CONSERVAR PATRIMÓNIO

ARTICLE / ARTIGO

Estimating the firing temperature of a brick sample from a church *convento* archway ruin in Quipayo, Camarines Sur, Philippines

Estimativa da temperatura de cozedura de uma amostra de tijolo de uma ruína do arco da igreja do convento em Quipayo, Camarines Sur, Filipinas

JAN-MICHAEL C. CAYME [1*]
ERIC T. MIRANDA [2]

1. Chemistry Department, De La Salle University, 2401 Taft Avenue, Malate, Manila, 0922 Philippines

2. School of Chemical, Biological and Materials Engineering and Sciences, Mapúa University, 658 Muralla Street, Intramuros, Manila, 1002 Philippines

*jm.cayme@gmail.com

Abstract

The firing of bricks is one of the most critical manufacturing steps that affect its durability. It also directly reflects the past artisan's skills and technological knowledge. This study estimates the firing temperature range of a brick material from a Spanish Colonial Period church *convento* archway ruin in Quipayo, Camarines Sur, Philippines. A combination of different analytical techniques, namely energy dispersive X-ray fluorescence (EDXRF), Fourier transform infrared (FTIR) spectroscopy, X-ray diffraction (XRD), scanning electron microscopy with energy dispersive X-ray (SEM-EDX), and thermogravimetric analyzer (TGA), were utilized to determine the mineralogical and chemical composition. From the resulting composition data, the firing temperature of the brick material was estimated to be within the range of 900 to about 1,100 °C and burned in an oxidizing atmosphere. The information derived from this study provides a baseline chemical data of historical bricks that can help assess future conservation works.

KEYWORDS
Brick
Chemical characterization
Firing temperature
Analytical techniques
Philippines

Resumo

A cozedura dos tijolos é uma das etapas de fabrico mais importantes que afetam a sua durabilidade. Também reflete as competências e os conhecimentos tecnológicos do artesão. Este estudo estima a gama de temperaturas de cozedura de um material de tijolo de uma ruína do arco de uma igreja do convento do Período Colonial Espanhol em Quipayo, Camarines Sur, Filipinas. Foi utilizada uma combinação de diferentes técnicas analíticas, nomeadamente a fluorescência de raios X dispersiva em energia (EDXRF), a espetroscopia de infravermelhos com transformada de Fourier (FTIR), a difração de raios X (XRD), a microscopia eletrónica de varrimento com raios X dispersivos em energia (SEM-EDX) e termogravimetria (TGA), para determinar a composição mineralógica e química. A temperatura de cozedura do material de tijolo foi calculada entre 900 e 1100 °C, numa atmosfera oxidante. A informação deste estudo fornece uma base de dados químicos de tijolos históricos que pode ajudar a avaliar futuros trabalhos de conservação.

PALAVRAS-CHAVE
Tijolo
Caracterização química
Temperatura de cozedura
Técnicas analíticas
Filipinas

Introduction

Cultural heritage materials are tangible sources of valuable information regarding the past. Through material evidence, fundamental questions about the traditions, customs, and practices during the olden times can be addressed [1-4]. A common heritage material typically used in old masonry constructions is bricks. Brick making has been practiced since ancient times when raw clays were processed and were either sun-dried or fired in a kiln [5]. This material was widely used in constructing sacred places, fortifications, and secular buildings, among others, where stone masonry is either unavailable or difficult to procure [6]. Unlike other masonry work, brick making involves many human interventions, beginning with choosing the appropriate clay type, adding tempers or not, drying time, and finally, the firing temperature reached either in an open fire pit or in a kiln. These series of processes differ depending on the location, availability of materials, and skills of the artisans, eventually making the entire manufacturing chain variable [7-9]. In the absence of historical records, the chemical analysis of old bricks is an excellent strategy that will generate scientific-based data on their provenance.

In the Philippines, making bricks was believed to have been introduced in the late sixteenth century by the Spanish Empire during the colonial era [10]. Historical records on how bricks were made are fragmentary and were considered local initiatives that are not normally documented. One example was a descriptive account in the late nineteenth century showing that a brickmaker used carabaos (water buffalos) to mix thoroughly equal proportions of three different soil types collected in rice fields and along streams. After mixing, water was added to the mixture, followed by drying, and fired in a kiln or *horno* [7]. Attempts to broaden the historical information on colonial era bricks have been reported in literature through the chemical and mineralogical composition of selected bricks from the provinces of Ilocos Norte, Laguna, and Camarines Sur in the Philippines [8, 10-12]. By investigating the post-firing transformations of the raw clay minerals (aluminosilicates) together with the other non-clay minerals in these bricks, knowledge of the possible technological strategies employed by artisans and the temperature capability of their kilns can be known. Moreover, the firing temperature employed is viewed as a crucial step in any brick-making procedure because it influences the brick's overall microstructure, which eventually dictates its physical deterioration in the long run [13-14].

A rough indication of a historical brick sample's firing temperature can be obtained by investigating the post-firing minerals formed through different analytical techniques, namely X-ray (i.e., energy dispersive X-ray fluorescence – EDXRF – and X-ray diffraction – XRD), microscopy (i.e., scanning electron microscopy with energy dispersive X-ray – SEM-EDX), spectroscopy (i.e., Fourier Transform Infrared – FTIR), and thermal (i.e., thermogravimetric analyzer – TGA). Combinations of these techniques were utilized to estimate the firing temperature (<850 °C) of colonial era bricks from the Philippines obtained at the church convents of Milaor, Camarines Sur and Pagsanjan, Laguna, and the church bell tower of Liliw, Laguna [10, 12]. This temperature estimate was attributed to the absence of calcium silicate mineral phases and traces of calcite in the reported brick samples. In other studies, the presence of diopside, a form of a calcium silicate mineral, was used as evidence to show that the firing temperature is not more than 900 °C [15]. A firing temperature of between 900 to 1,000 °C was ascribed to the production of various old brick samples due to the presence of aluminum-rich spinel mineral phase and the disappearance of feldspars [16]. Furthermore, the existence of undecomposed clay, such as kaolinite, was also reported as a basis that the firing temperature did not exceed 550 °C [17]. By using these approaches, an estimate firing temperature range of a fragment of brick material from a nineteenth century, Spanish Colonial Period church *convento* arch ruin at Quipayo in the Province of Camarines Sur, Philippines, was investigated in this study.

