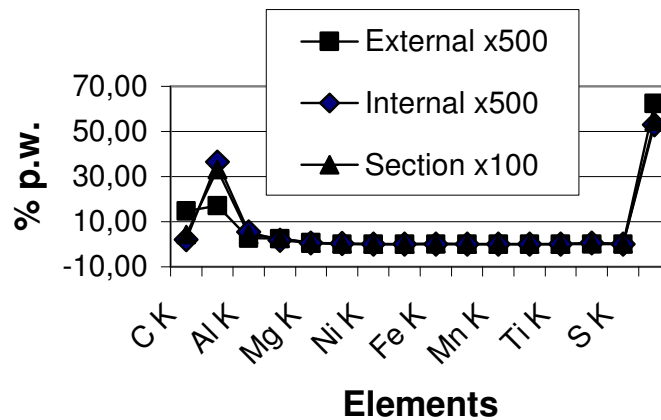
2. The Na is very low (<1%) in all cases. This is because the material has been leached away by the intense humidity present.

3. The K is too low ( $\approx 0\%$ ), this is because the material has been leached away by the intense humidity present and also because of a possible lack in raw material.

4. Ca is also generally very low (<5%), perhaps a little higher in the exterior surface because of calcium salt crust formation.

### Sample 2 (Y931)

### Elementary p.w. % - Sample 2



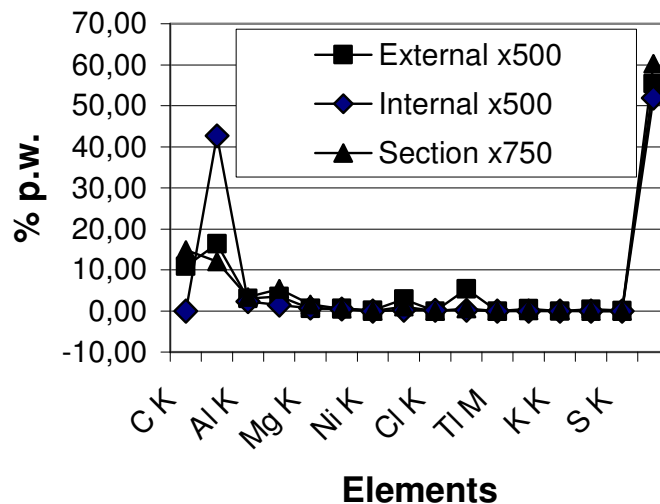
### CONCLUSIONS

The following conclusions have been drawn from the previous element analysis.

1. The Si is generally low (<37%) in the section and in the internal surface of sample and low (<17%) in the exterior surface of sample. This is because the material has been leached away by the intense humidity present.
2. The Na is very low (<1%) in all cases. This is because the material has been leached away by the intense humidity present.
3. The K is very low ( $\approx 0\%$ ), this is because the material has been leached away by the intense humidity present and also because of a possible lack in raw materials.
4. The Ca is also too low (<3%), but perhaps a little higher in the exterior surface because of the calcium salt crust.

### Sample 3 (Y934 A)

### Elementary p.w. % - Sample 3



## CONCLUSIONS

The following conclusions have been drawn from the previous element analysis.

1. The Si is generally low (<42%) in the section and in the internal surface of sample and low (<17%) in the exterior surface of sample. This is because the material has been leached away by the intense humidity present.

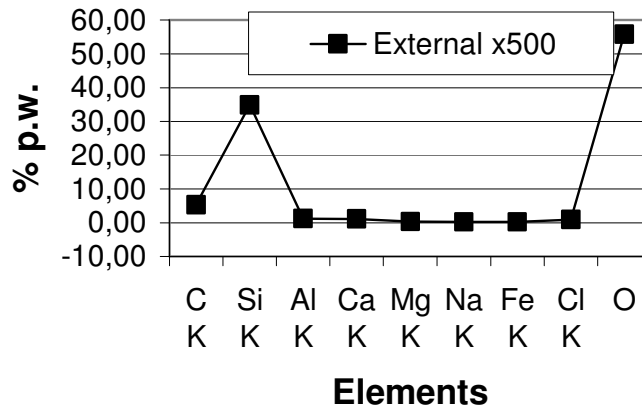
2. The Na is very low (<1%) in all the cases. This is because the material has been leached away by the intense humidity present.

3. The K is very low ( $\approx 0\%$ ), this is because the material has been leached away by the intense humidity present and also because of a possible lack in raw material.

4. The Ca is also too low (<5%), perhaps a little higher in the exterior surface because of the crust of calcium salt.

### Sample 4 (Y934 B)

#### Elementary p.w. % - Sample 4



## CONCLUSIONS

The following conclusions have been drawn from the previous element analysis.

1. The Si is generally low (<37%) in the exterior surface of the sample. This is because the material has been leached away by the intense humidity present.

2. The Na is very low (<1%) in all the cases. This is because the material has been leached away by the intense humidity present.

