



METAL CONTENT OF GROUNDWATER AND OIL OF THE SOUTH CASPIAN BASIN

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ABSTRACT

This article presents the results of a study examining the distribution of rare earth elements (REEs) in oil and groundwater in the South Caspian Basin. The region is unique due to its combination of thick sedimentary strata, active mud volcanism, and major oil and gas fields, resulting in distinct vertical hydrogeochemical zonation. Extracting REEs from groundwater represents a strategic opportunity for developing a new high-tech industry based on the existing oil and gas infrastructure. It is demonstrated that the REE composition in regional oil differs significantly from that in suspected source rocks and seawater, indicating the possible influence of deep processes on the formation of the trace element composition of oil. Potential sources of REEs in oil, including endogenous input from deep crustal zones, are discussed. The study results indicate a complex polygenic origin for the rare earth elements in oil of the South Caspian oil and gas basin. Along with biogenic elements inherited from the original organic matter, deep processes associated with mantle degassing and endogenous metal inputs play a significant role in shaping the trace element composition. It has been established that REEs form a regional deep fluid system genetically linked to petroleum complexes. The applicability of direct REE extraction technologies to the conditions of the Caspian shelf is substantiated.

Keywords: rare earth elements; microelements; oil; South Caspian Basin; geochemistry; metallogeny of naphthides; deep processes; lithium; groundwater; mud volcanoes.

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1. Introduction

The study of the microelement composition of oil is an important area of geochemical research, allowing us to estimate the concentrations of rare earth elements (REE). There are several generally accepted geochemical classifications of elements based on the Periodic Law of D. I. Mendeleev. The classifications of V. M. Goldshmidt (1923), V. I. Vernadsky (1927), A. E. Fersman (1933), N. A. Solodov (1932), A. N. Zavaritsky (1950), and others subdivide chemical elements according to their geochemical similarity, that is, according to the feature of their joint concentration in certain natural systems [1, 2]. The article presents the results of a study of the features of REE distribution in oil of the South Caspian Basin. This region is unique due to the combination of thick sedimentary strata, active mud volcanism and the largest oil and gas fields, which determines the pronounced vertical hydrogeochemical zonation.

2. Research methods and objects of research

The study of rare earth elements in formation waters is challenging due to their low concentrations and high sensitivity to sampling conditions. In the South Caspian Basin, these studies are of an indicator-geodynamic nature and are aimed at solving problems in petroleum geology and studying deep processes in one of the deepest sedimentary basins in the world. In summarizing, systematizing, and analyzing the hydrogeochemical data presented in this article, factual materials from published works on the South Caspian Basin by M. V. Abramovich, L. A. Abukova, I. S. Guliyev, D. A. Guseinov, V. A. Sulin, V. S. Melik-Pashayev, A. A. Kartsev, V. Yu. Kerimov, Sh. F. Mekhtiev, V. V. Semenov, S. A. Punanova, M. Z. Rachinsky, L. A. Buryakovsky, V. V. Kolodiya, D. I. Zulfugarli, F. R. Babayeva, A. Kurbanguradova, and others [3-6].

The study focused on formation waters from productive horizons, mud volcano waters, and waters from Azerbaijan and the adjacent Caspian Sea. During the field stage, samples were carefully collected and preserved, and in the laboratory, they were concentrated on ion-exchange columns, followed

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by analysis on a high-precision ICP-MS system. The following analytical methods were employed:

- Inductively coupled plasma mass spectrometry (ICP-MS) allows the analysis of highly mineralized brines after appropriate sample preparation.
- CP-OES was used in earlier studies to determine macro components and some REEs.
- A mandatory step was sample concentration and matrix removal using ion-exchange chromatography prior to ICP-MS analysis. The trace element composition (Mn, As, Co, Cr, Mo, Ti, Cu, Li, Ni, Pb, V, Zn, and Fe) of oil was analyzed using a Perkin Elmer NexION-300 D instrument. Detection limits for most elements are <0.001 g/t, the linear dynamic range reaches eight orders of magnitude, and allows for the simultaneous determination of trace element concentrations and the main sample components. A set of certified multi-element standards (Multiwave) was used for standardization.

