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X-ray diffraction (XRD), X-ray fluorescence (XRF) and Scanning Electron Microscopy (SEM) analysis of potsherds, Sungai Batu Complex, Bujang Valley, Kedah

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Abstract: Archaeological excavations at the Sungai Batu Archeological Complex have unearthed potsherds with monument structures. The discovery of the potsherds enables scientific studies of X-ray diffraction (XRD), X-ray fluorescence (XRF) and Scanning Electron Microscopy (SEM) analysis to be conducted and resolve related issues such as where the raw materials were obtained by the manufacturers. To solve the issue, potsherds were taken from around the ancient river, and scientific analyses was conducted for comparison purposes. Before the clay sample was subjected to the scientific analyses, the samples were cleaned and measured (for weight, thickness and width). Color sampling was also performed. Based on results of the analyses, it clearly shows that the potsherds was produced using raw materials from the ancient river in the Sungai Batu Complex itself and baked at a temperature between 550°C and 650°C.

Keywords: Potsherds, scientific analysis, raw material

INTRODUCTION

The archaeological research at the Sungai Batu Complex reveals evidence of the oldest structure and smelting sites in Southeast Asia. The dating was determined using the optical stimulate luminansen *(OSL)* and radiocarbon techniques. The results clearly show that the structure was built since 582 BCE (Figure 1 and Table 1) and the iron industry started to grown since 535 BC (Figure 2).

The structure here has been classified as river jetty, administrative and ritual sites (Naizatul, 2012; Iklil Izzati, 2014; Mohd Hasfarisham, 2014; Shamsul Anuar, 2015; Nurashiken, 2016; Suhana, 2016). Previous excavations at all monument sites in Sungai Batu have found potsherds that suggested pottery was part of the daily use in this area. This interpretation has similarities with Chia (1997, 2003a, 2003b) and Suresh (2011) who also proposed potsherds was used for cooking, storage and trading as well as in religious ceremonies.

According to Peacock (1959), Solheim (1990), Mohd Kamaruzzaman *et al.* (1991), Chia (1995, 1997, 2003a, 2003b) and Gani *et al.* (2015), a scientific study on pottery should be carried out to determine the raw material used in the process of producing the artifacts. In addition, by conducting a scientific analysis, the information on combustion technologies can also be known and classified. To obtain such information, quantitative and scientific analysis of XRD, XRF and SEM were applied to 15 potsherds and 17 soil samples from Sungai Batu Archaeological Complex. The scientific analysis carried out only involved potsherds fragments found at the river jetty

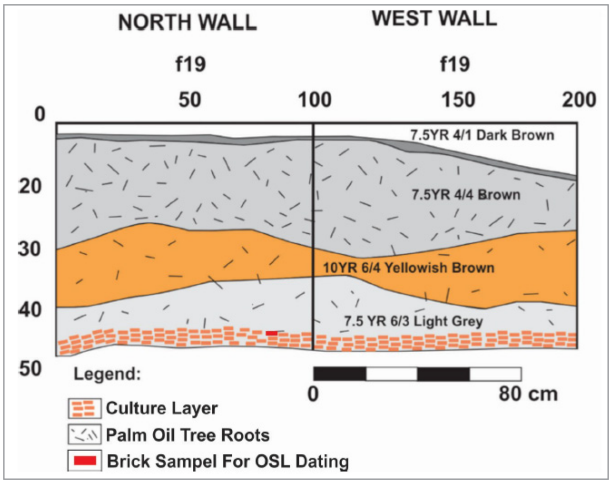

Figure 1: A stratigraphic layer showing the location of in-situ brick sample and revealing the date 582 BCE.

Table 1: Result of OSL Dating from f19 trench.

Site	Trench	Spit	Sample Classification	OSL Dating	BCE: Before Century
SB2D	F19	5 (40-50 CM)	Floor	-	582 BCE

and administrative sites to determine whether local raw materials were used in the process of potsherds production.

