Territorial distribution of germanium in the c_5 coal seam on the territory of the "Pavlohradska" mine

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Abstract. The actual issues of the distribution of germanium in the c_5 coal seam in the territory of the "Pavlohradska" mine of Western Donbas were studied. Three zones with high germanium content were found on the territory of the c_5 seam, and their spatial location was determined. It was established that the geological structure of the c_5 coal seam in places with the highest germanium content has common features: minimal thickness, the presence of one or two partings, as well as the presence of at least two low-amplitude northeast-trending disturbances, which can be used as predictive criteria for determining zones with the largest germanium content. The increased variability of the thickness of the coal seam, its structure, the presence of discontinuities, and the lithological-facies variability of the immediate and main roof contribute to the increase in the gradients of the germanium content. The growth of the regional component of germanium content in the north-eastern direction was established. It has been proven that both syngenetic and epigenetic factors influence the content of germanium in the coal seam. The regression equation between these parameters is calculated, which allows you to predict the germanium content without conducting new tests and analytical studies.

1 Introduction

The importance of studying germanium (*Ge*) in coal seams is due to its potential for industrial use. Basic for industry are the semiconductor characteristics of germanium, which is one of the widely distributed natural semiconductor materials [1]. Germanium is one of the 12 chemical elements known as elemental or simple semiconductors. The

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transparency in the infrared region of the spectrum of highly pure metallic germanium is of military and strategic importance [2, 3]. The use of alloys of germanium with copper, magnesium, and aluminum, which have increased stability in acidic and aggressive environments, has found wide application in many areas of the chemical industry [4, 5]. *Ge*-organic compounds with carbon ("*Ge-C*" bonds) are active in the life processes of organisms (oxygen transfer in the blood, strengthening of immunity, antitumor activity, etc.) [6]. Currently, germanium is mainly used as a semiconductor material in electronic devices, a key element in the construction of passive thermal vision systems, military infrared guidance systems, night vision devices, firefighting systems, as a component of special alloys, as well as the main component of some medical drugs for increasing immunity and possessing antitumor properties [7].

The following are successively produced from germanium raw materials: *Ge* – concentrate (from 5% to 30% *Ge*), germanium tetrachloride ($GeCl_4$), its oxide, poly- and single crystals [8]. All these intermediate products in this technological chain constitute commercial products for use in various fields [9, 10]. For example, $GeCl_4$ is used in the production of glass for optical fiber technology, GeO_2 with a purity of up to 99.999% in catalysts for the polymerization of PET plastics, in the production of BGO crystals ($Bi_{14}Ge_3O_{12}$), for scintillation sensors of high-energy photons – even purer GeO_2 is used, in infrared night vision devices – range uses poly- and single-crystal windows and lenses made of artificially grown germanium crystals [11]. It is important to note that the semiconducting properties of germanium are needed not only in the electronics industry, but also in solar converters and *Si-Ge* junctions [12]. Thus, for each commercial product from the processing of germanium raw materials, there is a special global market. Adequate geological and economic assessment of germanium raw material deposits must consider the level, dynamics, and trends of price changes in all these markets [13, 14].

Previous studies of the microelement composition of Donbas coal focused on the analysis of the distribution of the so-called "toxic" and "potentially toxic" trace elements in coal seams of the region [6, 8, 15]. A methodology was developed for the classification of coal deposits and oil fields of the Dnipro-Donetsk basin according to the content of various microelements [16 – 18]. Other studies focused on the analysis of the distribution of germanium in specific coal seams of the Pavlohrad-Petropavlivka area of Donbas [19 – 21]. But until now, the spatial distribution of germanium in the c_5 coal seam in the territory of the "Pavlohradska" mine has not been investigated.

The purpose of the research is to determine the characteristics of the spatial distribution of germanium in the c_5 coal seam on the territory of the "Pavlohradska" mine.

The object of the study is the c_5 coal seam, which is located within the boundaries of the "Pavlohradska" mine.

2 The choice of object to study

Germanium belongs to the category of geochemically scattered elements [22]. This characteristic results from the fact that it can manifest itself as a siderophilic, chalcophilic or lithophilic element depending on the specific conditions of geochemical processes [23]. As a result, germanium appears as an isomorphic impurity in the crystal lattices of most silicates, polymetallic sulfides, and some iron oxides [24, 25]. In addition, germanium can create its own minerals, which can appear as microinclusions (so-called "prisoner minerals") in the structure of other minerals (so-called "host minerals") or form independent aggregates and large groups (which are very rare). All these natural compounds are a potential resource base of germanium [18, 20, 26].

