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STUDY AND COMPARISONS BETWEEN PLOUGHING AND OTHER FORMS OF CORROSION OF GREEK ARCHAEOLOGICAL GLASS

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ABSTRACT

This paper is an initiative study of a form of corrosion of archaeological glass that until now has been recorded, but not studied. Seven samples of glass, that exhibit this type of corrosion, have been examined in the scanning electron microscope (S.E.M.) and analyzed by E.D.X.A. and three samples of the soil that they were found have been tested by X-ray diffraction (X.R.D.). The samples come from the excavations of the 22nd ephorate of prehistoric and classical antiquities in the city of Rhodes. The present study contains the description of "ploughing", the results of some characteristic analyses of the samples and the preliminary conclusions.

KEYWORDS: Glass, dulling, weeping, pitting, iridescence, ploughing.

OBJECTIVES

The forms of corrosion of glass objects from East Mediterranean area are usually dulling, weeping or sweating, crizzling, discolouration, pitting, crust formation, lamination, iridescences, milky or enamel like weathering and loss of vitreous nature (Lampropoulos *et al.*, 2002; Lampropoulos *et al.*, 2001; Lopez *et al.*, 2001; Moraitou *et al.*, 2001; Romich et al., 2001; Lampropoulos *et al.*, 1995; Newton, Davison, 1989). The above forms are depicted in the following figures 1 - 18.

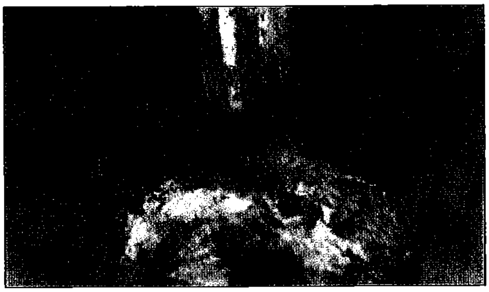

Fig. 1: Dulling, pitting and iridescences on glass object (Photo: V.N. Lampropoulos).

Fig. 2: Dulling, pitting and iridescences on glass fragment (Photo: V.N. Lampropoulos).

Fig. 3: Crizzling and iridescences on glass object (Photo: V.N. Lampropoulos).

Fig. 4: Crizzling on glass fragment (Photo: V.N. Lampropoulos).

Fig. 5: Discolouration on glass fragment (Photo: V.N. Lampropoulos).

Fig. 6: Discolouration and pitting on glass object (Photo: V.N. Lampropoulos).

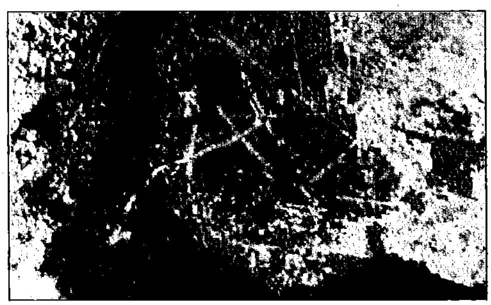

Fig. 7: Pitting and iridescences on glass object (Photo: V.N. Lampropoulos)

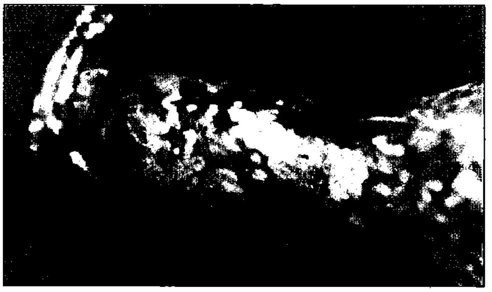

Fig. 8: Pitting and iridescences on glass object (Photo: V.N. Lampropoulos).

Fig. 9: Crust formation and pitting on glass fragment (Photo: V.N. Lampropoulos).

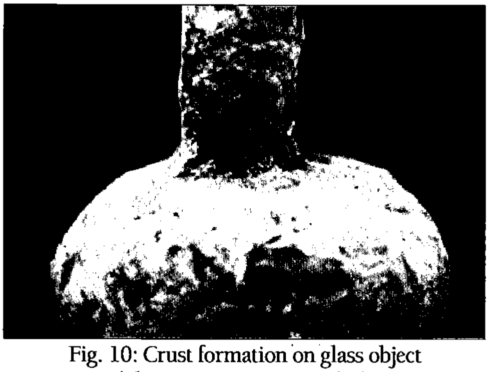

Fig. 10: Crust formation on glass object (Photo: V.N. Lampropoulos).

