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MINERALOGY AND GEOCHEMISTRY OF OIL SHALE IN AZERBAIJAN: CLASSIFICATION, PALAEOWEATHERING AND MATURITY FEATURES*

Ад. А. Алиев, О. Р. Аббасов, А. М. Агаев. МИНЕРАЛОГИЯ И ГЕОХИМИЯ ГОРЮЧИХ СЛАНЦЕВ В АЗЕРБАЙ-ДЖАНЕ: КЛАССИФИКАЦИЯ, ОСОБЕННОСТИ ПАЛЕОВЫВЕТРИВАНИЯ И ЗРЕЛОСТИ. В научно-исследовательской работе широко рассмотрены наземные выходы горючих сланцев Шамахы-Гобустанского и Апшеронского районов, а так-же среди выбросов грязевых вулканов Азербайджана. В соответствии с распространением в породах как главных, так и микроэлементов, на основании опубликованных материалов был проведен сравнительный анализ со средними, средне-черными сланцами, составом сланцев Северной Америки, пост-архейскими сланцами Австралии, а также горючими слан-цами Эстонии, Иордании, США и др. На основе известных классификаций рассматриваются характеристики стабильно-сти оксидов главных элементов и оцениваются признаки зрелости. Свойства выветривания широко прокомментированы на основании различных индексов, в том числе «Индекса изменения в соответствии с компонентом (ИИСК)», «Индекса хими-ческих изменений (ИХИ)», а также анализами результатов диаграмм, связанных с элементным составом.

В составе образцов определено 11 минералов 5 классов, в которых преобладают силикаты. Используемая классифика-ционная диаграмма log (SiO₂/Al₂O₃) и log (Fe₂O₃/K₂O) показывает, что все исследованные образцы соответствуют сланцам.

Соотношение K₂O/Al₂O₃ подтверждает превосходство глинистых минералов в составе горючих сланцев по сравне-нию с K-минералами, включая K-полевой шпат. Оценки на основе Al₂O₃/(CaO + MgO + Na₂O + K₂O) и Fe₂O₃/K₂O, SiO₂/Al₂O₃ подтверждают нестабильность оксидов и минералов в образцах. Кроме того, соотношения SiO₂/Al₂O₃ и Al₂O₃ > Fe₂O₃ > TiO₂ подтверждают незрелость и связь с глинистыми минералами.

Значения ИХИ и диаграммы зависимости ИХИ от ИИСК, ИХИ от Al/Na и A–CN–K, а также исследования, связанные с содержанием главного оксида, подтверждают среднюю и высокую степень выветривания. Протолит сланцев связан с мафическими и промежуточными изверженными источниками.

Ключевые слова: горючие сланцы, геохимия, минерал, классификация, зрелость, выветривание.

Ад. А. Алієв, О. Р. Аббасов, А. М. Агаєв. МІНЕРАЛОГІЯ І ГЕОХІМІЯ ГОРЮЧИХ СЛАНЦІВ В АЗЕРБАЙДЖАНІ: КЛАСИФІКАЦІЯ, ОСОБЛИВОСТІ ПАЛЕОВИВІТРЮВАННЯ І ЗРІЛОСТІ. У науково-дослідній роботі широко розгляну-ті наземні виходи горючих сланців Шамах-Гобустанський і Апшеронського районів, а також серед викидів грязьових вулка-нів Азербайджану. Відповідно до поширення в породах як головних, так і мікроелементів, на підставі опублікованих мате-ріалів був проведений порівняльний аналіз із середніми, середньо-чорними сланцями, складом сланців Північної Америки, пост-архейськими сланцями Австралії, а також горючими сланцями Естонії, Йорданії, США та ін. На основі відомих кла-сифікацій, розглядаються характеристики стабільності оксидів головних елементів і оцінюються ознаки зрілості. Власти-вості вивітрювання широко прокоментовані на підставі різних індексів, в тому числі «Індекса зміни відповідно до компоне-нта (ІЗВК)», «Індекса хімічних змін (ІХЗ)», а також аналізами результатів діаграм, пов'язаних з елементним складом.

У складі зразків визначено 11 мінералів 5 класів, в яких переважають силікати. Використовувана класифікаційна діа-рама log SiO₂ / Al₂O₃ і log (Fe₂O₃ / K₂O) показує, що всі досліджені зразки відповідають сланцям.

Співвідношення K₂O / Al₂O₃ підтверджує перевагу глинистих мінералів у складі горючих сланців в порівнянні з K-мінералами, включаючи K-польовий шпат. Оцінки на основі Al₂O₃ / (CaO + MgO + Na₂O + K₂O) і Fe₂O₃ / K₂O, SiO₂ / Al₂O₃ підтверджують нестабільність оксидів і мінералів в зразках. Крім того, співвідношення SiO₂ / Al₂O₃ і Al₂O₃> Fe₂O₃> TiO₂ підтверджують незрілість і зв'язок з глинистими мінералами.

Значення ІХЗ і діаграми залежності ІХЗ від ІЗВК, ІХЗ від Al / Na і A-CN-K, а також дослідження, пов'язані з утриман-ням головного оксиду, підтверджують середню і високу ступінь вивітрювання. Протоліт сланців пов'язаний з мафічними і проміжними виверженими джерелами.

Ключові слова: горючі сланці, геохімія, мінерал, класифікація, зрілість, вивітрювання.

Introduction. The South Caspian Basin (SCB) is located in the collision zone between the Arabian and Eurasian plates which is subjected to intensive sedimentation. Such tectonic and paledepositional features have created a favorable condition for the formation of hydrocarbons, mud volcanoes, especially oil shale in the Paleogene-Miocene sediments in Shamakhi-Gobustan and Absheron regions.

About 60 oil shale manifestations and deposits were recorded in these regions [41]. Along with outcrops, oil shale is also found in ejecta of mud volcanoes, which are widely spread both in Shamakhi-Gobustan and Absheron regions [1; 3; 4; 10; 22].

The study is aimed to investigate the chemical classifications, provenience, palaeoweathering and maturity characteristics of oil shale in the research regions based on the geochemical and mineralogical features.

Analysis of recent research and publications.

Information about oil shale in Azerbaijan is known as early as the beginning of the 20th century. This information was brief, because researchers, especially Russian scientists described only the outcrops of oil shale recorded during the study of the geological structure, tectonic properties and hydrocarbon potential of the territory of Azerbaijan [1].

In the middle of the century, the investigations on the study of oil shale have been relatively expanded, and several scientific papers and reports related to some fields and manifestations have been published [1; 3; 5; 6; 10; 22].

In later periods, the question of the study of non-traditional oil shale in Azerbaijan has not been enough actual. Of course, the main reason for this was the existence of large reserves of oil and gas in the territory of the Republic [1].

