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# CONTENTS

**Part 1 – Geology, Mineralogy and Mineral Deposits**

<table>
<thead>
<tr>
<th>Author(s)</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dimitar Sinnyovsky, Natalia Kalutskova, Nikolai Dronin, Illyana Tsvetkova, Nadezhda Atanasova</td>
<td>Geosite “Iron Gate” (“Demirkapiya”) in Rila</td>
<td>5</td>
</tr>
<tr>
<td>Gergana Meracheva, Efrosima Zaneva-Dobranova</td>
<td>3D Structural Model of Tertiary Sediments in NW Part of Thrace Basin</td>
<td>11</td>
</tr>
<tr>
<td>Bogdan Prodanov, Lyubomir Dimitrov, Valentina Doncheva, Todor Lambev</td>
<td>Integrated Geodatabase for the Coastal Zone between Sozopol and Tsarevo (South Bulgarian Black Sea Coast)</td>
<td>17</td>
</tr>
<tr>
<td>Kameliya Marinova, Stefka Pristavova</td>
<td>Petrographic Investigation of Ceramic Artifacts from the Thracian Sanctuaries in the Eastern Rhodopes</td>
<td>23</td>
</tr>
<tr>
<td>Boris Valchev, Sava Juranov</td>
<td>Campanian-Maastrichtian Benthic Foraminifera from the Byala Formation (Eastern Balkan)</td>
<td>30</td>
</tr>
<tr>
<td>Boris Valchev</td>
<td>Campanian Planktonic Foraminiferal Assemblages from the Chugovitsa Formation in the Area of Jelyava and Eleshnitsa Villages, Sofia District</td>
<td>37</td>
</tr>
<tr>
<td>Kamen Popov</td>
<td>The Hercynian Collisional Metallogeny in Bulgaria</td>
<td>43</td>
</tr>
<tr>
<td>Ivan Dimitrov, Valentina Nikolova, Iuli Paskov</td>
<td>Field Observation of the Buried Weathering Crust in the Oshtava Graben (Southwestern Bulgaria)</td>
<td>51</td>
</tr>
<tr>
<td>Dimitar Sinnyovsky</td>
<td>Unesco Geopark Initiative and Bulgarian Geoconservation</td>
<td>57</td>
</tr>
<tr>
<td>Radostina Rizova, Georgi Nachev, Ivan Dimitrov</td>
<td>Tectonomorphologic Characteristics of Zavalska Mountain, SW Bulgaria</td>
<td>63</td>
</tr>
</tbody>
</table>

**Part 2 – Geophysics, Hydrogeology and Engineering Geology, Drilling and Oil and Gas Production**

<table>
<thead>
<tr>
<th>Author(s)</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ivan Nikolov, Alexander Loukanov, Elena Ustinovich, Anatoliy Angelov, Seiichiro Nakabayashi</td>
<td>Catalytic Carbon Nanodots for Oxygen Reduction Reaction</td>
<td>69</td>
</tr>
<tr>
<td>Authors</td>
<td>Title</td>
<td>Page</td>
</tr>
<tr>
<td>---------------------------------</td>
<td>----------------------------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>Nikolay Stoyanov, Stefan Zeinelov</td>
<td>Mathematical Flow Model of the Krasnovo Thermomineral Field (Southern Bulgaria)</td>
<td>73</td>
</tr>
<tr>
<td>Martin Boyadjiev, Grigor Filkov</td>
<td>Research to Determine the Dependence Between the Environmental Temperature and the Temperature of Natural Gas Used for the Domestic Sector as a Consumption Factor</td>
<td>79</td>
</tr>
<tr>
<td>Dobri Dobrev, Mihail Mihailov</td>
<td>Incidents in Natural Gas Transport</td>
<td>84</td>
</tr>
<tr>
<td>Stanislav Yankov, Blagovesta Vladkova</td>
<td>Emergency Actions and Neutralization of Oil Spills</td>
<td>89</td>
</tr>
<tr>
<td>Denitsa Borisova, Banush Banushev, Doyno Petkov</td>
<td>Spectral Reference Library Filled with Reflectance Rock Features</td>
<td>97</td>
</tr>
<tr>
<td>Marjan Delipetrev, Blagica Doneva, Gorgi Dimov</td>
<td>Elements and Structure of the Normal Geomagnetic Field in the Republic of Macedonia</td>
<td>104</td>
</tr>
<tr>
<td>Stefan Zeynelov, Daniel Ishlyamski, Bozhurka Georgieva</td>
<td>A Complex Approach for Sedimentary Architecture Modelling of Fluvial Successions and Their Conversion into Hydrogeological Units</td>
<td>109</td>
</tr>
</tbody>
</table>
GEOSITE “IRON GATE” (“DEMIRKAPIYA”) IN RILA

Dimitar Sinovyovski¹, Natalia Kalutskova², Nikolai Dronin², Iliyana Tsvetkova¹, Nadezhda Atanasova¹

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ABSTRACT. Geosite “Iron Gate” (“Demirkapiya”) is situated on the territory of Samokov Municipality, Sofia District. It is in the glacier valley of Beli Iskar River between the summits of Golyam Skakavets (2705.9 m) and Musala (2925.4 m). Geosite “Iron Gate” is of aesthetic and scientific value. It includes the deepest part of the largest glacier valley on the Balkan Peninsula carved out by the Beli Iskar glacier during the Würm Ice Age. This is the deepest place in the valley called “Demirkapiya” or “Iron Gate”, due to the impressive displacement of 1250 m between the riverbed and the surrounding peaks. The Beli Iskar River valley is a typical U-shaped glacier trough valley with steep slopes and rounded bottom and a length of 21 km between Kanara Cirque and Beli Iskar village. Side glacier moraines on both slopes of the valley are formed during the ice age and covered later by supraglacial moraines (scree slopes). They consist of angular or somewhat rounded particles, ranging in size from large boulders to glacial flour, obtained as a result of the rocks disintegration. The monolith granite of the Musala Body of the Rila-West Rhodopean Batholith is cut by numerous pegmatite, aplite and quartz veins, vein-like granite bodies and dykes of diorite and granite porphyry, suitable for demonstration of the principle of cross-cutting relationships in geology. Other important geoconservation features of the site are the glacial and periglacial landforms and deposits, which may serve for demonstration of the manner in which glaciers work. The area is on the territory of the National Park Rila with restricted measures, according to the requirements of such category protected areas.

Keywords: Geosite “Iron Gate”, Geopark Rila

Introduction

Geosite “Iron Gate” (“Demirkapiya”) is situated on the territory of Samokov Municipality, Sofia District. It is in the glacier valley of Beli Iskar River between the summits of Golyam Skakavets (2705.9 m) and Musala (2925.4 m). Coordinates of the moraines near the road to Beli Iskar Dam are: 34°01'09.94" E, 46°37'56.4" N. This point is situated 14 km south of Samokov town and 8 km south of Beli Iskar village.

Category

Geosite “Iron Gate” is of aesthetic and scientific value. This is the deepest place of the deepest and longest glacier valley on the Balkans - the Beli Iskar River Valley with a displacement of 1250 m against Musala Peak. The geosite includes supraglacial moraines developed on both slopes of the glacier valley.

Geological setting

The area has a simple geological structure. The first data about the native rocks belong to Viquenel (1852) who noted that the granite forms peaks with a height of 2500-3000 m and occupies the heights from which Maritsa River expires. On the watershed between Maritsa and Iskar, the author described white coarse-grained granite and gray granite.

Hochstetter (1870) also noted Rila granite as the largest granite massive in the old crystalline body of the Rhodopes.
Entering the Beli Iskar River Valley from the north, he described mica gneiss with layers of amphibolite gneiss, crystalline limestone, serpentine, and up the valley, "the rock becomes totally granite-like with large orthoclase crystals."

Бончев (1908) made the first serious contribution to the petrography of Rila. He described biotite granite in the valley of Beli Iskar (Соколет и Демиркапия). Granites east of Beli Iskar are described as part of the Western Rhodopes. As far as their age is concerned, he states: "It can not be said that they are of a younger geological age than the archaic one."

Later these granites are described as part of the so-called South Bulgarian Granite (Димитров, 1939) with Paleozoic age.

Яранов (1943) described the so-called “West-Rhodopean Batholith” on the territory of the West Rhodopes. According to the author, "this is a typical batholith, the largest one of the entire Balkan Peninsula", which is associated with the granite batholith of Rila.

The leucocratic granite that crops out in the area, belongs to the Musala Body of the Rila-West Rhodopean Batholith, characterized by Бунхов et al. (1989) as a complicated igneous massive, with four phases of magmatic activity. The native rock representing the second phase is medium and coarse-grained biotite granite, intruded during the Lutetian Age of the Eocene (42-35 Ma ago) into the granodiorite of the first phase and Precambrian metamorphic rocks. In turn, this granite is cut by granites and plagiogranites of the third phase and apliteoid and pegmatoid granites of the fourth phase forming small stock-like bodies or veins. Каменов et al. (1997), Пейчева et al. (1998) and Каменов et al. (1999) combine the third and the fourth phases into a single third type.

Саров et al. (2011) described the granite according to the previous authors cited above as part of the Musala Body of the Rila-West Rhodopean Batholith.

Geodiversity of Rila was first reviewed in the light of the geopark development by Синьовски (2014), Sinnyovsky (2014, 2015) who outlined its petrographical and geomorphological diversity. The geopark potential of Rila Mountain, glacier formations and supraglacial activity in Rila were subject also of several other papers (Атанасова, Синьовски, 2015; Цветкова, Синьовски, 2015; Синьовски et al., 2017; Sinnyovsky et al. 2017).

The Beli Iskar Glacier valley is carved entirely in the medium-to coarse-grained biotite granite of the Musala body which is exposed on both slopes of the Beli Iskar River Valley between Musala Ridge to the east and Golyam/Malak Skakavets Ridge to the west. The granite is leucocratic, light grey to grey-white in colour with massive and equigranular structure. The texture is poikilitic and hypidiomorphic-granular. The main rock-forming minerals are plagioclase, K-feldspar, quartz, and biotite. Due to the good preservation and perfect outcrops of the rocks they are appropriate for demonstration of the mineral composition and magmatic crystallization processes leading to the formation of structures and textures in igneous rocks.

According to these authors the Rila-West Rhodopean Batholith consists of two differing in age and tectonic position plutons. They believe that the granodiorites of the first petrographic type are part of an older (~80 Ma) sinmetamorphic pluton with calcium-alkaline character and mantle magma and consider the granites of the second and third petrographic types in age 42-35 Ma as genetically related phases of postmetamorphic pluton with high potassium-calcium-alkaline character.
Morphology

In addition to the remarkable petrographic peculiarities other important geoconservation features of the geosite are the glacial and periglacial landforms and deposits, suitable for demonstration of the manner in which glaciers work.

The geosite includes the deepest part of the largest glacier valley on the Balkan Peninsula carved out by the Beli Iskar glacier during the Würm Ice Age. It covers both slopes of the valley, where lateral moraines of the glacier are preserved, covered by Holocene supraglacial deposits - scree slopes (Fig. 4). This is the deepest place in the valley called “Demirkapiya” or “Iron Gate”, due to the impressive displacement between the River Basin and the surrounding peaks.

Цви (1897) first established traces of glacial activity on the Balkan Peninsula in Rila during his field trip in 1895. However, he believed that there are only cirques glaciers, but not valley glaciers of alpine type, because he did not investigated the Beli Iskar Valley. He had only doubts about the Cherni Iskar Valley, where he found glacial terraces. Later the glacial landscapes in the area are described in the works of Радев (1920), Делпрадев (1928, 1932), Иванов (1954), Гловня (1958, 1963) and others.

The Beli Iskar River Valley is a typical U-shaped trough glacier valley with steep slopes and rounded bottom (Fig. 5). Its length is 21 km between Kanara Cirque and Beli Iskar village. Its accumulation zone includes also Beli Iskar and South Zelenivrah cirques. It has also been fed by numerous side cirques namely such as Kovach Cirque, East and West Nalbant Cirques, North Zelenivrah Cirque, Devil’s Cirque, Preka Reka Cirque, Darkev Cirque, Golyam Bliznak Cirque, South Skakavitsa Cirque, Ttrite Mushit, Golyama Skakavitsa and Sakan Dupka Cirques (Fig. 6), as well as several valleys with not well differentiated cirques such as Malak Bliznak, Toshov dol, Lyuti dol and others.

Цви (1897) considered as an end moraine the old rupee around Iskar River near Samokov, remaining from the extraction of spilled magnetite for the needs of traditional forge crafts. Later, his teacher Albrecht Penck (1925) found that the end moraine was at the village of Beli Iskar. The scree slopes are composed of unconsolidated and unsorted granite boulders ranging from several centimeters to...
more than a meter in size (Fig. 7). The fine-grained material (sandy and clayey till fraction) is washed away by the surface water and the moraine debris are without matrix.

Interpretation

Around 11 000 years ago as the ice advance began to melt, glacial deposits or drift were left behind. The active processes are related to direct reworking of the rock material due to the glacier movement (glaciotectonism). The moraines formed in this way consist of somewhat rounded particles, ranging in size from large boulders to glacial flour, obtained as a result of the rocks disintegration. These are usually the ground moraines and lateral moraines formed below the glacier surface.

Fig. 7. Lateral moraines formed as a result of the placing of chaotic supraglacial debris on the ice surface due to the frost shattering of the steep side slopes that remain there after the glacier retreat

After melting of glacier in the end of the Pleistocene and the beginning of the Holocene, the rock boulders remained on the slopes of a glacier valley, where they continue to slow down as a result of frost weathering. These lateral moraines are formed as a result of so called “passive processes” of the placing of chaotic supraglacial debris on the ice surface due to the frost shattering of the steep side slopes that remain there after the glacier retreat (Fig. 7). The continuous accumulation of angular boulders on the glacial moraines leads to formation of the so called scree slopes or supraglacial moraines. They are angular and coarse-grained with centimeter to boulder size without matrix. These scree slopes or supraglacial moraines are formed as a consequence of the frost weathering which attacks the rock massive through the joints and leads to the separation of blocks by „plucking” called glacial quarrying in the manner described by Matthes (1930).

The modern post-glacial alluvial deposits in Beli Iskar River Valley, initially formed out as the ground moraine material of glacier, are subsequently reworked and rounded by the river stream. They are represented by poorly sorted sediments containing stones up to boulder size (Fig. 8).

Surrounding landscape

Green Ridge Moraines are formed as supraglacial lateral moraines on both slopes of the Beli Iskar Glacier. West of the geosite is situated Geosite Skakavitsa including the second highest peak in Skakavitsa share of Rila Mountain Golyam Skakavets (2706 m). West of the geosite is the beautiful alpine landscape of Skakavitsa – deep cirques formed the pyramidal peaks of Golyam Skakavets (2706 m) and Malak Skakavets (2670 m) and wooded eastern slope of Zeleni Rid (Green Ridge). In the floor of the valley flows Beli Iskar River, which together with Cherni Iskar River gives rise to the longest Bulgarian river – Iskar River. Two kilometers east of the geosite is situated Musala Peak (2925 m), the highest peak in the Balkans.

Sensitivity and protection measures

The geosite is located in a restricted area because of the status of Beli Iskar Dam as a source of drinking water. The area itself is on the territory of the National Park Rila with restricted measures, according to the requirements of such category protected areas. Quarrying and other mining activities are forbidden in the whole park area.

Access

The access to the geosite is easily feasible on the road from Beli Iskar village to Beli Iskar Dam which is asphalt paved up to the entrance of Rila central reserve. It is part of the mountain road traversed through Dzhanka Pass in the early 20 century to connect Samokov with Yakoruda, Belitsa and Razlog.

Acknowledgements

This research has been supported by the National Science Fund under the contract DNST/Russia 02/14.
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3D STRUCTURAL MODEL OF TERTIARY SEDIMENTS IN NW PART OF THRACE BASIN

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ABSTRACT. The region in the most south-eastern part of Bulgaria (northwest flank of Thrace basin) is characterized with relatively poor geological, geophysical and drilling knowledge. The available and accessible field geological, geophysical and drilling information extremely irregularly describing the geology in that part of Bulgaria, as well as the information from the Thrace basin in Turkey became useful for building the 3D structural model of the Tertiary sequences in that region. The Thrace basin is characterized with very complex tectonic and lithological environment of sedimentation. This fact predetermined careful selecting the processes and steps in building the 3D model. Both the data from hypothetical faults and folds, which is mapped out at surface geological mapping, and the data from the same faults, which is interpreted on the sections of deep geophysical researches are used in order to build the tectonic model. In the next stage of creating the digital 3D model, by using the information obtained from research conducted on Bulgarian and Turkish area, lithological interpretation and correlation of lateral and vertical relations of the main stratigraphic boundaries and lithological formations in the region is done. After that interpretation, the data are applied and implemented to the already created tectonic model, thus the complete 3D geological model is formed. As a result of the 3D structural modelling of the NW part of the Thrace basin, the complex spatial and structural-tectonic relationships between the main stratigraphic boundaries and lithological formations and bodies can be traced, hydrocarbon potential prospects (structures, bodies, etc.) can be identified, and their area, thickness or volume can be calculated.

Keywords: 3D geological model, tectonic model, litho-structural interpretation, NW flank of Thrace basin

3D СТРУКТУРЕН МОДЕЛ НА ТЕРЦИЕРНИТЕ НАСЛАГИ В СЕВЕРОЗАПАДНАТА ЧАСТ НА ТРАКИЙСКИЯ БАСЕЙН

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РЕЗЮМЕ. Районът в най-югоизточната част на България (северозападен борд на Тракийския басейн) се характеризира със сравнително слаба геолого-геофизична и съдържания изученост. Наличната обширност на пловдова геоложка, геофизическа и съдържава информация, в основно едновременно отразяване геоложката на тази част на България, а така също и информацията от продължението на Тракийския басейн в Турция, послужи за изграждане на 3D структурен модел на терциерните наслаги в района. Тракийският басейн се характеризира със сложна тектоника и литофациална обстановка на седиментация, което предпределя впечатляващо подобряне на процесите и стъпките при изграждане на 3D модела. За изграждане на тектонски модел са използвани данните от предполагаемите структурно-тектонски нарушения, набелязани при повърхностните геоложки наблюдения и последващото им привързване с данните от дълбочинните геофизични изследвания. В следващия етап на изграждане на цифровия 3D модел, основаван се на информация, получена от изследвания на българска и турска територия, е направена геоложка интерпретация и проследяване на латералните и вертикалните взаимоотношения на основните стратиграфски граници и литоложки формации в изучавания район. След геоложка интерпретация данните са добавени и привързани към създаването вече тектонски модел, като по този начин е оформен целостен 3D геоложки модел. В резултат на създаването на 3D структурен модел на северозападната част на Тракийския басейн е възможно проследяване сложните пространствени и структурно-тектонски взаимоотношения на основните стратиграфски граници и литоложки формации и тела, набелязани на перспективни в нефтогазонасочено отношение обекти (структурни, тела и пр.), изчисляване на тяхната площ, дебелина или обем.

Ключови думи: 3D геоложки модел, тектонски модел, литолого-структурна интерпретация, северозападен борд на Тракийския басейн

Introduction

Identification and characterization of litho-stratigraphic units, subsequently distinguishing of potential reservoirs and seals in tertiary sequences in the most south-eastern part of Bulgarian territory (northwest flank of Thrace basin) is in the basis of the evaluation of the hydrocarbon potential of that region. In order to trace the complex vertical and lateral spatial and structural-tectonic relationships of these sedimentary rock sequences, it is necessary to illustrate and present them in three-dimensional space by means of digital geological model. Past research for the purpose of regional and ore geology and some separate wells drilled in different parts of the region present extremely irregular geological features of that part of Bulgaria. Oil, gas and gas-condensate fields and accumulations found in the Thrace basin in Turkey, as well as the increased interest of exploration companies in its Bulgarian section, are preconditions for the creation of 3D structural model for clearer presentation of the geological features of this region. A 3D structural model would allow and help to identify oil and gas prospects and objects as well.

Principal geological (tectonic and litho-stratigraphic) features of the region

The limited number and arsenal of research predetermine the existence of different concepts about tectonic belonging of the area under investigation to one or another tectonic unit (Fig.1). In earlier publication (Занева-Добранова, Мерачева, 2014) the issue is dealt with more details, where the area is called northwest flank of Thrace basin. Some authors (Boyanov and Goranov, 2001) call it South Sakar depression,
others (Йовчев и др., 1971) consider it as element of Madjarovo foreland depression.

Fig. 1. Tectonic structure of the region of investigation (according to Yovchev, 1971 with author’s additions)

The probable reason for the lack of accurate division of the tectonic units in this part of the country, is the fact that there is no single opinion about the faults. The most significant fault is the Maritza fault zone, a structural element still widely disputable according to dozens of authors, not traced on any geological map as a continuous line. Outlined tectonic structures are normal faults with east-west to NNW-SSE and NW-SE direction. It is considered (Мерачева и др., 2017) that these faults are an extension of the southeastward spreading North Osmancik fault zone in Thrace basin, where in the north part of it the faults with NW-SE direction prevail. Numerous studies in the Turkish part of the basin give grounds to most of the Turkish researchers (Turgut, Eseller. 2002.) to come to the conclusion, that in structural terms the Thrace basin is composed of great number of folds and faults oriented to greater or lesser extent parallel to the boundaries of the basin, which is observed on Bulgarian territory as well. The main right strike-slip fault zone in the north part of the basin is Terzili and it is located to the south of North Osmancik fault zone. On the other hand, close to our border with Greece lies the root system of Maritza fault zone, which could be a Bulgarian extension of the Turkish Terzili fault zone. Such a concept is also considered by Bulgarian researchers (Иванов и др., 2001; Герджиков и Георгиев, 2006), who, in a broad sense, assign all subequatorial or spreading NW-SE strike-slip faults located to the north of the Rhodope Mountains to the Maritza fault system. These faults control the distribution of thicknesses, relationships, and spreading of lithostatigraphic units with Tertiary Age. The thickness of the sediments with Tertiary age increases from north to south and from north-west to south-east. The largest drilled thickness of the Tertiary sequence is in R-1 Svilengrad well, where the value of 1136 m is registered.

Tertiary sequence in the region of research consists of sedimentary rocks with Paleogene and Neogene Age (Fig.2). It overlies discordantly above different level pre-Paleogene fundament and is partly or fully covered by eluvial, proluvial and alluvial-talus sediment of Quaternary (Кожухаров и др., 1995).

At the base of the Tertiary section, according to data from the seismic surveys, north of R-1 Svilengrad well, a zone with unclear configuration and characteristic sand-conglomerate facies is observed. These rocks, by lithological features, could be assigned to Biser and Leshnikovo formations with Paleocene-Eocene (?) age. In earlier publications (Палахарчеева, Стефанова, 2013), they were assumed as analogues of the Hamitabat formation in the Turkish part.

Above them or directly on the fundament overlay with transgression the clastic-carbonate rocks of the formations with Prabonian age. By litho-stratigraphic features the rocks are assigned to breccia-conglomerate, conglomerate-sandstone, terrigenous-limestone-shale and pyroclastic-marl formations and these are in complex spatial relationships. In some places a smooth lithofacies replacement of the rocks from one formation to the neighbouring is observed, and in other sectors of the area the lithological units pass through each other by gradual transition. In the south-east their probable correlates are the sediments of Koyunbaba and Ceylan formations. The rocks in the section are followed by the Oligocene deposits of the shale-marl formation, which could be correlated with the formations of the Muhacir group on Turkish territory - Mezardere, Osmancik, Danismen. The Paleogene deposits are transgressively and discontinuously covered by continental Neogene sedimentary rocks included within the scope of the Ahmatovo formation.
Model building methods

For visual presentation and characterization of the complex subsurface geological environment and relationships of rocks, a suitable geological computer program is used. The result of the applied processes of geological interpretation, geostatistical prediction for volumetric representation of the heterogeneity in the subsurface, and graphical visualisation, is the geological model. These processes, in which a geological characteristic of a given object is actually performed, can be described by a section or map of some surface, or by a block or a grid of cells. However, we should take into account the fact that the geological subsurface is not a set of surfaces or sections or blocks. Neither is it a continuum except in the broadest sense of the term. This is because every geological unit is an irregular volume with distinguishing characteristics. The boundaries between units create discontinuities that are further complicated by faulting, erosion and lack of sedimentation. Within this heterogeneous complexity we are concerned with variables that are continuously variable within the volume of a unit, but discontinuous across boundaries (Houlding, 1994). The spatial distribution of a geological characteristic frequently influences the spatial variation of a variable. In order to adequately represent such a complex geological environment, it is necessary to consider this set of discrete, irregular, discontinuous volumes that control the spatial variation of variables. Within this 3D context, using the necessary computer tools for geological characterisation, 3D geological modelling was performed in the following order:

1. Management of spatial information;
2. Geological interpretation of the available data, as a complex of points and lines;
3. Creation of structural framework containing the main surfaces – faults, horizons, unconformities, geological bodies;
4. Building of three-dimensional grid, based on the structural framework to support volumetric representation of heterogeneity in the subsurface by geostatistical prediction of data;
5. Enhanced graphical visualization.

Management of spatial information

The first step, before building the model, is a continuous process in which the relevant information from performed in the region research is collected, reviewed, analysed and implemented in the software program. The quality, representativeness and scale of the data used is important for the creation of the present model, as the area is characterised by poor knowledge. This fact determines the complexity of the next steps in the model creation and affects the spatial variation of the variables in creating the three-dimensional grid. The vast majority of the information - drilling, logging, seismic and geological data is imported into the geological software for use in the next stages.

Geological interpretation

During the geological interpretation, faults on each seismic section are picked and correlated, as well as the main seismic horizons and litho-stratigraphic boundaries (Fig.3).

Subsequent process at this stage is an interactive interpretation of faults and seismic horizons, which allows the correlation and control of the process in the three-dimensional space. Initially, on the seismic sections on which wells are projected, the main seismic horizons and stratigraphic boundaries are picked from the data on the welltops of the formations. In the same sections, the main tectonic breaks are identified, each in a different colour for easier visual recognition. Then, using the interactive drawing tools, all boundaries are interpreted and correlated in space when each seismic section is intersected with another. In this way, each of the interpreted components is oriented in the 3D space, while controlling the interpretation by simultaneous visualisation of the process both in the 2D window - the seismic section and in the 3D window - the three-dimensional viewpoint. In the process of interpretation of each of the elements on the sections it is possible to observe and model their direction, orientation and shape in real time in 3D space.

Structural framework creation

Fig. 3. Geological interpretation of faults and seismic horizons

The stratigraphic interpretation was performed using the data from the investigated wells in the studied area. In the process of interpretation, the geological intuition and experience of the authors, which are indispensable for the limited information on a large part of the geology in the area, are important. After determining the location of the wells in the three-dimensional space in the computer program, information from all available drilling studies is imported and used. The digitised in advance logging data help to perform a litho-stratigraphic interpretation and characteristic of subsurface 3D space. The data from the defined boundaries of the lithostratigraphic units in the wells became useful for basis during the geological interpretation and correlation of the seismic horizons. The geological information about the locations and geometry of mapped on the surface faults and formations from past geological and structural mappings in the research area are correctly performed in the software. They are then compared to seismic data.

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three-dimensional space (fig.4). At this stage, it is possible to reflect and represent any elements that arise from complex geological environment such as pinch-out, lithological replacement, faulting, folding, and so on.

There are three main steps that have been undertaken in creating the structural framework:

1) Structural framework geometry definition on X, Y and Z coordinates – on X and Y the model covers a large part of the study area, and Z coordinates of the model defines the bottom surface of the sediments with Tertiary Age.

2) Tectonic modelling – a grid of interpreted faults has been created, while the relationships between the connected faults are presented. In this case, the presence of listric and truncated faults, which in the places of their intersection require increased attention when connecting them.

3) Horizon modelling (main geological boundaries) – grid of points and subsequent surfaces creation, where geological features are considered – pinch-out, unconformity, erosion and so on.

Three-dimensional grid building

The structural maps and fault surfaces created in the previous stage are made up of points that are irregularly distributed in space. This means that the distances between the data points are randomly spaced and always create empty spaces (“holes”) between them. Gridding fills in the holes by extrapolating or interpolating Z values in those locations where no data exists. Thus, gridding produces a regularly spaced array of Z values from irregularly spaced XYZ input data. There are several methods of creating a three-dimensional grid, each of which is based on the calculation of the points’ values by a specific algorithm, resulting in different results in each interpretation. To create the current structural model, a method is used, that best describes the results of the geology of the area, namely the Minimum Curvature method. The preference of the method is based on the fact that it is used in the absence of data for much of the space. In addition, this method is efficient and fast enough. The interpolation process, in this case, is smooth, with minimal bending when using data values. Thus, the final stage of creating the 3D structural model is accomplished in the following steps:

1) A grid of pillars is built from the fault surfaces, the combination of which forms each fault surfaces by means of Pillar gridding process. The basic idea is to use the faults from the tectonic model as the basis for generating a 3D grid of corner points for each fault. Tectonic modelling processes are closely related to the process of creating a grid of pillars. This allows a return to the process of tectonic modelling and editing of the work on it in order to improve the 3D grid of pillars forming the fault surfaces. Of particular importance is the correct definition of the top, middle and bottom corner points of each pillar in the fault surfaces in terms of cell type, size, and orientation. Based on this Pillar gridding, it is possible to define the relationships between the surfaces representing the stratigraphic boundaries and the lithological formations. It is essential for building the three-dimensional grid to connect the intersecting fragments as early as the tectonic model. In the present case, the presence of listric and truncated faults predetermines the complexity of the realisation of this step as well as the need for adequate quality control of this process. The result from Pillar gridding is a set of pillars, both along the faults but also in between faults.

2) At the final stage of model creation, the surfaces have been created from the interpreted stratigraphic boundaries and litho-stratigraphic units, and subsequently those are implemented in the tectonic model. At the same time, the amplitude, the offset angle, the azimuth, and the impact zone in meters for each fault that has influenced the distribution of the geological units in the model are assigned and defined. For the region of investigation, the model is complicated by the presence of a syn-tectonic/syn-rift sedimentation zone, where the thickness of the lithological unit on both sides of the faults should be predefined. At this stage the relationships between the formations, such as unconformity, pinch-out, etc., have been defined, thanks to which the geological model fully represents the real paleo environmental conditions of sedimentation.

Graphical visualization

After building the geological model, it is possible to easily visualise each part of it (Fig. 5). This is done by reorienting the view plane or profile, changing the direction, changing the scale, or concentrating on a particular location of the model of particular interest. If necessary, using powerful workstations and appropriate visualization and viewing tools, it is possible to visualise the model from a certain angle, as well as access a particular object and use the information contained therein. This makes the model sufficiently informative for subsequent activities in 3D space.
Results of the 3D model

As a result of the performed modelling and geological analyses in the process of building of the 3D structural model, geology, tectonic structure and litho-structural features in the studied area were clarified and specified. The questions raised in the interpretation and analysis of the input data concerning the direction of spreading, the dip, the type and relationship of the faults found a response in the created tectonic model. The presence of normal faults on the north of our border with Greece, as well as the predominant direction of east-west, SSE-NNW to SE-NW, have been confirmed. The tectonic model became useful for correlation of the relationships between two main branches of the North Osmanchik normal fault, their extension to the west and their listric character (Fig. 6).

![Geological section](image)

Fig. 6. Vertical section of the 3D structural model with south-north direction

The boundaries of the spreading of the main litho-stratigraphic units with Tertiary Age, getting shallower on the north and northwest to the edges of the sedimentary basin, the unconformable relationships with the overlaying formation could be clearly observed. The 3D structural model allowed northwest tracking (Fig.7) in the three-dimensional space previously identified area, located to the north of the main fault, characterised by syn-tectonic processes of sedimentation during the Upper Eocene Age. The area south of the main fault zone, which has as thick sedimentary complex as the one found north of the fault is extremely interesting.

![Geological section](image)

Fig. 7. Vertical section of the 3D structural model with west-east direction.

Conclusions

Based on the created 3D structural model of the north-western part of the Thrace basin opportunities are revealed for:

- Correlation, observation and specifying the direction, dip, azimuth and type of the faults, as well as their impact on the general geological architecture;
- Correlation of the complex spatial and structural-tectonic relationships of the main stratigraphic boundaries and lithological units in the sequence with Tertiary Age;
- Identification of oil and gas potential prospects (structure, non-structure bodies etc.), calculation of their geometry and volume;
- Identification and observation of the spreading and relationships between litho-stratigraphic units with specific petrophysical properties;
- Prediction of migration paths for fluids with different phase state.

The created 3D structural model can be useful for subsequent analytical and research works related to:

- Stratigraphic modelling of geological bodies of varied genesis – riffs, channel-levee systems etc. (Geobody modelling);
- Facies modelling and paleo environmental modelling;
- Petroleum system modelling;
- Petrophysical modelling;
- Geomechanical modelling;
- Reservoir modelling and simulation.

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INTEGRATED GEODATABASE FOR THE COASTAL ZONE BETWEEN SOZOPOL AND TSAREVO (SOUTH BULGARIAN BLACK SEA COAST)

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ABSTRACT. For a complex study and interpretation of the geological conditions in the southern Bulgarian coastal zone between towns of Sozopol and Tsarevo, it was necessary to combine a wide spectrum of data. The creation of an integrated GIS database was the initial stage preceding a complex analysis of the coastal zone. For the purpose seabed data was used, collected by innovative remote sensing methods as multi-beam echo-sounding, mapping by SeaBat 7111 Multibeam Echosounder System (MBES) with 100% coverage of the surveyed area, side-scan imaging, LiDAR and autonomous unmanned system for 3D mapping. Primary sedimentological analyses of 625 sedimentary samples were presented as well as the lithology of the bottom sediments which was brought into a unified classification system (Folk 7 classes). A contemporary shoreline was digitized at a scale 1: 5 000 from airborne orthophoto images with accuracy 0.5 m. Digital models of the seabed and terrestrial relief were generated with an optimal horizontal resolution of 3 m and 30 m respectively. All sedimentary samples, sonar mosaics, terrain models and orthophoto mosaics were analyzed in GIS environment and combined into an integrated database. The information was divided into three main types of data: vector type data, raster elements and digital terrain models (DTM). Combining data of the shelf from contemporary surveys with modern technology and archival material from the Science Fund of the Institute of Oceanology “Fridtjof Nansen” into integral geodatabase allowed us to make a comprehensive study of the geomorphological setting and lithology of the seabed in the coastal zone between towns of Sozopol and Tsarevo.

Keywords: Bulgarian Black Sea, coastal zone, seabed substrate, Multibeam Echosounder System, GIS
sediment layer allow the creation of an interdisciplinary geo-
database. Its development is the initial step in the
implementation of the project “Seabed mapping of the southern
Bulgarian Black Sea coastal zone for habitat classification”,
funded by the Bulgarian Academy of Sciences (BAS) within the
frame of a Program for Supporting the Young Scientists at
BAS, Project № 17-103/28.07.2017. As the project is not
completed, the report will focus on the initial layout of the
available data and start-up results.

Survey Area

The survey area embraces the coastal zone between the
ports of Sozopol and Tsarevo. Geographically, the region is a
part of the southern Bulgarian Black Sea coast, whereas in
geomorphological terms the region falls entirely in front of the
Medni Rid-Strandzha coast (Tonev, Mkouev, 1984). The
western boundary is the contemporary shoreline with a length
of approximately 90 km. For the correctness of the study, a
terrestrial part which has a significant impact on the coastal
zone is also analysed. More specific is a determination of the
coastal zone – open sea boundary. Based on the title, we
accepted provisionally the 25-meter isobath for delimitation.
According to the Water Framework Directive, the surveyed
marine area falls into the water bodies of BG2BS000C011 and
BG2BS000C012 with wave exposure of the coast ranging from
Exposed, Very Exposed to Extremely Exposed (Valchev et al.,
2014). The area of the plots is approximately 1000 km² (Fig.1).

