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X-Ray Diffraction and X-Ray Fluorescent Analyses of Prehistoric Pottery Shards from Ulu Kelantan

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Abstract: Problem statement: X-Ray Diffraction (XRD) and X-Ray Fluorescent (XRF) were used in order to obtain mineralogical and elemental composition of seven pottery shards that have been unearthed during the excavation at *Peraling Cave* and *Cha Cave* in Ulu Kelantan, Malaysia. **Approach:** *Peraling Cave* and *Cha Cave* were prehistoric sites dating from 10, 000 BC which were inhabited by Hoabinhian people and then continuously used by people of Neolithic culture around 3000 BC. **Results:** Mineralogical and elemental analyses were carried out to determine whether the pottery found in the archaeological sites was locally made or trading items. Several clay samples from rivers in Ulu Kelantan such as *Perias* River, *Chai* River, *Peralon* River, *Nenggiri* River, *Betis* River and *Jenera* River were taken to be analysed. **Conclusion/Recommendations:** Mineralogical and elemental content of the pottery shards showed that the pottery shards did not originate from the Ulu Kelantan area and one of the samples contained clinochlore mineral. Clinochlore forms from the metamorphic and hydrothermal alterations of other iron and magnesium silicate minerals and is usually found in igneus rock and metamorphic rock formation.

Key words: X-Ray Diffraction (XRD), X-Ray Fluorescent (XRF), pottery, ulu kelantan

INTRODUCTION

Gua Peraling is a massive rock shelter located close to the *Perias* River, a tributary of *Nenggiri* River. The site at *Gua Peraling* produced much denser fragments of Hoabinhian habitation remains. The reason is that perhaps *Gua Peraling* is located near to water supply, allowing the Hoabinhian fragments to extend right to the surface layers of the sites. It seems that the people here had been in the shelter manufacturing their stone tools in huge quantities for a very long time. Some of the pebble tools had ground cutting edges like tools found in ancient deposits in northern Australia (Taha, 1981). A number of Hoabinhian burials were excavated, but mainly found in poor state of preservation. *Gua Peraling* lies close to a famous archaeological rock shelter called *Gua Cha*, which produced many well-preserved burials of Hoabinhian and Neolithic periods when excavated by Sieveking (1954). The re-excavations done by Taha (1981) showed that the Hoabinhian and Neolithic burials formed a continuous sequence, suggesting rapid culture change to Neolithic about 3000 years ago.

Gua Cha the site of archaeological finds dating back to Hoabinhian age (10,000-3,000 BC) is situated in the *Nenggiri* valley, in the district of *Gua Musang*. Certain archaeologists believe that a Malenesoid group of men from mainland China in a migratory exercise passed through the Malay Peninsula when it was part of the Sunda platform which included the present day Malaysia, Indonesia and the Philippines, to other parts of Asia, Pacific Island and Australia (Taha, 1981).

In 1953 and in 1979, Sieveking and Adi Taha had led teams to *Gua Cha* and found rock shelter burial grounds, primitive tools, pottery and cooked bones and eaten forest animals. The *Gua Cha* pottery assemblage comprised footed vessels, carinated bowls, biconical vessels, globular vessels, beakers, pot-stands, rounded container, jars, bucket-shape vessels and perforated cups (William-Hunt, 1952; Sieveking 1954; Peacock, 1959).

The latest research of the *Gua Cha* concludes that Sieveking's statement which stated the residents

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originated from China and India is incorrect. Sieveking stated, “Malaya is seen as an empty land without people and without culture, before the arrival of people and culture from the land of China and India”. If there were immigrants in the proto-historic period under the concept of ‘Greater India’ and during prehistoric period according to Dr. Benjamin it is parallel to the theory of ‘Kuih Lapis’. Sieveking’s hypothesis shows that the society that lived in *Gua Cha* was living during two different stages of time (Sieveking, 1954).

The cultures of the people were different and they were Hoabinhian and Neolithic cultures. In another specific research done by Adi Taha at *Gua Cha*, the research shows the continuity and change from Hoabinhian to Neolithic. These two different societies were related to each other. However, the migration issue of the two ethnic groups will not be discussed further in this study.

Scientific analysis of pottery plays special part in identifying the composition and morphology and more importantly the origin of the potteries (Glaccock *et al*., 2004; Hirshman *et al*., 2010) this can be done by determining the compositions of the pottery and comparing them with the raw materials obtained from the area. From interviews conducted by Stephen Chia in *Sayong*, *Kuala Kangsar*, Perak it can be concluded that the traditional pottery making communities obtained their raw materials about two or three kilometres away from their village. This corresponded well with the ethnographic studies of pottery making communities. For example, Ariffin (1990) showed that the potters did not travel more than seven kilometres to obtain their clays.

