Clay Minerals (2022), **57**, 114–119
doi:10.1180/clm.2022.28

CAMBRIDGE UNIVERSITY PRESS

Mineralogical Society

Article

Characteristics of the raw materials of glazed tile bodies in the southern area of the Bao'ensi site, Nanjing, China

Weijuan Zhao[1], Dan Zhao[1], Bo Wu[1], Bo Li[1], Baohua Zhou[2], Jianfeng Cui[3] and Qinlong Chen[4]*

[1]School of Physics and Microelectronics, Zhengzhou University, Zhengzhou 450001, China; [2]Nanjing Research Institute of Archaeology, Nanjing 210001, China; [3]School of Archaeology and Museology, Peking University, Beijing 100871, China and [4]School of History, Zhengzhou University, Zhengzhou 450001, China

Abstract

The Nanjing Bao'ensi site is the largest and highest-ranking royal temple from the Ming Dynasty, and it is famous for its full-body glass pagoda. In this study, the glazed tiles excavated from the southern area of the Bao'ensi site were selected and analysed using X-ray diffraction, thermal dilation and energy-dispersive X-ray fluorescence to determine their phase composition, firing temperature and chemical composition. The glazed tile bodies of the Bao'ensi site consist mainly of quartz and mullite, although some samples contain trace amounts of other minerals. All of the body samples were fired to the same temperature range (i.e. 1000–1100°C). The firing temperature combined with the phase composition indicate that the raw materials and firing process of the glazed tile body samples have similarities, but there are certain differences. The source of the raw materials for a portion of the glazed tile bodies is Dangtu, Anhui, whilst the source of the raw materials for the remaining materials remains to be discovered.

Keywords: Bao'ensi site, body of glazed tiles, firing temperature, source of raw material

(Received 14 April 2022; revised 9 October 2022; Accepted Manuscript online: 20 October 2022; Associate Editor: M. Dondi)

Bao'ensi Temple was built by Zhu Di, the emperor of the Ming Dynasty, on the foundations of Changgan Temple (长干寺) and Tianxi Temple (天禧寺). The Nanjing Bao'ensi site is located in the Ancient Changganli area outside the Gate of Ming Zhonghua in Nanjing, covering an area of ~250,000 m^2. The site is the largest and highest-ranking royal temple in the Ming Dynasty. The Bao'ensi pagoda of the temple is famous worldwide. It was destroyed during the war of the Taiping Heavenly Kingdom during the late Qing Dynasty (Wang, 1984). The site is generally divided into two areas: the southern area and the northern area. The Nanjing Institute of Archaeology conducted a comprehensive and systematic archaeological excavation in the northern area in 2007–2010 and in the southern area in 2017.

Ancient works (Nanjing Museum, 1962; Lu, 1996) present clear records of the firing of glazed tiles during the Ming Dynasty. The 'Collected Statutes of the Ming Dynasty' (明会典) state: 'In 1393, the bricks and tiles needed for Nanjing construction were fired in Jubaoshan kiln for glazed tiles every year, and the clay used for glazed tiles came from Taiping Palace.' Combined with archaeological reports, this has led some researchers to posit that the glazed tiles of the Bao'ensi site were fired mainly in the Jubaoshan kiln for use around Nengrenli Temple (能仁里) and Yanxiang Temple (眼香庙) in Nanjing, with the body clay coming from Dangtu in Anhui Province (Chen, 2009, 2015). Several scholars have selected five collections of yellow-coloured and green-coloured glaze components (Liu *et al.*, 2007) collected from the vicinity of Yanxiang Temple (眼香庙) in Yaogang Village (窑岗村) in Nanjing in the 1960s for scientific and technological investigation. These components were presumed to be glazed arch elements from the Bao'ensi site (Zhang, 2003). The results showed that the raw materials used in the bodies of these glazed components are the same as those from Dangtu.

Based on previous work (Ding *et al.*, 2011, 2013; Huang *et al.*, 2015; Qi, 2015, 2018; Qi & Zhou, 2015), 56 glazed tile samples unearthed from the archaeological excavation site in the southern area of the Bao'ensi site were selected to determine systematically and comprehensively the body-firing process used and the source of the raw material. The phase composition, firing temperature and chemical composition of the body samples were studied using X-ray diffraction (XRD), thermal dilation (TD) and energy-dispersive X-ray fluorescence (EDXRF). The EDXRF data were processed using multivariate statistical analysis. Our results can provide scientific and technological support for investigations into the production, circulation and management systems of imperial kilns from the Ming Dynasty.

