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Research Article

Looking for Noble and Rare Metals in Black Shale Formations of Armenia: The Primary Investigations

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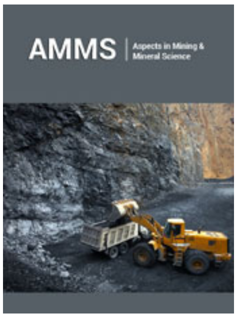
ISSN: 2578-0255



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Submission: May 24, 2023
Published: June 22, 2023

Volume 11 - Issue 4

How to cite this article: Arshavir Hovhannisyan, Yelena Panova, Shahen Khachatryan, Varduhi Siradeghyan, Karen Hambaryan And Yeghis Keheyan*. Looking for Noble and Rare Metals in Black Shale Formations of Armenia: The Primary Investigations. Aspects Min Miner Sci. 11(4). AMMS. 000769. 2023.
DOI: 10.31031/AMMS.2023.11.000769

Abstract

The shortage of liquid and gaseous fossil fuels in the world growing day by day has led to intensive searches for new energy sources. The focus on solid fuels has increased dramatically, particularly on oil shales and brown coals, the world reserves of which significantly exceed the known reserves of liquid hydrocarbons combined. Moreover, solid caustobiolites, in addition to being source of energy, also have another "merit" undiscovered until recent decades: they are natural accumulators of noble and rare metals. More than 40 deposits and occurrences of brown coal and oil shales are known within the borders of Armenia. Prospecting work of coal and oil shales, as well as of bituminous formations, has been done for decades. However, in general, the study of fuel and energy resources of the Republic was unplanned, unsystematic, and it is currently in unsatisfactory condition. Moreover, the existing preconditions for expanding the raw material base of solid fossil fuels require ongoing research, since coal and oil shales can have a significant share in the energy balance of the Republic of Armenia. More than 16 deposits of brown coal and oil shales were studied in detail in Armenia during the Soviet years. According to the data received, exploitation of those deposits was considered to be inefficient, and the resources of coals were considered to be non-perspective in terms of fuel raw materials. However, solid fossil fuels have another "aspect" of usefulness, i.e. metallogeny. Interest in the issue of black shales metallogeny has increased over the last 35 years. Targeted combined studies of noble and rare metals in the black-shale complexes are a fundamentally new phenomenon in our country, and they have been carried out for the first time.

Keywords: Armenia; Black shale; Noble and rare metals; Brown coals; Metal bearing

Introduction

Numerous studies on alpine geodynamics and patterns of spatial distribution of metallic and non-metallic deposits of the Lesser Caucasus, depending on the geodynamic regime of development of folded areas of Armenia [1], allowed to theoretically predict and later prove in practice the metallogeny of terrigenous-carboniferous complexes [2-6]. These complexes are widespread in Armenia. They are represented by terrigenous-coal-bearing and terrigenous-carbonate-coal-bearing deposits with small thickness of brown coals, oil shales, bituminous mudstones, sandstones and limestones, clay shales, and a lesser amount of andesites, tuffites, tuff-conglomerates and tuff breccias. The total thickness of the complexes is highly variable and is between 60-120 and 200m on average. They spread hundreds of meters, and in some cases from 2-3 to 5km [7-9]. The age of the complexes ranges from the Lower Triassic to Pliocene (Triassic, Jurassic, Eocene, Oligocene, Miocene, Pliocene), which indicates the multi-stage of mineralization all over Phanerozoic. In most cases, these deposits have gentle dips and they outcrop, or have subsurface emplacement and are easy for open-pit mining. The modest volume of work carried out so far are very insufficient to find out the mineral raw materials value of the Armenian solid caustobiolites in terms of metallogeny. It is necessary to implement large-scale complex projects, which will include both research and geological exploration work. Since 2021, within the scope of cooperation between the Institute of Geological Sciences of NAS RA and the Institute of Earth Sciences of Saint Petersburg State University, explorations have started related to the issue of noble and rare metals in brown coals and oil shales. In fact, in the work, an attempt is made to discuss the prospects of the metalbearing of gray coals and black shale in Armenia. This is especially relevant in the sense that the aforementioned geological formations have very low quality as combustible minerals. And their complex use: obtaining combustion energy and extracting metals can give a real economic effect in Armenia, which is poor in natural fuels.

