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Ceramic Materials Based on Clay Minerals in Cultural Heritage Study

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Abstract

The artifacts belonging to the ceramic heritage are mostly based on all clay types used by humans over the ages, because the sources of clays were easily available and people were interested to produce ceramics and pottery. This is the reason why the conservation of cultural heritage is of great concern. Ceramics (Greek κεράμιον Keramion) is a material obtained by shaping and firing clay. In the Romanian history, many ceramic pieces, of great diversity, have been discovered, and most of them are used in traditional households. Ceramic materials based on clay minerals in cultural heritage (ceramic heritage) involve techniques of characterization of raw materials and ceramic objects based on clays, discovered in different archaeological sites, leading to some results about the production technology, provenance, authentication, and historical appartenance on Romanian territory. The chemical composition of ancient ceramics and pigments decorating them, excavated from different Romanian archaeological sites, suggested a chemical composition of ceramic based on clay minerals (kaolinite, illite, and smectite), while the pigments belonging to them contained red pigments (hematite or ocher), manganese oxides (brown pigments), and magnetite or carbon of vegetable origin (black-pigmented layers).

Keywords: Cultural heritage, clays, pottery, ceramics, Transylvania tiles

1. Introduction

In ancient times, sources of clays were widely available, between them soils or surface sediments have been the proper sources for ceramics without further treatment, due to their natural mixture of plastic and nonplastic components [1]. Ceramics is an inorganic nonmetallic

material obtained through thermal processing of natural raw materials at relatively high temperature [2]. The raw materials are clays with finely divided quartz (sand) (0.02–0.04 mm) and feldspar, responsible for the rheology along the thermal processing. Clay is a group of minerals in earth that is granular; plastic, when mixed with a little water; or hard and brittle, if combusted. The clay is composed of hydrated aluminum silicates, with the addition of an appreciable amount of other elements: magnesium, iron, calcium, and potassium [3,4]. The clays retain fluid water (liquid) (from pores between clay particle aggregates) at low temperature, molecular water from the surface of particles or crystallites at medium temperature, and, sometimes, neutral molecules (H_2O) or ionic hydroxyl groups (OH^-) liberated at higher temperatures during thermal processing [5–7]. The production of ceramics was first implemented in the Neolithic period. The Greeks and Romans developed lime mortar cements, with a remarkable resistance, and some of these archaeological sites stand testimony to this day [8]. The Industrial Revolution of the eighteenth and nineteenth centuries registered significant improvements in the ceramic industry, while the twentieth century contributed to the scientific understanding of these materials. Conservation and restoration of cultural heritage has become one of the main concerns worldwide. In this respect, there is particular interest for investigations by nondestructive techniques some unique heritage ceramics for their subsequent preservation and restoration. These nondestructive analytical methods are able to provide information on composition/chemical nature of cultural artifacts, selected parts and materials in order to elucidate their origin, state of degradation (surface and/or internal) objects as a result of exposure over a period to environmental conditions, and the effects/effectiveness of strategies to conservation/restoration during their implementation.

1.1. Traditional ceramics

The traditional ceramics involve those materials that are derived from common, naturally occurring raw materials such as clay minerals and quartz sand. The traditional ceramics is manufactured from naturally occurring raw materials: silicates—compounds based on silica (SiO_2) and unmodified or chemically modified aluminosilicates (alumina [Al_2O_3] plus silica). In addition, the raw materials used in traditional ceramics could be classified into three groups: clay, silica, and feldspar [9].

Clay minerals such as kaolinite ($Al_2[Si_2O_5][OH]_4$) generated either by the weathering of igneous rocks under the influence of water, dissolved carbon dioxide, and organic acids, or from feldspar ($KAlSi_3O_8$) eroded from rocks such as granite and deposited in lake beds, which are aluminosilicates that contain sodium (Na), potassium (K), or calcium (Ca) with a composition from $NaAlSi_3O_8$ and $KAlSi_3O_8$ to $CaAl_2Si_2O_8$. Feldspar acts as fluxing agents to reduce the melting temperatures of the aluminosilicate phases where they are subsequently transformed into clay [10]. Except feldspar, silica, as the second major ingredient in refractories, is usually added as quartz sand, sandstone, or flint pebbles [11]. The role of silica is either to maintain the shape during firing (as filler) or to improve the final mechanical properties.

The behavior of ceramics depends on its chemical, physical, and mechanical properties [7]. In the ancient ceramics, the main minerals are gehlenite ($Ca_2Al_2SiO_7$), anorthite ($CaAl_2Si_2O_8$), quartz (SiO_2), belite (β-Ca_2SiO_4), and carbonates/calcite ($CaCO_3$) and/or dolomite

$(CaMg(CO_3)_2)$. For ceramics with limestone as raw material, the fired products may also contain akermanite $(Ca_2MgSi_2O_7)$, gehlenite $(Ca_2(Al,Fe,Mg)(Si,Al)_2O_7)$, and Mg-silicates (e.g., diopside and $CaMgSi_2O_6$) [12,13].

2. Background

2.1. Romanian history of ceramics

Ceramics, until the twentieth century, was essentially used for utilitarian purposes for ritual acts. At first, craftsmen did not know the potter's wheel, but they were very skilled at shaping and baking clay. Ceramic art painting in white, black and red, with models of great beauty and originality, was spread over a territory more extensive than present-day Romania and perfected for almost 2000 years [14]. The pottery techniques are extremely important for archaeologists as a source of results about cultural groups and their distribution areas. Through fragments of pottery, one can identify intercultural links or movements of populations in certain geographical areas [15]. For example, Romania's geographical region consists of Wallachia until Jiu Valley in Dobrogea, southwest Moldova and southeast Transylvania, and extending south to the Aegean Sea.