3. Research results

Hydrogeochemical characteristics and patterns of spatial distribution of groundwater in the South Caspian Depression

In the South Caspian Basin, two types of groundwater spatial distribution are distinguished [7]:

1. Lateral distribution: an increase in mineralization and a change in composition are observed from the periphery of

the basin to its central, most submerged part. Freshwater is confined to marginal depressions, while brines are confined to deep axial zones.

2. Vertical distribution: distinct hydrogeochemical zoning is observed. The depth of the zone boundaries varies depending on the tectonic structure and lithology. In areas of mud volcanism, vertical removal of deep fluids occurs, creating local anomalies.

The presence of hydrocarbon deposits directly influences redox conditions and the enrichment of waters with specific components (I, Br, NH_4 , HS^-). The characteristics of the waters by complexes are given in tables 1 and 2.

In the South Caspian Depression, three zones are distinguished based on the total mineralization of groundwater: upper (Pliocene complex), middle (Paleogene-Miocene complex), and lower (Cretaceous complex) (see fig. 1) [7].

- Pliocene complex:** The waters are represented by calcium chloride brines (mineralization up to 228 g/l) and relatively low-mineralized sodium hydrocarbonate waters (8.6–63 g/l). Hydrochemical inversion is noted: a decrease in mineralization with depth and a transition to alkaline waters (fig. 1a).
- Paleogene-Miocene complex (Maikop series):** All hydrochemical types are found with mineralization from 5.7 to 37.2 g/l. An increase in mineralization and a change in the water type to calcium chloride in the direction of folding subsidence are characteristic (fig. 1b).

Table 1
General characteristics of groundwater in sedimentary complexes of the South Caspian Basin

Aquifer complex	Water type (according to Sulin)	Total mineralization, g/l	Predominant chemical composition	Key features and distribution areas
Pliocene	GKN, SS, MC, CC	8.6 – 228.0	Calcium chloride, sodium bicarbonate	Two main types: Concentrated calcium chloride brines in the upper part of the section and less mineralized alkaline waters in the lower part. Regions: Absheron, Gobustan, Lower Kura Depression.
Paleogene-Miocene (Maikop)	GKN, SS, MC, CC	5.7 – 73.0	From sodium bicarbonate to calcium chloride	the calcium chloride type in the direction of folding. Regions: Apsheron, Gobustan.
Hauterivian (Lower Cretaceous)	GKN, SS, MC, CC	6.0 – 15.0	Chloride-hydrocarbonate sodium	Relatively low-mineralized waters. Southeastern subsidence of the Greater Caucasus meganticlinorium.
Middle Jurassic-Valanginian	State Committee for National Economy	5.2 – 12.1	Chloride sodium-calcium	Low-mineralized waters. Regional increase in the role of Ca^{2+} and Mg^{2+} . South-eastern immersion meganticlinoria of the Greater Caucasus.
Conventional designations of water types: GKN - sodium bicarbonate; SS - sodium sulfate; MC - magnesium chloride; CC - calcium chloride				

Table 2
Ranges of content of the main components (mg- eq /l) in groundwater of the South Caspian Depression

Aquiferous complex	Cl^-	SO_4^{2-}	HCO_3^-	Ca^{2+}	Mg^{2+}	$\text{Na}^+ + \text{K}^+$	General mineralization
Pliocene	10–420	next.–22	0.2–15	0.1–57	0.1–37	12–310	8.6–228 g/l
Paleogene-Miocene	8–128	0.1–8	0.1–8	0.1–7	0.1–6	12–116	6.9–73 g/l
Hauterivian Danish	9–25	0.1–2	0.4–5	0.1–2	0.1–1	10–23	6.0–15 g/l
Middle Jurassic-Valanginian	6–15	next.–2	2–12	0.1–0.2	0.1–0.4	9–21	5.2–12 g/l
Note: The table shows generalized ranges based on research data from various areas of the basin							

- *Cretaceous complex (depths >3–4 km):* Calcium-sodium chloride brines with mineralization >300–350 g/L predominate. They exhibit maximum concentrations of trace elements (Br, I, Li, Rb, etc.) and a relative enrichment in heavy rare earth elements (HREE). This is due to albitization, dolomitization, and ion exchange processes under high-temperature conditions (fig. 1c).

