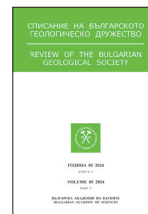




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Preliminary studies of Bulgarian natural raw materials as possible sources for the synthesis of high-quality ceramics of the “yellow” pavers type

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Предварителни проучвания на български природни суровини като възможни източници за синтез на висококачествена керамика от типа „жълти“ павеа

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Резюме. Представени са резултати от предварителни проучвания на български природни суровини като възможни източници за синтез на висококачествена керамика от типа „жълти“ павеа. За целите на сравнителен анализ е направен кратък геолого-минералогичен литературен обзор на български и унгарски находища на мергелни суровини и на български находища на немергелни богати на магнезий суровини. Демонстрирани са възможностите на рентгено-флуоресцентния (XRF) анализ и техниките на праховата рентгенова дифракция (PXRD) за експресно получаване на надеждни данни за фазово-химичната характеристика на изследваните материали. Направена е връзка между тези характеристики и физикохимичните и механичните свойства на евентуално синтезирани от тях продукти (цвет, твърдост и др.). Представени са съображения за избор на методики за обработка на първичната информация, допускащи известно опростяване без да се засяга достоверността на резултатите. Последните са анализирани и са дискутирани възможности за подобряване на качествата на изходната суровина с цел получаването на изделия с желани характеристики.

Ключови думи: жълти павеа, мергели, XRF, PXRD.

Abstract. The results of preliminary studies of Bulgarian natural raw materials as possible sources for the synthesis of high-quality ceramics of the “yellow” pavers type are presented. For the purposes of comparative analysis, a short geological-mineralogical literature review of Bulgarian and Hungarian deposits of marl raw materials and of Bulgarian deposits of non-marl raw materials rich in magnesium is made. The capabilities of the X-ray fluorescence (XRF) analysis and the powder X-ray diffraction (PXRD) techniques for the rapid acquisition of reliable data on the phase-chemical characteristics of the investigated materials have been demonstrated. A relation is made between these characteristics and the physicochemical and mechanical properties of possibly synthesized products (color, hardness, etc.). Considerations for choosing methods for processing the primary data are presented, allowing for some simplification without affecting the reliability of the results. The latter have been analyzed and possibilities for improving the qualities of the starting raw material have been discussed in order to obtain products with desired characteristics.

Keywords: yellow pavers, marls, XRF, PXRD.

Introduction

The characteristic yellow color of the pavement of some of the streets and squares in the center of

Sofia has long become emblematic of our capital. The expression “yellow pavers” itself has become a symbol denoting the location of historical monuments, cultural, educational, scientific, religious

and administrative buildings that house government and financial institutions taking important decisions for the country. The paving was produced using a special technology from natural raw materials in an enterprise located nearby Budapest, then within the borders of Austria-Hungary. After its purchase, it was placed in the center of Sofia between 1907 and 1909 on a total area of nearly 60,000 square meters. It has witnessed historical events and vicissitudes. However, over a hundred-year period of operation leaves its mark – broken integrity of the blocks, lacks, slippery surface, etc. Today, yellow pavers occupy an increasingly smaller area and are threatened with extinction. In 2013, they were declared as cultural heritage by a unanimous decision of the Metropolitan Municipal Council. In terms of the Law on cultural heritage, they are described as a cultural monument (https://yellowpavement-sofiabg.blogspot.com/p/7_16.html, last visited on 16 March 2024).

In addition to the desire and administrative measures for the protection of the yellow paving, this status also gives rise to various initiatives for the study of their composition, structure and properties with the prospect of organizing own production from Bulgarian natural raw materials with equivalent or better quality of the final product. For example, in 2014, with modest European funding, a project entitled “Study of the composition, structure, properties and method of obtaining the yellow pavers in Sofia” was launched, initiated by the Sofia municipality, for which a contract was concluded between it and the Bulgarian Crystallographic Society – a legal entity non-profit association (<https://www.bgcryst.com/>). For its implementation, research teams from the Bulgarian Academy of Sciences (Institute of Physical Chemistry and Institute of Mineralogy and Crystallography), University of Mining and Geology, Sofia and University of Architecture, Civil Engineering and Geodesy, Sofia, were involved. Initial data were obtained characterizing the composition and physicochemical properties of yellow pavers (Report of Ist stage of Project, “Study of the composition...., 2014). To date, the authors of the present study are aware of at least two projects that participated in competitive procedures and received funding from the National Research Institute in Bulgaria for research related to the topic. The results reported in specialized publications and at various scientific forums are: Encheva et al., 2016; Lakov et al., 2018a, b, 2021, 2022; Gacheva

et al., 2019a, b; Mutaftchieva et al. 2022a, b, 2023; Karamanov, 2023; Karamanova et al., 2023; Karamanov et al., 2024, etc.

When conducting research related to the production of ceramic products the accumulated knowledge about the influence of the type of mineral ingredients in the starting materials (composition, structure, properties) on the physical properties of the intermediates (plasticity, firing shrinkage, porosity) should be taken into account and from there to those of the final products (color, physical-mechanical properties, thermal conductivity), etc. (Wang et al., 2023). Previous research (Report of Ist stage of Project, “Study of the composition...., 2014; Karamanov et al., 2024) on the chemical composition (classical silicate and energy dispersive (EDS) chemical analyses) of yellow pavers have shown the following results: SiO₂ content over 50 wt%; Al₂O₃ – around and below 15 wt%; CaO – around and below 17 wt%; MgO and FeO contents of about and exceeding 5 wt% for each of the oxides; very low percentages of alkali oxides. Averaged elemental composition (in wt%) has been determined as follows: Si 45.37; Al 14.53; Ca 22.25; Fe³⁺ 6.41; Mg 5.53; K 4.56; Na 1.35. Phase identification and quantification (by the Rietveld method) of the same objects have shown the following results: formation of the high temperature synthetic phases pyroxene and anorthite in ratios ranging from 2:1 to 1:1; presence of X-ray amorphous (glassy) phase of about 15–25 wt%; minimal presence of quartz and aluminosilicates of probably residual origin from the initially used material (Report of Ist stage of Project, “Study of the composition...., 2014; Encheva et al., 2016; Karamanov et al., 2024). Recently, a sample of original yellow paver has been subjected to a quantitative phase analysis by the Rietveld method using an internal standard – silicon powder (Si) (to be published). The following results were obtained: 38 wt% anorthite solid solution (s.s.); 34 wt% pyroxene (diopside) phase; 4 wt% quartz; 4 wt% silicon powder (Si); and 20 wt% x-ray amorphous (glassy) phase. The elemental composition of the same sample was obtained by X-ray fluorescent (XRF) spectroscopy (Supermini 200 spectrometer – Rigaku, Japan; IMC-BAS) as follows: Si 37.86 wt%; Al 11.47 wt%; Ca 30.45 wt%; Fe³⁺ 8.74 wt%; Mg 3.31 wt%; K 5.83 wt%; Na 1.00 wt% and about 1 wt% of Ti, Mn, Sr and other elements-admixtures.