METHODOLOGY FOR ANALYSIS OF POTSHERDS

This study involves several methods for the purpose of field data collection. The main method used is the excavation to collect evidence of potsherds to conduct quantitative and scientific analysis. After the sample was obtained, quantitative analysis was conducted first to obtain basic information on the typology of the potsherds. After the quantitative analysis, scientific analysis of XRD, XRF and SEM were made on the potsherds samples. The scientific analysis results was compared with the results of the analysis of soil samples taken in the ancient river at the Sungai Batu Archaeological Complex. This was to resolve issues related to local or foreign raw materials have been used in the process of producing potsherds.

QUANTITATIVE ANALYSIS OF POTSHERDS FROM THE SUNGAI BATU ARCHAEOLOGICAL COMPLEX

Quantitative analysis of potsherds samples involved determination of weight, thickness and types of debris; either representing part of the lip, body or pottery base following classification determined by Rice (1987) and Nurhadi *et al.* (2008). The analysis for thickness is divided into three categories: 1) for less than 6 mm, 2) medium, for between 6-10 mm and 3) for thickness more than 10 mm. From the results of the study on 15 potsherds, the type of pottery classification is determined to be body (Plate 1) (nine pieces (60%)), lip (Plate 2) (three pieces (20%)) and base (Plate 3) (three pieces (20 %)). The thickness analysis of pottery fragmentation clearly illustrates that the pottery thickness at the river jetty and administrative sites is moderate, between 6-10 mm (Table 2). The thickness suggests its use for food preparation or for other daily use.

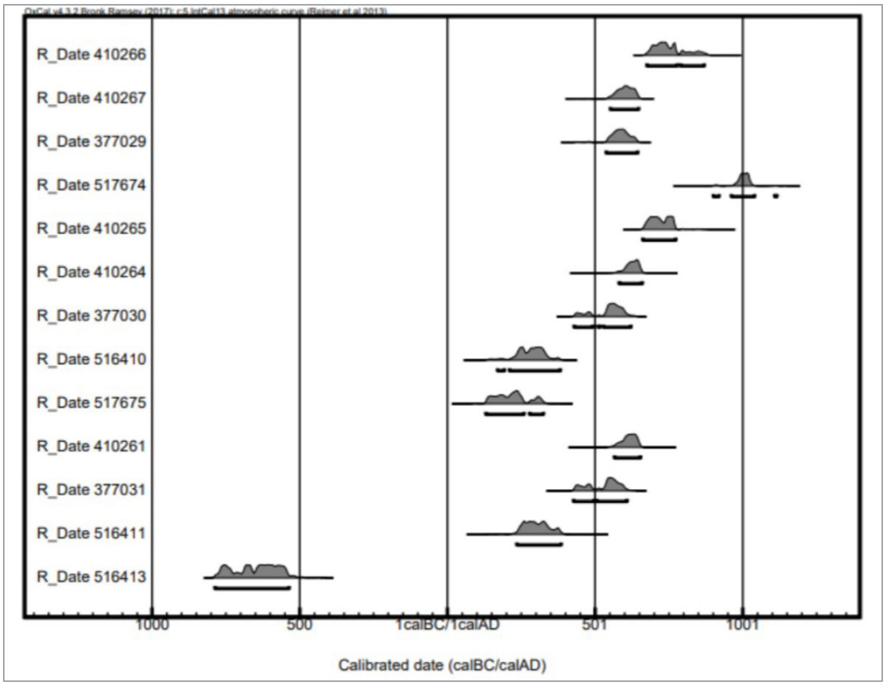

Figure 2: Chronological model of Site SB2H.

Plate 1: Classification of body part of fragmented potsherd found at river jetty and administrative sites.

