Science, Engineering & Education,8, (1), 2023, 3-20

Contribution of University of Chemical Technology and Metallurgy to the Development of Technical Mineralogy and Petrography in Bulgaria

Irena Kirilova Mihailova

University of Chemical Technology and Metallurgy, Sofia, Bulgaria

Received 26 September 2023, Accepted 20 October 2023

"The only way to do great things is to do what you love.
If you haven't found it yet, keep looking.
Don't settle for less."

Steve Jobs

ABSTRACT

This brief review of the scientific research activity of scientists from the field of Mineralogy and Petrography at University of Chemical Technology and Metallurgy (UCTM) for more than 40 years (in the period 1961-2007) clearly outlines the orientation towards experimental scientific research that crosses over the boundaries of Earth sciences such as classical geological sciences.

The scientific topics of all lecturers of Mineralogy at UCTM: Ivan Borissov, Julia Pavlova, Ivan Ivanov, Dobrinka Stavrakeva and Franz Dipchikov, are in accordance with its specifics and are focused on the needs of the silicate, chemical and metallurgical industries. The research of these specialists laid the foundations of technical mineralogy and petrography in Bulgaria.

Keywords: petrurgy, glass-ceramics, ceramics, industrial waste, technical mineralogy.

INTRODUCTION

In his article "Earth depths in the laboratory", which is an overview of the beginning of the experimental work in the geological sciences on a global scale [1], E.N. Gramenitsky asks the question: "Why do geologists need the experiment? In response, he presents vivid examples and convincing arguments. As early as the end of the 18th century, geologists, who were able to pose questions concerning the laws of nature not only in expeditions but also in laboratories, appeared. Sir James Hall (1761-1832) is considered the founder of experimental petrology, whose experiment resolved the scientific dispute between the "Neptunists" and "Plutonists". Norman Bowen and Orwell Tuttle, who stand out among the galaxy of experimenters from the Geophysical Laboratory of the Carnegie Institution in Washington, in the middle of the 20th century, presented experimental data that put an end to the dispute between the "Magmatist" and "Transformist"

**Correspondence to: Irena Kirilova Mihailova, University of Chemical Technology and Metallurgy, 8 Kliment Ohridski blvd., 1797 Sofia, Bulgaria, E-mail: irena@uctm.edu.*

camps about the origin of granites. Gramenitsky pointed out that despite the connection of experimental mineralogy and petrography with chemistry and physics, experimental geologists had their own achievements in the technique and methodology of experiments, as well as in the study of experimental results. On the other hand, the author emphasized that business relationships had also been established with technologists, especially in the field of metallurgy and silicate production. “At first, geologists looked for an analogy in technological processes with what happened in the depths of the earth. For technologists, the methods of evaluating mineral raw materials and the optical study of materials were useful. Thus, technical mineralogy arose. Then it turned out that mineralogists understood some technological processes more deeply than technologists themselves.” These words can be fully applied to the development of technical mineralogy at University of Chemical Technology and Metallurgy (UCTM). Since the 1960s, geologists teaching Crystallography and Mineralogy as fundamental disciplines and studying raw materials for chemical technology and metallurgy, have turned their scientific interests to experiment and to technogenic minerals and materials. In the team of UCTM, they have worked together and exchanged experience with scientists in the fields of chemistry, physical chemistry, inorganic chemical technologies, silicate technology and metallurgy. The experimental approach in scientific research is increasingly used. Thus, technical mineralogy and petrography not only arose in Bulgaria, but for several decades it developed, followed world trends and priorities and currently has its representatives, both in UCTM and other universities as well as in the Bulgarian Academy of Sciences.

Mineralogy in the modern world is closely related to experimentation and the application of modern analytical methods. On the website of the Institute of Mineralogy of the University of Hannover, in 2023 we are greeted with the words: “Traditionally, mineralogy includes the study of minerals and crystals that form the rocks on the Earth. Today, mineralogy has transformed into a multidisciplinary natural science, linking geosciences and environmental sciences with physics and chemistry“ [2].

The scheme proposed back in 1987 by V.A. Perepelitsyn [3], the interconnections of earth sciences with physics, chemistry and technical sciences are shown. Technical mineralogy and petrography are assigned a key place in this network (Fig. 1).

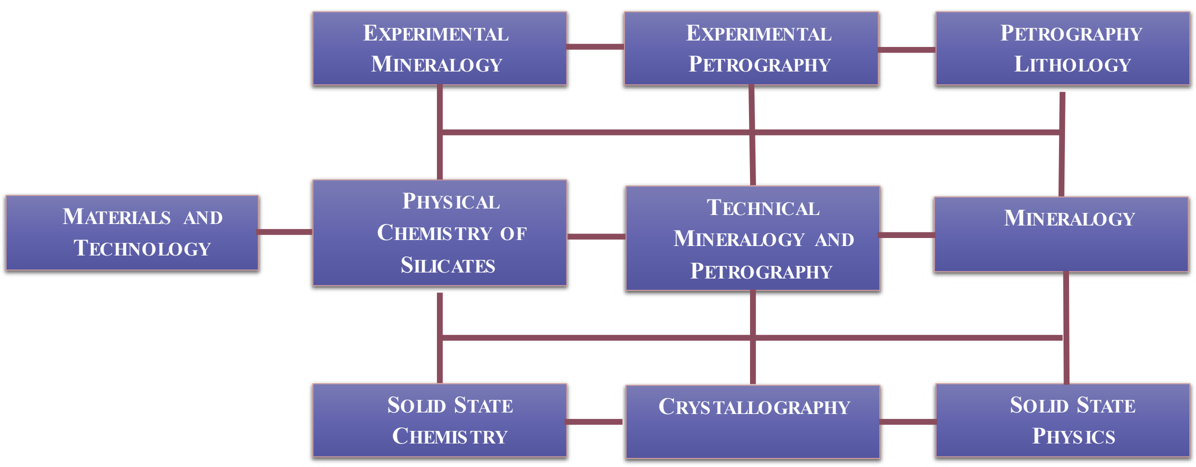

Fig. 1. Position of technical mineralogy and petrography among related sciences, in accordance with [3].

The classification of materials shown in Fig. 2 enables us to distinguish the objects of classical mineralogy and petrography (natural minerals and rocks) from the objects of technical mineralogy and petrography (synthetic minerals, synthetic inorganic compounds, technical stones, inorganic polyphase materials, composites). Unlike synthetic minerals, synthetic inorganic compounds have no natural analogues.

HISTORICAL OVERVIEW

The University of Chemical Technology and Metallurgy (UCTM) in Sofia has seventy years of history. The State Polytechnic was divided into four independent higher technical institutes by a decree of the Presidium of the National Assembly on the 10th of June, 1953. One of them was the Higher Institute of Chemical Technology, currently UCTM.