Experimental samples and methods

Samples

A total of 56 samples with yellow, green and black glaze colours were collected from the southern area of the Bao'ensi site. Typical samples are shown in Fig. 1.

Experimental methods

The phase composition of the body samples was analysed using XRD (SmartLab X, Japan) in the scanning range of 10–80°2θ

*Email: 12087725@qq.com

Cite this article: Zhao W, Zhao D, Wu B, Li B, Zhou B, Cui J, Chen Q (2022). Characteristics of the raw materials of glazed tile bodies in the southern area of the Bao'ensi site, Nanjing, China. *Clay Minerals* **57**, 114–119. https://doi.org/10.1180/clm.2022.28

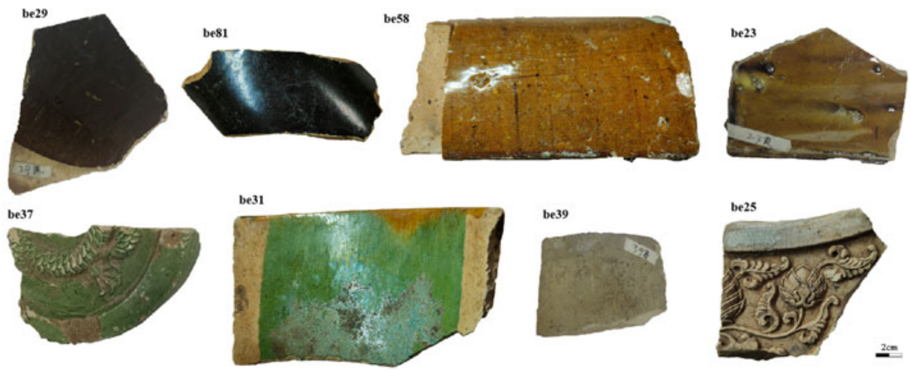

Fig. 1. Typical glazed tiles from Bao'ensi Temple in Nanjing.

with Cu-*K*α radiation at 30 mA/40 kV. The XRD traces were analysed using the *Jade 6* program, by which the phase composition of each sample body was obtained. The samples to be analysed using XRD were separated by cutting and cleaned with deionized water in an ultrasonic cleaner. After drying in an oven, the bodies were ground into powder in an agate mortar.

The thermal behaviour of the body samples was measured using TD (LINSEIS DIL L175, Germany) at a resolution of 0.05 nm from room temperature to 1200°C at a rate of 5°C min^{-1}. The glaze layer of the selected samples was removed and cut into rectangular bars, washed with deionized water in an ultrasonic cleaner and dried in a drying oven.

The chemical composition of the body samples was determined using EDXRF (XGT-7000, Japan) with a Si–Li detector with a beam spot of 1.2 mm, an operating voltage of 30 kV and an operating current of 250 μA. The data-acquisition time was 120 s. Na_2O was not determined because of the poor fluorescence yields and low counting signal obtained with the EDXRF instrument. The selected samples were cleaned and then dried in a drying oven.

Results and discussion

Phase-composition analysis of the glazed tile bodies from the Bao'ensi site

The XRD traces of the glazed tile bodies are shown in Fig. 2. The phase composition of each body sample was obtained, as shown in Table 1.

The glazed tile bodies of the Bao'ensi site consist mainly of quartz and mullite, along with trace amounts of albite, rutile, muscovite, hematite and pyroxene (Table 1). Therefore, the body materials have a comparable composition, along with certain differences, suggesting partial consistency in the selection of body materials.