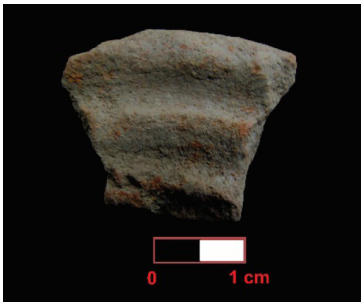

Plate 2: Classification of lip part of fragmented potsherd found at river jetty and administrative sites.

Plate 3: Classification of base part of fragmented potsherd found at river jetty and administrative sites.

Table 2: The results of the quantitative analysis of pottery samples at river jetty and administrative sites at Sungai Batu Archaeological Complex.

No. Sample	Thickness (mm)	Weight (g)	Color	Section
1	9.46	34	7.5YR 7/8 Reddish Yellow	Body
2	9.81	28	7.5YR 8/4 Pink	Body
3	9.43	46	7.5YR 7/4 Pink	Base
4	7.62	16	7.5YR 7/4 Pink	Base
5	9.45	31	7.5YR 7/3 Pink	Lip
6	9.93	14	7.5YR 7/6 Reddish Yellow	Lip
7	8.17	21	7.5YR 7/4 Pink	Body
8	5.04	17	7.5YR 5/3 Brown	Body
9	8.73	27	7.5YR 7/4 Pink	Body
10	8.66	38	7.5YR 6/3 Light Brown	Body
11	9.07	13	7.5YR 6/2 Pinkish Gray	Lip
12	8.66	16	7.5YR 5/3 Brown	Base
13	8.04	25	7.5YR 5/3 Brown	Body
14	8.89	14	7.5YR 5/3 Brown	Body
15	9.04	19	7.5YR 5/3 Brown	Body

The analysis also attempts to identify the potsherds' colors using Munsell Soil Color Charts. From the study, at least five colors were identified for potsherds found at the river jetty and administrative sites, which are reddish yellow, pink, brown, light brown and pinkish gray. According to Chia (1997), potsherds with these colors are commonly found in Peninsular Malaysia. Further, according to Chia (1997), the yellow-colored potsherds is also a clear indication that it was burned at an optimum temperature that allows oxidation to occur perfectly. This clearly illustrates that the society had been able to regulate the temperature of the combustion to produce quality potsherds Before Centuries.

The quantitative analysis of the 15 pieces of potsherds also revealed it originated from pottery without decorations. This is because on the body, base and lip parts of the potsherds, cord-marked, impressed, incised, circle, punctated and displacement technique are not detected. This find indicates a different type of potsherds than those found in Kuala Selingsing, Sungai Mas and Pengkalan Bujang, which revealed decorations on the potsherds (Ahmad Fawzi, 1986). Based on potsherds typology, this strongly suggests that the process of potsherds making at the Sungai Batu Complex was at an early stage and did not involve any form of beauty of appearance in its potsherds. This is because the ornamental patterns on potsherds represent the custom and growing artistic style of the time.

XRD, XRF AND SEM ANALYSIS OF POTSHERD SAMPLES

The results of XRD analysis on potsherd samples (Table 3) clearly reveal the presence of quartz and montmorillonite minerals that dominate the pottery samples. In addition, quartz, microline, rutile, zircon, anatase and muscovite were also detected in the pottery. Based on the presence of montmorillonite and illite minerals in the pottery samples, it is suggested that burning was at temperatures around 550 °C up to 650 °C, as suggested by Zuliskandar *et al.* (2008) and Palanivel & Rajesh (2011). Based on the scientific analysis, the results strongly suggest the possibility of open firing techniques being applied during the potsherds kiln process. This interpretation is submitted because burning the potsherds does not require high temperatures.