The training in Mineralogy at UCTM started from the very beginning and has continued without interruption until now. Prof. G. K. Georgiev was the first lecturer to teach a course in Mineralogy for students of Industrial Chemistry at the Polytechnic. He and Prof. S. Stoinov taught mineralogy and petrography to students of

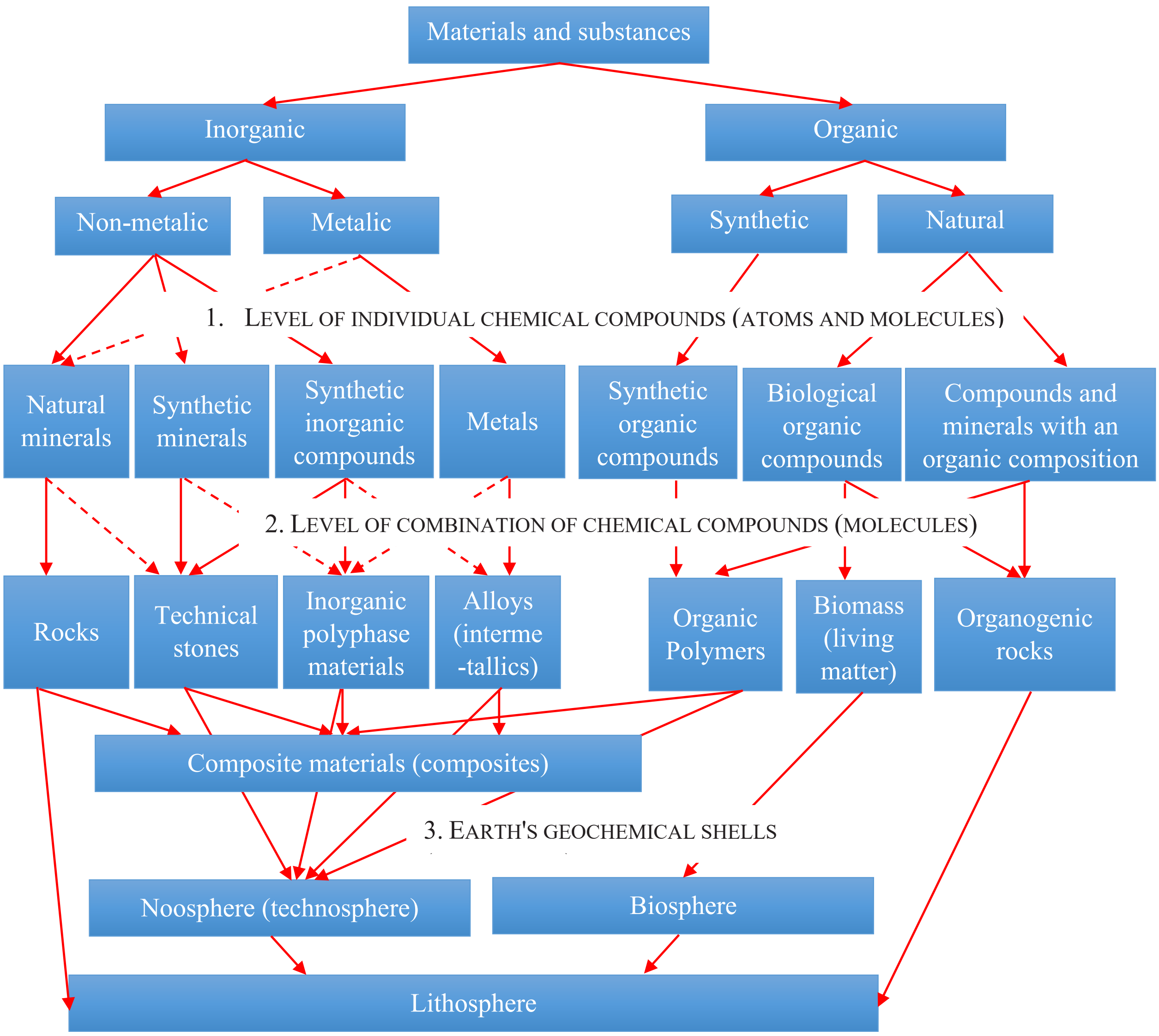

Fig. 2. Classification of materials by composition and origin in accordance with [3].

Metallurgy and Silicate Technology at the UCTM following the division of the Polytechnic.

The first assistants in Mineralogy and Petrography at UCTM were Dobrinka Stavrakeva, Ivan Ivanov, and Julia Pavlova. They were appointed to the Department of Silicate Technology in the period 1961-1963. Ivan Borissov was appointed an associate professor in 1964. Until 1967, the group of mineralogists and petrographers was part of the Department of Silicate Technology, then it became an independent Department of Mineralogy and Petrography. The department existed until 1981 and then merged with the Department of Silicate Technology. In 1969, Franz Dipchikov began his doctorate, later he became a research associate, and associate professor and worked at UCTM until 2007. Over the years, a number of specialists, chemists, laboratory assistants and other collaborators have been working in the department. Maria Chilova (1968-1978) worked for the laboratory of Silicate Analysis in the department as a chemist and as a part-time graduate student; there also worked the specialist-geologist - Violeta Georgieva, senior specialist Maria Konstantinova and laboratory assistants Galina Grigorova and Dimitrina Stoycheva.

Full-time Ph.D. students were: Julia Pavlova, Franz Dipchikov, Vanzetti Vassilev, Vivian Kazandzhieva, Dorina Bozova, Anka Dimitrova, Violeta Georgieva, Petrunka Mihailova, Irena Georgieva (Mihailova) and part-time graduate students: Isak Isakov, Ivan Donchev and Albena Tudjarska-Patsovska.

SCIENTIFIC TOPICS AND RESEARCH ACTIVITY OF MINERALOGISTS AT UCTM

The scientific topics of all lecturers of Mineralogy at UCTM are in accordance with its specifics and are focused on the needs of the silicate, chemical and metallurgical industries. Extensive research has been conducted on various metallurgical slags from non-ferrous and ferrous metallurgy, various ceramic and refractory materials, Portland cement clinker from all Bulgarian cement plants, ash and slag from thermal power plants, defects in glassware, and many other materials. Work has been done on the phase equilibrium in a number of multicomponent systems, interesting for the synthesis of new technical materials. The crystallization processes in a wide range of multicomponent silicate compositions from industrial waste (metallurgical slags, flotation waste from ore mining) and the whole series from basic to acidic magmatic rocks have been investigated, to study the possibilities for obtaining cast stone products (petrurgy) and glass-ceramics materials (petrositals, slag glass-ceramics, etc.). The research of these specialists laid the foundations of technical mineralogy and petrography in Bulgaria. Under the scientific guidance of the habilitated lecturers, a number of doctoral theses on industrial waste (metallurgical slags, ash from thermal power plants) and the synthesis of new silicate materials have been defended. More than 10 PhD students have studied at the Department.