Some of the most relevant ceramic types specific to Romania are:

* **Cucuteni** (village in the county of Iaşi) **mankind ceramics**, 5000–6000 years ago, between the Carpathians and Dnieper, for nearly a millennium, a remarkable Neolithic culture flourished, known as the most relevant example of the relationship between man and clay. These ceramics are widespread in Moldova, northeast Muntenia, and southeast Transylvania, and Bessarabia site is characterized by a very high-quality ceramic that is technically rich with varied paintings [15, 16]. One of the most well-known Cucuteni ceramics, a representative of Romanian culture, is shown in Figure 1. This civilization is a representative of the Chalcolithic period from southeastern Europe and as a valuable source of data on the transformations of the human social evolution, pointing out the following aspects: social, cultural, and technological development, which played a significant role in generating an early form of ranked societies.

* **Monteoru ceramics,** one of the most well-researched Bronze Age times at the north of the Danube, is formed in parts of hilly north and northeast Muntenia and spread quickly in southern Moldova (including east of Prut) and points toward the Carpathian Mountains.

* **Culture Wietenberg** was developed in central Transylvania together with Coţofeni culture that take potteries decorated with mature style, with some Schneckenberg influences.

* **In Gumelniţa culture**, the ceramics is especially black and sometimes brown (brick-red rare). Both are weathered, with various shapes and decorations, and the latter carved in relief and barbotined or graphite painted.

* **Hamangia culture** is the oldest Neolithic culture in Dobrogea with a long flowering period, which lasted until the birth of Pontic Gumelniţa period.

Figure 1. Cucuteni ceramics

For ancient ceramics, the methodological exact sciences have their beginning in the sixth decade of twentieth century, when it was widely used in X-ray diffraction (XRD) technique [18], investigation of thermal expansion [19], and optical microscopy ceramic artifact analysis [20]. In the next decade, new analytical methods such as Mössbauer spectroscopy [21], differential thermal analysis [22,23], and electron microscopy [24, 25] were explored. Through improvements in the investigation methods in the last decade of the twentieth century, the characterization of such ceramics reached impressive new levels [26–28]. The eighth decade of the twentieth century coincided with the development of some methods based on SEM that currently dominates the studies about pottery. The use of these methods allowed for a better understanding of structural changes due to the different types of clay burning at different temperatures [14], which allowed the extraction of information, enabling economic and social outline of the communities that produced these artifacts. At present, the world can identify and understand the most stages of the technological process of making ceramics in different chronological periods and in different cultures.

It is important to use modern chemical analysis, both nondestructive (which can be in some cases fully noninvasive) methods and destructive methods of modern microanalysis, for small samples analysis [29–32]. They may be extremely valuable in the provenance investigation of an object, the origin of the materials used for its manufacture, in determining its degradation state and, finally, to choose the most suitable methods of restoration and conservation, the type of materials for conservation, and also in monitoring the progress of conservation processes, or to identify the fake art objects [33]. The main aspects of ceramic characterization are classification, production technology, and provenance through specific techniques for chemical and mineralogical characterization: spectroscopic techniques (FT-IR, Raman, XRD, EDXRF, and ICP-AES) and thermoanalytical techniques [34].

2.2. Analytical techniques for investigation

Modern chemical methods and measuring techniques can be used for archaeometric purposes. Some analytical techniques have been investigated with exemplification for different Romanian artifacts.

2.3. Methods and apparatus

Thermal analysis presented in the following chapter helped in the characterization of pottery in order to conclude about the chemical and phase composition, and it was recorded with a Mettler 4000 TA, TG 50 analyzer system at a rate of 10°C min^{-1} in a static air atmosphere; PerkinElmer thermoanalyzer TG S-2; and DTA 1700 at a rate of 10°C min^{-1}. A sample (15 mg) of finely ground stones were subjected to analysis in a Pt plate at a temperature range of 35–1000 oC (10°C min^{-1}). This concluded that the archaeological pottery was fired at relatively high temperatures.

Energy-dispersive X-ray fluorescence (EDXRF) analyses were performed with an PW4025 apparatus, type Minipal PANalytical, with a Si(PIN)-detector and an Rh tube with an acceleration voltage of 30 kV. Due to varying surface structures and inhomogeneities in the surface composition of the samples, the analyses are usually performed on both sides of the objects and a mean value is calculated, when the analysis must be completely nondestructive. When possible, the sample is powdered, so a representative homogenous sample can be obtained. An XRF is known as the first powerful, commercial, fast, nondestructive, and relatively accurate technique for qualitative as well as semiquantitative chemical analysis.

Inductively coupled plasma—atomic emission spectrometry (ICP–AES) was used to quantify minor and trace elements. Detection limit for major elements is under the ppm level and the analytical precision calculated from replicate analysis is ±1%. For the ICP-AES measurements (usually with Varian equipments), the samples are finely powdered in an agate mortar and then mineralized with a microwave-assisted digestion oven with the use of high-pressure closed Teflon PFA vessels (with a mixture of 5 ml HF 40% and 5 ml HNO$_3$ 65%) and pressure and temperature control. Multielement matrix-matched standards were used for the quantitative determinations.

X-ray diffraction (XRD) patterns were recorded on a DRON UM1 diffractometer, operating at 32 kV and 25 mA, using Co Kα radiation (1.79021 Å) with an iron filter. The diffractometer is connected to the PC, so the collected data can be analyzed and interpreted using either the dedicated program or other specific data analysis software.

Fourier transform IR spectroscopy (FT-IR) standard spectra were collected by using a PerkinElmer Spectrum GX spectrometer, for a range of 400–4000 scans and a spectral resolution of 4 cm^{-1}. It was possible to use the drift accessory with the powdered pure substance, thereby allowing for a better and easier analysis.

The Raman spectroscopy analysis performed with **Raman spectra** has been recorded with a First Guard Raman apparatus, BaySpec with two wavelengths (1,064 and 785 nm). The Raman system includes a "superhead" optic fiber for noncontact measurements, with a 50× long

working distance (LWD)-visible Olympus lens. The spectral data were processed with a software application dedicated to the file generation of Raman spectra. The spectral resolution was 3 cm^{-1}. All the spectra were recorded in the 200–3,400 cm^{-1} domain.

3. Case studies

3.1. Ceramics from Schneckenberg culture (sixteenth century), Dealul Melcilor, Braşov, Romania

Sampling, reported in Table 1, was performed at the ruins of the Schneckenberg culture (sixteenth century), Dealul Melcilor, Braşov, Romania. Some examples of the investigated ceramic samples are shown in Figure 2.