From the XRF analysis, the main and trace element contents detected are silica (SiO_2), aluminum (Al_2O_3) and iron oxide (Fe_2O_3) between 69.05%, 13.31% and 5.13% (Shamsul Anuar, 2015) (Table 4). The high silica content obtained through this XRF analysis has amplified the XRD analysis results that revealed silica as the dominant content in potsherds samples. This is reinforced based on the SEM analysis that shows the wide range of sand content including circles and squares (Plate 4). In addition, the presence of aluminum (Al_2O_3) is similar to the presence of montmorillonite elements i.e. clay minerals which is the main raw material in potsherds production.

The CaO graph against K_2O plotted based on the XRF analysis (Figure 3) clearly shows that the source of the raw material for the process of potsherds production was taken from the same source material. The analysis results of 17 soil samples from the Sungai Batu Archaeological Complex also clearly revealed the presence of kaolinite and quartz or montmorillonite and quartz and silica

Table 3: Results of XRD analysis of potsherd samples.

No. Sample	Mineral Content	
	Mineral Name	**Chemical Name**
1	Quartz Montmorillonite	SiO_2 $Na\ O_3\ (Al, Mg)_2\ Si_4\ O_{10}\ OH_2\ 6H_2O$
2	Quartz Montmorillonite Microcline	SiO_2 $Na\ O_3\ (Al, Mg)_2\ Si_4\ O_{10}\ OH_2\ 6H_2O$ $(K_{95}\ Na\ O_5)\ Al\ Si_3\ O_8$
3	Quartz Muscovite Montmorillonite Rutile	SiO_2 $(K, Na)\ Al_2\ (Si\ Al)_4\ O_{10}\ (OH)_2$ $Na\ O_3\ (Al, Mg)_2\ Si_4\ O_{10}\ OH_2\ 6H_2O$ TiO_2
4	Quartz Montmorillonite Microcline	SiO_2 $Na\ O_3\ (Al, Mg)_2\ Si_4\ O_{10}\ OH_2\ 6H_2O$ $(K_{95}\ Na\ O_5)\ Al\ Si_3\ O_8$
5	Quartz Muscovite Montmorillonite Microcline	SiO_2 $(K, Na)\ Al_2\ (Si\ Al)_4\ O_{10}\ (OH)_2$ $Na\ O_3\ (Al, Mg)_2\ Si_4\ O_{10}\ OH_2\ 6H_2O$ $(K_{95}\ Na\ O_5)\ Al\ Si_3\ O_8$
6	Quartz Muscovite Montmorillonite Microcline	SiO_2 $(K, Na)\ Al_2\ (Si\ Al)_4\ O_{10}\ (OH)_2$ $Na\ O_3\ (Al, Mg)_2\ Si_4\ O_{10}\ OH_2\ 6H_2O$ $(K_{95}\ Na\ O_5)\ Al\ Si_3\ O_8$
7	Quartz Montmorillonite Microcline	SiO_2 $Na\ O_3\ (Al, Mg)_2\ Si_4\ O_{10}\ OH_2\ 6H_2O$ $(K_{95}\ Na\ O_5)\ Al\ Si_3\ O_8$
8	Quartz Microcline Montmorillonite Anatase	SiO_2 $(K_{95}\ Na\ O_5)\ Al\ Si_3\ O_8$ $Na\ O_3\ (Al, Mg)_2\ Si_4\ O_{10}\ OH_2\ 6H_2O$ TiO_2
9	Quartz Microcline Montmorillonite Anatase	SiO_2 $(K_{95}\ Na\ O_5)\ Al\ Si_3\ O_8$ $Na\ O_3\ (Al, Mg)_2\ Si_4\ O_{10}\ OH_2\ 6H_2O$ TiO_2
10	Quartz Montmorillonite Rutile Zircon	SiO_2 $Na\ O_3\ (Al, Mg)_2\ Si_4\ O_{10}\ OH_2\ 6H_2O$ TiO_2 $Zr\ O_2$
11	Quartz Microcline Montmorillonite	SiO_2 $(K_{95}\ Na\ O_5)\ Al\ Si_3\ O_8$ $Na\ O_3\ (Al, Mg)_2\ Si_4\ O_{10}\ OH_2\ 6H_2O$
12	Quartz Illite Montmorillonite Rutile	SiO_2 $(K, H_{30})\ Al_2\ (Si_3, Al)\ O_{10}\ (OH)_2\ xH_2O$ $Na\ O_3\ (Al, Mg)_2\ Si_4\ O_{10}\ OH_2\ 6H_2O$ TiO_2
13	Quartz Montmorillonite Microcline	SiO_2 $Na\ O_3\ (Al, Mg)_2\ Si_4\ O_{10}\ OH_2\ 6H_2O$ $(K_{95}\ Na\ O_5)\ Al\ Si_3\ O_8$
14	Quartz Muscovite Montmorillonite Microcline	SiO_2 $(K, Na)\ Al_2\ (Si\ Al)_4\ O_{10}\ (OH)_2$ $Na\ O_3\ (Al, Mg)_2\ Si_4\ O_{10}\ OH_2\ 6H_2O$ $(K_{95}\ Na\ O_5)\ Al\ Si_3\ O_8$
15	Quartz Montmorillonite Microcline	SiO_2 $Na\ O_3\ (Al, Mg)_2\ Si_4\ O_{10}\ OH_2\ 6H_2O$ $(K_{95}\ Na\ O_5)\ Al\ Si_3\ O_8$

