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IN SEARCH OF THE ORIGINS OF THE ROMAN CBM FOUND AT NOVAE

Abstract: The aim of the extensive research project on ceramic raw materials found in the vicinity of the Roman *castrum* of Novae was to test the hypothesis put forward by Prof. Piotr Dyczek (Antiquity of Southeastern Europe Research Center University of Warsaw) that most of the ceramic building material (CBM) used at Novae was made in workshops local to the Novae region — workshops whose output relied on ceramic raw materials locally available within that region. The results from the analysis of nineteen raw material samples were compared with the results of CBM analysis as well as the results of analysis of common ware, table ware and legionary pottery. The sampled ceramic fragments were subjected to various laboratory analyses. These included: chemical analysis by WD-XRF, thin-section studies, X-ray diffraction, MGR-analysis, estimation of physical ceramic properties (open porosity, water absorption and apparent density) and K-H analysis. Raw material analyses included: estimation of water of plasticity, a firing test, an *à la* ceramics test (MGR-analysis), chemical analysis by WD-XRF, thin-section studies, X-ray diffraction (XRD) of material at the green stage (natural sample, complexed with glycerol, calcined at 500^{o}C) and X-ray diffraction after firing *à la* ceramics at various temperatures. Of the 54 analysed CBM samples only five are outliers from beyond the region. The remaining CBM samples represent products made at workshops local o the Novae region.

Keywords: ceramic building material, legionary pottery, common ware, table ware, Novae, WD-XRF, MGR-analysis, thin-section studies, firing test, *à la* ceramics test, X-ray diffraction

Introduction

The aim of the extensive research project on ceramic raw materials found in the vicinity of the Roman *castrum* of Novae was to test the hypothesis put forward by Prof. Piotr Dyczek (Center for Research on the Antiquity of Southeastern Europe, University of Warsaw) that most of the ceramic building material (CBM) used at Novae was made in workshops local to the Novae region — workshops whose output relied on ceramic raw materials locally available within that region.

Fifteen raw material samples were collected during a field survey. Also available were a further two samples of raw material collected from the Novae site and analysed in 2007 (clay samples taken from a geological stratum beneath the *porta Praetoria*, and from beneath the floor of feature 9/2007), and two samples taken from the side of an escarpment. The map in Fig. 1 shows the underlying geology[1]

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[1] Geological map after Vangelov *et alii* 2013 with changes by M. Daszkiewicz and G. Schneider.

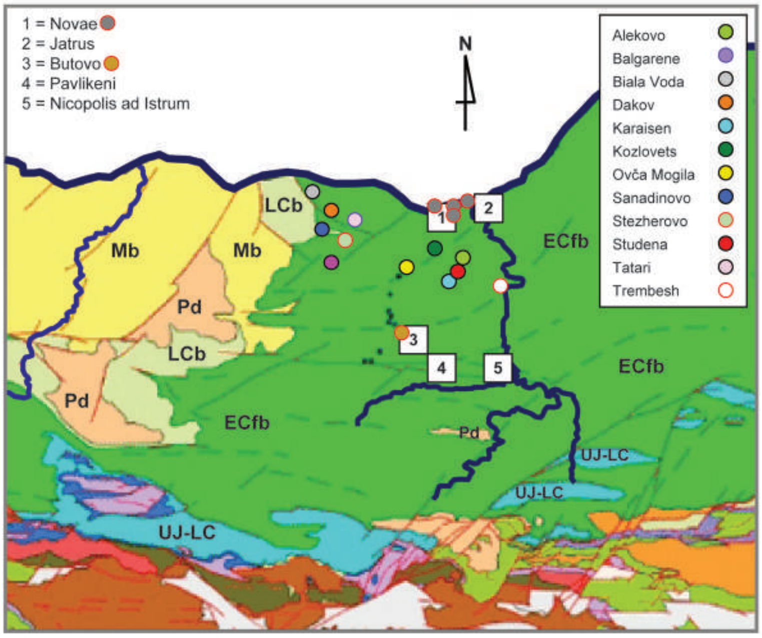

Fig. 1. Map with the underlying geology and the locations from which clay samples were taken (geological map after Vangelov *et alii* 2013 with changes by M. Daszkiewicz and G. Schneider).
Mb = Miocene basins; Pd = Paleogene deposits on the Moesian Platform;
LCb = Late Cretaceous basins on the Moesian Platform;
Ecfb = Early Cretaceous foreland basin;
UJ-LC = Upper Jurassic-Lower Cretaceous

and the locations from which samples were taken. The results from the analysis of nineteen raw material samples were compared with the results of CBM analysis. A total of 54 CBM fragments were examined.[2] Roof tiles (including two *imbrices*) were predominant among the analysed CBM, but bricks (including two *bessales* and one *sesquipedalis*), pipes, one *tubulatio* and a fragment of floor tile were also analysed. Sixteen CBM fragments came from features dated to the Flavian period, seven were dated to the early Antonine dynasty (Trajan period), thirteen to the latter half of the second / early third century, fourteen to the third century and three of the analysed CBM samples came from features dated to the fourth century. In addition, the results of both the CBM and raw material analyses were compared with the results obtained in 2007 from the analysis of pottery vessels: thirteen sherds of common ware dated to the Flavian period (recovered from hospital and bathhouse contexts) and nine sherds representing Flavian legionary pottery.

Because CBM, like most other categories of archaeological ceramics (various types of pottery, terracotta, lamps), was always made with the use of aluminosilicates and silicates as well as clay-carbonate raw materials,[3] the basic ingredient of the ceramic body consisted of various types of clay. The fabrics of the CBM used in Novae, which were analysed in this study, were made from bodies consisting of both a plastic and a non-plastic part. Each part comprises a raw material characterised by a specific chemical composition and mineralogical (petrographic) composition. This binary nature of the ceramic body composition had to be taken into account during the analysis

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[2] The first series was performed in 2007, when four samples of CBM were analysed (none of the results have previously been published). A further 50 CBM samples were analysed in 2020.

[3] Only a small proportion of ancient ceramics are made from raw materials with a clay mineral content of less than 40%. Examples include quartz ceramics (Egyptian faience, Islamic quartz pottery), frit, and bone china.

of the CBM. The same was true when analysing the raw materials, i.e., the composition of the plastic as well as the non-plastic parts of both ceramics and raw materials had to be determined. To this end, the sampled ceramic fragments were subjected to various laboratory analyses. These included: chemical analysis by WD-XRF, thin-section studies, X-ray diffraction, MGR-analysis, estimation of physical ceramic properties (open porosity, water absorption and apparent density) and K-H analysis. Raw material analyses included: estimation of water of plasticity, a firing test, an *à la* ceramics test (MGR-analysis), chemical analysis by WD-XRF, thin-section studies, X-ray diffraction (XRD) of material at the green stage (natural sample, complexed with glycerol, calcined at 500°C) and X-ray diffraction after firing *à la* ceramics at various temperatures.[4] Not all of these analytical methods were used on each sample. Analyses were performed according to a *step-by-step* strategy (both for the ceramic fragments and the raw material samples). The use of a *step-by-step* strategy greatly increased the time needed to perform all of the analyses and evaluate their results; however, it was essential to adopt this strategy in order to keep the cost of analysis to the required minimum.

The results of MGR-analysis, the firing test and *à la* ceramics test are presented at the end of this article in Pls. 1–15. Micrographs of typical fabric images seen in the polarising microscope can be seen in Pls. 16–28.

Terminology

Objects made from ceramic materials are produced by shaping and firing a ceramic mass. A ceramic material is defined as an inorganic, non-metallic material formed from a raw material at room temperature and converted into a permanent solid mass by firing. Contemporary ceramics are made from a broad range of materials.[5] However, archaeological ceramics, with only a few exceptions (see footnote 2), are clay-based ceramics referred to as "pottery" (pottery = all ceramic wares that contain clay when formed, except technical, structural, and refractory products). Thus, in the case of clay-based ceramics it is essential to define the term "clay".

The word "clay" is used as a textural term (referring to grain size) and as a material term (referring to a material with specific properties).

In addressing the definition of the word "clay" as a textural term, Anne D. Wilkins noted that "Various size terms are in common use and have been adopted by geologists, but due to the lack of standardisation, the terms often mean different things to different people".[6]

In sedimentology, the most commonly used grain-size scale for clastic sediments is the one which was introduced by Udden in 1914,[7] and modified by Wentworth in 1922[8] (known as the Udden-Wentworth scale). In this scale the clast diameter in millimetres is used to define the different sizes on the scale [Fig. 2a]. Gravel is defined as clasts of grain size larger than 2 mm in diameter (these are divided into granules, pebbles, cobbles and boulders depending on their size). Sand is material with a grain size ranging from 0.0625 mm to 2 mm in diameter. Sand grains can be further divided into five classes: very coarse, coarse, medium, fine and very fine. Silt is the term for clastic material with a grain size of between 0.0039 mm and 0.0625 mm in diameter, which can

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[4] Literature to methods, see, e.g., Daszkiewicz 2014; Daszkiewicz, Schneider, Bobryk 2021; Daszkiewicz, Maritan 2017; Daszkiewicz *et alii* 2016.

[5] It is worth noting that the Anglo-Saxon term "ceramics" can be used to refer to a variety of inorganic materials, including glass, enamel, and glass-ceramics as well as plaster, lime and cement.

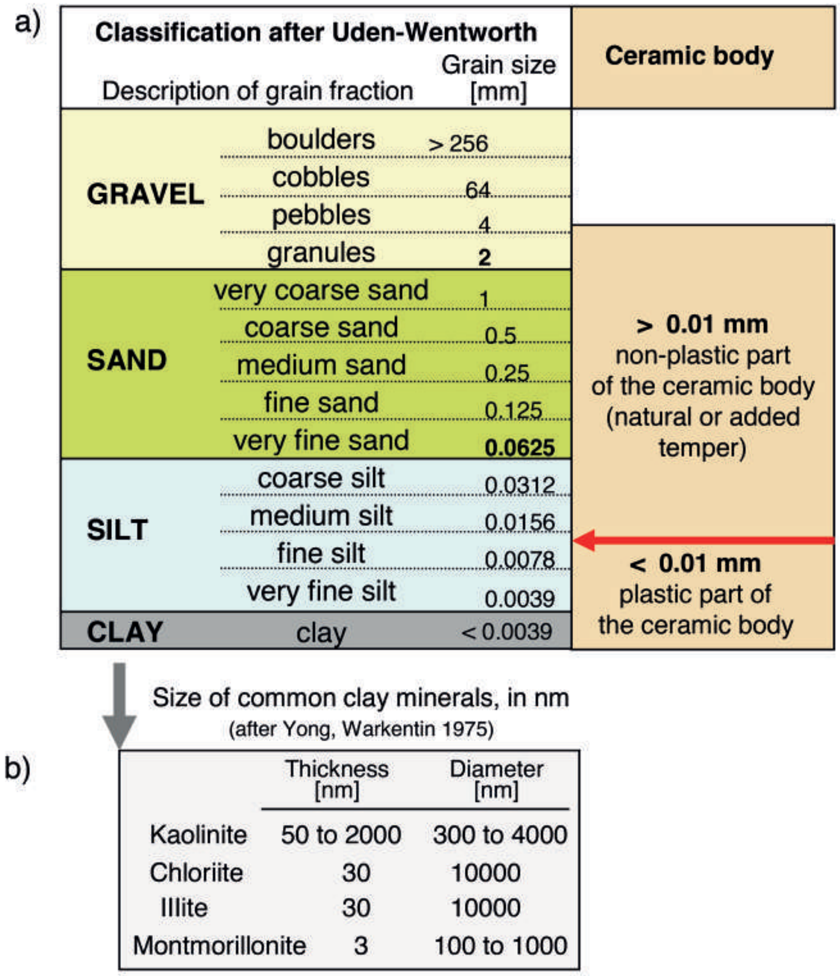
[6] Wilkins 2010, pp. 2–12.

[7] Udden 1914.

[8] Wentworth 1922.

be divided into coarse, medium, fine and very fine silt. “Clay” is the term used for the finest grade of clastic particles, namely particles smaller than 0.0039 mm in diameter (1/256 mm). In addition to this size limit for clay particles, other size limits are also used to separate clay particles from silt particles. An upper size limit of 1 µm in diameter for clay-sized particles is used by colloid chemists, whilst an upper size limit of 2 µm for clay-size material is currently used by engineers who have to adhere to the European Standard.[9]

Clay-sized particles consist primarily of a group of minerals known as clay minerals. The size of common clay minerals[10] is shown in Fig. 2b (the size of clay minerals is given in nanometres). The properties of clay minerals can make it difficult to correctly assess the content/distribution of silt-sized and clay-sized particles in a given material. This is due to the fact that clay minerals can form flocculants of 10–20 µm[11] that are resistant to disaggregation.[12]



a)

Classification after Uden-Wentworth

	Description of grain fraction	Grain size [mm]	**Ceramic body**
GRAVEL	boulders	> 256	
	cobbles	64	
	pebbles	4	
	granules	**2**	**> 0.01 mm** non-plastic part of the ceramic body (natural or added temper)
SAND	very coarse sand	1	
	coarse sand	0.5	
	medium sand	0.25	
	fine sand	0.125	
	very fine sand	**0.0625**	
SILT	coarse silt	0.0312	
	medium silt	0.0156	
	fine silt	0.0078	**< 0.01 mm** plastic part of the ceramic body
	very fine silt	0.0039	
CLAY	clay	< 0.0039	

b)

Size of common clay minerals, in nm
(after Yong, Warkentin 1975)

	Thickness [nm]	Diameter [nm]
Kaolinite	50 to 2000	300 to 4000
Chloriite	30	10000
Illite	30	10000
Montmorillonite	3	100 to 1000

Fig. 2. Grain size classification: a = grain-size scale for clastic sediments and size of common clay minerals; b = size of common clay minerals

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[9] Standard EN ISO 14689-1: 2003: Geotechnical investigation and testing — Identification and classification of rock — Part 1: Identification and description.

[10] Yong, Warkentin 1975, after Holtz, Kovacs 1981, p. 104.

[11] Sometimes 50–500 µm microflocs of clay minerals are also observed (Tan *et alii* 2017).

[12] Tan *et alii* 2017.

Unlike fine and very fine silt, coarse and medium silt can be seen with the naked eye or with a hand lens. However, individual clay-sized particles can be seen neither with the unassisted eye nor with a hand lens. Macroscopically, fine and very fine silt can be distinguished from clay particles using sensory analysis involving the tongue, teeth and palate: silt feels gritty, whilst clay feels smooth. The size of these grains is generally too small for optical techniques to be of any use in their identification. Scanning electron microscopy and X-ray diffraction can be used to identify minerals in these fractions.

In the case of textural classification of indurated fine-grained rocks, a popular means of classifying clay-silt-sand-grained rocks based on ternary diagrams is that proposed by Folk in 1974;[13] this classification system is shown in Fig. 3. Rocks in which most of the particles are clay-sized are classified as claystone. If silt-sized particles predominate, the rock is classified as siltstone; mixtures of more than one-third clay-sized and silt-sized particles are referred to as mudstone.[14] According to this classifications, claystone, mudstone and siltstone can also include up to 10% sand-size particles. If there is 10–50% sand-sized particles in any of these rocks then they are referred to respectively as sandy claystone, sandy mudstone and sandy siltstone.

Another term which is also used in the terminology of indurated fine-grained rocks is shale. According to Nichols: “The term shale is sometimes applied to any mudrock (e.g., by drilling engineers) but it is best to use this term only for mud rocks that show a fissility, which is a strong tendency to break in one direction, parallel to the bedding. (Note the distinction between shale and slate: the latter is a term used for fine-grained metamorphic rocks that break along one or more cleavage planes)”.[15]

In the case of textural classification of unconsolidated fine-grained sediments, there are many types of classifications that are based on ternary diagrams in which the vertices of the triangles are clay, silt and sand. Fig. 4a shows the classification of sediment based on sand-silt-clay ratios after

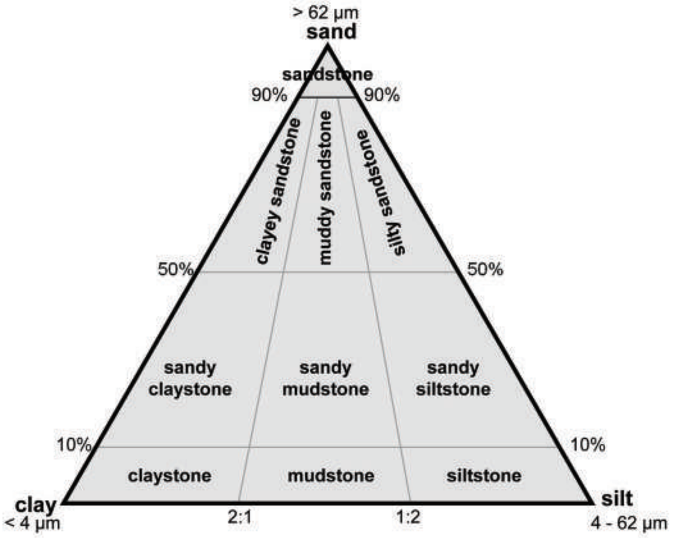

Fig. 3. Classification of fine grained rocks (after Folk 1974)

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[13] Folk 1974.

[14] For a discussion on the classification of mudstones, see Al-Rawas, Cheema, Al-Aghbari 2000.

[15] Nicols 1999, p. 21.

Shepard,[16] Fig. 4b shows the classification after Pettijohn[17] and Fig. 4c shows a simplified version of soil texture classifications of the United States Department of Agriculture (USDA).[18] As can be seen from these classifications, the term "clay" does not denote only particles of clay size. Clay may contain of up to 25% [Fig. 4a] or 20% [Fig. 4b] or up to 40% [Fig. 4c] sand or silt grains (or a mixture of sand and silt grains).

Generally, when clay-sized particles predominate in sediments, unindurated (unconsolidated) fine-grained sediment is called "clay" or "clayrock", and indurated (massive) fine-grained sediment is called claystone or clayshale if it is fissile.

In addressing the definition of the word "clay" as a term for a particular material, it should be noted that the fundamental property of a clay is that it comprises sediments of clay-sized particles that are sufficiently plastic when wet to allow the material to be formed into a desired shape, which is retained upon drying. The material becomes hard, brittle and non-plastic when fired, all the while retaining the shape into which it was formed.

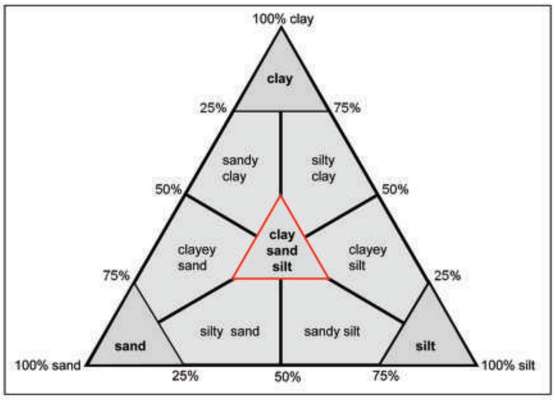

Fig. 4a. Classification of sediment based on sand-silt-clay ratios (after Shepard 1954)

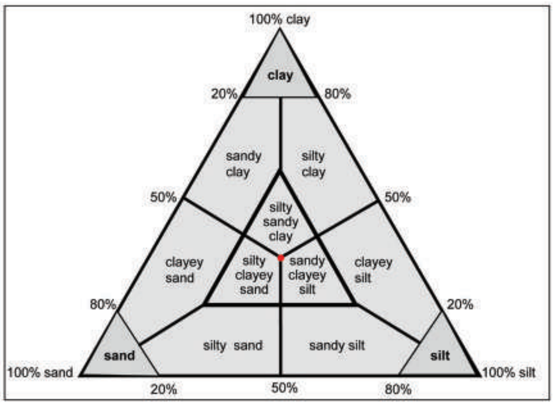

Fig. 4b. Classification of sediment based on sand-silt-clay ratios (after Pettijohn 1975)

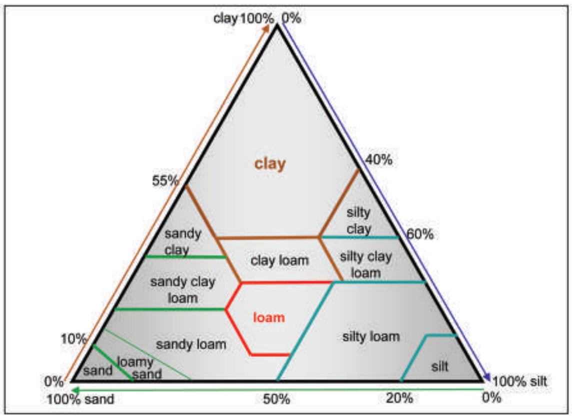

Fig. 4c. Simplified version of soil texture classifications of the United States Department of Agriculture (USDA)

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[16] SHEPARD 1954.

[17] PETTIJOHN 1975.

[18] Source: http://soils.usda.gov/technical/manual/print_version/complete.html.

As a general rule, clay is used as a raw material (clay raw material) to make clay-ceramics. However, it must be remembered that plastic ceramic raw materials (i.e., those that are readily formed) are all types of particles with a grain size of less than 0.01 mm in diameter, in other words materials with clay-sized particles as well as fine and very fine silt-sized particles: these fractions form the plastic part of the ceramic mass (particles of more than 0.01 mm in diameter comprise the non-plastic components [Fig. 2a]).

Clay minerals, which constitute the main clay-sized particles (i.e., they form the basis of the plastic part of every ceramic body in clay pottery), commonly develop as a result of the breakdown of feldspars and other silicates. Clay minerals are hydrated Al, Mg and Fe aluminosilicates belonging to the phyllosilicates (sheet silicates). Some clay minerals are rare, while others are common or very common. Depending on the layer structure of the octahedral and tetrahedral sheets, phyllosilicates can be divided into two-layer silicates (1:1 structure, an octahedral sheet is permanently bound on one side to a tetrahedral sheet), three-layer silicates (2:1 structure, an octahedral sheet is sandwiched between two tetrahedral sheets) and four-layer silicates (2:1:1 structure). Amorphous clay is known as allophane ($Al_2O_3 \cdot SiO_2 \cdot nH_2O$).

Two-layer silicates include clay minerals of the kaolinite group (1:1 layer silicates):

- kaolinite $Al_2(Si_2O_5)(OH)_4$
- dickite $Al_2(Si_2O_5)(OH)_4$
- nacrite $Al_2(Si_2O_5)(OH)_4$
- halloysite $Al_2(Si_2O_5)(OH)_4$.

Three-layer silicates include clay minerals (2:1 layer silicates):

- of the smectite group: montmorillonite $(Na,Ca)_{0.33}(Al,Mg)_2(Si_4O_{10})(OH)_2 \cdot nH_2O$
  beidelite $(Na,Ca_{0.5})_{0.3}Al_2((Si,Al)_4O_{10})(OH)_2 \cdot nH_2O$
  nontronite $Na_{0.3}Fe_2((Si,Al)_4O_{10})(OH)_2 \cdot nH_2O$
  saponite $Ca_{0.25}(Mg,Fe)_3((Si,Al)_4O_{10})(OH)_2 \cdot nH_2O$
- verniculite $Mg_{0.7}(Mg,Fe,Al)_6(Si,Al)_8O_{20}(OH)_4 \cdot 8H_2O$
- hydromicas: illite $K_{0.65}Al_{2.0}[Al_{0.65}Si_{3.35}O_{10}](OH)_2$.

Four-layer silicates include clay minerals of the chlorite group (2:1:1 layer silicates):

- clinochlore $Mg_5Al(AlSi_3O_{10})(OH)_8$
- chamosite $(Fe^{2+},Mg,Al,Fe^{3+})_6(Si,Al)_4O_{10}(OH,O)_8$
- nimite $(Ni,Mg,Al)_6((Si,Al)_4O_{10})(OH)_8$
- pennantite $Mn^{2+}_5Al(AlSi_3O_{10})(OH)_8$ (all formulas source: www.mindat.org).

There are also mixed-layer minerals: kaolinite-illite, illite-smectite, and smectite-chlorite. All this shows that the ceramic raw material known as clay is a very mineralogically complex sedimentary rock.

In summary, the term clay refers to fine-grained sediments comprising a predominance of variable amounts of clay-size grains (the majority of which are clay minerals) and of variable amounts of silt-size and/or sand-size particles (silt- and sand-sized grains = natural temper of non-plastic particles). It must be borne in mind that there are a multitude of clay minerals, and that a clay raw material is made up of more than one clay mineral. Clays often contain a mixture of numerous clay minerals, and the relative percentages of clay minerals within a single deposit of the same geological provenance is not necessarily constant. Because each clay mineral has different technological properties, changes in the proportions of individual clay minerals, especially those belonging to different groups, affect the thermal properties (e.g., fire resistance, shrinkage, swelling) and chemical composition of a ceramic raw material. Furthermore, the properties of a raw material are also affected by the type and quantity of silt and sand-sized grains. Therefore, the terms “typical clay” or “behaviour of typical clay” (which, unfortunately, appear in the archaeometric literature) should not be used — there is no such thing as typical clay; there is only "this particular clay" and we can determine the properties and specific chemical and mineralogical composition of "this particular clay".

Pottery is made of clay, hence unconsolidated fine-grained sediments containing grains in the clay-silt fraction or material with grains in the clay-silt-sand fraction. This material must contain a percentage of clay-sized clastic particles that will make it sufficiently plastic for a given forming technique. Intentional non-plastic temper usually comprises sand-sized grains (in some cases fine gravels occur). If the raw material for pottery making consists of indurated fine-grained sediments they will need to be crushed to make the material suitable for use.

In this article the term "ceramic raw materials" is used in reference to clay raw materials that are suitable for making clay-ceramics immediately after extraction, whilst the term "clay raw materials" is used in a broader sense, encompassing both "ceramic raw material" as well as raw materials that need to be processed before they can be used for pottery making.

Searching for a raw material — methodological approach

There are four approaches to analysing clay raw material: analyses performed by a sedimentologist, analyses carried out by a potter, analyses conducted for the requirements of modern ceramics production, and analyses for the needs of archaeometric research (analysis of archaeoceramics).

Sedimentology, a branch of geology concerned with the study of sedimentary rocks, deals with defining the texture and structure of rocks and identifying the minerals from which they are built. When analysing sedimentary rocks such as clays, the main laboratory techniques used in order to accurately identify clay minerals and minerals found in clay in fractions > 0.0039 mm are: X-ray diffraction, TG-DTG-DTA, heavy minerals analysis, optical microscopy, and electron microscopy. In the field, simplified identification of detritus can be performed using the hardness or HCl test.

A potter who produces wares in the traditional way will perform a test after obtaining a new clay to assess whether it is fat or thin and whether it needs tempering (and to determine what type of temper should be added and in what proportion) or slurrying, or whether it can be used as it is for the chosen forming method. The potter also does a firing test to assess the thermal behaviour of the ceramic body: to see the colour of the finished product and assess its shrinkage (i.e., the difference in size between the formed and dried product and the fired product) and to determine the optimal firing temperature for the given function of the product. The tests carried out by the traditional potter are classed as non-laboratory empirical analyses and have been performed by potters since ceramics were first produced.

Modern ceramics production based on technologies that use natural raw materials such as clays relies on a strictly defined technology which, as in the case of the traditional potter, is determined based on empirical analyses, but empirical analyses carried out in laboratories. However, just like potters across the millennia, a modern technologist must gain a good understanding of the thermal behaviour of the raw materials being used and the thermal behaviour of the given ceramic body. In current standardised production, it is important to define the dimensional tolerance of a product (standards are set for permissible deviations from shape depending on the accuracy class). The properties of a product made from a given raw material (ceramic body), fired at a given temperature, are analysed. These properties include: mechanical properties (hardness, resistance to compression, stretching and crushing), thermal properties (thermal conductivity), chemical properties (chemical reactivity), physical properties (density, porosity, water absorption) and functional properties (frost resistance, water resistance, resistance to thermal shock). Laboratory analysis of ceramic raw materials encompasses analysis of green raw materials as well as model tests of fired raw materials (de facto ceramics). They cover a wide spectrum of methods and techniques, such as sieve analysis, rheological analysis, TG-DTG-DTA analysis, dilatometric tests, chemical composition analysis, microscopic examinations (using optical and scanning microscopy), X-ray diffraction, Raman spectroscopy, and Moesbauer spectroscopy.

When analysing clay raw materials for the purposes of archaeoceramology, the aim of the analysis is in essence a 180-degree reversal of the analytical objectives of sedimentologists, potters and technologists in modern ceramics factories. The latter three all proceed from point A (raw material) to point B (end product), while the archaeoceramologist goes from point B to point A. This is a much more difficult task, even when attempting to recreate a recipe that is recorded in writing and uses a known raw material deposit, as in the case of some post-medieval wares or when attempting to recreate a ceramic body based on a known recipe and known clay extraction sites used by contemporary workshops (e.g., a pottery workshop in Mazzaro di Vallo[19]).

Thus, the first step in identifying the raw material used for making CBM was, as strange as it may sound, to analyse samples of CBM found at the Novae site. Knowing the thermal behaviour and original firing temperature of a ceramic product means that from the outset of the raw material analysis it is possible to select clay samples that can be taken into consideration as potential raw materials used in the production of CBM, legionary pottery (LegP) or common wares (CW).

In looking for the raw materials from which ancient CBM or indeed any other ancient ceramic product was made, it must be remembered that the fragment (or complete object) recovered during excavation is the end result of a *chaîne opératoire*.[20]

The *chaîne opératoire* begins with the procurement of raw materials, encompasses the technological process and does not end with the removal of the finished product from the potter's kiln, nor even with the effects that usage has on the given ceramic product. It also incorporates all of the changes that take place within the ceramic object during its existence from the moment it ceased fulfilling its functional purpose to the moment it reached the laboratory. Each component and each activity, starting with the acquisition of the raw material and ending with the submission of the sample to the laboratory, affects the analysed item to a different extent [Fig. 5].

Raw materials

Ceramic products can be made using clay without any additional refining processes (if such a raw material is available) or alternatively the raw materials can be specially treated by washing or levigating, or ceramic bodies can be made by adding non-plastic temper of certain grain sizes, or by mixing with other types of clay. This first important element of ceramic technology determines the properties of the final product.

Processing a ceramic body

a) Preparation of a ceramic body, stage 1 (plastic raw material + non-plastic raw material[21])

Combining raw materials results in a mixture that is characterised by a specific chemical composition as well as mineralogical and petrographic composition depending on the raw materials used and the recipe (the ratio of the individual components used in the mixture). This means that products made of clay[22] differ in chemical composition and mineralogical and petrographic composition from products made using a ceramic body[23] based on the same clay.

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[19] Daszkiewicz, Schneider forthcoming.

[20] Projektgruppe Keramik 1989.

[21] The non-plastic part consists of those ingredients of the ceramic body with a particle size fraction greater than 0.01 mm (various minerals, rock fragments, bioclasts, phytogenic matter, grog). The non-plastic part (temper) can be an integral component of the raw material deposit, but it can also be an intentional temper added to meet the needs of the technological process.

[22] Meaning the natural raw material.

[23] This term is used to describe blends of clay or clays and any non-plastic inclusions — the effect of the technological process.