The above reported results (within the corresponding compositional ranges) are a consequence

of both the mineral composition of the starting raw material – marl deposits from the surroundings of Budapest, and the specific procedures of the thermal treatment applied to obtain the paving stones. Undoubtedly, the relationships between the quantitatively predominant newly formed phases pyroxene, anorthite and X-ray amorphous (glassy) mass are responsible for both the characteristic color and the physico-mechanical properties of the finished product.

“Yellow pavers” are an interesting topic for the Bulgarian research community because it unites the efforts of scientists from various fields of material science (geology, mineralogy, physical chemistry, civil engineering, etc.) in the implementation of interdisciplinary research, the results of which can be:

(i) obtaining new knowledge about Bulgarian natural raw materials, suitable for obtaining high-quality ceramic products, such as “yellow paving stones”;

(ii) obtaining new knowledge about the methods and techniques for obtaining similar products;

(iii) opportunity to restore and supplement areas paved with the emblematic pavement in the historic center of our capital.

In the first part of this work, brief information is presented on the distribution and mineral composition of the Hungarian marl raw material – an assumed starting material for the production of the yellow paving stones, as well as those for the Bulgarian marl raw material with potential for the production of the identical product. Similar information is given for magnesium-containing non-marl natural materials from Bulgaria as a possible additive in synthesis procedures. In the second part, the results of preliminary studies of Bulgarian natural raw materials, suitable for the synthesis of high-quality ceramics of the “yellow” pavers type, are presented. Samples of marls, dolomite, talc, talc schist and magnesite from different localities were studied by powder X-ray diffraction (PXRD), X-ray fluorescence (XRF) analysis and in some cases Mössbauer spectroscopy (MS). In addition to phase identification, most samples were characterized by semi-quantitative phase analysis and where possible by quantitative Rietveld analysis. The obtained marl data are compared and analysed for advantages and disadvantages. Possibilities of using additives from other natural raw materials to correct missing components in order to obtain optimal mineral compositions of the starting material are discussed.

Brief information about available natural raw materials as a potential source for the production of yellow pavers

Hungarian Marls

The clay formation of Buda – Kiscell clay (KC) has been used for brick and tile production. Clay pits were already established in the middle of the 19th century in the Budapest region, Hungary (Görög, Török; 2006). This is an Oligocene clay formation and the bedrock is a massive Triassic limestone or dolomite. It is divided into two units having different properties. The lower layer is grey and impermeable, while the upper one is weathered, carbonate is leached and pyrite and other iron-containing minerals are oxidized to limonite. This causes a color change so the grey colour turns to yellow and the beds behave like clayey material. The mean carbonate content of the KC is approximately 15% and is primarily presented by a micritic calcite matrix (Duhović et al., 2022). In 2009 Tóth reported for the KC that “the clay mineral fraction comprises smectite (27 wt%), muscovite (36 wt%), mixed-layer clay minerals, i.e., illite/chlorite and kaolinite/chlorite (37 wt%). Quartz, calcite, dolomite and feldspars can also be recognized by X-ray diffraction (XRD)” (Tóth, 2009).

Assuming that together calcite from the matrix and the calcite and dolomite grains presented in it make up a total of 15 wt%, and quartz and feldspar – about 5 wt% amounts and ratios of the clay minerals should be as follows: smectite (21 wt%), muscovite (29 wt%), mixed-layer clay minerals, i.e., illite/chlorite and kaolinite/chlorite (30 wt%).

Bulgarian Marls

The geological formations to which marl deposits are attached are distributed mainly in Northern Bulgaria – Moesian Platform and Fore-Balkan Mts. The largest quarries for extraction of this raw material, important for the production of cement, building materials and ceramic products, are also concentrated there: Koritna, Yablanitsa (“Zlatna Panega Cement” – Titan Group Bulgaria); Beli Izvor, Vratsa (“Holcim Bulgaria” Ltd.); Mezdrinsky Vrah, Mezdra (“Stroykeramika” JSC); Karierata, Svetlen, town of Popovo, Targovishtko (“Rodna Industria-91” Ltd.), etc., reflected in the register of active concessions for the extraction of underground resources, taken

from the website of the Ministry of Energy of the Republic of Bulgaria (<https://www.me.government.bg/themes/koncesii-za-dobiv-735-1613.html>, current as of 03/13/2024). Such a lithostratigraphic unit with a wide distribution in Northeastern Bulgaria is the Gornooryahovska Formation (GOF) with a chronological range – Lower Barremian–Lower Aptian (Bonchev, 1957; Nikolov, 1969). It is almost entirely made up of marl rocks, among which slightly silty clay marls predominate and, to a lesser extent, pure marls (Cheshitev et al, 1992a; Cheshitev et al, 1992b; Filipov, 1992; Filipov, Cheshitev, 1992; Hrishev, Nedialkova, 1991; Hrishev et al., 1990; Nedialkova, Cheshitev, 1992). A characteristic feature is its relatively monotonous mineral composition. In 1955, Demirev reported the results of engineering geological studies of clayey marls from the same formation in the area of the future Rositsa dam (now Alexander Stamboliyski dam) north of the town of Sevlievo (Demirev, 1955). The petrographic characterization reported a clay fraction over 30%, an average CaCO_3 content of 20%, an amount of matrix (the main mass) up to 80% and clastic terrigenous material in an amount of up to 20–30%, represented by quartz grains and more rarely feldspar, calcite, pyrite oxidized to goethite and traces of muscovite. According to X-ray data, the clay mineral was identified as illite (a sericite-like mineral, muscovite).

