

Research Article

X-Ray Diffraction (XRD) and X-Ray Fluorescence (XRF) Analysis of Proto-historic Votive Tablets from Chawas Cave, Hulu Kelantan, Malaysia

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Abstract: This research was conducted to determine the origin of votive tablets found in prehistoric and proto-historic site of Chawas Cave in Hulu Kelantan. The votive tablets found in Chawas Cave showed several Buddhist images which are associated with the Srivijaya Kingdom which existed from 7th century AD until 12th century AD. To determine if the votive tablets were produced by communities that lived in Hulu Kelantan, hence the study of the chemical composition of the votive tablets should be carried out. Two techniques were employed in this research, namely the X-Ray Diffraction (XRD) and X-Ray Fluorescence (XRF) techniques. The techniques will determine the mineral content as well as the major and trace element content of the votive tablets. Analysis showed that all the votive tablet samples have mineral known as clinocllore. Clinocllore is one of the chlorites, namely a group of phyllosilicate minerals. Chlorite is commonly found in igneous rocks as an alteration product of mafic minerals such as pyroxene, amphibole and biotite. The votive tablets were found in a cave which consisted of limestone cave formation and it showed that the votive tablets were not produced by the local community of Hulu Kelantan. Major elements also showed that the chemical composition of the votive tablets is not similar to the composition of clay samples taken from several rivers in Hulu Kelantan.

Keywords: Chawas cave, hulu kelantan, srivijaya, votive tablet, X-Ray Diffraction (XRD), X-Ray Fluorescence (XRF)

INTRODUCTION

Chawas Cave is one of the rock shelters that exists in Hulu Kelantan valley. The first archaeological excavation was conducted in 1994 which unearthed several findings; these were mostly stone tools and animal remains which are associated with the Hoabinhian, Neolithic and proto-historic culture (Adi, 2007). Apart from the stone tools and animal remains, several cord mark pottery shards which are associated with the Neolithic culture were also found in this area. Radiocarbon dating by the Australian National University dated this site from 10,700 BC to 1000 CE. The most interesting finding in Chawas Cave was the Mahayana Buddhism votive tablet made from clay. More than a thousand votive tablets have been found in this area which indicated that maybe some of the communities living in Hulu Kelantan had been

influenced culturally by the Srivijaya Empire and practised Mahayana Buddhism. Several scholars have also associated the finding with the kingdom of Chih-tu where in the Sui Dynasty had sent their ambassadors to this area in 607 to 610 CE (Wheatley, 1961; Zulkifli, 2003).

Votive tablets are small Buddhist icons, usually made from baked or unbaked clay by a press-mold technique. In order to determine the origin of the clay, the chemical characteristics of the votive tablets therefore need to be studied. Based on their mineral content and major and trace elements, we can gather information about the origin of the clay. Several research of the same intent have been carried out on the ancient bricks of Bujang Valley temple of which the main objective was to determine the origin of the clay that were used. For example, chemical characteristics of

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the ancient bricks from Candi Sungai Mas (Site 32/34), Candi Bukit Kechil, Candi Bukit Pendiati (Site 17) and Candi Pengkalan Bujang (Site 23) showed that local clay was used to make the bricks (Zuliskandar *et al.*, 2011; Ramli *et al.*, 2012; Zuliskandar and Nik Hassan Shuhaimi, 2013; Zuliskandar *et al.*, 2013). Analysis on ancient glass beads from Sungai Mas also revealed that the beads were locally made based on the chemical characteristics of the beads (Ramli *et al.*, 2011a; Ramli *et al.*, 2009). Several pottery shards from prehistoric sites in Hulu Kelantan have also been analyzed and the results showed that most of the shards did not originate from Hulu Kelantan and probably originated from the coastal area (Chia, 1997; Ramli *et al.*, 2011b). Another analysis which involved ancient artefacts is the analysis carried out on ancient bronze drums found in several metal age sites in Malaysia (Adnan *et al.*, 2012). Analysis on pottery shards from Sharhr-I Sokhta, South Eastern Iran also showed some of the pottery shards probably came from Indus Valley which the indicator is showed by higher lead content in some of the pottery shards (Hossein *et al.*, 2013).