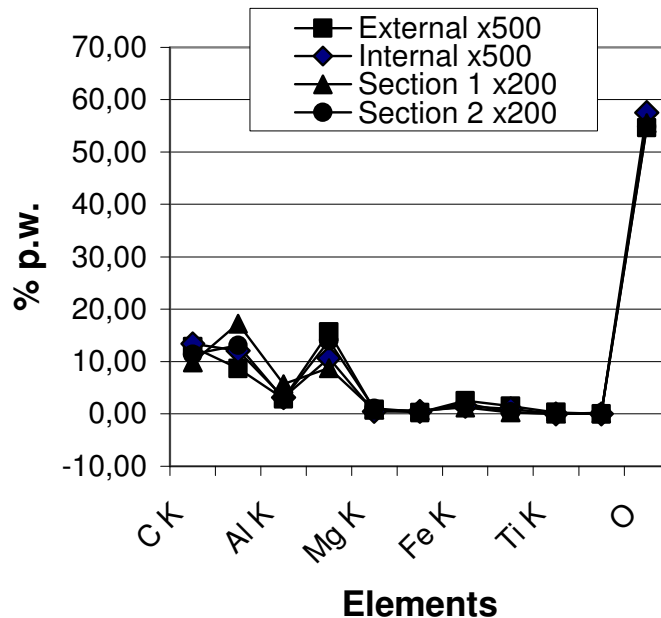
3. The Ca is also too low (<2%), this is because the material has been leached away by the intense humidity present.

4. The Al is very low ( $\approx 2\%$ ), this is because the material has been leached away by the intense humidity present.

### Sample 5 (Y941 big)



### Elementary p.w. % - Sample 5



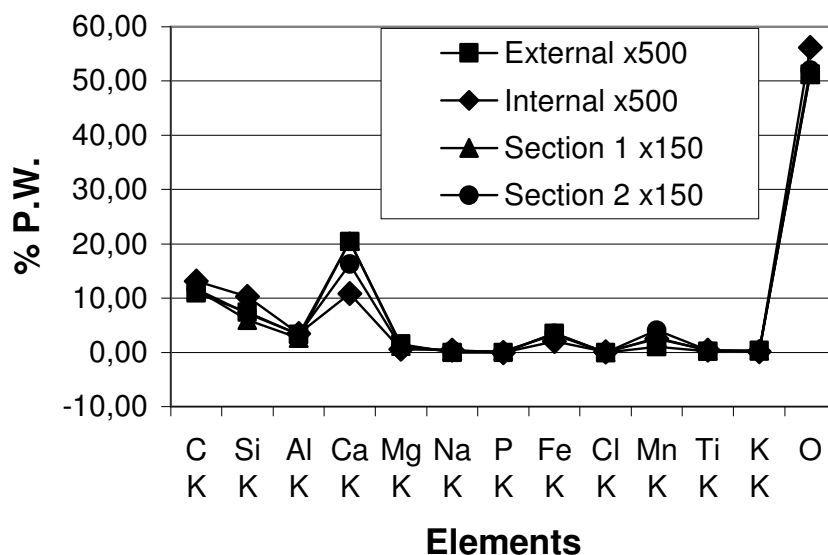
### CONCLUSIONS

The following conclusions have been drawn from the previous element analysis:

1. The Si is generally very low (<18%) in all the cases and specifically in the exterior surface of sample is very low (<10%).
2. The Na is too low (<1%). This is because the material has been leached away by the intense humidity present.
3. The K is really low ( $\approx 0\%$ ). This is because the material has been leached away by the intense humidity present, and also its lack in raw material.
4. There is a normal level of Ca, and it's especially high in the exterior surface in perhaps because the crust of calcium salt.

### Sample 6 (Y941 small)

### Elementary p.w. % - Sample 6



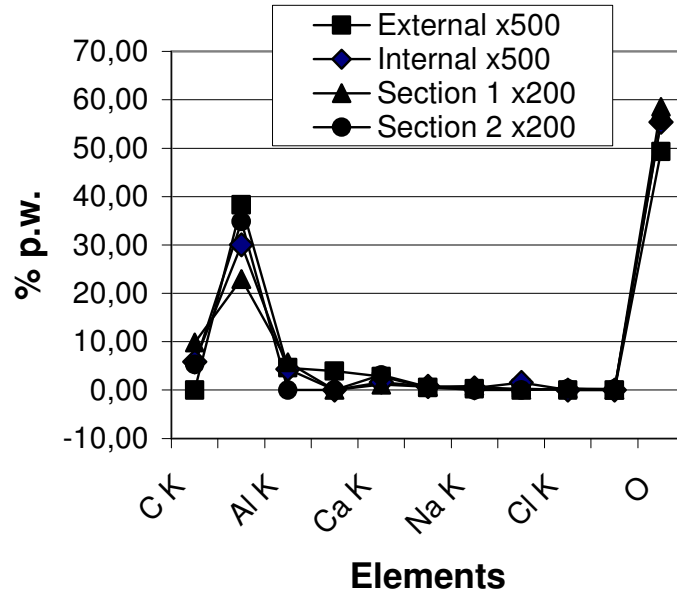
#### CONCLUSIONS

The following conclusions have been drawn from the previous element analysis:

1. The Si is generally very low (<10%) in all the cases this is because the material has been leached away by the intense humidity present
2. The Na is too low (<1%). This is because the material has been leached away by the intense humidity present
3. The K is really low ( $\approx 0\%$ ). This is because the material has been leached away by the intense humidity present, and also its lack in raw material.
4. There is a normal level of Ca it's especially high in the exterior surface, perhaps because the crust of calcium salt.