In 2015, Lenchev et al. report their results for clayey marls from Butovo and Ovcha Mogila deposits (Veliko Tarnovo), Razdelna (Varnensko), Tanyova Molgila (Gorna Oryahovitsa), etc., falling within the scope of the Gornooryahovska Formation (Lenchev et al., 2015). The clayey substance is reported to be composed of illite with admixtures of kaolinite and traces of montmorillonite. The content of CaCO_3 reaches up to 40 wt%, and the rest of the components vary within the following limits (in wt%): SiO_2 35–60; Al_2O_3 10–18; Fe_2O_3 4–6; MgO 2–3; $\text{Na}_2\text{O}+\text{K}_2\text{O}$ 2.1–2.8 (p. 82 in Lenchev et al., 2015).

X-ray phase analysis of marl from the Popovo deposit (GOF) shows that, in addition to calcite (CaCO_3) and kaolinite, it contains illite, quartz and chlorite and that it has the following chemical composition, wt%: SiO_2 – 41.56; Al_2O_3 – 11.90; CaO – 18.40; Fe_2O_3 – 5.00; MgO – 2.30; R_2O – 2.14 ($\text{R} = \text{Na}, \text{K}$); Loss on Ignition (LOI) – 18.70 (Koruderlieva et al., 2004). For the purposes of the comparative analysis further on in this work, this

composition of the marls from Popovo is presented by elements without considering LOIs, as follows: Si 42.80 wt%; Al 13.88 wt%; Ca 28.97 wt%; Fe^{3+} 7.70 wt%; Mg 3.07 wt%; $\text{R}=\text{K}+\text{Na}$ 3.58 wt%.

Dolomites (Delyan quarry, Dupnitsa Municipality)

The deposit is located about 20 km north of the town of Dupnitsa. It is built of Middle Triassic dolomites. The mineral composition is mainly represented by dolomite and in a very small amount of calcite and clay minerals (Chatalov, 1988).

Magnesite (abandoned quarry, “Seltse” area, Dorkovo village, nearby the town of Velingrad)

The quarry has been in operation for asbestos and vermiculite for several decades since the early 1960s. It falls within the scope of the Bogutevska Plagiogneiss Formation (bogPeD) on a lenticular metaserpentine body, the result of intensive alteration of primary ultrabasites with a probable peridotite composition under the successive influence of auto- and allotriomorphic processes (Kozhoukharov et al., 1992; Petrov, Nesheva; 2007). Magnesite occurs as subparallel veins up to 8 cm thick in the loose environment of highly weathered ultrabasite. It is often found in association with opal tridymite-cristobalite (opal CT) of later origin.

Talc (mineralization near the village of Ustrem, Topolovgrad Municipality)

Not far from the village of Ustrem, low-iron talc mineralization (Fe_2O_3 up to 0.48 wt%) is manifested. In a zone 120 m long and up to 5 m thick, small veins of talc are traced among dolomitized marbles (Zhelyazkova-Panayotova, Bozhinov, 1989).

Talc schists (Ovcharovo deposit, Harmanli Municipality)

The deposit has been in operation since 1969. It is attached to small ultrabasic bodies that have undergone strong alterations: serpentinization, talcification, amphibolitization, chloritization, and carbonation. The contact zones are often made of talc

with impurities of tremolite, chlorite and “ore dust”. The main mass is represented by talc (talc content 35–70%), in which small lenticular formations of almost monomineralic flaky talc are included (Zhe-lyazkova-Panayotova, Bozhinov, 1989).

Materials and methods

Localities, sampling and sample preparation

In the present work, clayey marls from three localities of the Gornooryahovska Formation have been studied: Karierata, town of Popovo, Municipality of Targovishte; Krusheto and Tanyova mogila, G. Oryahovitsa Municipality. The non-marl magnesium-containing raw materials are: dolomite from the quarry near the village of Delyan; magnesite from the village of Dorkovo-Seltse, mono mineral talc from the vicinity of the village of Ustrem and talc schists from the Ovcharovo deposit. The samples, in amounts of 5–10 kg each, were subjected to crushing, grinding in ceramic ball mill, and sieving to obtain fractions below 0.125 mm for further research.

Methodological approaches in relation to the characteristics of the main raw material

Among the possible methods and techniques for characterizing natural resources, similar to those listed above, those that are relatively express in their implementation have been selected. These are powder X-ray diffraction (PXRD) and X-ray fluorescence (XRF).

In the second method, sample preparation involves either manual pressing of the starting material or mixing it with a special adhesive and obtaining tablets by pressing. In both cases, there is no data on LOIs, which for the studied materials are mainly determined by the contents of CO_2 and H_2O . Both components play an important role in the technological processes for obtaining ceramics from the starting raw materials, related to the plasticity of the intermediates and the porosity of the final products. Their quantities can be determined indirectly from the mineral phases-carriers in the initial batch. These are carbonate minerals for carbon dioxide and clay minerals for water. Different techniques and preliminary procedures allow to control their contents before the actual firing of the

product. The above justifies the use of the above-mentioned sample preparation. The goal is through combined (PXRD, XRF-EDS) studies to obtain fast results for the phase-chemical characteristics of the starting materials previously studied at a very good level. Based on them, through appropriate calculations theoretical compositions and indices could be obtained in order to facilitate the application of portable hand-held X-ray fluorescence analyzers to search for suitable raw materials under field conditions. A disadvantage of these analyzers is that, most often, due to their technical characteristics, they cannot register sodium, and therefore, in the final result, there is no quantitative data for this element.

Ideally, the study should have a sample of very well processed starting material (grinding, sieving and homogenization). The combined PXRD and XRF data should provide adequate information on the mineral and chemical composition of the samples. In practice, things look different. Difficulties stem from various source, such as: the statistical representativeness of the samples taken in relation to the investigated geological body (layer, stratum, vein, etc.); the limitations of the analytical techniques used (portable XRF instruments (EDS) allow measurements in the range of Mg ($Z=12$) to U ($Z=92$) without including sodium at all in the final results); problems related to phase identification and quantification. For example, phase quantification by Rietveld method of substances with strong preferential orientation and/or consisting of small size particles which leads to profile broadening require the inclusion of a number of separate new refinable parameters in the procedure. However, this very often has negative consequences such as: strong correlation between individual parameters, time-consuming calculation procedures, instability and tendency to divergence of the specification process. Ultimately, this leads to a delay and often an inability to get the same results again.

Below are some basic characteristics of marl raw materials and problems that may arise in their characterization with the above methods and guidelines for eliminating or minimizing their effect are indicated. Some features of non-marl raw materials in their capacity as additives are also briefly discussed. The goal is optimization of activities to find or achieve suitable starting production material.