The main objective of this research is to determine whether the votive tablets found in Chawas Cave was made from local clay or otherwise. Mineral content of the votive tablets will be compared with mineral content of local clay especially clay taken from several rivers near the site. Comparison will also be performed on their major and trace elements. Final results should demonstrate whether the origin of the votive tablets is local and further show the involvement of the local communities in the production of the votive tablets. This is because initial indication only leads to the Kingdom of *Chih-tu* that existed in the state of Kelantan since the 6th century AD.

MATERIALS AND METHODS

A total of 10 votive tablet samples were taken from the excavation site of Chawas Cave and then taken to the lab for cleaning and labelled with the names KSGC1, KSGC2, KSGC3, KSGC4, KSGC5, KSGC6, KSGC7, KSGC8, KSGC9 and KSGC10. Samples weighing 0.4 g were refined and heated up for one hour at a temperature of 105°C and mixed until homogenous with the flux powder of a type of Spectroflux 110 (product of Johnson and Mathey). These mixtures were baked for one hour in a furnace with a temperature of 1100°C. The homogenous molten was moulded in a container and cooled gradually into pieces of fused glass with a thickness of 2 mm and a diameter of 32 mm. The samples were of 1:10 dilution. Samples in the form of fused glass were prepared for analysis of major elements such as Si, Ti, Fe, Al, Mn, Ca, Mg, Na, K and P₂O₅. Pressed pallet samples were prepared for analysis of trace elements such as Ba, La, Nb, Ni, Pb, Rb, Th, V,

Table 1: Mineral content for the votive tablet samples

No.	Sample	Mineral content
1	KSGC1	Quartz SiO ₂ Al ₂ Si ₂ O ₅ (OH) ₄ kaolinite KAl ₂ (Si ₃ Al)O ₁₀ (OH) ₂ muscovite (Mg _{2.8} Fe _{1.7} Al _{1.2}) (Si _{2.8} Al _{1.2}) O ₁₀ (OH) ₈ clinochlore, ferroan
2	KSGC2	Quartz SiO ₂ Al ₂ Si ₂ O ₅ (OH) ₄ kaolinite KAl ₂ (Si ₃ Al)O ₁₀ (OH) ₂ muscovite (Mg _{2.8} Fe _{1.7} Al _{1.2}) (Si _{2.8} Al _{1.2}) O ₁₀ (OH) ₈ clinochlore, ferroan
3	KSGC3	Quartz SiO ₂ Al ₂ Si ₂ O ₅ (OH) ₄ kaolinite KAl ₂ (Si ₃ Al)O ₁₀ (OH) ₂ muscovite (Mg _{2.8} Fe _{1.7} Al _{1.2}) (Si _{2.8} Al _{1.2}) O ₁₀ (OH) ₈ clinochlore, ferroan
4	KSGC4	Quartz SiO ₂ Al ₂ Si ₂ O ₅ (OH) ₄ kaolinite KAl ₂ (Si ₃ Al)O ₁₀ (OH) ₂ muscovite (Mg _{2.8} Fe _{1.7} Al _{1.2}) (Si _{2.8} Al _{1.2}) O ₁₀ (OH) ₈ clinochlore, ferroan
5	KSGC5	Quartz SiO ₂ Al ₂ Si ₂ O ₅ (OH) ₄ kaolinite KAl ₂ (Si ₃ Al)O ₁₀ (OH) ₂ muscovite (Mg _{2.8} Fe _{1.7} Al _{1.2}) (Si _{2.8} Al _{1.2}) O ₁₀ (OH) ₈ clinochlore, ferroan
6	KSGC6	Quartz SiO ₂ Al ₂ Si ₂ O ₅ (OH) ₄ kaolinite KAl ₂ (Si ₃ Al)O ₁₀ (OH) ₂ muscovite (Mg _{2.8} Fe _{1.7} Al _{1.2}) (Si _{2.8} Al _{1.2}) O ₁₀ (OH) ₈ clinochlore, ferroan
7	KSGC7	Quartz SiO ₂ Al ₂ Si ₂ O ₅ (OH) ₄ kaolinite KAl ₂ (Si ₃ Al)O ₁₀ (OH) ₂ muscovite (Mg _{2.8} Fe _{1.7} Al _{1.2}) (Si _{2.8} Al _{1.2}) O ₁₀ (OH) ₈ clinochlore, ferroan
8	KSGC8	Quartz SiO ₂ Al ₂ Si ₂ O ₅ (OH) ₄ kaolinite KAl ₂ (Si ₃ Al)O ₁₀ (OH) ₂ muscovite (Mg _{2.8} Fe _{1.7} Al _{1.2}) (Si _{2.8} Al _{1.2}) O ₁₀ (OH) ₈ clinochlore, ferroan
9	KSGC9	Quartz SiO ₂ Al ₂ Si ₂ O ₅ (OH) ₄ kaolinite KAl ₂ (Si ₃ Al)O ₁₀ (OH) ₂ muscovite (Mg _{2.8} Fe _{1.7} Al _{1.2}) (Si _{2.8} Al _{1.2}) O ₁₀ (OH) ₈ clinochlore, ferroan
10	SGC10	Quartz SiO ₂ Al ₂ Si ₂ O ₅ (OH) ₄ kaolinite KAl ₂ (Si ₃ Al)O ₁₀ (OH) ₂ muscovite (Mg _{2.8} Fe _{1.7} Al _{1.2}) (Si _{2.8} Al _{1.2}) O ₁₀ (OH) ₈ clinochlore, ferroan

