

Prediction of the chemical composition of ancient glass objects before weathering

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Abstract: This paper analyzes the differences and correlations in the composition of ancient glass artifacts and determines how they are classified. The surface weathering of known glass artifacts is analyzed in relation to their glass type, color, and decoration: and the statistical patterns of chemical composition content in different types of glass artifacts under different weathering conditions are analyzed according to glass type, and the chemical composition content before weathering is predicted by analysis of weathering point detection data.

Keywords: Ancient glass; correlation analysis; chi-square test.

1. Introduction

Since ancient times, the Silk Road has been an important channel of communication between China and the West, and we have exchanged porcelain and silk with them for glass products and so on. Glass products have also become a witness to the history of trade between China and the West. After glass products were introduced to China from West Asia and Egypt, our craftsmen improved the process by taking local materials, creating products with the same shape as the West but with different chemical composition.

Affected by the burial environment, the weathering process of ancient glass exchanged elements between the exterior and interior, resulting in a great change in the composition ratio, leading to errors in our judgment of his category. For example, the artifact in Figure 1 is marked as unweathered, but we can also distinguish it from its surface color and ornamentation to show local shallow weathering; the surface in Figure 2 is a weathering type, while there are also unweathered areas.



Figure 1: Glass sample of unweathered dragonfly eye



Figure 2: Sample of weathered glass chess pieces

2. Methods

The surface weathering of known glass artifacts is analyzed in relation to its glass type, color and ornamentation to determine the correlation between each sample variable, and the Spearman rank

correlation coefficient is adopted to solve this problem according to the non-linearity of the sample, which is relatively more widely used. The statistical patterns of chemical composition content in different types of glass artifacts under different weathering conditions are analyzed according to glass type, and visualized to observe the composition content of each content under different weathering conditions. Finally, to predict the unweathered composition of weathered glass artifacts, it is considered that the statistical law between the chemical composition variables in the above two states can be used to obtain the amount of change in chemical composition in unweathered and weathered conditions thereby achieving the purpose of predicting the chemical composition content before weathering.

3. Results and Discussion

3.1 Analysis of surface weathering of cultural relics in relation to their characteristics

Firstly, the data were pre-processed with the intention of excluding non-valid data and filling in the gaps, and the data were pivotally analyzed by Excel to obtain Table 1 below: Pivot table of surface weathering and data of each feature type.

Table 1: Surface weathering and pivot table for each feature type

Counting item:Surface weathering	Type	Ornamentation			Total high potassium	Lead Barium		Total lead barium	Total
Surface Weathering	Color	A	B	C		A	C		
Weathering			6		6	11	17	28	34
	Black					2		2	2
	Blue-Green		6		6	1	2	3	9
	Pale Blue					7	7	14	14
	light green						1	1	1
	Deep Blue					1		1	1
	Dark Green						5	5	5
	Purple						2	2	2
No weathering		6		6	12	5	7	12	24
	Blue-Green	5		1	6				6
	Green						1	1	1
	Pale Blue			4	4	4		4	8
	light green						2	2	2
	Deep Blue	1			1	1		1	2
	Dark Green			1	1		2	2	3
	Purple						2	2	2
Total		6	6	6	18	16	24	40	58

From the table, it is easy to know that both weathered and unweathered contain blue-green light blue light green dark blue dark green purple while weathered type alone has black and unweathered type alone has green: weathered type contains three types of ornamentation, while unweathered type lacks B type pattern, while weathered surface contains only B type pattern in high potassium type and weathered surface has only blue-green color in high potassium type. This does not show the relationship between the weathered surface and each feature. In order to obtain the relationship between the weathered surface and each feature, we need to conduct correlation analysis.

We performed Spearman correlation analysis by SPSS for weathered surfaces with pattern, color, and type, respectively, and obtained Table 2.

Table 2 Spearman correlation - detailed format

		Type	Ornamentation	Color
Surface weathering	Correlation coefficient	-0.344**	0.037	0.038
	p-value	0.008	0.781	0.777

* p<0.05 ** p<0.01

It is not difficult to find a significant relationship between the surface weathering and the type of its P-value of 0.008 reached a confidence level of 95% of the remaining features and surface weathering are not significant relationship, taking into account the type of cultural relics and the possible existence of disorderly ornamentation, we also through the chi-square test for its corroboration to obtain Table 3.