The catholic mission in Quipayo was established by the Order of Friars Minor (OFM) or the Franciscans in the late sixteenth century, making it one of the oldest in the Bicol or *Kabikolan* region. Quipayo was one of the original mission centers of the Franciscans in Bicol and an important coordinating center wherein nearby towns were evangelized, and smaller parishes were supervised [18]. The brick material from Quipayo was analyzed using a combination of EDXRF, FTIR, XRD, SEM-EDX, and TGA, respectively. The result of this study aims to highlight the vital role of chemical analysis in providing scientific data as a prelude to any planned intervention and restoration work. Chemical analysis using various instrumental methods provides information on the structure and composition of heritage materials, which is necessary for crafting proper conservation frameworks suitable for the material. The use of rigorous chemistry techniques is not generally employed in conservation works in the Philippines, and there is a scarcity of published data in the Southeast Asian region. Hence, this paper will serve as a baseline data for more detailed studies on heritage brick materials in the future.

Background of the structure

Quipayo, where the arch ruin of the brick *convento* is located, is within the Province of Camarines Sur and used to be an independent town during the colonial era. Currently, it is under the jurisdiction of the Municipality of Calabanga (Figure 1). From Manila, the capital of the Philippines, Quipayo is almost 300 km away, heading towards the southeastern part of the main island of Luzon.

Figure 1. Map of the Province of Camarines Sur where Quipayo is located within the Municipality of Calabanga. Manila, the capital of the Philippines, is also shown in the map (source: Google maps).

Figure 2. Quipayo church *convento* archway ruin: *a)* archival photo facing east (October 1973, photography: *Parroquia de la Inmaculada Concepcion* parish office); *b)* archway ruin facing east (April 2014, photography: J. C. Cayme); *c)* view of the archway ruin relative to the main church structure (photography: Google maps).

The archway ruin is the only visible part of the historical *convento* that remained (Figure 2a-b). Like any church structure in the Philippines which was originally made of bamboo or wood and thatch-roofed during the early Spanish Colonial Period, the frequency of strong typhoons and other natural disasters perennially destroyed church buildings. As a remedy, renovation works have used more permanent building materials such as bricks [7]. Based on the relative position of the archway ruin to the church facade, it is most likely located on the extreme end of the *convento* either as an extension or part of a series of arches spanning the ground level (Figure 2c). The archway ruin may have supported a deck above, which may have been used as an open area or a service area attached to a kitchen. The area below the arch can be used for either storage or a horse stable [19]. Scant historical records state that the original brick masonry structure was probably built in the early seventeenth century, and the present *convento* ruins were believed to be a nineteenth century construction [20]. The archway ruin's structural purpose and a construction year of about the early to mid-1800s was ascribed by rough comparison with existing church *conventos* in the Philippines having similar architectural features [19].

Materials and methods

Clay brick sample

The brick masonry comprising the archway ruins are composed of bricks with average sizes of approximately 30.48 (length) × 6.99 cm (height) relative to its outer surface. Biological growth is also apparent from the brick's surface, especially those near the base. This is due to the damp and moist environment conducive to the development of algae, molds, fungi, or lichens [21] (Figure 3a). The brick fragment used in this study was collected in April 2014 inside the lower western end side of the *convento*'s archway (Figure 3b-c).

