

Study on Chemical Composition of Ancient Glass Based on Standardized Model

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Abstract. In the study of ancient glass, identifying its chemical composition is an indispensable step to accurately classify it. However, the weathering of ancient glass in the buried environment will change the chemical composition, so the ability to properly process data such as chemical composition is crucial. In this paper, the relationship between the weathering of high-potassium glass and lead-barium glass and its color and pattern is studied respectively, and the existing data on the chemical composition of the sample glass in cultural relics are processed and analyzed by constructing a standardized model. Besides, the non-weathered standardized models of high-potassium glass and lead-barium glass were obtained, and their weathering trends were summarized. Based on this model, the chemical composition content of samples before weathering was predicted.

Keywords: Standardized Model, Ancient Glass, Chemical Composition.

1. Introduction

In the past, the Silk Road connected Europe and Asia. It was a channel for cultural exchanges between the East and the West in ancient times, and greatly promoted trade. Glass is one of the precious pieces of evidence [1-3]. Glass beads from early West Asia and Egypt were introduced to China through the Silk Road. On its basis, Ancient glass in China was made from local materials.

The main chemical composition of glass is silicon dioxide (SiO_2), which is commonly known as quartz sand. Pure quartz sand has a high melting point, so it is necessary to add flux to lower the melting point during glass refining [4-6]. Commonly used fluxes in ancient times include plant ash, natural natron, saltpeter and lead ore, etc., and limestone was added as a stabilizer, converted into calcium oxide after calcination. The use of different fluxes during calcination will lead to changes in the main chemical composition of the glass. High-potassium glass, common in South Asia, Southeast Asia, and southern China, uses plant ash as a combustion aid in the firing process, and its composition contains high potassium oxide (K_2O) and magnesium oxide (MgO), which are common in South Asia, Southeast Asia, and southern China. Lead-barium glass is added with lead ore as a flux during the firing process, and its content of lead oxide (PbO) and barium oxide (BaO) is relatively high. Academia believes that it is a unique glass variety in ancient China, and the glass of Chu culture is based on Mainly lead-barium glass [7-8].

The glass preserved in ancient times is often buried underground and is easily weathered due to the influence of the environment. During the weathering process, a large number of elements within the glass will exchange with elements in the external environment, which will eventually change the chemical composition of the glass and affect the judgment of the glass category. However, there are often weathered parts and unweathered parts on a piece of glass at the same time. Even in weathered parts, there may be differences in chemical composition due to different degrees of weathering [9-10]. Therefore, being able to reasonably process and deduce the data on the chemical composition of glass is very important for correctly judging the type of glass and conducting research on ancient glass.

2. The data and method

2.1. The data

The chemical composition data of ancient glass used in this article comes from Question C of the 2022 National Undergraduate Mathematical Contest in Modeling. (http://www.mcm.edu.cn/html_cn/node/5267fe3e6a512bec793d71f2b2061497.html)

2.2. The method

To find out the relationship between glass surface weathering and its proportion type, pattern, and color, this paper processes the original data, Classifies samples according to weathered ones and non-weathered ones, sorts out the number of each kind of samples, and figures out their characteristics, which are shown in the pie charts.

When it comes to the research on the content of chemical components, this paper first deletes invalid data which can be known by calculation, Then the rest of the data were organized into four categories: weathered high-potassium glass, non-weathered high-potassium glass, weathered lead-barium glass, and non-weathered lead-barium glass. Subsequently, to obtain the statistical law of the chemical composition of the two types of glass, this paper calculates the average and standard deviation of each chemical composition before and after weathering and tabulates them.

During the prediction, due to the different degrees of weathering of glass samples, this paper builds up two standardized models of each kind of glass. In this paper, the difference between the proportion of chemical composition of each weathered glass and its standardized model is calculated and averaged, which is used as the standardized amount of the change of chemical composition of high-potassium glass and lead-barium glass during weathering. Finally, the standardized amount is added to the chemical composition of each weathered glass sample, which is their chemical composition before weathering predicted in this paper.

3. Results

3.1. Analysis of Weathering Factors

Before analyzing the relationship between surface weathering and glass type, pattern, and color, this paper preliminarily processed the data in Form 1 to obtain pie charts as shown in Figures 1, 2, 3, 4, 5, 6, and 7.