Table 3 Cardinality test results

Title	Name	Surface weathering		Total	X ²	Calibration X ²	P
		No weathering	Weathering				
Type	High potassium	12	6	18	6.880	5.452	0.009***
	Lead Barium	12	28	40			
Total		24	34	58			
Ornamentation	C	13	17	30	4.957	4.957	0.084*
	A	11	11	22			
	B	0	6	6			
Total		24	34	58			
Color	Blue-Green	6	9	15	4.822	4.822	0.682
	Pale Blue	8	14	22			
	Purple	2	2	4			
	Dark Green	3	5	8			
	Deep Blue	2	1	3			
	light green	2	1	3			
	Black	0	2	2			
Green	1	0	1				
Total		24	34	58			

Note: ***, **, * represent 1%, 5%, 10% significance levels, respectively

Through the above table we found that the p-value of type and surface weathering is 0.009***, rejecting the original hypothesis that there is a significant difference, and the significance level is very high at 99%, while the rest are outside 95%, so we conclude that there is a significant difference between type and surface weathering under our two-sided corroboration.

3.2 Statistical rules for the content of chemical components with and without weathering on the surface

We analyze the statistical patterns of chemical content in different types of glass artifacts and under different weathering conditions according to glass type, and find the frequency of each chemical component within a certain content range in this random-like data, which generally takes the form of direct observation of histograms for statistical pattern analysis of such data. First, we divided the data into two categories: weathered and unweathered, and then visualized the histograms of the chemical components corresponding to all the artifacts one by one. Considering the existence of uneven distribution of different contents, we equalized the histograms in order to make the histograms uniform and reflect the changes and distribution of each content more clearly, which means that the 14 chemical components with the The difference between the maximum and minimum values were divided into five parts as the basis for frequency division. Due to the small number of data, we put the data before and after weathering under the same chemical composition in the same graph with different colors, which not only eliminates the situation that does not conform to the statistical law due to the small number, but also shows more intuitively the change of each chemical composition whether it is weathered or not. The following combined figure 3 was finally obtained.

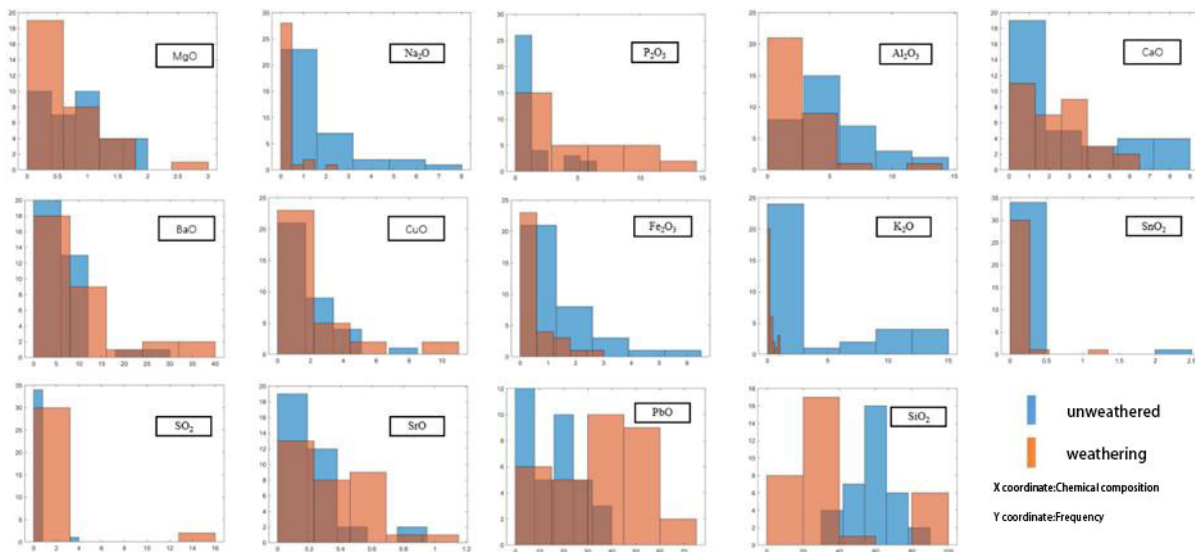


Figure 3: Summary of the frequency histogram of the distribution of the content of each chemical component

