Based on the analysis and identification of ancient glass products

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Abstract. The chemical composition of ancient glass in China is diverse, and it is very vulnerable to weathering under the influence of burial environment. This weathering will aggravate the difficulty of identifying ancient glass types. There are a number of relevant data on ancient glass products in China. Archaeologists have divided these cultural relics into two types: high potassium glass and lead barium glass according to their chemical composition and other detection methods. In this paper, Kappa consistency test, statistical law, principal component analysis, k-means clustering analysis, logical regression model, gray correlation analysis and other methods or models are used to analyze the composition of these glass samples and identify their types.The Kappa coefficient is used to test the consistency of these three groups of disordered classification variables, and the Kappa value is used to judge the correlation degree of the three groups of disordered classification variables. Through the test, it is found that the surface weathering of glass relics has a certain relationship with its glass type; Later, we tried to explore whether there would be a more obvious rule when the surface weathering was affected by two variables at the same time. It was found that when the glass type was fixed to high potassium, the type of its decoration would have an impact on its weathering.

Key words: Ancient Glass, Classification and Prediction, Cluster Analysis, Logical Regression

1. Research background

Although the appearance of ancient glass in China is similar to that of foreign glass products, its chemical composition is different. This is because ancient glass in China was made from local materials after ancient ancestors absorbed its technology. The main raw material of glass is quartz sand. Pure quartz sand has a high melting point, so in ancient times, plant ash, natural soda, saltpeter, lead ore and other fluxes were often added to reduce the melting temperature when refining glass, and limestone that will be converted into calcium oxide after calcination was added as a stabilizer. The main chemical composition of the glass is different with different fluxes added. The ancient glass is very vulnerable to weathering due to the influence of burial environment, and this weathering will increase the difficulty of identifying ancient glass types[1]. This is because the composition proportion of glass has changed due to the large exchange of internal elements and environmental elements during the weathering process.

According to the data, the classification rules of high potassium glass and lead barium glass are analyzed; For each category, select appropriate chemical components to classify its subclasses[2], give specific classification methods and results, and analyze the rationality and sensitivity of classification results.

2. Introduction

According to the relevant data of ancient glass products in China, archaeologists have divided these cultural relics into two types: high potassium glass and lead barium glass based on their chemical composition and other detection methods. The relationship between the surface weathering of these glass relics and their glass types, patterns and colors is analyzed; Based on the type of glass, the statistical rule of whether there is weathering chemical composition content on the surface of cultural relics samples is analyzed, and the chemical composition content before weathering is predicted according to the testing data of weathering points[3].The classification rules of high potassium glass and lead barium glass are analyzed; For each category, select appropriate chemical components to classify its subclasses, give specific classification methods and results, and analyze the rationality and sensitivity of classification results.

3. Analysis of the relationship between surface weathering of glass relics

3.1. Study on the Relationship among Glass Type, Color and Texture

These three variables can be paired with surface weathering to form three groups of disordered categorical variables. Below, Kappa consistency test and result comparison are conducted for them.

Table 1 Kappa consistency test chart

Kappa consistency test		
Pairs	Kappa value	pvalue
Surface weathering pairing type	0.336	0.009***
Surface weathering matching color	0.002	0.981
Weathered surface matching pattern	-0.04	0.709

Note: * * * represents the significance level of 1

From Table 1, we can read the Kappa value and p value of three pairs of variables. It is not difficult to find that only when the surface weathering matches the type, its Kappa value=0.336, showing general consistency; The p value is 0.009 * * *, which is significant at the level[4]. However, when surface weathering is paired with color or ornamentation, both of them are very low in generality and not significant in level. It can be concluded that the surface weathering of these glass relics is related to their glass types, but not to their colors and patterns.

3.2. Analysis on the statistical law of the content of weathering chemical components on the surface of cultural relics

In order to make the rule more obvious and the prediction more accurate, continue to refine the data. First, assign the content of all undetected components to 0, then use the 3sigma outlier recognition method to remove the abnormal values that do not conform to the normal distribution in each group of data, and replace them with the average of the remaining normal values. Finally, calculate the average values of various chemical components of these two types of samples, And make a broken line diagram with or without weathering on the horizontal axis, as shown in Figure 1 and Figure 2.