Data and methods

In 2012 – 2018 the area between Sozopol and Tsarevo was
studied predominantly by the Institute of Oceanology – BAS
and the Centre of Underwater Archaeology – Ministry of
Culture of the Republic of Bulgaria (CUA) for different
purposes: engineering, archaeological, hydrographic,
environmental monitoring of the bottom, habitat mapping, etc
(Fig.1, 2). Data used in the present study are acquired during
hydrographic surveys performed by Multibeam Sonar System
„SeaBat7111“, multibeam echorser „MB1 Teledyne Odom
Hydrographic“, Side Scan Sonars “StarFish 450H“ and „Klein3000“, as well as single beam echosounder „Hydro Star 4300“, as
well as sediment samples taken by Van Veen grab
(Assessment Report of Marine Environmental Status, 2013;
Todorova et al., 2015). A high-resolution sonar mosaic in a 16-
bit rusty colour scheme of the shallowest area south of the
town of Kiten (provided by the CUA) was also used and
combined with the other data (Fig.1, 3). For the verification
and assigning a lithological substrate type to each area with similar
backscatter characteristics, sediment samples taken by Van
Veen grab were analysed (Fig.3).

![Fig. 1. 3D visualisation of the integrated geodatabase (DTM, sediment sampling and sonar mosaics) along Southern Bulgarian Black Sea coast](image-url)
The integrated geodatabase is a set of data for the seabed of the southern Bulgarian coastal zone in front of the Medni Rid-Strandzha Coast. The data is divided into three basic types: raster, vector and digital terrain models (DTM).

The raster elements were selected with priority for marine research. They are a compilation of past studies done before the year 2000 and retrieved from the archives of the Institute of Oceanology and they include:

- sonar mosaics of the seabed with high resolution (Assessment Report of Marine Environmental Status, 2013; Todorova et al., 2015), some of them kindly provided by the Center for Underwater Archeology in Sozopol;
- 41 satellite images from Google Earth covering the land between ports of Sozopol and Tsarevo; high-resolution air...
born orthophoto mosaics captured by an autonomous unmanned system (Scientific Fund of the Institute of Oceanology);
- 1: 5000 topographic maps of the area compiled in the eighties of the twentieth century (Scientific Fund of the Institute of Oceanology);
- different kind of maps of the coastal zone: morpholithostratigraphic; geological and tectonic; geological and morphological; bathymetric; morphological and lithological (Petrova et al., 1992a, b; Kenderova et al., 1999; Kozhuharov et al., 2010; Вълчев, 2015, Scientific fund of the Institute of Oceanology);
- in addition, some thematic photographic material of geological formations, phenomena and others were incorporated in the database for more complex interpretation of coastal geology and morphology (Желев и др., 2012, Желев, Вълчев, 2013, 2015, Желев, Вълчев, 2015).

The vector type data include point, line and polygon which were produced by processing of DTM, digitization of the available raster materials and geological sampling:
- for detailed tracking of coastal formations, a shoreline in scale 1: 5000 was digitalized;
- from the map material, various elements of the geological base were digitalized: geological, morpho-lithostratigraphic, geological-tectonic, geomorphological, morphological and lithological units;
- from the sonar mosaics, the varieties according to physical characteristics of the seabed were outlined.

An essential part belonged to the large number of sediment sampling stations. 625 samples were unified according to different globally accepted classification systems of marine sediments (Assessment Report of Marine Environmental Status, 2013). The present-day practice of sediment study shows that depending on the needs (geoengineering, environmental or habitat mapping), in addition to Bulgarian state standard (БДС) 2761-86 (БДС, 1987), the sediment has to be unified according to the globally accepted classifications of Folk 15 classes (Folk, 1954), Folk 16 classes (Kaskela et al., 2015) and Wentworth (1922). Using the Gradistat software (Blott and Pye, 2001) all data were classified in all above-mentioned class schemes and organized in the database in such a way to display the preferable class according to the needs.

Digital terrain models. Based on data from topographic and bathymetric surveys, three digital terrain models were created:
- the first model covers the coastal zone between the mouth of Ropotamo River and Lozenets. The data were kindly provided by the Center for Underwater Archeology (Project E701/08 Bulgarian Black Sea bathymetric LiDAR, 2009);

![Fig.3. Integrating different types of data sets (digital terrain model, sonar mosaic, physical varieties and sediment samples) for seabed sediment classification](image)
bathymetric terrain models have also been generated at depths between 7 m and 30 m and between 30 m and 55 m with a resolution of 3 m (Todorova et al., 2015);
- by combining topography maps of 1: 5000 scale and 3 ASTER GDEM, bathymetric contours with depth interval of one meter, a digital terrain model with a resolution of 30 m was created for both terrestrial and marine parts of the coastal zone where no sounding data exist.

**Initial results**

Initially available data about seabed substrate were classified after Wentworth size class scheme (Wentworth, 1922), Folk 16 classes (Folk, 1954), Blott and Pye (2001) and БДС 676 (БДС, 1987) sediment grain size classifications, which enforced a comparison analysis. Discrepancies in grain size classes were established which led to a unification of the sediment data in the above-mentioned classifications. Figure 3 shows the application of the integrated database in the layout of the substrate map. The DTM allowed extraction of bathymetric contours at every 0.5 m for high accuracy bathymetric maps of the coastal zone. The sonar mosaics which represent the intensity of bottom sediments reflectivity were used to identify and outline seabed physical varieties. The lithology of these varieties was determined by means of verification using sedimentological data (Fig.3, 4).

Using a combination of different database layers a map of interest can be produced on a scale up to 1:5000. An example is given on Figure 4 - seabed substrate map which can be used for additional habitat characterization.

**Conclusions and challenges**

The initial results of the integration of the database completely follow the concept set up in the project “Seabed mapping of the southern Bulgarian Black Sea coastal zone for habitat classification”. The research demonstrates the effectiveness of multidisciplinary approaches to mapping and studying seabed morphology and geospatial distribution of the seabed substrate. The combination of high-resolution geophysical mapping of the seabed by multi-beam echosounder and side-scan sonar, supported by sediment sampling and video recording allowed drawing of precise large-scale sediment maps of the coastal zone of Primorsko. As a result of the conducted research the following results were achieved:

1. A digital terrain model was developed for the coastal zone between Sozopol and Tsarevo with a horizontal resolution of 30 m;
2. Using the Gradistat software (Blott and Pye, 2001), 625 geological stations were unified according to globally accepted classification systems Folk (Folk, 1954) and Wentworth (Wentworth, 1922);
3. An initial substrate map of the seabed of Primorsko coastal zone was made using Folk 7 classes.

The main goal, also outlined in the title of the project, is to map the seabed substrate (Folk 16 classes) as a geological
basis for determination of submarine habitats by integrating data from remote, geological and sedimentological surveys. It will be achieved through achieving the following objectives: creating an initial database of archive data in GIS environment that will be complemented by up-to-date geospatial data on coastal relief, underwater slope and new sediment data; based on the already summarized geospatial information the boundaries of the main lithological types in the studied area will be established and geomorphological and lithological maps of the coastal zone will be produced, which will be a basis for subsequent extraction of information about the natural habitats.

The results, apart from the benefit for the geological study of the Bulgarian continental shelf and the mapping of habitats, present a geodatabase which would be useful in solving future engineering, geological and geophysical tasks and implementing management plans for the Bulgarian Black Sea sector. The realization of such an interdisciplinary project will be a significant contribution to the activity of the Bulgarian Academy of Sciences which main goal is a gradual comprehensive study of the whole Bulgarian Black Sea sector.

Acknowledgements: The present study was developed under the research project „Seabed mapping of the Southern Bulgarian Black Sea coastal zone for habitat classification” funded by Bulgarian Academy of Sciences in the frame of “Program to support young scientists at BAS”, Project № 17-103/28.07.2017.

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Acknowledgements: The present study was developed under the research project „Seabed mapping of the Southern Bulgarian Black Sea coastal zone for habitat classification” funded by Bulgarian Academy of Sciences in the frame of “Program to support young scientists at BAS”, Project № 17-103/28.07.2017.

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PETROGRAPHIC INVESTIGATION OF CERAMIC ARTIFACTS FROM THE THRACIAN SANCTUARIES IN THE EASTERN RHODOPES

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ABSTRACT. The paper presents the petrographic investigation of ceramic artifacts found in two archaeological sites – the Thracian sanctuaries “Gluhite kamani” and “Ada tepe” in the Eastern Rhodopes. The studied ceramic fragments from Early Iron Age (EIA) are characterized by the methods of optical analysis. The results of this study give information related to the ceramic production techniques and also help us presume the raw material sources and the probable place of production sites. The results of the petrographic investigation of the representative ceramic artifacts from the two archaeological sanctuary sites show that most of the investigated EIA pottery has different temper composition (mineral and rock). The results give us information about the local raw material used for producing the pottery and a small amount of artifacts were probably imported.

Keywords: geoarcheology, ceramic artifacts, petrography, Eastern Rhodopes

The interdisciplinary study of archaeological sites has been taking place for many years, and their results complete the information about them to a great extent. Geoarchaeology is defined as the application of methods and concepts of Earth science for the needs of archaeological studies (Rapp, 2002). The petrographic study of ceramic artifacts has crucial importance in determining the way of manufacturing, the materials used to make the ceramics, the identification of fragment of igneous, sedimentary and metamorphic rocks in the ceramic form, allows to identify the source of clay, used for manufacturing the investigated ceramic (Kyne, 2012). The aim of this study is to investigate artifacts (ceramic fragments), which refer to the Early Iron Age (EIA) in Thrace from the two archaeological sanctuary sites “Gluhite kamani” and “Ada tepe” located in the Eastern Rhodopes using a petrographic method. The obtained results will help us characterize the temper (mineral and rock composition) of the artifacts, to presume the raw material’s sources and the probable place of production sites and give information related to the ceramic production techniques.

The archeological site “Gluhite kamani” is located 4.9 km south-west from the village of Malko Gradište and 3.5 km northeast of the village of Efrem. It is situated on a hill slope at an altitude of 500 m. The site represents a rock cult complex from the Early Iron Age, Late Iron Age and the Middle ages. (Fig. 1). The research of the site is made by G. Neghrizov, J. Cvetkova and others during the period 2008-2017 (Нехризов и др., 2017). Gluhite Kamani (meaning “Deaf Stones”) probably owes its name to the fact that there is practically no echo in the area. Its fame is due to the prominent rock formation on the top of the ridge. This rock formation is presented by Paleogene tuffs and rhyolites, dispersed in several groups from northwest to southeast (Алексиев et al., 2000; Желев и др., 2010). “Gluhite kamani” consists of rhyolites forming the region of summit Sveta Marina volcanic sub-complex, (Йорданов и др., 2008). Besides the acid volcanic rocks in the region, metamorphites from the Sakar metamorphic terrain, Paleogene breccia-conglomerates, sandstones, limestone siltstones, marls, tuffs, sandy and clastic limestones also crop out (Podrunchenska Formation, carbonate-tuff formation, Kurdzhaliterrigenous group and Vulchepolska Formation), as well as Neogene sediments (Йорданов и др., 2008).
The archaeological site “Ada Tepe” is located 2.8 km from the City Hall of the village of Ovchari at the top of the ridge at an altitude of 492.4 m (Fig. 2). The research of the site consists of rescue excavations made by G. Nekhrizov during the period 2001 – 2006 (Некризов и др., 2002; Nekhrizov et al., 2012). The site represents a cult place from the Late Bronze Age, Early Iron Age, and Late Iron Age.

Fig. 1. Archeological site “Gluhite kamani”

From the geological point of view, the area falls within the East Rhodope metamorphic terrain in the range of Krumovtsa lithotectonic unit built up by marbles, migmatized biotite gneisses, ultrabasites, amphibolites and Kesebir lithotectonic unit represented by metagranites. The Paleogene in the area is presented by breccias, breccia-conglomerates conglomerates, sandstones, limestone argillites, marls, organogenic and clayey limestone (Shavarska and Pardarska Formations) and Quaternary sediments along the Krumovtsa River. (Capov и др. 2008).

Fig. 2. Archeological site “Ada Tepe”

Methodology

The object of the study were 58 representative ceramic fragments (pottery samples) from the archeological sites “Gluhite Kamani” and “Ada tepe”. The microscopic investigation was made through ceramic thin-sections using microscope Meiji7390 and digital camera Olympus 5050 in transmitted light.

The petrographic thin-sections were used to characterize the various fabrics of artifacts by their typical texture and to obtain some information about the mineralogy and rock composition of their inclusions (temper). The information obtained by the petrographic research was statistically processed according to Sauer, 1995 (Bezecky et al., 2013). Detailed semi-quantitative analysis was performed only with thin sections of appropriate sample size and quality. For characterization of the temper and to enable graphical presentation of the results the method showed on Table 1 was applied.

Table 1. Grain proportion

<table>
<thead>
<tr>
<th>Occurrences within one (representative) field of view</th>
<th>number of grains</th>
<th>index</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dominant</td>
<td>more than 20</td>
<td>a</td>
</tr>
<tr>
<td>Very frequent</td>
<td>10-19 grains</td>
<td>b</td>
</tr>
<tr>
<td>Frequent</td>
<td>5-9 grains</td>
<td>c</td>
</tr>
<tr>
<td>Subordinate</td>
<td>2-4 grains</td>
<td>d</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Occurrences within five fields of view</th>
<th>number of grains</th>
<th>index</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moderate</td>
<td>5-9 grains</td>
<td>e</td>
</tr>
<tr>
<td>Rare</td>
<td>2-4 grains</td>
<td>f</td>
</tr>
</tbody>
</table>

The very rare constituents were classified as follows

<table>
<thead>
<tr>
<th>Very rare</th>
<th>more than one occurrence per thin section</th>
<th>index</th>
</tr>
</thead>
<tbody>
<tr>
<td>Traces</td>
<td>one occurrence</td>
<td>h</td>
</tr>
</tbody>
</table>

All samples were analyzed with the same magnification.

The X-ray diffraction method was used to determine the various minerals involved in the clay composition and to determine the probable ceramic firing temperature. Powder diagrams were photographed with a powder X-ray diffractometer TuR-M62 with gonimeter HZG3, modified for step scanning and electronic pulse dialing. The diffractograms were shot in the range of 4-8° 2Θ, with duration of exposure of 1.5s.

Results

The principal objective of this study was to assess the mineralogical and petrographic composition of the ceramic artifacts.

Site “Gluhite Kamani”
The ceramic artifacts from the “Gluhite Kamani” are divided into eight groups on the basis of the rock fragment inclusions. The mineral composition in all the groups is similar with exception of one group - BG (Fig. 4 A, B).

Group 1 (1G) - the ratio between matrix and temper is from 60 to 40 %. The rock fragments are represented by acid volcanic rocks, quartzites, volcanic rocks (rhyolites) with spherulitic texture, granoids and schists (Fig 3 a, b). The mineral fragments are presented by quartz, plagioclase, K-feldspar, micas, ore minerals, small amounts of epidote and amphibole. The main feature of the group is the presence of a large amount of volcanic rocks (acid), and volcanic rocks with spherulitic texture (Fig. 3b).

Group 2 (2G) - the ratio between matrix and temper is from 60 to 40 %. The rock fragments are represented by acid volcanic rocks, quartzites and granoids (Fig. 3c). Quartz,
plagioclase, K-feldspar, micas, ore minerals, small amounts of epidote and amphibole are distinguished in the composition of the mineral fragments. The presence of a large amount of small-size quartz grains and rock fragments mainly of acid volcanic and a small percentage of granitoid rocks are distinguishing for the group.

**Group 3 (3G)** - the ratio between matrix and temper is from 65 to 35%. The rock fragments are represented by acid volcanic rocks, quartzites and schists. The mineral fragments are quartz, plagioclase, muscovite and biotite, ore minerals, epidote and amphibole. The presence of muscovite in the amount of the muscovite in this group is more than in the previous ones. The group is distinguished by a large percentage of schists (Fig. 3d) in the temper component. The mineral fragments have a similar level and differ only by their quantity.

Site “Ada Tape”

The ceramic fragments from the archaeological site “Ada Tape” are divided into 4 groups according to their petrographic and mineralogical features (Fig. 4A,C). Only two pottery fragments are without analogue (Adt-15-14 and Adt-52-12) and they are not included in any of them. For all groups, the amount of included rock fragments is smaller than that of the mineral fragments. The variation rock fragments and their limited quantity do not allow their use for grouping.

**Group 4 (4G)** - the ratio between matrix and temper is from 60 to 40%. The rock fragments are varied: acid volcanic rocks, quartzites, schists, granitoids, intermediate volcanic rocks and volcanic rocks with spherulitic texture. The mineral fragments are represented by quartz, plagioclase, K-feldspar, mica, ore minerals and small amounts epidote and amphibole. The higher percentage of rock fragments with varied composition and appearance of medium-sized volcanoes is characteristic of this group.

**Group 5 (5G)** - the ratio between matrix and temper is from 65 to 35%. The rock fragments are from acid volcanic rocks, volcanic rocks with spherulitic texture, schists, gneisses. The mineral fragments are represented mainly by quartz, plagioclase, K-feldspar, muscovite (with increased percentage), biotite, ore minerals and small amounts of epidote and amphibole. The presence of large amounts of gneisses and schists in the temper is distinguishing for this group (Fig. 3e).

**Group 6 (6G)** - the ratio between matrix and temper is from 60 to 40%. The rock fragments are presented by quartzites, granitoids and schists. The mineral fragments are mainly of quartz, plagioclase (with an increased percentage), K-feldspar, muscovite, biotite, ore minerals, small amounts of epidote and amphibole. The presence of granitoids and schists in the composition of the rock fragment is determinative, here.

**Group 7 (7G)** - the ratio between matrix and temper is from 70 to 30%. The rock fragments are represented with almost the same percentage as the mineral fragments. The rock fragments are presented mainly by intermediate volcanic rocks (Fig. 3g) and fewer quartzites, granitoids and volcanic rocks with spherulitic texture. Typical for this pottery is the larger percent of matrix as compared to temper and the presence of rock fragments from intermediate volcanic rocks.

**Group 8 (8G)** - the ratio between matrix and temper is from 65 to 35%. The rock fragments are of small amount, represented mainly by granitoids, amphibolite and single enriched by epidote rocks. The mineral fragments here are represented by quartz, plagioclase, amphibole, epidote, ore minerals and small amounts of K-feldspar, micas and pyroxene. The high quantity of amphibole (Fig. 3f) and the epidote grains in the composition of the mineral temper are specific for this group.

The matrix in all the groups is optically active and represented by micaceous groundmass and clay minerals (illite–montmorillonite).

**Group 1 (1A)** - the ratio between matrix and temper is from 55 to 45%. The individual rock fragments are represented by quartzites, schists, granitoids, gneisses, acid volcanic rocks, intermediate and basic volcanic rocks and amphibolites. The mineral fragments are represented by quartz, plagioclase, K-feldspar, muscovite, biotite, ore mineral, amphibole and epidote. The main factor for the pottery of this group is a greater presence of quartz, feldspars and micas with sporadic grains of amphibole and epidote (Fig. 3i).

**Group 2 (2A)** - the ratio between matrix and temper is from 60 to 40%. The rock temper is represented by quartzites, altered volcanic rocks (Fig. 3j), tuffs, granitoids, schists and amphibole with low quantity compared to the mineral temper. The mineral fragments are represented by quartz, plagioclase, K-feldspar, muscovite, biotite, ore mineral, amphibole and epidote. In this group, the percentage of the quantity of amphibole and epidote increase at the expense of K-feldspar and quartz.

**Group 3 (3A)** - the ratio between matrix and temper is from 60 to 40%. The rock fragments are represented by quartzites, amphibolites, schists, gneisses and altered volcanic rocks. The mineral fragments are represented by quartz, plagioclase, K-feldspar, muscovite, biotite, ore minerals, amphibole, epidote and pyroxene. Typical for this group is the presence of a high percentage of amphibole and epidote in the temper component (Fig. 3i).

**Group 4 (4G)** - the ratio between matrix and temper is from 70 to 30% (Fig. 3h). The rock fragments are represented by altered intermediate, acid and basic volcanic rocks, volcanic glass and schists. The mineral fragments are represented by quartz, plagioclase, K-feldspar, muscovite, biotite, ore minerals. The presence of plagioclase among the mineral fragments and high amount in the matrix is typical for this group.

Ceramic artifact Adt-15-14 – the ratio between matrix and temper is 60/40%. It is characterized by a large amount of muscovite and biotite among mineral temper (Fig. 3k). Quartz, K-feldspar, plagioclase and ore minerals are also included in the temper. The rock fragments are limited, represented by single quartzites, schists and tuffs.
Fragment Adt-52-17 is made of matrix and temper in ratio from 65 to 35 %. The mineral fragments are represented mainly by quartz and in a small amount by K-feldspar, plagioclase, ore minerals and single epidote grains. The rock temper is presented by single granitoids and schists, fragments of chamotte (older ceramics) and carbonate. The last one fills all gaps and pores in the ceramic.

Fig. 3. Microphotos of ceramic artifacts: a – Rock fragment of the acid volcanic rock (centre) and quartzites among micaceous matrix. CPL, Observation field wide (Ob.F. W.) = 1900 μm; b – Rock fragment of volcanic rock with spherulitic texture. CPL, Ob.F. W. = 1900 μm; c – Rock fragment of granitoid (centre). CPL, Ob.F. W. = 3900 μm; d – Rock fragment of schist (centre). CPL, Ob.F. W. = 1900 μm; e – Rock fragment of gneiss. CPL, Ob.F. W. = 1900 μm; f – Enriched of amphibole ceramic artifact. PPL, Ob.F. W. = 1900 μm; g – Intermediate volcanic clast among micaceous matrix. CPL, Ob.F. W. = 1900 μm; h – Fragments of acid volcanic rock among fine crystalline matrix. CPL, Ob.F. W. = 1900 μm; i – Enriched of amphibole pottery. PPL, Ob.F. W. = 1900 μm; j – Fragment of altered volcanic rock (centre) and epidote. CPL, Ob.F. W. = 1900 μm; k – Enriched of micas (biotite and muscovite) and quartzites pottery. CPL, Ob.F. W. = 1900 μm; l – Ceramic artifact enriched of minerals – quartz, micas and ores. CPL, Ob.F. W. = 3900 μm.
The matrix in all the groups is optically active and represented by micaceous groundmass. The XRD analyses supplement the information for ceramic artifacts from the "Gluhite Kamani" (Янкова и др., 2013) and give the new data about those from the site "Ada tepe". The results confirm the optically specified mineral composition and register the presence of illite, montmorillonite-illite and montmorillonite. The supposed temperature of the firing of the studied ceramics is within the limit from 500-550°C to 800° (850°) according to the determined mineral phases. The upper limit of this temperature range is indicated by the presence of illite in some fragments (Fig. 5). The lower limit of this range is not very clear, due to the presence of montmorillonite and montmorillonite-illite, which indicate temperatures from 500° to 550°C.
Discussion and conclusion

The results of the petrographic investigation of the representative ceramic artifacts from the two archaeological sanctuary sites “Gluhite kamani” and “Ada tepe” with regard to the groups described above show that most of the investigated EIA pottery has different temper composition (mineral and rock). The differences could be summarized in the following way:

- The raw material used for the production of the pottery in the site “Gluhite kamani” is enriched by rock fragments compared to those from “Ada tepe” where the mineral inclusions are dominant (Fig. 4 A);
- The rock fragments included in the ceramic artifacts from the site “Gluhite kamani” are presented mainly by acid volcanic rocks, some of them with spherulitic texture;
- The pottery temper from the site “Ada tepe” consists of a large variety of rock fragments – schists, gneisses, granitoids, acid, intermediate and basic volcanic rocks, amphibolites and tuffs;
- The raw material used for the production of pottery from the site “Ada tepe” is characterized by the presence of lot of minerals like epidote, micas and amphibole (Fig. 4C);
- In the representative investigated pottery there is a small quantity of ceramic with different temper (minerals) which cannot be included into the divided groups (Adt-15-14, Adt-52-17).

All this evidence for the ceramic artifacts from these two archaeological sites gives us information about the local raw material used for producing the pottery. The site “Gluhite kamani” is situated on the Paleogene rhyolites and most of the included fragments in the pottery from this site are from these rocks. The other rock inclusions like bitolite, gneisses and schists are probably from the Thracian unit (Sacar metamorphic terrain) revealed to the north and northeast of the site.

In the “Ada tepe” site the presence of minerals like epidote and amphibole and rock inclusions of amphibolites, schists, granitoids and basic volcanic rocks are the most distinct mineral and rock temper for the divided ceramic groups (4a,c). These types of rocks crop out in the vicinity of the site (south and northwest) and suggest the presence of short transportation in the valley of the river Krumovitsa and Elbasan Dere. The possible local raw material of the EIA pottery was also investigated through the heavy mineral fraction of the site “Ada tepe” showed by the data published by Ajdanlìjsky et al. (2008). A small amount of ceramic artifacts (Adt-15-14, Adt 52-17) are probably imported in the site “Ada tepe”.

On the basis of the petrographic features in some of the studied artifacts (groups 8G and 3A) from the two archaeological sites was found similarity in the mineral temper especially in the content of the minerals like amphibole. There are, also, a similarity according to the type of the raw material (groups 7G and 4A) which indicates the similar way of production using more amounts of matrix and a small quantity of temper. These indicators could be presumed about the relation between these two archaeological sites during EIA and only future investigation will confirm this.

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CAMPANIAN-MAASTRICHTIAN BENTHIC FORAMINIFERA FROM THE BYALA FORMATION (EASTERN BALKAN)

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ABSTRACT. The Byala Formation, developed in the tectonically complicated boundary region between the Eastern Fore Balkan and Eastern Balkan, is well investigated from paleontological and stratigraphical point of view. Despite this fact, the small foraminiferal content of the Campanian-Maastrichtian part of the unit have not been studied micropaleontologically in details. The present article is focused on the benthic foraminiferal assemblages, which are rich and diverse. The studied samples were picked up from three sections (Byala-south and Byala-north, revealing the uppermost Maastrichtian levels, and Beliya Nos-Byala River, referred to the North-European type Upper Cretaceous (Гочев 1932; Koen, 1938; Ботев, 1953), but since the beginning of the 1960s they have been considered to belong to the Mediterranean type (Трифонова, 1960а; Атанасов, 1961; Синьовски, 2007; Дабовски et al., 2009). Detailed reviews on the geological investigations on the unit were given by Синьовски (2006) and Дабовски et al. (2009).

It should be noted that, despite the initial foraminiferal studies (Трифонова, 1960а, b), the detailed investigations on small foraminifers (biostratigraphical zonations – Juranov, 1983; Valchev, 2003а; paleoecological interpretations – Valchev, 2003b, 2004; taxonomical study – Вълчев, 2001) were focused predominantly on the Paleocene part of the Byala Formation. First planktonic foraminiferal data concerning the lowermost (Campanian) levels of the formation were recently published (Valchev, 2017). Therefore, the present article aims (i) to reveal the taxonomical composition and structure of the benthic foraminiferal assemblages from the Campanian-Maastrichtian levels of the Byala Formation, (ii) to elucidate the stratigraphical

Keywords: benthic foraminifers, Campanian, Maastrichtian, Byala Formation, Eastern Balkan

KEYWORDS. Беленска свита, развита в тектонски усложнения граничен район между Източния Предбалкан и Източния Балкан, е добре изучена в палеонтолошко и стратиграфско отношение. Независимо от този факт асоциациите от малки формацинери от кампан-мастрихтската част на единицата не са били обект на детайлни микропалеонтолошки изследвания. Настоящата статия е фокусирана върху асоциациите от бентосни формацинери, които са богати и разнообразни. Изследванияте проби са събрани от три разреза (Бяла-юг, Бяла-север, представляващ най-горните мастрихтски нива) и няколко единични разкрития, намиращи се на морския бряг в района на гр. Бяла, Варненска област. Изследванията са изградени от таксони с аглутинирана и хиалина черупка с широко стратиграфско разпространение и във варирящи съотношения. Те показват високо таксономично разнообразие (общо 84 вида) и изобилие от екземпляри. Този факт предоставя добър възможност за палеоеколожки интерпретации. Като цяло установената бентосна формацинерна фауна може да бъде отнесена към широко разпространената в Тетийски регион фауна от типа Velasco, характерна за хемипелагичната зона.

Ключови думи: бентосни формацинери, Кампан, Мастрихт, Беленска свита, Източна Стара планина

Introduction

The Campanian–Paleocene Byala Formation is developed in a small area in the Eastern Balkanides and it is well investigated from paleontological (calcareous nanofossils, ammonites, echinoids, incoeramids, and partly small foraminifers) and stratigraphical (lithostratigraphy, biostratigraphy, chronostratigraphy, cyclic and event stratigraphy) point of view. The first data on the rocks of the Byala Formation were published by Златарски (1907), who described them as “whitish limy marls”. Later on Бончев (1926) named the rocks “Byala clayey marls”. Джуранов, at first (Джуранов, 1984) united them into “limestone-marl formation”, and then (Джуранов, 1991) formalized the unit as “Byala limestone-marl Formation” (see also Джуранов, 1993). Initially the rocks were referred to the NorthEuropean type Upper Cretaceous (Гочев, 1932; Коен, 1938; Ботев, 1953), but since the beginning of the
range of the taxa and (iii) to estimate their paleoecological significance.

The Byala area is of great interest because here the Cretaceous/Tertiary boundary was first established in Bulgaria (Stoykova, Ivanov, 1992) in the frame of Bulgarian–Austrian project led by Prof. Anton Preisinger. Later on, the outcrops north of Byala beach were announced as protected geosite named “Belite Skali” (Синьовски, 2003) which is included in the “Register and Cadastre of the Geological Heritage of Bulgaria” (Синьовски и Желев, Синьовски, 2003*).

Geological Setting

The area of study is part of the Eastern Balkanides and it comprises the tectonically complicated boundary region between the Eastern Fore Balkan and Eastern Balkan (Fig. 1). It is characterized by the presence of numerous normal, reverse and thrust faults at a various scale (Fig. 2 shows the largest ones only). The biostratigraphical investigations conducted previously (e. g. Juranov, 1983; Джуранов, 1989, Синьовски, 2006) proved that there is no complete section of the Byala Formation revealing its total stratigraphical range. Moreover, it was established that there are cases of overturned stratigraphical successions or repeatedly occurring stratigraphical levels (Джуранов, 1989).

As a whole, the Byala Formation comprises rhythmic limestone-marl successions related to climatic oscillations (Preisinger et al., 1993a, b) which alternate with monotonous limestone-marl successions related to climatic oscillations (Sinnyovsky, 2001) described the rhythmic intervals as “typical periodite alternation” resulting from high frequency climatic cycles of Milankovich and proved, on the intervals as “marl” beds in fact are basis of sedimenthological analyses on samples from the Upper Campanian and Danian parts of the Byala Formation. They consist of couples of prominent limestone bed and soft back-weathering interbeds (Plate 1, a, b) with periodicities of about 1 m (Sinnyovsky, 2001; Синьовски, 2006).

![Fig. 1. Tectonic subdivision of Bulgaria (after Дабовски and Загорчев, 2009) with the location of the area of study](image1)

![Fig. 2. Geological map of the coastal part of the Byala area (after Джуранов et al., 1994P)](image2)

1. Dvoynitsa Fm.: medium to coarse-grained thick-bedded sandstones, alternating with thin-bedded fine-grained sandstones, siltstones, marls and conglomerates (Lower–Middle Eocene); 2–3, Byala Fm.: alternation of clayey limestones and marls (2. Paleocene, 3. Campanian–Maastrichtian); 4, thrust; 5, chroonostrophic boundary; 6, bedding; 7, section (a) and outcrop (b): 1. Byala-south, 2, Byala-north, 3, Beliya Nos–Byala Reka, 8, borehole

The studied samples were picked up from three outcrop sections located on the sea coast in the surroundings of the town of Byala (Figs. 2, 3). Two of them (Byala-south, exposed

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at the beach, and Byala-north, located north of the beach) reveal the uppermost Maastrichtian levels (Plate Ic, d). The third one crops out between Beliya Nos Cape and Byala River mouth north of the town of Byala, and it comprises Lower Campanian to Upper Maastrichtian levels (Plate Ie, f). Some small scale faults, but without data for visible displacement, are observed in the lower half of this section (Plate Ig).

Benthic foraminiferal assemblages

Taxonomical diversity and specimen abundance

The studied samples revealed high taxonomical diversity of the benthic foraminiferal assemblages – totally 84 species were recorded (see Appendix). The Lower Campanian levels demonstrate lowest diversity – 26 species established. The assemblages are dominated by taxa with hyaline tests such as Gavelinella beccariiformis (White), Nuttalides trümpyi (Nuttal), Nuttalides sp., Lenticulina velascoensis White, accompanied by the species with agglutinated tests Ammodiscus cretaceus (Reuss), A. glabratu Cushman and Jarvis, and Massonella oxycon (Reuss). All of them occur as rare specimens. The secondary contributors, including some representatives of nodosariids, heterolepids, bolivinoids, are represented sporadically by single specimens.

The Upper Campanian samples contain more diverse assemblages – up to 40 species were recorded. Here the dominating taxa are the same as in the Lower Campanian, but with increased occurrence of the species with agglutinated tests Clavulinoides amorphous (Cushman) and C. trilaterus (Cushman) in addition. Here, Gaudryina cretacea (Karrer), G. pyramidata Cushman, and Quadrimorphina allomorphinoides (Reuss) are present as rare specimens. The secondary contributors, occurring as single specimens, are the same as in the Lower Campanian.

The Lower Maastrichtian assemblages include up to 60 species. “New” elements of the dominating group, amongst the above mentioned, are Aragonia velascoensis (Cushman), which is represented by rare to common specimens, and Nodosaria longiscata d’Orbigny occurring as rare specimens. Gaudryina pyramidal Cushman and Oridorsalis megastomus (Grzybowski) are also rarely encountered characteristic species. The presence of Bulimina midwayensis Cushman & Parker and Guttulina ipatovcevi Vassilenko amongst the secondary contributors should be noted.

The highest taxonomical diversity was recorded from the Upper Maastrichtian levels. All the 84 taxa were established in the samples from this part of the Byala Formation. The
dominating species here are *Nuttalides trümpyi* (Nuttal), *Gavelinella beccariiformis* (White), *Osangularia velascoensis* (Cushman), *Aragonia velascoensis* (Cushman), *Clavulinoides trilaterus* (Cushman), *Gaudryina cretacea* (Karrer), *G. pyramidata* Cushman, *Marssonella indentata* (Cushman and Jarvis), *Bathyphysion discreta* (Brady), *N. semireticulata* (Cushman and Dusenbery) and *Pseudopecclavulina globulifera* (Reuss) are of broad stratigraphical range (Upper Cretaceous–Paleocene), therefore it is not possible to define biostratigraphical markers (FAD and LAD) on the base of benthic foraminifera.

**Biostratigraphical markers**

All the species, recorded in this study, apart from *Reussella szajnoche* (Grzybovskii) are characteristic for hemipelagic conditions. The last fact gives a good opportunity for paleoecological reconstruction and further paleogeographical interpretation of the position of the Byala Formation in the Late Cretaceous–Early Paleogene geological structure of Eastern Bulgaria.

**Types of assemblages**

The taxonomical composition and the structure of the benthic foraminiferal assemblages – dominating taxa such as *Gavelinella beccariiformis* (White), *Nuttalides trümpyi* (Nuttal), *Osangularia velascoensis* (Cushman), *Aragonia velascoensis* (Cushman), *Clavulinoides trilaterus* (Cushman), *Gaudryina cretacea* (Karrer), *G. pyramidata* Cushman, *Marssonella indentata* (Cushman and Jarvis), *M. oxycona* (Reuss) are typical for the Velasco-type fauna, characteristic for the hemipelagic realm and widely known from the Tethys region (Cushman, 1925, 1926; White, 1928a, b, 1929; Cushman, Jarvis, 1928; Braga et al., 1975; Proto Decima, Bolli, 1978; Tjalsma, Lohman, 1983; etc.).

**Conclusion**

The study of the Campanian–Maastrichtian benthic foraminiferal assemblages from the Byala Formation recovered from three sections and several outcrops on the sea coast in the surroundings of the town of Byala revealed that (i) they are of high taxonomical diversity, (ii) composed of taxa with broad stratigraphical range, and (iii) dominated by species, characteristic for hemipelagic conditions. The last fact gives a good opportunity for paleoecological reconstruction and further paleogeographical interpretation of the position of the Byala Formation in the Late Cretaceous–Early Paleogene geological structure of Eastern Bulgaria.

