Archaeometric analysis of architectural ceramics form the site
“Khustiin bulag” Tuv province, Mongolia

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ARTICLE INFO: Received: 25 Oct, 2019; Accepted: 16 Jun, 2020

Abstract: A series of architectural ceramics, including roof tiles and bricks from the excavation site at Khustyn Bulag, Mungunmorit soum, Tuv aimag (province) of Mongolia were subjected to detailed archaeometric analysis. We present here results of Fourier-transform infrared spectroscopy (FT-IR), Scanning electron microscopy (SEM-EDS) and Thermogravimetric analysis (TGA) and their potential to determine the composition of brick samples from one excavation site, and their firing temperatures. In addition, yellow ochre, which is a natural earth rock pigment that contains hydrated iron oxide and represents the most common pigment of antiquity, was revealed at this excavation site. The mineral composition of ochres will be determined and the possible use of it will be discussed.

Keywords: ceramic; ochres; clay mineral; firing temperature; SEM-EDS; FT-IR; TGA;

INTRODUCTION

Determining the composition of clayware and raw materials, production techniques and minerals occurring during firing is important for the study of archaeological and cultural studies. Archaeological finds, such as earthenware are regarded as an important tool that contains information about the timeframe, technology and origin. In fact, the application of the techniques of chemistry, physics, geology, and materials science provide a basis for understanding many questions about manufacturing techniques, history of technology, production organization, functional relationships between specific resource manufacturing combinations, and patterns of local, regional or extra-regional distribution of pottery [1].

While for the age determination of heated ceramic samples thermoluminescence (TL) was used; archæometric methods such as Fourier-transform infrared spectroscopy (FT-IR), X-ray diffraction, scanning electron microscope (SEM-EDS) and thermogravimetric analysis (TGA) are commonly combined together to
determine the mineral composition and
technological processes [2-3]. For decades, IR
spectroscopy has been one of the frequently
used methods to investigate the structure,
bonding and chemical properties of clay
minerals [4]. The examination of ancient
pottery with an analytical SEM is, therefore,
valuable for characterizing and distinguishing
between the traditions in ceramic technology in
antiquity because information is obtained on
both extent of vitrification and firing
temperature [5].

The compositional analysis of ceramic
materials in archaeological studies is carried out
with the purpose of understanding how the
ceramic might have been produced and used,
and also to determine the location and
techniques involved in its manufacture.
Mineralogical analysis of ancient pottery is
particularly useful in the understanding of the
manufacturing process, and appropriate
techniques may provide information about
temper addition, oxidation-reduction
conditions and temperatures of firing.

Clay minerals are determined by the
temperature and duration of firing. During
firing, the minerals change their structure, they
decompose and finally new minerals are formed
[6]. In archaeology, the firing temperature is
considered to be the benchmark of the
 technological level of ancient society. Such an

approach originated from the characterization
of contemporary ceramic manufacturing [7].
During firing, the color of the sample changes,
which is related to the iron (Fe) content of the
material. Iron oxide produces hematite at
temperatures higher than 600°C, and at > 890°C
it produces magnetite [8]. The authors [9-10]
believe that the firing at about 600-800°C, was
sufficient for decomposing calcareous material.

A series of archaeological ceramics,
including roof tiles and bricks from the
excavation site at Khustyn Bulag,
Mungunmorit soum, Tuv aimag were
previously subjected to rehydroxylation dating
of bricks, which gave a date of 2200±20 years,
proving that the construction materials were
from the Xiongnu period [9]. Analytical
methods conducted to determine the mineral
composition, production techniques and origin
of the clay [9, 11, 12] revealed the need for
further examining the samples. Particularly, a
detailed archaeometric analysis might also
verify the presence and impact of calcite
(CaCO₃) on the rehydroxylation dating method.
Therefore, in this work, TGA together with
microanalysis (SEM-EDS) and FT-IR were
used for characterization of the construction
materials excavated at a certain archaeological
site, as well the characterization of the different
layers of the roof tiles.

MATERIALS AND METHODS

Research materials

The site from the Khustyn Bulag,
Mungunmorit soum in Tuv aimag was
previously described elsewhere [13], [14] and
architectural samples were collected during the
excavations carried out by the Institute of
Archaeology of the Mongolian Academy of
Sciences. Ceramics: roof tiles MM1, MM2 and
MM3, tapestry brick MM4 and after refiring at
500°C for 4 hours are shown in Figure 1. Ochre
pigment sample MM_N was fired at 500°C,
700°C and 900°C for 1 hour and is shown in
Figure 2.
The samples were heated at 500°C for 4 hours. Initially, the color was grey, however, after refiring at 500°C for 4 hours, the color of samples MM1, MM2, MM3 turned red, while the color of the MM4 sample became grey, as can be seen from the insets in Figure 1.

Figure 2 shows ochre samples after heating at 500°C, 700°C and 900°C for 1 hour.

Water evaporates and the color changes when the hydrated iron oxide is heated.