Y, Zn, U, Cr, Sr, As, Ga, Cu, Hf, Co and Zr. These samples were prepared by mixing 1.0 g of samples together with 6.0 g of boric acid powder and then pressure of 20 psi was applied by using hydraulic pressure equipment. The samples of fused pallets and pressed pallets were then analysed using Philips PW1480 equipment. Samples in the form of very fine powder were put into the pellets (sample holder) and then analysed using the X-ray Diffraction instrument ((D500 Diffracto meter SIEMEN).

A scatter plot diagram of TiO₂ and MgO; Zr and V was then performed to demonstrate if there is any differences among the samples and analysed using Microsoft Excel software. The applicability of the analytical methods for the multi elemental analysis by XRF of the votive tablets is evaluated by the analysis of certified reference material, 315 Fire Brick (Calibration: G_FBVac 28 mm) for major elements and certified reference material, SY-2 (Calibration: Trace Element P_20) for trace elements. The CRM was also used as the quality control material of the analytical procedure.

RESULTS AND DISCUSSION

Mineral content analysis showed that the votive tablet samples have the same mineral content where all

of the samples contained minerals such as quartz (SiO_2), kaolinite ($\text{Si}_2\text{O}_5(\text{OH})_4$), muscovite $\text{KAl}_2(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_2$ and clinochlore, ferroan ($\text{Mg}_{2.8}\text{Fe}_{1.7}\text{Al}_{1.2}(\text{Si}_{2.8}\text{Al}_{1.2})\text{O}_{10}(\text{OH})_8$). Quartz is the general silica mineral that is usually found in soil samples while kaolinite is clay mineral. Muscovite is mineral from the mica group while clinochlore is mineral from the chlorite group that contains high magnesium and iron content. Analysis carried out showed that all the samples used the same clay source. The presence of decomposed kaolinite mineral at a temperature of 550°C showed that these samples if they were baked had been baked at a temperature of less

than 550°C . Nevertheless, there is a possibility that these samples were not baked but dried using sunlight. The mineral content in the votive tablet samples can be referred in Table 1 and the XRD diffraction pattern can be referred in Fig. 1 to 3.

