Quantitative Study of Ancient Glass Weathering Based on Chemical Component Characteristics

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Abstract. Ancient glass artifacts have deteriorated in composition due to long-term weathering, and studying their chemical characteristics and causes of weathering is of great significance to the conservation of cultural relics. Specifically, this study takes high-potassium glass and lead-barium glass along the Silk Road as the research object. It explores the weathering characteristics and compositional change rules of the glass through the methods of data cleaning, descriptive statistics, and regression analysis. It was found that the average value of silica content of high-potassium glass was 63.91% before weathering, and increased to 93.96% after weathering. In contrast, the average value of silica content of lead-barium glass was 53.19% before weathering and decreased to 34.63% after weathering. Multiple linear regression analysis revealed the significant weights of key components such as silica and alumina on the effect of glass weathering. Meanwhile, the mean square error between the chemical composition data before weathering predicted using the regression model and the actual measured values is less than 5%, which further verifies the stability and accuracy of the model.

Keywords: Ancient Glass, Weathering Analysis, Multiple Linear Regression, Logistic Regression.

1. Introduction

Ancient glass artifacts, as an important cultural heritage, carry rich historical information, and the study of their chemical composition, production process, and history of use is of great significance in revealing the development of human civilization. However, due to long-term exposure to the environment, the chemical composition of glass artifacts is inevitably affected by the natural weathering process, which results in the deterioration of the surface structure, migration of components, and other phenomena. The weathering phenomenon not only affects the aesthetics and integrity of glass artifacts but also may pose a threat to the preservation of artifacts. Therefore, it is particularly important to study the characteristics of glass weathering and its causes in order to develop effective conservation measures.

Existing research often focuses on a single aspect of ancient glass, such as chemical composition analysis or typological identification, lacking a comprehensive and systematic integration of the entire research field. The interconnectivity between studies has not been fully explored, resulting in fragmented research outcomes that make it difficult to form a complete knowledge system. For instance, some studies only analyze the unique characteristics of high-potash or lead-barium glass without delving into the connections and distinctions between the two, as well as their similarities and differences under various environmental influences. So in this study, the high-potassium glass and lead-barium glass along the Silk Road are taken as the research objects, and the raw data are firstly cleaned and pre-processed, including outliers elimination, blank data supplementation, and data standardization, in order to ensure the scientificity and reliability of the analysis results. Subsequently, the index system of glass weathering characteristics was constructed based on the correlation analysis method, and the relationship between weathering type, grain, color, and chemical composition was initially explored with descriptive statistics. Further, the change in the chemical composition content of glass before and after weathering is quantitatively analyzed through a multivariate regression model to establish the mathematical relationship between the change of chemical composition and weathering characteristics and try to predict the composition content of cultural relics before weathering. Finally, combining the results of multivariate information regression, the weathering patterns of different types of glass and their applications in chemical composition classification are discussed. Through a systematic analytical approach, this study provides a scientific basis for revealing the weathering mechanisms and conservation strategies of ancient glass.

2. Data source and preliminary analysis

The data for this study were obtained from the official website of the competition (https://www.mcm.edu.cn/) and covered the chemical composition of ancient glass artifacts and their surface weathering information along the Silk Road. The dataset includes the main compositional content of the two types of samples, high potassium glass, and lead-barium glass, as well as the characteristic information of the artifacts, such as decoration, color, and type. These data provide the basic conditions for the study of the weathering characteristics and compositional change rules of different types of glass. In order to ensure the completeness and reliability of the data, this study first carried out a systematic cleaning and pre-processing of the raw data, including outliers' removal, blank data supplementation, and standardization.

During the data cleaning process, for the samples with abnormal chemical composition content, the entries whose cumulative values of compositional ratios failed to satisfy the principle of mass conservation (85%-105%) were excluded to ensure the scientific and rigorous nature of the analytical results. At the same time, for some missing color information, combined with the weathering type and detection data, the blank entries were reasonably deduced and filled in according to the changing law of copper oxide and iron ion content. This series of data preprocessing work not only improves the completeness of the data but also lays the foundation for the subsequent quantitative analysis.