We can easily find that the content of weathered (orange) Na_2O , Al_2O_3 , SiO_2 , CaO , Fe_2O_3 and K_2O in the 14 plots is more than that of unweathered (blue) compared to the distribution near the vertical axis, which means that the weathered content of less artifacts is more frequent, which means that the weathered compared to unweathered these six chemical components are decreasing; conversely, the remaining eight chemical composition content weathered than unweathered is increasing trend. Since the amount of data of each chemical composition of high potassium and lead-barium glass are within 50, if we use the histogram again, we do not have the statistical law, which may lead to unconvincing data, so we will analyze the statistical law of the chemical composition content with and without weathering on the surface of the artifact samples under different types by combining the histogram of the mean change of chemical composition under each type with the above overall situation, and we get Figure 4 and Figure 5.

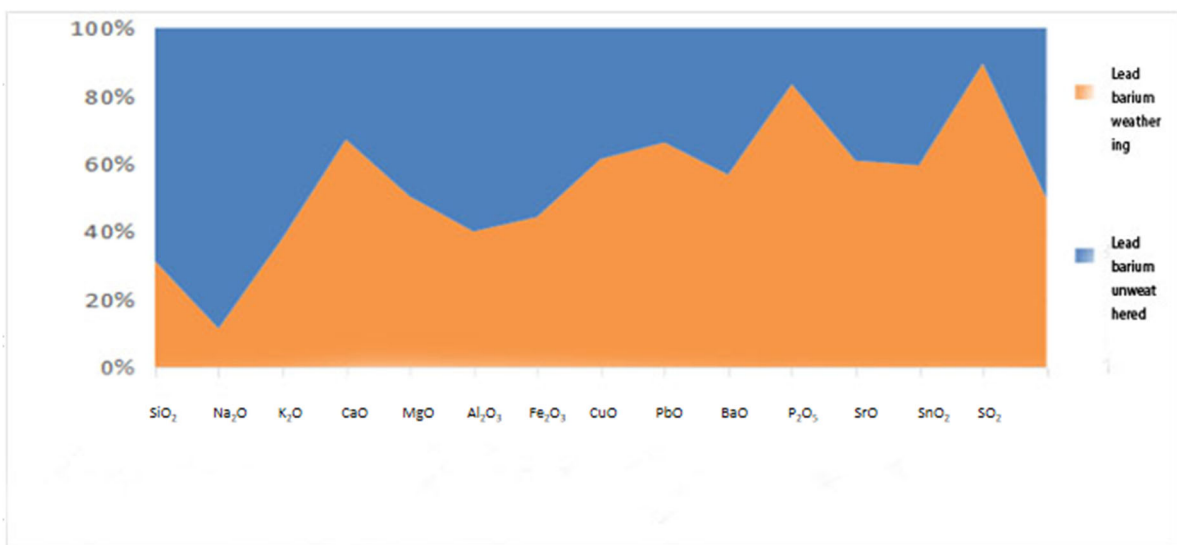


Figure 4: Percentage of each chemical composition under different weathering of lead-barium glass

