SYNCHROTRON STUDIES OF BAN CHIANG ANCIENT POTTERY

Waraporn Tanthanuch[1], Wanwisa Pattanasiriwisawa[1], Weenawan Somphon[3] and Sutham Srilomsak[2*]

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Abstract

The pottery shards excavated from the Ban Chiang archaeological site a UNESCO world heritage site, Thailand are well known for their distinctive red paint and exquisite designs. The pottery assemblages are found to span 3 periods: Pre-metal, Bronze, and Iron Ages. The aim of this research is to explore the firing techniques used for pottery production during these time spans. X-ray absorption spectroscopy carried out at Beam line 8 (BL-8) of the National Synchrotron Research Center (NSRC), Thailand was used to measure Fe^{2+} and Fe^{3+} distributions in the pottery. A range of other analytical techniques, including X-ray Diffraction (XRD), X-ray Fluorescence (XRF), Fourier Transform Infrared Spectroscopy (FT-IR), Differential Thermal Analysis (DTA), and Thermal Gravimetric Analysis (TGA) were also used to obtain the chemical compositions and information on changes in the thermal properties of the samples. The Fe K-edge absorption spectra of mixed standard iron compounds and the red clay ceramics fired under control conditions at various temperatures are used as a reference standard to determine the ferric/ferrous ratio in the pottery shards. Results revealed that all Ban Chiang pottery was likely fired under partial reducing conditions, but the firing temperature used was higher in the Pre-metal Age than those in the Bronze and Iron Ages.

Keywords: Ban Chiang, Synchrotron, Firing temperature, XANES, X-ray absorption spectroscopy, FT-IR

Introduction

The Ban Chiang archaeological site in the northeast of Thailand has been designated as a world heritage site by UNESCO since 1992. This site dates from circa. 2100 B.C. to A.D. 200, spanning the Pre-metal, Bronze, and Iron Ages (Pietrusewsky and Douglas, 2002). A team from the University of Pennsylvania and Thai Fine Arts Department suggested that Ban

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[1] *Synchrotron Light Research Institute, Nakhon Ratchasima, 30000, Thailand.*

[2] *School of Ceramic Engineering, Institute of Engineering, Suranaree University of Technology, Nakhon Ratchasima, 30000, Thailand. Tel.: 0-4422-4459; Fax: 0-4422-4612; E-mail: sutamsri@sut.ac.th*

[3] *Chemistry Department, Faculty of Liberal Arts and Science Kasetsart University, Kamphaeng Saen Campus Nakhon Pathom, 73140, Thailand.*

[*] *Corresponding author*

Chiang pottery represents the world's oldest bronze-casting and iron-working civilization (Gorman and Charoenwongsa, 1976). Ban Chiang pottery has a unique appearance with no Chinese or Indian influence seen in the pottery. Some pottery was printed with rice husk patterns. Interestingly, the bronze items from Ban Chiang appeared only as jewelry, not as weapons as often found in Europe and the rest of the world (Pietrusewsky and Douglas, 2002). This evidence indicates that Ban Chiang was a peaceful agricultural society. The excavations of Ban Chiang pottery are divided into 3 periods: Pre-metal Age pottery as characterized by black vessels and decorated with a cord-mark design is dated between 3000-5000 years ago. Bronze Age pottery, dated between 2300-3000 years old, comprises carinated pots with greyish-white clay, and a plain surface with a painted incision under their rims. Iron Age pottery, dated between 1800-2300 years old, is the most beautiful of all. The designs on dark clay covered with a buff slip are painted with red geometric patterns. The unique style of the pottery in each period suggested the possibility of different fabrication processes and firing temperatures during each period. Investigation of this may provide important clues to the evolution of these ancient societies as well as their technology transfer.

McGovern *et al.* (1985) and Bubpha (2003) studied Ban Chiang pottery by petrography and found that the major inclusions of Ban Chiang pottery are quartz, grog, and plant material. While plant material was the major inclusion in the Bronze Age pottery, it was rarely found in the Iron Age pottery. They also investigated the slips which coated the Iron Age pottery with a scanning electron microscope (SEM) and reported that the slips were a 10-50 microns thick fused clay. By examining with an energy dispersive spectrometer (EDS) they proposed that the chemical compositions of the slip are almost the same as those of the interior of the ware. The difference is that the slip has slightly more iron (Fe) and slightly less calcium (Ca) contents than that of the interior of the ware. Moreover, their studies of the red paint on the Iron Age pottery reveal that the paint has similar chemical compositions to that of the slip. The dissimilarity is that the red paint is composed of more Fe and less Ca. Glanzman and Fleming (1985) examined Ban Chiang pottery fabrication methods by xeroradiography. They noted that the Pre-metal Age pottery was predominately fabricated with a coil and slab method. The Bronze Age pottery was fabricated by both coil and slab and lump and slab methods. During the Iron Age the coil and slab technique was used to make pottery. However, the coils in the Iron Age period were rounded, not flat as in the earlier period. White *et al.* (1991) wrote an excellent reviewed paper about the ceramic technology at Ban Chiang.