PETRURGY

Prof. Ivan Iliev Borissov and Assoc. Prof. Dr. Julia Pavlova

“You and I in many respects belong to happy generations. The past generations would envy us, future ones will, too. To live in a time when there are transitions, turning points and decisive events when breakthroughs and great discoveries are made and sciences are born, is like drinking a glass of cold water in one breath after you have walked thirsty through a desert for days.” [4]

According to the definition of Ivan Borissov, in his book Petrurgy, the term “petrurgy” is understood as the melting of rocks, their casting into forms and their recrystallization. In other words, the reproduction of those phenomena that occur in nature under natural conditions with the solidification and crystallization of magma,

Fig. 3. Prof. Stavrakeva (in the middle) and Assoc. Prof. Ivanov (second from the right) together with colleagues from the "Technology of Silicates" Department - April 2015.

respectively lava." [5]

The beginning was marked by scientific research on the production of molten basalts, which were published in vol. VII of the "Geographic Journal" back in 1854. The first petrurgical plants began to work in 1921 and 1922 - Compagnie Générale de Basalte in France and "Schmelzbazalt A. G. Linz" am Rhein in Germany, respectively. In the following decades, interest in petrology grew and a number of new enterprises appeared on the territory of the former USSR, Czechoslovakia, Poland, etc. In 1966, the petrurgical plant in Bulgaria, located in the town of Plachkovtsi, came into operation. Its launch was preceded by a research activity in which Julia Pavlova participated but systematic research in the field of petrurgy in the Department of Mineralogy and Petrography at UCTM - Sofia began in 1966. For more than 20 years, this research topic was of great interest, which can be traced back to the topics of the dissertations, successfully defended under the supervision of Prof. Ivan Borissov and Associate Professor Julia Pavlova (Table 1).

Physical chemistry of multicomponent natural silicate systems

In its essence, scientific research on petrurgy can be defined as the study of the physicochemical relationships (changes in the solid state, melting,

Fig. 4. Professor Ivan Borissov (on the left) and Associate Professor Franz Dipchikov at the first cast stone conference in Mariánské Lázně, Czechoslovakia, 1976.

Table 1. Dissertation theses in the field of Petrurgy.

Dissertations with supervisor Prof. Ivan Borissov / * Julia Pavlova		
1972	Julia Pavlova	Petrurgical studies of basalts from Bulgarian deposits
1973	Franz Dipchikov	Research on waste from ore-concentration factories in Bulgaria as a raw material for cast stone products
1974	Anka Dimitrova	Heat treatment of alkaline rocks, syenites and monzonites and crystallization of melts and glasses obtained from them
1977	Dorina Bozova	Physicochemical studies on some medium-acid igneous rocks with a view to their use in petrurgy
1978	Vanzetti Vassilev	A study on the melting and crystallization conditions of granitoids from Bulgaria and some experiments on melt differentiation
1980	Vivian Kazandzhieva	Physicochemical studies of basic and ultrabasic igneous rocks from Bulgarian deposits
1988	Petrunka Mihailova*	Crystallization and properties of cast stone products with high heat resistance

crystallization of petroglass and petromelts and their chemical and physical properties, and of natural multicomponent silicate systems - already formed in nature [6]. The practical considerations for its development are explained by the fact that magmas and, to some extent, metamorphic rocks will become the main raw material for petrurgy, the silicate industry, inorganic chemical technology and a new type of metallurgy - petrometallurgy [6].

In numerous studies carried out by I. Borissov and his collaborators in this direction, the changes in rock-forming minerals during the thermal treatment of igneous rocks in an air-oxidizing environment, the conditions of rock melting, the changes of some properties of the vitrified melts of igneous rocks with an increase in temperature from 1200°C to 1500°C, and the conditions of crystallization of melts and petroglasses from igneous rocks were studied. Analyzing the results of these studies, I. Borissov formulated the following law for the anchieutectic (semi-eutectic) composition of magmas and igneous rocks: "The source magma, as well as the partial magmas obtained from the differentiation or other magmatic processes of one source magma, always tend to have eutectic composition. The temperature of the anchieutecticum at approximately 1 at pressure is Ea = 1175 ± 50°C" [7, 8]. Ivan Borissov also made a significant contribution to petrography - he is the author of a textbook on mineralogy and petrography [9]. He described a new specific type of alkaline volcanic rocks in the northwestern part of Burgas lowland, north of the town of Bulgarovo, which he called bulgarites [10]. In 1962 he dedicated a book to the first Bulgarian geologists [11], and in 1977 he published a book dedicated to the science of the Moon, with an emphasis on its geology [4].

The goals that stood before the researchers 50 years ago have their topicality and significance even today, namely to develop methods and technologies through fundamental research and derivation of laws that will serve to expand the raw material supply of the inorganic industry without producing waste that pollutes the environment [6]. They believed that the physical chemistry of multi-component natural silicate systems would play a huge role in the technical revolution of mankind, providing it with ferrous, non-ferrous and rare metals and alloys, oxides, salts and various other products [6].

Assoc. Prof. Dr. Eng. Julia Pavlova graduated from the Higher Institute of Mining and Geology in 1955. She worked as a geologist in the "Rare Metals" Company, then she became one of the first appointed assistants in Mineralogy and Petrography at UCTM. She prepared a

Fig. 5. Assoc. Prof. Dr. Julia Pavlova.

dissertation under the supervision of Prof. I. Borissov on the topic "Petrurgical studies of basalts from Bulgarian deposits", which was defended in 1973. She worked for over 30 years as a professor at UCTM. She was appointed as an associate professor of Mineralogy and Petrography. Her scientific interests were mainly in the field of petrurgy (the various types of cast stone products) [12 - 19].

But as a specialist in technical petrography, she also took an active part in a number of other scientific projects on ceramics and refractories, glass and enamels and others. Assoc. Prof. Dr. Julia Pavlova worked together with Prof. Borissov, Assoc. Prof. Dipchikov, Assoc. Prof. Emil Popov, Prof. Yordanka Ivanova and others.