Fig. 11: Lamination, iridescences and milky or enamel like weathering on glass object (Photo: V.N. Lampropoulos).

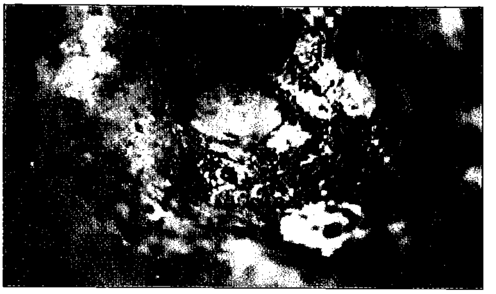

Fig. 12: Lamination, iridescences and milky or enamel like weathering on glass object (Photo: V.N. Lampropoulos).

Fig. 13: Iridescences on glass object (Photo: V.N. Lampropoulos).

Fig. 14: Iridescences on glass object (Photo: V.N. Lampropoulos).

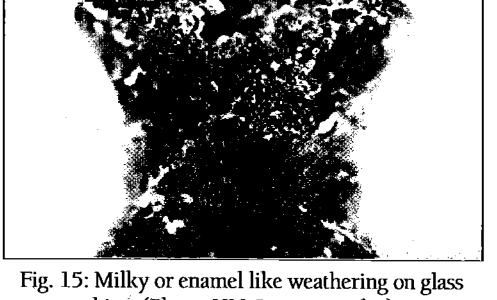

Fig. 15: Milky or enamel like weathering on glass object (Photo: V.N. Lampropoulos).

Fig. 16: Milky or enamel like weathering on glass object (Photo: V.N. Lampropoulos).

Fig. 17: Loss of vitreous nature on glass frag-ment (Photo: V.N. Lampropoulos).

Fig. 18: Loss of vitreous nature on glass fragment (Photo: V.N. Lampropoulos).

The paper deals with the development of this unusual form of corrosion (''ploughing''), which appears in the glass surface in the shape of channels with no specific direction. These vary from shallow grooves (Fig. 19, 20) to tunnels, cutting all the way through the material (Fig. 21, 22). Their sides are almost perpendicular to the surface, while their endings are circular. The grooves appear either singly on the glass surface (Fig. 24, 25) or with branches (Fig. 23), thus creating a network of channels throughout the object. Their direction and width is not specific.

This phenomenon was recorded for the first time by T. Buechner [Buechner, 1960] in glass frag-ments from the excavation in Tharra (south Creta island) in 1959. It was he who gave the phe-nomenon the name "ploughing" and speculated that it might be caused by the leaching down from a scratch on the surface or that it may be the effect of some kind of microorganism. According to previous research (Moraitou, 1996) there is also an agreement with this hypothesis, but has re-marked that the phenomenon needs to be studied, so as to enable a verification of the assumption.

After the examination under a stereoscopic microscope, it was observed that the decayed glass from the interior of the grooves was loosely connected to the concrete mass of the uncorroded material and that the degradation products are easily abstracted, leaving the sides of the groove almost perpendicular to the surface. One can also observe some kind of foliated arrangement of the corroded glass, which becomes looser in the center of the channel.

Fig. 19: Shallow bowl from the east necropolis of the city of Rhodes (early 3rd century B.C.) (Photo: Triantafillidis, 2000, p.165).

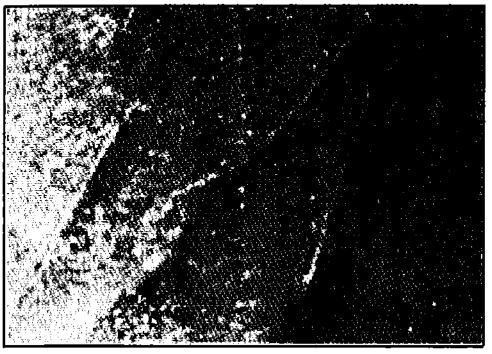

Fig. 20: Enlargement of figure 19 in a stereoscopic microscope (Photo: A. Leakou).

Fig. 21: Bowl from the central necropolis of the city of Rhodes (150 - 100 B.C.) (Photo: Triantafillidis, 1999; Triantafillidis, 2000, p. 47).

