EOCENE-MIOCENE OIL SHALES IN AZERBAIJAN: STRATIGRAPHIC CONTROLS ON FORMATION, DISTRIBUTION AND HYDROCARBON GENERATION

Based on the results of many years of field surveys, new information is presented on previously unknown oil shale outcrops in Azerbaijan. New boundaries of the distribution of oil shale-bearing facies were established. Role of stratigraphic controls in the distribution of oil shales within areas and outcrop sections, and their oil or gas generation capabilities were substantiated. The study of the source of oil shale parent rocks, and the features of oil shale basin that formed in the Eocene, Lower Maikop (first discovered in this study) and Miocene (Upper Maikop, Chokrakian and Diatom), made it possible to obtain some new regularities. Our results show that the kerogens of Eocene and Diatom oil shales demonstrate similar evolutionary histories that are noticeably different from the Maikop ones. Eocene oil shale kerogens, which show a closer connection with the marine environment demonstrate the ability to generate only oil, like Diatom kerogens, while the kerogen evolved in the Upper Maikop basin, which is subject to more terrigenous inputs and formed in a relatively freshwater environment, mainly shows the ability to generate gas.

Keywords: Azerbaijan, oil shale, formation, stratigraphic controls, regularity, oil generation capacity

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Introduction and research status

The territories of East Azerbaijan, which located in the zone of collision of large geodynamic units, were characterized by rapid and large-scale sedimentation, processes of regional compression and rich oil and gas formation (Aliyev et al., 2019; Aliyev and Abbasov, 2019; Odonne et al., 2021). In terms of the density of mud volcanoes, the region has no analogues in the world. In areas where rich hydrocarbon deposits, bituminous rock outcrops and mud volcanoes have been found, oil shale has also been discovered (Aliyev et al., 2014; Aliyev et al., 2018; Aliyev and Abbasov, 2020), which is considered the best source rock among sedimentary rocks.

Analyzing the published literature concerning the study oil shale of Azerbaijan in different directions, in two periods until the end of the 1930s and then the beginning of the 1960s, it is necessary to note the work done by K.N.Bogdanovich, I.M.Gubkin, V.V.Weber, Z.A.Mishunina, A.J.Sultanov, R.H.Sultanov, A.A.Ali-zadeh and others. Along with the identification of oil shale outcrop sections in the early periods, their lithostratigraphic features were studied. In the subsequent period, it includes the study of physical and chemical and geochemical characteristics of oil shale rocks, and the calculation of initial reserves of some deposits. If we exclude the book created by Salayev and his co-authors in 1989 (Salayev et al., 1989), then after a long break, precisely since 2000, the period began to study oil shale in Azerbaijan, along with oil sands, with more modern approaches and methods. During this period Ad.A.Aliyev and O.R.Abbasov restored the study of oil shale (Abbasov, 2009). In addition to surface outcrops, oil shales found in ejecta from mud volcanoes were included in their studies (Aliyev et al., 2018). In publications (Isaksen et al., 2007; Hudson et al., 2008; Baldermann et al., 2020; Aghayeva et al.,

2021) covering this period, along with samples taken from the mud volcano areas, several outcrop sections which contains oil shale layers were also investigated using modern approaches. In these studies, a small number of oil shale samples have been investigated not as oil shales, but as shale and argillite.

Long-term exploitation of rich oil and gas fields leads to a decrease in their production indicators. This necessitates a more detailed and appropriate study of oil shale (as well as oil sands) with a large reserve (Aliyev et al., 2014) that has not been used in Azerbaijan so far. In other words, the study of formation conditions of such rocks in previously known oil shale areas of Eastern Azerbaijan was not based on the methodological principles of the researches performed in this direction on a global scale, but at best, based on the hypotheses formed on the basis of analyzes of lithostratigraphic changes observed in the studied outcrop sections. However, in the few works published by foreign researchers together with local researchers (Baldermann et al., 2020; Aghayeva et al., 2021), more detailed studies were carried out in the study of two outcrops (Pirekeshkul and Islamdag sections). However, in these studies, oil shales found among the lithofacies of the sections were considered as argillaceous rocks. In addition, except for Eastern Azerbaijan, the possible distribution areas of oil shale in other regions of the country have not been specified, and the role of stratigraphic controls in their enrichment with the organic matter in the Middle Eocene-Upper Miocene stratigraphic range has not been substantiated. Another issue attracting attention is the type of oil shale kerogens associated with different stratigraphic units, as well as the as well as the definition of their ability to generate oil or gas hydrocarbons. This research work is devoted to the study of additional distribution areas of oil shale in Azerbaijan and the substantiation of the role of stratigraphic controls in distribution of oil shale lithofacies within areas (fold structures) and stratigraphic units, and their oil or gas generation potential.

Distribution of oil shale throughout the country, folded structures and outcrop sections

The results of our many years of field research show that the distribution of oil shale in Azerbaijan is characterized by Middle Eocene, Maikop, Chokrakian (partially) and Diatom deposits (Figure 1). With the exception of the Middle Eocene, oil shale stratigraphy correlates very well with Maikop and Diatom deposits, which contain potential oil and gas source rocks.

The oldest, Cretaceous oil shales of Azerbaijan are found along the southern slopes of the Greater Caucasus, including in areas extending almost to the Absheron Peninsula. They are established in the Altyaghaj, Bakhyshly (Atachay), Sarydashchay, Zarat, Talyshnuru, Gyzmeydan, Khilmilli, and Kurkechidagh outcrop sections belonging to the Albian stage of the Lower Cretaceous, as well as to the Cenomanian, Coniacian and Turonian stages of the Upper Cretaceous. Dark-colored oil shales of the Cretaceous period are not of economic interest due to the thinness of their layers traced in limited areas.

Middle Eocene deposits (mainly Paradashian (Bartonian) and relatively Lutetian stages (Figure 1)) can be considered as oil shale facies in Azerbaijan. If we do not take into account several meters of dark brown bituminous-paper oil shale in the area of the village of Susay on the left bank of the Guruchay, as well as local outcrop sections found in Gusarchay and other areas in the Pre-Caspian-Guba oil and gas region, significant outcrops of Middle Eocene oil shale in other areas were not recorded. Significant units of oil shale belonging to the Middle Eocene can be found in areas ranging from Ilkhydag to the centre of Gobustan, and from there to the western part of Shamakhy. In the north of the Shamakhy-Gobustan oil and gas region, the alternation of oil shale layers was established in the Agburun, Yashma, Chargyshlak and other areas. Particular attention is drawn to oil shale outcrops in the northwestern zones of the oil and gas region, especially in the Agsu, Gurjuvan, Girdimanchay, Sediyan, Diyalli, Juliyan, Erebshalbashy, Khilmilli and others. Middle Eocene oil shale, common in Central Gobustan, with a thickness of about 200–450 m, is present in the Jengichay and Kecheller outcrop sections with sufficient thickness and frequent alternation. Together with the Middle Eocene, thick layers of oil shale of younger Diatom are also characteristic of the Mayash, Kichik-Siyeki and other areas. In the course of fieldwork in Central Gobustan, we were able to discover several new outcrops of Eocene oil shales, such as Boyuk Siyeki and Chaily, which are of particular importance.

According to our estimates, the potential sites that give positive results in the search for Paleogene oil shale lithofacies are: the strip from Gusarchay to Shurabad; Inchechay and Terter interfluve zones in Naftalan; areas where Paradash stage of Middle Eocene sediments was recorded in Nakhchivan (especially in the interfluve zones Garadere-Dulyun); in Talysh, areas belonging to the Pirasora and predominantly Nesli facies (thin brown coal layers have also been identified (Babayev et al., 2015) correspond to Paradsh stage. According to the results of numerous previous studies (Sultanov, 1948; Abbasov, 2009) of the Gobustan region, the German fault was recognized as typical of the northern boundary of oil shales of the Middle Eocene.

