

Identification of causes of degradation of Gothic ceramic tiles by thermal analyses

Alexandra Kloužková¹ · Mária Kavanová¹ · Martina Kohoutková² ·
Petra Zemenová¹ · Zdeněk Dragoun³

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Abstract Thermal analyses are suitable methods when studying not only nowadays, but also archaeological ceramic materials. In this case, they were used to study the mineralogical composition and the ageing process of a collection of fragments of Gothic mosaic tiles which were found during archaeological research of Břevnov Benedictine Monastery in Prague. The ceramic bodies of the tiles were differently coloured and showed different degrees of degradation. The ageing process of low-fired ceramics is accompanied by irreversible moisture expansion of a ceramic body which can lead to its degradation. The expansion of ceramic bodies of selected tiles was evaluated by the modified dilatation method. Thermal analyses with the combination of other methods (XRF, XRD and IR) and induced hydrothermal treatment proved the presence of clays in raw materials and helped to identify the causes of different degrees of degradation of the studied tiles.

Keywords Ceramic tiles · Gothic · Thermal analyses · XRD · XRF

Introduction

Archaeological ceramic findings are being studied by material scientists to identify the provenance and raw materials, and to clarify technological procedures. The methods of characterization are similar to those used for modern ceramic materials, especially X-ray fluorescence (XRF), X-ray diffraction (XRD), optical microscopy (OM), infrared spectroscopy (IR), Raman spectroscopy (RS) and thermal analyses (TA). In case of some ceramic materials, it is necessary to study further characteristics which are related to the stability of a ceramic body. It is well known that ceramics prepared from clay materials fired at low temperatures below 1000 °C (common for historical ceramics, bricks, floor tiles, some types of roofing, etc.) can undergo rehydroxylation of clay minerals residua (meta-clays) by the influence of moisture [1–8]. This process is called ageing and is accompanied by a volume expansion of a ceramic body (moisture expansion) which can lead to its degradation. In 1928, Schurecht [9] firstly described crazing of glazed surfaces due to irreversible moisture expansion of ceramics. It was proved that in case of modern materials, the inaccurate technology of composite concrete–ceramic floor structures in civil engineering resulted in occasional failures [10–13], where moisture expansion was one of the dominant loadings.

The ageing of porous ceramics by rehydroxylation of meta-clays can be accelerated by curing in an environment of high temperature and humidity. There are several standard methods used for determination of a conventional irreversible moisture expansion such as boiling in water for 24 h [14, 15], steaming above boiling water for 4 h [16] or high-pressure steaming in an autoclave at 180 °C for 5 h [17]. These methods evolved for modern ceramic materials were, however, found unsuitable for archaeological ceramics,

✉ Martina Kohoutková
martina.kohoutkova@vscht.cz

¹ Department of Glass and Ceramics, University of Chemistry and Technology Prague, Technická 5, 166 28 Prague, Czech Republic

² Central Laboratories, University of Chemistry and Technology Prague, Technická 5, 166 28 Prague, Czech Republic

³ National Heritage Institute, Na Perštýně 12, 110 00 Prague, Czech Republic

where the amount of studied material is limited. For this kind of materials, the method based on dilatation thermal analysis was proposed [3]. The testing method consists of several stages (Fig. 1).

The first annealing is performed with a dried sample from the laboratory temperature to 700 °C. The strain–temperature relationship measured during first annealing is affected by thermal expansion and by contraction due to the elimination of hydroxyl groups. The second annealing is performed on the already annealed sample. The difference between the first and second annealing is due to the release of hydroxyl groups and is equal to the natural irreversible moisture expansion of an analysed sample. Similarly, the difference between the third measurement and the second measurement is equal to the irreversible expansion due to the accelerating test. The derivatives are plotted in Fig. 2, where the hatched area indicates the irreversible moisture expansion. Although we cannot assume a perfect thermal steady state, the transition point of quartz at 573 °C can be identified, as well as the coefficient of thermal expansion [3].

Hydrothermal loading at harsher conditions (230 °C, 100 h) was also used for identification of clay minerals in a ceramic body using different methods such as STA, IR or XRD [18–20].

Raw materials used for fabrication of prehistoric ceramics were usually from local sources. The ceramic products were fired at temperatures below 1000 °C, and so they contained mainly quartz, feldspars, micas and sometimes residua of carbonates, possibly also new phases as gehlenite, etc. Clay minerals (kaolinite, illite, etc.) were usually present in the form of reactive non-crystalline phases (meta-clays), but their presence in a crystalline form is also possible depending on the firing temperature. The

