Neutron activation analysis of bulk samples from Chinese ancient porcelain to provenance research

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Abstract Neutron activation analysis (NAA) is an important technique to determine the provenance of ancient ceramics. The most common technique used for preparing ancient samples for NAA is to grind them into a powder and then encapsulate them before neutron irradiation. Unfortunately, ceramic materials are typically very hard making it a challenge to grind them into a powder. In this study we utilize bulk porcelain samples cut from ancient shards. The bulk samples are irradiated by neutrons alongside samples that have been conventionally ground into a powder. The NAA for both the bulk samples and powders are compared and shown to provide equivalent information regarding their chemical composition. Also, the multivariate statistical have been employed to the analysis data for check the consistency. The findings suggest that NAA results are less dependent on the state of the porcelain sample, and thus bulk samples cut from shards may be used to effectively determine their provenance.

Introduction

Studies on of ancient ceramics are strenuous challenging for their because of the great variety, widespread distribution and complex chemical composition of shards excavated [1]. It is widely believed that the procedure of sample preparation, whatever whether standard samples or specimens to be investigated, do affects data veracity and reliability when determining the chemical composition of the ceramic sample. In general, samples for NAA are always ground into powders before analyzing in the reactor. However, it is difficult to grind highly-fired ceramic samples into fine, homogeneous grains. Experimental errors resulting from contamination during the process of sample preparation, both complicated and time consuming, are also likely to occur. In addition, samples in powdery state are often prone to be scattered during the

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Table 1 Elements values of samples from different areas (ppm)

Elements	La	Lu	Nd	Sm	U	Yb
M48-1 powders	45.13	0.51	39.83	7.15	3.54	3.30
M48-2 powders	47.40	0.53	39.92	7.47	4.45	3.30
M48-3 powders	47.87	0.50	38.62	7.63	3.76	3.37
M48-4 powders	46.08	0.52	38.15	7.42	4.66	3.35
M48-5 powders	47.55	0.54	38.84	7.70	5.06	3.39
M48-1 bulks	46.70	0.51	36.98	7.46	3.64	3.35
M48-2 bulks	48.14	0.54	38.04	7.68	4.27	3.33
M48-3 bulks	49.50	0.53	39.06	7.95	4.06	3.50
M48-4 bulks	47.35	0.53	39.30	7.62	4.02	3.44
M48-5 bulks	44.95	0.53	39.56	7.32	4.44	3.50
RZ1 powders	62.69	0.67	53.52	10.98	5.17	4.44
RZ2 powders	57.72	0.63	47.20	9.93	5.15	4.14
RZ4 powders	56.15	0.57	46.20	9.48	4.73	3.64
RZ5 powders	62.78	0.73	49.17	10.71	6.97	4.62
RZ6 powders	52.32	0.57	45.38	9.18	4.24	3.70
RZ7 powders	58.93	0.54	45.65	9.58	4.71	3.74
RZ8 powders	62.13	0.64	53.57	11.14	5.09	4.24
RZ9 powders	60.14	0.63	48.52	10.74	4.54	4.09
RZ10 powders	52.01	0.51	40.93	8.34	3.42	3.34
RZ1 bulks	61.70	0.65	51.04	10.57	5.03	4.23
RZ2 bulks	59.33	0.64	50.29	10.32	4.85	4.21
RZ4 bulks	56.12	0.58	47.25	9.58	4.97	3.72
RZ5 bulks	63.20	0.73	50.70	10.85	6.95	4.64
RZ6 bulks	53.61	0.57	45.51	9.44	4.25	3.67
RZ7 bulks	59.14	0.58	48.68	9.76	4.0	3.78
RZ8 bulks	62.06	0.63	52.51	11.06	5.15	4.18
RZ9 bulks	57.67	0.59	50.84	10.31	4.46	3.89
RZ10 bulks	52.07	0.50	44.20	8.41	3.82	3.42