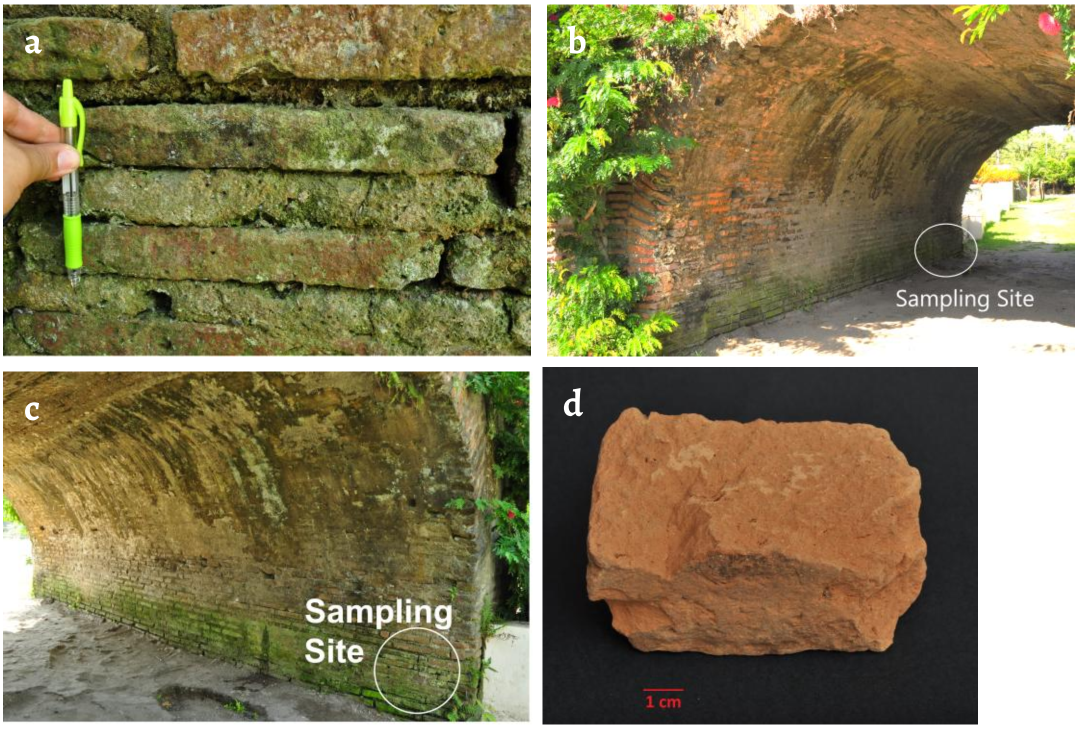


Figure 3. Archway ruin: *a)* Portion of the brick masonry wall where the sample fragment was retrieved; *b)* View of the front portion of the inner archway facing the east side; *c)* View of the back portion of the archway facing the west side (the approximate sampling site is indicated); *d)* The brick fragment, where the representative sample was obtained and tested with the different analytical techniques (photographs: J. C. Cayme, April 2014).

A brick fragment measuring about 7.87 × 3.81 × 2.54 cm was removed from an inconspicuous part of the structure approximately 30.48 cm from the base (Figure 3d) using a hammer and chisel. Extreme care was exercised in obtaining the fragment, and only an adequate amount was taken, which is enough for all the chemical characterizations used in this study. This precaution was practiced to ensure the historical authenticity of the ruins is maintained and preserved. From this fragment, a 16.2 g representative sample was scraped off from the inner portion about 1-2 cm from the surface to guarantee that no contaminants from the surroundings would affect the chemical analyses. This representative sample was homogenized and was dried completely at room temperature (around 37 °C) before testing using EDXRF, FTIR, TGA, SEM-EDX, and XRD analyses, respectively.

Analytical methods

Energy dispersive X-ray fluorescence (EDXRF) analysis

A Shimadzu EDX-7000 Energy dispersive X-ray fluorescence spectrometer was used to determine the elemental composition of the brick sample. A small bulk piece, enough to fit in the polypropylene cup holder, was run through a detailed analysis mode program (about 10 min run time) operated under a vacuum. The collimator was set to 3 mm. After the run, the results were reported as elemental oxides and undetected elements, such as absorbed crystalline water and organic compounds, are labelled LOI (loss on ignition).

Fourier Transform infrared (FTIR) analysis

The brick sample was homogenized and tested for qualitative mineral content and possible organic compounds using a Thermo Scientific Nicolet 6700 Fourier Transform Infrared spectrometer. The homogenized sample was prepared for analysis by using the KBr pellet method with a mixture ratio of roughly one part brick sample to three parts KBr. The pellet formed was scanned repeatedly for 16 times in the mid-infrared region (4000 to 500 cm^{-1}) at a resolution of 4 cm^{-1}. The FTIR spectrum was reported in the transmission mode.

X-ray diffraction (XRD) analysis

The mineralogical characterization of the brick sample was acquired using a Shimadzu Maxima XRD-7000 X-ray diffractometer. The sample was prepared by pressing a homogenized brick powder into an aluminum holder using a glass slide. XRD measurements were carried out through CuK_α radiation at a continuous scan range mode from 3-90°2θ. A scan speed of 2 deg/min was applied. The XRD pattern was graphed, and the mineral phases were analyzed using MATLAB program (The MathWorks Inc., Massachusetts, USA). The possible identity of the mineral phases in the sample was compared to the reference mineralogy database from the RRUFF Project (RRUFF Project, Arizona, USA) [22] and Web Mineral (www.webmineral.com).

Scanning electron microscopy with energy dispersive X-ray (SEM-EDX) analysis

SEM-EDX was employed to visualize the brick sample's microstructural changes and the corresponding elemental composition. A small, smooth cross-section representing the brick fragment was removed from the bulk and mounted into the SEM holder using a double-sided conductive adhesive tape, afterward coated with a thin layer of gold (JEOL JFC-1200 Fine Coater). The SEM image (1,500× magnification) was obtained using SEM/EDX JEOL JSM-5310 and analyzed by an Oxford Link Isis in spot-profile mode. Simultaneously, an EDX elemental profile of the SEM image region was also acquired at a 62 eV resolution.

Thermogravimetric analysis (TGA)

The brick fragment's thermal properties were measured using TA Instruments Discovery TGA55. The sample was placed in a platinum pan (Platinum HT), and the mass (24.96 mg) was weighed automatically by the TGA. The run program was set from 25 to 1,000 °C at a ramping rate of 10 °C/min under nitrogen atmosphere. The weight loss was monitored as the temperature increased.

Results and discussion

Chemical and mineralogical composition

Chemical elements originating from natural clays and their transformation products in the brick material after firing are reflected in the EDXRF and FTIR data shown in Table 1 and Figure 4, respectively. Clays are rarely pure and always include non-clay mineral impurities, most of which come from sand. EDRXF shows that the brick sample primarily comprises of silicates (SiO_2) at 46.51 %, which form part of the elements in quartz, feldspar, and clay phyllosilicates (i.e., clay minerals). Quartz is the primary source of SiO_2 in the sample and supported by the FTIR results showing characteristic infrared absorption bands assigned to Si-O stretching vibrations at 1061 cm^{-1} (υ3; asymmetrical) and 795 cm^{-1} (υ1; symmetrical), and bending vibration at 472 cm^{-1} (υ4; asymmetrical), respectively [10, 12].