A series of physical and chemical changes took place during the firing process of the glazed tiles. The mineralogical composition of the tiles reflects the heating changes of the original materials, mainly clays. Clays with various mineralogical compositions yield various end products when heated, which may be used to identify the mineralogical composition of the original clay (Li, 2001). The glazed tiles were fired under low temperatures. Kaolinite ($Al_2O_3{\cdot}2SiO_2{\cdot}2H_2O$) is the main source of mullite ($3Al_2O_3{\cdot}2SiO_2$) detected in all of the samples (Dubois *et al.*, 1995). Therefore, the quartz phase in the body materials belongs to α-quartz. The main component of quartz is SiO_2, which often contains a number of impurities such as Al_2O_3, Fe_2O_3, CaO, MgO, TiO_2, etc. These impurities represent other minerals (e.g. carbonate (dolomite, calcite and magnesite), feldspar, rutile, mica and iron oxide) being included in the process of mineral formation. The structural water in kaolinite is released during hydroxylation and the crystal structure is destroyed to form metakaolinite in the temperature range of 450–650°C (Equation 1). Metakaolinite begins to transform into Al–Si spinel-type structures at 925°C (Equation 2), and the Al–Si spinel begins to transform into mullite and cristobalite at 1050–1100°C (Equation 3). Due to the presence of flux oxides (such as K_2O and CaO), the formation temperature of mullite in the body is reduced, and cristobalite does not form in the body phase, implying that the firing temperature of the body was ~1000°C. Through thermal expansion analysis (Tite, 1969), it can be inferred that the firing temperature of the glazed tile body was 1000–1100°C (Table 1).

$$\underset{\text{(kaolinite)}}{Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O} \rightarrow \underset{\text{(metakaolinite)}}{Al_2O_3 \cdot 2SiO_2} + 2H_2O \quad (1)$$

$$2(Al_2O_3 \cdot 2SiO_2) \rightarrow 2Al_2O_3 \cdot 3SiO_2 + SiO_2 \quad (2)$$

$$3(2Al_2O_3 \cdot 3SiO_2) \rightarrow \underset{\text{(mullite)}}{2(3Al_2O_3 \cdot 2SiO_2)} + \underset{\text{(cristobalite)}}{5SiO_2} \quad (3)$$

The melting point of albite ($NaAlSi_3O_8$) is ~1100°C, and the melting of quartz and mullite at high temperatures is rapid in the presence of albite flux. Muscovite usually coexists with feldspar and quartz. Pyroxene is a common silicate mineral. Hematite is the main mineral form of Fe_2O_3, and it has a melting point of ~1250–1270°C. Rutile, a TiO_2 polymorph generally containing >95% TiO_2, has a melting point of ~1500–1600°C.

The phase composition combined with the firing temperature indicate that the raw material was concentrated and that the firing processes of the glazed tile body samples had similarities.

Analysis of the chemical composition of the glazed tile bodies

The chemical compositions of the 56 glazed tile sample bodies were determined using EDXRF. Some of the EDXRF data are shown in Table 2.

Archaeological reports show that the Nanjing Jubaoshan kiln site was the main location for providing royal and official buildings in Nanjing with glazed pottery products (Nanjing Museum, 1962; Chen, 2009). In addition, ancient works such as the 'Collected Statutes of the Ming Dynasty' (明会典), 'Exploitation of the Works of Nature' (天工开物) and 'Taiping Prefecture Chorography' (太平府志) report that the material that makes up the body of the Jubaoshan glazed tiles consists of a white clay

https://doi.org/10.1180/clm.2022.28 Published online by Cambridge University Press