TECHNICAL MINERALOGY AND PETROGRAPHY

In the 60s and 70s of the last century, metallurgy, the chemical industry, construction, and the production of silicate materials - glass, ceramics, cement, etc., were developing intensively in Bulgaria. These gave rise to specific research work to solve emerging practical problems in various industries. Meanwhile, the production work of metallurgical plants, other

Fig. 6. Assoc. Prof. Franz Dipchikov and Assoc. Prof. Julia Pavlova (in the second row on the right) at the 7th Scientific and Technological Conference on Glass and Fine Ceramics, October 22-24, 1981 in Varna.

industrial enterprises, and thermal power plants led to the formation and accumulation of a huge amount of industrial waste, and its utilization was on the agenda of both society and science. At that time, the development of Bulgaria was closely related to that of the USSR. Technical petrography was already established with the scientific works of Soviet petrographic scientists in response to the rapidly developing industry in the years of Stalin's five-year plan. In 1952, the impressive book "Petrography of Technical Stone" [20] was published, where refractories, ceramics, slags, non-metallic inclusions in steel, binders and "stones" (crystalline inclusions, defects) in technical glasses were characterized. The authors were Dmitry Stepanovich Belyankin, B.V. Ivanov and Vladimir Vasilievich Lapin, who established themselves as leading scientists in this field. In the preface to the book, it is noted that the methods used in technical petrography are analogous to those for the study of rocks, namely: optical microscopy in transmitted and reflected light, chemical analysis, X-ray diffraction analysis, spectral analysis, thermal analysis, etc. A few years later Lapin published another serious and thorough study "Petrography of metallurgical and fuel slags" [21]. These books became fundamental for all researchers who later entered this new scientific field. Among them are the Bulgarian scientists working at UCTM, namely Ivan T. Ivanov, Dobrinka Stavrakeva, Julia Pavlova and Franz Dipchikov. Except for Prof. Borissov, whom I do not know in person but I have impressions from his articles and books, I have had the honour of knowing the other colleagues I mentioned briefly above.

For those who know ***Assoc. Prof. Dr. Ivan Todorov Ivanov*** *he is a great erudite and scientist, a true citizen of the world, with the free spirit of a discoverer and traveller, with a fine sense of humour and an aristocrat at heart.*

Ivan Ivanov graduated in Geology-Geochemistry at Sofia University "St. Kliment Ohridski" in 1959 after defending a diploma thesis, under the supervision of Prof. Ivan Kostov. In 1967, he won a competition and became a part-time postgraduate student at IGEM Academy of Sciences of the USSR, Moscow. His academic supervisor was Prof. Dr. Vladimir Vasilievich

Fig. 7. Assoc. Prof. Ivan Ivanov in Leipzig, 1996.

Lapin. In January 1972, he successfully defended a dissertation on the topic: "Investigation of the phase composition and structure of blast furnace and synthetic slags with a high content of manganese and barium oxides" in the presence of the Scientific Council of Institute Ore Geology, Geochemistry, Mineralogy and Petrography (IGEM, RAS) Moscow under the chairmanship of Academician D. Korzhinsky. He was appointed associate professor of Mineralogy and Petrography on 09.01.1976 and worked as such at UCTM until his retirement in 2000. He is the author of 92 publications in specialized scientific publications, the distribution of which by topic is presented in the Table 2. Associate Professor Dr. Ivan Ivanov specialized in Applied Mineralogy and Petrography under Prof. Chetverikov at Moscow State University, USSR (1967-1968) and in Finland under Prof. Niini (1983). For more than 30 years, I. Ivanov has had professional and personal contacts with Prof. Dr. Peter Schreiter, Germany. He has participated several times with reports at traditional colloquiums on Technical Petrography at the University of Leipzig at his invitation. In 2000, he participated with an overview report on the mineralogy of metallurgical slags in Bulgaria at the VI International Congress on Applied Mineralogy in Göttingen, Germany [22]. He has professional contacts with Prof. R. Khodakovskaya from the Institute of Chemical Technology, Moscow, Institute Ore Geology,

Table 2. Publications of Assoc. Prof. Ivan Ivanov in the period 1961-2000.

Scientific Topics	Number of articles
1. Mineralogy and petrography	4
2. Applied Mineralogy	88
2.1. Slags and matte from non-ferrous metallurgy [22, 24]	8
2.2. Slags from ferrous metallurgy [22]	20
2.3. Phase composition of ferroalloy slags [25, 26]	5
2.4. Oxidation of sulfides	5
2.5. Phase studies on manganese and iron ore agglomerates [27, 28]	15
2.6. Slag glass-ceramics – obtaining, phase composition and properties	16
2.7. Technical ceramics [29]	14
2.8. Phase studies in the system $BaO – MnO – SiO_2$ [30-33]	5

Geochemistry, Mineralogy and Petrography IGEM, RAS, Moscow, Prof. V.V. Lapin from the Institute of Metallurgy of the RAS, Moscow, and with Prof. T.Y. Malysheva and Dr. A.V. Arakcheeva [23]. He has participated in a number of congresses, conferences, symposiums, etc., in Germany, Greece, Turkey and Bulgaria.

Under the supervision of Assoc. Prof. Ivanov, Ivan Donchev defended a dissertation on "Mineralogical-petrographic studies of metallothermal slags from the production of special ferroalloys" in 1991. Together with Professor Stavrakeva, they were supervisors of my dissertation work "Phase studies in the system BaO-MnO-SiO_2 and synthesis of melilite glass ceramics", which was defended in 1998.

The scientific and applied contributions of Assoc. Prof. Ivan T. Ivanov can be briefly summarized as follows: he investigated the phase composition and structure of almost all types of solid metallurgical slags to study possibilities for their application in practice. In the composition of copper converter slags, for the first time in our country, he found out a phase with the composition Fe_7SiO_{10}. Later, it was detected in steelmaking slags in South Africa and called iscorite. In the blast furnace slag of Kremikovtsi, containing an increased content of barium, he found α- and β-celsian for the first time in world practice, as well as a kind of transitional high-temperature phase, called by him bredigite-merwinite, with an increased content of Ba and monoclinic symmetry, proved by single-crystal X-ray studies. In the composition of ferrovanadium slags, a new phase Ca-Al-V silicate with variable composition and original structure was established [25]. A detailed crystallographic and structural characterization of the new phase was made together with Dr. A.V. Arakcheeva from the Institute of Metallurgy, Academy of Sciences of the USSR [26]. Glass-ceramic materials were obtained from blast furnace slags with original melilite-wollastonite composition and properties. Manganese and iron ore agglomerates with a complex phase composition specific to Bulgarian ores were studied [27, 28]. In the field of technical ceramics, willemite, celsian, anorthite, spinel, and tialite [29] were synthesized and samples

Table 3. Authorship certificates of Assoc. Prof. Ivan T. Ivanov and team.

