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PIXE/RBS Studies on Ancient Pottery from Jinsha Ruins Site of Chengdu^{*}

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Abstract: Jinsha Ruins Site, Chengdu, China, spanned the age from late Shang Dynasty to Western Zhou Dynasty (B. C. 1200—B. C. 650), was generally considered as the inheritance of Sanxingdui Culture. This paper focuses on the studies of the pottery unearthed from Jinsha. PIXE and RBS experimental setup was preliminarily established and these techniques were employed to find the elemental composition of those collected shards. From the results of factor analysis, the differences can be seen among pottery shards from different stratum, which may suggest that the clay gathered from different sites was used in different periods. The authors also found that there was no obvious assemblage phenomenon in the factor analysis among the pottery shards from different pits, this may be the evidence for “no special clay for special use”.

Key words: PIXE; RBS; pottery; Jinsha Ruins

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1 Introduction

The Jinsha Ruins Site, only 5 km away from the downtown of Chengdu, China, discovered in 2001, was generally considered as the inheritance of the 38 km far away Sanxingdui Culture after 8 year excavation. In the 3 km² relics area, there exists a lot of ancient remnants, such as the base address of large buildings, large-scale festival area, residential area and graveyards. All these suggest that Jinsha was the capital of ancient Shu Kingdom and was another political, economic, religious and cultural center after Sanxingdui Culture. Jinsha Ruins Site covered the age from late Shang Dynasty to Western Zhou Dynasty (B. C. 1200—B. C. 650)

which was just after the age of Sanxingdui Culture. The research about Jinsha relics can help archaeologists to understand the history of Sichuan or even the whole China^[1].

Together with the precious gold, copper, jade, stone wares and tons of ivory, numerous pieces of pottery were also dug up from earth^[2]. As artifacts for daily use, the pottery has a lot of important information, for example, the information contained in the pictures drawn on the surface of pottery and the level of handicraft of that age represented by the quality of pottery and so on. In this paper, we focused on the studies of the elemental composition of these pottery shards. By

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studying the elemental composition in pottery or porcelain, much information of ancient ages can also be revealed^[3–17]. At the Jinsha Site, the pottery pieces were collected from different stratum and different pits, this means that they were made at different ages and maybe for different purposes. If the pottery shards from different stratum have the same or close elemental composition, it can be told that the ancient people of Jinsha always obtained pottery clay at one site all the hundred years. On the contrast, if different elemental composition was found, it can be told that there were two or more clay gathering sites for the ancient people of Jinsha. For those potteries from different pits, whether or not they were made of special clay because of their special use, such as being used in sacrifices, could also be answered in such a study.

Ion beam analysis techniques (e. g., proton induced X-ray emission (PIXE))^[3–6], instrumental neutron activation analysis (INAA)^[7–13] and X-ray fluorescence analysis (XRF)^[14–17] are often used to determine the elemental composition in pottery shards. In this paper, PIXE technique was employed to obtain the contents of Mg, Al, Si, K, Ca, Ti, Fe, etc in the pottery shards unearthed in the Jinsha Ruins Site while Rutherford backscattering analysis (RBS) technique was used to determine the matrix elements.

2 Samples

Twelve pieces of pottery were chosen for the present study. They were taken from several different excavation pits and four different archaeological stratum^[2]. We prepared seventeen samples from these shards, and the details were given in Table 1. Sample Nos. 1 and 2 are the outside layer and the inside layer of one piece of pottery, and so are Nos. 3 and 4, Nos. 5 and 6, Nos. 7 and 8, Nos. 9 and 10. See that these five pieces of pottery have a difference in color between the outside and the inside layers, they are divided into two samples for each, i. e., an outside one and an in-

side one. In the “excavation pit” row, capital T means probe gird. The capital H means ash pit, where the ancients put their trash in. M means burial pit, Y means kiln remains, and G means funerary objects channel. The number of stratum means the earth layer where the samples were unearthed. The bigger the number is, the older the pottery is.

Table 1 The sample information

Sample number	Excavation pit	Stratum	Color	Outside/inside
No. 1	T7676-7575	6	white and gray	outside
No. 2			brown	inside
No. 3	M2471	5	orange	outside
No. 4			brown	inside
No. 5	H6638	6	brown	outside
No. 6			dark brown	inside
No. 7	H6711	5	white	outside
No. 8			gray	inside
No. 9	G426	5	white	outside
No. 10			gray	inside
No. 11	H6466	1	black	none
No. 12	H6638	6	brown	none
No. 13	Y206	5	brown	none
No. 14	H6466	1	orange	none
No. 15	H2471	5	black	none
No. 16	H6432	7	brown	none
No. 17	Y206	5	black	none

All the samples were made by the following steps^[6]. Firstly, it was necessary to wash off the superficial mud and other contamination in an ultrasonic cleaner. Ethanol was used to clean the surface after the shards were dried in an oven for about 12 h. Secondly, for the “two samples” shards, the outside layer was scraped down by a knife lightly, and the powder was carefully collected. For the other shards, we put them into an agate mortar and crushed carefully. At last, after some large pebbles were removed, the remaining powder was pressed into disks with a diameter of 15 mm. In all this process, ethanol was used to

clean the used tools and avoid sample pollution.