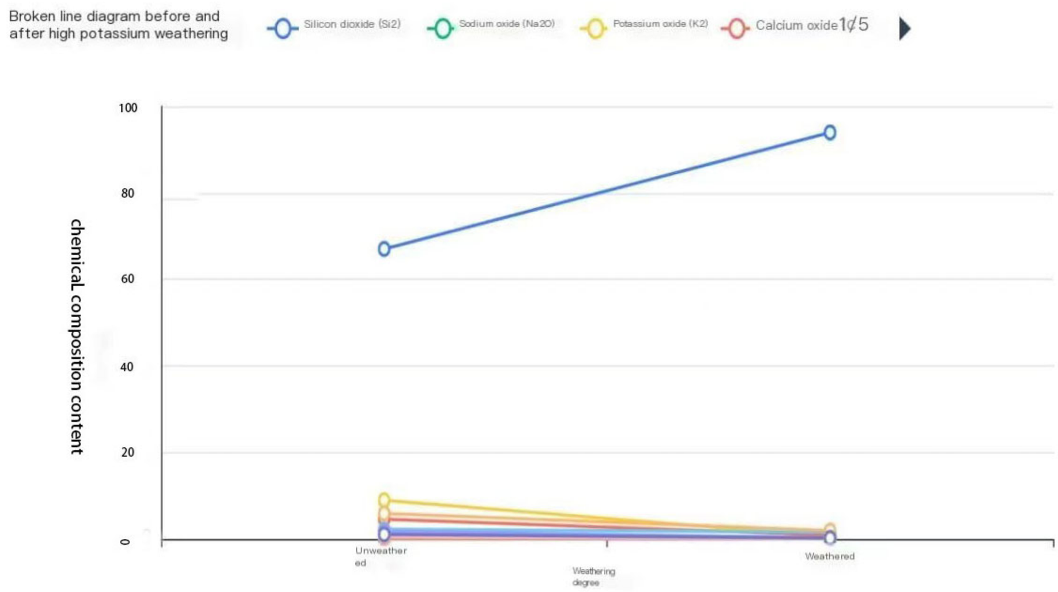

Figure1 Chemical composition of high potassium glass before and after weathering line diagram

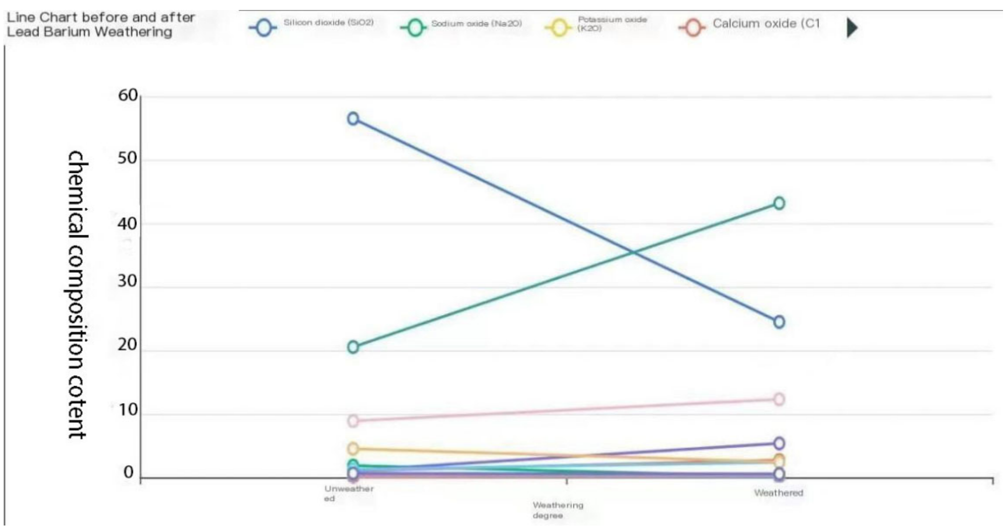

Figure2 Broken line chart of chemical composition of lead-barium glass before and after weathering

It can be seen intuitively from the broken line diagram that only the content of silicon dioxide (SiO_2) increases significantly after weathering of high potassium glass[5], while the content of other chemical components decreases, and some even become zero after weathering; However, after weathering of lead barium glass, the content of silicon dioxide (SiO_2) decreased significantly, the content of lead oxide (PbO) increased significantly, and the content of other chemical components did not increase significantly.

