ҚАЗАҚСТАН РЕСПУБЛИКАСЫ ҰЛТТЫҚ ҒЫЛЫМ АКАДЕМИЯСЫ

Satbayev University

ХАБАРЛАРЫ

ИЗВЕСТИЯ

НАЦИОНАЛЬНОЙ АКАДЕМИИ НАУК РЕСПУБЛИКИ КАЗАХСТАН Satbayev University

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NAS RK is pleased to announce that News of NAS RK. Series of geology and technical sciences scientific journal has been accepted for indexing in the Emerging Sources Citation Index, a new edition of Web of Science. Content in this index is under consideration by Clarivate Analytics to be accepted in the Science Citation Index Expanded, the Social Sciences Citation Index, and the Arts & Humanities Citation Index. The quality and depth of content Web of Science offers to researchers, authors, publishers, and institutions sets it apart from other research databases. The inclusion of News of NAS RK. Series of geology and technical sciences in the Emerging Sources Citation Index demonstrates our dedication to providing the most relevant and influential content of geology and engineering sciences to our community.

Қазақстан Республикасы Ұлттық ғылым академиясы «ҚР ҰҒА Хабарлары. Геология және техникалық ғылымдар сериясы» ғылыми журналының Web of Science-тің жаңаланған нұсқасы Emerging Sources Citation Index-те индекстелуге қабылданғанын хабарлайды. Бұл индекстелу барысында Clarivate Analytics компаниясы журналды одан әрі the Science Citation Index Expanded, the Social Sciences Citation Index және the Arts & Humanities Citation Index-ке қабылдау мәселесін қарастыруда. Webof Science зерттеушілер, авторлар, баспашылар мен мекемелерге контент тереңдігі мен сапасын ұсынады. ҚР ҰҒА Хабарлары. Геология және техникалық ғылымдар сериясы Emerging Sources Citation Index-ке енуі біздің қоғамдастық үшін ең өзекті және беделді геология және техникалық ғылымдар бойынша контентке адалдығымызды білдіреді.

НАНРК сообщает, что научный журнал «Известия НАНРК. Серия геологии и технических наук» был принят для индексирования в Emerging Sources Citation Index, обновленной версии Web of Science. Содержание в этом индексировании находится в стадии рассмотрения компанией Clarivate Analytics для дальнейшего принятия журнала в the Science Citation Index Expanded, the Social Sciences Citation Index и the Arts & Humanities Citation Index. Web of Science предлагает качество и глубину контента для исследователей, авторов, издателей и учреждений. Включение Известия НАН РК. Серия геологии и технических наук в Emerging Sources Citation Index демонстрирует нашу приверженность к наиболее актуальному и влиятельному контенту по геологии и техническим наукам для нашего сообщества.

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GEOCHEMICAL STUDIES OF CONDENSATE, GAS AND CORE SAMPLES DERIVED FROM GAS-CONDENSATE FIELDS IN THE MOYNKUM SAG (KAZAKHSTAN)

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Abstract. This paper presents the interpretations of geochemical studies of condensate, gas and core samples from five fields (Amangeldy, Anabay, Ayrakty, Sultankuduk and Zharkum,) of the Moyunkum sag to characterize source rocks and determine the genetic sources of condensates and gas. Based on the results of biomarker analysis, all condensates were generated from shaly lacustrine source rocks with terrigenous organic matter input. The thermal parameters of the biomarkers showed that the condensates of Amangeldy field possess the highest thermal maturity among the studied samples, which is also consistent with the results of the carbon isotopic composition of its gases. Different distributions of biomarkers in the condensates of Avrakty, Amangeldy, and Zharkum fields may attest to their different genetic origins. All gases have a thermogenic genesis and were generated from a terrigenous source rock (kerogen type III). Ayrakty gases contain relatively high concentrations of nitrogen, although Amangeldy and Zharkum gases have similar nitrogen concentrations. The condensate of well № 4 Zharkum was found to have a different chemical composition indicating its genetic difference from the rest of the condensates of this field. According to the results of Rock-Eval pyrolysis, the studied samples relate to kerogen type III and some of them reached the zone of dry gas generation window, which is also consistent with the result of maceral analysis and Ro value of one sample (Anabai–2779m).

Key words: gas chromatography, biomarkers, fingerprinting, sterane, terpane, isotopic composition of carbon, Rock-Eval, vitrinite, maceral composition

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МОЙЫНҚҰМ ТЕРЕҢДІГІНІҢ ГАЗОКОНДЕНСАТТЫ КЕН ОРЫНДАРЫНАН АЛЫНҒАН КОНДЕНСАТ, ГАЗ БЕН КЕРН ҮЛГІЛЕРІНІҢ ГЕОХИМИЯЛЫҚ ЗЕРТТЕМЕСІ