Since the beginning of 2000, the issue of studying oil shale has been resumed in the Department of "Mud Volcanism" of the Institute of Geology and Geophysics, Azerbaijan National Academy of Sciences. The geological and organic-geochemical features, as well as the probable resources and using the potential of oil shale of the Shamakhi-Gobustan, Absheron, Guba, Ismayilli regions of Azerbaijan, have been widely commented in the papers of a number of scientists of the Department [1-6; 9; 10; 12-14; 22; 41].

There are no any available studies conducted by Azerbaijani and foreign researchers that have been devoted to issues such as mineralogy, classification, provenance, etc. based on the inorganic chemical properties of oil shale found in Paleogene-Miocene sediments in the country. Though there are many published literature devoted to these studies in countries where oil shale has long been investigated [8; 15; 17; 28; 30; 38; 44; 45]. In this regard, this study is the first attempt to investigate the classifications, provenience, palaeoweathering and maturity characteristics of oil shale in Azerbaijan.

Geological settings. Shamakhi-Gobustan region – occupies a significant part of the south-eastern plunge of the Greater Caucasus. The Meso-Cenozoic and Quaternary formations take part in the geological structure of the region [1; 11]. About 40 outcrops of oil shale associated with Upper Cretaceous-Miocene sediments were registered here [5; 6; 22; 41]. The layers of oil shale of the Upper Cretaceous are thin, and the content of organic matter is relatively low [1; 2]. The region is characterized by a change in the thickness of sediments of the Middle Eocene. The thickness of oil shale layers vary in intervals of up to 10 meters in arches of the anticline, synclinal and mould structures (Boyuk Siyaki, Kichik Siyaki, Jangichay, Jangidagh, etc.) [1; 9]. The layers, containing oil shale in sediments of the Upper Maikopian are associated with shale lithofacies of the "Riki horizon". The sediments of the Middle Miocene (Konkian) are characterized by light gray, brown-gray shale and carbonate rocks. In the northwest and southwest of Gobustan, these lithofacies alternate with layers of oil shale of various thicknesses. The layers of oil shale were also registered in the sections of the Upper Sarmatian sediments [6; 10].

The geological and tectonic positions of the region are very complex, and two microblocks (Bayanata and Toragay) were established here that bound to the Goradil-Masazir underthrust zone and Gujur-Gyzyldash thrust [11].

Absheron region – 18 outcrops of oil shale were registered in the region [41]. In the geological structure of the region, the terrigenous and carbonate rocks of the Upper Cretaceous and Cenozoic deposits are noted [11]. Oil shale in the sections of the Eocene was registered only in the areas of Goytepe and Govundag [6]. The sediments containing oil shale in the region are associated mainly with the Upper Maikopian series and Upper Miocene [2; 5; 9]. The alternation of layers of black bituminous oil shale is registered on the northern slope of the mountains Uchtepe-Shorchala, as well as in the outcrops of the mountains Goytepe, Orjandagh and Fatmai. In the terrigenous and carbonate sediments of the Middle Miocene, the shale-bearing layers with a thickness of 30 m were observed within the Western Absheron in the Shorbulag and Garaheybat areas. The outcrops of laminated oil shale were recorded in Uchtepe-Ilkhidagh area, within the southern pericline of the Kecaldagh-Zigilpiri fold and further east of the village of Binagadi. The outcrops of oil shale were recorded in the Meotian sections that are characterized by a different thickness

in the region. Due to tectonic and orographic settings, the region is a bottom of the south-eastern part of the Greater Caucasus. Most of the tectonic zones are gradually deepening in the direction of the expansion of the Greater Caucasus – from the northwest to the south-east, and complicated with mud

volcanoes (Keyreki, Lokbatan, Bozdagh-Qobu, etc.) [11]. The samples of oil shale were taken from the outcrops of Jangichay and Boyuk Siyaki of the central part of Shamakhi-Gobustan region, as well as from ejecta of mud volcanoes in the studied regions (Fig. 1).
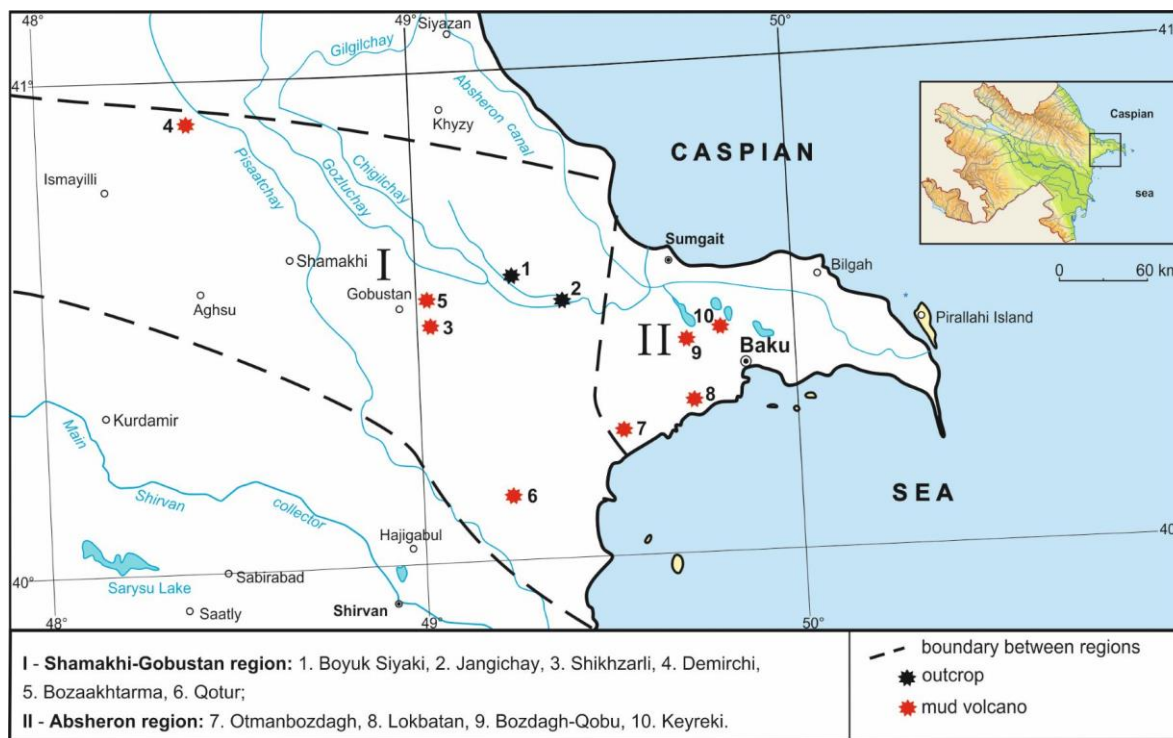

Fig. 1. Location map of the studied oil shale from outcrops and mud volcanoes

The accuracy of the age of oil shale from the outcrops is beyond doubt. Thus, the geological structure of the studied areas has been studied accurately. The geological age of oil shale found in the ejecta of mud volcanoes was determined according to the genus and species of fauna contained in the rocks assemblages. The *Globigerina bulloides (Orbigny)*, *Cibicides sp.*, *Globigerina triloculinoides (Plummer)*, etc. planktonic and benthic foraminifera belonged to Eocene were determined in the studied rocks.