Figure 2. Different ceramic samples

It is interesting that this region conserved many cultures (Vatina, Gârla Mare, Luciu de Sus, Wietenberg and Otomani). Eight differently fabricated contemporary pottery samples were selected for characterization, as shown in Table 1.

Clay minerals, as the main material for production of ceramics and pottery, show some characteristic reactions—dehydroxylation, decomposition, transformation—during the firing (heating effects, 20–800°C), and several steps for reconstruction of former production conditions are identified, knowing that the temperature at which ancient ceramics and pottery were fired varies over a wide range (600–800°C) depending on the type of clay used. Thermogravimetric (TG) analysis and differential thermogravimetric (DTG) analysis are very important characterization methods used for the control of the reaction process and of the properties of the materials obtained [35–38]. The presence of some minerals is related to the ceramics firing process, giving information about the manufacture technology of the pottery. For a firing temperature higher than 900°C (observed for all the analyzed samples), a certain conclusion had been reached that the glazed ceramics was usually fired at temperatures ranging from

900°C to 950°C, mostly due to the reaction between quartz and carbonates when the temperature reaches 900°C.

No.	Sample	Color/location
1	Ceramic	Black/Dealul Melcilor
2	Ceramic	Grey/Dealul Melcilor
3	Ceramic	Red/Dealul Melcilor
4	Ceramic	White/Dealul Melcilor
5	Ceramic	Green/Dealul Melcilor
6	Ceramic	Brown/Dealul Melcilor
7	Ceramic	Braşov tile
8	Ceramic pot	Braşov medieval customs/Bran-Braşov

Table 1. The ceramic samples analyzed

Thermal analysis enables detection of exothermic and endothermic peaks (effects due to gain/loss of enthalpy) occurring in the sample when undergoing controlled heating and compares to an inert reference material [39–46]. The endothermic peak around 100°C is due to moisture water, whereas those appearing at about 200–250°C are attributed to "bound" water, or to "hydrated" interlayer cations (as in swelling clay minerals). The TG/DTG diagrams for different colored ceramics are shown in Figure 3.

Figure 4 shows the TG/DTG diagram for the Transylvania tile ceramics.

Some effects have been observed as follows:

- endothermic effects attributed to gypsum appear in the range 120–160°C [47];

- endothermic peak that could be attributed either to water lost from iron hydroxides, or to recrystallization of amorphous and/or crystallized Fe-oxy hydroxides appears at 300°C, through an exothermic peak in the range 300–350°C.

- some exothermic peaks in the range 550–650°C could be attributed to some organic matter (binder used in the preparation of the ceramic paste, or external coating).

In both cases, an abrupt increase in weight starts immediately at room temperature and lasts up to 200°C. To our knowledge, such thermoanalytical behavior of pottery samples has never been observed previously.

Usually, the ceramic heritage contains mostly the following clay types: kaolinites (kaolinite, dickite, nacrite, and halloysite), illites (illite, hydrous micas, phengite, glauconite, and celadonite), smectites (montmorillonite, beidellite, and saponite), vermiculites, and palygorskite (palygorskite and sepiolite). Some minerals, such as kaolinite, illite, and smectite, show strong endothermic peaks (in the range 550–650°C (higher for chlorite)), and some endothermic peaks are at 840°C (single peak)—for calcite and dublets at 780°C and 860°C—for dolomite. They are
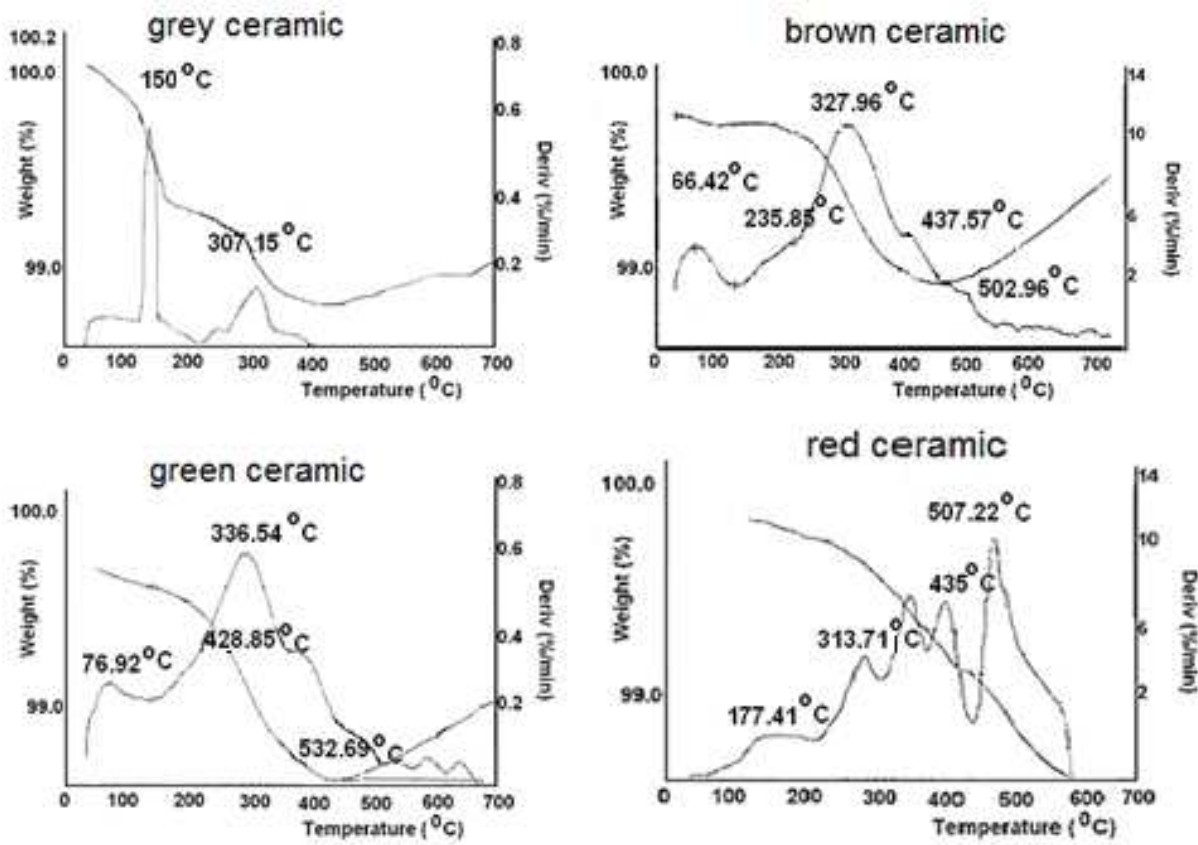
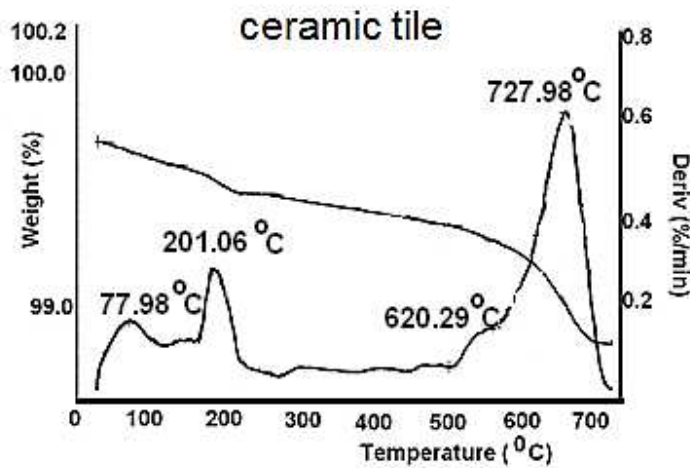**Figure 3.** Thermal analyses of colored ceramics