**Appendix**

**Alphabetical list of benthic foraminiferal species**

*Allomorphina conica* Cushman and Todd

*Ammodiscus cretaceus* (Reuss)

*A. glabatus* Cushman and Jarvis

*A. peruvianus* Berry

*Anomalinaeoides* sp.

*Aragonia velascoensis* (Cushman)

*Astacolus gladius* (Philippi)

*Bannerella retusa* (Cushman)

*Bathyphysion discreta* (Brady)

*B. microcladus* Samuel

*Bolivina midwayensis* Cushman

*Bolivinoides delicatus* Cushman

*Bullimina midwayensis* Cushman and Parker

*Chilostomelloides* sp.

*Cibicidoides dayi* (White)

*Clavulinoides amorphous* (Cushman)

*C. trilaterus* (Cushman)

*Cyclammina* sp.

*Dendrophya* sp.

*Dentalinoides fallax* (Cushman and Dusenbery)

*Ellipsoglandulina chlortoma* (Rhehak)

*Gaudryina cretacea* (Karrer)

*G. pyramidata* Cushman

*Gavelinella beccariiformis* (White)

*Globobulimina sutera* (Cushman and Renz)

*Guttulina ipatovecvi* Vassilenko

*Gyroidinoides globosus* (Hagenow)

*Haplophragmoides suborbicularis* (Grzybovskii)

*H. walteri* (Grzybovskii)

*Haplophragmoides* sp.

*Hormosina ovuloide* (Grzybovskii)

*Hyperammina* sp.

*Kalamopsis grzybovskii* (Dylazanka)

*Karreria fallax* Rhehak

*Karreria* sp.

*Laevidentalina laticolis* (Grzybovskii)

*Lenticulina velascoensis* White

*Lenticulina* sp.

*Marginulina* sp.

*Marssonella indentata* (Cushman and Jarvis)

*M. oxycona* (Reuss)

*Neoflabellina jarvisi* (Cushman)

*N. semireticulata* (Cushman and Jarvis)

*Nodosarella hedbergi* Cushman and Renz

*Nodosaria limbata* d’Orbigny

*N. longiscata* d’Orbigny

*Nodosaria* sp.

*Nonion* sp.

*Nuttalides trümpyi* (Nuttal)

*Nuttalides* sp.

*Oridorsalis megastomus* (Grzybovskii)

*Osangularia velascoensis* (Cushman)

*Osangularia* sp.

*Paliolatella crebra* (Mathes)

*Paliolatella* sp.

*Pleurostomella kugleri* Cushman and Renz

*Praeglobobulimina* sp.

*Pseudonodosaria manifesta* (Reuss)

*Pseudoclavulina globulifera* (ten Dam and Sigal)

*Pseudonodosaria manifesta* (Reuss)

*Pseudonodosaria* sp.

*Pullenia coryelli* White

*P. quinqueloba* (Reuss)

*Pygmammoseisitron laevis* (Montagu)

*P. oxystomum* (Reuss)

*Pyramidulina raphanus* Linnè

*P. velascoensis* (Cushman)

*Pyramiduloides* sp.

*Quadrimorphina allomorphinoides* (Reuss)

*Q. cretacea* (Reuss)
Rhizammina indivisa Brady
Recurvoides sp.
Reptaminia charoides (Jones and Parker)
Reussella szajnoche (Grzybovski)
Reussolina globosa (Montagu)
Reussolina sp.
Saccammina complanata (Franke)
S. placenta (Grzybovski)
Saracenaria arcuata (d’Orbigny)
S. hantkeni (Cushman)
Textularia plummerae Lalicker
Trochamminia sp.
Trochamminoides sp.
Vaginulopsis longiformis (Plummer)
V. pedum (d’Orbigny)

References


PLATE I

a) periodites in the upper part of Byala–north section (Upper Maastrichtian); b) cyclic limestones at Beliya Nos Cape section (Lower Campanian); c) general view of Byala-north section; d) Byala-south section: the uppermost Maastrichtian and the lowermost Danian levels; e) general view of the base of Beliya Nos Cape section (lowermost Campanian levels); f) the Maastrichtian levels north of Beliya Nos Cape towards Byala River mouth (view to north); g) a fault without data for visible displacement north of Beliya Nos Cape; h) thrusted and folded levels of the Byala Formation between Byala-north section and Beliya Nos Cape.
CAMPANIAN PLANKTONIC FORAMINIFERAL ASSEMBLAGES FROM THE CHUGOVITSA FORMATION IN THE AREA OF JELYAVA AND ELESHNITSA VILLAGES, SOFIA DISTRICT

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ABSTRACT. The Campanian turbidites of the Chugovitsa Formation, belonging to the Mediterranean type Upper Cretaceous in Bulgaria and cropping out in a narrow strip with west-east direction in the area of the villages of Jelyava and Eleshnitsa, Sofia district, are investigated herein in terms of their planktonic foraminiferal content. The area of study is part of the Panagyurishite Unit of the Srednogorie Zone and the samples were picked up from two sections located along the Jelyavska and Eleshtiska rivers' valleys. The lower part of the Chugovitsa Formation in both sections comprises a 60 m package of grey, motley and violet marls referred to the Voden Member. The samples contain poor planktonic foraminiferal fauna including predominantly Early Campanian taxa like Globotruncana elevata (Brotzen), and species with broader stratigraphic range – Globotruncanita arca (Cushman), Globotruncanita lapparenti Brotzen, Globotruncanita stuartiformis (Dalbiez), Rugoglobigerina rugosa (Plummer). The upper levels are composed of about 300 m turbidite deposits containing more diverse and abundant assemblages represented by Early to Late Campanian taxa including, apart from the above mentioned, Globotruncanita ventricosa White, Globotruncanita stuarti (de Lapparent), Heterohelix globulosa (Pattenden), Pseudotextularia elegans (Rzehak). Two biostratigraphical zones were defined following Premoli Silva and Verga’s (2004) zonation – Globotruncanita elevata and Globotruncanita ventricosa.

Keywords: planktonic foraminifers, Chugovitsa Fm., Campanian, Srednogorie zone, Sofia District.

Introduction

The sections near the villages of Jelyava and Eleshnitsa, Sofia district, reveal almost complete succession of the Mediterranean type Upper Cretaceous in Western Bulgaria. They comprise Turonian marls, Coniacian glauconitic sandstones, Coniacian–Campanian carbonate and turbidite deposits. Златаровски (1910) first described the rocks near the village of Eleshnitsa referring them to the “Campanian substage”. Later on Цанков (1965) determined Maastrichtian age for the carbonates in the same section (the village was named Yordankino in the period between the 1960s and the 1980s) and Dimitrova et al. (1981) divided three levels in the section near Jelyava: Coniacian (113 m), Santonian (200 m) and Campanian (677 m). Dimitrova et al. (1984) refined this subdivision into Coniacian (totally 113 m including 15 m glauconitic sandstones in the base and 98 m carbonates), Santonian (200 m carbonate deposits) and Campanian (including 170 m carbonate and 250 m turbidite sequences). The basal terrigenous level and the carbonate one the authors described as “limestone-marl formation” (corresponding to the “first”, “second” and “third horizon” of the Maastrichtian of Връблянски et al., 1961) and the turbidite level – as “flysch formation” (“fourth horizon” of the Maastrichtian of Връблянски et al., 1961). Начев и Начев (1989, 2003) followed this subdivision.

Чунев (1995) referred the rocks of the “limestone-marl formation” to the Mirkovo Formation and these of the “flysch formation” – to the Chugovitsa Formation. The two formal units were introduced and described by Moes and Антонов (1976, 1970) in the Stargel–Chelopech strip. Later on Попов (2005)
united them into the Popintsi Group in Panagyurishte ore region.

Sinnyovsky (Sinnyovsky, 2005; Синьовски, 2007), Дабовски et al. (2009) and Antonov (2010) followed Moev and Антонов’s subdivision as the first author recognized the Voden Member of Моеv and Антонов (1978) comprising 60 m at the base of the Chugovitsa Formation in the sections near Jelyava and Elelnitsa. He also noted that “none of the previous investigators reported the presence of large-scale slump structures, resulting in significant augmentation of the thickness”.

From micropaleontological point of view, the sections have been investigated by means of planktonic foraminifers and calcareous nannoplankton. Dimitrova (in Dimitrova et al., 1981; Димитрова et al., 1984) examined planktonic foraminifers in thin sections. She gave lists of species representing the most characteristic taxa for every individual package in Jelyava section. Later on Dimitrova and Valchev (2007) summarized these data and indicated the presence of Globotruncanita elevata and Globotruncanita stuartiformis zones. Sinnyovsky, at first indicated three nannofossil zones (Синьовски, 1993), and later on (Sinnyovsky, 2005; Синьовски, 2007) published a detailed Campanian nannofossil zonal scheme concerning the upper levels of the Mirkovo Formation and the entire Chugovitsa Formation.

The present article aims to elucidate in details the taxonomical composition and the structure of the planktonic foraminiferal assemblages on the basis of isolated specimens recovered from the Chugovitsa Formation and to estimate their biostratigraphical importance.

**Geological Setting**

The area of study is part of the Panagyurishte Unit of the Srednogorie Zone (according to Дабовски and Загорчев, 2009, Fig. 1). The outcrops of the Mediterranean type Upper Cretaceous form a narrow strip with west-east direction in the southernmost part of Western Balkan. The samples were picked up from two sections located along the valleys of Jelyavsk and Elelnishka rivers in the northern outskirts of Jelyava and Eleshnitsa villages (Fig. 2).

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**Fig. 1. Tectonic subdivision of Bulgaria (after Дабовски and Загорчев, 2009) with the location of the area of study**

**Fig. 2. Geological map of the area of Jelyava and Elesnitsa villages (after Angelov et al., 2010 with modifications)**

1-3) Quaternary (1 - alluvium, Holocene; 2 - deluvium, Pleistocene–Holocene; 3 - proluvium, Pleistocene); 4–6) Upper Cretaceous (4 - Chugovitsa Formation: rhythmic alternation of limy sandstones, siltstones, mudstones, marls and clayey limestones, Campanian; 5 - Mirkovo Formation: red to rose and gray-greenish clayey limestones, Santonian-Campanian; limestone-marl formation: gray and motley limestones and marls, Coniacian; sandstone formation: carbonate glauconitic sandstones, Coniacian; 6 - coal formation: conglomerates and breccia-conglomerates, sandstones, siltstones, limy mudstones, marls, clays and coal, Turonian); 7) Lower–Middle Jurassic (Gradets Formation: quartz sandstones, Aalenian-Bajocian; Ozirovo Formation: sandy bioclastic limestones and silty marls, Sinemurian–
The base of both sections (Fig. 3) is composed of marls referred to the coal formation of Turonian age (Plate la). They are overlaid with parallel unconformity by 7–15 m carbonate glauconitic sandstone with inoceramid and rare echinid remains comprising the sandstone formation of Coniacian age (Plate la, b). The next level is composed of 220 m gray and molley predominantly thick-bedded to massive limestones and marls belonging to the Mirkovo Formation (Plate Ib, c). In Eleshnitsa section a thin package of tephra layers (190 m above the base) is observed. In the section near the village of Jelyava this interval is not well exposed and it is characterized by the presence of slump structures. The base of the Chugovitsa Formation is represented by 60 m grey to violet marls referred to the Voden Member (Plate ld-f). They are overlaid by a 300 m thick turbidite succession with dominance of the marl interbeds and marl packages in its lower levels (Plate lf-h).

Planktonic foraminiferal assemblages and zones

The samples from the Voden Member contain poor planktonic foraminiferal fauna including predominantly Early Campanian taxa like *Globotruncanita elevata* (Brotzen), and species with broader stratigraphic range – *Globotruncanita arca* (Cushman), *Globotruncanita lapparenti* Brotzen, *Globotruncanita stuartiformis* (Dalbiez), *Rugoglobigerina rogosa* (Plummer). The samples from the typical Chugovitsa Formation contain more diverse and abundant assemblages represented by Early to Late Campanian taxa including apart from the above mentioned *Globotruncanita ventricosa* White, *Globotruncanita stuarti* (de Lapparent), *Heterohelix globulosa* (Ehrenberg), *Pseudotextularia elegans* (Rzehak).

![Fig. 3. Stratigraphical columns of Eleshnitsa and Jelyava sections (after Sinnyovsky, 2005, Синьовски, 2007, with modifications) with the distribution of the planktonic foraminiferal taxa](image-url)
Two biostratigraphical zones were defined following Premoli Silva and Verga’s (2004) zonation – Globotruncanita elevata and Globotruncana ventricosa.

**Globotruncanita elevata Partial Range Zone**

*Author.* Postuma (1971). In Bulgaria it was introduced by Banuapoza (1975) as “Globotruncana elevata” Zone.

*Definition.* Interval, with Globotruncanita elevata (Brotzen), from last occurrence of Dicarinella asymetrica (Sigal) to first occurrence of Globotruncana ventricosa White.

*Common taxa.* In the lower levels (the lowermost 50 m) of the zone, despite the zonal marker Globotruncanita elevata (Brotzen), Globotruncana arca (Cushman), G. lapparenti Brotzen, Globotruncanita stuartiformis (Dalbiez) were recorded as rare specimens, while taxa like Globotruncana falsostuarti Sigal, G. hilli Pessagno, Heterohelix globulosa (Ehrenberg), and Rugoglobigerina rugosa (Plummer) occur as singles among species only. The middle and upper levels reveal the same taxonomical composition, but with higher specimen abundance.

*Age.* Early Campanian.

*Correlation.* The zone is cosmopolitan. Its taxonomical composition is the same as in the zones described by Wonders (1980), Robaszynski et al. (1984), Caron (1985), Abdel-Kireem et al. (1995), Salaj (1980). In Bulgaria it was established by Vaptzarova (1976, 1980) in the western and central north parts of the country.

*Remarks.* Premoli Silva and Verga (2004) limited the range of the zone in the Lowermost Campanian only.

*Boundaries.* The lower boundary was not fixed in the present study. The upper one was established at 400 m above the base of the sections.

*Thickness.* At least 150 m.

**Globotruncana ventricosa Interval Zone**

*Author.* Dalbiez (1955).

*Definition.* Interval from first occurrence of Globotruncana ventricosa White to first occurrence of Radotruncana calcara (Cushman).

*Common taxa.* In the lower levels the zonal marker Globotruncana ventricosa White occurs predominantly as single to rare specimens and it increases gradually its abundance in the middle and upper levels. Common taxon throughout the entire interval is Globotruncanita stuartiformis (Dalbiez). Species like Globotruncana falsostuarti Sigal, G. hilli Pessagno, Heterohelix globulosa (Ehrenberg), and Rugoglobigerina rugosa (Plummer) are additional elements to the assemblages. In the uppermost levels Globotruncanita stuarti (de Lapparent), Pseudotextularia elegans (Rzehak), Globotruncanella havanaensis (Voorwijk), and Rugoglobigerina penyi Broennmann were recorded as single or rare specimens.

*Age.* Latest Early Campanian–Late Campanian.

*Correlation.* The zone corresponds entirely to the zone of the same name of Abdel-Kireem et al. (1995), partly to ventricosa zone of Caron (1985), Robaszynski et al. (1984), and Wonders (1980), arca and rugosa zones of Salaj (1980). In Bulgaria it could be correlated to Globotruncanita stuartiformis zone of Dimitrova and Valchev (2007) and Globotruncana rugosa zone of Vaptzarova (1976).

*Remarks.* In the sections near the villages of Jelyava and Eleshnitsa the zonal marker Radotruncana calcara (Cushman) was not found and therefore the upper boundary of this zone was not defined. Thus, the entire interval above Globotruncanita elevata zone is referred to Globotruncana ventricosa zone.

*Boundaries.* The lower boundary was established at 400 m above the base of the sections.

*Thickness.* 200 m.

**Conclusion**

The turbidite deposits of the Chugovitsa Formation are well exposed in the northern outskirts of the villages of Jelyava and Eleshnitsa and they provide a good opportunity for a biostratigraphical study of the Campanian interval – four nanofossil zones have been previously defined. In terms of planktonic foraminifers the investigated assemblages are low to moderately diverse and with low abundance of specimens. On the other hand, the assemblages are dominated by species of broad stratigraphical range. This fact is an obstacle to find biostratigraphical markers (FAD and LAD) for a detailed zonation – only the FAD of Globotruncana ventricosa White was recorded in the sections and therefore only two zones were defined.

**References**


PLATE I

a) the base of the Mediterranean type Upper Cretaceous 1 km north of the village of Eleshnitsa representing the coal and the sandstone formations; b) the sandstone formation and the base of the Mirkovo Formation 1.5 km north of the village of Jelyava; c) the Mirkovo Formation in the Eleshnitsa River valley 800 m north of the village of Eleshnitsa; d) the Voden Member of the Chugovitsa Formation in the northern outskirts of the village of Eleshnitsa; e) the Voden Member in the valley of Jelyavska River 1 km north of the village of Jelyava; f) the uppermost levels of the Voden Member and the base of the typical Chugovitsa Formation on the left riverside of Jelyavska River; g, h) the lower levels of the Chugovitsa Formation in the northern outskirts of the village of Eleshnitsa (g) and on the left riverside of Jelyavska River (h).
THE HERCYNIAN COLLISIONAL METALLOGENY IN BULGARIA

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ABSTRACT. Ordovician – Lower Carboniferous sedimentation, calc-alkaline and potassium-alkaline magmatism and tectonic deformations mark the Hercynian collisional stage within the frame of the Neoproterozoic – Hercynian epoch. Mainly the magmatic processes define the metallogenic characteristic. The calc-alkaline plutons control the Stara Planina Metallogenic Zone with iron, lead, copper, gold, fluorite and other deposits. The potassium-alkaline magmatism defines the Berkovitsa-Shipka Metallogenic Zone with uranium deposits as well as with tungsten, copper, polymetallic and other ore occurrences.

Keywords: Hercynian magmatism, metallogeny, iron, lead, gold, uranium deposits.

Introduction

Neoproterozoic and Paleozoic rocks are exposed in the cores of the Alpine orogeny structures. They are formed during the Neoproterozoic – Hercynian cycle, including spreading, subduction and formation of magmatic arcs, collision and post-collisional orogenesis. The collisional events from this cycle are demonstrated by the presence of typical sedimentary and magmatic complexes. The metallogenic processes are marked mostly by the formation of iron, lead-zinc, gold, uranium and other deposits related to the evolution of the magmatic structures.

Geology

The Hercynian collisional stage covers the time from the Ordovician to the Lower Carboniferous, when the sedimentary or volcano-sedimentary rocks, Stara Planina granodiorite-granite and Stara Planina potassium-alkaline complexes and the associating mineral deposits were formed (Fig. 1). The pre-collisional basement consists of Neoproterozoic ophiolite (ultramafite, gabbro, cumulates, dikes and pillow lava), high grade metamorphites as well as by Neoproterozoic – Cambrian low grade metamorphic rocks, as green schist, marble, meta-diabase, tuff, meta-gabbro to meta-granitoid and others (Haydutov et al., 1979; Хайдутов и др., 2012; Marinova et al., 2008; Zagorchev et al., 2015, etc.).

The Ordovician – Lower Carboniferous sedimentary complexes were formed as a result of the epicontinental terrigenous marine sedimentation, with interruptions, transgressions and tectonic deformations. Green schist terrigenous rocks (Dalgidel Group) overlay Cambrian rocks in the Stara Planina Mountain area. The Ordovician – Devonian section is compounded by aleurolite, argillite, less sandstone, quartzite, lyde and conglomerate. Calcareous-turrigenous (Stakevo Formation) and terrigenous-volcanogenic (Rayanovo Formation) Lower Carboniferous (?) deposits were noted (Haydutov et al., 1979; Хайдутов и др., 1995а, b; Angelov et al., 2010, etc.). The Ordovician – Lower Carboniferous complexes in SW Bulgaria are in green schist facies, and the terrigenous-metarocks with meta-gabbro-dolerite intercalations predominate (Zagorchev, et al., 2015; Marinova et al., 2008).
Куйкин и др., 1971; Иванов и др., 1974; Каменов и др., 2002; Дюлгеров и др., 2006, 2010а; Марнова и др., 2008, etc.). On the basis of the rare elements ratios Каменов et al. (2002) define these rocks as calc-alkaline to high potassium calc-alkaline, and of island-arc type. Furthermore, Дюлгеров et al. (2010а) show that the rocks have crustal-mantle origin with predominant crustal component. The calc-alkaline plutons cut the Old Paleozoic rocks and are covered by the Upper Carboniferous sediments, which mark their Upper Devonian – Lower Carboniferous age (Хайдутов и др., 1995а,b). The absolute age data (360–314 Мa) of these rocks confirm this conclusion (Армов et al., 1981; Каменов et al., 2002; Валев и др., 1995а,b). The complex includes the described by Попов et al. (1988) Зверино вулкан-плутонический комплекс (трахиандезит, тро/entities in the text.}

The collisional stage is characterized by development of fold and fault structures. The antiform positions of the rock complexes are delineated, as Caledonian and Neoproterozoic units are outcropped within them. Small fold structures are noted, most often with subequatorial to east-southeastern direction, as the planar and linear structural elements mark three to four deformations (Angelov et al., 2010).
Metallogeny


In the general metallogenic analysis of the Bulgarian territory (Iovchev 1960, Miliev and Bogdanov 1974 and Dimitrov 1988) noted part of the studied Paleozoic deposits, connected to the Hercynian or Caledonian (?) magmatism, in the frame of the Balkan or West Balkan Metallogenic Zone. However, this zone is formed during the Alpine tectonogenesis, with typical Alpine ore mineralizations. The described ores, related to the Paleozoic magmatism, are formed as a result of earlier tectonomorphic processes and are included in other metallogenic units.

The modern methods of the metallogenic analysis are based on paleo-tectonic principle. Thereby, within the Neoproterozoic – Hercynian geotectonic cycle is differentiated the Hercynian collisional stage. It is characterized by the calc-alkaline and potassium-alkaline hypabyssal magmatic complexes, which determine the positions of the Stara Planina and Berkovitsa-Schipka Metallogenic Zones respectively (Fig. 1).

The Stara Planina Metallogenic Zone is determined by the plutons from the Stara Planina granodiorite-granite complex and the ore deposits connected with them. Skarn iron and hydrothermal lead-zinc, gold, copper, fluorite and smaller polymetallic, gold-polymetallic, molybdenum, barite, iron and other ores are found. The ore formation associates with metasomatic alterations represented by Ca-skarn around the contacts with marbles, as well as with the distinct silification accompanied by sericitization, epidotization, carbonatization, etc. The ore bodies are lens-like, bedding, irregular, columnar, and nest-like in the marble beds or veins and share zones in the fault structures cutting the different rocks. Depending on the ore type, the main ore minerals are magnetite, galena, native gold, chalcopyrite, fluorite, pitchblende, molybdenite. The Berkovitsa and Tran Ore Regions and individual ore manifestations are differentiated (Table 1).

The Berkovitsa Ore Region is controlled by the Sveti Nikola, Mezdra, Petrohan and some smaller plutons. They are intruded in Neoproterozoic ophiolite, Neoproterozoic – Cambrian green schist, volcano-sedimentary and metaplutonic rocks and Ordovician – Lower Carboniferous sediments. The Chiprovtsi, Gorni Lom and Pesochintsia Ore Fields are distinguished.

The Gorni Lom Ore Field (S from the town of Belogradchik) is marked by the copper-pyrite massive sulfide Gorni Lom deposit and series of ore occurrences (Nikolaev and Tonev, 1964; Dragov, 1971). They are represented by complicated ore veins in faults along the pluton’s contacts.

The Chiprovtsi Ore Field is developed SW from the Sveti Nikola pluton, in Neoproterozoic – Cambrian rocks. The Martinovo skarn iron deposit, the hydrothermal Chiprovtsi lead-zinc (Fig. 2) and Lukina Padina fluorite deposits, and barite, lead-zinc and copper ore occurrences are traced consecutively. The ore is developed in a zone of boudinaged marble (Nikolaev and Tonev, 1964; Dimitrov, 1964; Dragov and Obretenov, 1974; Atanasov and Pavlov, 1982).

The Pesochintsia Ore Field (NW from the town of Berkovitsa) is connected to the Mezdrea pluton. The skarn iron Pesochintsia-1 (Drena) ore occurrence, the hydrothermal copper Pesochintsia-2 (Bistrovets) ore occurrence, etc., are localized in its contacts with the Paleozoic marble (Стамболски, 1961ф).

The Bov-2, Kobilaya, Hristo Danovo and Kazanita molybdenum ore occurrences are individually formed, outside the ore fields.

The Tran Ore Region (W Bulgaria) is determined by the Ruy and Lyutskan plutons, intruded in the high grade metamorphic rocks and in the green schist, meta-biotite, tuff and gabbro. The Lyutskan and Ruy Ore Fields and the separate Zlogosh ore occurrence are distinguished.

The Lyutskan Ore Field (W from the town of Tran) (Fig. 2) is controlled by the Lyutskan pluton. The Zlata, Yamka, Krushev Dol and Krastato Dere gold deposits and numerous ore occurrences are found. They are represented by quartz-sulfide ore veins within NNE faults cutting the granitoid and metamorphic rocks (Dragov, 1960; Miliev and dr., 2007). The Beli Bryag and Vodopada uranium ore occurrences are also noted (Stoykov, 1976).

The Ruy Ore Field (NW from the town of Tran) is determined by the ores related to the Ruy pluton. The Ruy, Lomnitsa-1, Zabel, Zelenigrad polymetallic and Logo and Nadezhda gold-polymetallic ore occurrences are found. They are represented by quartz-sulfide ore veins or brecciated zones (Димитров, 2007ф).

The Zlogosh gold ore occurrence (NNW from the town of Kyustendil) is marked by quartz-sulfide veins, concordant to or intersecting the foliation (Miliev and dr., 2007).

The Berkovitsa-Schipka Metallogenic Zone is controlled by the magmatic bodies from the Stara Planina potassium-alkaline complex and the associated ore deposits. It covers Western Stara Planina Mountain, between the towns of Belogradchik and Shipka. Considerable uranium deposits and tungsten, copper, polymetallic and rare earth mineralizations are found. The host rocks are represented by alkaline plutons, older granitoids and different Paleozoic schists and marbles. In the individual areas they associate with metasomatic alterations as silicification, sericitization, berylization, greisenization, albitization, K-feldsparization, low temperature Na-metasomatites, etc., and with Ca-skarn in some places. The ore bodies were formed along the contacts between the plutons and host rocks or in faults, often complicated in structure. The ore formation was favored by the host marbles and schists. Lens-like, nests, stockwerks, columnar, vein and
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<th>Ore Region</th>
<th>Ore Field</th>
<th>Deposit, Ore occurrence</th>
<th>Main minerals</th>
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<th>Structural position</th>
<th>Ore bodies, morpholog y</th>
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**STARA PLANINA METALLOGENIC ZONE**

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**BERKOVÍTSA – SIPHKA METALLOGENIC ZONE**

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<th>Ore Region</th>
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<th>Deposit, Ore occurrence</th>
<th>Main minerals</th>
<th>Secondary of importance and rare minerals</th>
<th>Structural position</th>
<th>Ore bodies, morpholog y</th>
<th>Host rocks</th>
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Table 1.
Characteristics of the Hercynian collisional ore deposits in Bulgaria
### Ore Region | Ore Field | Deposit, Ore occurrence | Main minerals | Secondary of importance and rare minerals | Structural position | Ore bodies, morphology | Host rocks | Metasomatic alterations
--- | --- | --- | --- | --- | --- | --- | --- | ---
Individual occurrence | Prekop (W, Mo, U) | molybdenite | scheelite, uraninite | contact marble – montzodiorite | lens-like, irregular | montzodiorite | Ca-skarns (andradite, diopside, hedenbergite)
Shipka mineralized area | Bedek, Shiroka Polyana, Tsiganski Ushetsi, Sofia, (Fe) | magnetite, hematite, pyrite | concordant fault zones, faults | share zone, vein-like | greenschist Pz1; syenite Pz2; |
share zone types of ore bodies are observed. The main ore mineral in the uranium ores is nusturan (pitchblende), and in the other ores are molybdenite, magnetite, galena, sphalerite, and chalcopyrite. The Svoge Ore Region and some small individual tungsten-molybdenum mineralizations are differentiated (Table 1).

The Svoge Ore Region is defined by the development of Seslavtsi, Svidnya and Proboynitsa intrusives, Zverino volcano-plutonic structure and smaller bodies and dikes. The Buhovo, Proboynitsa and Kurilo Ore Fields and the Zverino mineralized area are distinguished. Rare earth and uranium mineralizations within faults has also been observed (Бахнева и др., 1963ф).

The Buhovo Ore Field (NE from Sofia City) is controlled by the Seslavtsi pluton. The Seslavtsi 1, 2, 3 (Fig. 2), Goten, Chora, Borcha and Chamilov Kamak uranium deposits are found here (Стойков, 1976; Тонев, 1980). The ore is formed along the northern and eastern contacts of the pluton with Paleozoic marble. The Svoge Ore Region and some small mineralized area are distingui shed. Rare earth and uranium mineralizations are formed in the cutting areas between sub-equatorial and terrigenous sediments. The Kurilo uranium deposit and several other ores are molybdenite, magnetite, galena, sphalerite, and chalcopyrite. The Svoge Ore Region and some small bodies and dikes. The Proboynitsa Ore Field (in the area of Bov and Lakatnik villages) is related to the homonymous pluton. The Proboynitsa uranium deposit (Fig. 2) and several ore occurrences are found (Стойков, 1976; Драгоманов и др., 1995ф). The ore is developed in complicated fault structure, which cut the pluton and the Paleozoic metamorphic rocks.

The Kurilo Ore Field (NE from Sofia City) is controlled by small bodies of K-alkaline rocks intruded in Paleozoic terrigenous sediments. The Kurilo uranium deposit and several ore occurrences are found. The ore mineralization is developed in the cutting areas between sub-equatorial and northeastern faults (Стойков, 1976; Драгоманов и др., 1995ф).

The Proboynitsa Ore Field (in the area of Bov and Lakatnik villages) is related to the homonymous pluton. The Proboynitsa uranium deposit (Fig. 2) and several ore occurrences are found (Стойков, 1976; Драгоманов и др., 1995ф). The ore is developed in complicated fault structure, which cut the pluton and the Paleozoic metamorphic rocks.

The Kostova-Shipka Metallogenic Zone with important uranium deposits and some tungsten-molybdenum, iron and copper mineralizations originates with the Devonian – Lower Carboniferous Ca-alkaline, predominantly crustal plutonism. The Berkovitsa-Shipka Metallogenic Zone with important uranium deposits and some tungsten-molybdenum, iron and copper mineralizations is formed in relation to the Lower Carboniferous K-alkaline mantle magmatism.

The Svidnya rare earth ore occurrence (west of the town of Svoge) is related to the homonymous pluton. The increased contents of La, Ce, Nd and less Pr, Sm, Gd and Y are determined in the apatite (Срдяванова, 1973ф). Uranium mineralization within faults has also been observed (Бахнева и др., 1963ф).

The Zverino mineralized area (Zverino village, the Iskar River defile) is defined by the development of Zverino volcano-plutonic structure. The Ignatitsa and Levishte coper, Gabrovitsa polymetallic and other ore occurrences are found (Popov et al., 1988).

The Prekop molybdenum-tungsten, uranium-bearing ore occurrence (NE from the town of Chiprovtsi) is related to the homonymous pluton. The ore type is skarn, along the contact of the Prekop pluton with Paleozoic marble.

The Shipka mineralized area is located in the Shipka area in Stara Planina Mountain. The Bedek, Shiroka Polyana, Solta and Tsiganski Ushetsi iron ore occurrences are related to the K-alkaline magmatic bodies and are developed in brecciated zones or faults (Костов, 1949).

Conclusion
Ca and K-alkaline magmatic processes are of primary importance for the Hercynian collisional metallogeny in Bulgaria. The Stara Planina Metallogenic Zone with iron, lead-zinc, gold, copper, fluoride deposits and other small mineralizations originates with the Devonian – Lower Carboniferous Ca-alkaline, predominantly crustal plutonism. The Berkovitsa-Shipka Metallogenic Zone with important uranium deposits and some tungsten-molybdenum, iron and copper mineralizations is formed in relation to the Lower Carboniferous K-alkaline mantle magmatism.

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Geofund Reports


FIELD OBSERVATION OF THE BURIED WEATHERING CRUST IN THE OSHTAVA GRABEN (SOUTHWESTERN BULGARIA)

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ABSTRACT. Geological and geomorphological features of the area of Oshtava graben (southwestern Bulgaria) are presented in the paper. The area is characterized by fault tectonics and the predominant basement rocks are granites. In the current research special attention is paid to the weathering crust which is covered by Neogene sediments. This deep weathering is related to the subtropical conditions in the late Neogene. The weathering crust is preserved under the clastic sediments, formed as a result of the deep erosion. The accumulation of these clastic materials is connected to the Messinian salinity crisis in late Neogene when changes in local and regional erosion bases (Aegean Sea level) led to the deep river incision, followed by areal erosion and deposition. Buried under these sediments the rocks of the denudation surfaces weathered chemically but without washing and removal of the weathering products, which continue to accumulate under the clastic formations.

The aim of the current paper is to direct the attention of researchers and experts to the deep weathering in Southwest Bulgaria, which has not been investigated in detail until now. The topicality of the research is determined by the significance of the buried weathering crust and the impact that it could have on the environmental processes and infrastructure.

Keywords: weathering crust, granite, Oshtava graben

INTRODUCTION

At the beginning of the Cenozoic a circum-equatorial sea current existed that spanned the entire Earth. It flowed unimpeded through the Tethys Sea and warmed the planet. As the continents continued to separate, the Tethys Sea gradually closed, cutting off the circum-equatorial currents (Bryden and Kinder, 1991). It cooled the Earth as the cooling culminated in the ice ages. These events shifted significantly the global sea level. The isolation of the Mediterranean from the world ocean, happened in the Burdigalian (20-15 Ma) but the most pronounced climatic event happened 7-5 million years ago and is known as the Messinian Salinity Crisis (MSC), also referred to as the Messinian Event (Hsu et al., 1977). This event was first discovered in 1970 by drilling on a number of localities in the Mediterranean of several hundreds of meters of salts by Glomar Challenger. The culmination of the crises led to desiccation of the Mediterranean that took place about 5.5 Ma ago. Such a catastrophic event had a great impact on the landscape of the entire region. The lowering of the base-level of erosion led to deep incision of rivers that drained in the Mediterranean. Deep Messinian canyons are recorded throughout the region. It also led to unusually active Late Miocene groundwater movement and karstification. The climate became drier and cooler. This was a change from the generally warmer climate of the Neogen.

In this paper, the effects of the late Neogene erosion and deposition in part of Southwest Bulgaria are discussed. The aim is to direct the attention of researchers and experts to the deep weathering in the Southwest Bulgaria, which has not been investigated in detail until now. The paper has been
elaborated on the basis of field observation and literature review.

**Study area**

The area of study of the current research is located in southwestern Bulgaria and is part of the western slopes (foothills) of Pirin mountain (Fig. 1). It is situated into a regional tectonomorphologic domain known as the Struma lineament (Загорчев, 1988). The area comprises a series of tectonic troughs named: Blagoevgrad graben, Simitli graben and Sandanski graben. The orientation of this chain of troughs is NNW – SSE. They are constrained by the Vlahinski, Verilski, Ograzhdenski and Belasishki elevated blocks to the west, and to the east they border the mountains Rila and Pirin. The time of initiation of this linear structure cannot be accurately defined, but it dates back at least to the beginning of the Eocene. Although the troughs are constrained by faults, the evolution of the lineaments could be related to the global climatic events too.