3.3. Prediction of chemical composition content of samples before weathering

According to the average value data of each chemical composition of the two types of glass, the horizontal axis is the histogram of various chemical compositions, Fig. 3 and Fig. 4.

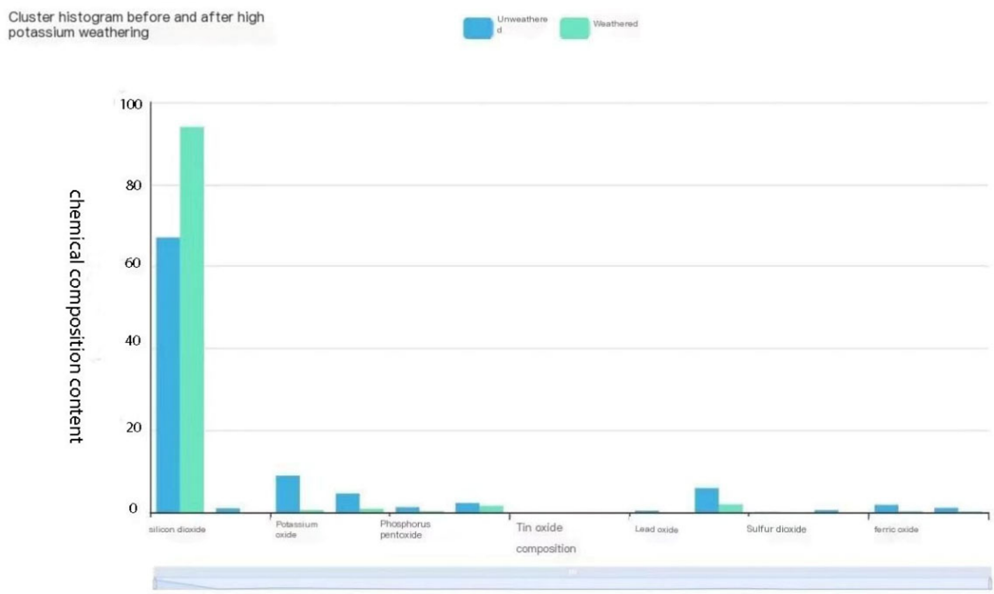

Figure 3 Bar chart of chemical composition content of high potassium glass before and after weathering

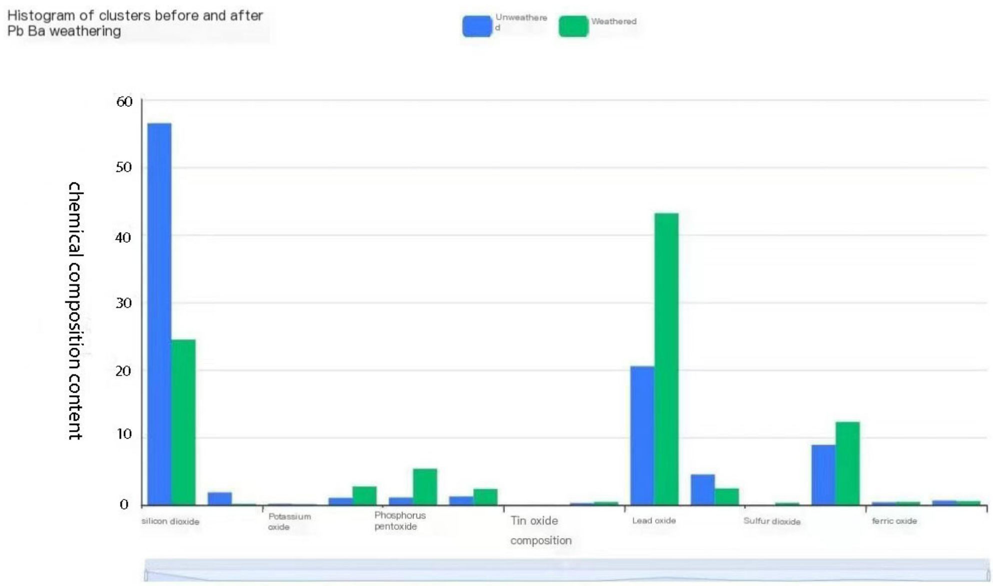

Figure 4 Bar chart of chemical composition of lead-barium glass before and after weathering

From these two histograms, it can be seen that the approximate content of each chemical component in the weathered samples of two types of glass before weathering should be near the average value of each chemical component content in the samples before weathering[6]. In order to make the prediction results more accurate, the Class A uncertainty of the samples before weathering is calculated. After the effective figures are unified according to the rules, the prediction interval of the chemical composition content before weathering is finally obtained, as shown in Table 2.