Traditionally, marls are called clay-carbonate sedimentary rocks, made up of a uniform fine-

grained mixture of **clay** and **carbonate minerals** in the ratio of 35–65% clay and 65–35% carbonate. Not infrequently they contain clastic, **terrigenous material** in varying amounts and grain sizes.

Carbonate minerals. They are represented most often by calcite, but can also be aragonite, dolomite, siderite, etc. They are most often present in the micritic matrix, but can also form part of the terrigenous material. Their quantity in the starting raw material affects the type and properties of the final product, because in the course of the thermal reactions they release gas – CO_2 , which can have an impact on the porosity. Preliminary procedures for degassing the material for the initial batch are possible. As a rule, during firing, a part of calcium, together with most of the aluminum present, is directed to the formation of the anorthite s.s. phase, whereas magnesium and iron tend to the pyroxene phase. PXRD patterns of calcite and dolomite clearly differ in the positions of their most intense reflections.

Clay minerals. They may belong to any of the following larger groups: (i) Smectite group with the most common representatives being montmorillonite and vermiculite; (ii) A group of micas with the most common representatives being muscovite, illite and their varieties (sericite), often formerly designated as hydromicas, glauconite; (iii) Chlorite group with clinocllore and chamosite as the most common representatives; (iv) Kaolinite subgroup with the most common representatives – kaolinite and its polymorphs. The representatives of the individual groups clearly differ in the positions of their main reflections on the diffractograms. There are difficulties in separating kaolinite (Kln) from typical chlorites (Chl) due to peak overlapping of their most intense basal reflections with a particularly strong effect in the case of small crystallite sizes (below 100 Å): $\text{Kln}(001) + \text{Chl}(002)$, $d \approx 7 \text{ Å}$ at about $12.4\text{--}12.6^\circ 2\theta$ and $\text{Kln}(002)$, $d = 3.57 \text{ Å} + \text{Chl}(004)$, $d = 3.53 \text{ Å}$ at about $24.9\text{--}25.1^\circ 2\theta$. This is overcome with increased demands on the quality of the X-ray diffraction experiment. It is almost impossible to identify the individual phases within each of the groups. Quantitative determinations are hampered by a strong preferential orientation along the basal reflections, characteristic of all clay minerals, and the often small particle size leading to profile line broadening. It should be kept in mind that in the absence of a dolomite component, the amount of Mg^{2+} , Fe^{2+} , Fe^{3+} , Cr^{3+} and other transitional elements is determined by the presence of representa-

tives from this group of minerals, mainly chlorites and to a lesser extent smectites and micas. Particular attention is required for the presence and quantity of smectite representatives, due to their property to increase their volume when in contact with water, which leads to significant changes in the plasticity of the starting material and more special requirements to the molding process to avoid unwanted phenomena such as “firing shrinkage”.

Terrigenous material. It is typically dominated by quartz, feldspar, clay minerals, iron oxides, and terrestrial organic matter. The presence of carbonate minerals is possible. Besides the quantity, for some minerals (quartz, feldspars) the size of the particles is also important. In the course of petrification procedures, it is possible that larger particles fail to dissolve and then they are also stored in the final product, which can degrade some of its mechanical properties. A possible way to minimize this result is to pre-treat the raw material by grinding and sieving to fractions of a certain size. Unproblematic identification of quartz and data from quantitative phase determinations performed on PXRD data are one means of approximating the amount of terrigenous material in the sample as a whole.

Preliminary studies of Bulgarian marl raw material (Report of Ist stage of Project, “Study of the composition...”, 2014; Lakov et al., 2018a; (Cheshitev et al, 1992a; Cheshitev et al, 1992b; Filipov, 1992; Filipov, Cheshitev, 1992; Hrishev, Nedialkova, 1991; Hrishev et al., 1990; Nedialkova, Cheshitev, 1992; Lenchev et al., 2015) and own data from the present study from the described areas show relatively low and persistently spatially monotonous sodium contents in the samples taken from them (0–1 wt%). During the thermal synthesis, this element is directed either to the anorthite s.s. phase, where it is in a subordinate amount compared to calcium, or possibly remains in the X-ray amorphous phase. The behavior of potassium (about 1–4 wt%) is expected to be similar. This is due to the increased miscibility of the feldspar end members – albite $\text{NaAlSi}_3\text{O}_8$, orthoclase/microcline KAlSi_3O_8 and anorthite $\text{CaAl}_2\text{Si}_2\text{O}_8$ with increasing temperature, well known from the widespread triangular diagrams for this group. It follows that the absence of sodium content data is not essential in this study and can therefore be ignored. The results of the X-ray fluorescence analysis can be used to construct indicators to serve as a guide to the phase composition and quantitative phase relationships in the samples. Such can be, for example: $(\text{Mg} + \text{Fe} + \text{Mt})/(\text{Ca})$,

where Mt – transition metals (Ti, Cr, Mn, etc.), which gives an indication of the approximate ratio of clay to carbonate minerals; (Si+Al)/Ca, which makes the same for the ratio between the aluminosilicate component (clay minerals+part of the terrigenous ones) and the carbonate material, etc.

The $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio and its change during heat treatment is also of great importance. One of the methods for establishing and controlling this indicator is Mössbauer spectroscopy. In the present study, it was applied only to the marl samples. The aim is to be able, after the thermal experiments carried out with them, to compare the ratios of the iron atoms in the divalent and trivalent state and to draw conclusions about their evolution during the oxidation-reduction processes taking place and regarding their coordination number in the final products.

In the non-marl raw materials used, sodium should, as a rule, be absent if the material under study is pure. Its presence is an indication of unwanted admixtures. Therefore, the correctly conducted phase identification of the samples is a first indication of the possible presence of sodium-containing compounds and largely justifies their subsequent investigation with portable XRF analyzers, despite the limitations of the latter.

The above-mentioned difficulties related to quantitative phase determinations by the Rietveld method direct research to the use of semi-quantitative phase analysis (e.g. Reference Intensity Ratio – RIR values – I/I_c). The procedure is quick and although the information is not complete and accurate, the results obtained are reliable enough to establish some quantitative relationships. Thus, for example, the kaolinite/chlorite ratio can be determined by the ratio of the peak heights of the partially overlapping strongest lines of the two minerals, when there are conditions and grounds for this. Other important parameters that can be deduced from quantitative phase determinations made from PXRD data can be: amount of clay minerals/amount of carbonate minerals; quartz/(clay + carbonate minerals), etc. They generally provide information on the relationships between some initial phases, and subsequently guidelines for conducting the firing procedures in order to obtain final products with desired qualities and properties.