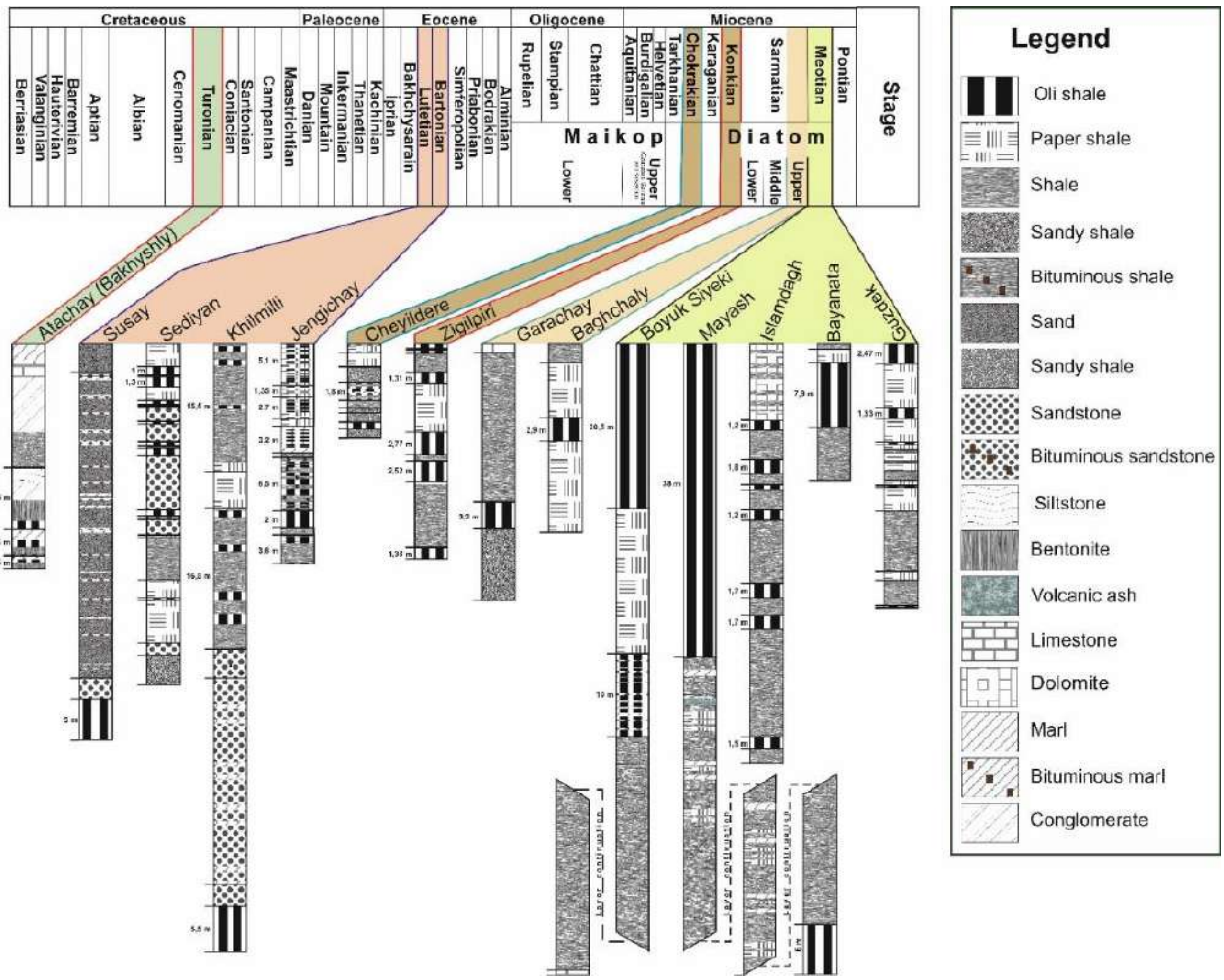

Figure 1. Cretaceous-Miocene sections of some oil shale-bearing outcrops in Eastern Azerbaijan

But our new research shows that the distribution areas of oil shale are typical for a more northern zone, including the Guba basin. In our opinion, the prospect of discovering Middle Eocene oil shales in the northern zones of Eastern Azerbaijan should be limited to the zones that continued until the Imamgulukend-Khachmaz fault.

Oil shales are not considered typical of the Lower Maikop deposits identified in the country. However, in our studies, black oil shales of the Lower Maikop age of considerable thickness are traced over large areas in Guba (Figure 2A), in the northwest of Gobustan (in Lahij (Figure 2B)) and in its center (Figure 2C), as well as in Yardimly (Figure 2D).

The identification of oil shale facies of the Lower Maikop age, which are not considered typical for Azerbaijan, in large areas in Pre-Caspian-Guba region and Talysh necessitates the expansion of the search for their analogues in the south of Guba, including in Gobustan. The presence of oil shales in sedimentary lithofacies of the Maikop age, known in Nakhchivan as volcanogenic facies, is called into question.

The Upper Maikop deposits, which play the main feeding role for the hydrocarbon reservoirs of Azerbaijan, are also of particular importance in terms of oil shale facies. The areas located to the east of the zones of the Girdimanchay current are characterized by a denser manifestation of the Lower Miocene facies, which preserve oil shale. They are observed in Kurkechidagh, Kemishdagh, Khilmilli, Engikharan, Aghdere, Erebshalbashy, Gibledagh, Shikhzerli, Shaibler, Gaibler, Jengidagh, Bayanata, Islamdagh and other areas. In the course of field research in Central Gobustan, we discovered previously unknown areas of oil shale in the Upper Maikop. They are located: southeast of the Kichik-Mereze mud volcano, northeast of Mount Gaibler; about 2.6 km southwest of Mount Gaibler, 1.2 km east of the cemetery, on the right and left banks Baku-Shamakhy-Yevlakh highways; in a low field between the mountains of Boyuk-Siyeki and Kichik-Siyeki; in the northwest of the Iyimish mud volcano. To date, oil shale facies related to the Upper Maikop have not been found in the south of Shamakhy-Gobustan, but as a result of our field research, we were able to establish them in several areas: in the in the northwest East Cheyildag volcano; about 1 km southwest of the Gylynj mud volcano. The most important new outcrops on the Absheron Peninsula are related to the southern flanks of Agchala Lake, located southeast of the Uchtepe volcano. The next new outcrop in Western Absheron was discovered exactly 1.3 km south of the Aghchala field, on both sides of the Tagiyev-Sahil road. The oil shale rocks found in this area, which we have named the "Mushvigabad road", are covered with abundant jarosite rocks. In our opinion, it is highly probable that analogues of the oil shale facies of Maikop series extending east of Girdimanchay can also be observed in the west of this river, especially in the Naftalan region and in the near-surface intervals of the sites, located between the Kura and Gabirri rivers. Conducting exploration work in this direction will most likely make it possible to discover new oil shale-bearing areas.

Figure 2. Lower Maikop-aged oil shale outcrops discovered for the first time in Guba (**A**), Lahij, Gobustan (**B** and **C**) and Talish (**D**)

The surface outcrops of oil shale in the Chokrakian deposits, representing the Middle Miocene, were revealed by us only in the southern limb of the Cheyildagh fold, covering the extreme eastern part of the Sundu-Cheyildag anticline zone of South Gobustan.

Oil shales of Middle and Upper Miocene in East Azerbaijan are associated with the Konkian, Upper Sarmatian and Meotian (together called Diatom (Figure 1)). The Upper Sarmatian deposits of the Pre-Caspian-Guba region require special attention in for Diatom oil shale facies. Here, the lower part of the Upper Sarmatian lithofacies is confined to the Rostov suite, which is composed of carbonate and shale deposits together with oil shale. A long strip of o shale facies stretches from Gilgilchay in the southeast to Gudiyalchay in the northwest, up to the watersheds of Gusarchay-Tahyrzhalchay and the village of Enig. However, more significant outcrops are established in a small-scale strip between Velvelechay and Gudiyalchay, which reaches about 30 km. Moving south, in the Shamakhy-Gobustan oil and gas region, the Rustov analogue (Akhudag suite) is found in the central parts of Gobustan, including between the Akhudag and Baygushlu sites, as well as in Kichik Siyeki and others. The unsatisfactory thickness of oil shale layers does not attract attention.