During the Neogene, until the beginning of the Quaternary temperature drop, the region of the present southwestern Bulgaria was affected by subtropical climatic conditions. The global climatic changes in the late Neogene, related to the drying of Mediterranean Sea (MSC) shifted the erosional bases of the rivers, which combined with tectonic reasons, resulted in deep area erosion and deposition of coarse clastic sediments in Messinian time. Buried under these sediments the granites and metamorphic rocks of the denudation surfaces continued to weather chemically but without washing and removal of the weathering products, which continued to accumulate under the clastic formations. During the Quaternary the main river acquired its present valley and the flows from west and east cut and partially removed the late Neogene sediment cover, although parts of it are still on place. The sediments of the Struma lineament recorded the change of the rivers erosional bases. Very distinctive rock formations were deposited in the lineament area during the Messinian time. These formations known as Kalimantsi and Sandanski Formations (Kojumdjgieva et al., 1982) have been dated and it appears that their deposition corresponds to the time of the deepest erosional incision of the rivers flowing towards the Aegean Sea (Zagorchev, 2002). In the time span 7-5 million years ago very fast and deep erosion and deposition, and subtropical weathering, happened in the troughs of the Struma lineament. The clastic rocks are locally derived, poorly sorted and usually very coarse. They covered denudation - accumulation surface carved over variegated fundament.

**Geological settings**

**Extends of the Oshtava graben**

In the Bulgarian literature (Загорчев и Маринова, 1990, 1993) the Sandanski graben is shown as containing two dissimilar parts. The northern part is an elevated terrace at the western slopes of Pirin Mountain that has fundament of granites and metamorphic rocks. This part comprises a hilly terrain, east of the Kresna gorge, and separated from the gorge by an elevated ridge (Figures 1 and 2). The southern part of the Sandanski graben, south of Kresna, comprises a wide fluvial plane of the river Struma.

![Fig. 1. Location of the area of study with colored representation of the topographic elevation.](image)

Features of the northern part of the graben will be discussed in the paper. The difference between the northern and southern part is that the northern part is considerably elevated compared to the southern one and it seems to reflect different geologic evolution. Most of all it contains evidence of a river flow, presumably the predecessor of river Struma, that flowed easterly, and on elevated level, compared to the present position of the river in the Kresna gorge. This older river we call Paleo-Struma in accordance with other authors (f.e. Ivanov, Bozukov, 2017). The area east of the Kresna gorge is best described with the name of Oshtava graben, rather than naming it as Sandanski graben.

The generalized geomorphic situation of the Oshtava graben (or Oshtava area of the Sandanski graben) is shown on Figures 2 and 3. North of the village of Brezhani it borders the Oranovo-Simitli graben and south of Kresna it passes into the wider fluvial plane of Struma. Both the northern and the southern border domain are lower in hypsometric sense and lacking the ridge of fencing hills from west, thus the area of the Oshtava graben can be examined as an elevated older terrace compared to the northern and southern domains.

Judging from the coarse clastic sedimentary rock, that once covered it completely, the Oshtava graben was fluvial valley between the Messinian and the beginning of the Quaternary but remained as an elevated terrace after river Struma acquired it present valley in the Kresna gorge.
Fig. 2. Morphological features of the terrain east of the Kresna gorge, between the settlements of Brezhani and Kresna. From west to east, zones elongated in north-south direction are recognized and named as: Kresna gorge, fencing hills, paleodislocation; denudation plane, and mountain slope. The paleodislocation is a deep, and relatively straight valley of fault predisposition that is interpreted as the valley of the predecessor or the river Struma. The fencing hills, paleodislocation and the denudation plane are transected by the present tributaries of the river Struma. The depression between the fencing hills and the mountain slope can be discerned also on the slope map shown on Figure 3.

Fig. 3. Slope map of the terrain east of the Kresna gorge, between the settlements of Brezhani and Kresna.

Rock formations in the Oshtava graben

The following rock formations outcrop in the Oshtava graben:
1. Predela metamorphic complex of inferred neoproterozoic age (Милованов и др., 2008, 2009). It comprises tectonically inserted sleeve of various iron-rich metamorphics in amphibolite facies;
2. Maleshevska metamorphic complex, comprising mostly sialic rocks - gneisses and schists, injected with anatectic melts;
3. Granites of the North Pirin pluton. The dating of these granites by Бояджиев и Лилов (1971, 1976) yielded 30-41 Ma. Age of 92 +/- 22 Ma was accepted for the national geological map of Bulgaria (Загорчев и Маринова, 1993). Age of 32.99 +/- 0.39 Ma was accepted for the national geological map in scale 1:50 000 (Милованов и др. 2008, 2009).
4. Sandanski Formation (Kojumdjigieva et al., 1982) that contains sandstones, alevrolites, sandy clays, grits and conglomerates of the Late Miocene - Meotian to Pontian registages. These registages from the Central Paratethys domain correspond to the Messinian and Zanclean of the ISC stage division (Gozych, et al., 2015), spanning between 7.2 and 3.6 Ma.
5. Kalimantsi Formation (Kojumdjigieva et al., 1982), comprising very coarse conglomerates with various proportions of pebble, cobble and boulder fragments in sandy matrix and
Meotian, Pontian and Dacian fauna. It has rich assemblage of giraffes' remains of late Miocene age (Geraads et al., 2005).

Alluvial deposits of Quaternary age are found only in the valley of river Struma and in narrow river terraces in the area.

The granites covered with discontinuous cover of the Kalimantsi Formation are the most widespread in Oshtava graben. Small exposures of boulder conglomerates and sandstones reveal that the entire area of the Oshtava graben was covered by Late Neogene clastic rocks.

Fault network

Three fault orientations dominate in the region. These are N-S, NW-SE and NE-SW. The N-S faults seem to be older than the rest. They control the boundaries of the sedimentary basins and the flow of the larger rivers prior to the Quaternary. At present, they are intersected and locally displaced by the active NE-SW faults. The entire length of the Oshtava graben is controlled by the splays of one such fault. It controlled the river flow of the predecessor of Struma and was sealed by coarse clastic sediments of the Kalimantsi Formation. Wedges of conglomerate still exist on several places in its valley.

The Quaternary rivers following the NE-SW faults, such as Mechkulska, Oshtavska, Krivodlaska, Vlahinska and Solunska transected the older N-S valleys, partially removing their clastic infilling (Fig. 4).

Paleotopography and water flow

Since the Neogene topographic features are partially buried by clastic rocks, the water follows a complicated path in the Oshtava graben. Surface waters are drained by the N-S valleys and are driven under the Neogene sediments, where they run as subsurface flows until they discharge into the E-W valleys of the Quaternary streams. Thus, the fault network, combined with the barrages of still uneroded Late Neogene sediments deposits in the N-S trending fault valleys, creates two distinct water pathways: hidden subsurface pathway from north to south and visible surface pathway from east to west.

Quantification of the weathering crust

There is stark contrast between the degree of weathering of the granites in the Quaternary Kresna gorge, where the granites are virtually fresh, and those in the region to the east of the fencing hills, where granites are deeply weathered. This can be explained with the fact that the weathering products that formed in dry subtropical conditions, were trapped under the Neogene sediments without the opportunity for washing and removal. Under the sedimentary cover there was abundant supply of water, so the weathering has continued until present day. In contrast, in the Kresna gorge all weathering products are immediately washed out.

Given that the Oshtava graben was formed predominantly on granitic basement, the ISRM (International Society for Rock Mechanics) chart (Fig. 5) is used for quantitative description of the weathering.

Geomorphological settings

In the unpublished geological reports (Костадинов и др., 1968) for the region are recognised 7 erosion-denudation levels, 2 levels of floodplains and 6 upper river terraces. The average height of the planation surface on Figure 2 varies between 600 and 800 meters a.s.l. and the heights of the fencing hills, that separate it from the Kresna gorge, are also between 600 and 800 meters a.s.l., however, because the planation surface is inclined to the west, the fencing hills stand higher compared to it. The planation surface and the fencing hills have some flat tops at different levels, which imply that they represent different erosional levels related to the different position of the local erosional base but the Quaternary erosion and likely tectonic denivelation complicate their differentiation.

Fig. 4. Junction of the Paleo-Struma valley of Neogene age, striking N-S and Vlahinska river valley, of Quaternary age, striking E-W. The Vlahinska valley displaces Paleo-Struma at least 250 m to east (left on the picture). At the junction, in front on the picture, a sleeve of Kalimantsi Formation is exposed in the old valley that is partially eroded by the river Vlahinska.

Fig. 5. Chart of weathering staged after ISRM (1978).

All six weathering stages can be found in the area of study and the only thing that varies is the thickness of the layers. The variation is due to: 1. geomorphological position of the outcrop, which is: valley bottom, slope, wide or narrow hilltop; 2. time of removal of the clastic cover, and 2. the tectonic predisposition of rocks, as the faulted rocks weather much deeper.

In general, wide and flat surfaces have thicker crust of class W5 and W4 and the weathering of classes W3 and W4 reaches much deeper. In the vicinity of fault zones weathering of class W4 was found in boreholes at depths of 90m and beyond. In the slopes of the N-S trending valleys, where the
Neogene cover was recently stripped the weathering crust is much thicker than in the slopes of the Quaternary streams flowing from east to west.

The Kalimantsi Formation in the area was locally derived and it contains boulders of granite, included in sandy matrix, which was also derived from granite, so sometimes it is difficult to distinguish it from the spherically weathered granite. For this purpose a field test can be used using steal tipped hand tool like hammer or mattock. It was found that the steel tool cannot penetrate in spherically weathered granite (Fig. 6) for more than 1-2 cm, while is can penetrate in the matrix of Kalimantsi conglomerates (Fig. 7) considerably deeper.

The weathering of the metamorphic rocks produces clay rich diluvium that is thicker than in unweathered domains.

Engineering geological effects of the weathering

Weathering strongly influences the strength properties of the rocks. It alone, without any other negative influence, can shift the position of the rock in the widely used rock mass classification systems such as RMR or GSI (Bieniawski, 1989, Hoek and Brown (1997) towards the classes of poor and very poor rocks, with regards to the road and tunnel construction. Since the uppermost, strongly weathered part of the section, is thick at least several meters most of the excavations and many foundations are done inside it. These make the foundations vulnerable to soil creep (Fig. 8 and Fig. 9) and water erosion (Fig. 10). The geodynamic processes that accompany the weak layers of weathered rock are easily recognizable on the slopes of Oshtava graben. Inclined trees and ravines are common in contrast to the modern Kresna gorge, where the rock falls are a danger.
The hysteresis is expressed in that rain water is accumulated in the porous weathering crust and does not immediately impact the surface runoff.

Conclusions

Subtropical weathering crust was sealed under the late Neogene clastic formations of the Struma lineament. Under the cover of clastic sediments the chemical weathering continued until recent days. There is a sharp contrast in the weathering profile of the Quaternary rivers and those of the Neogene fault valleys that were buried under clastic sediments. At present, in the region east of the Kresna gorge, the erosion of the valleys that were buried under clastic sediments. At present, in the region east of the Kresna gorge, the erosion of the weathering crust was sealed under the late Subtropical weathering. The expansion of the road construction projects east of the Kresna gorge shall take into account challenging engineering conditions, which are not well known to this moment.

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UNESCO GEOPARK INITIATIVE AND BULGARIAN GEOCONSERVATION

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ABSTRACT. Twenty years ago at the ProGEO’98 meeting in Belogradchik, Bulgaria, the UNESCO GEOPARK initiative was announced. This year the scientific conference “Geoparks and Modern Society” devoted to this event will be held in the small northwest town with participation of geoscience from more than 15 countries from four continents. The Geopark initiative was launched as an instrument for coordination of the efforts to promote the international recognition of significant examples of the Earth’s geological heritage, popularize knowledge on the Earth’s history and trigger local sustainable development. Its original version was designed to set up a world network of areas called “geoparks”, where significant geological features are recognized. Despite the initial enthusiasm, after a series of procedures, in 2001 the UNESCO Executive Board surprisingly decided that the UNESCO geosites/geoparks programme should not be pursued. Meanwhile the initiative received a huge international response and dozens of geoparks were developed in the frame of several years. At present, the European Geoparks Network comprises 71 Geoparks from 23 countries and the Global Geoparks Network includes more than 120 geoparks. Bulgaria was one of the first countries in Europe with geopark projects are completely different and require individual approaches. Regarding the growing requirements of the Global Geoparks Network, development of an upgraded evaluation methodology for geosites in geopark environment, including both generally accepted and specific characteristics is necessary. This should be among the main purposes of the newly established National Committee of Geodiversity and Geoparks which has to take up its mandate as recommended by UNESCO’s International Geoscience and Geoparks Programme from 2015.

Keywords: UNESCO GEOPARK Initiative, Bulgarian geoparks initiatives

Introduction

This year marks 20 years since the announcement of the UNESCO GEOPARK Initiative at the ProGEO’98 Meeting in Belogradchik (Patzak and Eder, 1998). This event produced a big impact on the Bulgarian geoconservation. It prompted the financing of a big project for compilation of a National inventory of geosites and designation of areas with significant geological heritage appropriate for geoparks establishment. Within four years after the meeting a State Registry and Cadastre of the Bulgarian Geological Phenomena was created on the basis of a remarkable database including well illustrated scientific dossiers of 188 geosites in Bulgarian, English and Russian, evaluated according to the original Bulgarian methodology developed specifically for assessment and characterization of the nominated geosites. At the same time, as the essence of the project, the scientific foundations of the first Bulgarian geopark Iskar Gorge were laid, presented at the 3rd European Geoparks Meeting in Eggenburg, Austria (Jelev et al., 2002).
Historical review of the GEOPARK initiative

The idea for creation of a global network including areas with geological heritage of international value under the auspices of UNESCO was first hinted in the “Draft Programme and Budget 1998-1999” (document 29 C/5, para. 02036) as an initiative to “promote a global network of geo-sites having special geological features” (UNESCO General Conference, 1997). It was announced at the ProGEO’98 Meeting in Belogradchik as a new UNESCO GEOPARK Programme which acts in the framework of two internationally agreed action plans (Patzak & Eder, 1998): the Agenda 21 for Environment and Development into the 21st century including education, public awareness, training and capacity building, and the 1972 Convention for protection of the World cultural and natural heritage. This initiative was launched to create a UNESCO GEOPARK Programme “in response to the numerous requests from the Member States expressing their interest in improving the international recognition of their national geological heritage” (Patzak & Eder, 1998).

At least initially, it was planned to make use of the existing structures of the IGCP Programme for the further development of this new initiative. Geoparks, designated to integrate geocervation with biological conservation like “natural parks”, were envisaged to be under the exclusive authority of the government in the country where it is situated. As a consequence the Geopark initiative encouraged identification of geodiversity in many nature parks with established infrastructure, budget and management plans to provide a geological framework of their natural heritage.

Considering the approval of this initiative by the 29th UNESCO General Conference (1997) and having examined document 156 EX/11 Rev. of the UNESCO Ex. Board (1999a), at its 30th session the Director-General was invited to implement the corresponding plan of action by preparing a feasibility study on developing a UNESCO geosites/geoparks programme and to submit it to the Executive Board preferably at its 159th session but not later than the 160th session (UNESCO Ex. Board, 1999b, Decision 3.3.4, p. 11).

The result of the feasibility study was reported at the 160th session of the UNESCO Executive Board (2000a) with a conclusion that geological heritage promotion is an important recognized need, and that an alternative to the World Heritage List is required for the recognition of geological/geomorphological sites of national, regional and international importance that may not rank as of World Heritage value. In other words, geoparks are proposed as an alternative UNESCO designation because not all of the world’s scientifically or historically important geosites could meet the ‘outstanding universal value’ criterion required by the 1972 UNESCO World Heritage Convention (Hose, 2012).

After considering various approaches to geological heritage conservation and referring to the support expressed by governmental and scientific agencies in many countries, the feasibility study recommended that the geoparks activity should be integrated into the World Network of Biosphere Reserves within the MAB programme, through developing a “Geoparks seal of excellence”. It should have three main purposes: 1) the use of geological sites in educating the broad public, 2) the use of their potential as a tool ensuring sustainable development, and 3) the conservation of the geological heritage for future generations.

The Director-General presented the results of the feasibility study at the sixteenth session of the MAB International Coordinating Council in November 2000 (UNESCO Executive Board, 2000b). Some delegations agreed on the importance of safeguarding geological sites, but disagreed on making such activity an integral part of the function of the World Network of Biosphere Reserves. Following the recommendation of the MAB International Coordinating Council against inclusion of a Geoparks programme as part of the World Network of Biosphere Reserves the UNESCO Executive Board made the same conclusion and invited the Director-General “not to pursue the development of a UNESCO geosites/geoparks programme, but instead to support ad hoc efforts with individual Member States as appropriate” (UNESCO Ex. Board, 2001a,b).

This short but dramatic period of the early history of the UNESCO geoparks initiative is indicative of the enormous difficulties faced by its supporters in the Member States. However, the idea turned out to be attractive and was well accepted in many European countries. Meanwhile in June 2000 the European Geoparks Network was established at

Fig. 1. Participants in the ProGEO’98 meeting in Belogradchik among the Belogradchik rocks

The Division of Earth Sciences took the initiative to coordinate international efforts to prepare the framework of future conservation activities and launching of a new dedicated programme endorsed at the 156th session of the UNESCO Executive Board (UNESCO Ex. Board, 1999a). It was aimed to promote the international recognition of significant examples of the earth’s geological heritage, popularize knowledge on the earth’s history and trigger local sustainable development. Its original version was designed to set up a world network of natural “parks” where “significant geological features” are recognized. Pursuant to the programme, the Executive Board undertook an initiative on geoparks, focused on the preservation of significant examples of the geological environment intended to contribute to the local sustainable development. According to this document the Geoparks programme was envisaged as a separate entity designed to complement the World Heritage Convention and the Man and the Biosphere (MAB) programme.

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This short but dramatic period of the early history of the UNESCO geoparks initiative is indicative of the enormous difficulties faced by its supporters in the Member States. However, the idea turned out to be attractive and was well accepted in many European countries. Meanwhile in June 2000 the European Geoparks Network was established at
Lesvos, Greece, by four regions of different European Countries—France, Germany, Spain and Greece. Over the next few years many natural parks in Europe applied to join it. Many countries started to recognize and estimate geological sites or landscapes of international value within their national boundaries. In February 2004 in Paris, the UNESCO international group of experts decided to establish Global UNESCO Network of Geoparks. It was also decided to include the existing 17 European Geoparks and 8 new Chinese Geoparks in the Global UNESCO Network of Geoparks which now includes more than 120 global geoparks. In October 2005 the European Geoparks Network signed the ‘Madonie declaration’ according to which it is recognized as the official branch of the UNESCO—Global Geoparks Network in Europe.

Despite UNESCO’s central role in establishing this network, its relationship to Geoparks has been defined as ‘ad hoc’ for over a decade. However, this ‘ad hoc’ arrangement does not allow UNESCO and Geoparks to capitalise upon many of the potential benefits of a more formalised relationship (UK National Commission for UNESCO, 2012). The growth of the Geoparks network has also created potential long-term risks which need to be addressed. According to the UK National Commission for UNESCO (2012) the geopark access to UNESCO branding could help raise the profile of sites, strengthen recognition of Global Geoparks as a brand and convey internationally recognized quality and standards. As a result of the long term international efforts UNESCO’s General Conference approved, on 17 November 2015, the International Geoscience and Geoparks Programme (UNESCO General Conference, 2015) in order to provide an international status to a former Global network of sites of geological significance UNESCO. Thus, the Geopark concept underwent a new development and the existing geoparks received the label “UNESCO Global Geopark”.

Bulgarian initiatives

The first Bulgarian geopark “Iskar Gorge” was developed under the project of the Ministry of Environment and Water for the Register and Cadastre of the Bulgarian geological phenomena. The problems and perspectives of this area were discussed at the 3rd European Geoparks Meeting in Eggenburg (Jelev et al., 2002).

The Iskar Gorge is a remarkable 100 km long canyon crossing the Balkan Mountain, where metamorphic, igneous and sedimentary rocks of the whole Phanerozoic Earth history are exposed: Neoproterozoic-Ordovician diabase-phylliloid complex, Early Paleozoic (Ordovician, Silurian and Devonian) graphitithic black shales, Carboniferous anthracite coal deposits with well preserved megafloa, continental terrigenous and volcano-sedimentary Permian deposits, complete Triassic section including the famous Buntsandstein facies and Alpine carbonate Triassic, representative Jurassic section, Urgonian type Lower Cretaceous, Mediterranean (volcano-sedimentary) and North European (platform) type Upper Cretaceous, Cretaceous/Tertiary boundary iridium layer, Paleocene, Eocene and Neogene sediments, as well as different genetic types of Quaternary deposits including loess. It includes unique geological phenomena of scientific and educational value as for example Ordovicin-Silurian, Silurian-Devonian, Jurassic-Cretaceous and Cretaceous-Tertiary chronostratigraphic boundaries, sequence-stratigraphic successions, global impact events, deformational phases marked by angular unconformities, neotectonic events, different genetic types of ore deposits and deposits of industrial minerals. Besides its geological advantages as a real canyon with its neotectonic evolution, forming it as one of the most impressive canyons on the Balkans, the Iskar Gorge preserved several outcrops of historical value for the Bulgarian geology, as for example the outcrop near Chelopek village, which is one of the first fossil deposits in Bulgaria, where in its “Inoceramid Cretaceous” marked with “1” on Fig. 2, Franz Toula (1878) described first Upper Cretaceous fossils in Bulgaria – ammonites, echinoids and bivalves.

Fig. 2. Part of the first map of the Iskar Gorge by Franz Toula (1878) at a scale 1:288000 made in 1875 during his route Sofia-Berkovitsa-Vratsa-Ljutibrod-Sofia: 1 – Inoceramid Cretaceous; 2 – Orbitolinid Cretaceous; 3 – bryozoan sandstones; 4 – Caprotina (Requienia) type limestone
together; 5) it could be part of a global network that will demonstrate and share best practices with respect to Earth heritage conservation and its integration into sustainable development strategy.

Unfortunately, due to lack of funding, this geopark remained in a working version for many years. Now a new initiative of three Iskar municipalities – Mezdra, Svoge and Novi Iskar is about to revive this wonderful project and reinforce the efforts to create “Iskar Canyon” Geopark (Fig. 3).

The concept of the next geopark project “Belogradchik Rocks”, founded in one of the most disadvantaged areas in Europe – Northwest Bulgaria, is based on the famous rock ensemble of the Belogradchik Rocks, considered to be the most famous geological phenomenon in Bulgaria with global significance. It is based also on the remarkable geodiversity of the area between the Balkan ridge and the Danube, including almost all petrographic types of sedimentary, igneous and metamorphic rocks belonging to all Phanerozoic systems. Despite the perfectly developed documentation and professional scientific description of 72 geosites, it underwent two unsuccessful applications in the European Geoparks Network for the same reason as geopark “Iskar Gorge”.

Nevertheless, during all these years the Bulgarian geoconservationists continued to work on identifying geodiversity in three perspective geopark areas – “Belogradchik Rocks”, “Rila” and “Burgas Lakes”.

Documentation of the aspiring Geopark “Belogradchik Rocks” is entirely completed on the basis of the existing methodology for evaluation and characterization of geosites, and only financial support to fulfill the recommended by the GGN Bureau actions is required. Recently the geological setting of the area was reviewed by Tronkov and Sinnyovsky (2012). Up to now this wonderful geological phenomenon has been estimated by many experts and ordinary people. Words of admiration over the beauty of Belogradchik Rocks have been expressed by many writers and poets. It is not possible to mention all the works of art and science inspired by their appearance, as for example the famous aquarelle of Felix Kanitz from 1873 (Fig. 4). However, it is worth to remember the inspiring comparisons to other remarkably beautiful places of nature in different parts of Europe made by the French traveler Jerom Adolf Blanqui (1843): “The narrow mountain gorges of Olioul in Province, Pancorbo Pass in Spain, the Alps, the Pyrenees, the wildest mountains of Tirol and Switzerland hold nothing that can be compared to this”.

Recently the Belogradchik Rocks became the most famous opera scene in the world and the cannons from Kanitz’s aquarelle have been replaced by stage sets (Fig. 5).

Now the rocks are the majestic background of the spectacles of the summer festival of the Sofia Opera and Ballet „Opera of the Peaks – Belogradchik Rocks“ where spectacles are performed in the open air inside the Belogradchik Fortress. This wonderful idea attracts many visitors from Bulgaria and abroad and contributes to the global promotion of the natural and cultural potential of the Belogradchik Rocks.

Fig. 3. The mayors of the Iskar municipalities Svoge, Mezdra and Novi Iskar decided to use the remarkable geological heritage of the Iskar Gorge, as for example of its entrance near Lyutibrod village, and to reinforce the development of Geopark “Iskar Canyon”

Fig. 4. View of the Roman fortress “Kaleto” at the top of the Belogradchik Rocks - aquarelle by Felix Kanitz from 1873

Fig. 5. The summer festival of the Sofia Opera and Ballet „Opera of the peaks – Belogradchik Rocks 2018“

Geopark Rila (Синьовски, 2014; Sinnyovsky, 2015; Sinnyovsky et al., 2017a) is at a stage of scientific characterization of geomorphosites related to the main theme of the geopark – fossil glacial geomorphology and alpine landscapes. Additionally, several geotrails of historical value for the Balkan geology and geomorphology are under development. Rila Mountain is the highest mountain on the Balkan Peninsula. It has wonderful alpine landscapes but also remarkable cultural heritage dating back to Roman times. The famous middle age Rila Monastery attracts millions of visitors every year. This makes the task of creating Geopark Rila very difficult and responsible, because the main theme of the geopark should be involved in the context of the remarkable spiritual heritage of the mountain.
Besides places and events related to its centuries-old history, the mountain also offers many opportunities for popularizing well-forgotten events occurring during the new history of Bulgaria. The so-called Kaiser’s roads which were built by Tzar Ferdinand 100 years ago to connect Bulgaria with the newly liberated Bulgarian territories south of Rila, can be turned into wonderful geotrails (Синьовски и др., 2017) to demonstrate both the Quaternary glacier formations and the wonderful alpine landscapes (Fig. 6). These roads are known for having passed the high guest of Tzar Ferdinand, the German Emperor and King of Prussia Kaiser Wilhelm II at the end of the Second World War. At the sight of Pirin Mountain from Nehtenitsa area under Yakoruda Cirque he exclaimed: “O wonderful incomparable picture! Who in Europe has ever thought that the Balkan Peninsula hides such magnificent scenarios and mountain landscapes”.

Fig. 6. The Kaiser’ Road through Zavrachitsa Pass

Geopark “Burgas Lakes” (Sinnyovsky et al., 2017b) is the newest idea, devoted to the wonderful maritime landscapes, focused on the Quaternary sea level changes, lagoon formation and beach sand modeling. Its initial stage includes investigation of the concepts concerning the sea level changes of the Black Sea due to a Bosporus two-way exchange of water between the brackish or freshwater Black Sea and the fully marine Mediterranean Sea driven by the Milankovitch climatic cycles. The catastrophic sea-level rise due to an abrupt Early Holocene saltwater flooding of the Black Sea announced by Ryan et al. (1997a,b), linked to the biblical legend about Noah’s Flood, triggered tremendous interest by the wide public.

Important part of the region’s geodiversity are the old marine terraces outlining the ancient shorelines of the Black Sea basin: the Nymphen, the Neoeuxinian, the Karangatian, the Early Euxinian and the Chaudinian (Fig. 7). They are represented by flattened surfaces or sediments dated on the basis of rich bivalvian fauna. Ramsar sites and dune habitats are subject of intensive research due to the rare and protected inhabiting species. These biotopes are the link between geodiversity and biodiversity within the lake complex and have a high potential for geomorphosites and geocotrails to be developed for geotourism purposes (Sinnyovsky et al., 2017b). The remarkable geodiversity of the area is complemented by the ruins around the ancient towns Anhialo (Pomorie) and Apolonia (Sozopol) testifying to the long history of life on the Black Sea coast. The establishment of a Geopark on the Black Sea coast will add this unique seaside to the European Geoparks Network and will expand its geography to the lullaby of the ancient European civilization – Pontus Euxinus.

Fig. 7. The Atanasovsko Lake is part of the Burgas Lake Complex, formed after the subsidence of the Black Sea coast in the last several thousands of years

Conclusions

The main themes of the Bulgarian geopark projects are completely different and require individual approaches. The diverse themes presuppose development of an upgraded evaluation methodology for geosites in geopark environment, including both generally accepted and specific requirements. The present paper represents the history of the UNESCO Geoparks which was discussed at the International Conference “Geoparks and modern society - protection, promotion and sustainable use of Earth heritage in park environment” in Belogradchik, dedicated to the 20th Anniversary of the UNESCO GEOPARK Initiative announced at the ProGEO’98 Meeting in the small northwest Bulgarian town. The Bulgarian experience in geopark development and the previous achievements of the Bulgarian geocconservation shows that many efforts should be made for recognition of the Bulgarian geoparks as Global Geoparks. Despite its natural beauties and advantages, surpassing many geoparks with the label "Global Geoparks", without administrative and legal changes, Bulgarian geoparks have no chance to become part of the Global Geoparks Network. Although Geoparks initiative is a bottom-up process, without state funding, this idea is condemned to failure in Bulgaria. An important role in this direction could be taken by the establishment of a National Committee of Geoconservation and Geoparks, according to the recommendations of the International Geoscience and Geoparks Programme (IGGP). This committee, recognized by the National Commission for UNESCO, will coordinate identifying and evaluation of the geological heritage, raising public awareness of its importance, and will promote the development of new UNESCO Global Geoparks, provide information at the national level about the global and regional networks of UNESCO Global Geoparks, and initiate supporting actions for sustainable development of geopark areas in the country.

Acknowledgements

This research has been supported by the National Science Fund under the contract DNTS/Russia 02/14.
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TECTONOMORPHOLOGIC CHARACTERISTICS OF ZAVALSKA MOUNTAIN, SW BULGARIA

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ABSTRACT. Zavalska Mountain (Kitka peak, 1180 m) is the westernmost morphographic edifice from the Zavalsko-Planska mountain chain of the Western Srednogorie. In geologic sense it was studied extensively in the course of mapping initiatives in different scale but in geomorphologic sense it is insufficiently studied. The purpose of the paper is to analyze the lineament pattern of the Zavalska Mountain using modern technical tools. For the purpose of the investigation detailed digital topographic model of the terrain was made. Analysis of the lineament network was performed in GIS media. The lineament data were processed using stereoanilic software. The results were analyzed in the context of the known geological fabric with emphasis on the tectonomorphic significance of the lineament directions. The results shed light on the mechanism of formation of the Zavalska Mountain.

Keywords: tectonomorphic characteristics, linear structure, lineament network, neotectonic

Introduction

The purpose of this article is to make a detailed analysis of the lineament network of Zavalska Mountain, using modern GIS tools, with the aim to clarify the neotectonic evolution of the area.

Zavalska Mountain (Kitka, 1180.7 m) is the westernmost mountain of the Zavalsko-Planska mountain range of the Western Srednogorie (Fig. 1). The main ridge of Zavalska Mountain stretches from northwest to southeast. The length of the ridge reaches 20 km and the width is 4-5 km. The higher part of the mountain reaches the village of Zavala, and to the southeast it continues with the ridges of Tsrancha and Breznitshi Greben.

On the northwest, a saddle near the village of Prodancha (971 m) separates it from the Ridge Greben, then passing on to Serbian territory. The northwestern and western slopes of the mountain are limited by the Vrabcha and Butriniti depressions. To the northeast, the hills reach the small Burelska valley - the westernmost of the Sub-Balkan valleys.

To the east, the connection between Zavalska and Viskyar Mountains is made by a water dividing ridge over the Zavala Village, along which passes the main water divider of the Balkan Peninsula. To the southeast, the valley of the Yablanitsa River separates the Zavalska Mountain from the Ezdemirska Mountain and the Stara, and a saddle at 875 m connects it to Lubash Mountain.

Fig. 1. Geographic position of Zavalska Mountain in SW Bulgaria.
Stratigraphy

Zavalska Mountain is built-up of Upper Cretaceous volcanic and sedimentary rocks and Quaternary deposits (Fig. 2). The Upper Cretaceous rocks in the area are well studied (Синьовски и др., 2012). Most of the sedimentary and volcanic rocks are considered to be of Campanian age (Маринова и др., 2010).

The marl-limestone unit, introduced by Загорчев и др. (1995), reveals from the village of Vishan to the southeast. It overlies with sharp lithological transition the limestone-marl unit, limestone unit or conglomerate-sandstone unit. It is covered with a sharp lithological contact by the marl-tuffite unit.

Fig. 2. Geological map of Zavalska Mountain, SW Bulgaria (by Маринова и др., 2010).

The Babski volcanic complex, introduced by Grozdev (Ангелов и др., 2010), is exposed as a wide strip (2-4 km) from the state border near the village of Vrabochka to Breznik. It contains volcanic products with a distinct basic composition, as well as highly alkaline latites and trachytes.

The Vidrishki volcanic complex was introduced by Grozdev (Ангелов и др., 2010). The complex includes pyroclastics and various sediments, named as pyroclastic-tuff unit as well as crosscutting bodies of andesites. The area reveals also the effusive and sub-volcanic bodies of the complex.

The tuffite–marl unit, introduced by Grozdev (Ангелов и др., 2010), is exposed as a relatively wide NW-SE oriented strip south of the village of Prodancha.

The Flish unit (Загорчев и др., 1995) is exposed as two broad (500-800 m) strips with NW-SE direction passing through the outskirts of the villages of Prodancha and Krusha. This is a folded package underlying the Krasava syncline.

Sandstone un İte, introduced by Grozdev (Ангелов и др., 2010), is exposed as two broad (400-800 m) strips with NW-SE direction, passing in the vicinity of the villages of Prodancha and Krusha. They build-up the linearly extended ridges of Tsrancha, Greben and others, which represent the main folded limb that shapes the Krasava Syncline.

The sandstone–marl unit was introduced by Загорчев и др., (1995). The unit has a large areal spread to southeast of the village of Garlo. It is the main rock assemblage of the Krasava Syncline.

Quaternary.(Holocene). Alluvial deposits from flood-plains and flooded terraces. The alluvial deposits form the floodplains of the Yablanitsa, Konska, Kalia Barra and other rivers. They are made of quartz sands and clayey sands with thin layers of impure, sandy clays. Among them gravel lenses are found.

Tectonics

In tectonic terms, the study area falls within the Sofia Unit of the Western Srednogorie (Ivanov, 1998). The northern boundary of the unit is placed on the Sub-Balkan fault zone (outside the survey area) and the southwestern border is placed along the Pernik fault zone with a general direction of 120-140°, located southern of the area of study. The larger structures recognized in the studied area from south to north are the south vergent Dragovska Anticline, the south vergent Krasavskya Syncline and the Galabovska Anticline. In the past, Late Subhercynian (Pre-Maastrichtian) onset of the earliest folding was inferred, because Maastrichtian shallow sea sandstones and clays were believed to cover discordantly the sedimentary and volcanic rocks of Koniacian-Santonian age (I.e. Nachev and Nachev, 2003). Later studies (Симовски и др., 2012, 2013) have proven that Maastrichtian rocks are not present in the region, so the earliest onset of folding deformation must be ascribed to the Late Campanian. Since that time the total deformation progressed significantly, for example the limbs of the Krasava Syncline are isoclinally folded and locally overturned (Димитров, Бенев, 1970). The stages of this deformation are difficult to recognize, however the opening of small, fault controlled sedimentary basins filled with Oligocene sediments mark the Post-Lutetian, Illyrian deformation stage as particularly important for the region. In general the geological maps for the area show a uniform strike of the fault formation in the range 120 - 140° although this appears an oversimplification of a more complex structural setting, in which more westerly striking beds overprint the NW striking once (Fig. 3).

Methods and analysis of the lineaments

To make precise relief pattern for the selected area, topographic maps in 1:25 000 scale are used. All are georeferenced in the WGS84. UTM35N. Horizontals are vectorized in the ArcGIS environment and the ArcScan tool after color division in PhotoShop. For better accuracy and reliability in inscribing and verifying the geometry of plotting, topology and error checking of this type were built in ArcGIS Workstation.