Powder X-ray Diffraction (PXRD)

The powder XRD patterns of the studied samples were recorded on Empyrean Powder X-ray dif-

fractometer (Malvern Panalytical, Netherlands) equipped with PIXcel^{3D} detector, using Cu radiation ($\lambda = 1.5406 \text{ \AA}$) at 40 kV and 30 mA, in the range $3\text{--}100^\circ 2\theta$ range, a scan step of 0.013° for 69 s/step (total time 35 min). Phase identification was carried out using the HighScore Plus (HS+) program (Degen et al., 2014) and/or through X-ray powder diffraction patterns simulated on the basis of appropriate crystal structural models derived from the available databases (retrieved, NIST Inorganic Crystal Structure Database, 2020; Downs, Hall-Wallace, 2003) using the PowderCell (PC) program (Kraus, Nolze, 1996). The semi-quantitative phase analysis was also conducted in the same environments. Where appropriate Rietveld refinement procedures have been carried out with the GSAS program and EXPGUI (Toby, 2001; Larson, von Dreele, 2000).

X-ray fluorescent (XRF) spectroscopy

The X-ray fluorescence analyses were performed using Supermini 200 spectrometer – Rigaku, Japan with data collection at 50 kV and 4.00 mA, capable to detect sodium ($Z = 11$) (SUPERMINI XRF). Each sample was ground and then pressed to obtain a tablet. The sample/tablet was placed in a holder with an irradiated area of 30 mm in diameter. The weight ratio of the amount of sample to the amount of glue (Acrawax C powder) was 5:1. A semi-quantitative method (SQX) was used to determine the elemental composition. In addition and according to the methodological purpose of the research, S1 TITAN Bruker Handheld XRF Analyzer, Model 800, Germany with excitation parameters 15–30 kV and 9.2–17 μA , application Geo-Mining, unable to quantify sodium (TITAN XRF).

Mössbauer spectroscopy (MS)

The Mössbauer spectrum was measured on an electromechanical spectrometer (Wissenschaftliche Elektronik GMBH, Germany) operating in constant acceleration mode at room temperature. $^{57}\text{Co}/\text{Rh}$ (activity $\cong 10 \text{ mCi}$), standard- $\alpha\text{-Fe}$ was used as a source. The experimentally obtained spectrum was processed using the WinNormos program. The parameters of hyperfine interactions are determined – isomer shift (δ), quadrupole splitting (Δ), quadrupole shift (2ε), effective internal magnetic field (B_{hf}), as well as line width (Γ_{exp}), and relative weight of partial components (G) of the spectra.

Results

Figure 1 shows the localities sampled for the present studies. Marl raw materials are marked with yellow markers, and non-marl, magnesium raw materials - with light blue markers.

Figure 2 shows powder X-ray patterns/PXRD patterns of representative samples from the studied localities. The following abbreviations of names of mineral species and groups were used in the phase identification: Amp amphibole; Cal calcite; Chl chlorite; Crs cristobalite; Dol dolomite; Ilt illite; Kln kaolinite; Mgs magnesite; Qz quartz; Sme smectite; Tlc talc; Trd tridymite; Vrm vermiculite.

Figure 3 presents Rietveld refinement plots of some of the studied raw materials including data from the quantitative phase analysis.

Below are presented quantitative data on the available phases, determined by quantitative phase analysis performed with the GSAS software package (GSAS) or the PowderCell program routine (PC), as well as data on the chemical composition of the studied raw materials obtained by X-ray fluorescence analysis (SUPERMINI XRF, detecting Na or TITAN XRF without Na). For all chemical analyses, results are normalized to the sum of 100% and do not account for CO₂ and H₂O, which would be released during heat treatment from decarbonation and release of chemically bound water as losses on ignition (LOI) and therefore are not present in the

final products after firing. This makes the results of the chemical analyses of the starting and final products comparable. Data on the composition of original yellow pavers (average of 5 samples) obtained by TITAN XRF and by SUPERMINI XRF analyses (see Introduction) have been added for the purpose of comparative analysis (Table 1).

Non-marl magnesium-rich natural materials

Dolomites (Delian): GSAS: dolomite 90 wt%; calcite 7 wt%; quartz 3 wt%. Chlorite and mica are available in quantities up to 5 wt% total, which should reduce the dolomite content to 85 wt%; TITAN XRF (elements, wt%): Si 4.96; Al 1.91; Ca 59.72; Fe 1.03; Mg 32.04; K 0.34.

Magnesite (Seltse): GSAS: Magnesite 95 wt%; montmorillonite 3 wt%; cristobalite+tridymite 2 wt%. TITAN XRF (elements, wt%): Mg 84.22; Si 15.22; Ca 0.4; Fe 0.16.

Talc (Ustrem): PC: talc 95 wt%; vermiculite+chlorite+amphibole+montmorillonite 5 wt %. TITAN XRF (elements, wt%): Si 55.34; Al 1.94; Ca 6.48; Fe 1.45; Mg 34.79.

Talc schiests (Ovcharovo): PC: talc 85 wt%; quartz 4 wt%; vermiculite 7 wt%; calcite 4 wt%. SUPERMINI XRF (elements, wt%): Si 57.24; Al 1.65; Ca 0.94; Fe³⁺ 6.55; Mg 33.62. TITAN XRF (elements, wt%): Si 51.35; Al 2.32; Ca 0.66; Fe³ 0.33; Mg 39.16.