Figure 4. Thermal analyses of tile ceramics

due to the escape of CO during the breakdown of their structure (other carbonates are unusual in ancient ceramic materials). The presence of these characteristic thermal effects indicates that the primary minerals survived the firing processes required to destroy the structure of the minerals. The DTA curves of salts are complex, and their interpretation needs familiar

experience with the technique, and also information from other analytic techniques, such as XRD, XRF, ICP-AES, FT-IR [48], micro-chemical tests, and microanalyses (scanning electron microscopy and energy-dispersive X-ray microanalysis (SEM-EDX)).

The X-ray diffraction, as one of the most important techniques for potteries analysis, led to the identification of the following mineral phases: quartz, kaolinite, illite, gibbsite, goethite, feldspar, and mixed layers (smectite/illite). The presence of illite peak in X-ray diffraction patterns indicates the presence of calcite, too. We observe that quartz, kaolinite, and K-feldspar are common elements. These are basic constituents of the original clay matrix.

From profile of the DTG curves, the clays could be classified as Ca-rich and Ca-poor raw clays. **Ca-poor ceramics** include quartz, feldspar, and micas.

For them some processes could be observed:

- for calcite presence, which decomposes by oxidation at lower temperature than illite, generated CaO is visible until 800°C.

- hygroscopic water is visible at 80°C, and gypsum at 145°C.

- for almost all clay minerals, their decomposition is visible in the region 580–640°C [33,49–54].
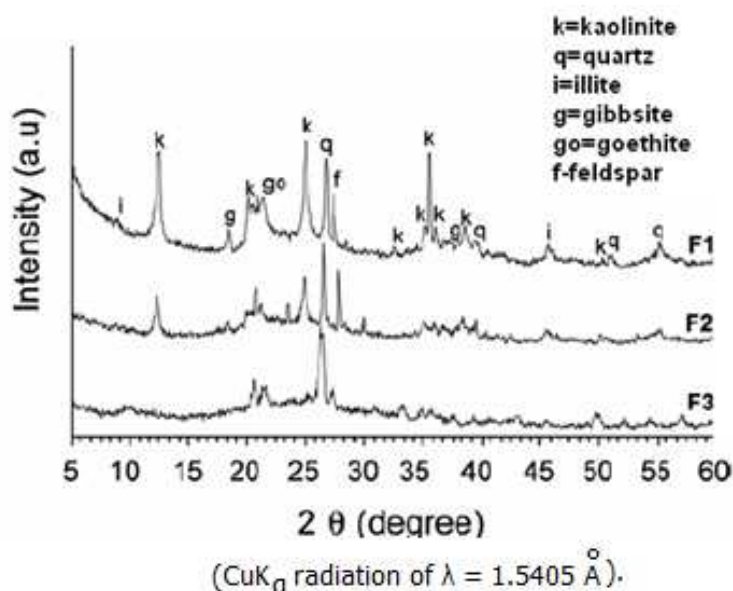

Figure 5. XRD diagram for tile (F1) and ceramics (green (F2) and brown (F3))