Linear structures are generated using Global Mapper and its Generate Watershed feature. ArcGIS tables are then generated, containing information about the direction of each line. The received data is processed in a text file, maintained by Stereonet. A rose-diagram with 24 classes and 1252 linear structures was generated.

Introduction in the terminology

In the beginning of the last century the term lineament was introduced in the works of some tectonicians such as Hobbs (1904). In their view, the lineaments are "characteristic lines in the face of the earth" (Challinor, 1964). The most significant lineaments are the ridges of hills, the boundaries of the elevated mountain areas, the river valleys, the coastal lines, as well as the boundary lines of the geological formations of different petrographic types. They are believed to be associated with deep faults or zones of intense fracturing, along which vertical or horizontal movements of the crust happened.
Tectonicians, such as Moody and Hill (1956), Moody (1966) etc. as well as geomorphologists (e.g. Герасимов, Раппсман, 1964) consider the linear structural elements on the surface of our planet for morphostructural elements. These are all areas of linear tectonic discontinuities.

Lineaments are studied using structural-geological, structural-geomorphologic and morphotectonic analyses. The study of the lineaments clarifies the relation of the orographic directions with the fault structures.

In Bulgaria, the terminology of lineaments was introduced by the tectonician E. Bonchev in a number of works (e.g. Бончев, 1963, 1971). Later this topic was also adopted by some geomorphologists. From morphostructural point of view, the problem of the lineaments and lineament zones in Bulgaria was examined by Мичев и др. (1986). According to these authors, 5 series of lineaments can be discerned on the territory of Bulgaria — two diagonal (NW and NE), two orthogonal (E-W and N-S) and one local (NNW). According to their study, the territory of Zavalska Mountain is in the so called Kraishtid lineament series, which encompasses lineaments striking 160°–170°. They can be classified as local according to Hobbs (1904).

According to Бончев (1971), Zavalska Mountain is localized in the Kraishtid structural zone, located in Western Bulgaria, south of the Western Stara Planina Mountain. The specific feature of this area is that it is split in blocks, separated by faults. There are a number of faults striking at 160°, to which almost the entire river-valley network is attached.

Analysis of the lineaments and discussion

The rose diagram of the linear structures is shown on Figure 4. It has a very strong maximum of 136°, another at about 105° and two weaker at N-S and at 44°.

![Fig. 4. Rose diagram of the 1252 linear structures](image)

The map of the linear structures in Zavalska Mountain is shown on Figure 5. In the Bulgarian tectonic literature, no model has been presented so far to explain the overall picture of the occurrence of these lineaments. However, it is quite clear that the area is dominated by folds with northwest and southeast striking axes and there is a significant number of proven faults with similar strike.

These data fit into a well-known and well-studied tectonic model, which seems to be valid for this region as well. This is the wrench faulting model, which gained popularity with the classic publication of Moody and Hill (1956) and was further developed by authors such as Wilcox et al. (1973), Sylvester (1988), and others. What is important is that in this model the formation of folds and fractures is considered as a single process.

In short, the geotectonic development of the area can be reduced to the following events and processes:

There was strike slip shear motion statistically averaged by the direction of 136°. Probably this shear has been active from late Cretaceous to present day with periods of higher intensity, for example during the Illyrian phase.

The strike slip motion does not exclude reverse and normal fault translations but they are subordinate to it. Parallel to the fault shearing is the folding of the volcanics, the folding being the geometric effect of the shear movement.

The folding can be also a result of transpression (Sanderson and Marchini, 1984), which includes a portion of pure shear in addition to the simple shearing. In any case, the axes of the folds, being formed in this way, are oblique to the direction of shear.

In case of a left shear, they rotate counterclockwise, and in case of a right shear they rotate clockwise to the direction of shear.

At the onset of deformation they are initiated at a higher angle to the direction of shear but with its advance this angle diminishes never reaching full parallelism between the fold axes and the direction of shear.

From the geological maps (Загорчев и др., 1990; Ангелов и др., 2010), it is established that the strike of bedding does not coincide completely with the direction of the faults (Fig. 3), as it tends towards more westerly strikes, correspondingly to counterclockwise motion of the fold axes, compared to the strikes of the faults. This results from the fact that there are parasitic folds of a lower order on the terrain whose axes are oriented obliquely to the general direction of the strike-slip shear. In this sense, the maximum of lineaments of 105° reflects these folds. This maximum reflects both erosion of susceptible beds in fold limbs and extensional faults parallel to the fold axes. In theory these faults would be mainly reverse faults but limited strike and reverse motion is possible. On the other hand, the maximum of 136° corresponds mainly to strike slip faults. The kinematic sketch of these relationships is shown of Figure 6.

The results of the study comply with paleostress reconstructions in Northwest Bulgaria made by Kounov et al. (2011). Paleostress reconstruction from fault plains inferred that "From the late Oligocene to the earliest Miocene, SSE-NNW transtension generated coal-bearing sedimentary basins and anticlockwise rotation of the main tensive axis happened by almost 50° with respect to the previous tectonic stage".
Our study confirms the anticlockwise rotation of the structural elements, which can be result only from regional sinistral strike slip shear. On the other hand it is not obvious that this rotation happened only from late Oligocene to the earliest Miocene as it may have been initiated by even earlier sinistral shear contemporaneous with the opening of the basin that contains this volcano sedimentary assemblage.

To answer this question further studies and dating of the faults and folds have to be made in this seeming simply folded assemblage. It is noteworthy that a rose (Fig. 7) generated by the beds shown of Figure 3 produces very similar pattern as the lineament picture on Figure 5. This is a clear indication that the lineaments are produced predominantly by selective erosion of beds and thus are controlled by the folds.

Based on paleostress reconstruction from fault plains the authors inferred that “From the late Oligocene to the earliest Miocene, SSE-NNW transtension generated coal-bearing sedimentary basins and anticlockwise rotation of the main tensile axis happened by almost 50° with respect to the previous tectonic stage”. Our study confirms the anticlockwise rotation of the structural elements which can be results only from regional sinistral strike slip shear.

Fig. 5. Digital elevation model and linear structure derived from the hydrographic network of the region.

Fig. 6. Kinematic sketch of the tectonic elements inferred from the lineament analysis and the geological descriptions of the study region.

Fig. 7. Rose of 52 bedding planes from the studied area after Загорчев и др. (1990).
Conclusions

The studied region has a pronounced linear structure. The lineaments network is due to tectonic predisposition in which tight folds and numerous faults dominate. The data from the geological literature and these of the lineament analysis are in accordance and allow for a tectonomorphological model that includes simultaneous sinistral strike slip motion and folding in which erosional forms are formed in directions visible on the rose diagram.

The data shed light on the mechanism of formation of Zavalska Mountain. Moody (1966) classified the orogenic edifices into the following types: (1) linear uplifts with longitudinal fault zones; (2) autochthonous fold belts; (3) uplifted fault blocks; (4) domal uplifts; and (5) volcanic chains. The data accumulated so far suggest that Zavalska is a mountain from the first class. It is one of the pop ups related to the strike-slip tectonics of the region.

References


CATALYTIC CARBON NANODOTS FOR OXYGEN REDUCTION REACTION

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ABSTRACT. This report provides a new perspective for practical application of the electronics properties of carbon nanodots as an electrocatalytic layer on the graphite working electrode. For that purpose, ultra-small nitrogen doped carbon nanodots (C-dots) with average diameter between 1.5-2 nm were synthesized by microwave assisted pyrolysis and after that were immobilized chemically onto the graphite surface of the electrode. As environmentally friendly electrocatalyst for oxygen reduction reaction (ORR) our data show that the bare C-dots alone are not able to form stable electro-catalytic film for ORR because of their high water solubility. However, the chemically conjugated nanoparticles exhibit ORR electrocatalytic activity in acid or basic media. These properties open a new range for practical application in the field of ecotechnology and environmental protection.

Keywords: carbon nanodots, environmental friendly electrocatalyst, oxygen reduction reaction

In basic environment:

\[
\begin{align*}
\text{O}_2 + 4e^- + 2H_2O & \rightleftharpoons 4OH^- & E_0 = 0.401 \text{ V} \\
\end{align*}
\]

In acidic environment:

\[
\begin{align*}
\text{O}_2 + 4e^- + 4H^+ & \rightleftharpoons 2H_2O & E_0 = 1.229 \text{ V} \\
\end{align*}
\]

In order to increase the performance of the working electrode (cathode) our efforts are concentrated on the development of effective and low cost electrocatalysts (known as platinum-free) that are able to increase ORR peak current and reduce the electrochemical overpotential. The reason is because the noble metals as platinum and its compounds are considered as the most effective ORR catalysts, however the high cost and poor global distribution limit its practical application (Lin et al., 2014).

Introduction

The negative consequences of the anthropogenic environmental pollution create a prerequisite for the development of modern ecotechnology for clean energy generation. One such approach is the development of membrane fuel cells, microbial fuel cells, etc., which utilize the reduction of oxygen in order to generate electrical energy (known as oxygen reduction reaction or ORR) (Huang et al., 2017). The reduction of oxygen in water solution can proceed basically by two general pathways and the reaction occurred on the cathode electrode. The pathways are dependent on pH conditions and thus ORR mechanism basically differs in basic or acidic conditions (Yeager 1984), as shown on the equation below:
During the last decades a lot of efforts have been made to develop an effective and non-precious electro-catalysts as alternatives of the platinum based on light elements (carbon, hydrogen, boron, oxygen, etc.). The recent studies have focused on carbon based nanomaterials, which are of particular interest, because they have various attractive benefits (Li et al., 2012), such as electrocatalytic activity dependent on their structure and morphology, cheap production, easy chemical modification and long-term stability. Herein we employed nitrogen-doped carbon nanodots (C-dots) as electrocatalyst of ORR in both basic and acidic aqueous solutions. C-dots are reported to be composed of polyatomic carbon domains surrounded by amorphous carbon frames (Zhu et al., 2013). The nanoparticles are highly fluorescent and can be fabricated in one step reaction by microwave assisted pyrolysis. Their abundant of organic groups shell allows to be immobilized on the graphite electrode through chemical conjugation. Thus, the presented report suggests a novel approach for producing effective electro-catalyst as alternative to platinum for ORR.

**Experimental Procedures**

**Materials.** Citric acid, 1,2-ethylenediamine, sodium nitrite, sodium bicarbonate, potassium hydroxide, sulfur acid and concentrated hydrochloric acid were purchased from Wako. All the chemicals used within the experiments were of an analytical grade without any further purification. All solutions were prepared with deionized water. Graphite rods (model: Uni 0.5 Mm Hb Nano Dia Blended Hi-quality Mechanical Pencil Leads, made in Japan) with 1.2 nm diameter were used as a working electrode (cathode).

Fabrication of graphite electrode chemically coated with carbon nanodots. The nanoparticles were prepared by the so called “bottom up” method. For that purpose 1 g of citric acid was mixed with 10 ml deionized water and 0.2 ml of 1,2-ethylenediamine was subsequently injected in the reaction mixture. The precursors were well mixed by magnetic stirrer to obtain a clean transparent solution. Then the mixture was subjected to microwave pyrolysis in 150 ml Beher glass for 180 sec in conventional microwave oven (600 W). After the pyrolytic reaction a yellow-brown pellet was formed at the bottom of the glass vessel. Its aqueous solution has acidic pH = 3.5. The pellet was dissolved again in 10 ml deionized water and cooled down in an ice bath. In another glass vessel blue nitrous acid (HNO₂) was prepared by simple mixing of ice, concentrated hydrochloric acid and sodium nitrite (NaNO₂) at temperature close to 0 °C. 2 ml of the freshly prepared nitrous acid was mixed with the solution of carbon nanodots. During the formation of diazonium salts the fluorescence of nanoparticles disappeared. This fluorescence quenching effect was an indicator for the monitoring of reaction end. The chemically activated nanoparticles [C-dots-N=N⁺] Cl⁻ were mixed with the graphite electrodes in sodium bicarbonate (NaHCO₃) buffer solution. Thus, an energetic reaction of chemical conjugation occurred on the graphite surface. During the reaction bubbles were formed on the fabricated electrode surface as a result of neutralization of the bicarbonate buffer with the acidic solution of the nanoparticles.

**Electrochemical measurements.** The measurements were conducted by a conventional three-electrode system utilizing a Saturated Calomel electrode (SCE) and a platinum wire as a reference and counter electrode. The working electrodes were (i) unmodified graphite electrode, (ii) graphite electrode chemically modified with carbon nanodots and (iii) polycrystalline platinum disk electrode as a control experiment. For ORR measurements, 0.1 M KOH and H₂SO₄ solutions saturated with oxygen were used. Before measurement the solutions were subjected to bubbling with oxygen for 30 min to achieve their complete saturation at ambient temperature (Gara & Compton, 2011). One control experiment with solutions saturated with nitrogen was performed too.

**Result and discussion**

**Physicochemical characterization of the carbon nanodots.** The physicochemical characterization of C-dots was performed using Fourier transform infrared spectroscopy (FT-IR), dynamic light scattering (DLS) and X-ray photoelectron spectroscopy (XPS). DLS analysis showed nanoparticles size distribution in the range 1.5-2.5 nm with 2 nm average diameter. By this analysis no aggregations were found. FT-IR analysis showed absorption bands at 3000~3500 cm⁻¹, which were associated to the combination of stretching vibrations of amino (H₂N–), hydroxyl (HO–), and alkyl (C–H) functionalities. These organic groups are responsible also for the hydrophilic nature and stability of C-dots in aqueous solution. The transitions at 1566, 1402, 1184 and 768 cm⁻¹ are assigned to ν(C=O), ν(C=C), ν(C=O) and ν(C=C) vibrations, respectively (Zhu et al., 2013). XPS analysis was performed, focusing on the C 1s, N 1s and O 1s regions of the carbon nanodots. XPS analysis for C 1s region shows main binding energy (BE) peaks at 285.1 eV and 287.0 eV, which correspond to functional groups of aliphatic carbons and to carbons in C=O, C-O-H and C-O-C, respectively. The region for nitrogen (N 1s) at 407.5 eV was observable with a dominant peak.

**Electrochemical activity of unmodified graphite electrodes.** Cyclic voltammograms were measured for the unmodified graphite macroelectrodes (as control experiment) in a range of scan rates in H₂SO₄ solution saturated with either oxygen or nitrogen gas. As we expected, in the majority of experiments with saturated oxygen there was a response for ORR electroactivity of the graphite. Nevertheless, the control experiment with solution saturated with nitrogen gave very little response with most nothing except a response for the breakdown of solvent (in case of organic solvent as methanol).

**Electrochemical activity of graphite electrode coated with C-dots.** The ORR electroactivity of the immobilized C-dots on the graphite electrode was evaluated in basic and acidic media as explained above. On Fig. 1 are shown typical linear sweep voltammograms obtained from (i) unmodified graphite electrode, (ii) graphite electrode coated with carbon nanodots, and (iii) polycrystalline platinum disc electrode. The experiments were performed in oxygen saturated solutions of 0.1 M potassium hydroxide (Fig. 1A) and 0.1 M sulfuric acid (Fig. 1B). The figure shows that the unmodified electrode and the platinum electrode have an ORR peak current (ιp) and ORR onset at ~ 552 μAcm⁻² and ~0.35 V, and at ~559 μAcm⁻² and ~0.038 V.
(vs SCE), respectively in basic solution. In acidic solution the unmodified electrode and platinum disk have ORR peak current and ORR onset at –662 $\mu$A cm$^{-2}$ and –0.51 V, and at –717 $\mu$A cm$^{-2}$ and –0.47 V (vs SCE), respectively. In both experiments as theoretically expected the polycrystalline platinum disk electrode displays optimal oxygen reduction reaction activity. It is clear further on both figures that in basic or acidic solution modified graphite electrode becomes less electronegative. In case of KOH the ORR onset of the coated electrode shifted from –0.35 V to –0.27 V (shifting by 0.08 V) and the peak shifted from –552 $\mu$A cm$^{-2}$ to –484 $\mu$A cm$^{-2}$ (shifting by 68 $\mu$A cm$^{-2}$). In the case of the acidic solution the change is even more significant. The ORR onset of the coated electrode shifted from –0.51 V to –0.16 V (shifting by 0.35 V) and ORR peak current shifted from –662 $\mu$A cm$^{-2}$ to –597 $\mu$A cm$^{-2}$ (shifting by 65 $\mu$A cm$^{-2}$). The analysis of the figure proved that the modification of the electrode with carbon nanodots enables ORR to occur at a less electronegative overpotential compared to that of unmodified electrode. As a result the electrochemical reaction proceeds at less electronegative ORR onset and the achievable current density is increasing.

![Graph](image)

**Fig. 1.** Linear sweep voltammograms of unmodified graphite, graphite electrode chemically coated with nitrogen doped carbon nanodots and platinum disk electrode in (A) 0.1 M solution of KOH and (B) 0.1 M solution of H$_2$SO$_4$.

The obtained data concluded that the addition of fluorescent nitrogen doped carbon nanodots on the electrode surface caused beneficial alteration to the ORR signal output. The reason is because in both basic and acidic solution the nanoparticles have a 2 electron pathway ORR mechanism. In the case of H$_2$SO$_4$ the obtained H$_2$O$_2$ was the major reaction product (Martínez-Perinan et al., 2018). It was important to test the operational stability during longer period of exploitation of the modified electrode in order to claim for its practical industrial applications. All experiments show that the modified electrodes have initial increase in their relative current output (during 90 min exploitation). These were important results for the practical use of the electrode as cathode in fuel cells. However, after few hours’ exploitation (less than 4) their current gradually decreases. Note that the nature of graphite electrode is with low adhesion which enables dissolution of its rough surface into the electrolyte during the friction with liquids.

Another practical advantage of the fabricated electrode is the resistance of the carbon nanodots to poisoning as inhibition of the catalytic centers with hydrogen sulfide, carbon oxide and methanol. These mentioned compounds have been shown to reduce significantly the ORR activity of all platinum based electrocatalysts. In addition, the presence of the nano-layer on the electrode reduces the charge transfer resistance and thus improves the electrochemical response. This property could find application in the biosensors technologies too.

**Conclusion**

We reported the fabrication and electrochemical characterization of graphite electrode modified with nitrogen doped carbon nanodots towards the ORR in basic and acidic media. All experiments show increasing of the ORR signal output, which caused increasing of the achievable current too. Thus, the electronegativity of the ORR onset potential of the modified electrode was decreased. Future work is orientated to improve the stability of the nano-layer on the electrode surface. This might offer cheap, stable and effective alternative of the platinum based cathode materials.
Acknowledgment

Funding from Bulgarian National Science Found, Grant № DN07/7, 15.12.2016. This study was accomplished thankful to the bilateral agreement between Saitama University-Japan and the University of Mining and Geology “St. Ivan Rilski”-Bulgaria.

References

MATHEMATICAL FLOW MODEL OF THE KRASNOVO THERMOMINERAL FIELD (SOUTHERN BULGARIA)

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ABSTRACT. A generalized conceptual scheme of the hydrogeological conditions in the region of the Krasnovo thermomineral field is developed. This concept is implemented in a three-dimensional model of the flow structure. The modeled area includes the upper part of the thermomineral reservoir to a depth of 400 m and covers a territory of about 72 km². Within these boundaries four hydrogeological units are determined: a fault-fissure conductive complex, a fractured poor water-bearing complex, a fault-drainage spring complex, and a Quaternary-Neogene aquifer complex. The developed flow model is used to calculate the water balance revenue and expenditure elements for the fault-fissure complex and for the spring complex. The obtained model solutions are used as a base for the performed quantitative assessment of the Krasnovo field water resources. The boundaries of the sanitary protection zone around the existing facilities for extraction of thermal mineral waters are determined. The computer programs Modflow and Modpath are used.

Keywords: hydrogeological model, mineral water resources, thermomineral field, water budget

MATEMATически ФИЛТрационен модел на термоминерално находитие Красноvo (Южна България)

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РЕЗЮМЕ. Разработена е общ концепция за геоложките условия в района на термоминерално находитие Красноvo. Концептуалната схема е реализирана в тримерен математически модел на филтрационното поле. Моделният обект обхваща площад със площ около 72 km² и до дълбочина около 400 m. В тези граници са детерминирани четири геоложки единици - разломно-пукнатинен проводящ комплекс, пукнатинен слабоводоносен комплекс, разломно-дренажен изворен комплекс и кватернерно-неогенов водосборен комплекс. С филтриационния модел са изчислени приходните и разходните елементи от водния баланс на разломно-пукнатинния проводящ комплекс и разломно-дренажния изворен комплекс. Въз основа на моделните решения е направена количествена оценка на водните ресурси на находище Красноvo. Определена е санитарно-охранителна зона около действащите съоръжения за добив на термоминерални води. Използвани са компютърните програми Modflow и Modpath.

Ключови думи: геоложки модел, ресурси на минерални води, термоминерално находитие, воден баланс

Introduction

One of the areas rich in thermal mineral water in Bulgaria is the Sredna gora thermomineral-bearing system, formed in the deep parts of the granite-gneiss massif of Sashtinska Sredna gora (Figure 1). Separate parts of this system are the thermal mineral fields Hissarya, Pesnopoy, Krasnovo, Strelcha and Banya (Panagyrishite), where some of the most famous national balneological centers are built. The listed fields have been known and used since ancient times, and in the last 100-150 years they have been increasingly exploited and thoroughly researched. Detailed data and different estimates of the genesis, water and heat resources, chemical composition, yield and use of the thermal mineral waters are presented in a large number of monographs, articles, scientific reports and notes. Systematic information on the thermal system and its composite fields is contained in a number of summary reports (Азманов, 1940; Щерев, 1964; Петров и др., 1970, 1998; Бенderev et al., 2016; Pentcheva et al., 1997, and others).

The schemes and resource assessments, presented in various information sources for the Krasnovo field are too general, mainly based on data on the flow rate of the drainage water facilities, without taking into account, analyzing and assessing the characteristics of the composite and boundary hydrogeological units, the hydraulic connections and the water exchange between them, the influence of the boundary conditions and possible external impacts, the flow structure, the water budget, the boundaries of the sanitary-protection zones (SPZ), etc. In fact, there are similar deficiencies in the published data about most of the thermal fields and manifestations of the Sredna gora thermomineral water-bearing system.

For a detailed, well-grounded and more precise assessment of the water budget, a three-dimensional (3D) model of the Krasnovo field was developed using Modflow program. Based on the model solutions, the flow structure is determined, the elements of the water budget are calculated and the local and regional resources of the thermal-mineral waters are estimated. Using the Modpath program, the boundaries of the SPZ around the exploited water sources are defined. Publications and archive sources for the area of the thermomineral field (Христова, 1981; Щерев, 1964; Петров и др., 1970, 1998; Пенчев, 1999) were also used.

73
General information about the thermomineral field

Thermomineral field Krasnovo is located at the southern foot of Sashinska Sredna gora Mountain, about 2 km east of the village of Krasnovo. The main reservoir is formed in the deep parts of a fissured and tectonically disturbed rock complex, including parts of the Matenica pluton (mtyC), the Smilovene pluton (smyδC) and the Arda group (ArPeC) (Figure 1). Thermomineral waters circulate by faults, and on the terrain they appear from the Quaternary-Neogene sediments, filling the Krasnovograben.

The warm springs have been used since ancient times, and documented studies and activities for more efficient utilization of the field began in the early 20th century. In 1928, Krasnovo capture was built, which captured two springs with a total flow rate of 2 l/s and a temperature of 53.5 °C. In the period 1958-1961, based on detailed geophysical and drilling studies, the main normal dip-slip faults which formed the Krasnovograben,
tectonic disturbances and thermal anomalies in the spring zone were mapped (Xρξτος, 1961). At a regional level, studies outline a stepped graben filled with clayey and sandy-clayey sediments. From the three deep boreholes (C-1, C-2 and C-3) drilled in the graben bedrock, the most perspective is C-1 (Figure 1). It is built in the spring area, at about 150 m from the existing capture. Its depth is 160 m. At 127 m below the ground, it enters the cracked and fissured granite bedrock, where it reveals a very conductive pressure zone hydraulically connected to the main reservoir. The other two deep boreholes (C-2 and C-3) have been identified as being without potential due to very low artesian flow rate (up to 0.3 l/s), insignificant relative flow rates at pump mode and temperature below 35 °C. The uncaptured spring Gyola located in the spring area with a flow rate of 0.2 l/s and a temperature of 21 °C is also of no significance. The water drained from these sources is not directly connected to the main reservoir but is a result of the mixing of thermal mineral water and fresh cold water.

![Image](image-url)

Fig. 1. Location of the studied area. Geological background

Note: The maps and the profile are compiled on the basis of the geological map of Bulgaria M 100000 – map sheet Panagyurishte and Karlovo (Krueve u Kauke, 1990; Pyceea u d., 1990) and unpublished materials (Xρξτος, 1961)

The capture and C-1 borehole are the only existing water abstraction facilities in the Krasnovo thermomineral field. They are with artesian character, forming a complex drainage system very sensitive to external and internal impacts. Observations on the flow rate and the temperature of the drained waters also show that the exploitation resources of the field in the last six decades have been gradually decreasing, which is explicable for deep high pressured water-bearing structures. In the initial stage of the joint operation of the two facilities (1960), the outflow from C-1 was 24.5 l/s at 55 °C and the initial flow rate (2 l/s) decreased to 1.2 l/s. For ten months,
the flow rate of C-1 decreased to 14 l/s at 55.2 °C, and the flow rate of the capture increased to its initial value of 2 l/s. In 1998/1999 the flow rate of C-1 was about 6-7 l/s at a temperature of 55.4 °C and the flow rate of the capture – 1.5 l/s at 52 °C. In the beginning of 2018, the outflow from C-1 was 5.5 l/s at a temperature of 53 °C, and the flow rate of the capture was 1.25 l/s at 49.6 °C. According to its chemical composition, the water from the Krasnovo field refers to the nitrogenous thermae, but besides N contains also H2S. Its total dissolved solids (TDS) concentration is about 0.3 g/l, and the type of the water is HCO3-SO4-Na, with a neutral to alkaline
pH. The microcomponents Li, Be, Ga, Ge, Se, Rb, Cs etc. are presented. The helium content is 234 Pa, and the radioactivity is 25 Em. Water is suitable for the treatment of kidneys, gallbladder, liver, digestive system and musculoskeletal apparatus. The resource assessments made so far, on the thermomineral field, are based on observations on its flow rate, chemical composition and temperature regime.

**Conceptual model of the thermomineral field**

On the basis of the current geo-tectonic knowledge of the region and the available information about the studied site (Христова, 1961, Кацков и Ильеви, 1994, Русева и др., 1994), the following general conception for the hydrogeological settings in the range and the adjacent territories of the Krasnovothermomineral field was assumed (Figure 2).

**Watershed area.** The watershed area of the field covers an area of 72 km², including parts of the Gerenska River basins and its northern tributaries (Krasnovska, Banski Dol, Drenov Dol etc. (Figures 1 and 2). The terrain is heavily intersected, with altitudes varying from 1273 m on the ridge of Sashinksa Sredna gora to 320-350 m in the spring zone. The river network density is about 1.4 km/ km² and the average value of the surface runoff is 2 1/s/km².

**Fig. 2. Hydrogeological map of the watershed area of Krasnov field**

**Basic hydrogeological units.** According to the assumed working hypothesis, four main hydrogeological units are separated in the watershed area of the thermomineral field and its periphery, the surface outcrop and boundaries of which are illustrated in Figure 2.

- **Fault-fissure conductive complex (fA-Pz-cmx).** It is developed by the Krasnov graben tectonic structures, and the associated river and deep gullies fault zones. It is built of faulted, fissured and secondary altered intrusive and metamorphic rocks. The Palaeozoic granites (mty-C) dominate the graben and SE part of the watershed area, where the main thermomineral reservoir is formed at a depth of about 1000 m. In the central part of the watershed area, the fault-fissured complex is attached to the Precambrian gneisses (ArPeC) and in the N-NW – to the Palaeozoic granites and granodiorites (smyC-C). The hydraulic conductivity k is most often in the range of 0.01 to 0.1 m/d, with the high values being associated with the upper part of the cross-section – up to a depth of 100-200 m.
- **Fractured poor water-bearing complex (fA-Pz-cmx).** Includes parts of the Palaeozoic and Precambrian rocks that are not affected by the tectonic deformations. Up to a depth of 50-100 m, the rocks are very fractured and secondary altered, and below in the cross-section the open fissures gradually dwindle or are completely absent. The hydraulic conductivity varies widely from about 0.02 m/d in the upper part of the rock massif to 0.001 m/d and is lower in depth.
- **Fault-drainage spring complex (fA-Pz-cmx).** It is formed in the most fractured parts of Palaeozoic granites (mty-C), where several sub-parallel and sub-meridian faults intersect. It covers a small territory in the SE part of the Krasnovo graben (the area of drainage of the thermomineral waters), which includes the Krasnov capture, C-1 borehole, the spring Gyola and other smaller scattered springs along the Banski Dol River. Fault-drainage spring complex is the main path to the surface for the deep thermomineral flow and is a very important factor that determines the quantitative and qualitative parameters of the spring waters and partially limits the resources of the thermomineral field. The hydraulic conductivity in this zone ranges from 0.1 to 1 m/d.
- **Quaternary-Neogene aquifer complex (Q-N-cmx).** It is formed in the sediments that fill the Krasnovski graben and is built of conglomerates, clayey sands, sandy clays and clays with a total thickness of 100-150 m. The predominant presence of the fine-dispersed fractions implies the low water permeability of the medium. The hydraulic conductivity is about 0.03 m/d, and in some parts it is up to 0.2-0.3 m/d.

**Recharge and discharge.** The main recharge is from infiltration of rainwater and river water. It occurs in the outcrop parts of the rock complexes. It is most intense in the outcrops of the fault-fissure conductive complex. The average infiltration rate W is between 3.0E-05 and 7.5E-05 m/d. It is determined by the assumption that between 2 and 5 % of the precipitations, whose annual sum in the area is 538 mm (Ковчева и Левева, 1990), are infiltrated in the subsurface space. The cold water infiltrating by faults maintains the water budget and the high pressure in the main reservoir. In depth, their temperature reaches 55-60 °C under the influence of the geothermal anomaly in the deep parts of the Palaeozoic plutons. The main direction of the thermomineral flow is S-SE and the average gradient is 0.015. The piezometric heads in the bedrock of the graben are very high, and at the lowest SE part of the catchment area are 10-15 m above the terrain, which generates the ascending thermomineral flow in the fault-drainage spring complex. Part of this stream is drained by the capture and C-1 borehole, and another part is discharged and mixed with the cold waters of the Quaternary-Neogene complex and emerging on the surface as scattered springs with low flow rate and low temperature (20-25 °C).
Composition of the flow 3D model

The flow model FM3D is a 3D simulation of the flow structure in the region of Krasnovo thermomineral field, taking into account the complex hydrogeological conditions and all external influences, including the activity of the capture and C-1 borehole. The basic points and input parameters in its composition are as follows:

- FM3D is compiled with Modflow computer program. The model area covers the subsurface in the watershed area of the thermomineral field with an area of 72 km² and up to a depth of about 400 m.
- Spatial discretization is made with an uneven orthogonal grid. FM3D includes two model layers - ML-1 and ML-2 (Figure 3). According to the differences of the hydrogeological parameters in the model layers, four model zones are defined (Tables 1 and 2), which simulate the spatial distribution of the hydrogeological units of different rank (Figure 3).
- The relief of the lower and upper boundaries of the model layers and zones are consistent with the morphological features of the terrain and the spatial forms of hydrogeological units. The ground surface is set as the upper boundary of the ML-1.
- The regional flow is modeled with a boundary condition of third kind under the General Head Boundary (GHB) scheme along parts of the outer boundaries of the model area.
- The Gerenska River and its tributaries are simulated as 3D objects with relevant geometry and hydraulic characteristics. They are defined as a boundary condition of third kind using the River program package.
- The infiltration recharge is set in all cells of the first model layer with the Recharge program package. According to the permeability of the surface layer, 3 model zones with different infiltration rates were introduced – MZ-W1, MZ-W2 and MZ-W3 (Figure 4), which respectively simulate the surface propagation of $IA-Pz-cmx$, $A-Pz-cmx$ and $QN-cmx$. The introduced values of W in these zones are: $W1 = 2.0E-04$ m/d, $W2 = 1.0E-04$ m/d and $W3 = 5.0E-05$ m/d.
- The upstream flow from the main reservoir is set on the bottom of the ML-2 layer in the MZ-2.3a zone with a boundary condition of second kind by the Specified Flow program package. The initially accepted flow value was corrected for model calibration.
- The capture and C-1 borehole are modeled as 3D objects with corresponding coordinates and construction parameters. They are set to work with a constant level of drainage with a boundary condition of first kind by the Specified Head program package.

The model calibration uses data from the long-term exploitation of the facilities and data on water levels in the rivers.

![Fig. 3. Geometry of the model layers and zones. Boundary conditions.](image)

### Hydrogeological units, model layers and model zones

<table>
<thead>
<tr>
<th>Hydrogeological unit</th>
<th>Geological unit</th>
<th>Lithological characteristic</th>
<th>Geology index</th>
<th>Model layer</th>
<th>Model zone</th>
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</thead>
<tbody>
<tr>
<td>1st rank</td>
<td>2nd rank</td>
<td></td>
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<td>Fractured poor water-bearing complex</td>
<td>Near-surface zone</td>
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<td>$\gamma_c$, smy$\beta_c$, ArPeC</td>
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<td>MZ-1.1</td>
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<td>Arda group</td>
<td>granites, schists, gneisses</td>
<td>ML-2</td>
<td>MZ-2.1</td>
</tr>
<tr>
<td>Fault-drainage spring complex</td>
<td>Deep zone</td>
<td>Mavetica pluton</td>
<td>$\gamma_C$, ArPeC</td>
<td>ML-1</td>
<td>MZ-1.2</td>
</tr>
<tr>
<td>Quaternary-Neogene aquifer complex</td>
<td>Spring zone</td>
<td>Proluvial and alluvial-proluvial deposits</td>
<td>pQp</td>
<td>ML-2</td>
<td>MZ-2.3a</td>
</tr>
<tr>
<td>Quaternary-Neogene aquifer complex</td>
<td>Perennial zone</td>
<td>Ahmatovo formation</td>
<td>pQp</td>
<td>ML-1</td>
<td>MZ-1.3</td>
</tr>
<tr>
<td>Quaternary-Neogene aquifer complex</td>
<td>Spring zone</td>
<td>Sand and clay</td>
<td>$\alpha_N$</td>
<td>ML-1</td>
<td>MZ-1.4</td>
</tr>
</tbody>
</table>
Table 2.
Hydraulic conductivity $k$ and active porosity $n_0$ of the model zones

<table>
<thead>
<tr>
<th>Hydrogeological unit</th>
<th>Model zone</th>
<th>$k$, m/d</th>
<th>$n_0$,-</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fractured poor water-bearing complex</td>
<td>MZ-1.1</td>
<td>1.5E-02</td>
<td>2.0E-03</td>
</tr>
<tr>
<td></td>
<td>MZ-2.1</td>
<td>7.0E-03</td>
<td>1.0E-03</td>
</tr>
<tr>
<td>Fault-fissure conductive complex</td>
<td>MZ-1.2</td>
<td>5.0E-02</td>
<td>3.0E-03</td>
</tr>
<tr>
<td></td>
<td>MZ-2.2</td>
<td>2.5E-02</td>
<td>2.0E-03</td>
</tr>
<tr>
<td>Fault-drainage spring complex</td>
<td>MZ-2.3a</td>
<td>1.0E00</td>
<td>1.0E-02</td>
</tr>
<tr>
<td></td>
<td>MZ-2.3b</td>
<td>1.5E-01</td>
<td>7.5E-03</td>
</tr>
<tr>
<td>Quaternary-Neogene aquifer complex</td>
<td>MZ-1.3</td>
<td>1.0E-01</td>
<td>5.0E-03</td>
</tr>
<tr>
<td></td>
<td>MZ-1.4</td>
<td>3.0E-02</td>
<td>2.5E-03</td>
</tr>
</tbody>
</table>

Note: The values of $k$ and $n_0$ are defined by literary data (Spitz and Moreno, 1996; Cmaovoe, 2015, and others).

