Investigation of trace elements in Guangxi ancient pottery by INAA*

Peng Zi-Cheng[1], Sun Wei-Dong[1], Huang Yun-Lan[2],
([1] *Department of Earth and Space Science,* [2] *Structure Research Laboratory, University of Science and Technology of China, Hefei 230026*)
Satoshi Koshimizu, Kenji Tomura, Minoru Suzuki,
(*Yamanashi Research Institute of Cultural Properties, Japan*)
Jiang Tin-Yu and Chen Wen
(*The Museum of Guangxi Zhuang Nationality Autonomous Region, Nanning 530022*)

Abstract Guangxi Zhuang Nationality Autonomous Region is an original place for manufacture of ancient pottery in China since Zenpiyan site, dated 9240-10370 years ago, was excavated. Contents of trace elements La, Ce, Nd, Sm, Eu, Tb, Yb, Lu, U, Th, Sc, Ta, Ba, Cs, Rb, Sr and Zr in 44 porttery shards from Guangxi sites, dated from 1450 B.C. to 200 A.D., were determined by INAA and XRF. The proveniences of the 44 samples are postulated by the analyses of geochemical parameters.

Keywords INAA, Ancient pottery, Provenience postulation, Rare earths

1 Introduction

Since Ambrosino (1953) first reported their researches on analyzing archaeological materials by means of nuclear methods, more and more workers[1] have widely made a series of studies on instrumental neutron activation analysis (INAA) of ancient objects including glass, metal, ceramics, stone and mineral products. With regard to INAA studies on Chinese ancient ceramics, Li[2] determined the contents of more than 20 elements in Longquan, Cizhou, Yaozhou, Yuezhou and Jizhou wares and found that the rare-earth elements (REE) patterns and the Th/U and Hf/Ta ratios could be used for recognition of producing areas . Chen *et al* [3] investigated the contents of Al, As, Ba, Ca, Co, Cr, Cs, Fe, Mn, Sc, Th, U and V in 93 shards of pottery and proto-porcelain, unearthed from Zhengzhou, Panlong Cheng, Jiangnan Shi, Tonggou Shan and Wucheng sites and inferred that all the proto-porcelain samples were produced from Wucheng site. This conclusion is in agreement with that by archaeologists.

Guangxi Zhuang Nationality Autonomous Region is located in the southern of China, where the minority nationalities live in compact communities. That area has been an original place for manufacture of the ancient pottery in China since Zenpiyan site was excavated. That site was dated 9240-10370 years ago by TL method. The chemical composition of 17 trace elements in 44 pottery shards from Guangxi sites (1450 B.C. to 200 A.D.) is reported in this paper. On the basis of the INAA data, the archaeological groups related with their proveniences are also discussed .

2 Experimental

The powders of pottery shards were irradiated together with U.S. Geological Survey standard GSP-1 and Japanese standard AGV-1 at neutron flux $5\times10^{11}\,n\cdot cm^{-2}\cdot s^{-1}$ for 24 h in a Triga Mark II reactor at the Institute for Atomic Energy, Rikkyo University.[4] The gamma ray spectrometer consisting of a coaxial Ge(Li) detector and a 4096-channel pulse height analyzer has an efficiency of 0.12 relative to 7.5 cm× 7.5 cm NaI(Tl) crystal and a resolution of 2.0 keV for 1332 keV photons of ^{60}Co. Counting was carried out for 1000 s on the seventh day and for 3000 s on the fortieth day after the end of pile bombardment. The analytical method used in this study is simple and non-destructive. The contents of the 15

*The Project Supported by the USTC-TKU Committee
Manuscript received date: 1996-07-20

trace elements including La, Ce, Nd, Sm, Eu, Tb, Yb, Lu, U, Th, Sc, Ta, Ba, Cs and Rb in the samples have been determined. The relative errors were < 0.03 for La, Ce, Sm, Sc, and Th; 0.04~0.08 for Rb, Cs and Ba; 0.10 for Eu; and 0.05~0.15 for Tb, Yb, Lu, Nd, U and Ta. The contents of trace elements Sr and Zr were measured by XRF and their errors were 0.10. The general description and the analytical results of the samples are shown in Table 1.