#### Sample 7 (Y933)

### Elementary p.w.% - Sample 7



### CONCLUSIONS

The following conclusions have been drawn from the previous element analysis:

1. The Si is generally very low (<40%) in all the cases and specifically in the section 1 of the sample it is very low. This is because the material has been leached away by the intense humidity present.
2. The Na is too low (<1%). This is because the material has been leached away by the intense humidity present.
3. The K is really low ( $\approx 0\%$ ) this is because the material has been leached away by the intense humidity present and also its lack in raw material.
4. The Ca is very low (<5%). This is because the material has been leached away by the intense humidity present.
5. The Al is very low (<1%) in the case of section 2. This is because the material has been leached away by the intense humidity present.

### ENVIRONMENTAL STUDY

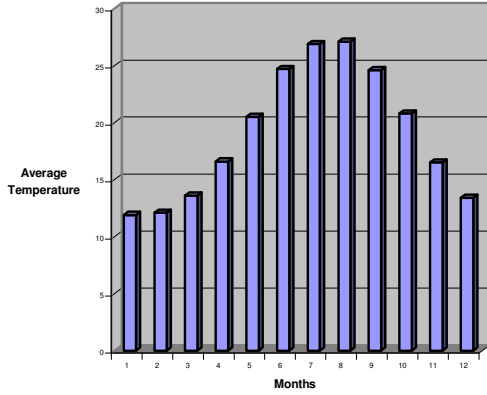
During the environmental study, data regarding winds, temperature and relative humidity from the area of the excavation was collected.

#### Climate data - study.

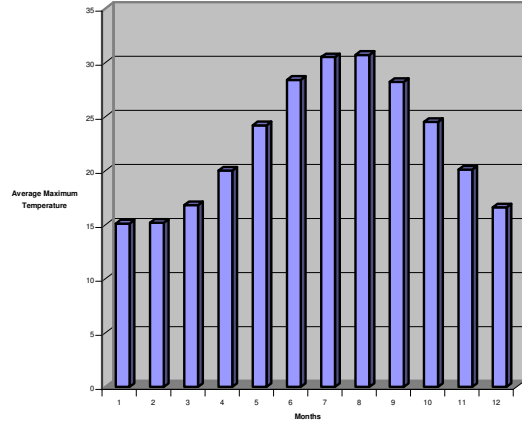
MONTHS	AVERAGE TEM- PERATUR E	AVERAGE MAXIMUM TEMPERA- TURE	AVERAGE MINIMUM TEMPERA- TURE	ABSOLUTE MAXIMUM TEMPERA- TURE	ABSOLUTE MINIMUM TEMPERA- TURE	RELATIVE HUMIDITY (%)	HEIGHT OF RAINFALL	WIND DIREC- TION
JANUARY	11,9	15,1	8,8	22,0	-4,0	70,1	149,6	NW
FEBRUARY	12,1	15,2	8,8	22,0	-2,2	69,1	105,7	NW
MARCH	13,6	16,8	10,1	27,4	0,2	68,7	75,6	W
APRIL	16,6	20,0	12,5	30,6	5,2	66,5	27,8	W
MAY	20,5	24,2	15,8	34,8	5,0	64,4	18,6	W
JUNE	24,7	28,4	19,9	37,4	12,6	58,5	2,3	W
JULY	26,9	30,5	22,3	40,0	14,6	57,6	0,4	W
AUGUST	27,1	30,7	22,7	42,0	17,0	59,9	0,2	W
SEPTEMBER	24,6	28,2	20,5	36,6	10,6	61,4	5,8	W

<b>OCTOBER</b>	<b>20,8</b>	<b>24,5</b>	<b>16,9</b>	<b>33,2</b>	<b>7,2</b>	<b>67,5</b>	<b>65,5</b>	<b>W</b>
<b>NOVEMBER</b>	<b>16,5</b>	<b>20,1</b>	<b>13,2</b>	<b>28,4</b>	<b>2,4</b>	<b>71,4</b>	<b>94,1</b>	<b>W</b>
<b>DECEMBER</b>	<b>13,4</b>	<b>16,6</b>	<b>10,4</b>	<b>22,8</b>	<b>1,2</b>	<b>72,4</b>	<b>157,4</b>	<b>NW</b>