Table 3.
Water budget of the fault-fissure conductive complex (fA-Pz-cmx)

<table>
<thead>
<tr>
<th>FLOW IN, $Q^{IN}$, l/s</th>
<th>FLOW OUT, $Q^{OUT}$, l/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inflow from adjacent to the water catchment area complexes</td>
<td>24.45</td>
</tr>
<tr>
<td>Inflow from rivers</td>
<td>6.48</td>
</tr>
<tr>
<td>Inflow from the Quaternary-Neogene aquifer complex</td>
<td>5.69</td>
</tr>
<tr>
<td>Inflow from the fractured poor water-bearing complex</td>
<td>81.37</td>
</tr>
<tr>
<td>Inflow from the fault-drainage zone and upstream flows by deep faults from the main reservoir</td>
<td>16.72</td>
</tr>
<tr>
<td>Recharge from infiltration of precipitation</td>
<td>17.82</td>
</tr>
<tr>
<td><strong>Balance error 0.03 % (difference)</strong></td>
<td></td>
</tr>
</tbody>
</table>

Table 4.
Water budget of the fault-drainage spring complex (f1A-Pz-cmx)

<table>
<thead>
<tr>
<th>FLOW IN, $Q^{IN}$, l/s</th>
<th>FLOW OUT, $Q^{OUT}$, l/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inflow from the fault-fissure conductive complex and upstream flows by deep faults from the main reservoir</td>
<td>24.81</td>
</tr>
<tr>
<td>Inflow from the fractured poor water-bearing complex</td>
<td>1.58</td>
</tr>
<tr>
<td>Inflow from the Quaternary-Neogene aquifer complex</td>
<td>2.12</td>
</tr>
<tr>
<td><strong>Total flow in: 28.51</strong></td>
<td><strong>Total flow out: 28.49</strong></td>
</tr>
</tbody>
</table>

Model solutions

Structure of the flow field. The model solution for the distribution of the hydraulic heads in the two model layers (Figure 5) presents the flow structure in the watershed area of the thermomineral field under the conditions of continuous exploitation of the capture and C-1 borehole.

Water budget. Groundwater resources. Using FM3D, the water budgets of the fault-fissure conductive complex (fA-Pz-cmx) and the fault-drainage spring complex (f1A-Pz-cmx) are composed, which are very closely related to the formation, circulation and drainage of the thermomineral waters (Tables 3 and 4). The presented results provide the basis for the following summaries and conclusions regarding the water resources of the thermomineral field.

- The total discharge of the circulating groundwater in the spring zone is 28.5 l/s.
- The regional water resource of the field is estimated at 26.4 l/s, assuming that it is formed from the upstream flow of the main thermomineral reservoir and the hot water entering the spring zone from the deep parts of the fault-fissure conductive complex and the fractured poor water-bearing complex.
- The local water resource of the water abstraction facilities (the capture and C-1 borehole) is 6.75 l/s, with guaranteed chemical composition and temperature of the abstracted thermomineral water and with a tendency for a slight decrease in the outflow in the near decades.

Models for determination of SPZ boundaries

The boundaries of subzone II and subzone III of the SPZ around the capture and C-1 borehole are calculated using the ModPath program. Two mass-transport models, MP3D-1 and MP3D-2 are compiled, taking into account the determined by FM3D flow structure. The values of the active porosity $n_0$ specified in the model zones are accepted according to the lithology and/or the secondary alterations in the water-bearing medium (Table 2). By MP3D-1, the boundaries of subzone II have been determined at a computing time of 400 days, and with MP3D-2 the boundaries of subzone III at a calculation time of 25 years (Figure 6). These periods have been chosen with accordance to the normative documents in Bulgaria.
Conclusion

A modern concept of the hydrogeological structure and the
recharge conditions, circulation and drainage of the
thermomineral and cold waters in the watershed area of
Krasnovo field was implemented by the developed models.
The model solutions determine the complex flow structure in
the artesian aquifer system and quantify the water resources
of the field as well as the parameters of the optimum yield
and the boundaries of the SPZ around the water abstraction
facilities. The obtained results enable a better understanding
of the mechanisms of formation and movement of thermomineral
waters and provide new data about their resources. These
results have also an important practical significance for a more
efficient exploitation of the field. The presented methodological
approach can be successfully used in solving of other similar
hydrogeological problems.

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RESEARCH TO DETERMINE THE DEPENDENCE BETWEEN THE ENVIRONMENTAL TEMPERATURE AND THE TEMPERATURE OF NATURAL GAS USED FOR THE DOMESTIC SECTOR AS A CONSUMPTION FACTOR

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ABSTRACT. In this report we present a current issue related to the recalculating of the volume of natural gas used in the domestic sector and the dependence on the weather conditions of the coefficients involved in these corrections. Several methods of data processing were used, including: regression analysis and artificial neural networks ANN. The gas distribution companies in the course of the operation of the gas distribution networks solve this problem, related to the accuracy of reporting the consumed quantity of gas, depending on its priorities and expert capacity. To this end, colleagues from Sofia Gas have conducted a study and observed differences in readings of the reported amount of gas per user, in which the consumption was measured with a gasmeter without temperature correction and with a temperature correction gasmeter. On this basis, by additionally mounted temperature sensors and volume correctors of the Gas Center experts, we have conducted an experiment to specify the impact of environmental parameters on a model for adjusting the volume of gas. On the basis of the data used for the heating periods in 2016/2017, the report presents a mathematical model, which defines a function describing the gas temperature dependence on the daily air temperatures. Using Artificial Neural Networks (ANN), relationships between air temperature and soil temperature are determined for different gas flows. A software application has been developed to predict the temperature of the soil depending on the climate zone and average air temperature. The results of solving this problem and the possibility to forecast are the opportunities to improve the effective management of the Gas Distribution Networks.

Keywords: natural gas, applications for natural gas consumption, flow measurement, correction factors for natural gas consumption

Introduction

The purpose of this report is to systematize and present information on the result of a study to establish a relationship between the volume and temperature of the natural gas used in the domestic sector and the relationship of these parameters to the ambient temperature as a key factor in predicting the consumption of natural gas.

Natural gas, like all gases, is a highly compressible fluid and its volume depends on and varies according to the pressure and temperature at which it is measured. In the gas practice basic conditions are defined, characterized by a fixed temperature and pressure conditions under which to trade with natural gas. For basic comparison conditions, when measuring physical quantities such as volume, reference and measurement conditions are used, which are published in BDS EN 13443 and are 20 °C (293.15 K) and 1 atmosphere (101 325 Pa).
Correct determination and metrologically accurate measurement of the volume of compressible fluids, as well as the natural gas used in households, is related to the ability to obtain accurate gas pressure and temperature data in the so-called working conditions. This data must be consistent with the exact moment at which the flowmeter reads the volume of the gas passing through it.

The consumption of natural gas in household consumers is measured by flowmeters without built-in temperature or pressure correction. The technology for determining gas consumption in this case is related to adjusting the monthly reporting volume in accordance with the average temperature \( T \) and atmospheric pressure \( P \), and not so much with a compressibility factor \( Z \) which is acceptable to the extent that the correction coefficient of over-compression \( K_z \) at compressibility factor \( Z \) which is acceptable to the extent that the correction coefficient of over-compression \( K_z \) at atmospheric pressure is with a value determined by BDS EN ISO 12213-2 (http://www.bgc.bg/zfactor/AGA8-92DC_clear.php?).

In accordance with the state-of-the-art technology in the measurement, the temperature and pressure correction can also be performed on-site by using temperature and pressure sensors that are mounted in place called “Smart” flow meters that are integrated into the Commercial Metering Tool (CMT) and are capable of a one-way or a two-way commands and data transfer. As long as this type of flow meters is not yet widely used, correction factors are used to recalculate the volume of gas, mainly related to the need to recalculate the volume of gas from temperatures close to 0° C (for the heating season) to 20 ° C (КЕВР, Показатели за качество..., 2004).

Most EU countries have solved this problem by selecting 0° C for base conditions and thus minimizing the error of lack of temperature correction in the winter months, Table 1 (BDS EN 13686; 1998).

In real terms, for companies supplying gas to consumers, most of the commercial metering devices (CMDs) are from batches that do not have the ability to recalculate the volume of gas at a standard temperature (20 °C). In these cases, the use of a technique to give an idea of the actual temperature of the gas used (Филков, 2010) is important for the accuracy of reporting and gaining confidence from gas users.

This study ends with several conclusions and suggestions that, in our opinion, would minimize the possibility of technical discrepancies between the actual amount of household gas used and that reported by the flow meter.

Table 1  
Basic temperature conditions at which natural gas is traded in countries around the world

<table>
<thead>
<tr>
<th>#</th>
<th>Country</th>
<th>Conditions</th>
<th>Temperature, °C</th>
<th>Pressure, Pa</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Austria</td>
<td>0</td>
<td>101 325</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Belgium</td>
<td>0</td>
<td>101 325</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Bulgaria</td>
<td>20</td>
<td>101 325</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>UK</td>
<td>15</td>
<td>101 325</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Germany</td>
<td>0</td>
<td>101 325</td>
<td></td>
</tr>
</tbody>
</table>

Scope of the problem

The reached length of the urban distribution network in the developed gas supply regions is more than 1590 km and continues to increase. In these networks-260000 potential of consumptions (Николоу, 2007), the distances that natural gas passes from the point of reading its physical parameters into the points of entry to the populated areas, the automatic gas regulator stations (AGRC), to the points for measuring and reporting natural gas to consumers, are significant. The measurement of these input parameters can not be related to the physical state of the gas in the places where the consumed amount of household gas is taken into account. In addition, the use of temperature correction (temperature-correcting and volume-correcting) commercial metering devices (CMDs), as discussed above, is not wide-spread.

At the same time, precise information about temperature and absolute gas pressure is essential for the accuracy in accounting for and invoicing the actual amount of gas consumed.

To solve the problem described, a survey was conducted and three control samples were collected to gather data about:
- Average monthly air temperature for the surveyed region;
- The hourly consumption of gas for three types of objects surveyed;
- The air temperature in the vicinity of the flow meter location;
- Soil temperature in the studied region.

Processing of the task

Experiments include the sequential installation of two flow meters that measure the volume of gas simultaneously. The flow meter (1) is of the GMT G 2.5 type, with no gas temperature readout, and the second flowmeter (2) is the Galus 2100 TCE type, which recalculates the gas volume according to its temperature. In the monthly reports on flowmeters 1 and 2 there is a difference between the registered gas volumes due to the use of the temperature correction in the flowmeter 2 automatically performed by the CMD. From the ratio of the reported quantity of gas from the two flow meters, applied to a specific period (month), it is also possible to establish the value of the correction coefficient for the studied region under the conditions specific to it. With the obtained coefficient, the readings of the flowmeters in the region are corrected for each reported period.
The sequentially located flow meters are a very good basis for continuing the experiment. However, they do not provide sufficient data which, by processing as information, allows us to conclude how the temperature of the gas is influenced by the ambient temperature and what the dependence of gas consumption on this temperature is. To achieve these goals, the experiment has been extended and has passed the next scheduled stage.

In order to establish the actual gas parameters (temperature and pressure) recorded at the sale to the customer, an experimental set up with two electronic temperature and pressure correctors connected to existing diaphragm volumetric flowmeters was built. The flow chart is shown in Figure 1. The temperature of the gas and the impulses from the counter of the flow meter are input at the inlet of the corrector 1. At the output of the same corrector, the same pulses are output synchronously, entering the input of the corrector 2. In this way, the corrector 2 simulates the same expense as the pulses are synchronized over time. At the same time, the temperature input of the corrector 2 is fed by the ambient temperature signal. Both pressures of the pressure inlet are supplied with atmospheric pressure. For the purpose of the experiment, the two correctors are synchronized over time and report the data in their memory every hour. Flowmeters are approved under MID, Measuring Instruments Directive.

To find differences and analogies for different types of clients, this scheme has been transferred to 3 sites with the following features:

Object 1: Multi-family house. Research in the period: January-February 2016; High monthly consumption of natural gas; Flow meter located in a cabinet outside the building near the ground;

Object 2: Apartment in a residential building. Research in the period: March 2016; Low monthly consumption of natural gas; Flow meter located on floor 4 of the building;

Object 3: Office space. Research period: December 2015; Flow meter located outside the building at a height of one meter from the ground elevation; Average monthly consumption per customer type.

Essential laws and anomalies in the survey

Considering the daily consumption data and comparing them with the changes in the temperatures of the gas and the air by hours for all three sites, the results are in the direction of:

- In terms of household gas consumption in settlements, the temperature of the gas is strongly influenced by the air temperature, regardless of where the flow meter is located: inside or outside the building (Figs. 2, a, b, c);
- The temperature of the gas follows the temperature of the air tightly, exceeding it by one degree;
- In the case of consumption close to the maximum, realized at minimum temperatures, the gas temperature falls by half to one degree below the air temperature due to the throttle effect obtained in the regulator at the flow meter inlet;
- For all objects, 60 to 70% of gas consumption accumulates during a period when minimum temperatures are measured.

The three studies clearly outline the characteristic dependence of the two measured temperatures. Accordingly, at lower air temperatures the gas temperature is lower and the gas consumption is increased. This difference is in some cases up to 30% and the reason for this is the higher energy consumption associated with compensating for heat loss at low ambient temperatures.

In Figure 2,a in red there is a line describing the change of the gas temperature, and in blue is the line of the change of the air temperature. The measurement period is limited to the broken green line, after which the setup is transferred to another object.

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In this case, the dependence that is obtained when the temperature and the amount of gas used in the household are reduced. In the surveyed period, about 65% of the consumption was recorded at the minimum set temperatures.

The third study has a clearly expressed sine wave of the temperatures obtained during the light and dark of the day. Regardless of the typical increase of the air temperature during
the day, the gas temperature without delay changes in parallel with the air temperature. In this case, there is an increased consumption at minimum temperatures (Fig. 2 c). Figure 2c clearly shows the relationship between air temperature (blue line) and gas temperature (red line).

Fig. 2 c. Temperature in object „C“

At lower temperatures, the consumption is higher and due to the throttle effect, there is a decrease in the temperature of the gas below the air temperature by another degree, a degree and a half.

Impact of soil temperature

Regarding the influence of the temperature of the soil on the gas temperature, we can say that it is essential and determinant in the gas transmission system and does not affect the temperature of the gas from the gas distribution networks. Of relevance to this topic are the following observations.

The 24-hour temperature fluctuations in the snow cover penetrate into small depths (20-30 cm) and as a result, on a monthly basis, they remain relatively constant. The average diurnal temperature of the soil in the depth decreases during the summer and grows in the winter, in the transition seasons (spring and autumn) there is a much more complex distribution of this temperature with depth. The vertical distribution of the soil temperature has a significant effect on the surface layer. In the summer, when the direct sunlight is the main factor in the warming of the soil, the soil under grassy areas at all depths is colder than in the streets and pavements.

In winter, when the predominant role plays the radiation, the soil under the vegetation is warmer than the bare terrain, but in winter the snow cover plays a major role in the formation of the thermal regime of the soil. Snow reflects strongly the solar radiation and at the same time radiates almost as a black body a long wavelength radiation. For this reason, the radiation balance on the surface of the snow, as a rule, is negative. Under the influence of radiation heat loss the surface of the snow is heavily cooled. At the same time, the snow has a small thermal conductivity, increasing with its density.

As a result of the small heat conduction, the temperature inside the snow layer sharply increases with the depth. As a result, the surface temperature of the soil under the snow is always higher than the temperature of the non-snow-covered parts and may affect the ambient temperature of the gas panel in which the flow meter is located.

In addition, the criterion for the thermal properties of the soil is its thermal conductivity. Soil is a bad heat conductor and its average thermal conductivity is 26 times lower than that of water. That is why if the soil is dry the heat transfer is slow. This explains the heating rate on wetter and drier soils. Slow heating of moist soils is due not only to evaporation but also to faster heat transfer to deeper layers. Accordingly, their slow cooling during the night is due to the compensation of heat from the deeper layers.

As a result, we can conclude that the change in the surface layer of the soil may affect the ambient temperature, but since in Bulgaria the CMDs are located in panels and are not outdoors, the main factor influencing the temperature of the gas remains the temperature of the air. These results can also be seen through the SCADA system of the gas company.

Possibility for gas demand prediction

From hourly consumption for the period and gas temperatures, analyzes were made to determine a function describing dependencies between the two parameters.

After a series of samples, it was found that a function of type (1) best describes the daily gas consumption according to the average daily temperature. This function is (Бояджиев, 2012):

$$Y= -1E-04x^3 + 0.0047x^2 – 0.0772x + 0.6197$$ (1)

Investigating the results of the analysis, it was assumed that the functions obtained through data using air temperature gave more accurate estimates.

It can certainly be assumed in the specific case of this study that the ambient temperature (in this case the air) is most correlated with the gas temperature. This conclusion requires that the air temperature be used when determining the correction coefficient for calculating the volume of gas under standard conditions (1 atm. and 20°C).

Conclusions

The survey and research covered a period of 4 months and was realized with the logistic support of colleagues from the gas distribution company of Overgas Network AD.

Investigating the results of the analysis, it was assumed that the functions obtained through data using air temperature gave closer results to those with the gas temperature. It can certainly be assumed in the specific case of this study that the ambient temperature (in this case the air) is most correlated with the gas temperature. This conclusion makes it necessary to use the air temperature when determining the correction coefficient for calculating the volume of gas under standard conditions (1 atmosphere and 20°C).

Most of the gas consumption is realized in the periods when the air temperature is close to the minimum registered value. This observation determines the need to adjust the volume to
give a greater weight to the average minimum temperature to form a correction factor when needed.

In the case of correction coefficients for temperature set on the basis of average monthly temperatures possible technical losses on the volume of natural gas for thin client (100 m³ / monthly consumption) could reach 2.8% relative value, while for large domestic customers (300 m³ / month) - a relative error in the order of 2.4%.

The possible SOLUTION is in two directions: The first option does not require capital costs but requires a change in the regulatory environment and consensus in the gas community.

We propose the basic conditions for trade in natural gas to be changed to 0°C. Such is the good practice studied in developed gas countries like Germany, France, Spain, the Netherlands, Italy and others.

The second option will give the most objective results with respect to the reported gas quantity both for the seller and the customers and is related to the replacement of flowmeters with those capable of performing at least temperature correction of the measured volume of gas.

We consider this correction to be key in measuring accuracy. The other pressure adjustment is also important, but the pressure at the flow meter input is a controllable quantity and the process itself is under the control of network operators.

Only in this option it is not necessary to apply a medium-weighted coefficient to all users, which will inevitably place a particular group in a more favorable situation and will be less favorable as an approach to other consumer groups.

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INCIDENTS IN NATURAL GAS TRANSPORT

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ABSTRACT. Attempting to reduce greenhouse gas emissions makes natural gas highly preferred fuel, as evidenced by statistics. Safety and efficient fuel transportation to distribution networks have been posing more and more challenges to facilities and people. Statistical analysis of gas pipeline incidents in production and transportation is presented. This shows different types and frequency of incidents. Quantitative analysis of the main reasons for emergency leakage from transmission pipelines is made. Event trees are mapped showing likelihood of various emergency scenarios leading to fire, jet fire, vapor cloud explosion, and non-ignition dispersion. There is a need for a national regulation of different standards for emergency planning that are not yet in place in our country.

Keywords: natural gas, transport, incidents

INCIIDENTI ПРИ ПРЕНОСА НА ПРИРОДЕН ГАЗ

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РЕЗЮМЕ. Стремежът към намаляване на вредните емисии в околната среда прави природния газ изключително предпочитан гориво, което се доказва от статистиката на добива. Предизвикателствата пред съоръженията и човека стават все по-големи в усилията им да транспортират безопасно и по най-ефективен начин горивото до разпределителните мрежи. Направен е статистически анализ на данни свързани с добива, транспорта, вида и честотата на инцидентите при тръбен пренос на природен газ. Характеризирани са количественно основните причини за аварийно изтичане от преносни газопроводи. Постройки са държата на събитията, показващи вероятността за реализиране на различни аварийни сценарии, водещи до пожар, факелно горене, експлозия на облак от пари и дисперсия без запалване. Обоснована е необходимостта от национален регламент на различни норми за аварийно планиране, както в страната, така и в света

Ключови думи: природен газ, транспорт, инциденти

Introduction

Natural gas is driving a number of economies around the world, because it is compliant with modern environmental standards. The increased demand has led to the development of gas transmission networks to satisfy the markets. The more the transmission network evolves, the closer they are to settlements and sites. Such gas installations hide potential risks of a larger accident or ecological disaster. To avoid any incidents, it is necessary to thoroughly study documented cases of uncontrolled leakage of natural gas and to analyze the applied prevention methods. For this purpose, a statistical analysis of the frequency of the incidents was made, which allows quantifying the main causes of emergency leakage. This data would allow us to describe possible scenarios of development in case of potential accidents. The survey is centered on the gas transmission network in the European Union. It would serve to assess the risk of future projects in real gas distribution facilities.

Trends in natural gas extraction

The methods of exploration, extraction, storage and transport of natural gas have changed in recent years thanks to technological advances. Initially, the search was carried out by examining folded structures with traces of hydrocarbon accumulation. Given the location of the deposits, this is a long and difficult process. As consumption increases, there is a growing need for more efficient ways to detect raw material. The main purpose of the prospecting is to obtain a detailed picture of the depth and volume of the field before the start of the actual extraction process. In the past the preferred fields were the ones of small depth, great potential and easy access. Nowadays these preferred natural gas sources are exhausted. This fact forces geologists to look for non-standard and innovative methods for discovering new natural gas deposits. The most commonly exploited are the conventional ones, which are located in the so-called “traps”. They are accompanied by the presence of oil and water. With the help of new and innovative technologies in recent years, more and more unconventional fields are being discovered and developed. The raw material is placed in coal or shale layers beneath the surface. In the shale deposits most of the natural gas has already migrated from the rock. Due to the considerable geological differences between the conventional and unconventional fields different technologies for their extraction and processing have been developed (Павлова, Костова, 2012).

As more and more fields are being developed natural gas has become an extremely attractive product. It is expected that the share of natural gas in the global energy market will reach 40% by 2020. This is due to increased electricity consumption
and the replacement of liquid fuels in transportation. (Николов, Божков, 2011). Figure 1 shows the growth of natural gas production over the last quarter of a century. Statistics show that more than one third of the world’s yield is shared almost equally between the USA and Russia.

![Trend of world natural gas extraction](image)

**Fig. 1. Global natural gas extraction**

### Natural gas transport

Due to objective (engineering) and subjective (geopolitical) reasons, transport is perhaps the most difficult part of the gas market. Innovative methods such as Liquefied Natural Gas (LNG), Compressed Natural Gas (CNG), Natural Gas Hydrates (NGH), and others are alternatives to pipeline transport. According to sociological studies, CNG technology is beneficial in small fields and at small distances. For larger distances and fields it is economically advantageous to apply LNG technology or a pipeline transport.

When it is necessary to cross water basins of considerable depth and length, LNG transport in vessels is overpaying the pipeline method. But the LNG technology has significant limitations from economic point of view. The construction of a re-gasification terminal is economically justified with natural gas consumption greater than 12,106 m³/day (Николов, Божков, 2011).

Despite the scientific and industrial advances in natural gas transportation methods, the pipeline remains the main and most preferred one. Different types of gas pipelines are differentiated depending on their purpose. In the primary yield prior to purification and obtaining the final product, the gas together with the desired and undesirable substances are transported to processing plants through small diameter pipelines. After processing the raw product to the desired state the product is distributed via a gas transmission pipeline system. This way the gas reaches the global distribution network.

The aim of this report is to provide more information on the transmission gas pipelines. They operate under high pressure and they are controlled by different compressor stations depending on the length of the pipeline and its capacity. Feed stations that lower the working pressure of the main gas pipeline are the ones that manage the gas distribution network in urban and industrial areas.

### Accidents in gas pipeline transport

Highway pipelines are facilities of fundamental importance for the security of energy supply. Any failure in them causes delays, reductions or suspensions of deliveries. This results in inconveniences and/or losses to the end user. This conclusion is based on studies and reports conducted by European Gas Pipeline Incident Data Group (10th Report of the European Gas Pipeline Incident Data Group 2018, 9th Report of the European Gas Pipeline Incident Data Group 2015, 8th Report of the European Gas Pipeline Incident Data Group 2011). These reports have collected data from 17 gas distributors and from stations across 142,794 km of gas pipelines.

The frequency of accidents on transmission pipelines is calculated as the number of incidents over a given period of time is divided by the total length of functioning gas pipelines in the same period as presented in Table 1. An accident is any uncontrolled (unmanageable) leakage of natural gas from a steel pipeline which is on shore.

<table>
<thead>
<tr>
<th>Year</th>
<th>Number of incidents</th>
<th>Frequency [10^-6 km⁻¹]</th>
<th>50% LL</th>
<th>50% UL</th>
</tr>
</thead>
<tbody>
<tr>
<td>1977</td>
<td>38</td>
<td>0.372</td>
<td>0.351</td>
<td>0.394</td>
</tr>
<tr>
<td>1978</td>
<td>45</td>
<td>0.358</td>
<td>0.340</td>
<td>0.375</td>
</tr>
<tr>
<td>1979</td>
<td>44</td>
<td>0.350</td>
<td>0.333</td>
<td>0.372</td>
</tr>
<tr>
<td>1980</td>
<td>47</td>
<td>0.345</td>
<td>0.328</td>
<td>0.363</td>
</tr>
<tr>
<td>1981</td>
<td>46</td>
<td>0.340</td>
<td>0.324</td>
<td>0.356</td>
</tr>
<tr>
<td>1982</td>
<td>42</td>
<td>0.342</td>
<td>0.327</td>
<td>0.359</td>
</tr>
<tr>
<td>1983</td>
<td>53</td>
<td>0.360</td>
<td>0.341</td>
<td>0.379</td>
</tr>
<tr>
<td>1984</td>
<td>48</td>
<td>0.350</td>
<td>0.332</td>
<td>0.369</td>
</tr>
<tr>
<td>1985</td>
<td>51</td>
<td>0.360</td>
<td>0.341</td>
<td>0.379</td>
</tr>
<tr>
<td>1986</td>
<td>51</td>
<td>0.360</td>
<td>0.341</td>
<td>0.379</td>
</tr>
<tr>
<td>1987</td>
<td>58</td>
<td>0.372</td>
<td>0.351</td>
<td>0.394</td>
</tr>
</tbody>
</table>

The statistical data from the EGIG reports show that by increasing the diameter and thickness of the tube wall the number of incidents decreases. This information is a basis for starting an average frequency of 95% above the upper limit confidence interval.

\[
F = 0.275 \text{ events}/(\text{km} \cdot \text{year})
\]  

The occurrence of an emergency event is a consequence of many factors which may subsequently be established or not. The reasons for uncontrolled leakage of natural gas are classified by EGIG statistics as:

- External impact from activities carried out by "third parties" near the pipeline leading to external damage to the pipe, including: agricultural activities, construction, road construction, etc.;
- Construction defects and material defects, including tearing, installation errors, poor welding, etc.
- Corrosion - external and internal, galvanic, cracks;
- Earth moving - landslides, earthquakes, breakdowns, floods and mining activities;
- Operator error during hot tap made;
- Other and unknown - project error, lightning, maintenance, and other uncertain.

Figure 2 presents the distribution of incidents occurrence according to the registration periods.
The accidents caused by gas leakage can damage the gas pipeline to varying degrees, which requires a fault classification. According to the latest 10th EGIG report from 2018 they are directly related to the size of the facility. Depending on the size of the hole, we distinguish three types of uncontrolled leaks through:

- Pinhole – a hole less than 2 cm in diameter;
- Hole – a hole greater than 2 cm in diameter and less than or equal to the diameter of the pipe;
- Rupture - the diameter of the hole is larger than the diameter of the pipe.

Table 2.  
Frequency [F] of accidents for reasons  

<table>
<thead>
<tr>
<th>Reason</th>
<th>Hole size</th>
<th>F per 1,000 km/year</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pinhole</td>
<td>Hole</td>
</tr>
<tr>
<td>External impact</td>
<td>0.0169</td>
<td>0.0197</td>
</tr>
<tr>
<td>Corrosion</td>
<td>0.0360</td>
<td>0.0014</td>
</tr>
<tr>
<td>Construction defects</td>
<td>0.0227</td>
<td>0.0016</td>
</tr>
<tr>
<td>Operator error</td>
<td>0.0043</td>
<td>0.0014</td>
</tr>
<tr>
<td>Earth moving</td>
<td>0.0069</td>
<td>0.0085</td>
</tr>
<tr>
<td>Others</td>
<td>0.0126</td>
<td>0.0016</td>
</tr>
</tbody>
</table>

The listed variables are as follows:

\[ P(A|B) = \frac{P(B|A)P(A)}{P(B)} \]  \hspace{1cm} (2)

The Modeling of emergency events

For the purpose of this study, a probability of random events are modeled. Such events can occur everywhere. For example, in the case of failure of a technical device the data presented in the incident reports using Basis theorem [2], it is possible to calculate the conditional probability of realization of each scenario, to construct events trees and to determine the relative frequency of the accident scenarios to the final consequences (losses).

Different types of pipeline structure problems: breakthrough, hole or rupture. The distribution of frequencies between these three types in gas pipeline is shown in Figure 3.

Fig. 3. Event tree

Applying the model shown in combination with statistics from EGIG reports allows us to build event trees for each type of uncontrolled leakage (breakthrough, hole, rupture) of natural gas, depending on the cause of occurrence. Figures 4, 5 and 6 show contingency probabilities for accidents.

Fig. 4. Events tree – Pinhole

Any development (scenario) of the emergency leakage leads to a different, eventually extreme emergency event - different forms of combustion or dispersion.

- EX - Explosion. Rapid combustion (deflagration or detonation). Very often after the explosion the gas continues to jet fire (JF);
- JF – Jet fire (Jet Fire). It is combustion in the gas stream, limited by the range of gas ignition, i.e. by mixing it with air that the jet ejects upon its leakage from the pipeline breakdown;
- FF - Deflagration burn (Flash Fire) in an unlimited gas cloud, which creates a limited overpressure for a short time. It occurs in an environment where combustible gas and air form a combustible gas-air mixture. The flame front moves rapidly into the combustible mixture and accelerates but does not reach the speed of the sound. This is deflagration burning at a speed of several tens of meters. Compared to the explosion, combustion is so slow that the combustion gas expands prior to the ignition and can not form an open airborne wave with energy sufficient to cause damage;
- VCE - Vapor Cloud Explosion;
- Dispersion (DISPERSION) or distribution of gas without ignition.
gas transport projects. These new projects must also be safer than before.

For conventional pipe conveyance, the analysis of the incidents outlines the following main conclusions:

As the depth of laying increases as well as the wall thickness of the main pipelines, the incidents decrease. Modern solutions are rightly oriented to anti-corrosion protection - both internal and external, in view of the events (Fig. 2).

Increasing the age of existing pipelines increases the likelihood of incidents caused by corrosion.

Incidents caused by the movement of earth masses and of unexplained nature have increased in recent years.

The extensive study of accidents in the natural gas facilities has led to constantly decreasing incidents in the growing gas pipeline network across the EU.

The EU’s clear policy of achieving energy independence for its member states, including Bulgaria, recommends of interconnector links in the Union. The implementation of these projects is related to the assessment of safety risks in the design, construction and operation of the facilities.

New natural gas facilities will require a thorough examination of the problems related to the lack of standards for emergency (short-term) planning of atmospheric pollution from natural gas combustion products in incidents.

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Fig. 7. Emergency natural gas event tree with probability in cases of kilometer per year (events/year)
EMERGENCY ACTIONS AND NEUTRALIZATION OF OIL SPILLS

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ABSTRACT. In the exploitation, production, transport and storage of oil resources there is a risk of oil spills. In the marine environment, these spills cause serious environmental damages. The International Convention for the Prevention of Pollution from Ships (MARPOL 73/78) and other international conventions have led to a significant reduction of oil spills worldwide, regardless of the increasing volume of oil trade and the expansion of exploration and production of oil at sea. Despite these remarkable improvements, oil spills continue to occur throughout the world. Statistics show that between 1.7 and 8.6 million tons of oil are spilled each year in the world seas and oceans, more than 70% of which are directly related to human activity. Every oil spill has different characteristics and most appropriate neutralization method should be selected according to the spill type. In the present material are presented various engineering solutions for neutralizing oil spills, aiming at minimizing the negative effects and securing the affected areas.

Keywords: oil spills, neutralization, health, safety, impact on the environment, sustainable development

Introduction

The contemporary period of development of society is characterized by ever-growing contradictions between man and the surrounding environment.

Such a contradiction is the use of hydrocarbons as a major source of energy, as well as of vital products such as plastics, lubricants, fertilizers and chemical raw materials, all of which will continue to be necessary in the future. Current trends in energy consumption show that this situation is unlikely to change much in the future. In fact, the production and consumption of oil and petroleum products are increasing globally (Figure 1), and hence the risk of pollution. The growth of the Bulgarian economy leads to a significant increase in energy consumption and with it the import of liquid fuels. The ports, as part of the transport and technology infrastructure, represent strategic entry portals for the supply of petroleum products. At the same time, they are trying to attract transit oil-gas transmission complexes and to develop exploration wells in the exclusive economic zone of the Bulgarian Black Sea section (Shutko, Gavrilov, 2009).

Fig. 1. Global crude oil production (https://commons.wikimedia.org/wiki/File:World_Oil_Production.png)

All this leads to an unavoidable increase of the risk related to developing emergency situations such as oil spills.
Sources of oil spills and their consequences

The discharge of oil from ships, offshore platforms or the transport of oil through pipelines is the result of both accidental and "normal" operational discharges.

Accidental discharges (oil spills) arise when vessels collide or are at distress into the sea (engine disruption, fire, explosion) and break down near the shore, when there is a leak from offshore drilling rig or when a pipeline breaks down. Many things can be done to avoid incidents, but there will always be unfortunate situations that cause incidents.

Operational discharges, on the other hand, are predominantly intentional and "routine" and, to a very large extent, can be effectively controlled and avoided. The main sources of oil spills are all transport - technological and transportable engineering - technical facilities, namely:

Sea ports and oil terminals

Some of the most common risk areas for possible oil spills are the approaches to ports and waterways, ports themselves and especially oil terminals (Fig. 2), which by definition are with intensive maritime traffic, hence it always involves risk. Oil terminals are high-risk facilities due to the significant quantities of oil and petroleum products stored in them as well as due to the need to be in close proximity to the sea, since the main method of supplying them is through tankers.

Stationary and floating oil production and oil exploration platforms

The platforms (Fig. 3) intended for permanent use are designed with a very high safety factor and increased criteria for preventing oil spills and ensuring environmental protection. However, the security measures taken are not always sufficient. The most typical oil "eruptions" are caused by equipment failure, corrosion, human error and extreme natural impacts.

Pipelines

As risk areas for possible emergency oil spills from pipelines can be defined all modular connections and overload hoses of the pipelines (Fig. 4). They are usually equipped with highly reliable and duplicated system pressure monitors as well as early warning systems for faults, and their cellular structure limits possible spills to the amount of a single section. The reasons for these spills can be varied - defects and corrosion of the material, erosion of the underlying earth layer, tectonic movements, damages from ship anchors and bottom trawls.

Maritime transport and specialized vessels for oil transport

Maritime transport is one of the least polluting types of transport. Nevertheless, the tankers are huge, not maneuverable and despite the modern tendencies for their construction with double hull, very vulnerable as construction vessels (Fig. 5). Several times a year ships deviate from their course due to technical failure, bad weather or human error and cause more than 50% of the total spilled oil each year. From the point of view of the risk of terrorist attacks, the tankers have no protection.
Natural sources
Hydrocarbons have been discharged into the oceans and seas by natural hydrocarbon seepages (oil springs) on the seabed and along the coast for thousands of years (Fig. 6). These springs are fed by naturally accumulated hydrocarbons that emerge on the surface through faults and cracks.