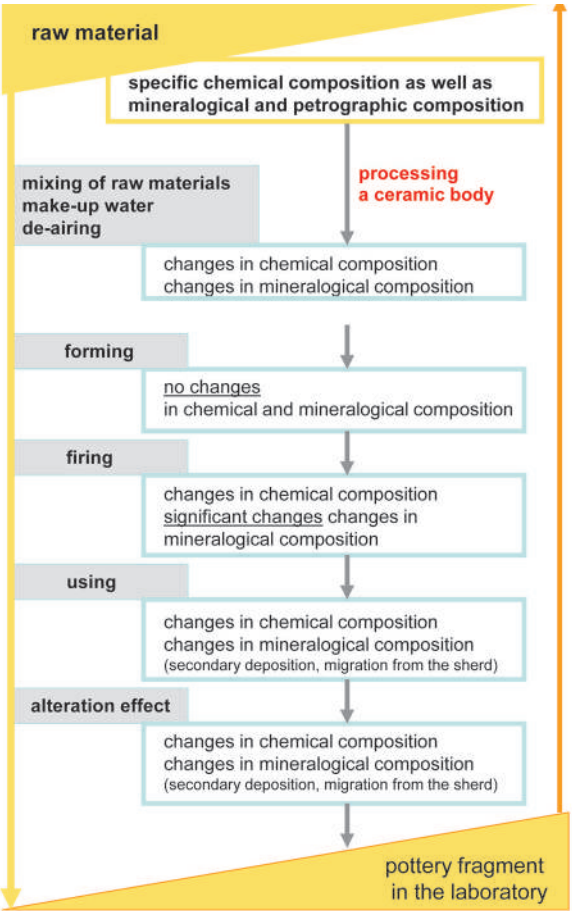

Fig. 5. The *chaîne opératoire* begins with the procurement of raw materials and ending with the submission of the sample to the laboratory. Each component and each activity affects the analysed item to a different extent

b) Preparation of a ceramic body, stage 2 (plastic raw material[24] *+ non-plastic raw material + make-up water)*

In order to obtain a plastic ceramic body of a consistency appropriate for the chosen forming method, an amount of water appropriate for a given raw material is needed. Depending on its mineralogical composition, this make-up water can affect the melting point temperature and cause changes in the mineralogical composition of the ceramic body (e.g., the presence of NaCl and/or KCl_2 can be observed) and also has an impact on the chemical composition of the ceramic body (increased levels of sodium, chlorine, potassium, and magnesium, among others). Notably, the chemical composition of the make-up water also has a significant effect on the colour of the ceramic product.[25]

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[24] The plastic part is composed chiefly of clay minerals, while the matrix is deemed to consist of all minerals with a particle size fraction less than 0.01 mm. The plastic part of the ceramic body hardens during the firing process and becomes the non-plastic matrix.

[25] In the case of pottery made from marly clay, the use of sea water or water from salt lakes causes it to change colour from red to white (Daszkiewicz 2014). In contemporary workshops at Djerba (Tunisia), potters use either sea or freshwater as make-up water depending on what colour they want the pottery to be.

c) Preparation of a ceramic body, stage 3

The way in which the ceramic body is processed (mixing of ingredients, de-airing) affects the size and number of pores, the distribution of the non-plastic particles, and the heterogeneity of the matrix, and thus leaves a mark on the end product in the form of a specific structure and texture. Different approaches to mixing and de-airing can result in products made according to the same recipe having very different structures and textures.

Forming

The shaping and forming process causes changes in the pores (shape, distribution, additional pores) and affects the relative density.[26]

Firing

During the firing process a series of changes occur within the ceramic product. Depending on the temperature and gas conditions of the firing, products made from the same ceramic body may differ in: colour, extent of linear changes (shrinkage, expansion), degree of vitrification, open porosity (as well as closed and total porosity), apparent density and water absorption, functional properties (permeability, thermal shock resistance), magnetic and mechanical properties (e.g., resistance to compression and crushing). Significant changes in mineralogical composition and changes in chemical composition will also occur.

Usage

Changes occur to the inner and outer surfaces, such as surface matting, and loss of slip/glaze. Soot can be deposited on the outer surfaces of cooking vessels and organic matter (residues of food cooked or stored inside the vessel) can be deposited in the open pores of the ceramic fabric, mostly those open on the internal surface of the vessel walls. In technical ceramics such as salt evaporation vessels, remnants of salt can be observed in the open pores and on the sides of these vessels.

Deposition in archaeological context (the alteration effect[27])

The chemical composition of ceramic fragments can differ markedly from their original composition due to the secondary deposition of phosphorus, which is most often accompanied by the secondary deposition of strontium and barium. This effect is often associated with the migration from the ceramic body of elements such as rubidium, potassium, sodium, calcium, and sometimes magnesium, manganese, and silicon. In consequence, the content of elements that occur in more stable compounds, such as titanium, aluminium, iron, and chromium, is exaggerated. Furthermore, secondary deposits of calcium carbonates, gypsum and iron compounds are also very frequently observed in the pores of the ceramic material, which results in elevated concentrations of calcium, sulphur, iron and manganese and causes changes in the content of geochemically correlated trace elements (e.g., calcium is geochemically correlated with strontium, and iron is correlated with vanadium). Ceramics that have been exposed to seawater (recovered from underwater excavations or shipwrecks) have exaggerated magnesium levels. Changes in concentrations of lead, copper and tin are also observed as a result of the migration of these elements from metal artefacts deposited in the vicinity of the pottery. In addition to changes in the chemical composition, changes may also occur in the phase composition: partial rehydroxylation of clay minerals, reconstruction of thermally decomposed carbonates, changes in the diopside-gehlenite-calcite system, deposition of gypsum and/or secondary calcite in the pores.

[26] Daszkiewicz, Bobryk, Wetendorf 2017.

[27] On the subject of the alteration effect in archaeological pottery, see Schneider 2017.

Later changes

Changes associated with the cleaning and storage of artefacts. (e.g., a decrease in CaO content in surface layers, new phases in open pores, surface weathering).

In conclusion, there is no such simple equation as raw material = product = laboratory sample. The artefact at the end of the *chaîne opératoire*, the sample in the laboratory, is characterised by a chemical composition and mineralogical composition that differs to a greater or lesser degree from the chemical composition and mineralogical composition of the raw materials used to make the ceramic product represented by the sample that reached the laboratory [Fig. 5]. When analysing samples of ancient pottery and looking for the raw materials from which a given ceramic product was made, we seldom encounter a situation like that presented, for example, by the Roman ceramic workshop at Rheinzabern.[28] More often the story is one of various researchers spending many years trying, and ultimately failing, to find raw material sources and places of production (as, for example, in the case of Italian sigillata[29]).

Measurement strategy and analysis results — CBM, CW and LegP

Abridged MGR-analysis (refiring at 1100, 1150 and 1200°C)[30] and chemical analysis by WD-XRF were performed for each of the 54 CBM fragments as well as for each of the nine LegP fragments and 13 CW samples. After the samples had been classified on the basis of these results, some of them were selected for K-H analysis (9 CBM samples), and thin sections were made from 14 samples (five LegP samples, three CW samples and six CBM samples). Additionally, XRD analysis was carried out on one CBM fragment.

Pls. 1–10 show the results of MGR-analysis for all 76 samples, while MGR-groups are listed in the first column of Table 1 and Table 2. The results of chemical analysis are also detailed in these tables.[31] Micrographs of typical fabric images seen in the polarising microscope are presented in Pls. 16–24. The original firing temperature of the CBM was determined based on the results of K-H analysis (results for six of the samples are shown in Fig. 6); the diffractogram of one of these CBM samples is shown in Fig. 7.

Generally speaking, CBM, CW and LegP fabrics differ sufficiently to allow even small non-diagnostic sherds to be attributed to one of these three groups based on macroscopic analysis of a fresh fracture surface, with only one exception. One sample of CBM (MD7241) can be classified as LegP. The results of MGR-analysis showed that differences in the macro-fabric are not related to the original firing temperature or solely to different recipes, but to the use of decidedly different types of plastic raw material in the manufacture of CBM, CW and LegP. CBM was made of mixed clays of the NC-CC type with no deliberate addition of non-plastic particles (with the exception of sample MD7241), CW was made of MC clays with the intentional addition of various medium-coarse grains, whilst LegP was made of NC clays or NCcc+

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[28] Schneider 1978.

[29] Schneider, Daszkiewicz 2020a; 2020b.

[30] Thin slices were removed from each sample in a plane at right angles to the vessel's main axis. Firing was done in a Carbolite electric laboratory resistance furnace, in static air, at a heating rate of 5°C/min, a soaking time of 1 hour at the peak temperature, a cooling rate of 5°C/min up to 500°C and then cooling with the kiln for 1 hour.

[31] The contents of major elements listed in table 1 are calculated as oxides and normalized to a constant sum of 100%. Si = silicon, calculated as SiO_2; Al = aluminium, calculated as Al_2O_3; Ti = titanium, calculated as TiO_2; Fe = iron, total iron calculated as Fe_2O_3; Mn = manganese, calculated as MnO; Mg = magnesium calculated as MgO; Ca = calcium calculated as CaO; Na = sodium calculated as Na_2O; K = potassium calculated as K_2O; P = phosphorus calculated as P_2O_5.The element concentrations determined are valid for samples ignited at 900°C (measurements were performed on specimens melted after ignition).

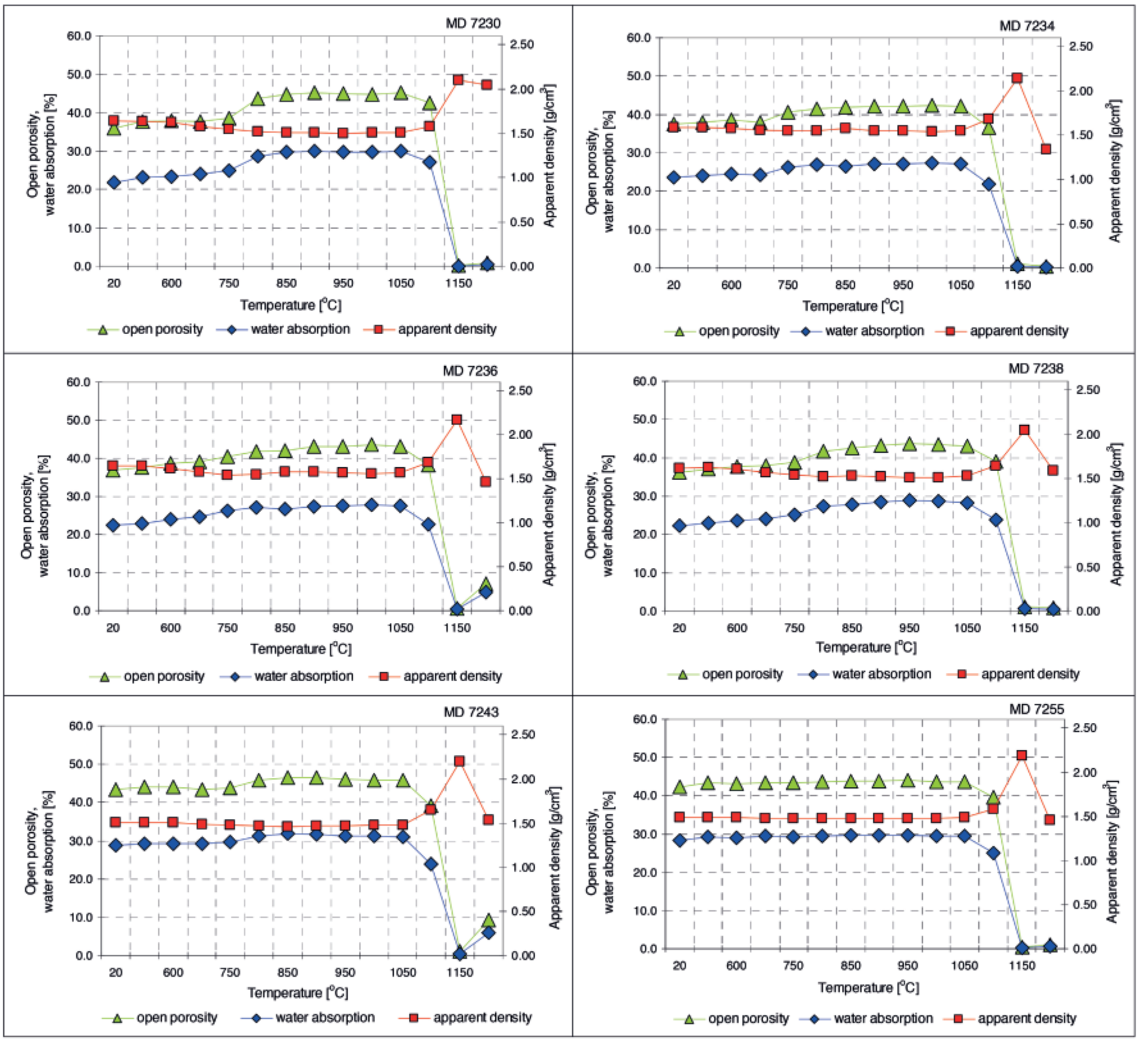

Fig. 6. Results of K-H analysis for six of the CBM samples. Curves showing the values of open porosity, water absorption and apparent density vs. refiring temperature (compiled by H. Baranowska)

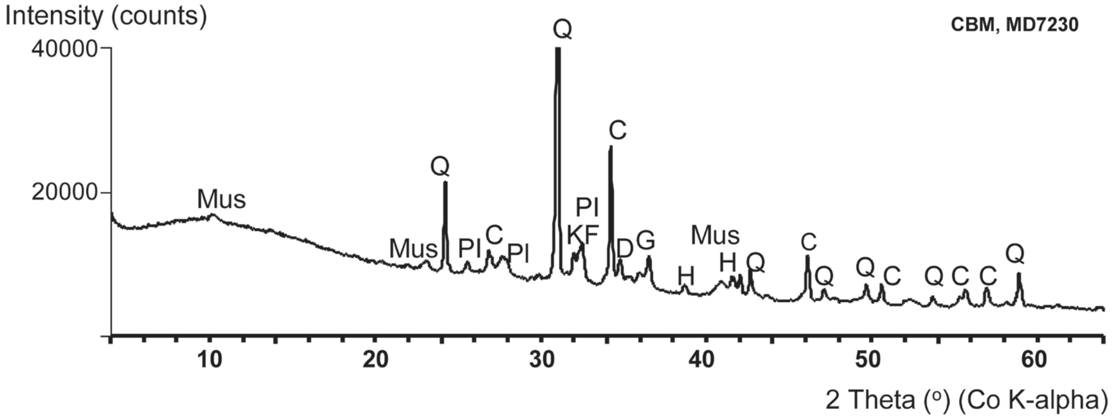

Fig. 7. Diffractogram of CBM sample MD7230

clays. Various clays were used within each group, as evidenced by the number of MGR-groups [Table 1, first column]. In the case of CBM samples, 41 MGR-groups were identified among 54 samples [Table 2, first column], meaning that 35 CBM samples each represent a different MGR-group,[32] LegP fragments represent four MGR-groups, and CW samples represent nine MGR-groups. In addition, the largest of the MGR-groups were further divided into MGR-subgroups. All CBM samples and CW samples attain melting point at temperatures < 1200^{o}C, resulting in the total deformation of the sample with surface vitrification after refirng at 1200^{o}C. After refiring at this temperature CBM samples (with four exceptions) have a semi-melted (sMLT[33]) or melted (MLT[34]) matrix type. A floated (FL[35]) matrix type predominates among the CW samples (only three samples have an sMLT or MLT matrix type). However, even refiring at 1150^{o}C already causes the breakdown of the matrix of all CW samples and CBM samples (except for two: MD7241 and MD3892). LegP samples differ very distinctly from CBM and CW samples because at 1200^{o}C they have a sintered matrix type (SN[36]), the only exceptions being two samples attributed to the LegP-2 MGR-group [Table 1], which have an over-melted matrix type.[37]

The results of chemical analysis confirm the groupings resulting from MGR-analysis. CW pottery is especially distinctive due to its high CaO content [Table 1], which MGR-analysis shows is related to the matrix and not to carbonates in the > 10 µm fraction (non-plastic particles). Eight of the LegP samples are also distinctive due to their CaO content — in this case a low CaO content. The ninth of the analysed LegP samples (MD3872) differs very markedly (from the CBM and CW samples also) in having high levels of Al_2O_3, a very high Sr/CaO ratio, a high cerium (Ce) content and a very low chromium (Cr) content.

MGR	Dat.	Lab.	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	V	Cr	Ni	Cu	Zn	Rb	Sr	Y	Zr	Nb	Ba	La	Ce	Pb	Th	l.o.i.
group		No.	% by weight										ppm															%
Legionary pottery																												
LegP-1	1	MD3866	76.65	0.520	11.74	3.41	0.050	1.18	4.23	0.56	1.44	0.22	85	112	41	24	52	63	110	19	151	10	374	29	56	50	20	3.3
LegP-1	1	MD3870	75.84	0.522	12.09	3.29	0.053	1.23	4.62	0.60	1.50	0.25	78	122	43	19	51	62	118	18	156	11	357	18	53	23	19	3.8
LegP-3.1	1	MD3867	74.04	0.505	15.46	6.54	0.015	1.06	0.32	0.17	1.77	0.12	127	94	44	23	68	101	55	17	167	11	248	24	45	33	19	0.5
LegP-3.2	1	MD3869	77.11	0.503	12.72	5.08	0.019	0.99	1.48	0.22	1.76	0.12	110	127	40	42	59	87	70	18	180	10	348	15	52	161	21	1.8
LegP-3.4	1	MD3874	76.35	0.492	13.17	5.60	0.017	1.06	1.24	0.24	1.73	0.10	114	93	38	19	62	94	67	19	167	11	256	15	51	80	21	0.7
LegP-3.3	1	MD3873	72.92	0.490	14.62	5.79	0.018	1.05	3.01	0.27	1.68	0.16	92	110	44	31	64	92	88	17	178	11	256	20	45	47	23	3.1
LegP-2	1	MD3871	70.40	0.677	13.00	5.06	0.044	1.58	5.89	0.55	2.32	0.48	121	107	47	29	103	89	210	24	200	12	400	26	77	25	16	2.8
LegP-2	1	MD3868	69.49	0.690	13.62	5.39	0.068	2.04	4.64	0.88	2.30	0.90	113	114	60	34	77	86	171	28	189	13	501	31	68	26	18	4.7
LegP-4	1	MD3872	62.45	0.725	22.68	5.77	0.085	0.97	2.13	2.61	2.45	0.13	115	47	24	10	63	113	609	33	286	15	932	67	127	27	35	0.4
Common Ware																												
CW-1.1	1	MD3875	50.99	0.631	12.91	5.22	0.149	1.67	24.98	0.85	2.22	0.39	126	117	56	37	74	70	435	29	138	13	432	27	72	22	10	12.5
CW-1.1	1	MD3877	53.31	0.714	12.01	5.22	0.129	1.88	23.00	0.87	2.39	0.48	122	126	47	51	74	67	413	23	161	13	396	16	63	958	27	12.6
CW-1.1	1	MD3878	52.29	0.757	13.42	5.53	0.125	1.82	22.60	0.99	2.12	0.34	140	102	50	35	75	71	448	28	156	13	403	25	57	32	15	10.2
CW-1.2	1	MD3876	49.30	0.796	12.57	5.55	0.121	2.31	25.76	1.13	1.94	0.52	137	82	35	27	71	69	470	20	144	12	434	8	41	<5	15	11.5
CW-1.3	1	MD3887	48.58	0.699	12.72	5.78	0.147	2.25	25.73	0.63	2.35	1.11	131	138	56	26	76	67	504	26	145	11	493	22	63	21	17	11.5
CW-2	1	MD3879	54.90	0.715	12.71	5.10	0.129	1.60	21.75	0.80	2.10	0.19	123	102	46	31	69	65	386	27	166	16	436	23	55	24	12	11.4
CW-3	1	MD3880	55.89	0.842	13.78	5.77	0.115	2.02	17.58	1.25	2.39	0.37	150	96	34	29	63	63	335	21	153	13	396	9	41	75	16	7.9
CW-4	1	MD3881	49.49	0.766	10.92	5.82	0.143	3.42	26.02	0.63	2.48	0.30	148	166	57	35	73	60	375	24	147	14	461	16	57	31	13	19.3
CW-5	1	MD3882	52.06	0.710	13.84	5.44	0.114	2.08	22.53	0.67	2.19	0.37	102	120	51	34	65	71	393	26	147	14	359	18	65	20	13	9.6
CW-6	1	MD3883	50.94	0.813	11.78	5.69	0.158	2.71	24.99	0.52	1.88	0.52	140	171	59	37	72	69	464	28	167	13	415	30	55	12	16	10.6
CW-7	1	MD3884	55.64	0.759	14.31	6.03	0.125	2.14	17.60	0.75	2.31	0.34	131	132	63	43	87	77	349	32	162	14	392	26	69	20	16	7.5
CW-8	1	MD3885	49.61	0.712	10.72	5.27	0.177	2.55	27.45	0.77	2.23	0.51	116	144	47	32	64	65	484	24	193	9	450	27	46	10	15	14.1
CW-9	1	MD3886	51.05	0.718	12.98	5.38	0.146	2.02	24.20	0.71	2.34	0.45	126	131	48	33	76	69	427	26	153	13	337	12	60	24	13	11.1

Table 1. The results of chemical analysis by WD-XRF. Concentration of major elements normalised to 100%, measurement of melted, ignited samples; l.o.i. = loss on ignition at 900°C

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[32] It is unlikely that only one product was made from one ceramic body, therefore it is assumed that any sample submitted by archaeologists for analysis represents a group of products made from a given ceramic body. Therefore, the term "group" is used even in cases where the so-called group comprises only one of the analysed samples.

[33] sMLT = semi-melted: over-melting of the surface occurs, changes in sample shape are noted (not just rounded edges) but no bloating.

[34] MLT = melted: the sample becomes spherical or almost spherical in shape.

[35] FL = flowed: the sample flows into a thin layer.

[36] SN = sintered: the sherd is well compacted, it may or may not become smaller in size in comparison to the original sample, whilst its edges remain sharp.

[37] ovM = over-melted: the surface of the sample becomes over-melted and its edges rounded.

MGR	Dat.	Lab.	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	V	Cr	Ni	Cu	Zn	Rb	Sr	Y	Zr	Nb	Ba	La	Ce	Pb	Th	l.o.i.
group		No.	% by weight										ppm															%
CBM-1.1	1	MD7206	56.79	0.637	14.75	5.27	0.058	2.06	17.04	0.66	2.58	0.15	101	82	54	28	87	125	340	26	183	14	316	25	60	27	5	6.7
CBM-1.2	1	MD7222	59.82	0.663	14.62	5.32	0.060	2.02	13.77	0.65	2.87	0.21	93	86	53	36	87	127	312	24	188	14	332	33	60	28	7	5.9
CBM-1.3	1	MD7228	59.96	0.662	14.57	5.12	0.045	2.12	13.89	0.77	2.75	0.12	98	80	53	34	84	127	321	26	193	15	316	40	64	43	7	2.5
CBM-1.4	1	MD7238	59.47	0.649	14.49	5.19	0.049	1.96	14.46	0.69	2.92	0.12	98	91	55	37	81	125	303	25	184	15	338	<5	42	39	<5	6.8
CBM-1.5	1	MD7230	59.31	0.650	14.67	5.23	0.056	2.11	14.31	0.67	2.78	0.19	103	78	55	43	92	127	322	27	188	12	329	20	49	32	6	6.1
CBM-1.6	1	MD7253	57.74	0.634	14.67	5.17	0.064	2.05	15.45	0.69	2.65	0.88	94	82	53	37	109	123	372	25	180	15	355	45	39	31	<5	5.6
CBM-2	3	MD7207	61.12	0.688	14.74	5.23	0.050	2.06	11.99	0.64	3.28	0.20	100	75	54	31	87	120	305	26	191	15	369	35	57	37	<5	6.3
CBM-3	1	MD7208	63.81	0.743	14.27	5.17	0.058	2.47	9.51	0.87	2.75	0.36	78	94	53	36	111	119	302	28	222	14	380	39	65	38	7	3.5
CBM-4	4	MD7209	59.24	0.673	14.55	6.00	0.071	2.35	12.88	0.66	2.89	0.69	85	76	61	39	90	126	369	26	192	14	424	40	68	41	7	6.8
CBM-5	4	MD7210	58.77	0.681	15.22	5.49	0.059	2.12	13.64	0.65	3.02	0.34	100	88	59	37	96	134	314	26	192	14	343	23	50	32	8	6.1
CBM-6	4	MD7211	62.21	0.712	15.19	5.36	0.061	2.19	10.09	0.79	2.90	0.50	83	93	62	58	136	135	336	27	197	15	370	35	45	20	5	3.0
CBM-7	1	MD7212	62.12	0.666	14.24	5.04	0.051	2.01	12.38	0.69	2.61	0.20	81	72	51	43	89	124	342	25	196	13	347	37	62	32	7	4.7
CBM-7	4	MD7213	62.74	0.664	13.95	5.09	0.055	2.12	11.72	0.73	2.68	0.25	68	79	53	32	92	123	292	29	194	14	330	28	60	29	11	4.7
CBM-8	?	MD7214	60.01	0.660	14.40	5.22	0.054	2.03	13.93	0.66	2.79	0.24	105	70	53	71	91	127	320	24	194	15	368	49	70	33	6	6.2
CBM-9	4	MD7215	61.20	0.694	14.96	5.61	0.057	2.11	10.87	0.78	3.28	0.43	128	85	48	47	100	130	314	26	191	15	349	16	72	44	9	6.3
CBM-10.1	3	MD7216	61.56	0.715	15.29	5.65	0.055	2.22	10.83	0.80	2.74	0.15	114	96	55	34	97	133	332	27	194	14	324	20	74	46	7	2.1
CBM-10.2	3	MD7221	61.84	0.711	14.68	5.41	0.049	2.26	11.34	0.81	2.75	0.15	103	93	55	28	92	129	351	25	209	14	318	48	62	32	6	2.4
CBM-11	4	MD7217	61.61	0.705	14.88	5.39	0.074	2.25	11.22	0.68	2.90	0.29	96	84	54	53	123	134	309	30	199	13	347	9	61	32	5	4.3
CBM-12	3	MD7218	61.27	0.704	15.16	5.48	0.056	2.32	10.92	0.71	3.13	0.25	101	85	58	43	97	135	309	29	194	15	318	19	59	35	5	4.6
CBM-13	4	MD7219	63.47	0.729	14.95	5.45	0.051	2.03	9.40	0.78	2.93	0.22	115	98	57	28	84	132	356	25	207	16	409	9	39	52	7	3.9
CBM-14	2	MD7220	62.09	0.688	14.48	5.39	0.050	2.17	11.25	0.76	2.89	0.23	90	86	54	36	92	126	278	26	201	15	341	42	79	36	4	5.0
CBM-15	3	MD7223	59.20	0.727	16.48	6.16	0.061	2.33	11.22	0.75	2.91	0.16	103	95	62	44	98	142	337	27	182	17	347	41	73	37	7	3.2
CBM-16	3	MD7224	59.25	0.725	16.04	6.05	0.066	2.50	11.36	0.69	3.05	0.27	101	96	62	35	90	141	340	27	187	16	389	38	70	30	8	4.8
CBM-17	3	MD7225	58.85	0.716	16.31	6.07	0.061	2.30	11.62	0.74	2.81	0.52	106	93	62	48	99	135	364	28	185	16	388	33	55	39	6	3.5
CBM-18	1	MD7226	60.59	0.678	14.64	5.12	0.055	3.06	11.84	0.62	3.23	0.16	96	65	61	37	94	121	254	24	189	14	262	30	52	47	8	7.9
CBM-19	4	MD7227	61.28	0.706	14.87	5.25	0.044	2.31	11.92	0.78	2.68	0.16	98	88	52	41	93	125	334	27	206	15	332	33	78	35	5	3.2
CBM-20	4	MD7229	60.82	0.710	15.23	5.38	0.054	2.22	11.69	0.77	2.86	0.27	90	97	62	45	100	133	343	26	201	16	358	60	71	45	8	3.6
CBM-21.1	4	MD7231	64.59	0.746	14.90	5.21	0.047	2.13	8.32	0.72	3.08	0.26	89	85	55	33	93	134	300	27	201	15	374	20	52	37	5	3.5
CBM-21.2	2	MD7234	65.22	0.744	14.81	5.23	0.044	2.24	7.93	0.87	2.79	0.13	98	88	57	59	103	120	303	27	204	14	310	30	59	39	8	2.4
CBM-22.1	4	MD7239	65.04	0.747	14.53	5.23	0.056	2.26	7.84	0.90	2.92	0.49	86	93	56	32	162	130	311	29	217	16	362	25	53	23	5	1.7
CBM-22.1	4	MD7240	60.96	0.729	15.44	5.73	0.054	2.16	9.87	0.67	3.09	1.28	89	83	58	112	160	138	359	26	196	15	418	44	59	48	10	3.2
CBM-22.2	5	MD7237	62.48	0.746	15.06	5.31	0.049	2.52	9.82	0.89	2.90	0.23	95	92	54	35	103	131	316	30	220	16	341	20	73	39	6	4.2
CBM-22.3	1	MD7232	62.84	0.711	14.79	5.30	0.051	2.13	10.39	0.76	2.87	0.16	92	90	52	33	87	128	294	28	200	14	350	48	80	26	6	3.4
CBM-22.4	3	MD7235	63.97	0.733	14.84	5.26	0.048	2.11	8.10	0.76	3.42	0.77	119	77	58	31	97	130	278	26	198	16	346	29	68	33	4	5.9
CBM-23	3	MD7233	63.74	0.691	13.95	5.27	0.064	1.98	10.31	0.78	2.91	0.32	108	88	54	35	91	123	272	29	211	12	405	46	59	47	5	6.3
CBM-24	4	MD7236	64.39	0.672	13.53	4.97	0.059	1.87	10.33	0.79	3.05	0.33	108	80	49	42	95	112	244	25	199	14	379	13	43	31	5	8.2
CBM-25	4	MD7241	63.87	0.754	15.48	5.93	0.102	2.82	6.49	1.25	3.02	0.28	106	119	80	43	94	118	175	34	209	15	510	26	69	38	<5	5.7
CBM-26	1	MD7242	61.75	0.702	14.88	5.20	0.052	2.25	11.17	0.72	3.11	0.16	106	116	51	33	94	130	297	27	194	15	351	49	55	34	9	5.2
CBM-27	3	MD7243	62.79	0.735	15.01	5.53	0.047	2.46	9.41	0.92	2.92	0.17	106	97	54	37	99	130	364	24	207	15	335	<5	62	36	<5	1.2
CBM-28	2	MD7244	63.55	0.715	14.65	5.28	0.050	2.34	9.52	0.72	3.00	0.18	107	73	56	31	91	129	313	25	199	15	351	38	53	29	6	4.6
CBM-29	2	MD7245	61.52	0.734	14.88	5.47	0.057	2.17	11.26	0.87	2.84	0.18	101	92	54	34	94	129	350	28	219	14	346	47	60	32	8	4.0
CBM-30	5	MD7246	63.95	0.732	15.09	5.35	0.067	2.05	8.37	0.78	3.37	0.25	116	84	62	34	96	129	261	26	197	16	389	7	81	35	10	5.9
CBM-31	5	MD7247	64.03	0.716	14.63	5.25	0.049	2.19	9.36	0.71	2.91	0.16	93	80	55	30	91	130	294	26	203	15	340	56	61	35	<5	3.8
CBM-32	3	MD7248	62.99	0.732	14.83	5.64	0.052	2.08	9.68	0.80	2.94	0.26	107	86	52	22	87	129	343	28	205	14	338	42	65	45	5	3.8
CBM-33	3	MD7249	63.68	0.710	14.40	5.20	0.056	2.12	9.56	0.83	3.24	0.20	125	89	56	34	92	126	238	25	203	16	360	35	69	38	8	6.5
CBM-34	2	MD7250	62.71	0.716	14.71	5.31	0.049	2.23	10.32	0.79	2.90	0.26	88	97	55	33	99	132	288	24	210	16	359	17	64	33	<5	4.0
CBM-35	3	MD7251	60.39	0.731	16.15	6.05	0.060	2.16	10.36	0.71	3.20	0.18	127	80	61	31	91	140	293	28	182	15	379	43	67	35	7	4.0
CBM-36	1	MD7252	60.86	0.709	15.14	5.60	0.053	2.26	11.61	0.82	2.79	0.15	90	93	58	25	94	131	327	27	195	15	400	<5	86	41	8	3.2
CBM-37	2	MD7254	61.65	0.705	14.77	5.41	0.062	2.31	11.18	0.78	2.89	0.24	107	94	59	29	91	129	351	28	200	16	386	20	87	31	7	4.5
CBM-38	2	MD7255	63.83	0.751	15.19	5.30	0.045	2.19	8.90	0.83	2.82	0.15	91	98	54	30	94	133	303	26	202	16	326	17	59	36	<5	1.7
CBM-39	1	MD3892	62.12	0.809	12.85	4.90	0.135	2.75	11.99	1.12	3.06	0.28	112	94	53	23	69	89	270	31	273	13	419	24	79	24	21	7.6
CBM-40	1	MD3893	63.72	0.808	15.38	5.95	0.093	3.00	6.88	1.01	2.95	0.22	118	121	79	27	96	104	176	31	215	16	419	35	70	28	25	4.2
CBM-40	1	MD3894	63.46	0.816	15.59	6.11	0.108	3.36	6.37	1.02	2.94	0.23	116	131	85	46	121	106	180	32	217	14	454	29	89	83	20	4.0
CBM-41	1	MD3895	63.72	0.887	15.61	6.02	0.107	3.29	6.26	1.42	2.51	0.19	133	159	78	35	103	110	164	36	250	15	461	36	86	38	25	2.6

Table 2. The results of chemical analysis by WD-XRF. Concentration of major elements normalised to 100%, measurement of melted, ignited samples; l.o.i. = loss on ignition at 900°C

The next analytical step was a thin-section study (as a reminder, the term "matrix" refers to all grains < 10 μm, while inclusions observed "in the matrix" refers to non-plastic particles, hence those > 10 μm).