Information on the history of ceramic production can be obtained from archaeological assemblages through standardization of raw material composition and manufacturing technique (Rice, 2005), form and dimensions (Balfet, 1965; Sinipoli, 1988) and surface decoration (Hangstrum, 1985).

MATERIALS AND METHODS

Two pottery shards from *Gua Peraling* and four shards from *Gua Cha* were randomly chosen, then catalogued and photographed. Six clay samples from *Perias* River, *Nenggiri* River, *Betis* River, *Peralon* River, *Chai* River and *Jenera* River were also taken. All the pottery shards and clay samples were cleaned and dried at 115°C and ground into very fine powder. Clay samples were also heated in furnace at the temperature of 600°C. For the characterisation of the shards and clay samples, analytical instruments used included X-Ray Diffraction SIEMENS D5000 Diffractometer and XRF Spectrometer Philips Model PW1480. The important of XRD tecnique was also used in the ceramic industry (Ridha *et al*., 2009; Woon *et al*., 2009), herbs industry (Shujun *et al*., 2005), medical rsearch (Parekh *et al*., 2009) and etc. Physical properties of the shards such as water absorption capacity, porosity, density and pottery thickness were also analysed.

Samples for XRF analysis then are grinded into very fine powder form. A mixture of 0.4 g of sample in powder form (heated at 105°C) and 4.0 g of flux powder (Johnson Matthey Spectroflux 110) homogeneously been mixed together. The mixture was fused in an electric furnace at 1100°C, being set for one hour to make a glass. Homogeneous molten sample than was casted into container and let to be cooled in stages to become fuse glass with diameter of 32 and 2 mm thickness. Fused glass samples are prepared for major elements analysis such as Si, Na, K, Ca, Fe, Al, Ti, Mn and Mg. Press pallet samples then be prepared for trace elements analysis such as Cu, Pb, Zr, Sr Ba, La, U, Ni and Cr. Press pallet samples was prepared by mixing 1.0 g of sample and 6.0 g of powder boric acid in a sample container and the be pressed to 20psi pressure by hydrolyte pressure instrument.

RESULTS

Compositional and morphological analyses showed that the same technology was used for making the pottery, for example, the firing method, thickness and porosity. The thickness of the six pottery shards was measured in order to predict the function of the pottery. For example, thick walled pottery was often used for storage where as thin walled potteries were mainly used as tableware. Two pottery shards from *Gua Peraling* and four from *Gua Cha* are classified as medium and thin hence it may be assumed that the potteries in this area had been used for storage and as tableware.

The ranges of colour from grey to black suggest that the pottery was under incomplete oxidation and some had been smudged. It was probably caused by carbonaceous clay that was not sufficiently fired to totally oxidise the organic components to allow colour development of any iron present (Rice, 2005; Ertem and Demirci, 1999). The shards were found to range from incompletely to relatively well oxidized forms. The physical properties of the pottery shards are shown in Table 1.

Table 1: Physical Properties of pottery Shards at *Gua Cha* and *Gua Peraling*, Ulu Kelantan, Kelantan

	Physical properties				
Sample	Water absorption capacity (%)	Porosity (%)	Density (g/cm^3)	Thickness (mm)	Vessel Parts
GP1	12.78	25.75	2.03	5.57	Body
GP2	9.85	23.07	2.34	7.74	Body
GC1	13.65	26.44	1.93	4.35	Body
GC2	12.30	17.96	1.46	6.14	Body
GC3	8.24	16.19	1.97	9.15	Body
GC4	13.59	21.25	1.56	8.95	Body

Table 2: Elemental contents (Major Element) of pottery shards in *Gua Cha* and *Gua Peraling*, Ulu Kelantan

	Dry weight (%)							
-Sample	Al	K	Ca	Fe	Mg	Ti	Na	Si
GP1	20.50	5.61	1.16	7.49	0.61	1.27	0.92	54.34
GP2	17.69	4.43	1.32	4.51	0.87	0.69	0.56	63.44
GC1	20.99	5.24	1.59	6.96	0.86	1.16	0.64	52.49
GC2	17.15	2.31	1.77	4.30	0.51	0.59	0.62	69.12
GC3	17.00	2.83	2.29	8.01	1.15	1.15	1.08	62.09
GC4	20.97	3.08	1.45	4.80	0.66	1.21	0.14	59.30