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Аннотация. Бұл ғылыми мақалада көмірсутек шығаратын жынысқа сипаттама беру және конденсаттардың генетикалық шығу тегін анықтау мақсатында Мойынқұм алқабының 5 кен орнынан (Амангелді, Айрақты, Анабай, Жарқұм және Сұлтанқұдық) алынған конденсат, газ және керн үлгілерін геохимиялық зерттеу нәтижелерінің интерпретациясы берілген. Биомаркерлік талдау нәтижелері бойынша барлық зерттелген конденсаттардың көлдік ортада шөккен балшықты органикалық заттантүзілгені анықталды. Биомаркерлердің термиялық параметрлері зерттелген үлгілердің ішінде Амангелді кен орнының конденсаттарының ең жоғары термиялық пісіп-жетілуін көрсетті, бұл оның газдарының көміртегі изотоптық құрамының нәтижелерімен де расталады. Айрақты, Амангелді, Жарқұм кен орындарының конденсаттарында биомаркерлердің әртүрлі таралуы олардың әртүрлі генетикалық шығу тегін көрсетуі мүмкін. Көміртектің изотоптық құрамы бойынша барлық зерттелген газдар термогендік генезиске ие терригендік көмірсутек шығаратын жынысынан түзілген. Айрақты газдарының құрамында азоттың концентрациясы салыстырмалы түрде жоғары, бірақ Амангелді және Жарқұм газдарының азот концентрациясы ұқсас. Сондай-ақ, тағы бір қызық құбылыс болғаны, барлық талдаулар бойынша Жарқұмдағы No4 ұңғысының конденсатының химиялық құрамы басқаларынан өзгеше, бұл оның осы кен орнының қалған конденсаттарынан генетикалық айырмашылығын көрсетеді. Rock-Eval пиролизінің нәтижелері бойынша зерттелген үлгілер керогеннің ІІІ түріне жататыны және кейбірі майлы көмірсутекті газдардың түзілу аймағына жеткені анықталды, бұл нәтиже бір үлгідегі(Анабай–2779м) мацеральды талдау және витриниттің шағылыстыру қабілетін өлшеу нәтижесімен де сәйкес келеді.

Түйін сөздер: газ хроматографиясы, биомаркерлер, саусақ ізі, стерандар, терпандар, көміртектің изотоптық құрамы, Rock-Eval, витринит, мацеральды талдау

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ГЕОХИМИЧЕСКОЕ ИССЛЕДОВАНИЕ ОБРАЗЦОВ КОНДЕНСАТА, ГАЗА И КЕРНА, ОТОБРАННЫХ ИЗ ГАЗОКОНДЕНСАТНЫХ МЕСТОРОЖДЕНИЙ МОЙНКУМСКОГО ПРОГИБА

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Аннотация. В данной научной статье представлены интерпретации результатов геохимических исследований образцов конденсата, газа и керна пяти месторождений Мойнкумского прогиба (Амангельди, Анабай, Айракты, Жаркум и Султанкудук) в целях характеристики материнских толщ и определения генетического происхождения конденсатов и газа. По результатам биомаркерного анализа все исследованные конденсаты образовались из глинистых материнских толщ, осаждавшихся в озерной среде с вкладом терригенного органического вещества. Термические параметры биомаркеров показали, что среди исследованных проб конденсаты месторождения Амангельды обладают самой высокой термической зрелостью, что также подтверждается результатами изотопного состава углерода его газов. Разные биомаркеры в конденсатах месторождений Айракты, Амангельды и Жаркум могут свидетельствовать об их разных генетических происхождениях. Все газы имеют термогенное происхождение и сгенерировались из терригенной материнской породы (тип керогена III). Газы Айракты содержат относительно высокие концентрации азота, хотя газы Амангельды и Жаркум имеют схожие концентрации азота. Также интересным феноменом было то, что по всем анализам конденсат скважины №4 Жаркум обладает другим химическим составом, что указывает на его генетическое отличие от остальных конденсатов данного месторождения. По результатам пиролиза Рок-Эвал было установлено, что исследованные пробы относятся к типу керогена III и некоторые из них достигли зоны генераии жирных углеводородных газов, что также хорошо согласуется с результатом мацерального анализа и измерения отражательной способности витринита одной пробы (Анабай – 2779м).

Ключевые слова: газохроматография, биомаркеры, фингерпринтинг, стераны, терпаны, изотопный состав углерода, Рок-Эвал, витринит, мацеральный состав

Introduction

Geology. The Shu-Sarysu basin is traditionally distinguished as a gas-bearing region in South Kazakhstan and is the first largest sedimentary basin in the country in terms of gas and condensate reserves. The main information about the gas content of this basin became known in the 1960s, after the discovery of a gas inflow with a high content of

nitrogen and helium in the Usharal-Kempirtobe area from the subsalt Lower Permian deposits. The Shu-Sarysu basin has 10 main sags and uplifts (Fig.1), whose regional structures show their sufficient isolation from each other, creating closed hydrodynamic systems (Turkov, 2020). In the Shu-Sarysu basin, the industrial gas potential of three complexes has been proven: Devonian, Carboniferous and Lower Permian. Three identified layers in the Lower Carboniferous complex are serpukhovian (c1sr), visean (c1v), and turnian (c1t) (Fig.1).