Five fragments of LegP were selected to make thin sections. Two LegP samples (MD3866 and MD3870) represent the same chemical group and MGR-group, while the remaining samples (MD3871, MD3872 and MD3873) represent various chemical groups and various MGR-groups.

Samples MD3866 and MD3870 are very similar to each other in terms of petrofabric [Pl. 16]. They contain angular to subangular grains of quartz and polycrystalline quartz of up to 2 mm in size (in MGR slices some grains are up to 4 mm). It is not clear whether these grains represent an intentional temper added as part of the technological process. The matrix of these samples contains some quartz and pale mica in very fine silt fraction and fine silt up to 10 μm in size. In both samples fine inclusions, mostly up to 0.15 mm (sparse inclusions up to 0.4 mm), of cryptocrystalline carbonate aggregates are observed, as is one bioclast. Carbonates are not homogenously distributed in the matrix. One large inclusion (1 mm in diameter) in MD3870 is a piece of micaceous siltstone.

Sample MD3871 [Pl. 16] has a matrix containing many very fine opaque minerals (iron compounds) and carbonates finely distributed in the matrix. Non-plastic particles include iron-rich minerals and cryptocrystalline carbonate aggregates of up to 0.2 mm. The large inclusions are of polycrystalline quartz of up to coarse-sand size, but in a much smaller quantity than in the two previous samples.

Sample MD3872 [Pl. 17] has a matrix that differs very much from the other samples of LegP and was undoubtedly made using a different clay. Crushed inclusions of up to 1mm are observed among the non-plastic material. There are more plagioclase than quartz inclusions. This probably explains the high Na content of this sample's chemical composition.

It is equally certain that another clay was used to make sample MD3873 [Pl. 17]. In comparison to the other LegP samples, the matrix of this sherd is characterised by a near total absence of inclusions [Pl. 17d]. The non-plastic material visible in the matrix is dominated by grains of subangular quartz; plagioclases are rarely observed [Pl. 17c]. The hiatus in grain sizes suggests that the non-plastic particles were probably added intentionally to the clay (fat clay needs a temper to make it more workable). Some inclusions of carbonate aggregates are observed which seem to be secondarily recarbonized after thermal decomposition [Pl. 17d].

Further thin sections [Pls. 18–20] were made from three sherds of common ware (MD3876, MD3879, MD3886). Each of these sherds was made from calcareous clays, and microfossils (foraminifera) are observed in all three thin sections; in some cases they can be better seen with parallel polarisation filters [Pls. 18e–f, 19f, 20f]. In all three thin sections the non-plastic inclusions consist of volcanic material. Abundant hornblende, orto- and clinopyroxene (mostly clinopyroxene), plagioclase and volcanic rock fragments (andesite/ basalt) can be seen. Rare inclusions of quartz and sedimentary rocks such as fine sandstone or siltstone are also observed. Most of the volcanic inclusions are between 0.1 mm and 0.6 mm in size, with only isolated grains in the fine fraction (up to 0.1 mm). The < 0.1 mm fraction is dominated by bioclasts and opaque minerals (most probably iron compounds) with some quartz. This grain size distribution suggests that the volcanic material represents ingredients that were added deliberately (intentional temper) to calcareous (with a high bioclast content) clays.

In contrast to common ware sherds, the table wares are characterised by a very fine material without any coarse temper. Only two[38] thin sections were available [Pl. 21]. The matrix of both samples contains very fine mica and opaque minerals [Pl. 21 a and d]. The non-plastic inclusions are of silt size (up to 0.06 mm) and consist mainly of quartz and mica and rare feldspar. Recarbonized carbonate aggregates and clay-carbonate aggregates are also observed as rare grains in fine sand fraction [Pl. 21c]. Microfossils are observed only very rarely, as seen in the example in Pl. 21f.

Five thin sections of CBM samples were studied. Samples MD3892 and MD3894 represent other clays. The raw material used for these two specimens of CBM obviously differ from each other and also from those of the other CMB, LegP and CW examined in thin section [Pl. 22]. The first one was made from a very silty clay (calcareous clay). The same inclusions are observed in the matrix and in the > 10µm fractions (up to *ca.* 100µm); they comprise: grains of quartz, pale and dark mica, few hornblende, few plagioclases, finely distributed carbonates as well as some opaque minerals. There are only rare grains of fine sand size (quartz and carbonate aggregates). In sample MD3894, which was made from a much less silty non-calcareous clay (parts of the matrix are enriched with carbonates), non-plastic inclusions observed in silt size comprise grains of quartz, pale and dark mica, opaque minerals and inhomogeneously distributed carbonates (crystalline and cryptocrystalline). In addition to grains of silt size, rare grains of sand fraction

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[38] MD2544 — this sample was submitted for analysis by E. Klenina, see Daszkiewicz, Bobryk, Schneider 2006; sample MD3242 was submitted for analysis by M. Baranowski, see Baranowski, Daszkiewicz 2009.

(including medium sand) of polycrystalline quartz and crystalline carbonates are also observed. Secondary cryptocrystalline carbonates are also observed as a fill in some pores.

Two further CBM samples (MD7230 and MD7238) are similar to each other. They were made from a silty calcareous clay. The fine inclusions are predominantly quartz grains, with a few larger inclusions of fine sand size [Pl. 22]. Mica plates are not visible at high magnification, only quartz, opaque minerals and inclusions of foraminifera [Pl. 23 b and f] as well as some inclusions of small gypsum crystals (pore fill left by gypsum remnants [Pl. 25 e]). The presence of gypsum is reflected in the results of chemical analysis by elevated sulphur contents. Several clay aggregates strongly coloured by iron compounds are visible in sample MD7230 [Pl. 23 c and d].

Another CBM sample (MD7234) was made from a silty clay. Quartz, mica, and opaque minerals are observed in the matrix. Some feldspars and few bioclasts are also observed in the > 10 µm fraction. The sample is heterogeneous, and a chain of quartz grains of fine sand size can be seen [Pl. 24 c] dividing the sample into two parts: one with fine sand grains and the other featuring only silt-size grains. Parts of the matrix are also coloured by iron compounds to various degrees [Pl. 24 d–f] — these areas represent parts of the sample that exhibit different thermal behaviour in MGR-analysis.

The presence of few microfossils in the CBM samples MD7230, MD7234 and MD7238 [Pl. 25d] as well as in brick MD3455,[39] which has a similar petrofabric, possibly indicates that the clays used to make these products are of a similar provenance.

The equivalent original firing temperature (Teq) of CBM samples, as estimated by K-H analysis,[40] was no lower than 800°C (with one exception) and not much higher than 1050°C (<1100°C). Most CBM was fired at a Teq of 850–950°C. Curves showing the values of open porosity, water absorption and apparent density vs. refiring temperature for six examples of CBM are shown in Fig. 6. In theory, during refiring up to the original firing temperature these values should remain constant. The first changes should appear above a temperature higher than the original firing temperature. But, in several CBM samples, an increase in the value of open porosity and water absorption with a simultaneous decrease in the value of apparent density was observed after refiring at 750°C, which is related to the thermal decomposition of carbonates (secondary cryptocrystalline carbonates within the pores and/or recarbonised carbonates) and not to the original firing temperature having been exceeded. X-ray diffraction performed on CBM sample MD7230 confirms the conclusions drawn from K-H analysis and observation of thin sections, namely that both calcite as well as gehlenite and diopside are present in this sample [Fig. 7].

All CBM samples, which were subjected to K-H analysis, are characterised by high values of open porosity (35–45 vol.%), high values of water permeability (21–29 vol.%[41]) and apparent density values varying from 1.49 up to 1.69 g/cm^3. The highest value of apparent density (2.07–2.20 g/cm^3) was estimated after refiring at 1150°C.[42] After refiring at 1200°C most of the samples exhibited secondary porosity.

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[39] This brick fragment was submitted for analysis in 2006 by T. Sarnowski (unpublished report).

[40] In K-H analysis values of open porosity, water absorption and apparent density were determined by hydrostatic weighing. These values were determined before and after refiring a fragment weighing 2–3 grams in controlled conditions at incremental temperatures (refiring carried out using the same procedure as for MGR-analysis, see footnote 30). After each refiring the samples were weighed for a third time in air. This process yielded three values: m_s – mass of dry sample; m_w – mass of wet sample weighed in air; m_{ww} – mass of sample weighed in water (with pores saturated by boiling in water). The values of physical ceramic properties were then calculated. Precision of the estimation of physical ceramic properties by hydrostatic weighing is about 1%.

[41] Given these high values of open porosity and water absorption, it would have been advisable to determine the water permeability of the roof tiles; however, this measurement could not be performed due to the size and shape of the briquettes submitted for analysis.

[42] MGR-analysis shows that maximum apparent density is attained in these sherds when they are fired at temperatures above 1100°C but below 1150°C.

The Teq determined for the majority of TW sherd samples fell within a range of 1000–1100°C; only two samples yielded a range of 700–800°C.[43] Estimation of original firing temperature was not performed on CW and LegP.

Measurement strategy and analysis results — clay raw materials

Regardless of its chemical and mineralogical-petrographic composition, the plasticity of the ceramic body from which all types of pottery and CBM are formed must be suitable for the given moulding technique, otherwise the end product will not retain the desired shape when it dries out. In light of this fact, analysis of clay raw materials began with a plasticity test, which was performed on all nineteen samples. This included an assessment of the water of plasticity (make-up water) content. This is calculated by determining how much water is needed for 100 grams of dry clay to become fully workable (i.e., the clay will not crack when shaped into a ball, and when pressure is applied to the ball it will become deformed but without developing any cracks). The analysed clay samples are characterised by a water of plasticity content that ranges from 24 g to 30 g H_2O/100g dry clay. Only one of the nineteen samples, the silty raw material (MD7195) with a content of 27 g H_2O/100g dry clay, could not be made into a plastic mass suitable for forming as required. The rest of the analysed raw materials could be made into a plastic mass that could be formed satisfactorily.

A firing test was performed as the next step in this study. The briquettes required for this test were made from a plastic mass (homogenised by hand) that was shaped in non-porous porcelain moulds. The resulting dome-shaped samples were dried in an electric laboratory dryer and then fired in a laboratory furnace.

The four clay samples from the series analysed in 2007 had been fired at eight temperatures: 400, 600, 700, 800, 900, 1000, 1100 and 1200°C [Fig. 8]. Firing at this range of temperatures (referred to as a full firing test) allows us to estimate the shrinkage on firing and colour of the

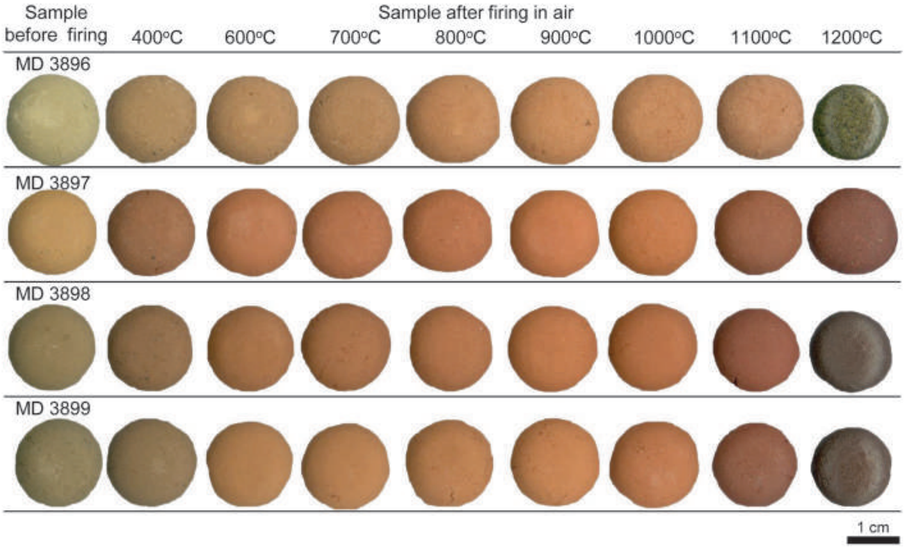

Fig. 8. Firing tests of four clay samples. The briquettes were made from a plastic mass (homogenised by hand) shaped in non-porous porcelain moulds (compiled by H. Baranowska)

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[43] Elena Klenina and Andrzej Biernacki project, see Daszkiewicz, Bobryk, Schneider 2006.

end product and also allows us to check whether there is a range of firing temperatures at which a briquette made from a given raw material will exhibit macroscopically visible structural and textural properties (macrofabric) similar to those of the ceramics whose raw materials we are trying to identify.

The clay samples analysed in 2020 were fired at only five temperatures: 800, 900, 1100, 1150 and 1200°C [Pls. 28–30]. It was not possible to perform the firing test at eight temperatures, therefore the number of firings was reduced to the three temperatures needed for comparison with the results of the MGR-analysis of CBM, CW and LegP (1100, 1150 and 1200°C) plus an additional two temperatures: 800 and 900°C. These two temperatures were selected because 800–900°C is the lowest probable temperature range at which the roof tiles that made up the bulk of the analysed CBM could have been fired. The samples were fired in a Carbolite electric laboratory resistance furnace, in static air, at a heating rate of 5°C/min, and a soaking time of 1 hour at the peak temperature. After the firing process had been completed, the samples were not removed from the furnace immediately, but were left inside it until they had cooled to room temperature (thus simulating the original firing of ceramics). Of the two briquettes that were fired at each temperature, one was left whole, whilst a thin slice was cut out from the middle of the second briquette. The surface of the fired briquette corresponds to the surface of a ceramic product, and the surface of the thin slice corresponds to the cut-section of a ceramic product (cut-section taken in a plane perpendicular to the axis of the vessel). Thus, a slice removed from a sample of CBM, CW or LegP for the purposes of MGR-analysis (original samples shown in Pls. 6–15) will look the same as (or very similar to) a slice removed from a briquette, as long as that particular briquette is made of the same clay that was used in the production of the given CBM, CW or LegP, and is fired in similar kiln conditions (temperature and atmosphere). At this stage, it is already possible to carry out a preliminary classification of the clays based on their suitability as ceramic raw materials for making the analysed CBM, CW and LegP. Comparing the results of MGR-analysis for samples of CW and LegP with the clay samples after the firing test revealed that only one raw material sample (clay MD3897) has a firing behaviour similar to the thermal behaviour of some of the refired LegP samples. In contrast to CW and LegP, at this stage of research fourteen raw materials can be considered as potential clay raw materials for the production of CBM.

As MGR-analysis consists of refiring slices removed from ceramic sherds, its results cannot be compared directly with the firing test results for clay raw materials. In MGR-analysis the thermal behaviour of the surface of a cut-section is observed, whilst in a firing test it is the behaviour of ceramic bodies (surface effect as well as texture and structure of cut-section of fabric) that is observed. A direct comparison with MGR-analysis results can be achieved by performing an *à la* ceramics test on the raw material samples. The differences between the firing test and the *à la* ceramics test are shown in Fig. 9 using the example of Bâla Voda clay. Cut slices in the *à la* ceramics test lose the appearance of cut-sections from the firing test and exhibit thermal behaviour like that of the surfaces of the briquettes from the firing test. All of the samples were made from the same ceramic body, therefore the thermal behaviour of the refired slices is the same as the thermal behaviour of the briquettes in the firing test after refiring/firing at 1150 and 1200°C. An *à la* ceramics test was carried out on only fourteen raw material samples. Five samples that could not have been clay raw materials used for making CBM were excluded: four of them because their firing behaviour (as revealed by the firing test) was markedly different to the thermal behaviour of the CBM samples (clay samples MD3896–3899) and one (clay MD7195) because it was not even suitable for making bricks. At this point, twelve further briquettes were made from each clay, and these were fired in the same conditions as described above at 800 and 900°C. Samples fired in this way simulated ceramic goods fired in an oxidising atmosphere at 800 or 900°C. The fired samples (ceramic goods) were then treated like fragments of archaeological ceramics, hence they

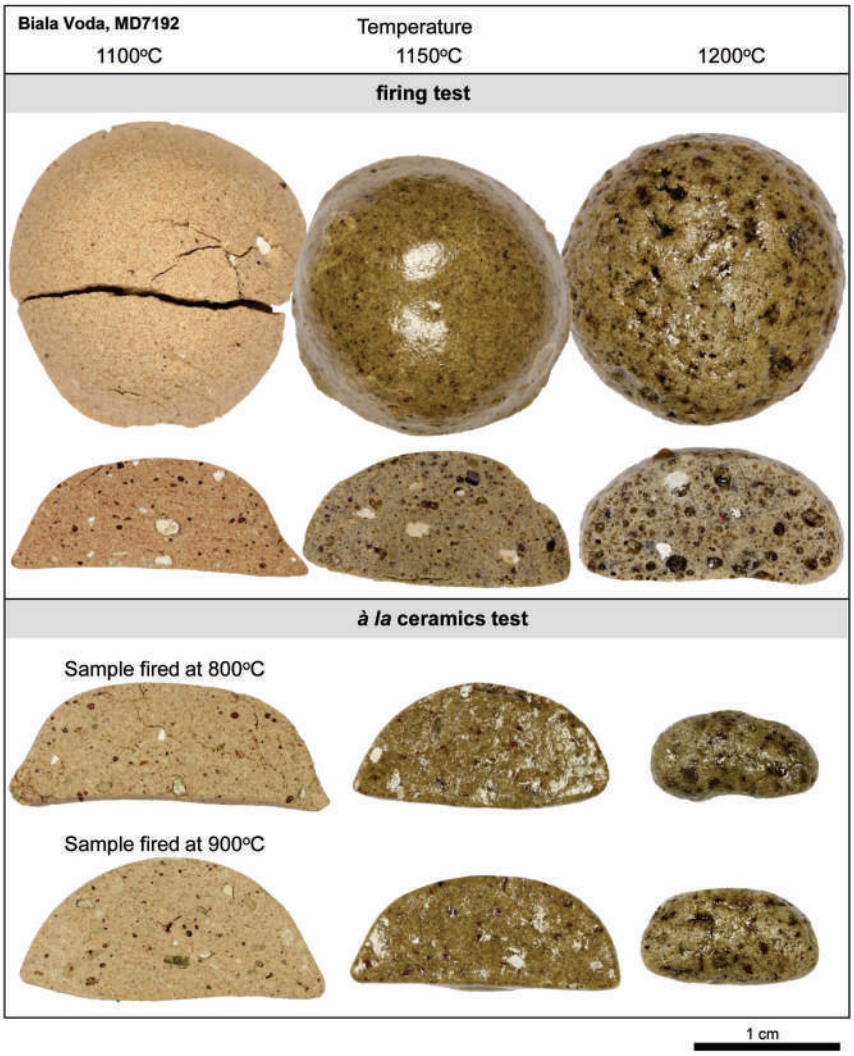


Fig. 9. Differences between the firing test and the *à la* ceramics tests
(briquettes made from Bâla Voda clay)
(compiled by H. Baranowska and M. Daszkiewicz)

were subjected to MGR-analysis in exactly the same way that MGR-analysis[44] is carried out on samples of pottery recovered from archaeological sites. This means that thin slices were removed from each briquette and these were subsequently refired at the standard range of temperatures for abridged MGR-analysis, namely at 1100, 1150 and 1200°C. Additional refiring was also performed at 800 and 900°C [Pls. 31–32]. After refring at these temperatures only minimal changes in the thermal behaviour of the surface of cut-sections were observed.

One of the clays (Bâla Voda clay, MD7192) is a calcareous clay with natural temper in the form of clay-carbonate aggregates (hereinafter referred to as grains of marl) measuring up to 1.5 mm. These grains undergo thermal decomposition during the firing process and cause cracks in the end product. However, clays of this type are used to make bricks after the marly grains have been neutralised. Marl can be neutralised in a variety of ways.[45] The mechanical method involves

[44] See footnote 30.

[45] Rybka 1963.

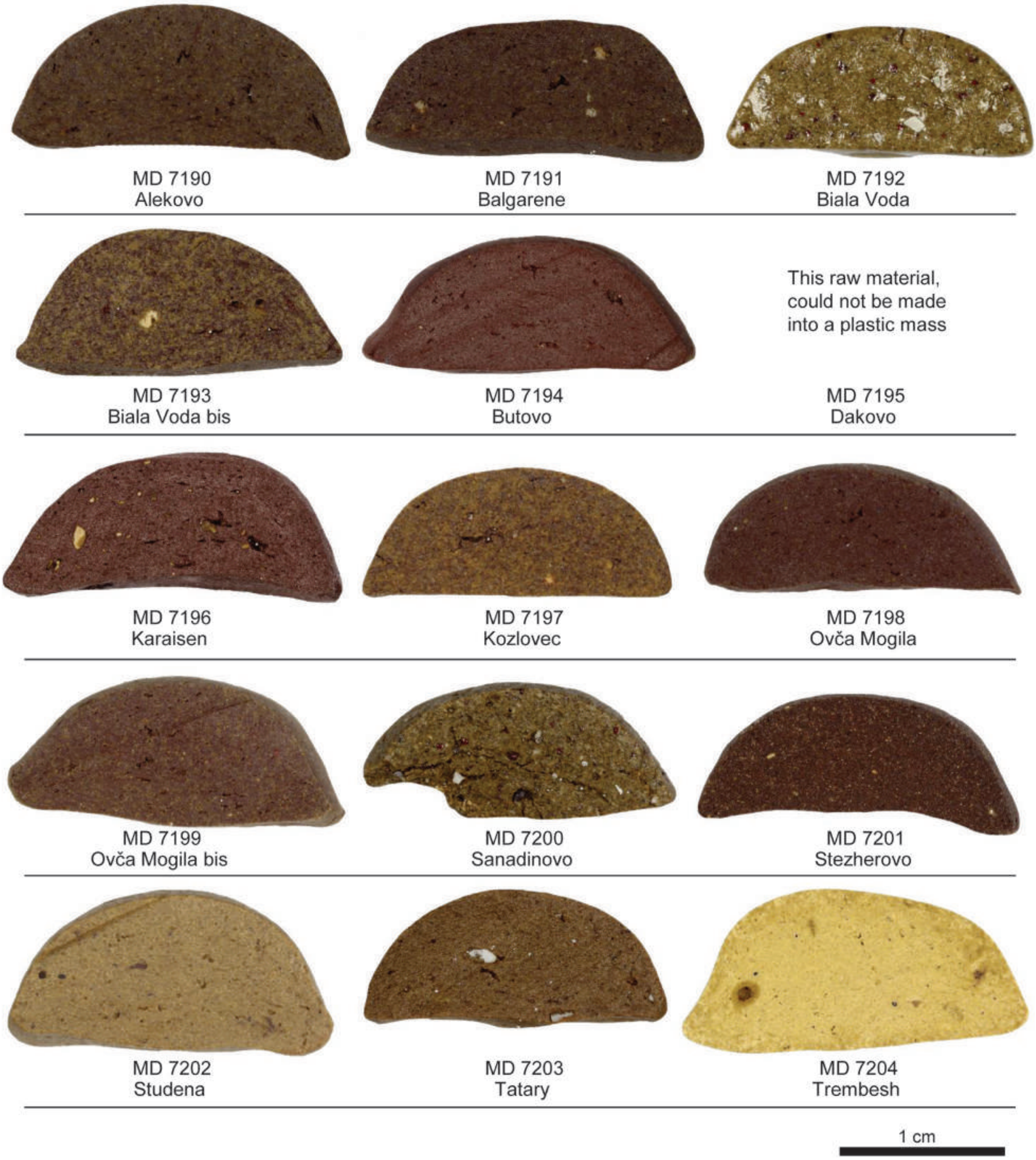
breaking down the marl grains to a harmless size by drying the clay, crushing it in specially adapted disintegrators and sieving it using vibrating sieves, which yields good results but is too expensive a method to use in small, traditional pottery workshops or brickmaking works (only manual strength is used). The thermal method involves firing products at a temperature high enough to produce CaO and SiO_2 compounds that do not undergo hydration. This method is effective at firing temperatures above 1100°C. There is also a chemical method, in which chemical compounds such as sodium, potassium or calcium chlorides are added to the ceramic body, and a mechanico-chemical method, which involves immersing fired ceramic products in water immediately after they have been removed from the kiln and while they are still warm.

In traditional pottery/brickmaking it is fairly common to add table salt to the ceramic mass (which leads to the formation of water-insoluble calcium silicates during firing), or to use saline make-up water. In brickmaking marly grains are also neutralised by quenching the product in a water bath.

Two methods of neutralising marly grains were investigated using model tests performed for the purposes of this study. These tests were conducted in order to assess whether Bâla Voda clay is suitable for making CBM without first removing / breaking down the natural temper of marly grains. Two series of briquettes were made with the addition of table salt (5 wt.% and 10 wt.%), and another series was made without any added salt. All series were fired at 800°C (in a firing test carried out the next day samples cracked after firing at 800°C). One part of the briquettes with added salt was cooled according to the same procedure as that used for briquettes in the firing test; however, the second part of the briquettes with added salt and the briquettes with no added salt were removed from the kiln after the temperature had dropped to 30°C and were immersed in water at room temperature. The model tests showed that both the addition of table salt and quenching in a water bath neutralised the marl grains. The briquettes were observed for four months after the marl grain neutralisation tests had been performed, after which time no carbonate blooms appeared on the samples, which were stored in an air-dry state, and no cracks were observed. However, crack propagation occurred and continues to occur in samples after the firing test: the samples shown in Pl. 11 fall apart into small pieces.

Model tests carried out on products made of Bâla Voda clay, in which the marl grains were neutralised using only a mechanico-chemical method (i.e., by quenching in a water bath), also revealed that the briquettes with no added salt were characterised by a uniform beige-red colour, in contrast to the briquettes with added salt, which fired unevenly and featured parts with a lower saturation of red. Thus, Bâla Voda clay is a clay raw material that can be used to make CBM if the appropriate technology is applied.

As shown by the firing test, only one of the clay raw materials is fireproof after firing at 1200°C (MD3897). Most of the other clay raw material samples analysed are not fireproof once they have been fired at 1150°C — just like 52 of the 54 CBM samples. Each of the analysed clay raw materials is characterised by a different thermal behaviour, which proves that the phase and chemical compositions of these materials are markedly different. Fig. 10 shows the cut-sections of briquettes fired at 1200°C. Given that all of the briquettes were the same shape and size before they were fired, the differences observed in thermal shrinkage and thermal expansion are significant, number and size of pores also exhibit equally marked differences. Fig. 11 shows cut-sections after the *à la* ceramics test for the same samples refired at 1150°C (the optimal temperature for comparing with refired CBM samples). After the *à la* ceramics test some of these samples exhibit similar thermal behaviour to that observed in CBM samples defined as mixed clays of the NC-CC type. Fig. 12 shows briquettes made of Bâla Voda Bis and Ovča Mogila Bis clays. In both cases a matrix of the "mixed clays of the NC-CC type" is clearly visible; however, this is not a result of the intentional mixing of two types of clay but a feature of the original raw material.



MD 7190
Alekovo

MD 7191
Balgarene

MD 7192
Biala Voda

MD 7193
Biala Voda bis

MD 7194
Butovo

This raw material, could not be made into a plastic mass

MD 7195
Dakovo

MD 7196
Karaisen

MD 7197
Kozlovec

MD 7198
Ovča Mogila

MD 7199
Ovča Mogila bis

MD 7200
Sanadinovo

MD 7201
Stezherovo

MD 7202
Studena

MD 7203
Tatary

MD 7204
Trembesh

Fig. 10. Cut-sections of briquettes fired at 1200°C (firing test)
(compiled by H. Baranowska)

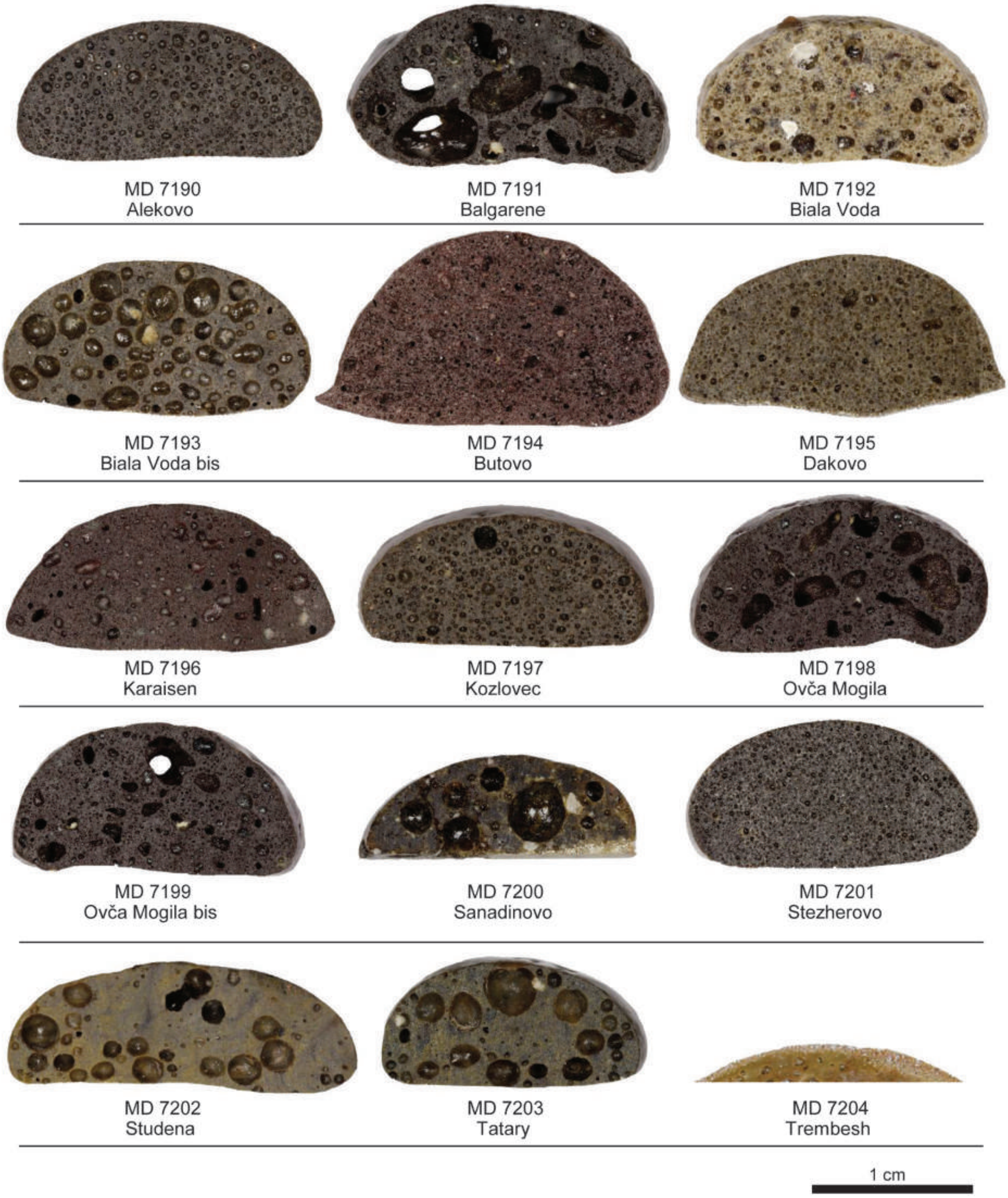


Fig. 11. Cut-sections of briquettes, refired at 1150°C of samples beforehand fired at 900°C (*à la* ceramics test) (compiled by H. Baranowska)

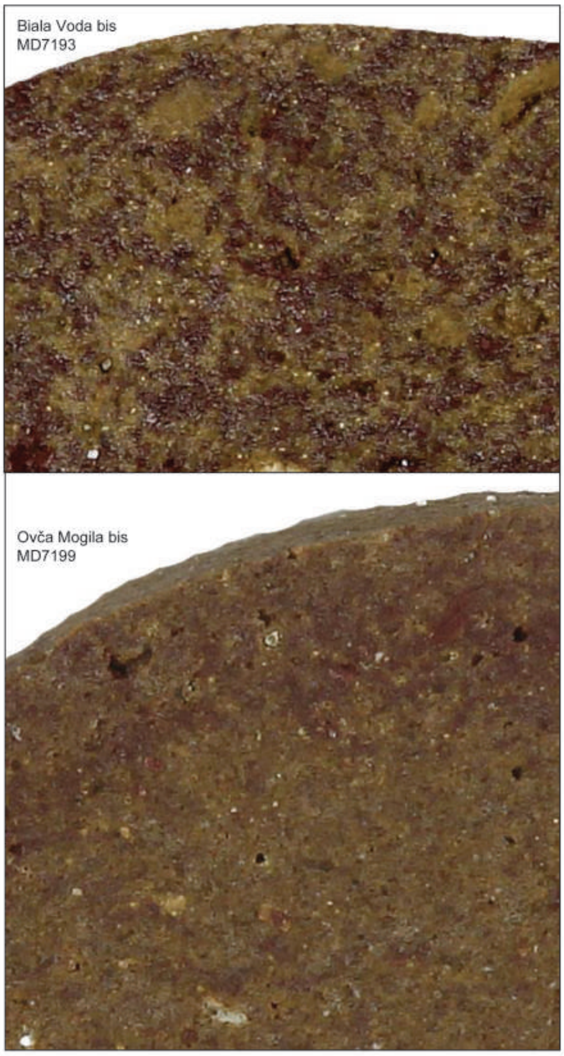


Fig. 12. Briquettes refired at 1150°C of samples made of Bâla Voda Bis and Ovča Mogila Bis clays beforehand fired at 900°C (*à la* ceramics test). In both cases a matrix of the "mixed clays of the NC-CC type" is clearly visible; however, this is not a result of the intentional mixing of two types of clay but a feature of the original raw material

Next, chemical analysis was conducted on all of the clay raw material samples [Table 3]. The chemical composition of the samples is just as diverse as their thermal properties [Figs. 10–11]. But, generally speaking, all of the clay raw materials are characterised by a low chromium content of 62–112 ppm (one clay sample, taken from a geological stratum beneath the *porta Praetoria*, has Cr content of 122 ppm) and a low nickel content of 25–70 ppm.