From the EDXRF data, aluminates (Al_2O_3) account for 17.54 % of the sample, which forms part of layered aluminosilicates in clay minerals and is also found in feldspars. An indication for montmorillionite type clays in the sample is implied by the SiO_2/Al_2O_3 ratio of 2.66, while a possible mixed layered illite/smectitic clays are indicated by K_2O having < 1.0 % abundance and Fe_2O_3 at 4.0 to 7.0 %, respectively [10, 23]. Studies have reported that montmorillionite is one of the dominant clay types in the Camarines Sur province, where Quiapayo is located [24-25]. Furthermore, another historical brick from a church convent in Milaor which is within the same province also identified montmorillonite as a possible clay type [10]. K_2O and CaO are likely part of the potassium and calcium endmembers of feldspars in the sample and interlayer cations in clays as Ca^{+2} and K^+. A CaO content of 2.16 % based on the EDXRF data, which is less than 6.0 %, signifies a non-calcareous clay was used as raw material [26-27] in manufacturing the brick.

On the other hand, clay minerals, according to the FTIR data, generally have key absorption peaks situated at 3750 to 3400 cm^{-1} for the O-H stretching modes, 1200 to 700 cm^{-1} for the Si-O and Al-O stretching modes, with its corresponding bending modes at 600 to 400 cm^{-1} and metal-OH bending modes at 950 to 600 cm^{-1}, respectively [8]. Since the vibrating groups in clay phyllosilicates are more rigid than the loosely held Si-O group in quartz, overlapping with quartz is usually observed in a brick's FTIR spectrum. Furthermore, absorbed water can also have overlapping peaks, as demonstrated by the broad FTIR peak centered at 3448 cm^{-1} (O-H stretching mode) and 1637 cm^{-1} (H-O-H bending mode) [28].

Iron oxide minerals formed during the firing process are evident from the weak FTIR absorption bands at 542 and 579 cm^{-1}, assigned to hematite (Fe_2O_3) and magnetite (Fe_3O_4), respectively [8]. Besides the FTIR absorption peak for Fe_2O_3 being sharper compared to Fe_3O_4, XRD has also identified hematite as the primary mineral phase in the brick sample (Figure 5). These observations suggest that the brick sample was fired in open air or a perfectly oxidizing atmosphere when manufactured [10]. The total amount of iron oxide (5.05 %) is reported as Fe_2O_3 from the EDXRF.

The content of mineral fluxes which in the case of the sample are the total amount of K_2O, Fe_2O_3, CaO, and TiO_2, from the EDXRF, provided information on the vitrification process during firing. Since the total amount of fluxes (8.18 %) is less than 9.0 %, the raw clay material used for the brick is considered high refractory [27]. This result implies that a relatively higher firing temperature is needed to form a glassy material to bind the minerals together.

Historical accounts show that ashes from plant materials like coconut husks were mixed with clay in colonial period brick-making in the Philippines [12]. These burned plant materials served as a temper to prevent cracking at high temperatures and for the wet clay material to not stick on the brick mould [29]. This would explain the loss on ignition (LOI) in the EDXRF data at 26.34 %, which is attributed to these organic compounds left during firing in the clay matrix and other elements that are outside the limit of detection of the EDXRF. Furthermore, these organic compounds transformed into amorphous carbon ashes, which can be attributed to the large amount of carbon in the EDX analysis.

Table 1. Element oxides composition from the EDXRF

Element oxides	Percentage (%)
SiO_2	46.51
Al_2O_3	17.45
Fe_2O_3	5.05
CaO	2.16
SO_3	0.62
K_2O	0.51
P_2O_5	0.51
TiO_2	0.45
Cl	0.17
MnO	0.12
SrO	0.04
V_2O_5	0.03
ZrO_2	0.01
CuO	0.01
ZnO	0.01
Ir_2O_3	0.00*
LOI**	26.34

* Ir_2O_3 - 0.004 %; **LOI - loss on ignition

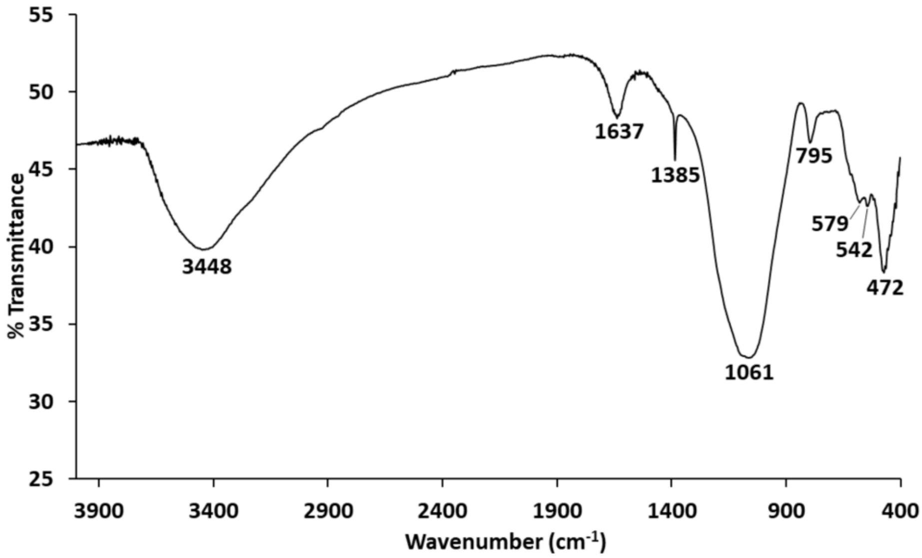


Figure 4. FTIR spectrum showing the significant absorption peaks.