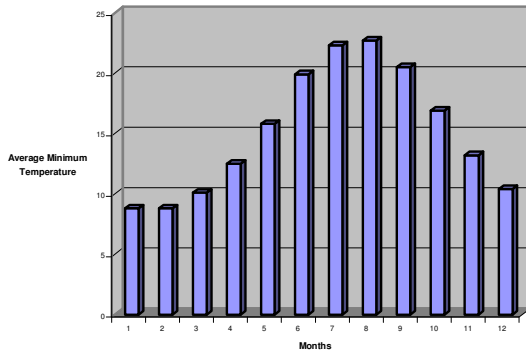
Months - Average Temperature



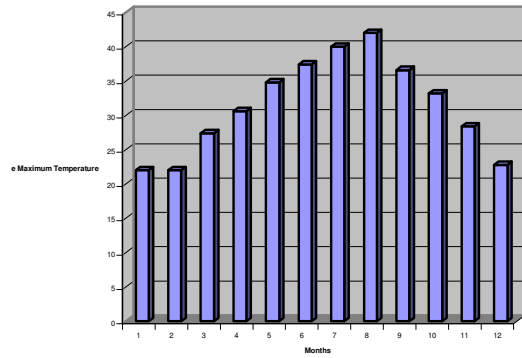
Months - Average Maximum Temperature



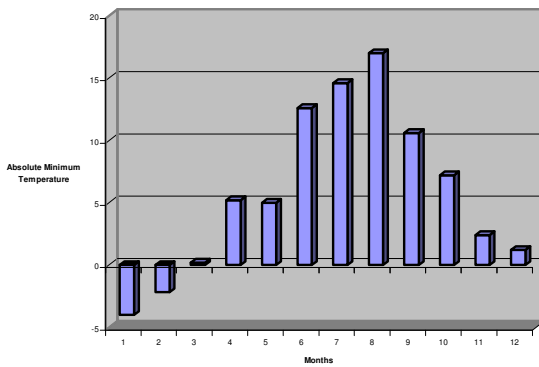
Months - Average Minimum Temperature



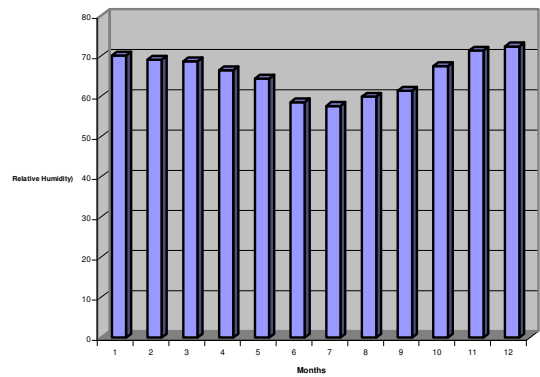
Months - Absolute Maximum Temperature

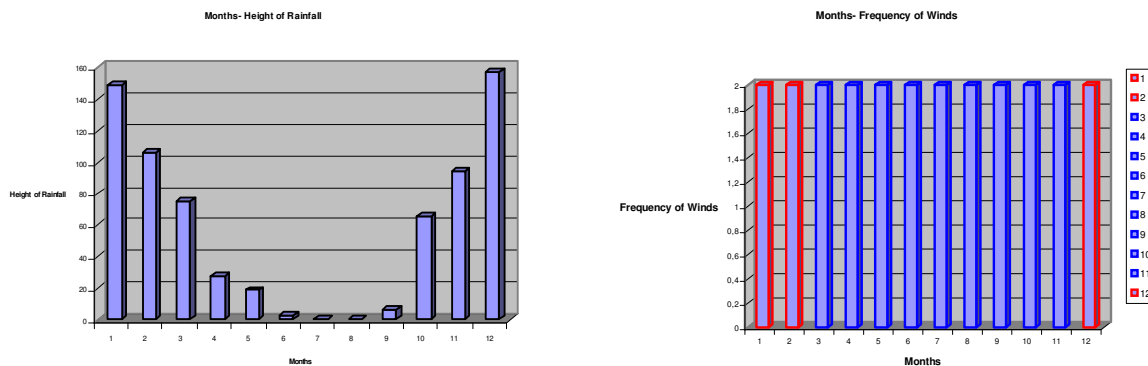


Months- Absolute Minimum TemperatureA



Months-Relative Humidity (%)





The climate data elements were provided by the department of statistics of National Meteorological Service for the period from 1955 up to 2004. During the examination of this data, the following things were observed:

1. The average temperature from January to December was a minimum of 11.9°C in January and a maximum of 27.1 °C in August. Also, the average maximum temperature for January was recorded at 15.1 °C while the average minimum was 8.8 °C. However, the absolute maximum temperature was 22 °C and the absolute minimum -4 °C. Respectively, during August, the average maximum temperature observed was 30.7 °C and the average minimum was 22.7 °C, while the absolute maximum temperature reached 42 °C and the absolute minimum 17 °C.
2. Relative humidity (RH%) indicated percentages of between 57.6% and 72.4% at all times throughout the year, with the most times recorded 67 - 69%
3. The height of rainfall begins from 0.2 mm during the summer months (August) and reaches 157.4 mm over the winter (December). Also it has to be noted that on the island powerful western winds blow all year round apart from the winter period when they change to northwestern.

### Conclusion.

The presence of humidity constitutes one of the most important causes of physiochemical deterioration of structural materials of monuments, archaeological finds and works of art. In the atmosphere, the relation of existing contents in water to saturated content on percentage (%) gives a degree of relative humidity (RH). By observing the average RH per month, during the period from 1955 to 2004, high RH percentages have been noticed, although the height of rainfall decreases drastically from June to September and is quite low from April to May. According to the data of atmospheric humidity (condensation), the rainfall and the ground-water level (capillary rising), the result is likely to be a high percentage of relative humidity (RH%) in the ground.

With regard to the temperature changes, it is comprehensible that the layers of ground that are very deep remain detached from them, while the layers near the surface are affected by them. The temperature in the deep layers is theoretically lower than that of the surface ground. This multiplies the problems, when the excavated objects are revealed and transported from a cooler to a warmer ground environment.

Finally, in the region of excavation of the glass unguentaria, conditions of frost nor particularly high temperatures have not been observed.