The only clay sample (MD3897) which is not over-fired at up to and including 1200^{o}C, contains 80.9 wt.% of SiO_2, but with quartz grains not visible to the naked eye [Fig. 8] and in spite of its high silicon content is plastic.

Clay	Lab. No.	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	V	Cr	Ni	Cu	Zn	Rb	Sr	Y	Zr	Nb	Ba	La	Ce	Pb	Th	l.o.i.
		% by weight										ppm															%
Nov-clay-1	MD3896	65.23	0.900	13.36	4.86	0.094	3.44	7.92	1.73	2.29	0.16	115	112	46	16	69	89	196	36	342	12	430	37	85	20	19	9.1
Nov-clay-2	MD3897	80.88	0.486	10.30	3.87	0.048	0.91	1.66	0.19	1.57	0.09	92	62	35	18	54	74	46	19	155	10	203	24	50	85	16	3.8
Nov-clay-3	MD3898	71.58	0.958	14.30	5.85	0.064	1.88	1.15	1.59	2.48	0.17	135	122	54	25	83	104	138	39	354	13	406	36	93	21	22	3.4
Nov-clay-4	MD3899	73.63	0.922	13.46	5.04	0.100	1.58	0.88	1.37	2.82	0.21	125	111	50	20	65	94	99	36	355	12	375	34	95	18	23	3.4
Alekovo	MD7190	62.68	0.768	15.36	6.02	0.080	2.43	8.98	0.92	2.61	0.15	139	97	59	35	94	133	250	29	202	16	366	30	54	50	7	10.2
Balgarene	MD7191	65.66	0.741	14.49	5.63	0.076	1.93	7.95	0.86	2.54	0.14	127	90	53	29	85	125	267	28	224	16	311	38	62	47	6	8.6
Biala Voda	MD7192	70.47	0.566	8.02	4.27	0.039	1.47	12.75	0.47	1.81	0.14	76	66	25	9	49	87	236	27	322	13	205	6	46	17	<5	10.9
Biala Voda bis	MD7193	64.81	0.802	14.00	5.10	0.063	3.00	9.43	0.92	1.75	0.13	98	96	51	18	79	87	204	44	299	16	326	47	66	25	6	10.7
Butovo	MD7194	61.22	0.896	19.75	7.46	0.110	2.11	3.92	0.99	3.37	0.17	155	112	68	54	109	158	211	32	187	17	382	24	63	68	9	6.9
Dakov	MD7195	72.95	0.930	9.98	3.73	0.076	2.29	6.27	1.70	1.86	0.23	82	100	28	16	53	77	181	40	455	17	329	52	97	24	<5	7.0
Karaisen	MD7196	68.65	0.979	14.71	5.97	0.113	2.35	3.19	1.33	2.54	0.18	117	112	56	28	81	120	126	40	326	19	450	46	82	44	8	5.7
Kozlovets	MD7197	65.98	0.919	13.32	5.19	0.095	2.97	7.93	1.31	2.14	0.15	100	109	47	20	72	104	230	42	387	17	444	32	71	40	<5	9.1
Ovča Mogila	MD7198	62.99	0.791	16.24	6.16	0.080	2.06	7.85	0.86	2.84	0.14	141	98	61	34	93	142	249	30	210	16	289	33	80	43	7	9.2
Ovča Mogila bis	MD7199	62.15	0.781	16.79	6.13	0.075	2.11	7.99	0.87	2.95	0.15	148	100	63	35	92	144	245	30	198	16	312	52	60	46	8	9.2
Sanadinovo	MD7200	60.03	0.656	11.78	5.84	0.074	2.57	15.22	0.95	2.42	0.47	90	92	44	24	66	108	314	36	273	12	317	30	53	32	11	13.5
Stezherovo	MD7201	67.95	0.959	13.48	5.26	0.099	3.29	4.61	1.73	2.43	0.20	106	105	50	18	74	105	151	41	362	17	477	13	75	34	7	6.7
Studena	MD7202	54.33	0.660	16.82	6.05	0.057	2.41	15.82	0.91	2.74	0.21	157	103	69	47	113	149	355	31	172	13	335	49	44	39	7	14.9
Tatari	MD7203	53.88	0.668	16.52	7.00	0.068	2.11	16.20	0.65	2.76	0.13	136	95	70	25	107	140	565	26	183	14	308	20	67	33	<5	14.4
Trembesh	MD7204	50.86	0.584	15.05	5.14	0.072	2.22	22.72	0.79	2.44	0.12	121	84	54	31	90	122	742	26	175	13	301	14	54	31	<5	17.9

Table 3. The results of chemical analysis by WD-XRF. Concentration of major elements normalised to 100%, measurement of melted, ignited samples; l.o.i. = loss on ignition at 900°C

This sample is also characterised by a low Zr content and the highest SiO_2/Zr (0.52) ratio of all the analysed raw materials, as well as by low levels of Fe_2O_3, MgO and K_2O, and very low concentrations of TiO_2 and Na_2O. In contrast, the only non-plastic raw material, Dakot clay (MD7195), is characterised by a low Al_2O_3 content, a high Zr content, which is the highest among all of the analysed raw materials, but also by the lowest SiO_2/Zr (0.16) ratio. Bâla Voda clay (MD7192) is also distinctive, among other things because of having the lowest Al_2O_3 content of all 19 analysed raw material samples and the lowest SiO_2/Zr (0.11) ratio. These three clays also have very low levels of nickel (Ni 25–35 ppm). Butovo clay differs from all of the other raw material samples in having the highest concentration of Al2O3 and F2O3. Only six clay samples have a CaO content of up to 4.6 wt.%; three of these samples were collected from Novae. Five samples have a CaO content of 12.8–16.2 wt.% and the Trembeš sample (MD7204) has a CaO content of 22.7 wt.%. The high levels of CaO in these samples are attributable to carbonates connected with the matrix [Figs. 10–11]. Elevated CaO content is correlated with the proportion of the matrix that fires various shades of olive-green, and the intensity of these shades in the colour of the matrix, after the firing test [Fig. 10]. There is only one sample (Bâla Voda, MD7192) in which the CaO content is related to the matrix as well as to grains in coarse fraction, as shown by the results of the firing test [Pl. 11, and see description four paragraphs ago].

After comparing firing and refiring behaviour as well as chemical composition of clay raw materials with the thermal behaviour and chemical composition of the CBM, two clay samples were selected for XRD analysis [Figs. 13–16], and thin sections were made from green raw materials and fired briquettes [Pls. 37–39].

The decision to perform X-ray diffraction analysis on only two clay samples should come as no surprise given that this technique, which is widely used by geologists to determine mineral composition, is of limited use in the study of archaeological ceramics. X-ray diffraction analysis makes it possible to determine mineral phases in a clay sample. However, one recording is not enough to accurately identify clay minerals. In X-ray diffractograms of individual groups of layered silicates, the location of even the most intense reflexes is not characteristic of a single mineral. Accurate identification of clay minerals can be achieved by threefold recording on oriented preparations (after separating the clay fraction), using air-dry natural samples, samples saturated with glycerol and samples calcined at 500^{o}C. The results obtained from three such measurements are used for a more precise interpretation of general diffractograms of the analysis of whole clay samples.

Figs. 13 and 14 show diffractograms of two clay samples: Ovča Mogila Bis clay and Studena clay.[46] For kaolinite and chlorite there is a coincidence of basal 001 (kaolinite) and 002 (chlorite) reflexes, and for smectites, a coincidence of basal 001 reflexes (chlorite and air-dry smectite) is possible. After calcination at 500°C, kaolinite is transformed into an amorphous phase (metakaolinite), and therefore the reflexes originating from this mineral "disappear" from the diffractogram. In a preparation saturated with ethylene glycol, the 001 smectite reflex changes position (swelling).

The following clay minerals were identified in Ovča Mogila Bis clay (MD7199): chlorite, a mixed-layer mineral of the chlorite-smectite type, illite (and/or mica), and kaolinite. The presence

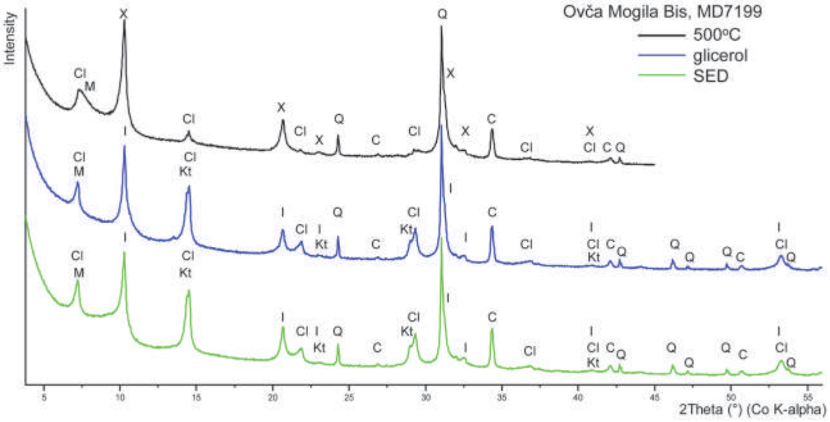


Fig. 13. X-ray diffractograms of Ovča Mogila Bis clay: 500°C = preparation after calcination at 500˚C for 3 hours; glicerol = air-dry preparation saturated with ethylene glycol; SED = air-dry natural sample; samples separated by the sedimentation method

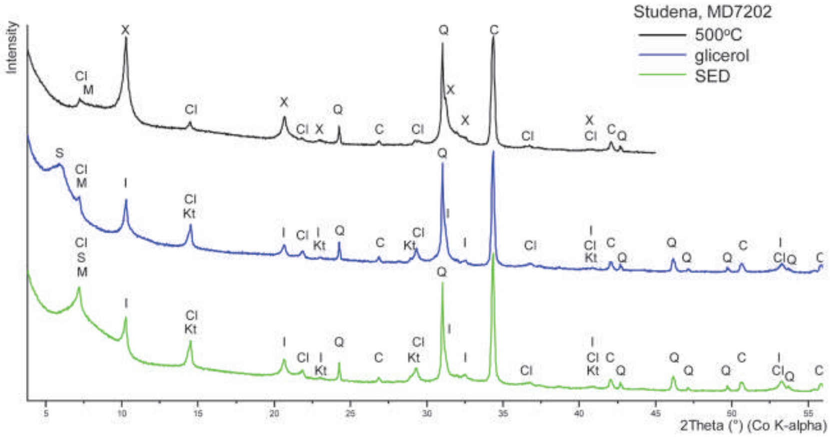


Fig. 14. X-ray diffractograms of Studena clay: 500°C = preparation after calcination at 500˚C for 3 hours; glicerol = air-dry preparation saturated with ethylene glycol; SED = air-dry natural sample; samples separated by the sedimentation method

[46] Oriented preparations were made from samples separated by the sedimentation method and recorded on a diffractometer using the Bragg-Brentano method in the following ranges: 3.8–56˚ 2θ (air-dry preparation saturated with ethylene glycol), 3.8–45˚ 2˚ (preparation calcined at 500˚C for 3 hours). The total measurement times of a single recording were: 1 hour 30 minutes (air-dry preparation saturated with ethylene glycol); 1 hour 12 minutes (preparation calcined at 500˚C for 3 hours). Measurement parameters: step 0.026˚ 2θ. Filtered CoKα radiation (Fe filter) with current parameters of 30 mA and 40 kV. Radiation detection — fast line PIXcel detector (analysis by G. Kapron, UW).

of quartz and calcite was also detected, and in the calcined preparation, a mica-like phase formed after heating of the clay minerals [Fig. 13].

The following clay minerals were identified in Studena clay (MD7202): smectite, chlorite, a mixed-layer mineral of the chlorite-smectite type, illite (and/or mica), and kaolinite. The presence of quartz and calcite was also detected, and in the calcined preparation, a mica-like phase was formed after calcination of the clay minerals [Fig. 14].[47]

Due to the thermal properties of clay minerals (i.e., their dehydroxylation and the formation of new phases produced by collapsed clay minerals depending on the firing temperature), as already mentioned, the application of XRD is of limited use in the analysis of archaeological ceramics. Figs. 15 and 16 show the results of XRD analysis of two raw material samples before and after firing. Six briquettes made of each clay were fired using the same procedure for preparing the briquettes and the same firing conditions as those used in the firing test. In the diffractograms of two different raw materials fired at 800°C, the clay mineral reflexes disappear, but in both cases a muscovite reflex is visible. A faint muscovite reflex is also visible after firing at 900°C; it is not visible in the diffractograms of the briquettes fired at 1000°C and at higher temperatures.

The most likely original firing temperature range for historic CBM is 800–1000°C. Comparing the diffractograms of the two raw materials fired at 800, 900 and 1000°C (which corresponds to ceramics made of these clays fired at these temperatures without the intentional addition of

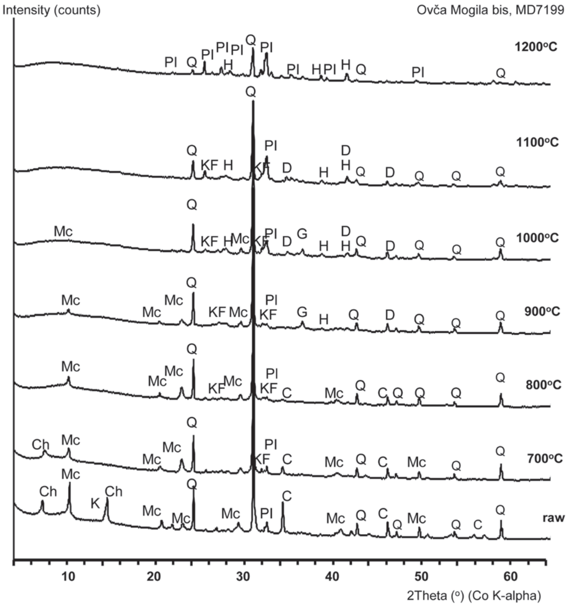


Fig. 15. X-ray diffractograms of briquettes made of Ovča Mogila Bis clay fired at various temperatures (Ch = chlorite, Mc = micas, K = kaolinite, Q = quartz, Pl = plagioclases, KF = K-feldspars, C = calcite, D = dolomite, H = hematite, W = wollastonite, G = gehlenite)

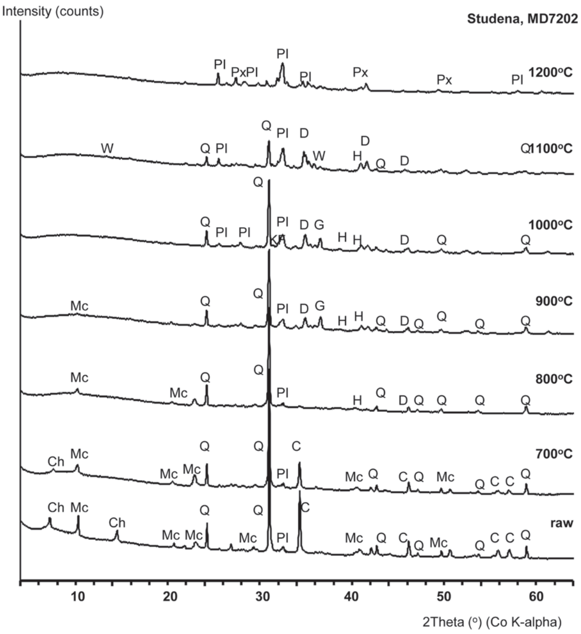


Fig. 16. X-ray diffractograms of briquettes made of Studena clay fired at various temperatures (Ch = chlorite, Mc = micas, K = kaolinite, Q = quartz, Pl = plagioclases, KF = K-feldspars, C = calcite, D = dolomite, H = hematite, W = wollastonite, G = gehlenite)

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[47] The results correspond to the clay minerals identified in Regosols from Lom-Svištov region (Hristov, Atanasova, Teoharov 2010).

non-plastic particles) reveals that there is no reflex characteristic of clay minerals. The observed differences are related to the intensity of calcium aluminosilicate reflexes (new phases related to thermal changes of calcite). But if only XRD analysis is performed for a given ceramic product, it will not be possible to determine whether the carbonates are associated with the plastic or the non-plastic part (e.g., with an intentional temper of crushed carbonates) of the ceramic body. In order to correctly interpret the results, the necessary minimum required is the results of macroscopic ceramic fabric analysis, and preferably the results of MGR-analysis and/or thin-section studies.

Generally speaking, XRD analysis can be used to give a rough estimation of the original firing temperature,[48] but it is rarely (or even very rarely) useful in provenance studies. Determining the composition of the types of clay minerals present in a given raw material will not help in provenance studies when, for comparison with the phases present in the raw material, we have the phases present in the ceramic product. To some extent, it may be helpful to determine the mineral composition of the ceramic body by using rational analysis,[49] i.e., analysis of the rational composition, or in other words the hypothetical minerals that make up a given raw material determined on the basis of its chemical composition presented in the form of oxides, whose content was determined by classical chemical analysis. SEM/EDS analysis can be used to determine the matrix composition, but it must be borne in mind that rather than yielding comprehensive mineralogical data, this analytical method simply provides information about chemical elemental composition from which we can draw conclusions about mineralogical composition based on what we know about the given sample, including details of its shape, appearance, etc. (the same chemical composition does not equate to the same mineral).

If, for example, in a CBM sample we detect the presence of inclusions with a chemical composition corresponding to that of kaolinite, this does not unequivocally mean that there is any kaolinite in the sample, as after firing kaolinite undergoes structural collapse (at *ca*. 500°C), and kaolinite could not exist as a mineral phase in CBM (i.e., in a stable ceramic product). On the other hand, the presence of primary kaolinite (primary meaning the clay mineral in the raw material used for pottery making, not impurities connected with the secondary contamination of the sherd during its deposition in an archaeological context) would indicate firing at too low a temperature (a temperature so low that dehydroxylation of kaolinite and transformation into methakaolinite did not take place),[50] and such a pseudo-ceramic product would disintegrate on contact with water.

A water conditioning test was carried out on fifteen raw materials sampled in 2020, from which briquettes were made and fired at 500°C and then immersed in distilled water. Eleven of the briquettes regained plasticity in the water — a suspension formed either immediately after immersion or after several hours had elapsed, and after the evaporation of any excess water the samples regained plasticity to varying degrees. Four of the briquettes disintegrated (leaving small nodules) but did not regain plasticity (Karajsen, Kozlovec, Sanadivevo and Stežerovo clays).

The next step in analysing the raw materials was a thin-section study. When analysing clay, thin-sections should be prepared from green raw materials, and, in order to compare them with finished ceramic products, further thin sections should be prepared from briquettes made of a given clay that has been fired in various firing conditions. Fig. 17 shows micrographs of thin sections of Studena clay in the green stage[51] and fired at 800°C — the differences in the microscopic images, as expected, are very clear.

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[48] This is one of the so-called static methods used for the estimation of original firing temperature. Static methods focus on analysing specific characteristics from which the firing temperature is then estimated. In the case of XRD analysis estimation of firing temperature is based on the presence or absence of particular mineral phases.

[49] The concept of rational composition was introduced by the German chemist Herman Bollenbach.

[50] In technological terms this is drying not firing.

[51] For the purposes of this study, one thin-section was prepared from green clay.

The thin sections described below were made from briquettes made from three samples of clay (Studena, Ovča Mogila Bis and Bâla Voda Bis clays) after they had been fired.

The Studena clay (MD7202) thin section was made from a briquette fired at 800°C (see description of firing test), thus the microscopic image should be like that of a ceramic product made without any intentional temper and fired in an oxidising atmosphere at 800°C. The matrix is unevenly coloured by iron compounds; small, randomly distributed patches of matrix very strongly coloured by iron compounds are clearly visible [Pl. 37a]. Only inclusions of silt size are observed in the field of view as well as some mica consisting of quartz [Pl. 37a–f]. Microfossils are also observed [Pl. 37d–f]. This makes this clay similar to CBM sample MD7230 and sample MD7238 [Pls. 23–24].

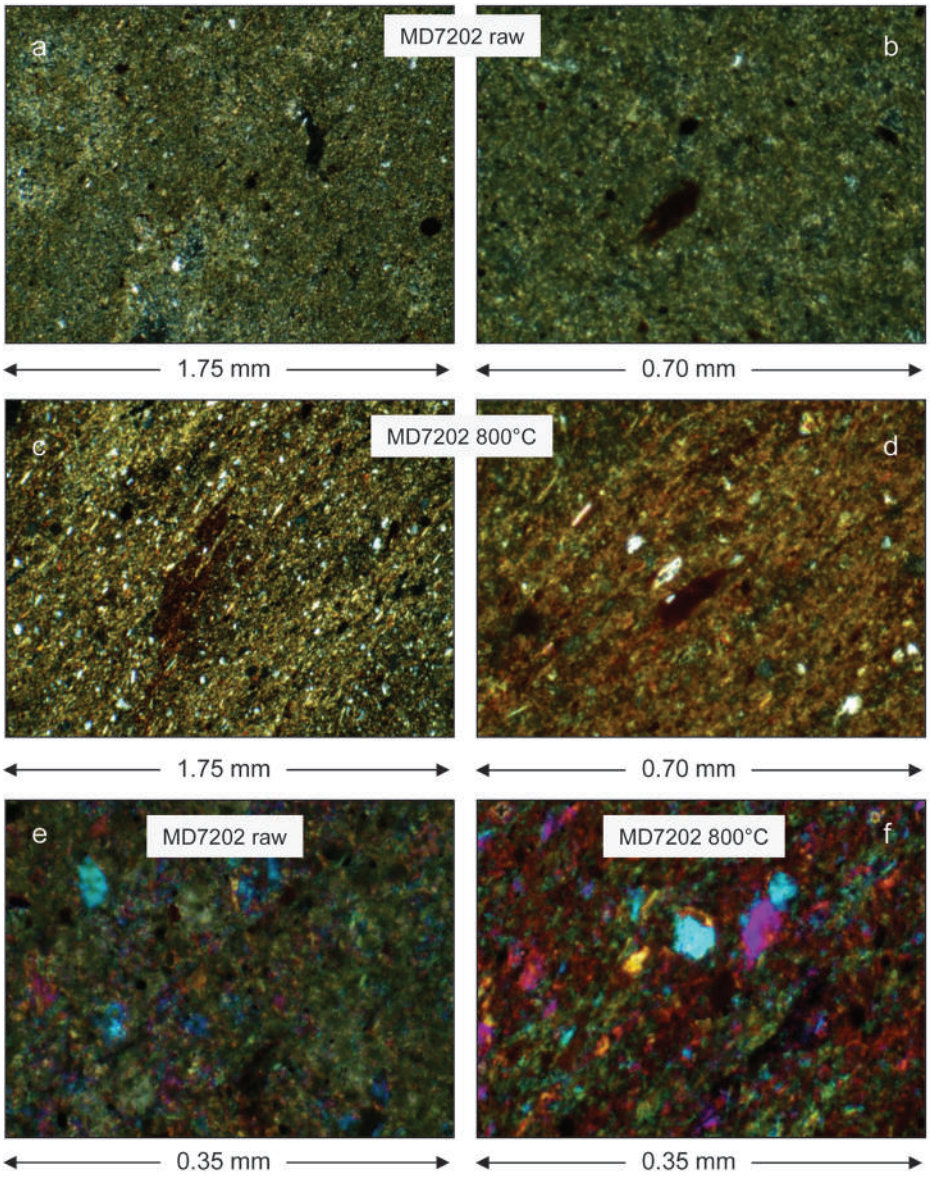

Fig. 17. Typical image of thin sections of Studena clay in the green stage
and of briquettes made of Studena clay fired at 800°C
(Micrographs, XPL, e and f with quartz plate)

The clay sample from Ovča Mogila Bis (MD7199), like the Studena clay, was examined in the form of a thin section taken from a briquette fired at 800°C. As with the Studena clay, all of the inclusions are of silt size and represent quartz and some mica, as well as opaque minerals (iron compounds) inhomogeneously distributed in the matrix [Pl. 38]. Only some inclusions of former gypsum crystals are larger than the quartz [Pl. 39a and c]. The gypsum content is confirmed by chemical analysis. This sample also features microfossils like the foraminifera in CBM samples [Pl. 39 e and f].

Two clay samples fired at 1150°C were also examined [Pl. 38a and b]. No shapes that would indicate the original presence of gypsum and bioclasts are observed in the briquette made from Ovča Mogila Bis clay. In contrast to the sample fired at 800°C, patches of matrix variously coloured by iron compounds are clearly visible, with a predominance of patches very strongly coloured by iron compounds. Those areas which are lightly coloured are small and finely distributed, which is easily visible macroscopically in the firing test. A similar effect can be seen in some of the CBM samples in MGR-analysis.

As in the case of the briquette made from Ovča Mogila Bis clay, no remains of microfossils are observed in the briquette made from Bâla Voda Bis clay (MD7193). Patches of matrix variously coloured by iron compounds are also clearly visible, but areas that are lightly coloured predominate and individual patches are larger [Pl. 38c–f]. The sample of Ovča Mogila Bis clay is somewhat different from the sample of Bâla Voda Bis clay (MD7193) which, however, is only very clear in the chemical data regarding K and Rb and in the firing test.

Combining the results obtained from analysis of CBM, CW, LegP and clay samples

The first step in writing up these analysis results was to group the samples according to their chemical composition using the finger method.[52]

This preliminary comparative analysis incorporates the results of chemical analysis performed on all of the ceramic sherds recovered from Novae that were submitted to the laboratory, including the various types of amphorae analysed in 1999.[53] This analysis revealed that several Zeest 64 amphorae[54] have a similar chemical composition to that of CW pottery, and therefore these amphorae were included in the second stage of the comparative study. Four major groups and six outlier samples were identified using the finger method. Several groups and subgroups can be distinguished within each major group, most of which in the case of CBM are represented by no more than one sample.[55]

Multivariate statistical analyses[56] were employed to confirm the groupings defined using the finger method. Firstly, to reliably assess which elements best distinguish samples from specific groups, a principal components analysis (PCA) was performed[57] on the results obtained by

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[52] Or "by eye" as it is sometimes referred to.

[53] Daszkiewicz *et alii* 2000.

[54] These sherds were found during excavation of the *thermae legionis*, and the amphorae were dated to the late first century AD based on their archaeological context (Daszkiewicz *et alii* 2000).

[55] The term "group" is used even when that group is represented solely by one sample. Because it is improbable that only a single vessel would have been produced from one ceramic body, it is assumed that the analysed sample represents a group of vessels made from the same material. This is why the term "group" is used even in those cases where groups are represented by just a solitary sample.

[56] All multivariate clusters analysis, principal components analysis and discriminant analysis were carried out using a licensed copy of the SYSTEM Package obtained from the Weierstrass Institute for Applied Analysis and Stochastics, Leibniz Institute in Forschungsverbund Berlin e.V.

[57] Using concentrations of the following elements: Si, Ti, Al, Fe, Mn, Mg, Na, Ca, K, V, Cr, Ni, Zn, Rb, Sr, Y, Zr, Nb, Ba and Ce.

WD-XRF. In the PCA, the two first components explain only 45% of the variation (component 1 [PComp1] explains 25.2% of the variation, and component 2 [PComp2] explains 19.8%,), component 3 (PComp3) explains 16.8.0% of the variation and the remaining seventeen components explain 38.2%. The results of PCA, PComp1 vs. PComp2 are shown in Fig. 18a — pottery types were defined as separate clusters[58] and all clay samples as one cluster. As can be seen from the loadings plot [Fig. 18b], combinations of positive and negative loadings (mixed loadings) are not prevalent; only two variables have mixed loadings where positive and negative loadings are similarly high — concentrations of calcium (CaO) and rubidium (Rb). Three variables have a similar correlation with PC1 as well as with PC2 — concentrations of magnesium (MgO), vanadium (V) and barium (Ba). The highest component positive loadings correlated with PCompl have a concentration of Ca whilst the highest component loadings correlated with PCom2 have concentrations of silicon (SiO_2). Concentrations of aluminium (Al_2O_3), iron (Fe_2O_3), potassium (K_2O) and strontium (Sr) are present in the highest component loadings correlated with PComp3. The PCA results confirmed the groupings and the significance of particular chemical elements determined using the finger method. The PCA showed that the samples of CW, along with Zeest 64 amphorae and LegP sherds, are very distinct from all of the others ceramic fragments [Fig. 40a]. High CaO as well as high MnO and Sr concentrations and low SiO_2 concentrations play a significant role in distinguishing the cluster made up of CW and cluster of Zeest 64 amphorae.

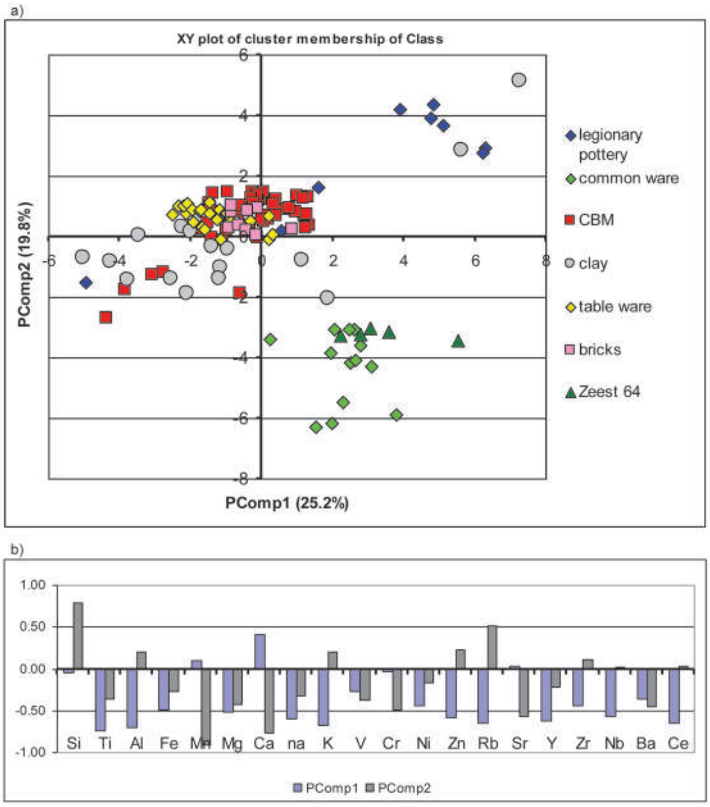

Fig. 18. Results of a PCA of chemical analysis results
(the concentration of the following elements were used:
Si, Ti, Al, Fe, Mn, Mg, Na, Ca, K, V, Cr, Ni, Zn, Rb, Sr, Y, Zr, Nb, Ba and Ce)

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[58] Individual clusters encompass LegP, CW, CBM, TW, bricks submitted by T. Sarnowski (referred to as “bricks -TS” hereinafter) and Zeest amphorae found in Novae.