In most of the territory of Gobustan and Absheron, outcrops of oil shale of Konkian age, identified under the name of the Baygushgaya suite, are registered in some outcrop sections along with the Birgut suite (Meotian), which is considered as another stratigraphic composition of Diatom. Outcrops of Meotian oil shales are widespread in Gobustan and on the Absheron Peninsula. Moving to the north and northwest of Gobustan, they are marked in small layers only in certain local areas, such as the Jeyirli and Nabur sections. In the north, Meotian oil shales do not attract much attention. Thus, with the exception of the Yashma region, there are none in nearby places. To the south, Birgut paper oil shale lithofacies are exposed along the low-mountain sections of the Langebiz and Alat rige, and also extend eastward from large mud volcanic fields traced south of Gobustan. The oil shale layers of Meotian age, together with the Konkian ones (tens of meters thick), are very significant in the thick (up to 500 m) sections of Birgut, recorded in the area of the Kichik Siyeki, Boyuk Siyeki and Baygushgaya mountains, located in the central part of Gobustan. In addition to, Meotian oil shale was found in Bayanata, Islamdagh, Mayash, Sungur, Akhudagh, Baygushlu, Alagyshlag, Garagyshlag, Saridash and other areas almost together with Konkian one in Central and South Gobustan.

At the transition to the Absheron Peninsula, outcrops of Diatom oil shale are observed in the areas of Shorbulag, Garaheybat, Damlamaja, Uchtepe, Goytepe, as well as in areas continuing to Ilkhydagh. Along with the southern outskirts of Central Gobustan, the western part of the Absheron Peninsula is the most common zone for recording oil shales belonging to the Konkan and Meotian ages. Here, attention is drawn to the alternation of oil shale layers of different thicknesses in the sections of Diatom, belonging to the Kecheldagh, Khyrdalan, Shabandagh, Masazyr, Zigilpiri (Figure 1), Binegedi, Fatmayi, Saray and other outcrops. In areas where, along with Diatom oil shales, outcrops of other bituminous rocks (oil sands and marls) were recorded, both in the southern suburbs of Gobustan and in Western Absheron, we regularly found signs of oil during field studies.

In our opinion, there is a high probability of finding analogues of Diatom oil shale facies of the Shamakhy-Gobustan and Absheron peninsulas, in the interfluve of the Kura and Gabirri, as well as in the northern zones of Talysh and especially in the western and northwestern parts of Nakhchivan.

Summarizing the results of our many years of field research, from a spatial point of view, it is clear that deposits containing surface oil shale in the territory of Azerbaijan are distributed over large areas belonging to the Pre-Caspian-Guba, Shamakhy-Gobustan, Absheron and

Talysh (Jalilabad) oil and gas regions. However, an analysis of the published literature on the lithostratigraphic characteristics of outcrop sections identified on the territory of the country gives good reason to assume that some areas belonging to the Ganja and Nakhchivan oil and gas regions are also oil shale-bearing. Figure 3 shows the identified areas of oil shale in the territory of Azerbaijan, as well as the proposed potential areas for their prospecting in the future.

With a few minor exceptions, the location of more than 70 oil shale outcrops we identified in East Azerbaijan (Aliyev and Abbasov, 2019), also correlates very well with basins where mud volcanoes have also been recorded. Of particular importance for the distribution of oil shale in East Azerbaijan are the areas of the Paleotethys Sea basin, corresponding to the zones of the accretionary prism (southern slope of the Greater Caucasus), or the Bayanata microblock located in the Jeyrankechmez-South Caspian Megabasin. (Figure 4). To the north of the Zangi-Garajuzlu fault, the areas corresponding to the accretionary prism are more favourable for the distribution of Eocene oil shale outcrops. This fault and its southern zones, as well as Western Absheron, located east of the Boransyz-Jylgha fault, are more distinguished by the distribution of Diatom oil shales.

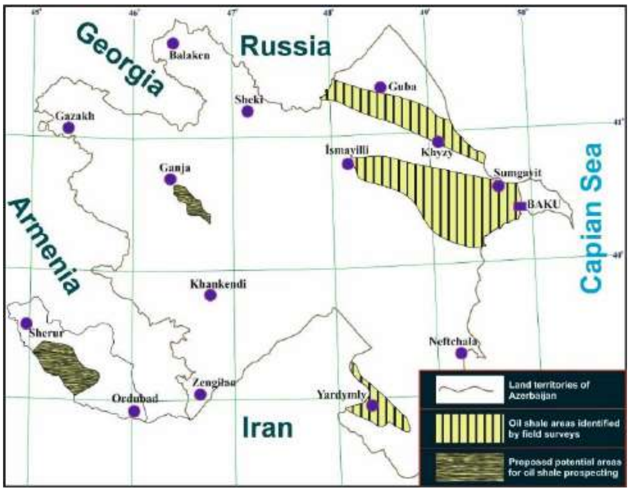

Figure 3. Exacted and assumed distribution areas of oil shale in the territory of Azerbaijan

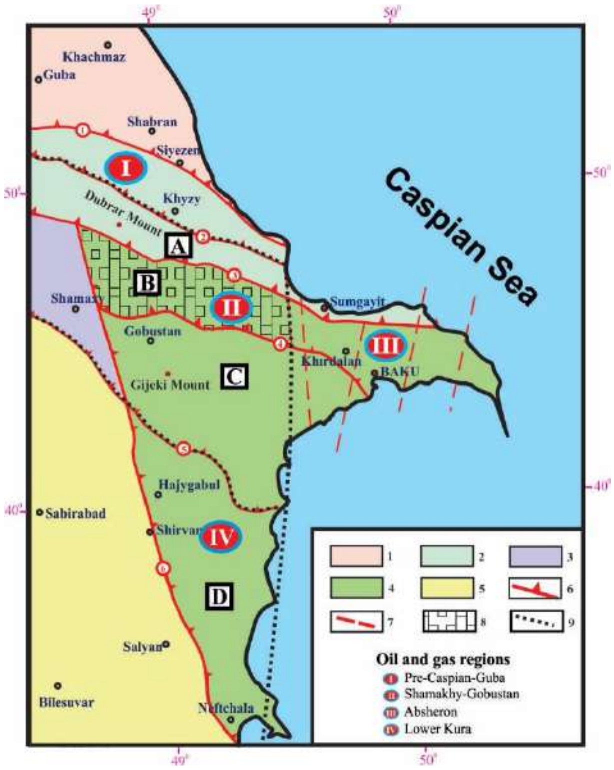

Figure 4. Tectonic scheme of oil shale-bearing and mud volcanic regions of East Azerbaijan (Modified after (Aliyev et al., 2015; Kengerli et al., 2012): **1** – Guba basin (Megazone of Gusar-Devechi); **2** – Shahdagh-Khizi basin (Megazone of the Lateral Range of the Greater Caucasus), Zagatala-Govdagh and Absheron basins (Megazone of the Southern Slope), Shamakhy-Gobustan basin (Megazone of Kakheti-Vendam-Gobustan (**A** – Northern Gobustan Allochthonous)), **3** – Shamakhy zone; **4** – Jeyrankechmez-South Caspian Megabasin (**B** – Bayanata microblock (accretion prism areas), **C** – Toraghay microblock, **D** – South-Eastern Shirvan); **5** – South Caucasus island arc system; **6** – Deep faults (**1** – Siyezen, **2** – Main Caucasus; **3** – Goredil-Masazyr convergence zone (Suvagil fault); **4** – Gujur-Gyzyldash (Zangi-Garajuzlu fault); **5** – Ajıchay; **6** – Shamakhy-Neftchala; **7** – Fault (from left to right: Boransyz-Jylgha and left sided slides); **8** – Parautochthonous; **9** – Border of the oil and gas region

Oil shale rocks are also recorded in the ejecta of mud volcanoes erupting in Azerbaijan. They are mainly found in a median zone (Figure 5), characterized by conjugate logarithmic spirals showing axial symmetry with respect to the emission centre that have been established

(Odonne et al., 2020, p. 10) on the breccia area of the volcanoes. The zone closest to the vent (corresponding to the feeding area of a mud volcano, consisting of the most recent mudflows) is called a central zone, and the zone covering the outer part of the plateau and upper slopes is called a distal zone (Figure 5 (Odonne et al., 2020)), which are not typical for oil shale rock ejecta.