## TOPOGRAPHICAL DATA

### Ground-water lever.

According to studies of the National Institute of Geology and Mining Research, it is observed that quadrants of the ground in the city of Rhodes - and similarly in the region of the excavation - is level and hypsometric differences from the sea do not exist. Also, the upper level of the ground-water level is 5 m underground, near enough to the depth where the artifacts that were used in this study were excavated (according to the excavation diaries)

Finally, petrographically the ground is constituted by alluvium of certain diluvial depositions (sand, gravel, mica) and also few neogenic rocks (clay, metamorphic)

### Conclusions.

From the above elements we are led to the conclusion that the sea influences the height of the ground-water level. Also the ground-water level is too small in order to allow contact of the rising humidity, according to the phenomenon of capillary rising, with the level of excavation.

## ACIDITY - ALKALINITY - SALINITY OF GROUND OF EXCAVATION

Six samples were taken from the soil environment of the excavation. These samples were used for the measurement of pH, electric conductivity and concentration of sulfate ( $\text{SO}_4^{2-}$ ) and chloride ( $\text{Cl}^-$ ) ions. The results of these measurements appear in the following table:

$\alpha/\alpha$	pH	Conductivity ( $\mu\text{S}/\text{cm}^2$ )	$\text{SO}_4^{2-}$ (ppm)	$\text{Cl}^-$ (ppm)
<b>Sample 1 (Y931)</b>	<b>7,40</b>	<b>110</b>	<b>3,5</b>	<b>25,0</b>
<b>Sample 2 (Y932)</b>	<b>7,10</b>	<b>50</b>	<b>1,0</b>	<b>10,0</b>
<b>Sample 3 (Y933)</b>	<b>6,40</b>	<b>50</b>	<b>1,0</b>	<b>9,0</b>
<b>Sample 4 (Y934)</b>	<b>6,15</b>	<b>37</b>	<b>0,5</b>	<b>7,0</b>
<b>Sample 5 (Y941 small)</b>	<b>6,50</b>	<b>45</b>	<b>0,5</b>	<b>7,0</b>
<b>Sample 6 (Y941 big)</b>	<b>6,80</b>	<b>42</b>	<b>0,5</b>	<b>6,5</b>

### Conclusions.

From the measurements of the soil samples that were taken from the surface of artefact deposits the following conclusions can be drawn:

The pH indicates the content in ions of hydrogen ( $\text{H}^+$ ) in an environment and it constitutes an important factor for an environment that contains water.

1. The first sample (unguentaria with record No Y931) the pH shows alkaline ground that shows a presence of calcium carbonate ( $\text{CaCO}_3$ ).
2. The second sample (unguentaria with record No Y932) the pH shows light limestone ground.
3. The third and fourth sample (unguentaria with record No Y933, Y934) the pH shows acidic ground that identifies a presence of aluminosilicates (quartz, clays etc.).
4. In the fifth and sixth sample (unguentaria with record No Y941 small and Y941 big) the pH is light acidic to neutral, which means ground of aluminosilicates composition.

The conductivity expresses the concentration of soluble salts in a solution. According to the measurements, low conductivity has been observed that involves low concentration of chlorides and salts in general. This shows that the content in chloride (Cl<sup>-</sup>) and sulfate ions (SO<sub>4</sub><sup>2-</sup>) belongs mainly to the bed level that is high enough to be affected by the height of rainfall and the sea level.

### FORMS OF DETERIORATIONS

The humidity is the most important factor that led to the deterioration of glass<sup>6</sup>. When a glass comes in contact with water or with a water solution, a number of chemical changes take place on its surface. These reactions can expand at a later date in the main body of the glass, depending on the quality of the surface that has been created. Certain surfaces are protected, while others aren't, and their quality depends on various factors, mainly on the composition of glass and the pH of the glaze<sup>5</sup>.

The processes of chemical reactions that happen when there is contact between glass and a water solution can be described as follows:

1. Exchange of glass's cations with ions of oxon (H<sub>3</sub>O<sup>+</sup>) of the water solution, with diffusion that takes place within the already shaped diffusion layer.
2. Dissolution of diffusion layer controlled by the prevailing surface tendency. This process decreases the thickness of diffusion layer and consequently increases the effect of previous erosive reactions<sup>6</sup>.

Also, in the sodium glasses the wastewater of alkalis and silicon happens at the same time<sup>5</sup>.

The main sources of humidity in archaeological glasses are the water of subsoil (ground-water level), the rain and the atmosphere (condensation)<sup>9</sup>. As already, noted in the environmental study chapter. The ground-water level is found to be quite narrow (5 m) and near the depth that the artifacts were found (≈2 m). This fact had an immediate reaction to the artifacts, as a result of the ground water capillary rise. But, still, the subsoil waters sweep mainly but not exclusively through the soil and the soluble components of the aluminosilicates, so that they contain ions of sodium (Na<sup>+</sup>), potassium (K<sup>+</sup>), calcium (Ca<sup>2+</sup>), sulfates (SO<sub>4</sub><sup>2-</sup>), chlorides (Cl<sup>-</sup>) and silicates (SiO<sub>3</sub><sup>2-</sup>)<sup>9</sup> which are dissolved in various proportions. In the case of Rhodes, the underground water is also connected with the sea. This means that apart from the phenomenon of salt spray, by which salts are transported to the soil, important quantities of chloride and silicon salts can be found in the subsoil water itself, caused by the sea, as it is at the same hypsometric level as the ground.