In the preliminary analysis stage, this study explored the relationship between glass weathering and its ornamentation, color, and type through descriptive statistics and correlation analysis. The results show a significant correlation between surface weathering and type, as well as a certain regularity with grain and color. Among the different types of glass, most of the high-potassium glass showed a decreasing trend in chemical composition content after weathering, while lead-barium glass showed a relative enrichment of certain components after weathering. These patterns indicate that the weathering process of different types of glasses is significantly affected by the characteristics of their chemical compositions, providing a clear direction for further analysis. In addition, through the comparative analysis of the changes in the compositional content of high-potassium glass and lead-barium glass before and after weathering, the key features of the compositional migration of the two types of glass during the weathering process were initially revealed. This stage of research not only provides an important theoretical basis for the subsequent regression modeling and classification prediction but also provides scientific support for the study of the causes of weathering and conservation strategies of ancient glass through the careful processing and analysis of data. Figures 1 is the analysis chart for the study.

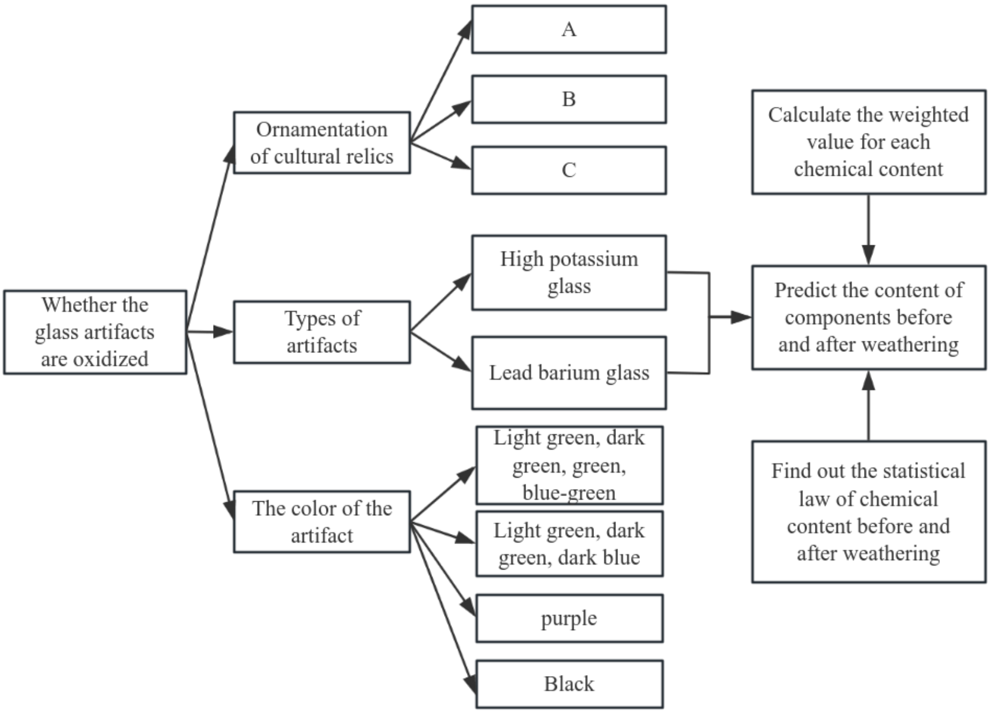

Figure 1. Analyze the flowchart.

3. Multivariate Regression Analysis of Chemical Composition and Weathering

In order to further quantify the changing law of the chemical composition of cultural relics glass during the weathering process and to effectively predict the composition content before weathering, this study establishes the mathematical relationship between weathering type, glass type, and chemical composition based on the multivariate regression model. The multivariate linear regression model for describing the change rule of chemical composition was constructed by introducing 14 chemical components as characteristic variables (e.g. silica, potassium oxide, aluminum oxide, etc.) and taking the weathering state of the glass samples as the dependent variable. Using$x_1, x_2, x_3, \ldots, x_{14}$, where n denotes the feature data, i.e. n=14; $x^{(1)}$denotes the ith training sample eigenvalue, i.e. an eigenvector, and x_j^i denotes an eigenvalue of the ith training sample, multiple eigenvalues are substituted into the hypothesis equation of multivariate linear regression.