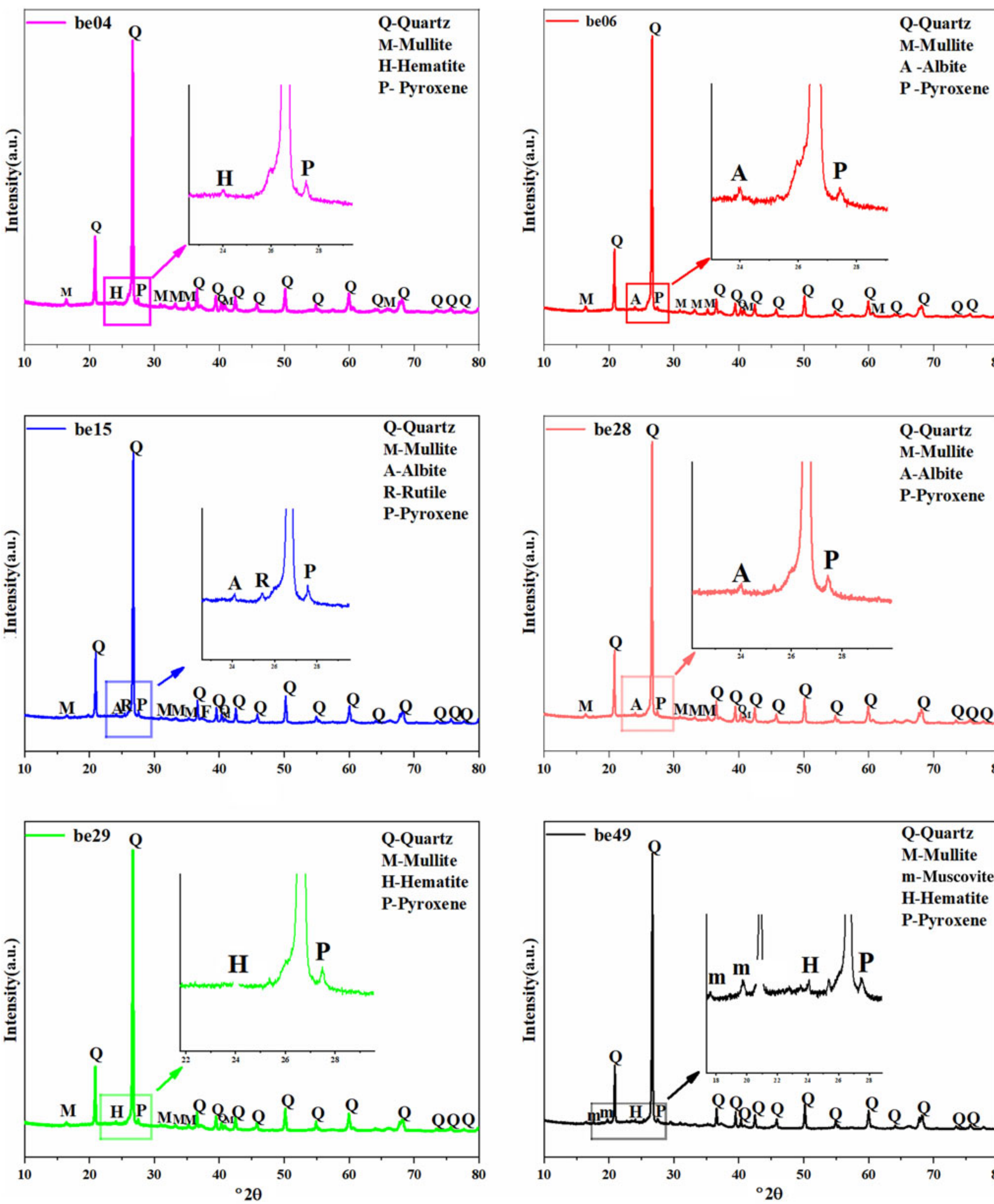

Fig. 2. XRD traces of representative body samples.

from the Dangtu area, Anhui (Chen, 2009). Based on this information, the data from the Dangtu glazed tile body samples from previous research (Ding et al., 2011; Yang, 2018), numbered as AM (DY), were used to explore whether the raw material of the glazed tile bodies from the Bao'ensi site originates from Dangtu.

Analysis of the EDXRF data

The chemical composition of the glazed tile bodies analysed (Fig. 3) was used to determine the possible differences between the glazed tile bodies from the Bao'ensi area and the Dangtu area.

https://doi.org/10.1180/clm.2022.28 Published online by Cambridge University Press

Table 1. The phase compositions and firing temperatures of representative Bao'ensi site body samples.

Sample	Phase composition	Firing temperature (°C)
be04	Quartz, mullite, hematite, pyroxene	1017 ± 20
be06	Quartz, mullite, albite, pyroxene	1032 ± 20
be15	Quartz, mullite, albite, rutile, pyroxene	1030 ± 20
be28	Quartz, mullite, albite, pyroxene	1031 ± 20
be29	Quartz, mullite, hematite, pyroxene	1018 ± 20
be49	Quartz, mullite, muscovite, hematite, pyroxene	1024 ± 20