Currently (according to data for 2022 – 2023), there are no published reliable estimates of global reserves or production of germanium and its compounds [27]. Estimates made at the beginning of the 21st century are based on different approaches and often do not consider some potential sources of germanium, especially those that are not yet fully exploited in production, including many germanium-bearing coal seams [28, 29]. The importance of coal as the main source of germanium is noted in many countries, including Ukraine, China, Uzbekistan, Canada, and the USA [30, 31]. Also, the strategic importance of germanium ores for the sustainable development and defense capabilities of countries was confirmed by the decision of the National Security and Defense Council of Ukraine dated July 16, 2021, and the Decree of the President of Ukraine No. 306/2021 "On stimulating the search, extraction and beneficiation of minerals that are of strategic importance for sustainable development and defense capabilities of the state".

Global demand for germanium is expected to grow to 320 – 400 tons annually by 2030, and production could increase by about one-and-a-half times, according to the US Geological Survey [32]. The cost of germanium single crystals, depending on their quality characteristics, can reach 10 – 15 thousand dollars per kilogram [33]. Meanwhile, approximately 100 tons of germanium are lost each year during coal mining in Donbas, which is about 45% of the known total annual production of this metal in the world.

The territory of the "Pavlohradska" mine field of PJSC "DTEK Pavlohradvuhillia" is in the administrative boundaries of the Pavlohrad area of the Dnipropetrovsk region. Geologically, it is part of the Pavlohrad-Petropavlivka geological and industrial area of Donbas. The geological structure of the mine field includes coal deposits of C_1^3 formation of the Lower Carboniferous, which are covered by seams of Paleogene, Neogene, and Quaternary sediments. The total thickness of Cenozoic sediments reaches 55 meters. Carboniferous coal-bearing seams are represented by the lower part of the Sarmatian coal-bearing world of the Serpukhivskyi horizon, which mainly contains argillites, siltstones, sandstones, limestones, and coal. The Carboniferous rocks within the mine field have a gentle (2 – 5º) and weakly undulating monoclinal bedding with an inclination to the north and northeast. The tectonic complexity of the field is due to the presence of discontinuous deformations of different amplitudes. The northern boundary of the field is determined by the Pivdenno-Ternivskyi downthrown fault, along which the rock displacement amplitude varies from 83 to 140 meters, and the thickness of the zone of their crushing varies from 10 to 100 meters.

On the territory of the "Pavlohradska" mine field, the c_5 coal seam has a relatively simple structure and is defined as stable. According to the average indicators of ash content, the coal of this seam is classified as low- and medium-ash in different areas; according to the content of total sulfur – as low- and medium-sulfur. According to the technological characteristics according to DSTU 3472-96, the coal of seam c_5 belongs to the "DG" brand (long-flame gas) and can be used as a high-quality energy fuel or a component of the charge for coking. The thickness of the c_5 coal seam in the field varies from 0.2 to 1.5 meters.

Within the boundaries of the Pavlohradska field, the germanium concentration in the c_5 seam varies from 8.8 g/t to 24.7 g/t with an average value of 17.62 ± 0.47 g/t, which is 6.08 times higher than the germanium clark for world reserves of hard coal specified in [34]. The median and modal values of germanium content are 18.05 g/t and 20.6 g/t, respectively. The standard deviation, variance, kurtosis, and skewness of the sample are 4.02 g/t, 16.18 g/t, -0.61 and -0.42, respectively.

3 Research methods

The primary focus of this research lies in the challenge of directly observing geological processes responsible for the accumulation and distribution of elements within geological formations. In such instances, dynamic analysis is conducted through statistical data comparison and examination of cartographic materials depicting the distribution of chemical elements within the studied objects. Subsequently, the obtained results are scrutinized, considering physico-chemical and geological characteristics. Initially, information gathering on chemical element distribution in geological formations marks the inception of the research. It progresses from consolidating factual data, through theoretical comprehension, culminating in verifying established patterns through experimental methods.

Sample collection occurred within mine workings (seam samples obtained using the furrow method [35] and from core duplicates), conducted by researchers in collaboration with personnel from coal mining enterprises' geological services and various geological exploration organizations from 1981 to 2014. The control test volume constituted 5% of the total sample volume.

