Glass weathering chemical composition prediction model

Junchi Liao *

School of Information Engineering, China University of Geosciences, Beijing 100083, China

* Corresponding Author Email: liaojunchi7007@icloud.com

Abstract. This paper analyzes the relationship between glass surface weathering and glass type, decoration, and color, and predicts the chemical composition content of weathered glass before weathering. In this paper, firstly, the glass type and surface weathering were subjected to a chi-square test, and then the relationship between glass color, decoration and surface weathering was statistically analyzed using the control variable method: controlling for constant glass type. It is concluded that when the glass is high potassium glass, it tends to be non-weathered glass, while lead-barium glass tends to be weathered glass. High potassium glass with A ornamentation corresponds to all weathered glass, while B or C ornamentation corresponds to all unweathered glass, and the colors are dark blue, light blue, and dark green, corresponding to all weathered glass. The color of lead barium glass is black, blue-green, decorated with A; the color is light blue, decorated with C, all weathered glass. When the color is dark blue, the conclusion of the pattern is A. Then the average content changes of each chemical composition before and after the weathering of the two types of glass were counted separately, and the chemical composition content of the two types of weathered glass before weathering was calculated according to equation (3), respectively, and the specific results are shown in Table. 4.

Keywords: Weathered glass, chi-square test, control variables.

1. Introduction

Glass, as a precious physical evidence of early trade exchanges, was often introduced to China after being made into bead-shaped ornaments in West Asia and Egypt after the emergence of the Silk Road for cultural exchanges between China and the West in ancient times, and was made into ancient Chinese glass after China absorbed its technology and locally sourced materials, so that ancient Chinese glass and foreign glass products are similar in appearance, but their chemical compositions are different [1].

Since pure quartz sand [2] has a high melting point and the main raw material of glass is quartz sand, whose main chemical composition is SiO2, fluxes [3] are added during refining in order to lower the temperature of glass melting [4]. Grass wood ash, natural bubble soda and lead ore, which were commonly used as fluxes in ancient times, are added in addition to limestone as a stabilizer [5]. The added fluxes differed in their main chemical composition. For example, lead-barium glass [6], which is the main component of Chu culture glass, has a higher content of PbO and BaO when lead ore is added as a flux in the firing process [7], and it is also usually considered as a glass variety invented by China itself. Potassium glass [8], on the other hand, is made by adding substances with high potassium content, such as grass wood ash, as a flux during the firing process, and it is mainly popular in regions such as Lingnan, Southeast Asia and India in China.

Because of the influence of the burial environment, ancient glass can be weathered [9], and in this process of weathering, its internal elements are exchanged with the environmental elements in a large amount, resulting in a change in its composition ratio, which can affect the correct determination of its category.

Based on the data provided by question C of the National University Mathematical Modeling Competition of the Gaojiao Cup 2022, this study intends to solve the following problems: first find out the relationship between the type of glass, decoration, color and its surface weathering of these glasses, and then analyze them; then combine these types of glass [10], after deriving the statistical pattern of the presence or absence of weathering on the surface of the artifact samples and their chemical composition content, analyze them, and based on the weathering point detection data, the chemical composition and its content before weathering were predicted.

2. Model building and solving

2.1. Data pre-processing

1. The data in Table 1 shows that there are missing values for the color attributes, but there are only four missing values, and the proportion is only 7.27% of the total sample, so this paper chooses to delete the missing samples.

2. The data with the sum of the components of the artifacts between 85% and 105% are considered as valid data, so the data that do not meet the requirements are eliminated in this paper, and the samples with artifact numbers 15 and 17 are eliminated.

2.2. A control variable analysis model based on chi-square test

For high potassium glass: there are 6 samples of surface weathered and 12 samples of surface unweathered. For lead-barium glass: there were 28 samples of surface weathered glass and 12 samples of non-weathered.

The results of the chi-square test using SPSS software are shown in Table .1.

Table 1. Cardinality test results

Type		Total	X^2	Correction X^2	P
High potassium glass	Barium lead glass				
12	12	24	6.88	5.452	0.009***
6	28	34			
18	40	58			

The result is significant at P=0.009, so the original hypothesis is rejected and the type of glass and surface weathering are considered to be correlated. When the glass is high potassium glass, it is more inclined to be non-weathered glass, while lead-barium glass is inclined to be weathered glass.