Many analytical techniques and approaches have been applied to identify the firing temperatures of ancient ceramics. Uda *et al.* (1999) estimated the firing temperature of ancient Chinese pottery by applying various analytical techniques, for instance XRD, X-ray Emission (PIXE), and DTA. Mössbauer Spectroscopy provided relevant information on the firing techniques in many publications (Wagner *et al.*, 1997; Matsunaga and Nakai, 2004; Maritan *et al.*, 2005). Recently, the Synchrotron X-ray Absorption Near-Edge Spectroscopy (XANES) technique has been developed, which provides advantages in archaeological research (Pantos *et al.*, 2002). This technique was applied for iron (Fe) valence state analysis in the samples the same as that used in the Mössbauer's Spectroscopy technique, but it also provided oxidation states of the Fe-ion and local symmetries of transition metal ions (Bianconi, 1988; Lamberti *et al.*, 2003). The XANES technique has been known to be used for determination of iron oxidation states in other samples such as silicate glass (Berry *et al.*, 2003), minerals (Wilke *et al.*, 2001), and ancient pottery from the Kaman-Kalehöyük site (Matsunaga and Nakai, 2004).

The XAS beamline (BL-8) of the National Synchrotron Research Center (NSRC), Thailand, has been successfully constructed and opened for users since 2006 (Klysubun *et al*., 2007). Therefore, it is a good opportunity for us to conduct archaeological research using the XAS beamline in Thailand. The objective of this work was to determine whether the Ban Chiang pottery of the 3 chronological periods was fired under different conditions by using XANES. The relationships between potential changes of the Fe redox state in controlled experimental fired clay across various firing temperatures and conditions were examined. The resulting spectra of these red clay samples were used as a fingerprint for the firing characterization of Ban Chiang pottery. Moreover, analysis techniques including XRF, XRD, thermal analysis, and FT-IR were combined in this research investigation to obtain other relevant information.

Materials and Methods

Sample Preparation

Three different types of samples were used in this present study including pottery shards, reference fired clays, and Fe standard compounds. The Fe standard compounds were analyzed to obtain the standard curve of the Fe redox state and Fe *K*-edge energy. The reference fired clays prepared in the laboratory were used for comparison with the XANES spectra of the shard samples.

Pottery shards

The pottery shards excavated from Ban Chiang archaeological site in the Northeastern of Thailand were used in this study. Ten representative shards (Figure 1) from 3 different Ages were selected for investigation as follows:

i) For Pre-metal Age: 3 pottery shards with a cord-marked design of simple geometric incising; PSN-2 (S10E13) (Figure 1(a)), excavated at 237 centimeter depth (cmdt); 5423 (Figure 1(b)), excavated at 400-410 cmdt; and 5424 (Figure 1(c)), excavated at 410-420 cmdt.

ii) For Bronze Age: 2 pottery shards with a puff rim and red paint; 5412 (S6E15) (Figure 1(d)), excavated at 330-340 cmdt; and 5414 (Figure 1(e)), excavated at 350-360 cmdt.

iii) For Iron Age: 5 pottery shards painted with red-on-buff; 8027 (Figure 1(f)), excavated at 130-160 cmdt; 0602 (Figure 1(g)), excavated at 190-200 cmdt; 7083 (Figure 1(h)), excavated at 160-180 cmdt; 8033 (Figure 1(i)), excavated at 160-180 cmdt; and 0042 (Figure 1(j)), excavated at surface-150 cmdt.

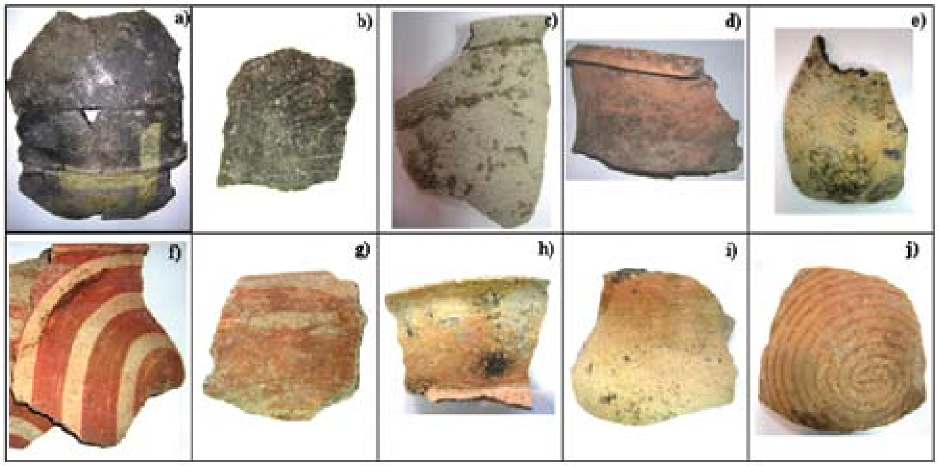

Figure 1. Ban Chiang pottery shards; a), b), and c) Pre-metal Age; d), and e) Bronze Age; f), g), h), i), and j) Iron Age

Reference Fired Clays

Natural clay, of which the chemical composition is provided in Table 1 was used to fabricate the reference fired clay. The clay was extruded and prepared to get the sample size of 20×100×10 mm (W×L×H) and dried at 100°C. Samples were fired at 500, 700, 900, and 1200°C in an electric kiln under oxidizing or reducing conditions with the heating rate of 5°C/min. Samples were soaked at the preset temperature for 1 h. Afterwards, they were cooled to room temperature at a rate of 5°C/min.