3 Experiments

The 2 MeV collimated proton beam was provided by the Van de Graaff accelerator at Institute of Nuclear Science and Technology, Sichuan University. In this study, PIXE and RBS experimental setup was preliminarily established. All samples were analyzed in a 2×10^{-7} Pa target chamber. The beam direction was vertical to the surface of samples. A semiconductor Au(Si) barrier detector, placed in the target chamber, was used to obtain RBS spectra at an angle of 160° with respect to the beam direction. On the other side of the beam at an angle of 135° , there placed a Canberra X-PIPS[®] detector (25 μm beryllium window, active area 5 mm^2) with a resolution of 185 eV at 5.9 keV to detect the X-rays emitted from the samples. There was a 9 μm Mylar film between the vacuum chamber and the X-PIPS[®] detector. The two detectors and the beam direction were on the same plane as shown in Fig. 1. As we know, the conventional X-ray detector for PIXE measurements has lower efficiencies for detecting light elements ($Z < 13$), therefore, in this studies RBS was employed to find if the light elements existed and at the same time to determine the matrix elemental composition. The beam current was adjusted to keep a appropriate counting rate. The RBS spectra were

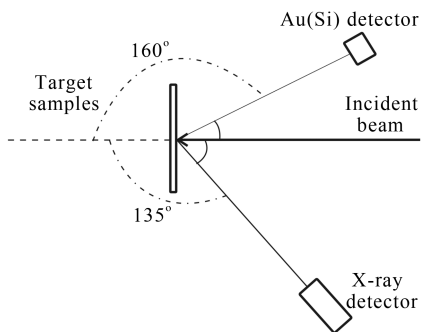


Fig. 1 Experimental arrangement inside the target chamber.

fitted by SIMNRA code^[18], and the relative chemical composition in the samples was calculated by

the program GUPIX95^[19].

4 Results and Discussion

A typical PIXE spectrum from a sample is shown in Fig. 2. Several peaks which correspond to Al, Si, K, Ca, Ti, Mn and Fe elements can be seen in this figure. From the measured PIXE spectra of samples the relative chemical composition in the samples are obtained. Fig. 3 shows a RBS spectrum which represented the information from the same point of the same sample where the PIXE spectrum was obtained. We can see several steps in Fig. 3. From the right to the left, they correspond

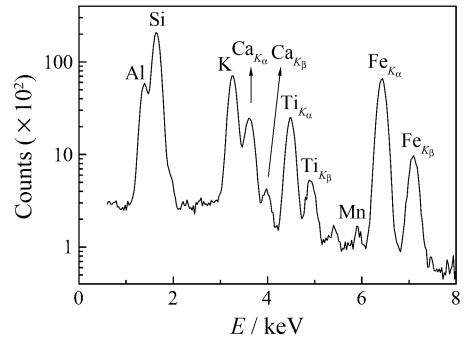


Fig. 2 A typical PIXE spectrum with 2 MeV protons of a pottery sample from Jinsha Relics.

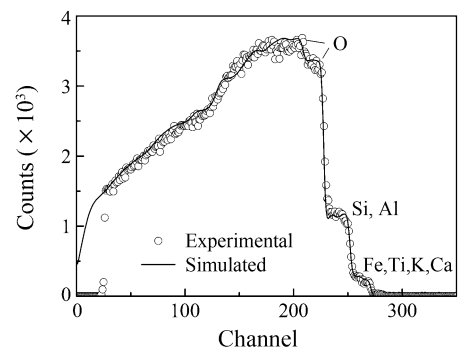


Fig. 3 A typical RBS spectrum with 2 MeV protons and the SIMNRA fit result of a pottery sample from Jinsha Relics.