Since the type of glass has an effect on whether it is weathered or not, the relationship between the type of glass, color, and decoration and surface weathering should be analyzed controlling for the same type of glass. The sample data of surface weathering and color of high potassium glass were obtained by using EXCEL software as shown in Figure 1.

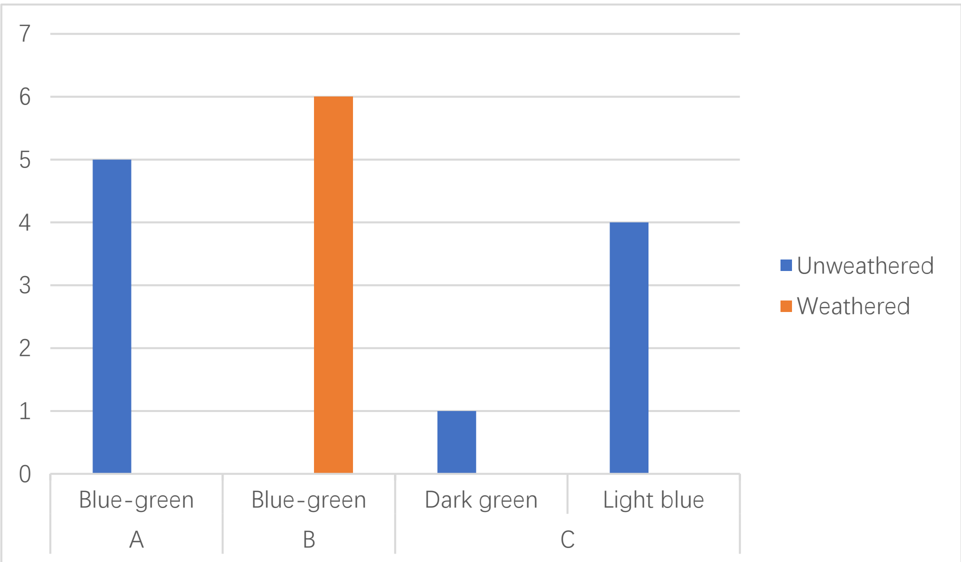

Figure 1. Color pattern and weathering statistics of high potassium glass

Analysis shows that: high potassium glass ornamentation for A corresponds to all weathered glass, ornamentation for B or C corresponds to all unweathered glass, the color is dark blue, light blue, dark green, corresponding to all for weathered glass.

Statistical data on surface weathering and color samples of lead barium glass were obtained as shown in Figure 2.