Table2Prediction intervals of chemical components before weathering

	silicon dioxide	Sodium oxide	Potassium oxide	calcium oxide	magnesium oxide	alumina	ferric oxide
High potassium, not weathered	68±2	1.0±0.4	9±1	4.6±0.9	1.1±0.2	5.9±0.8	1.9±0.4
Lead barium not weathered	57±2	1.9±0.5	0.15±0.02	1.1±0.2	0.7±0.1	4.5±0.7	0.4±0.1
	Copper oxide	Lead oxide	Barium oxide	Phosphorus pentoxide	Strontium oxide	Stannic oxide	sulfur dioxide
High potassium, not weathered	2.3±0.4	0.4±0.1	0.6±0.2	1.3±0.4	0.04±0.01	0.02±0.01	0.09±0.05
Lead barium not weathered	1.3±0.3	21±1	9±1	1.1±0.4	0.26±0.05	0.0010±0.0005	0.008±0.008

4. Analysis of Classification Rules of High Potassium and Lead barium Glasses

First, after comparing the content data of each chemical component of the two types of glass without weathering, magnesium oxide (MgO), phosphorus pentoxide (P_2O_5), strontium oxide (S_rO), tin oxide (S_nO) and sulfur dioxide (SO_2) are removed, and the remaining chemical components are subject to principal component analysis. We set two principal components, named principal component 1 and principal component 2 respectively, to obtain the factor load matrix thermodynamic diagram under the non weathering conditions, as shown in Figure 5.

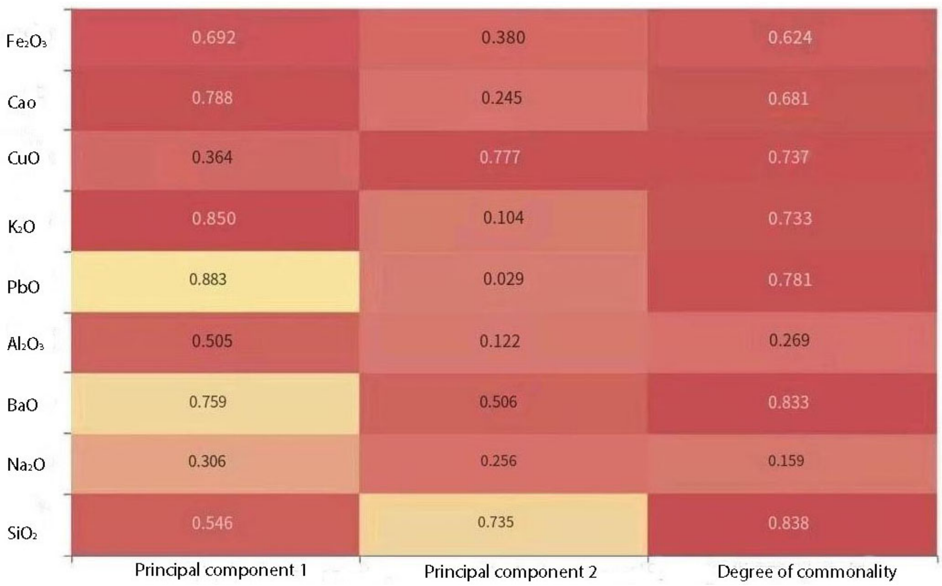

Fig. 5 Factor loading matrix thermal map without weathering

It can be seen from the figure that the weight of potassium oxide (K_2O) and calcium oxide (CaO) in principal component 1 is large, while the weight of lead oxide (PbO) and barium oxide (BaO) is small; It is not difficult to find that the weight of copper oxide (CuO) and barium oxide (BaO) is larger and the weight of potassium oxide (K_2O) is smaller when principal component 2 is compared with principal component 1. The specific formula is as follows [7]:

F1=0.138×Silica(SiO_2)-0.077×Sodium oxide (NaO_2)-0.192×Barium oxide (BaO)+0.127×Alumina (BaO)-0.223×Lead oxide (PbO)+0.215×Oxidation (K_2O)+0.092×Copper oxide (CuO)+0.199×Calcium oxide (CaO)+0.175 × Iron oxide (Fe_2O_3) (1)