Table 1 The general description and the analytical results of Guangxi pottery shards

Code	Dynasty	La	Ce	Nd	Sm	Eu	Tb	Yb	Lu	U	Th	Sc	Ta	Ba	Cs	Rb	Sr	Zr	$F_1\times100$	$F_2\times100$
		/$\mu g\cdot g^{-1}$																		
P01	EH	30.4	49.1	16.9	3.62	0.95	0.62	4. 13	0.73	7.19	33.2	13.9	2.51	106.3	13.9	98	39	314	2.29087	-2.64235
P02	EH	31.1	50.3	N.D.	4.01	1.04	0.79	2.96	0.45	4.25	9.11	10.2	1.38	97.6	12	88	40	265	1.25295	-2.48419
P03	EH	38.1	58.3	47.5	4.72	1.19	0.75	3.43	0.49	11	43.5	14.2	2.31	131.1	27.3	163	32	264	2.02487	1.4461
P04	EH	34.9	55.7	17.7	4.08	1.22	0.64	3.69	0.44	7.25	26.2	15.6	1.48	83.1	10.2	74	20	284	3.49204	-3.04697
P05	EH	29.8	50.0	31.5	3.06	0.54	0.46	2.91	0.43	5.06	20.8	12.2	1.31	111.8	12.0	80	41	300	1.81176	-3.03124
P06	EH	27.0	51.6	24.3	4.08	1.18	0.53	2.99	0.48	4.38	19.0	8.21	1.06	64.9	8.14	51	28	255	2.45692	-4.19174
P07	EH	30.4	49.8	13.2	3.99	0.52	0.69	3.48	0.52	8.15	26.6	12.6	2.10	117.7	18.0	104	30	317	2.88912	-2.03577
P08	EH	36.6	62.5	21.0	4.81	0.69	0.86	3.83	0.50	6.00	24.4	12.4	1.70	74.1	14.5	94	33	329	2.98524	-3.91812
P09	EH	45.0	67.2	36.3	5.97	1.12	1.00	4.12	0.49	12.5	39.7	14.8	2.24	79.4	23.7	116	29	220	1.91431	.10065
P10	EH	36.9	61.0	17.0	3.96	1.32	0.77	3.29	0.53	6.05	27.2	11.2	1.83	103.9	19.8	123	46	301	1.46204	-1.81466
P11	EH	38.2	63.1	N.D.	4.53	1.46	0.70	3.07	0.53	7.08	27.2	12.2	1.94	113.3	22.2	133	38	276	1.66809	-.47876
P12	EH	40.0	64.4	28.8	5.09.	1.22	0.82	3.57	0.52	7.30	27.4	12.9	1.99	112.4	20.2	118	37	293	2.02352	-1.33199
P16	EH	40.7	65.2	49.5	5.06	1.36	1.13	4.00	0.51	9.29	34.7	16.7	2.20	78.7	14.1	87	20	266	3.32007	-2.06369
P17	EH	28.8	47.5	17.2	3.51	0.89	0.60	3.15	0.41	5.57	24.6	12.2	1.55	82.8	13.8	73	33	353	3.33904	-4.90143
P21	EH	36.2	60.2	19.7	4.08	1.34	0.68	3.41	0.51	6.13	20.1	13.0	1.54	110.8	16.1	110	48	334	1.71059	-2.93066
P22	EH	31.3	58.8	33.4	3.98	1.20	0.57	3.38	0.48	6.35	30.4	13.5	1.89	82.3	12.2	84	33	332	3.08598	-4.04398
P18	WE	37.3	56.8	18.5	4.20	1.27	0.99	3.95	0.52	8.95	37.8	16.4	2.07	109.4	18.3	119	40	264	1.52580	-.64654
P19	WE	35.0	54.9	24.4	4.24	1.03	0.85	3.39	0.49	8.29	31.9	13.1	2.01	111.5	22.8	132	38	258	1.48580	-.03632
P13	WH	41.0	67.1	18.8	4.80	0.74	0.59	3.64	0.56	10.2	36.3	14.2	2.73	120.1	25.5	143	44	296	1.60978	-.44722
P14	WH	43.5	64.7	17.2	5.80	0.78	0.74	4.06	0.54	16.3	46.9	17.0	2.97	167.8	32.5	201	34	227	1.32008	4.11749
P15	WH	44.7	66.4	30.7	5.01	1.20	0.68	3.71	0.59	13.2	40.1	13.5	2.42	146.6	28.6	168	41	256	1.22472	1.89384