**TGA analysis**

Thermogravimetric analysis is a technique in which the mass of a substance is monitored as a function of temperature of time, in as much as the sample specimen is subjected to a controlled temperature program in a controlled atmosphere. The powders of each layer were ground in a mortar to a high degree of fineness. TGA analysis was then performed on the fine powders using a TGA-2100D from Analytical Technologies Limited. Temperatures were probed in the range between room temperature (RT) to 900°C at a heating rate of 10°C min⁻¹, in a flowing nitrogen atmosphere at 100 ml/min. For data analysis the software from TGA-2100D was used.
FT-IR analysis

The firing temperature of the samples was determined from the FT-IR (IR) spectra using the following procedure [10]. FT-IR was recorded using an IR Prestige spectrometer. Spectra of powdered samples of the pottery were obtained using KBr disks. The disks were prepared using 1 mg of the sample in 100 mg of KBr. The transmission spectra obtained were in the range of 4000-400 cm\(^{-1}\).

RESULTS AND DISCUSSION

TGA analysis

TGA is a technique when a material is heated, its weight either increases or decreases. The mass loss due to the thermal process was determined by thermogravimetric analysis and the peak intervals of the dehydration and dehydroxylation were determined accordingly [7]. When heated, clays show significant mass loss due to dehydration (20~350\(^{\circ}\)C), dehydroxylation (350\(^{\circ}\)C~600\(^{\circ}\)C), and decomposition of carbonates, mainly calcite (700\(^{\circ}\)C- 800\(^{\circ}\)C). The TGA curves of samples MM1, MM2, MM3 are shown in Figures 3 (a, b, c) separately and is shown in one plot in Figure 3 (d) in order to reveal the differences in their thermogravimetric curves.

SEM-EDS analysis

Microstructural and elemental analysis of cross-sections and powder samples (separated from individual layers) were performed on a Hitachi TM-3000 (Hitachi High-Technologies Corporation, Japan) scanning electron microscopy at the Mongolian University of Science and Technology.

Figure 3. Representative TGA curves of samples MM1, MM2 and MM3
The mass loss due to dehydration (20, 9 and 12%), dehydroxylation (3, 2 and 3%) and due to decomposition of carbonates (4 and 9%) are shown in Table 1. Only samples MM1, MM3 contain calcite; the presence of calcite decomposition was observed in the 700-800°C region. For samples MM1, MM2 and MM3 there was no mass loss relative to a particular region and further decay continued.

| Sample code | Mass increase, % | Weight loss, % |
|-------------|------------------|----------------|
|             | (20~350°C)       | Dehydroxylation (350~600°C) | Decomposition of calcite (700~800°C) |
| MM1         | 20               | 3              | 4               |
| MM2         | 9                | 2              | 1               |
| MM3         | 12               | 3              | 9               |
| MM1 core    | 12               | 3              | 3               |
| MM1 outer   | 6                | 11             | 1               |
| MM1 inner   | 2                | 6              | 14              |

According to [7], the outer surface, core and inner surface of the sample MM1 were also measured using thermogravimetry; the results are shown in Figure 4. The conventional statement says: if the sample contains calcite, the firing temperature was below 800°C [7]; the presence of calcite is observed for the inner surface and core. However, for the outer surface no calcite decomposition was observed. It should be noted that the outer surface was grey colored with hard surface, while the core and inner surface of sample MM1 were red-brown.

**FT-IR measurements**

FT-IR is a spectroscopy technique that is typically used to determine the functional structure of organic chemicals. It is advantageous in that it can reveal the presence of organic and inorganic substances [16]. The spectras of roof tile samples MM1, MM2 and MM3 along with brick sample MM4 were processed. Figure 4 shows the results of FT-IR measurements.
Figure 5. FT-IR results of samples MM1, MM2, MM3 and MM4

The spectra revealed microline and magnetite at 461 cm\(^{-1}\), 584 cm\(^{-1}\) [6], quartz at 775 cm\(^{-1}\), and organic compounds at 2883 cm\(^{-1}\); the bands at 1643 cm\(^{-1}\), 3450 cm\(^{-1}\), 3743 cm\(^{-1}\) are assigned to O-H stretching of inter layer and inner O-H group of absorbed water (O-H-O bend). The band at 3896 cm\(^{-1}\) revealed an inter layer O-H group, which was detected in samples MM1 and MM2, but not yet detected in samples MM3 and MM4. Furthermore, a band in the region of 3423 cm\(^{-1}\) was detected in sample MM4, which was not detected in the other samples.

[17-18] proposed that calcite decomposition occurs at 600-800°C. In our samples MM1, MM3 and MM4, a low intensity band and calcite band were detected around 1427 cm\(^{-1}\), no calcite was observed in MM2. TGA measurements detected a decomposition at around 700-800°C for ceramic samples.