Elements	Ce	Co	Cr	Cs	Eu	Fe
M48-1 powders	85.50	8.45	78.30	9.24	1.41	27235.19
M48-2 powders	89.61	8.71	76.89	9.56	1.45	26973.72
M48-3 powders	90.03	9.46	84.62	10.28	1.54	28623.64
M48-4 powders	88.70	8.69	78.53	9.44	1.47	27342.90
M48-5 powders	90.95	9.45	79.09	9.43	1.49	29627.64
M48-1 bulks	88.72	8.71	80.90	9.61	1.44	27124.06
M48-2 bulks	91.21	8.68	78.67	9.61	1.52	27385.72
M48-3 bulks	93.24	9.78	92.81	10.55	1.57	30301.24
M48-4 bulks	91.14	8.32	78.59	9.60	1.46	25787.38
M48-5 bulks	88.31	8.68	74.27	9.21	1.42	26677.72
RZ1 powders	119.23	8.47	56.19	9.05	2.11	20921.40
RZ2 powders	113.54	9.54	56.24	8.84	1.86	22247.67
RZ4 powders	112.05	8.55	81.32	12.66	2.02	20381.82
RZ5 powders	126.72	8.58	69.96	12.51	1.74	19027.76
RZ6 powders	103.59	8.48	50.09	10.99	2.00	26051.30
RZ7 powders	119.62	9.30	50.55	10.72	2.18	23355.03
RZ8 powders	117.30	7.36	52.57	13.92	1.94	18819.82
RZ9 powders	116.46	8.19	49.72	14.10	2.21	21334.61

Table 1 continued

Elements	Ce	Co	Cr	Cs	Eu	Fe
RZ10 powders	98.31	10.35	85.44	19.64	1.54	22952.03
RZ1 bulks	115.58	7.79	56.85	9.30	2.02	18440.74
RZ2 bulks	116.86	11.29	57.89	8.93	1.92	20846.83
RZ4 bulks	113.61	8.84	74.13	12.94	2.03	20591.82
RZ5 bulks	129.06	8.87	70.34	12.74	1.77	18580.61
RZ6 bulks	107.48	8.39	50.64	11.17	2.07	25690.06
RZ7 bulks	121.37	9.52	51.76	11.05	2.23	23647.17
RZ8 bulks	120.06	7.44	57.93	14.48	1.96	18491.96
RZ9 bulks	113.50	8.09	47.03	13.65	2.15	20408.54
RZ10 bulks	99.23	11.33	84.89	20.07	1.52	22140.94

Elements	Hf	Rb	Sb	Sc	Ta	Tb
M48-1 powders	8.88	113.13	1.25	13.14	1.50	0.94
M48-2 powders	9.05	114.77	1.24	13.27	1.45	0.97
M48-3 powders	8.75	117.44	1.20	14.19	1.58	1.04
M48-4 powders	9.24	113.13	1.27	13.32	1.48	1.02
M48-5 powders	9.11	111.75	1.23	13.37	1.50	0.97
M48-1 bulks	9.36	113.84	1.28	13.60	1.56	0.94
M48-2 bulks	9.51	119.72	1.32	13.50	1.53	1.03
M48-3 bulks	8.96	120.59	1.37	14.84	1.60	1.04
M48-4 bulks	9.32	117.56	1.27	13.45	1.53	1.00
M48-5 bulks	8.31	111.39	1.20	12.71	1.38	0.90
RZ1 powders	10.15	134.26	1.14	12.22	1.67	1.39
RZ2 powders	10.21	125.21	1.13	12.16	1.73	1.41
RZ4 powders	7.83	129.53	1.02	15.10	1.52	1.28
RZ5 powders	8.26	150.11	1.05	15.45	1.95	1.44
RZ6 powders	9.08	118.22	1.15	13.51	1.48	1.17
RZ7 powders	9.43	135.78	1.18	12.04	1.59	1.16
RZ8 powders	8.95	152.38	1.11	13.74	1.69	1.39
RZ9 powders	8.84	154.64	1.22	14.53	1.57	1.37
RZ10 powders	7.30	135.80	2.28	15.32	1.54	1.03
RZ1 bulks	9.78	135.55	1.13	12.45	1.71	1.34
RZ2 bulks	10.43	127.75	1.11	12.40	1.76	1.37
RZ4 bulks	7.98	132.25	0.98	15.24	1.54	1.26
RZ5 bulks	8.35	153.38	1.05	15.65	1.98	1.50
RZ6 bulks	9.16	123.84	1.10	13.85	1.55	1.22
RZ7 bulks	9.40	140.51	1.19	12.26	1.67	1.27
RZ8 bulks	9.19	158.18	1.17	14.00	1.70	1.40
RZ9 bulks	8.55	149.06	1.22	14.03	1.52	1.34
RZ10 bulks	7.39	138.42	2.26	15.35	1.57	1.11