Estimation of firing temperature

The FTIR spectrum (Figure 4) provides insights into the brick material's firing temperature range based on the absorption peak's intensity. The absence of detectable peaks at 1100 cm^{-1} (Si-O stretching) and 915 cm^{-1} (Al-OH bending), but instead, an intense broad peak centered at 1061 cm^{-1} was present, are typical spectrum patterns that resulted from the dehydroxylation and rearrangement of aluminum octahedral sheets in clay minerals. This transformation usually occurs when the material is fired above 650 °C [30]. The shift of the Si-O band toward higher frequencies accompanied by the intense broad peak is also indicative of a firing temperature that has reached 800 °C [31].

The existence of certain mineral types in the brick sample can also be utilized as an indicator of firing temperature. As seen in Figure 5, the transformation of quartz from the α- to the β-structure occurs abruptly at 573 °C [32]. The brick sample originated from a highly sandy montmorillionitic soil; hence the sand content minimized the amount of Ca and Na detected in the EDXRF and EDX. Montmorillonite, which was originally present in the raw clay material based on the EDXRF data, was absent in the XRD pattern, implying a firing temperature above 850 to 900 °C. Montmorillonite decomposes within this temperature range, and this property was employed to ascribe a possible lowest firing temperature limit of about 900 °C [33], consistent with the FTIR results. A similar analysis reported in literature for Spanish Colonial Period bricks in the Philippines from Pagsanjan and Liliw, both in the Laguna Province, have montmorillonite still present in the XRD pattern, hence have a lower temperature range compared to the Quipayo brick sample [12]. The brick sample was also made from a non-calcareous raw clay based on the EDXRF (Table 1) explaining the absence of newly formed calcium-silicate mineral phases [34]. Furthermore, since β-quartz is the only predominant polymorph of SiO_2 in the brick sample, as opposed to the high-temperature variety, which is cristobalite, the highest firing temperature should not exceed 1,100 °C [35].

SEM results (Figure 6) show the appearance of buckling in the clay plates (marked as 1) and starting to coalesce (marked as 2). These developments are classified as an extensive vitrification that typically forms at a temperature exceeding 950 °C in an oxidizing atmosphere [26, 36]. The presence of high refractory fluxes, as determined by the EDXRF data and confirmed through EDX (Table 1), implies that a higher temperature is needed to completely vitrify the brick's microstructure. The SEM did not detect any significant bloating pores, which are usually influenced by the decomposition of calcite or the release of CO_2 in $CaCO_3$. Since the brick sample is non-calcareous based on the EDXRF data and the EDX detected only < 1.0 % of calcium on the representative SEM image, calcite is found to be negligible and not involved in the formation of pores.

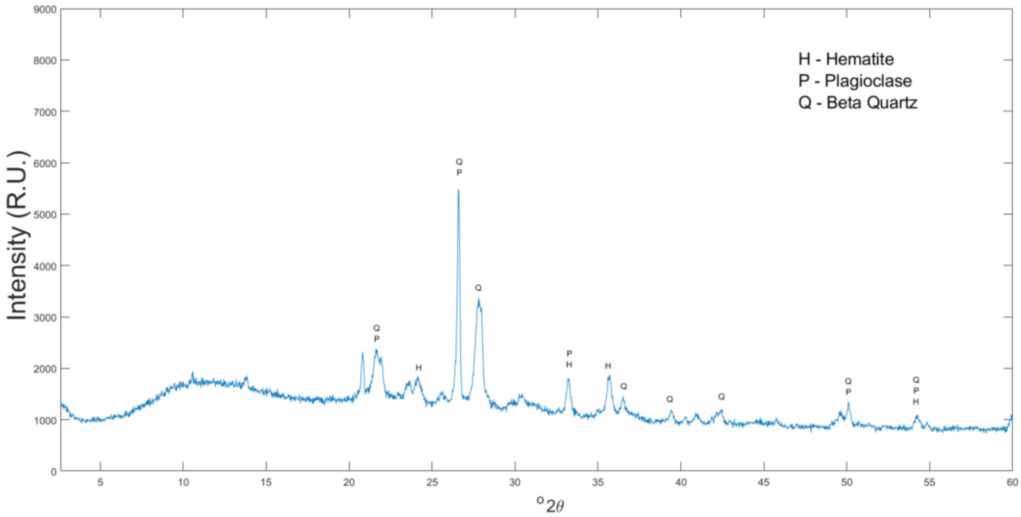
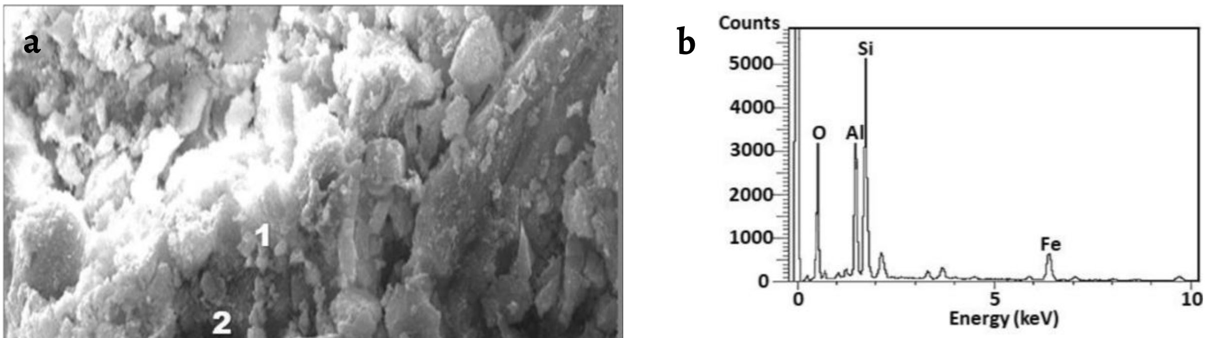


Figure 5. XRD patterns showing the different mineral phases.