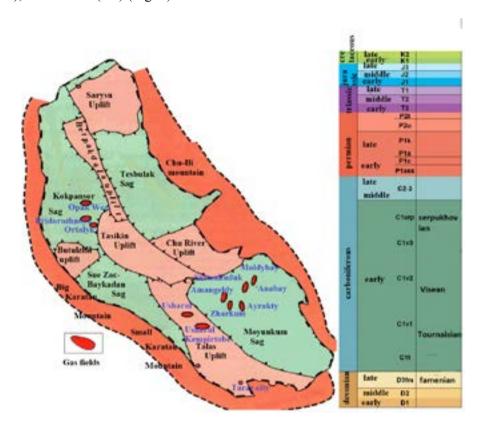


Fig. 1 Overview map of the Shu-Sarysu gas condensate basin and chronostratigraphic column of the region (modified after)

Among all the regions, the most promising and largest gas-bearing one is the Moyunkum sag, where the well-known gas condensate fields such as Amangeldy, Ayrakty, Zharkum, Anabay and Sultankuduk are located, although Anabay and Sultankuduk fields have not commercially developed yet. The largest reserves in the Moiynkum deep are found in the Lower Visean deposits, in which gas condensates are produced in Amangeldy, Ayrakty and Zharkum fields. Serpukhov deposits are in active production only in Zharkum field. At present within the basin, the development of gas condensates is carried out only in three fields (Amangeldy, Zharkum and Ayrakty) and the establishment of the genetic origin of their gas condensates, migration pathways and

the genetic relationship have become one of the important and widely discussed topics among researchers.

Previous research and importance of the work

Despite the study of the region by different methods, there has not been generally accepted consensus about the origins of hydrocarbons yet, due to scarce published papers on geochemical studies of hydrocarbons in the Shu-Sarysu basin. For example, according to the results of core studies of the Marcel block in the Kokpansor deep (Zhao et al., 2016), the studied intervals in Ortalyk and Pridorozhnoye fields were found to have relatively high values of total organic matter (>1%) and mainly relate to kerogen type III. As for geochemical studies of the Moyunkum sag, in 2017, 15 core samples derived from the intervals of 2577–4498 m of well R-1 in the Sultankuduk field were analyzed on Source Rock Analyzer (SRA) in Weatherford company, and in 2020 a similar study was carried out for 8 cutting samples (interval 2034–4494 m) from the same well (Ismagulova et al., 2020).

In 2021, in Atyrau branch of "KMG Engineering" LLP was carried out a comprehensive geochemical study of condensate and gas samples from Moyunkum sag fields (Amangeldy, Zharkum, and Ayrakty) and core samples from the Amangeldy–102, Anabay–12, and Sultankuduk R–1 fields (Seitkhaziyev, 2021), whose results are presented in this paper. It should be noted that all studied samples were derived from different hydrocarbon pay zones of the Visean and Serpukhov deposits.

Research objectives

The main purpose of this work was to compare the results of various geochemical studies of condensate, gas and core samples derived from gas-condensate fields in Moyunkum sag to characterize their source rocks in terms of environmental condition, lithology of organic matter, thermal maturity, and discern the genetic links between the hydrocarbons. Also "condensate-source rock" correlations were performed. The novelty of this study is that such work has not carried out for the hydrocarbons of the aforementioned fields before and the results of this paper can serve as the one of the main literary sources in assessing the source of HC fluids and gases of this deep.

Materials and basic methods

In October 2021 condensate and gas samples were sampled at the wellheads in Amangeldy, Ayrakty and Zharkum fields using glass bottles and an MKB-200 samplers respectively (Fig. 2a and b).

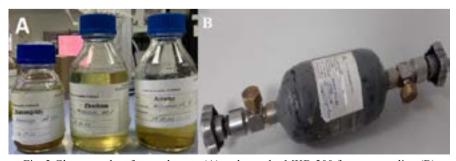


Fig. 2 Glass samplers for condensate (A) and sampler MKB-200 for gas sampling (B)

7 core samples were collected from shale intervals by visual inspection of the core (Fig.3), which was also confirmed by the results of gamma ray logging and macro-description of the core. The n-alkanes and isoprenoids distributions of the condensates were studied on GC-FID, while fingerprinting and biomarker analysis of condensates were performed on LTM-MD-GC and GCMSD in SIM mode. The study of the carbon isotopic composition of gases was performed on GC-IR-MS, while the component composition of the gas was carried out on GC. Geochemical study of core materials was carried out on Rock-Eval 6 and the microscope.

The work was carried out in laboratory of geochemical studies of oil, water and rocks of the Atyrau branch of "KMG Engineering" on special software Malcom (Schlumberger, France) and PIGI (IGI, England), the plots of which were based on literature papers (Seithaziyev et al., 2022).

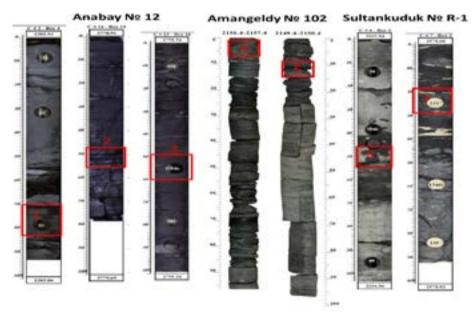


Fig.3 Chosen core intervals from wells for geochemical analysis

Results of research

The results of this study were explicitly given in another published paper (Seithaziyev et al., 2022).