Elements	Th	Zn	Zr
M48-1 powders	15.62	56.66	270.72
M48-2 powders	15.53	64.93	245.24
M48-3 powders	15.97	64.88	253.56
M48-4 powders	15.79	62.17	273.89
M48-5 powders	16.20	61.10	274.75

Table 1 continued

Elements	Th	Zn	Zr
M48-1 bulks	16.07	58.20	284.18
M48-2 bulks	16.11	60.83	319.95
M48-3 bulks	16.71	64.46	283.66
M48-4 bulks	16.02	56.01	294.72
M48-5 bulks	15.30	63.45	241.74
RZ1 powders	17.57	64.67	309.33
RZ2 powders	18.32	60.86	297.28
RZ4 powders	17.61	74.26	256.93
RZ5 powders	22.30	89.88	292.29
RZ6 powders	16.68	52.38	304.34
RZ7 powders	15.80	51.84	306.77
RZ8 powders	19.13	72.75	305.68
RZ9 powders	17.99	69.78	288.16
RZ10 powders	16.27	69.36	226.68
RZ1 bulks	17.77	65.39	332.70
RZ2 bulks	18.51	63.12	324.08
RZ4 bulks	17.91	74.58	288.77
RZ5 bulks	22.65	90.24	257.96
RZ6 bulks	17.29	54.94	310.67
RZ7 bulks	16.07	53.09	314.41
RZ8 bulks	19.63	68.15	290.91
RZ9 bulks	17.52	65.46	282.16
RZ10 bulks	16.42	74.51	216.88

process of sample preparation and measurement, thus resulting to the increase the waste of samples that are precious and nonrenewable. Consequently, it is necessary to control the procedure of sample preparation to avoid contamination and reduce specimen consumption. If measurement can be carried out on bulk samples directly, it will be promising for the reduction of specimen cost and improvement of data accuracy if powder grinding is not needed during sample preparation.

In 1991, Bode and Overwater [2] described challenges associated with neutron activation analysis (NAA) of kilogram-sized samples at the 8th International Conference on Modern Trends in Activation Analysis (Vienna, 1991). After years of development, the large sample neutron activation analysis (LSNAA) theory and technique improved greatly [3–5]. Most of the majority of the LSNAA development work for archaeological research has been focused on scanning the entire geometry of sample with the purpose of determining the heterogeneity of the sample structure. But there is a need to also study the provenance of cultural relics. By understanding the provenance of samples obtained from a given site, it is possible to obtain clues about the culture and migration patterns of ancient humans which is the really usage of the chemical analysis. In this work, we report the results from a NAA study using multivariate statistical method for comparing bulk and powder samples. Samples were taken from ancient archeological shards and the chemical compositional results used to verify the shards provenance and infer cultural implication.