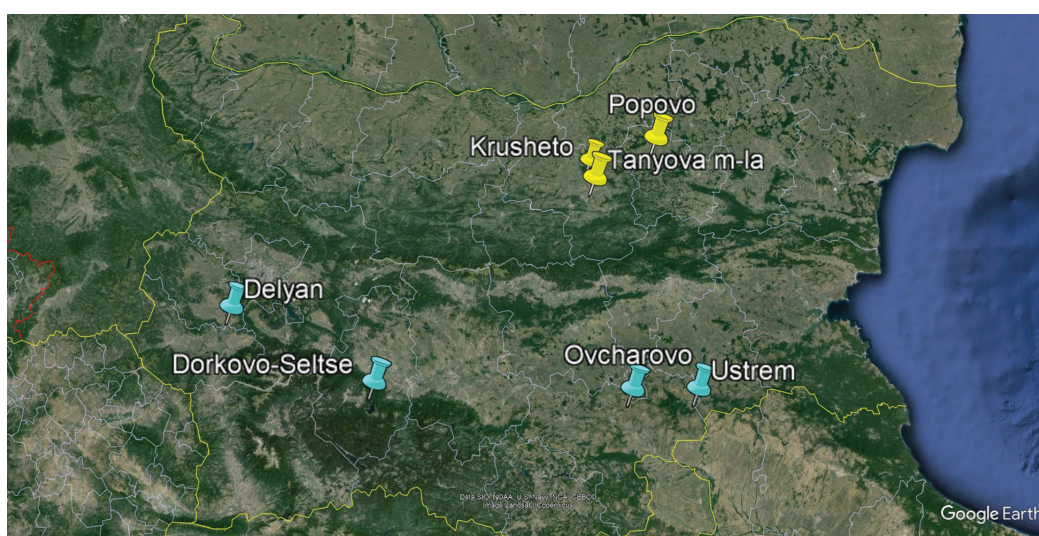


Fig. 1. Localities of sampling. Marl raw materials – yellow pin markers; non-marl, magnesium-rich raw materials – light blue pins.

Фиг. 1. Локалитети на пробоотбор. Мергелни суровини – жълти маркери; немергелни богати на магнезий материали – светлосини маркери.

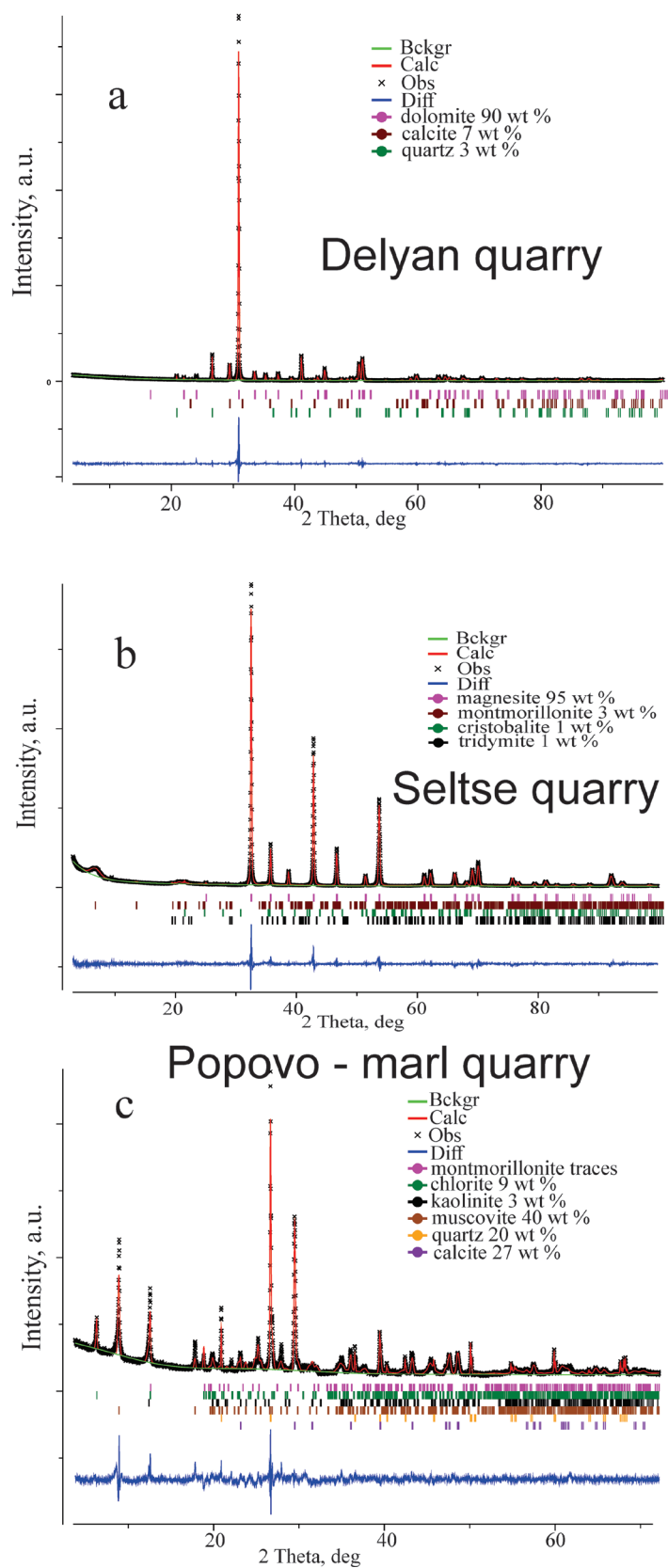


Fig. 3. Rietveld refinement plots of raw materials from: a) Delyan dolomite quarry; b) Seltse asbestos quarry; c) Popovo marl quarry

Фиг. 3. Плотове от уточнения по метода на Ритвелд на природни материали от: а) доломитова кариера Делян; б) кариера за азбест Селце; в) кариера за мергели Попово

Table 1

Data on the amount of mineral phases (PC) and information on the chemical composition (TITAN XRF) of samples of Bulgarian marl raw material.

Таблица 1

Данни за количеството на минералните фази (PC) и сведения за химичния състав (TITAN XRF) на образци от българска мергелна суровина.

Locality	Mineral phases wt% (PC)						Chemical composition, wt%, indicators, (TITAN XRF)		
	Ilt	Cal	Qz	Chl	Kln*	Sme	Mg+Fe	(Mg+Fe)/Ca	(Si+Al)/Ca
<i>I</i>	<i>2</i>	<i>3</i>	<i>4</i>	<i>5</i>	<i>6</i>	<i>7</i>	<i>8</i>	<i>9</i>	<i>10</i>
Popovo	47.5	17.5	16	13	6	-	11.93	0.57	2.97
Tanyova mogila	43	20	16	12	9	-	10.06	0.63	4.33
Krusheto	29.7	34.5	18.5	12.6	4.7?	-	10.33	0.32	1.70
Yellow paver (SUPERMINI XRF)							12.05	0.40	1.62
Yellow pavers (average of 5 TITAN XRF analyses)							12.20	0.66	3.57

* Chl and Kln were quantified as one phase in the PC routine. Subsequently their amounts were apportioned using the RIR values of their strongest lines at about 12.4–12.6° 2 θ after applying profile fitting in the (HS+) program. Data for Krusheto marl Kln is dubious since no peak is observed at this position (Fig. 2f, right).