Discussion

In this paper interpretation of the results of complex geochemical studies of condensate, gas and core samples consists of three parts:

The first part (4.1) presents the interpretation of geochemical study results of 18 gas and condensate samples (gas chromatography, fingerprinting and biomarker analysis) derived from three fields (Amangeldy, Zharkum and Ayrakty) of the Moyunkum sag to characterize their source rocks, assess genetic typing and reservoir continuity within each field and on the scale of the explored fields.

In the second part of the work (4.2), geochemical studies of the core from three fields of this deep (Amangeldy № 102, Sultankuduk R-1 and Anabay № 12) were carried out using the Rock-Eval pyrolisis and a microscope to measure the vitrinite reflectance and study the maceral composition in the samples. Also, based on the results of analyzes of gas chromatography and biomarkers, a "condensate-source rock" correlation was carried out to discern genetic links between samples of condensates and extracts from potential source rocks.

The third part (4.3) of this paper presents the interpretation of the results of geochemical analyzes (component composition and carbon isotopic composition) of 6 gas samples from the above fields to determine the gas types and environmental condition of OM, thermal maturity and genetic relationships between gas samples.

Geochemical study of condensates

According to the values of density and depth of condensates, condensates in the Lower Visean (clv1) deposits of the Amangeldy field (perforation interval 2000–2400 m) are lighter than the overlying condensates in the Lower Visean deposits of Ayrakty (2050–2150m) and lower -Visean and Serpukhov deposits in Zharkum (perforation intervals 1500–1950m).

Gas chromatography

Gas chromatography study of condensates was carried out to assess the distribution of normal and isoprenoid alkanes at the molecular level. Based on the results of this study, the quality of the sample and its suitability for further analysis can be assessed.

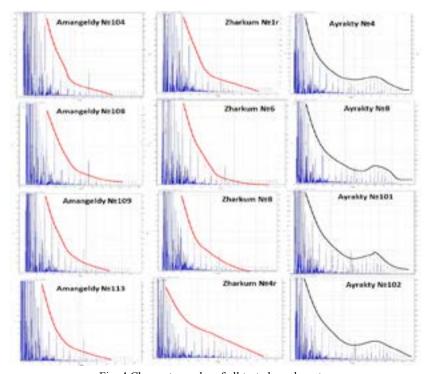


Fig. 4 Chromatography of all tested condensates

On fig.4 Chromatograms of condensates from the Amangeldy, Zharkum and Ayrakty fields are presented. Unlike other samples, the chromatogram of the Ayrakty condensate shows relatively high concentrations of heavy molecular n-alkanes in the form of a second peak, which may indicate its genetic difference from the Amangeldy and Zharkum condensates.

Such a bimodal distribution of n-alkanes often indicates a large input from terrestrial OM, although the absence of heavy n-alkanes in the Zharkum and Amangeldy samples is most likely due to their high thermal maturity, at which high-molecular-weight n-alkanes are cracked into low-molecular homologues in kerogen. Therefore, on the chromatograms of condensates, a narrow range of the HC series is noted in comparison with those of oils.

According to the chromatograms, gas condensate samples are not biodegraded, as evidenced by the presence of all n-alkanes mainly up to $C_{20}-C_{31}$. (fig. 4).

Chromato-mass-spectrometric (biomarker) analysis

Biomarker analysis of condensates was carried out to characterize the source rocks of the studied samples in terms of environmental conditions, lithology of OM, thermal maturity, and discerning genetic links between condensates, although it should be noted that biomarkers in oils rather than those in condensates are usually studied for the above purposes.

As diagnostic ions of the saturated fractions m/z 191, 217, and 218 were used for identifications for terpanes, steranes, and isosteranes, respectively, while m/z 178, 184, and 192 were chosen to identify the ions of the aromatic fraction such as phenanthrene, dibenzothiophene, and methylphenanthrenes.

Environmental condition of OM. To determine environmental conditions of OM was used plot of pristane/phytane vs C_{29} sterane/ C_{30} hopane, according to which source rocks of all samples were deposited in lacustrine environment. Relatively high Pr/Ph values in all samples might indicate the presence of a predominantly oxidizing environment during OM sedimentation (fig.5).

OM lithology. The low C_{29}/C_{30} ratios of hopane (29H/30H<1) in the mass fragmentograms of terpanes (m/z 191) in all samples indicate shaly source rocks (Seitkhaziyev et al., 2021; Seitkhaziyev et al., 2022;) (fig.6).

Thermal maturity. In this paper plot of 29Ts/29Tm vs. Ts/Tm was used to determine the thermal maturity of condensates, due to their growth with increasing thermal maturity (fig.7). According to these parameters, among the studied samples the condensates of the Amangeldy field were shown to have the highest thermal maturity. This means that the condensates in the Lower Visean (clv1) deposits of this field (perforation interval 2000–2400 m) experienced relatively higher thermobaric conditions than the overlying condensates in the Lower Visean deposits of Ayrakty (2050–2150m) and the Lower Visean and Serpukhovian deposits of Zharkum (perforation intervals 1500–1950m). It is obvious that this was due to the relatively deep occurrence of the productive formations of Amangeldy, where high temperatures and pressures led to compositional alterations of HC. Moreover, the relatively low density values (710–728 kg/m3) in Amangeldy condensates also confirm their high thermal maturity, since with maturity in the source

rocks, high-molecular n-alkanes are cracked to low homologues, resulting in density decrease of HC. As for the thermal maturity within the same field, the thermal maturity of the condensate of well \mathbb{N}_2 4 differs from the rest of the Zharkum condensates, although according to the customer data, wells \mathbb{N}_2 8 and \mathbb{N}_2 4 penetrate only the Serpukhov deposit, and the remaining wells (\mathbb{N}_2 . 1G and 6) exploit the lower Visean deposit. Condensate from the well \mathbb{N}_2 1G is more thermally mature than that of the well \mathbb{N}_2 6.