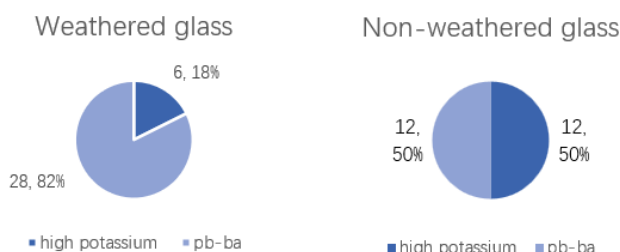


Figure 1. Number and proportion of weathered glass and non-weathered glass in 2 types

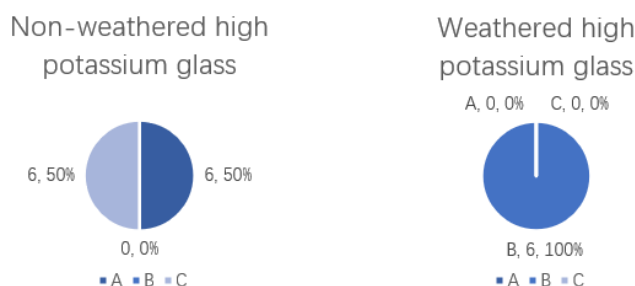


Figure 2. The number and proportion of high-potassium glass with different patterns

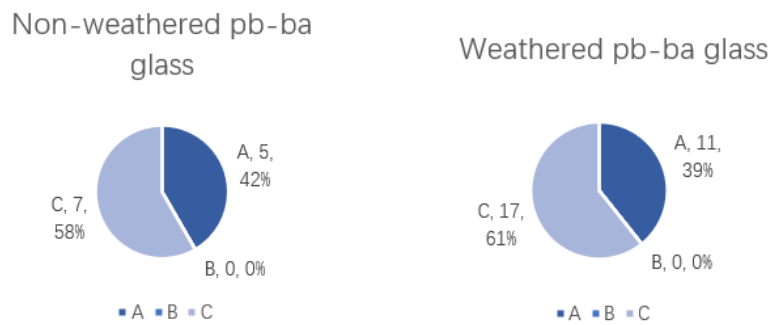


Figure 3. The number and proportion of lead-barium glass with different patterns

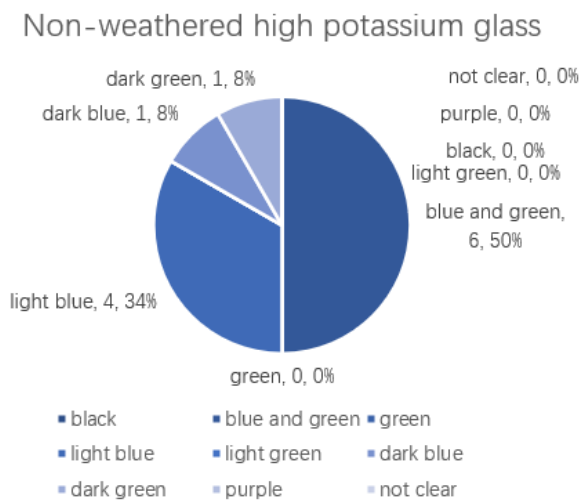


Figure 4. The number and proportion of each color of the non-weathered high-potassium glass

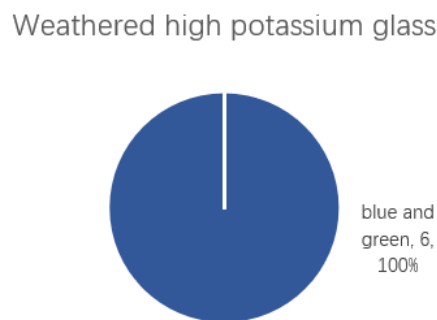


Figure 5. The number and proportion of each color of the weathered high-potassium glass

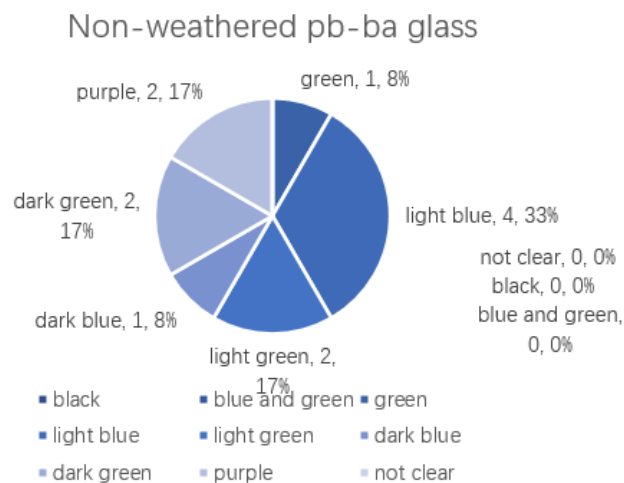


Figure 6. The number and proportion of each color of the non-weathered lead-barium glass