All analytical procedures were conducted in certified central laboratories of geological exploration industries. The concentration of germanium was determined using the photocolorimetric method according to [36]. Internal laboratory control utilized 7% of duplicate samples, while external laboratory control utilized 10% of duplicates. Analysis quality (precision and reproducibility) was evaluated based on the significance of mean systematic error, tested via Student's t-test, and the significance of mean random error, tested using Fisher's test. Given the insignificance of both errors at the 0.95 significance level, the analysis quality was deemed satisfactory.

In the initial processing stage of primary geochemical data, Excel 2016 and Statistica 11.0 were employed to compute main descriptive statistical indicators, construct frequency histograms of content, and analyze germanium distribution characteristics. The Surfer 11 program was utilized for all map creation, graphing, correlation coefficient calculations, and regression equation derivation. During these processes, all germanium concentration values and coal technological parameters were normalized according to the formula:

$$X_{norm} = \frac{(X_i - X_{\min})}{(X_{\max} - X_{\min})},$$

where X_i is the result of a single value of element concentration; $X_{\max}$ is the result of the maximum concentration value of the element; $X_{\min}$ is the result of the minimum concentration value of the element.

Normalization was carried out to unify the sample to the same scale, regardless of the used units of measurement and the scope of the data.

4 Research results

For visual analysis and a better idea of the nature of the sample of germanium contents and the peculiarities of their distribution, a histogram was constructed (Fig. 1).

Visual analysis of the presented histogram demonstrates: 1) the lack of compliance of the sample with a normal or lognormal distribution; 2) the presence of polymodality in the distribution of germanium; 3) shift of the main mass of the distribution to the right, to higher values. Additional analytical calculations were also carried out to check the correspondence of the empirical distribution of the studied parameter to the normal distribution. For this, the Kolmogorov-Smirnov, Shapiro-Wilk, Lilliefors, and Pearson's chi-square tests were used. In all cases, the results confirmed that the sample did not follow a normal or lognormal distribution. Therefore, for an adequate assessment of the central tendency of the germanium level, it is better to use the median instead of the arithmetic mean.

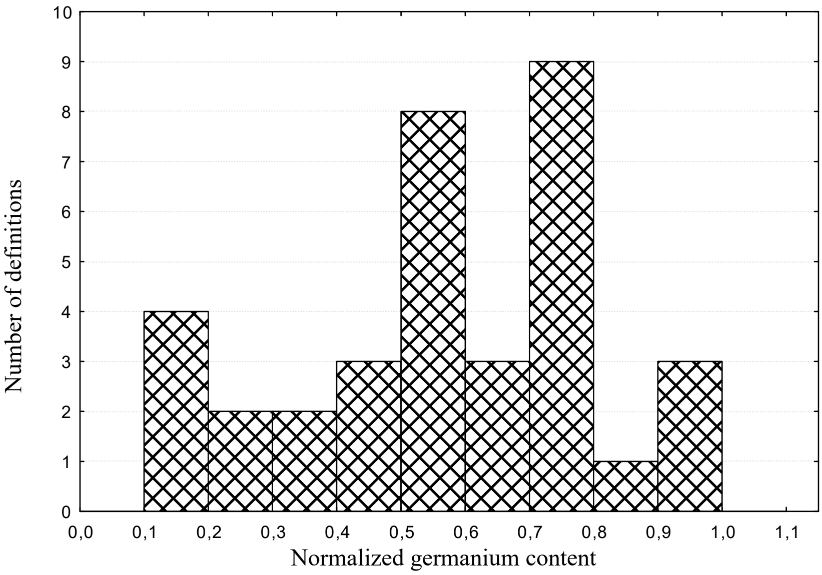

Fig. 1. Histogram of the distribution of normalized germanium content in seam c_5 within the boundaries of the "Pavlohradska" mine.

On the constructed map of isoconcentrations (Fig. 2), one significant and two relatively local zones of increased germanium content are distinguished, which were detected at the isogypsum level of 0.7.