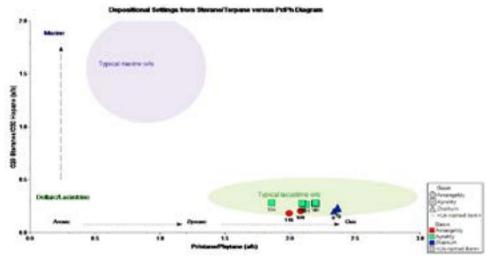


Fig. 5 Pr/Ph versus C29 sterane/C30 hopane ratio plot

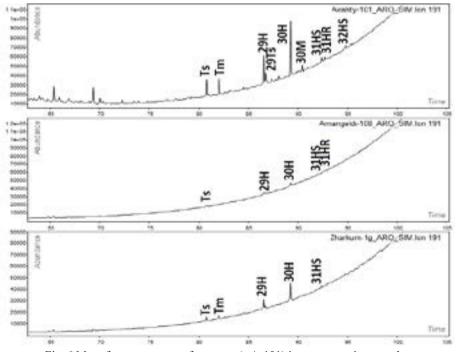


Fig. 6 Mass-fragmentogram of terpanes (m/z 191) in representative samples

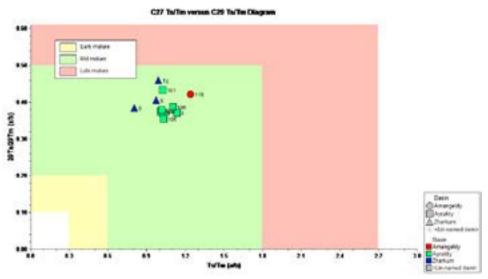


Fig. 9 Plot of C27Ts/Tm versus C29Ts/Tm in condensates

Fig. 8 Plot of methylphenanthrene index(MPI-1) versus methylnaphthalene index(MNR) in studied condensates

Condensate fingerprinting

Condensate fingerprinting was determined on LTM-GC based on 11 aromatic peaks in their compositions (fig. 9). Internal standard (IS) was added to each sample to calculate concentrations of aromatic compounds in ppm (Ganz et al., 1999).

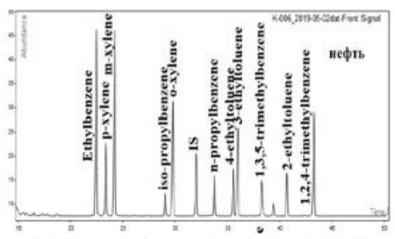
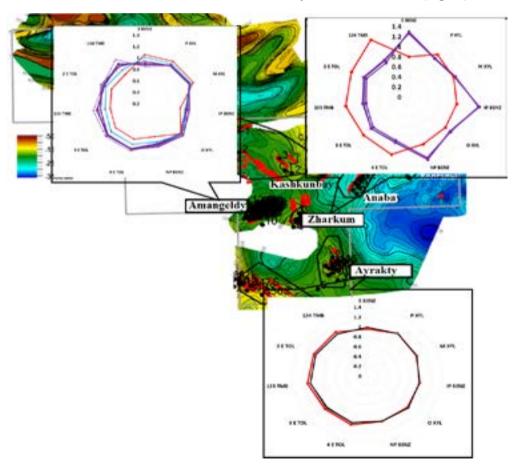


Fig. 9 Chromatogram of a representative condensate on LTM-MD-GC

When the identified groups were plotted on the structural map of fields, it was revealed that the condensates of each studied field have different fingerprintings, which indicate the absence of a hydrodynamic connection between the studied fields (fig.10).

Based on the fingerprinting of 7 condensate samples from wells developing deposits of the Visean deposit of the Ayrakty field, 2 groups were distinguishable, as marked in black and red colors (fig.11). Despite their identical pay zones, it is likely that the reservoirs of the eastern part do not completely mix with the reservoir of the western part, or there is a certain barrier between the identified groups that prevents from the movement of fluids, although there is no fault or barrier on the map and, according to the genetic characteristics of biomarkers, all condensates of this field have a single genetic group. Figure 10 Identified condensate groups in the structural map based on the result of their fingerprinting

Comparisons of aromatic components in the condensates in the form of star diagrams do not reveal significant differences in the composition of the studied samples of Zharkum condensates, except for N = 4. The identity of star diagrams in the condensates of wells N = 8, 6 and 1 indicates reservoir continuity beteen these wells (fig.12).