Concentrations of the same elements play a significant role in distinguishing the cluster consisting of LegP sherds (except for three samples), but there is an opposite correlation. In contrast, samples belonging to those groups of cluster LegP located almost symmetrically on the other side of the X axis are distinguished by a low concentration of CaO as well as MnO and Sr and a higher content of SiO_2.

In the PCA results, five CBM samples are outliers from the group of CBM samples. The remaining CBM samples, as well as bricks-TS and TW clusters form a relatively compact group in which most of the TW samples exhibit a clear shift towards lower PCom1 values [Fig. 18a]. Generally speaking, samples representing the TW cluster have a higher Al_2O_3 content than most CBM samples.

Multivariate cluster analysis was performed next. Fig. 19 presents the results of this analysis in the form of a dendrogram.[59] Eleven clusters were singled out (cluster numbers are given in column C), and most of them can be further divided into sub-clusters. These clusters can be grouped in five major groups of clusters: major cluster groups A, B, C, D and E. The first major cluster group, group A, consists of two clusters (clusters 1 and 2) jointly made up of six samples. Five of them are LegP samples, and one is a clay sample (MD3897, Nov-2, samples taken from the side of an escarpment). The second major cluster group, group B, comprises four clusters (clusters 3–6). These clusters contain all five CBM samples and two LegP samples that were outliers in the PCA results. The first cluster of group B (cluster 3) consists of two samples of LegP (MD3871 and MD3868) and four outliers of CBM samples (MD3893, MD3894, MD3895 and MD7241). The next cluster (cluster 4) features two clay samples, whilst cluster 5 is made up of seven clay samples and one outlier sample of CBM (MD3892). The last cluster of group B (cluster 6) comprises only one clay sample (Bâla Voda clay, MD7192). The next major cluster group (group C) consists of only one cluster (cluster 7) represented by a third LegP sample that was an outlier in PCA (sample MD3872 with an exceptionally high content of Al_2O_3 and Na_2O). Major cluster group D, divided into two clusters (8 and 9) is the most numerously represented of all the groups, comprising a total of 90 samples. Cluster 8 consists mostly of CBM samples, but also includes eight of the nine analysed bricks-TS samples, four TW samples and one sub-cluster made up of three clay samples (Studena, Trembeš and Tatari clays). Cluster 9 brings together the remaining TW samples, four CBM samples and one sub-cluster made up of four clay samples (Ovča Mogila, Ovča Mogila Bis, Alekovo and Bălgarene clays). The last major cluster group (group D) is also divided into two clusters (10 and 11), the first of which features eleven CW samples and one Zeest 64 amphora, the other consisting of another two CW samples and four Zeest 64 amphorae (amphora samples were not included in subsequent multivariate and bivariate analyses due to the fact that, despite their similarities with CW sherds, CW pottery does not belong to any of the groups determined for amphora samples[60]).

The next step was discriminant analysis. LegP, CW, CBM, TW, brick-TS and clays were defined as clusters in this discriminant analysis, and the same elements were used as in multivariate cluster analysis and PCA. Fig. 20 shows canonical variation 2 versus canonical variation 1. This result shows that the group discrimination is unequivocal. CBM, TW, bricks-TS and eighteen clay samples form a compact group. One clay sample is well separated (MD3897), as are the LegP samples, which do not form one compact group, and the CW pottery samples, which are well separated from other sample groups.

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[59] Square Euclidean Distance, Ward clustering, using logged values of the concentrations of the following elements: Si, Ti, Al, Fe, Mn, Mg, Na, Ca, K, V, Cr, Ni, Zn, Rb, Sr, Y, Zr, Nb, Ba, Ce and La.

[60] Daszkiewicz *et alii* 2000.

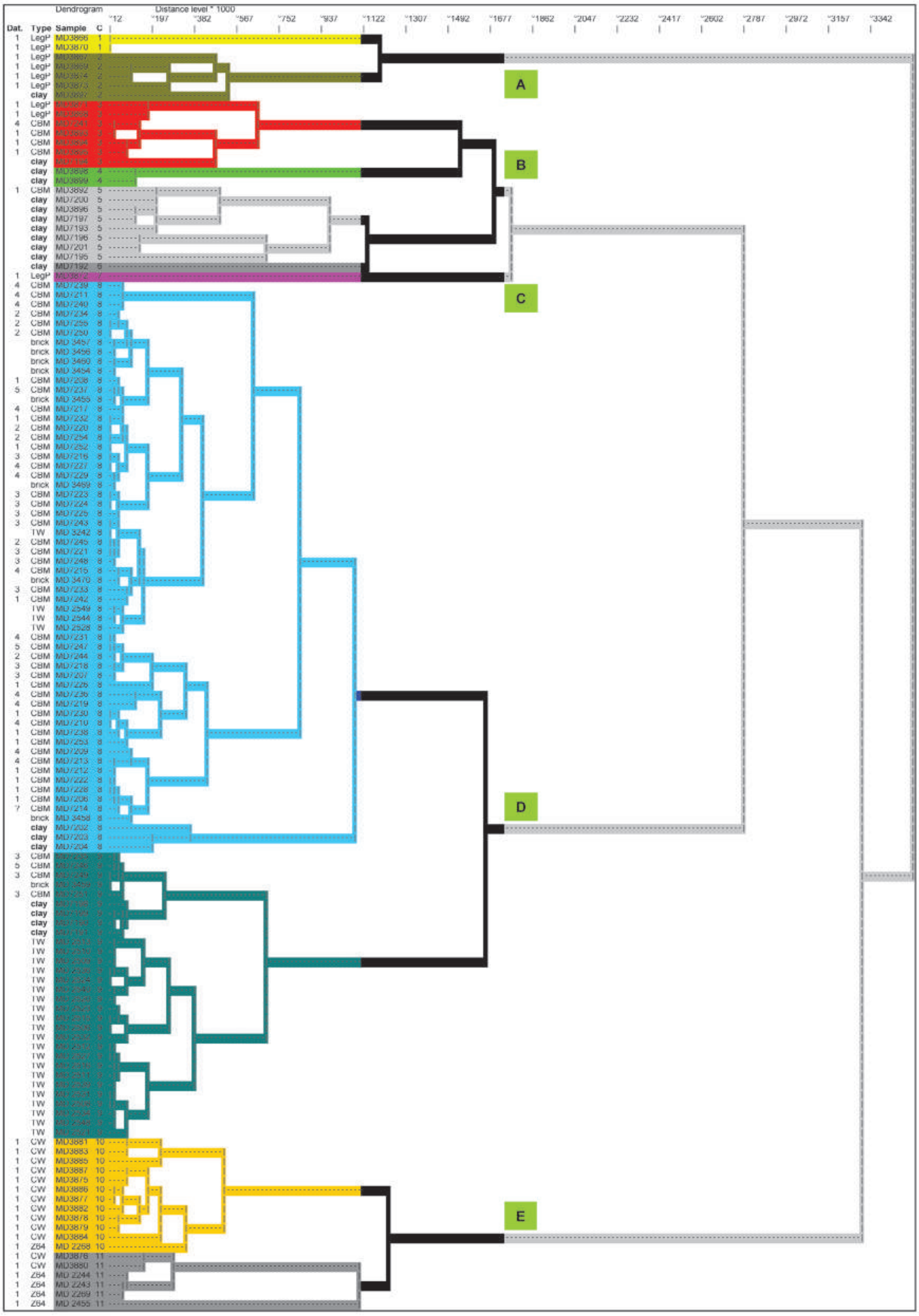

Fig. 19. Results of multivariate cluster analysis in the form of a dendrogram (Square Euclidean Distance, Ward clustering, logged values of the concentrations of the following elements were used: Si, Ti, Al, Fe, Mn, Mg, Na, Ca, K, V, Cr, Ni, Zn, Rb, Sr, Y, Zr, Nb, Ba and Ce)

Fig. 20. Results of a discriminant analysis (the concentration of the following elements were used: Si, Ti, Al, Fe, Mn, Mg, Na, Ca, K, V, Cr, Ni, Zn, Rb, Sr, Y, Zr, Nb, Ba and Ce)

Fig. 21 presents all of the analysed sherds and clay samples in the form of a biplot showing the ratio of Al_2O_3/SiO_2 versus Mn content (as MnO in wt.%). MnO content was one of the criteria that distinguished pottery produced in Butovo and Pavlikeni from pottery from Novae in work carried out as part of the IATRUS project.[61] In Fig. 21, the green ellipse shows the same field that that signified pottery production at Novae in the published diagram.[62] The black rectangle in Fig. 21 encompasses this field, and also includes all bricks-TS and most CBM samples as well as some clay samples. The only samples that do not fall within this area are five CBM samples that are outliers in all of the analyses, and clay samples that can be ruled out as raw materials for CBM.

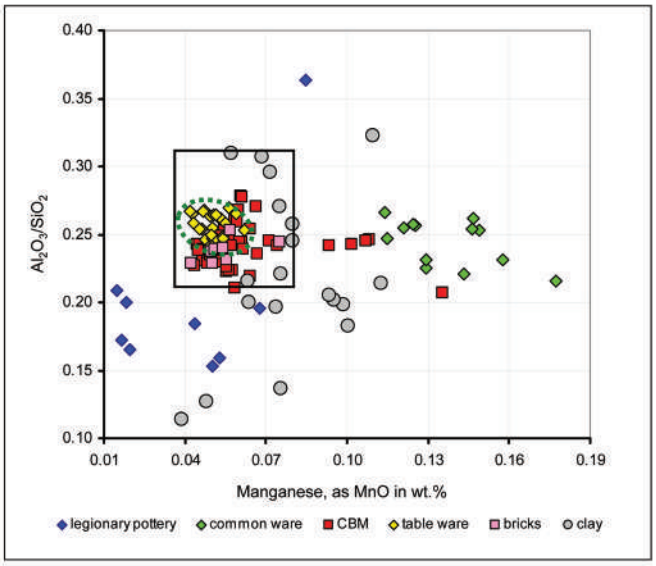

Fig. 21. Bivariate diagram of Al_2O_3/SiO_2 vs. MnO contents in wt% of various ceramics, clay and CBMs found in Novae

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[61] Daszkiewicz, Schneider 2007.

[62] Daszkiewicz, Schneider 2007, p. 480.

In addition to determining which, if any, of the sampled clay raw materials could potentially have been the raw materials used for making CBM, an attempt was also made to establish whether there is a correlation between chemical composition and individual types of CBM: roof tiles, bricks, pipes, floor tiles. Fig. 22 shows the results of the PCA[63] in which these types of CBM were defined as clusters. They indicate that pipes were made at many different workshops. Checks were also made to see whether there was a correlation between chemical composition and dating. There is a clear tendency for some of the CBM samples dated to the Flavian Period to separate from the remaining samples [Fig. 23].

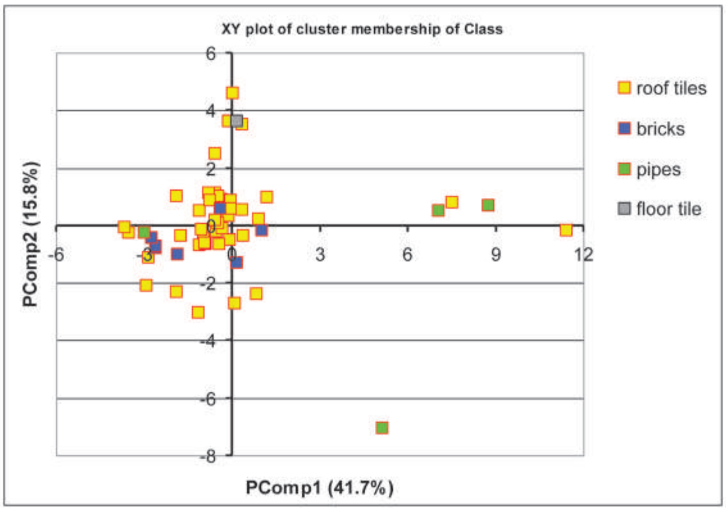

Fig. 22. Results of a PCA of chemical analysis results (the concentration of the following elements were used: Si, Ti, Al, Fe, Mn, Mg, Na, Ca, K, V, Cr, Ni, Zn, Rb, Sr, Y, Zr, Nb, Ba and Ce). CBM types are defined as clusters

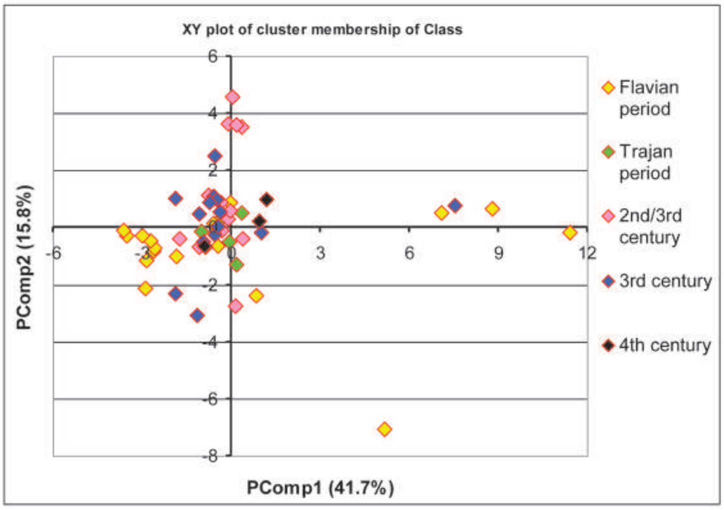

Fig. 23. Results of a PCA of chemical analysis results (the concentration of the following elements were used: Si, Ti, Al, Fe, Mn, Mg, Na, Ca, K, V, Cr, Ni, Zn, Rb, Sr, Y, Zr, Nb, Ba and Ce). CBMs dating are defined as clusters

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[63] The same elements were used in the PCA as in all of the multivariate analyses presented in this article.

Finally, there is one question left to answer: Which of the clay samples is the best match for the CBM used in Novae? Looking at the results of all analyses, Studena clay, Ovča Mogila and Ovča Mogila Bis clays are the ones that should be taken into consideration as potential raw materials. Naturally, it is not possible to say that this is exactly the same clay as the analysed sample, but we can say that these are clays "of the same family". Multivariate cluster analysis,[64] the results of which are shown in the form of a dendrogram in Fig. 24, was performed taking into account all

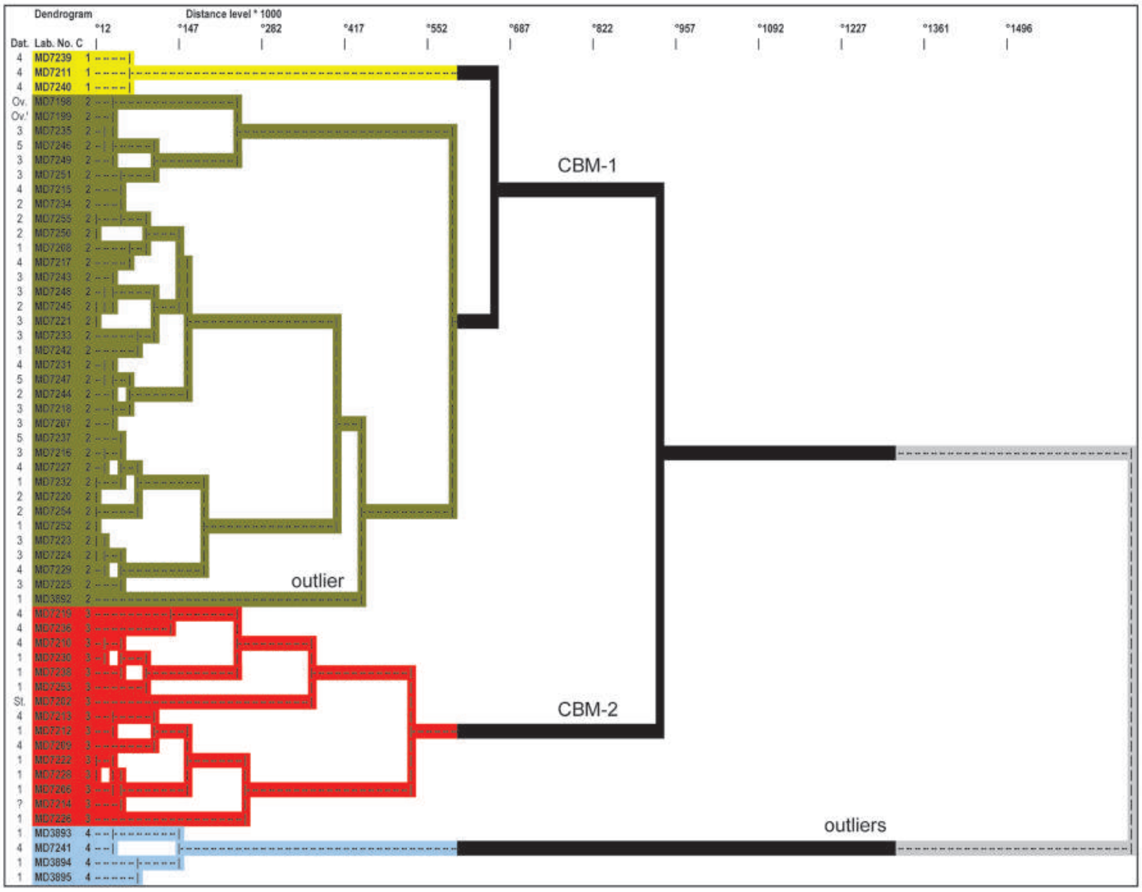

Fig. 24. Results of multivariate cluster analysis in the form of a dendrogram (Square Euclidean Distance, Ward clustering, logged values of concentrations of the following elements: Si, Ti, Al, Fe, Mn, Mg, Na, Ca, K, V, Cr, Ni, Zn, Rb, Sr, Y, Zr, Nb, Ba and Ce). The numbers in the first column (dat.) mean that samples came from features dated to:
1 = Flavian period;
2 = early Antonine dynasty (Trajan period);
3 = latter half of the second / early third century;
4 = third century;
5 = fourth century

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[64] Square Euclidean Distance, Ward clustering, using logged values of the concentrations of the following elements: Si, Ti, Al, Fe, Mn, Mg, Na, Ca, K, V, Cr, Ni, Zn, Rb, Sr, Y, Zr, Nb, Ba, Ce and La..

CBM samples and the three aforementioned clay samples. Four clusters were singled out (cluster numbers are given in column C), each of which can be divided into sub-clusters, but three CBM groups can be distinguished: CBM-1, CBM-2 and outliers. The first group, CBM-1, is made up of 35 CBM samples as well as Ovča Mogila and Ovča Mogila Bis clays (sample MD3892 is excluded from this group). CBM-2 comprises 14 CBM samples and Studena clay. Cluster 4 consists solely of CBM outliers. Most of the CBM samples in CBM-2 represent wares dated to the Flavian Period [Fig. 24, first column]. The results of discriminant analysis confirm the groupings resulting from multivariate cluster analysis [Fig. 25], with the exception of sample MD7219, which is linked to its slightly lower CaO content and higher TiO_2 content. Figs. 26 and 27 show CBM samples divided according provenance and dating. A summary of all these analyses results is presented in the form of a diagram in Fig. 28. It shows the correlation between dating and product type and its provenance attribution. Each of the CBM samples is presented as a separate rectangle (colours indicate dating and the outline of each rectangle indicates the CBM type).

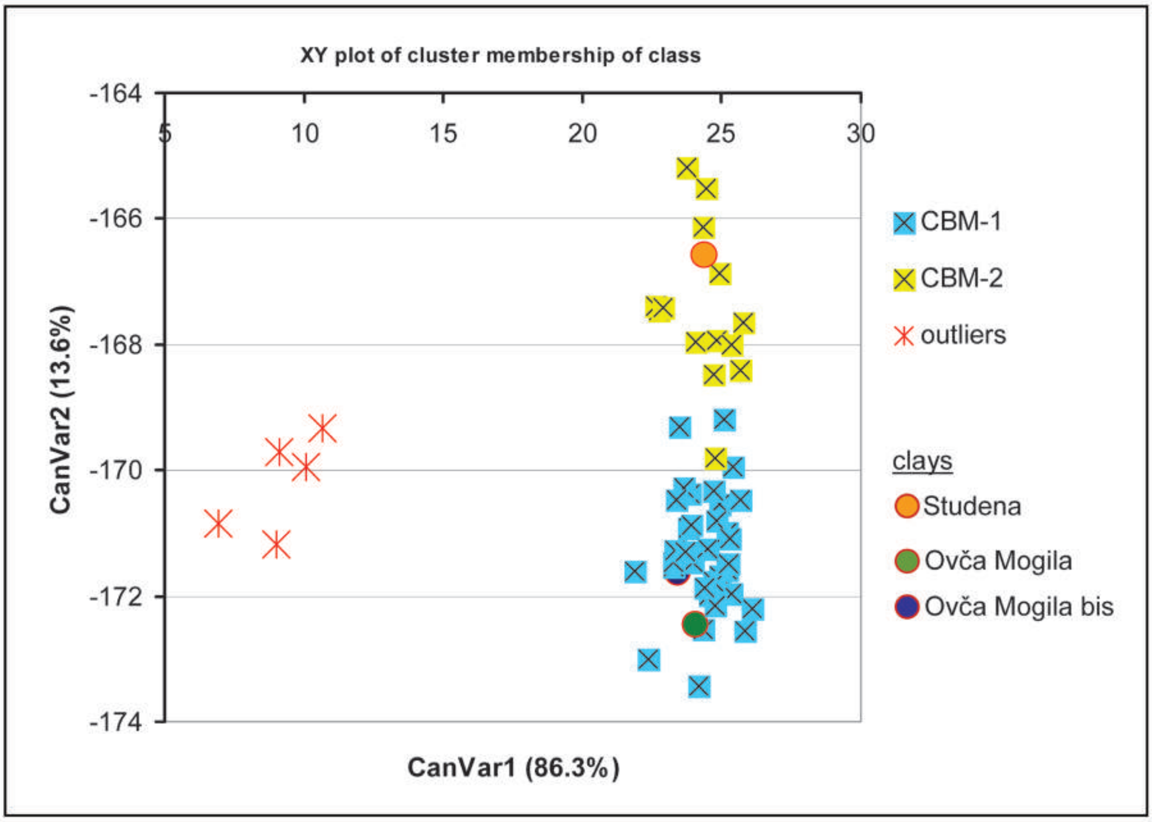

Fig. 25. Results of a discriminant analysis (concentrations of the following elements were used: Si, Ti, Al, Fe, Mn, Mg, Na, Ca, K, V, Cr, Ni, Zn, Rb, Sr, Y, Zr, Nb, Ba and Ce). All CBM samples and clays from Ovča Mogila, Ovča Mogila Bis and Studena were included

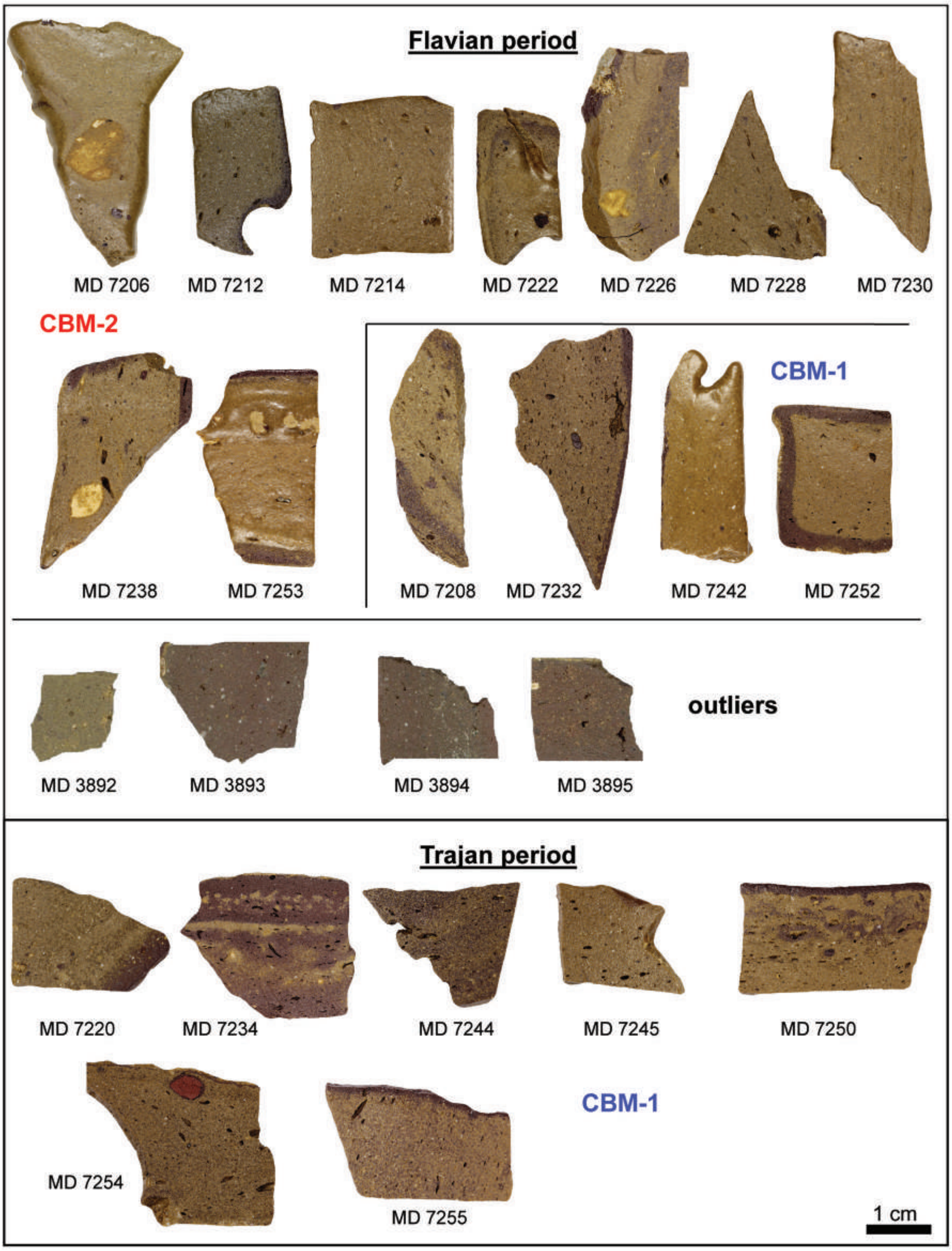

Fig. 26. CBM samples after refiring at 1150°C grouped according provenance and dating (compiled by H. Baranowska and M. Daszkiewicz)

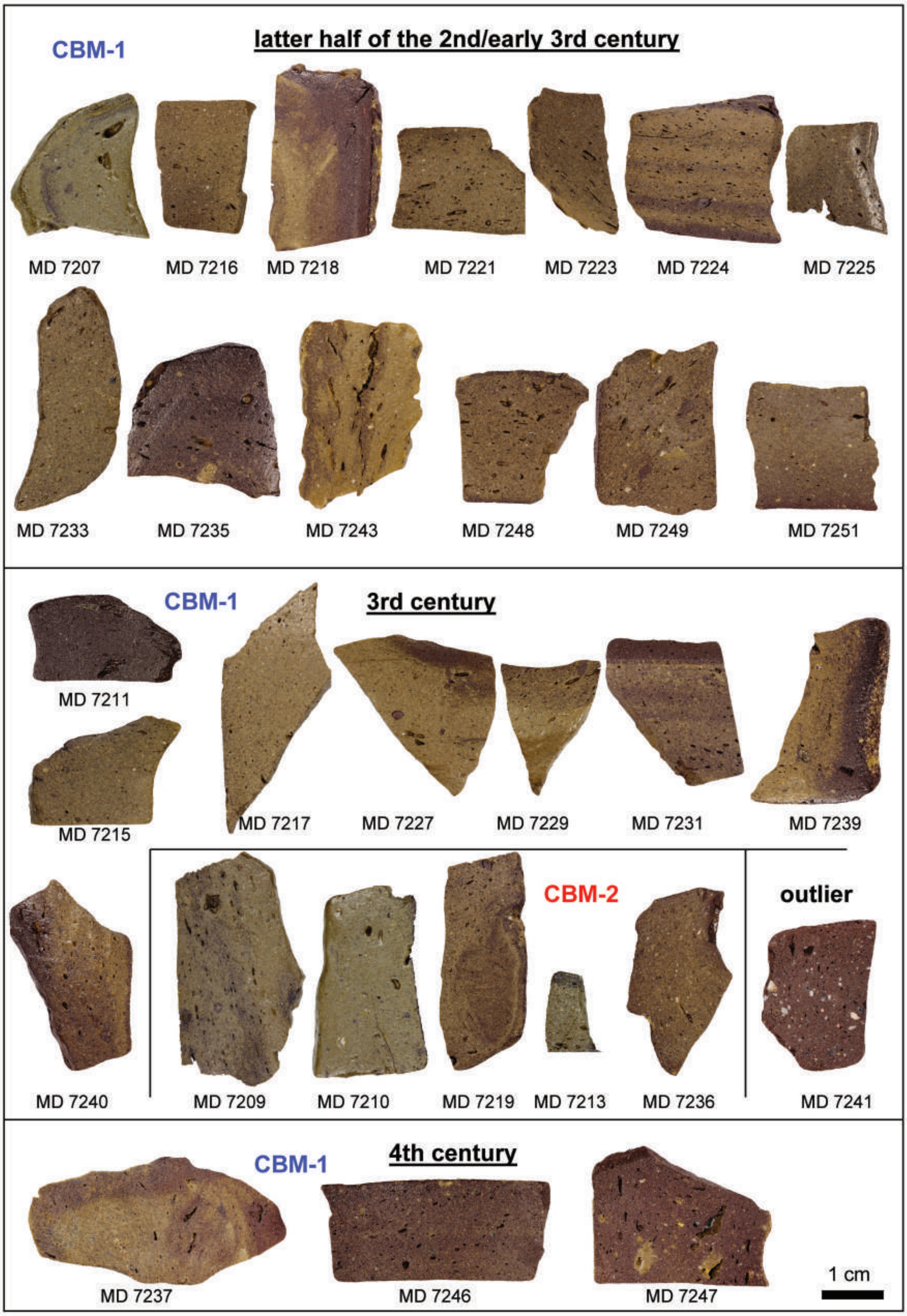

Fig. 27. CBM samples after refiring at 1150°C grouped according provenance and dating (compiled by H. Baranowska and M. Daszkiewicz)

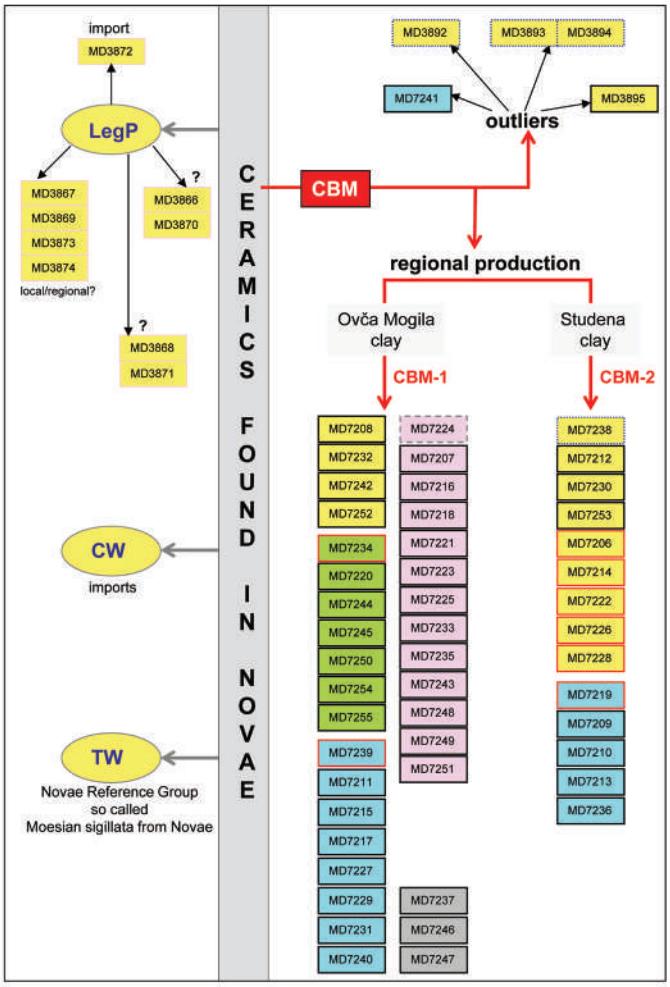

Fig. 28. Ceramics found in Novae, correlation of product type, dating and provenance attribution. Each of the CBM samples is presented as a separate rectangle, colours indicate dating (yellow = Flavian period; green = early Antonine dynasty [Trajan period]; violet = latter half of the second / early third century; blue = third century; grey = fourth century), the frame of each rectangle indicates the CBM type: points = pipes; black line = roof tiles; red line = bricks; dashed line = floor tile

Conclusions

Legionary pottery samples represent wares produced at various workshops, albeit four of the nine analysed fragments were made in the same provenance centre, probably connected with the Novae region. One clay (clay MD3897, samples taken from the side of an escarpment) has a firing behaviour similar to the thermal behaviour of these four refired LegP samples, and its chemical composition also shows some similarities.