P20	WH	21.7	34.1	25.7	2.85	0.62	0.56	2.96	0.41	7.37	24.4	11.5	2.56	72.7	15.1	79	30	381	3.97112	-5.41980
P44	WH	46.9	88.8	20.7	5.42	1.80	0.88	3.37	0.56	3.09	18.6	22.1	1.16	175.8	20.6	204	680	174	-32.6445	-7.06580
P31	WS	36.7	57.0	22.2	4.03	0.95	0.46	2.41	0.37	2.58	16.3	21.0	0.93	115.2	21.6	141	69	99	-3.95688	3.57997
P32	WS	69.2	114	53.7	10.2	1.92	1.42	4.23	0.52	17.2	47.2	18.7	1.93	191.7	32.9	239	41	108	-.93021	8.38336
P35	WS	45.6	69.0	23.3	4.61	0.84	0.72	4.02	0.61	9.40	31.9	14.2	3.18	55.8	17.9	99	32	296	2.80366	-3.23619
P23	SW	34.2	54.4	16.3	4.06	0.45	0.85	3.68	0.55	8.34	35.2	11.7	2.43	63.7	12.7	90	39	372	3.27155	-5.18565
P24	SW	77.2	137.1	74.4	12.0	2.28	2.13	5.38	0.67	22.2	54.9	17.5	2.43	209.0	29.9	248	50	128	-1.11489	8.07451
P25	SW	66.3	127.4	66.0	12.17	4.60	2.05	7.22	0.89	13.7	34.4	15.4	1.92	174.5	22.1	289	34	238	1.10288	5.69578
P26	SW	56.6	74.9	33.3	6.72	1.36	0.84	3.79	0.65	12.8	30.5	14.7	3.37	165.7	30.0	190	43	215	.35362	3.71549
P36	SP	53.4	79.4	35.3	6.16	0.95	0.70	3.76	0.65	14.5	40.2	15.7	3.31	121.6	13.5	130	19	337	4.01251	-1.19525
P40	SP	42.4	74.6	33.8	5.99	2.01	1.40	3.51	0.39	5.09	18.2	10.5	1.30	270.7	9.60	94	54	242	-0.40205	1.95792
P41	SP	42.7	74.6	43.0	6.34	2.14	0.97	3.95	0.53	6.36	18.2	11.4	1.40	185.1	8.62	79	30	295	2.30652	-.96469
P27	NS	27.8	38.9	11.6	3.03	0.72	0.55	3.32	0.54	4.93	17.8	13.3	1.38	171.5	14.0	131	57	259	.22781	.45692
P28	NS	52.3	82.2	46.9	7.35	1.28	1.47	4.33	0.65	5.61	20.9	9.93	1.22	191.2	15.1	237	73	87	-4.13293	7.64757
P29	NS	69.7	123.4	53.5	10.8	1.56	1.99	6.91	0.93	6.86	28.5	9.06	1.82	221.7	16.4	211	105	149	-5.00066	5.05819
P30	NS	40.0	69.0	23.6	3.84	1.09	0.65	3.68	0.62	5.53	20.9	15.6	2.08	203.1	17.1	140	65	239	-1.05451	1.72150
P33	NS	15.9	33.4	N.D.	2.13	0.40	0.46	2.48	0.43	3.47	15.6	12.4	0.33	147.7	18.7	119	36	328	2.27359	-1.47238
P34	NS	14.1	22.9	9.59	1.94	0.37	0.52	2.17	0.32	3.01	15.5	13.3	0.70	112.7	14.4	121	24	101	-.25995	4.25641
P37	NS	10.3	20.3	7.63	1.91	0.37	0.51	2.44	0.36	3.75	16.6	13.7	0.61	132.1	12.6	110	16	161	1.49979	2.65551
P38	NS	46.5	98.2	38.2	7.04	2.33	1.26	4.78	0.65	6.70	32.7	17.6	1.06	73.6	18.6	127	14	164	2.14233	2.03972
P39	NS	18.7	31.1	N.D.	2.17	0.29	0.25	2.39	0.36	3.01	15.1	9.65	0.61	63.5	7.97	73	13	206	2.92192	-1.81563
P42	NS	83.6	150	44.5	11.9	2.03	1.85	8.97	1.28	9.55	44.9	13.2	2.56	286.2	17.1	201	62	376	1.03067	1.94984
P43	NS	40.1	72.0	21.7	4.70	1.54	0.65	2.98	0.36	3.46	14.6	88.7	0.70	199.7	23.8	86	126	170	-6.64208	.41925
CAV	–	.310	.808	.600	.195	.0735	.0474	.209	.0322	–	–	–	–	–	–	–	–	–	–	–