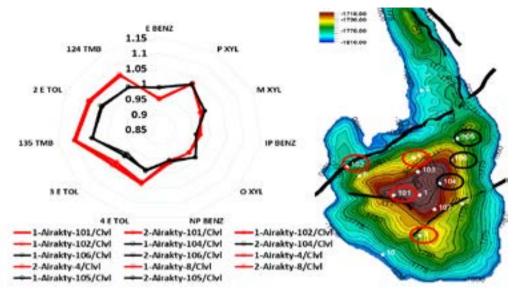


Fig. 11 Distribution map of identified types of condensate by fingerprinting in the Ayrakty field

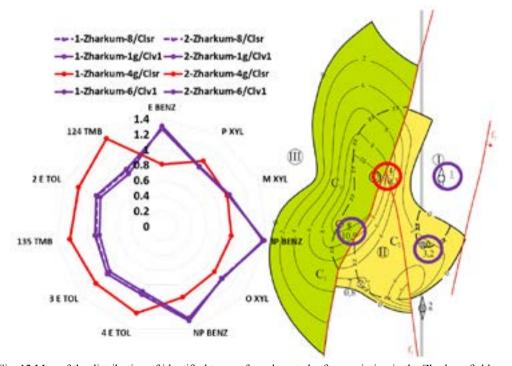


Fig. 12 Map of the distribution of identified types of condensate by fingerprinting in the Zharkum field

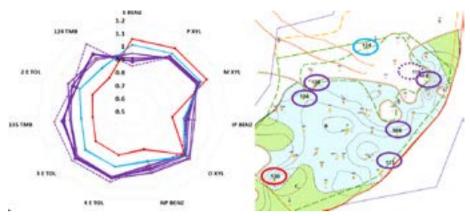


Fig. 13 Map of the distribution of identified types of condensate by fingerprinting in the Amangeldy field

Fringerprinting results of 7 condensate samples in Amangeldy field indicate that they differ slightly from each other, as clearly illustrated in fig.13 with red, blue and purple colors. The compositions of the condensates of wells № 120 and № 124 differ slightly from each other and from the rest of the condensates, which indicates reservoir discontinuity. This difference is also confirmed by different daily flow rates of gases and condensates of the studied wells. For example, the daily production rates of gas and condensate in well № 120 are two to three times higher than those of well № 108 (Ismagulova et al., 2021).

Geochemical studies of core samples

Rock-eval pyrolysis

Seven core samples were analyzed on Rock-Eval 6 in Bulk Rock mode to characterize potential source rocks in terms of organic matter type, kerogen type, thermal maturity, and determine their generating potentials.

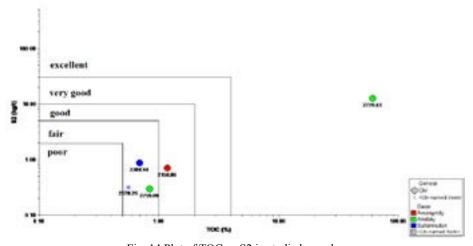


Fig. 14 Plot of TOC vs S2 in studied samples

Since the correctness of the results depends on the amount of organic matter (TOC) in the studied rock, samples with low values of TOC (<0.5) and S2 (<0.20) were excluded from further interpretation and the results of only 5 out of 7 samples were used to correctly interpret the data pyrolysis (Bordenave, 1993).

The generative potential. The amount of organic matter in the rock, kerogen, and the hydrocarbons present in the sample are determined by the Total Organic Carbon (TOC) parameter. As seen in fig.14. TOC values for the studied samples of Anabay, Sultankuduk and Amangeldy range from 0.56 to 61.16 mgHC/g of rock, which gives a possible generative potential from scarce to excellent. The high TOC values (61.16 %) for sample Anabay № 12 from the interval 2779.43m can be explained by the high value of its residual carbon (RC-59.99), which has a low generative potential. Samples from the Amangeldy and Sultankuduk fields have very scarce generation potentials, which is also in good agreement with the SRA results.

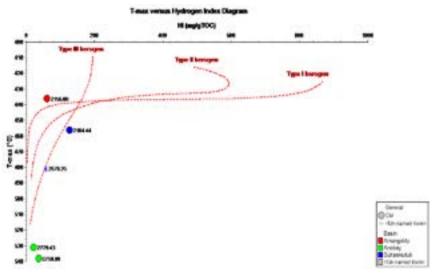


Fig. 15 Plot of Hydrogen index against Tmax in the studied samples

Kerogen type. In this work, the characterization of kerogen and initial OM was also carried out by analyzing 5 samples and plotting the dependence of the Hydrogen Index (HI) and the temperature of maximum HC generation (T-max). The low HI values in the samples are easily explained by the absence of a noticeable concentration of organic matter. All studied samples are located close to kerogen type III (gas generating) (fig.15).

Thermal maturity. Values of production index (PI) in the samples vary from 0.03 to 0.23. The largest scatter (0.030.12) of PI was established for core samples derived from the intervals (2759.09–2779.43 m) of the well № 12 in Anabay field. The plot of T-max versus PI was used to determine the thermal maturity of the studied samples and shows that all the studied samples except Amangeldy (interval 2156m) ones are thermally overmature, which can be explained by the anomalous thermal regime (fig.16). An

analysis of the paleogeographic and paleotectonic conditions for the accumulation of sediments in this basin shows that the sedimentation of oil and gas source rocks occurred at different rates. A linear increase in T-max values with increasing depth of sediments was also established, except for the Sultankuduk samples (fig.16). The plot of T_{max} values versus vitrinite reflectance values which is a reliable indicator of thermal maturity showed that sample N0.12 (int. 2779.43m) almost entered the gas formation phase of high thermal maturity (fig.17).