A comprehensive study of hydrogeochemical parameters, including trace elements and rare earth elements, is a promising tool for solving problems in petroleum geology and understanding geodynamic processes in deep sedimentary basins.

A study of the hydrogeochemical characteristics and spatial distribution patterns of groundwater in the South Caspian Basin allows us to draw the following conclusions:

- The South Caspian Basin exhibits a distinct three-dimensional vertical hydrogeochemical zonation, controlled by depth, geothermal conditions, and the difficulty of water exchange.
- The spatial distribution of groundwater has a pronounced lateral direction: from freshwater at the periphery to brines in the central, submerged part of the basin.
- The composition and distribution of groundwater are closely linked to tectonic dislocation and the presence of

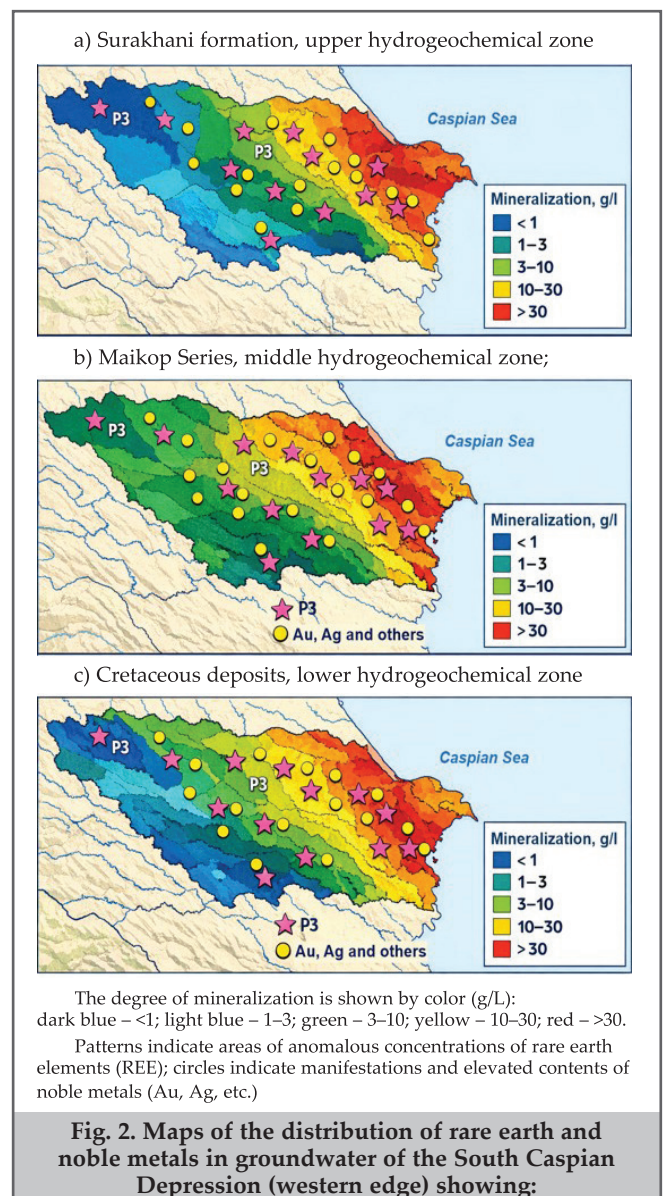
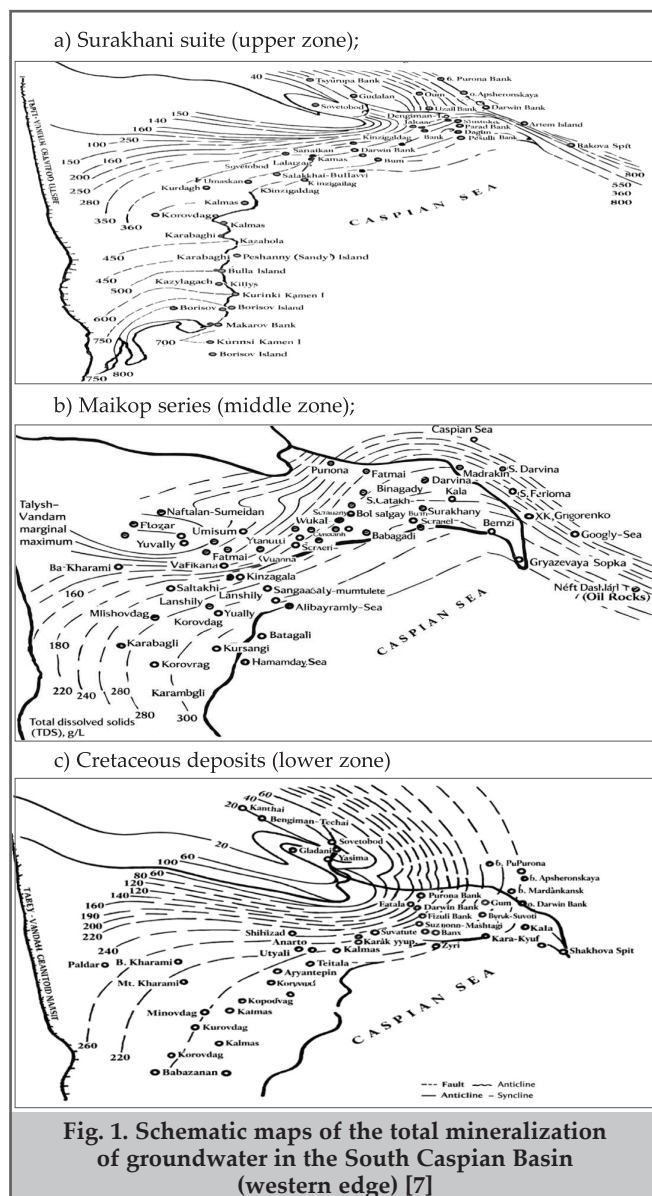
hydrocarbon deposits, which is reflected in specific hydrochemical anomalies (iodine-bromine and sodium bicarbonate waters).