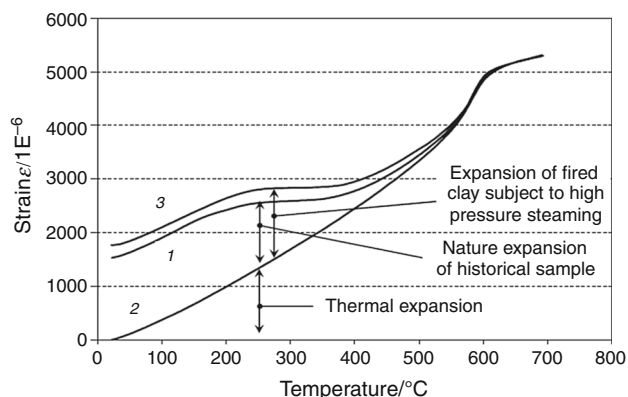


Fig. 1 Strain–temperature relationships measured using a dilatometer on a sample from historical clay ceramics (1 first measurement of a historical sample, 2 second measurement of the same sample, 3 third measurement of the sample subjected to an accelerating test by high-pressure steaming) [3]

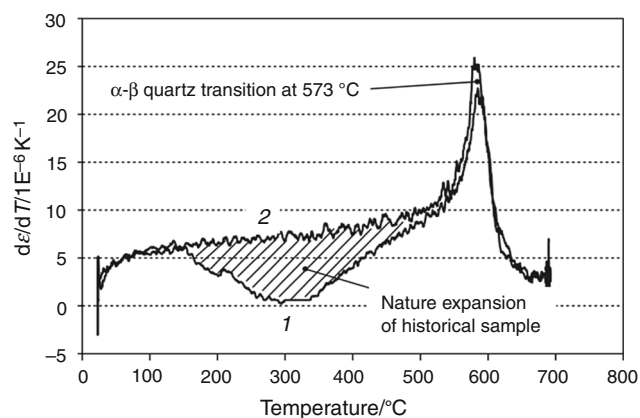


Fig. 2 Derivatives of strain–temperature relationships of sample from historical clay ceramics (1 first measurement of a historical sample, 2 second measurement of the same sample) [3]

presence of particular minerals then can help to estimate the approximate firing conditions [21–23].

Ceramic pavements have been indivisible and significant part of buildings already from ancient times. Ceramic material was preferably used for its colour scheme, texture, possibility of detail elaboration and decoration. Among the oldest types of ceramic tiles in Europe were especially geometric fair-faced (unglazed) tiles. They differed in the colour of the ceramic body according to the origin of raw materials and also the process of firing [22, 23]. One of the most significant types is represented by unglazed mosaic tiles which were manufactured in different shapes and colours. Tiles were subsequently set together to form geometric patterns and fixed in a lime mortar. Later, tiles started to be glazed by lead or lead–tin glazes. This type of floor mosaic tiles was produced substantially by Cistercian monasteries, e.g. in Pontigny in France, during the twelfth century or in Eberbach in Germany in the second half of the thirteenth century. The unique three-coloured geometric Gothic floor tiles were found also in the Benedictine Monastery in Břevnov in Prague in the Czech Republic [24, 25].

This work deals with characterization of the ceramic bodies of the floor mosaic tiles of Břevnov. The main aim was to evaluate the mineralogical composition by thermal analyses, to consider the similarity of ceramic bodies and to determine causes of the destruction of white tiles.

Experimental

The subject of this study was a collection of fragments of Gothic tiles which were found during archaeological research of Břevnov Monastery in 1991–1992. (Břevnov Monastery was established in 993 by Prince Boleslav II and Saint Adalbert, the Bishop of Prague and the oldest

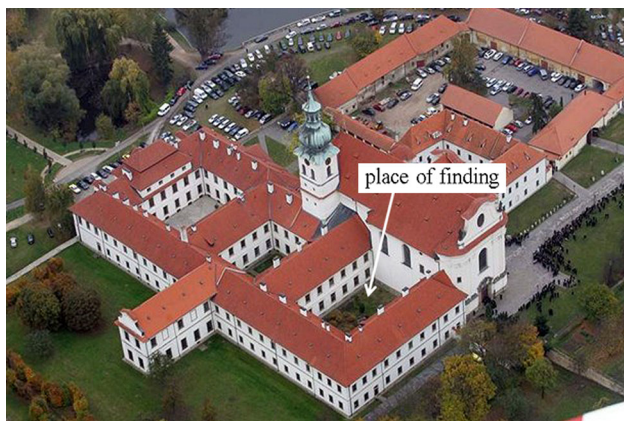


Fig. 3 Břevnov Monastery [26]

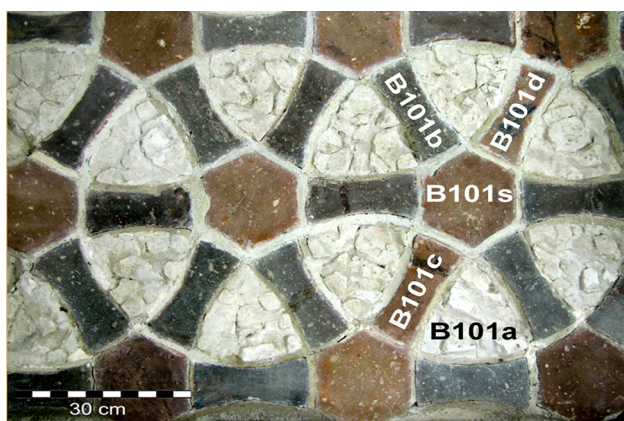


Fig. 4 Partial restoration of the Gothic ceramic mosaic

male monastery in the Czech Republic, Fig. 3.) Ceramic tiles formed the floor of the west cloister of the monastery. A part of fragments of tiles constituted a ceramic mosaic that was made of circles. Each circle was formed by three different types of colour-contrasting ceramic tiles (Fig. 4).