Authorship certificate	Number
Composition and method of obtaining Celsian ceramics	No 24459, Reg. No 35019, 1976
Composition of Willemite ceramics	No 27149, Reg. No 40281, 1978
Willemite ceramics	No 33064, Reg. No 53721, 1981
Composition of a plastic self-hardening mixture to make moulds and foundry cores	No 34212, Reg. No 57343, 1982
Ceramics for multilayer capacitors	No 36406, Reg. No 58831, 1982
Slag sital (slag glass-ceramics)	No 38542, Reg. No 66249, 1984
Wollastonite-melilite slag glass-ceramics	No 38543, Reg. No 66967, 1984
Ceramic composition for multilayer capacitors	No 38549, Reg. No 67025, 1984
Slag sital (slag glass-ceramics)	No 38692, Reg. No 66250, 1984
A method for extracting manganese and iron from liquid metallurgical slags	No 39037, Reg. No 67676, 1984
Ceramic composition for heat- and slag-resistant products	No 40553, Reg. No 71737, 1985
Ceramic glaze	No 51712, Reg. No 93016, 1990

with good utilitarian properties were obtained. I had the chance, working under the guidance of Assoc. Prof. Ivanov, to participate with him in the synthesis of new phases in the BaO-MnO-SiO_2 system [30 - 33], some of which were accepted as standards of the database of powder diffraction patterns maintained by The International Centre for Diffraction Data (ICDD) (e.g. $Ba_3MnSi_2O_8$, $BaMnSi_2O_6$ and $BaMnSiO_4$). Assoc. Prof. Ivanov synthesized a new phase with the composition $BaCa_2Mg[SiO_4]_2$ and characterized it in detail by X-ray crystallographic methods [34].

Fig. 8. Prof. Dr. Eng. Dobrinka Stavrakeva.

Prof. Dr. Eng. Dobrinka Anastasova Stavrakeva

"Industrial waste should be perceived as secondary minerals - one of the alternatives to mineral raw materials. By utilizing them, let us preserve nature and its natural raw materials for a longer time" 2021, D. Stavrakeva, [35].

Dobrinka Stavrakeva graduated from the Dnipropetrovsk Mining Institute (Mining Academy) with a degree in Mineral Exploration in 1958. Since 1961, she was an assistant professor of Mineralogy and Petrography at HICT (now the University of Chemical Technology and Metallurgy). In 1966-1967, she was on a 7-month specialization in France on phase and microstructural features of Portland cement clinker. She graduated with a second degree in "Silicate Technology" at UCTM in 1970. She defended her doctoral thesis at the Laboratory of Physico-Chemical Experiments at the IGEM of the Academy of Sciences of the USSR - Moscow under the supervision of Prof. Dr. V.V. Lapin in 1971. The topic of her dissertation was "Study of crystallization and optimal conditions for obtaining castings from copper mining slag". In 1975, she was appointed associate professor in Mineralogy and Petrography. She defended her doctoral dissertation in 1995 before the specialized Council for Geological Sciences of the Higher Attestation Commission on the topic "Phase formation, phase equilibria and microstructural features in oxide and silicate systems with practical significance". In the same year, she did a teaching internship in Paris. She was appointed Professor of Mineralogy and Crystallography. Prof. Stavrakeva's scientific research includes phase-structural and mineralogical-petrographic studies of a large number of technogenic materials. A number of waste slags from the mining industry, manganese-containing converter slags, refractories before and after their use, pyrite slags from the chemical industry, and various copper-zinc, iron and cobalt catalysts for the chemical industry were characterized. A significant amount of research was devoted to the microstructure and phase characteristics of various types of ceramic glazes, specialty ceramics and archeological ceramics [58]. In a special series, a complete mineralogical-petrographic characterization of the Portland cement clinker of the Bulgarian plants, as well as of the ashes and cinders from the thermal power plants in Bulgaria, was made. A number of studies were conducted on crystal phases and phase equilibria in insufficiently studied systems containing lithium, rubidium, boron, tellurium, and vanadium. She is the author of over 140 publications in specialized scientific journals at home and abroad. Table 4 shows her publications up to 2005, but her research work has continued after that. She published a number of overview articles dedicated to the possibility of industrial waste utilization as an alternative to the use of mineral raw materials [35]. In 2020, a book on ancient mining metallurgical slags on the territory of Bulgaria was published and she was a co-author [40]. She also published a number of articles in this area in recent years [41 - 45]. The results were reported at scientific forums in our country with international participation and at international forums (Paris, Strasbourg, Germany). She was the co-author of 9 inventions. She was the supervisor of 3 doctoral students: Liliana Zashkova, Al. Patsovska, Irena Georgieva (I. Mihailova) and 30 graduates. She is the author and co-author of 7 textbooks and study aids [46 - 52]. Prof. Stavrakeva was the president of the Bulgarian Mineralogical Society from 1999 to 2005, which is a well-deserved recognition and testifies to her scientific prestige in the scientific community.

The research activity of Prof. Dobrinka Stavrakeva has the following main scientific contributions: as a result of the study of the phase equilibrium in some tellurium- and vanadium-containing oxide and silicate systems, a number of double and triple phase diagrams were constructed. A scheme, for determining the type of phase image and the number of crystal phases depending on the field strength of the cations, the geometric size (ionic radius) and the coordination number of the cations, was proposed. As a result of studying the phase formation, the liquidus curves were proposed, and the fields of the crystal phases and the phase formation schemes of a number of multi-component silicate systems with or without the participation of $BaSO_4$ were outlined.

For the first time, a number of new crystal phases, modification conversions of previously known compounds, and new limits of isomorphic substitutions were defined and their crystal-chemical formulas were presented (Ag_2TeO_3, Ag_2TeO_4, $Cu_5Te_2O_9$, $Cu_5Te_2O_{11}$ (two structural modifications) $PbTe_4O_9$, $Pb_2Te_5O_{12}$, $Pb_2Te_3O_8$, Pb_2TeO_4, Pb_5TeO_7, $PbTeV_2O_8$ - dimorphic, Ba-silicates, Ba-aluminosilicates, etc.). A number of controversies regarding the nature of some crystalline phases and solid solutions were resolved. Facts regarding barium-calcium, barium-magnesium and barium-aluminum silicates were established.

Table 4. Publications of Prof. Stavrakeva in the period 1961-2005.