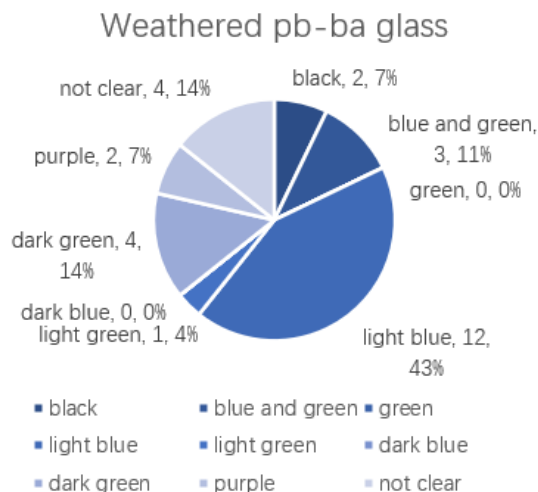


Figure 7. The number and proportion of each color of the weathered lead-barium glass

Analyzing the obtained pie chart, the conclusions are as below.

First, lead-barium glass is more susceptible to weathering than high-potassium glass. According to data, the weathering rate of high-potassium glass is 33.3%, and that of lead-barium glass is 70%.

Second, as for high-potassium glass, Pattern B is highly related to weathering, while blue-green is a necessary and insufficient condition for weathering.

Third, as for lead-barium glass, those which are light blue or with Pattern C have the highest probability of weathering, while darker-colored glass (such as black or purple) has a lower probability of weathering, and the probability of those with Pattern B is 0.

3.2. Standardized Model

For high-potassium glass, weathered samples were selected in this paper, and Table 1 shows the composition ratio of weathered high-potassium glass in the samples.

Table 1. Composition list of weathered high potassium glass (excerpt)

Sampling site	SiO ₂	K ₂ O	CaO	MgO	Al ₂ O ₃	Fe ₂ O ₃	CuO	P ₂ O ₅
07	92.63	0	1.07	0	1.98	0.17	3.24	0.61
09	95.02	0.59	0.62	0	1.32	0.32	1.55	0.35
10	96.77	0.92	0.21	0	0.81	0.26	0.84	0
12	94.29	1.01	0.72	0	1.46	0.29	1.65	0.15
22	92.35	0.74	1.66	0.64	3.5	0.35	0.55	0.21
27	92.72	0	0.94	0.54	2.51	0.2	1.54	0.36

Before constructing the standardized model, this paper calculated the average and standard deviation of the proportions of chemical components before and after weathering. The results are shown in Tables 2, 3, 4, and 5:

Table 2. The proportion of chemical components of weathered high potassium glass

	SiO ₂	K ₂ O	CaO	MgO	Al ₂ O ₃	Fe ₂ O ₃	CuO	P ₂ O ₅
Average	93.96	0.54	0.87	0.20	1.93	0.27	1.56	0.28
Standard deviation	1.58	0.41	0.45	0.28	0.88	0.06	0.85	0.19

Table 3. The proportion of chemical components of non-weathered high potassium glass

	SiO ₂	Na ₂ O	K ₂ O	CaO	MgO	Al ₂ O ₃	Fe ₂ O ₃	CuO	PbO	BaO	P ₂ O ₅	SrO	SnO ₂	SO ₂
Average	66.29	1.05	9.62	4.56	1.05	5.88	1.76	2.19	0.33	0.40	1.24	0.04	0.18	0.09
Standard deviation	7.94	1.37	2.74	3.44	0.62	3.00	1.56	1.57	0.52	0.83	1.39	0.05	0.63	0.17

Table 4. The proportion of chemical components of weathered lead-barium glass

	SiO ₂	Na ₂ O	K ₂ O	CaO	MgO	Al ₂ O ₃	Fe ₂ O ₃	CuO	PbO	BaO	P ₂ O ₅	SrO	SnO ₂	S ₂ O ₂
Average	24.91	0.22	0.13	2.70	0.65	2.97	0.58	2.28	43.31	11.81	5.28	0.42	0.07	1.37
Standard deviation	10.40	0.55	0.24	1.63	0.69	2.58	0.72	2.77	11.99	9.78	4.12	0.26	0.26	4.12

