

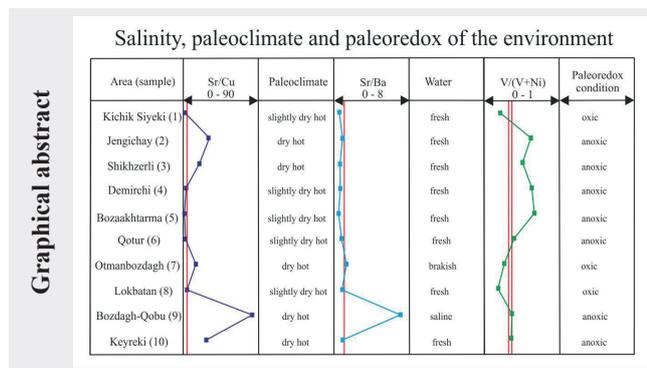
# Mineralogical and geochemical proxies for the Middle Eocene oil shales from the foothills of the Greater Caucasus, Azerbaijan: Implications for depositional environments and paleoclimate

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**Abstract:** The sedimentary environment of the Middle Eocene oil shales in the foothills of the Greater Caucasus (Shamakhi-Gobustan region and Absheron Peninsula), including the salinity, redox, and climate conditions were restored using mineralogical and bulk-rock geochemical signatures of 10 samples taken from the outcrop sections and ejecta of mud volcanoes. Obtained results are in agreement with the evolutionary history of the Middle Eocene sediments, being described in the literature. The samples demonstrate their formation feature within the aquatic environments - lagoons and lakes, having a depth of 10 meters. With the exception of some areas of the Absheron Peninsula, all samples can be associated with freshwater, mixed redox (mostly reducing), and arid/semi-arid environments.

**Key words:** oil shales, mineralogy, geochemistry, depositional environment, paleoclimate, Greater Caucasus



Highlights

- The gradual transition of the sedimentary environment from continental to marine is typical for genesis of Middle Eocene oil shales.
- The depositional conditions of the Middle Eocene oil shales most likely correspond to isolated coastal-marine zones - lagoons and lakes with a depth of 10 meters.
- Except of some samples of the studied regions, oil shales are associated with freshwater, mixed paleoredox (mostly reducing) and arid/semi-arid environments.

## Introduction

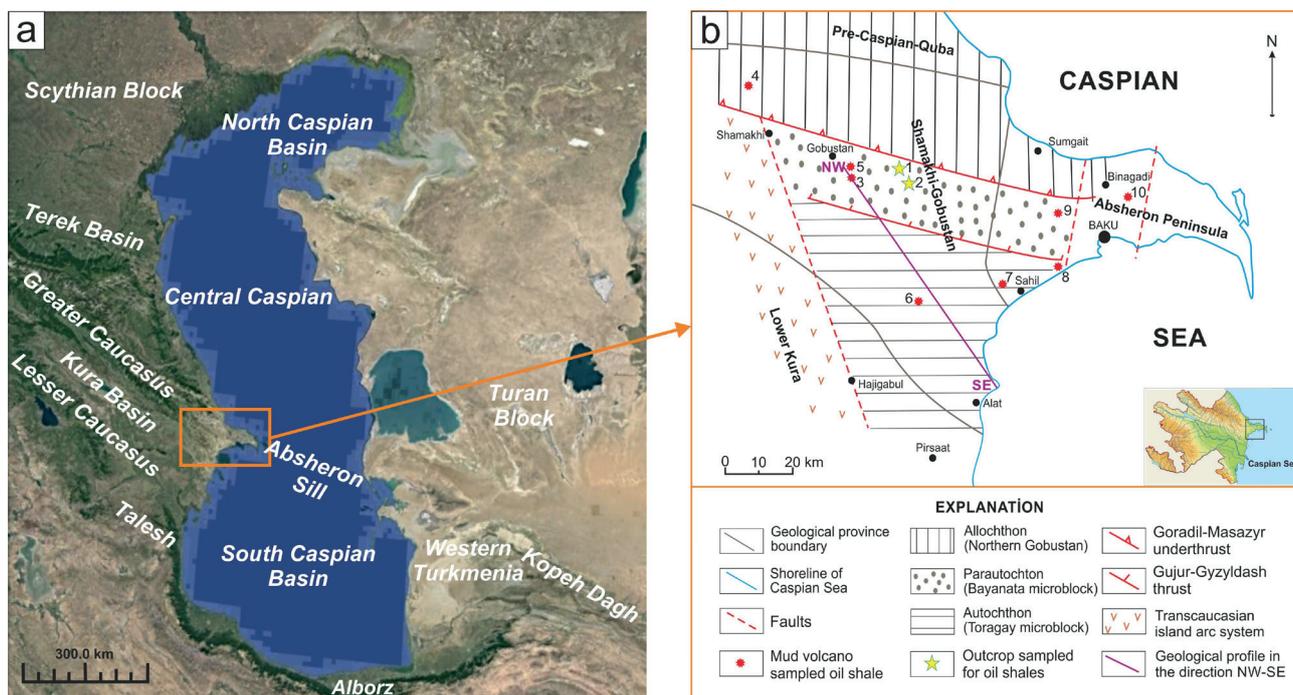
The Shamakhi-Gobustan region and Absheron Peninsula at the foothills of the Greater Caucasus (Fig. 1a) are located in the collision zone between the Arabian and the Eurasian lithospheric plates (Aliyev & Abbasov, 2019). The specific geodynamic and depositional environments provided favorable conditions for the formation of rich oil and gas fields, mud volcanoes and especially oil shales in the Eastern Azerbaijan, including the adjacent Caspian Sea (Aliyev et al., 2019).

Oil shales are very important for Azerbaijan, being considered as an alternative source of energy and raw materials (Sultanov & Sultanov, 1947; Ali-zade et al., 1962; Salaev et al., 1990; Aliyev et al., 2002, 2015; Abbasov et al., 2013; Aliyev & Abbasov, 2019). It was determined that the main qualitative parameters (organic matter 15–31 %, sulfur 0.4–1.2 %, ash content 65–85 % and caloric value 6.0–12 MJ . kg<sup>-1</sup>) in oil shale deposits such as Guba, Diyally, Jengichay, Kichik Siyeki and others in Azerbaijan exceed low-caloric deposits of some other countries, like

Germany, Romania, China, etc. (Abbasov, 2015; Aliyev et al., 2015a; Aliyev & Abbasov, 2018). In addition, this shale in Azerbaijan has a great potential as a source rock of oil (Abbasov et al., 2012, 2015; Abbasov, 2016a). The beds of oil shales in Central Gobustan, located at relatively shallow depths, are considered as future sources of shale gas for the country (Abbasov, 2016a).

In the Upper Cretaceous–Middle Miocene sedimentary sequences in Eastern Azerbaijan, about 60 oil shale outcrop sections were recorded (Aliyev et al., 2014). However, the main deposits of Middle Eocene oil shales are very thick and have wide spatial distribution (Abbasov, 2009). Oil shales were also found in the ejecta of mud volcanoes (Abbasov et al., 2012; Aliyev & Abbasov, 2018). In these rocks, the *Globigerina bulloides* (ORBIGNY), *Cibicides* sp., *Globigerina triloculinoides* (PLUMMER), benthos and planktonic foraminifers, as well as fish teeth and bones were found, belonging also to Middle Eocene.

In the published literature, an extended research was devoted to the general geological, organic-geochemical, and other characteristics of oil shales in Azerbaijan



**Fig. 1.** Location maps (after Aliyev & Abbasov, 2019; Aliyev et al., 2015b) of study regions and samples collected from outcrop sections (1 – Kichik Siyeki, 2 – Jengichay) and ejecta of mud volcanoes (3 – Shikhzarli, 4 – Demirchi, 5 – Bozaakhtarma, 6 – Qotur, 7 – Otmanbozdagh, 8 – Lokbatan, 9 – Bozdagh-Qobu, 10 – Keyreki).

(Sultanov & Sultanov, 1945; Sultanov, 1948; Ali-zade et al., 1962; Salaev et al., 1990; Aliyev et al., 2002, 2014, 2015, 2018a; Aliyev & Abbasov, 2018; Abbasov, 2009, 2016, 2017; Abbasov et al., 2013). Because the studies of depositional environments and paleoclimate conditions were insufficient, this study is devoted to the reconstruction of depositional environments and paleoclimate conditions in relation to the mineralogical and geochemical proxies for the Middle Eocene oil shales of researched areas.

### Geology and tectonics: a general overview

The Shamakhi-Gobustan region, located in south-eastern side of the Greater Caucasus, is built of Mesozoic and Cenozoic sediments. About 40 oil shale outcrop sections were registered in the region (Sultanov, 1948; Salaev et al., 1990; Abbasov, 2009; Aliyev et al., 2014). The oil shale interbeds are associated with the sediments of the Upper Cretaceous–Upper Miocene (Sultanov & Sultanov, 1947; Salaev et al., 1990; Aliyev & Abbasov, 2018).

The Middle Eocene sediments are also very important for Azerbaijan (Sachsenhofer et al., 2018), including the Shamakhi-Gobustan region in terms of oil shales-bearing lithofacies (Aliyev & Abbasov, 2019). Besides the outcrops, the Middle Eocene oil shale samples were collected also from the mud volcanoes (Shikhzarli, Demirchi, Bozaakhtarma and Qotur), which brought

additional information. In the region, the thickness of Middle Eocene sediments varies from 1.7 km (Central Gobustan) to 3.8 km (Southern Gobustan; Fig. 2).