Scientific Topics	Number of articles
1. Applied Mineralogy – Phase composition, phase formation and phase equilibrium	116
1.1. Slags from non-ferrous metallurgy [36]	7
1.2. Slags from ferrous metallurgy	5
1.3. Flotation waste	2
1.4. Portland cement clinker	6
1.5. Catalysts. Salts. Waste from the chemical industry	11
1.6. Ceramic materials, glazes and refractories	20
1.7. Glass-crystalline, glass-ceramic and composite materials	11
1.8. Phase formation and phase equilibrium [37-39]	40
1.9. Waste from thermal power plants (fly ashes and slags)	6
1.10. Other	2
2. Mineral raw materials and alternative sources [35]	7
3. Science Journalism	8

Regularities of the phase-forming processes related to glass formation, microliquation and crystallization in multicomponent silicate systems involving Al, Ba, Cr, Pb, B, Ti, Cu, and Mo, etc. were established. The role of a number of components in the general course of crystallization, which predetermines phase formation and which must be taken into account in the synthesis of new materials and the utilization of a number of industrial wastes and non-scarce natural raw materials, was explained. It was established that a number of elements such as Fe, Ti, Cr, Cu, Sn, Mo in silicate systems exhibited independent behaviour during crystallization in an air-oxidizing environment. Regardless of their low contents in the general silicate system, they transformed into independent oxide phases. The established micro-inhomogeneities of liquation origin in the glasses of almost all investigated multi-component compositions allowed us to confirm a constant tendency towards micro-liquation, determined by the different strengths of the chemical bond of cations with oxygen. Microliquation begins at temperatures in the superliquidus region, precedes and predetermines the crystallization process. The well-established regularities in the phase-forming processes from melt in multicomponent silicate systems allow to interpreting and explaining some petrological processes. The different self-consistencies of the elements during the cooling of the melts lead to crystallization differentiation. The research expands and enriches the scientific basis for the synthesis of new materials in Te- and V-containing oxide systems, in silicate systems with the participation of BaO, in multicomponent silicate systems with the participation of $BaSO_4$, and many other silicate systems of practical importance, using non-deficient natural raw materials and industrial waste.

The established new barium-silicate, barium-aluminium, and barium-magnesium phases and the series of solid solutions based on Ba-Ca and Ca-Ba orthosilicates and those based on Celsian with a number of Ba-silicates are of practical importance for the synthesis of new special cements, refractories, glass crystal and glass-ceramic materials.

Assoc. Prof. Dr. Eng. Franz Pavlov Dipchikov
For his colleagues, he is smiling, modest, and responsive - a good person who can always be relied on.

F. Dipchikov completed his higher education in 1967 at UCTM majoring in “Silicate Technology”. He was a full-time postgraduate student in the period 1969-1973 at the Department of Mineralogy and Petrography. Under the scientific supervision of Prof. I. Borissov, he prepared a dissertation on the topic: “Research on waste from ore-concentration factories in Bulgaria as a raw material for cast stone products”. This period is particularly important for the improvement of his qualification in the field of mineralogy and petrography and for his further development. After a successful defence of his dissertation in 1973, he was appointed a research associate II degree, and in 1981 - a research associate I degree. Since 1994, he was the Assistant Professor in the “Technology of Silicates” Department, and in 2000 he was awarded the scientific title of “Associate Professor”.

The scientific research activity of Associate Professor Dr. F. Dipchikov, which includes over 70 publications, is aimed at the synthesis of cast stone products and silicate glass-ceramic materials based on natural raw materials and industrial waste [53 - 57]. This subject area is extremely interesting from a scientific point of view, due to the complexity of the systems and the physicochemical processes taking place. On the other hand, it opens up opportunities to obtain materials with practical physical and chemical properties. The research work of Assoc. Prof. Dipchikov can be systematized mainly in the following directions: Cast stone products - research and optimization of melting and crystallization, new raw materials, electric arc melting; Glass-ceramic materials from rocks and industrial waste, including waste from the concentration of ores and industry, metallurgical slags, ashes from thermal power plants; Synthesis of new materials: binders, foam glass, mineral wool, enamel, ceramic glazes, ceramics. An important contribution of his scientific research is related to the production of pyroxene cast stone products with high physico-mechanical and chemical indicators based on natural raw materials and waste. It was established that a number of types of igneous rocks and industrial waste can be used for the synthesis of pyroxene materials. Original combinations of raw materials were proposed, and a wide range of additives were used as crystallization initiators. The syntheses of new glass-ceramic, glass-crystalline and composite materials based on non-scarce natural raw materials and industrial waste: hercynite glass-ceramic (from ferroalloy production slag), hercynite composite material with high hardness (from waste nickel catalyst and fayalite waste), a glass-ceramic material with a low coefficient of thermal expansion in the system Li_2O-Al_2O_3-SiO_2 (of perlite quartz sand, lithium carbonate and additives) are of scientific and applied importance; as well as nepheline glass-ceramics, glass-ceramics subject to mechanical processing in the system K_2O-Na_2O-Al_2O_3-MgO-FeO-SiO_2-F, glass ceramics with melilite-wollastonite composition (from blast furnace slag and glass crumb), Celsian glass

Table 5. Authorship certificates of Assoc. Prof. Franz Dipchikov and team.

Authorship certificate	Number
Pyroxene petrosital	No 35941, 13.05.1983
Glass-ceramic material	No 36246, 05.05.1983
Glass-ceramic material	No 36247, 05.07.1983
Slag sital	No 38542, 13.07.1984
Wollastonite-melilite slag	No 38543, 25.07.1984
Slag sital	No 38692, 10.07.1984
Glass-ceramic material	No 38693, 10.07.1984
Glass-ceramic material	No 38694, 10.07.1984
Mica-containing glass-ceramic material	No 38695, 10.07.1984
Cast stone material	No 40547, 17.09.1985
Glass-ceramic material	No 41198, 12.02.1986
Mineral wool	No 42894, 27.03.1987
Sintered composite material	No 43590, 27.03.1987
Sintered composite material	No 43591, 27.03.1987
Composite glass-ceramic material	No 43592, 27.03.1987
Foam glass-ceramics	No 44770, 01.12.1987
Styrofoam material	No 45910, 17.05.1988
Silicate binder	No 46670, 15.11.1988
Acid-resistant silicate binder	No 47269, 13.12.1987
Ceramic glaze	No 50089, 06.03.1990
Ceramic glaze	No 51713, 16.10.1990

ceramic (from waste ferroalloy slag), etc. In the synthesis of numerous silicate materials, the following technologies were used: crystallization from a melt resulting in cast stone products, crystallization of monolithic glass samples in a one-step or two-step temperature regime, and sintering of crystal and/or glass powders resulting in glass-ceramic or composite materials.

Associate Professor Dipchikov implemented 7 of his industrial rationalizations, as a result of which an economic effect was produced, amounting to over BGN 400,000 (at 1989 prices).

To present the research work of my colleagues I searched for their publications extensively. In addition to publications in foreign journals, Comptes rendus de l'Académie bulgare des sciences, and Review of the Bulgarian Geological Society, I found a number of publications typical of the time in the Bulgarian specialized magazines *Building Materials and Silicate Industry and Metallurgy*. It should be noted that their articles published in these journals are often based on a skilful combination of several experimental methods and numerous experimental compositions (for example, 31 samples of basalts, each one melted at two temperatures 1450°C and 1500°C [13] and this is no exception). Some industrial experiments were also described. The journals were oriented towards scientific and scientific-applied research and were closely related to real practical problems and to the development of these sectors of industry in the 1970s and 1980s. The first journal had sections: *Chronicle*, which covered important Bulgarian and international scientific forums, and *Technical Novelties* - short news from the world of science and new applications and patents. It even presented the graduated engineers and the topics of their diploma theses. These profiled national journals provided a good and easily accessible way for up-to-date scientific information to engineers working in Bulgarian enterprises in the field of chemical technologies and metallurgy. On the other hand, the publication of a number of scientific studies in Bulgarian language has inevitably limited the access of the international scientific community to them and their timely reaction and response.

