'Ploughing', an unusual form of corrosion of archaeological glass

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Summary

This paper is a preliminary study of a form of corrosion of archaeological glass that until now has been recorded, but not studied. Ten samples of glass that exhibit this type of corrosion have been examined with the scanning electron microscope (S.E.M.) and analysed by energy dispersive X-ray analysis (E.D.X.A.). In addition, three samples of the soil in which they were found have been tested by X-ray diffraction (X.R.D.). The present study contains a description of 'ploughing', the results of some analyses of the samples and some preliminary conclusions.

Description

This unusual form of corrosion appears in a glass surface in the shape of channels with no specific direction. These vary from shallow grooves to tunnels cutting all the way through the material (Figures 1 and 2). Their sides are almost perpendicular to the surface, while their endings are circular. The grooves appear either singly on the glass surface (Figure 3) or with branches (Figure 4), 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 Tomas Buechner [BUECHNER, 1960] in glass fragments from the excavation in Tharra (southern Crete) in 1959. It was he who gave the phenomenon the name 'ploughing', and speculated that it might be caused by leaching down from a scratch on the surface or that it may be the effect of some kind of micro-organism. The conservator Anita Moraitou

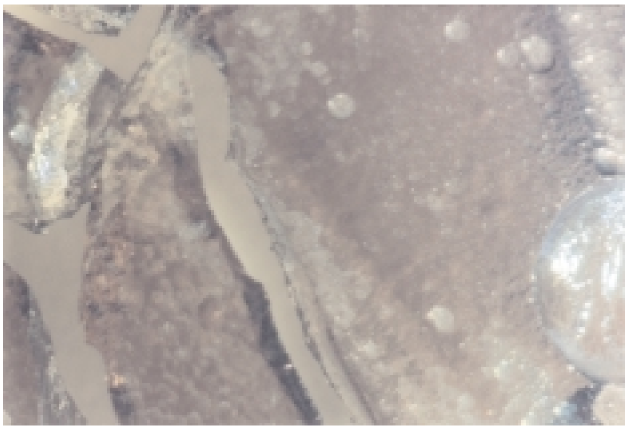

Figure 2. Enlargement of Figure 3 in a stereoscopic microscope. Grooves cutting all the way through the material.

Figure 3. Single grooves on a Rhodian bowl, dated early 1st century BC.

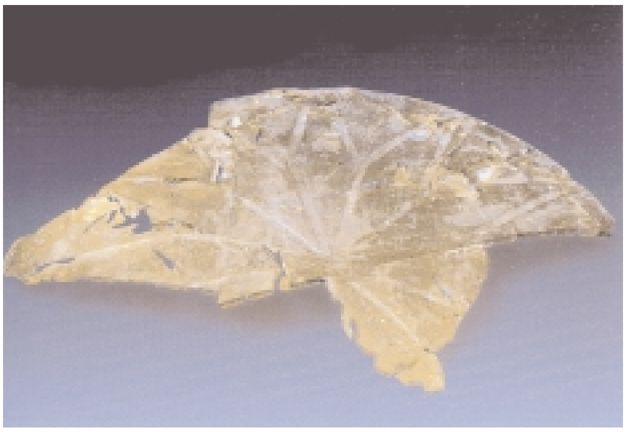

Figure 1. Bowl from the central necropolis of the city of Rhodes, dated 150-100BC (ΤΡΙΑΝΤΑΦΥΛΛΙΔΗΕΣ, 2000, p.47).

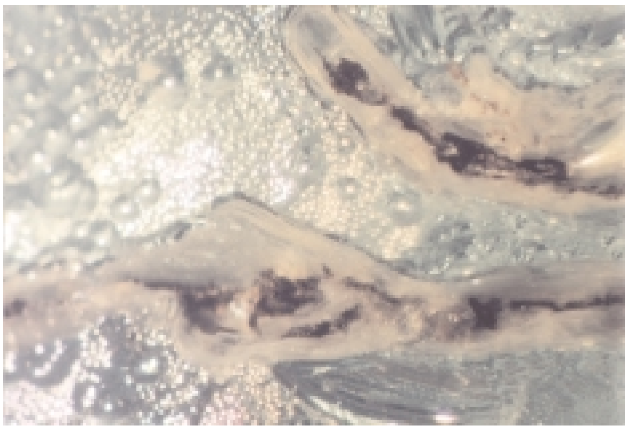

Figure 4. 'Ploughing' in a glass fragment from Rhodes.