F2=-0.433×Silica(SiO_2)+0.151×Sodium oxide (NaO_2)+0.298×Barium oxide (BaO)+0.072×Alumina (Al_2O_3)+0.017×Lead oxide (PbO)+0.061×Potassium oxide (K_2O)+0.458 × Copper oxide (CuO)+0.145 × Calcium oxide (CaO)+0.224 × Iron oxide (Fe_2O_3) (2)

Combined with the thermodynamic diagram and formula, it can be obtained that in the case of no weathering, the larger the value of F_1, the more the glass sample has the characteristics of high potassium glass; The higher the value of F_2, the more characteristic the glass sample is of lead barium glass F_1 and F_2 correspond to the principal components 1 and 2 respectively. Therefore, under this condition, the rule can be drawn as follows: under no weathering conditions, the samples containing more potassium oxide (K_2O) and calcium oxide (CaO) are potassium rich glasses; Lead barium glass contains more copper oxide (CuO) and barium oxide (BaO) in the sample.

Continue to compare the content data of each chemical component of the two types of glass during weathering and remove sodium oxide (NaO_2), potassium oxide (K_2O), magnesium oxide (MgO), iron oxide (Fe_2O_3), strontium oxide (S_rO), tin oxide (S_nO), sulfur dioxide (S), and reset principal component 1 and principal component 2. Perform principal component analysis on the remaining chemical components to obtain the factor load matrix thermodynamic diagram under weathering conditions, as shown in Figure 6.

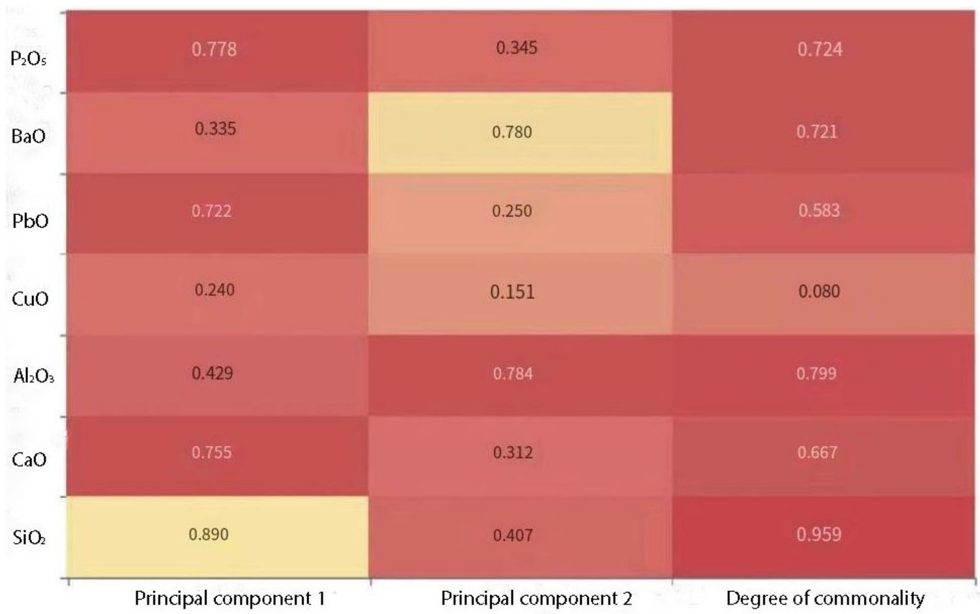

Fig.6 Factor loading matrix thermal map under weathering conditions

F1=-0.313×Silica(SiO_2)+0.266×Calcium oxide (CaO)+0.151×Alumina (Al_2O_3)+0.084×Copper oxide (CuO)+0.254 × Lead oxide (PbO)+0.118 × Barium oxide (BaO)+0.274 × Phosphorus pentoxide (P_2O_5). (3)

F2=0.241×Silicon dioxide (SiO_2)+0.185 × Calcium oxide (CaO)+0.463 × Alumina (Al_2O_3) -0.089 × Copper oxide (CuO) -0.148 × Lead oxide (PbO) -0.461 × Barium oxide (BaO)+0.204 × Phosphorus pentoxide (P_2O_5). (4)

From the figure, we can see that the weight of lead oxide (PbO), phosphorus pentoxide (P_2O_5) and calcium oxide (CaO) in principal component 1 is large, while the weight of silicon dioxide (SiO_2) is small; It is not difficult to find that the weight of alumina (Al_2O_3) and silicon dioxide (SiO_2) is larger, and the weight of lead oxide (PbO) and barium oxide (BaO) is much smaller by comparing the main component 2 with the main component 1[8].