The Al_2O_3 content of the Bao'ensi site body samples varies between 22.10% and 25.60%, while the Al_2O_3 content of the Dangtu glazed tile body samples varies between 20.11% and 24.78% (Fig. 3a & Table 2). The two sets of samples have generally comparable Al_2O_3 contents, with only a few samples having different Al_2O_3 contents. The SiO_2 content of the Bao'ensi site body samples varies between 65.30% and 72.10%, while the SiO_2 content of the Dangtu glazed tile body samples varies between 64.60% and 70.67%. Hence, the two sample sets have comparable SiO_2 contents. In addition, the K_2O contents of the Bao'ensi site body samples and the Dangtu glazed tile body samples are comparable (3.40–5.40% and 3.47–4.58%, respectively). In contrast, the Bao'ensi site body samples have a greater CaO content than their Dangtu glazed tile body sample counterparts (0.30–3.60% and 0.19–0.44%, respectively; Fig. 3b). In addition, the TiO_2 contents of the two sets of samples are generally variable (Fig. 3c). Finally, the Fe_2O_3 contents of the Bao'ensi site bodies and the Dangtu glazed tile body samples are generally comparable (1.60–3.50% and 1.63–2.74%, respectively), with some samples from the Bao'ensi site having a greater Fe_2O_3 content. Therefore, the two sites have comparable chemical compositions overall.

Factor analysis of the EDXRF data

Factor analysis converts multiple variables into a few uncorrelated comprehensive indicators, establishes the possible correlations between multiple variables and extracts two to three factors that most reflect the data. Based on such an analysis, the results (data points) reflect the relationships between samples (i.e. adjacent sample points have similar properties and belong to the same group) and the relationships between elements and samples (variables). Thus, data points within the same area will be characterized by adjacent variables (Xue, 2013).

Figure 4 depicts the factor-loading diagram of the glazed tile body samples from the Bao'ensi site and the Dangtu glazed tile body samples. Factor analysis was performed using the *SPSS* software package. Five chemical components, namely Al_2O_3, SiO_2, K_2O, CaO and Fe_2O_3, were selected for factor analysis, and two factors (i.e. F_1 and F_2) were extracted, explaining 73% of the total variance (Equations 4 and 5):

$$F_1 = 0.327Al_2O_3 - 0.4SiO_2 + 0.3K_2O + 0.155CaO + 0.21Fe_2O_3 \quad (4)$$

$$F_2 = -0.208Al_2O_3 + 0.062SiO_2 - 0.353K_2O + 0.587CaO + 0.511Fe_2O_3 \quad (5)$$

Table 2. Chemical composition of the Bao'ensi glazed tile body samples (wt.%).

