Analysis of Glaze on Ceramics from the 'Akko Marina

Irina Segal

Among the ceramic sherds dredged from the seabed of the 'Akko Marina were some bowls of well-known types from land excavations, but with a glaze of unusual silvery-black appearance. In order to investigate this phenomenon, two sets of the same types of glazed ceramics were submitted for analysis: ceramics with black glaze from beneath the sea and ceramics with ordinary glaze from the Knights' Hotel excavation on land (Stern 2012). The underwater ceramics included the following types: Cypriot Thirteenth Century Sgraffito and Slip Painted Ware (Sample 1; Stern, this volume: Fig. 2:22; see Stern 2012:60–65), Port St. Symeon Ware (Sample 2; Stern, this volume: Fig. 2:15; see Stern 2012:55–58), Byzantine Sgraffito Ware (Sample 3; Stern, this volume: Fig. 3:25; see Stern 2012:65–69) and Proto-maiolica Ware (Sample 4; Stern, this volume: Fig. 4:46; see Stern 2012:77–80). The aim of this study was to define the main factor leading to the changes in color under sea water, from yellow to black.

The chemical composition of the glaze was defined by using inductively coupled plasma atomic emission spectrometry (ICP-AES; Table 1) and a scanning electron microscope employed with energy dispersion analyzer (SEM-EDS). Mineralogy of the glaze was checked with an X-ray powder diffraction spectrometer (XRD).

Thin layers of glaze were recovered from both sets of ceramics and divided into two parts: one of them was ground in agate mortar and the other, mounted on stubs and covered by a thin layer of carbon. The ground samples were used for XRD analysis in the solid state and for ICP-AES analysis after dissolution.

Table 1. Chemical Composition of Glaze on Ceramics from 'Akko (ICP-AES)

Element / Sample	Wt. %										ppm						
	SiO_2	Al_2O_3	CaO	MgO	Fe_2O_3	TiO_2	P_2O_5	SO_3	Pb	Cu	Zn	Co	Ni	Ba	Sr	Mn	Cr
Ordinary Glaze from Land Excavation																	
1	46.3	9.8	1.1	0.5	1.3	0.7	<0.1	0.1	38	0.10	100	9	345	217	110	65	65
2	48.3	4.7	2.7	1.0	1.2	0.3	<0.1	0.3	39	0.08	235	8	173	1490	535	170	65
3	37.9	10.0	1.7	0.4	1.9	0.4	<0.1	0.3	45	0.62	54	6	85	231	80	118	75
4[i]	58.4	10.7	13.7	1.9	4.1	0.5	1.1	0.4	4	0.01	90	13	310	308	373	595	110
Black Glaze from Sea																	
3000 (1)	49.0	8.6	1.3	1.0	1.5	0.6	<0.1	2.5	36	0.05	90	10.0	50	145	130	70	105
A14/334 (2)	45.0	5.5	5.6	1.6	1.5	0.4	<0.1	7.1	36	0.26	70	10.0	42	590	300	90	245
A18, 19 (3)	45.0	5.7	0.5	0.6	2.5	0.3	<0.1	3.8	38	0.05	130	4.5	20	120	1.6%	130	43
A14/332 (4)	36.0	1.5	1.0	0.5	1.4	0.1	<0.1	8.4	46	0.05	73	5.2	95	30	95	103	225

[i] Destroyed glaze layer, which explains the low lead and copper content

The carbon-covered samples were used for SEM-EDS analysis. The SEM-EDS method was employed in addition to ICP-AES analysis because of possible contamination of glaze with underlying ceramic layers in the powder used for ICP. Only elements leading to color change were checked by SEM-EDS, viz., iron, lead, copper and sulfur.

Table 2. Normalized Results of SEM-EDS Analysis of Glaze from ʻAkko (in Weight %)

Element / Sample	Fe	Pb	Cu	S
Ordinary Glaze from Land				
1	0.5	99.5	n.d	n.d
2	1.3	98.7	n.d	n.d
3	0.8	97.4	1.2	n.d
4	1.4	99.2	n.d	n.d
Average	*1.0*	*98.7*	*0.3*	*n.d*
Black Glaze from Sea				
3000 (1)	0.7	93.9	0.6	4.8
A14/334 (2)	1.2	93.5	1.1	5.3
A18, 19 (3)	0.6	94.1	0.4	5.0
A14/332 (4)	1.6	88.0	0.3	9.3
Average	*1.0*	*92.4*	*0.6*	*6.1*

n.d = not determined (lower than limit of detection)

Results of the ICP-AES analyses (major, minor and trace elements) are shown in Table 1. Sample No. 4 had a thin, almost totally eradicated glaze layer and for this reason the amounts of lead and copper are lower than in the other three samples. These elements are commonly present in glaze. Sulfur content in the samples from the sea is higher than in the four samples derived from land excavations, indicating that underwater conditions are conducive to conversion of some minerals to sulfidic form.

Results concerning lead, copper, iron and sulfur detected by SEM-EDS are given in Table 2. They are normalized to 100%. As can be seen from Tables 1 and 2, there are significant differences in sulfur content between the two sets of glaze. In comparison to the glazes on vessels found on land, which contains no sulfur, in glazes from the sea the sulfur content increases up to 9.3%. The presence of sulfur in sea water obviously leads to the creation of sulfides of lead present in the glaze.

Structural analysis by XRD shows that the main mineral in the black samples is galena (PbS) and there are no iron and copper sulfides in visible amounts (Fig. 1). A small amount

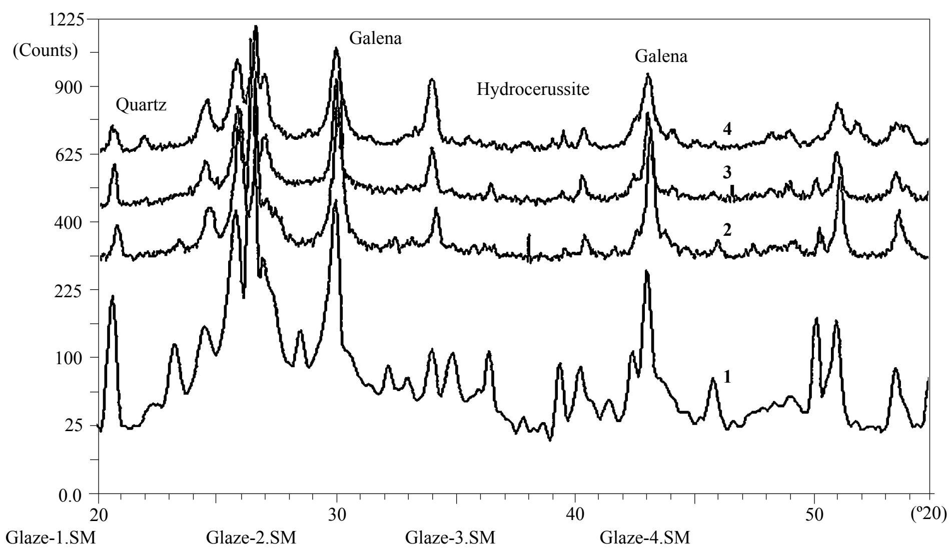

Fig. 1. XRD-spectra of the glaze on sherds from the sea.

of hydrocerussite—$Pb_3(CO3)_2(OH)_2$—(which was initially cerussite) remained in the black glaze, implying that the process of sulfide creation was not yet finished.

REFERENCES

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