Marl raw materials

Marls from the quarry in the town of Popovo, Targovishte district, were studied in the most detail.

Marls (Popovo): GSAS (wt%): illite (muscovite) 40; calcite 27; quartz 20; chlorite 9; kaolinite 3; smectite (montmorillonite) traces. PC (wt%): illite 47.5; calcite 17.5; quartz 16; chlorite 13; kaolinite 6. SUPERMINI XRF (elements, wt%): Si 34.84; Al 15.12; Ca 31.49; Fe 8.86; Mg 2.19; K 6.41; Na 1.09. TITAN XRF (elements, wt%): Si 43.40; Al 19.23; Ca 21.08; Fe 7.07; Mg 4.86; K 4.36.

For the purpose of a better comparison, results of the studies of marl raw materials from the three deposits obtained by PowderCell program routine (PC) and TITAN XRF are presented in Table 1.

Original yellow pavers

Averaged chemical composition of the yellow pavers obtained by TITAN XRF from five samples of the original pavement are presented here in the following sequence: element (range, wt%)–average arithmetic value, wt%: Si (50.18–52.1)–50.62; Al (14.78–15.38)–15.02; Ca (18.02–18.92)–18.40; K (3.61–3.90)–3.76; Mg (5.50–6.64)–5.98; and Fe (5.46–6.49)–6.22. The following indicators were additionally calculated (average of 5 analyses): (Mg+Fe) (10.96–12.93)–12.2; (Mg+Fe)/Ca 0.66;

(Si+Al)/Ca 3.57. The same indicators have been derived from the chemical data obtained by the SUPERMINI XRF analyses (see Introduction): (Mg+Fe) 12.05; (Mg+Fe)/Ca 0.40; (Si+Al)/Ca 1.62.

Figure 4 compares the Mössbauer spectra of a sample of marl (the quarry in the town of Popovo) and of a sample of yellow paver from the original capital pavement. Mathematical processing has been performed according to the type of spectra, using a model with three doublets. The relative weight of the partial components (G) of the spectra are indicated in the figure caption. Similar to that of Figure 4a are the spectra of the samples from the other two marl localities (not shown here).

Discussion

Analysis of the obtained results

In general, data on non-marl magnesium-rich raw materials show that the content of the main and practically interesting phases in them (dolomite, magnesite, talc) exceeds 85–90 wt% which designates them as suitable materials for supplementation.

Differences are observed in the values reflecting the quantities of the established phases, as well as in those related to the chemical composition of the studied samples, obtained by different methodolo-

gies and techniques (see the data for the talc schists from subsection Talc schists (Ovcharovo) and for the marls from Popovo). However, their order and approximate ratios are preserved. In such a case, the use of more express methods for phase quantification (e.g. PC and HS+ vs GSAS) and techniques for obtaining chemical contents (TITAN vs SUPER-MINI XRF) are justified to the extent that the meas-

ured samples are statistically representative and in achieving the best possible “a high degree of agreement” between the data from the chemical analyses and those for the quantitative phase relationships.

The data from Table 1 reveal that the investigated marls have a rather monotonous mineral composition. The differences are determined by the ratios between the clay and carbonate phases, as well as

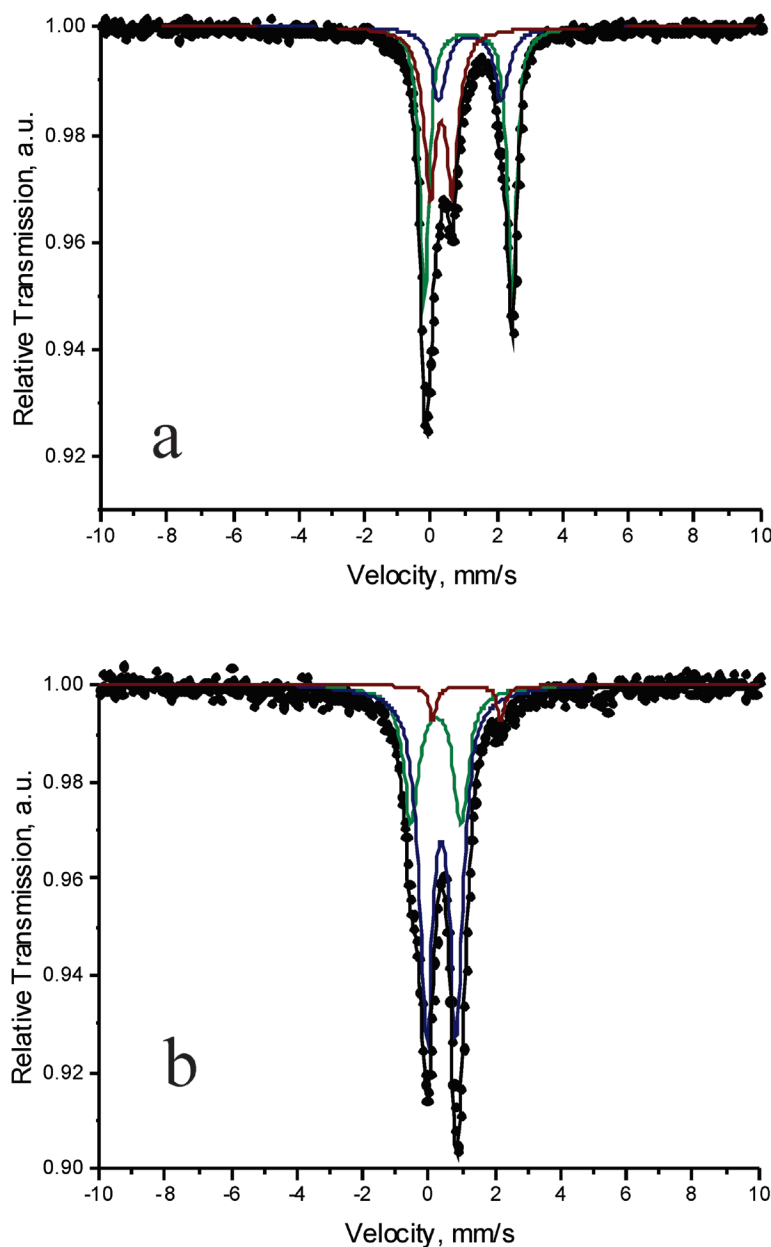


Fig. 4. Mössbauer spectra of a) marl sample (Popovo quarry): Db1-Fe²⁺ – green line (45%); Db2-Fe²⁺ – blue line (19%); Db3-Fe³⁺ – red line (36%) and b) sample of original yellow paver: Db1-Fe³⁺_{tetra} – green line (30%), Db2-Fe³⁺_{octa} – blue line (66%), Db3-Fe²⁺ – red line (4%)