Combined with the thermodynamic diagram and formula, it can be obtained that the larger the value of F_1 is, the more characteristic the glass sample has of lead barium glass; The larger the value of F_2, the more characteristic the glass sample has of high potassium glass. F_1 and F_2 correspond to principal components 1 and 2 respectively. Therefore, under this condition, the rule can be drawn as follows: under weathering conditions, the samples containing more silicon dioxide (SiO_2) and less lead oxide (PbO) and barium oxide (BaO) are high potassium glasses; The samples containing more lead oxide (PbO) and phosphorus pentoxide (P_2O_5) and silicon dioxide (SiO_2) are lead barium glasses.

4.1. Select appropriate chemical components for classification

The glass samples are divided into four categories: high potassium weathering, high potassium weathering, lead barium weathering and lead barium weathering. Next, we will first use silica (SiO_2) to classify the glass samples that are not weathered with high potassium.[9] The results are shown in Figure 7.

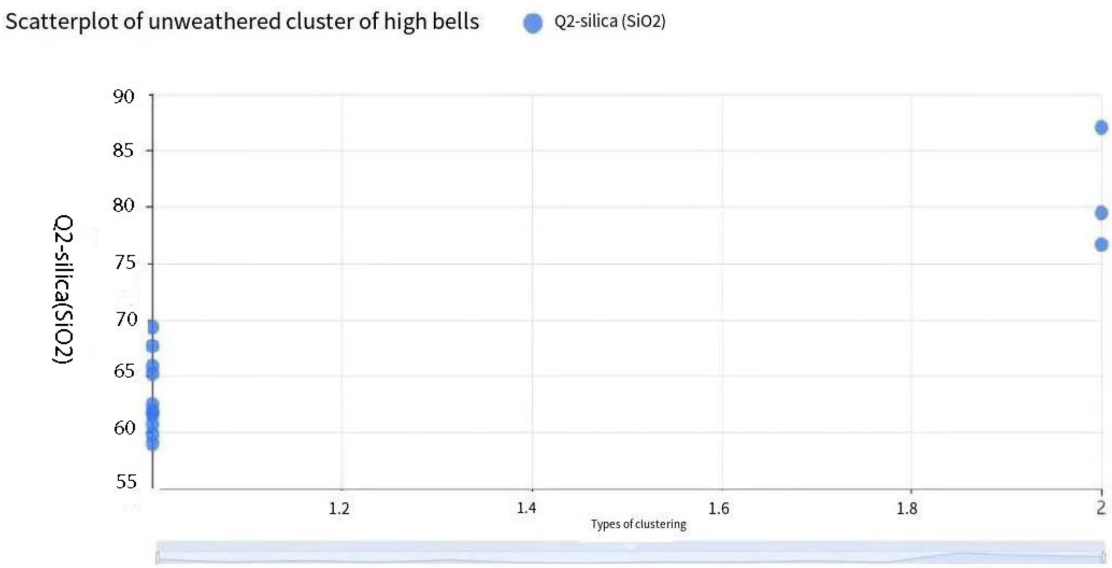

Fig 7 Scatter plot of high potassium unweathered cluster

Silica (SiO_2) divides the high potassium fresh glass into two clusters. Cluster I has eleven sample points, and their distribution interval is roughly [58,70]. Cluster II has three sample points, and their distribution interval is roughly [76,87].

Use calcium oxide (CaO) to classify the high potassium weathered glass samples, and the results are shown in Fig 8.