Table 5. The proportion of chemical components of non-weathered lead-barium glass

	SiO ₂	Na ₂ O	K ₂ O	CaO	MgO	Al ₂ O ₃	Fe ₂ O ₃	CuO	PbO	BaO	P ₂ O ₅	SrO	SnO ₂	SO ₂
Average	56.47	1.84	0.17	1.03	0.63	4.49	0.58	1.57	20.52	8.88	1.08	0.25	0.01	0.17
Standard deviation	10.42	2.37	0.17	0.87	0.55	3.34	1.04	1.96	6.53	5.95	1.87	0.24	0.05	0.78

The standardized models are built up. The standardized model for the composition ratio of non-weathered high-potassium glass is shown in Table.6., and the standardized model for the composition ratio of non-weathered lead-barium glass is shown in Table.7.

Table 6. Standardized model of the composition ratio of non-weathered high-potassium glass samples

	SiO ₂	Na ₂ O	K ₂ O	CaO	MgO	Al ₂ O ₃	Fe ₂ O ₃	CuO	PbO	BaO	P ₂ O ₅	SrO	SnO ₂	SO ₂
Standard	66.29	1.05	9.62	4.56	1.05	5.88	1.76	2.19	0.33	0.40	1.24	0.04	0.18	0.09

Table 7. Standardized model of the composition ratio of non-weathered lead-barium glass samples

	SiO ₂	Na ₂ O	K ₂ O	CaO	MgO	Al ₂ O ₃	Fe ₂ O ₃	CuO	PbO	BaO	P ₂ O ₅	SrO	SnO ₂	SO ₂
Standard	56.47	1.84	0.17	1.03	0.63	4.49	0.58	1.57	20.52	8.88	1.08	0.25	0.01	0.17

3.3. The prediction

This paper takes the difference between each weathered sample and its standardized model and then takes the average value, and obtains the average array of differences as shown in Table.8.

Table 8. Average differentials of high potassium glass(excerpt)

	SiO ₂	Na ₂ O	K ₂ O	CaO	MgO	Al ₂ O ₃	Fe ₂ O ₃	CuO	PbO	BaO	P ₂ O ₅
Average differentials	27.68	-1.05	-9.08	-3.69	-0.85	-3.95	-1.50	-0.63	-0.33	-0.40	-0.96

Next, this article processed the weathered samples again and obtained the prediction of the chemical composition content before weathering as shown in Table.9.

Table 9. Prediction of the chemical composition ratio of high-potassium glass before weathering

Sampling site	SiO ₂	Na ₂ O	K ₂ O	CaO	MgO	Al ₂ O ₃	Fe ₂ O ₃	CuO	PbO	BaO	P ₂ O ₅	SrO	SnO ₂	SO ₂
07	64.95	1.05	9.08	4.76	0.85	5.93	1.67	3.87	0.33	0.4	1.57	0.04	0.18	0.09
09	67.34	1.05	9.67	4.31	0.85	5.27	1.82	2.18	0.33	0.4	1.31	0.04	0.18	0.09
10	69.09	1.05	10.00	3.9	0.85	4.76	1.76	1.47	0.33	0.4	0.96	0.04	0.18	0.09
12	66.61	1.05	10.09	4.41	0.85	5.41	1.79	2.28	0.33	0.4	0.81	0.04	0.18	0.09
22	64.67	1.05	9.82	5.35	1.49	7.45	1.85	1.18	0.33	0.4	1.17	0.04	0.18	0.09
27	65.04	1.05	9.08	4.63	1.39	6.46	1.70	2.17	0.33	0.4	1.32	0.04	0.18	0.09

Similarly, the predicted chemical composition content of lead-barium glass before weathering is shown in Table.10.