The FT-IR spectra recorded a low intensity absorption band at 584 cm\(^{-1}\) for samples MM1, MM2 and MM3 and medium intensity band for MM4 turned out to be magnetite. A medium intensity hematite band at 584 cm\(^{-1}\) [6, 15] was observed in sample MM4. The absorption band at 1043 cm\(^{-1}\) revealed the production temperatures for MM1 and MM2 as 700°C and 900°C for MM3 and MM4 [19]. It must be noted that after the RHX measurements were carried out at 500°C, the color of tiles (MM1, MM2, MM3) became red and the brick (MM4) dark blue.

**Ochre analysis**

Natural iron-rich oxides provided red-yellow-brown paints and dyes for a wide range of antique application, including but in no way limited to rock art paintings, pottery, wall paintings and cave art, and human tattoos. Generally speaking, ochres are natural earth pigments varying from dull yellow to red and brown. The colour shown by ochres depends on the nature of the iron oxide chromophore. Thus, the darker red ochres richer in hematite, Fe\(_2\)O\(_3\), while the paler, yellow ochres mainly contain hydrated iron oxide, goethite, Fe\(_2\)O\(_3\)\(\cdot\)H\(_2\)O or FeOOH [20].

Ochres is a natural earth rock pigment contains hydrated iron oxide and ranges in various color from red, yellow to deep orange or brown. Color changes are observed by heating ochre: pigments were fired at 500°C, 700°C and 900°C for 1 hour and the mineral composition was measured using FT-IR. Furthermore, this is the first time that ochre samples from the Mongolian ancient architectural ceramics were examined.
The FT-IR spectra recorded the absorption bands at 431 cm\(^{-1}\) assigned to illite (O-M-O) \[2\], 3453 cm\(^{-1}\) indicated inter layer O-H, and absorption bands at 778 cm\(^{-1}\) and 797 cm\(^{-1}\) \[16, 21\] indicated (Si-O). The spectra of ochre sample MM_N revealed high intensity peaks at 913 cm\(^{-1}\), 1031 cm\(^{-1}\) indicated Al-OH and Illite stretching and the weak intensity band at 3622 cm\(^{-1}\) is due to O-H stretching of illite (O-Hstr) \[22\]. For sample MM_500, weak intensity absorption bands at 1643 cm\(^{-1}\), 2880 cm\(^{-1}\) indicated absorbed water (O-H-O bend) and organic compounds respectively. The high intensity peak at 1082 cm\(^{-1}\) in sample MM_700 indicated a presence of quartz.

High intensity peaks were observed for samples MM_N and MM_500 and medium intensity peaks were observed for samples MM_700 and MM_900 at 465 cm\(^{-1}\) and 534 cm\(^{-1}\), indicating microcline and hematite \[6\]. As a result of this observation it is possible to maintain that the high iron content in the ceramic was used for pigmentation.

**SEM-EDS analysis**

A scanning electron microscope provides detailed surface information by tracing a sample in a raster pattern with an electron beam. The typical SEM image of the selected MM1 and MM4 samples are shown in Figure 7 [9].
Figure 7. SEM-EDS Measurements: left MM1, right MM4

Table I. Results of SEM-EDS measurements

| Element | Weight, % |
|---------|-----------|
| MM1     | MM4       |
| Mg      | 1.8       | 13.4     |
| Al      | 13.9      | 13.4     |
| Si      | 40.7      | 36.3     |
| K       | 6.9       | 6.9      |
| Ca      | 7.7       | 9.5      |
| Ti      | 1.8       |          |
| Fe      | 27.1      | 33.8     |

A high concentration of iron was confirmed in the clay sample, which is in agreement with the results of IR measurements, and additionally, the clay sample was identified as illite (KAl₂Si₄O₁₀).

CONCLUSIONS

The architectural samples collected from the excavation site “Khustyn bulag”, Mungunmorit soum, in Tuv aimag were investigated using TGA, FT-IR, and SEM-EDS to determine the firing temperatures and production techniques. The following conclusions were made.

1. It is advantageous to combine the TGA, FT-IR, and SEM-EDS methods to determine the production techniques. FT-IR measurements revealed the possibility that MM1 and MM2 samples were manufactured at 700°C, while samples MM3 and MM4 were manufactured at 900°C, however FT-IR method
is more suitable for determining the mineral composition of the sample.

2. TGA measurements revealed that samples MM1 and MM3 were manufactured at below 800°C, whereas sample MM2 was manufactured at 700°C. Measurements of the samples from different layers of the roof tile MM1 revealed evident differences in the results. These detailed thermogravimetric results provided us information about the variations in the clay paste during the manufacturing period and also the possible variations in firing.

3. The FT-IR method revealed the presence of ochre in the samples, which probably was a very important feature of the technology for coloring of the samples. The very fact that ochre revealed from this site is interesting and further research into this topic will be done in our next research.

Acknowledgements

The research was partly financed under the project ShuSS 2017/63 from the Science and Technology Foundation of Mongolia. Suvd-Erdene B. received the Master scholarship from TWAS research grant RGA No: 17-521RG/PHYS/AS_G.

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