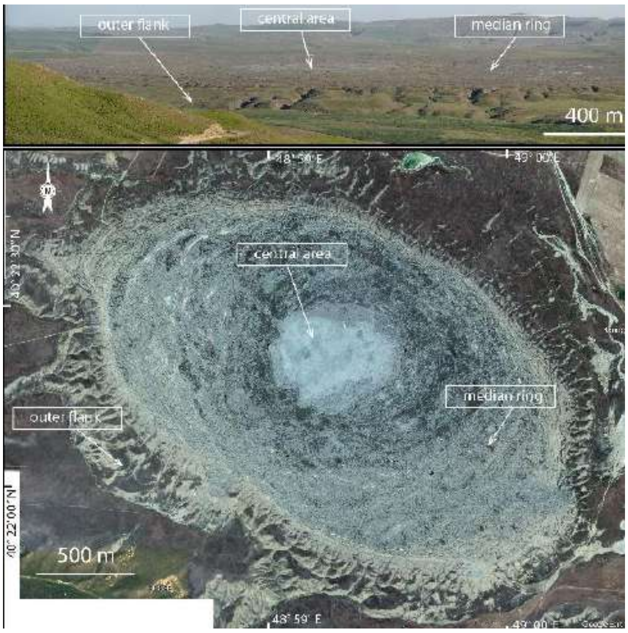

Figure 5. Central, median and distal zones were established in the breccia zone of the Ayazakhtarma mud volcano **(**Odonne et al, 2020)

The conical shape and large dimensions are more characteristic of mud volcanoes, whose eruption centres are located in the areas of distribution of younger deposits (mainly Pliocene and Quaternary) (Figure 6B), not related to the geological age of Azerbaijan oil shales. (Abbasov et al., 2022). Such mud volcanoes are characterized by ejections of Eocene, Upper Maikop and younger Diatom oil shales. They were recorded in deeper, i.e., in places of the greatest subsidence of the Cretaceous deposits (Figure 6B), where the thickness of the Cenozoic deposits is much higher. Volcanoes identified in Western Absheron, south of Gobustan, which are part of the Jeyrankechmez-South Caspian megabasin, can serve as an example (see Figure 3). On the contrary, for volcanoes in areas whose geological structure is composed of older (mainly Eocene and Miocene) deposits **(**Figure 6A and 6B), the mud chambers are located at a relatively shallow depth, the breccia extends over a more limited area and cannot be stacked and demonstrate a plateau-like extension. With the exception of Diatom, they are mainly characterized by ejections of the Eocene and Upper Maikop oil shale rocks. A large number of oil shale outcrops have been recorded in areas with such geological characteristics (Figure 6A). An example of such territories is the central part of Gobustan (Bayanata microblock (see Figure 4 and Figure 6)).

With the exception of the steepest north-eastern zones of the Lower Kura oil and gas region, where the mud volcanoes Injabel, Kelameddin, Akhtarmaardy, Akhtarma-Pashaly, etc. were found, no oil shale was found in the ejecta of mud volcanoes located in its southern zones. This pattern can only be explained by the geological structure of the Lower Kura basin. Thus, the thickness of sedimentary layer here reaches 20 km, and more than half of the deposits in lower regions located near the sea belong to the Upper Neogene and Anthropogene (Aliyev and Rahmanov, 2018). In our opinion, this factor makes it impossible for the mud volcanoes located in this part of the Lower Kura to erupt Paleogene-Miocene deposits (as well as oil shale rocks), in contrast to other oil and gas regions.

Our studies have revealed some regularities in relation to the folded structures of the occurrence of oil shale. Thus, the Middle Eocene oil shales developed mainly in synclines. Examples in this respect are Shahandagh, Chargyshlag, Embizler, Aghdere, Boyuk Siyeki, Kichik Siyeki and others. In addition, very few anticlines, including the Diyally (Sediyan) and Jengichay, contain Middle Eocene oil shales, and the thickness of their layers is noticeable in the sections found in these areas (see Figure 1). In most oil shale-bearing synclines, the limbs dip at angles >60°. The Koun oil shales, found in the northern parts of Shamakhy-Gobustan, are often associated with the cores of synclines. Eocene oil shales appear in the limbs of structures in the south. The oil shales identified in the northern flank of the anticline at the Diyalli deposit belong to layers that occur at a lower angle. In addition to the limbs of the Jengichay anticline, oil shale layers were found in its core part.