Fe Standard Compounds

Fe standard compounds were prepared by mixing $FeSO_4.7H_2O$ (Fe^{2+}) and $FePO_4.2H_2O$ (Fe^{3+}) in the ratios of 20%, 30%, 50%, 70%, and 80% (w/w in Fe of ($Fe^{3+}/(Fe^{2+}+Fe^{3+})$)). Then they were finely ground to a powder for homogeneity before use.

Chemical Analysis by XRF

Chemical analyses of the samples were determined by XRF using a Philips PW-2404 spectrometer equipped with a Cr tube.

Phase Analysis by XRD

The phase of samples was characterized by XRD using a Bruker Analytical X-ray Systems model D5005 X-ray diffractometer equipped with a Cu Kα sealed tube X-ray source operating at 40 kV and 35 mA. The data were collected in the range of 4.0-70.0° 2 theta with a 0.02° step size and a scan speed of 0.1 sec/step.

FT-IR Analysis

The samples were manually ground in an agate mortar for about 5 min for infrared analysis. FT-IR spectroscopy was performed using a Bruker infrared spectroscopy, ATR, Alpha, equipped with a Globar source. The spectra were obtained covering the 4000-400 cm^{-1} range. The spectra were recorded with a spectral resolution of 2 cm^{-1} and 128 scans. Data processing was performed by OPUS version 5.5 (Bruker Optic GmbH, Germany).

Table 1. Chemical composition of reference clay and Ban Chiang pottery shards

Compounds	Chemical composition (wt%)			
	Reference clay	Pre-metal Age (PSN-2)	Bronze Age (5412)	Iron Age (8027)
SiO_2	74.57	57.90	55.70	67.10
Al_2O_3	16.14	17.70	16.20	14.10
Fe_2O_3	5.38	3.52	3.16	1.43
TiO_2	0.88	1.00	0.78	0.85
K_2O	1.13	1.33	2.47	2.61
Na_2O	0.43	0.14	0.29	0.31
CaO	0.32	0.74	1.81	1.11
MgO	0.67	0.71	0.57	0.35
P_2O_5	0.04	0.15	0.79	0.82
MnO	0.07	0.07	0.28	0.08
ZrO_2	0.01	0.02	0.03	0.02
BaO	0.01	-	0.11	0.09
SiO_2/Al_2O_3	4.62	3.27	3.43	4.76

Thermal Analysis by TGA/DTA

TGA/DTA measurements were performed on a Perkin Elmer model DTA7 under air atmosphere from room temperature up to 1200°C at a heating rate of 20°C/min.

XAS Data Collection

Samples and reference compounds were ground manually in an agate mortar until homogenized fine powders were obtained. Sample powders were filled into the rectangular frames of the sample holders, which were taped with Kapton tape. The sample holder size was 12 mm × 6 mm, covering the beam size of the measuring station. The Fe *K*-edge XANES spectra were measured in the transmission mode using the BL-8 beamline of the National Synchrotron Research Center (NSRC, Thailand). Monochromatized 1.2 GeV SR X-rays, obtained from a Ge (220) double-crystal monochromator, was used to select the photon energy with a spectral resolution ($\Delta E/E$) of 10^{-4} (Klysubun *et al.*, 2007). While scanning the photon energy, the absorption spectrum was measured with 2 ionization chambers located before and after the sample. Incident beam energies were set from 50 eV below the main absorption edge energy (about 7112 eV for Fe) to about 200 eV above the Fe *K*-edge, with 0.2 eV steps for the 7050–7150 eV region and 1 eV steps after that region. The photon energy was calibrated in the region around the iron *K*-edge absorption using the maximum of the absorption peak (white line) of iron foil at 7112 +/- 0.2 eV. All of the XANES spectra were averaged and normalized using IFEFFIT software version 9 software (Ravel and Newville, 2005). The energy of the absorption edge (E_0) is defined as the edge crest in the normalized XANES spectra throughout this paper.

Results and Discussion

Chemical Analysis by XRF

Investigation of the chemical composition of Ban Chiang pottery using XRF is shown in Table 1. In this Table the SiO_2/Al_2O_3 ratio is also shown. All the samples contain a high amount of SiO_2 and low amount of Al_2O_3, of which the SiO_2/Al_2O_3 ratio varied between 3.27 and 4.76. The amount of alkaline oxides (K_2O and Na_2O) of the Pre-metal Age shard is lower than those found in both the Bronze Age and Iron Age shards. The amounts of alkaline-earth oxides (CaO and MgO) which are auxiliary fluxes are also low. In contrast, the amount of Fe oxide in the Pre-metal Age shard is higher than those in both the Bronze Age and Iron Ages shards. It is known that iron oxide causes the reddish color of the clay-based products after firing at low temperature, but gives a grayish color under high temperature. In this investigation, only Pre-metal Age pottery showed a grayish color throughout, while the Bronze Age and Iron Age shards exhibited a lighter color on the surface but showed dark-grey to black colors in the interior of the shards.

The composition of the reference clay (Table 1) contains higher amount of SiO_2 and Fe_2O_3 than those found in the pottery shards. However, the amount of these compositions did not effect the change of the iron redox states after firing. Therefore, it is acceptable to compare the iron redox states in the controlled samples to those in the pottery shards.