Notes: EH: Eastern Han Dynasty, WE: West-Eastern Han Dynasty, WH: Western Han Dynasty, WS: Warring States, SW: Spring- and Autumn-Warring States, SP: Spring and Autumn Period, NS: Neolithic Age, F_1 and F_2: Loading F_1 and F_2 factors of Q mode. CAV: Chondrite average value from Ref.[5]. P01~20 samples are excavated in Guigang; P44, Quanzhou Jianansi; P31, Zhongshan Baotashan; P32, Shenxi Landu; P35, Gongcheng Tongle; P23~24, 26, Hegui Sanzhen; P52, Beiliu Lianwu Tangling; P36, Fuyang Daba Shan; P40~41, Fuyang Liyushan; P27~30, 42~43, Pingnan Shijiaoshan; P33~34, 37~39, Qinzhou Duliao.

3 Results and discussion

3.1 As well known, rare earth elements (REE) all have very similarly chemical properties and always coexist in the mineral. The raw materials for preparation of ceramics, such as pottery clay and porcelain stone, are usually composed of several minerals. This makes the ancient pottery appear in different patterns of the REE composition, which is related with their original proveniences. On principle of geochemistry[5] the REE follows the even-even rule, i.e. the plot of atomic number vs the absolute content of single REE shows the sawtooth shape. It indicates that the REE patterns caused by the raw materials, will hard be recognized. But, the sawtooth shape of REE could be eliminated by the normalized treatment[5]. For our study, the chondrite normalization would be used. Table 1 shows that the total contents of eight REE are 100~200μg/g for most of the samples, while for a few samples more than