The variability of the Middle Eocene lithofacies in this region is characteristic. The basal sequence is made up of black shales with interbeds of light brown oil shales (Sultanov & Sultanov, 1947; Aliyev & Abbasov, 2019). The thickness of the interbeds of oil shales found on the wings and ridges of anticlines and synclines, such as Kichik-Siyeki, Jengichay, Jengidagh, a.o., varies from a few centimeters to about 10 meters (Salaev et al., 1990; Abbasov, 2009).

The tectonic block identified between the Altyagaj-Kurqachidagh fault and the Goradil-Masazyr underthrust is called the Northern Gobustan allochthon. This allochthon is related to the Baskal overthrust mass that the Cretaceous flyschoid sequences cover the Paleogene-Miocene sediments (Aliyev & Bayramov, 1999). A microblock located south of the Goradil-Masazyr underthrust and bounded by the Gujur-Qyzyldash thrust is Bayanata parautochthon (Fig. 1). The total thickness of the Paleogene-Miocene sediments in this microblock is 2.5–4.5 km (Fig. 2), and it is the largest exposed area (Boyuk Siyeki, Kichik Siyeki, Jengichay, a.o.) of the Middle Eocene oil shale in the Shamakhi-Gobustan region (Sultanov & Sultanov, 1947; Abbasov, 2009). A microblock located south of the Gujur-Qyzyldash thrust is named Toragay autochthon (Fig. 1b) that made up of

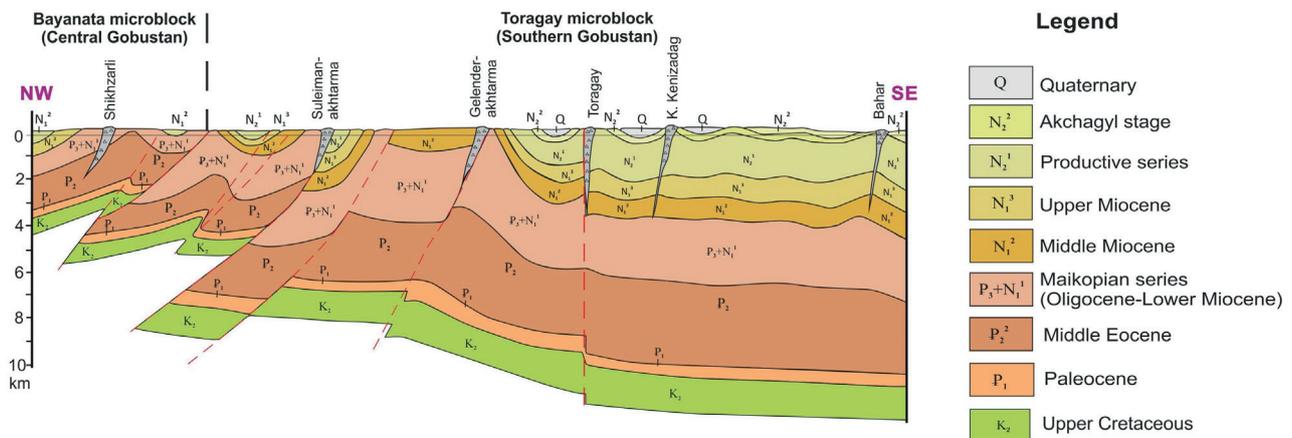


Fig. 2. Geological profile of the Bayanata and Toragay microblocks (after Aliyev et al., 2015b).

the Cenozoic sediments. In this microblock, the top of the Upper Cretaceous lies at a depth of 8–11.5 km (Fig. 2). In addition, the largest and active mud volcanoes (Toragay, Boyuk Kenizadagh, Qotur, a.o.) of the region crop out here (Aliyev et al., 2015b). The ejected mud of these mud volcanoes typically originates from the Maikopian series (Inan et al., 1997; Aliyev et al., 2015) and Middle Eocene sediments (Aliyev et al., 2015b) that have been buried to depths of 4–10 km (Odonne et al., 2020).

On the Absheron Peninsula, which is the southeastern end of the Greater Caucasus, 18 oil shale outcrops have been discovered (Sultanov, 1948; Aliyev et al., 2002). The Peninsula is built of Upper Cretaceous-Cenozoic sediments (Aliyev et al., 2015). The oil shale outcrops related to the Middle Eocene have been found only in Goytepe and Govundagh areas, and they associated mainly with the Upper Maikop and the Upper Miocene (Abbasov, 2016b, 2017).

The tectonic zones studied here dip to the southeast, in the direction of the extension of the Greater Caucasus. The Mesozoic complex in the south of the Absheron Peninsula abruptly descends (Aliyev et al., 2015). The Paleogene-Pliocene sediments dominate in the geological structure of the uplifts, which was found in some outcrop sections (Khirdalan, Zigilpiri, a.o.).

Four tectonic zones have been established in the Peninsula, and there is a morphological connection between the anticlines and the synclines. The dislocations in the Peninsula are indicated also by mud volcanoes Keyreki, Lokbatan, Bozdagh-Qobu, etc. (Aliyev et al., 2015).

### Sampling and methods

Sampling collected two samples of oil shales from the outcrops (1 – Kichik Siyeki, 2 – Jengichay) 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; Fig. 1b). The samples were black, grey and brown in colour, having laminated structure.

**Mineralogical composition of rocks.** Bulk rock mineralogical composition of oil shale samples was determined by XRD “MiniFlex 600” at the Institute of Geology and Geophysics, Azerbaijan National Academy of Sciences. The samples were first wet-ground to fine powders (~5 µm), and then they were loaded onto a zero-back-ground sample holder. After running on the XRD, the resulting diffraction patterns were scanned over the 2θ range of 5 to 65° using Cu-Kα radiation (accelerating voltage of 40 kV and current of 15 mA) with a D/tex high-speed detector using 0.02° steps and a scan rate of 2° per minute. XRD patterns were analysed with the CRYSTAL IMPACT software Match!, and mineral abundances were determined by the RockJock XRD pattern fitting program.

**Bulk rock geochemistry.** The major elements were determined by X-ray fluorescence spectrometry with wavelength energy dispersion on the S8 TIGER Series 2 WDXRF. The sample was prepared via a hydraulic press at 25 tons. The fire loss was determined at 1000 °C. The quality of the data was verified by analysing the certified sample SRM 2709 (NIST, 2002).

The trace elements were analysed using an Agilent 7700 Series ICP-MS. All samples were finely ground until they could be sieved through a 75 µm sieve. A total of 50 mg of the powder of each sample was dissolved by cleavage with ultrapure acids in three stages. The solutions were transferred to clean flasks and diluted with 1 % HNO<sub>3</sub> to 50 ml. Acids were purified using acid purification equipment. Analytical uncertainties (relative standard deviations) related to measuring elements were less than 5 %. The analyses of major oxides and trace elements were also performed at the Institute of Geology and Geophysics, Azerbaijan National Academy of Sciences.

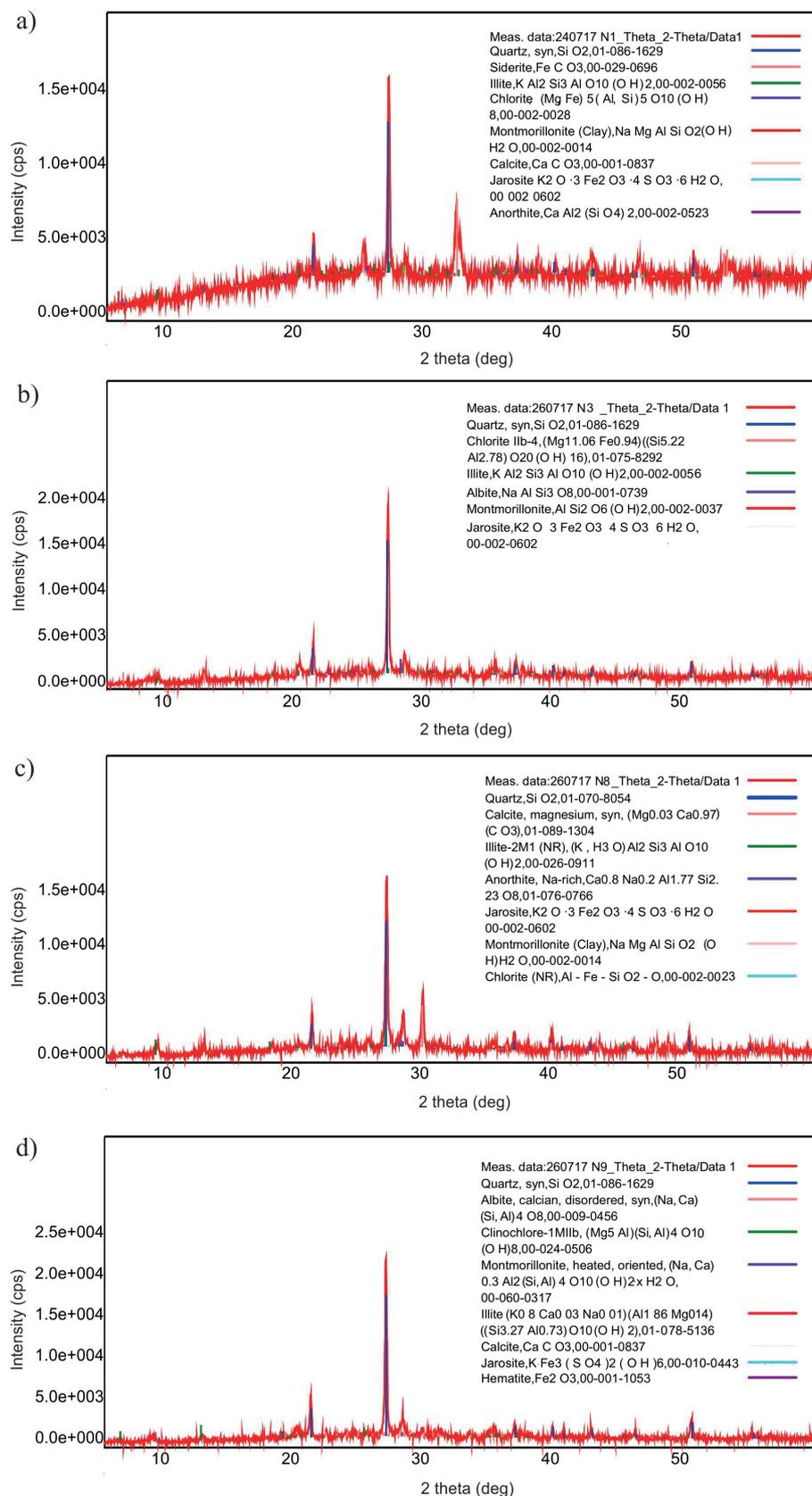
**Age of rocks.** The ages of samples collected from the mud volcanic areas were studied at the Integrated Engineering Exploration Production, Department of Geophysics and Geology, SOCAR. The studied samples were carefully grounded and washed to remove sludge and clay particles. The dried powder samples is scattered on a black board measuring 9 x 12 cm. Microfaunas were studied at magnification x200–300, using the Loupe Zoom Paralux XTL 745 and МБС-10 microscopes. Microscope images were transferred to a computer using a digital camera OptixCam.