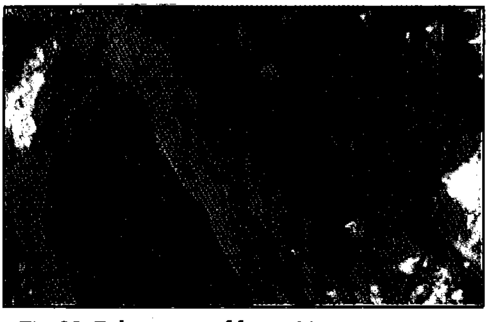

Fig. 22: Enlargement of figure 21 in a stereoscopic microscope. Grooves cutting all the way through the material (Photo: A. Leakou).

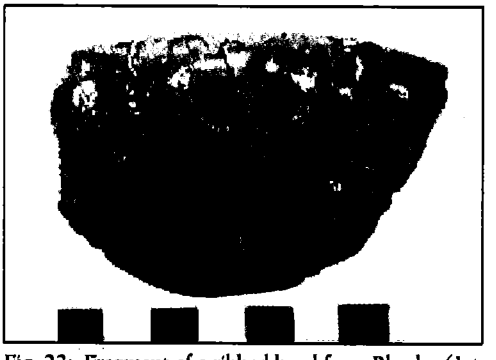

Fig. 23: Fragment of a ribbed bowl from Rhodes (1st century B.C.) (Photo: A. Leakou).

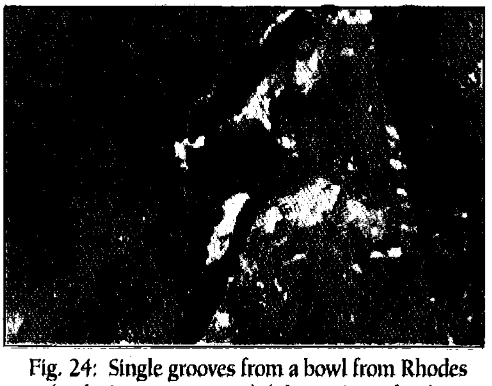

Fig. 24: Single grooves from a bowl from Rhodes (early 1st century B.C.) (Photo: A. Leakou).

Fig. 25: "Ploughing" in a glass fragment from Rhodes (Photo: A. Leakou).

METHODS - RESULTS

The analyses were performed in samples, according to previous researches (Brill 2001 ; Brill 1994), concerning Roman and Hellenistic soda glass from the island of Rhodes, in south-eastern Greece. The glass vessels and fragments that are examined in this paper come from the excava-tions of the 22nd ephorate of prehistoric and classical antiquities in the city of Rhodes. They date from the 4th century B.C. to the 1st century A.D. In all of the samples an area of uncorroded glass was selected to make an elementary analysis and then various areas in the interior of the grooves to observe the morphology of this phenomenon and perform analyses. In the areas where it was judged necessary, a mapping of the elements was made to create a clear image of the distribution of the elements, as well as the difference of their concentration from one point to the other. In figure 26 the wide area of a groove from a glass sample from Rhodes is observed and the elements are mapped using the scanning electron microscope. It can be noticed that sodium has been almost totally leached out in the interior of the groove. It can be also noticed that in the center of the channel, silicon appears reduced. This is due to the gradual loss of the corroded material. It can be clearly seen that in this area there are only grains of glass and this leads to the conclusion that the loss of the material, that leads to channels cutting through the glass, begins from the center and proceeds to the walls of the grooves.

In the rim of the groove and for some distance to the interior there is evidence of the presence of the network former, which proves the existence of glass at that area. At the same point one can notice that the concentration of calcium and potassium is not changed, while sodium does not ap-pear at all. The same conclusions can be reached by observing the pit that is next to the groove.