Table 3: Elemental Contents (Trace Elements) of Pottery Shards in *Gua Cha* and *Gua Peraling*, Ulu Kelantan

	m/g (ppm)						
Sample	Mn	Zn	Ba	Cu	Pb	Au	Ag
GP1	343	105	13	3	47	1.0	10
GP2	184	96	12	6	59	0.5	4
GCI	215	70	40	1	37	1.0	2
GC2	363	111	41	1	48	0.5	1
GC3	465	179	44	6	61	1.0	1
GC4	303	127	71	5	38	1.0	1

Table 4: Elemental Contents (Major Elements) of Clay Samples Taken Around Ulu Kelantan

	Dry weight (%)							
Sample	Al	K	Ca	Fe	Mg	Ti	Na	Si
Sc	21.52	3.31	0.22	3.13	1.58	0.87	0.22	65.53
SS	25.29	3.16	0.32	4.13	0.91	0.89	0.27	60.35
SP	28.87	3.42	0.09	4.35	1.56	1.01	0.34	66.35
Si	22.13	2.45	1.19	3.96	1.31	0.98	0.31	65.24
SB	23.27	2.33	0.18	1.99	0.89	0.81	0.24	61.59
SN	22.35	3.52	0.37	3.41	1.29	0.95	0.24	69.20

Compositional analysis showed that there are differences between the pottery samples and clay samples. The elemental content of major and trace elements of the pottery shards are shown in Table 2 and 3, whilst the elemental content of the clay samples are shown in Table 4 and 5. The mineral contents of the pottery (Table 6), clay sampels (Table 7) and also the major and trace elements indicate that some of the pottery shards are probably of local origin, but four of the shards (GP2, GC1, GC3 and GC4) might have been brought in from outside Ulu Kelantan. Figure 1 shows as a binary plot the amount of K_2O versus the amount of CaO (De Raedt *et al*., 2000), which reveals the existence of two compositional groups. Three of the samples, GP2, GC2 and GC4 have elements that are most similar to the clay sample from *Jenera* River, but sample GC4 is totally different in its mineral contents and therefore suggesting that only samples GP1 and GC2 are probably the locally made pottery. Majority of the shards showed that they were not locally produced. This may suggest the strong possibility of some trading activities taking place around this area involving the inland people of Ulu Kelantan with coastal community which has more advance in culture.

Table 5: Elemental contents (Trace elements) of clay sample Taken around Ulu Kelantan

Sample	m/g (ppm) Mn	Zn	Ba	Cu	Pb	Au	Ag
Sc	106	19	6	27	24	0.5	4
SS	546	99	11	53	21	1.0	6
SP	424	106	3	46	7	1.0	4
Si	428	84	5	18	11	0.5	11
SB	86	67	6	4	7	0.5	11
SN	15	34	3	15	5	0.5	11

Table 6: Mineral Contents of Pottery Shards in *Gua Peraling* and *Gua Cha*, Ulu Kelantan

Location	Sample	Mineral
Gua Peraling, Ulu Kelantan	GPl	$KAlSi_3O_8$ Microcline Intermediate SiO_2 Quartz
	GP2	$KAlSi_3O_8$ Orthoclase SiO_2 Quartz
Gua Cha, Ulu Kelantan	GC1	$KAlSi_3O_8$ Microcline Intermediate SiO_2 Quartz
	GC2	$KAlSi_3O_8$ Orthoclase SiO_2 Quartz
	GC3	$KAlSi_3O_8$ Microcline Intermediate SiO_2 Quartz
	GC4	($Mg_313Fe_2AI_{0.87}$) $Si_3.AI_{0.7}O_{10}(OH)_8$ Clinochlore $NaAlSi_3O_8$ Albite SiO_2 Quartz

Table 7: Mineral Contents of Clay Samples from Ulu Kelantan, Kelantan

Location	Sample	Mineral
Nenggiri River	SN	SiO_2 Quartz $KA1_2Si_3AIO_{10}(OH)_2$ Muscovite
Betis River	SB	SiO_2 Quartz $KA1_2Si_3AIO_{10}(OH)_2$ Muscovite
Perias River	SS	SiO_2 Quartz $KA1_2Si_3AIO_{10}(OH)_2$ Muscovite $KAlSi_3O_8$ Orthoclase
Chai River	SC	SiO_2 Quartz $KA1_2Si_3AIO_{10}(OH)_2$ Muscovite
Jenera River	SJ	SiO_2 Quartz $KA1_2Si_3AIO_{10}(OH)_2$ Muscovite
Peralon River	SP	SiO_2 Quartz $KA1_2Si_3AIO_{10}(OH)_2$ Muscovite