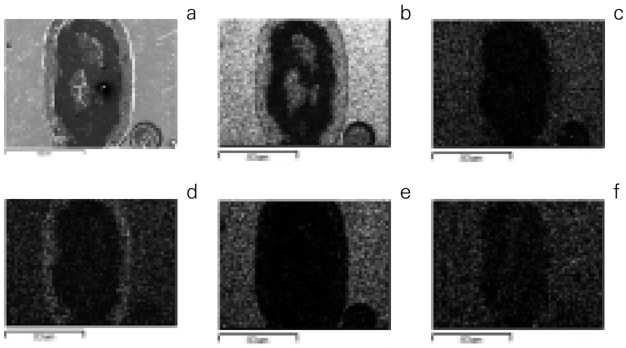

Figure 5. Mapping of the elements of a glass sample from Rhodes – a) picture of the area of the groove (x 75), b) silicon, c) calcium, d) aluminum, e) sodium, f) potassium.

[ΜΩΡΑΙΤΟΥ, 1996] also agrees with this hypothesis, but remarks that the phenomenon needs to be studied, so as to enable a verification of the assumption.

After the examination with 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 centre of the channel.

Results

In all of the samples an area of uncorroded glass was first 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 their distribution, as well as the difference in their concentration from one point to another. Moreover, in all cases a ratio of concentration of the network modifiers to the concentration of the silicon was calculated, so as to estimate the leaching of the elements. This proportion will be referred to further on as λ ($\lambda = C_{alkalis}/C_{silicon}$).

In Figure 5 a wide area of a groove in 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 centre of the channel the silicon appears reduced. This is due to the gradual loss of the corroded material. 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 in that area. At the same point one can notice that the concentration of calcium and potassium has not changed, while sodium does not appear at all. The same conclusions can be reached by observing the pit that is next to the groove.

The area near the side of the groove appears in Figure 6 and the elementary analysis of this field is compared in Table 1 to that of uncorroded glass from the same sample. The numbers in Table 1 confirm the observations described above regarding the mapping of the elements. Thus, the λ values for the elements indicate that sodium has been leached out, while the concentrations of calcium and potassium remain at the same level in relation to the concentration of silicon. Moreover, the λ value for aluminum, which appears to have increased, reveals that a small amount of silicon has been leached out.

Two channels almost conjoined are shown in Figure 7. The glass surface is very corroded and exhibits iridescence and pitting, in addition to 'ploughing'. If the groove is observed closer (Figure 8) the arrangement

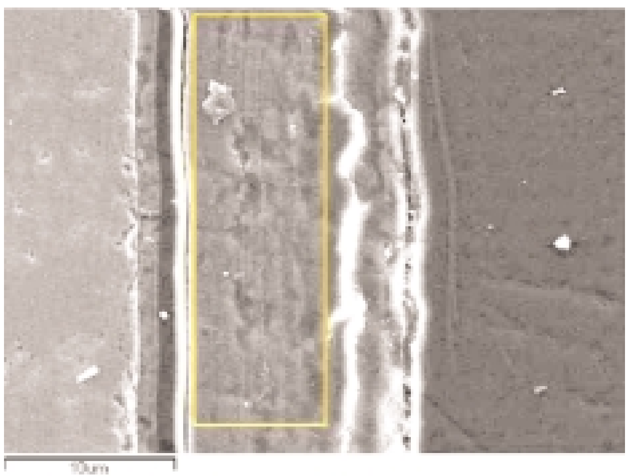

Figure 6. The edge of the groove (x500, S.E.M.).

Table 1.

El.	**Uncorroded glass Weight %**	**λ**	**'Ploughing' Weight %**	**λ**
O	43.85 +/- 0.31		40.73 +/- 0.53	
Si	22.39 +/- 0.08		16.33 +/- 0.12	
C*	20.23 +/- 0.42		34.51 +/- 0.66	
Na	8.07 +/- 0.07	0.36	0.65 +/- 0.05	0.04
Ca	3.05 +/- 0.05	0.13	3.07 +/- 0.07	0.19
K	0.83 +/- 0.03	0.04	0.96 +/- 0.05	0.06
Al	0.71 +/- 0.03	0.03	3.26 +/- 0.06	0.20
Cl	0.48 +/- 0.02		0.25 +/- 0.04	
Mg	0.19 +/- 0.03		0.23 +/- 0.04	

*The presence of carbon in the elementary analyses is due to the graphite with which the samples were covered during their preparation for the scanning electron microscope.