(Table 5). Based on the match of the analysis, it clearly illustrates that the raw material for the manufacture of potsherds was taken in the vicinity of Sungai Batu itself. This is because kaolonite originates from the granite rocks located in the vicinity of Mount Jerai (Bradford, 1972) while montmorillonite was derived from the shale rocks in Sungai Petani Formation (Bradford, 1972; Burton, 1988). This area is close to the study area based on the geological map.

The results of the trace element analysis showed that the lead content (Pb) in potsherds was low which strengthened the interpretation that it was produced using local material. This is because the potsherds analysis from India has recorded high lead content, as suggested by Zuliskandar *et al.* (2001). This enabled the interpretation that the potsherds found in the river jetty and administrative sites were made using the raw material in the vicinity of Sungai Batu.

Table 4: Results of XRF analysis of potsherd samples.

Content (%)	Sample No.				
	1	**2**	**3**	**4**	**5**
SiO_2	65.06	62.22	60.02	60.30	64.56
Ti_2O	0.91	0.91	0.92	1.17	0.90
Al_2O_3	18.60	18.08	18.55	20.16	18.07
Fe_2O_3	4.01	5.95	6.40	3.70	3.59
MnO	0.01	0.01	0.01	0.01	0.01
MgO	0.80	0.76	0.63	0.23	0.69
CaO	0.06	0.05	0.04	0.06	0.09
Na_2O	0.14	0.14	0.13	0.10	0.12
K2O	1.04	1.02	0.99	0.80	0.96
P_2O_5	0.04	0.03	0.04	0.05	0.03
	6	**7**	**8**	**9**	**10**
SiO_2	62.69	68.73	61.23	67.51	59.89
Ti_2O	0.89	0.87	0.82	0.82	1.04
Al_2O_3	17.67	16.78	18.30	17.92	20.79
Fe_2O_3	5.79	2.55	5.79	3.02	4.94
MnO	0.01	0.01	0.12	0.01	0.01
MgO	0.74	0.66	0.89	0.77	0.28
CaO	0.07	0.03	0.05	0.04	0.04
Na_2O	0.15	0.11	0.15	0.11	0.12
K_2O	0.99	0.93	0.91	1.00	1.05
P_2O_5	0.03	0.03	0.04	0.03	0.05
	11	**12**	**13**	**14**	**15**
SiO_2	59.95	59.56	59.90	63.17	64.15
Ti_2O	0.96	1.06	0.93	1.10	0.92
Al_2O_3	19.67	19.26	19.15	21.96	18.74
Fe_2O_3	5.85	6.33	5.21	1.83	3.56
MnO	0.01	0.01	0.01	0.01	0.01
MgO	0.60	0.25	0.66	0.25	0.56
CaO	0.04	0.06	0.04	0.04	0.06
Na_2O	0.13	0.15	0.12	0.07	0.13
K_2O	0.89	1.06	0.92	0.87	0.91
P_2O_5	0.04	0.04	0.05	0.03	0.03

Table 5: Raw data of soil samples from the Sungai Batu Comples taken for XRD analysis.