Фиг. 4. Мьосбауерови спектри на а) образец от мергел (кариерата в гр. Попово): Db1-Fe²⁺ – зелена линия (45%); Db2-Fe²⁺ – синя линия (19%); Db3-Fe³⁺ – червена линия (36%) и б) образец от оригинално жълто паве: Db1-Fe³⁺_{tetra} – зелена линия (30%), Db2-Fe³⁺_{octa} – синя линия (66%), Db3-Fe²⁺ – червена линия (4%)

the amount of quartz (of possible terrigenous origin) in them. Clay minerals (illite, chlorite and kaolinite) predominate in the samples from Popovo and Tanyova Mogila, while calcite and quartz are more common in the marls from Krusheto. Visually, this is also evident in Figure 4f, when comparing the peak intensities of the corresponding minerals. The results for sodium in the samples from Popovo confirm those of earlier studies of its limited content (about 1 wt %), there. It is most likely that it is included in the composition of representatives of illites, such as glauconite, for example. The carbonate component is represented solely by calcite. Even if it contains certain amounts of magnesium, they are insufficient to form an independent dolomite phase. In such a case, the registered amount of iron and magnesium in the sample is most likely due to the presence of these elements in the chlorites and to a lesser extent in the illites.

This is justified when comparing the data in columns 5 and 8 of Table 1. However, there is a discrepancy when comparing the peak intensities of the respective phases presented in Figure 2, which can for now only be explained by poor homogenization of the sample from the Krusheto locality.

The results of Mössbauer spectroscopy for marl from Popovo (Fig. 4a) show that two of the doublets have parameters characteristic of Fe^{2+} and one has parameters corresponding to Fe^{3+} . The Db1 doublet is characterized by higher quadrupole splitting values than those of Db2, which is an indication of a smaller symmetric electrostatic field around the iron core. Generally speaking, the doublet parameters Db1 and Db2 correspond to Fe^{2+} in two non-equivalent positions in the crystal lattice of phyllosilicates (Dyar, 2002; Biedermann et al., 2014; Czaja et al., 2014). The Db3 doublet is probably due to Fe^{3+} in the tetrahedral layer. In the spectrum of the yellow paver sample, three positions of the iron with the corresponding doublet components were determined. Two of the doublets have parameters characteristic of Fe^{3+} and one with 4% relative weight has parameters corresponding to Fe^{2+} (Fig. 4b). The parameters of the doublets are close to those of iron in the different positions (tetrahedral and octahedral) in synthetic ferri-diopside according to Hafner and Huckenholz (1971). In general, it should be noted that Fe^{2+} predominates in the marls, while in the yellow paver it is subordinated to Fe^{3+} . This is undoubtedly related to the oxidation processes that occur during heat treatment.

Comparative characteristic in order to optimize the composition of the starting raw material for the process of thermal synthesis

If it is assumed that the production of the original yellow pavers was carried out without the use of additives and the only losses during firing were due to dehydration of the clays and decarbonization of the limestones, the chemical composition of the finished products should reflect to a large extent that of the starting raw material. It is then logical to assume that in order to obtain products with similar and better physico-mechanical indicators, the starting materials should have similar characteristics to those from which the original pavers were made. Below, the data on the phase-chemical composition of Bulgarian marls obtained in the present study are compared with those of the Hungarian marls. The indicators from Table 1 (columns 8–10) were also compared with their analogous ones for the yellow pavers (subsection Original yellow pavers).

The carbonate component of the Bulgarian marls consists exclusively of calcite, while there is evidence of the presence of dolomite in the Hungarian raw material. In general, with lower amounts of carbonate minerals (about 15 wt%), Hungarian marls are more enriched in mafic components (MgO and FeO). The corresponding indicators Mg+Fe also show this. The two elements have a significant influence on the amount of the newly obtained synthetic pyroxene phase, as well as probably on the degree of crystallinity. Both parameters are closely related to the physical (color, hardness) and mechanical (wear resistance) characteristics of the final products. The absence of smectite representatives in the Bulgarian marls is striking, whereas in the Hungarian marls their amount reaches about 20% of the total raw materials weight. This has a direct bearing on ductility and hence on the molding processes during the manufacturing. It should be noted that the original yellow pavers contain about five wt% quartz, probably a residual phase from the starting material. Bulgarian marls contain over 15 wt% of this mineral. If in the course of the synthesis this quartz does not dissolve, it is likely that additional sieving procedures will be required in order to achieve a lower fraction thus reducing its amount in the initial batch. An alternative is the choice of another raw material. The comparison of the indicators (Mg+Fe)/Ca and (Si+Al)/Ca show that in terms of chemical composition, the Bulgarian marls from

the quarries in the town of Popovo and at Tanyova mogila are closest to the Hungarian raw material.

It follows from the above that adjustments are possible in the composition of the starting materials, made by adding other ingredients. In this case, these can be natural non-marl materials rich in magnesium, depending on whether they should be carbonate-containing or silicate-based.

Conclusions

Bulgaria has diverse and high-quality non-metallic mineral raw materials of important meaning for various branches of the national economy. The analysis of the existing geological and mineralogical data and characteristics of their deposits in our country and the good knowledge of the opportunities of the firing processes allow researchers to target those of them that can provide sources for the synthesis of high-quality ceramics of the type “yellow” pavers. Such are the deposits of marl and non-marl rich in magnesium raw materials available in Bulgaria. Their preliminary phase-chemical characteristics are a nec-

essary prerequisite for correct selection of starting materials for the production of final products with desired physical and mechanical characteristics (color, hardness, wear resistance, heat resistance, etc.). In this regard, X-ray fluorescence analysis and powder X-ray diffraction techniques offer fast investigations and sufficiently reliable results. In the case of handheld portable XRF instruments, data collection can also be carried out in the field. The processes related to the collection of this kind of information bring new knowledge, both about the natural mineral raw materials available in Bulgaria, and about the applied firing and densification processes, and the final products obtained from them.

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