- Active mud volcanism is an important factor disrupting regional zonation and causing vertical transport of deep fluids, which forms local geochemical anomalies in the upper horizons.

REE distribution characteristics:

- Rare earth element distribution characteristics (Ce and Eu anomalies, LREE/HREE ratio) serve as effective indicators of hydrogeochemical conditions, redox environment, and deep processes, such as water-rock interaction under high-temperature conditions.
- *Cerium anomaly (Ce/Ce*):* A negative anomaly in the oxidizing conditions of the upper zone is replaced by a slightly positive or zero anomaly in the reducing conditions of the depths.
- *Europium anomaly (Eu/Eu*):* A positive anomaly may indicate high-temperature interaction of water with feldspars in the deep zones of the basin [7].

In the South Caspian Basin, each vertical hydrogeochemical zone is dominated by rare earth and non-ferrous metals (fig. 2). The following indicators are observed at the Absheron



Archipelago fields (Oil Rocks, Bahar, Sangachaly-Deniz): total rare earth element (REE) content is 0.1–5 µg/g (g/t); light rare earth elements (LREE) predominate: La, Ce, Nd; heavy rare earth element (HREE) concentrations (Yb, Lu) are an order of magnitude lower. At offshore fields (Azeri-Chirag-Gunashli, Shah Deniz), oil exhibit anomalously high Eu/Sm ratios and specific REE spectra, distinct from those found in sedimentary rocks (table 4).

Correlation with other geochemical indicators shows that SKNB oil with high Eu/Eu* ratios often have elevated V contents (50–200 ppm) and V/Ni ratios >1. This is consistent with the hypothesis of a reducing environment and possible hydrothermal influence. Gottich [8] demonstrated that oil with anomalous REEs have a lighter carbon isotope composition ($\delta^{13}\text{C}$ from -28 to -30‰), which may indicate the presence of deep-seated organic matter. High S concentrations (up to 2–3%) correlate with a positive Eu anomaly, which also supports the model of reducing sedimentation/diagenesis conditions

1. Upper zone — Surakhani formation (fig. 2a)

The map shows the distribution of relative water-exchange horizons in the upper part of the section. Within the western flank of the basin, moderately mineralized waters predominate, confined to areas of infiltration recharge from the Greater Caucasus and Gobustan fold system. Color differentiation shows a lateral increase in mineralization in the southeast direction, toward the more submerged coastal-marine part.