Element	Atomic %
Si	11.07
Al	6.55
Fe	2.94
Ca	0.79
K	0.38
Cu	0.31
Ti	0.19
Na	0.12*
Mn	0.09*
Mg	0.04*
O	44.30
C	33.21
Total	100

*trace amount

Figure 6. Brick sample (inner core): *a)* SEM image (magnification of 1,500×); *b)* EDX spectrum and quantitative atomic percentage.

Thermal analysis

TGA methods were used to evaluate the dehydroxylation of clay minerals and the possible presence of calcite or $CaCO_3$ in the brick's microstructure. The TGA graph (Figure 7) recorded a continuous weight loss having a total mass loss of 10.3 %wt. from room temperature (~ 26 °C) to 1,000 °C. Two distinct weight losses were observed from the graph, one at 236 °C attributed to the absorbed hygroscopic water (1.5 %wt.) and another at 356 °C (1.7 %wt.). The latter is due to the combustion of highly volatile organic compounds, possibly from organic residues embedded in the ceramic matrix during the manufacturing process, clay mineral dehydration, and hydroxide decomposition, respectively [37]. There is no indication that $CaCO_3$ is present in the brick sample due to the absence of massive weight loss between 700 to 850 °C.

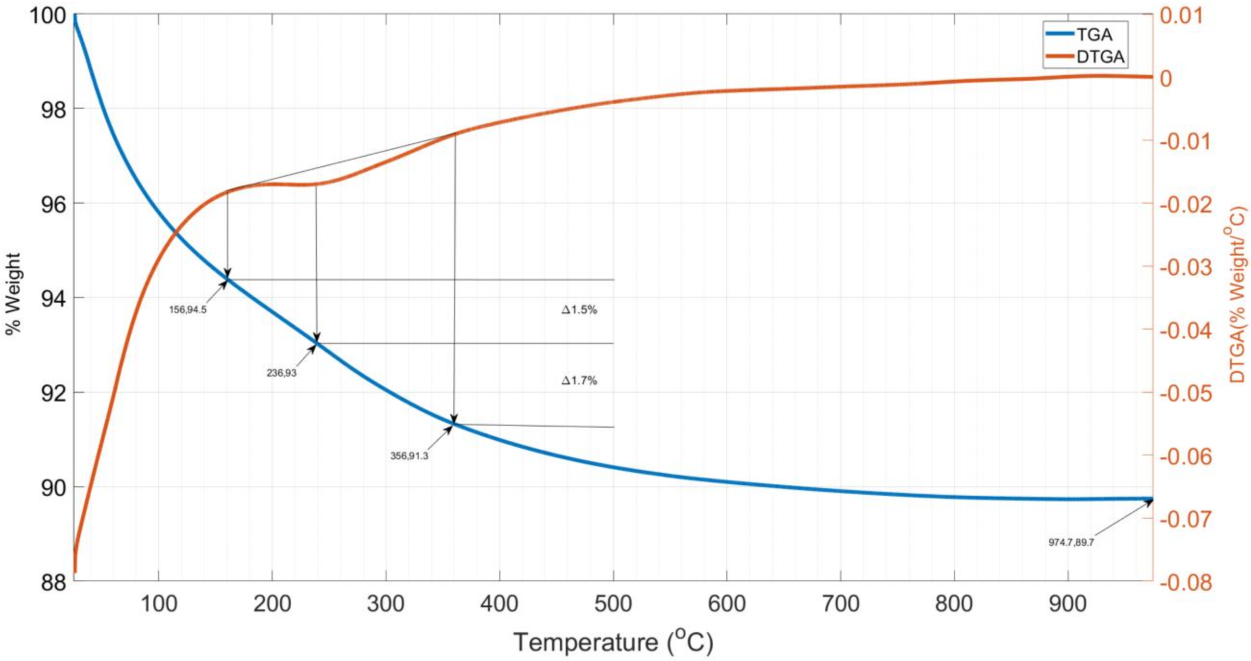


Figure 7. Thermogravimetric data of the brick sample. The blue line corresponds to the weight loss and the orange line is the first derivative plot.

Conclusion

The characterization of the Spanish Colonial Period brick from a church *convent* arch ruin in Quipayo was mainly produced from clay deposits that are non-calcareous, containing montmorillonite as one of the clay types and possible mixed layered illite/smectite clays, which are consistent with the geology of the surrounding soils in the province. Mineral phases, namely hematite, ß-quartz, and plagioclase, have also been identified. Based on the mineralogical content and phase transitions, it led to the conclusion that the firing temperature is within the range of 900 °C to about lower than 1,100 °C. The hematite also implies that the brick was fired in an oxidizing environment. The knowledge of the firing temperature will contribute to the understanding of historical methods, which will aid in crafting proper conservation protocols consistent with the original materials. Increasing the brick sample size in future studies should be done to highlight the variability in the firing temperature within similar colonial period structures.

Acknowledgements

The authors are very grateful to Ms. Yem M. Garcillanosa, parish office staff of the *Parroquia de la Inmaculada Concepcion* church in Quipayo, Camarines Sur for providing the old pictures and the historical background of the parish. She also supervised and assisted in removing the old brick material from the arch way ruin of the *convento* wall. Sincere gratitude is also given to Fr. Michael M. Macario, parish priest of the *Parroquia de la Inmaculada Concepcion* church and the local Parish Pastoral Council (PPC). The EDXRF data was provided by Shimadzu Philippines Corporation and Mr. Sean Dalawampu did the analysis. This study would not have been possible without the support of the Chemistry Department of De La Salle University (DLSU), Manila, and the helpful insights of the following persons from DLSU: Dr. Jaime Raul Janairo, Mr. Michael Ajero, Dr. Maria Carmen Tan, Mr. Aniano Asor Jr and Mr. Reynaldo Coria (SEM-EDX data).