**Mineralogy**

The provenance and tectonic setting of used 10 samples were widely discussed in previous papers (Aliyev & Abbasov, 2019; Aliyev et al., 2019).

In this study, related to the bulk rock mineralogical composition, it should be briefly noted that 11 minerals of 5 classes were found in the samples. The samples consist mainly of silicates, as well as carbonates and sulphates. Only one sample contains 1 % of halite. Hematite was found in three samples taken from mud volcano areas Demirchi, Bozdagh-Qobu and Keyreki.

Quantitative analysis of clay minerals shows that montmorillonite (mean = 15.1 %) and chlorite (mean = 16.2 %) are more abundant than illite (mean = 10.9 %). As for silicates, the value of quartz is 25.8 %, and feldspar – anorthite (Fig. 3a, c) and albite (Fig. 3b, d) – 8.2 %. Calcite was determined in eight samples (mean = 7.0 %), and siderite only in two areas (mean



**Fig. 3.** XRD images of oil shale samples: a – Kichik Siyeki (1), b – Shikhzarli (3), c – Lokbatan (8), d – Bozdagh-Qobu (9).

**Tab. 1**  
Mineralogical composition of samples [wt.%].

	Area (sample)	Quartz	Feldspar	Calcite	Illite	Montmorillonite	Chlorite	Jarosite	Halite	Siderite	Hematite	Gypsum
Shamakhi – Gobustan region	Kichik Siyeki (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
Absheron Peninsula	Otmanbozdagh (7)	20.0	15.0	9.0	12.0	17.0	17.0	7.0	–	–	–	–
	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

= 2.9 %) with carbonates (Tab. 1). The most common sulphate in the samples is jarosite (mean = 11.8 %). In addition, 5 % of gypsum was defined in the Qotur sample. The mean value of hematite is 1.2 %.

### Major oxides

The value of SiO<sub>2</sub> ranges from 45.72 to 55.55 %, with an average value of 49.81 %. Compared to the mud volcanoes of the Shamakhi-Gobustan region, the value of this major oxide differs in samples taken from the outcrop sections (Kichik Siyeki and Jengichay) in some regions. The maximum values were recorded in the Northern Gobustan allochthon. The concentration of Al<sub>2</sub>O<sub>3</sub> varies from 12.69 to 16.81 % (with an average value of 14.64 %) and the same regularity can be given for this major oxide. The highest Fe<sub>2</sub>O<sub>3</sub> value was determined only in Kichik Siyeki,

and in the remaining nine samples its value is much lower (Fig. 4).

The compositions of Na<sub>2</sub>O (0.97–1.76 %, average value 1.34 %), MgO (2.25–3.20 %, aver. 2.65 %), P<sub>2</sub>O<sub>5</sub> (0.03–0.39 %, aver. 0.17 %), SO<sub>3</sub> (0.35–7.37 %, aver. 2.93 %), K<sub>2</sub>O (2.06–3.89 %, aver. 3.36 %), CaO (0.29–9.67 %, aver. 3.97 %), TiO<sub>2</sub> (0.61–0.90 %, aver. 0.76 %) and MnO (0.02–0.18 %, aver. 0.09 %) are shown in Tab. 2. The regularity of the abundance of oxide compounds in the samples was as follows: SiO<sub>2</sub> > Al<sub>2</sub>O<sub>3</sub> > Fe<sub>2</sub>O<sub>3</sub> > CaO > K<sub>2</sub>O > SO<sub>3</sub> > MgO > Na<sub>2</sub>O > TiO<sub>2</sub> > P<sub>2</sub>O<sub>5</sub> > MnO.

### Trace elements

The maximum Zr values were recorded in the samples of the mud volcanoes Lokbatan and Bozdagh-Qobu (317 and 419 ppm). Unlike the Otmanbozdagh sample, the Sr

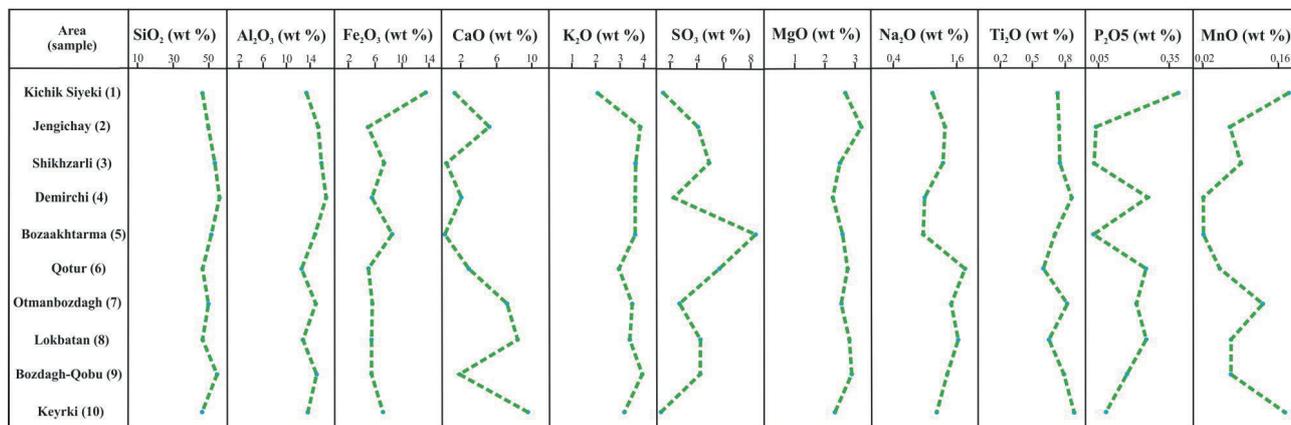


Fig. 4. Variation of major oxides in the samples.

value is higher in samples from three other mud volcanoes (426 ppm in Lokbatan and Keyreki, and 1000 ppm in Bozdagh-Qobu) of the Absheron Peninsula. According to the distribution of Mo, an absolute superiority of the Shamakhi-Gobustan region was established. The value of Zn reaches 112 ppm in the sample of mud volcano Demirchi, 100 ppm in the Lokbatan, 114 ppm in the Keyreki and 541 ppm in the Bozdagh-Qobu. The Absheron Peninsula has a significant advantage in the Cr content

distribution. The highest value of V was recorded in the sample of the Bozaakhtarma mud volcano. In addition, the value of this element in other samples, such as Jengichay reaches 104 ppm, Demirchi – 241 ppm and Shikzarli – 246 ppm. The values of Ga and U are characterized by low concentrations. The regularity of the abundance of trace elements in the samples was as follows: Ba > Sr > Zr > Rb > V > Cr > Zn > Ni > Mo > Cu > Pb > Br > Ga > As > U = Se (Tab. 2).