The Ca-rich ceramics (with CaO content >5%) include kaolinite, illite, and chlorite. They show peaks at about 640°C, where clay minerals decompose. The samples present very low firing temperatures (740°C), and CaO has an important role in the transformation process of the ceramic matrix. The red bricks show extensive vitrification with iron oxide phases dispersed almost homogeneously in the vitreous matrix (allocated to large hematite crystals surrounded by lemonite) [55]. In the ceramics with higher percentage of CaO, calcium aluminosilicate microcrystalline is obtained, simultaneously with a color difference, due to the trapping of iron
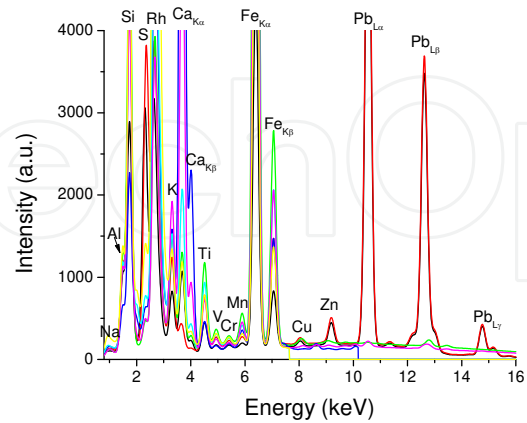
in the augite lattice [56]. A denser, less porous, and more durable ceramics is observed for the red bricks, mostly due to a higher vitrification.
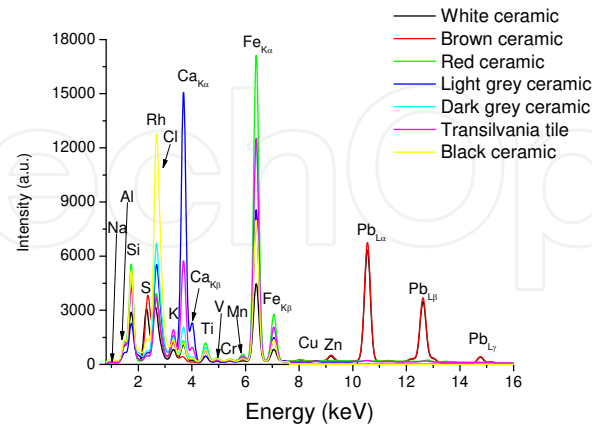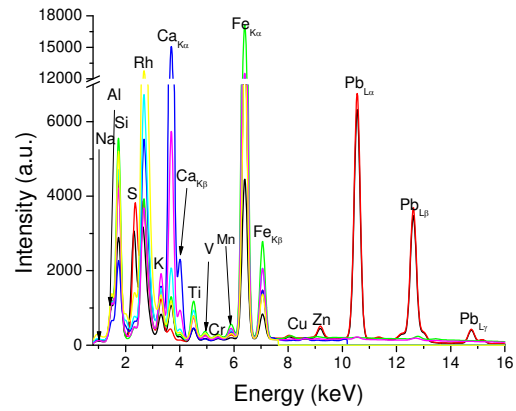
Figure 6. (a) XRF spectra of the analyzed samples. (b) XRF spectra of the analyzed samples: a break was inserted in order to observe the variation of the elements; the color codes are the same as for Figure 6 a. (c) XRF spectra of the analyzed samples: the intensity scale was modified in order to observe the variation of the minor elements; the color codes are the same as for Figure 6 a.

Quartz, feldspar, white mica, biotite-like mica, iron oxides, and calcite are the main phases present, but the archaic ceramics contain smaller amounts of detrital feldspar. Also, ilmenite, sphene, zircon, rutile, spinel, epidote, apatite, and monazite have been identified by EDXRF (Figure 6 a,b,c) and SEM in some samples [57]. Cs and Rb concentrations are influenced by the presence of K-feldspar and mica (Cs and Rb are substitute for K). This observation, coupled with their low K_2O and Na_2O content and high Al_2O_3 content, suggests that during the preparation of the raw materials, the potters production followed a procedure, probably "levigation," separating the less fine nonplastic particles such as K-feldspar and albite. Th and Sc are considered as proper sensors for ancient ceramics provenance due their insolubility and their reduced effects on metamorphism, weathering, and diagenesis [58,59].

Element	Ceramic	Enamel
Si	25.3%	5.56%
Ti	10.1%	15.3%
Al	3,34%	6.42%
Fe	3.05%	4.17%
K	1.21%	0,49%
Na	1.19%	2,97%
Ca	0.28%	0.93%
Ba	0.11%	2.27%
Mg	702 ppm	0.15%
Zr	147 ppm	0.056%
Mn	355 ppm	0.025%
Cr	85.3 ppm	84 ppm
Zn	71.2 ppm	97 ppm
Sr	46.4 ppm	0.026%
Li	24.9 ppm	41%
Ag	1.99 ppm	49 ppm
Pd	—	0.015%
Pb	—	26.2%
Cu	—	0.68%
Tl/Bi	—	26%
P	—	0.22%
Sb	—	0.17%
As	—	5.4 ppm
Au	—	55%

Table 2. Major and trace elements ICP-AES analytical results for ancient ceramics and raw material sample (in wt.% and ppm)

The presence of certain chemical elements in the composition of ceramic samples and in the composition of the enamel can provide interesting data on the types of materials used in the

medieval period. Some of these elements are found in the recipes used in painting [60–64]. The fact that the composition was found in zirconia ceramics is proof of the use of bentonite as raw material [15,33].

The degradation of the ceramic parts can be explained by the presence of potassium. Depending on environmental conditions, potassium becomes potassium hydroxide by artifact drying and then potassium carbonate by reacting with CO_2 from the atmosphere. The presence of KOH makes the area around the vessel to become alkaline, this being responsible for corrosion layer present only in enamel. This is the reason that it should be kept in a controlled humid environment to prevent the subsequent artifacts degradation [30].

Piesa/element	Green paint	Blue paint	White paint	Ceramics
Na_2O	—	3	4.2	—
MgO	2	—	2.1	2.9
Al_2O_3	20.2	18.5	24.2	17.6
SiO_2	30.2	36.9	36	52.6
SO_3	12.1	—	—	0.63
Cl	5.46	3.4	5.79	2.1
K_2O	2.23	3.89	1.67	3.45
CaO	2.16	2.2	3.27	9.66
TiO_2	1.29	1.21	1.63	0.985
V_2O_5	0.02	0.03	0.03	—
Cr_2O_3	0.04	0.05	0.041	0.04
MnO	0.043	0.04	0.079	0.22
Fe_2O_3	1.53	2.17	1.96	9.17
Co_3O_4	0.070	0.24	0.02	0.069
NiO	0.1	0.36	0.02	—
CuO	0.047	0.064	0.042	0.02
As_2O_3	0.03	0.35	—-	—
PbO	22.3	36.9	18.7	0.17
ZnO		—	—	0.03

Table 3. Chemical composition of artifacts detected by XRF and XRD

From Tables 2 and 3, similarities for different tempers can be observed, as a proof that most samples fall close, but the ceramic fragment containing sand and feldspar are less similar.

SiO_2 and Al_2O_3 together comprise more than 50 wt.% of the ceramic chemical composition. The alkali oxides (K_2O, Na_2O, CaO, and MgO) constitute together less than 5 wt.% and Fe_2O_3

reaches 10 wt.% on average. A high H_2O value (10 wt.% on average) is observed, which is too high for burned ceramic material. The Al_2O_3 and H_2O contents explain the great abundance of clay-derived minerals, and confirm the abundance of partial dehydroxylation of clay material derived from kaolinite (main mineral of the ceramics) [65].