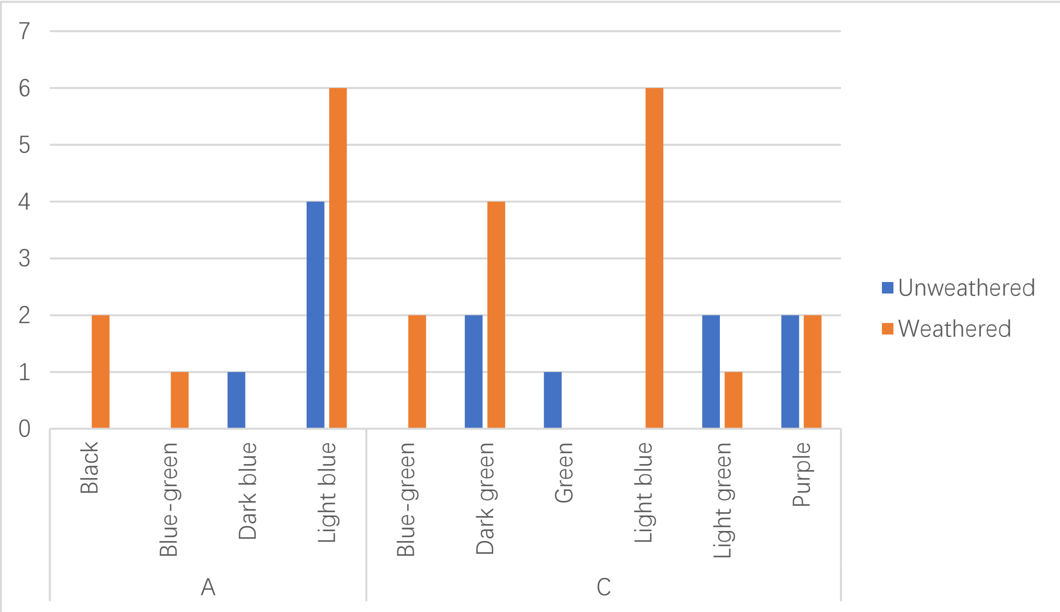

Figure 2. Lead barium glass color Decoration and weathering statistics

Analysis shows that: the color of lead barium glass is black, blue-green, and the ornament is A; the color is light blue, and the ornament is C. All weathered glass. When the color is dark blue, the ornamentation is A.

2.3. Weathering chemical composition statistics

In this paper, the types of glass are classified into four categories: weathered high potassium glass, unweathered high potassium glass, weathered lead-barium glass, and unweathered lead-barium glass. The box line diagrams of the percentage of chemical composition of the glass are also plotted to observe the differences before and after weathering.A box line diagram of the composition of unweathered high-potassium glass is shown in Figure 3.

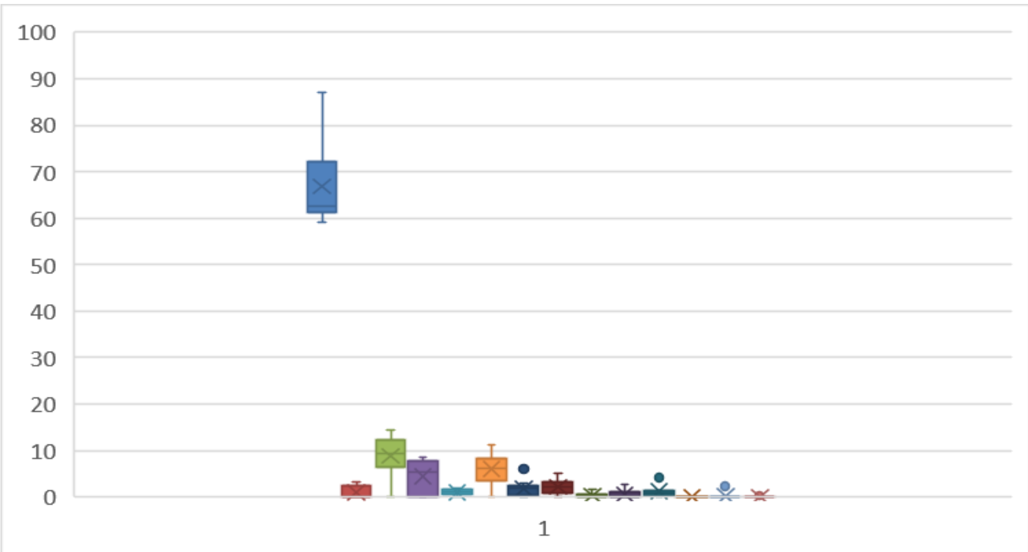

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Figure 3. Composition box diagram line of unweathered high potassium glass.

Figure 4. shows a box line diagram of the composition of weathered high-potassium glass.