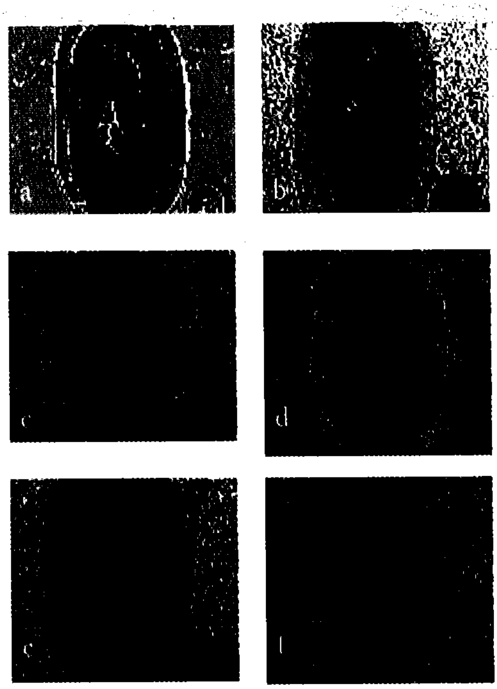

Fig. 26: Mapping of the elements of a glass sample from Rhodes. a. Picture of the area of the groove (x75, S.E.M.), b. silicon, c. calcium, d. aluminium, e. sodium, f. potassium (Photo: A. Karampotsos).

The area near the side of the groove appears in figure 27 and the elementary analysis of this field is compared in table I (sample 1) to that of uncorroded glass from the same sample. The numbers in table I confirm the observations, which were described above, regarding the mapping of the elements. So it is noticed that sodium has been leached out, while the concentration of potassium remains in the same level. The concentrations of aluminum, calcium and silicon appear increased at the edge of the groove due to the soil depositions between the perpendicular glass layers. These depositions cannot be removed without harming the loosely connected corroded material that ex-ists in the interior of the groove.

Two channels almost conjoint are shown in figure 28. The glass surface is very corroded and ex-hibits iridescence and pitting in addi-

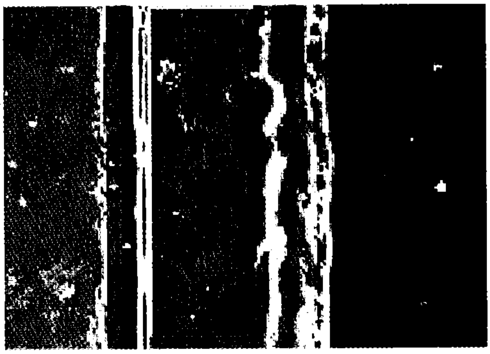

Fig. 27: The edge of the groove (x500, S.E.M.). Marked area: Corroded glass (Photo: A. Karampotsos).

tion to "ploughing". If the groove is observed closer (fig. 29) the arrangement of the decayed glass in perpendicular layers is clearly seen. The elementary analysis at this point (Table I, sample 4) leads to the same conclusions as in the previous sample. A large pit close to the borders of "ploughing" is shown in figure 30. The reduction of the con-centration of sodium is obvious in this case too, while the remaining network modifiers do not seem to have been leached out. This is shown more clearly in the table of the elementary analysis (Table I, sample 4), from the concentrations of these elements. The reduction in sodium content in this case is less than in the case of "ploughing". Thus, it can be concluded that the image created by the distribution of the elements, as revealed in the mapping, is similar to that of "ploughing", but in the case of "ploughing" the leaching out of the elements is more substantial than in the case of pitting.

Fig. 28: "Ploughing" in a glass sample from Rhodes (x3,2/0,06A, metalographic microscope) (Photo: A. Leakou).

The observations mentioned above are valid for all of the samples examined and the results of the analyses are displayed in Table I,

Fig. 29: Enlargement of the side of the groove of figure 28 (x20/0,40A, metalographic microscope) (Photo: A. Leakou).

where the changes of the concentrations of the elements and oxides can be observed in the cases of "ploughing" and pitting, in comparison to uncorroded glass from the same samples. The results are also presented graphically in Diagram I, where the con-centrations of the oxides in the cases of "ploughing" and pitting are presented in comparison to uncorroded material from the same samples.

An examination of samples of the soil, where the glass fragments were found, has also been per-formed. The samples were analyzed by X- ray diffraction and the main minerals traced were cacite ($CaCO_3$) and quartz (SiO_2). In smaller amounts montmorilonite ($(Al_{1,67}Na_{0,33}Mg_{0,33})(Si_2O_5)_2(OH)_2$), kaolinite ($Al_4(Si_2O_5)_2(OH)_8$) and calcium oxide ($CaO$) were traced. Moreover, throughout the year, the soil presented high levels of humidity, salinity and al-kalinity, which are main factors of corrosion of excavated glass material (Lampropoulos, 2003) .