CONCLUSIONS

A brief review of the scientific research activity of scientists from the field of Mineralogy and Crystallography for more than 40 years clearly outlines the orientation towards experimental scientific research that crosses over the boundaries of Earth Sciences such as Classical Mineralogy and Petrography.

This activity is in tune with modern scientific trends of the time such as the production of cast stone products (petrurgy) and synthesis of functional glass-ceramic materials with specified properties and corresponding applications. The interrelation of the scientific subject areas with the industrial development of Bulgaria from those years is visible. The progressive ideas of expanding the raw material base of inorganic technologies and utilization of industrial waste have acquired even greater importance in the modern world.

On the other hand, each of the researchers has his own individuality and specific interests and strengths. I was truly lucky to be a doctoral student of Assoc. Prof. Ivanov and Prof. Stavrakeva, to work with Assoc. Prof. Dipchikov, to know Assoc. Prof. Julia Pavlova. This allowed me to see the breadth of their professional interests, not only in the development of geology and mineralogy but also in silicate technologies and metallurgy. Their scientific interests are combined with a strong individuality, extensive general knowledge, an active civic position and a gift of speech. As a PhD student, I became familiar with a number of experimental methods for materials synthesis, as well as methods for phase and structural analysis. I was impressed by their experience and mastery of optical microscopy, X-ray diffraction analysis, infrared spectroscopy, differential thermal analysis and a number of other methods, the data from which they interpreted themselves. Moreover, they successfully worked in different teams and enjoyed indisputable scientific prestige and well-deserved respect among their colleagues. I was learning a lot from their personality, their strive for work, perseverance and patience. I learned how important it is for the researchers to be honest and correct in describing the obtained results. I could feel their endless benevolence, tolerance and support, and perhaps most importantly, they conveyed to me the sense of challenge and the excitement of seeing the results of one's experiment, the thrill of facing the unexpected and the scientific mystery and searching for the right path. For me, they are my true teachers in profession and life, to whom I thank.

REFERENCES

1. E.N. Gramenitsky, Earth depths in the laboratory, Chemistry and Life, 5, 2015, 18, (in Russian).
2. https://www.mineralogie.uni-hannover.de/en/institute/about/
3. V.A. Perepelitsyn, Fundamentals of Technical Mineralogy and Petrography, 1987, (in Russian).
4. I. Borissov, Selenology, Narodna mladezh, Sofia, 1977, (in Bulgarian).
5. I. Borissov, Petrurgy, Science and Art, Sofia, 1969, (in Bulgarian).
6. I. Borissov, Physical chemistry of the multi-component natural silicate systems – essence, achievements and problems, Review of the Bulgarian geological society, 37, 1976, 31-35, (in Bulgarian).
7. I. Borissow, A hypothesis on the anchieutectic composition and differentiation of the matter, Review of the Bulgarian geological society, 44, 1983, 235-247, (in Bulgarian).
8. I. Borissow, On the anchieutectic composition of magmatic rocks, C. R. Acad. Bulg. Sci., 32, 1979, 67-70.
9. I. Borissov, Mineralogy and petrography, Technique, Sofia, 1978, (in Bulgarian).
10. I. Borissow, Die Bulgarite - eine neue Eruptivgesteinsart, Chem. Erde, 38, 1979, 169-193.
11. I. Borissov, Our First Geologists, People's Education (Narodna Prosveta), Bulgaria, 1963, (in Bulgarian).
12. I. Borissov, J. Pavlova, Thermal treatment and melting of basalts in Bulgaria, Construction Materials and Silicate Industry, 11-12, 1968, 18-20, (in Bulgarian).
13. I. Borissov, J. Pavlova, Secondary crystallization of vitrified basaltic melts, Construction Materials and Silicate Industry, 5, 1971, 23-28, (in Bulgarian).
14. I. Borissov, J. Pavlova, Chemical characteristics and preliminary estimate of the economic value of Bulgarian basalts, Przeglad Geologiczny 19, (2), 1971, 103-106, (in Russian).
15. I. Borissov, J. Pavlova, Petrographic studies of basalts in Bulgaria with a view to their use in petrology, Annual Journal of the Higher Institute of Chemical Technology, 20, 1972, 331-342, (in Bulgarian).
16. I. Borissov, J. Pavlova, Crystallization of melts from the basalts of Northern Bulgaria, Stara Planina and Sredna Gora, Review of the Bulgarian Geological Society, 36, 1975, 25-28, (in Bulgarian).
17. J. Pavlova, Ch. Coshujarov, Obtaining composite materials with a micro-grained structure from rocks. IV Petrurgical Conference, Czechoslovakia, 1981, pp. 47-50, (in Russian).
18. J. Pavlova, Studies on the mechanism of crystallization of petrurgical melts and glasses, Construction Materials and Silicate Industry, 10, 1983, 34-36, (in Bulgarian).
19. P.A. Abella, S.M. Manent, I.Q. Mitjans, M. Kanazirski, J. Pavlova, F. Dipchikov, Basaltic raw materials of Catalonia in the production of glass ceramics, Ceramics International, 16, 1990, 143-149.