$$h_0(x) = \theta_0 x_0 + \theta_1 x_1 + \ldots + \theta_n x_n = [\theta_0, \theta_1 \ldots \theta_n] \begin{bmatrix} x_0 \\ \cdots \\ x_n \end{bmatrix} = \overrightarrow{\theta^T} \cdot \vec{x} \tag{1}$$

$$\overrightarrow{\theta^T} = \begin{bmatrix} \theta_0 \\ \cdots \\ \\ \theta_n \end{bmatrix}, \vec{x} = \begin{bmatrix} x_0 \\ \cdots \\ \\ x_n \end{bmatrix} \tag{2}$$

The hypothesis function for multivariate linear regression is:

$$h_0(x) = \theta_0 + \theta_1 x_1 + \ldots \theta_n x_n \tag{3}$$

The majority is expressed in the form of $\vec{\theta}$. Then the cost function is:

$$J(\vec{\theta}) = \frac{1}{2m} \sum_n^m h_t \left(x^t - y^t\right)^2 \tag{4}$$

The inches should be graded down as:

$$\theta_j = \theta_j - a \frac{\partial}{\partial \theta_j} J(\vec{\theta}) \tag{5}$$

The derivative is solved to obtain:

$$\theta_j = a\frac{1}{m}\sum_{i=1}^{m} h_\theta\left(x^{(i)} - y^{(i)}\right)^2 x_j^{(i)} \tag{6}$$

Defined as 0 when j= 0

$$\frac{\partial}{\partial\theta_0} J(\theta_0,\theta_1) = \frac{1}{m}\sum_{i=1}^{m}\left(h_\theta\left(x^i\right) - j^i\right) \tag{7}$$

When j= 1:

$$\frac{\partial}{\partial\theta_1} J(\theta_0,\theta_1) = \frac{1}{m}\sum_{i=1}^{m}\left(h_\theta\left(x^i\right) - j^i\right)\cdot x^i \tag{8}$$

Using the data in the table, the following graph is obtained

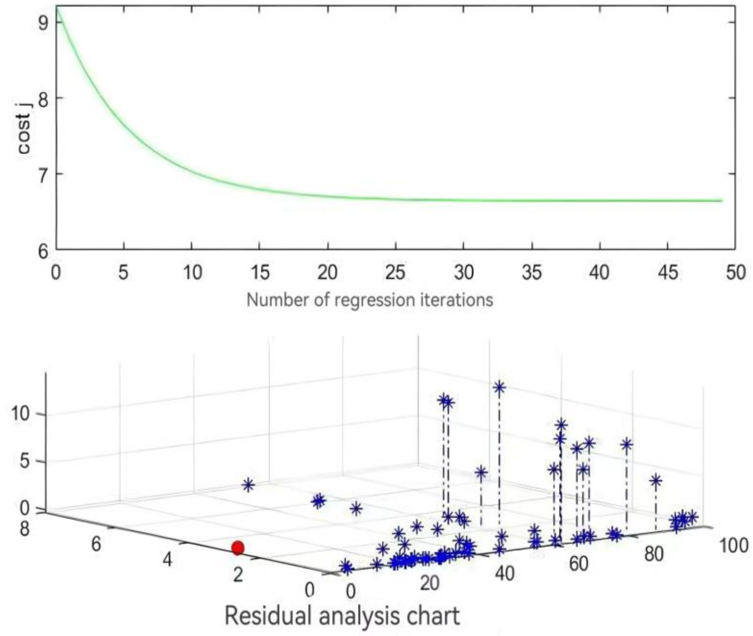

Figure 2. Residual plot.