The collection of excavated fragment of ceramic tiles was dated to the end thirteenth century and contained fragments of the ceramic mosaic (Fig. 4) and also

fragments of individual tiles of different types [24, 25]. Samples for analyses of ceramic bodies were taken from six different tiles: five (B101a, B101b, B101c, B101d, and B101s) from the mosaic (Fig. 4) and one (B57a) from the individual tile of a geometric shape and grey-brown colour. The samples of ceramic bodies were ground in an agate mortar to the form of fine powder, well dried (at 105 °C) and used for the following analyses:

- X-ray fluorescence analysis (XRF); ARL 9400 XP sequential WD-XRF spectrometer equipped with a Rh anode end-window X-ray tube type 4GN fitted with 50- μm Be window. All peak intensity data were collected by software WinXRF in vacuum. The generator settings—collimator—crystal—detector combinations were optimized for all 82 measured elements with an analysis time of 6 s per element. The obtained data were evaluated by standardless software Uniquant 4. The analysed powders were pressed into pellets of about 5 mm thickness and diameter of 40 mm without any binding agent and covered with 4- μm supporting polypropylene (PP) film. The time of measurement was about 15 min.
- X-ray diffraction analysis (XRD); X-ray powder diffraction data were collected at room temperature with an X’Pert PRO θ - θ powder diffractometer with parafocusing Bragg–Brentano geometry using $\text{CuK}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$, $U = 40 \text{ kV}$, $I = 30 \text{ mA}$). Data were scanned with an ultrafast detector X’Celerator over the angular range 5° – 60° (2θ) with a step size of 0.0167° (2θ) and a counting time of $20.32 \text{ s step}^{-1}$. Data evaluation was performed in the software package HighScore Plus 3.0e.
- Thermal analyses (DTA, TG, DSC)—STA LINSEIS STA PT1600/1750 °C HiRes using $45 \pm 0.06 \text{ mg}$ of sample in Pt crucible and the heating rate of $10 \text{ }^\circ\text{C min}^{-1}$ in the temperature range of 25 – $1000 \text{ }^\circ\text{C}$ in helium flow. H_2O and CO_2 release was measured by mass spectrometer OmniStar, Pfeiffer Vacuum, in the range of 300 AMU.

Table 1 Semiquantitative chemical composition of the samples determined by XRF (mass%), presented in oxides

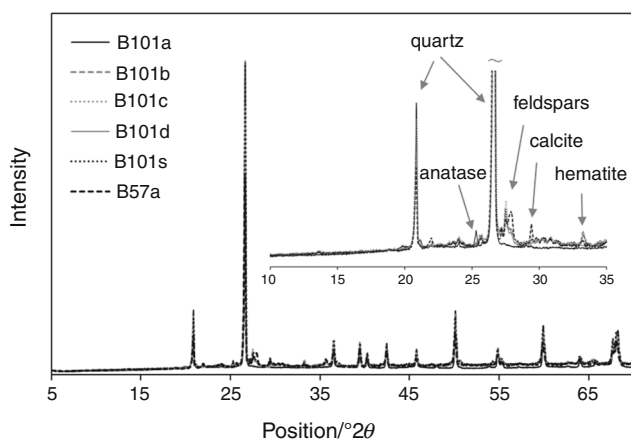
Sample	Content/mass%								
	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	K_2O	Na_2O	Others
B101a	63	33	1.1	1.6	0.6	0.3	0.4	0.1	0.18
B101b	72	16	4	0.9	2.0	1.3	2.6	0.9	0.51
B101c	75	14	4	0.8	1.9	1.0	2.4	0.9	0.80
B101d	72	16	4	0.9	1.6	1.3	2.7	1.0	0.46
B101s	74	13	3	0.8	1.6	1.0	2.3	0.8	2.98
B57a	67	15	4	0.9	7	1.9	2.4	1.2	0.46

Others— P_2O_5 , V_2O_5 , Cr_2O_3 , MnO , ZrO_2

Table 2 Mineralogical compositions of raw materials of the samples calculated from chemical composition by software MINLITH

	Q	Kn	Ill	Chl	Mm	Ab	An	Cc	Ank	Rt	Ht	Sd
101a	19	70	4	1	3	0	0	0	2	1	0	0
101b	40	4	26	0	19	2	0	0	6	1	0	1
101c	46	4	25	0	13	4	0	0	6	1	0	0
101d	40	3	28	0	19	4	0	0	5	1	1	0
101s	49	2	24	0	14	3	0	0	5	1	0	0
57a	35	0	24	4	18	5	1	9	4	1	0	0

Q quartz, Kn kaolinite; Ill illite, Chl chlorite, Mm montmorillonite, Ab albite, An anorthite, Cc calcite, Ank ankerite, Rt rutile, Ht haematite, Sd siderite