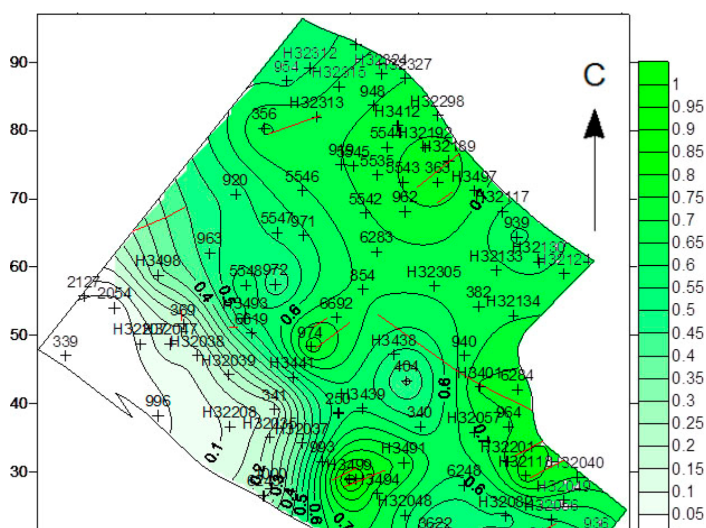

Fig. 2. Map of isoconcentrations of the normalized content of germanium in the coal of seam c_5 of the "Pavlohradska" mine.

The first zone with an increased content of germanium occupies almost half of the area of the mine seam and is in the northeastern part. This zone is characterized by a complex corrugated surface, on which there are three areas with abnormally high concentrations of the element in question. The axes of these corrugations fan out from the first of them, which is located near the northern edge of the mine field near wells 5543, H32189 and 363. The maximum value of germanium content within this section is 21.4 g/t.

The second section is located southwest of the first, along the second fan axis, in wells 6283, 854, 6692 and 974. Coal samples from well 974 showed the maximum germanium content for this section, which is 21.3 g/t.

The third area with abnormally high concentrations of germanium is in the southeastern part of the first zone along the third axis of the fan near wells 6284, H3401, H3211, H32040 and H32049. The highest content of germanium here was recorded in coal samples from well H3211, where it reached 23.6 g/t, which is the highest indicator for the entire first zone.

The second relatively local zone with an increased content of germanium was found to the southwest of the first significant zone, almost in the southern part of the mine seam, in wells H3491, H32048 and H3494. The maximum value of germanium here, found in samples from well H3494, is 21.3 g/t.

The third local zone with an increased content of germanium is in the southernmost part of the mine field near wells 992, H32111, H32112, 995 and 3023. The highest content of germanium in this area and in the entire mine seam was recorded in coal samples from well 992, where it reached 24.7 g/t

Analysis of the drilling data of each well and information from the mine geological surveying service revealed several common characteristics in the geological structure of the c_5 coal seam in all areas with the maximum germanium content: 1) the minimum capacity of the coal seam; 2) availability of one or two partings; 3) the presence of at least two small-amplitude disturbances with a northeasterly extension.

On the map of local deviations of the standardized content of germanium in the c_5 coal seam of the "Pavlohradska" mine (Fig. 3), one large and almost continuous zone of positive local deviations is clearly distinguished, separated by the 0.05 isogypsum.

This zone stands out as a wide strip starting from wells H32312, H32315 and H3498 on the northern and northwestern border of the mine field, narrows near wells 250 and H3439 in the central part and widens again to the southern border of the field, reaching its maximum width near wells 993. 3023 and H32111. It passes through the center of the mine seam in the meridional direction. The map shows a significant undulation of the surface of this zone. The maximum indicators of positive local deviations are recorded in places adjacent to wells 356 (first site), 974 (second site), H3499, H3494 (third site) and 992 (fourth site). The other two less pronounced zones of positive local deviations are concentrated near wells H3401 and H32118. The analysis of the geological structure and spatial location of zones with positive local deviations of germanium in the c_5 seam allows us to establish that they are associated with local reductions in the power of the coal seam.

On the map of the gradients of the normalized content of germanium in the c_5 coal seam of the "Pavlohradska" mine (Fig. 4), two bands of maximum gradients of the content of this element are clearly visible.

Both zones are in the southern part of the mine field and are separated by a thin meridional strip that extends through the area of wells H3221, H32048, H3491 and 340. The first zone includes the area near wells 2054, H3498, H3220, H32038, H32039, 6619, H3493, 5548, 972, 974, H3441, 341, H32035, H32037, 1000, 6243, 993, H3499, H3494. The second strip covers the area around wells H32196, 3622, 992, 995, H32112, H32111, H32089, 348, H32082, H32056, H32118, H32201. In the territory of these two strips, the increased variability of the power of the coal seam, its structural features, the presence of tectonic disturbances and the facies variability of the nearest and main roof is recorded.