**Tab. 2**  
Major and trace element concentrations of oil shale samples.

Area (sample)	Kichik Siyeki	Jengichay	Shikzarli	Demirchi	Bozaakhtarma	Qotur	Otmanbozdagh	Lokbatan	Bozdagh-Qobu	Keyreki	Mean
Major oxide [wt %]											
SiO <sub>2</sub>	46.04	49.55	53.39	55.55	51.23	46.43	49.71	46.07	54.39	45.72	49.81
Al <sub>2</sub> O <sub>3</sub>	13.36	15.36	16.06	16.81	14.93	12.69	15.10	12.96	15.27	13.82	14.64
Fe <sub>2</sub> O <sub>3</sub>	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 <sub>2</sub> O	1.15	1.38	1.34	1.00	0.97	1.76	1.50	1.63	1.42	1.23	1.34
K <sub>2</sub> O	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 <sub>2</sub>	0.74	0.75	0.76	0.87	0.71	0.61	0.83	0.66	0.80	0.90	0.76
P <sub>2</sub> O <sub>5</sub>	0.39	0.04	0.03	0.26	0.03	0.25	0.21	0.25	0.17	0.08	0.17
SO <sub>3</sub>	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

## Interpretation of analytical data based on knowledge from earlier researches

**Depositional environments.** The mineralogical assemblages of the studied areas have provided information on the depositional environments during the Middle Eocene age.

Mason and Moore (1982) considered illite as the applicable mineral for the marine environment analysis. Illite associates with a K-rich alkaline environment. A decrease in water depth leads to a decrease in illite concentration (Freed, 1980). Powers (1957) found the genesis of chlorite in a marine environment. However, in addition to an open sea, Weaver (1956) believed this mineral may also be associated with sedimentation occurring in a freshwater environment. Parham (1966) suggested a general clay zonation from a coast to deep ocean environment in the following order: kaolinite, illite, chlorite, palygorskite, and sepiolite. Together with montmorillonite, mixed I/S minerals can be formed at almost all paleodeposition ranges. A typical pattern of distribution of clay minerals from shore to open sea is determined as follows: kaolinite – illite – smectite (Galán, 2006). Transformation of smectite to illite occurs due to the absorption of  $K^+$  and the release of  $Na^+$ . Removed  $Na^+$  leads to albitization, which was found in some samples (Fig. 3b, d). Hence, replacing  $Na^+$  with  $K^+$  contributes to albitization in sandstones and shales. The process of converting of kaolinite to illite requires a relatively high temperature (100–130 °C), which leads to removal of a certain amount of  $K^+$  (Saigal et al., 1988).

The genesis of calcite is associated with shallow phreatic zones (De Ros et al., 1994). In addition, there is an evidence that calcite occurs in alluvial environment (Leeder, 1975; Wright & Tucker, 1991).

Jarosite occurs in an aqueous and acidic environment (Singh et al., 2016). Hematite is more susceptible to oxidation and can be considered a replacement product of magnetite. In many igneous rocks, this mineral is a solid solution in the composition of ilmenite. Higher contents of hematite produce a strip-like iron formation. The origin of this mineral is related to geothermal waters, as well as to a stagnant water environment at the bottom of lakes, sometimes also anhydrous conditions and volcanic

activity (Nelson, 2014). Zolotov and Shock (2005) considered that the genesis of hematite spherules is associated with mineral deposition in an aqueous environment. They concluded that the occurrence of a jarosite-goethite-gypsum assemblage is a result of precipitation of acidic solutions formed through near-surface aqueous oxidation of pyrite mineral. Unlike a marine environment, the content of Ca and Mn in siderite mineral, associated with the deposition of freshwater, is relatively higher. Such a difference is explained by various activities of  $Fe^{2+}$ ,  $Mg^{2+}$ ,  $Ca^{2+}$ , and  $Mn^{2+}$  in a marine environment and porous meteoric water (Mozley, 1989). In addition, the formation condition of halite, which was found in lower concentrations in two samples, is associated with an evaporite deposition occurring in a saline lake.

Geochemical proxies of lithofacies assemblages provide useful information on paleodepositional environments. Some ratios and plots based on the major oxides, such as  $Al_2O_3$ ,  $K_2O$ ,  $Na_2O$ ,  $CaO$ ,  $Fe_2O_3$ , etc., and trace elements, were used to reconstruct the deposition processes of oil shale samples during the Middle Eocene.

Englund and Jørgensen (1973) established a ternary classification diagram based on a study of soil and shale samples from different geographical regions of the world to ascertain the depositional environments of the sediments. The position of samples, associated with various geochemical, mineralogical and paleoweathering conditions, in various parts of AKF ternary diagram [ $Al_2O_3$  – ( $K_2O + Na_2O + CaO$ ) – ( $Fe_2O_3 + MgO$ )] reveals whether

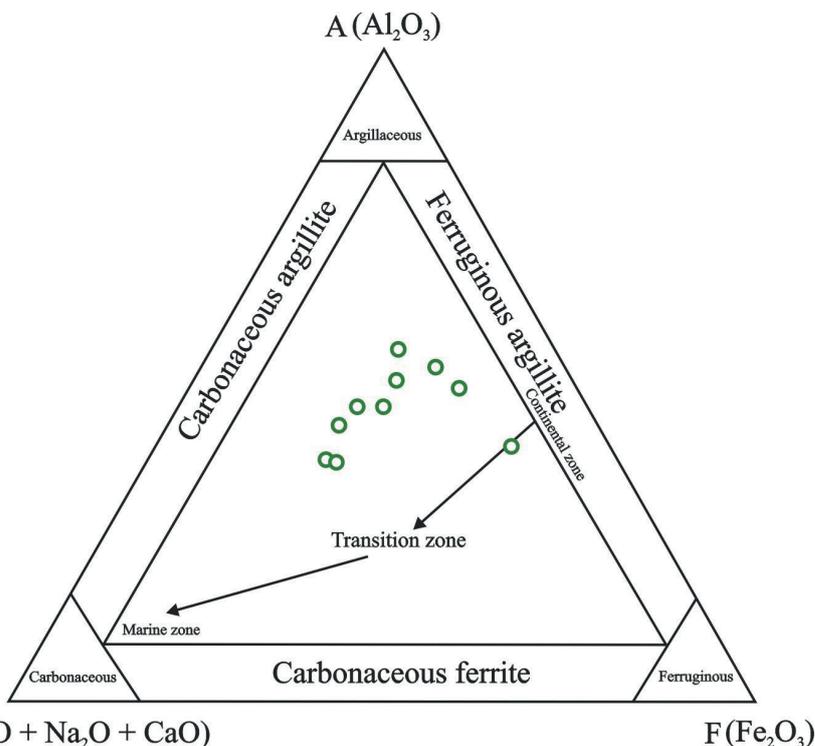


Fig. 5. Oil shale samples in AKF diagram (after Englund and Jørgensen, 1973).

the sediments were deposited in continental, transition and/or marine zone. Fig. 5 shows a gradual transition of sediments of the basin from freshwater to marine environment, majorly falling within the transition zone.

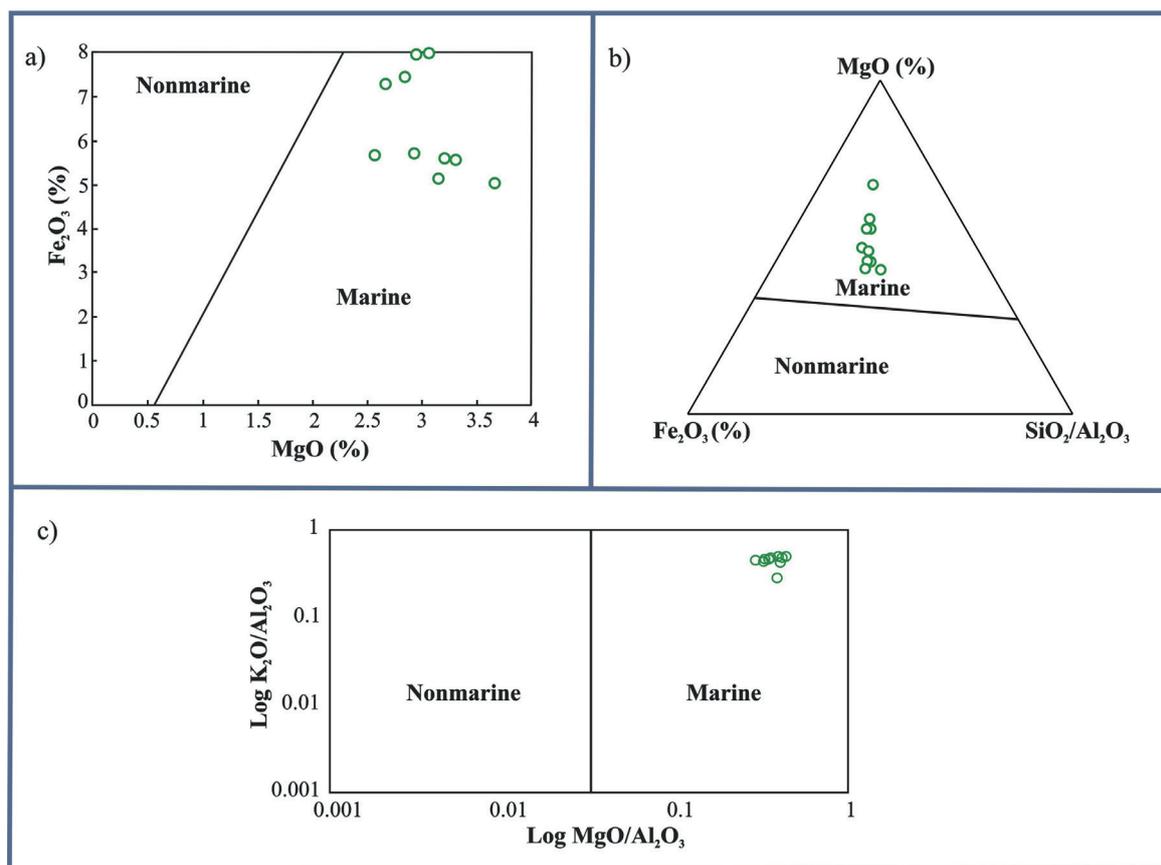
Na is often transported in the form of a solvent. Its high concentration indicates a continental sedimentary environment and arid climate. However, within the sea and lake conditions, this element is associated with a humid climate. Low amount of Na is considered typical for a coastal marine condition. The amount of Al increases when this clay-forming element relates to an open sea environment (Engalychev & Panova, 2011). In addition, the ratio of  $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$  provides information on the relationship of rocks with clay minerals or plagioclase (Ratcliffe et al., 2007). Such a specific feature creates this ratio to be a favorable indicator for assessing a paleodepositional environment. The  $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$  values are characterized by an increased tendency from the Northern Gobustan to Absheron.