Also, the high percentages of relative humidity encouraging the creation of erosion centres and the condensation of erosion products on the glass surface have already been noticed. As well as the growth of microorganisms that can indirectly and immediately affect glass have been noted<sup>6</sup>. The various microorganisms can corrode the glass indirectly because of the water condensation on the glass surface that results in the creation of an erosive environment<sup>9</sup>. According to other studies, it has been proved that the action of the microorganisms can cause the washing off of elements such as Sodium (Na), titanium (Ti), calcium (Ca), magnesium (Mg), iron (Fe), manganese (Mn) and aluminum (Al). Bio-deposits that are formed by their presence can cause changes of the diffusion, the conductivity and the natural behavior of surfaces with regard to the environmental conditions<sup>6</sup>.

The effect of water on a glass surface apart from the changes that are caused on the glass surface, reactions take place also in water that is transformed into light acidic or alkalic solution. This depends on whether the glass washes off the alkalis

and silicon dioxide. The pH of the solution depends on the alkalis concentration, as well as on the proportion of alkaline oxides to silicon dioxide. These two factors change with the passage of time and consequently change the pH of the water solution<sup>6</sup>.

The leaching off of silicon dioxide on the glass in the solution is very small and is continuous for pH lower than 9, while it increases with the further increase of pH. More specifically, the solubility of silicon dioxide presents differences in the three regions of pH. In the first area, with  $\text{pH} < 10$ , the solubility reaches roughly  $6,31 \times 10^{-6}$  moles/lit with the shaping and the presence of orthosilicate acid ( $\text{H}_2\text{SiO}_3$ ). In the second area with  $10 < \text{pH} < 12$  it has relatively high solubility as a result of the shaping and the presence of orthosilicate ions ( $\text{HSiO}_3^-$ ). In the third area with  $\text{pH} > 12$  it shows higher solubility as result of the shaping and the presence of ions oxides of silicon ( $\text{SiO}_3^{2-}$ )<sup>6</sup>.

The leaching away of alkali in conditions with pH lower than 9, has been recorded to be linear and with no effect by the pH of the solution. For pH higher than 9 the process is slowing down as the pH increases. More specifically the glasses that contain sodium are corroded under all the pH conditions; however it is worth of noticing the drop of erosion tendency when pH is higher than 9<sup>6</sup>.

Finally, the leaching away of calcium oxides are encouraged under pH conditions lower than 10. On the other hand, when pH is higher than 10 the oxides are more resistant to corrosion<sup>6</sup>. By measuring the pH of the samples soil it is observed that solubility of silicon dioxides applied to the first conditions and is considered very low and continuous. On the other hand, intense erosion of the samples has been observed by the washed away of the sodium calcium oxides the applied conditions of low pH.

The following notes are the result of the observations during the recording of samples from Rhodes:

**Perfume unguentaria with record no Y931:** They were two unguentaria by which was saved a neck, the body of one of them, as well as roughly 21 fragments of very low thickness (0,5 - 1 mm). Under macroscopic observation on the artifact's surface, noted that a deposition of clay (both inside and outside of the artifact) and insoluble salts crusts. Also extended formation of foliar erosion that resulted to Iridescences.

**Perfume unguentaria with record no Y932:** They were two unguentaria by which they are saved from the first one 32 fragments and 21 chips with thickness roughly 2,5 mm, while from the second one 11 chips with thickness around 2 mm. Depositions of clay (both inside and outside of the artifact) and insoluble salts hard crusts were also noted under macroscopic observation. Also extended formation of foliar erosion that resulted to iridescences has also noted. Crizzling and pitting were observed on the surface, by examination of surface samples under a Scanning Electron Microscope (S.E.M.).

**Perfume unguentaria with record no Y933:** it was an unguentaria with the base saved and the neck with verge, while exist roughly 19 fragments with really low, thickness (0,5 - 1 mm). Depositions of clay (both inside and outside of the artifact) and insoluble salts hard crusts were also noted under macroscopic observation. Also extended formation of foliar erosion, iridescences and biological decay had also been noted. Pitting was observed on the surface, by examination of surface samples under a Scanning Electron Microscope (S.E.M.).

**Perfume unguentaria with record no Y934:** it was saved almost entire in two fragments, very thin 1 mm and three moreover fragments from different unguentaria



with thickness of 4 mm. On the one fragment depositions of clay (both inside and outside of the artifact) and insoluble salts hard crusts were also noted under macroscopic observation. Also extended formation of foliar erosion, iridescences. Pitting was observed on the surface, by examination of surface samples under a Scanning Electron Microscope (S.E.M.). On the second fragment, depositions of clay and dulling were observed along with surface anomaly observed by S.E.M.

**Perfume unguentaria with record no Y941:** they were two unguentaria. The big one had the neck with verge and part of the base, along with 56 fragments with very low thickness (roughly 1mm). Depositions of clay (both inside and outside of the artifact) and insoluble salts hard crusts were also noted under macroscopic observation. Also extended formation of foliar erosion, iridescences that was also confirmed by the S.E.M. analysis. The second smaller unguentaria had one part of the neck and its verges as well as fragments of its base, along with 49 splinters 0,5-1 mm thick. Depositions of clay and insoluble salts hard crusts were also noted under macroscopic observation. Also extended formation of foliar erosion that resulted to iridescences has also noted. Pitting and surface degradation was observed on the surface, by examination of surface samples under a Scanning Electron Microscope (S.E.M.).