Mineral Phase Analysis by XRD

The mineral phase composition that was analyzed using XRD is shown in Figure 2. All Ban Chiang pottery shards have Quartz as main mineralogical phase. Quartz is also found to be the main phase of the reference clay samples.

Thermal Analysis by TGA/DTA

Figure 3(a) displays the TGA curves of Ban Chiang pottery shards from various ages. It is clear that the TGA curve of the Pre-metal Age shard PSN-2 is significantly different from those of the other ages. From the TGA curves it appears that the weight loss of the Pre-metal, Bronze, and Iron Ages pottery when heated from room temperature to 300°C are 1%, 5%, and 6% respectively. In the 300-600°C temperature range, the Pre-metal Age shard lost about 2% of its weight while the Bronze Age and Iron Age shards lost approximately 8% of their weights. These results suggest that the Pre-metal Age pottery was fired to a higher temperature than the 2 later Ages pottery.

Figure 3(b) illustrates the DTA curves of Ban Chiang pottery. It is clear that the DTA curve of the Pre-metal Age pottery has 2 different characteristics from the other Ages pottery. First, its peaks are both shorter and boarder. Second, its curves show downward slopes at high temperature which may be caused by baseline drift. From Figure 3(b) it is obvious that the DTA curves of Ban Chiang pottery of all ages show 1 large endothermic peak between room temperature and 350°C and 1 exothermic peak in each of the 350-500°C and 800-1050°C ranges. The peaks which occurred in the room temperature -350°C and 800-1050°C ranges were very broad, indicating that reaction occurred over large temperature intervals. Normally, the DTA curve of clay shows a first endothermic peak between room temperature and 200°C from the removal of adsorbed moisture reaction. This peak is much sharper than the endothermic peak found between room temperature and 350°C in the Ban Chiang pottery. The reason for this difference may be attributed to the fact that moisture which was absorbed into the ancient pottery for thousands of years reacted to some compounds inside the pottery to form new compounds of a hydrate form. These compounds may be tightly bonded to the pottery. Therefore they are more difficult to remove. In addition, the peak shifting and broadening in the Ban Chiang pottery's DTA curve may be caused by the high heating rate used in this experiment. The DTA curve of general clay shows a large and broad exothermic peak at 300-500°C, attributed to burn out of organic materials. It appears that peaks of this

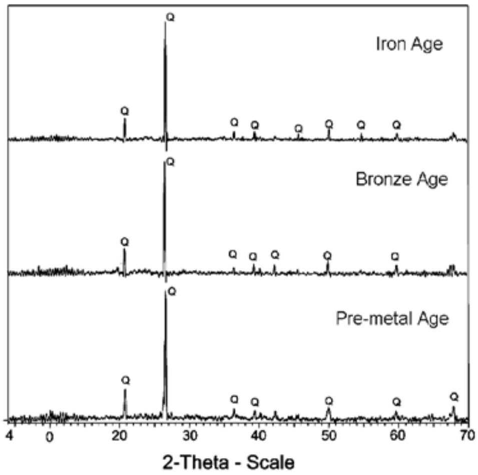

Figure 2. X-ray diffractograms of following Ban Chiang pottery shards: PSN-2, Pre-metal Age; 5412, Bronze Age; and 8027, Iron Age. Note K is Kaolinite and Q is Quartz

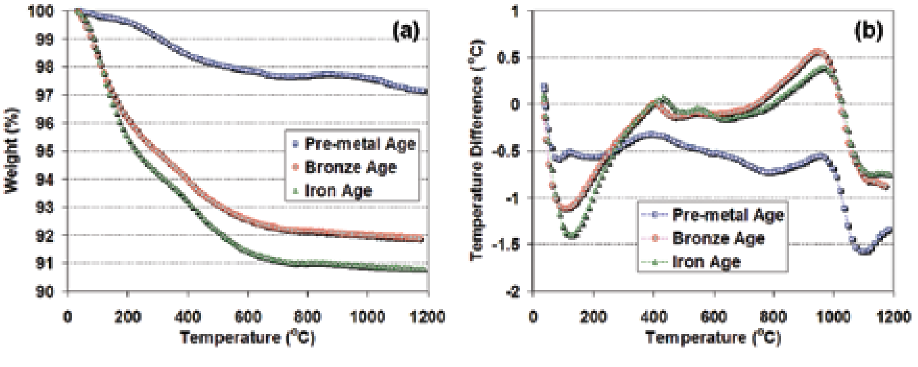

Figure 3. (a) TGA curve; and (b) DTA curve of Ban Chiang pottery shards

temperature range in Figure 3(b) are small especially the peak of the Pre-metal Age period. This result suggests that all periods of Ban Chiang pottery were fired to higher temperatures than this temperature range and the Pre-metal Age pottery was fired to a higher temperature than the other ages. The small peaks at 300-500°C in Figure 3(b) are likely to be caused by the burning out of organic materials which were not completely burned thousands of years ago when the pottery was fired in a reducing atmosphere heated by burning wood. The large exothermic DTA peaks in the range of 800-1050°C, shown in Figure 3(b), may be caused by a reaction between alumina and silica to form crystals. However, the exothermic peak of the same reaction of clay is normally sharper and longer than those in Figure 3(b). The discrepancy may be caused by the high heating rate used in this experiment. It is important to note that all DTA peaks of the Bronze Age and Iron Age shards are not only sharper but also larger than those of the Pre-metal Age shards. Both the TGA and DTA data suggest that the Bronze Age and Iron Age specimens were fired at lower temperatures or/and different atmosphere than the Pre-metal Age specimens.