Since a high MgO value indicates marine lithofacies, then an increase in this major oxide in the samples characterizes a broad transition from the terrestrial to marine lithofacies. The use of the binary diagram MgO vs.  $\text{Fe}_2\text{O}_3$  and the ternary diagram (MgO –  $\text{SiO}_2/\text{Al}_2\text{O}_3$  –

$\text{Fe}_2\text{O}_3$ ) excludes a formation condition associated with the nonmarine assemblages (Fig. 6a, b).

K is mainly transported as solvent in a humid climate condition. Lower concentration of this element is associated with a coastal-sea basin environment (Engalychev & Panova, 2011). Taking into account the role of K in the reconstruction of a paleodepositional environment of sedimentary rocks, Roaldest (1978) established a classification diagram based on  $\text{K}_2\text{O}/\text{Al}_2\text{O}_3$  vs.  $\log \text{MgO}/\text{Al}_2\text{O}_3$ . Our samples in the diagram confirm the marine provenance of studied oil shales (Fig. 6c).

An important issue represents a determination of the water type (seawater or freshwater), as well as the structure (delta, coastal, lagoon, etc.) and depth of the paleobasin of the studied oil shale. To clarify these parameters, detailed chemical characteristics are investigated. Mn and Fe are mobile in the water,  $\text{Fe}^{+2}$  oxidizes more easily than  $\text{Mn}^{+4}$ . Mg tends to be reduced faster than Fe. In addition, these two elements, mobile in water, freely transfer from the rock to a reducing environment. Vertical and horizontal flows occurring in a water column cause a separation of Fe and Mg ions from the sediment, so no precipitation of these ions occurs in sediment. However, Fe precipitates in a colloidal form in a low saline environment, while Mn



**Fig. 6.** Diagrams showing depositional conditions of samples: a) MgO vs.  $\text{Fe}_2\text{O}_3$ ; b) MgO  $\text{SiO}_2/\text{Al}_2\text{O}_3$  –  $\text{Fe}_2\text{O}_3$  (after Ratcliffe et al., 2007); c)  $\log \text{K}_2\text{O}/\text{Al}_2\text{O}_3$  vs.  $\log \text{MgO}/\text{Al}_2\text{O}_3$  (after Roaldest, 1978).

is more stable and its precipitation occurs only when an environment is too saline (Liang et al., 2014). Lower Fe values indicate a sedimentation environment associated with a pelagic zone, but higher values represent a zone close to a shelf. The value of Fe/Mn indicates that the studied samples correspond to sedimentation occurring at shallow depths (Fig. 7).

better preservation of Zr in comparison to Ti. A higher value of this ratio corresponds to deep water, a lower – to coastal marine environment (l.c.). The ratio values for samples range from 9.55 to 42.74. Sr and Ba as alkaline earth metals reflect a similar chemical feature. However, Br salts have a lower solubility than those of Sr. On the other hand, the radius of its ion is larger. In the process of paleoweathering

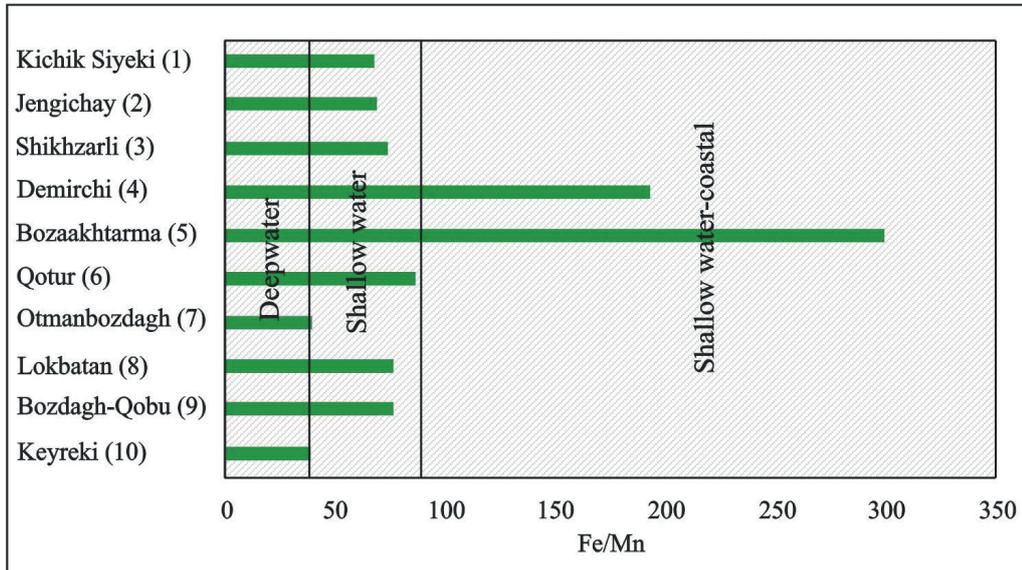


Fig. 7. Paleodepositional conditions of oil shales based on the Fe/Mn ratios of samples.

In sedimentary rocks, a Ti/Mn ratio increases in a nonmarine zone. Resistance to chemical weathering of Ti mineral leads to association with an alluvial and coastal marine region. Ti concentration in saline water basins is characterized by low values, which is associated with the absence of their solutions (Engalychev & Panova, 2011). For the samples studied, the Ti/Mn ratio ranges from 3.14 to 21.5. The obtained results are well-correlated with a shallow water basin.

Indicators such as Mn/Ni and Mn/Ga are widely used to determine a sedimentation conditions. Genetic significance of these indicators is based on a migration characteristics of these elements. As mentioned above, a rich Mn content is characteristic for pelagic zone located far from the coast, but Ga most likely precipitates close to coast, and its value decreases sharply in the direction of deep sea. From the point of view of nickel, a rich concentration of this element is associated with a closed basin – a lagoon, which is rich in organic matter. As a pyroxene exchange product, Ni is incorporated with high concentrations of chloride (Ratcliffe et al., 2007). Therefore, it is used as a facial indicator of a coastal-marine environment to explain the sedimentation process in published literature (Engalychev & Panova, 2011). For the studied samples, the value of Mn/Ni ranges from 2.67 to 31.25, and Mn/Ga from 18.18 to 108.33.

Ti/Zr ratio provides information on the transportation of terrigenous material. Such an estimate is based on the

and sedimentation, Ba containing clay minerals can easily be adsorbed by colloids and organic particles (l.c.; Liang et al., 2014). In mixed marine and freshwater environments, the main part of this element is deposited as BaSO<sub>4</sub>. A higher Ba concentration is associated with coastal-marine environment, including an outflow of large rivers. However, the presence of this element in an open sea is very limited (Engalychev & Panova, 2011). In contrast to Sr, an increase in salinity leads to early precipitation of Ba (Liang et al., 2014). However, Sr has the same feature as a crisis limit of salinity. Thus, this element is practically not chemically precipitated, since a salinity becomes higher in seawater. Also, the Sr migration occurs together with Ca (Engalychev & Panova, 2011). Based on the specific chemical characteristics of both elements, a Sr/Ba ratio is considered as an favorable indicator for assessing the water salinity. It was established that the ratio >1 indicates seawater (saltwater) and <1 – freshwater (Couch, 1971; Miknis & McKay, 1983). Except for two samples (Otmanbozdagh and Bozdagh-Qobu), the calculated values of this ratio for oil shales are lower than one.

