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ARTICLE

# Archaeometric analysis of architectural ceramics form the site "Khustiin bulag" Tuv province, Mongolia

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***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; archeometric 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

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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 600ºC, and at > 890ºC it produces magnetite [8]. The authors [9-10] believe that the firing at about 600-800ºC, was sufficient for decomposing calcareous material.

A series of architectural 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 ($CaCO_3$) 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 500ºC for 4 hours are shown in Figure 1. Ochre pigment sample MM_N was fired at 500ºC, 700ºC and 900ºC for 1 hour and is shown in Figure 2.

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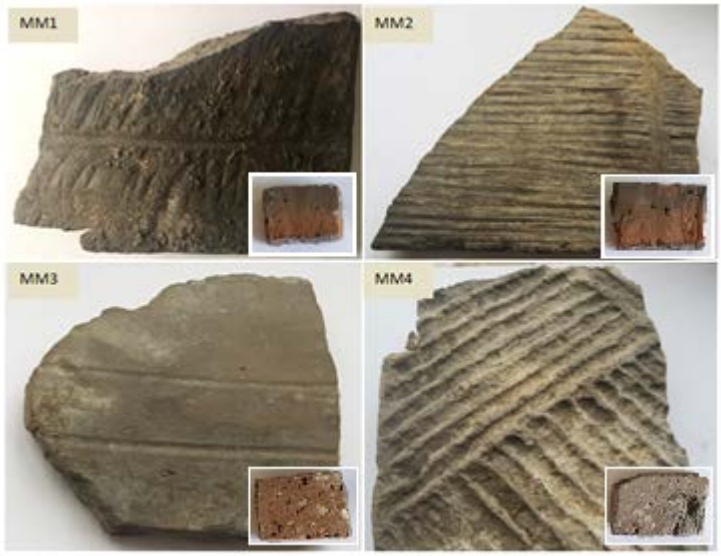


***Figure 1. Roof tiles of MM1, MM2, MM3 and brick of MM4; inset shows the corresponding fragments after refiring at 500°C for 4h***

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.

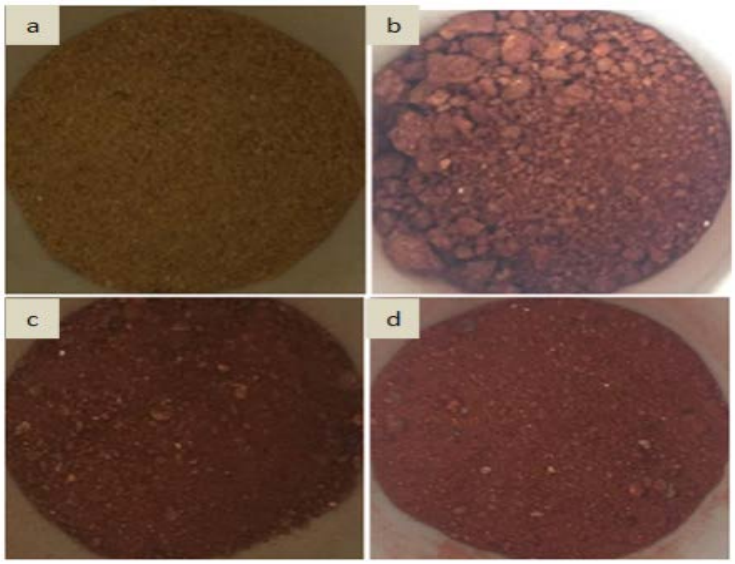


***Figure 2. Ochre pigments sample (a) MM_N raw, (b), (c), (d) refired at 500°C, 700°C, 900°C***

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.

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### 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 $cm^{-1}$.

### 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.

## 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 (20~350ºC), dehydroxylation (350ºC~600ºC), and decomposition of carbonates, mainly calcite (700ºC- 800ºC). 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 thermogavimetric curves.