Fieldwork, Materials and Methods

In fact, we try to determine the possibilities of the detailed and comprehensive analysis of black-shale formations of Armenia, with the assessment of their current hypsometric level and the perspectives of their application. To study the problem, our geological-geochemical group has already sampled the previously known 9 occurrences and deposits of brown coals, oil (black) shales, and bituminous limestones (Figure 1). Among more than 40 geological sites we have chosen the ones which are physically more accessible and are more representative. The total number of samples is 30. The material for research was samples of coals, oil shales, and bituminous limestones of deposits and occurrences of Armenia, which are shown in the schematic map (Figure 1). The samples were taken according to the stratum thickness, from bottom to top. The distribution of rhenium and trace elements in black shales has been analyzed through inductively coupled plasma mass spectrometry (ICP MS).

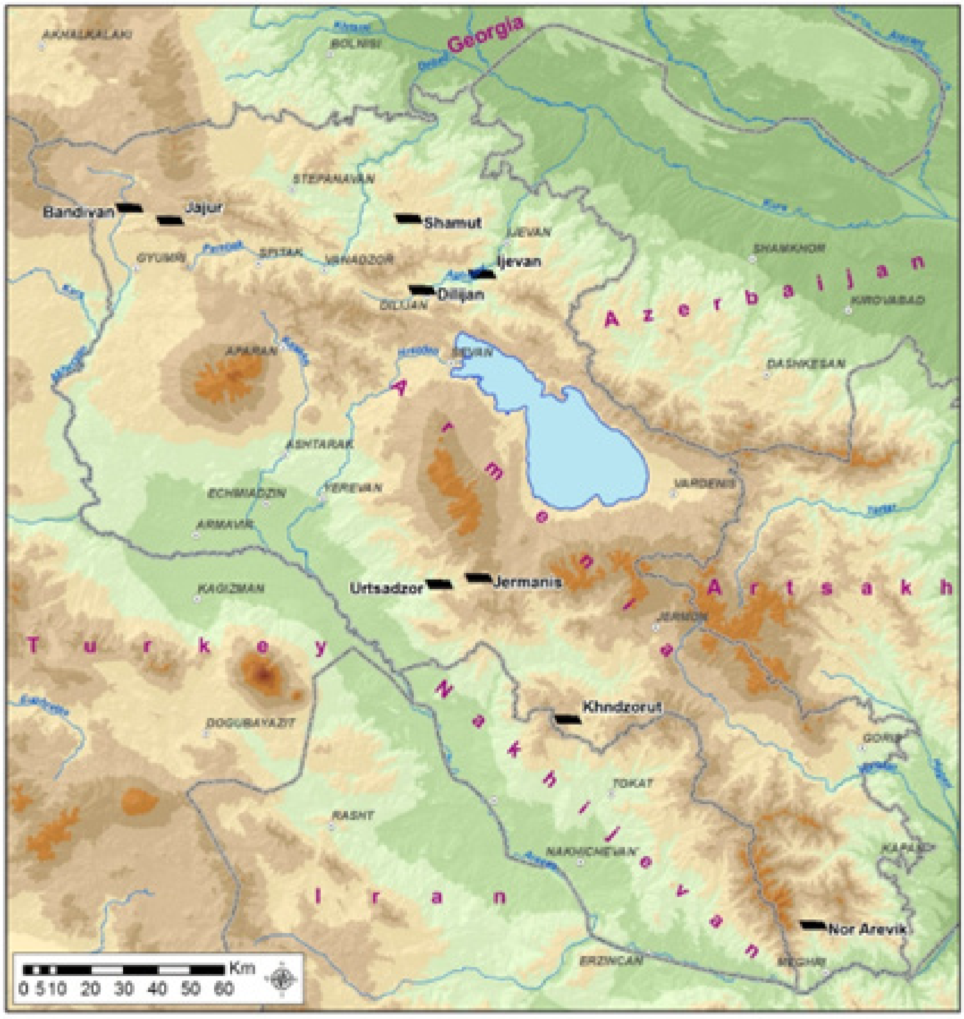

Figure 1: The schematic map and areas of distribution of sampled deposits and occurrences.

In this case, we used the methodology and analysis algorithm developed for brown coals [10]. To decompose the samples and dissolve salts, nitric and hydrofluoric acids, hydrochloric acid of special purity, further cleaned through distillation, and deionized water were used. The prepared solutions were analyzed with Agilent-7700 and ELAN-6100 DRC devices. The spectrometry of atomic absorption allows to implement quantitative analysis for determining the contents of noble metals (Au, Pt, Pd, Os, Ir, Ro, Ru), which was carried out according to the method of full opening with the help of acid with additional melting of the residue. The weighed portion of the powdered sample weighing 10g was decomposed according to the method developed in the laboratory. The sample decomposition method is based on partial, non-oxidative destruction of the sample by acid mixture, washing, drying, and ashing the residue, fusing it with sodium peroxide and dissolving the mixture in hydrochloric acid. The introduction of oxalic acid into the mixture of destructive reagents prevents the passage of noble metals into the solution and ensures separation of metals in the solid phase, if they are present in the sample in the form of soluble salts. Hydrofluoric acid destroys the silicate matrix of the sample, as a result, silicon is removed in the form of fluoride, and the mixture of sulfuric and phosphoric acids contributes to the displacement of fluoride ions from the resulting salts of other metals. The destruction of carbon substances is of particular importance: it eliminates the need for pre-ashing process of carbon samples. The analyses of the prepared solutions were carried out by the method of atomic absorption spectrometry with electrothermal atomization on Analyst-800 devices.