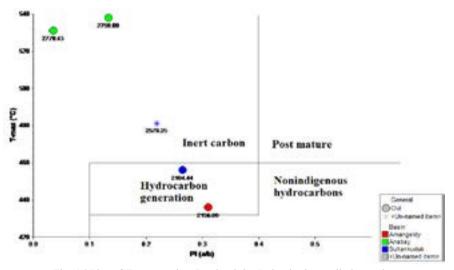


Fig. 16 Plot of T-max against Productivity Index in the studied samples

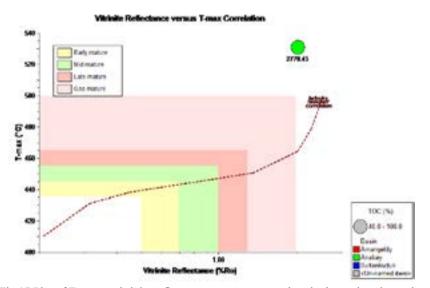


Fig.17 Plot of Tmax vs vitrinite reflectance measurement values in the analyzed samples Figure 25

Maceral analysis

Among the studied core samples, the maceral composition was possible to determine only for one sample (Anabay, 12), whose values in maceral ternary showed to be gasgenerating kerogen, which is also consistent with its Rock-Eval result (fig.18). In the remaining samples, there is very little organic matter and it is in a dispersed state, which makes it difficult to determine percentage of maceral groups.

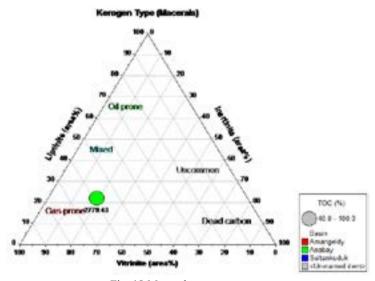


Fig. 18 Maceral group ternary

"Condensate-source rock" correlation

Visual comparison of the gas chromatographic analysis chromatogram and the Rock-Eval pyrolysis pyrolysis of all the studied core samples was carried out to verify the reliability of the obtained quantitative results. Then a visual correlation "condensate-extract from source rock" was carried out. Pyrograms of pyrolysis and distributions of n-alkanes suggest a high concentration of mobile and free HC S1 in the core even after extraction(fig. 19).

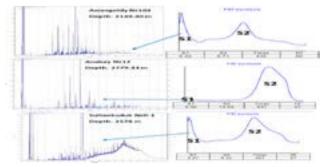


Fig.19 Integration of the results of Rock-Eval pyrolysis and gas chromatographic analysis of extracts from the core

Geochemical studies of gases Molecular analysis of gases

According to the results of the molecular analysis of gases, the values of methane in the studied gases of Ayrakty, Amangeldy and Zharkum fields vary from 76.37 % to 87.54 %, and gases can be characterized as wet owing to their methane composition (methane <95 %). Non-hydrocarbon gases CO₂ and N₂ are also present in all samples. In contrast to the gases of the Amangeldy (6.34–6.50 mol) and Zharkum (4.59–7.92 mol) fields, Ayrakty gases are characterized by a relatively high content of nitrogen (10.92–13.67 mol), although the concentration of carbon dioxide in the studied samples varies from 0.07 to 0.44 mol.

Isotope analysis of carbon in gases

The results of molecular analysis and carbon isotope composition in gases were used to characterize gases in terms of gas type, environmental condition, biodegradation, thermal maturity, and discern the genetic links between gases, although sometimes secondary processes associated with migration or mixing with gases from another source and biodegradation can significantly alter their original molecular and stable isotopic compositions. Compared to methane, the isotopic values of gases C_{2-5} are less affected by secondary processes and therefore provide more reliable information on the source and thermal maturity (Seitkhaziyev et al., 2020, 2021, 2022).

Gas type. There are basically two types of gas: biogenic gas and thermogenic. Biogenic gases are formed by anaerobic bacteria at low temperatures and are slightly enriched in δ^{13} C (up to–60 %). The ratios $C_1H_4/C_2H_6+C_3H_8+C_4H_{10}$ in such gases are usually very high, due to the formation of a very high concentration of methane by bacterial activity with a scarce concentration of microbial ethane, propane and butane (Peters et al., 2005). Thermogenic gases are directly related to the cracking of hydrocarbons in kerogen (Zhongying, 2012). Based on this assumption, Bernard plot was built, where all the studied gases of the fields are of thermogenic origin (fig.20).

Environmental condition. The isotopic composition of carbon can provide information about the environmental condition where the accumulation of OM took place. Thermogenic gases can be divided into two groups: the first group includes gases produced from coal, obtained from terrestrial humic OM, whereas the second one includes petroleum-associated gases obtained from marine sapropelic OM. Methane derived from terrigenous sources (kerogen type III) is usually more enriched in the heavy isotope δ^{13} C compared to that of marine origin. Based on this, the Bernard plot was applied (fig.20), where all the studied samples are in the zone of terrigenous origin.