The chemical and mineralogical data, as well as textural aspects, conclude that the main raw material for ceramic elaboration comes from fine-grained clay quartz-rich material. Some important conclusions could be reached:

• When SiO_2 concentration is high, the sample contains quartz sand.

• When the sample contains feldspar, the concentration of K, Na, Ca increases the firing temperature. Kaolinite is the main mineral of the ceramics [66].

• K_2O, Na_2O, MgO, and CaO build the feldspar (microcline and albite) and together indicate the presence of illite, hematite, maghemite, goethite, and anatase in the raw material.

• The extremely high SiO_2 contents correspond, besides clay-derived material and the abundance of quartz, to sand grains and rock fragments. The predominance of SiO_2 (61.2%), Al_2O_3 (34%), Fe_2O_3 (2%), CaO (<10%), MgO (<3%), and 1.3% loss on ignition confirm clay-derived minerals, quartz, and some iron oxyhydroxides as the main minerals of ceramic fragments. The chemical composition of high-quality refractory clays is as follows: silicon oxide, aluminum oxide, and 2% iron oxide.

• The P_2O_5 contents relatively high for clay material normally are responsible for amorphous to criptocrystalline (Al,Fe) phosphate.

• The water contents are still high (5.6–8.9 wt.%) showing the rehydration of the ceramic vessel after their discharge and the formation of the soil with black earth.

• Barium, phosphorus, and even Pb seem to be the anomalous elements found in the ceramic fragments of Scheneckenberg. The anomalous values of Ba were frequently found in the ceramic fragments with temper.

• The iron contents represent hematite and goethite, and some maghemite, minerals also identified in the studied ceramic fragments. Maghemite is responsible for the red color of the potteries. This phase is formed by partial dehydroxylation of clay material (visible at 600 °C). These potteries are used for cooking. They contain elements such as Mg, Ca, Ba, Zn, Pb, Y, from aluminum phosphates and Ba-Mn oxyhydroxides.

• After breaking, these potteries in long contact with soil concentrate in P, Mg, Ca, Mn, Ba, Zn, and Pb. In this phase, hematite and maghemite rehydrate and form kaolinite and goethite, respectively.

3.2. Archaeometric investigation of medieval polychrome glazed pottery

The composition and origin of the tile sample taken from the Medieval Customs archaeological site, Bran region, Braşov County, dating back to the seventeenth and the eighteenth centuries, have been used at first for ceramic composition for making ceramics and for the composition

of paints used to decorate this tile. The chemical composition of ancient pigments is an important criterion for the identification of pottery preservation, decoration, and technology used. The study was focused on red, brown, and black pigments from a pre-Roman pottery—a Transylvania tile, Figure 7 [67].
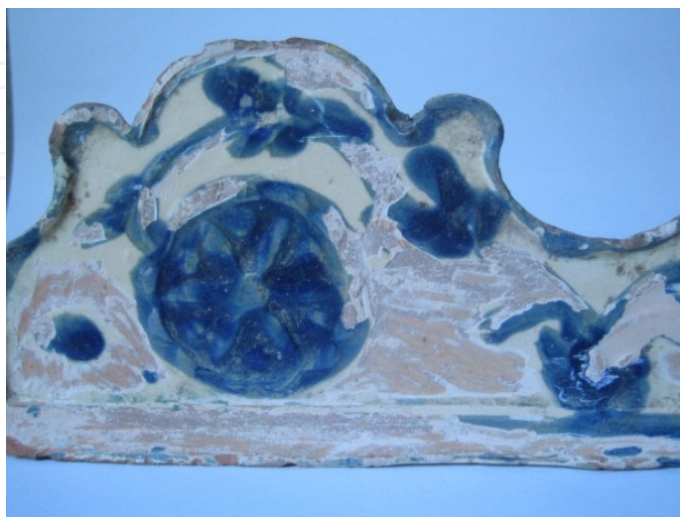
Figure 7. Transylvania tile

3.2.1. Historical aspects

It seems like ancient tiles appeared in Germany around 1300. The tiles were more advantageous than open fireplace due to storage of warmth and for elimination of smoke in the room. Their use is common in our country and quickly spread throughout Europe, thanks to their advantages. The oldest tile known to us dates from the early fifteenth century. These are unglazed and they represent biblical scenes, mythological strange mermaids with fish or snake tail and wing, real or fantastic animals, pictures knighthood, geometrical, and floral motifs. The tiles could be glazed and polychrome painted with cobalt blue, green, yellow, and brown pigment-based enamel. Besides functionality, tiles were always meticulously decorated in relief. They had to be not only stove plates, but beautiful objects, providing protection and comfort family space. We have too few studies about the representations that appear on Transylvania tiles, how they were chosen, who were favorite reasons, motivations, and their symbolism elections. It is interesting to follow the trail forms and reasons in the European recurrence in different cultures. It seems that often the choice of decoration for tiles was linked to beliefs and rituals apotropaic, popular superstitions. In this respect, chimney, hearth were considered passageways, as well as threshold or window. Transitional spaces were exposed to evil spirits, evil eye, magic outside. And inside the house, the stove was considered a dangerous object, which could cause fire and smoke poisoning of the occupants of the house. Hence the need for home care through icons and symbols apotropaic fireplace [68]. An analysis of the compositions of the Roman ceramics reveals that the latter tend to have lower concentrations in Cs, Rb, K_2O, Na_2O, and CaO and higher in Al_2O_3.