Sample	Al_2O_3	SiO_2	K_2O	CaO	TiO_2	Fe_2O_3
be00	22.90	68.50	3.90	0.90	0.70	2.10
be01	22.60	69.40	3.90	0.50	0.70	2.20
be03	23.50	69.20	4.10	0.60	0.70	1.80
be04	21.80	70.90	3.50	0.30	0.60	3.00
be05	25.40	65.30	5.40	0.70	0.70	2.20
be06	22.40	70.50	3.80	0.90	0.60	1.70
be07	22.50	70.90	3.80	0.30	0.70	1.70
be08	24.90	68.70	3.50	0.50	0.60	1.70
be10	23.80	69.00	3.80	0.70	0.70	1.70
be11	23.00	69.30	3.80	1.30	0.80	1.80
be12	25.50	65.80	4.20	0.80	0.60	2.70
be13	23.30	69.60	4.10	0.50	0.70	1.80
be15	21.80	68.10	3.70	3.60	0.70	2.10
be16	23.50	69.70	3.90	0.30	0.70	1.80
be17	23.30	69.70	3.80	0.50	0.70	1.90
be18	23.80	69.40	3.90	0.40	0.70	1.80
be19	24.20	69.20	3.80	0.30	0.60	1.70
be21	22.60	70.80	3.90	0.30	0.60	1.80
be22	23.00	70.10	3.80	0.40	0.70	1.90
be23	23.70	68.50	4.30	0.90	0.70	1.90
be25	25.10	68.20	3.90	0.40	0.70	1.70
be27	22.30	66.40	3.90	2.90	0.80	3.50
be28	23.60	69.60	4.00	0.40	0.60	1.80
be29	23.70	69.60	3.70	0.60	0.70	1.60
be30	22.30	68.90	3.60	0.80	0.70	3.40
be31	23.10	69.40	3.90	0.70	0.80	1.80
be32	24.00	68.80	3.70	0.60	0.60	1.90
be36	21.60	72.10	3.80	0.30	0.70	1.60
be37	23.60	69.10	4.10	0.60	0.70	1.60
be38	21.90	70.60	3.90	0.50	0.60	2.20
be39	25.60	66.70	4.20	0.60	0.60	2.30
be43	24.20	67.40	4.20	1.20	0.70	2.20
be44	24.00	69.40	3.90	0.40	0.60	1.60
be47	23.10	70.20	3.80	0.30	0.60	1.90
be49	23.60	68.80	3.70	0.40	0.70	2.80
be51	23.20	70.10	3.80	0.30	0.70	1.80
be53	24.00	68.90	4.00	0.40	0.70	2.00
be54	22.10	70.50	4.30	0.50	0.60	1.70
be55	21.70	70.50	4.00	0.80	0.70	2.20
be58	23.90	67.90	3.80	1.30	0.70	2.50
be59	23.20	69.50	4.00	0.60	0.70	1.80
be61	22.20	71.10	4.10	0.30	0.60	1.60
be62	23.30	70.00	3.90	0.30	0.60	1.80
be63	23.90	68.90	3.40	0.70	0.60	1.90
be65	22.60	70.50	4.00	0.30	0.70	1.90
be66	24.70	65.30	4.10	1.10	0.70	2.10
be67	22.40	68.50	4.30	0.30	0.70	1.90
be68	23.30	69.50	4.00	0.40	0.70	1.70
be70	22.90	69.70	4.20	0.80	0.60	1.80
be71	22.00	71.00	4.00	0.40	0.80	1.80
be72	22.80	69.00	4.20	1.00	0.60	2.30
be73	23.30	67.10	3.60	1.40	0.70	1.90
be74	23.20	69.20	4.10	0.90	0.70	1.90
be79	23.10	68.80	4.00	1.10	0.80	2.20
be80	21.70	70.80	4.20	0.70	0.70	1.70
be81	22.40	70.90	3.80	0.50	0.60	1.80
Average	23.23	69.21	3.95	0.71	0.68	1.99
Maximum	25.60	72.10	5.40	3.60	0.80	3.50
Minimum	21.60	65.30	3.40	0.30	0.60	1.60

Figure 4 shows that the data points for the Bao'ensi site glazed body samples display considerable scattering, and those for the Dangtu glazed tile body samples plot in the same area, overlapping with a significant proportion of the Bao'ensi site glazed body samples thus indicating similarities in the chemical composition of the two groups of glazed tile samples. Therefore, the raw materials for some of the Bao'ensi site glazed body samples may