No. Sample	Content	Location of Sampling	No of Sampling
1	Kaolinite and quartz	Ancient river near jetty site SB1K	3
2	Kaolinite, montmorillonite and quartz	Ancient river near jetty site SB1J	3
3	Kaolinite and quartz	Ancient river near administrative site SB1M	3
4	Kaolinite and montmorillonite	Ancient river near jetty site SB2B, SB2D and SB2E	5
5	Kaolinite and montmorillonite	Ancient river near administrative site SB2ZZ	3

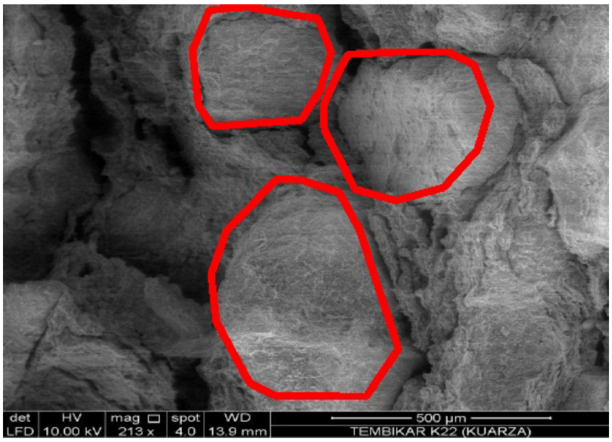

Plate 4: The SEM analysis results show the size of sand (red circle) that reinforces XRD and XRF analysis data related to the use of silica as the raw material in potsherds (after Shamsul Anuar, 2015).

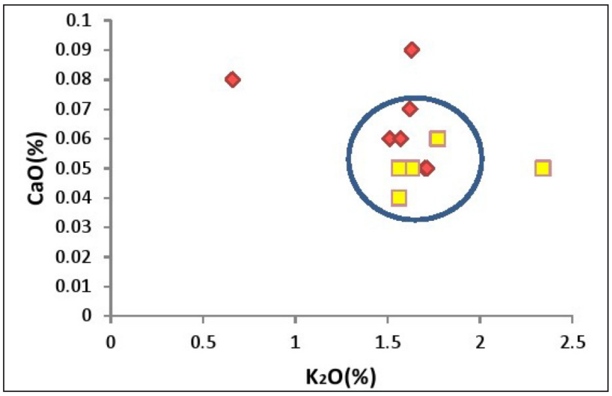

Figure 3: CaO graph against K_2O for potsherds. It is clearly shown that the raw material was taken from the same area in Sungai Batu (after Shamsul Anuar, 2015).

CONCLUSION

The results of XRD, XRF and SEM analysis clearly reveal the raw material of potsherds found at the jetty and administrative sites in the Sungai Batu area. This is suggested based on the presence of quartz and montmorillonite minerals as the dominant minerals, and the presence of low lead (Pb) elements which differed from the analysis of imported potsherds that have high lead elements. The results of soil sample analysis illustrate that the basic ingredients for pottery making was taken around the Jerai and Mahang formations near the Sungai Batu site. The results of potsherd analyses in the Sungai Batu area have reinforced the analysis of the local material as the main medium for pottery production in Sungai Bujang, Sungai Baru, Mukim Merbok, Mukim Bujang and Sungai Merbok Kecil (Zuliskandar *et al.,* 2014).

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