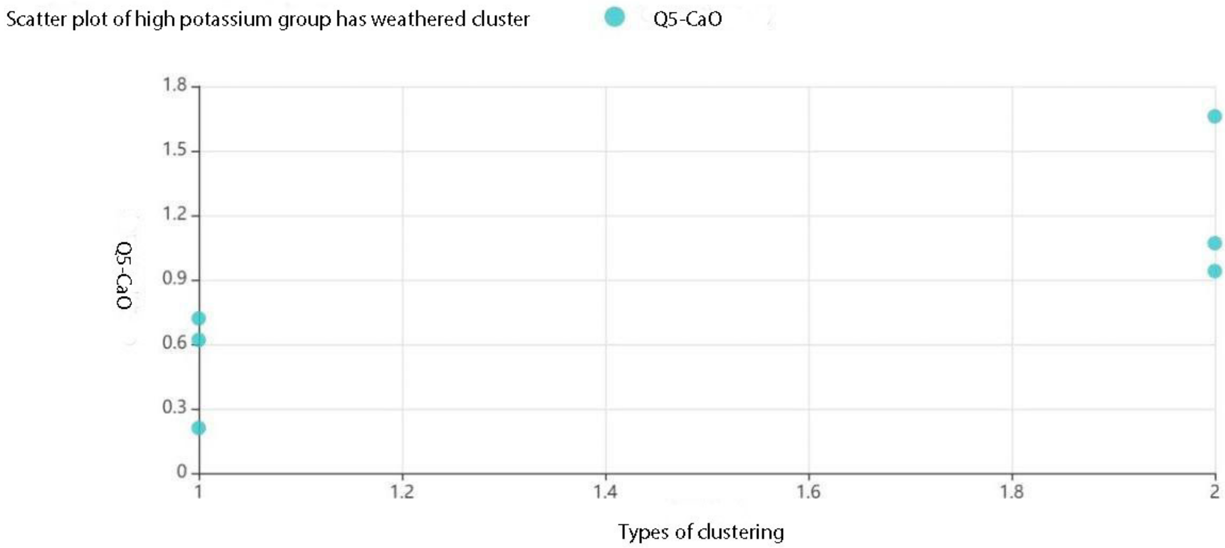

Figure8 Scatter diagram of high potassium weathered cluster (1)

Calcium oxide (CaO) divides the high potassium weathered glass into two clusters. Cluster I has three sample points, and their distribution interval is roughly [0.2,0.75]. Cluster II also has three sample points, and their distribution interval is roughly [0.9,1.7].

The aluminum oxide (Al_2O_3) is used to classify the high potassium weathered glass samples, and the results are shown in Figure 9.

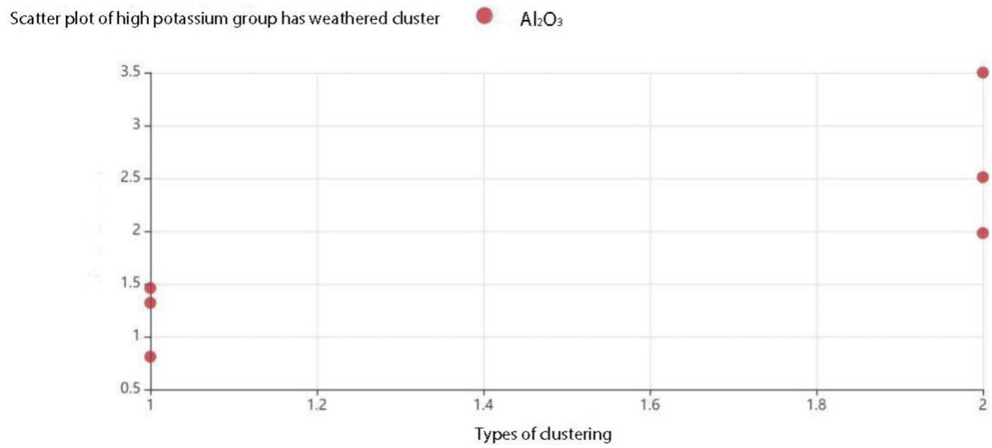

Figure 9 Scatter diagram of high potassium weathered cluster (2)

Alumina (Al_2O_3) divides the high potassium weathered glass into two clusters. Cluster 1 has three sample points, and their distribution interval is approximately [0.8,1.5]. Cluster 2 also has three sample points, and their distribution interval is approximately [2,3.5].

Use silica (SiO_2) to classify the high potassium weathered glass samples, and the results are shown in Fig 10.