Normally, porcelain is defined as having a body made of Kaolin, or porcelain clay, that was fired at above high temperature (around 1,200 °C). The glaze on the surface of the porcelain body usually formed at temperatures around 1,100 °C, in contrast to the pottery body, which had no glaze or a low-fired glaze. Before the production the mature high-fired glazed porcelain (celadon), there was a transitional period from Shang (c. 1700–1027 BC) to Han Dynasty (206 BC–220 AD), during which the so called proto-porcelain or proto-celadon products fired at a temperature higher than that for pottery but with low body qualities manufactured in rough handcrafts [6]. However, scholars have never reached an agreement so far on the provenance of those kind of shreds excavated in the sites located in North China. Many scholars [7, 8] claimed that proto-porcelain wares excavated in North China were produced in South China and exchanged to the North. On the other hand, other scholars [9, 10] believed that proto-porcelain in North China may have its own origin and produce in locale area. In this paper, a total of 25 proto-celadon shards of Han Dynasty (206 BC–220 AD) from both Southern and Northern China were selected for analysis, and each shard was sampled separately into bulk and powder state respectively, thus making all samples fall into two groups noted as group A (powder group) and group B (bulk group). This novel method we bring about for sample preparation seems promising for NAA experiments.

Materials and methods

Site description

Haiqu Han Cemetery, in Rizhao city Shandong province, which is the best preserved cemetery so far, locates in a low upland about 1 km away from southwest of Shilibao country of Rizhao, Shandong. The northern portion of this site is approximately 1 km from Haiqu Town of Han Dynasty. In 2002, Archaeology Institute of Shandong Province initiated a rescue excavation in this area in order to cooperate with the construction of freeway by the government. More than 240 skillfully manufactured proto-porcelain shreds, most of which were believed to be from middle to late Han Dynasty according to the ware styles and grave structures, were excavated in this site. It is widely deemed that the earliest provenance of northern China porcelain much later than Han dynasty. Given the history of the site, these ceramics shreds are thought to be crucial in the provenance study. In this aim, shards from the Haiqu site were select to determine the

Fig. 1 PCA analysis of ceramics elements of bulk samples (*filled symbols*) and powder samples (*open symbols*) by NAA
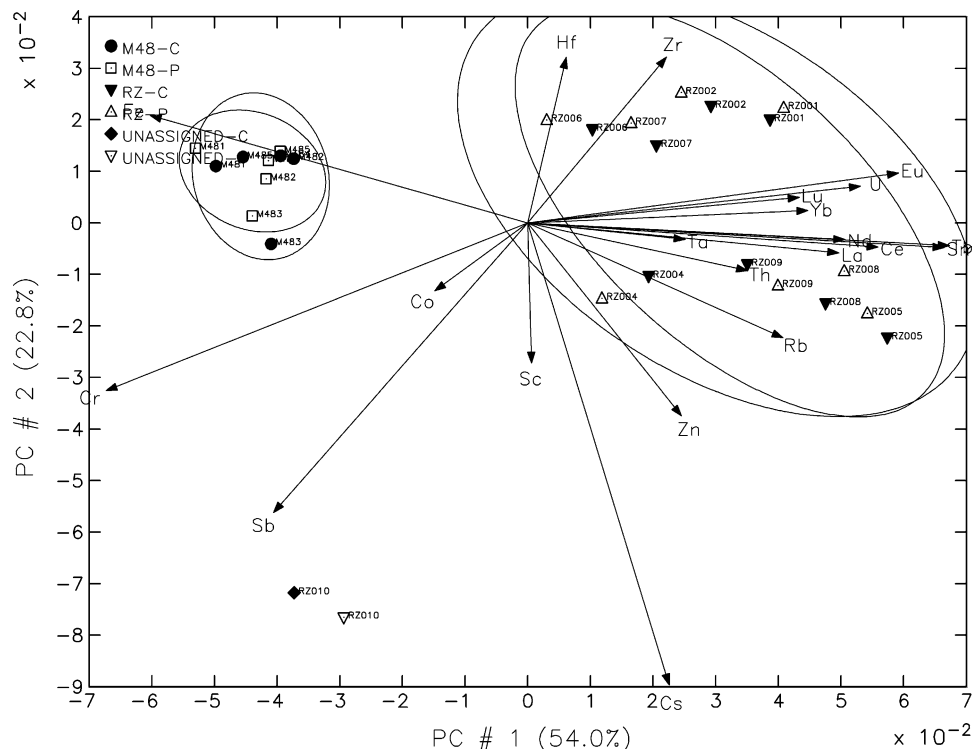
chemical compositions, and comparative the samples from Southern China in same period to study its provenance. Among all the shreds, nine pieces were from Haiqu site (given ID: RZ), and six pieces were from Xiaolongjing site (given ID: M48), in Zhejiang province, in Southern China.