The effects of the oil spills
They can be as different as the sources themselves. The size of the spill affects the type of the environmental damage though it is not the only factor of significance. In some cases, like that of Atlantic Empress, for example, despite the huge amount of oil spilled, the observed environmental consequences are negligible. While the effects of a spill from Exxon Valdez, which is almost 8 times smaller than that of the Atlantic Empress, are colossal.

Fig. 6. Natural hydrocarbon seepage on the seabed

Exxon Valdez oil spill covered about 2100 km of coastline and caused the death of between 100,000 and 250,000 seabirds, about 2,800 otters, about 12 river otters, 300 seals, 247 eagles, 22 orcas, and an unknown number of salmon and herring. 1400 ships, 85 helicopters and 1100 people were involved in the cleaning of the spill, and Exxon paid up to $ 4.5 billion for cleaning and damages. The effects of the oil spills can be divided into two main types - environmental and economic.

The environmental consequences are related to the effect, damage or complete destruction of animal species, plant species and even entire habitats. Typically, for oil spills at sea, most affected are the animal species whose natural environment and existence are closely related to water.

The economic consequences are related to disruption of the normal functioning of various sectors of the economy dependent on the sea. If an oil spill reaches, for example, tourist beaches, they become unfit for visitors, from which coastal communities and businesses (hotels, restaurants, and attractions) depend heavily. Another sector which is heavily affected by oil spills is fishing and fish farming.

Historical overview of oil spills
Oil spills had occurred into the environment through cracks and breaks before mankind began its use. Probably the first man-made oil spills occurred shortly after Aug. 27, 1859, when industrial mining began after Edwin Drake’s oil drill reached oil for the first time in Pennsylvania.

Although catastrophic spills nowadays occur relatively rarely, smaller ones are frequent phenomena. Such spills occur from oil exploration, oil extraction activities, shipments of oil through ships, pipelines, rail and road tankers. In addition, frequent spills are caused by the consumption of petroleum products, e.g. by vessels that transport oil only as fuel.

It is important to note that in most sources of information, oil spills are measured in tons, with one tonne approximately equal to 7.33 barrels or 1165 liters. In this calculation, an average value of 0.858 (33.5 API) is used for the specific gravity of the oil, although these values may range from below 0.770 to above 1. For this reason, the actual volume of spilled oil is difficult to be measured, in most cases the values that are given are approximate.

Analysis of the trends in the oil spills
An integral part in the planning of measures for oil spill response is the study of oil spills over the previous years as well as the study of possible sources (Fig. 7). Such sources, for example, are vessels, pipelines, oil platforms, land transport, etc., often requiring different methods of response.

![Fig. 7. Ratio between the different sources of oil spills and the quantities spilled oil for a decade between 1970 and 1999](image)
An analysis of the trends of areas suffered oil spills was made by analysts of the Oil Spill Intelligence Report, who reported that since 1960, spills of 10000 gallons and more have occurred in 112 countries. However, some areas suffer more spills than others, such as:

- The Gulf of Mexico - 267 spills;
- Northeastern US coast - 140 spills;
- The Mediterranean Sea - 127 spills;
- Persian Gulf - 108 spills;
- North Sea - 75 spills;
- Japan – 60 spills;
- Baltic Sea - 52 spills;
- Great Britain and La Manche Channel - 49 spills;
- Malaysia and Singapore - 39 spills;
- The west coast of France and the northern and western coasts of Spain - 33 spills;
- Korea - 32 spills.

According to the International Tanker Owners Pollution Federation (ITOPF), as a result of vessel incidents (without calculating spillages from oil drills and spillages during wars such as that in the Gulf 1990-91, which totaled over 1.5 million tons of crude oil) for the 1970-2016 period globally, vessels have spilled approximately 5.73 million tons of oil, with more than half of that quantity being spilled in the 1970s (Fig. 8).

The spills in recent years have dropped drastically, from around 319,000 tons per year in the 1970s to around 19,600 tons per year in 2000-2009 and slightly below 5,600 tons per year over the period 2010-2016 (Table 1).

### Table 1
**Quantities of oil spilled from vessels during the decades 1970-2016 (ITOPF 2017).**

<table>
<thead>
<tr>
<th>Year</th>
<th>Quantities of oil spilled from vessels (t)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1970-1979</td>
<td>3 192 000</td>
</tr>
<tr>
<td>1980-1989</td>
<td>117 5000</td>
</tr>
<tr>
<td>1990-1999</td>
<td>1 134 000</td>
</tr>
<tr>
<td>2000-2009</td>
<td>196 000</td>
</tr>
<tr>
<td>2010-2016</td>
<td>39 000</td>
</tr>
</tbody>
</table>

Today, the volume of oil spilled by vessels is a small part of the total volume delivered safely to its destination each year (Fig. 9). The reported total quantity of oil spilled in the environment in 2016 is approximately 6000 tons and the total quantity of oil and oil products transported by sea in the same year is approximately 3055 million tons.

It is important to note that the volume of spilled oil for a year can be seriously affected by just one large spill. Such examples are the spills from AMOCO CADIZ (1978) - 227,000 t, ATLANTIC EMPRESS (1979) - 287,000 t, Kxtoc 1 (1979) - 470,000 t, CASTILLO DE BELLVER (1983) 250 000 t, EXXON VALDEZ - 37 000 t, ABT SUMMER (1991) - 260 000 t, Deepwater Horizon (2010) - 670 000 t.

**Behaviour of the oil spill**

When an Oil or petroleum product is spilled into the sea, it undergoes many processes. The aggregation of these processes is called the behavior of the oil spill (Fig. 10).

The development and the effect of a spill is determined by its behavior. For example, if the oil evaporates quickly, the cleaning will be easier and more dangerous, due to saturation of the atmosphere with the evaporated hydrocarbons. In another case, the oil spill may be attributed to surface currents or winds in the vicinity of polluted areas or to the coast where it will cause severe damage to the environment as well as to the economy of the state. On the other hand, the slick can be taken to the sea where it is naturally dispersed and has less direct impact on the environment and almost none on the economy.

For this reason, a detailed knowledge of the behavior of the oil spill is essential to anticipate its environmental impact and to develop effective cleaning strategies.
The first group of processes that influences the behavior of the oil are those of the weathering, they represent a series of processes in which the physical and chemical properties of oil are changing. These processes are not permanent and change over time (Fig. 11) and are almost entirely determined by the type of oil or petroleum product, as well as by environmental conditions.

Fig. 11. Time characterization of processes influencing the behavior of the oil spill (ITOPF 2011)

The second group of processes is related to the movement and distribution of oil on the sea surface. Unlike weathering processes, they depend to a lesser extent on the type of oil or petroleum product and more on the weather conditions.

When looking at the behavior of an oil spill in the sea, a distinction is often made between persistent and non-persistent oil (Fig. 12).

Fig. 12. Sustainability of spilled oil in the marine environment (ITOPF 2011)

As a general rule, persistent types of oil and petroleum products dissolve and disperse slowly in the marine environment and usually require cleaning. They usually include some types of crude oil, lubricants and heavy diesel used by ships. These types of oil pose a potential threat to natural resources when spilled, in terms of impacts on wildlife, habitat suffocation, and oiling of tourist beaches.

By contrast, non-persistent types of oil and petroleum products are rapidly dispersed by evaporation. As a result, the spill of such petroleum products rarely requires active cleaning. Non-persistent types of petroleum products include gasoline, light diesel and kerosene. The effects of such spills may include staining on vessels in ports and at high concentrations - acute toxicity to marine organisms.

Oil spill response methods

There is not yet a fully satisfactory method of dealing with large oil spills, although many of them in the last decades of the 20th century have made great advances in the technologies for monitoring, response and cleaning, as well as in their management and coordination.

In essence, the response to oil spills aims to hold, collect and remove enough of the spilled oil to resume the affected economic activities, and the processes of natural recovery of the marine environment to cope with the remaining quantity as quickly as possible and with minimal residual negative impact.

The methods currently in place to treat oil spills are diverse and their knowledge is essential.

For example, in order to determine the likely migration path and potential spill area, different monitoring tools such as aero monitoring, GPS tracking buoys, and satellite imagery may be used.

Floating containment booms can be used to limit the spill, which may be positioned around the spill source or the inlets of rivers and canals, ports, water inlets, and around sensitive areas such as protected areas and reserves. For collecting spilled oil, it is possible to use skimmers and pumps to physically separate the oil from the water and collect it in collecting tanks. Another approach to such separation is the use of various natural or artificial sorbents (e.g. straw, sawdust, polyester and polyester fibers, polyurethane, polypropylene, etc.) to absorb the oil from the water, and afterwards to retrieve it after their collection. Where appropriate, it is permissible, to use surfactants and solvents and to disperse them over the slick to aid the natural dispersion of oil into the sea and thus to accelerate its biodegradation.

In any case, the most important decision-making point - which method of response to oil spill to be applied is the "Net Environmental Benefit Assessment" (NEBA). This is a structured approach and an important process used by the authorities involved with the management and stakeholders during the preparation, planning and cleaning of the oil spill.

Operations to tackle oil spills depend to a large extent on their size. For this reason, depending on the amount of spilled oil, spills are classified into three groups (Национален аварийн план, София, 2011):

- Small spill - from 1 to 25 t;
- Average spill - from 25 to 1000 t;
- Large spill - more than 1000 t.

Means of monitoring

The concept of pollution monitoring includes the comprehensive set of measures and systems for assessment and remote monitoring of oil pollution. These are, for example, vessels and aircraft specially equipped with Side Looking
Airborne Radar (Fig. 13); sensors for measurement in different areas of the electromagnetic spectrum (optical, infrared or ultraviolet); drones for visual observation; tracking buoys; satellite imagery; sampling equipment.

Spill monitoring tools allow us to: accurately determine the coordinates of the slick; determine the size of the slick and the direction of growth; determine the direction of movement of the slick, the prevailing meteorological conditions and the state of the sea; determine the slick's proximity to economically important sites and ecologically sensitive areas; determine locations for cleaning operations where they will perform most efficiently; identify the highest concentrations of hydrocarbons; target the means for treating the spill; report on the effectiveness of cleaning operations; monitor the natural dispersion of the spill.

The active method of application is where the booms are actively used to contain and recover offshore oil through a variety of systems and configurations depending on the intended purpose and available resources.

The active use of oil booms is the most commonly used and preferred method of oil spill response. The collection is carried out by their controlled dragging through the oil slick, retaining and concentrating the oil from the water surface into a dense layer to allow more efficient subsequent pumping by skimmers and pumps.

Such a dragging is usually done by a combination of boats in the "J" (Fig. 15), "U" or "V" (Fig. 16) configuration, by single-vessel oil spill recovery systems (Fig. 17) or through utilization paravane systems (Fig. 18).

Oil Booms

Actions to control/liquidate oil spills begin by physically restraining or stopping of the oil leakage from the source, limiting and collecting freely floating oil before spreading over large areas and reaching the shore. Such physical retention and collection is a preferred method in the oil spills response and is usually carried out by the deployment oil booms. There are two basic methods for the use of booms - Passive and Active:

In the passive method, the booms are fixed at key positions in order to minimize the impact of the oil on the protected zone (Fig. 14).

In the active method, the booms are used to contain and recover offshore oil through various systems and configurations depending on the intended purpose and available resources.
Fig. 17. Single-vessel double-sided oil spill recovery system (IOGP Report 522, 2015)

Fig. 18. Paravane (IOGP Report 522, 2015)

System for collecting of oil spills through collection screens (Sweeping arms)

These systems are very similar to the single-ship two-sided collection systems, but solid collection screens are used instead of booms (Fig. 19). These systems allow oil spills to be collected at worse meteorological conditions than the maximum allowable for use of oil booms; therefore, they are often preferred as reserve equipment.

System for controlled in-situ burning

This is a process of controlled burning of oil floating on the water surface near the spill site (Fig. 20). In order to carry out such combustion, the oil should be concentrated and a source of ignition applied. Under ideal conditions, incineration on site has the potential to remove relatively large quantities of oil from the sea surface and hence the dangers it can cause to ecosystems and the environment.

Fig. 19. Oil collection system via sweeping arms

Fig. 20. Controlled burning of oil on the sea surface (IOGP Report 523, 2015)

Dispersants

The use of dispersants is one of the most effective methods to minimize the environmental and socio-economic consequences of a spill. With proper and timely implementation, they can significantly hamper the penetration of a spill in coastal habitats and tourist areas as their use significantly increases the rate and degree of natural dispersion of the oil under the action of the waves, thus promoting the processes of its natural biodegradation, by reducing the surface tension in the contact surface between oil and water, which facilitates oil breakdown of very small oil droplets under the influence of waves.

Dispersants are a mixture of two or more surfactants in a solvent. Each surfactant molecule contains an oleophilic part (attracts oil) and a hydrophilic part (attracts water), thus engaging with both the oil molecules and the water simultaneously (Fig. 21).

The formation of small droplets of dispersed oil in the water column makes oil much more easily available to naturally occurring hydrocarbon-degrading microorganisms (Fig. 22), so that the possibility of biodegradation increases significantly.

Fig. 21. Operation method of surfactant (IOGP Report 532, 2015)

Fig. 22. Hydrocarbon-degrading microorganisms - converting hydrocarbons into carbon dioxide (CO₂) and water (H₂O) (IOGP Report 532, 2015)
Sorbents

Sorbents are a wide range of organic, inorganic and synthetic products designed to collect and retain oil from the water. Their composition and configuration depend on the material used and their intended use.

Sorbents are most effectively used during the final stages of coastline cleaning to collect small amounts of oil that cannot easily be recovered by other cleaning techniques.

They are not suitable for use on the high seas and are generally less effective in more viscous types of oil (such as heavy fuel oil) and in highly weathered or emulsified oil, although some sorbents are specially formulated for use in more viscous oil types.

A wide variety of materials can be used as sorbents. These include: organic materials such as peat, sawdust, paper pulp, agricultural crops, cork, chicken feathers, straw, wool and even human hair; inorganic materials such as vermiculite and pumice; synthetic materials (Fig. 23) such as polypropylene and other polymers.

Synthetic sorbents are usually most effective in extracting oil. In some cases, they can achieve a ratio of collected oil to sorbent of 40:1 compared to 10:1 for organic products and only 2:1 for inorganic materials (National Aromatic Plan..., Sofia, 2011).

Fig. 23. Sorbent sheets. (ITOPF 2012)

Conclusion

Today there is a wide variety of methods for oil spill response. The ultimate goal of all of them is the complete liquidation of the oil spill and the reduction of its harmful effects on the environment and human health.

Achieving this goal requires an adequate strategy based on detailed knowledge of these methods, the impact of weather conditions on them, and the biology and ecology of the endangered region. An essential component of such a comprehensive strategy is to ensure the safety of personnel involved in its implementation.

Oil spill response is a complex process that cannot be managed only by the use of a particular method but must be a combination of multiple techniques and methods for achieving maximum efficiency of cleaning and protecting biological resources.

Another major component in the preparation of an operational plan to respond to oil spills is to ensure safe working conditions for the personnel involved in its cleaning.

Containment and recovery operations are mainly carried out in a variable, unpredictable and hazardous environment (fire and toxic fumes, poor weather conditions). Work in such environments may further increase the operational risks arising from the handling of engineering and technical means to neutralize oil spills. Long working shifts and the non-routine activities that staff must perform should also be taken into account.

For this reason, it is essential to carry out an overall risk assessment of the planned work activities.

The planning and choice of methods for oil spill response should be based on a comprehensive understanding of operational, environmental and logistical constraints, application techniques, as well as knowledge of the potential benefits and negatives which arise by them. It is also important to bear in mind that the effectiveness of all these methods can be seriously affected by the environment.

In any case, such decision-making should be based on an assessment of the net environmental benefit analysis and risk assessment for the health and safety of the working teams involved in the application of these methods.

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SPECTRAL REFERENCE LIBRARY FILLED WITH REFLECTANCE ROCK FEATURES

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ABSTRACT. Remote sensing is applied often in Earth observations. It includes acquiring, processing, and interpreting images and multispectral data, acquired from optical sensors mounted on airborne and satellite platforms. For better object-oriented interpretation of remotely sensed data the reference spectral features of well-described objects are required from laboratory, field, and satellite sensors. In-situ laboratory and field remote sensing measurements provide a significant part of the spectral data for interpreting spectral images with different spatial resolution and creating thematic spectral reference libraries. Including data from different experiments into an accessible reference spectral library ensures their continued exploitation, provides a basis for their qualitative assessment, and allows them to be exchanged between specialists from different research and applied sciences. Creating, updating and maintaining a spectral reference library requires periodic laboratory and field experiments, including spectrometric and other type of measurements, in this case, of rocks. The reflectance rock features are used for updating regularly the library with the necessary information. This study suggests that collected spectral data from the field spectrometric measurements of the different exposed rocks and laboratory spectral measurements of the samples collected in the field campaign will be used for filling in the reference spectral library. The obtained spectral reflectance features could be used in airborne and satellite image classification and for comparison with reference reflectance spectra from other spectral libraries. To obtain the data for filling in the presented spectral reference library, spectrometric systems, assembled in the Department of Remote Sensing Systems at the Space Research and Technology Institute of the Bulgarian Academy of Sciences, based on models of Ocean Optics spectrometers Inc. were used. The spectrometric system TOMS /Thematically Oriented Multi-Channel Spectrometer/ was used to perform laboratory and field spectrometric measurements. Field spectrometric measurements were performed during petrology training on established geological routes. Laboratory spectrometric measurements were performed in the Spectral and Photometric Measurements Laboratory of the Remote Sensing Systems section. The resulting reflecting spectra can be used to classify satellite images and compare them with the reference reflection spectra from other spectral libraries.

Keywords: Earth and planets remote sensing, Earth observations, laboratory and terrain spectrometric measurements, spectral data, spectral library

СПЕКТРАЛНА РЕФЕРЕНТНА БИБЛИОТЕКА ЗАПЪЛНЕНА С ОТРАЖАТЕЛНИ ХАРАКТЕРИСТИКИ НА СКАЛИ
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РЕЗЮМЕ. Известно е, че за изучаване на планетите, се използват различни дистанционни методи на изследване. Също така, при наблюденията на Земята дистанционните изследвания са често използвани. Те включват процесите на получаване, обработка и интерпретация на изображения и многочленни спектрални данни, регистрирани от различни сензори, които са монтирани на самолетни и спътникови платформи. За повишаване на точността при обектио-ориентирана интерпретация на данните от дистанционните изследвания на изучените и добре описани обекти се използват изследванията на измерванията на еталони спектрални характеристики, които се получават от лабораторни, полеви и спътникови сензори. Лабораторните и полевите дистанционни измервания осигуряват значителна част от спектралните данни за интерпретиране на спектрални изображения с различна пространствена разделителна способност и за създаване на тематични спектрални референтни библиотеки. Включването на данни от различни експерименти в достъпна референтна спектрална библиотека гарантира тяхната продължителна експлоатация, осигурява основа за тяхната качествена оценка и позволява получените данни да се обменят между специалисти от различни научни и приложни области. Създаването, актуализирането и поддържането на референтна тематична спектрална референтна библиотека изисква периодични лабораторни и полеви експерименти, включително спектрометрични и други видове измервания на отделни обекти на изследване, в конкретния случай - на скали. Спектралните отражателни характеристики на скали се използват за редовно попълване на създаваната библиотека с необходимата информация. Такъв вид изследване предполага измеряването на спектрални отражателни характеристики на скали при терени експерименти на различни скални разкрития и провеждане на лабораторни спектрометрични измервания на скални образци, събрани от места на провеждане на теренините измервания. В настоящия доклад авторите представят етапите за получаването на даните, генерирането на спектралната референтна библиотека във вида на база от данни и запазването им с получените спектрални отражателни характеристики на скали. За получаване на данните, с които ще бъде запълнена представената спектрална референтна библиотека, са използвани спектрометрични системи, асемплирани в секция „Системи за дистанционни изследвания“ в Института за космически изследвания и технологии към Българска академия на науките, базирани на модели на спектрометри на Ocean Optics Inc. Със спектрометричната система TOMS /Thematically Oriented Multi-Channel Spectrometer/ са проведени лабораторни и полеви (терени) спектрометрични измервания. Теренните спектрометрични измервания са реализирани по време на учебни практики по горноречената програма по утвърдените геоложки маршрути. Лабораторните спектрометрични измервания са осъществени в лаборатория „Спектрални и фотометрични измервания“ към секция „Системи за дистанционни изследвания“. Получените отражателни спекти могат да се използват за класификация на спътникови изображения и да се съпоставят с референтните отражателни спекти от други спектрални библиотеки.

Ключови думи: дистанционни изследвания на Земята и планетите, наблюдения на Земята, лабораторни и терени спектрометрични измервания, спектрални данни, спектрални библиотеки
Introduction

The in-situ reference spectral data are very important in Earth observations for supporting mineral exploration and mapping geology, for recognizing minerals and rocks by their spectral signatures, and for the future planning of satellite missions. Remote sensing measurements made in laboratory and on the field (in-situ) provide helpful information for research studies and for analyzing data from sensors located on airborne and satellite platforms. Analysis of spectral data obtained in the laboratory and on the field, and from various other platforms, requires a knowledge base that consists of different spectral features for known and well-described different objects.

The U.S. Geological Survey (USGS) spectral library is the biggest one and is related both to Earth observations and spacecraft mission planning (Kokaly et al., 2017). The USGS spectral library presents a knowledge base for the characterization and mapping of materials and provides important compositional standards. As part of the spectral library and at the same time as independent thematic spectral libraries the Jet Propulsion Laboratory (JPL) (https://speclib.jpl.nasa.gov/documents/jpl_desc, July 2018), John Hopkins University (JHU) (https://speclib.jpl.nasa.gov/documents/jhu_desc, July 2018), Arizona State University (ASU) (http://tes.asu.edu/spectral/library/index.html, July 2018), the ASTER/ECOSTRESS projects (https://speclib.jpl.nasa.gov/, July 2018), collect spectral data from laboratory and field spectrometric measurements. The JPL and JHU libraries contain reflectance spectra, the ASU library contains emittance spectra and the ASTER library contains both of them. Another spectral library for the storage of spectrometer data and associated metadata is the SPECCHIO spectral database system (Huener et al., 2011). Spectroscopic data are also acquired at the Keck/NASA RELAB (Reflectance Experiment Laboratory) supported by NASA as a multi-user spectroscopy facility (http://www.planetary.brown.edu/relab/, July 2018) and these data are used for filling in the RELAB Spectral Database (http://www.planetary.brown.edu/relab/docs/relab_disclaimer.html, July 2018).

For processing the spectral data from the ASTER Spectral Library and the ENVI Spectral Libraries Spectral Python (SPy) a pure Python module is used. SPy is free, open source software distributed under the GNU General Public License (http://www.spectralpython.net/, July 2018). Thematic spectral libraries in ENVI software could be created using the Spectral Library Builder from a variety of spectra sources, including ASCII files, spectral files produced by spectrometers, other spectral libraries, and spectral profiles and plots. The collected spectra are automatically resampled to an input wavelength space using Full-Width Half-Maximum (FWHM) information (https://www.harrisseospatial.com/docs/spectrallibraries.html, July 2018). In the RELAB the Modified Gaussian Model (MGM) software is used (http://www.planetary.brown.edu/mgm, July 2018).

The USGS spectral library contains information about spectral features and characteristics mainly of minerals and rocks but also of soil and vegetation. Based on the specifics of the researched object, thematically oriented spectral libraries started to be created (Ruby and Fischer, 2002; Fang et al., 2007; Rivard et al., 2008).

The thematic spectral libraries have a significant application in the integration of in-situ measured spectra and specific properties of the studied objects and remotely sensed spectral data (Tits et al., 2013). Applications of the spectral libraries using various methods for processing and interpreting of spectral data have been made (Rivard et al., 2008; Xu et al., 2018).

Laboratory and field spectrometric measurements of rocks have been continuing for more than 30 years performed by different teams from the Space Research and Technology Institute at the Bulgarian Academy of Sciences /SRTI-BASI/. The authors of this study aimed to collect spectral data both from previous own experiments (Avanesov et al., 1989; Borisova, 2002, 2003, 2004, 2013, 2015; Borisova and Kancheva, 2005; Borisova, 2007; Borisova et al., 2008, 2009; Borisova and Iliev, 2008; Borisova et al., 2009, 2010; Borisova and Petkov, 2014), from colleagues’ previous experiments with their agreement (Spiridonov and Chervenyashka, 1984; Lukina et al., 1992; Kancheva, 1999; Stoimenov et al., 2014) and from new ones in order to create a reference thematic spectral library filled with reflectance rock features. It consists of spectral data with metadata and additional information for better interpretation of spacecraft images with different spatial resolution.

The reflectance spectra of representative samples of magmatic rocks from different regions in Bulgaria (Rila Mountain, Stara Planina Mountain, Sredna Gora Mountain) are studied as an example in the present paper. The study proposes collected spectral data from field spectrometric measurements of different rocks and from laboratory spectrometric measurements of the samples collected during the same field campaigns to be used for filling the reference spectral library. For easy access to the spectral library without specialized programs, simple text versions of the spectral data, their visualizations, and text files in HyperText Markup Language (HTML) format with the metadata and additional information are planned to be used. The authors aim to offer the possibility for using the spectral data to specialists working in different research and applied sciences following the procedures for accessing the spectral library and downloading the spectral data.

Materials and Methods

The information for the proposed spectral library will include description of: field and laboratory spectrometric instruments; short petrographic description of the region and studied objects (in this case – rocks); field and laboratory spectrometric measurements.

Field and laboratory instruments

The spectrometric measurements of rock reflectance spectra are performed using laboratory and field spectrometer. The used spectral instrument works in the wavelengths covering the spectral ranges from the visible /VIS/ to the near infrared
The spectrometer used to measure reflectance rock spectra for filling in the reference spectral library is based on models of Ocean Optics Inc. covering the spectral range from 400 to 900 nm. Spectrometric measurements of representative samples of rocks are made in laboratory and field conditions. In some cases, samples were purified, so that the unique spectral features of the studied objects could be related to their typical structure. The field reflectance spectral signatures were obtained with a TOMS /Thematically Oriented Multi-channel Spectrometer/ assembled at the Remote Sensing System Department at SRTI-BAS in collaboration with Alabama State University, USA (Petkov et al., 2005).

In the spectral libraries each spectral characteristic has a description, called also metadata, associated with the obtained spectrum. The metadata describe what was measured and can include details about the measurements made and other supporting information about the nature and composition of the studied object.

**Short petrographic description**

The area of the locality Kirilova polyana (Rila Mountain) consists of high-grade metamorphic rocks, metamorphosed ultrabasic and basic igneous rocks, called South Bulgarian granitoids, aplite-pegmatoid granites and fine-grained biotite granites. (Димитрова, 1960; Кожухаров, 1984; Kamenov et al., 1999)

Spectrometric studies were made of the fine-grained biotite granite. They expose near Kirilova polyana in the west direction and form the Monastic Body. Fine-grained biotite granites are light gray with massive structure and hypidiomorphic texture. The rock-forming minerals are magmatic K-feldspar, quartz, plagioclase, biotite and zircon and secondary - sericite, chlorite and clay minerals (Банушев и др., 2012).

On the road to the village Barziya, about 3 km after the Petrohan pass in Stara Planina Mountain, are revealed magmatic rocks from the Petrohan pluton. It is a complex magma body emplaced into rocks of Berkovska and Dalgidelska groups. It is made of several magmatic phases: the first is gabbro, widespread in the northern part of the pluton near Berkovitsa; the second is represented by diorites, and the third - by granodiorites. The largest areas are occupied by diorites and granodiorites. (Чунев и др., 1965; Хайдутов, 1979; Хайдутов и др., 2012)

Field spectrometric studies have been made of the diorites. They are gray, grey-greenish, medium-grained, and uniform-grained. Their structure is massive, and the texture – prismatic granular. The main rock-forming minerals are plagioclase (andesine) and amphibole, secondary – biotite and augite, and accessory - titanite and magnetite (Банушев и др., 2012).

About 10 km south of the town Zlatitsa in Sredna Gora Mountain on the road to Panagyurishhte, outcrop of the South Bulgarian granitoids is embedded in metamorphic rocks of the Prarodopska group. To the South there are Bulgarian granitoids intrusive bodies of Palaeozoic age, of different sizes and composition, divided into three intrusive complexes. The first set includes intrusive granites, granodiorites and small bodies of diorite and quartz-diorites. In this complex the Smilovenski, Hisanski and Poibrenski plutons are included. The composition of the second intrusive complex includes amphibole-biotite, biotite and light granites. The Koprivshtenski, Kilsurski and Matenishki plutons belong to this complex. The third intrusive complex is represented by granular biotite, biotite-muscovite and pegmatite granitoids. The Strelnchenski, Karavelovski, Lesichovski and Varshilski plutons are presented in this complex. (Дабовски и др., 1972; Мурбат и Загорчев, 1983; Загорчев и Мурбат, 1986; Peycheva et al., 2004)

At the point of the field measurement biotite granites of the Northwest Koprivshtenski pluton are revealed. They are light gray, sometimes rusty colored by iron hydroxides, medium-to coarse-grained, with a clear lineal porphyroid parallelism. They are formed by K-feldspar, plagioclase, quartz, biotite, apatite and zircon (Банушев и др., 2012).

**Field and laboratory measurements**

The results from the terrain spectrometric measurements of pure surface of granites, granodiorites and diorites in the Mountains of Rila, Stara Planina and Sredna Gora in Bulgaria for the period 2007-2017 will be used for filling in the reference thematic spectral library. As a result of these measurements spectral features of the investigated objects will be acquired. The obtained data are processed statistically, and the registration of 100 spectra and their average values is set in the company software used on the spectrometer.

The reference spectral library will also include data from laboratory measurements. The laboratory spectrometric measurements using the TOMS spectrometer are performed by the Remote Sensing Systems Department at SRTI-BAS. The reference spectral library will be filled in with reflectance rock features.

**Example of the structure and content of the presented spectral reference library**

**Spectral data**

Since this will be a spectral library, first come the spectral data, i.e. the results from the spectrometric measurements, both on the field and in the laboratory, for filling in the proposed spectral reference library.

The results of the performed laboratory and field spectrometric measurements are presented as text files containing description of the measured rocks in the presented example: granite, granodiorite and diorite. These spectral data are visualized as plots of spectra. The examples of the spectral reflectance signatures as a result of the laboratory and field measurement are shown on Figure 1 (a,b).

**Metadata**

The next information needed for filling in the proposed spectral reference library is the metadata.

The metadata include information about each measurement such as: dark spectrum, reference spectrum, number of sampled component spectra, integration time, spectra
averaged, correction for electrical dark, number of pixels in processed spectrum, etc. The description of each studied object is also included. Petrographic description of each rock sample, chemical composition of minerals, etc. are given for the presented example. The metadata will be presented in separate text files.

Additional information

In some cases it is possible to collect more information for filling in the proposed spectral reference library called additional information.

The photographs of the studied objects could also be added in the reference spectral library. The photos will be included as files in related image formats (.jpg, .gif).

Fig. 1a. Plot of spectral reflectance signatures of granites (white line), granodiorites (grey line) and diorites (black line) acquired during the laboratory measurements.

Fig. 1b. Plot of spectral reflectance signatures of granites (white line), granodiorites (gray line) and diorites (black line) acquired during the field measurements (all on pure rock surface).

Samples of granite (a,b) studied in the laboratory are presented on Figure 2. Photos of the granites studied in some field measurements are shown on Figure 3.

Fig. 2. Porphyroid granites (a, b) from Šredna Gora Mountain, Bulgaria.
The main aim of the performed spectrometric measurements is to acquire and collect spectral data, in this case - about rocks, for the creation of a specialized thematic reference spectral library and the possibility for exchanging information between existing open access spectral libraries.

Conclusions

In-situ laboratory and field spectrometric measurements provide a significant part of the spectral data for interpreting spectral images with different spatial resolution and in creating thematic reference spectral libraries, in this case – of rocks. Including data from different experiments into an accessible spectral library ensures their continued exploitation, provides a basis for their qualitative assessment, and allows them to be exchanged between specialists from different fundamental and applied sciences. Therefore, it is necessary to have the possibility for complementing the spectral libraries in short periods of time depending on the subject of the survey. Creating, updating and maintaining a reference spectral library requires periodic laboratory and field experiments, including spectrometric and other type of measurements.

At the same time, laboratory and field spectrometric measurements are part of an integrated system for Earth and planets remote sensing and ground observations. In-situ spectrometric measurements have potential for long-term practical application when used to verify data which increases their accuracy. This leads to an optimal correlation between the different methods for measuring and observing the different types of land cover: soils, vegetation, water, rocks, minerals, etc. The creation of a spectral library increases the effectiveness of scientific research in the field of remote sensing on the Earth’s and planets' surfaces, creates synergy between different scientific fields and helps the exchange of information.

For future work, the authors suggest collecting field reflectance spectral features of different rocks and laboratory spectrometric measurements of the samples collected in the field campaign. The obtained spectra could be used for airborne image classification and comparison of the results with the reference spectra of the USGS and other spectral libraries.

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ELEMENTS AND STRUCTURE OF THE NORMAL GEOMAGNETIC FIELD IN THE REPUBLIC OF MACEDONIA

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ABSTRACT. This paper presents the research of the normal geomagnetic field of the Republic of Macedonia. The complex geological structure of the explored area of regional and local character, has an important impact on the geomagnetic field. The geomagnetic field is composed of two components: normal and anomalous field. The geomagnetic field represents an important segment in the regulation of the natural processes on the Earth, which makes its permanent observation and study of special importance. Conducted investigations of the geomagnetic field maintain the continuity of monitoring and studying of the field changes in the area of the Republic of Macedonia which started in 2000.

Keywords: geomagnetic field, total field, declination, inclination, normal field, geomagnetic models and maps

Introduction

The geomagnetic field reflects the Earth’s structure, the processes within it, as well as the external influences. The field is presented as a sum of three components: (Delipetrov, 2003).

- Normal geomagnetic field which reflects the causes of magnetism in the core and the mantle. This component includes agents that are in the depths of the earth’s crust, but they are spread throughout the territory of the Republic of Macedonia;
- Regional geomagnetic anomalous field affected by characteristic generators of the magnetic field in the separated neotectonic zones in the Republic of Macedonia;
- Local geomagnetic field which is in direct correlation with the geological structures in the upper part of the Earth’s crust with expressed magnetic features (increased concentration of ferrous magnetic minerals).

The territory of the Republic of Macedonia, as part of the Alpine orogen in the Balkan Peninsula, is characterized by a very complex geological structure, where structural segments are separated - zones which are widespread in the Balkan Peninsula. In recent geological history, neotectonic phase, different geological processes have divided these areas in separated units. The different geological structure and processes in these regions have significant impact on the structure of the geomagnetic field. There is no other such small area as the Republic of Macedonia with so complex geological structure and hence, with such structure of the local geomagnetic field in whole Europe.

Models and maps of the elements of the normal geomagnetic field in the Republic of Macedonia

Two methods of modeling of the geomagnetic field prevail today, one is the method of spherical harmonic analysis and the other is the method of polynomial analysis.

The normal field for a territory can be expressed by:

\[ E(\Delta \phi, \Delta \lambda) = a_1 + a_2 \cdot \Delta \phi + a_3 \cdot \Delta \lambda + a_4 \cdot \Delta \phi^2 + a_5 \cdot \Delta \lambda^2 + a_6 \cdot \Delta \phi \cdot \Delta \lambda \]

where:

- \( E(\Delta \phi, \Delta \lambda) \) – is the value for the normal field of the point with coordinates \( \phi_1 \) and \( \lambda_1 \);
- \( \phi_0 \) and \( \lambda_0 \) – is the geographic latitude and longitude of the place;
- \( \phi_0 \) and \( \lambda_0 \) – is the geographic latitude and longitude of the point depending on which measurements are being reduced; for the Republic of Macedonia the central point is \( \phi_0 = 41,50^\circ \) and \( \lambda_0 = 22^\circ \);
$$\Delta \phi = \phi_1 - \phi_0 \quad \text{is the difference of geographic latitudes in minutes;}$$

$$\Delta \lambda = \lambda_1 - \lambda_0 \quad \text{is the difference of geographic longitudes in minutes;}$$

$a_i$ – are the coefficients for corresponding differences in nT/min (\(\gamma/\text{min.}\)), i.e. minutes / minutes or gammas and minutes.