Generally, in all the above cases the same types of deterioration have been observed. These can be categorized as follows:

**Dulling.**

It is the simplest form of corrosion, according to that a glass loses its initial lucidity and transparency, while it becomes progressively non-transparent. This type of erosion can be separated easily from dulling that is caused by scratches or deposits<sup>6</sup>.

**Crizzling.**

Crizzling of a glass can be the result of either pressure application on its surface, or spontaneous (without certain reasons) glass crizzling. At the case of the perfume unguentaria crizzling is the result of pressure application<sup>6</sup>.

**Lamination.**

The phenomenon of repeated layers creation is a form of corrosion according to which the glasses surface layers exfoliation. These layers are usually water saturated to a high percentage and the fluctuations of humidity can lead to shrinkage or their dilation with result exfoliation of the glass surface<sup>6</sup>

**Iridescences.**

The term characterizes an optical phenomenon, when the glasses with foliar erosion present a variety of colors, both in reflection and transit light<sup>6</sup>.

**Pitting.**

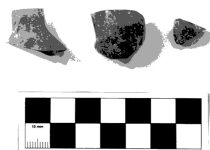
Pitting usually begins from the erosive centers that are found on or under the surface of glass and it is directed to all the directions under high speed, with an inside direction, shaping circular cavities. Pitting is created under the defective regions of glass surface, regarding their size is characterized as micro-pitting with diameter 0,1 - 0,2 mms, macro-pitting of 2 - 4 mms diameter and prima-pitting of <4mm diameter<sup>6</sup>.

**Crusting.**

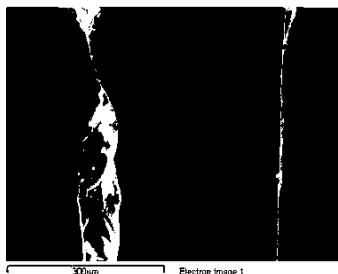
The formation of crust on a glass surface is related to the phenomenon of pitting. During the formation of the crust the surface of glass darkens in color, because of the presence of insoluble salts. When a surplus of calcium oxide is washed off the glass, it is deposited on the glass surface or between its deteriorated layers by forming a common phase.

According to other studies, during the erosion of glass in the ground the alkalis, the alkaline grounds as well as certain other components are eliminated gradually

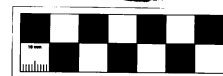
from its mass. While aluminum, iron, titanium and certain other elements that form insoluble compositions, remain in the network of silicon dioxide.



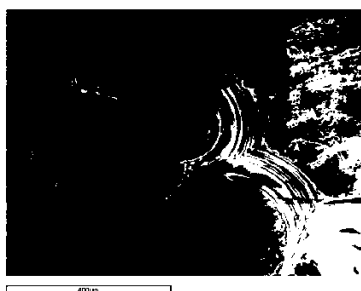
*Dulling.*



*Crizzling.*



*Iridescences.*



*Pitting.*



*Crust.*

### **CONSERVATION PROCESSES**

The conservation process of archaeological glass objects begins immediately after it has been excavated, by immediately applying first aid measures that are carried out more systematically when the objects are moved to the laboratory.

No previous conservation work has been observed when referring to the glass unguentaria from Rhodes, which were the subject of this case study. For this reason, we initially collected photographic documentation and recorded the objects as they were received; we also drew sketches of pieces that in our opinion were considerably more important. Afterwards, fragments were chosen to use in the examination and material analysis of the objects, as well as the soil samples for the examination of the burial environmental conditions. It is important to note that no destructive analytical methods were used for the observation of the material structure of the objects so the splinters were returned. The next step was choice of suitable conservation methods and materials. As a result of the lamination decay the object's surface had become extremely fragile. It is for that reason they were primarily fixed with a low concentration solution of Paraloid B72 and acetone. The solvent was initially applied on its own to the surface and then the fixative solution was periodically introduced and gradually increased, starting at 1% and rising to 4%. According to the bibliography the solvent that exists within the material's pores helps the resin's molecules to increase their mobility and ability to penetrate the pores, as well as achieve even distribution of the fixative within the material's mass.

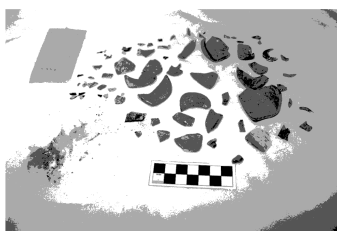
Also, the use of solutions with increasing concentration facilitates the diffusion of the fixative solution<sup>6</sup>. After each application of the fixative the splinters were left to dry out, the solvent on sheet Melinex (polyethylenterephthalic acid).

The next step was the cleaning of the fragments. The cleaning process involves the removal of soluble and insoluble deposits from the objects surface. To begin with we undertook a number of cleaning tests with deionised water, neutral detergents, various solvents and reagents in paste form. More specifically, deionised water applied with a cotton baton was used for the removal of soluble deposits. It was observed on application that the use of water ensures high solubility, and low penetration in the pores and in the corroded layers of the glass surface. After the application of various organic solvents ethanol and white spirit), with a cotton baton, it was observed that the organic solvents caused low solubility, but high penetration. Thus, a combination of water - ethanol in proportion 1:1 was selected as the cleaning method for deposits.