The major element analysis that was carried out showed that the dry weight percentage for the silica element was between 66.61 to 75.42%. KSGC2 sample contained the lowest silica content while KSGC1 sample contained the highest silica content. Dry weight percentage for the titanium element was between 1.23 to 1.51%. The iron content in the votive tablet samples was quite high where the dry weight percentage was

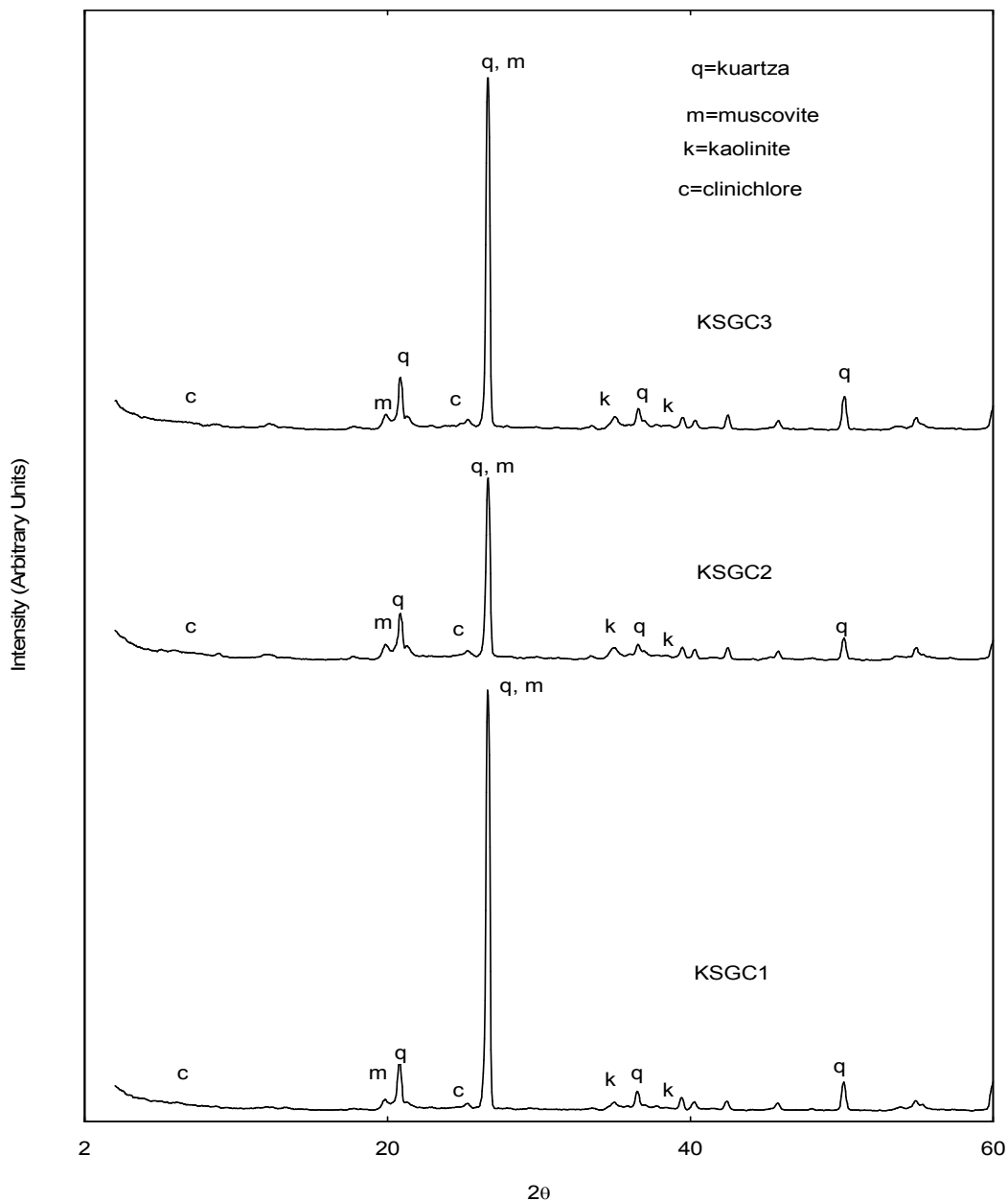


Fig. 1: XRD diffraction pattern for the KSGC1, KSGC2 and KSGC3 sample

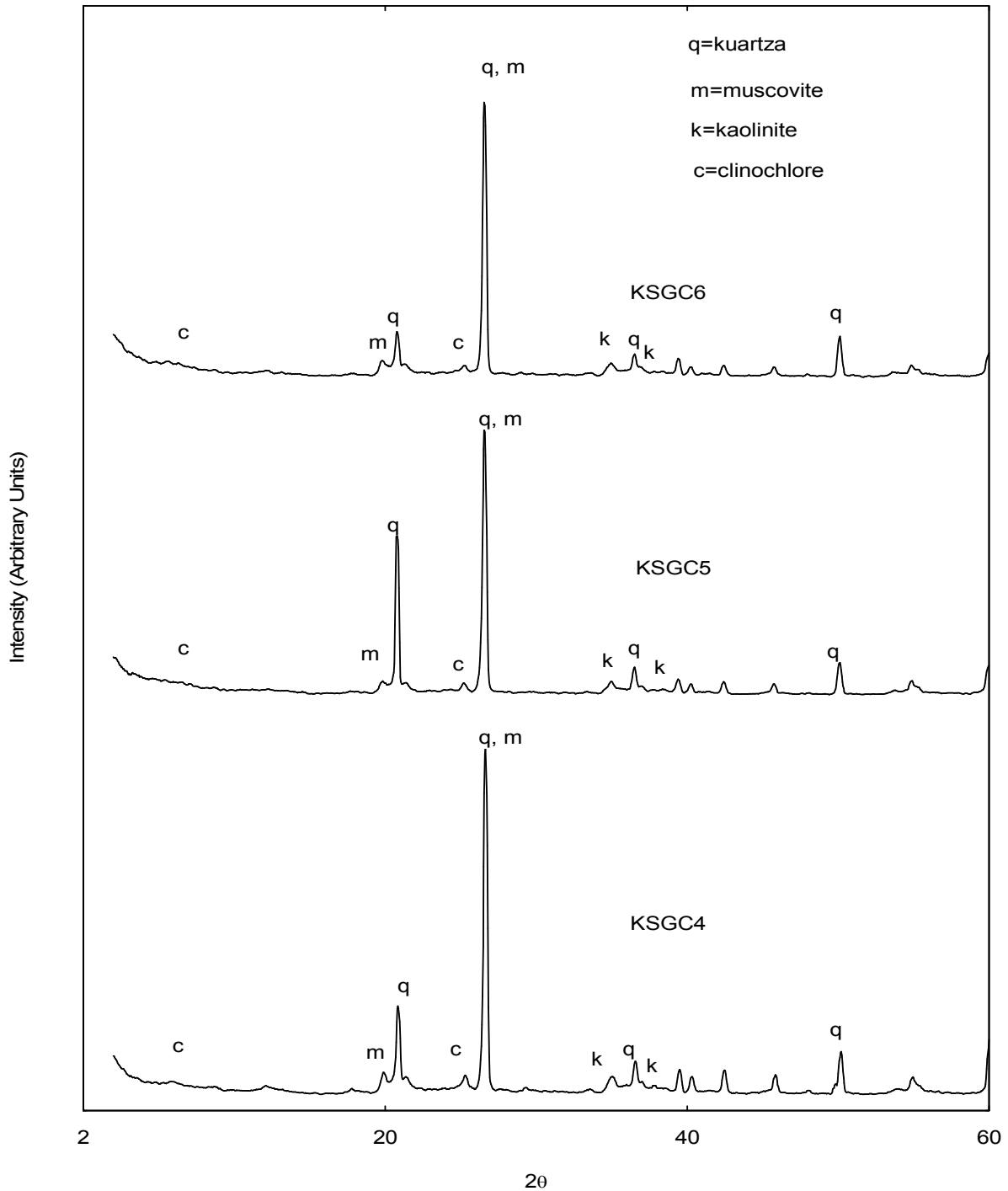


Fig. 2: XRD diffraction pattern for the KSGC4, KSGC5 and KSGC6 sample

between 5.18 to 6.94%. KSGC9 sample contained the highest iron while KSGC1 and KSGC7 sample contained the lowest iron content. The high iron content is caused by the presence of the clinochlore mineral. The aluminium element content was between 13.04 to 17.46% of which KSGC2 sample contained the highest aluminium content while KSGC1 sample contained the lowest aluminium content. Dry weight percentage for

the manganese and calcium content was between 0.14 to 0.29% and 0.60 to 0.99% respectively. Magnesium and sodium content was between 0.43 to 0.68% and 0.20 to 0.47% respectively. Dry weight percentage for potassium element was between 1.19 to 1.60% of which KSGC7 sample contained the lowest potassium element while KSGC2 contained the highest potassium element. Dry weight percentage for the phosphorous element