to the Fe, Ti, K and Ca elements, Si and Al elements, and the last two steps are both caused by O element. The program SIMNRA can provide perfect fits to the spectra. After the analysis by using SIMNRA code, we can know how much O element

were contained in the samples, and whether or not there existed other light elements in the samples and we can also know the approximate contents of other heavier elements in the samples. These element contents can be used as matrix element contents which will be employed in the PIXE analysis. It should be explained why the O element caused two steps in Fig. 3. In the fitting process, we found that the concentration of O element is not always distributed homogeneously from the surface to the inside part. We divided the surface into 3 layers, and found that the first and third layers contained less O element than the second layer (about 6% atom concentration less than the second layer). The most possible cause is that firstly the samples were prepared by pressing the dry pottery powder into disk shape, and then the sample surface will absorb the moisture in the air. When the samples were placed into the vacuum target chamber, we believed that the moisture contained in the sample surface could be partly pumped out. There-

fore, the inhomogeneous distribution of the O element on the sample surface was formed. The element contents in the samples such as Si, Al, Fe, Ti, K, Ca and O are more accurately calculated by the GUPIX95 program (in 10^{-6}). The final results are shown in Table 2, all elements are given in oxide form. From Table 2 it can be inferred that SiO_2 and Al_2O_3 take a large part of the mass of the samples, this is consistent with other experimental results^[6]. The existence of Fe and Mn is just the evidence why the pottery appeared orange or black. For the five “two layers” samples (i. e., samples Nos. 1—10), main element contents of inner and outer layer is very similar, with the exception of samples No. 3 and No. 4, whose contents of Al_2O_3 and Fe_2O_3 are different to some extent. In addition, for improving the detection for high-Z trace elements, in the future we will plan to use a dual-detector system^[20] or try to use a so-called “funny filter”^[21].

Table 2 The chemical composition measured by PIXE and RBS of all the 17 samples

wt. %

	Al_2O_3	SiO_2	P_2O_5	K_2O	CaO	TiO_2	MnO	Fe_2O_3
No. 1	32.68±0.53	54.09±0.80	0.84±0.08	2.75±0.30	0.78±0.10	1.52±0.30	0.04±0.01	7.28±0.31
No. 2	30.46±0.64	54.55±0.83	1.01±0.11	3.22±0.24	1.08±0.08	1.56±0.21	0.04±0.02	8.08±0.42
No. 3	31.91±0.50	48.50±0.92	0.37±0.03	2.28±0.17	0.90±0.16	1.86±0.16	0.08±0.02	14.12±0.51
No. 4	42.13±0.91	44.96±0.77	0.40±0.02	1.26±0.09	1.02±0.13	1.35±0.24	0.02±0.01	8.86±0.26
No. 5	34.10±0.78	49.03±0.86	1.25±0.06	3.49±0.12	1.82±0.04	1.50±0.22	0.04±0.01	8.76±0.31
No. 6	32.80±0.44	51.33±0.72	1.51±0.04	3.64±0.29	2.14±0.09	1.45±0.14	0.12±0.02	7.01±0.20
No. 7	37.42±0.52	47.33±0.87	0.68±0.04	3.52±0.14	0.88±0.11	1.49±0.23	0.09±0.01	8.59±0.27
No. 8	35.92±0.67	47.27±0.64	1.45±0.10	3.69±0.21	1.28±0.06	1.67±0.20	0.18±0.01	8.54±0.24
No. 9	40.01±0.92	46.93±0.84	0.52±0.08	3.55±0.32	0.61±0.13	1.42±0.22	0.03±0.01	6.92±0.31
No. 10	36.51±0.75	47.72±1.13	1.61±0.06	3.92±0.18	1.32±0.11	1.65±0.11	0.08±0.02	7.19±0.16
No. 11	33.95±0.60	49.30±0.52	0.45±0.02	2.94±0.29	1.25±0.08	1.33±0.17	0.40±0.03	10.37±0.26
No. 12	34.92±0.74	48.22±0.85	1.28±0.03	2.78±0.21	1.71±0.17	1.03±0.08	0.14±0.01	9.91±0.18
No. 13	34.16±0.52	47.34±0.98	0.57±0.04	2.59±0.19	1.05±0.21	1.37±0.12	0.11±0.02	12.81±0.22
No. 14	33.89±0.68	46.48±0.86	0.89±0.03	2.20±0.23	1.14±0.02	1.28±0.13	0.13±0.02	13.99±0.34
No. 15	31.67±0.54	48.39±1.05	0.23±0.04	2.75±0.16	1.45±0.16	1.09±0.03	0.88±0.05	13.55±0.32
No. 16	34.16±0.71	45.64±0.64	0.82±0.02	2.73±0.24	1.26±0.14	1.46±0.20	0.25±0.01	13.68±0.19
No. 17	31.99±0.32	50.78±0.87	0.48±0.11	3.02±0.22	1.41±0.21	1.18±0.11	0.30±0.03	10.85±0.20