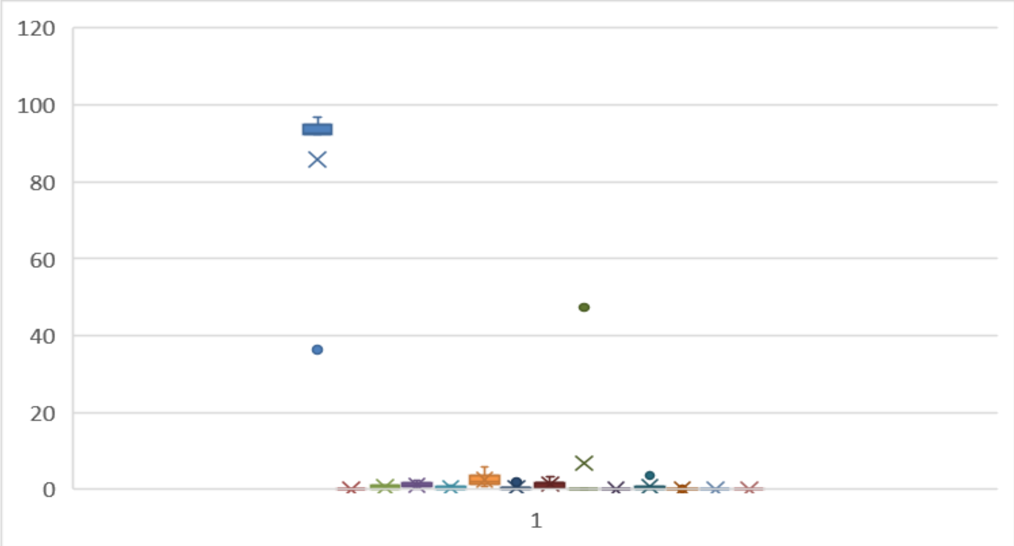

Figure 4. Box line diagram of weathered high potassium glass composition

The observation and comparison show that there are data points with excessive deviations, which are eliminated in this paper.

The statistical pattern of weathering chemical composition of high-potassium glass: the overall proportion of silica increases after weathering, while the proportion of the remaining chemical components decreases. The distribution range of silica after weathering is reduced mostly in 92%~96%, and the percentage of the remaining chemical components is basically less than 5%, and the fluctuation range is small.

The statistical law of the weathering chemical composition content of lead barium glass: the same analysis shows that, contrary to the high potassium glass, the overall percentage of silica of lead barium glass decreases after weathering, and the percentage of calcium oxide, copper oxide, lead oxide, barium oxide, and phosphorus pentoxide increases, among which the percentage of lead oxide, barium oxide, and phosphorus pentoxide increases most obviously, and the percentage of the remaining chemical components all decrease. Before and after weathering, the fluctuation range of silica content decreases, from 38% to 63% to 18% to 28%. The fluctuation range of barium oxide increased, from 5%~11% to 6%~16%, and phosphorus pentoxide changed from 0%~3% to 0%~7%. The rest of the chemical components accounted for the fluctuation range of little change.

2.4. Weathering chemical composition statistics

In this paper, the mean is used to represent the percentage of a certain chemical composition before and after weathering of different types of glass. The difference between the mean values of chemical composition ratios before and after weathering is calculated to represent the change of chemical composition ratios after weathering. Then, the range of the percentage of chemical composition before weathering is predicted based on the range of fluctuation of the percentage of chemical composition before weathering.

$$a_i = \frac{\sum_{j=1}^{n} a_{ij}}{n} \tag{1}$$

$$q_i = \frac{a_i - b_i}{b_i} \tag{2}$$

As Table .2 shows the data of composition change of lead-barium glass.

Table 2. Changes in composition of lead barium glass

type	SiO_2	Na_2O	K_2O	CaO	MgO	Al_2O_3	Fe_2O_3
Weathered lead barium	24.6418	0.3582	0.0891	2.6714	0.5818	2.8632	0.4864
Unweathered lead barium	51.0192	1.4369	0.2112	1.5131	0.6788	4.2688	0.7531
Weathering change amount	-26.377	-1.0787	-0.1221	1.1583	-0.097	-1.4057	-0.2667
Type	CuO	PbO	BaO	P_2O_5	SrO	SnO_2	SO_2
Weathered lead barium	2.3955	42.0114	12.9636	5.1341	0.4359	0.0214	1.6145
Unweathered lead barium	1.5054	25.4781	8.8012	1.7238	0.2796	0.0915	0.1408
Weathering change amount	0.8901	16.5333	4.1625	3.4102	0.1563	-0.0702	1.4738

Analysis of Table. 2 shows that for lead-barium glass, silica, potassium oxide, iron oxide, barium oxide, and tin oxide all decrease after weathering. Among them, silica, potassium oxide, and iron oxide have the highest reduction ratio, with the reduction ratio reaching 63%, 86%, and 72% of the preweathering ratio, respectively. Barium oxide and tin oxide have a very low reduction ratio of 2.8% and 19%, respectively. The remaining components have increased in percentage. Among them, calcium oxide, phosphorus pentoxide, and sulfur dioxide increased especially after weathering, reaching 46%, 77%, and 70%. The overall chemical composition of lead barium glass increased as a percentage. Table .3 shows the data on the change of composition of high potassium glass.