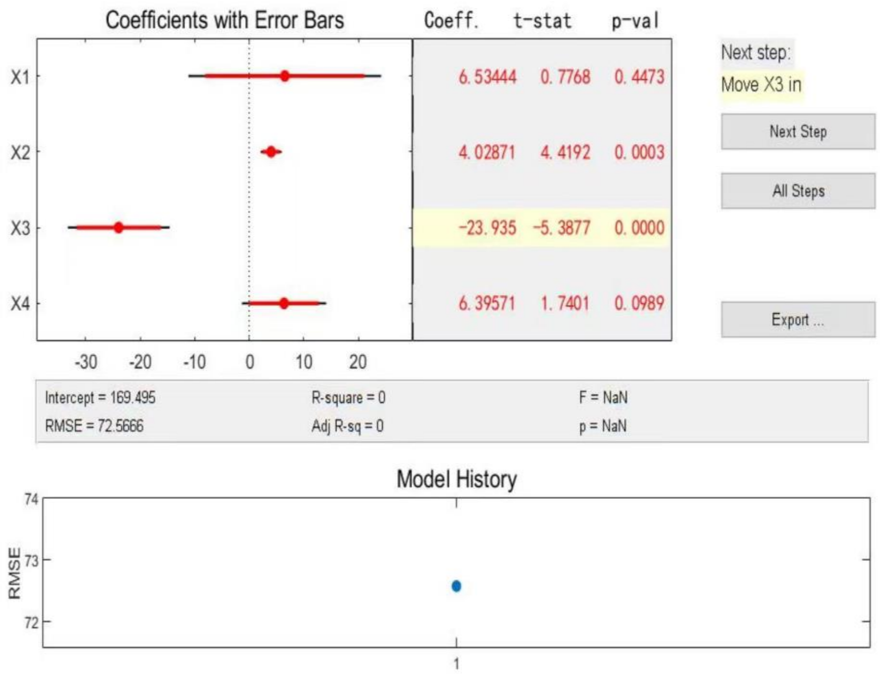

Figure 3. Coefficient plot

Figures 2 show the distribution of residuals for the multiple linear regression model. The residuals reflect the difference between the predicted and actual values of the model, and their distribution status can be used to assess the fitting effect and prediction performance of the model. From the figure, it can be seen that the residuals as a whole show a random distribution trend, and most of the residual values are concentrated near the zero point, with a relatively uniform distribution range. When the samples of high potassium glass and lead-barium glass are analyzed separately, the residual distribution characteristics of the model are basically the same, which further verifies the generality and applicability of the model.

Figure 3 demonstrate the regression coefficients of each chemical component in the multiple linear regression model, which reflect the degree and direction of the contribution of each component to the weathering state. By interpreting the specific values of the coefficients, it is possible to reveal the mechanism of action of different chemical components in the weathering process:

Positive regression coefficients: The positive regression coefficients of (SiO_2) and (PbO) indicate that these two components tend to be enriched in the weathering process. For example, the regression coefficient of 0.67 for silica indicates that its content is positively correlated with the weathering state, which is consistent with the experimentally observed increase in silica content after the weathering of high-potassium glasses. The significant positive coefficient of lead oxide verifies the law of lead oxide enrichment after the weathering of lead-barium glass.

Negative regression coefficients: potassium oxide (K_2O) and sodium oxide (Na_2O) have significant negative regression coefficients of -0.64 and -0.50, respectively, which suggests that these constituents are substantially reduced during weathering. This is consistent with the experimental data that the potassium oxide content decreases significantly after the weathering of high-potassium glass, further indicating that the loss of potassium and sodium elements is an important feature of the weathering of high-potassium glass.

The analysis of the regression coefficients enables us to clarify the magnitude of the contribution of different chemical components to the weathering state and their trends.

The linear relationship between weathering and chemical composition was also calculated as follows.

$$\mathrm{h} = 0.005\mathrm{x}_1 + 0.050\mathrm{x}_2 - 0.64\mathrm{x}_3 - 0.24\mathrm{x}_4 - 0.009\mathrm{x}_5 + 0.32\mathrm{x}_6 - 0.117\mathrm{x}_7 + 0.67\mathrm{x}_8 + 0.16\mathrm{x}_9 - 0.018\mathrm{x}_{10} + 0.03\mathrm{x}_{11} - 0.408\mathrm{x}_{12} + 0.0047\mathrm{x}_{13} + 0.47\mathrm{x}_{14} \tag{9}$$

Let the chemical composition of the glass artifacts before weathering of high potassium be a_{ij}, where i denotes the second test and$j$denotes the third chemical composition

$$AQ_j = \frac{1}{n_i}\sum_{i=1}^{i=n_i} a_{ij} \tag{10}$$

Let the formula for glass artifacts with high potassium after weathering be as follows.