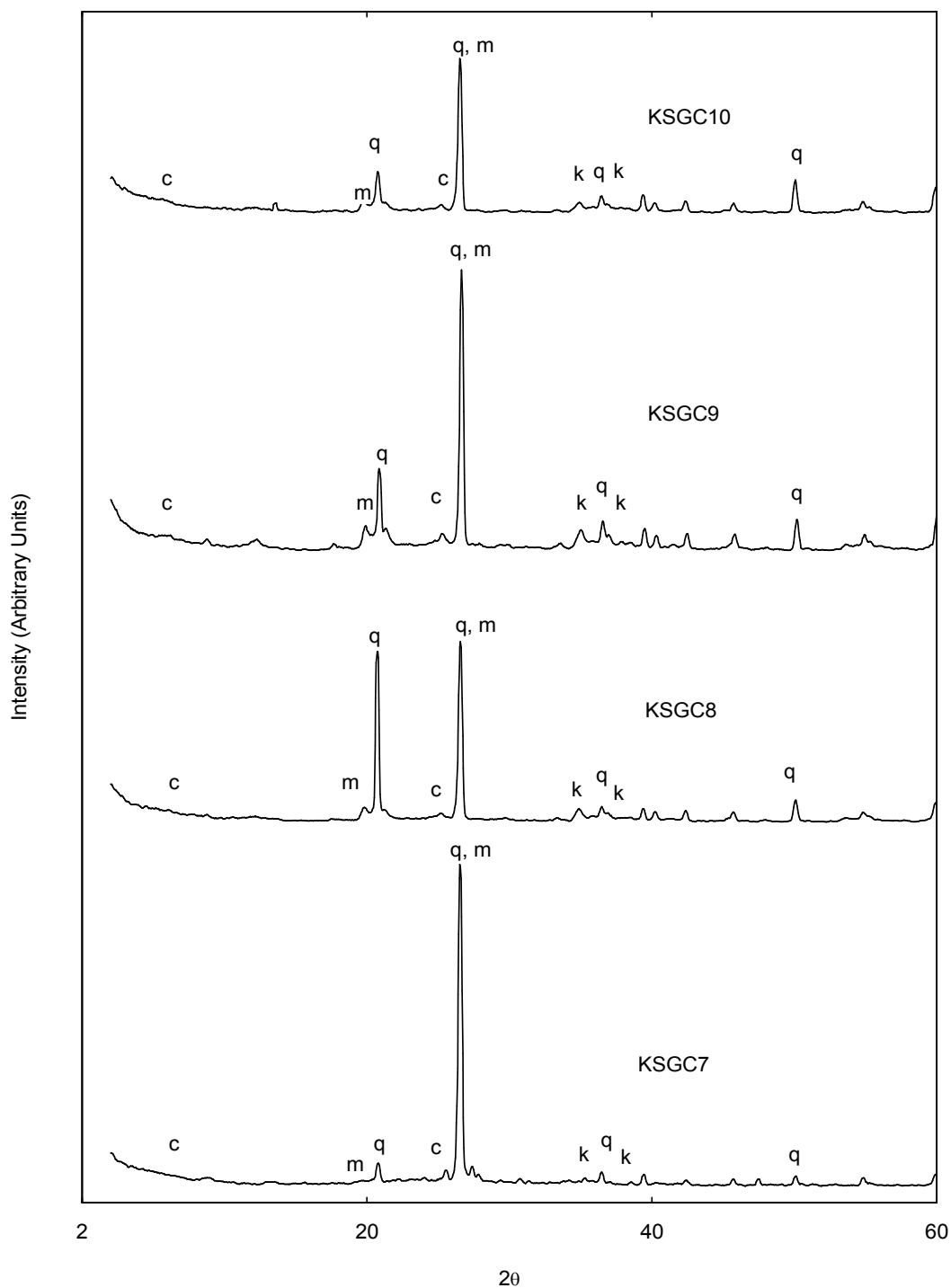


Fig. 3: XRD diffraction pattern for KSGC7, KSGC8, KSGC9 and KSGC10 sample

was between 0.08 to 0.17%. Major element content for the votive tablet samples can be referred to in Table 2. Scatter plot of TiO_2 and MgO (Fig. 4) was plotted to see the difference of each sample studied (De Readt *et al.*, 2000). Differences of elements for each samples need to be known to determine whether each sample contained the same elements or different elements.

After the graph was plotted, it was found that the votive tablet samples contained major elements that are almost similar. It is suggested that these samples used the same source of clay. Comparison to clay taken from surrounding area also indicated that the sources of the votive tablet were taken from another area and not came from clay in Hulu Kelantan.