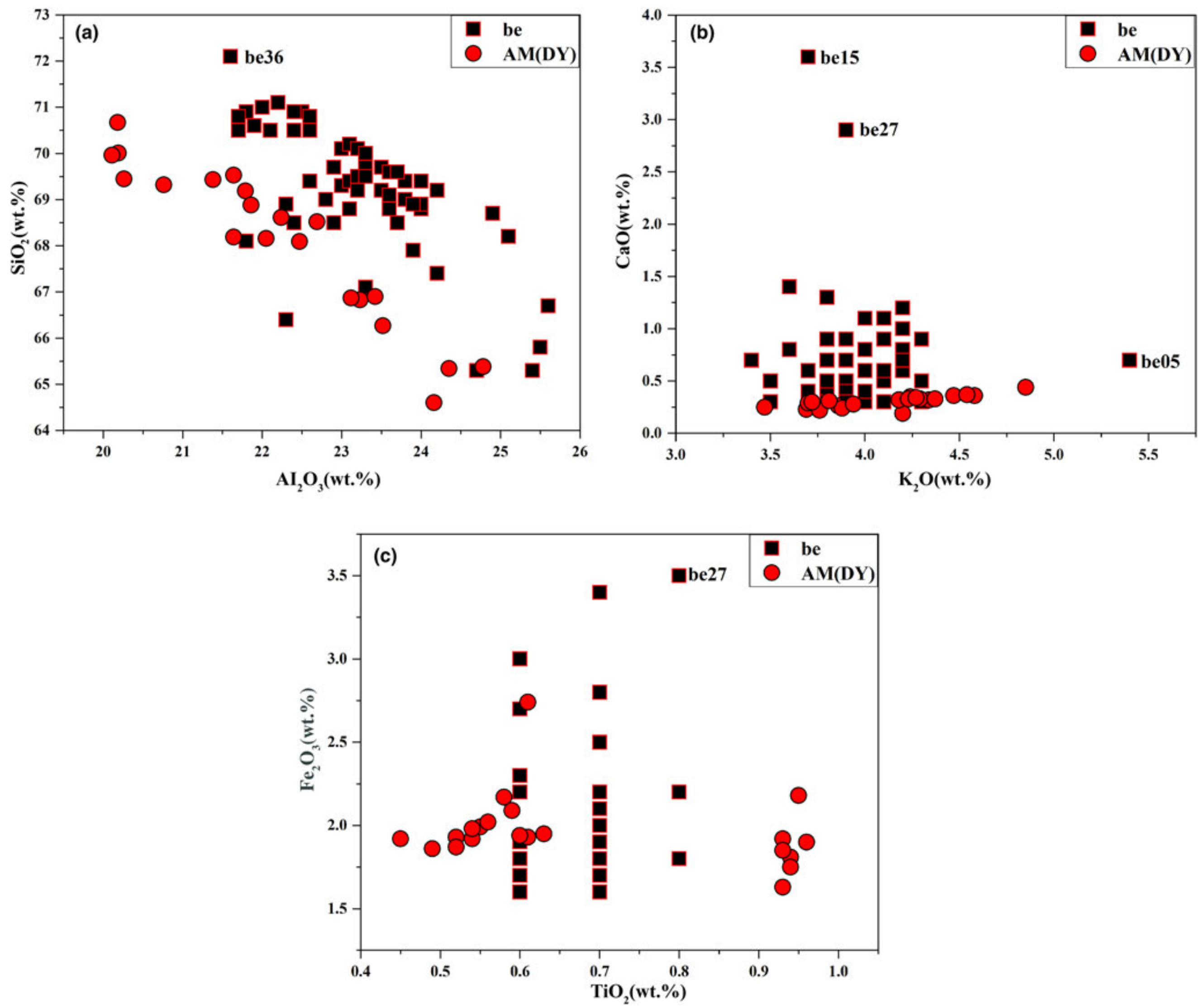

Fig. 3. Dispersion analysis of the glazed tile body samples. AM(DY) = Dangtu glazed tile body samples.

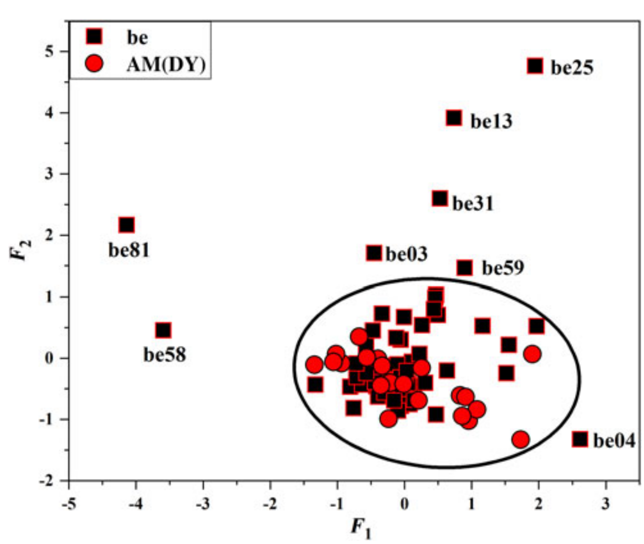

Fig. 4. Factor analysis of the glazed tile body samples. AM(DY) = Dangtu glazed tile body samples.

originate from Dangtu. However, some of the Bao'ensi site glazed body samples do not match the composition of the Dangtu samples (Fig. 4), indicating that there was another source of the raw materials for these samples.

Conclusion

The glazed tile samples from the Bao'ensi site in Nanjing, China, consist mainly of quartz and mullite, with some samples also containing trace amounts of albite, rutile, muscovite, hematite and pyroxene. The firing temperature of the glazed tile matrix samples from the Bao'ensi site was ~1000–1100°C. The firing temperature combined with the mineralogical composition indicate that the different Bao'ensi site glazed tile body samples had concentrated raw materials and underwent similar firing processes, indicating a strict and unified management system of official kilns and high-level manufacturing. Most samples from the Bao'ensi site and their counterparts from the Dangtu kiln for glazed tiles in Anhui have a comparable chemical composition, indicating a common origin. The raw material of the majority of the glazed tile bodies in the Bao'ensi site come from the Dangtu kiln, whereas the sources of the rest of the samples remain to be studied further.