Materials and methods. Samples – two samples from the outcrops (1 – Boyuk Siyaki, 2 – Jangichay) and eight samples from ejecta of mud volcanoes (3 – Shikhzarli, 4 – Demirchi, 5 – Bozaakhtarma, 6 – Qotur, 7 – Otmanbozdagh, 8 – Lokbatan, 9 – Bozdagh-Qobu, 10 – Keyreki) were taken. The samples are black, gray and brown in color with a laminated structure.

Chemical composition of rocks – analysis of major element oxides were performed on the "S8 TIGER Series 2 WDXRF" spectrometer and trace elements on the "Agilent 7700 Series ICP-MS" mass spectrometer at the Institute of Geology and Geophysics, Azerbaijan National Academy of Sciences.

Mineralogical composition of rocks – studied using the XRD "MiniFlex 600" at the same Institute.

Age of rocks – the microscopes "Loupe Zoom Paralux XTL 745" and "МБС-10" and a digital camera "OptixCam" were used. The study was carried out at the Integrated Engineering Exploration Production, Department of Geophysics and Geology, SOCAR.

Methodology. The published literature was used to obtain information about average shale [47], average black shale [49], North American shale composite [25], post-Archean Australian Shale [46] as well as oil shale from the Green River Formation of USA [45], Gurun basin and Hatildag deposit of Turkey [38; 44], Sultani deposit of Jordan [8], Baltic deposit of Russia [28] and Estonia deposit of Estonia [15] for comparative studies based on the distribution of major oxides and trace elements. A diagram and index proposed by [27] and [24] were used for the classification and determination of maturity of samples. The palaeoweathering characteristics were studied based on two indexes – Index of Compositional Variability [18] and Chemical Index of Alteration [35], and also plots proposed by [18; 31; 35; 43].

Results and discussions. Mineralogy – 11 minerals belonging to 5 classes: mainly carbonates, sulphates and silicates were found in the samples. Only one sample contains 1% of halite (halogen class), and hematite was found in three samples (Table 1).

Table 1

Mineralogical composition of samples (%)

Region	Area (sample)	Quartz	Feldspar	Calcite	Illite	Montmorillonite	Chlorite	Jarozit	Halite	Siderite	Hematite	Gypsum
Shamakhi-Gobustan	Boyuk Siyaki (1)	26.7	10.0	2.0	9.0	10.0	15.0	1.5	-	25.8	-	-
	Jengichay (2)	28.0	6.0	8.0	10.0	13.0	20.0	15.0	-	-	-	-
	Shikhzarli (3)	23.0	7.0	-	15.0	15.0	20.0	20.0	-	-	-	-
	Demirchi (4)	28.0	13.0	4.0	15.0	15.0	18.0	4.0	-	-	3.0	-
	Bozaakhtarma (5)	27.0	5.0	-	7.0	26.0	10.0	22.0	-	3.0	-	-
	Qotur (6)	23.0	5.0	12.0	10.0	12.0	16.0	16.0	1.0	-	-	5.0
	Otmanbozdagh (7)	20.0	15.0	9.0	12.0	17.0	17.0	7.0	-	-	-	-
Absheron	Lokbatan (8)	23.0	5.0	14.0	10.0	16.0	15.0	17.0	-	-	-	-
	Bozdagh-Qobu (9)	35.0	8.0	3.0	11.0	12.0	16.0	12.0	-	-	3.0	-
	Keyreki (10)	24.0	8.0	18.0	10.0	15.0	15.0	4.0	-	-	6.0	-
	Mean	**25.8**	**8.2**	**7.0**	**10.9**	**15.1**	**16.2**	**11.8**	**0.1**	**2.9**	**1.2**	**0.5**

The analyze of mineral assemblages in the shale samples showed the presence of clay minerals – illite, chlorite and montmorillonite. The value of montmorillonite (mean = 15.1 %) and chlorite (mean = 16.2 %) higher than illite (mean = 10.9 %) (Table 1).

Illite is widely distributed in clay and shale associated with the marine origin as a result of weathering of feldspar and muscovite. In the process of converting muscovite to illite, some part of K^{+1} is replaced by Ca^{+2}, Mg^{+2} and $H3O^+$ [7]. On the other hand, in a process of metamorphism of clay, its crys- tallization provides an indicator between diagenesis and low-temperature metamorphism [23].

Chlorites are formed in a result of physical and chemical change in the minerals of a mafic type such as pyroxene, amphibole, biotite, talc, and pyrophyllite. In coastal areas, where the degree of metamorphism is low, iron-enriched chlorite is formed. This type of chlorite is more unstable. At low temperatures, chlorite converts to montmorillonite, while and at high temperatures to talc, cordierite and garnet [7].

Montmorillonite belonging to the group of smectite forms as a result of hydrothermal changes or weathering of aluminum-rich minerals, in particular, bentonites – volcanic ash and tuff. Formation of this mineral often occurs together with other clay minerals, including illite. In the process of formation, the role of weathering and transformation of aluminosilicate rocks, especially, feldspar as well as rivers and streams are not excluded [29]. This mineral is an authigenic, and its origin related to an accumulation of shale and a change in detrital materials in a relatively calm condition.

The mean value of quartz in samples is 25.77%, feldspar – 8.2 % (Table 1). Quartz is a wide- spread accessory mineral associated with siliceous eruptions, such as volcanic rhyolite and plutonic granite [33]. Taking part in all degrees of metamorphism, and having a high resistance to chemical weathering, this mineral is widely distributed in sedimentary rocks including metamorphosed oil shale.

Anorthite (Fig. 2a and 2c) and albite (Fig. 2b and 2d) are present in the studied samples. Anorthite is the calcium-rich endmember of the plagioclase solid solution series, the other endmember being albite (the sodium endmember). Albite twinning is characteristic for plagioclase associated with igneous rocks, such as basalt, andesite, dacite, rhyolite, etc. Along with the metamorphic rocks, they are found in the composition of detrital sedimentary rocks. At shallow depths, close to the Earth's surface, they are relatively less stable in comparison with alkaline feldspar (orthoclase, anorthoclase, etc.) and quartz, and decompose to clay mineral during weathering [33]. Quartz and feldspar are associated with coastal zones [29]. During diagenesis, various processes occur in sediments, such as activation of silicate source for quartz cementation, as well as a replacement of quartz and feldspar with calcite or clay transformation [26; 42].