Sample preparation

Samples were cut into cubes by $1 \times 1 \times 1$ cm^3, whose surface layer and glaze were then removed using a diamond drill. After that they were placed into deionized water and cleaned with a brush. Then we rinsed them using a ultrasonic cleaner with pure alcohol solution, aiming at eliminating pollution arising from burial environment. Each purified sample (~ 1.0 g) was sliced into part A, which was ground into fine powder in an agate mortar, and part B that was diced coarsely. Archival portions were retained from each specimen for future research.

Neutron activation analysis

Measurements were undertaken in the reactor of University of Missouri (USA) using instrumental neutron activation analysis (INAA). Neutron activation analysis at MURR, which consists of two irradiations and three gamma counts, constitutes a superset of the procedures used at most NAA laboratories [11]. Ceramic specimens were analyzed together with two standard samples SRM-278 (Obsidian Rock) and Ohio Red Clay (a standard developed for in-house

applications) in order to control the determinate quality of the samples. Concentrations of a total of 24 elements were obtained in our experiment while results of only 21 among them (La, Lu, Nd, Sm, U, Yb, Ce, Co, Cr, Cs, Eu, Fe, Hf, Rb, Sb, Sc, Ta, Tb, Th, Zn and Zr) were employed for statistical analysis because of the high standard errors and/ or low concentrations of the rest.

Results and discussion

The experiment result

The results of the NAA measurements are shown on the Table 1. Under intuitive observations, the most elements of samples with different status were pretty close to each other and indicate that the status of samples, powder or bulk status, are not have strong affection to the NAA testing obviously.

Multivariate statistical analysis

Geochemical methods for provenance research usually generate vast amounts of data, which often show a high degree of correlation among various elements and generally require simplicity by multivariate statistical methods to summarize the compositional information. To obtain further insights into the origins of artifacts, compositional groups of samples with specific provenances should be defined on purpose of comparing with the unknown artifacts.
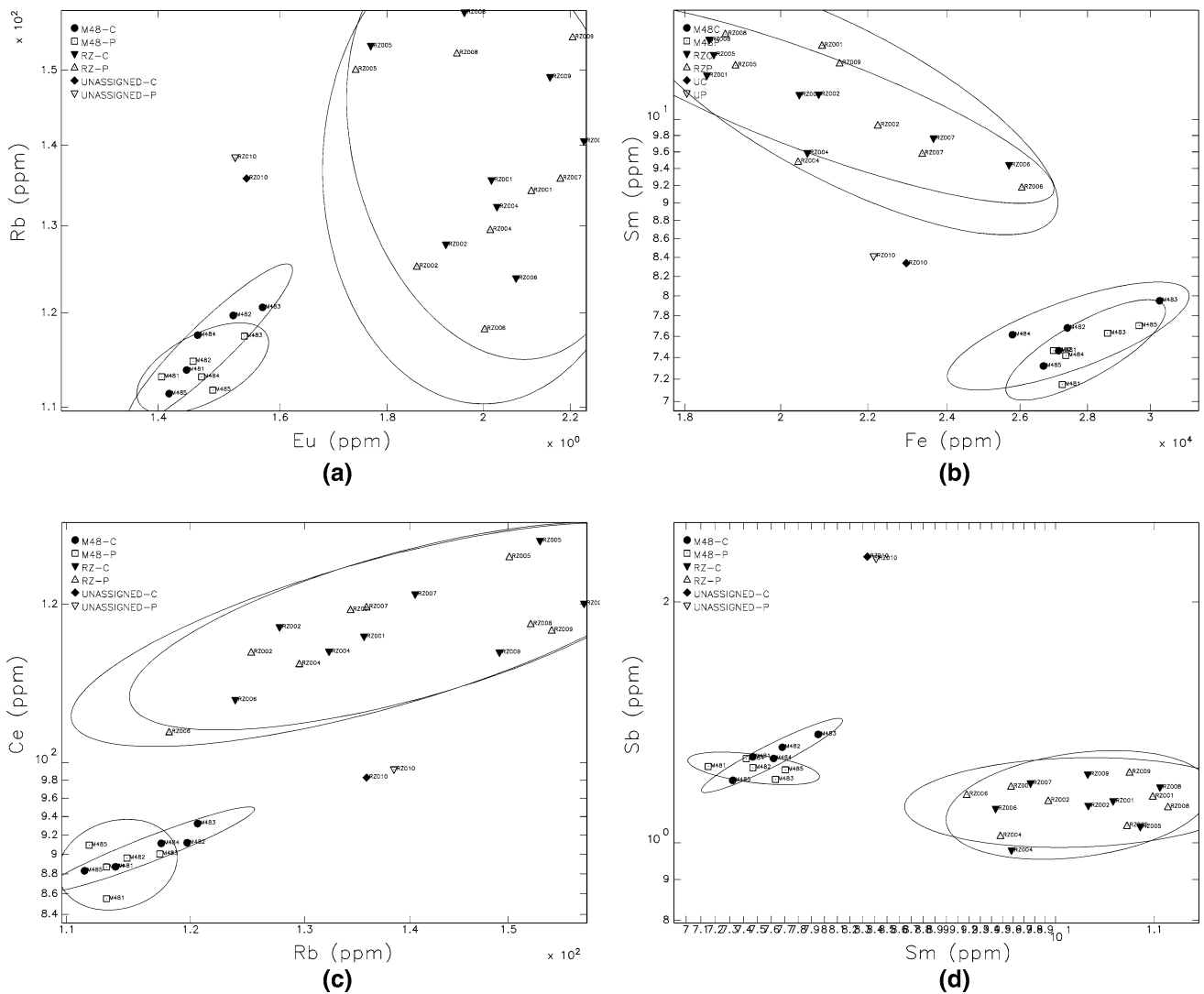
Fig. 2 Results of Cr/Eu, Sm/Fe, Co/La, and Sb/Sm ratios