For the removal of insoluble crusts various chemicals were used in the form of solutions and pulps. More specifically, solution 2% w/w E.D.T.A. (disodium salt of ethylenediaminetetraacetic acid) with 2% w/w  $\text{NH}_4\text{HCO}_3$  (ammonium bicarbonate) in deionised water was used. The solution was applied with a cotton baton. According to the bibliography it is known that the action of bicarbonate salts, lies on the formation of insoluble carbonate salts with metal ions of crust and on the other hand in the creation of an alkaline environment, that encourages the removal of soluble salts that are contained in the crust. Therefore, it was observed, that the solution softened the crust and with mechanic method and it was possible to remove it with a scalpel. Also, the cleaning method using pastes of absorbant clays (sepiolite) with E.D.T.A. for the removal of calcium ions ( $\text{Ca}^{2+}$ ) and magnesium ( $\text{Mg}^{2+}$ ) was tested. Once the paste was applied it was observed that the upper crust surface softened and could be removed relatively easily with a scalpel. Then the process of consolidation the fragile surface of glass splinters with successive coverings with low concentration solutions of acrylic resin Paraloid B72 and acetone was applied, and after that the resetting of fragments, joining and adhesion procedure was followed, with a concentrated solution of Paraloid B72 in acetone.



*Vessel before conservation.*



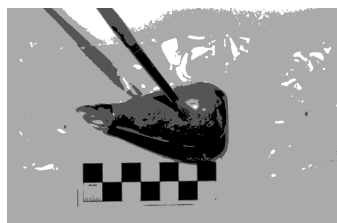
*Vessel before conservation.*



*Vessel before conservation.*



*Vessel before conservation.*



*Pre-consolidation procedure.*



*Pre-consolidation procedure.*



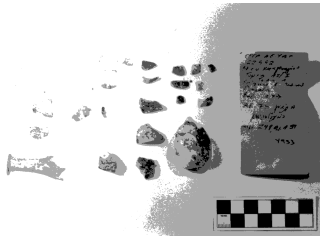
*Cleaning procedure with pulps of E.D.T.A. and sepiolite.*



*Cleaning procedure with pulps of E.D.T.A. and sepiolite.*



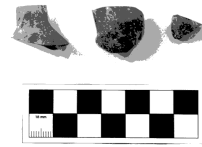
*Cleaning procedure with pulps of E.D.T.A. and neutral paper.*



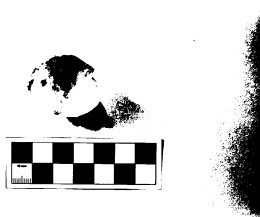
*Vessel after cleaning.*



*Vessel after cleaning.*



*Fragments of vessel after cleaning.*



*Fragments of vessel after cleaning.*



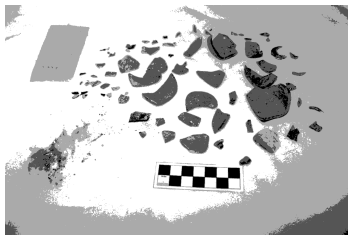
*Fragments of vessel after cleaning.*



*Fragments of vessel after cleaning.*



*Fragments of vessel after cleaning.*



*Fragments of vessel after cleaning.*



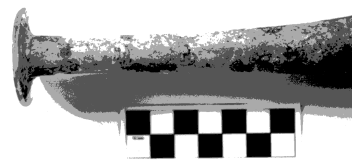
*Fragments of vessel after cleaning.*



*Αγγείο μετά τον καθαρισμό.*

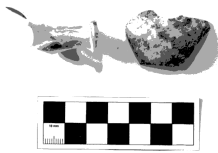


*Fragments of vessel after*



*Fragment of vessel after cleaning.*

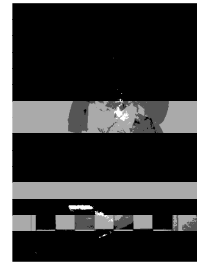
*cleaning.*



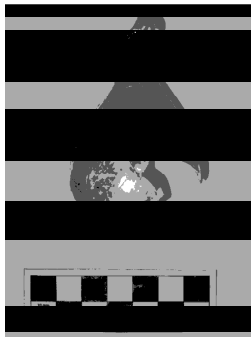
*Fragments of vessel after cleaning.*



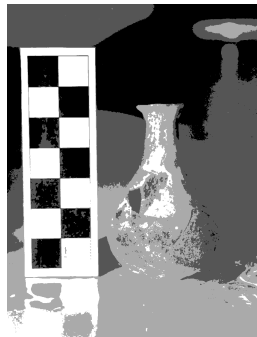
*Joining procedure.*



*Joining and adhesion procedure.*



*Joining and adhesion procedure.*



*Joining and adhesion procedure.*



*Joining and adhesion procedure.*

### **PROPOSED CONDITIONS FOR DISPLAY AND STORAGE**

For the display of vessels, it is proposed that showcases are used with dehydrated material of silica gel and these standard conditions; relative humidity 35 - 40%, temperature  $21 \pm 1,5$  °C, lighting 150 lux. For the storage of vessels, it is proposed that they are kept in air-conditioned storage areas and placed in bookshelves with the following standard conditions; relative humidity <42%, temperature 18 - 23 °C, lighting <150 lux.

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