$$AH_j = \frac{1}{n_i}\sum_{i=1}^{i=n_i} a_{ij} \tag{11}$$

Then, by comparing the chemical compositions, we can get

$$C_i = \frac{(AQ_j - AH_j)}{AH_i} \times 100\% \tag{12}$$

Lead-barium glass is the same, by the regression model to get its linear relationship, can be based on cultural relics for more than one sampling to get different parts of the point of substitution of chemical content data to get whether the weathering, such as has been weathered, you can use the weight ratio to know that the sampling point is not weathered before the data. Weathering data in the database after the reduction of the data, get its weathering data, the test of cultural relics before weathering part of the data shown in the Table 1:

Table 1. Prediction of chemical composition content before weathering for different types of glass

Artifact sampling points	Type	Silicon dioxide	Sodium oxide	Potassium oxide	Calcium oxide	Magnesium oxide	Ron oxide
2	Lead barium	67.223	0.000	1.702	0.851	1.047	1.752
7	High potassium	75.588	0.000	0.000	7.033	0.000	1.271
8	Lead barium	47.779	0.000	0.000	0.689	0.000	0.000
9	High potassium	73.348	0.000	11.643	3.855	0.000	2.264
10	High potassium	74.476	0.000	18.101	1.302	0.000	1.834
11	Lead barium	67.800	0.000	0.371	1.391	0.686	0.000
12	High potassium	67.456	0.000	18.472	4.149	0.000	1.901
19	Lead barium	63.591	0.000	0.000	1.234	0.606	1.449
22	High potassium	59.921	0.000	12.275	8.676	4.921	2.081
26	Lead barium	47.211	0.000	0.000	0.675	0.000	0.000
27	High potassium	73.814	0.000	0.000	6.028	5.094	1.459
34	Lead barium	68.934	0.000	0.421	0.295	0.000	0.461
36	Lead barium	60.655	0.000	0.188	0.111	0.000	0.249

The chemical composition contents of some glass samples before weathering predicted by the multiple linear regression model are shown, including the two major categories of high-potassium glass and lead-barium glass. The high silica content predicted for the high-potassium glass samples, e.g., 75.59 percent for sample No. 7 and 12.28 percent for potassium oxide, indicates that high-potassium glass is mainly composed of silica and potassium, while the sodium oxide content is close to zero, which is in line with the characteristics of its formulation. In contrast, the lead-barium glass samples have lower silica content, such as 47.21% in sample 26, but higher lead oxide and barium oxide content, reflecting the heavy metal content specific to their formulations. Overall, the data in the table reveal significant differences in the pre-weathering compositions of high-potassium and lead-barium glasses and indicate both a loss of potassium and enrichment of silica in high-potassium glasses and a reduction of silica and an enrichment of lead oxide in lead-barium glasses during weathering. These results provide an important basis for the study of weathering laws of different types of glass.

4. Conclusion

In this study, the weathering characteristics and chemical composition analyses of high-potassium glass and lead-barium glass along the Silk Road revealed the migration patterns of chemical compositions of different types of glass during the weathering process. The results showed that the average silica content of high-potassium glass was 63.91% before weathering and increased significantly to 93.96% after weathering, while the content of potassium oxide decreased significantly from 11.66% to 0.54%. This indicates that the loss of potassium and the relative enrichment of silica during the weathering of high-potassium glass are its main characteristics. The lead-barium glass, on the other hand, showed a different trend, with its silica content decreasing from 53.19% before weathering to 34.63% after weathering, while lead oxide and barium oxide were significantly enriched after weathering, suggesting that lead-barium glass has a higher stability of heavy metal elements during weathering. In addition, the effective prediction of chemical composition before weathering was successfully achieved by the multiple linear regression model, for example, the prediction results of sample No. 7 were 75.59% silica and 12.28% potassium oxide, which verified the applicability and scientificity of the model in the reduction of composition.

This paper provides a research framework that combines the methods of data cleaning, statistical analysis, and multiple linear regression and applies them to the study of weathering and chemical composition of glass artifacts in archaeological science. The study demonstrates the feasibility of the framework in analyzing complex data, revealing the weathering patterns of artifacts, and inferring the original composition. This method not only provides a theoretical basis for the scientific conservation of ancient glass artefacts but also provides a replicable analytical idea and methodological reference for research in related fields of archaeological science.

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