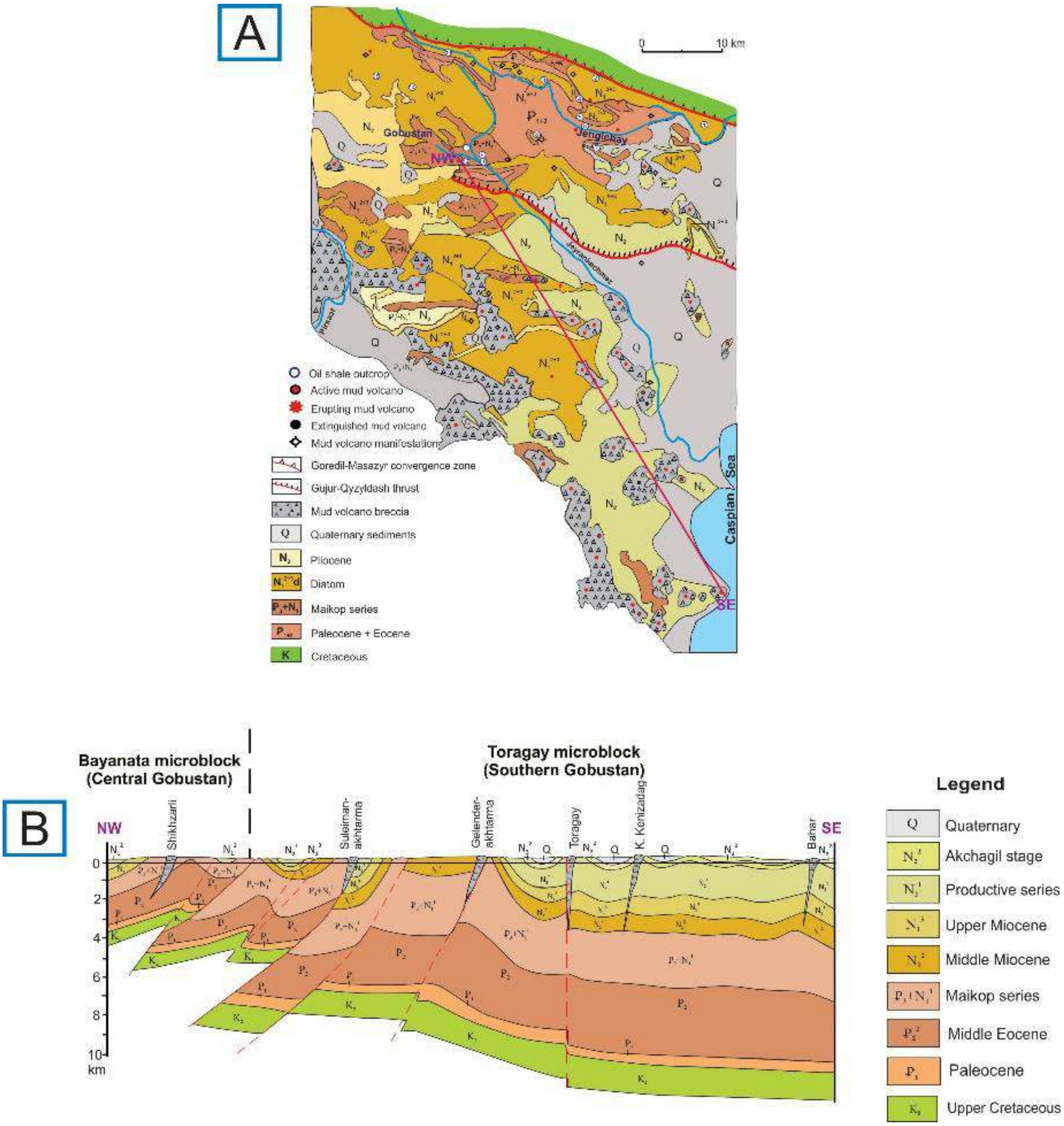

Figure 6. Geological map (**A**) and geological profile (**B**) of Gobustan (modified after (Aliyev et al., 2015; Abbasov, 2009)). Previously known and newly discovered shale outcrops. **1** – Mayash; **2** – Boyuk Siyeki; **3** – Kichik Siyeki; **4** – Siyekilerarasy; **5** – Jengidagh; **6** – Jengichay; **7** – Bayanata; **8** – Iyimish; **9** – Gaibler; **10** – Jeyrankechməz; **11** – Kichik Mereze; **12** – Shihkzerli; **13** – Nabur; **14** – Jeyirli; **15** – Erebshalbashy

In Talysh, Guba, Lahij, and Central Gobustan, the oil shales belonging to the Lower Maikop were also registered in the synclinal folds.

Oil shales of Lower Miocene age are found in the cores and limbs of most synclines in the north, northeast of Gobustan and east of Shamakhy. However, as in some western outcrops of Gobustan (between Aghsu and Girdimanchay rivers), in the direction of Absheron (for example, in the Uchtepe and Agchala regions) and in areas to the north-west of it (for example, in Orjandagh), Upper Maikop oil shale provides outcrops mainly in the cores, as well as on the lims of the anticlines.

As mentioned above, the Chokrak oil shale layers were identified by us only in the southern flank of the Cheyildagh anticline; their total thickness is slightly more than 1 m (Figure 1).

As for oil shales of Diatom age, the main stratigraphic complex that attracts attention among them undoubtedly belongs to the Sarmatian (Figure 1). The outcrops of this stage, identified in the Guba basin (see Garachay and Baghchaly sections in Figure 1), have a monoclinal occurrence. The angles of occurrence of shale layers fluctuate between 50 and 70°.

In the Bayanata microblock, Meotian oil shales are exposed in some synclinals, including Kichik Siyeki and Boyuk Siyeki (Figure 1), as well as on the Baygushgaya structure. The oil shale layers belonging to the Meotian and Konkian stages in all three of these areas lie at an angle of about 40–50° on the limbs of the structures. In the direction of Shamakhy, they are also exposed on the limbs of the Khydyrli anticline. The layer of Diatom oil shales found in the village of Jeyirli has a very low angle of occurrence. South of Gobustan, in the syncline defined between the Akhtarma and Cheyil anticlines, as well as on the limbs of the latter and Gungormez anticlines, Konkian, Sarmatian and Meotian oil shale are distinguished. Continuing towards the western Absheron, the Buransyz-Jylgha anticline can be mentioned as the next structure where oil shale associated with Diatom has been found. The Meotian oil shale section on the northeastern slope of Mount Bayanata (Figure 1) is also very important. Analogous of wich are also observed in the centroclinal of the Garaislam syncline, where the number and thickness of Diatom oil shale layers (in Figure 1 see Islamdagh section) are especially important in the sections observed here.

The Diatom oil shales more characteristic of the Western Absheron, are recorded in the structures of large anticlinal structures. Zigilpiri, Binegedi, Fatmayi, Novkhani, Saray, Ateshgah, Damlamaja and others contain shale outcrops in almost satisfactory areas. In general, in the zones corresponding to the arches (for example, Lokbatan and Shorbulag) and periclinals (for example, Bozdag-Guzdak and Deveboynu) of anticlines in Peninsular, especially in the crests of mud volcanoes in the south and southeast of Western Absheron, almost no oil shale outcrops were found on the surface, but the erupting volcanoes here are quite typical for the ejection of oil shale of Eocene-Miocene age. Mud volcanic manifestations are also characteristic of the central and northern zones of Western Absheron, since the anticlines found here are complicated by the intersections of tectonic lines. The Diatom oil shales have also been found in the periclinal and arch parts of these structures (Zigilpiri, Saray, Binegedi, Jorat, Fatmayi, and others). The fact that their outcrops are often lenticular in shape and most often refer to areas in which oil seeps have also been found (Aliyev et al., 2014). This dependence indicates that their high content of organic matter is enriched due to allochthonous hydrocarbons.

Beridash, Solakhay, Ayrantoken, Goturdagh, Gyrdagh and other structures are registered along the Langebiz-Alat tectonic zone. Oil-bearing sands and marls with large reserves were found here, associated with the outcrops of those structures that are complicated by mud volcanoes of the same name. In the sections studied by us in these structures, oil shales of the facies overlying the oil sand unut, contain paper oil shale with a strong bituminous content. Visually, such shale is difficult to distinguish from oil shale. Unlike oil shales, which are associated with kerogen, the bitumen concentrated in such shales is allochthonous in nature. In other words, the bitumen released from the bottom layer of oil sand saturates the top layer of shale, resulting in the formation of bituminous shale. In this regard, such oil shales are widespread in Cheyldere, Solakhay, especially in Rahim, Gyrgyshlag and others, which are considered areas of oil sands and marls. The lenticular outcrops of bituminous shale in the areas of distribution of oil-bearing gryphons and salsas, which we have identified in Iyimish, Gotur and many other areas of mud volcanoes, do not escape attention. On the northeastern flank of the Gyrgyshlag anticline, where the oil-bearing mud volcano Gyrdag is located, Sarmatian and Meotian deposits are also noted in the area dominated by oil-bearing deposits of the Chokrakian age. Approximately 1.2 km northwest of the oil-producing Gyrdag oil gryphons, strong bituminous features are observed in the dolomite deposits on both lower slopes of the valley stretching for hundreds of meters. Here, the Diatom paper oil shale overlays carbonate facies accompanied by oil seeps (Figure 7). It is assumed that the organic parts of such oil shales are similar to the underlying dolomite oil reservoirs. According to our visual observations, the contribution of allochthonous hydrocarbons to the rich bituminous content of paper oil shales of Chokrakian and Diatom ages is quite large.

With the exception of some shale deposits in the transition zones from Gobstan to Absheron (Uchtepa, Aghchala, Guzdek, etc.), shale deposits of the Apsheron Peninsula are currently used as objects for various purposes, so their economic efficiency is doubtful.

Stratigraphic control on formation and hydrocarbon generation

By studying the mineralogical-chemical, organic-geochemical composition and petrographic characteristics of oil shale sampled from outcrops and mud volcano eruption areas, we have identified some regularities related to the formation of oil shale of the Eocene, Lower Maikop and Miocene epochs. The main points of interest regarding the mineralogical composition are related to quartz, calcite and jarosite. Miocene-aged oil shales significantly exceed the Lower Maikop and Eocene, according to quartz and jarozite. In contrast to the Eocene and Lower Maikop shales, calcite is relatively less important for the Miocene oil shales. The concentration of this mineral in the oil shales of Yardymly is around 40%.