**Paleoredox conditions.** Inorganic contents provide indicators of oxygenation of bottom sediment and water column. A number of indices and plots have been identified for the reconstruction of paleoredox conditions of sedimentary rocks, some of which are associated with metals (Jones & Manning, 1994). The value of V in the composition of oil shales increases sharply from the

center to the north in Gobustan. A downward trend was established for oil shale sampled from the Absheron Peninsula (Tab. 2). The general analysis shows that, the V value of oil shale (mean = 184 ppm) is much higher than that of NASC (130 ppm; Gromet et al., 1984), PAAS (150 ppm; Taylor & McLennan, 1985) and UCC (97 ppm; l.c.). Such enrichment corresponds to a marine environment (Ernst, 1970). From the point of view of the incorporation of  $V^{4+}$  into porphyrins, V binds to rich organic matter, including oil shale. Such incorporation is the result of substitution for Mg in porphyrins, which are degradation products of chlorophyll (Emerson & Huested, 1991). V is not always correlated with organic matter, and Glikson et al. (1985) found it may be physically hosted by detrital silicate sources (Jones & Manning, 1994). Mangini et al. (2001) explained the richness of U and V during sedimentation due to an anoxic-euxinic environment in bottom sediment and water column. Organic compounds rich in V and other metals are always correlated with Type I and II kerogens. This is due to the organic origin of these kerogens, including their relationship with phytoplankton. However, Type III kerogen is not rich in metals (less than 100 ppm), such as V and Ni. The high stability of V and Ni in organic compounds plays a key role in their connection with tetrapyrrole complexes. The preservation of organic matter associated with tetrapyrroles is also favored under anaerobic conditions. In general, the abundance of these metals in organic matter depends on the concentration of tetrapyrrole complexes contained in organic composition (highly aliphatic material of algal origin). The amount of preservation of such complexes in organic compounds is a function of exposure time to aerobic conditions (Lewan & Maynard, 1982). Huerta-Diaz and Morse (1992) believed that in reducing conditions, which sulfate reduction is more efficient, V accumulates preferentially over Ni (Watitemsu et al., 2014). Emerson and Huested (1991) note that the content of Mo and V in a water column of anoxic condition are usually lower than in oxic seawater environment due to uptake into highly anoxic sediments. Anderson et al. (1989) also established this pattern for U. Shaw et al. (1968) made a conclusion that during early diagenesis under oxygen conditions, V is mobilized from biogenic material, although its mobilization is limited under anoxic environments (Watitemsu et al., 2014). V is more likely to be enriched under acidic conditions, while Ni can be enriched in both basic and acidic conditions (Lewan & Maynard, 1982). In addition, Hatch and Levental (1992) note that high Mo, U, V, Zn and S contents provide an indication on the presence of dissolved  $H_2S$  in a strongly stratified water column. Their low contents indicate a weakly stratified, dysoxic water column. Organic sediments are rich in heavy metals such as Cu and Cr. They are well-uptaken and stored by organic matter (Glikson et al., 1985).  $Cu^{2+}$  can be reduced to  $Cu_2S$

and precipitates in an environment bound to reducing state (Liang et al., 2014). Cr is always bound to detrital fractions of sedimentary rocks.

The tendency to a decrease in Ni/V ratio indicates that the genesis of sedimentation environment associated with hydrocarbons is more reductive (Telnaes et al., 1991). This is bound to the fact that the unavailability of V under oxic conditions, and the removal of nickel as sulfide under anoxic environments (Jones & Manning, 1994). Unlike the Kichik Siyeki sample, the Ni/V ratio is characterized by lower values in the samples of Central Gobustan compared to the Absheron Peninsula.

In general, the suboxic and anoxic intermediate environments show an average V/Cr value  $>4.25$ , while the dysoxic state ranges from 2 to 4.25, and the oxic condition  $<2$ . The values around 1 suggesting the  $O_2$ - $H_2S$  interface is within the sediment (Jones & Manning, 1994). Interpretation of this ratio shows the distinctive features of two studied regions. Thus, with a few exceptions, there is a tendency showing that the oxic state dominates on the Absheron Peninsula compared to the Shamakhi-Gobustan region (Fig. 8).

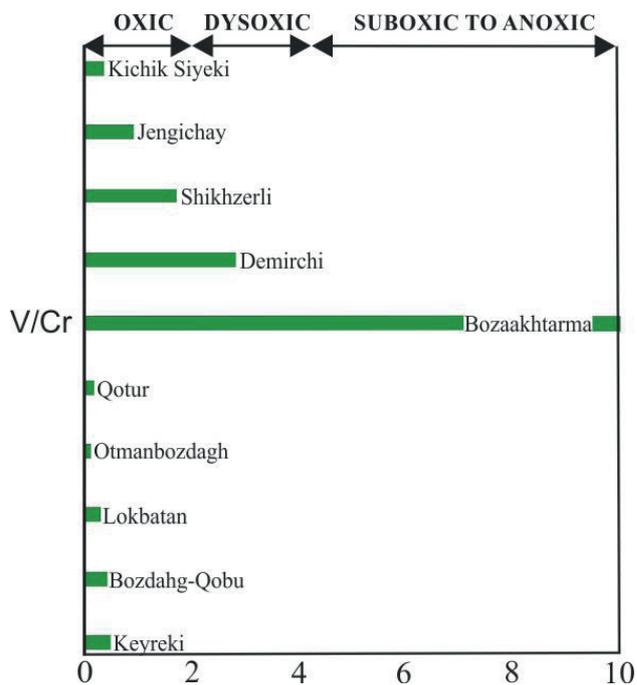


Fig. 8. V/Cr plot showing paleoredox conditions of oil shale samples.

Depending on the content of some metals in sedimentary rocks, the  $V/(V + Ni)$  value  $\geq 0.84$  presents a significant indicator of dissolved  $H_2S$  in the deeper part of a strongly stratified water column, which corresponds to euxinic, while the value is between 0.54 and 0.72 indicating minimal dissolved  $H_2S$  (anoxic) and a less strongly stratified water column. The dysoxic, weakly

stratified water column shows an average  $V/(V + Ni)$  value of 0.46–0.60 (Hatch & Leventhal, 1992). In addition, some other researchers have almost similar classifications on the same ratio (Lewan & Maynard, 1982; Lewan, 1984; Hoffman et al., 1998; Rimmerr, 2004). The values of  $V/(V + Ni)$  for the samples range from 0.26 to 0.93, suggesting that except for Kichik Siyeki and Qotur, the reducing anoxic states are characteristic in other areas of the Shamakhi-Gobustan region. A  $(Cu + Mo)/Zn$  ratio is proposed as an indicator for the oxidation of bottom waters (Hallberg, 1982). In the process of sedimentation that occurs in the presence of  $H_2S$ , Cu precipitates more than Zn. The abundance of Mo in the water content, which is rich in  $H_2S$ , led to its inclusion in this ratio. In addition, under anoxic and sulfide (euxinic) conditions, the adsorption nature of Mo on humic substances provides a favorable environment to transfer this element to the sediment–water interface (Hoffman et al., 1998). The  $(Cu + Mo)/Zn$  values increase in reducing conditions (Hoffman et al., 1998). Unlike the sample taken from the Lokbatan mud volcano, the calculated values of this ratio are higher in the samples of the Shamakhi-Gobustan region compared to the whole Absheron Peninsula.

**Paleoclimate.** Study of the nature of mineral formation is only informative in assessing of paleoclimatic conditions. Westermann et al. (2013) found that in marine settings, the variations in bulk-rock mineralogical proxies may record paleoenvironmental changes and/or diagenetic overprint (Madhavaraju et al., 2016). On the other hand, variations in paleoclimate affect the water basin, including pH, redox conditions, etc. Therefore the general paleoclimate characteristics of some minerals, discovered in the content of oil shale samples, are reviewed. Chamley (1977) made a conclusion that sediments rich mainly in chlorite and quartz relate to arid climates, while humid periods lead to an alteration in primary minerals, and formation of kaolinite and degraded mixed layers (Singer, 1984). In relatively low-relief areas, arid climatic conditions replaced by short-term humid seasons are characteristic by high concentrations of smectites (i.c.). Chamley (1979) found in semi-arid conditions the smectite bound to moderately hot and only periodically wet seasons. Keller (1970) noted that the formation of smectites of detrital origin is more associated with the semi-arid conditions. Like smectite and chlorite, illite is one of the major minerals forming in arid or semi-arid climates (Khormali & Abtahi, 2003). The widespread distribution of chlorite and illite in sedimentary rocks formed during the initial stage of weathering (Nesbitt & Young, 1989), associated with rapid erosion, occurring in source area (Fursich et al., 2005). This condition is considered as a typical change in the paleoclimate from warm and humid (seasonal) to arid or semi-arid one (Madhavaraju et al., 2016).

The dominance of semi-arid climatic conditions is favourable for carbonate minerals, including calcite (Emadi et al., 2008). Like potassium and iron hydroxide, jarosite demonstrates the genesis of the weathering associated with arid climate conditions. Diagenetic processes and semi-arid fluid environments occurring at shallow depth are characteristic for hematite (Walker, 1976). Paleoclimate environment of calcium is bound to semi-arid zones (Leeder, 1975).

Liu et al. (1984) noted the relative lower mobile properties of Al, Fe, and Mg, and leaching of the other more-easily and more-rapidly deliberating elements, which provides very useful information in assessing paleoclimatic conditions (Chandra et al., 2016). K and Na are the most rapidly and easily deliberating, which leads to their accumulation in dry climatic condition (i.c.). Transient climatic conditions, such as sub-arid and sub-humid, influence some properties of Ca (dissolution, accumulation, etc.; Shang et al., 2013). The arid/semi-arid paleoclimatic states in the above-mentioned mineralogical properties should prevail in the case of higher concentrations of Al, Fe, Mg and Ca (Gao et al., 2011) (Tab. 2).

Suttner and Dutta (1986) established a binary diagram based on  $(Al_2O_3 + K_2O + Na_2O)$  versus  $SiO_2$  to constrain the paleoclimatic condition during sedimentation of siliciclastic rocks. The result of this plot confirms the arid climatic conditions for the studied oil shale samples (Fig. 9).