Because as many as 9 elements were found in these samples, it is not easy to compare the samples with each other if no further analysis is adopted. Here a factor analysis are performed for all these elemental composition. Fig. 4 shows the results from a factor analysis. The factor number is reduced to two, which are shown as follows:

$$F_1 = 0.024Al_2O_3 + 0.456SiO_2 + 0.830P_2O_5 + 0.755K_2O + 0.284CaO + 0.477TiO_2 - 0.544MnO - 0.798Fe_2O_3,$$

$$F_2 = -0.835Al_2O_3 + 0.511SiO_2 + 0.132P_2O_5 + 0.232K_2O + 0.665CaO - 0.394TiO_2 + 0.629MnO + 0.247Fe_2O_3,$$

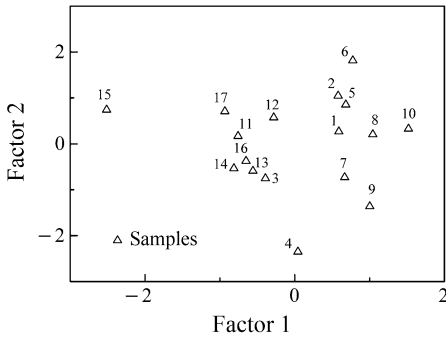


Fig. 4 Result of factor analysis.

At first, we classified these points by the stratum as shown in Fig. 5. It can be seen that the the shards from the stratum 5 mainly occupy the lower right part . The points of stratum 6 points of are

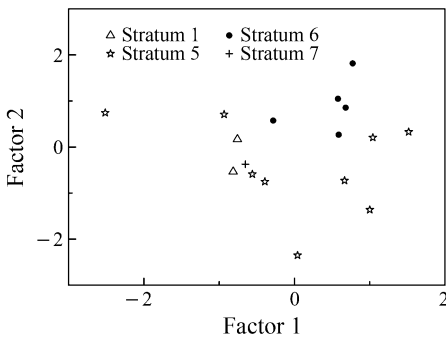


Fig. 5 Samples classified by stratum.

located on the upper right part while the points of other stratum stay in the middle. So we can find out that the shards from the same stratum have a

close composition, and to the shards from different stratum there is clearly a difference in elemental composition, which maybe suggests that in different periods of Jinsha culture the ancient people didn't gather clay for pottery manufacture from the same site.

In Fig. 6, we also classified all the seventeen samples into five groups by the kind of pits in which they were found. The samples of Nos. 5, 6, 7, 8, 11, 12, 14, and 16 were from ash pits, the samples of Nos. 13 and 17 were buried in a kiln remains, the samples of Nos. 3, 4 and 15 were found in burial pit, the samples of Nos. 9 and 10 were dug out in a funerary objects channel, and the samples of Nos. 1 and 2 were excavated in a probe gird. From Fig. 6, it can be seen that there is no obvious assemblage phenomenon. The points from all kinds of pits were interspersed with each other, this maybe can be understood in a way that at the time of Jinsha there was no special clay for special use, i. e. , there was no clear distinction between the potteries used for daily life, sacrifice, mortuary objects or other kinds, and they were all made from the same clay.

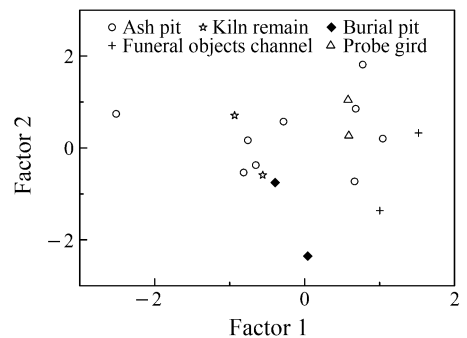


Fig. 6 Samples classified by pits.

5 Conclusion

In the studies presented in this paper, the chemical composition of seventeen samples excavated from Jinsha Relics in Chengdu was compared with each other. It was found that the pottery shards from different stratum have different elemental composition, which maybe suggested that

the ancient people of Jinsha Relics collected different clay at different ages for producing the pottery, and that there was no clear distinction between the potteries used for daily life, sacrifice, mortuary objects or other kinds. The studies performed in this paper are preliminary, we still need more pottery samples and conduct more systematic researches.

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References.