The mineral calcite (carbonate class) was found in eight rock samples (mean = 7.0 %) and siderite in only two samples (mean = 2.9 %) (Table 1). The ma-
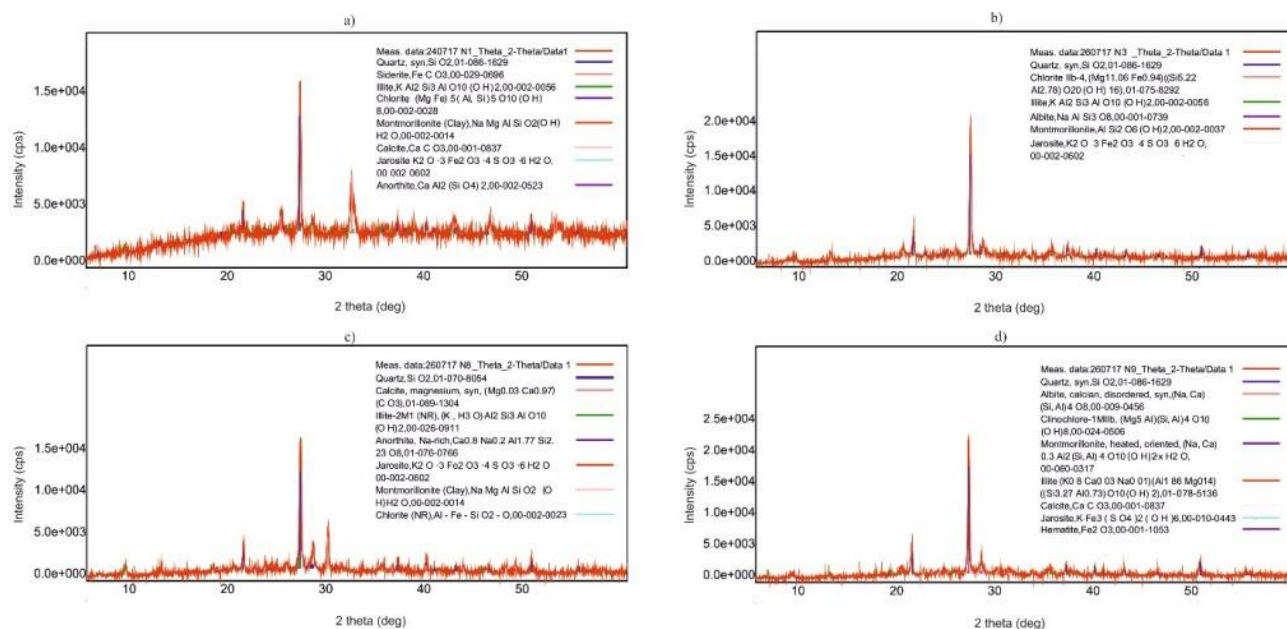
Fig. 2. XRD images of oil shale samples: a – Kichik Siyaki (1), b – Shikhzarli (3),
c – Lokbatan (8), d – Bozdag-Qobu (9)

in components of carbonate minerals are limestone and dolomite. The main element structure center of the carbonate minerals consists of an equilateral triangle in which a C^{+4} ion is located, and oxygen ions in its hills. Each Ca^{+2} ion is surrounded by six oxygen ions. The carbonate minerals, found as a result of analytical studies, belong to the calcite group. Calcite is the most common carbonate mineral, mainly consist of limestones that their fine-grained powder as a cementing agent plays a key role in the formation of sedimentary rocks, oil shale and skeletal structures of living organisms. This group of mineral is associated with rare products of magmatic eruptions called carbonatites. They form as a veinlet associated with sulphide ores after precipitation from hydrothermal fluids. Unlike calcite, aragonite forms as a result of high pressure and temperature related to depths close to the surface. According to this feature, the presence of the aragonite mineral in metamorphic oil shale can be considered as an indicator of metamorphism, reflecting a condition of low temperature and high pressure. In terms of temperature, a relatively hot paleosource is characterized by aragonite, and cold by calcite [33]. The common genesis of calcite mineral identified in the samples is bound to cold sources. Another calcium-containing mineral is diagenetic siderite, often presents in the composition of oil shale and sandstone. Forming in shallow water and taking part in the formation of concretion, this mineral gives a reason to take this factor into account during the study of the genesis of oil shale.

A widespread mineral of sulphate class in the content of samples is jarosite, with an average value of 11.85%. In addition, 5% of gypsum was found in sample No. 6. Jarosite is an alunite group mineral, which is the main potassium and iron hydrosulfite. The mineral is considered as a secondary mineral associated with the oxidized part of sulphide-containing rocks. The genetic feature of this mineral related to a weathering occurring in an arid climate. This mineral often forms due to weathering of iron sulphide. Gypsum is an aqueous sulfate of calcium. As a less dense mineral, genetically forms in a lake, sea and geothermal water as well as also in a veinlet that is rich in sulphate precipitation.

Unlike magnetite, hematite is more prone to oxidation and can be considered a changing product of magnetite. In many igneous rocks, hematite is a solid solution in the composition of ilmenite. Larger sediments of hematite are found in strip-like iron formations. The mineral origin is associated with geothermal waters, as well as with stagnant water environments at the bottom of the lakes, sometimes anhydrous conditions and volcanic activity [33].

Major oxides. The SiO_2 value in the samples ranges from 45.72 to 55.55 % (mean = 49.81 %). The values of this major oxide in the samples taken from the Boyuk Siyaki and Jangichay outcrops differ from oil shale sampled from ejecta of mud volcanoes in Shamakhi-Gobustan region. A tendency on decreasing of the value for this oxide was recorded towards the south-east from North Gobustan. In addition to Si, the second major oxide in the chemical composition of samples is Al. It is nearly impossible to give statistical distributions for this element on the studied areas and regions. The Al_2O_3 values in the samples range from 12.69 to 16.81 % (mean = 14.64 %). Compared to the Eocene samples, the Fe_2O_3 value is significantly higher (13.54 %) in

sample No. 1 of the Upper Miocene. The Fe_2O_3 values are significantly lower (4.92-8.54 %) in the other nine samples.

The mean value of Fe_2O_3 is 6.84 %. Other major oxides, such as Na_2O (0.97-1.76 %, mean = 1.34 %), MgO (2.25-3.20 %, mean = 2.65 %), P_2O_5 (0.03-0.39 %, mean = 0,17%), SO_3 (0.35-7.37 %, mean = 2.93 %), K_2O (2.06 to 3.89 %, mean = 3.36 %), CaO (0.29-9.67 %, mean = 3.97 %), TiO_2 (0.61-0.90 %, mean = 0.76 %), MnO (0.02-0.18 %, mean = 0.09 %) were determined for all samples (Table 2).