Table 10. Prediction of the chemical composition ratio of lead-barium glass before weathering

Sampling site	SiO ₂	Na ₂ O	K ₂ O	CaO	MgO	Al ₂ O ₃	Fe ₂ O ₃	CuO	PbO	BaO	P ₂ O ₅	SrO	SnO ₂	SO ₂
02	67.84	1.63	1.09	0.68	1.16	7.25	1.85	0	24.64	0	0	0.03	0	0
08	51.70	1.63	0.04	0	0	2.86	0	9.70	5.89	28.30	0	0.21	0	1.39
08 severe	36.17	1.63	0.04	1.53	0	2.63	0	2.43	9.66	27.69	3.36	0.37	0	13.84
11	65.15	1.63	0.25	1.85	0.69	4.21	0	4.22	2.60	11.68	5.18	0.21	0	0
19	61.20	1.63	0.04	1.27	0.57	5.09	1.32	2.80	20.03	2.42	4.63	0.03	0	0
26	51.35	1.63	0.04	0	0	2.22	0	9.86	6.74	29.32	0	0.29	0	0.77
26 severe	35.28	1.63	0.44	1.35	0	2.70	0	2.89	7.13	32.52	1.84	0.46	0	14.76
34	67.34	1.63	0.29	0	0	3.14	0.46	0.80	23.76	7.07	0	0.06	0	0
36	71.13	3.85	0.18	0	0	3.12	0.31	0	18.82	7.90	0	0.06	0	0
38	64.49	3.01	0.04	0	0	4.09	0.28	0.02	26.52	6.86	0	0.25	0	0
39	57.81	1.63	0.04	0	0	2.02	0	0.17	38.24	4.29	0	0.45	0	0
40	48.27	1.63	0.04	0.21	0	1.97	0.18	0	47.42	3.76	0	0.52	0	0
41	50.02	1.63	0.48	3.30	2.71	4.85	1.78	0	21.33	6.83	3.26	0.31	0	0

43 spot1	43. 97	1.6 3	0.0 4	3.5 8	0.8 7	3.77	0.75	4.6 4	37. 06	4.3 6	0	0.4 8	0	0
43 spot2	53. 26	1.6 3	0.0 4	4.7 4	0.9 3	4.93	1.38	0.8 0	21. 96	0.3 3	8.6 3	0.3 1	0	0
48	84. 89	2.4 3	0.3 6	1.1 6	1.5 2	15.1 7	1.02	0	0	4.3 8	0	0.0 9	1.2 5	0
49	60. 35	1.6 3	0.0 4	2.9 2	1.4 5	6.90	2.73	0	11. 39	3.1 7	6.9 0	0.3 0	0	0
50	49. 54	1.6 3	0.0 4	1.5 3	0.4 5	3.39	0.32	0.4 2	21. 21	11. 27	2.1 4	0.5 0	0	0
51 spot1	56. 17	1.6 3	0.0 4	1.9 2	1.1 7	6.77	1.18	0.6 6	17. 45	6.0 1	3.9 0	0.2 3	0.4 1	0
51 spot2	52. 91	1.6 3	0.0 4	3.4 7	1.4 3	4.03	0.41	0.0 4	28. 55	0	4.5 5	0	0	0
52	57. 30	2.8 5	0.0 4	0.6 1	0.5 3	2.68	0.22	0	24. 63	5.7 1	1.5 1	0.2 8	0	0
54	53. 84	1.6 3	0.3 6	1.5 3	1.2 6	5.67	0	0.1 2	32. 67	4.1 1	0.0 4	0.7 2	0	0
54 severe	48. 67	1.6 3	0.0 4	0	1.0 9	5.17	0	0.6 3	35. 67	0	9.9 3	0.9 6	0	0
56	60. 71	1.6 3	0.0 4	0	0	3.37	0	0.0 8	18. 46	12. 52	0	0	0	0
57	56. 98	1.6 3	0.0 4	0	0	3.70	0	0.4 5	22. 31	14. 37	0	0	0	0
58	61. 95	1.6 3	0.3 8	1.8 3	0.7 7	5.04	0.85	2.4 2	16. 56	4.7 3	4.7 9	0.0 8	0	0

4. Conclusions

In this paper, by constructing a standardized model, the analysis of the weathering factors of the sample glass and the prediction of the chemical composition before weathering are completed, and it is found that lead-barium glass is easier to weather than high-potassium glass. For high-potassium glass, the pattern is a significant weathering feature, while the weathering factors of lead-barium glass are relatively complex, related to both pattern and color. For lead-barium glass, glass samples with a C-type pattern or light blue have the highest probability of weathering, and glass samples of darker colors (such as black and purple) have a lower probability of weathering. According to the prediction, the loss of potassium in high-potassium glass is relatively serious, which leads to a substantial increase in silicon's content to a certain extent. More than half of the lead is lost in lead-barium glass, while the loss of barium is slightly less than that.

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