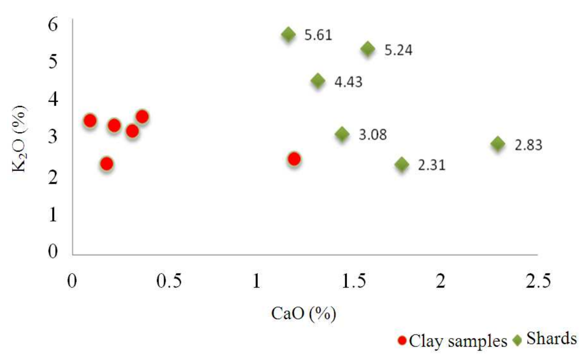

Fig. 1: Binary plot the amount of K_2O versus the amount of CaO

DISCUSSION

Lead (PbO) content in all samples is found to be in the normal range (Hornbostel, 1991), thus suggesting that there was no colouring material being added during the pottery making. Study done in *Gua Angin*, *Kota Gelanggi Jerantut*, *Pahang* showed that some potters added lead to their pottery as a colouring agent. Based on mineral content, samples GP2 and GC2 can be grouped together, sample GP1, GC1 and GC3 in the second group while sample GC4 is by itself. Analyses showed that the sample GC4 contain minerals known as quartz, clinochlore and albite, sample GP2 and GC2 contain minerals known as quartz and orthoclase, while sample GP1, GC1 and GC3 contain minerals known as microcline and quartz.

Clinochlore is one of the minerals in the chlorite group. Chlorite is commonly found in igneous rocks as an alteration product of mafic minerals such as pyroxene, amphibole and biotite. Chlorite is a common mineral associated with hydrothermal ore deposits and commonly occurs with epidote, sericite, adularia and sulfide minerals. In this environment, chlorite may be a retrograde metamorphic alteration mineral of existing ferromagnesian minerals, or it may be present as a metasomatism product via addition of Fe, Mg, or other compounds into the rock mass. Chlorite is also a common metamorphic mineral, usually indicative of low-grade metamorphism. It is the diagnostic species of the zeolite facies and of lower greenschist facies. It occurs in the quartz, albite, sericite, chlorite and garnet assemblage of pelitic schist. Within ultramafic rocks, metamorphism can also produce predominantly clinochlore chlorite in association with talc. Experiments indicate that chlorite can be stable in the peridotite of the Earth's mantle above the ocean lithosphere carried down by subduction and chlorite may even be present in the mantle volume from which island arc magmas are generated.

Analyses on the clay samples taken from the rivers near the *Cha Cave* and *Peraling Cave* such as *Nenggiri* River, *Betis* River, *Perias* River, *Chai* River, *Jenera* River and *Peralon* River showed that they all contain minerals known as muscovite and quartz accept that from the *Perias* River which has an additional mineral known as orthoclase. Muscovite decomposed at temperature of 600 and 700°C and since samples GP2 and GC2 also contain mineral known as quartz and orthoclase, this may suggest that these two samples have similar mineral contents with clay from *Jenera* River.

No kaolinite was found in the clay samples and this may be most likely due to the loss of kaolinite during heating of the clay at 600°C since kaolinite decomposes when the temperature exceeds 550°C (Stout and Hurst, 1985). Absence of kaolinite may also due to the absence of kaolinite in the clay used to make the pottery. However by looking at the colour and the mineral content of the shards, it can be suggested that the firing temperature used might be in range of 600-750°C. The effect of grain size on selected physico-chemical properties of clay in Malaysia can be refered from (Ahmad *et al*., 2009).

CONCLUSION

Elemental and mineral analyses of the pottery shards from *Gua Cha* and *Cha Peraling* showed that they do not contain similar type of minerals and elements as the clay sources taken around the area. Six samples from *Gua Cha* and *Gua Peraling* were analysed and only two samples that is GP1 and GC2 are similar with clay from *Jenera* River. Other samples were found to be of different elemental contents or types of minerals or both. Sample GC4 for example, has a similar elemental content with clay from *Jenera* River but totally different in mineral type where sample GC4 contain minerals known as clinochlore, albite and quartz while *Perias* River contain minerals known as muscovite, orthoclase and quartz.

Physical and chemical analysis showed that the same technology has been used for making the pottery. Thickness of the pottery showed that they were used for storage and also as tableware. The firing range is from 600-750°C and the colour ranges from black to grey. Elemental analysis also showed that no colouring agent had been added to the potteries.

Majority of the pottery shards showed that they are not similar to the clay samples taken from six different rivers in Ulu Kelantan although sample GP2 and GC2 are similar in composition with the clay from *Jenera* River. These potteries might have been imported into *Gua Cha* and *Gua Peraling*, or the other possibility is that the inhabitants in *Gua Cha* and *Gua Peraling* were from other places, probably from the coastal community. More samples needed to be analysed systematically from these two sites including pottery samples from the other sites in Ulu Kelantan in order to establish better comparison.

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