Figure 7. Paper oil shales of Diatom age in lithofacies above the dolomitic oil-bearing unit in the Gyrgyshlag section

The average CIA value of Azerbaijan oil shale is 67, which is higher than NASC (Gromet et al., 1984) and UCC, and about the same number as PAAS (Taylor and McLennan, 1985) and Average shale (Turekian and Wedepohl, 1961). An analysis of the CIA values shows that the studied oil shales are derived from source rocks that have undergone moderate chemical weathering. With some exceptions, along with feldspars, minerals consisting of Fe associations can be considered as typical primary components of the studied oil shales. In general, the role of deposits brought from areas of tholeiitic volcanism in the formation of the studied oil shales is obvious. Although iron-containing basalts are the main source of sediments entering the oil shale paleobasin, intermediate magmatic formations consisting of andesites also played a role in the accumulation of sediments. In particular, it is an indisputable fact that a number of Upper Maikop samples belonging to Agchala, Siyakilerarasi, and Jengidagh have different protolith characteristics, and at the same time, belong to relatively higher acid igneous associations. It is also necessary to note that among the samples of Absheron and Shamakhy-Gobustan, the group of oil shale of the Eocene age reveals a greater connection with andesitic volcanism.

Along with the significant presence of a representative of the smectite group in some Eocene samples, the identification of other clay minerals characteristic of ash formations (for example, about 12% clinoptilolite), as well as the fixation of signs of dacite in their protolithic nature, shows the role of tephra in their genesis. In addition, the calculation of the amount of terrigenous material brought by erosional igneous sources showed that in some Eocene samples (for example, in Otmanbozdagh, Shekikhan and Aghtirme), the degree of participation of terrigenous material is relatively low compared to other samples. To elucidate the role of terrigenous and pyroclastic composition, our analysis based on several metals including V, Cr, Ni, Zn, Fe and Al confirms the volcanoclastic nature of some Eocene samples. We hypothesize that those samples that reflect weak paleoweathering, retain carbonate minerals, and are associated with tephra, probably formed from volcanic ash. Our idea that some samples can be formed from volcanic ash under the influence of wind is supported by the fact that some explosive volcanisms registered in the Lesser Caucasus and Talysh in the Eocene.

The results of the approach based on the Fe_2O_3/TiO_2 and $Al_2O_3/(Al_2O_3+Fe_2O_3+MnO)$ indices of the samples show that all the analyzed samples exhibit a close nature to PAAS and NASC, indicating that they are not associated with hydrothermal sources.

The results of paleoclimatic reconstruction studies unambiguously reflect the arid-climatic conditions of the formation of the analyzed samples. In terms of regularity, it is concluded that the Eocene was subjected to relativly higher temperature conditions than the Miocene. This is in good agreement with the results (Zachos et al., 2001) on global climate changes occurring 65 million years ago.

The enrichment of oil shale with organic matter is facilitated by a number of factors, including the trophic nature of the basin, its connection with the sea, salinity, primary productivity, depth, redox conditions, sedimentation rate, etc. Thus, our approaches related to Al, Fe, Mn, and other compositions show the relationship of the studied oil shales with oligotrophic water bodies. The mineralogical composition of the rocks also confirms this idea. In the case of carbonates, with the exception of some samples, their amount in samples is low in terms of general indicators.

Most of Miocene samples formed in the more peripheral zones of the basin. An increase in the amount of quartz in their composition also confirms this possibility. In the formation of most Eocene samples, a relatively high influence of the marine environment is evident. The oil shales of Nardaranakhtarma, Khilimilli and Yardymly areas are more prone to the marine zone.

Ca, Fe, Sr, Br, and Mn analyzes also suggest that the Miocene shale basin was fresher than the

Eocene. With few exceptions, in the Absheron Peninsula and in Shamakhi-Gobustan, the Miocene basins were shallower (<20 m), while the Eocene basins were of medium depth (>20 m). On the other hand, the oil shale basins near the Caspian Sea were deeper than others located in Gobustan and Absheron. For comparison, the deepest shale-forming basins in Azerbaijan were located in the Lower Maikop, which is typical for the Guba and Talysh regions.

Predominantly oxic-dysoxic conditions can be considered typical for the environments of the oil shale paleobasin. Most of the Eocene samples were deposited in environments containing more oxygen than in the Miocene. Some samples of the Upper Maikop correlate with the depths at which sulfate reduction occurred.

The presence of intensive tectonic activity during the Eocene, especially the transport of volcanic ash into the paleobasin, created favorable conditions in terms of providing essential nutrients such as Fe, P and Cu. In the analyzed samples, a change in the aluminum concentration within 6–8% has a greater effect on the enrichment of Eocene and Diatom oil shale with organic matter (Figure 8). As terrigenous inputs increase in the pleobasin, when the Al concentrations reach the range of about 7–10%, the sediments provide a not-too-high content of organic matter, which is typical for most Maikop oil shales. Therefore, the Eocene sediments were subjected to less terrigenous inputs than the Miocene. In this regard, the role of primary bioproductivity was key in the enrichment of Eocene and, probably, Diatom kerogen with organic matter. For the Miocene, on the contrary, terrestrial plants were the dominant source. This supports our conclusion that the Eocene was associated with saltier seawater and the Miocene with fresher aquatic environments with abundant river flow. Volcanic ash was more involved in the accumulation of Eocene basin, and this nutrient-rich igneous association probably influenced the growth of algae in the water as well as the redox state of the water column.

Our extraction studies also confirm the results obtained for the kerogen type according to the data of inorganic chemistry. So, in Miocene oil shales, alcohol-benzene bitumen (1.69%) prevails over chloroform bitumen (1.24%). However, for the Eocene samples, the opposite trend is recorded. These different geochemical characteristics may be related to the more soluble chloroform bitumen in Eocene oil shales, where such organic molecules are associated with lipids, i.e. algae (source of autochthonous organic matter). On the other hand, the obvious predominance of the alcohol-benzene fraction in Miocene oil shales can be explained by the contribution of terrestrial plants to the formation of Miocene oil shale.

The average parametric indices of structural groups calculated from the ^{1}H NMR spectra of extracted bitumen from the Eocene samples of the Keyreki volcano and the section of the Bayanata outcrop of Diatom age show that the degree of aromaticity of bitumen belonging to the Bayanata oil shale is significantly lower (only in asphaltenes it reaches 11.5%). On the contrary, noteworthy is the high rates of paraffin compounds (in benzene = 61.4%, in 4:1 alcohol-benzene = 45.2%). In the Keyreki sample, the degree of aromaticity is 14% in total due to the sum of all extracted fractions. Spectral analysis showed that the kerogen of Bayanata sample of Diatom age is significantly enriched in organic matter of autochthonous origin.

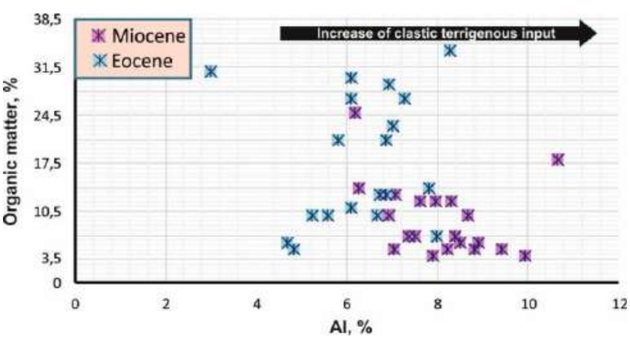

Figure 8. Diagram showing the effect of terrigenous inputs on the concentration of organic matter in Miocene and Eocene oil shale

According to the results of the diagrams associated with the corresponding parameters of "Rock-Eval" (Figure 9), the Eocene and Diatom oil shales sampled from both the mud volcanic area and from the outcrop sections clearly correspond to type II kerogen, as was seen in the above discussion. The samples belonging to the Upper Maikop are plotted in areas corresponding to the mixed type II–III and III.