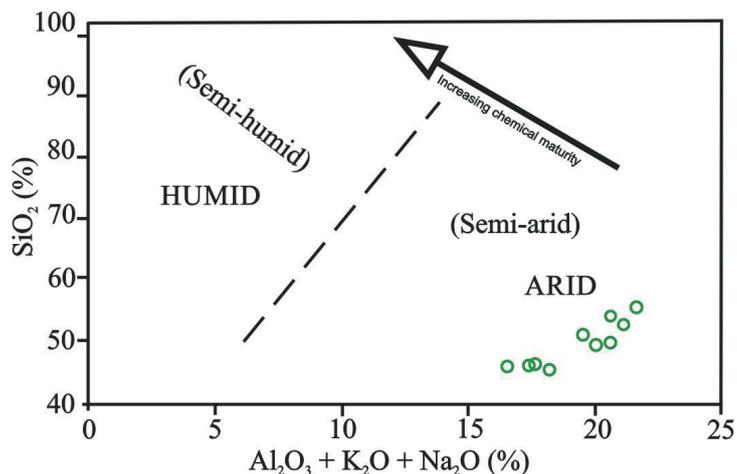


Fig. 9. Discriminant diagram showing paleoclimatic properties of oil shale samples (after Suttner & Dutta, 1986).

In our study we used various ratios such as  $Na_2O/Al_2O_3$ ,  $Na_2O/K_2O$ ,  $Na_2O/CaO$ , and  $Na_2O/TiO_2$  to get more information on paleoclimate changes. Fig. 10 shows that there are some variations for the curves depending on the areas in which the analysed samples are located. Commonly, in response to chemical weathering and precipitation, the values of these ratios decrease as a result of rapid loss of

Na<sup>+</sup> (Chandra et al., 2016). In addition, depletion in CaO, MgO, TiO<sub>2</sub>, and K<sub>2</sub>O, and enrichment in these ratios are also interpreted as an indicator of cold and arid climatic conditions. The detailed analysis of the research areas shows that values of Na<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub>, Na<sub>2</sub>O/K<sub>2</sub>O and Na<sub>2</sub>O/TiO<sub>2</sub> ratios for samples taken from the northern part of Gobustan (Demirchi) and the adjacent Central Gobustan (Bozaakhtarma) are relatively lower (Fig. 10), which is typical for hot and comparatively humid conditions. For some samples (Qotur and Lokbatan), the depletion in values of some major oxides, such as Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, and enrichment in these ratios indicate the prevalence of colder and arid climatic conditions.

of weathered rocks. Its higher concentration indicates the salty environment of the basin in arid season, which limits the flow of seawater in it (Couch, 1971). Accumulation of Cu is favourable for oil shale, which is enriched in organic matter, deposited in warm and humid climates (Liang et al., 2014). The Sr/Cu ratio is used to reveal paleoclimatic conditions: a warm humid climate is manifested by the value of 1.3–5.0, whereas Sr/Cu >5.0 suggests a hot arid climate (Abraham, 1978). In our case, the Sr/Cu ratio is expressed by the much higher values (1.4–83.33), which suggests a hot arid climatic conditions for the majority of samples.

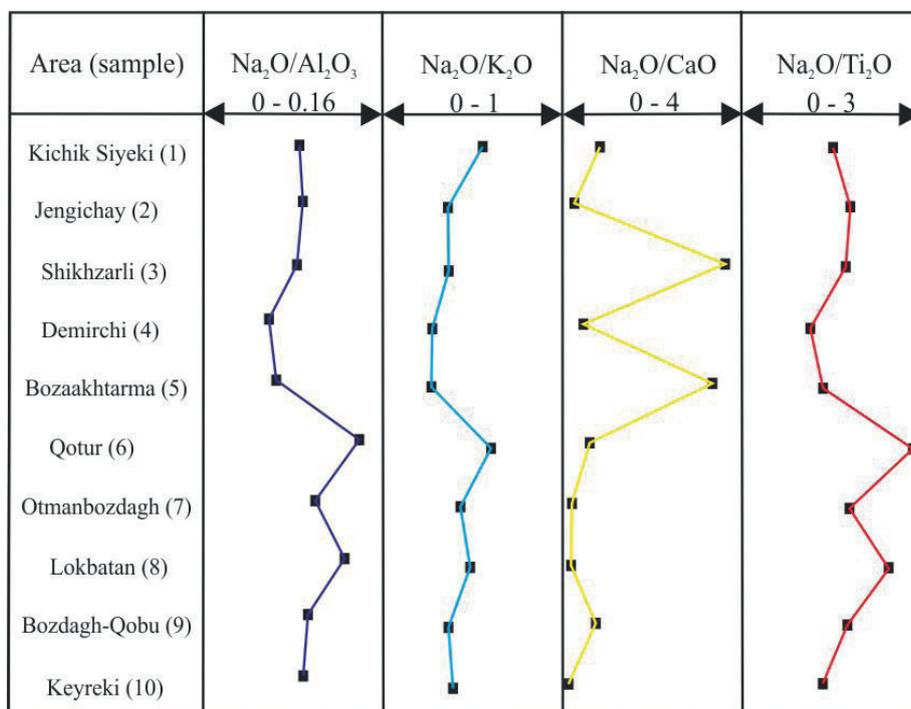


Fig. 10. Profiles of selected ratios, showing the paleoclimatic conditions of the samples.

An eluvial coefficient is used to obtain information on weathering of sediments (Zhang et al., 2013). In its formula

$$K_i = R_2O_3 / (RO + R_2O)$$

RO represents the value of CaO and MgO in the sample and R<sub>2</sub>O is a sum of Na<sub>2</sub>O and K<sub>2</sub>O. R<sub>2</sub>O<sub>3</sub> indicates trivalent oxides, including Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub>. The calculated values for the samples range from 6.1 to 13.15, indicating weak to moderate leaching of elements, which corresponds to semi-arid climatic conditions.

Concerning specific features of trace elements, various ratios are used to understand paleoclimate environments. Thus, the Sr, found in the samples, represents one of the most active trace elements – easily dissolving in the content

## Discussion

The genetic properties of clay mineral assemblages and also calcite, jarosite, hematite, etc., found in the samples indicate that the studied oil shales were formed in an aqueous environment. The determined values of illite suggest an idea that the samples are associated with peripheral zones. Also, the presence of calcite in the composition of mineral complexes (Tab. 1) indicates a condition of sedimentation related to shallow water zones. Studied oil shales are rich in chlorite (Tab. 1), which indicates both – marine and freshwater sedimentary conditions, so the freshwater basin conditions should not be

excluded in our interpretation.

Since the lagoon systems are characterized by a high concentration of smectite, illite, chlorite, calcite, and quartz (Sabatier et al., 2010; Abidi et al., 2019), data on the bulk-rock mineralogy of our samples (Tab. 1) confirm the idea that the paleodepositional conditions in studied areas are associated with isolated coastal marine areas.

The AKF diagram indicates that the paleosedimentation conditions of oil shale can be associated with transition zones located between continental and marine areas (Fig. 5). The use of classification diagrams based on the chemical composition of oil shales clearly indicates the bound of samples to aqueous environments (Fig. 6a, b, c).

Moreover, published works (Sultanov & Sultanov, 1945; Aliyev & Abbasov, 2018) show the traces of fauna, such as fish larvae and planktonic crustaceans, often

recorded in oil shale-containing assemblages located in both studied regions, which provide a sign of aquatic faunas. This fact is confirmed by the fauna (benthos, planktonic foraminifers, as well as the teeth and bones of fish), determined in recent studies and providing the age of samples from mud volcanoes. The values of Fe/Mn ratio suggest the shallow Middle Eocene sedimentation basin during the deposition of oil shale samples (Fig. 7). The comparison of these values from the Absheron Peninsula, located in a short distance from the South Caspian Basin, as well as from the Central and South Gobustan, manifests an increasing tendency of the water column in the direction to North Gobustan, which is situated at a high hypsometric level. The values of Fe/Mn ratio in the samples from the mud volcanoes of Bozaakhtarma and Demirchi are higher, which indicates the shallow-coastal water conditions (Fig. 7).

The maximum values of Ti/Mn were also recorded for the samples of the Bozaakhtarma (21.5) and Demirchi (26) mud volcanoes, which confirms the finding of the relatively shallow water column in comparison with other areas. The Mn/Ni and Mn/Ga values indicate that the paleodepositional environments of oil shale collected from Kichik Siyeki (Mn/Ni = 18.92; Mn/Ga = 82.35), Jengichay (Mn/Ni = 31.25; Mn/Ga = 62.5), Otmanbozdagh (Mn/Ni = 24.39; Mn/Ga = 71.43) and Keyreki (Mn/Ni = 17.57; Mn/Ga = 108.33) areas are associated with relatively deeper water levels.

Based on values obtained for the Ti/Zr ratio, it can be assumed that the transfer distance of terrigenous materials derived from the source terrains to the sedimentary basin was relatively long.