Geochemical features of studied rocks

Comparisons of the contents of Armenian black-shale rocks (coals, oil shales and bituminous sedimentary rocks, in general, 30 samples) sampled by us with the Clark numbers of other similar occurrences in the world are presented in Table 1. Compared to Clarke numbers, the highest values in the black-shale formation rocks of Armenia (Table 1) are set for gold and silver. Platinum and palladium are traditionally present in small amounts but can be considered as accompanying elements. The high content of rhenium has been recorded for the first time. The accompanying -elements - vanadium and uranium should not be ignored. Among the chalcophile elements, the following are distinguished according to their high contents (in descending order of Clark numbers of concentration): Co, Cu, Ni, Mo, Zn, Pb. Due to the fact that there are deposits of different genesis (primary and secondary) and ages in the territory of Armenia, an individual approach to the study of each of them is required. It is known that the formation of deposits in carbonaceous terrigenous-volcanogenic strata is of a complex nature and is caused by the processes of sedimentation, metamorphism, and superimposed metasomatism. It is established that elevated contents of noble metals in black shales can be controlled by faults and are due to the appearance of hydrothermal-metasomatic processes, with redistribution and introduction of noble metals by deep solutions [11-17]. In recent decades, close attention has been paid to rhenium in carbon shales, in which it is accumulated in high contents. Rhenium extremely rarely occurs as an independent mineral therefore, it is present as an isomorphic admixture in the composition of more than 50 minerals, and in an organic and argillaceous matter, it is in a dispersed condition. The Clarke of rhenium in black shales is 0.3-0.8g/t [18], which is six times more than its Clarke in other sedimentary rocks. Possessing organophilic properties, it is a characteristic element of carbon shales [19,20].

Table 1: The average geochemical contents of analyzed elements in clayey and black shales, in ppm.

Chemical Elements	Black-Shale Rocks of Armenia	Clay Shales by Sklyarov et al. [31]	Black Shales By Ketris, Yudovich [18,19]
U	1-75	3,7	8,5
V	3-134	130	205
Mo	1-40	2,6	20
Cu	3-170	48	70
Co	5-435	19	19
Ni	3-104	74	70
Zn	2-133	93	130
Pb	1-120	20	21
Rb	5-150	150	74
Sr	25-504	330	190
Au	0,002-0,83	0,0033	0,007
Ag	0,06-10,5	0,072	1
Pt	0,002-0,0061	0,001	0,0009
Pd	0,002-0,027	0,001	-
Re	0,005-0,042	0,0001	0,3-0,8

In the last decades, thanks to the development of modern analytical methods of determination of rhenium in a carbon matrix, new data have been obtained on the content of rhenium in the geological bodies of the sedimentary cover [21]. Improvement in analytical equipment and methods for the determination of rhenium has made it possible to carry out mass analyzes with a low detection threshold. The geochemical "specialization" of oil shales is given below (Table 2) within the sedimentary cover of the East European Platform [21,22]. It has been established that Dictyonema shales, oil shales-kuckersites and carbon shales of different basins have "rhenium specialization". The connection of metals with black shales may be of genetic nature or be spatially linked [23]. In the first case, the presence of a connection is determined by the presence of an organic component, in the second - by the common sedimentary basins, which are equally favorable for the formation of carbon rocks and accumulation of metals [23]. Currently, black-shale formations, along with ores of magmatic origin, are considered to be a potential source of stratiform mineralization of precious metals. Black shales provide a new source of raw materials for the metals e.g., gold, rhenium, and platinum group.

In this regard, it is important to understand their distribution and type of formation in black-shales, to create a basis for forecasting, developing prospecting methods for sites of this type, and creating technological enrichment schemes for the metals present in them.

Table 2: Geochemical specialization formulas of oil shales in Eastern Europe and Russia and its vicinity [19]. Note: the number before the element sign indicates the concentration Clarke of the element.