3.2.2. Ceramics support

Ceramic is a type of kaolin as hydrated aluminum silicate double, feldspar formed by the decomposition of igneous rocks and by the action of carbonic acid and water, under pressure, and subjected to high temperatures. The clays are some of the most common rocks from the earth, with smaller grains of 0.002 mm, composed of a complex mixture of clay minerals: kaolinite, illite, montmorillonite, etc. These are aluminum and magnesium silicate hydrate, made from altered feldspar and other silicates. They add muscovite, feldspar, heavy minerals (zircon, ilmenite, rutile, magnetite, garnets, etc.), fragments of shells, and other sulfide minerals as diagenetic, glauconite, calcite, and very fine particles of minerals from rock unspoiled page of complex colloidal silicate, hydrated, and the remnants of organic substances. The chemical composition of clays varies by minerals they contain. Ceramic clays and semi-acid clays are used in brick masonry construction, terracotta tiles, or cement. Semi-acid clays have a content of approximately 30%. Al_2O_3 can be used for the extraction of alumina in the synthesis process; and strong base and basic clays (refractory clays) are used in the manufacture of refractory chamotte for the manufacture of fine ceramics. Clays always contain a greater or lesser amount of impurities, which reduce refractoriness [69].

3.2.3. Pigments for glazed tile

For aesthetic and for a consistent colored ceramic, pigments are used with metallic oxides and different salts. Pigments vary from green to blue-green to blue. They can be used as dyes in clay bodies and glazes, directly or mixed with water. The coating is constituted of lead-alkali glass with the addition of copper or iron ions as coloring agents.

The presence of the oxides is vital. For example, chrome oxide gives green color, but it may fume or volatilize. If tin is present in a white or pastel glaze, the chrome reacts with the tin to create a pink coloration. If zinc oxide is present in the glaze, a dirty-brown color will be obtained. For green color, cobalt-zinc-alumina-chromite blue-green pigment system could be used, where varying the amounts of cobalt and chrome oxides produces a green ceramic color. Many pigments have mineral origin with different colors; for example, ocher: red and yellow; cinnabar: bright red; azurite: blue; malachite: green; lime: white; carbonized bone: black. As organic pigments red madder and murex shell purple are used, and as binding media, egg, casein, and wax.

The chemical compositions of the ancient ceramics and pigments used are shown in Table 4.

Except all these techniques, FT-IR has been used for ceramic composition identification, including the assignment on the basis of the typical wavenumbers of the contributions to the FTIR absorbance spectra of minerals given in the Sadtler database "Minerals and Clays" [70]. Making a distinction of clays present in the samples was also a difficult task: the contribution centered at ~1033 cm^{-1} can be attributed both to illite and montmorillonite. Montmorillonite is visible at the peak from ~615 cm^{-1}, while the band centered at ~1,633 cm^{-1} could be attributed to illite spectrum. Montmorillonite could be derived from hydrolysis process occurring during the burial period of the findings [71]. Calcite, as clearly shown by the FT-IR spectrum in which the large band centered at about 1444 cm^{-1} and the contribution at about 870 cm^{-1}, typical of

this mineral, is present. The absorptions from the main quartz phase (Si–O) could also be easily identified in the FTIR spectrum of ceramics and pigments used for glaze (Figure 8; 1163, 1083, 798, 778, 695, 514 cm $^{-1}$) [72]. The several intense bands in the range 800–550 cm $^{-1}$ (725, 646, 584 cm $^{-1}$) are characteristic of the metal–oxygen vibrations in the ceramic samples [73]. However, additionally the characteristic carbonate (calcite phase) vibrations at 1795, 1430, 876, 713 cm^{-1} [74] and M–O vibrations at 725, 685, 642, 580, 531 cm^{-1} could also be determined. Characteristic Si–O, C–O, and M–O stretchings could be easily identified in all FT-IR spectra. Broadbands between 3700–3000 cm^{-1} can be assigned to the adsorbed water (or water of crystallization) and O–H vibrations of glazed pottery. This could be associated with specific surface properties of pottery, which stimulate adsorption of moisture from atmosphere at ambient conditions.

Compound	Green pigment	Blue pigment	White pigment	Ceramic
Na_2O	–	3	4.2	–
MgO	2	–	2.1	2.9
Al_2O_3	20.2	18.5	24.2	17.6
SiO_2	30.2	36.9	36	52.6
SO_3	12.1	–	–	0.63
Cl	5.46	3.4	5.79	2.1
K_2O	2.23	3.89	1.67	3.45
CaO	2.16	2.2	3.27	9.66
TiO_2	1.29	1.21	1.63	0.985
V_2O_5	0.02	0.03	0.03	–
Cr_2O_3	0.04	0.05	0.041	0.04
MnO	0.043	0.04	0.079	0.22
Fe_2O_3	1.53	2.17	1.96	9.17
Co_3O_4	0.070	0.24	0.02	0.069
NiO	0.1	0.36	0.02	–
CuO	0.047	0.064	0.042	0.02
As_2O_3	0.03	0.35	–	–
PbO	22.3	36.9	18.7	0.17
ZnO		–	–	0.03

Table 4. Chemical composition of the Transylvania tile

The Raman spectra collected have to be compared with those obtained previously from reference materials. Published libraries of spectra are now widely available in the literature on historical pigments [75,76], enamel and glazing pigments [77], modern synthetic pigments [78],

modern inks [79], gums, waxes, varnishes, resins and other binders of historical and archaeo‐
logical importance [80,89], minerals [70,90,91], and plant fibers [92]. As already mentioned,
Raman scattering is a very weak phenomenon that requires an intense monochromatic light
source to generate a readily detectable effect. Also, the use of lasers has allowed a wider choice
of excitation lines, with wavelengths ranging from 351.1 nm to 1064 nm. In Raman spectra, the
hematite (α-Fe$_2$O$_3$) bands are identified at 613 (s); 408 (s); 227 (m); 204 (w) cm^{-1}, whereas 663
cm^{-1} band indicates the presence of magnetite (Fe$_3$O$_4$) [94]. The 1329cm^{-1} band is also assigned
to hematite. When the sample has been produced in an oxidizing atmosphere, the most
important indicator is the hematite [90,93]. If magnetite is present, this is an indicator of its
incomplete phase transformation into hematite [91].