Firing Temperature Analysis by FT-IR

The FT-IR absorbance measurements were performed on the whole set of experimentally fired clay and pottery shards. The FT-IR spectra were obtained covering the range of 4000-400 cm^{-1}. However, the typical spectra presented similar features ranging from 1400-600 cm^{-1}. These spectra ranges allowed us to use them as fingerprint spectra for the firing temperature characterization. The clay mineral (kaolinite) has characteristic absorption peaks at 917, 1012, 1038, and 1117 cm^{-1} (De Benedetto *et al.*, 2002). Investigation of the reference fired clays reveals that the intense absorbance peak of 1038 cm^{-1} corresponds to the clay mineral and is obviously seen in the 500°C fired clay of both the oxidizing and reducing atmosphere. At 700°C in both conditions, the absorption peak of the clay mineral slightly shifts to higher wave numbers by about 8-10 cm^{-1}. Interestingly, at 900°C oxidizing conditions, the peak shape of the experimental clays shifted significantly toward a higher wave number (1093 cm^{-1}) and has an extra shoulder peak at 1066 cm^{-1} (Figure 4(a)), while the 900°C reducing condition (Figure 4(b)) still has a peak shape similar to the 700°C fired

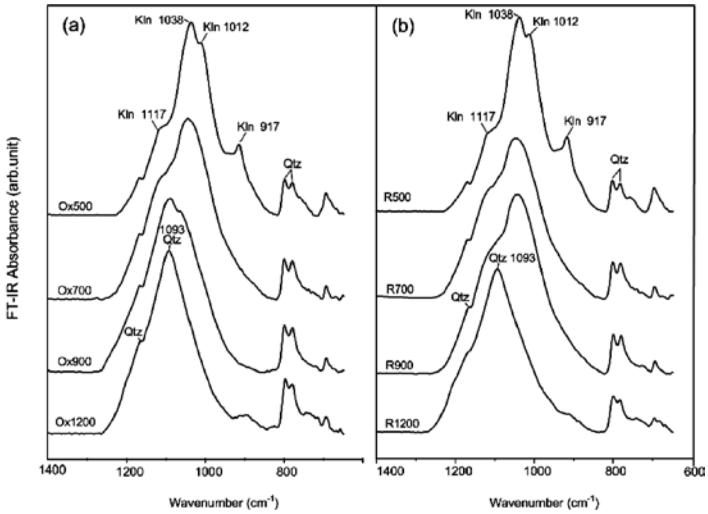

Figure 4. FT-IR absorbance spectrum of reference fired clays. R, Reduction firing; Ox, Oxidation firing; Kln, kaolinite; Qtz, quartz

clay. These results imply that under oxidation firing, the temperature reaches a higher degree than that of reduction firing. The intense band of 1038 cm^{-1} shifts to a higher wave number of 1093 cm^{-1} as the firing temperature increases (Figure 4(a)), suggesting the decreasing of clay minerals and the mineral phase transformation during firing. The 1200ºC fired clay showed peak positions at 1170, 1093, 802, and 782 cm^{-1} which corresponds to the SiO stretching of quartz. It is known that when the temperature reaches 1200ºC, the complete breakdown of clay mineral occurs; therefore the clay mineral could not be observed. It would be due to the fact that silica in clay material transforms into quartz continuously during firing, thus changing the FT-IR spectrum shape. The result suggests that the FT-IR spectrum reflects the phase changing of the mineral in clay fired under different conditions. Therefore, the FT-IR spectra of the reference fired clays were used as reference spectra to determine the firing temperature of Ban Chiang pottery.

The FT-IR absorbance of the Bronze Age and Iron Age shards shows minor differences, while 2 Pre-metal Age shards present a distinct feature (Figure 5). The spectra of 2 Bronze Age shards (5412 and 5414) and 3 Iron Age shards (8027, 8033, and 7083) are clearly matched to 700ºC fired clays under oxidizing conditions and 700ºC and 900ºC fired clays under reducing conditions. The spectra peak of 2 Iron Age shards (0042 and 0602) have shifted close to 500°C fired clays but are different in shape. Results suggest that these 2 shards were fired at a lower temperature than others. The Pre-metal Age shards (PSN-2 and 5424) exhibited an intense absorbance peak at 1093 cm^{-1} corresponding to a 1200ºC firing temperature of both oxidizing and reducing conditions. Another one of the Pre-metal Age shards presented a spectrum similar to 700°C fired clays under oxidizing conditions and to 700ºC and 900ºC fired clays under reducing conditions. Even though the FT-IR spectra could not tell the differences between clays fired under oxidation or reduction conditions, it provided more insight on the firing temperature estimation which could support the XANES data.