Common ware pottery was made of marly clay (with some microbioclasts) intentionally tempered with volcanic rock fragments (andesite/basalt). According to the results of chemical composition analysis, refiring and thin-section studies, CW pottery exhibits not only a similar chemical composition but also a similar thermal behaviour and similar composition/size/distribution of non-plastic components to some amphorae. We can assume that CW pottery was made in the same region as one group of Zeest 64 amphorae. The provenance of these amphorae is still in question. Given the available published data[65] these amphorae were not made at workshops in Sinope. However, there is no doubt that CW pottery must have been made in a region where both marly clay and volcanic rocks occur, both of which were used as temper. It is highly unlikely that these wares were made in the vicinity of Novae. Although marly clay (Trembeš clay, MD7204) suitable for making ceramics does occur there, volcanic rocks definitely do not (reusing items such as damaged andesite millstones as a source of temper would not have met the demands of mass production).

All analysed TW pottery fragments (red slipped fine wares — so-called Moesian sigillata from Novae) are a homogeneous group in terms of chemical composition representing wares deemed to be local to Novae — Novae Reference Group.[66]

Of the 54 analysed CBM samples only five are outliers from beyond the region. The remaining CBM samples represent products made at workshops local o the Novae region. Two groups associated with two different clay raw materials can be distinguished: CBM-1, associated with Ovča Mogila clay, and CBM-2, associated with Studena clay.

Analyses showed that two samples taken from the Ovča Mogila deposit at a depth of around 50 cm and from a depth of around 1.80 m exhibit identical firing behaviour and have the same chemical composition. This allows us to make a direct comparison between clay samples taken from this deposit and CBM samples used at Novae (a depth of *ca.* 1.80 m corresponds to the foundation level of Flavian Period buildings at Novae — height level *ca.* 47.20–47.30 m a.s.l.).

It is interesting to compare the location of the spots from which clay samples were taken with chemical composition and firing behaviour. Comparing three clay raw materials sampled from spots located close to one another revealed that each of these clay samples is significantly different in firing behaviour and chemical composition. However, clay samples taken from spots a long distance from one another differ slightly in chemical composition and the differences are more pronounced in the firing test. This should be borne in mind when looking for the raw materials from which ancient ceramics were made.

Translated by Barbara Gostyńska

Abbreviations

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[65] Türkmen 2003; Slusallek *et alii* 1983.

[66] Daszkiewicz, Bobryk, Schneider 2006; Daszkiewicz, Schneider 2007; Baranowski, Daszkiewicz, Schneider 2021

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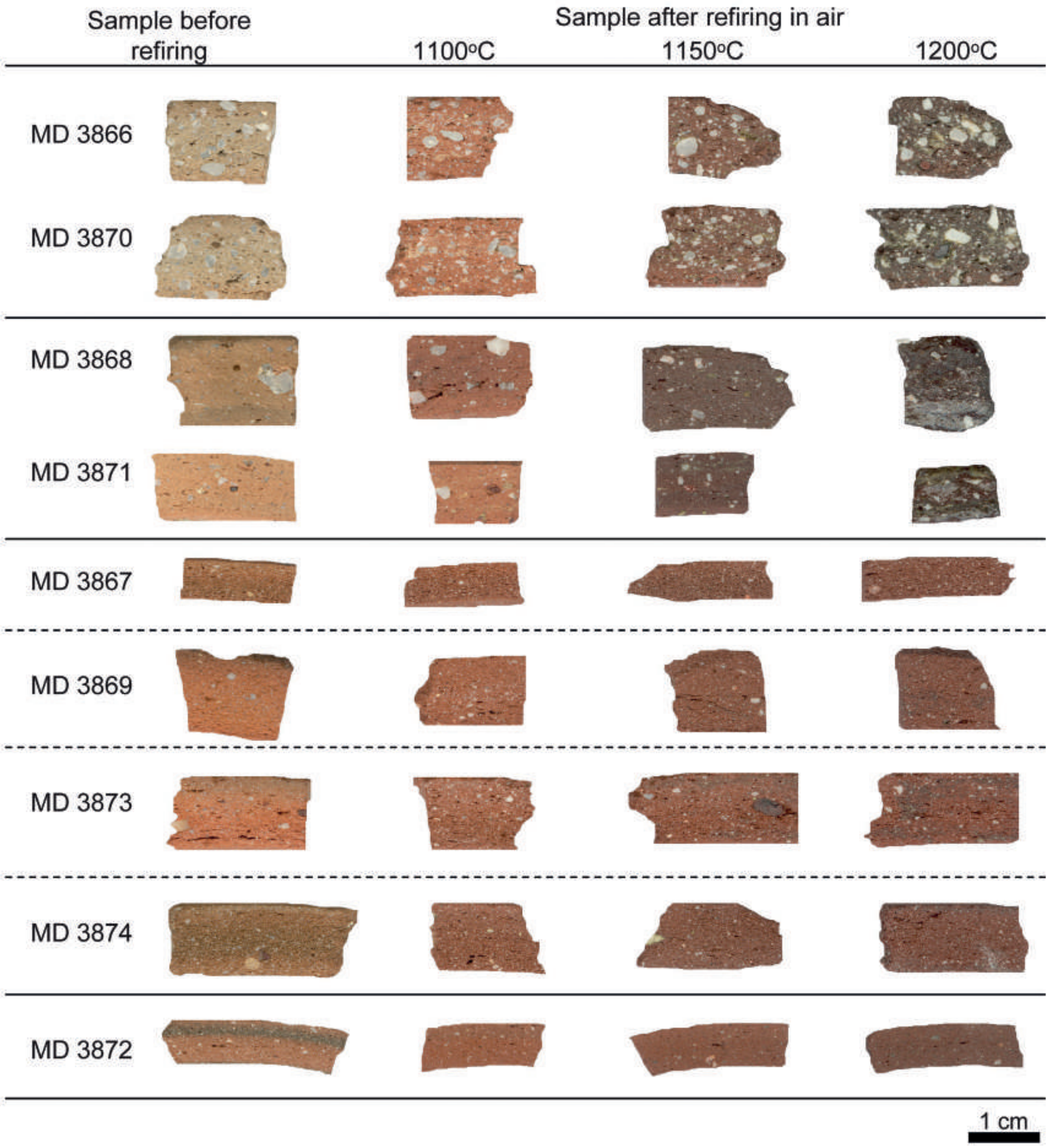
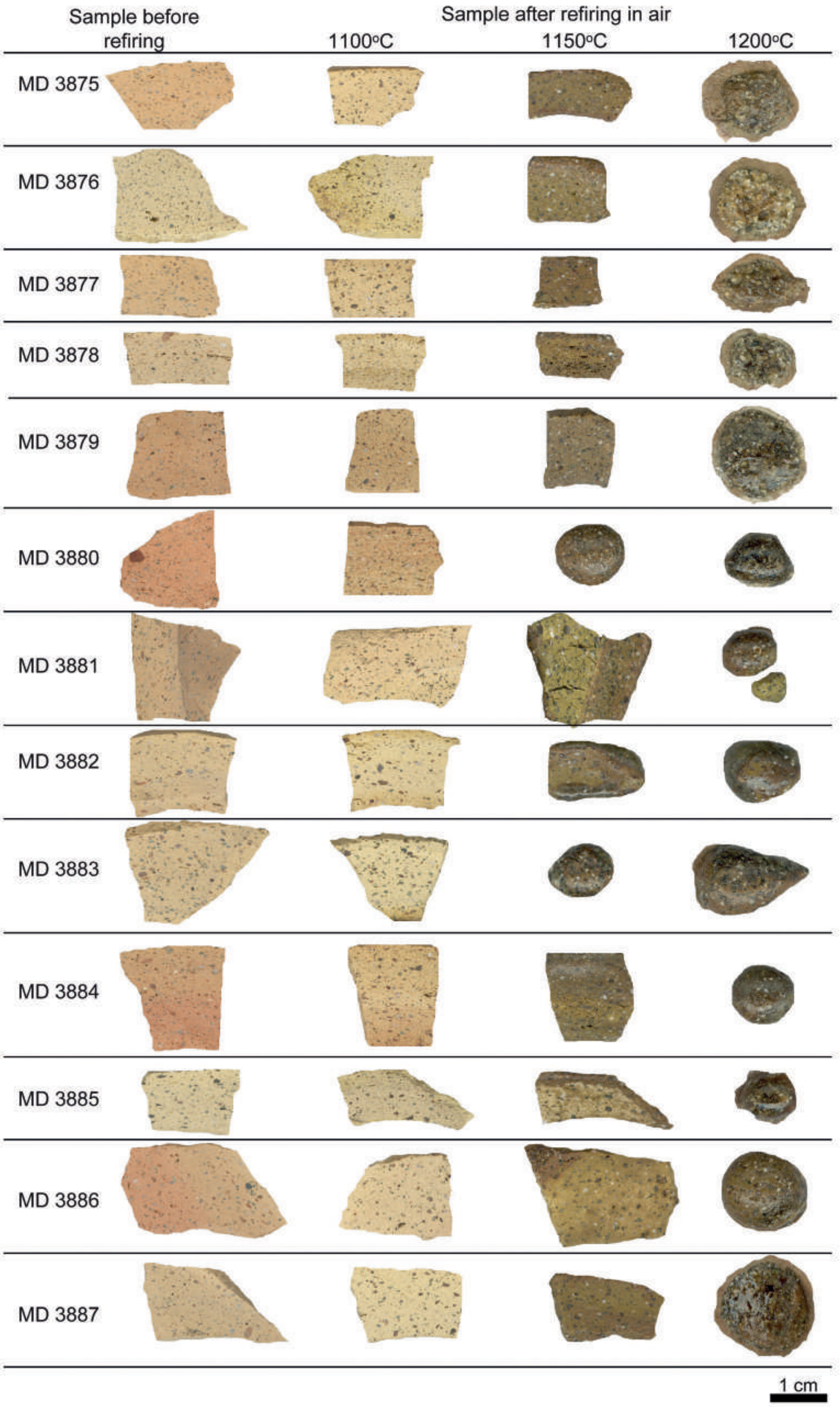


Pl. 1. MGR-analysis, LegP samples MD3866–MD3874, grouped according MGR-groups (compiled by H. Baranowska and M. Daszkiewicz)



Pl. 2. MGR-analysis, CW samples MD3875–MD3887
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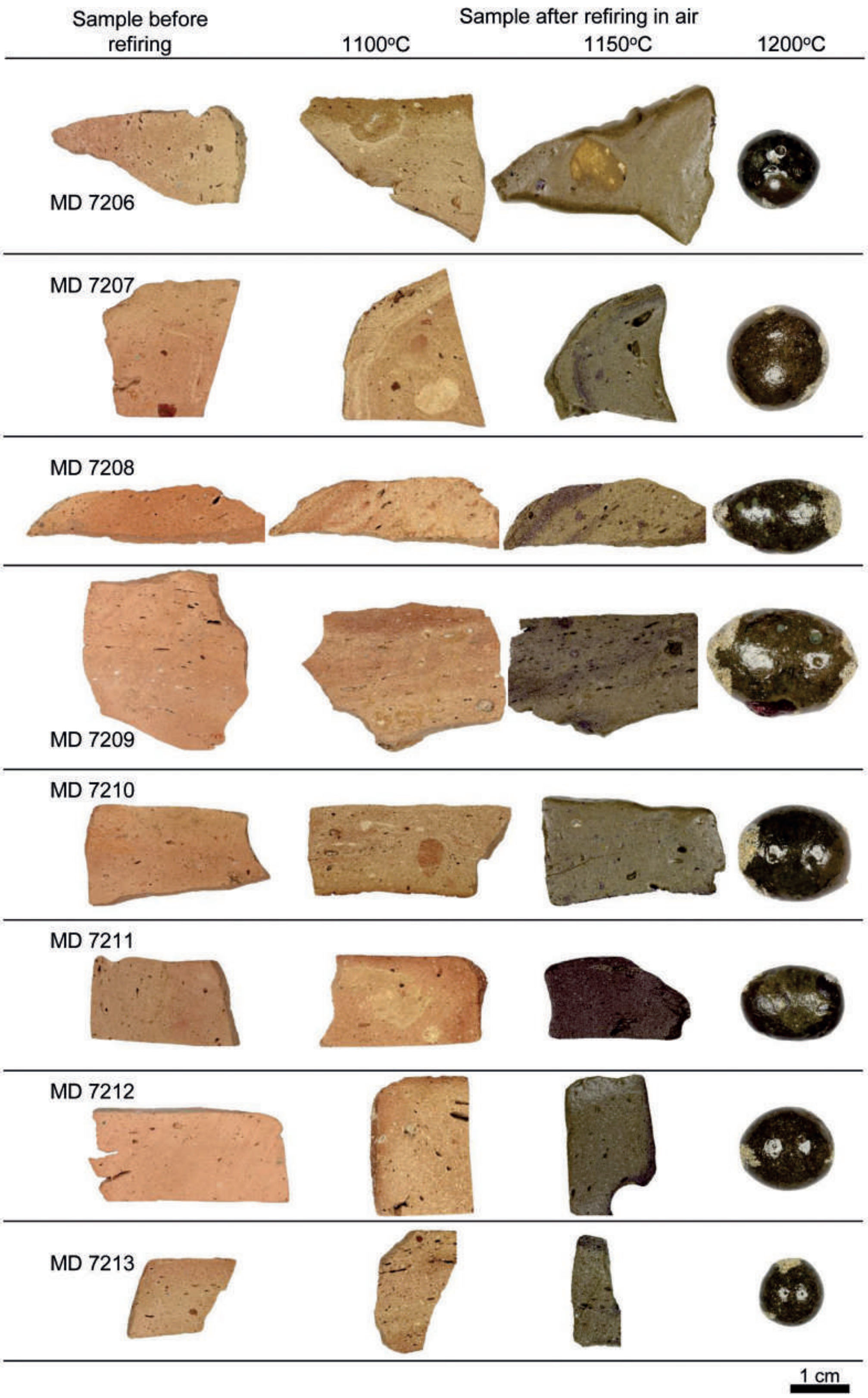

Pl. 3. MGR-analysis, CBM samples MD7206–MD7213
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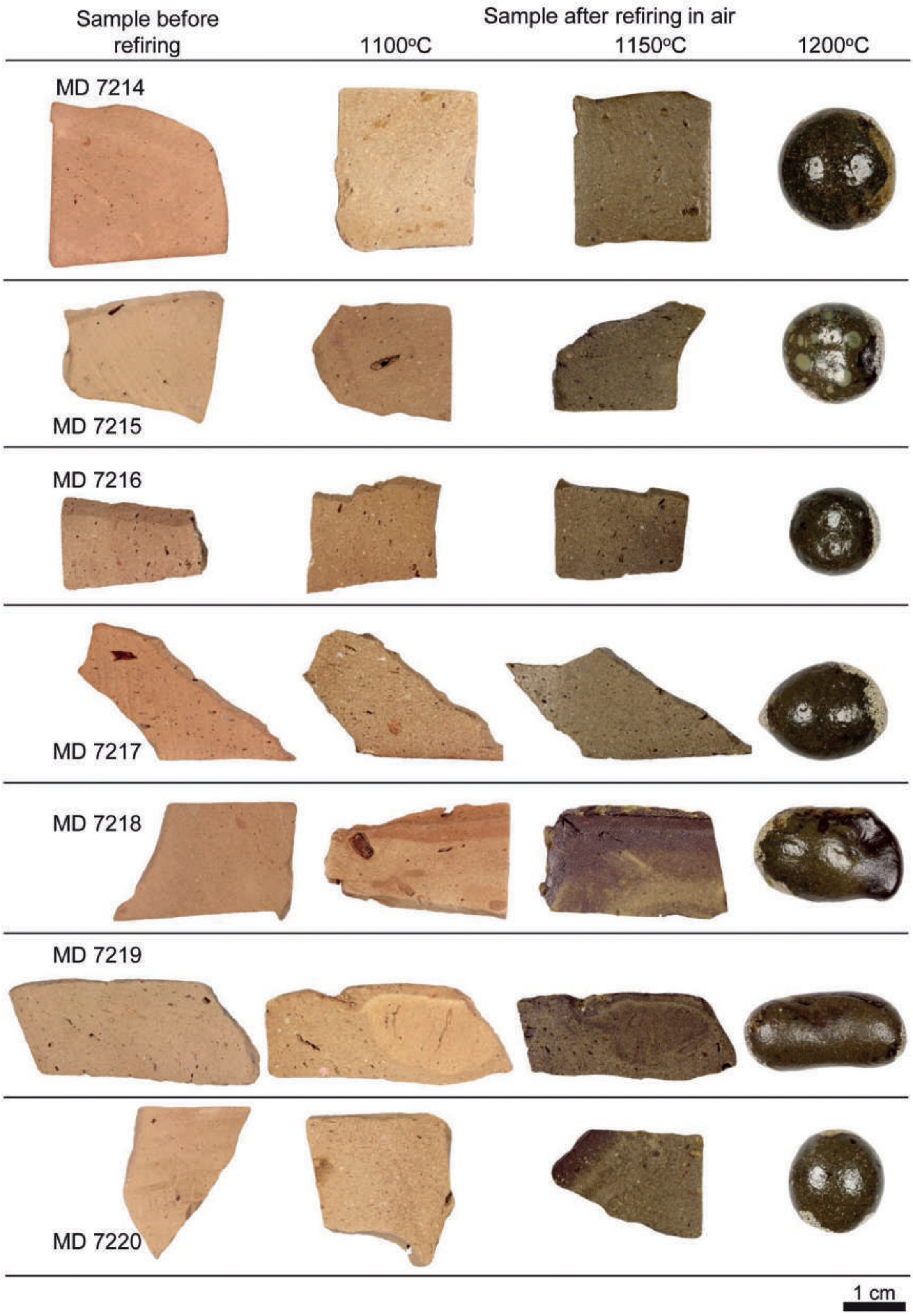

Pl. 4. MGR-analysis, CBM samples MD7214–MD7220
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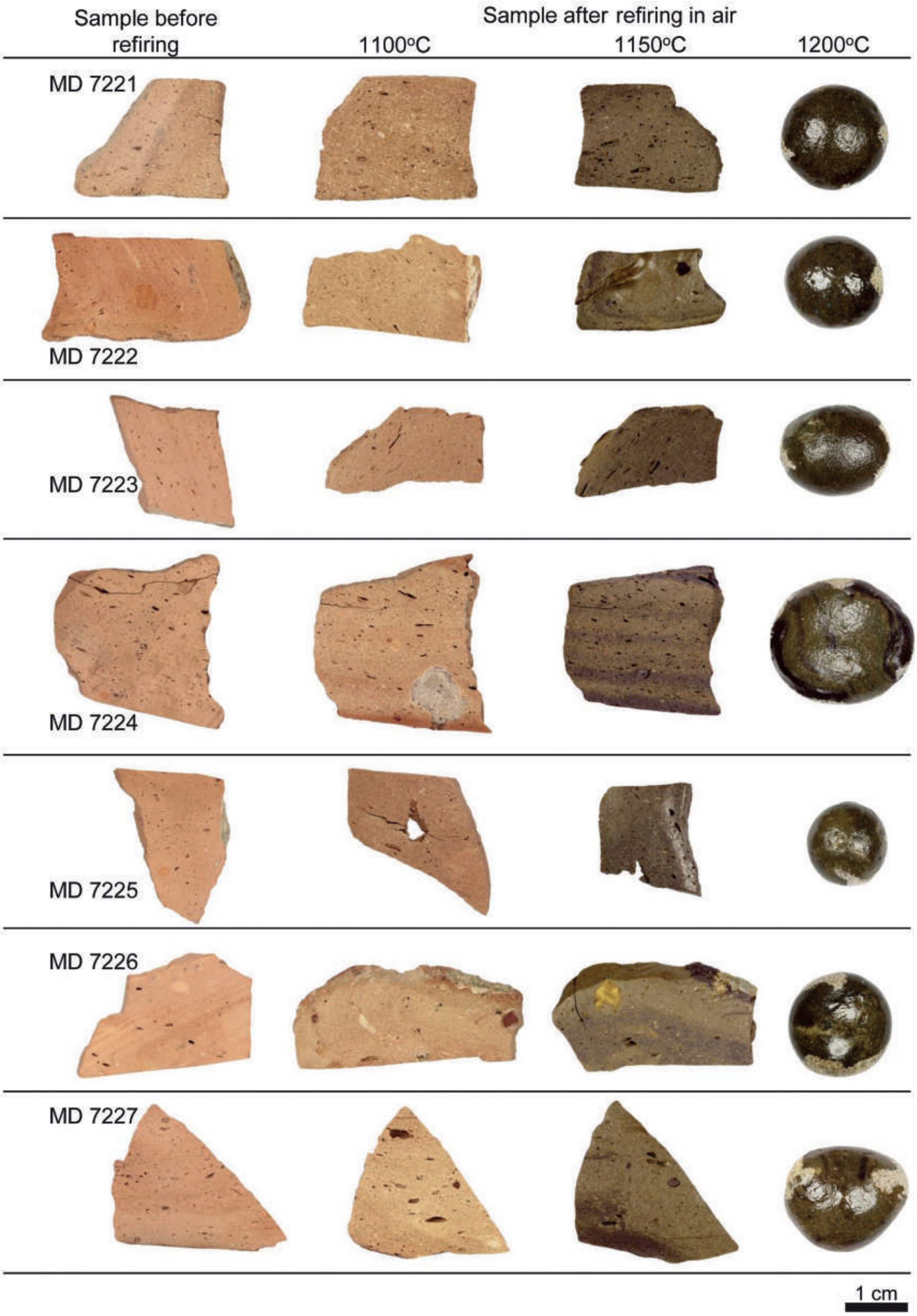

Pl. 5. MGR-analysis, CBM samples MD7221–MD7227
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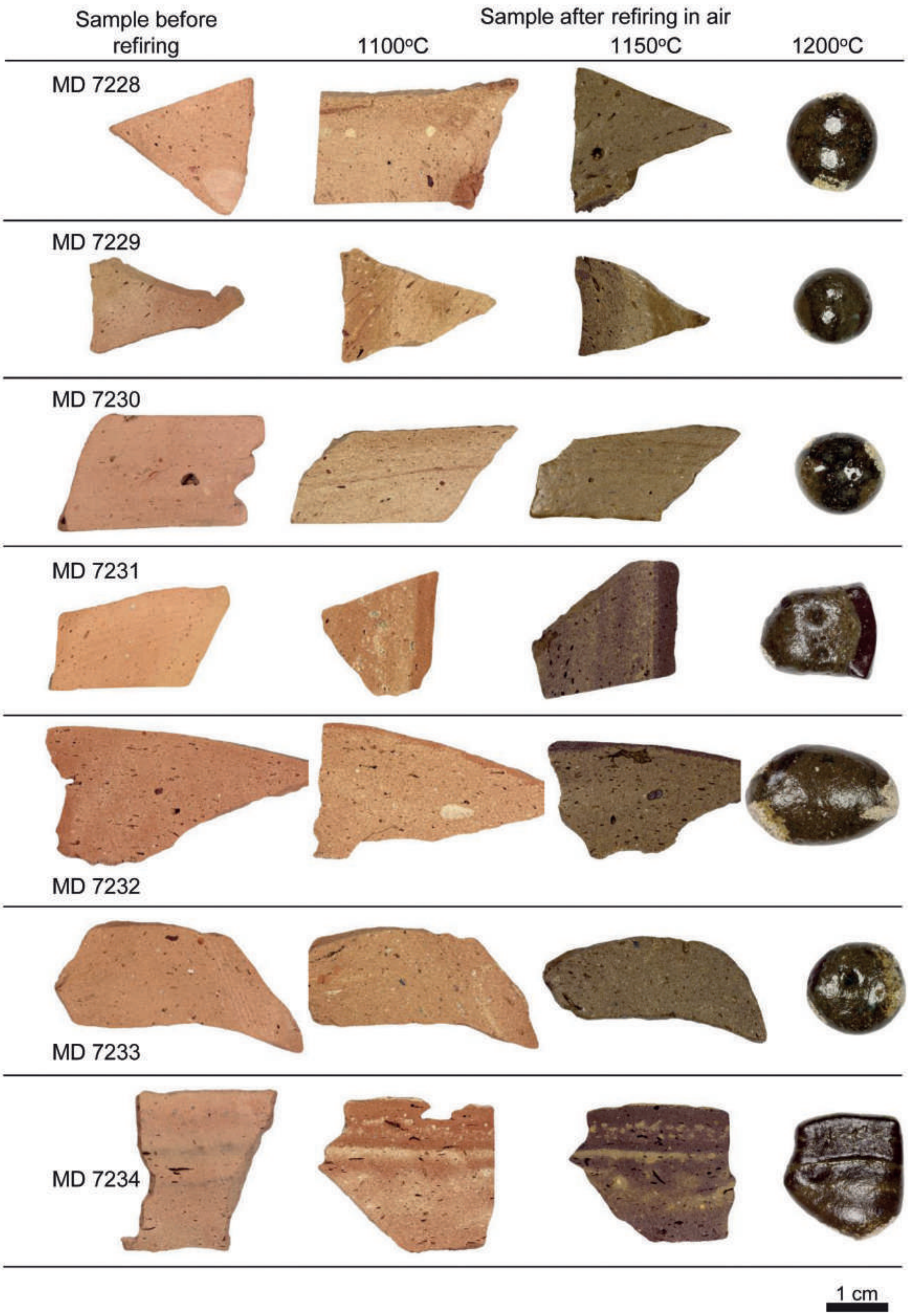

Pl. 6. MGR-analysis, CBM samples MD7228–MD7234
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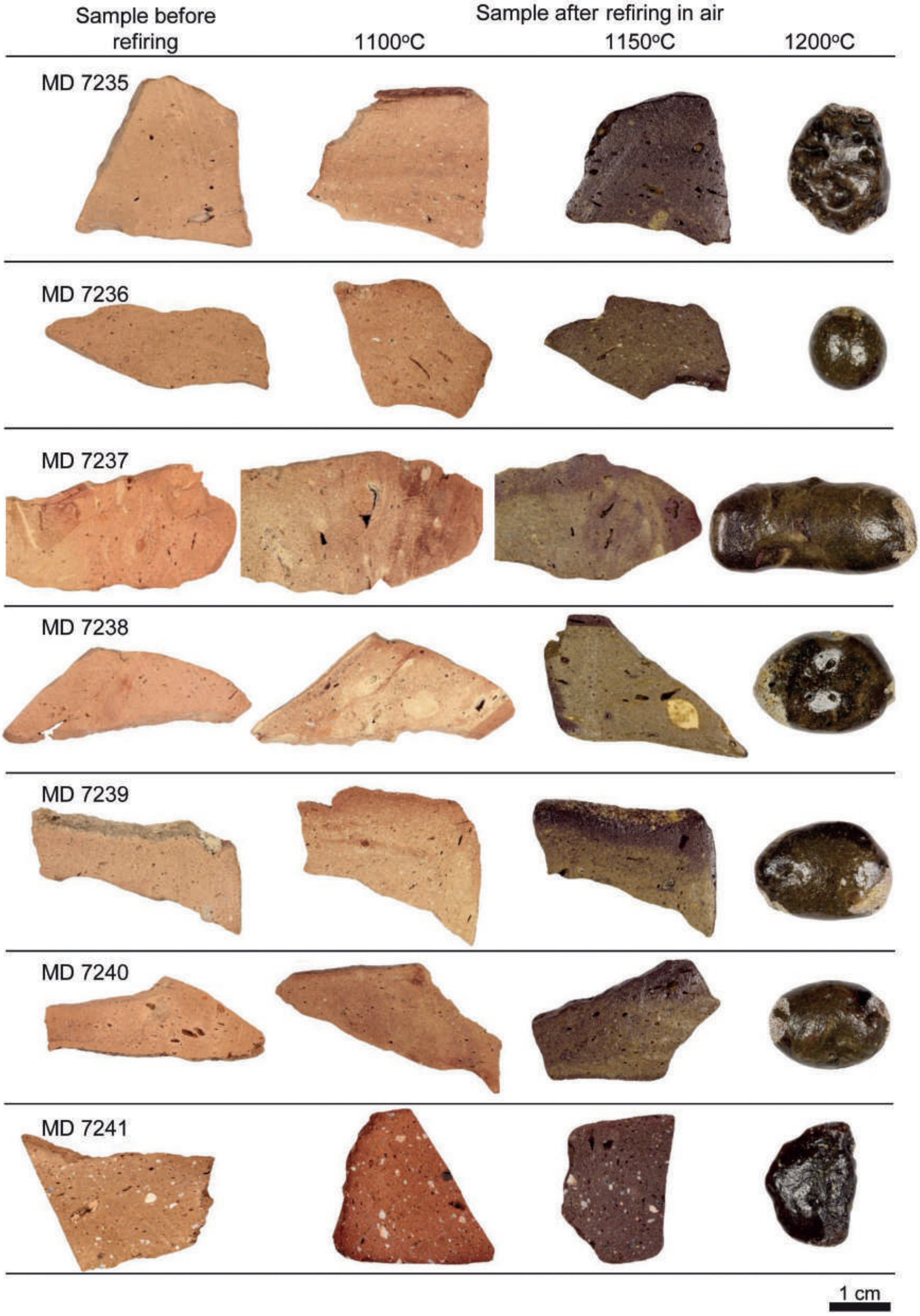

Pl. 7. MGR-analysis, CBM samples MD7235–MD7241
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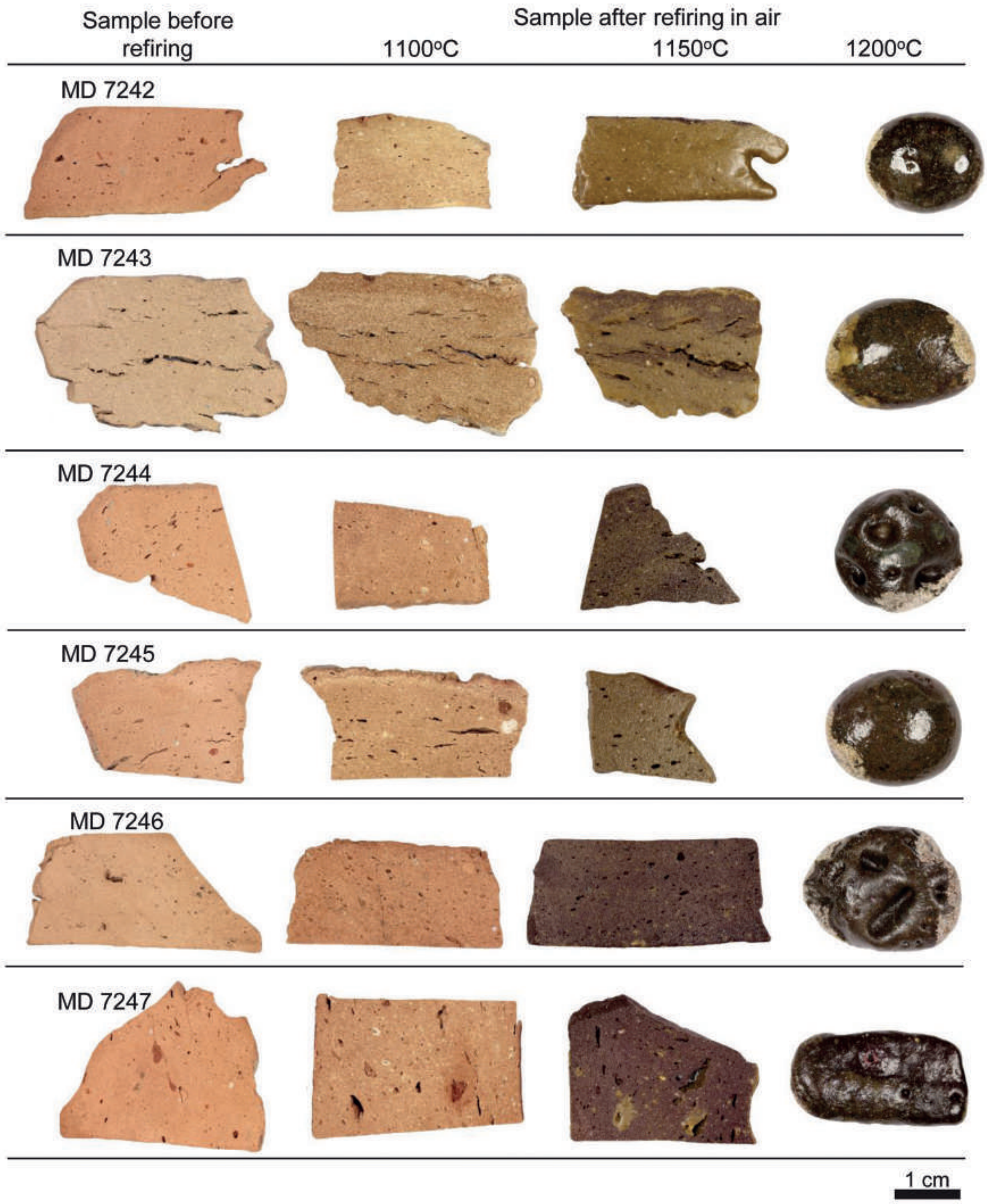