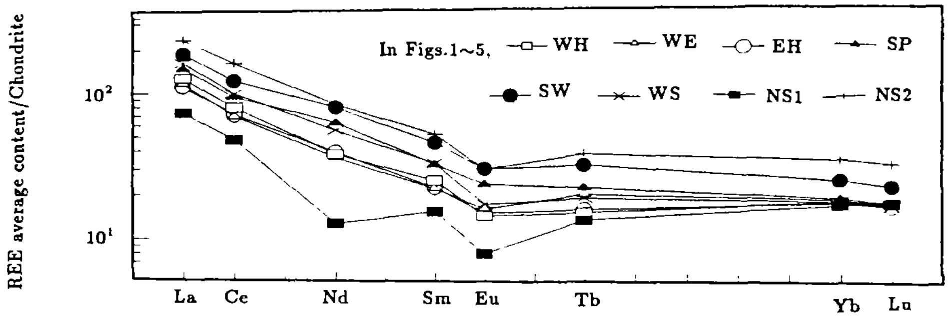

Fig.1 Atomic number of REE vs REE average content normalized by chondrite

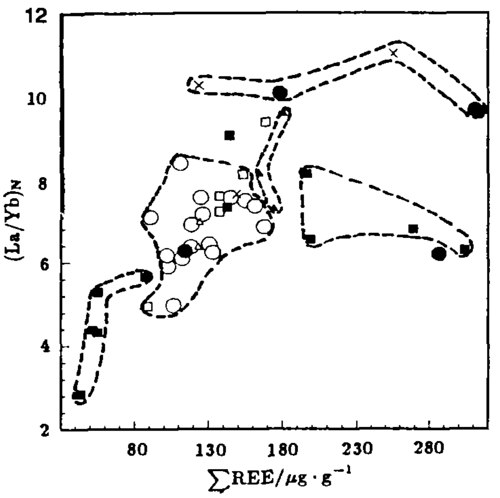

Fig.2 ΣREE vs $(La/Yb)_N$

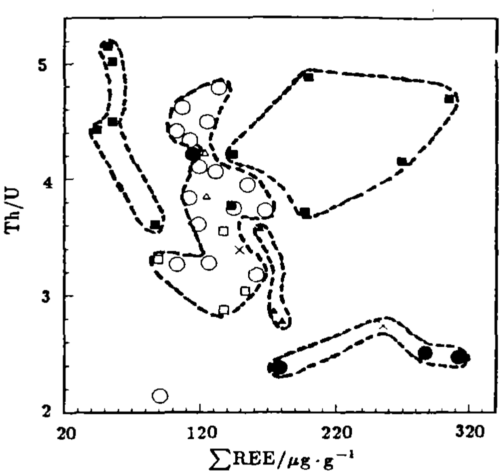

Fig.3 ΣREE vs the content ratio of Th to U

200μg/g or less than 100μg/g. In Fig.1, NS samples can be divided into two groups, NS1 and NS2, which represent high and low REE average contents, respectively. All 8 curves appear in typical, enriched-light REE patterns and Eu negative abnormality, similar to the REE patterns of the sediments. The distributive sequence of the curves from the upper to the lower is NS2→SW→SP→WS→WH→WE →EH→NS1. It implies that the raw material made for pottery, is composed of the sediments, therefore, their REE patterns are very similar. However, the materials came from various places, so that REE contents were different. The Han Dynasty samples (EH-WE-WH) were collected from one site of Guigang and the three curves are much close. The Neolithic Age samples were excavated from Qinzhou and Pingnan sites, which are far from each other, so these samples are mostly situated at two curves, NS2 and NS1. The WS, SW and SP samples were basically situated at three curves, respectively while a few points were overlapped.

3.2 The geochemical parameters of REE usually apply to the provenience postulation. $(La/Yb)_N$ vs ΣREE can be used to explain the sample's origin. Here, the subscript N means that the contents of La and Yb were normalized by those of the chondrite (see Table 1). Fig.2 shows that the samples were mainly situated in five areas, which correspond to their ages and/or origins. The Han Dynasty and Spring Autumn samples were concentrated in single area, respectively because they were excavated from single place. As described above, the NS samples were also distributed in two areas, corresponding to the high and low REE contents. The SW-WS samples were briefly located in one area, but three ones were scattered due to the seven samples are from two places far from each other. Fig.2 reflects that the statistical precision for 44 samples reaches to 0.86. Similarly, the statistical precision of the samples' points in Fig.3 does to 0.86 also.

3.3 The triangle plot (see Fig.4) of Th%, La% and Sc% can show the similar distribution of the samples. But, it is worth noticing that sample P36 was far from its SP area, because of sample P36 from Dabashan site, Fuyang county, while the other two from Liyushan site, Fuyang county. There are tens of kilometers between two sites. The statistical precision of distribution of the plotting points is 0.82. La/Sc vs Sr/Rb can also show the similar distribution of the samples. However, Sample SP44 and SP43 were out of the diagram scale. It indicates that different parameters of the trace elements will supply the diversified information for the pottery provenience study.