Aliyev and Abbasov (2019) found that the Middle Eocene sedimentation was probably associated with the final Eocene basin, which represented the northern branch of Meso-Tethys in the Crimea-Greater Caucasus-Kopet Dag system. The evolution of that independent deepwater basin, fed on the left – north branch of Meso-Tethys (Rustamov, 2005, 2008) is associated with areas covering the shale-flysch trough of the axial zone, which formed as a result of Jurassic rifting (Zonenshain & Le Pichon, 1986; Khain, 1995; Babayev et al., 2015) in the North Crimea-Greater Caucasus-Kopet Dag system, and extended to the east of Kopet Dag. The shale-flysch and non-compensated (Babayev et al., 2015; Rustamov, 2015) deep basin played a role as a border between the Scythian-Turan plate of the Eurasian continent and the intra-Transcaucasian plate (Rustamov, 2005). The beginning of the late Alpine tectogenesis corresponds to the period of regional uplift in the Caucasus-Caspian region and Iran (Shixalibeyli, 1967; Rustamov, 2008; Babayev et al., 2015). The flysch basin of Meso-Tethys covered the southern slopes of the Greater Caucasus and the Absheron Sill, playing a role in transporting terrigenous material during the Tufan and Vandam uplifts, and being completely closed in the Upper Eocene (Brunet et al., 2003; Rustamov, 2015). The intensification of regional uplift processes in the transitional phase of the Upper Cretaceous-Paleogene (in the tectonic phase of Laramie; Babayev et al., 2015) probably led to a decrease in the depth of the final Eocene basin (Aliyev & Abbasov, 2019). Such an interpretation corresponds well with the results obtained in the present study for the depths of the Middle Eocene sedimentary basin and the transport distance of terrigenous materials.

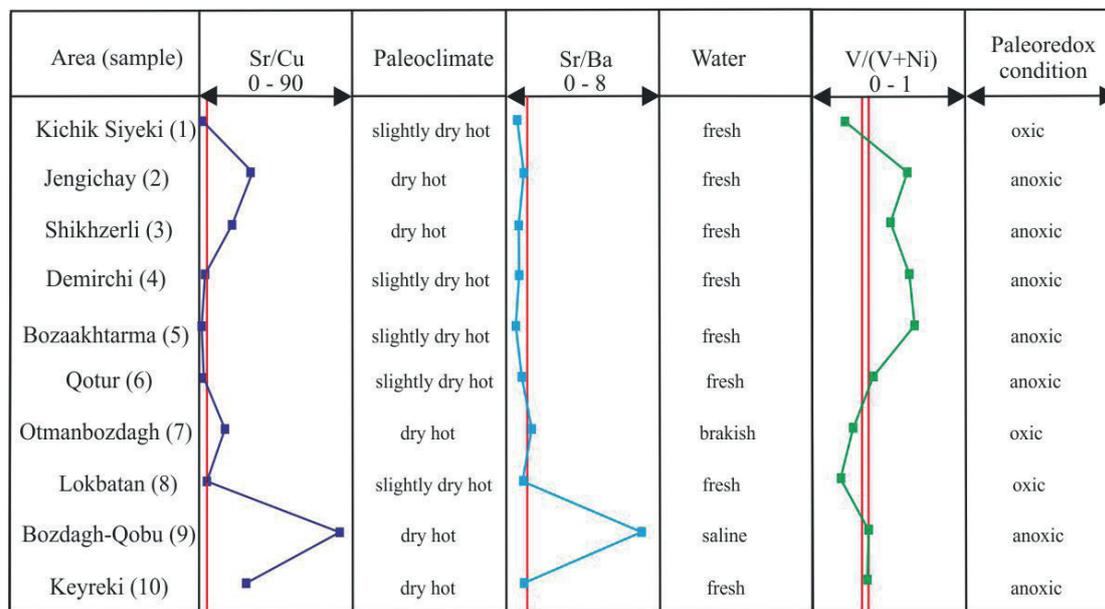


Fig. 11. Vertical profiles showing salinity, paleoclimate and paleoredox of samples.

Taking into account an analog (Engalichev & Panova, 2011) of the obtained results, the paleodepositional conditions for the Middle Eocene oil shales are most likely associated with isolated coastal-marine zones, in more detail, lagoons and lakes, which depth was 10 meters.

The results of the well-known approaches used in the reconstruction of the paleo-redox conditions of oil shales do not coincide. In more detail, although the amount of V determined in oil shales exceeds 100 ppm (mean = 184.4 ppm) but the average value of Ni is lower than this indication (mean = 68.3 ppm). In addition, it was established that the kerogen of oil shale samples is a mixture of type II and III (Aliyev et al., 2018b).

Unlike the Kichik Siyeki area in Central Gobustan and all areas of the Absheron Peninsula, the reducing conditions were established based on lower Ni/V values for the Shamakhi-Gobustan region. The same result was also recorded for the V/Cr ratio (Fig. 8). Except for the Lokbatan sample, the (Cu + Mo)/Zn values are lower in the Absheron samples. Jones and Manning (1994) found that the Ni/V and (Cu + Mo)/Zn are not reliable ratios in the interpretation of the palaeo-redox conditions.

The study of the nature of the minerals found in oil shales, which related to paleoclimatic conditions shows the samples are more strongly associated with arid/semi-arid seasons. In addition, the results of the widely used diagram ( $\text{Al}_2\text{O}_3 + \text{K}_2\text{O} + \text{Na}_2\text{O}$ ) vs.  $\text{SiO}_2$  (Fig. 9),  $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ ,  $\text{Na}_2\text{O}/\text{K}_2\text{O}$ ,  $\text{Na}_2\text{O}/\text{CaO}$ , and  $\text{Na}_2\text{O}/\text{TiO}_2$  ratios (Fig. 10), and also the eluvial coefficient confirm the dominance of arid paleoclimatic conditions.

In general, the obtained results of the map of vertical variabilities of salinity, paleoclimate and paleoredox of samples (Fig. 11) can be considered as characteristic features of oil shale from the foothills of the Greater Caucasus.

### Conclusion

The nature of the clay minerals found in the samples and the results of used ratios and diagrams based on the analysis of the bulk rock geochemistry data indicate that the oil shale is associated with the paleodepositional environment bound to a transition zone located between continental and marine zones. The AKF plots show a gradual transition of the sediments of the basin from continental to marine environment. The process of sedimentation in the aquatic environments was probably associated with the final Eocene basin, which was the northern branch of Meso-Tethys in the Crimea-Greater Caucasus-Kopet Dagh system. The intensification of regional uplift movements in the Upper Cretaceous-Paleogene periods probably led to a decrease in the depth of the final Eocene basin. The paleodepositional conditions of the Middle Eocene oil shales most likely correspond to isolated coastal- marine

zones, in more detail, lagoons and lakes, which depth was 10 meters.

The mineralogical and geochemical proxies of the Middle Eocene oil shales suggest an idea that except for some samples of the Apsheron Peninsula, all oil shales can be associated with freshwater, mixed paleo-redox (mostly reducing), and arid/semi-arid environments.

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## Aplikácia mineralogických a geochemických údajov zo strednoeocénnych roponosných bridlíc na úpätí Veľkého Kaukazu v Azerbajdžane pri rekonštrukcii environmentálnych a paleoklimatických podmienok ich genézy

Produktívna oblasť na úpätí Veľkého Kaukazu je situovaná v kolíznej zóne medzi arabskou a euroázijskou litosférickou platňou. Špecifické geodynamické a depozičné podmienky v tejto zóne prispeli k vytvoreniu bohatých akumulácií ropy a zemného plynu (cf. Aliyev & Abbasov, 2019).

Roponosné bridlice v Azerbajdžane sa vyznačujú vysokou kvalitou (energetická hodnota 6,0 – 12 MJ · kg<sup>-1</sup>, zastúpenie organickej substancie 15 – 31 %, síry 0,4 – 1,2 % a popola 65 – 85 %), prevyšujúcou kvalitu roponosných bridlíc v iných štátoch. Keďže vystupujú v hrubých polohách s veľkým plošným rozšírením, predpokladá sa, že

sa v tejto krajine v budúcnosti stanú dôležitým zdrojom ropy a zemného plynu (Abbasov, 2015, 2016a, b).

Tento článok má za cieľ preklenúť doterajší nedostatok poznatkov o depozičnom prostredí a paleoklimatických podmienkach počas strednoeocénnej evolúcie roponosných bridlíc. Výskum sa realizoval na 10 vzorkách z odkryvov a bahenných vulkánov v oblasti medzi lokalitami Gobustan a Baku, nachádzajúcimi sa na polostrove Abšeron na východnom úpätí Veľkého Kaukazu v susedstve Kaspického mora (obr. 1). Produktívne strednoeocénne súvrstvie je v tejto zóne situované v hĺbke len niekoľko stoviek metrov, prípadne vychádza až na povrch (obr. 2).

Metodika výskumu zahŕňala štúdium mineralogického a geochemického zloženia hornín (hlavné oxidy a stopové prvky; tab. 1 a 2, obr. 3 – 6) spojené s datovaním. Depozičné prostredie bridlíc sa určovalo na základe pomerov determinujúcich prvkov (obr. 7 – 11), pričom pri interpretácii sa brali do úvahy aj publikované zistenia a rekonštrukcie iných autorov aj z iných častí sveta.

Výsledkom výskumu je doloženie sedimentačných podmienok strednoeocénnych roponosných bridlíc v prostredí izolovaných príbrežno-morských oblastí – lagún

a jazier – s hĺbkou okolo 10 m. Doložený bol postupný prechod z kontinentálneho sedimentačného prostredia do morského. Roponosné bridlice v študovanom regióne, s výnimkou niekoľkých vzoriek, vznikali dominantne v sladkovodnom a prevažne redukčnom prostredí v aridných a poloaridných podmienkach.

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