Pl. 8. MGR-analysis, CBM samples MD7242–MD7247
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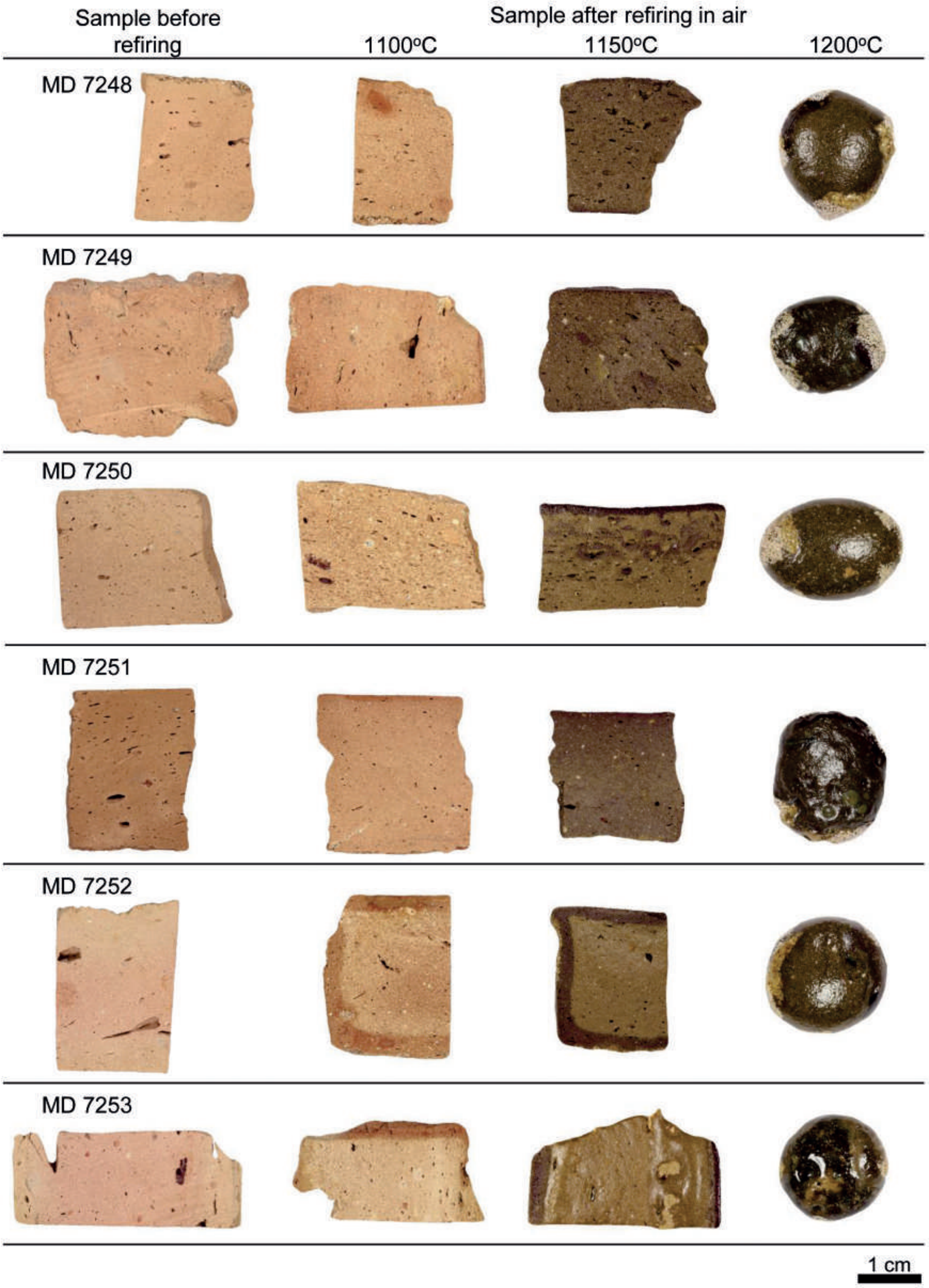

Pl. 9. MGR-analysis, CBM samples MD7248–MD7253
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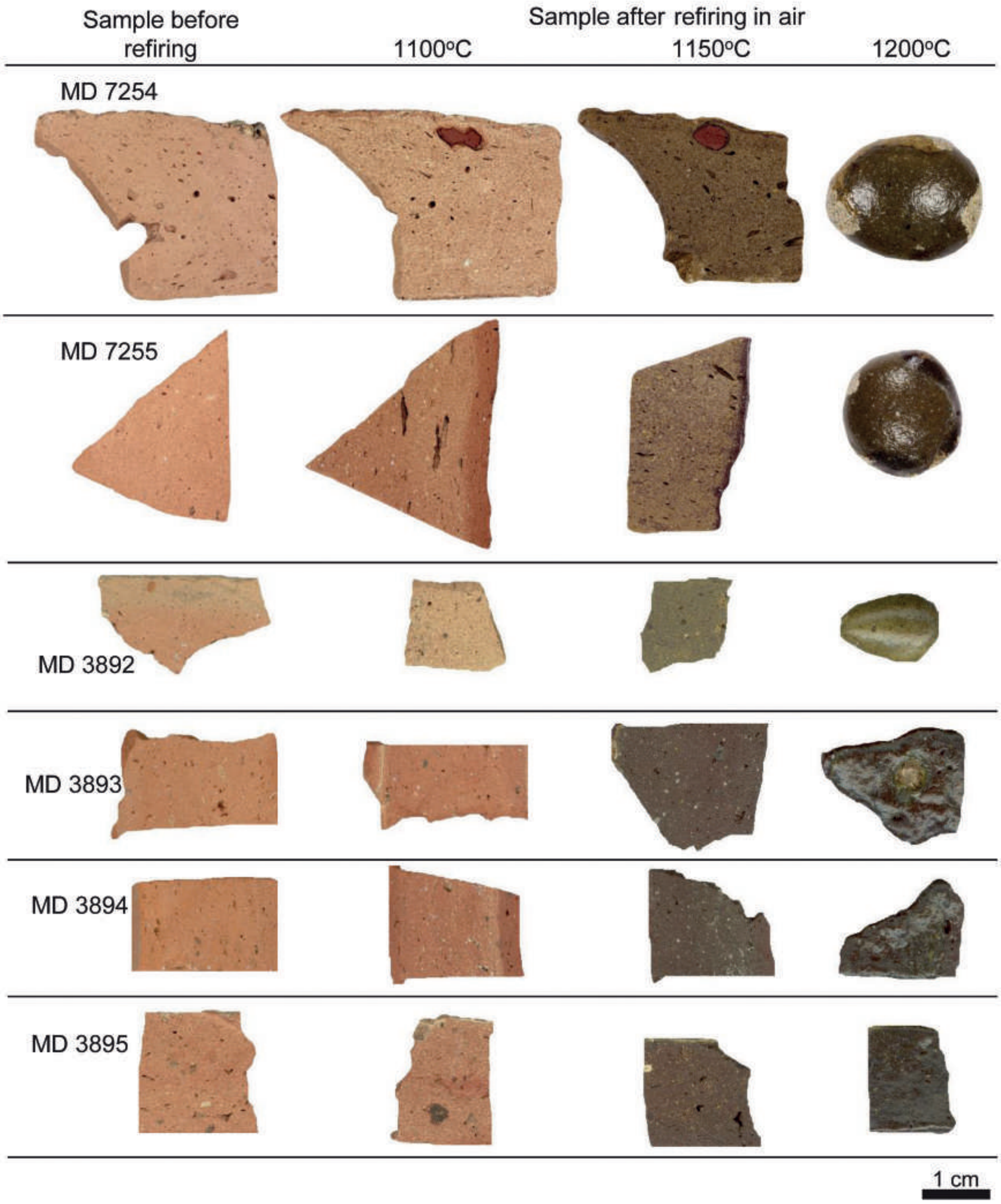


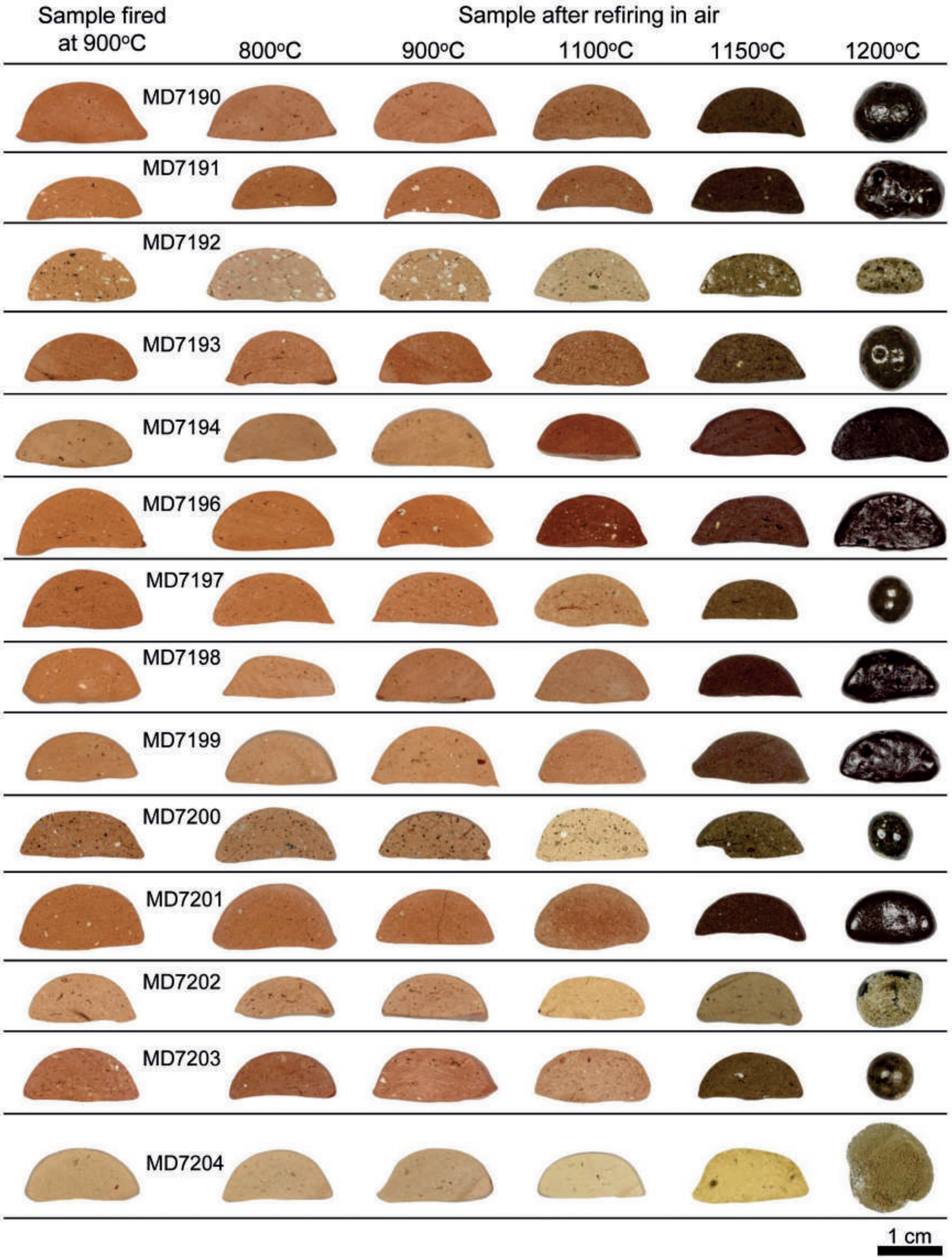
Pl. 10. MGR-analysis, CBM samples MD7254–MD7255 and MD3892–MD3895
(compiled by H. Baranowska and M. Daszkiewicz)

Pl. 11. Firing test, clay samples MD7190–MD7194
(compiled by H. Baranowska and M. Daszkiewicz)

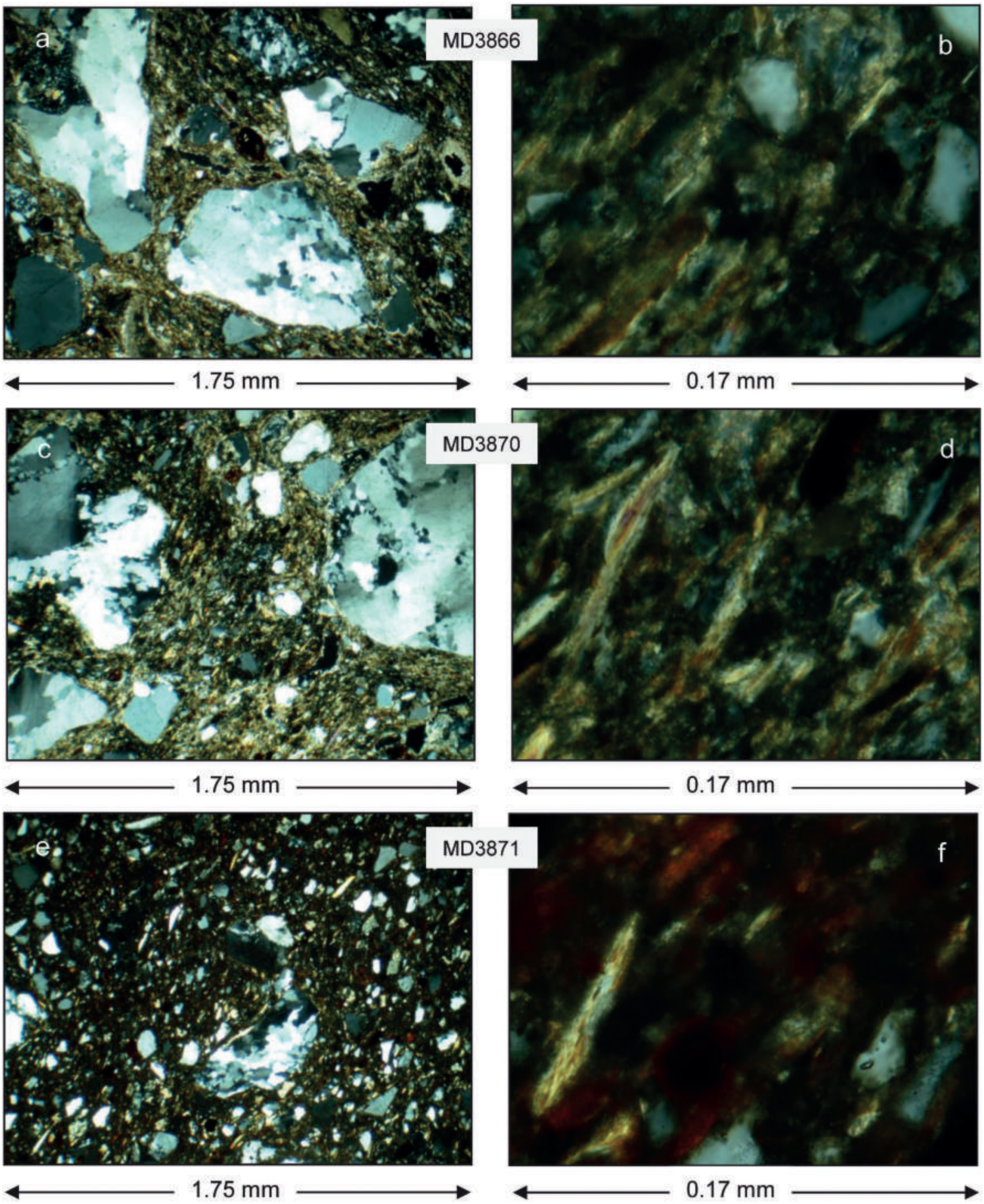
Pl. 12. Firing test, clay samples MD7195–MD7199
(compiled by H. Baranowska and M. Daszkiewicz)

Pl. 13. Firing test, clay samples MD7200–MD7204
(compiled by H. Baranowska and M. Daszkiewicz)

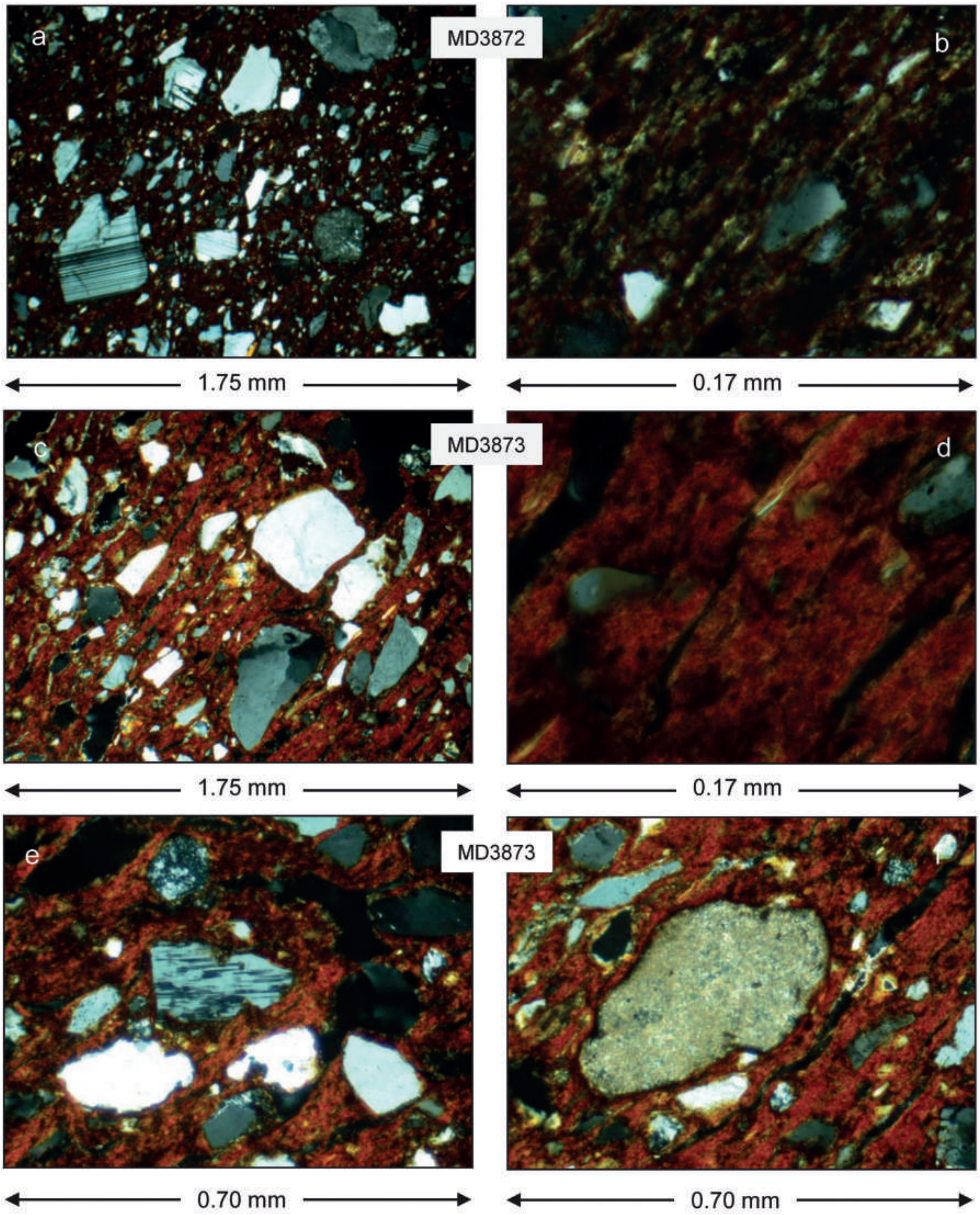
Pl. 14. Test *à la* ceramics of clay samples MD7190–MD7204, briquettes fired at 800°C (compiled by H. Baranowska and M. Daszkiewicz)



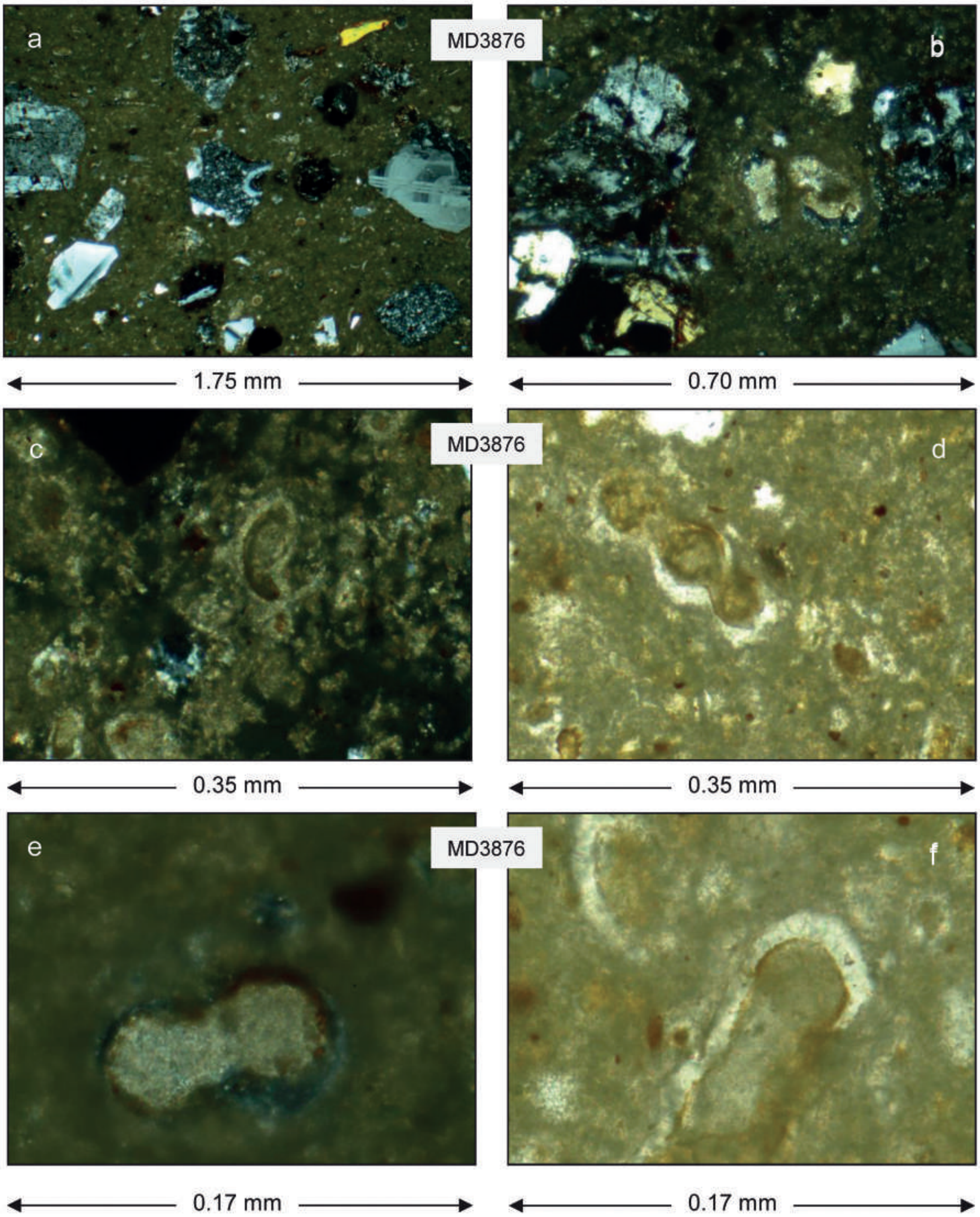
Pl. 15. Test *à la* ceramics of clay samples MD7190–MD7204, briquettes fired at 900°C (compiled by H. Baranowska and M. Daszkiewicz)



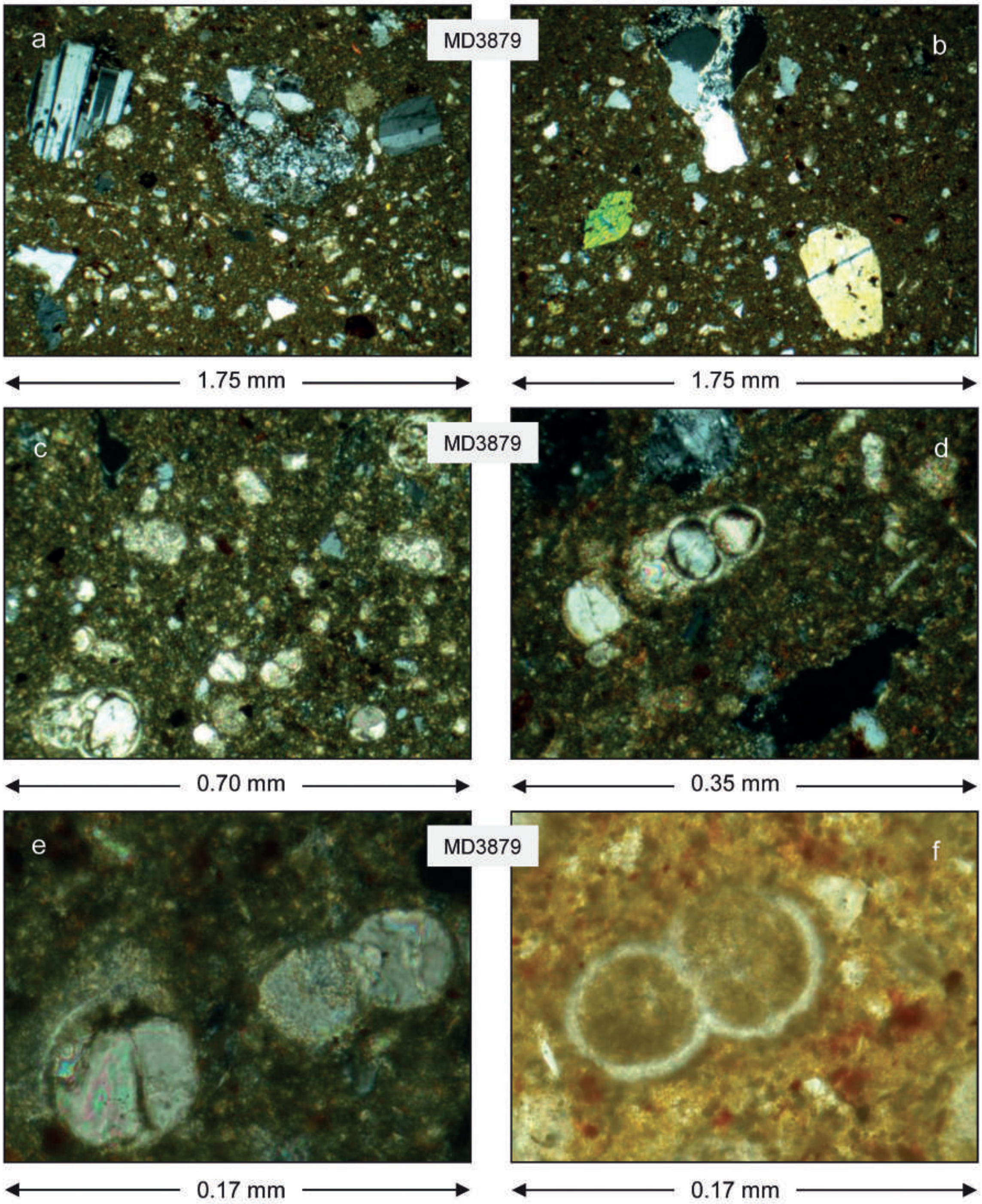
Pl. 16. Micrographs of typical fabric images of LegP samples MD3866, MD3870, MD3871 (XPL) (micrographs G. Schneider, compiled by H. Baranowska)



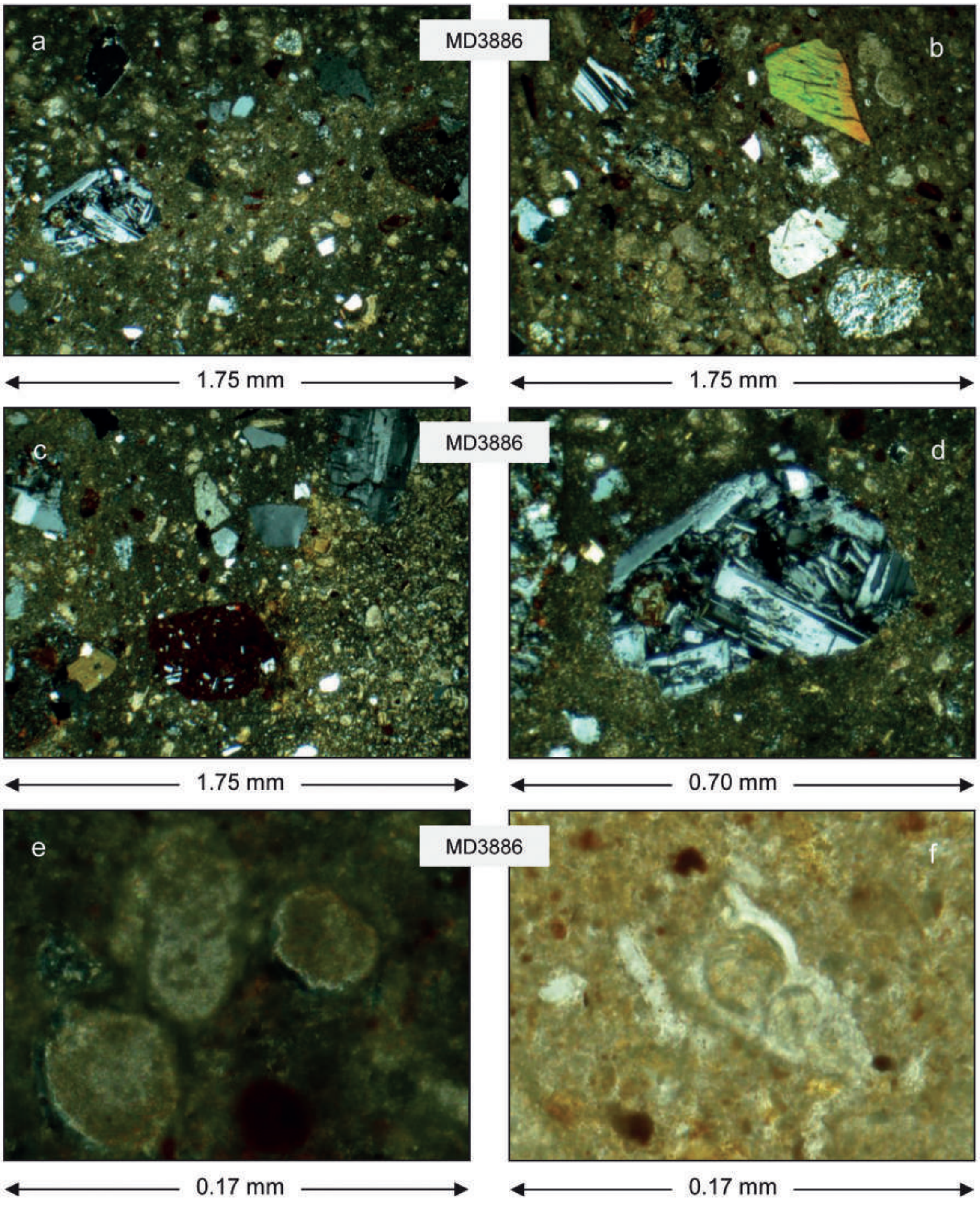
Pl. 17. Micrographs of typical fabric images of LegP samples MD3872, MD3873 (XPL)
(micrographs G. Schneider, compiled by H. Baranowska)