Table 2

Major and trace element concentrations of the samples

Region	Shamakhi-Gobustan						Absheron				
Area	Boyuk Siyaki	Jəngichay	Shikhzarli	Demirchi	Bozaa-khtarma	Qotur	Otman-bozdagh	Lokbatan	Bozdagh-Qobu	Keyraki	Mean
Sample	1	2	3	4	5	6	7	8	9	10	
Major oxide (%)											
SiO_2	46.04	49.55	53.39	55.55	51.23	46.43	49.71	46.07	54.39	45.72	**49.81**
Al_2O_3	13.36	15.36	16.06	16.81	14.93	12.69	15.10	12.96	15.27	13.82	**14.64**
Fe_2O_3	13.54	4.92	7.29	5.53	8.54	4.97	5.63	5.42	5.46	7.12	**6.84**
FeO	12.18	4.43	6.56	4.98	7.68	4.47	5.07	4.88	4.91	6.41	**6.16**
CaO	1.37	5.22	0.37	2.09	0.29	2.97	7.32	8.47	1.97	9.67	**3.97**
Na_2O	1.15	1.38	1.34	1.00	0.97	1.76	1.50	1.63	1.42	1.23	**1.34**
K_2O	2.06	3.84	3.65	3.61	3.61	2.93	3.47	3.38	3.89	3.15	**3.36**
MgO	2.67	3.20	2.49	2.25	2.58	2.76	2.56	2.81	2.89	2.34	**2.65**
TiO_2	0.74	0.75	0.76	0.87	0.71	0.61	0.83	0.66	0.80	0.90	**0.76**
P_2O_5	0.39	0.04	0.03	0.26	0.03	0.25	0.21	0.25	0.17	0.08	**0.17**
SO_3	0.45	3.06	3.90	1.26	7.37	4.69	1.69	3.30	3.20	0.35	**2.93**
MnO	0.18	0.07	0.09	0.02	0.02	0.05	0.13	0.07	0.07	0.17	**0.09**
Trace element (ppm)											
Ba	235	405	426	555	384	412	241	516	142	434	**375**
Zr	116	196	215	142	184	214	117	419	317	154	**207.4**
Br	8	12	5	1	5	72	5	5	8	3	**12.4**
Mo	80	77	64	48	126	5	19	16	34	12	**48.1**
Sr	116	325	214	317	134	294	295	426	1000	426	**354.7**
Cu	49	11	11	83	94	88	19	89	12	15	**47.1**
Cr	87	112	141	84	96	214	216	212	134	142	**143.8**
Rb	53	218	191	94	175	184	710	114	41	81	**186.1**
Zn	83	71	86	112	85	84	77	100	541	114	135.3
Ni	74	16	102	31	75	34	41	176	60	74	68.3
Se	0.4	0.1	0.6	0.3	11.6	0.7	0.3	0.5	0.1	0.4	1.5
As	5	3	5	8	2	7	23	3	9	7	7.2
Ga	17	8	15	11	7	12	14	5	8	12	10.9
V	31	104	246	241	964	41	24	61	61	71	184.4
U	3	1	2	1	1	1	1	1	3	1	1.5
Pb	7	34	12	19	19	18	9	18	11	21	16.8

The major oxides in the composition of samples were compared with average shale [47], NASC [25] and average black shale [49]. The SiO_2 and Al_2O_3 values corresponds to the average shale, while the Fe_2O_3 value proper to NASC and the CaO, Na_2O, K_2O, MgO, TiO_2. The P_2O_5 values coincide with both shales. Only for the Al_2O_3 value and alkaline compounds were established a correspondence compared with the average black shale (Table 3).

The major oxides in the samples were compared with the cognominal rocks of some countries that have extensive experience in the oil shale industry. The studied oil shale demonstrates similarity with the oil shale of the Estonian kukersite deposit [15] and Green River Formation of USA [45]. A associative similarity was recoded in the concentration of SiO_2, Al_2O_3 and CaO. The studied samples prevail on the oil shale of the Gurun basin of Turkey [38], Baltic basin of Russia [28] and Sultani deposit of Jordan [8] on the mean SiO_2 value. Referred to the CaO content, these three countries have a significant advantage (Table 4). High concentrations of CaO characterize a relationship with biochemical source, including cementing in the center of the basin [52]. The CaO value is significantly higher in the samples taken from the mud volcanic areas in Absheron region (excluding Bozdagh-Qobu) than in Shamakhi- Gobustan region (excluding Jangichay) (Table 2). This factor may be related to a depositional environment, in which the samples formed; instabilities at the level of lake, lagoon, etc., as well as intensity of transport of dissolved chemical components.

Trace elements. The mean Zr value in oil shale is 207 ppm, and there is a coincidence for this trace element compared to NASC [25] and PAAS [46]

Table 3

Comparison of chemical composition of the studied shales with published averages

	Present study	NASC [25]	Average shales [47]	Average black shales [49]	Post-Archean Australian Shale [46]
Major element oxide (%)					
SiO_2	45.81	64.82	58.50	-	62.80
Al_2O_3	14.64	17.05	15.00	13.00	18.90
Fe_2O_3	6.84	5.70	4.72	3.00	7.08
CaO	3.97	3.51	3.10	2.10	1.30
Na_2O	1.34	1.13	1.30	0.90	1.20
K_2O	3.36	3.97	3.10	2.40	3.70
MgO	2.65	2.83	2.50	1.20	2.20
TiO_2	0.76	0.80	0.77	0.33	1.00
P_2O_5	0.17	0.15	0.16	-	0.16
MnO	0.09	-	-	0.02	0.11
Trace element (ppm)					
Sr	354.7	142	300	200	200
Ba	375	636	580	300	650
V	184.4	130	130	150	150
Ni	68.3	58	68	50	55
Cr	143.8	125	90	100	110
Zn	135.3	-	95	300	85
Cu	47.1	-	45	70	50
Zr	207.4	200	160	-	210

Table 4

Comparison of the major oxides of the studied samples and oil shale of some countries with published averages (%)

	Present study	Gurun Basin (Turkey) [38]	Baltic basin (Russia) [28]	Sultani deposit (Jordan) [8]	Estonia deposit (Estonia) [15]	Green River formation (USA) [45]
SiO_2	49.80	16.13	33.22	26.26	59.80	53.71
Al_2O_3	14.64	4.67	7.69	2.87	16.10	13.53
Fe_2O_3	6.84	3.18	4.26	1.12	2.80	5.40
TiO_2	0.76	0.24	1.32	0.13	0.70	0.58
MgO	2.65	7.27	0.98	0.95	0.40	6.08
CaO	3.97	29.42	39.95	26.3	0.70	5.47
Na_2O	1.33	1.58	-	0.27	0.80	2.37
K_2O	3.36	2.10	7.18	1.37	6.30	1.26
P_2O_5	0.17	0.16	0.47	3.48	-	0.20
MnO	0.09	0.01	0.11	-	-	0.05

(Table 3). This indication differs sharply from some of the world's oil shale deposits and basins, including the Hatildag deposit of Turkey (14 ppm) [44] and Sultan deposit in Jordan (46 ppm) [8]. The mean Sr and Ni values for the oil shale are 355 and 68 ppm (Table 3). Relatively, the Sr content in average shale is 300 ppm [47], which roughly corresponds to oil shale in the present study (Table 3). However, the values of the same trace element in the NASC [25], average black shale [49] and PAAS [46] considerably less (142, 200 and 200 ppm) (Table 3). The mean Sr value is 430 ppm in the Hatildag oil shale deposit [44], Sultani – 707 ppm [8].