Table 3. Changes in composition of high potassium glass

type	SiO_2	Na_2O	K_2O	CaO	MgO	Al_2O_3	Fe_2O_3
Weathered lead barium	93.96333	0	0.815	0.87	0.59	1.93	0.265
Unweathered lead barium	67.98417	2.78	10.1791	6.399	1.295	6.62	2.318
Weathering change amount	25.97916	-2.78	-9.36409	-5.529	-0.705	-4.69	-2.053
Type	CuO	PbO	BaO	P_2O_5	SrO	SnO_2	SO_2
Weathered lead barium	1.561667	0	0	0.336	0	0	0
Unweathered lead barium	2.675455	0.70571	1.795	1.53	0.08333	2.36	0.40667
Weathering change amount	-1.11379	-0.70571	-1.795	-1.194	-0.08333	-2.36	-0.40667

Analysis of Table 3 shows that for the high potassium glass, only the proportion of silica component increases after weathering, and the proportion of the rest of components decreases. The percentage of sodium oxide, lead oxide, barium oxide, strontium oxide, and tin oxide are all 0% after weathering, and the percentage of potassium oxide, calcium oxide, aluminum oxide, iron oxide, and phosphorus pentoxide decreases a lot, 91%, 86%, 71%, 88%, and 78%, respectively. The percentage of silicon dioxide increased significantly to 38%. The overall chemical composition percentage of high potassium glass decreases.

In conclusion: the overall chemical composition of lead-barium glass increases after weathering, and the overall chemical composition of high potassium glass decreases. The percentages of potassium oxide, iron oxide, barium oxide, and tin oxide are decreased for both glasses.

The chemical composition of the weathered lead-barium and weathered high-potassium glass was firstly compiled, and then the chemical composition change rates of different types of glass weathering were calculated based on the previous calculations, and the chemical composition content of each weathered artifact before weathering could be calculated and predicted.

$$b_i = \frac{a_i}{1+q_i} \tag{3}$$

Statistics were obtained for each chemical composition to account for the size of the fluctuation range before and after weathering, and the upper and lower limits of the predicted pre-weathering chemical composition were calculated accordingly.

The final predicted weathering glass pre-weathering chemical composition content data are shown in Table 4. (The table is too large, only 1, 3 sampling points are shown)

Table 4. Predicted content before weathering

Sampling site 1	SiO_2	Na_2O	K_2O	CaO	MgO	Al_2O_3	Fe_2O_3
Average value	72.1032	0	11.2887	6.7624	0.9048	4.1658	2.001
Fluctuation cap	72.1032	0	11.2887	6.7624	0.9048	4.1658	2.001
Fluctuation lower limit	72.1032	0	11.2887	6.7624	0.9048	4.1658	2.001
Sampling site 1	CuO	PbO	BaO	P_2O_5	SrO	SnO_2	SO_2
Average value	4.5279	0	0	1.2987	0	0	0.4485
Fluctuation cap	4.5279	0	0	1.2987	0	0	0.4485
Fluctuation lower limit	4.5279	0	0	1.2987	0	0	0.4485
Sampling site 3	SiO_2	Na_2O	K_2O	CaO	MgO	Al_2O_3	Fe_2O_3
Average value	84.4385	0	5.4495	1.6683	0	3.4104	0
Fluctuation cap	97.10428	0	5.66748	1.968594	0	4.09248	0
Fluctuation lower limit	76.83904	0	4.46859	1.434738	0	2.864736	0
Sampling site 3	CuO	PbO	BaO	P_2O_5	SrO	SnO_2	SO_2
Average value	0.8736	0.2225	0	0.7458	0	0	0
Fluctuation cap	1.04832	0.202475	0	0.850212	0	0	0
Fluctuation lower limit	0.751296	0.193575	0	0.67122	0	0	0

3. Conclusion

In this paper, when correlating surface weathering with glass, decoration, and color attributes, the glass type attributes are controlled to be constant, and then the influence of decoration and color on surface weathering is analyzed, using the control variable method, and the correlation analysis results are more reliable. When predicting the chemical composition content before weathering, the influence of glass type is also considered, and the fluctuation range is given for reference.

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