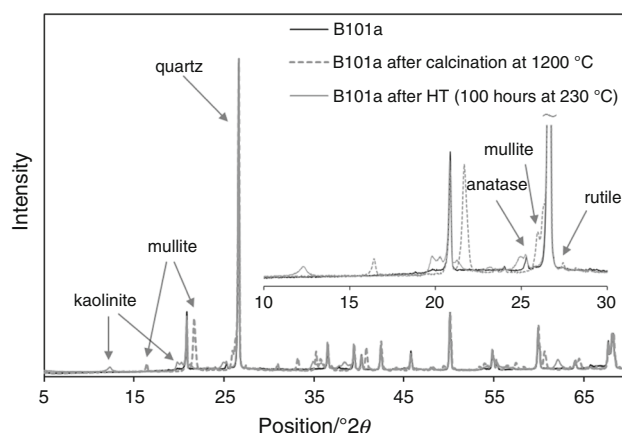
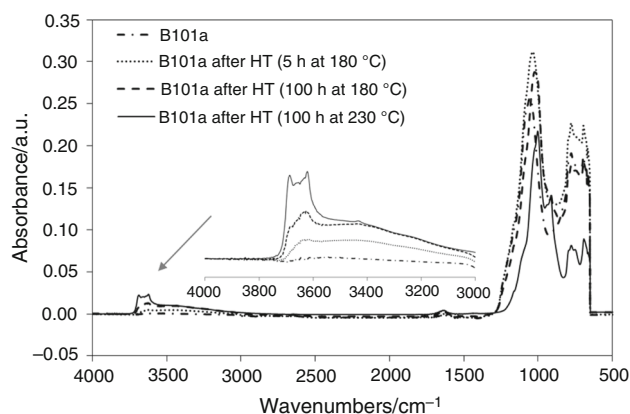
**Fig. 5** XRD pattern of ceramic bodies of selected samples of tiles

The accelerated ageing process was induced by hydrothermal conditions in Teflon-lined autoclaves at 230 °C (2.77 MPa) for 100 h and at 180 °C (1.00 MPa) for 5 and 100 h. A solid/solution ratio of 1 g sample/20 mL water was used in the experiments [20, 21].

Values of irreversible moisture expansion were measured by the dilatometric method using dilatometer LINSEIS L75 Platinum Series Horizontal in helium flow at the rate of 5 °C min⁻¹. Compact samples (20 × 10 × 8 mm) of tiles B101a, B101b, B101d, B57a dried at 105 °C to constant mass were used for the measurements.

Results and discussion

Table 1 shows chemical composition of the studied Gothic tiles measured by X-ray fluorescence analysis (XRF). It was found that the composition of samples B101b, B101c, B101d, and B101s was very similar and if we consider typical heterogeneity of an archaeological material, it can be denoted as the same. The other two samples differ especially in calcium content. While the sample B57a

**Fig. 6** XRD pattern of ceramic body B101a (original, calcinated, hydrothermally treated)**Fig. 7** IR spectra of ceramic body B101a before and after hydrothermal treatment (HT) at different conditions of temperature and time

contained the highest amount of calcium from all the samples (7 mass%), the lowest content of calcium (0.6 mass%) was identified in the sample of the white tile B101a. This information displaced the presumption about the use of a highly calcareous white material for manufacturing white parts of the mosaic as the monastery owned a limekiln from 996 [27].

The results of XRF analysis were used for the calculation of a theoretical mineralogical composition by the program MINLITH (Table 2). This program is used especially in geology [28–30], and the results do not provably determine the mineralogical composition as, e.g., XRD analysis, but give an idea what the composition could be. The program generated similar mineralogical composition for samples with the very similar chemical composition (B101b, B101c, B101d and B101s) as could be expected. The dominant mineral for these samples should be quartz, followed by clays as illite and montmorillonite. Quartz should be the dominant mineral also in the sample B57a.

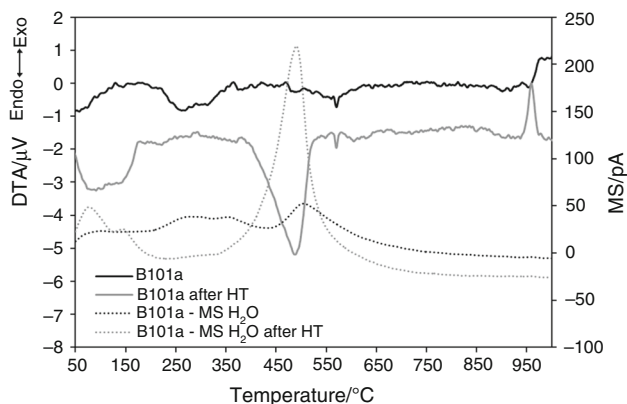


Fig. 8 DTA curves and the curves of H₂O release of the ceramic body B101a before and after hydrothermal treatment (HT)