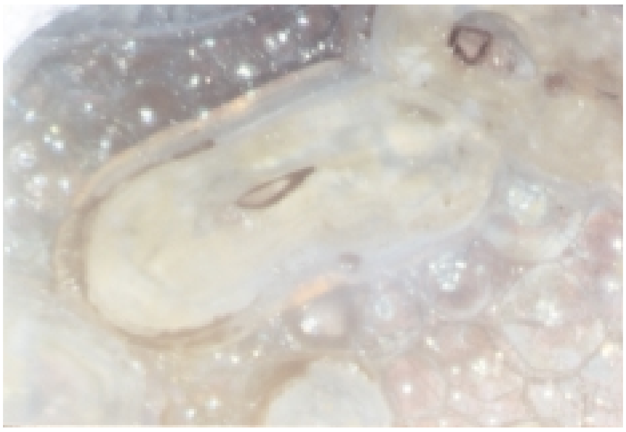

Figure 7. 'Ploughing' in a glass sample from Rhodes (x 3.2/0.06∞, metalographic microscope).

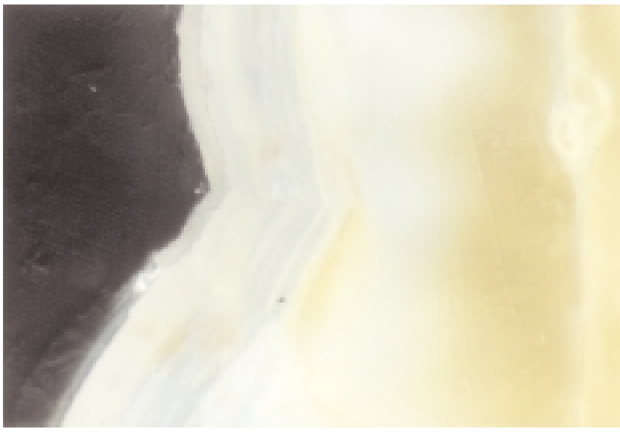

Figure 8. Enlargement of the side of the groove of Figure 7 (x 20/0.40∞, metalographic microscope).

of the decayed glass in layers is clearly seen. The elementary analysis at this point (Table 2) indicates that all of the elements appear reduced in the groove, in comparison to uncorroded glass, due to the non-concrete nature of the decayed material and the gradual loss of it. The same conclusions as for the previous sample can be deduced from the λ values for the elements. Proceeding to the centre of the same groove and performing an elementary analysis (Table 3), one can clearly see that in this area there are only grains of glass and calcium depositions. This leads to the conclusion that the loss of the material, which leads to channels cutting through the glass, begins from the centre and proceeds to the walls of the grooves.

A large pit close to the borders of the 'ploughing' is shown in Figure 9. The reduction of the concentration 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 by the λ values for these elements in Table 4 containing results of the elementary analysis. The reduction in sodium content in this case is less than in the case of 'ploughing' and there has been no leaching out of silicon. 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.

An examination of samples of the soil in which the glass fragments were found has also been performed. The samples were analysed by X-ray diffraction, and the main minerals traced were calcite ($CaCO_3$) and quartz (SiO_2). 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 in smaller amounts. Their conductibility was also measured and was found to be between 102 – 118 μS. The conductibility is relatively low, which allows one to assume that the glass samples were not being attacked by soluble salts. The pH of the soil samples was found to be between 7.09 –7.21, which indicates that the glass fragments were buried in a slightly alkaline environment, where silicon is not very stable. Overall, the original environment in which the glass

Table 2.

	Uncorroded glass		'Ploughing'	
El.	**Weight %**	**λ**	**Weight %**	**λ**
O	37.21 +/- 0.32		65.85 +/- 0.32	
C*	28.98 +/- 0.43		24.63 +/- 0.36	
Si	21.41 +/- 0.08		6.04 +/- 0.04	
Na	6.54 +/- 0.06	0.30	0.20 +/- 0.02	0.03
Ca	3.43 +/- 0.05	0.16	1.12 +/- 0.03	0.18
K	0.86 +/- 0.03	0.04	0.40 +/- 0.02	0.06
Al	0.70 +/- 0.03	0.03	1.28 +/- 0.02	0.21
Cl	0.46 +/- 0.02		0.12 +/- 0.02	
Fe	0.20 +/- 0.05		0.26 +/- 0.05	

*see Table 1

Table 3.