Compared to other samples, the Islamdag oil shale shows a relatively high CIA value with several other Diatom samples. Chemical weathering is known to play an important role in the regulation of primary productivity. Thus, the increasing intensity of chemical weathering stimulates the entry of biogenic elements into the paleobasin, which has a positive effect on the primary production of organic carbon. Petrographic studies have also shown that Diatom paper oil shales are rich in alginite. The total content of vitrinite and inertinite is about 30%. In general, such oil shales contain diatoms and fossil fish, as well as an abundance of lamalginite and telalginite. The oil shales of the Upper Maikop section of the Islamdag are dominated by vitrinite and pyrite (Aghayeva et al., 2021). (Isaksen, et al., 2007) also stated that the organic-rich rocks of the Upper Maikop, selected from the mud volcanic area and outcrops, mainly contain organic matter of plant origin, consisting of spores and pollen, as well as amorphous and woody materials as secondary components.

The results of mineralogical, inorganic chemical, organic-geochemical, extraction, spectral and petrographic studies demonstrate the history of the evolution of Eocene and Miocene (mainly Upper Maikop) oil shale in various basin conditions and with different types of kerogen, generalized in schematic illustration showing in Figure 10.

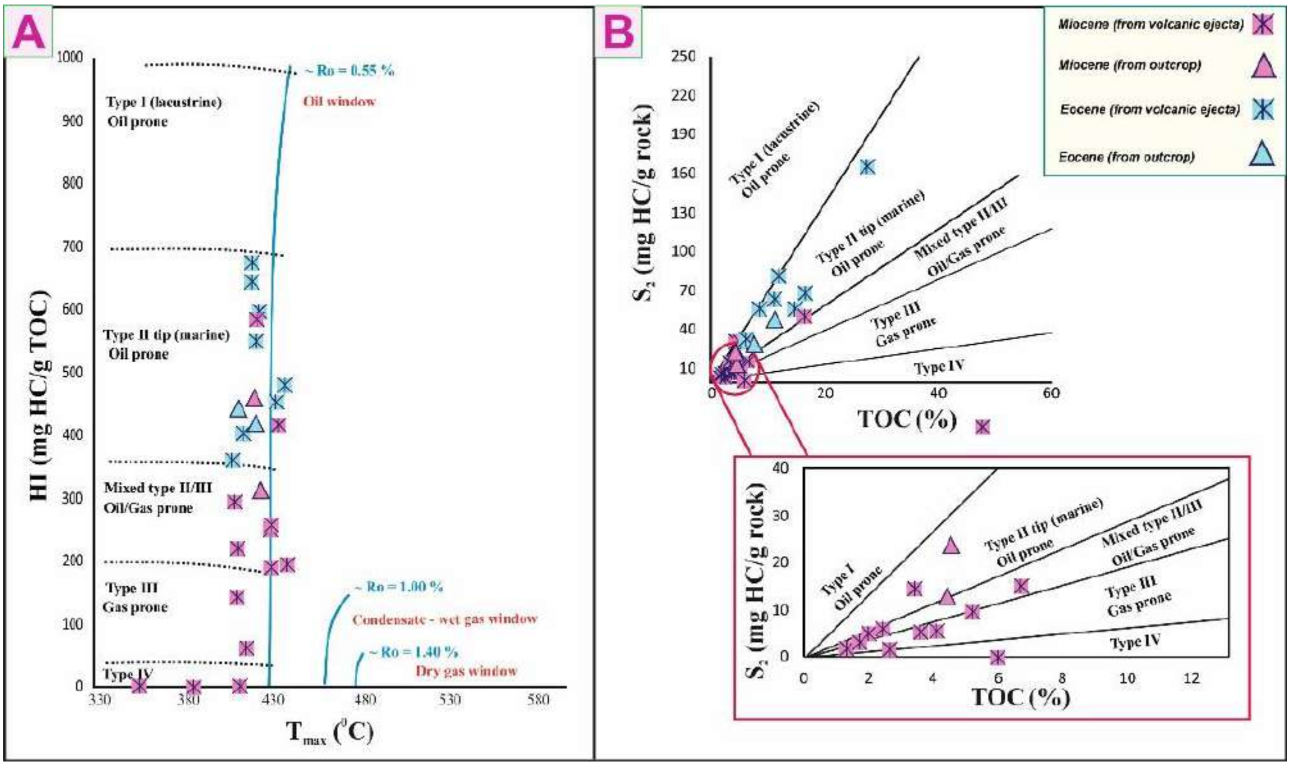

Figure 9. Cross plots between hydrogen index versus maximum pyrolysis temperature, and S_2 versus TOC indicating the kerogen types of Eocene-Miocene oil shale samples

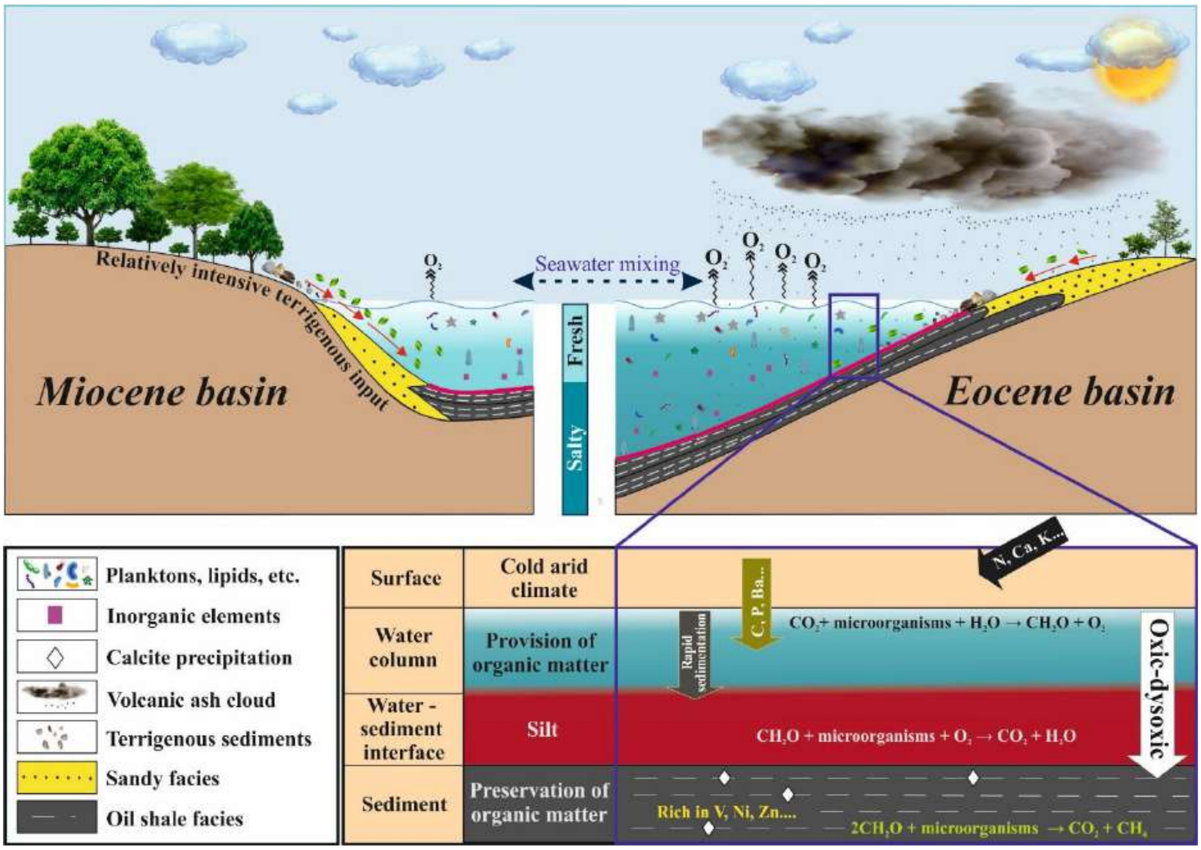

Figure 10. Generalized schematic illustration showing the evolutionary history of the Miocene and Eocene oil shale