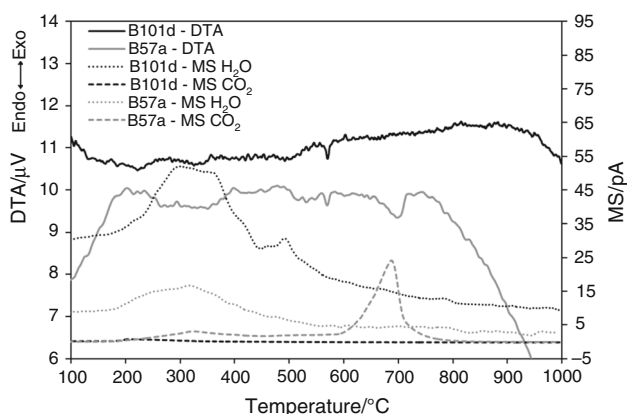


Fig. 9 DTA curves of calcareous (B57a) and non-calcareous (B101d) sample of tiles

This sample should contain unlike other samples calcite. The program generated a very different mineralogical composition for the sample B101a, where kaolinite should be the dominant crystalline phase.

Mineralogical compositions of differently coloured ceramics bodies of tiles were determined also by X-ray diffraction analysis as shown in Fig. 5. The analysis confirmed the results of XRF about the similarity of samples B101b, B101c, B101d and B101s; all the samples contained quartz as the dominant crystalline phase, then small amount of feldspars. The different grey colouring of the B101b tile compared to the reddish-brown of the other samples was probably caused by the firing in reducing atmosphere. Sample B57a contained quartz, feldspar and also a small amount of calcite. In the sample of the white tile (B101a), besides quartz only a very small amount of TiO₂ in the form of anatase was detected. This sample was subsequently subjected to accelerated ageing process (hydrothermal treatment in an autoclave at 230 °C for 100 h). The experiment proved the presence of kaolinite in the

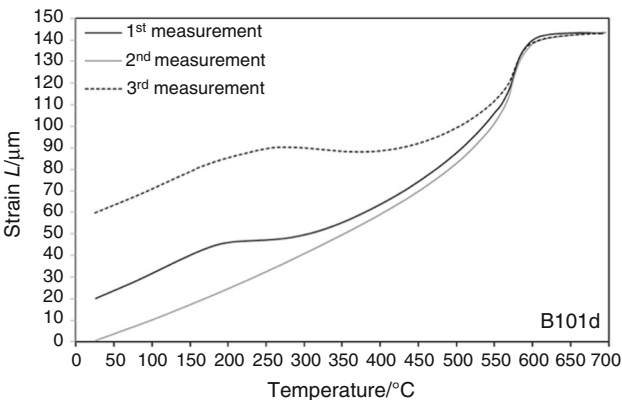
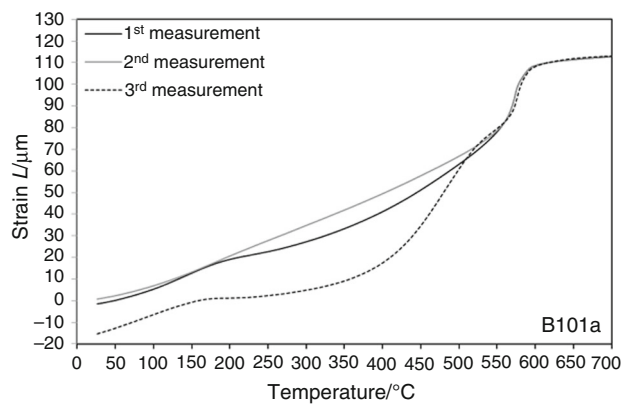


Fig. 10 Strain–temperature relationships of B101a and B101d (1 first measurement, 2 second measurement of the same sample, 3 third measurement of the sample subjected to hydrothermal steaming)

treated sample (Fig. 6). The sample was also fired at 1200 °C, and XRD then proved the presence of mullite and rutile (Fig. 6). The results of XRD are in good agreement with the theoretical mineralogical composition determined by program MINLITH. The difference can be seen only in determination of a clay mineral illite, which was not identified by XRD. The reason can be that the illite is present in the form of a non-crystalline meta-clay (fired clay) and so cannot be detected by XRD.

Figure 7 shows IR spectra of the sample B101a, illustrating the process of metakaolinite rehydroxylation under different hydrothermal conditions. Only the sample treated by the harshest hydrothermal conditions (100 h at 230 °C) showed the pronounced degree of ordering of the kaolinite structure represented by bands at ~3687, 3659 cm⁻¹ belonging to inner surface bonds and the band of inner OH bond at 3622 cm⁻¹ [31, 32].