REFERENCES

1. Eusebio, M. S.; Ceron, J. R.; Acabado, S. B.; Krigbaum, J., 'Rice pots of not? Exploring ancient Ifugao foodways through organic residue analysis and paleoethnobotany', *National Museum Journal of Cultural Heritage* **1**(1) (2015) 11-20.
2. Abdrabou, A.; Abdallah, M.; Nabil, E.; Matsuda, Y.; Kamal, H. M., 'Preliminary investigation of the materials and techniques used in a decorated wooden stick of king Tutankhamun', *Conservar Património* **30** (2019) 9-19, https://doi.org/10.14568/cp2017033.

3. Goemaere, E.; Sosnowska, P.; Golitko, M.; Goovaerts, T.; Leduc, T., 'Archaeometric and archaeological characterization of the fired clay brick production in the Brussels-Capital Region between the XIV and the third quarter of the XVIII centuries (Belgium)', *Acheosciences* **43**(1) (2019) 107-132, https://doi.org/10.4000/archeosciences.6429.
4. Cayme, J.-M. C., 'Analytical chemistry methods of estimating the hydraulic lime characteristics of mortars from a Spanish Colonial Period fortification in the Philippines: perspective of a Southeast Asian country', *SPAFA Journal* **6** (2022) 5fabjq9471, https://doi.org/10.26721/spafajournal.5fabjq9471.
5. Fernandes, F. M.; Lourenço, P. B.; Castro, F., 'Ancient clay bricks: manufacture and properties', in *Materials, Technologies and Practice in Historic Heritage Structures*, ed. M.B. Dan, R. Přikryl & Á. Török, Springer, Dordrecht (2010) 29-48, https://doi.org/10.1007/978-90-481-2684-2_3.
6. Javellana, R. B., *Wood and Stone*, Ateneo de Manila University Press, Quezon City (1991).
7. Jose, R. T., '*Palitada*: skin of the church', in *Zero in: skin surface essence*, Ateneo Art Gallery, Ayala Foundation, Inc., Eugenio Lopez Foundation, Inc. and Museum *Pambata* Foundation, Inc, Manila (2003) 20-25.
8. Cayme, J.-M. C.; Asor Jr, A. N., 'Extraction methods for quantifying iron, calcium and magnesium in a historic brickwork produced during the Spanish colonial period in the Philippines', *KIMIKA* **26**(1) (2015) 27-37, https://doi.org/10.26534/kimika.v26i1.27-37.
9. Neri, L. A. M.; Basilia, P. G. A.; Luga, E. A. C., 'The Alubijid Spanish kiln: the archaeology, colonial history, and cultural significance', *Journal of Philippine Local History & Heritage* **6**(1) (2020) 107-142.
10. Cayme, J.-M. C., 'Analytical chemistry methods of estimating the original firing temperature of bricks from a 19th century convent in the Philippines: Perspective of a Southeast Asian country', *SPAFA Journal* **5** (2021), https://doi.org/10.26721/spafajournal.2021.5.651.
11. Cayme, J.-M. C.; Asor Jr, A. N.; Alano, M. K. A. T.; Miranda, E. T., 'Chemical characterization of historical brickwork of the church *convento* in Pagsanjan, Laguna', *KIMIKA* **27**(1) (2016) 29-40, https://doi.org/10.26534/kimika.v27i1.29-40.
12. Cayme, J.-M. C.; Bermejo III, A. F.; Francia, C. A. E. T.; Asor Jr., A. N.; Miranda, E. T., 'Spanish Colonial Period bricks from churches in Laguna, Philippines: a preliminary chemical characterisation using X-ray diffraction, energy dispersive X-ray fluorescence and Fourier transform infrared', *Journal of Physical Science* **32**(2) (2021) 105-124, https://doi.org/10.21315/jps2021.32.2.8.
13. Elert, K.; Cultrone, G.; Navarro, C. R.; Pardo, E. S., 'Durability of bricks used in the conservation of historic buildings - influence of composition and microstructure', *Journal of Cultural Heritage* **4**(2) (2003) 91-99, https://doi.org/10.1016/S1296-2074(03)00020-7.
14. Cultrone, G.; Sebastián, E.; Elert, K.; de la Torre, M. J.; Cazalla, O.; Rodriguez-Navarro, C., 'Influence of mineralogy and firing temperature on the porosity of bricks', *Journal of the European Ceramic Society* **24**(3) (2004) 547-564, https://doi.org/10.1016/S0955-2219(03)00249-8.
15. Cardiano, P.; Ioppolo, S.; De Stefano, C.; Pettignano, A.; Sergi, S.; Piraino, P., 'Study and characterization of the ancient bricks of monastery of "San Filippo di Fragalà" in Frazzanò (Sicily)', *Analytica Chimica Acta* **519** (2004) 103-111, https://doi.org/10.1016/j.aca.2004.05.042.
16. Ghale, D. B.; Bohara, N. B.; Duwal, N.; Bhattarai, J., 'Investigation on the mineralogical phase of ancient brick samples of Kathmandu Valley (Nepal) using XRD and FTIR analysis', *Rasāyan Journal of Chemistry* **12**(1) (2019) 402-408, http://dx.doi.org/10.31788/RJC.2019.1224034.
17. Ramli, Z. B.; Rahman, N. H. S. N. A.; Samian, A. L.; Yarmo, Y., 'X-ray diffraction and X-ray fluorescence of ancient bricks of *Candi bukit pendiat* (Site 17), Bujang Valley, Kedah', *Research Journal of Applied Sciences, Engineering and Technology* **6**(6) (2013) 1094-1100.
18. Totanes, S. H. S., 'From missions to mainstream: Franciscan efforts in *Nueva Cáceres, Kabikolan, 1578-1768*', in *The Journal of History: Selected Papers on Cultural History and Ethnohistory*, ed. D.B. Apilado, Philippine National Historical Society, Inc, Manila (2006) 97-127.
19. Jose, R. T., 'A visual documentation of Fil-Hispanic churches. Part VI: Parish church of Saints Peter and Paul, Calasiao, Pangasinan', *Philippiniana Sacra* **XLVII**(141) (2012) 731-760.
20. De Huerta, F., *Estado geografico, topografico, estadistico, historico-religioso de la provincia apostolica de San Gregorio Magno*, Binondo, Manila (1887).
21. Lopez-Arce, P.; Garcia-Guinea, J., 'Weathering traces in ancient bricks from historic buildings', *Building and Environment* **40**(7) (2005) 929-941, https://doi.org/10.1016/j.buildenv.2004.08.027.
22. Lafuente, B.; Downs, R. T.; Yang, H.; Stone, N., 'The power of databases: The RRUFF project', in *Highlights in Mineralogical Crystallography*, ed. T. Armbruster & R. M. Danisi, De Gruyter, Berlin (2015) 1-30, https://doi.org/10.1515/9783110417104-003.
23. Andrade, G. R. P.; Cuadros, J.; Partiti, C. S. M.; Cohen, R.; Vidal-Torrado, P., 'Sequential mineral transformations from kaolinite to Fe-illite in two Brazilian mangrove soils', Geoderma **309** (2018) 84-99, https://doi.org/10.1016/j.geoderma.2017.08.042.
24. Miura, K.; Badayos, R. B.; Briones, A. M., 'Characteristics of soils of lowland areas in the Philippines with specific reference to parent materials and climatic conditions', *Japan International Research Center for Agricultural Sciences Journal* **5** (1997) 31-42.
25. Miura, K.; Badayos, R. B.; Briones, A. M., 'Morphological characteristics and distribution patterns of lowland soils in the Philippines', *Soil Science and Plant Nutrition* **44**(2) (1998) 217-225, https://doi.org/10.1080/00380768.1998.10414442.
26. Maniatis, Y.; Tite, M. S., 'Technological examination of Neolithic-Bronze age pottery from Central and Southeast Europe and from the Near East', *Journal of Archaeological Science* **8**(1) (1981) 59-76, https://doi.org/10.1016/0305-4403(81)90012-1.
27. Musthafa, A. M.; Janaki, K.; Velraj, G., 'Microscopy, porosimetry and chemical analysis to estimate the firing temperature if some archaeological pottery shreds from India', *Microchemical Journal* **95**(2) (2010) 311-314, https://doi.org/10.1016/j.microc.2010.01.006.
28. Daghmehchi, M.; Rathossi, C.; Omrani, H.; Emami, M.; Rahbar, M., 'Mineralogical and thermal analysis of the Hellenistic ceramics from Laodicea Temple, Iran', *Applied Clay Science* **162**(15) (2018) 146-154, https://doi.org/10.1016/j.clay.2018.06.007.
29. Witt, J. C., 'Philippine paving-brick materials: a preliminary report', *Philippine Journal of Science* **11**(5) (1916) 203-221.