High Sr value in sedimentary rocks is associated with nano-calcareous planktons [32] and also aragonite sources. The mean Ni value is distributed in approximate concentrations in the noted shales (Table 3). However, the content of this trace element in the oil shale of the Hatildag deposit is 103 ppm [44], Sultani – 139 ppm [8], Baltic basin –10 ppm [30], Kukersit of Estonia – 17 ppm [48] and Green River – 1-10 ppm [17]. The origin of Ni in the studied oil shale is most likely associated with organic sources. The Zn and Cu values in oil shale are 135 and 47 ppm (Table 3). The Zn value is relatively high in the average shale and in PAAS (95 and 85 ppm) (Table

3). The mean Zn value for average black shale is 300 ppm. The average Zn value in the oil shale deposit in Turkey is 15 ppm [44], Sultani – 649 ppm [8], Baltic basin – 75 ppm [30], Kukersit deposit – 49 ppm [48] and Green River formation – 10 ppm [17]. The mean value of Cu does not differ much from the average shale and PAAS (45 and 50 ppm). In black average shale, the value of this trace element is slightly greater, 70 ppm (Table 3). The average Cu value of the Hatildag deposit is 38 ppm [44], Sultani – 115 ppm [8] and Baltic basin – 10 ppm [30].

Geochemical classifications and maturity. Based on the chemical classification diagram of $\log (Fe_2O_3/K_2O)$ versus $\log (SiO_2/Al_2O_3)$ [27], it was determined that most of samples correspond to shale, and only one sample with a rich Fe_2O_3 content correlate with Fe-shale (Table 2, Fig. 3). Shale is clastic sedimentary rock consisted of clay minerals, as well as quartz and calcite. The biological, chemical and coastal-mechanical erosions, as well as the shelf, lagoon, deep but relatively stagnant water environments, are characteristic for its genesis.

A ratio K_2O/Al_2O_3 differs sharply in clay min-

Fig. 3. Log (Fe_2O_3/K_2O) versus log (SiO_2/Al_2O_3) classification diagram [27] for the selected oil shale samples

erals and feldspar. The ratio value forms an idea of the original composition of sedimentary rocks. K_2O/Al_2O_3 ratio was established for clay minerals 0-0.3 %, but for feldspar 0.3-0.9 %. $K_2O/Al_2O_3 > 0.5$ indicates the content of alkaline feldspar associated with other minerals. The ratio varies from 0.15 to 0.26 for the studied oil shale (mean = 0.23). This result indicates the absolute superiority of clay minerals over K-containing minerals, including K-feldspar and micas.

Higher Na_2O/Ka_2O values indicate a bond with plagioclase. Relatively low values characterize change in extracellular cations of clay minerals. This feature provides an association between sodium and illite. The determined ratio for samples varries from 0.27 to 0.60 (mean = 0.41), corresponds to a low degree of maturity. A result of the correlation between Na_2O and Al_2O_3 is negative (r = –0.37), which can be explained by the fact that sodium does not bind to plagioclase in the samples, and the main bond is associated with illite. The K_2O/Na_2O ratio is 1.66-3.72 (mean = 2.56), which is characteristic for K-bearing minerals.

$Al_2O_3/(CaO + MgO + Na_2O + K_2O)$ ratio indicates the mobility of major oxides that form rocks [24]. The oxides present in the content of samples are unstable since the determined values of this ratio are lower (0.80-2.05).

The ratios of SiO_2/Al_2O_3 and Fe_2O_3/K_2O are very informative as an indicator of mineralogical stability in sedimentary rocks. Lower SiO_2/Al_2O_3 and higher Fe_2O_3/K_2O values are considered mineralogically less stable and more prone to reactivity under supercritical CO2 exposure [20; 39]. The ratio of SiO_2/Al_2O_3 is lower than that of Fe_2O_3/K_2O, and this result leads to the fact that the studied samples are classified as mineralogically unstable.

A ratio of SiO_2/Al_2O_3 is used to determine the maturity properties of sedimentary rocks, as well as to assess the presence of quartz associated with clay minerals or feldspar [16; 19]. In this regard, high ratios characterize mineralogical mature (quartzose, rounded) and while low ratios represent chemically immature rocks [40]. Since the sizes of fine-grained rocks have a positive effect on maturity, but rocks, mainly consist of clay minerals, have a negative im-

pact on this feature. Thus, maturity can be recorded in rocks, which rich with quartz, fine-grained sands, and feldspar. If the SiO_2/Al_2O_3 ratio is characterized by high values, up to 5, it indicates progressive maturity for quartz and feldspar. The value of this ratio for present study range from 3.22 to 3.66, the mean value is 3.4. Such values point to the superiority of clay minerals in the studied rocks. The Al_2O_3, Fe_2O_3 and TiO_2 values for the composition of samples shows a tendency like $Al_2O_3 > Fe_2O_3 > TiO_2$ (Table 2). The obtained result corresponds to clay minerals [37]. A positive result of the correlation between TiO_2 and Al_2O_3 (r = 0.57) also confirms this conclusion.

Unstable and recrystallization features of clay minerals lead to acute mineralogical changes during diagenesis and low-temperature metamorphism [50]. Isochemical features for such processes is characteristic. Index of Compositional Variability (ICV), which indicates a richness of alumina relative to the cations of some major oxides in rocks, is determined by the formula [$ICV = (Fe_2O_3 + K_2O + Na_2O + CaO + MgO + MnO + TiO_2)/Al_2O_3$ (%)] [18]. The index also allows detecting detrital mineralogical properties of rocks. The calculated ICV value for samples is 0.91-1.78 (mean = 1.32). Since rocks characterized by low ICV values are associated with the cratonic enviroments and clay minerals. Most of the samples have a higher value than 1, indicating the presence of fewer clay minerals and more rock-forming minerals, such as plagioclase, alkali-feldspar, etc.