Basin (Area)	Geochemical Specialization Formula
Eastern (Russian) part of the Baltic basin. Dictyonema shales	350Mo 160Sc 143Re 111Bi 75As 52U 24Cd 13Cu 12V 11Tl 10Ag 10Au 7Pb 6Sb 5Hg 4B 4Co 3Zn 2F 2Sn 2Ni 2Nb
Eastern (Russian) part of the Baltic basin. Kuckersites	1000Re 160Sc 14Ag 11Mo 5Hg 4Pb 4B 3Zn 2Sn
Yarenga basin	112Re 101Cd 66Mo 27As 12Zn 7V 5Ag 5Ni 4Cu 3P 2Ba 2Cr
Timan-Pechora basin	165Re 150Bi 50Mo 12U 7B 3Ag 3Pb 2Sn 2Tl 2V 2Zn 2Hg

The forms of occurrence of chemical elements in nature

According to Safronov [24], chemical elements are found in nature in mineral and non-mineral forms. The latter include simple and complex ions, colloidal, adsorbed, and suspended particles. In addition, they are divided into mobile and strongly bonded ones according to extraction from rocks (through simple leaching without destroying the mineral lattice). At the same time, it is a fact that the non-mineral mass of an element in nature is greater than its proportion in the mineral form [24]. Literature data show that the form of occurrence of noble metals in black shale complexes is complicated and diverse, and it is not always possible to confirm that. It is due to dispersed precipitation of noble metals (about 1μm), which are hard to determine by modern analytical methods [25,26]. If platinoid minerals are quite distinguishable in Poland, Australia, Karelia (20-30μm), then in South China and the USA, as well as most regions of Russia, the presence of platinoids is determined only by chemical-analytical methods [23]. At the same time, they can occur in soluble and insoluble organic matter, i.e., in nickel, copper, silver, molybdenum, zinc, lead and mercury minerals, in form of platinoid admixtures.

According to Gurskaya [12], The minerals of noble metals, revealed in black shales, form a complicated complex, which is divided into several classes: 1) native metals, 2) metallic solid solutions and intermetallic compounds (natural alloys), 3) sulfides, 4) arsenides and sulfo-arsenides, 5) selenides, 6) tellurides, 7) bismuthides, 8) antimonides. Lots of new minerals were revealed in black-shale rocks, including, their compounds with biophilic elements - selenium, phosphorus, and arsenic. Since the forms of occurrence of noble metals and the range of satellite elements determine their technological properties, the issue of determining the mineral composition in black-shale rocks becomes a primary one. Traditionally, the forms of occurrence of chemical elements in nature are divided into the following types: easily extractable; ores in which noble metals are included in the composition of sulfides and arsenides; ores in which noble metals are part of organic matter [27]. Traditional technological processes of extraction of refractory ores do not take into account the behavior characteristics of noble metals in shales, as a result, it is impossible to completely extract them. The following forms of noble metals are known in black shales: mineral and micromineral, dispersed, i.e., in associations with clay and organic matters, and water-soluble substances. Studies in this direction will be carried out for Armenian samples in the near future. Obviously, each type requires certain processing conditions. Mineralogical research of black shales of Cambrian-Ordovician of the Baltic paleo-basin has allowed detecting, native metals and intermetallic compounds in the siltstone-sandstone, admixture: Aunat (native), Pd, Os-Ir, Au-Ag, Au-Cu, Au-(Cu)-Hg, Au-Hg, Ag-Cu, Pt-Fe. Along with them, the samples contain native Fe, Al, Cu, Fe-Ni, Ni-Fe, Cu-Zn, as well as tellurides and bismuth oxides [23]. Further, the following mineralization phases of noble metals were revealed in the concretion complex (diagenetic sulfides): Aunat, chalcopyrite with an admixture of gold. In association with pyrite, the native elements occur with the admixtures of Ni, Co, Zn, Cu, As, with sphalerite - with the admixtures of Cd, Fe and pentlandite.

Noble metals and organic matter: The most important forms of existence of these elements in carbon rocks can be absorbed (in organic matter and clay minerals) and colloidal-saline. In recent years, the method of bio-oxidation based on the action of iron- and sulfur-oxidizing bacteria has been applied to the complex types of black-shale ores. In this case, it is important to have the presence of mobile, weakly bonded, colloidal-water-soluble forms of metals in the rock. The method is successfully used on an industrial scale in many countries around the world, e.g., in Poland, Canada, South Africa, and Finland [13,27-29]. The black-shale formations contain up to 50 rel.% of Corg (organic). A close correlation between rheium and organic matter has been established. The increase in rhenium concentration up to 0.1-0.2g/t is accompanied by an increase in the amount of Corg.