Fe-K XANES Analysis of Standard Fe Compounds

The Fe *K*-edge XANES spectra of the mixture Fe^{2+} ($FeSO_4$) and Fe^{3+} ($FePO_4$) standard compounds showed that there are distinct features in each individual spectrum (Figure 6). The structure at the main crest is significantly different between the oxidized and reduced forms of the samples. For example, the Fe *K*-edge spectra of samples containing 20% Fe^{3+} show an absorption edge at 7128.83 eV, while, the 80% $Fe^{3+}/(Fe^{2+}+Fe^{3+})$ sample peaked at about 7133.99 eV. Therefore, the absorption edge shifted to a higher energy with an increased amount of

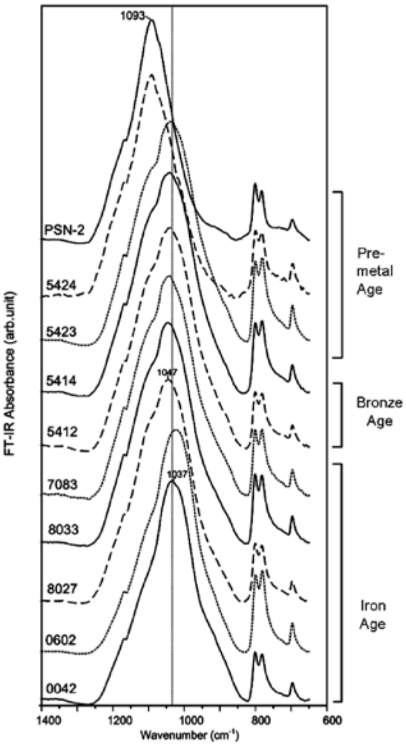

Figure 5. FT-IR absorbance spectra of Ban Chiang Pottery shards. R, Reduction firing; Ox, Oxidation firing

Fe^{3+} in the Fe^{3+} /(Fe^{2+}+Fe^{3+}) ratio. This result is in agreement with the XANES spectra of a series of quenched synthetic basaltic melts, in which the edge positions are shifted to higher energies with an increasing Fe oxidation state (Wilke *et al.*, 2005). The XANES results of the present work were used to draw the standard curve plotted between the Fe^{3+}/(Fe^{2+}+Fe^{3+}) ratio and the absorption energy. The standard plotted curve (Figure 7) shows clear positive relationships between the Fe^{3+}/(Fe^{2+}+Fe^{3+}) ratio and the absorption energy, with the R-squared value of 0.992. With this certainty, we concluded that it is safe to use the Fe^{3+}/(Fe^{2+}+Fe^{3+}) ratio resulting from the controlled experimental clay measurements as a standard curve for the estimation of the mixture of iron valence state of an unknown material as in the pottery shards.

Oxidation State Analysis with Fe-*K* XANES of Reference Fired Clays

The Fe *K*-XANES spectra of the reference clays fired under various conditions are shown in Figure 8 and the characteristic energies for the XANES spectra of each sample are summarized in Table 2.

The absorption edges of the clays fired under oxidizing conditions at various temperatures showed approximately the same energy level for each treatment; 7134±0.2 eV (Figure 8(a) and Table 2). The iron oxidation state of the clays fired under an oxidizing atmosphere was determined from the standard curve of the mixed Fe^{2+} and Fe^{3+} compound. Ninety-four percent are found to be mainly trivalent iron. These results correlate with the finding of Matsunaga and Nakai (2004) that the iron atoms that remained in fired clay are in a trivalent state after oxidation firing. We also observed slight increases of pre-edge peak intensities of the fired clays with increased firing temperatures. It might be due to the hematite formation after heating as reported by Matsunaga and Nakai (2004) that the hematite has a strong pre-edge peak because the iron atoms occupy distorted octahedral sites.

The Fe *K*-XANES spectra of clays fired under reducing conditions are shown in Figure 8(b). The spectrum shape of the reduced fired clay under 500°C is very close to the oxidized fired clay under 500°C, while the absorption energy of the reduced fired clay under 700°C shifted 0.72 eV to the lower energy. The trivalent Fe contained in the

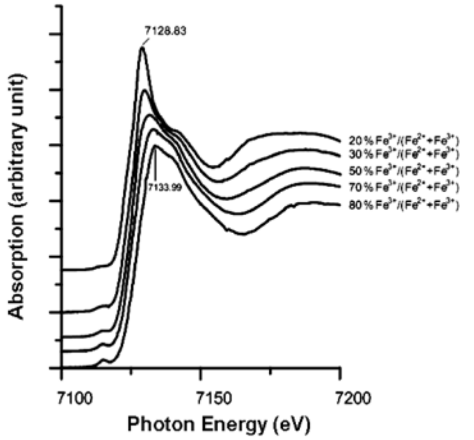

Figure 6. Fe *K*-XANES spectra of mixture Fe^{2+} and Fe^{3+} standard compounds

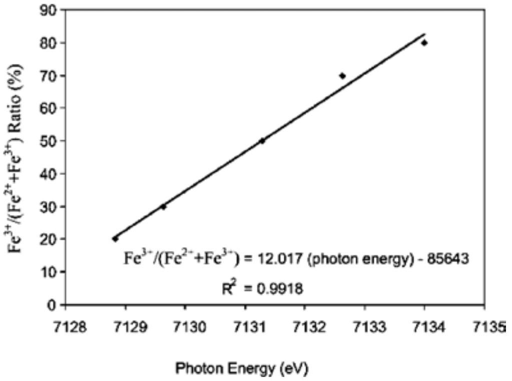

Figure 7. Plot depicting the percentage ratio Fe^{3+}/(Fe^{2+}+Fe^{3+}) versus Fe *K*-edge energy of standard Fe compounds