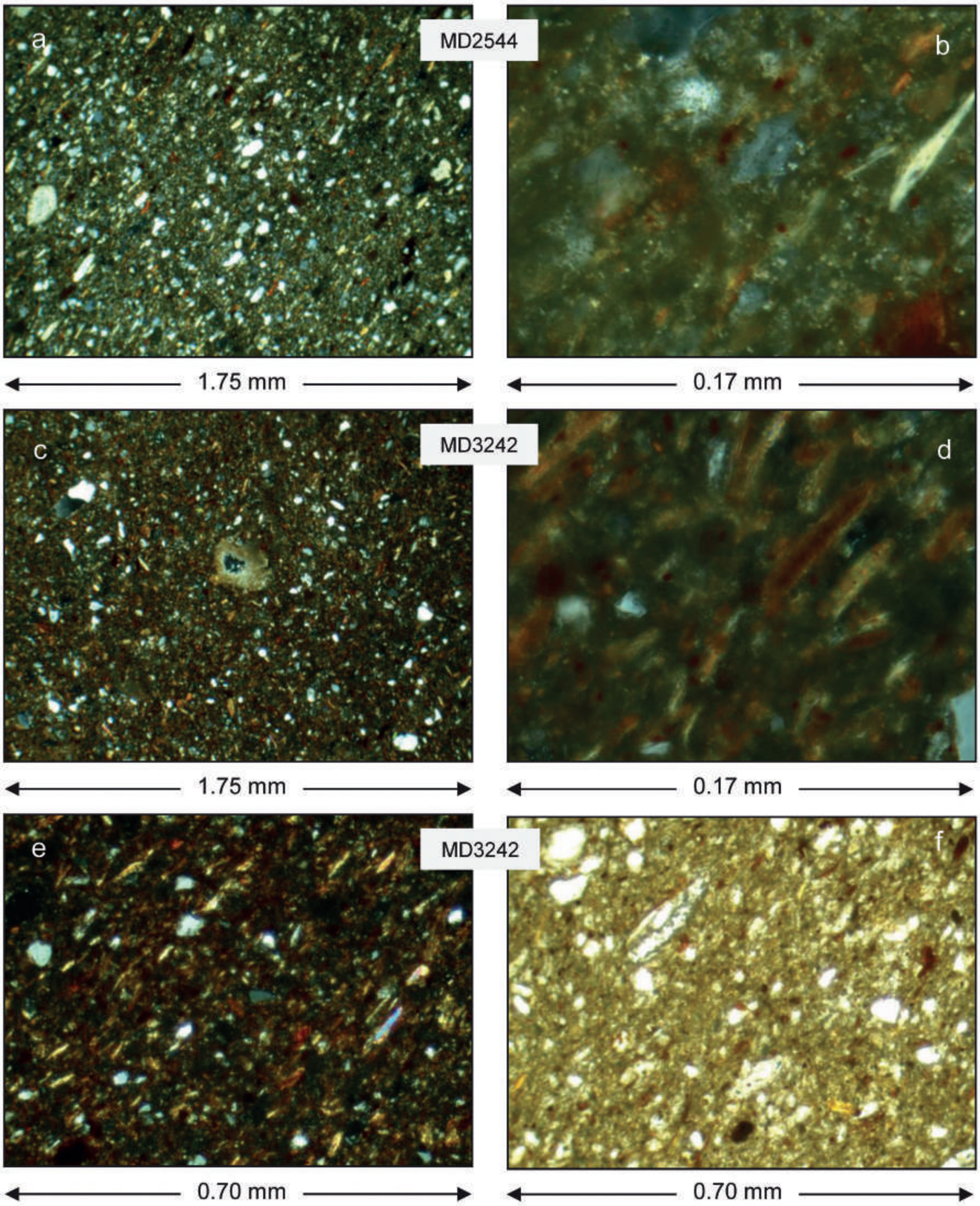
Pl. 18. Micrographs of typical fabric images of CW sample MD3876 (XPL)
(micrographs G. Schneider, compiled by H. Baranowska)



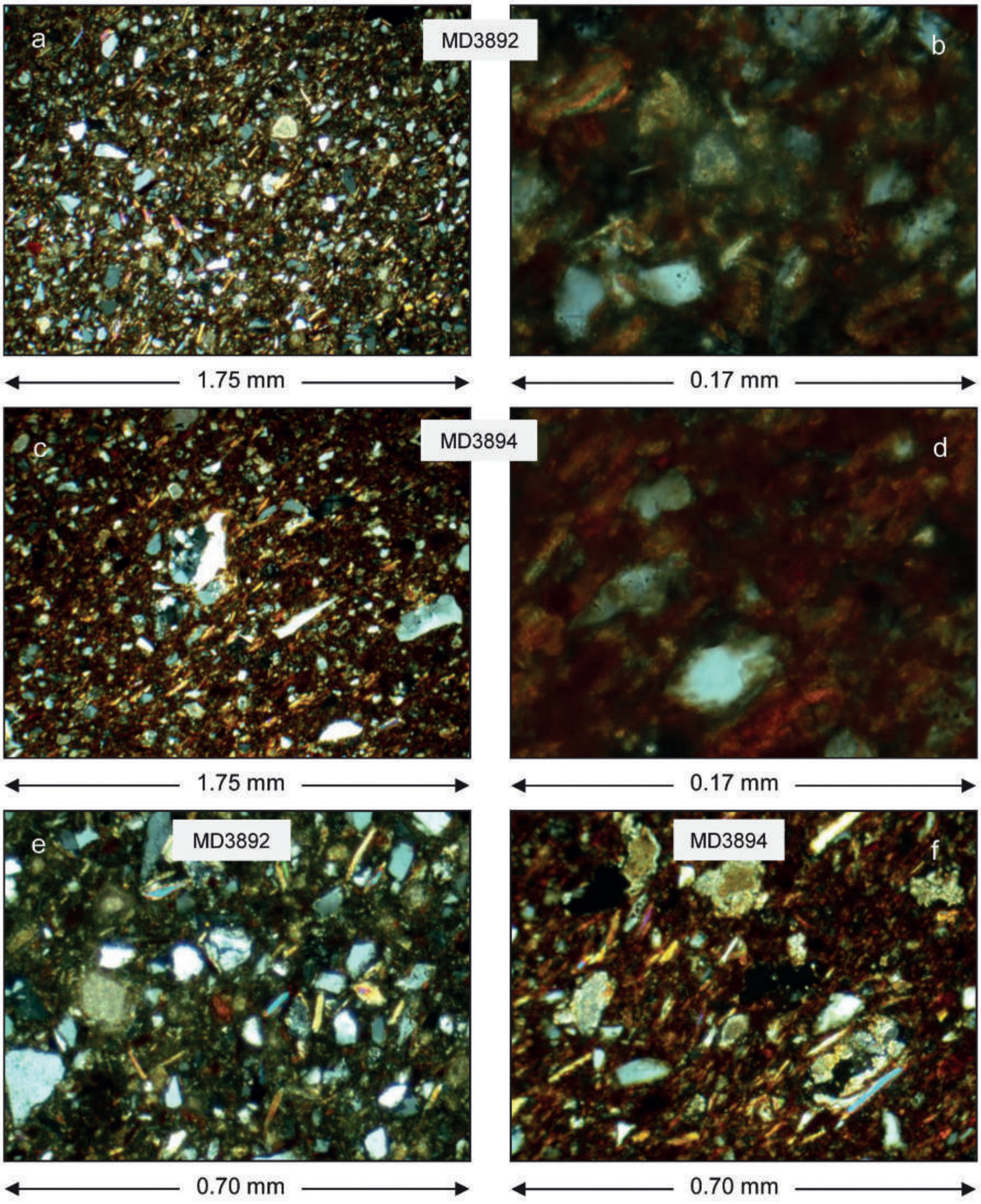
Pl. 19. Micrographs of typical fabric images of CW sample MD3879 (XPL)
(micrographs G. Schneider, compiled by H. Baranowska)



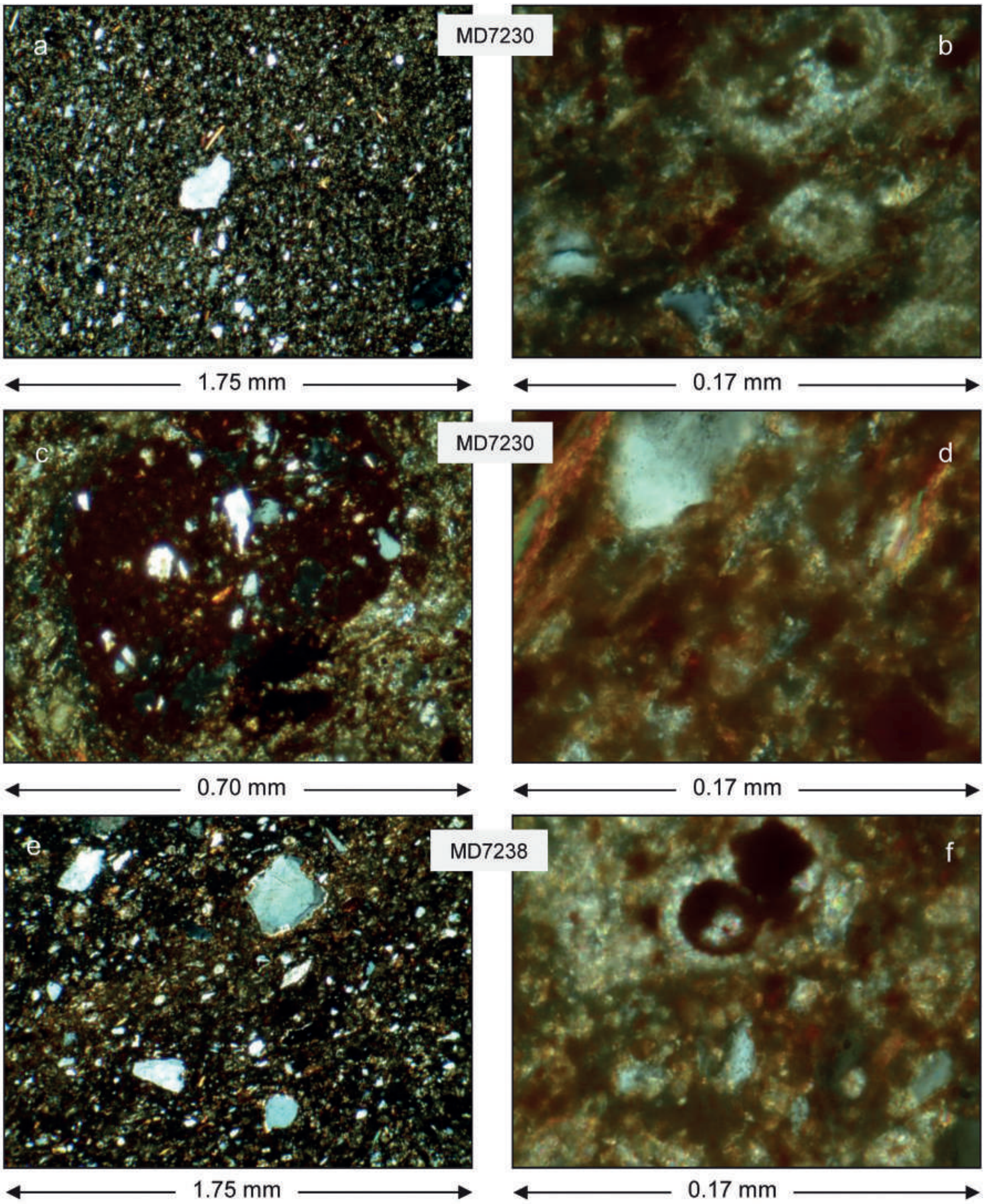
Pl. 20. Micrographs of typical fabric images of CW sample MD3886 (XPL)
(micrographs G. Schneider, compiled by H. Baranowska)



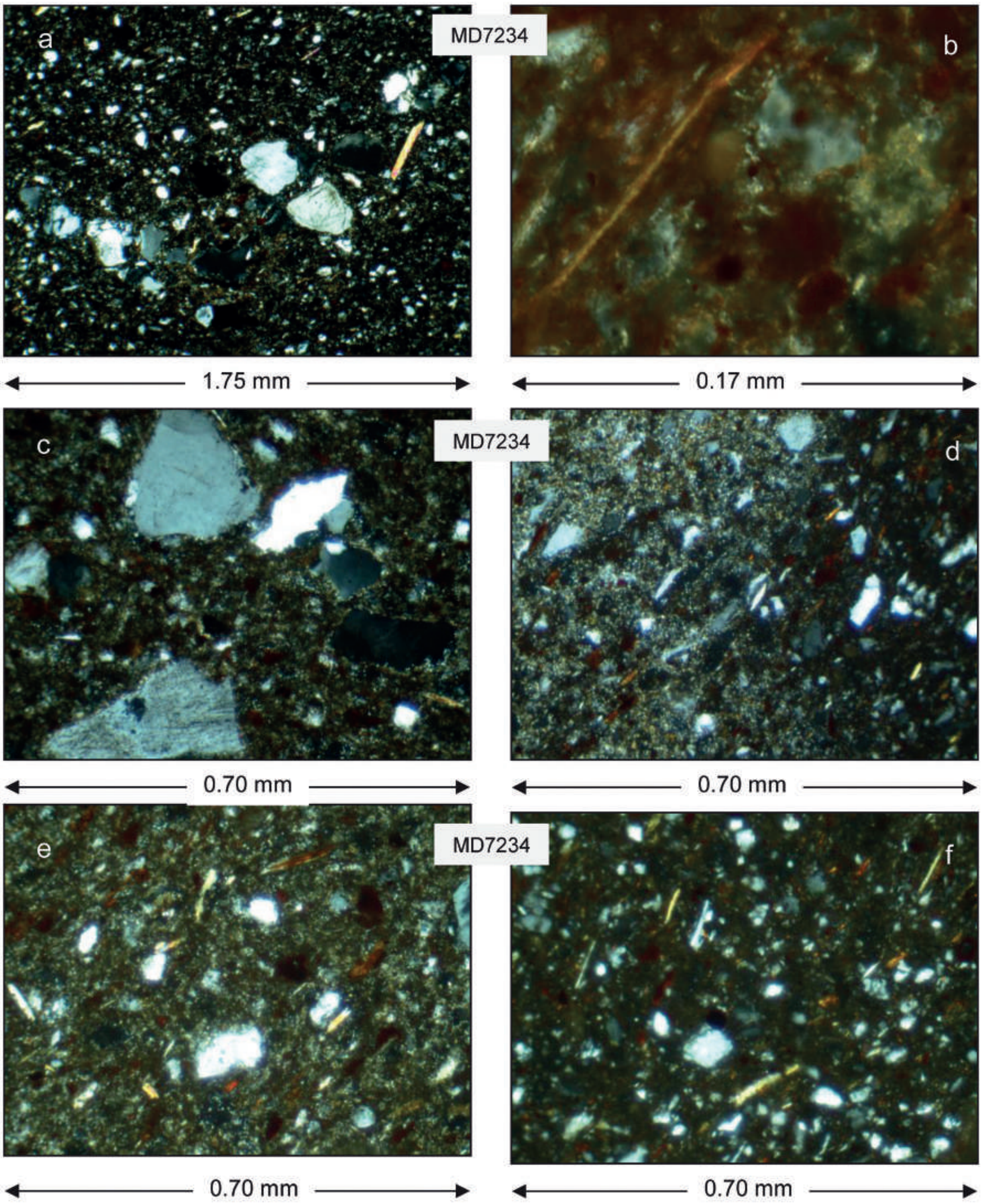
Pl. 21. Micrographs of typical fabric images of TW samples MD2544, MD3242 (XPL)
(micrographs G. Schneider, compiled by H. Baranowska)



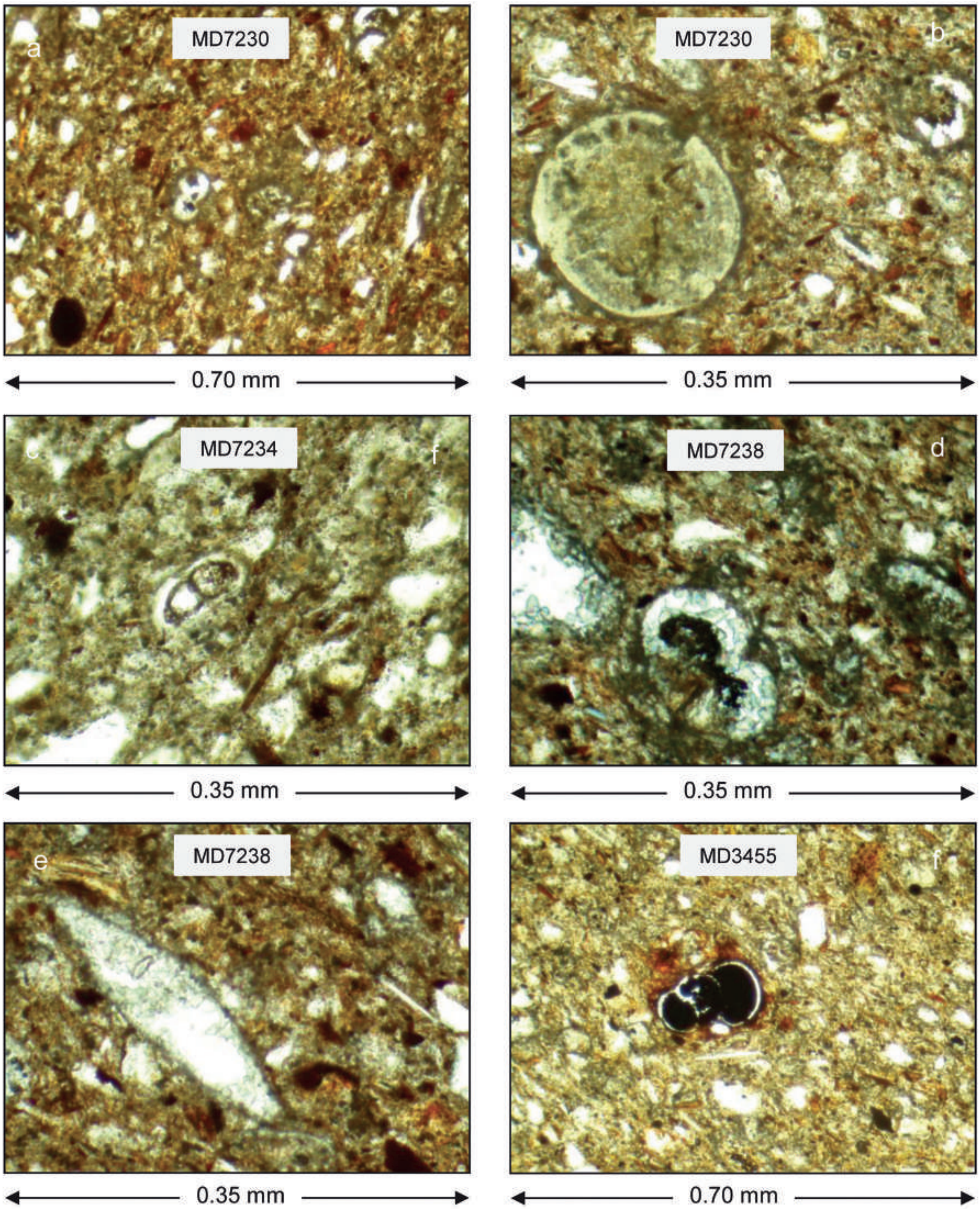
Pl. 22. Micrographs of typical fabric images of CBM samples MD3892, MD3894 (XPL)
(micrographs G. Schneider, compiled by H. Baranowska)



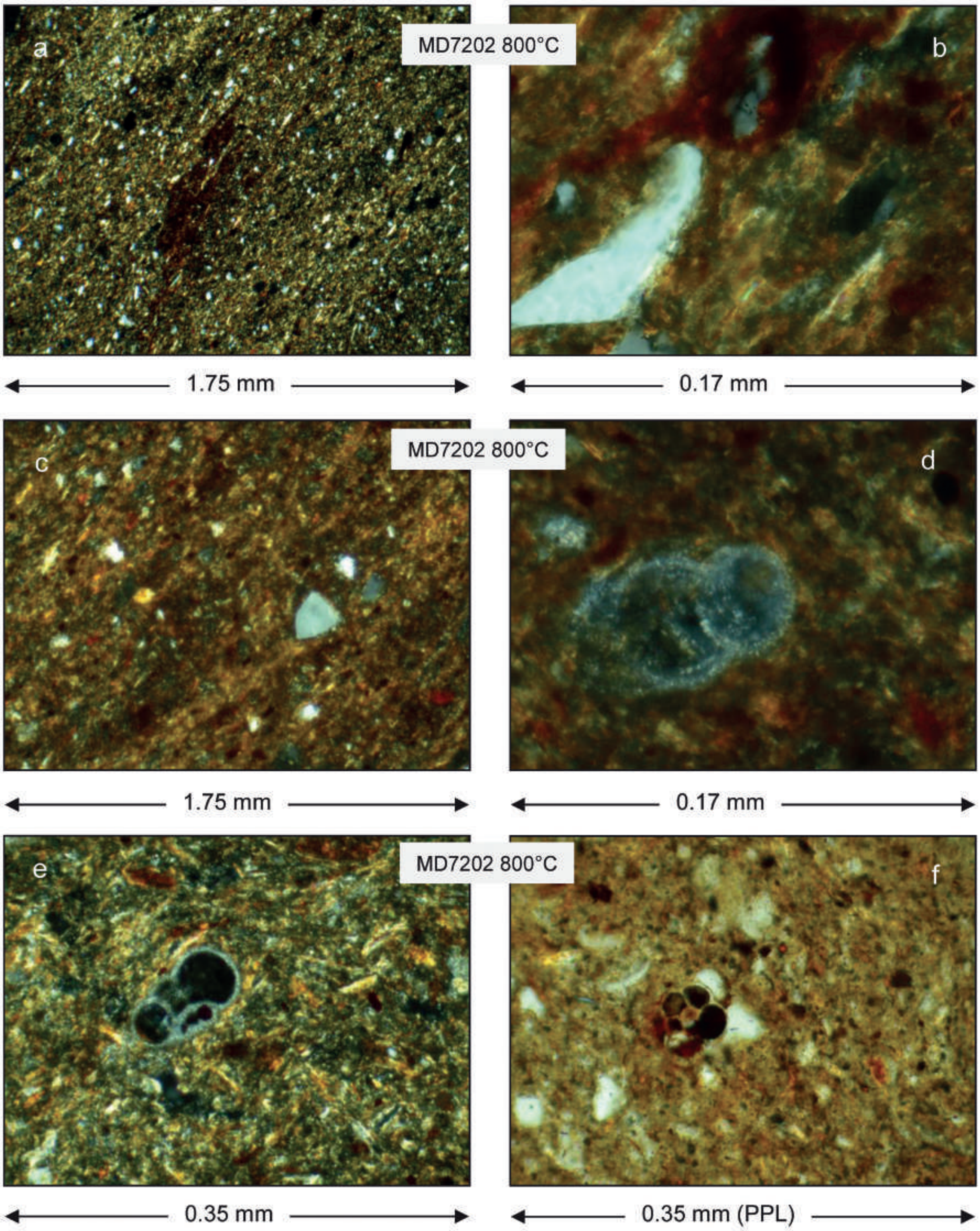
Pl. 23. Micrographs of typical fabric images of CBM samples MD7230, MD7238 (XPL)
(micrographs G. Schneider, compiled by H. Baranowska)



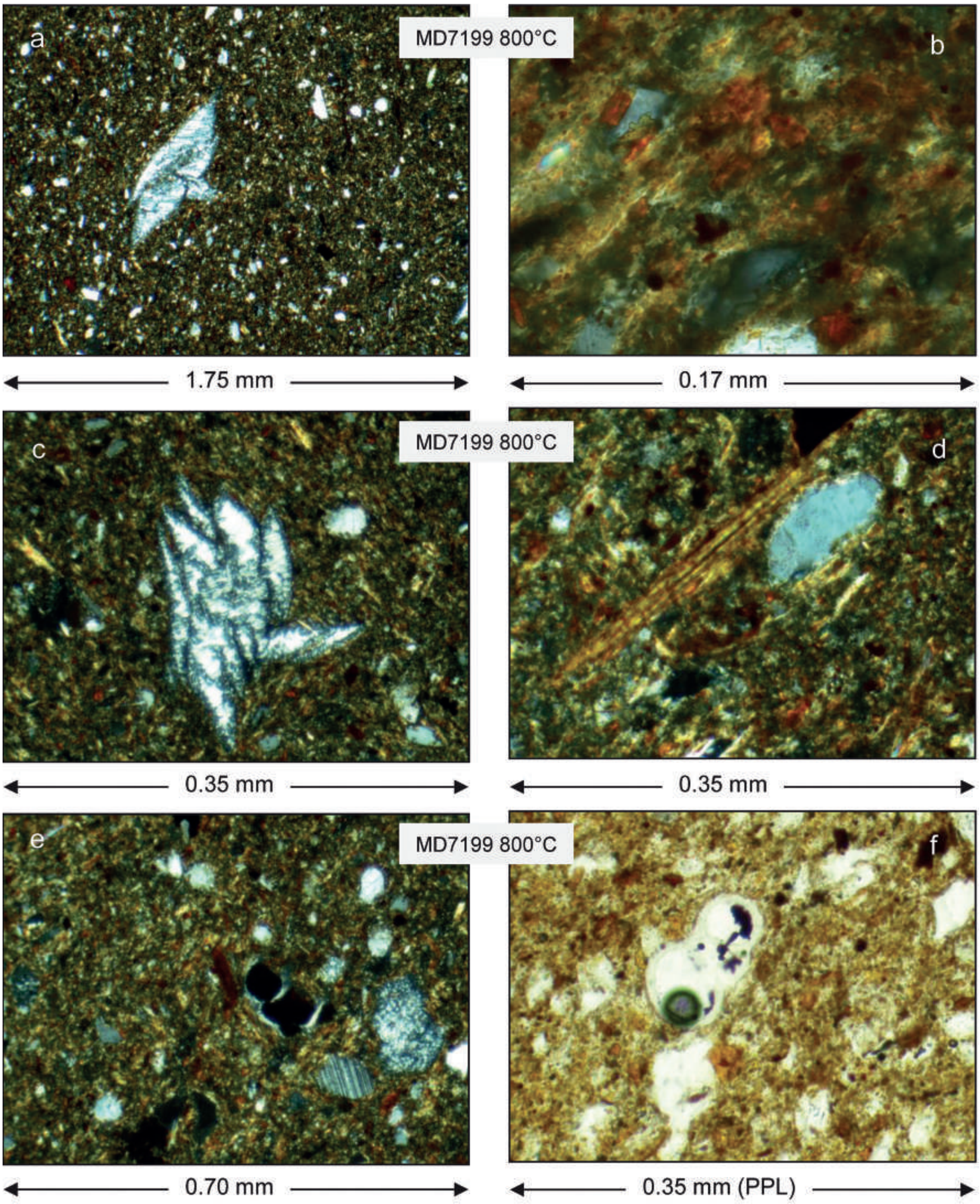
Pl. 24. Micrographs of typical fabric images of CBM sample MD7234 (XPL)
(micrographs G. Schneider, compiled by H. Baranowska)



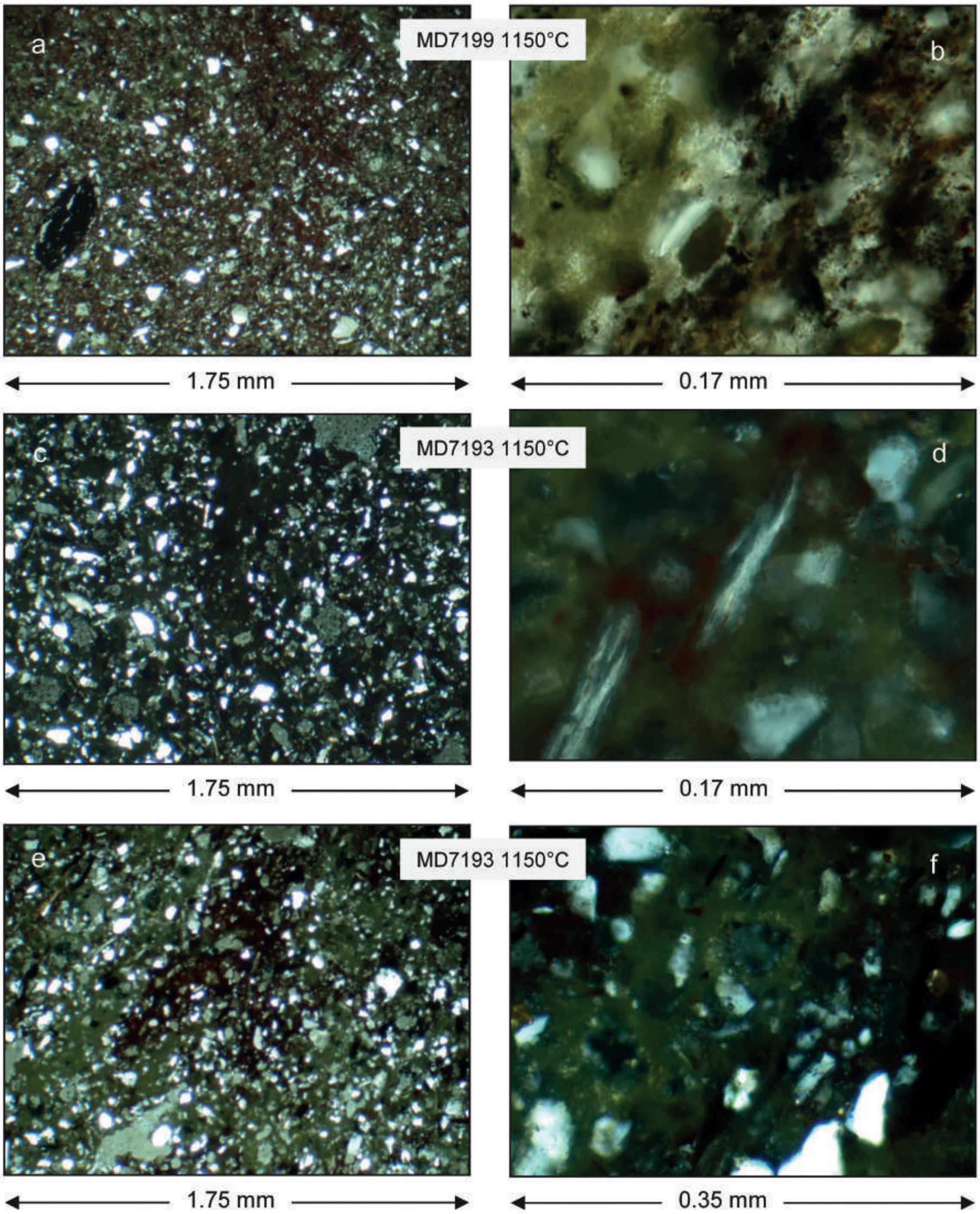
Pl. 25. Micrographs of typical fabric images of CBM samples MD7230, MD7234, MD7238, MD3455 (XPL) (micrographs G. Schneider, compiled by H. Baranowska)



Pl. 26. Micrographs of typical fabric images of clay sample Studena (MD7202) fired at 800°C (XPL) (micrographs G. Schneider, compiled by H. Baranowska)



Pl. 27. Micrographs of typical fabric images of clay sample Ovča Mogila Bis (MD7199) fired at 800°C (XPL) (micrographs G. Schneider, compiled by H. Baranowska)



Pl. 28. Micrographs of typical fabric images of clay sample Ovča Mogila Bis (MD7199) and clay Bâla Voda Bis (MD7193) fired at 1150°C (XPL) (micrographs G. Schneider, compiled by H. Baranowska)