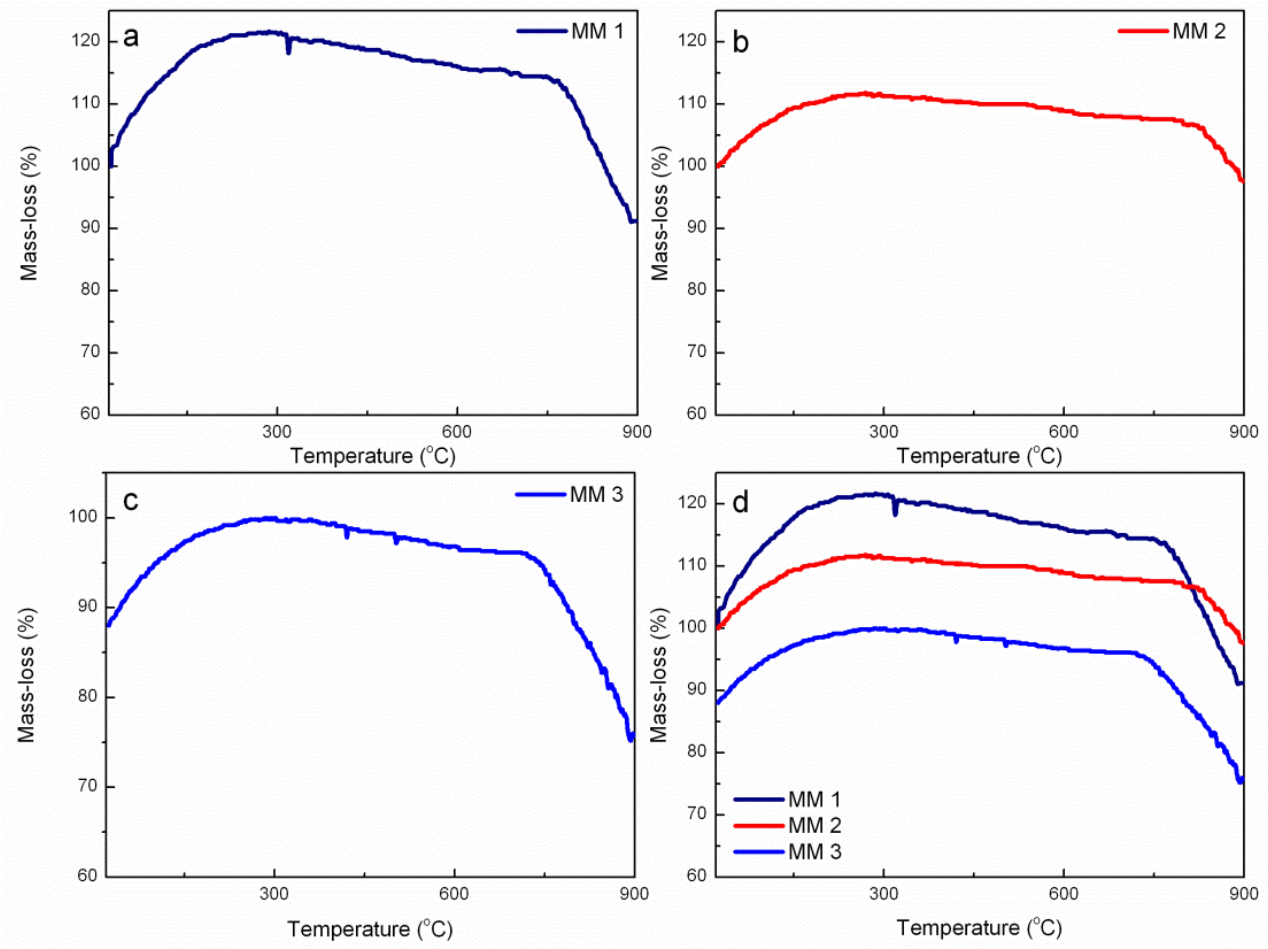


*Figure 3. Representative TGA curves of samples MM1, MM2 and MM3*

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*Table 1. Thermal data in TGA of samples*

| Sample code | Mass increase, % | Weight loss, % | |
|---|---|---|---|
| | (20~350ºC) | Dehydroxylation (350~600 ºC) | Decomposition of calcite (700~800 ºC) |
| 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 |

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.

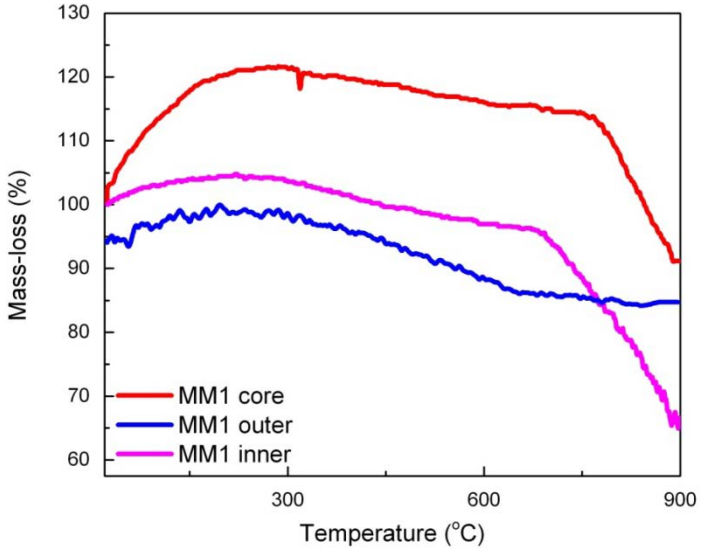


*Figure 4. Representative TGA curves of sample MM1 (core, outer surface, inner surface)*

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 800ºC [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.