Table 2: Major element content for the votive tablet samples

Sample	Dry weight (%)									
	Si	Ti	Fe	Al	Mn	Ca	Mg	Na	K	P ₂ O ₅
KSGC1	75.42	1.45	5.18	13.04	0.27	0.88	0.44	0.31	1.21	0.14
KSGC2	66.61	1.23	6.75	17.46	0.16	0.87	0.70	0.47	1.60	0.14
KSGC3	71.31	1.35	6.41	15.58	0.23	0.99	0.60	0.39	1.52	0.11
KSGC4	74.45	1.44	5.20	13.69	0.25	0.78	0.43	0.20	1.22	0.08
KSGC5	72.62	1.47	5.63	14.47	0.26	0.88	0.44	0.31	1.24	0.12
KSGC6	69.79	1.45	6.30	16.66	0.29	0.60	0.57	0.38	1.36	0.08
KSGC7	75.01	1.49	5.18	13.09	0.14	0.86	0.44	0.32	1.19	0.17
KSGC8	70.56	1.31	6.58	15.65	0.21	0.68	0.57	0.36	1.45	0.10
KSGC9	69.12	1.23	6.94	16.95	0.21	0.80	0.68	0.28	1.59	0.10
KSGC10	71.43	1.51	5.93	15.11	0.23	0.97	0.57	0.30	1.22	0.22

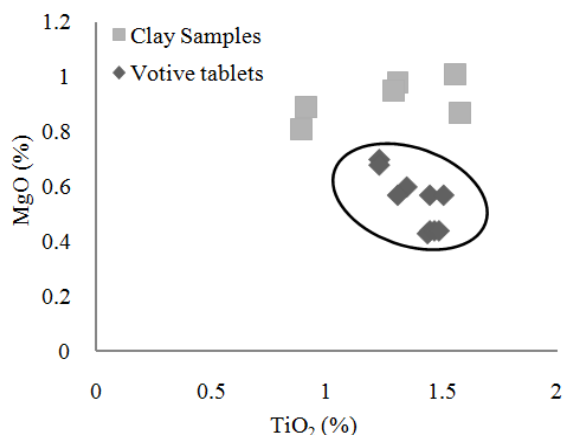


Fig. 4: Scatter plot of Ti (%) versus Mg (%)