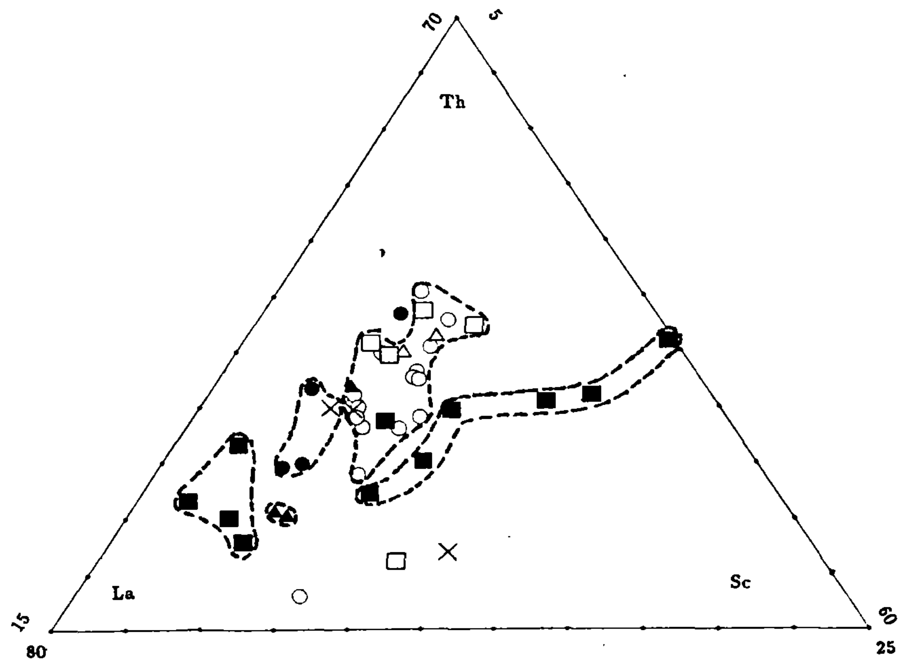

Fig.4 The triangle diagram of Th%, La%, and Sc%, where Σ(Th%+La%+Sc%) is equal to 100%

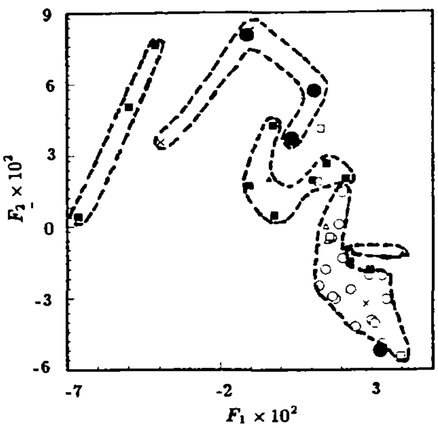

Fig.5 F_1 vs F_2

3.4 The statistical mathematics has been used as a potential tool to recognize the pottery provenience. For our study, the correspondence analysis with the multiple variables made of U, Th, Sc, Ta, Ba, Cs, Sr, Rb and Zr is applied. On the basis of the computer processing, the values of the accumulated variances reach to 0.621 and 0.893, which correspond to loading factors F_1 and F_2, respectively. It means that the data are highly correlated. The basically same distribution patterns are also obtained by F_1vs F_2 (see Fig.5).

4 Conclusion

The chemical compositions of 17 trace elements including the large-ion lithophile elements (eight RE elements and Cs, Rb, Sr, Ba, U, Th) and the transitive elements (Sc, Zr, Ta), have been used for discriminating the pottery proveniences. The all plots of geochemical parameters show that the 44 samples were distributed in five areas. The NS samples were mainly situated in two areas due to they came from two original places. The Han Dynasty (HD) samples made of EH, WE and WH, were relatively concentrated in one area due to they came mainly from one origin. The SP samples were distributed in one area as the same as the HD ones, while one of the SP samples was usually scattered to another area. In certain case, it implies that the SP samples are from two places. Seven of the SW and WS samples were excavated from two regions including five original sites, therefore, they could not be concentrated in one area. As usual, two or three of the samples were scattered to the other areas. In view of statistics, the more samples are participated in mathematical processing, the more reasonable results will be obtained.

Our results show that the chemical compositions of the trace elements have large potential to recognize the pottery proveniences, which is not only significant for research on basic sciences, promotion and evolution of pottery manufacture, but also benificial to discriminating between the genuine and false ceramics. Therefore, INAA becomes a powerful method for study of the archaeological science.

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