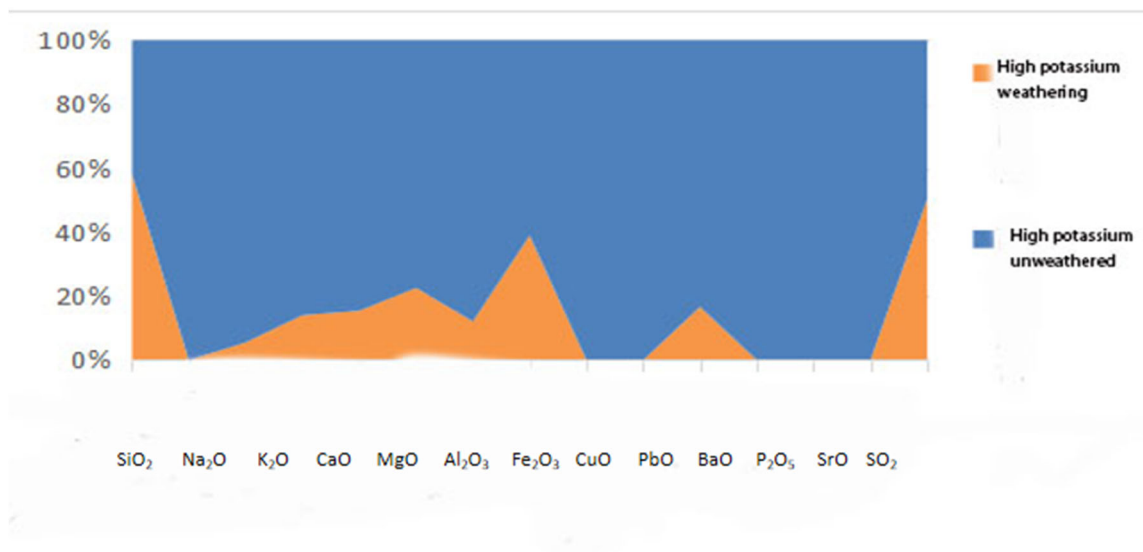


Figure 5. Percentage of each chemical composition of high potassium glass under different weathering

These two plots we find that the chemical composition of lead-barium glass weathering is almost all above the 50% cut-off except for the four types of sodium oxide, silica, alumina and iron oxide, while the chemical composition of high potassium glass weathering is almost all below 50%. Therefore, combined with the above histogram statistics, we conclude that except for a few chemical components, the overall chemical composition of lead-barium glass weathering is increasing compared to that of unweathered artifact samples, while sodium oxide and silica show a more obvious negative growth trend; the overall chemical composition of high-potassium glass weathering is decreasing compared to that of unweathered artifact samples. The overall chemical composition of high potassium glass weathered compared to unweathered samples tends to decrease. The amount of data for lead-barium glass is also much more than that for high-potassium glass, and the above conclusions for the overall histogram are also consistent with the trend of lead-barium glass type, which also reflects the reasonableness of the conclusions.

3.2 Prediction of chemical composition content before weathering

The final requirement is to predict the unweathered composition of weathered glass artifacts. We first predicted by machine learning random forest and found that the statistical data was too small leading to large errors in the predicted data, so we changed the scheme. By using the statistical law between the chemical composition variables in the above two states, we can obtain the change in chemical composition between unweathered and weathered glass artifacts to predict the chemical composition content before weathering. In this regard, we take the mean value of each chemical composition content before and after weathering as a percentage of the data.

to find the mean value of each variable:

$$x^* = \frac{1}{n} \sum_{i=1}^n x_i \tag{1}$$

Difference between pre-weathering and post-weathering

$$x = x_1^* - x_2^* \tag{2}$$

Finally, each independent variable is added to the corresponding difference to be the predicted value, and the predictions are shown in Table 3.