500°C fired clay and 700°C fired clay (calculated from the standard curve in Figure 7) are 92.8% and 84.1%, respectively (Table 2). Furthermore, the absorption spectra of the fired clay shifted significantly to the lower energy as the firing temperature increased. For example, the 900°C fired clay gave a broad absorption shape and edge crests at 7132.09-7132.97 eV. The energy at the middle of the edge crests was used to calculate the iron valence of the fired clay, and it was found that this clay contains 63% of trivalent iron. It is known that the broadened edge crests are often observed in mixed-valent compounds and compounds in which the absorber atoms occupy several different energy sites (Matsunaga and Nakai, 2004). Noticeably, the absorption feature of the 1200°C fired clay was different from other fired clays; it has a shoulder peak at 7128.29 eV and a sharp edge crest at 7132.39 eV. This sharp edge feature is defined as "white line", in which the typical species of iron atoms are located at highly symmetric sites and the valency of the absorber atom is expressed as an integer (Waychunas *et al.*, 1983). Therefore, the divalent Fe atom might be present predominantly in the clay fired at 1200°C under a reducing atmosphere. The shape of the shoulder can be attributable to the transitions of the bounded Fe atom from the 1s orbital to the 4s orbital (Shulman *et al.,* 1976; Waychunas *et al.*, 1983). The different features of the shoulder presumably reflect changes in the

Table 2. The energy of Fe *K*-edge features in reference fired clay and Ban Chiang pottery and Fe redox state contained in sample (calculated from the standard curve of Figure 7)

Sample			Edge crest energy (*ke*V)	Fe content (% $Fe^{3+}/(Fe^{2+}+Fe^{3+})$)
Reference fired clay				
Oxidizing conditions	:	500°C	7134.65	94.07
	:	700°C	7134.70	94.69
	:	900°C	7134.75	95.31
	:	1200°C	7134.80	95.94
Reducing conditions	:	500°C	7134.55	92.83
	:	700°C	7133.82	84.16
	:	900°C	7132.09	63.33
	:	1200°C	7132.39	63.93
Archaeological pottery				
Pre-metal Age	:	PSN-2	7132.09	63.33
	:	5424	7131.33	54.19
	:	5423	7132.56	68.97
Bronze Age	:	5414	7132.86	72.58
	:	5412	7133.45	79.67
Iron Age	:	8027	7133.72	82.91
	:	0042	7133.88	84.84
	:	7083	7133.17	76.30
	:	0602	7133.60	81.47
	:	8033	7133.07	75.10

Fe coordination number associated with the silicon crystal when being fired at different processes. Therefore, the features of Fe *K*-absorption of both the edge crest and shoulder might need to be taken into consideration for distinguishing the temperature and firing conditions of unknown pottery shards.

The Characterization of Ban Chiang Pottery Shards by XANES Spectra

In order to distinguish whether the pottery from different periods were produced under the same firing conditions, it is important that comparison is made of the XANES spectra of pottery samples (Figure 9) with the reference fired clays (Figures 8(a) and 8(b)), and the redox state of standard iron compounds (Figure 6). The Fe *K*-XANES spectra of pottery shards present different characteristics (Figure 9). It was found that 5 Iron Age shards have absorption edges in a range between 7133.07 and 7133.88 eV, in which the trivalent iron distributions are between 75.1% and 84.84% (Table 2). Two shards of the Bronze Age have absorption edges close to the Iron Age shards (7132.86 and 7133.45 eV), in which the trivalent iron distributions are 72.58% and 79.64%, respectively (Table 2). Results suggest that this pottery from 2 periods was fired under reducing conditions at temperatures between 700° and 900°C. By thin section, an obvious black core was present within the pottery of both the Bronze Age and Iron Age shards. It might be due to incomplete burning of carbonaceous materials (impurities in the clay) in a low firing temperature, which is caused by sealing off of the clay surface when temperatures reach 800°C, then trapping unburned carbonaceous materials and sulfides. These observations support the conclusion that the Bronze Age and Iron Age pottery was produced at a temperature between 700°C to 900°C under reducing conditions.

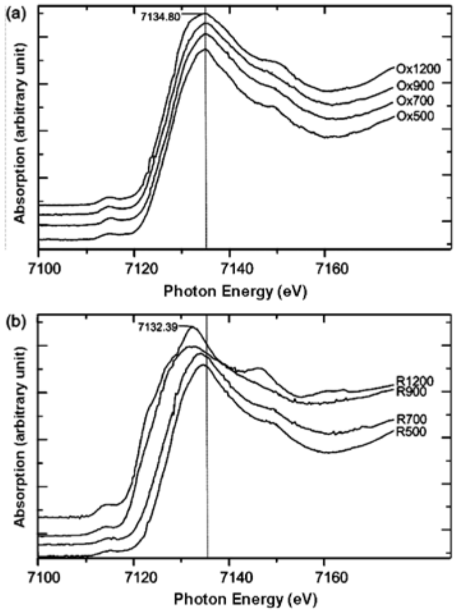

Figure 8. Fe *K*-edge XANES spectra of reference fired clays at various temperatures under: (a) oxidizing conditions (b) reducing conditions. Ox, Oxidation firing; R, Reduction firing