The Raman spectrum of the tile ceramic is shown in Figure 9. The representative Raman band
for beta-quartz is located at 462 cm^{-1}, while the medium intense 507cm^{-1} band is assigned to
albite (Na-feldspar). Specific bands appear here: 462, 401, 356 cm^{-1}, all being attributed to
quartz. The band from 506 cm^{-1} together with the shoulder around 600 cm^{-1} indicates the
presence of hematite. All these are more pronounced for not-glazed face (red colored spec‐
trum). The broadband around 1350–1500cm^{-1} is due to amorphous carbon, 461 cm^{-1} band is
assigned to β-quartz. Also, in the Raman spectrum of the ceramic supports, the medium intense
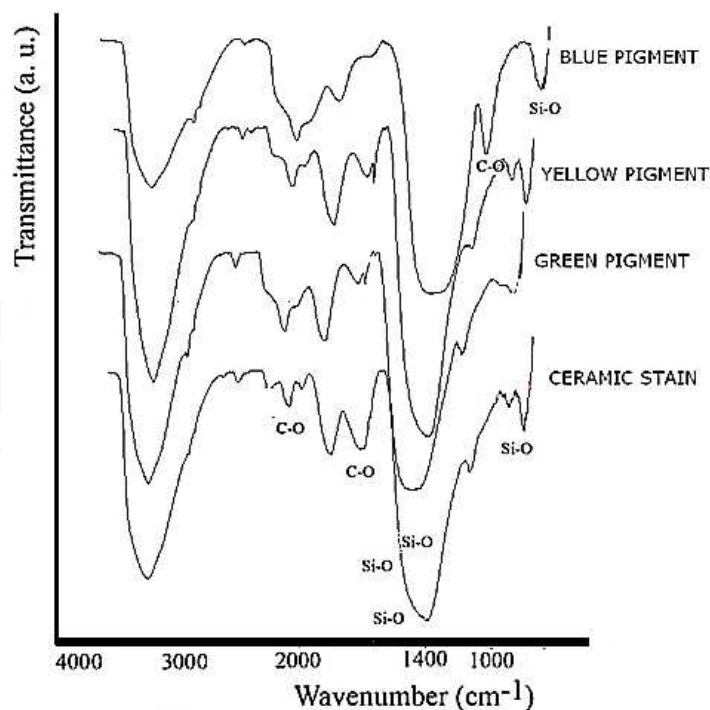—550 cm^{-1}—band reveals the presence of hematite, as shown in Figure 10.

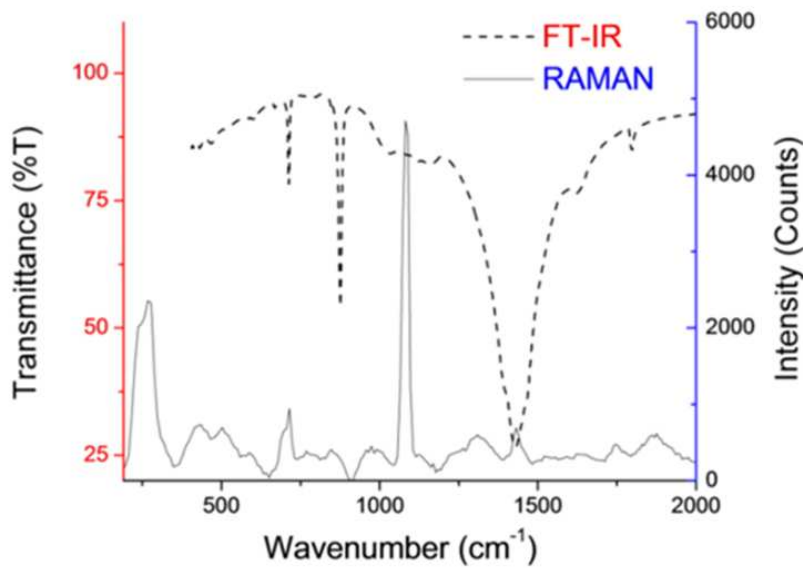**Figure 8.** FT-IR spectra of the pigments

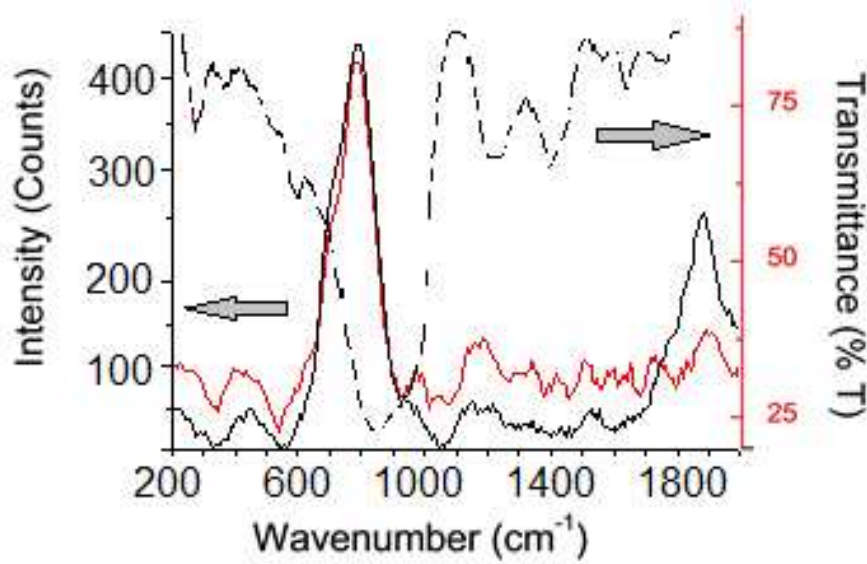**Figure 9.** FT-IR and RAMAN spectra of calcite

Figure 10. FT-IR and RAMAN spectra of the ceramic tile

4. Conclusions

Many ceramic pieces known as ceramic heritage have been discovered, characterized by specific techniques of characterization either for raw materials or ceramic objects based on clays, discovered in different archaeological sites, leading to some results about the production technology, provenance, authentication, and historical appartenance. The chemical composi-

tion of ancient ceramics and pigments decorating them, excavated from different Romanian archaeological sites, suggested a chemical composition of ceramic based on clay minerals (kaolinite, illite, and smectite), while the pigments belonging to them contain hematite or ocher (a red pigment), manganese oxides (brown pigments), and magnetite or carbon of vegetable origin (black-pigmented layers).

Acknowledgements

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