Compared with the Upper Maikop, it has been established that the Diatom and especially Eocene oil shales, provided with organic matter of autochthonous origin and having a high hydrogen index, bitumen index, generation potential and pyrolyzable carbon indicators, mainly have the potential to generate oil hydrocarbon. Agayeva and her co-authors in their paper (Aghayeva et al., 2021, p. 380), based on the study of only a few samples from the Pirekeshkul outcrop, note that in the Middle Eocene section, there are layers rich in organic matter containing type II kerogen, which cannot be considered an important source of rocks on onshore of Eastern Azerbaijan because for their low thickness. However, according to our studies, the total thickness of the Middle Eocene in East Azerbaijan, especially in Gobustan (> 300 m (Aliyev et al., 2015, p. 44)) and the Absheron Peninsula, as well as the frequent alternation and significant thickness of oil shale layers in their sections (see Figure 1), especially the presence of thick and large fragments of oil shale, often found in the ejecta of mud volcanoes shows that the opinion formed in the study of only one section is incorrect. In addition, the fact that the Upper Maikop deposits, considered in many studies to be the best source rocks, have satisfactory indicators of the quality and productivity index and the generation potential index of allochthonous organic compounds in oil shale samples, but contain low hydrogen and bitumen index, indicates their potential for gas generation.

Compared to other stratigraphic units, the Chokrakian oil shales, which have a negative impact on the general organic-geochemical parameters of the Miocene deposits, are characterized by the highest values of the average productive index, but the lowest values of pyrolyzable carbon and maximum pyrolysis temperature (see Figure 9), associated with the presence of organic compounds of allochthonous origin, corresponding to the peak S_1 in their hydrocarbon composition. This is also confirmed by the fact that strong oil shows are characteristic of sandstone and dolomite formations of the same age deposits in the oil and gas regions of Azerbaijan (see Figure 7).

The average geochemical parameters of oil shale samples currently do not show positive feature in terms of the possibility of oil and gas generation. But in some coastal regions, where the Upper Cretaceous roof descends deeper, the Upper Maikop and Middle Eocene deposits promise favourable signs for hydrocarbon generation. On the other hand, the Eocene and Maikop oil shales have great prospects for obtaining synthetic oil and gas, respectively.

Conclusion

The results of many years of field research made it possible to discover new areas of oil shale within Azerbaijan and remap (Figure 1) their distribution areas.

Surface outcrops of oil shale are found mainly in the distribution areas of Middle Eocene, Maikop, Chokrakian (partially) and Diatom deposits.

Lower and Upper Cretaceous shales found in the north of Gobustan are associated with low net thickness and limited areas, which reduces their economic significance.

In Central Gobustan, zones of distribution of accretionary-prismatic deposits are characteristic of significant outcrops of Middle Eocene and Upper Maikop oil shale.

Analogues of surface oil shale of Upper Samatian age, characteristic only for the Guba basin, were not found in Shamakhy-Gobustan and Absheron.

The oil shale outcrops of Konkian and Meotian, which are manifested in thick layers in Central Gobustan, are more common, especially in its east, in Western Absheron. These Diatom oil shales are also noted in the periclinal and arch parts of anticlines, the outcrops of which are often lenticular in shape and most often touch areas of seepage of oil and oil-bearing rocks (sands and marls). We believe that their high organic content is enriched in allochthonous hydrocarbons. The role of allochthonous hydrocarbons in the formation of organic matter in the Chokrakian oil shale is also substantiated.

In the formation of Guba oil shale, the uplift zones of the Greater Caucasus Megazone, called the Lateral Range, served as the source area, and in the evolution of the Shamakhi-Gobustan oil shale, the sediments brought from the Tufan and Vandam uplifts were of special importance. Volcanic ash brought by the wind into the basin also contributed to the formation of oil shale in some Eocene areas of East Azerbaijan.

Both Eocene and Diatom oil shales, which have closer contact with seawater and contain the largest amount of organic matter, sampled from the ejecta of mud volcanoes and outcrop sections, are compatible with type II (oil-bearing) kerogen. However, oil shales of Upper Maikop age, which show a closer relationship with freshwater sources (rivers), mainly correspond to type III (gas-generating) kerogen.

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AZƏRBAYCANIN EOSEN-MİOSEN YAŞLI YANAR ŞİSTLƏRİ: ƏMƏLƏGƏLMƏYƏ, YAYILMAYA VƏ NEFT-QAZTÖRƏTMƏYƏ STRATİQRAFİK NƏZARƏT

O.R. Abbasov

Məqalədə, çoxillik çöl-tədqiqatları əsasında Azərbaycan yanar şistlərinin daha əvvəllər məlum olmayan açılışlarına dair yeni məlumatlar təqdim olunur. Yanar şistli fasiyaların yeni yayılma areal-ları müəyyənləşdirilir. Onların sahə və kəsilişlər üzrə paylanmasında, həmçinin neft və yaxud qaztö-rətmə xüsusiyyətlərinin formalaşmasında stratiqrafik nəzarətin rolu əsaslandırılır. Eosendə, Alt Maykopda (ilk dəfə olaraq bu tədqiqatda aşkarlanıb) və Miosendə (Üst Maykopda, Çokrakda və Diatomda) formalaşan çökmə hövzələrin və bura gətirilən ana süxurların genezisi ilə əlaqəli tədqiqatlar bəzi qanunauyğunluqların əldə olunmasına imkan vermişdir. Nəticələrimiz, Maykopdan fərqli olaraq, Eosen və Diatom yaşlı yanar şistlərə aid kerogenlərin oxşar təkamül xüsusiyyətləri ehtiva etdiklərini göstərir. Dəniz mühiti ilə daha yaxın əlaqə göstərən Diatom kimi, Eosenə məxsus kerogenlər yalnız neft, lakin şirinsulu və nisbətən intensiv terrigen daxilolmaları şəraitində təkamül tapmış Üst Maykop yaşlı kerogenlər isə əsasən qaz törətmək imkanına malikdirlər.

ЭОЦЕН-МИОЦЕНОВЫЕ ГОРЮЧИЕ СЛАНЦЫ АЗЕРБАЙДЖАНА: СТРАТИГРАФИЧЕСКИЕ РЕГУЛЯТОРЫ ФОРМИРОВАНИЯ, РАСПРЕДЕЛЕНИЯ И ГЕНЕРАЦИИ УГЛЕВОДОРОДОВ

О.Р. Аббасов

В данной статье представлена новая информация о ранее неизвестных обнажениях горючих сланцев в Азербайджане, полученная по результатам многолетних полевых исследований. Установлены новые границы распространения фаций, содержащих горючие сланцы. Обоснована роль стратиграфического контроля над распределением горючих сланцев по площади и разрезам обнажений, показан их нефте-газообразующий потенциал. Исследование источников сноса пород – горючих сланцев и выявление особенностей эоценовых, нижне-майкопских (определены впервые в ходе данного исследования) и миоценовых (верхне-майкопских, чокракских и диатомовых) бассейнов седиментации горючих сланцев, позволили выявить новые закономерности. Согласно результатом проведенных работ, керогены эоценовых и диатомовых сланцев прошли схожий эволюционный путь, заметно отличающийся от майкопских горючих сланцев. Так, керогены горючих сланцев эоцена и диатомового яруса больше связаны с морской средой и могут генерировать преимущественно нефть. В то же время керогены, образовавшиеся в бассейнах верхнего майкопа, содержат больше терригенного органического материала, образовались в сравнительно пресноводных условиях и могут производить, в основном, газ.