Palaeoweathering. Intensity of chemical weathering is directly related to a number of factors, such as the composition of the parent rock, climatic condition, the duration of weathering, the degree of uplift tectonic movement, etc. The chemical weathering has a certain effect on the composition of silicate rocks. This is characterized by more stable properties of large cations (Ba, Rb, etc.) compared to small ones (Na, Ca, etc.) in weathered residues [34]. During weathering, an element with a smaller ionic radius is separated from feldspar and the abundance of such an element compared to a stable element in the content of rocks indicates the degree of chemical weathering. A comparison of arid and humid conditions indicates that arid is characterized by relatively poor chemical weathering. A climatic condition accompanied by heavy rainfall leads to the loss of unstable minerals. In addition, CO_2 in the atmosphere and temperature condition has a positive effect on the intensity of weathering. Thus, the high temperature increases the decomposition of plagioclase and potassium feldspars, as well as hydrolysis. The lack of plants, the intensification of temperature and rainfall can lead to strong weathering.

Some methods are used for the determination of weathering based on the abundance of mobile or immobile major oxides in the rock. Chemical Index of Alteration ((CIA), [35]) is an index indicates of the conversion of plagioclase and potassium feldspar into clay minerals. The computational formula of the coefficient is: $CIA = 100 \times [Al_2O_3/(Al_2O_3 + CaO^* + Na_2O + K_2O)]$. A value of CaO^* indicates only CaO in silicates. Since this value is different from CaO, the following formula [$CaO^* = CaO - calcite - dolomite - apatite$] was used for the index calculation. The calculation of the index was performed within the molar proportions of the oxides. For the studied rocks, the CIA values are between 72 and 80 (the mean value is 75), which indicate moderate to high degree of weathering. CIA versus Al/Na plot for the samples is almost identical to the PAAS (Fig. 4). Such a trend characterizes N^+ diagenetic loss.

According to the ICV-CIA plot, the samples were subjected to intensive weathering in the source area and only after the post-sedimentation processes; there were changes in their composition (Fig. 5). Up to 50 CIA values indicate unchanged plagioclase, as well as K-feldspar. The minimum values of CIA for all samples > 70. Since CIA values approach 100 indicate the conversion of feldspar to clay minerals, such as gibbsite, kaolinite [21]. The CIA values and silicate clay minerals in the shale samples (Table 1) also confirm moderate to high degree of weathering. The obtained values may be related either of the original sources or during transport before deposition and may reflect low-relief and arid climatic state in the source area [51].

The results of the ternary diagram of Al_2O_3, $CaO^* + Na_2O$ and K_2O (A–CN–K) [36] was used to determine the chemical weathering properties, show that all the samples plot parallel to the A–CN join. The normal weathering tendency is focused toward illite, but in general, the effect of K-metasomatism is not excluded. The obtained result supports a conclusion that the protolith of oil shales coincides with mafic and intermediate types of igneous rocks (Fig. 6).

The plot based on the amount of Al_2O_3 and K_2O of samples indicates a relationship with illite (Fig. 7). Such a conclusion is most likely based on the conversion of K-feldspar and muscovite into clay minerals as a result of weathering in arid/semiarid climatic conditions. In addition, the relationship between potassium and illite is confirmed by the result of correlation Ka_2O versus Al_2O_3 (r = 0.65).

Conclusions. 11 minerals belonging to 5 classes were determined in the samples which silicates predominate.
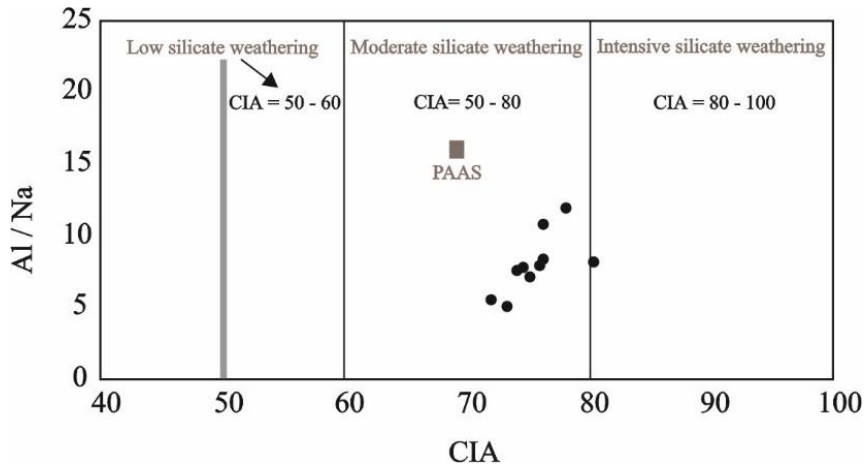
Fig. 4. Scatter plot of CIA versus Al / Na ratio [43] for the studied samples. PAAS range from [46]
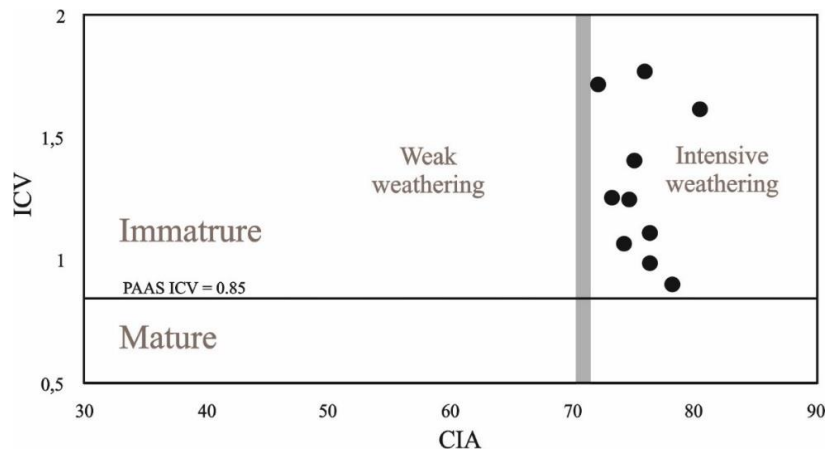