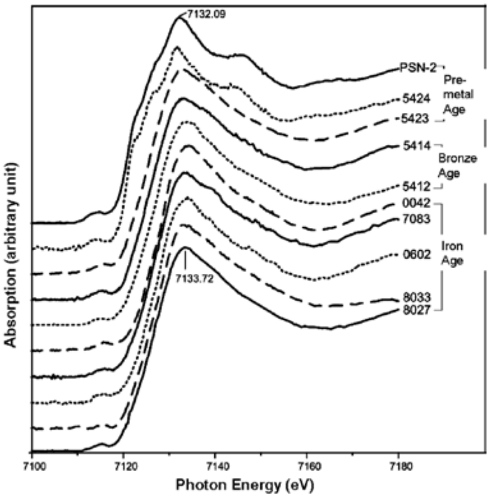

Figure 9. Fe *K*-edge XANES spectra of Ban Chiang pottery shards from different period of times. Ox, Oxidation firing; R, Reduction firing

The XANES features of 3 Pre-metal Age shards presented 2 different characteristics. The first 2 shards (PSN-2 and 5424) have a similar shape of XANES spectrum with 2 positions of absorption energy, the shoulder at 7128.29 eV and edge crest at 7132.09 eV and 7131.33 eV, respectively. The shape and absorption energy of these shards are very close to the clay samples produced under reducing conditions at 1200°C (Figure 8 and Table 2). Calculation of the trivalent iron distributions of the PSN-2 and 5424 shards found them to be 63.33% and 54.19%, respectively. However, the XANES feature of the 5423 shards shows a similar spectrum to the reference fired clay processed at 900°C under reducing conditions. Therefore, some pottery from the Pre-metal Age might have been fired under higher temperatures than that of the Bronze Age and Iron Age.

The characteristic of a Pre-metal Age shard is a dark-grey to black state which is believed to occur from ferric oxide (Fe_2O_3) or red iron oxide reduction at temperatures around 1200°C under reducing conditions to form ferrous oxide (FeO). Likewise, those of Grey Ware from Kamen-Kalehöyük, Turkey and grey shards from the Chinese terracotta figures in Matsunaka and Nakai (2004) and Qin and Pan's (1989) papers, respectively.

This study has concentrated on the original firing temperature and atmosphere conditions used on Ban Chiang pottery production during the historical period. The XANES technique has been applied for these analyses. This technique is proven as a potential way to identify the Fe reduction state of various materials, particularly pottery shards. The Fe reduction state in clay provides information on conditions used during firing, since the iron oxide in clay material undergoes transformation when being fired in different conditions, occurring in 2 valence states, Fe^{2+} and Fe^{3+}. Most iron undergoes transformation in a silicate matrix, therefore there was a low possibility of chemical alterations while the pottery was buried. The iron oxides remaining in the pottery body allow us to track back the original firing temperature in an ancient period. In this present work we found that Ban Chiang pottery shards in all 3 periods were fired under reducing conditions, but at different temperatures.

Five Iron Age shards, 2 Bronze Age shards and 3 Pre-metal Age shards were produced under reducing conditions at a temperature between 700°C and 900°C. And 2 Pre-metal Age shards were produced at 1200°C under reducing conditions. The XANES results are confirmed by FT-IR analyses, which presented a similar outcome. Even though the FT-IR measurement is not straightforward to find the firing conditions, the transformation of clay minerals after being fired could be determined. Thus, the FT-IR results can support the XANES analysis. This finding is also consistent with the TGA/DTA analysis as stated above.

An original firing temperature of Ban Chiang potteries has previously been reported by McGovern *et al.* (1985). By comparing the degrees of vitrification of 3 different ages of pottery with those of the refired tiles cut from the same specimens, they proposed that Ban Chiang pottery of all periods was fired at 500-700°C in the open air by piling wood and rice straw up and around the vessels. Our finding is inconsistent with McGovern *et al*'s. (1985) work. One possible reason for this discrepancy is the variation of shard samples. Most of our samples were excavated in 2003 while McGovern's samples were excavated earlier. Furthermore, McGovern *et al.* (1985) and our studies used different analytical techniques to interpret firing temperatures.

Since our result showed that some Pre-metal Age Ban Chiang pottery was fired at a rather high temperature and no evidence of an ancient kiln has been found, we consider that termite mounds could be used as kilns by Ban Chiang ancient people. It is highly possible that ancient Ban Chiang villagers used wood as fuel in their kilns, which could introduce reducing conditions. The firing technology of Ban Chiang in the Pre-metal Age might be relevant to pottery from Non Nok Tha and Ban Na Di (prehistoric sites close by Ban Chiang), which, according to Meacham and

Solheim's (1980) studies could be fired in kilns at 800-1150°C.

Conclusions

XANES has proven to be a technique of great potential for interpreting original firing temperatures and conditions of archaeological pottery production. The detailed shape and position of the edge, including the shoulder and the absorption *K*-edge are informative and relevant for Fe ion characterization. Combining XANES results with other common techniques used in materials science analyses, including FT-IR and TGA/DTA, strengthens the XANES analysis and is useful for archaeological research. Our results showed that all Ban Chiang pottery was likely fired under partial reducing conditions; the firing temperature used in the Pre-metal Age was higher than those in the Bronze and Iron Ages.

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