Financial support. This work was supported by the National Natural Science Foundation of China 11975210 and the National Social Science Fund of China 17CKG016.

References

Chen Q.L. (2009) Some problems of Jubaoshan kiln for glazed tiles in Nanjing in Ming Dynasty. *Jiangsu Local Chronicles*, **1**, 30–33.

Chen Q.L. (2015) The excavation of the glazed-tile kiln site at Yaogang village in Yuhuatai district, Nanjing, Jiangsu. *Cultural Relics*, **10**, 27–48.

Ding Y.Z., Duan H.Y., Kang B.Q., Wu J.M. & Miao J.M. (2011) Study on the provenance of raw materials of the body of the architectural glazed tiles from Nanjing Bao'ensi pagoda. *China Ceramics*, **1**, 70–75.

Ding Y.Z., Li H., Duan H.Y., Kang B.Q., Chen T.M. & Miao J.M. (2013) Study on the architectural glazed tiles from Nanjing Bao'ensi pagoda. *Cultural Relics in Southern China*, **2**, 81–84.

Dubois J., Murat M., Amroune A., Carbonneau X. & Gardon R. (1995) High-temperature transformation in kaolinite: the role of the crystallinity and of the firing atmosphere. *Applied Clay Science*, **10**, 187–198.

Huang L.R., Wang Q., Lei Y., Dong B.S., Zhang J.G., Wang H., *et al.* (2015) The excavation of the pagoda foundation and underground palace of the grand Bao'en temple in Nanjing. *Cultural Relics*, **5**, 4–52.

Li, J.J. (2001) *Ceramics Processing*. China Light Industry Press, Beijing, China, 549 pp.

Liu X.Y., Li Y.P., Jiang X.M., Quan K.S., Zhang W.J., Jiang J.X. & Meng Y.Z. (2007) Brief excavation report on imperial kiln of the Ming and Qing dynasties located in Jingdezhen City of Jiangxi Province. *Cultural Relics*, **5**, 4–47.

Lu M.C. (1996) Investigation of Ming Dynasty kiln for glazed tiles in Dangtu County. *Southeast Culture*, **1**, 113–114.

Nanjing Museum (1962) Jubaoshan kiln for glazed tiles in Nanjing in Ming Dynasty. *Cultural Relics*, **2**, 41–48.

Qi H.N. (2015) The No.6 well of the grand Bao'en temple and the loyalty well in Nanjing: a discussion on their connections. *Southeast Culture*, **5**, 59–72.

Qi H.N. (2018) A relic of a royal monastery – a buddhist statue and six commonly sacred bricks from the Ming Dynasty are found at the site of Bao'en temple in Nanjing. *Cultural Relics*, **5**, 69–87.

Qi H.N. & Zhou B.H. (2015) Study on the age, nature and related issues of the taki of the site of da Bao'en temple in Nanjing. *Cultural Relics*, **5**, 66–73.

Tite M.S. (1969) Determination of the firing temperature of ancient ceramics by measurement of thermal expansion: a reassessment. *Archaeometry*, **11**, 131–143.

Wang Y.P. (1984) The world-famous glazed tower from Nanjing Bao'ensi pagoda. Pp. 214–222 in: *Proceedings of the Ancient Chinese Capital Society*. Zhejiang People's Publishing House, Hangzhou, China.

Xue, W. (2013) *SPSS Statistical Analysis Method and Application*. Publishing House of Electronics Industry, Beijing, China. 396 pp.

Yang G.M. (2018) *Studies on Manfacturing Techniques's Information and Provenance of Glazed Tiles from Mingzhongdu*. Doctoral dissertation. University of Science and Technology of China, Hefei, China. 140 pp.

Zhang Z.X. (2003) Flat brackets in the glass pagoda of the Bao'en temple in Nanjing. Pp. 545–549 in: *Archaeological Collection of Nanjing Museum of Cultural Relics*. Cultural Relics Publishing House, Nanjing, China.