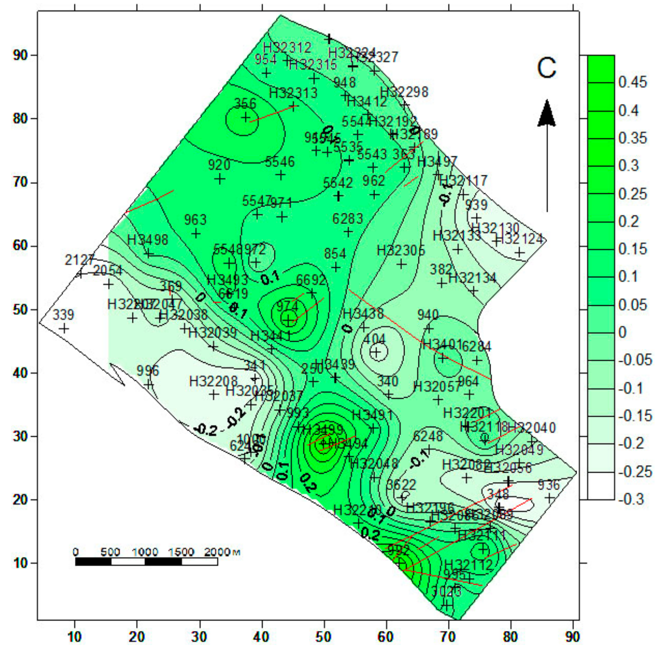

Fig. 3. Map of local variations of the normalized content of germanium in the coal of seam c_5 of the "Pavlohradska" mine.

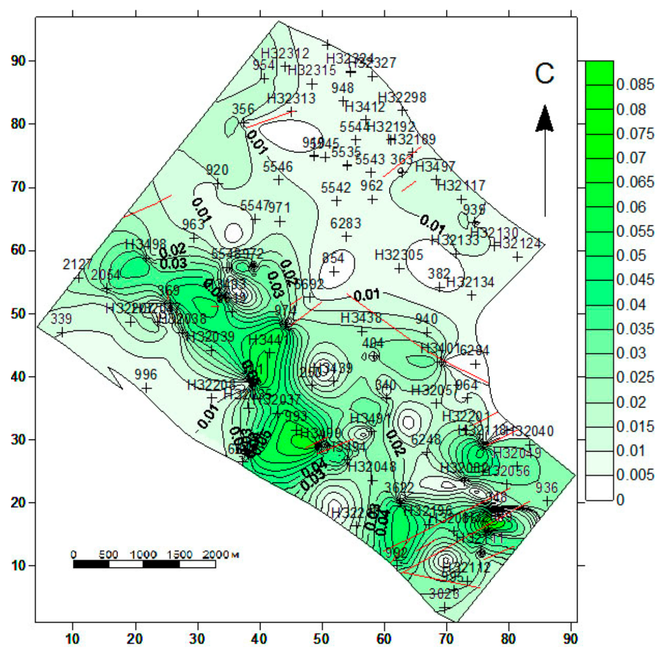

Fig. 4. Map of the gradients of the normalized content of germanium in the coal of seam c_5 of the "Pavlohradska" mine.

The map of regional changes in the normalized content of germanium (Fig. 5) shows an increase in its concentration in the northeastern direction.

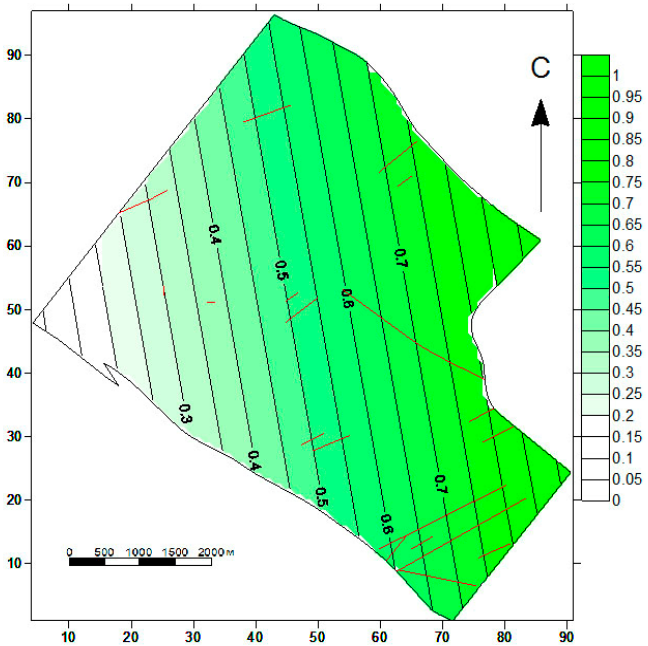

Fig. 5. Map of the gradients of the standardized content of germanium in the coal of seam c_5 of the "Pavlohradska" mine.