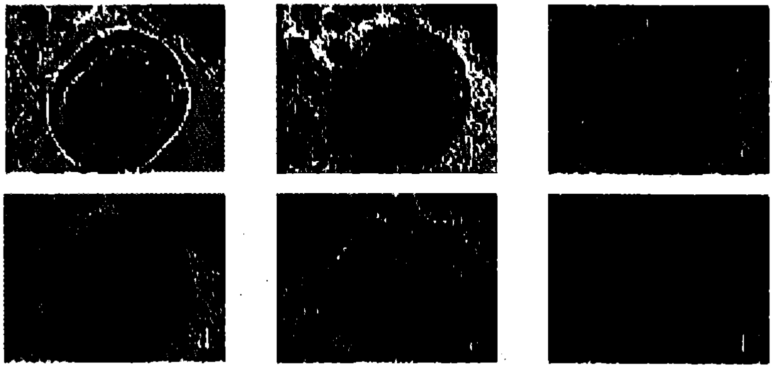

Fig. 30: Mapping of the elements in a large pit of a glass sample from Rhodes. a. picture of the pit (x75, S.E.M.), b. silicon, c. calcium, d. sodium, e. aluminium, f. potassium (Photo: A. Karampotsos).

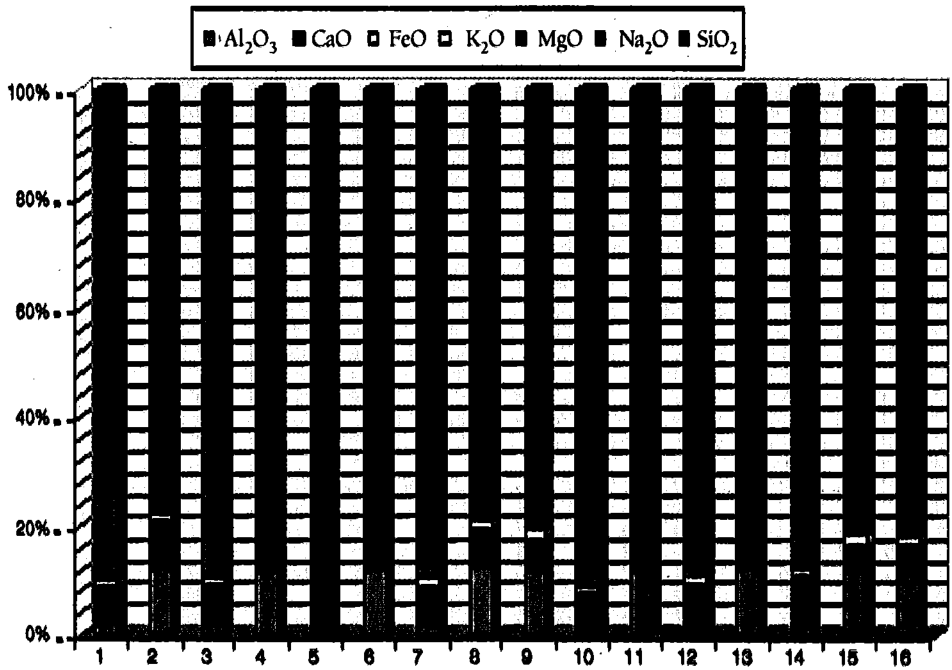

Fig. 31: Sample 1 (uncorroded glass), 2: Sample 1 ("ploughing"), 3: Sample 2 (uncorroded glass), 4: Sample 2 ("ploughing"), 5: Sample 3 (uncorroded glass), 6: Sample 3 ("ploughing"), 7: Sample 4 (uncorroded glass), 8: Sample 4 ("ploughing"), 9: Sample 4 (pitting), 10: Sample 5 (uncorroded glass), 11: Sample 5 ("ploughing"), 12: Sample 6 (uncorroded glass), 13: Sample 6 ("ploughing"), 14: Sample 7 (uncorroded glass), 15: Sample 7 ("ploughing"), 16: Sample 7 (pitting).