20. D.S. Belyankin, B.V. Ivanov, V.V. Lapin, Petrography of Technical Stone, Publishing House of the Academy of Sciences of the USSR, Moscow, 1952, (in Russian).
21. V.V. Lapin, Petrography of metallurgical and fuel slags, Publishing House of the Academy of Sciences of the USSR, Moscow, 1956, (in Russian).
22. I.T. Ivanov, Phase composition of metallurgical slags in Bulgaria, Applied Mineralogy, 2, 2000, 815-817.
23. B. Mavrudchiev, Associate Professor Dr. Ivan Todorov Ivanov turns 80 years old, Review of the Bulgarian Geological Society, 78, 2017, 159-160, (in Bulgarian).
24. I. Ivanov, P. Bakardzhiev, I. Grozdanov, Phase composition and structure of the waste copper slags from CMP "G. Damyanov" – Pirdop, Mining and metallurgy, 9, 1967, 13-17, (in Bulgarian).
25. I.T. Ivanov, vanadium-bearing phases in crystallized ferroalloy slags, Eur. J. Mineral., 7, 1995, 183-186.
26. A.V. Arakcheeva, I.T. Ivanov, Crystal structure of disomatic type of crystal phase with variable composition $CaAl(Al,V,M')_2(V,M'')(Si,Al)_2O_{10}$, its polytypic modifications and structural homologues, Crystallography, 1993, 38, 144-161, (in Russian).
27. I.T. Ivanov, New data on the composition of ferritic phases in iron agglomerate, Cristal Chemistry of Minerals, 1985, 865-875.
28. I.T. Ivanov, A.M. Todorov, Phosphorous distribution in the minerals of manganese agglomerates, C. R. Acad. Bulg. Sci., 35, 1982, 1399-1402.
29. S. Djambazov, D. Lepkova, I. Ivanov A study of the stabilization of aluminium titanate, Journal of Materials Science, 29, 1994, 2521-2525.
30. I. Georgieva, I. Ivanov, O. Petrov, X-ray powder diffraction data for $Ba_3MnSi_2O_8$ - A new phase in the system BaO – MnO – SiO_2, Powder Diffraction*,* 11, 1996, 26-27.
31. I. Ivanov, D. Nihtianova, I. Georgieva**,** X-ray powder diffraction and transmission electron diffraction data for $BaMnSi_2O_6$ - A new phase in the system BaO – MnO – SiO_2, Powder Diffraction, 11, 1996, 284-287.
32. D. Nihtianova, I. Ivanov, I. Georgieva**.** Crystallographic data for $BaMnSiO_4$: A new phase in the system BaO – MnO – SiO_2, Powder Diffraction, 12, 1997, 167-170.
33. I. Georgieva, I. Ivanov, V. Dimitrov, E. Gatef, Y. Dimitriev, Synthesis and structure of glasses in the system BaO – MnO – SiO_2, Journal of Materials Science, 31, 1996, 3197-3200.
34. I.T. Ivanov, G.N. Kirov, Synthesis and crystallographic characterization of $BaCa_2Mg[SiO_4]_2$, Proc. Acad. Sci. USSR, Proceedings of the Academy of Sciences of the USSR Inorganic Materials, 13, 569-571, (in Russian).
35. D. Stavrakeva, Industrial waste - one of the alternatives to mineral raw materials, Mining and Geology, 3-4, 2021, 32-38, (in Bulgarian).
36. D. Stavrakeva, R. Stoytseva, Chemical-petrographic characteristics of the waste slags from SMME "G. Dimitrov", Eliseina station, Mining and metallurgy, Metallurgy, 2, 1966, 15-18, (in Bulgarian).
37. D. Stavrakeva, Method for calculation of the valence of transitional elements in the composition of crystal phases, C. R. Acad. Bulg. Sci., 43, 1990, 57-60.
38. D. Stavrakeva, I. Georgieva, New data on the composition of melilite during solid phase and solid-liquid phase synthesis, C. R. Acad. Bulg. Sci., 48, 1995, 91-94.
39. D. Stavrakeva, Y. Ivanova, Y. Pyrov, New data on the composition of the crystalline phases in the Cu-Te-O system, Journal of Materials Science, 25, 1990, 2175-2180.
40. N. Tzankova, D. Stavrakeva, Early mining and metallurgy in the Eastern part of the Srednogorian metallogenic zone. Metallurgical by-products from copper extraction (copper

slags) found in the archaeological sites in Burgas and Yambol ore regions (phase chemical and structural characteristics), Publ. "St. Ivan Rilski", Sofia, 2020.
41. D. Stavrakeva, N. Tzankova, Chemico-mineralogical characterization of ancient slags from Rosen Ore Field. Part 1 - Propadnala voda deposit, Ann. Univ. Min. Geol., 59, Geol., 2016, 55-60, (in Bulgarian).
42. N. Tzankova, D. Stavrakeva, P. Leshtakov, K. Dimitrov, Chemico-mineralogical characterization of ancient slags from Rosen Ore Field. Part 2 - Korucheshme and Rosen deposits, metallurgical center „Atiya", Ann. Univ. Min. Geol., 59, Geol., 2016, 61-66, (in Bulgarian).
43. D. Stavrakeva, N. Tzankova, Ancient metallurgical slags from the Rosen Ore Region - a potential raw material for the production of copper and lanthanides, Geology and mineral resources, 6, 2016, 36-40, (in Bulgarian).
44. N. Tzankova, D. Stavrakeva, Mineralogical study of archaeological copper slags found in the area of the Boyadzhik village, Yambol region, Southeast Bulgaria, Journal of Mining and Geological Sciences, 63, 2020, 267-271.
45. N. Tzankova, D. Stavrakeva, Mineralogical study of archaeological copper slags found in the area of Krushevets Village, SE Bulgaria, Geologica Balcanica, 49, 2020, 3-23.
46. S. Bachvarov, B. Kostov, B. Samuneva, D. Stavrakeva, Manual for exercises on silicate technology, Technique, Sofia, 1964 (First edition), 1978, (2nd ed.), (in Bulgarian).
47. D. Stavrakeva, Iv. Ivanov, Manual for exercises in crystallography, mineralogy and petrography, Higher Institute of Chemical Technology, Sofia, 1988, (in Bulgarian).
48. D. Stavrakeva, P. Grozdanova, Raw materials and materials in silicate production, Technique, Sofia, 1989, (in Bulgarian).
49. D. Stavrakeva, P. Grozdanova, Raw materials and materials in the glass industry, Technique, Sofia, 1990, (in Bulgarian).
50. D. Stavrakeva, I. Ivanov, Manual for exercises in crystallography, mineralogy and petrography, Martilen, Sofia, 1993, (in Bulgarian).
51. D. Stavrakeva, I. Mihailova, Fundamentals of crystal chemistry, UCTM, Sofia, 2012, (in Bulgarian).
52. D. Stavrakeva, F. Dipchikov, CaRIne Crystallography Software: Manual for practical exercises, (in Bulgarian).
53. I. Borissov, F. Dipchikov, Untersuchungen zur petrurgischen Verwendung von Flottionsabgangen, Silikattechnik, 7, 1971.
54. F. Dipchikov, Building materials and silicate industry, 8, 1977, 19, (in Bulgarian).
55. F. Dipchikov, Building materials and silicate industry, 1, 1978, 22, (in Bulgarian).
56. F. Dipchikov, Bulgarite-based glass-ceramics, Building materials and silicate industry, 11, 1978, 24-28. (in Bulgarian)
57. I. Donchev, F. Dipchikov, O. Petrov, N. Zidarov, M. Tarassov, Synthesis of Artificial Rocks (Synroc Type), C. R. Acad. Bulg. Sci., 55, 2002, 53-56.
58. Liliana Pernicheva-Perets, Małgorzata Grębska-Kulow, Ilija Kulov, Balgarchevo. The prehistoric settlement, volume I – Annex, Craft House Bulgaria Ltd., Sofia, 2011.