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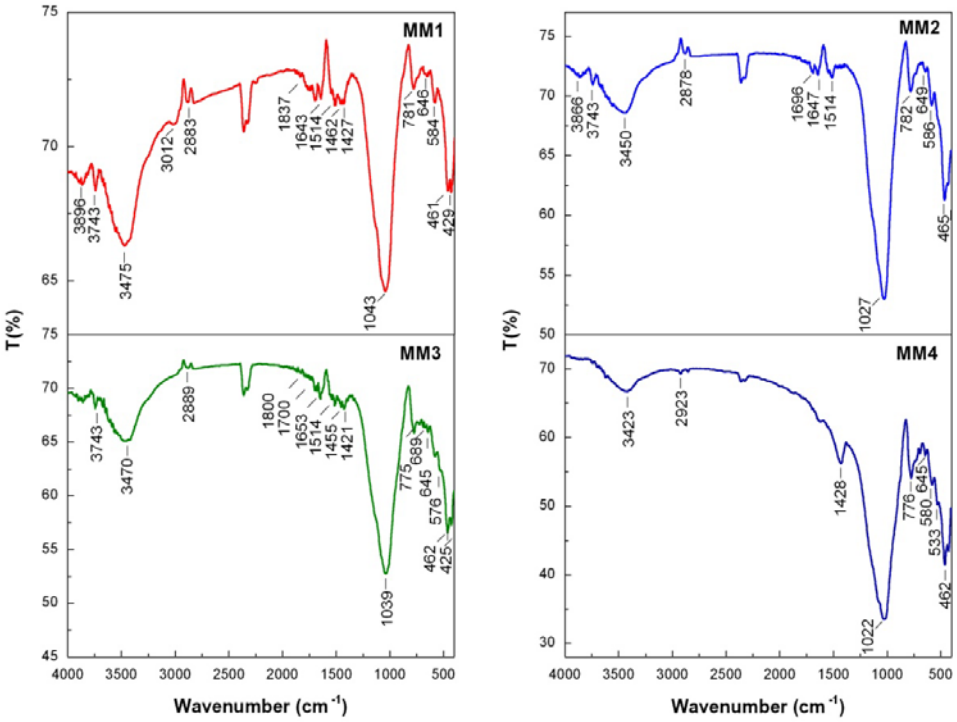


*Figure 5. FT-IR results of samples MM1, MM2, MM3 and MM4*

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 700-800ºC 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 700ºC and 900ºC for MM3 and MM4 [19]. It must be noted that after the RHX measurements were carried out at 500ºC, 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, $Fe_2O_3$, while the paler, yellow ochres mainly contain hydrated iron oxide, goethite, $Fe_2O_3 \cdot H_2O$ 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 500ºC, 700ºC and 900ºC 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.

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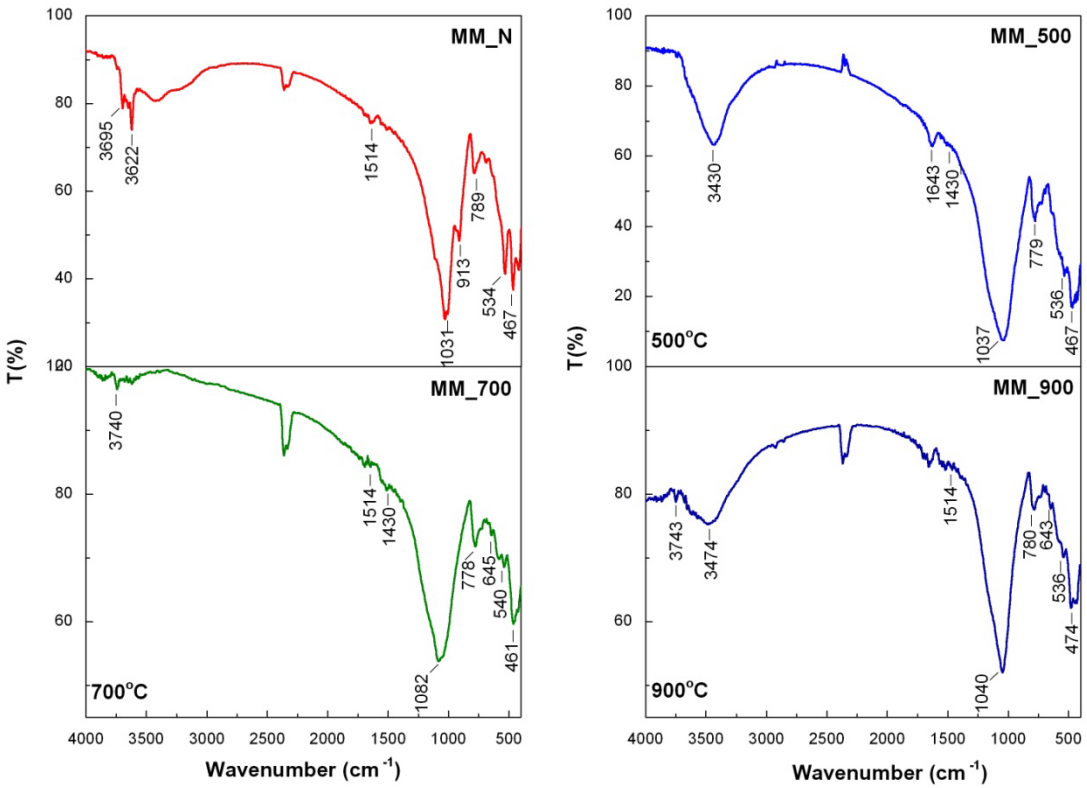