Table 3: Statistics of Forecast Results

Heritage Sampling Sites	SiO ₂	Na ₂ O	K ₂ O	CaO	MgO	Al ₂ O ₃	Fe ₂ O ₃
02	36.28	0	1.05	2.34	1.18	5.73	1.86
07	92.63	0	0	1.07	0	1.98	0.17
08	20.14	0	0	1.48	0	1.34	0
09	95.02	0	0.59	0.62	0	1.32	0.32
10	96.77	0	0.92	0.21	0	0.81	0.26
11	33.59	0	0.21	3.51	0.71	2.69	0
12	94.29	0	1.01	0.72	0	1.46	0.29
19	29.64	0	0	2.93	0.59	3.57	1.33
22	92.35	0	0.74	1.66	0.64	3.5	0.35
26	19.79	0	0	1.44	0	0.7	0
27	92.72	0	0	0.94	0.54	2.51	0.2
34	35.78	0	0.25	0.78	0	1.62	0.47
36	39.57	2.22	0.14	0.37	0	1.6	0.32
38	32.93	1.38	0	0.68	0	2.57	0.29
39	26.25	0	0	1.11	0	0.5	0
40	16.71	0	0	1.87	0	0.45	0.19
41	18.46	0	0.44	4.96	2.73	3.33	1.79
43 part 1	12.41	0	0	5.24	0.89	2.25	0.76
43 part 2	21.7	0	0	6.4	0.95	3.41	1.39
48	53.33	0.8	0.32	2.82	1.54	13.65	1.03
49	28.79	0	0	4.58	1.47	5.38	2.74
50	17.98	0	0	3.19	0.47	1.87	0.33
51 part 1	24.61	0	0	3.58	1.19	5.25	1.19
51 part 2	21.35	0	0	5.13	1.45	2.51	0.42
52	25.74	1.22	0	2.27	0.55	1.16	0.23
54	22.28	0	0.32	3.19	1.28	4.15	0
56	29.15	0	0	1.21	0	1.85	0
57	25.42	0	0	1.31	0	2.18	0
58	30.39	0	0.34	3.49	0.79	3.52	0.86
43_mean	75.975	0	8.19	4.70375	0.54375	3.97875	1.0875
51_mean	73.76	0	8.79	5.2425	0.6525	3.9625	1.305
54_mean	78.19	0	7.59	4.165	0.435	3.995	0.87
CuO	PbO	BaO	P ₂ O ₅	SrO	SnO ₂	SO ₂	type
0.26	47.43	0	3.57	0.19	0	0	Lead Barium
3.24	0	0	0.61	0	0	0	High Potassium
10.41	28.68	31.23	3.59	0.37	0	2.58	Lead Barium
1.55	0	0	0.35	0	0	0	High Potassium
0.84	0	0	0	0	0	0	High Potassium
4.93	25.39	14.61	9.38	0.37	0	0	Lead Barium
1.65	0	0	0.15	0	0	0	High Potassium
3.51	42.82	5.35	8.83	0.19	0	0	Lead Barium
0.55	0	0	0.21	0	0	0	High Potassium
10.57	29.53	32.25	3.13	0.45	0	1.96	Lead Barium
1.54	0	0	0.36	0	0	0	High Potassium
1.51	46.55	10	0.34	0.22	0	0	Lead Barium
0.68	41.61	10.83	0.07	0.22	0	0	Lead Barium
0.73	49.31	9.79	0.48	0.41	0	0	Lead Barium
0.88	61.03	7.22	1.16	0.61	0	0	Lead Barium
0	70.21	6.69	1.77	0.68	0	0	Lead Barium
0.19	44.12	9.76	7.46	0.47	0	0	Lead Barium
5.35	59.85	7.29	0	0.64	0	0	Lead Barium
1.51	44.75	3.26	12.83	0.47	0	0	Lead Barium
0	15.71	7.31	1.1	0.25	1.31	0	Lead Barium
0.7	34.18	6.1	11.1	0.46	0	0	Lead Barium
1.13	44	14.2	6.34	0.66	0	0	Lead Barium
1.37	40.24	8.94	8.1	0.39	0.47	0	Lead Barium
0.75	51.34	0	8.75	0	0	0	Lead Barium
0.7	47.42	8.64	5.71	0.44	0	0	Lead Barium
0.83	55.46	7.04	4.24	0.88	0	0	Lead Barium
0.79	41.25	15.45	2.54	0	0	0	Lead Barium
1.16	45.1	17.3	0	0	0	0	Lead Barium
3.13	39.35	7.66	8.99	0.24	0	0	Lead Barium
2.41875	0.09375	0	0.73125	0	0	0.24375	Lead Barium
2.9025	0.0625	0	0.8775	0	0	0.2925	Lead Barium
1.935	0.125	0	0.585	0	0	0.195	Lead Barium

3.3 Discussion

The quantitative treatment of the stereotypical variables was carried out so that they could be analyzed by correlation analysis and chi-square test, and more exact relationships were obtained through the mutual corroboration of the two. For the analysis of their statistical laws we first analyzed the combination of histograms for both weathering cases, and also visualized the two types to draw conclusions under their joint analysis, with convincing results.

4. Conclusion

The main findings of this paper are as follows.

- (1) there is a significant difference between glass type and surface weathering.
- (2) The overall chemical composition of lead-barium glass weathered compared to unweathered artifact samples is an increasing trend, with sodium oxide and silica showing a more significant negative growth trend.
- (3) The overall chemical composition of the high potassium glass weathering is decreasing compared with that of the unweathered artifacts.
- (4) The chemical composition of the glass before weathering was predicted.

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