	Uncorroded glass		'Ploughing'
El.	**Weight %**	**λ**	**Weight %**
O	37.21 +/- 0.32		31.34 +/- 1.49
C*	28.98 +/- 0.43		40.30 +/- 2.98
Si	21.41 +/- 0.08		4.48 +/- 0.00
Na	6.54 +/- 0.06	0.30	–
Ca	3.43 +/- 0.05	0.16	7.46 +/- 0.00
K	0.86 +/- 0.03	0.04	–
Al	0.70 +/- 0.03	0.03	–
Cl	0.46 +/- 0.02		–
Fe	0.20 +/- 0.05		0.26 +/- 0.05

*see Table 1

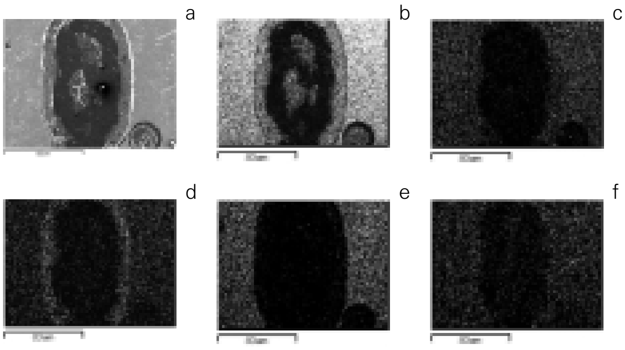

Figure 9. Mapping of the elements in a large pit in a glass sample from Rhodes – a) picture of the pit (x 75, S.E.M.), b) silicon, c) calcium, d) sodium, e) aluminum, f) potassium.

Table 4.

El.	Uncorroded glass Weight %	λ	'Ploughing' Weight %	λ
O	37.21 +/- 0.32		49.54 +/- 0.32	
C*	28.98 +/- 0.43		32.28 +/- 0.28	
Si	21.41 +/- 0.08		12.79 +/- 0.05	
Na	6.54 +/- 0.06	0.30	1.51 +/- 0.03	0.12
Ca	3.43 +/- 0.05	0.16	1.59 +/- 0.03	0.12
K	0.86 +/- 0.03	0.04	0.54 +/- 0.02	0.04
Al	0.70 +/- 0.03	0.03	1.12 +/- 0.02	0.09
Cl	0.46 +/- 0.02		0.23 +/- 0.02	
Fe	0.20 +/- 0.05		0.13 +/- 0.03	
Mg	0.17 +/- 0.03		0.07 +/- 0.02	

*see Table 1

samples were found, does not seem to have been exceedingly aggressive, since silicon is unstable when the pH is above 9. Nonetheless, even slightly alkaline circumstances can cause it to begin leaching out.

Conclusions

Recapitulating the observations concerning the morphology of glass, one can state that in all of the samples the weathered glass inside the grooves appears in the form of layers, perpendicular to the surface, which are loosely connected to the healthy glass and exhibit iridescence (Figure 10).

The corroded material is easily removed and its loss begins from the centre 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, while at the same time the concentration of silicon appears reduced. 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 further study to be confirmed. In regard to the hypothesis that has been mentioned about the existence of some kind of microorganism, 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 type of weathering that has only just begun to be examined and which requires further study, so that specific and clear conclusions can be drawn.

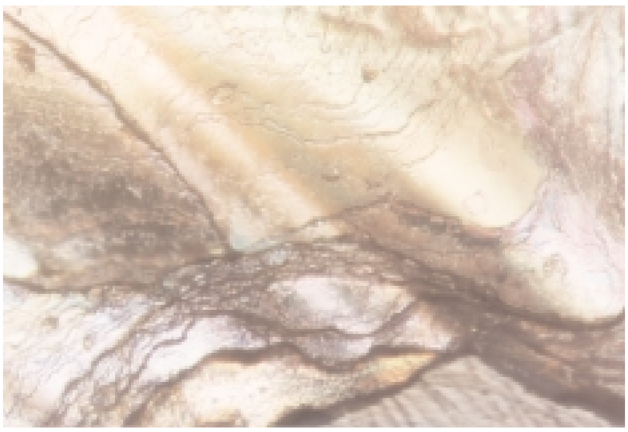

Figure 10. Vertical section of a groove. Layers of corroded glass that exhibit iridescence. Glass sample from Rhodes (x 10/0.20∞, metallographic microscope).

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