In this study, principal components analysis (PCA) was employed to convert the original variables to a set of uncorrelated principal component (PC) scores in multi-dimensional Mahalanobis space. In this new space, each sample is designated as a point, and samples with similar compositions will group together on plots while those with dissimilar compositions will lie separate from one another. The task of data processing and graphics generating were carried out using the special multivariate software called GAUSS developed by researchers of MURR [12].

PCA results are shown on the Fig. 1. The first two principal components, which contain most information, can serve to explain 76.8 % of the total square deviations, suggesting that final results can be represented by PCA.

Ceramics from different areas fall into distinct groups, illustrating different elements features of diverse areas. In the confidence level of 90 %, samples can be divided into

different groups. The first group with high Fe, Cr, Co, Sb and low U, Rb, Zn and most of rare-earth elements concentration is from Southern China (group ID: M48). While samples from Rizhao site in another group contain high concentrations of rare-earth elements as well as Cs and Zr and low contents of Fe, Cr, Co and Sb (group ID: RZ).

To all appearances, products from different areas can be distinguished by content of metallic impurities and rare-earth elements. Generally, minerals with high content of Fe and Cr, like chromites and rubies, are probable to gather transition metals such as Sc, Zn, Cr, rather than rare-earth elements. In addition, fine procession like elutriation will reduce content of metallic impurities but have nothing to do with rare-earth elements that are undissolving. It is obvious that ceramics from northern China are rich in Fe, Co, and several transition elements including Sc, Zn, and Cr, which may concern beneficiation of minerals,

indicating the rough process of manufacture of ceramics there. On the contrary, southern shards display lower content of metallic impurities, rare-earth elements, as well as some trace elements like Sb, Cs, and Zn.