30. Velraj, G.; Janaki, K.; Musthafa, A. M.; Palanivel, R., 'Spectroscopic and porosimetry studies to estimate the firing temperature of some archaeological pottery shreds from India', *Applied Clay Science* **43**(3-4) (2009) 303-307, https://doi.org/10.1016/j.clay.2008.09.005.
31. Yan, B.; Liu, S.; Chastain, M. L.; Yang, S.; Chen, J., 'A new FTIR method for estimating the firing temperature of ceramic bronze-casting moulds from early China', *Scientific Reports* **11** (2021) 3316, https://doi.org/10.1038/s41598-021-82806-z.
32. Johnson, S. E.; Song, W. J.; Cook, A. C.; Vel, S. S.; Gerbi, C. C., 'The quartz α ↔ß phase transition: Does it drive damage and reaction in continental crust?', *Earth and Planetary Science Letters* **553**(1) (2021) 116622, https://doi.org/10.1016/j.epsl.2020.116622.
33. Grim, R. E.; Kulbicki, G., 'Montmorillonite: high temperature reactions and classifications', *The American Mineralogist* **46**(11-12) (1961) 1329-1369.
34. Yanik, G.; Bozer, R.; Çeken, M.; Esenli, F.; Gocmez, H., 'The characterization of medieval ceramics excavated from the Eğirdir Caravanserai (Turkey)', *Ceramics-Silikáty* **56**(3) (2012) 261-268.
35. El Ouahabi, M.; Daoudi, L.; Hatert, F.; Fagel, N., 'Modified mineral phases during clay ceramic firing', *Clays and Clay Minerals* **63**(5) (2015) 404-413, https://doi.org/10.1346/CCMN.2015.0630506.
36. Chatfield, M., 'Tracing firing technology through clay properties in Cuzco, Peru', *Journal of Archaeological Science* **37**(4) (2010) 727-736, https://doi.org/10.1016/j.jas.2009.11.003.
37. Hanein, T.; Thienel, K. C.; Zunino, F.; Marsh, A. T. M.; Maier, M.; Wang, B.; Canut, M.; Juenger, M. C. G.; Haha, M. B.; Avet, F.; Parashar, A.; Al-Jaberi, L. A.; Almenares-Reyes, R. S.; Alujas-Diaz, A.; Scrivener, K. L.; Bernal, S. A.; Provis, J. L.; Sui, T.; Bishnoi, S.; Martirena-Hernández, F., 'Clay calcination technology: state-of-the-art review by the RILEM TC 282-CCL', *Materials and Structure* **55** (2022) 3, https://doi.org/10.1617/s11527-021-01807-6.

RECEIVED: 2023.8.29
REVISED: 2023.9.19
ACCEPTED: 2024.5.31
ONLINE: 2024.8.22