Usually, the differences of latitude and longitude are calculated in terms of coordinates of the geomagnetic observatory located on that territory.

Observations of the geomagnetic field of a given territory (usually state) are carried out in two parallel procedures. One is permanent monitoring of the geomagnetic field in an observatory. Another procedure that is performed periodically every 3 to 5 years are terrestrial observations of the basic network of repeat stations, and observations of the secondary net within a period of 10 years.

Based on this data collection about the geomagnetic field every five years, maps and models of the elements of the normal geomagnetic field for a given epoch are made.

**Model of the elements of the normal geomagnetic field in the Republic of Macedonia**

Field measurements were conducted on the fifteen repeat stations in Macedonia. ([Delipetrev, 2011])

During the field measurements, the following instruments were used:

- DI Fluxgate magnetometer – an instrument that measures values of the geomagnetic declination D and inclination I. The instrument consists of a non-magnetic theodolite and fluxgate sensor mounted on the telescope, so the optical and magnetic axes are parallel (fig. 1).

- Proton - magnetometer - GEOMETRICS G-856.

A model of the elements of the normal geomagnetic field in the Republic of Macedonia (Table 3) is made on the basis of the measured data (Table 1).

![Fig. 1. DIFlux magnetometer - theodolite with Fluxgate sensor on the top](image)

### Table 1.

Measured data on the repeat stations

<table>
<thead>
<tr>
<th>Station</th>
<th>H (nT)</th>
<th>X (nT)</th>
<th>Y (nT)</th>
<th>Z (nT)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tetovo</td>
<td>24233.26</td>
<td>24169.74</td>
<td>1546.12</td>
<td>39704.21</td>
</tr>
<tr>
<td>Egri</td>
<td>24751.17</td>
<td>24716.87</td>
<td>1302.71</td>
<td>39237.34</td>
</tr>
<tr>
<td>Mavrovo</td>
<td>24264.10</td>
<td>24251.20</td>
<td>1463.12</td>
<td>39704.21</td>
</tr>
<tr>
<td>Plackovica</td>
<td>24288.75</td>
<td>24251.75</td>
<td>1340.17</td>
<td>39822.61</td>
</tr>
<tr>
<td>Slivnica</td>
<td>24379.72</td>
<td>24337.21</td>
<td>1439.08</td>
<td>39790.33</td>
</tr>
<tr>
<td>Vodno</td>
<td>24207.50</td>
<td>24169.74</td>
<td>1351.72</td>
<td>39950.88</td>
</tr>
<tr>
<td>Bajlovce</td>
<td>23883.98</td>
<td>23853.08</td>
<td>1214.61</td>
<td>40156.53</td>
</tr>
</tbody>
</table>

### Table 2.

Coefficients of the model of the normal geomagnetic field

<table>
<thead>
<tr>
<th>Element</th>
<th>(a_0)</th>
<th>(a_1)</th>
<th>(a_2)</th>
<th>(a_3)</th>
<th>(a_4)</th>
<th>(a_5)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D</td>
<td>3.6278</td>
<td>0.118</td>
<td>-0.0386</td>
<td>0.078</td>
<td>0.0154</td>
<td>-0.3455</td>
</tr>
<tr>
<td>I</td>
<td>58.088</td>
<td>-0.037</td>
<td>-0.1578</td>
<td>0.119</td>
<td>0.0928</td>
<td>-0.4256</td>
</tr>
<tr>
<td>T</td>
<td>46550</td>
<td>-24.449</td>
<td>-172.278</td>
<td>-20.585</td>
<td>197.784</td>
<td>-449.635</td>
</tr>
<tr>
<td>H</td>
<td>24607</td>
<td>11.072</td>
<td>17.149</td>
<td>-95.376</td>
<td>38.900</td>
<td>57.755</td>
</tr>
<tr>
<td>X</td>
<td>24558</td>
<td>7.939</td>
<td>18.218</td>
<td>-97.322</td>
<td>37.095</td>
<td>66.862</td>
</tr>
<tr>
<td>Y</td>
<td>15560</td>
<td>46.635</td>
<td>-15.966</td>
<td>23.628</td>
<td>13.308</td>
<td>-145.088</td>
</tr>
</tbody>
</table>

### Table 3.

Values of the normal geomagnetic field calculated with the coefficient from Table 2

<table>
<thead>
<tr>
<th>Stations</th>
<th>D</th>
<th>I</th>
<th>T</th>
<th>H</th>
<th>X</th>
<th>Y</th>
<th>Z</th>
</tr>
</thead>
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<td>Galicica</td>
<td>3.378</td>
<td>57.276</td>
<td>46271</td>
<td>25014</td>
<td>24970</td>
<td>1474</td>
<td>39827</td>
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<tr>
<td>Egri</td>
<td>3.465</td>
<td>57.367</td>
<td>46330</td>
<td>24984</td>
<td>24938</td>
<td>1510</td>
<td>39016</td>
</tr>
<tr>
<td>Mavrovo</td>
<td>3.533</td>
<td>58.039</td>
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<td>24590</td>
<td>24543</td>
<td>1515</td>
<td>39411</td>
</tr>
<tr>
<td>Plackovica</td>
<td>3.666</td>
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<td>24531</td>
<td>24486</td>
<td>1483</td>
<td>39445</td>
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<tr>
<td>Vodno</td>
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<td>57.854</td>
<td>46567</td>
<td>24777</td>
<td>24731</td>
<td>1517</td>
<td>39428</td>
</tr>
<tr>
<td>Bajlovce</td>
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<td>58.850</td>
<td>46675</td>
<td>24144</td>
<td>24099</td>
<td>1477</td>
<td>39945</td>
</tr>
<tr>
<td>Ponikva</td>
<td>3.721</td>
<td>58.603</td>
<td>46750</td>
<td>24355</td>
<td>24304</td>
<td>1581</td>
<td>39905</td>
</tr>
<tr>
<td>Slivnica</td>
<td>3.698</td>
<td>58.217</td>
<td>46575</td>
<td>24531</td>
<td>24480</td>
<td>1582</td>
<td>39591</td>
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<tr>
<td>Luke</td>
<td>3.737</td>
<td>59.005</td>
<td>46235</td>
<td>23609</td>
<td>23759</td>
<td>1552</td>
<td>39633</td>
</tr>
<tr>
<td>Tetovo</td>
<td>3.617</td>
<td>58.346</td>
<td>46683</td>
<td>24499</td>
<td>24450</td>
<td>1546</td>
<td>39738</td>
</tr>
<tr>
<td>Island Gradot</td>
<td>3.946</td>
<td>57.667</td>
<td>46327</td>
<td>24777</td>
<td>24719</td>
<td>1685</td>
<td>39144</td>
</tr>
<tr>
<td>Nikolic</td>
<td>3.499</td>
<td>57.823</td>
<td>46493</td>
<td>24759</td>
<td>24713</td>
<td>1511</td>
<td>39352</td>
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<tr>
<td>Silvnicna</td>
<td>3.983</td>
<td>58.166</td>
<td>46607</td>
<td>24583</td>
<td>24524</td>
<td>1708</td>
<td>39596</td>
</tr>
<tr>
<td>Cma Skala</td>
<td>3.769</td>
<td>58.244</td>
<td>46903</td>
<td>24685</td>
<td>24632</td>
<td>1623</td>
<td>39881</td>
</tr>
</tbody>
</table>

Maps of the elements of the normal geomagnetic field of the Republic of Macedonia

The declination of the observed territory varies form 3.378° on the measuring point Galicica to 3.983° on the station Silvnicna. Declination varies in the interval $\Delta D = 0.605°$ (Fig. 2).
Analysis of the declination field shows that on the observed territory the extreme stands in the central southern part, near the measuring station Island Gradot. The field is quiet in the west and northwest, which should be expected according to the geological structure.

From the observations, the inclination varies from Galicica $57.276^\circ \leq I \leq 59.005^\circ$ Luke. The mean value of inclination is $I_{sr} = 58.125^\circ$. The field of inclination I related to that of the declination is more homogenous and relatively quiet. There is a slight twisting of isolines in the central southern part (Fig. 3).

Values of the measured points for the total field vector $T$ varies in the interval from 46 235 nT on the repeat station Luke to 46 903 nT on the point Crna Skala. The interval of variation is $\Delta T = 371.0$ nT. The field is relatively quiet with a twisting of the isolines in the central southern part and in the northeastern part (Fig. 4).

Analyzing the map of the horizontal component $H$ (Fig. 5) from north in the area of Bajlovce with a minimum value of 24150 nT toward south shows an increase to $H_{max} = 25000$ nT in the area of Ohrid and Prespa Lake, i.e. in the region of the repeat station Galicica. The average value of the field is $H_{sr} = 24575$ nT. The interval, in which the horizontal component on the observed territory varies, is $\Delta H = 850$ nT. The field is homogenous and relatively quite.

The field of the northern component $X$ (Fig. 6) is relatively quiet and with a maximum value $X_{max} = 24900$ nT from southwest, decreasing toward north and in the northeastern part it has a minimum value $X_{min} = 24100$ nT. The average value of the northern component is $X_{sr} = 24500$ nT. The interval of variation is $\Delta X = 800$ nT.

The field of the eastern component $Y$ (Fig. 7) varies from $Y_{min} = 1470$ nT in the area of the repeat stations Galicica and Bajlovce to $Y_{max} = 1700$ nT at the repeat stations Slivnica and
Island Gradot. The western part of the Republic of Macedonia has a quieter field related to the central and the eastern part. The expressed extreme is present in the southern part. The value of the component varies in the interval of $\Delta Y = 250$ nT. The average value is $Y_{sr} = 1595$ nT.

The field of the vertical component $Z$ (Fig. 8) is relatively quiet with expressed twisting of the isolines in the northeastern and central southern part. The maximum value is in the area of the repeat station Bajlovce $Z_{max} = 39945$ nT, and minimum value is in the region of the repeat station Galicica $Z_{min} = 38927$ nT. The average value of the component is $Z_{sr} = 39435$ nT. The interval of variation is $\Delta Z = 1018$ nT.

The comparison of maps of the relevant elements of the normal field from previous measurements in 1990 showed lower degree of similarity with these maps because of the use of a different network of repeat stations, the greater distance and difference in applied technology.

**Structure of the geomagnetic field**

The geomagnetic field on the Earth’s surface is a sum of vectors of many different magnetic fields:

$$T = T_0 + T_m + T_a + T_e + \delta T.$$  

The implemented geomagnetic field observation and the applied methodology of data processing have eliminated the influence of the local anomaly field $T_{al}$, the electromagnetic field $T_e$, and the impact of short time variations of the field $\delta T$.

In order to eliminate the influence of geomagnetic causes that are deep underground, and because their dimensions and area of influence are far beyond the territory of the investigated area, an IGRF (International Geomagnetic Reference Field) model is used as a filter that reflects the impact of normal geomagnetic field, in this case shown by two components: the field $T_0$ and the axial dipole field $T_a$ on the continent.

Maps of the differences of the normal geomagnetic field's elements between the IGRF model and our model were created (Figs. 9 - 12). (Panovska et al., 2006)

The analysis of the components of the regional anomaly of the geomagnetic field $T_r$ reflects the neotectonic regionalization of the Republic of Macedonia in three mega blocks:

- Eastern Macedonian zone;
- Vardar zone;
- Western Macedonian zone including Pelagonian block.
Conclusion

From the data presented on the elements and structure of the normal geomagnetic field in the Republic of Macedonia, it can be concluded the following:

- The maps and the elements' models of the normal geomagnetic field express the specificity of the area of the Republic of Macedonia;
- The presented data for the declination can have wide application in all activities where compass is used;
- Maps of the differences of the normal geomagnetic field elements between the IGRF model and our model were created.

References

A COMPLEX APPROACH FOR SEDIMENTARY ARCHITECTURE MODELLING OF FLUVIAL SUCCESSIONS AND THEIR CONVERSION INTO HYDROGEOLOGICAL UNITS

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ABSTRACT. Often the clastic fluvial deposits demonstrate significant lateral and temporal variability that significantly impedes the correct evaluation and modelling of their hydrodynamic properties. On the basis of lithological studies and aerial and terrestrial photogrammetric documentation of representative logs and 2D outcrops of fluvial successions study the main lithofacies and architectural-element units are determined. The fluvial successions are converted into hydrogeological units after a detailed grain size analysis and a correlation between the obtained results and the hydraulic conductivities. The application of an integrated geophysical approach (incl. ground-penetrating radar, electrical resistivity methods, geomagnetics, kappametry, etc.) enables the development of specific for the investigated sites key techniques used for indirect mapping of fluvial successions and hydrogeological units. This is useful for their depth profiling and spatial mapping. The presented multidisciplinary approach is developed for studying the Galata Formation in the area north of the Kamchia River firth.

Keywords: hydrogeological model, geophysical methods, hydrogeological units, water budget

INTRODUCTION

The main objective of contemporary surveys in the field of petroleum geology and hydrogeology in continental successions is 3D geometrization and characterization of sedimentary bodies that are typified by specific porosity and permeability. For decades, a set of sedimentological field and laboratory methods has been used for this purpose, where the form and degree of exposure of the sedimentary outcappings are of key importance for achieving credible results.

The combination of detailed lithofacial profiling and 2D mapping of outcrops with extensive detection of textures-indicators of sediment paleo-transport is the basis of the architectural-element analysis of fluvial successions - one of the most advanced 3D methods for facial and paleographic modeling, reconstruction and stratigraphic division of continental successions (Stoyanov and Ajdanlijsky, 2002; Ajdanlijsky and Stoyanov, 2003). Along with the many limitations associated with the nature of the outcropping of the investigated sedimentary successions, the application of this method is connected to the accessibility of these outcrops and the possibility of their detailed and extensive documentation.

Substantial progress in this area is the combination of relatively inexpensive modern Remotely Piloted Aircraft Systems (RPAS) and a standard high resolution camera (or other type of sensor), which emerges as a powerful tool for remote sensing. There are also a number of budget software solutions providing further processing of the information. Modern drones are an efficient and highly productive tool for near-terrestrial mapping and documentation of substantial in scale outcrops, which are otherwise inaccessible to conventional field methods. They also allow extremely high levels of detailization (Kysyov and Chankov, 2016).

Parallel to the development of computing machinery and measuring equipment, geophysical methods (electrical resistivity surveying, ground-penetrating radar, geomagnetic surveying, etc.) find wider application in detailed mapping of the near-surface geological section. Their geological efficiency is determined by the differentiation of rocks according to different physical properties (Dimitovski and Dr., 2007, 2014; Dimitovski and Stojanov, 2011; Stojanov, 2004; Stoyanov et al., 2017)
Methodology of geophysical research

Different geophysical methods (ground-penetrating radar, geomagnetic surveying, electrical resistivity surveying, kappametry, etc.) can be applied successfully for mapping of the near-surface geological section. The major advantage of these methods is that they are convenient non-invasive instruments for a relatively rapid and effective determination of the spatial boundaries of geological and hydrogeological units of different rank, as well as zones with different characteristics. The common scheme for their application to each specific subject involves three main steps:

- **Field measurements.** They are carried out on predefined profiles and/or areas covering characteristic parts or the whole area of the object under study. The depth of study is decisive for the choice of techniques and schemes used in field measurements.
- **Development of two-dimensional or three-dimensional computer models of the physical field,** based on the performed measurements. Based on the model solutions and depending on the method used, a series of surface maps at different hypsometric levels can be obtained and vertical sections of the geoelectric or geomagnetic field can be derived. The acquired distributions of the studied physical parameters (electrical resistivity, total vector of the geomagnetic field, etc.) are a function of the mineral composition, the granulometric characteristics and the geometry (architecture) of the studied geological bodies, the presence and the degree of their secondary alterations (weathering, cracking, karstification, compaction), the degree of water-saturation, the physical properties and chemical composition of groundwater, etc.
- **Interpretation of the computer models.** In the process of transformation of the geophysical models in geological and/or hydrogeological models, different approaches are applied, based on correlation dependencies and complex comparative analysis of model solutions with data from studies performed in the area under investigation - geological mapping, drilling, field tests, laboratory tests, etc. Depending on the applied geophysical method and on the character and required precision of the study, most common well-known relationships and theoretical dependencies are used, or transformation keys, ensuring high reliability and quality of interpretation, are developed for each specific object.

Basic geophysical methods for mapping of the near-surface geological section

The most suitable geophysical methods for mapping geological and hydrogeological units of different rank are electrical resistivity methods (electrometrolimetry), ground-penetrating radar, geomagnetic methods and kappametry. Practice shows that their integrated implementation gives greater confidence in the analysis and interpretation of the results from the geophysical study.

**Electrical resistivity methods.** The resistivity methods and, in particular, electrometrolimetry have a leading role in the geometrization of geological and hydrogeological units that compose the near-surface section. Their geological efficiency is determined by the differentiation of rocks according to their electrical properties and mainly the specific electrical resistance. The variations of this parameter are uniquely related to the degree of ionic conduction. In the near-surface geological section, the ionic conductivity is associated with the presence of a saturated porous media where the ground water acts as an electrolyte. Therefore, the influence of three factors should be taken into account when assessing the ionic conductivity: the porosity coefficient, the degree of saturation of the porous media with groundwater, and the specific electrical resistance of the groundwater (electrolyte), i.e. the degree of mineralization of groundwater. Research has shown that practically always a very good, even in many cases unambiguous, connection is present between the electrical resistance differentiation and the specifics of the studied near-surface geoelectrical section.

**Ground-penetrating radar (GPR).** The GPR uses radar pulses to image the subsurface. This nondestructive method uses high-frequency (usually polarized) radio waves, usually in the range of 10 MHz to 2.6 GHz. A GPR transmitter emits electromagnetic energy into the ground. When the energy encounters a buried object or a boundary between materials having different permittivity, it may be reflected or refracted or scattered back to the surface. A receiving antenna can then record the variations in the return signal. The principles involved are similar to seismology, except GPR methods implement electromagnetic energy rather than acoustic energy, and energy may be reflected at boundaries where subsurface electrical properties change rather than subsurface mechanical properties as is the case with seismic energy. The electrical conductivity of the ground, the transmitted center frequency, and the radiated power all may limit the effective depth range of GPR investigation. Increases in electrical conductivity attenuate the introduced electromagnetic wave, and thus the penetration depth decreases. Because of frequency-dependent attenuation mechanisms, higher frequencies do not penetrate as far as lower frequencies. However, higher frequencies may provide improved resolution. Thus, operating frequency is always a trade-off between resolution and penetration. The GPR registers changes in the electrical characteristics of the media (conductivity and dielectric permeability), which are directly related to the type of sediments, their humidity and porosity. In such a way, it reproduces in real time vertical sections (the so-called ground-penetrating radargrams), which reflect the geological, hydrogeological and anomalous conditions. Individual lines of GPR data represent a sectional (profile) view of the subsurface. Multiple lines of data systematically collected over an area may be used to construct three-dimensional or tomographic images. Data may be presented as three-dimensional blocks, or as horizontal or vertical slices. Horizontal slices (known as “depth slices” or “time slices”) are essentially planview maps isolating specific depths. With the application of the ground-penetrating radar one can clearly localize lithological boundaries, inclusions, water-saturated zones, etc.

**Geomagnetic surveying.** The magnetic methods in geophysics enable the study of the geological structure based on the anomalies of the geomagnetic field. These anomalies are due to the varying content or absence of ferromagnetic minerals in sediment rocks. Under certain conditions, there is the possibility of depositing different ferromagnetic minerals in the riverbeds. Such are ferromagnetic magnetite, low-magnetic ilmenite, hematite and others. The iron-ore mineralization
accumulated along the palaeochannels can be recognized using magnetic methods as low-intensive elongated anomalies, which repeat the form of the covered ancient riverbeds. Therefore, the geomagnetic method is very effective for the localization and geometrization of channel-belt bodies (some of the most attractive in terms of porosity and permeability building elements of fluvial clastic successions), in their lower part similar minerals are frequently present, formed as residual depositions. Because of its proven rapidity and effectiveness, the method can be used to localize the presence of hematite deposition, to track the route of paleoflows, etc.

**Kappametry.** The magnetic susceptibility depends on the type and quantity of magnetic minerals contained in the studied rock samples. This parameter is most often related to the presence of ferromagnetic minerals (iron oxides or sulphides such as magnetite and/or pyrrhotite). There is sometimes a strong dependence on some paramagnetic minerals (mafic silicates such as olivine, pyroxene, amphibolite, mica, tourmaline, and garnet) and very rarely diamagnetic minerals (calcite, quartz). The magnetic susceptibility (kappa) of the various rocks is related to their ability to “seal” the magnetic field of the Earth during their formation. For sediments, the magnitude of this parameter is in functional dependence on the physical prerequisites of their deposition. Fluctuations in the magnetic susceptibility values provide an appropriate tool for identifying cyclical changes in the physical processes of sedimentation, which are often associated with different climatic factors such as warming or cooling.

**Aero-photogrammetry.** The airborne photogrammetry deals with the determination of the shape, dimensions, position and other quantitative and qualitative characteristics of different objects on the Earth's surface according to photographic images made by an airborne device. There are geometric relationships between the objects in the area and their photographic image, as the photo is a central projection of the captured land surface. Nevertheless, photos can not be used directly for geodetic purposes. The different remoteness of the captured objects from the projection center (this can be associated with the center of the lens) is the reason for the different scale of the objects on the captured surface.

The main task of photogrammetry is the transformation of photographic images into plans and maps that are orthogonal projections of the captured land surface. With scale bars, basically a known distance of two points in space, or known fixed points, the connection to the basic measuring units is created. Algorithms for photogrammetry typically attempt to minimize the sum of the squares of errors over the coordinates and relative displacements of the reference points. This minimization is known as bundle adjustment and is often performed using the Levenberg–Marquardt algorithm. At least two photographic images are needed to generate a stereo model. It is necessary to capture a series of mutually overlapping photos along a predefined route in order to create the orthophoto mosaic. Common points are identified on each image. A line of sight (or ray) can be constructed from the camera location to the point on the object. The intersection of these rays (triangulation) determines the three-dimensional location of the point.

**Interpretation of geophysical models**

For the transformation of geophysical models into geological and/or hydrogeological models, the so-called geophysical keys are applied that are expressing the connection between the determined in the cross section zones, characterized by different physical properties, and their corresponding geological and/or hydrogeological units of different rank. Generally, when developing a geophysical key for a particular object, three different in degree of authenticity approaches can be applied. They are based on value tables, available lithology data and laboratory tests.

**Approach 1. Using value tables.** This is a very fast and inexpensive way for pre-processing the results of a geophysical study. In this approach, as a key for the transformation of a geophysical model into a geological or hydrogeological one are used published in specialized literature tables of values for the specific physical properties of the basic rocks, minerals and compounds, as well as data for rocks saturated with fresh, brackish or saline water (Daniels and Alberty, 1966; Keller and Frischknecht, 1981, Stoyanov et al., 2017). Unfortunately, the results of the interpretation are a little bit fairly accurate and usually variative, as the specific physical property values for different environments vary in wide and often overlapping boundaries (Tables 1, 2 and 3).

**Table 1.**

**Specific electrical resistance of some basic rocks and chemical compounds (Keller and Frischknecht, 1981, Daniels and Alberty, 1966).**

<table>
<thead>
<tr>
<th>Material</th>
<th>Specific electrical resistance $\Omega \cdot m$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Magmatic and metamorphic rocks</strong></td>
<td></td>
</tr>
<tr>
<td>Granite</td>
<td>$5 \times 10^3 - 10^6$</td>
</tr>
<tr>
<td>Basalt</td>
<td>$10^3 - 10^6$</td>
</tr>
<tr>
<td>Shale</td>
<td>$6 \times 10^2 - 4 \times 10^7$</td>
</tr>
<tr>
<td>Marble</td>
<td>$10^2 - 2.5 \times 10^4$</td>
</tr>
<tr>
<td>Quartzite</td>
<td>$10^2 - 2 \times 10^8$</td>
</tr>
<tr>
<td><strong>Sedimentary rocks</strong></td>
<td></td>
</tr>
<tr>
<td>Sandstone</td>
<td>$8 - 4 \times 10^3$</td>
</tr>
<tr>
<td>Argillite</td>
<td>$20 - 2 \times 10^3$</td>
</tr>
<tr>
<td>Limestone</td>
<td>$50 - 4 \times 10^2$</td>
</tr>
<tr>
<td><strong>Dispersive soils</strong></td>
<td></td>
</tr>
<tr>
<td>Clays</td>
<td>$1 - 100$</td>
</tr>
<tr>
<td>Alluvial sands and gravels</td>
<td>$10 - 800$</td>
</tr>
<tr>
<td><strong>Water</strong></td>
<td></td>
</tr>
<tr>
<td>Groundwater</td>
<td>$10 - 100$</td>
</tr>
<tr>
<td>Sea water</td>
<td>$0.2$</td>
</tr>
<tr>
<td><strong>Chemical compounds</strong></td>
<td></td>
</tr>
<tr>
<td>0.01M KCl</td>
<td>$0.708$</td>
</tr>
<tr>
<td>0.01M NaCl</td>
<td>$0.843$</td>
</tr>
<tr>
<td>0.01M CH$_3$COOH</td>
<td>$6.13$</td>
</tr>
<tr>
<td>Xylene</td>
<td>$6.99 \times 10^{16}$</td>
</tr>
</tbody>
</table>
Table 2.
Criteria for estimating sea salt water intrusion in the region of the Nile delta – District Rashid, Egypt (Stoyanov et al., 2017)

<table>
<thead>
<tr>
<th>Object of study</th>
<th>Water type</th>
<th>Resistivity (Ohm.m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unsaturated zone (dry sediments)</td>
<td>-</td>
<td>&gt; 150</td>
</tr>
<tr>
<td>Aquitard (clay and silt)</td>
<td>fresh water</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>slightly brackish water</td>
<td>20 – 45</td>
</tr>
<tr>
<td></td>
<td>moderately brackish water</td>
<td>10 – 20</td>
</tr>
<tr>
<td></td>
<td>brackish water</td>
<td>5 – 10</td>
</tr>
<tr>
<td></td>
<td>very brackish water</td>
<td>2.5 – 5</td>
</tr>
<tr>
<td></td>
<td>saline (salt) water</td>
<td>&lt; 2.5</td>
</tr>
<tr>
<td>Aquifer (gravel and sand layers)</td>
<td>fresh water</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>moderately brackish water</td>
<td>10 – 20</td>
</tr>
<tr>
<td></td>
<td>brackish water</td>
<td>5 – 10</td>
</tr>
<tr>
<td></td>
<td>very brackish water</td>
<td>2.5 – 5</td>
</tr>
<tr>
<td></td>
<td>saline (salt) water</td>
<td>&lt; 2.5</td>
</tr>
</tbody>
</table>

Approach 2. Employing available lithology data. This is the most frequently used methodology for transforming geophysical sections into results that reconstruct the geological structure of the studied areas. For this purpose a complex analysis and interpretation of the obtained sections is performed and they are compared with the available information for specific elements of the geological structure derived on the basis of geological mapping and exploratory drilling data.

Approach 3. Using laboratory tests data. They can be applied for the development of a local geophysical key, which gives the direct connection between the determined in the section media characterized by different physical properties and their corresponding geological and hydrogeological units in the studied area.

For example, in case electrical resistivity measurements are performed, it is advisable to use the following general scheme. During the stage of geological mapping or exploratory drilling, representative soil samples are taken from each low-rank geological unit. In case of layers that are very heterogeneous with respect to their granulometric composition, sampling is desirable to cover all dominant varieties. Water samples having TDS corresponding to the natural background are also taken. In laboratory conditions, the electrical resistance is measured first when the soil samples are dry and later when they are saturated. Watering is performed using the available water samples. The values for the electrical resistivity determined in such a way are used as local criteria for the transformation of geoelectrical computer models into geological or hydrogeological models.

An essential element in this approach is the measurement of the electrical resistivity of dry and saturated soil samples. For this purpose a device was designed and constructed, in which the electrical resistivity of a small volume of the studied media can be modeled and measured (Crowe, 2004). The device is a four-electrode geoelectrical column for measuring the electrical resistivity of dry and saturated samples (Figure 1).

Table 3.
Values for the specific electrical conductivity and the dielectric constant of some basic materials.

<table>
<thead>
<tr>
<th>Material</th>
<th>Specific electrical conductivity $\sigma$ [S/m]</th>
<th>Dielectric constant $\varepsilon$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>Distilled water</td>
<td>$10^{-2}$ – $3.10^{-2}$</td>
<td>81</td>
</tr>
<tr>
<td>Sea water</td>
<td>4</td>
<td>81</td>
</tr>
<tr>
<td>Ice</td>
<td>$10^{-3}$</td>
<td>4</td>
</tr>
<tr>
<td>Granite(dry)</td>
<td>$10^{-4}$</td>
<td>5</td>
</tr>
<tr>
<td>Limestone(dry)</td>
<td>$10^{-9}$</td>
<td>7</td>
</tr>
<tr>
<td>Clay (wet)</td>
<td>$10^{-1}$ – 1</td>
<td>8 - 12</td>
</tr>
<tr>
<td>Snow firn</td>
<td>$10^{-4}$ – $10^{-5}$</td>
<td>1.4</td>
</tr>
<tr>
<td>Sand (dry)</td>
<td>$10^{-7}$ – $10^{-3}$</td>
<td>4 – 6</td>
</tr>
<tr>
<td>Sand (saturated)</td>
<td>$10^{-4}$ – $10^{-2}$</td>
<td>30</td>
</tr>
<tr>
<td>Sediments(saturated)</td>
<td>$10^{-3}$ – $10^{-2}$</td>
<td>10</td>
</tr>
<tr>
<td>Sandy sediments (dry)</td>
<td>$2.10^{-3}$</td>
<td>10</td>
</tr>
<tr>
<td>Swamp forest and plain depositions</td>
<td>$8.10^{-3}$</td>
<td>12</td>
</tr>
<tr>
<td>Agricultural land and pastures</td>
<td>$5.10^{-3}$</td>
<td>13</td>
</tr>
<tr>
<td>Basalt(wet)</td>
<td>$10^{-2}$</td>
<td>8</td>
</tr>
<tr>
<td>Granite(wet)</td>
<td>$10^{-3}$</td>
<td>7</td>
</tr>
<tr>
<td>Clayey shale(wet)</td>
<td>$10^{-1}$</td>
<td>7</td>
</tr>
<tr>
<td>Sandstone(wet)</td>
<td>$4.10^{-2}$</td>
<td>6</td>
</tr>
<tr>
<td>Limestone(wet)</td>
<td>$2.5.10^{-2}$</td>
<td>8</td>
</tr>
<tr>
<td>Frozen soil / Permafrost</td>
<td>$10^{-5}$ – $10^{-2}$</td>
<td>4 – 8</td>
</tr>
<tr>
<td>Concrete (dry)</td>
<td></td>
<td>6</td>
</tr>
<tr>
<td>Concrete (wet)</td>
<td></td>
<td>2.5</td>
</tr>
<tr>
<td>Asphalt</td>
<td>3 – 5</td>
<td>3</td>
</tr>
<tr>
<td>PVC, plastics, rubber, latex, etc.</td>
<td></td>
<td>3</td>
</tr>
<tr>
<td>Sandy soils (dry)</td>
<td>$1.4.10^{-4}$</td>
<td>2.6</td>
</tr>
<tr>
<td>Sandy soils (wet)</td>
<td>$6.9.10^{-3}$</td>
<td>25</td>
</tr>
<tr>
<td>Clayey-sandy soils (dry)</td>
<td>$1.1.10^{-4}$</td>
<td>2.5</td>
</tr>
<tr>
<td>Clayey-sandy soils(wet)</td>
<td>$2.1.10^{-2}$</td>
<td>19</td>
</tr>
<tr>
<td>Clayey soils(dry)</td>
<td>$2.7.10^{-4}$</td>
<td>2.4</td>
</tr>
<tr>
<td>Clayey soils (wet)</td>
<td>$5.10^{-2}$</td>
<td>15</td>
</tr>
</tbody>
</table>

Measurements are made applying standard resistivity meters used in field geoelectrical surveys or conventional electrical measuring equipment. The necessary requirement for this apparatus is to generate alternating current, thereby eliminating or limiting the polarization of the potential electrodes. The geoelectrical column is made of a thick-walled tube of electro-insulating material. The current and the potential electrodes (C1, C2, P1 and P2) are located in the central part of the column and represent a Wenner-Alpha array. The column calibration constant is $k = 0.054$ m.

The sequence of operation for measuring the resistivity of dry and saturated samples is as follows. First, the column is filled and packed (without segregating) with sand having a...
known grain size and its resistivity is measured. The column is then placed in a higher container made of an electro-insulating material. The container is filled with water that penetrates along canals to the bottom end of the column and through the perforated base gradually saturates the built-in sample from the bottom upwards. The water inflow is stopped when the sand sample is completely saturated. This approach eliminates the presence of any unsaturated voids. Measurement is performed a few hours after the sample is saturated. It has been confirmed that this time is adequate to establish a relative physical-chemical equilibrium between the solid phase and the liquid phase and in such a way to ensure the reliability of the obtained result.

**Principles for attachment of fluvial architectural units towards aquifer and aquitard layers and zones**

The description and definition of architectural elements includes:
- Nature and morphology of confining surfaces;
- Unit scale: thickness, lateral development (parallel and perpendicular to the direction of the sedimentation paleo-transport);
- Surface geometry of the unit;
- Inner structure of the unit: lateral and vertical lithofacial assemblages and sequences, presence and orientation of low-rank erosion surfaces, orientation of the indicators of the sedimentary paleo-transport, interaction of bedding with respect to the limiting surfaces.

Based on the results from the performed grain-size analyses, the degree of sorting of the sediments in each separate lithofacies unit is determined. After that, this parameter is estimated for the architectural-element units that they compose. The representation and analysis of grain size data in standard phi-scale allows an accurate hydrodynamic and genetic interpretation of the established sedimentary bodies.

Employing connections, achieved by many authors, between granulometric composition and degree of sorting of sediments, on the one hand and hydraulic conductivity on the other, a correlation diagram (Figure 2) is compiled. It allows the lithofacies and architectural-element units to be interpreted as hydrogeological units (Stoyanov and Ajdaniljsky, 2002).

Using this correlation diagram, at first approximation, aquifers and zones with specific geometry and characteristics can be determined in the subsurface space of each particular studied site (Ajdaniljsky and Stoyanov, 2003). According to laboratory and "in situ" filtration and tracer tests, values of hydrodynamic and migration parameters can be assigned to each layer and zone.

**Conclusions**

The main objective of the proposed approach is the formation of an optimal complex of field sedimentological and geophysical methods for studying and 3D modeling of main lithofacies and architectural-element units and assessment of reservoir properties of young fluvial successions. It can be accompanied by an efficient and high-productive technique for near-terrestrial mapping and documentation of substantial in scale outcrops.
For this purpose, a variety of procedures aimed towards studying the near-surface geological section can be applied, including lithological analysis, geophysical methods, remote sensing, etc. They all are directed at:
- Development of specific detailed lithofacial sections and 2D profiles;
- Definition and documentation of architectural elements that are typical for terrestrial fluvial complexes;
- Precise 2D and 3D mapping of these elements in substantial scale outcrops that are inaccessible for the application of conventional field methods;
- Characterization of the architectural units with regard to their reservoir properties;
- Tracing the units' boundaries by application of geophysical methods (ground-penetrating radar, electrical resistivity methods, geomagnetics, kappametry, etc.).

The presented complex approach is developed for studying the Galata Formation in the area north of the Kamchia River firth.

Acknowledgment
The presented complex approach for sedimentary architecture modelling of fluvial successions and their conversion into hydrogeological units is based on unpublished authors' work in the frames of the Contract No: FGE-216 / 2018. Contract topic: “A multidisciplinary approach for sedimentary architecture modelling and evaluation of reservoir properties of fluvial successions”, funded by the scientific-research fund of the University of Mining and Geology "St. Ivan Rilski" for 2018.

References