- [1] Zhu Zhangyi, Zhang Qing, Wang Fang. *Sichuan Cultural Relics*, 2002, **2**: 3(in Chinese).
(朱章义, 张擎, 王方. *四川文物*, 2002, **2**: 3.)
- [2] Su Bai, Zhang Zhongpei, Wang Wei, *et al.* *Yearbook of Chinese Archeology*. Beijing: Cultural Relics Publishing House, 2008, 373—374(in Chinese).
(宿白, 张忠培, 王巍, 等. *中国考古学年鉴*. 北京: 文物出版社, 2008, 373—374.)
- [3] Zhang B, Pan B H, Zhang Z Q, *et al.* *Nucl Instr and Meth*, 2004, **B219—220**: 26.
- [4] Cheng H S, Zhang Z Q, Zhang B, *et al.* *Nucl Instr and Meth*, 2004, **B219—220**: 16.
- [5] Cheng Lin, Ding Xunliang, Feng Songlin, *et al.* *Nucl Instr and Meth*, 2006, **B244**: 409.
- [6] Cheng H S, Zhang Z Q, Song J, *et al.* *Nucl Instr and Meth*, 2006, **B249**: 601.
- [7] Xie Guoxi, Feng Songlin, Feng Xiangqian, *et al.* *Nucl Instr and Meth*, 2009, **B267**: 821.
- [8] Zhu Jihao, Feng Songlin, Fan Dongyu, *et al.* *Journal of Radioanalytical and Nuclear Chemistry*, 2007, **272**: 545.
- [9] Feng X Q, Feng S L, Fan C S, *et al.* *Journal of Radioanalytical and Nuclear Chemistry*, 2007, **272**: 551.
- [10] Zhao Weijuan, Zhang Xuehua, Han Guohe, *et al.* *Chinese Physics*, 2008, **C32**(Suppl. 2): 274.
- [11] Feng Xiangqian, Feng Songlin, Zhang Wenjiang, *et al.* *Nuclear Physics Review*, 2005, **22**(1): 142(in Chinese).
(冯向前, 冯松林, 张文江, 等. *原子核物理评论*, 2005, **22**: 142.)
- [12] Feng Songlin, Fan Dongyu, Feng Xiangqian, *et al.* *Nuclear Physics Review*, 2005, **22**(1): 138(in Chinese).
(冯松林, 范东宇, 冯向前, 等. *原子核物理评论*, 2005, **22**(1): 138.)
- [13] Wu Zhanjun, Zhao Weijuan, Lu Xiaoke, *et al.* *Nuclear Physics Review*, 2007, **24**(4): 284(in Chinese).
(吴占军, 赵维娟, 鲁晓珂, 等. *原子核物理评论*, 2007, **24**(4): 284.)
- [14] Cheng Lin, Ding Xunliang, Liu Zhiguo, *et al.* *Acta Physica Sinica*, 2007, **56**: 6894(in Chinese).
(程琳, 丁训良, 刘志国, 等. *物理学报*, 2007, **56**: 6894.)
- [15] Feng Songlin, Feng Xiangqian, Zhu Jihao, *et al.* *Chinese Physics*, 2008, **C32**(Suppl. 2): 284.
- [16] Cheng Lin, Li Rongwu, Pan Qiulin, *et al.* *Nucl Instr and Meth*, 2009, **B267**: 117.
- [17] Wen Chang, Zhao Huixian, Li Rongwu, *et al.* *Nuclear Physics Review*, 2009, **26**: 356 (in Chinese).
(温昶, 赵会仙, 李融武, 等. *原子核物理评论*, 2009, **26**: 356.)
- [18] Mayer M. *Nucl Instr and Meth*, 2002, **B194**: 177.
- [19] Campbel J L, Hopman T L, Maxwell J A, *et al.* *Nucl Instr and Meth*, 2000, **B170**: 193.
- [20] Calligaro T, Dran J C, Dubernet S, *et al.* *Nucl Instr and Meth*, 2005, **B240**: 576.
- [21] Roumié M, Wicenciak U, Bakraji E, *et al.* *Nucl Instr and Meth*, 2010, **B268**: 87.

成都金沙遗址古代陶片的 PIXE 和 RBS 分析*

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摘 要: 成都金沙遗址的年代覆盖了商代晚期至西周时期(公元前 1200 年—公元前 650 年), 一般被认为是三星堆文化的延续。初步建立了质子激发 X 射线发射(PIXE)和卢瑟福背散射(RBS)实验装置, 并采用 PIXE 和 RBS 方法研究了从金沙遗址出土的部分陶片的元素组成。通过因子分析, 观察到来自不同地层的陶片的元素组成存在一定的差异, 这可能意味着制作陶器的陶土在不同时期取自不同的地点。也观察到来自不同发掘坑的陶片的元素组成没有明显的聚类现象, 这可能意味着制作不同使用用途的陶器所用的陶土是没有区别的。

关键词: PIXE; RBS; 陶器; 金沙遗址

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