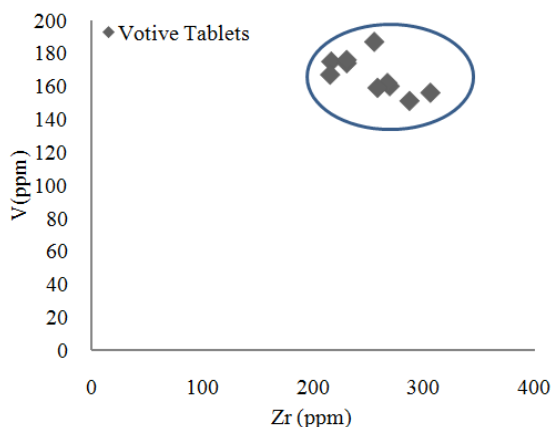


Fig. 5: Scatter plot of Zr (ppm) versus V (ppm)

Analysis of the trace elements was given attention if there were elements that exceeded 100 ppm. Most of the trace elements were of low content while trace elements with content exceeding 100 ppm were such as Ba, La, V and Zr. Ba element content was between 229 to 434 ppm; La element was between 83 to 170 ppm; V element between 151 to 187 ppm and Zr element was between 215 to 306 ppm. Scatter plot of Zr and V element (refer to Fig. 5) was plotted to find out whether the trace element content has similar element content. After the graph was plotted, it was found that the votive

Table 3: Trace element content for the votive tablet samples

Element (ppm)	Sample				
	KSGC1	KSGC2	KSGC3	KSGC4	KSGC5
Ba	434	299	386	388	330
La	170	122	117	83	85
U	26	25	31	31	27
Th	78	32	5	5	92
Ni	5	12	10	7	2
Cr	75	99	72	58	78
V	151	175	167	160	162
Nb	21	21	19	20	21
Zr	287	216	215	269	267
Y	23	37	34	34	47
Sr	31	25	29	24	28
Rb	67	78	77	78	80
Pb	84	118	58	77	35
As	5	9	9	8	10
Ga	20	20	20	20	20
Zn	59	95	80	84	84
Cu	-	-	-	-	-
Hf	7	7	6	6	3
Co	18	12	8	27	10

Table 4: Trace element content for the votive tablet samples

Element (ppm)	Sample				
	KSGC6	KSGC7	KSGC8	KSGC9	KSGC10
Ba	398	304	329	345	429
La	101	142	143	78	98
U	34	37	27	33	22
Th	92	13	78	21	37
Ni	19	3	10	16	4
Cr	79	69	80	86	85
V	187	156	174	176	159
Nb	21	21	17	18	23
Zr	255	306	230	230	258
Y	24	26	25	37	20
Sr	19	21	28	27	23
Rb	89	74	73	82	81
Pb	32	57	100	29	5
As	9	6	3	7	4
Ga	20	20	20	21	21
Zn	97	90	70	96	110
Cu	-	-	-	-	-
Hf	10	6	7	6	8
Co	5	9	5	16	19

tablets contained almost similar trace elements. This shows that the source used was similar. Trace element content in the votive tablet samples can be referred to in Table 3 and 4.

CONCLUSION

Analysis has shown that all the votive tablet samples have the mineral called clinocllore. Clinocllore is one of the chlorites which are a group of phyllosilicate mineral. Chlorite is commonly found in igneous rocks as an alteration product of mafic minerals such as pyroxene, amphibole and biotite. The votive tablets were found in a cave which comprised of limestone cave formation and it shows that the votive tablets were not produced by the local community of Hulu Kelantan. Major elements also showed that the chemical composition of the votive tablets were not similar to the composition of the clay samples taken from several rivers in Hulu Kelantan.

ACKNOWLEDGMENT

This research was conducted using the II/004/2012 grant; and therefore, we would like to express our gratitude to the Ministry of Higher Education for the research grant awarded.

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