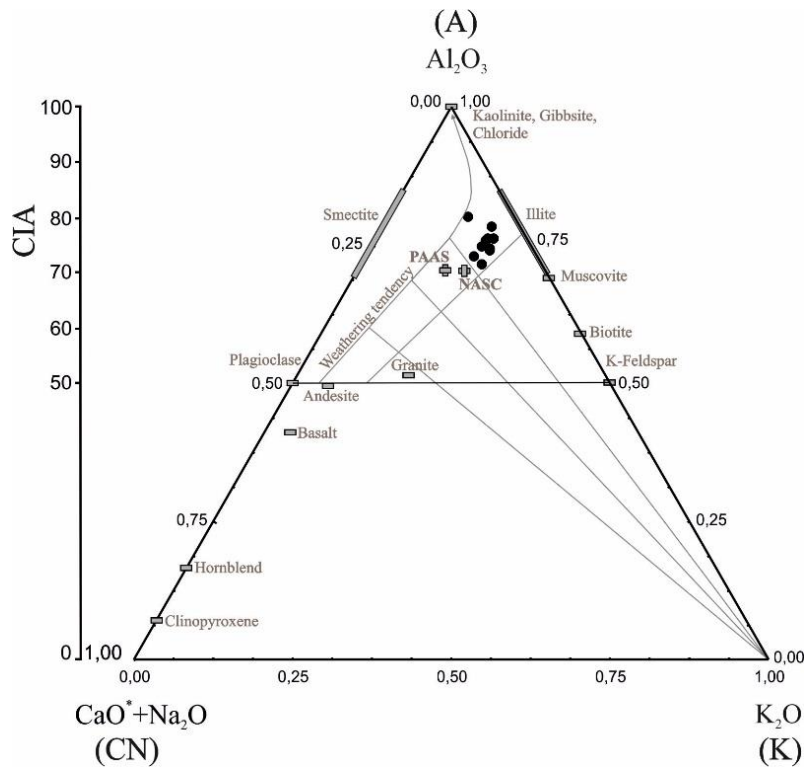Fig. 5. CIA-ICV plot [31] for the samples. PAAS range from [46]

Fig. 6. A–CN–K ternary diagram [36] of molecular proportions of $Al_2O_3 - (CaO^* + Na_2O) - K_2O$ for the oil shale samples. PAAS range from [46] and NASC [25]
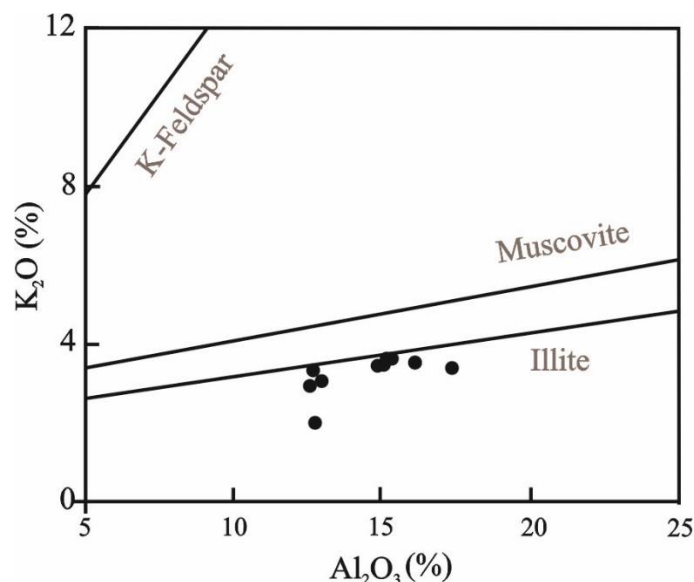
Fig. 7. Al_2O_3 versus K_2O plot [18] of oil shale samples

The coincidence between samples and shale was established using the classification plot based on log (SiO_2 /Al_2O_3) versus log (Fe_2O_3/K_2O).

The K2O/Al2O3 ratio confirms a superiority of clay minerals in the composition of oil shale compared to K-minerals, including K-feldspar. The estimates based on the Al_2O_3/($CaO + MgO + Na_2O + K_2O$) and Fe_2O_3/K_2O, SiO_2/Al_2O_3 ratios confirm the instability of oxides and minerals in the composition of samples. In addition, the ratios of SiO_2/Al_2O_3 and $Al_2O_3 > Fe_2O_3 > TiO_2$ support an idea that the samples are immature and associated with clay minerals.

The values of the CIA, and the plots for CIA versus ICV, CIA versus Al/Na ratio and the ternary diagram A–CN–K, as well as the study related to major oxide confirm moderate to high degree of weathering. The result of A–CN–K ternary diagram support that the weathering tendency of the samples plots close to the illite. The effect of K-metasomatism in this process is also not excluded. The role of post-sedimentation processes were most likely involved in the conversion. The protolith of oil shale samples is associated with mafic and intermediate igneous sources.

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MINERALOGY AND GEOCHEMISTRY OF OIL SHALES IN AZERBAIJAN: CLASSIFICATIONS, PALAEOWEATHERING AND MATURITY FEATURES

Shamakhi-Gobustan and Absheron regions (Azerbaijan) are a part of the South Caspian Basin, which is a subsiding basin located between the colliding of Arabian and Eurasian plates. The intensive rate of sedimentation process creates a favorable condition for the formation of oil shale, hydrocarbon and as well as mud volcanoes in these regions.

The purpose of the article. The study of oil shale in Azerbaijan has been mainly devoted to their geological and organic-geochemical characteristics, etc. However, the chemical classifications, provenience, palaeoweathering and maturity characteristics have not been studied. This study is the first attempt to investigate noted issues.

The research methodology. 10 samples from the outcrops and eject of mud volcanoes were analyzed. The concentrations of major and trace elements and minerals were measured by "S8 TIGER Series 2 WDXRF", "Agilent 7700 Series ICP-MS" mass spectrometers and XRD "MiniFlex 600". The microscopes "Loupe Zoom Paralux XTL 745" and "MC-10" and a digital camera "OptixCam" were used to determine the age of the samples.

The major and trace elements in the composition of samples were compared with average shale, NASC, PAAS and average black shale as well as oil shale from the Green River Formation of USA, Kukersit of Estonia, etc. studied in the published literature. A diagram and index were used for the classifications and determination of maturity of rocks. The palaeoweathering characteristic was determined based on CIA versus ICV and some other plots and ratios.

Research results. The minerals found in oil shale were classified according to their classes. According to the used classification diagram, it was established that all studied samples correspond to shale. A superiority of clay minerals in the composition of oil shale compared to K-minerals, including K-feldspar was found.

The estimates based on geochemistry and some ratios of elements confirm the instability of oxides and minerals, and immaturity of the samples.

The values of the CIA, CIA versus ICV plot, etc. confirm moderate to high degree of weathering. The results confirm a conclusion that the original sediments were derived from mafic and intermediate source terrain.

The scientific novelty. The scientific analysis presented in the paper is based on several substantial theoretical conclusions, which related to the factual material of research conducted by the co-authors.

The mineralogy, classification features, stability characteristics of the major oxides and minerals as well as chemical maturity and palaeoweathering were studied based on the chemical composition of the samples.

The practical significance. The results of the current study can be used for the further utilization of oil shale in Azerbaijan and the selection of promising areas in terms of mineral raw materials.

Keywords: oil shale, geochemistry, mineral, classification, maturity, weathering.

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