Figure 8 shows results of thermal analyses (DTA-MS mode) of the white tile B101a used for identification of clay minerals in a plastic component of the ceramic raw material. The DTA curve of the hydrothermally treated sample B101a shows strong endothermic effect in the temperature interval ~400–550 °C, which corresponds to dehydroxylation of kaolinite (removal of chemically bound

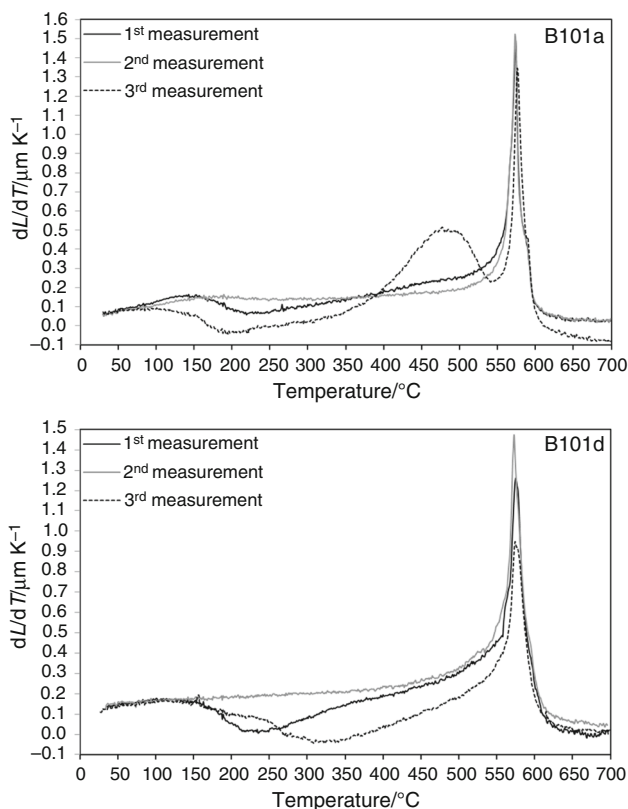


Fig. 11 Derivatives of strain–temperature relationships of B101a and B101d (1 first measurement, 2 second measurement of the same sample, 3 third measurement of the sample subjected to hydrothermal steaming)

water). Other endothermic peaks were registered at ~ 570 °C, which are related to a transformation from β -quartz to α -quartz. The DTA curve of hydrothermally treated sample also shows an exothermic peak related to the crystallization of defect spinel structure.

Figure 9 shows the results of thermal analyses (DTA–MS mode) of the calcareous sample B57a and the sample B101d representing the group of mosaic samples with the similar chemical and mineralogical composition. The presence of calcite in the sample B57a detected by XRD was confirmed by the endothermic peak between ~ 600 °C and 750 °C due to its decarbonation. This endothermic peak corresponds to MS line of CO_2 . DTA curves of both samples showed endothermic peaks related to transformation from β -quartz to α -quartz (~ 570 °C) and then a broad endothermic effect between ~ 200 and 500 °C due to dehydration and dehydroxylation of clays. The MS lines of H_2O confirm the dehydroxylation in wide temperature ranges for both samples; however, in case of the sample B101d, additional small endothermic effect in the temperature interval ~ 400 – 550 °C which probably corresponds to dehydroxylation of kaolinite was monitored.

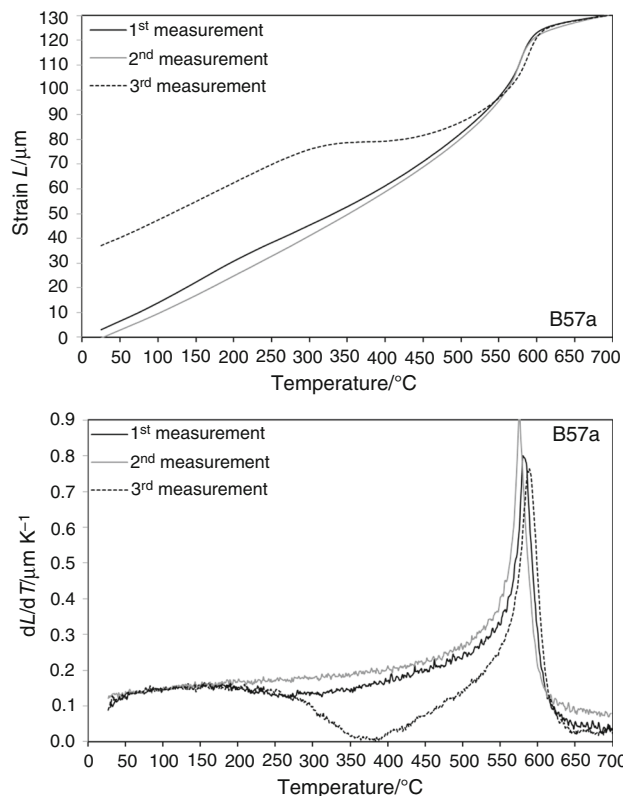


Fig. 12 Strain–temperature relationships of B57a on the top and derivates on the bottom (1 first measurement, 2 second measurement of the same sample, 3 third measurement of the sample subjected to hydrothermal steaming)

Table 3 Natural irreversible moisture expansion determined by dilatometric measurement

Sample	Irreversible moisture expansion/ $\mu\text{m m}^{-1}$	Standard deviation/ $\mu\text{m m}^{-1}$
B57a	289	10
B101a	1329	122
B101b	687	47
B101d	768	98

Values of irreversible moisture expansion were measured by the dilatometric method. Figure 10 shows dilatation curves of the samples B101a and B101d representing a typical example of rehydroxylation. The difference between the first and second annealing is due to the release of chemisorbed water from the ceramic body and is equal to the natural irreversible moisture expansion of the samples B101a and B101d. After the second annealing, the samples were subjected to the hydrothermal steaming (100 h at 230 °C) and then measured for the third time. The difference between second and third measurement