	Sample 1		Sample 2		Sample 3		Sample 4		
	Weight %		Weight %		Weight %		Weight %		
Oxides	Uncor-roded glass	"Plough-ing"	Uncor-roded glass	"Ploughi ng"	Uncor-roded glass	"Ploughi ng"	Uncor-roded glass	"Plough-ing"	Pitting
Al_2O_3	2.16	12.16	2.17	11.71	2.05	12.44	2.05	12.82	11.85
CaO	6.41	8.91	7.12	5.33	9.40	3.85	6.18	5.81	5.38
FeO	0.39	0.11	0.41	0.41	0.39	0.31	0.94	1.01	0.61
K_2O	1.45	1.32	0.99	0.25	0.69	0.31	1.34	1.47	1.78
MgO	0.58	0.67	0.36	0.43	0.57	0.84	0.64	0.42	0.41
Na_2O	15.82	1.18	16.32	1.23	14.22	0.81	16.23	0.79	1.96
SiO_2	73.18	75.63	72.61	80.63	72.67	80.68	72.62	77.69	78.01
Ele-ments									
Al	1.15	6.43	1.15	6.20	1.09	6.62	1.08	6.79	6.27
Ca	4.58	6.37	5.09	3.81	6.72	2.13	4.42	4.15	3.84
Fe	0.31	0.09	0.14	0.32	0.30	0.26	0.52	0.78	0.48
K	1.20	1.74	0.82	0.21	0.57	0.26	1.11	1.22	1.47
Mg	0.35	0.40	0.22	0.26	0.35	0.90	0.39	0.25	0.24
Na	11.74	0.87	12.11	0.92	10.55	0.60	12.04	0.59	1.21
Si	34.21	35.00	34.14	37.69	33.97	37.70	34.38	36.32	36.45
O	46.47	49.09	46.59	50.60	46.45	51.82	47.07	49.91	50.04

	Sample 5		Sample 6		Sample 7		
	Weight %		Weight %		Weight %		
Oxides	Uncorroded glass	"Ploughing"	Uncorroded glass	"Ploughing"	Uncorroded glass	"Ploughing"	Pitting
Al_2O_3	1.82	12.49	1.84	12.13	2.16	12.66	12.42
CaO	5.78	6.20	7.48	7.83	8,24	4.13	3.96
FeO	0.35	0,30	0.39	0.28	0.67	1.75	0.62
K_2O	1.03	0.63	1.16	0.76	1.35	0.70	1.25
MgO	0.58	0.69	0.25	0.44	0.41	0.51	0.46
Na_2O	15.36	0.43	16.51	0.98	14.93	0.44	1.79
SiO_2	75.08	79.26	72.37	77.58	72.85	79.81	79.5
Ele-ments							
Al	0.97	5.96	0.98	6.45	1.15	6.21	6.15
Ca	4.13	4.43	5.34	5.59	5.78	2.95	2.71
Fe	0.28	0.24	0.31	0.22	0.33	0.27	0.24
K	0.85	0.52	0.96	0.63	1,12	0.58	1.05
Mg	0.35	0.42	0.15	0.27	0.18	0.31	0.28
Na	11.38	0.32	12.23	0.73	11.06	0.33	1.19
Si	33.87	35.46	33.56	33.98	34.32	35.85	35.32
O	48.17	52.65	46,47	52.13	46.06	53.50	53.06

TABLE 1: Analyses of samples. Comparison between the concentrations of the elements in the area of "ploughing" to that of uncorroded glass from the same samples

DISCUSSION - CONCLUSIONS

Recapitulating the observations concerning the morphology, one can state that in all of the sam-ples the weathered glass inside the grooves appears in the form of layers (Fig. 31), perpendicular to the surface, which are loosely connected to the healthy glass material and exhibit iridescence (Fig. 32). The corroded material is easily removed and its loss begins from the center of the groove and moves on to the walls, until the channel cuts all the way through. From a chemical point of view it can be noted that in the interior of the grooves sodium has been almost totally leached out. This type of corrosion shows some similarities to pitting, regarding the arrangement and the leaching out of the elements. In the case of "ploughing" the leaching out is more intense, which indicates that it might be some kind of evolution or conjunction of the large pits, but this assumption requires farther study to be confirmed. In regard to the hypothesis that has been men-tioned about the existence of some kind of microorganisms, no such proof or evidence has been found. There still remain many questions to be answered on the subject of this unusual form of corrosion in archaeological glass. It is a weathering type that has only just begun to be examined and which requires farther study, so as specific and clear conclusions can be drawn.

Fig. 32. Perpendicular layers in the interior of a groove. Glass sample from Rhodes (x20/0,40A, metallographic microscope). (photo: A.Leakou)

Fig. 33: Vertical section of a groove. Layers of corroded glass that exhibit iridescence. Glass sample from Rhodes (x10/0,20A, met-allographic microscope). (photo: A.Leakou)

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