Ceramic products from Rizhao site have a wider distribution than those from southern China areas, and their low content of metallic impurities and good quality of products can be evidences of their high rank status. It is important to notice that their trace elements characteristics are totally distinct from the southern ones, implying that proto-porcelain excavated in Rizhao site were not manufactured in the south and then exchange to here. Generally, ancient ceramic wares were manufactured with local raw materials reflecting unique geochemical features there, thus making products from different areas display distinct elemental characters. Although the specific provenance of Rizhao site samples is difficult to know for the lack of geological background information, it can be still assured that proto-porcelain shards from Rizhao site have an independent source based on the totally different elements characters.

According to our results of samples in different states, it is suggested that no obvious distinctions appear as sample state varies, indicating that bulk samples could be measured by NAA methods directly without the need of grinding procedure, thus reducing the cost and contaminated risks of precious artifacts and decreasing the workload for sample preparation.

Trace elements features

As a kind of multivariate statistical analysis, PCA method is not so powerful to provide detail elemental distinctions of samples although it has been widely employed in provenance study. Consequently, biplot are also used give an intuitive characterization picture. Figure 2a–d shows ratios results of values of Rb/Eu, Sm/Fe, Ce/Rb, and Sb/Sm which present diversity of the rare-earth and metallic element contained in samples. Most of samples could separated to each groups according with the production area then supported the PCA estimation via the individual elements concentration.

Conclusion

In this paper, NAA measurements were carried out on ancient proto-porcelain samples both in bulk and powder states followed by elements biplot and multivariate statistical analysis. Conclusions drawn from the paper are as followings:

First, NAA results of bulk samples are in accordance with those of powder ones, and status of samples has nothing to do with the PCA results, implying that our method for sample preparation provides a novel approach that is promising applicant to ancient ceramic samples.

Second, celadon shreds from different areas can be distinguished by element contents of metallic impurities and rare-earth elements. For northern products, contents of metallic impurities are usually high, and features of rare earth elements as well as some other trace elements (Cr, Fe, and Sb etc.) are also distinct from those from the south, although they share similar appearances. This may suggest that the producing provenance of ceramics of Rizhao site was not trade or exchanged from Southern China.

References

1. Glascock MD (1992) Ceramic at MURR by neutron activation analysis and multivariate statistics. In: Neff H (ed) Chemical characterization of ceramic pastes in archaeology. Prehistory Press, Madison, WI, pp 11–26
2. Bode P, Overwater RMW (1993) J Radioanal Nucl Chem 167:169
3. Stamatelatos IE et al (2010) Large sample neutron activation analysis of a ceramic vase. J Radioanal Nucl Chem 283:735–740
4. Bedregal PS et al (2012) Neutron activation analysis of archaeological artifacts using the conventional relative method: a realistic approach for analysis of large samples. J Radioanal Nucl Chem 291:37–42
5. Tzika F et al (2007) Neutron activation analysis of large volume samples: the influence of inhomogeneity. J Radioanal Nucl Chem 271:233–240
6. Wang CS, Zhu J (2009) The provenance of ancient Chinese proto-celadon, The forth Forbes symposium-scientific research on historic Asian ceramics. Archetype Publications, London, pp 69–76
7. Li JZ (1998) History of Chinese science and technology (ceramics). Science Press, Beijing, pp 11–12
8. Chen TM, Rapp JG, Jing ZC (2003) Instrumental neutron activation analysis of chinese proto-celadon and some discussion. Archaeology 7:69–78
9. Zhu J et al (2010) Technology and provenance of proto-porcelain of Yingguo Graveyard in Henan province. Spectrosc Spectr Anal 30(7):1990–1994
10. Wang CS, Zhu J, Zhu TQ (2006) Enlightenment from provenance study of protoporcelain, China cultural relic news
11. Glascock MD (1992) Characterization of archaeological ceramics at MURR by neutron activation analysis and multivariate statistics. In: Neff H (ed) Chapter in chemical characterization of ceramic pastes in archaeology. Prehistory Press, Madison, WI, pp 11–26
12. Glascock MD, Neff H (2003) Neutron activation analysis and provenance research in archaeology. Meas Sci Technol 14:1516–1526