***Figure 6. FT-IR spectra of: Ochre pigments sample (a) MM_N raw, (b), (c), (d) refired at 500°C, 700°C, 900°C***

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 AI-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].

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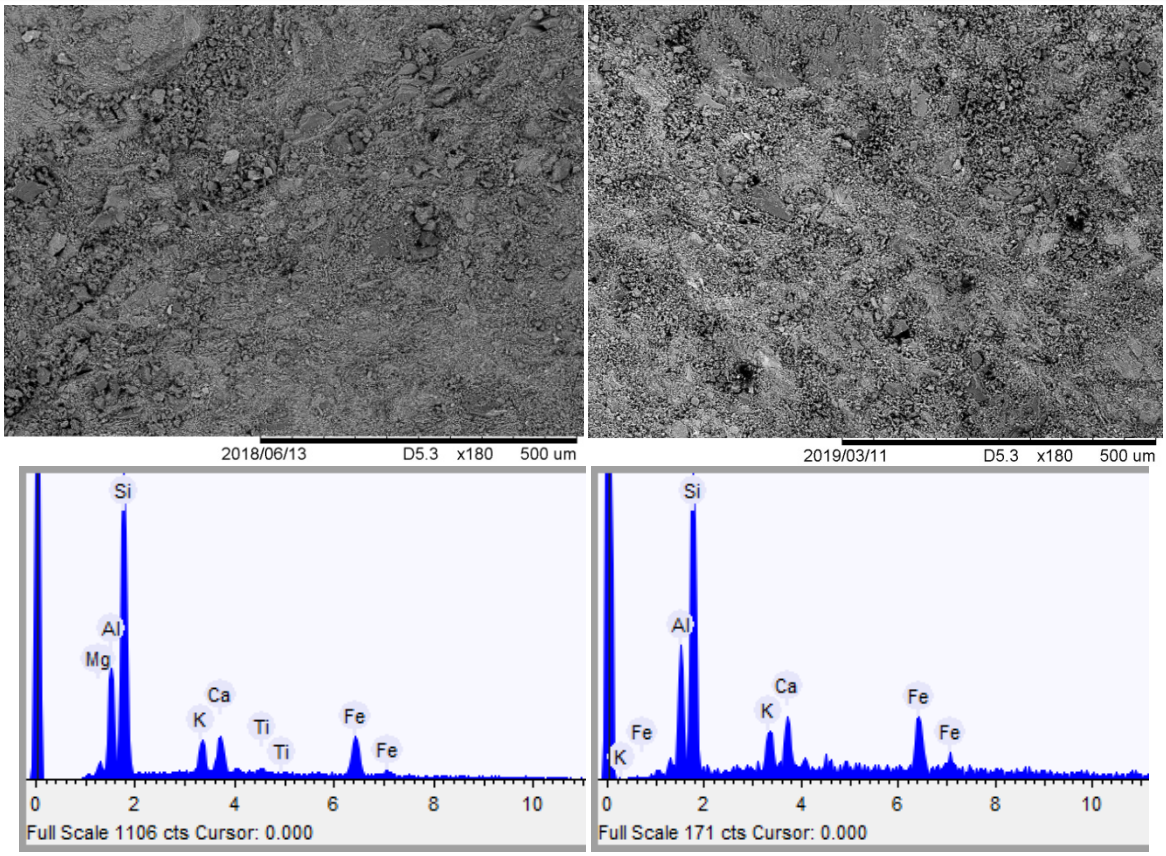


***Figure 7. SEM-EDS Measurements: left MM1, right MM4***

***Table I. Results of SEM-EDS measurements***

| Element | Weight, % | |
|---|---|---|
| | MM1 | MM4 |
| Mg | 1.8 | |
| 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 ($KAl_2Si_4O_{10}$).

## 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

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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.

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