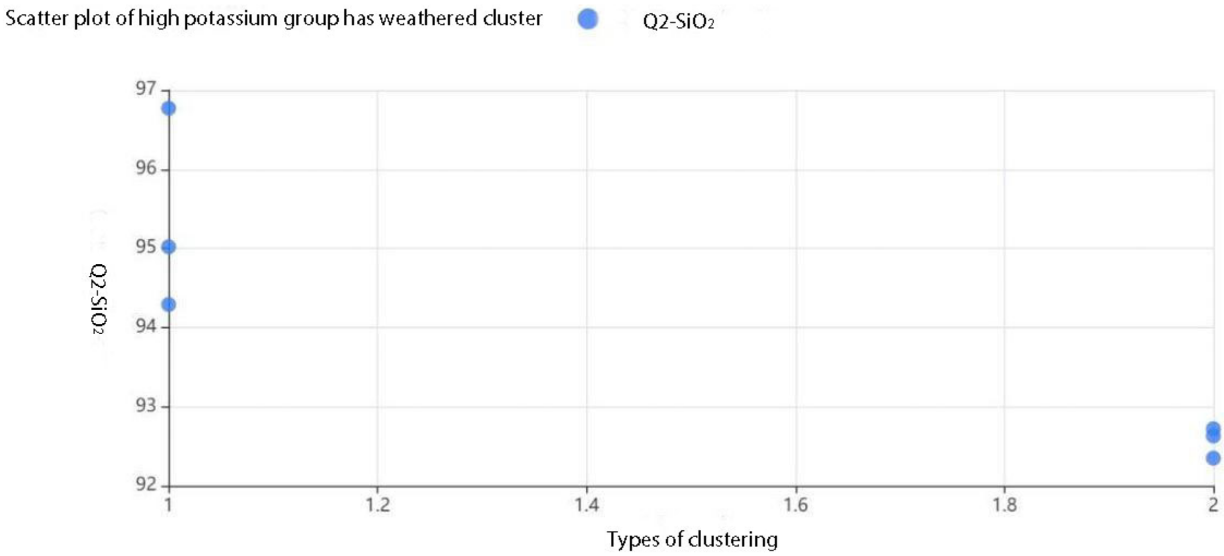

Figure 10 Scatter diagram of high potassium weathered cluster (3)

Silica (SiO_2) divides the high potassium weathered glass into two clusters[10]. Cluster I has three sample points, and their distribution interval is roughly [94,97]. Cluster II also has three sample points, and their distribution interval is roughly [92.93].

Use barium oxide (BaO) to classify the fresh lead barium glass samples, and the results are shown in Fig 11.

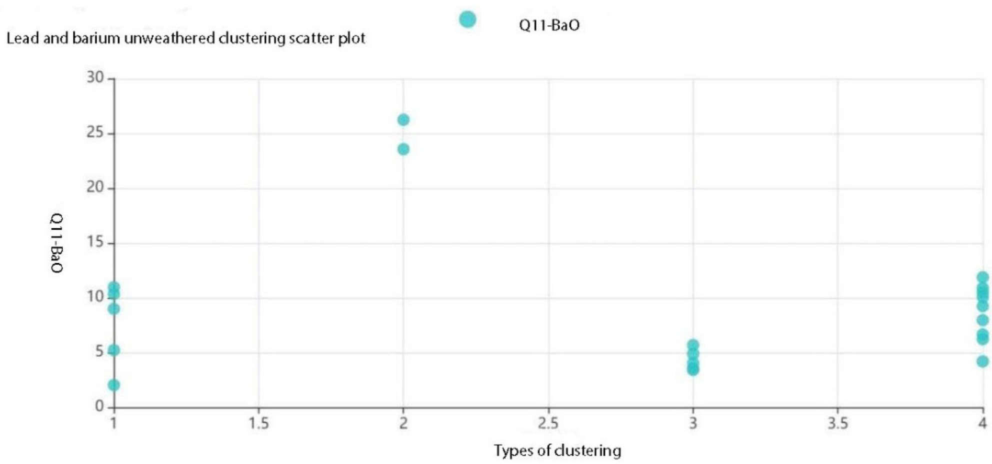

Figure 11 Lead and barium unweathered clustering scatter diagram (1)

5. Conclusion

In this paper, the composition and identification of glass products have been studied in depth, and the interaction of multiple variables, such as glass type, color, texture, weathering, chemical composition content, has been comprehensively considered, which has certain reference significance for the detection of material composition and category in real life. For example, when testing the year, composition and category of wine, we can learn from the methods and models in this paper to summarize certain rules and find the optimal method, which can improve the speed and accuracy of detection to a certain extent.

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