Correlation and regression analyze were conducted to test the hypothesis of a correlation between the germanium content in the coal seam and its power. The results of the correlation analysis showed the presence of an inverse and very close relationship between the germanium concentration and the seam thickness (m), while the linear correlation coefficient is -0.94. Based on the regression analysis, a linear regression equation was calculated:

$$Ge = 0.917 - 0.9577 \text{ m}.$$

The graph of this regression equation is presented in Fig. 6.

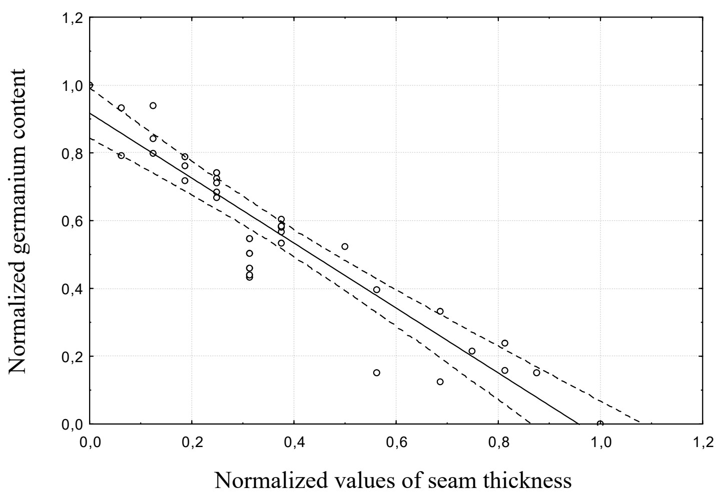

Fig. 6. Graph of the linear regression equation between the germanium content and the capacity of the coal seam c_5 of the "Pavlohradska" mine.

5 Conclusions

The conducted research made it possible to formulate the following key conclusions: 1) Within the mine field, the concentration of germanium in the c_5 seam ranges from 8.8 g/t to 24.7 g/t, with an average of 17.62 ± 0.47 g/t, which is 6.08 times more than the germanium clark for world coal reserves. This highlights the significant germanium enrichment of this reservoir and makes it an important potential source of this strategically important raw material. 2) It was found that the distribution of germanium does not correspond to a normal or lognormal law, while polymodality is observed in the distribution, which indicates the variety of forms of its concentration, which were realized in the specific geological conditions of seam c_5 of the "Pavlohradska" mine and the polygenetic nature of its accumulation in this seam. The results demonstrate that it is better to use the median instead of the arithmetic mean for a more accurate estimate of the central tendency of the germanium level. 3) Three zones with high Ge content were found on the territory of the c_5 seam, and their spatial location was determined. 4) It was established that the geological structure of the c_5 coal seam in places with the highest germanium content has common features: minimal thickness, the presence of one or two partings, as well as the presence of at least two low-amplitude northeast-trending disturbances, which can be used as predictive criteria for determining zones with the largest germanium content. 5) It was found that the local decrease in the capacity of the c_5 coal seam contributes to the formation of zones with positive local deviations in the content of germanium. 6) The increased variability of the thickness of the coal seam, its structure, the presence of discontinuities, and the lithologic-facies variability of the immediate and main roof contribute to the increase in the gradients of the germanium content. 7) The growth of the regional component of germanium content in the north-eastern direction was established. 8) The existence of a close and inverse correlation between the concentration of germanium and the power of the c_5 coal seam was proved, as well as the regression equation between these parameters was calculated, which allows you to predict the germanium content without conducting new tests and analytical studies.

The scientific novelty of the obtained results lies in the fact that the existence of genetically different forms of germanium in the c_5 coal seam was discovered, an inverse and close correlation between the concentration of germanium and the thickness of the seam was established, and it was also proved that the content of germanium in the coal seam is affected by both syngenetic, as well as epigenetic factors.

The practical value of the research lies in the justification of the method of accurate estimation of the central tendency for a sample population of germanium concentrations, the construction of maps reflecting the spatial distribution of the element in the reservoir, and the calculation of the regression equation for forecasting the germanium content without additional tests and analytical studies.

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