Thermal maturity. According to Raleigh distillation effects, the liberated hydrocarbons are isotopically lighter relative to its kerogen, while the rest of the kerogen becomes progressively heavier. Based on this, a plot of $\delta^{13}C_{propane}$ and $\delta^{13}C_{ethane}$ was plotted, since their values increase with increasing thermal maturity. According to this plot, among all studied gases Amangeldy gases have the highest thermal maturity with an equivalent value of vitrinite reflectance (R₀) of 2.0–2.2 % (fig. 21). It should be noted that the higher thermal maturity of gases (Ro-2.5–2.6 %) than condensates (Ro-1.72 % according to MPI -1) of the Amangeldy field might indicate that gases were generated later than condensate and migrated into the considered accumulation zones later than liquids.

Biodegradation. Gases are also susceptible to biodegradation, especially in the water-gas contact zone or in shallow reservoirs. Bacteria eat the light isotopes of propane and the remaining gas becomes heavier (less negative values) (Gaspar et al., 2016). According to the value of the isotopic composition of carbons, the studied gases did not experience biodegradation, which is also confirmed by the results of gas chromatographic analysis of their condensates (fig.21).

"Gas-gas" correlation. For "gas-gas" correlation, star diagrams of gases were plotted by normalizing the values of the isotopic composition of carbon C₁–C₅, according to the results of which it can be seen on the map that different "fingerprinting" of the gases of Ayrakty, Zharkum and Amangeldy indicate their genetic difference (fig. 22), which is also consistent with "fingerprinting" of their condensates (fig. 10).

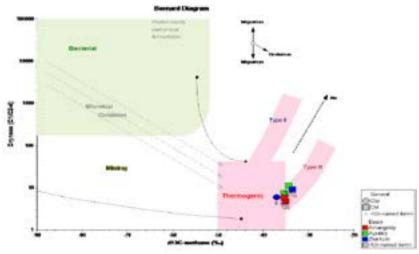


Fig. 20 Bernard diagram for gas type classification

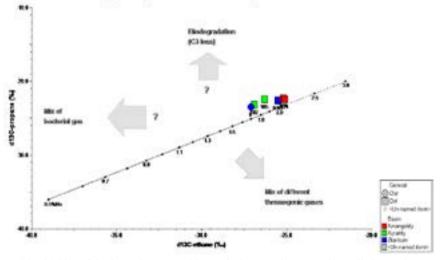


Fig. 21 Plot of the isotopic compositions of ethane and propane in studied samples

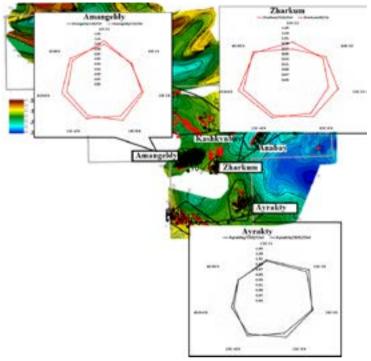


Fig. 22 Distribution map of selected types of gases by carbon isotopic composition

Conclusion

Comparison of the results of geochemical studies of samples of condensate, gas and core samples from gas-condensate fields of the Moyunkum sag enabled to draw the following conclusions:

According to the biomarker composition, all studied condensates were generated from lacustrine shaly source rocks. The condensates of the Amangeldy field have the highest thermal maturity, inferring that condensates and gases in the Lower Visean deposits of the Amangeldy field experienced relatively higher thermobaric conditions than the overlying condensates and gases in the Lower Visean deposits of Avrakty and the Lower Visean and Serpukhovian deposits of Zharkum. Higher thermal maturity of gases (Ro-2.5-2.6 %) than condensates (R₀-1.72 % according to MPI-1) of the Amangeldy field indicate that the gases were generated later than the condensates and migrated to the pay zones later than the liquid. Due to the high maturity, most terpanes and other biomarkers are absent in the Amangeldy condensates, which made it difficult to discern the genetic links between Ayrakty and Zharkum condensates. However, different distributions of steranes and aromatic hydrocarbons in the condensates of the Ayrakty, Amangeldy, and Zharkum fields may indicate their different genetic origins, which is also confirmed by the results of carbon isotopic composition of their gases. All studied gases are of thermogenic origin and were generated from terrigenous source rock (kerogen type III) with an equivalent R₀ value of 1.8-2.0 %. According to the analysis of the gas, the Ayrakty gases contain relatively high concentrations of nitrogen,

although the Amangeldy and Zharkum gases have similar nitrogen concentrations. The condensate of well №. 4 Zharkum was found to have a different chemical composition, which indicates its genetic difference from the rest of the condensates of this field.

According to the Rock-Eval results, only two samples (Sultankuduk № R-1 interval –2104.44m and Amangeldy № 102, interval–2156 m) are almost in the main zone of hydrocarbon generation, although the remaining samples are thermally overrmature and unable to generate HC. The studied samples relate to kerogen type III. Such gas-prone kerogen was also supported by maceral composition of one sample (Anabay–2779m).

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