Table 4 Coefficients of thermal expansion (CTE) determined by dilatometric measurement

CTE _{(20–550 °C)/K⁻¹}	Expansion measurement					
	Ceramic body					
	First	Second	Third	Δ_{2-1}	Δ_{2-3}	Ratio of rehydroxylation/%
B57a	8.93×10^{-6}	9.09×10^{-6}	5.67×10^{-6}	0.16	3.42	4.68
B101a	7.7×10^{-6}	11.8×10^{-6}	5.82×10^{-6}	4.1	5.98	68.56
B101d	7.18×10^{-6}	8.39×10^{-6}	4.75×10^{-6}	1.21	3.64	33.24

indicates the maximum of the possible expansion. The derivatives of the measured dilatometric curves are plotted in Fig. 11. The derivative curve of the sample B101a confirms pronounced dehydroxylation of metakaolinite in the temperature interval 450–550 °C, which is in good agreement with the results of thermal analyses presented in Fig. 8. Also, the dilatometric results of the sample B101d are consistent with the DTA-MS H₂O curves (Fig. 9), that is the release of water from meta-clays.

Figure 12 shows dilatation curves of the sample B57a. The curves display minor differences between the first and second annealing, so the ceramic body expanded less. This was as expected as the presence of CaO reduces irreversible moisture expansion [3]. The mean values of the natural irreversible expansions are listed in Table 3. The highest value (1329 $\mu\text{m m}^{-1}$) was obtained for the sample of the white tile B101a, where high amount of kaolinite was proved. The lowest value was obtained for the sample of the calcareous tile B57a.

Table 4 shows the values of coefficients of thermal expansion (CTE) of the samples B101a, B101d and B57a determined by dilatometric measurement. The column Δ_{2-1} represents values of the natural rehydroxylation, whereas the column Δ_{2-3} represents values of the maximum rehydroxylation induced by the hydrothermal treatment in an autoclave. The measured values were used for calculating the ratio of rehydroxylation in the studied samples. The calculated ratios of rehydroxylation along with dilatation curves show the different degrees of the natural rehydroxylation in the ceramic bodies of the studied samples by the influence of soil moisture. High degree of natural rehydroxylation (~70 %) was proved in the sample of the white tile B101a. Volume expansion of meta-clays and a low degree of kaolinite sintering caused extensive degradation of the white tile. Apparently lower degree of degradation showed terracotta ceramic bodies represented by the sample B101d with the ratio of rehydroxylation ~30 %. The lowest ratio of rehydroxylation (~5 %) was calculated for the tile B57a, which is related to the content of calcium restraining the volume expansion of meta-clays. Accordingly, this calcareous tile showed the lowest degree of degradation.

Conclusions

Thermal analyses (STA and dilatometry) with the combination of other methods (XRF, XRD and IR) were used to study the causes of degradation of ceramic bodies of Gothic mosaic tiles which were found during archaeological research of Benedictine Monastery in Prague. Analyses of hydrothermally treated (100 h, 230 °C) ceramic bodies proved that the raw material for fabrication of white tile (B101a) was mainly kaolin. Due to a low firing temperature (below 1000 °C), the ceramic body contained a high amount of an unstable phase—metakaolinite, which underwent rehydroxylation accompanied by volume expansion (the ratio of rehydroxylation was nearly 70 %). This process along with a low degree of sintering due to high amount of kaolinite caused extensive degradation of the white tiles. Apparently lower degree of rehydroxylation ~30 % was proved in the coloured ceramic body of terracotta tile B101d. The lowest degree of degradation showed the tile B57a, which was as expected due to the presence of calcium restraining the volume expansion of meta-clays.

Thermal analyses confirmed the presence of clay minerals or meta-clays in all samples, which is typical for archaeological material.

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References

1. Hanykř V, Kloužková A, Bouška P, Vokáč M. Ageing of historical ceramics. *Acta Geodyn Geomater.* 2009;6(1):59–66.
2. Hanykř V, Kloužková A, Bouška P, Vokáč M. Stárnutí pórovitého keramického střepu. *Sborník ze semináře Objemové změny pórovité keramiky.* Praha: Silikátový svaz, 2009, 33–43.
3. Vokáč M, Kloužková A, Hanykř V, Bouška P. Dilatometric analysis of ceramic roof tiles for determining irreversible moisture expansion. *Ceramics-Silikáty.* 2009;53(4):303–9.
4. Savage SD, Wilson MA, Carter MA, KcKay B, Hoff WD. Mass gain due to the chemical recombination of water in fired clay brick. *J Am Ceram Soc.* 2008;91(10):3396–8.
5. Drelich J, Bowen PK, Scarlett TJ. Effect of humidity instability on rehydroxylation in fired clay ceramics. *J Am Ceram Soc.* 2013;96(4):1047–50.