Noble metals and clay components of shales: In order to detect the connection between the clay components and noble metals of black shales we have analyzed the whole-rock composition of black shales and the clay fraction separately by the ICP MS method (Table 3). As seen in Table 3, the clay component is mostly several times enriched by noble metals and other elements compared to the BSh. Enrichment of the clay part of shale is typical for rhenium, uranium, molybdenum and vanadium. This is due to the higher absorption capacity of clay minerals. The clay fraction is enriched by platinum and palladium by about 7-10 times, and rhenium content in the clay part is 3-7 times more than in the black shale sample.

Table 3: Concentration of chemical elements in the studied samples of black shale (BSh) and in its clay component (CC), in g/t.

Sample	Pd		Pt		Au		Re		U		V		Mo	
	BSh	CC	BSh	CC	BSh	CC	BSh	CC	BSh	CC	BSh	CC	BSh	CC
9	0,06	0,45	0,012	0,11	0,067	0,093	0,15	1,23	14	119	279	1760	43	782
35	0,05	0,36	0,011	0,089	0,034	0,089	0,22	1,14	172	310	1483	2360	176	217
114	0,07	0,77	0,078	0,55	0,078	0,13	0,29	1,56	152	204	860	653	214	118

Colloidal-water-soluble forms of noble metals in black shales: Chemical elements in the black shale rocks can be in a dispersed form and be represented by particles of ultra-small size - less than 1000nm. The content of this fraction varies in different types of deposits; it is difficult to count, and it "is lost" during the analysis and use of traditional technology schemes of extraction. At the same time, there is evidence that rare and dispersed elements are naturally concentrated in porous sections of rocks with content several times higher than in the sample as a whole, and higher than the limit of detection by analytical methods [22,30]. The important results that shed light on the issue of the forms of occurrence of noble metals and rhenium in black shales were obtained during the segregation of the so-called "submicron fractions" from the rock [10]. Submicron fraction is a part of the sample in which chemical elements are in ionic, molecular and colloidal forms, 1-1000nm in size, which is extracted by water solution under specially selected conditions.

Experiments on a sample with the content of rhenium of 1.75g/t and the output of submicron fraction from the sample - 1.94 weight % allowed to determine the content of rhenium in submicron fraction of 22.6g/t. The extraction of this element in the colloidal-saline fraction was 25.3 rel.% [10]. The analysis of water solutions makes it possible to realize the possibilities of the ICP MS method to the maximum extent, since there is no negative effect of additionally introduced chemical reagents on the results, which leads to decrease in the limits of detection of elements. The content of petrogenic oxides in the solution of Submicron Fraction (SMF) is significantly lower than in the shale sample [10]. This enables us to obtain real values of microelements without introducing additional corrections. The result of the work with real concentrations, and not near detection limits is the high reproducibility of the analysis and decrease in determination error. The accumulation factor for the noble metals and rhenium is quite high, except for silver (Table 4). We assume that this may indicate the accumulation of silver in mineral form, unlike the noble metals and Re. Thus, analysis of matters according to the mineralogical and geochemical features of carbon rocks allows expressing an opinion about the content of gold, silver, platinoids, and rhenium in four possible forms. Each of them is associated with a specific part of the rock: a) sulfide mineralization (pyrite-marcasite, chalcopyrite, galenite and other sulfides), which are present in shales in the form of fine admixtures, concretions or merged sulfide layers; b) in the clay matter, which is determined by its high absorption capacity, c) in organic matter of rocks, d) in the composition of mobile (ionic, molecular and colloidal) forms [31-33].

Table 4: Noble metals in black shales and their submicron fractions, g/t [17].

Element	Average for the Baltic Paleobasin		Accumulation Ratio (SMF/BSh)
	SMF 70 Samples	BSh for 70 Samples)	
Pt	0,20	0,018	11,2
Pd	4,86	0,654	7,4
Au	0,29	0,034	8,4
Ag	0,91	1,309	0,7
Re	2,1	0,214	9,8

Conclusion

a. Black-shale formations are widely spread and are in significant volumes in the territory of Armenia. Their age is from the Lower Triassic to Pliocene and they are represented by terrigenous-carbonate formations, brown coals (lignite), oil shales, bituminous mudstones, sandstones, and limestones.

b. Black-shale formations in Armenia are enriched by gold, silver, rhenium, and platinoids. Among the satellite elements, there are Co, Cu, Ni, Mo, Zn, and Pb.

c. It is necessary to clarify the macro- and micro-mineral forms of noble metals, rhenium and satellite-elements in the black-shale formations of Armenia.

d. It is possible to detect a significant part of colloidal-saline forms of the above-mentioned chemical elements, however, their extraction will require an integrated approach.

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