6. Shoval S. Rehydroxylation of clay minerals and hydration in ancient pottery from the Land of Geshur. *J Therm Anal.* 1991;37:1579–92.
7. Burakov KS, Nachasova IS. Archaeomagnetic study and rehydroxylation dating of fired clay ceramics. *Izv-Phys Solid Earth.* 2013;49(1):111–9.
8. Moinester M, Piasezky E, Braverman M. RHX dating of archaeological ceramics via a new method to determine effective lifetime temperature. *J Am Ceram Soc.* 2015;98(3):913–9.
9. Schurecht HG. Methods for testing crazing of glazes caused by increases in size of ceramic bodies. *J Am Ceram Soc.* 1928;11:271–7.
10. Bouška P, Hanykýř V, Vokáč M, Pume D. Failures of floor structures made from concrete and fired clay units. In: Proceedings of construction materials'05 and Mindess Symposium. The University of British Columbia, Vancouver 2005, 1711–20.
11. Hauck D, Hilker E. Moisture expansion behaviour of brick. *Ziegelindustrie-Jahrbuch: Bauverlag Wiesbaden;* 1989.
12. Albenque M. Action de la vapeur d'eau sur les silicates ayant pris naissance à la cuisson de pâtes céramiques. Dissertation thesis. Université de Paris VI, 1974.
13. Pavlovic LJ, Tosic M. Kinetics of moisture expansion in some fired clay bricks. *Tile Brick Int.* 1997;13(2):105–9.
14. ČSN EN 772-19. Methods of test for masonry units—part 19: determination of moisture expansion of large horizontally perforated clay masonry units. Prague: Český normalizační institut, 2000. p. 12.
15. ČSN EN ISO 10545-10. Ceramic tiles—part 10: determination of moisture expansion. Prague: Český normalizační institut, 1998. p. 8.
16. AS/NZS 4456.11. Standard, masonry units and segmental pavers—methods of test. Method 11: Determining coefficients of expansion. Australian/New Zealand: Standards Australia, 1997. p. 12.
17. NF P 13–302. Entrevous en terre cuite pour planchers a poutrelles préfabriquées, Paris: AFN, 1983. p. 26.
18. Kloužková A, Zemenová P, Kohoutková M, Mazač Z. Ageing of fired-clay ceramics: comparative study of rehydroxylation processes in a kaolinitic raw material and moon-shaped ceramic idol from the Bronze Age. *Appl Clay Sci.* 2016;119(2):358–64.
19. Kloužková A, Zemenová P, Kohoutková M, Kloužek J. Hydrothermal rehydroxylation of kaolinite studied by thermal analysis. *Ceramics-Silikáty.* 2013;57(4):342–7.
20. Zemenová P, Kloužková A, Kohoutková M, Král R. Investigation of the first and second dehydroxylation of kaolinite. *J Therm Anal Calorim.* 2014;116:633–9.
21. Kloužková A, Zemenová P, Kohoutková M, Mazač Z. Characterisation of a prehistorical ceramic object: moon-shaped idol, by means of thermal analysis. *J Therm Anal Calorim.* 2014;116:641–5.
22. Quinn PS. Ceramic petrography. The interpretation of archaeological pottery & related artefacts. In *Thin Section.* Oxford: Archaeopress; 2013.
23. Reedy C. Thin-section petrography of stone and ceramic cultural materials. London: Archetype Books; 2008.
24. Dragoun Z. Středověké podlahy a dlaždice z břevnovského kláštera. *Zprávy památkové péče.* 1993;53(5):170–6.
25. Dragoun Z, Tryml M, Mjartan J. Restaurování torz středověkých podlah z Dolních Chaber a Břevnovského kláštera. *Staletá Praha.* 2010;26(2):122–9.
26. http://praha.idnes.cz/brevnovsky-klaster-musi-zaplatit-pokutu-zakaceni-stromu-pnb-/praha-zpravy.aspx?c=A110406_104053_praha-zpravy_jj.
27. Rovnaníková P. Omítky: Chemické a technologické vlastnosti. Praha: STOP; 2002.
28. Rosen OM, Abbyasov AA, Tipper JC. MINLITH—an experience-based algorithm for estimating the likely mineralogical compositions of sedimentary rocks from bulk chemical analyses. *Comput Geosci UK.* 2004;30:647–61.
29. Gregerová M, Čopjaková R, Beránková V, Bibr P, Goš V, Hanuláková D, Hložek M, Holubová Z, Závadná B, Kristová L, Kuljovská Z, Macháček J, Mazuch M, Procházka R, Škoda R, Všíanský D. Petroarcheologie keramiky v historické minulosti Moravy a Slezska. 1. vyd. Brno: Masarykova univerzita, 2010.
30. Adams AE, Mackenzie WS, Guilford C. Atlas of sedimentary rocks under the microscope. Essex: Longman Scientific & Technical; 1984.
31. Vaculíková L, Plevová E, Vallová S, Koutník I. Characterization and differentiation of kaolinites from selected Czech deposits using infrared spectroscopy and differential thermal analysis. *Acta Geodyn Geomater.* 2011;8(1):59–67.
32. Madejová J, Komadel P. Baseline studies of the clay minerals society source clays: infrared methods. *Clay Clay Miner.* 2001;49(5):410–32.