The metal content of the upper zone is focal. REE anomalies are mainly associated with areas of active mud volcanism and fault permeability zones, indicating the possible input of components from deep fluid systems. Gold and silver occurrences (circles) are concentrated in areas where alkaline sodium hydrocarbonate waters mix with calcium chloride brines.

2. Middle zone — Maikop series (fig. 2b)

The map characterizes waters of the Paleogene-Miocene complex, characterized by a narrower range of mineralization compared to the upper zone. The color gradient emphasizes the transition from low-mineralization waters in the northwest to calcium chloride waters in the direction of meganticlinorium subsidence.

The REE distribution in the waters of the Maikop Group is often enriched in light REEs, consistent with the influence of terrigenous material and diagenetic processes. At the same time, the presence of patterns in individual coastal blocks again demonstrates a connection with vertical migration channels. Noble metals are observed predominantly in reducing zones of the section, where hydrocarbon deposits and hydrogen sulfide are present.

3. Lower zone — Cretaceous sediments (fig. 2c)

The map of deep horizons shows the dominance of highly mineralized brines (>30 g/L), which form a regional axial fluid system. Maximum values were recorded in the coastal-marine part of the western flank, corresponding to zones of impaired water exchange and elevated geothermal temperatures.

Here, the highest density of rare-earth element (REE) and precious metal anomalies is observed. The relative increase in the proportion of heavy REE and the positive europium anomaly, characteristic of deep waters, are interpreted as the result of interaction with feldspars and possible hydrothermal-endogenous influence. Au and Ag are concentrated in

the same blocks where mineralization is highest, emphasizing the complex nature of the metal content of Cretaceous brines.

The western flank of the South Caspian Basin includes several structurally distinct regions—the Apsheron, Gobustan, and Lower Kura regions—within which mud volcanism is widespread. Maps (fig. 2) allow us to trace how changes in groundwater mineralization in each zone of the section correlate with the distribution of rare earth elements (REE) and precious metals

Absheron Province

In the upper zone of the Absheron Peninsula, contrasting mineralization fields are observed, ranging from freshwater to 10–30 g/L. The most significant REE anomalies are found in the areas of the Pirallahi, Lokbatan, and Binagadi volcanoes, where well data indicate vertical fluid mixing. Gold and silver concentrations are concentrated in the coastal-marine zone (Sangachaly-Deniz, Oil Rocks), consistent with the presence of iodine-bromine waters and the increased role of organic matter in the oil-water system. In the Maykop Group (fig. 2b), the Absheron is characterized by a more uniform mineralization of 5–37 g/L; however, REEs are again concentrated along faults controlling the Gushchu, Bozdag-Gobu, and Zykha volcanoes. This indicates stable deep recharge of the middle horizons.

In the Cretaceous sediments (fig. 2b), it is beneath the Absheron and the adjacent shelf that maximum metal content is predicted: areas around the Shikhsagirdly and Dashgil volcanoes coincide with red fields of >30 g/L. The presence of Eu²⁺-enriched fluids capable of forming organometallic complexes of Au and U in the process ash of oil is likely here.

Gobustan Region

Gobustan is a key region of the upper and middle zones. Map 2a highlights the green-yellow fields of 3–10 and 10–30 g/L, encompassing the Dashgil, Kalmas, Solakhay, and Ayrantekan volcanoes. The REE spectra of these waters are typically enriched in light elements (La, Ce, Nd), consistent with the involvement of terrigenous material from the Greater Caucasus. Precious metals (circles) are concentrated predominantly in the northwestern part, where the waters are alkaline and biodegraded oil are present in the Mishovdagh and Kurovdagh fields.

In the Maykop region (fig. 2b), Gobustan exhibits a gradual increase in Ca²⁺ and a transition to the calcium chloride type; REE anomalies are concentrated near the Bozdag, Cheildagh, and Girmaki volcanoes, indicating the role of diagenetic concentration and local hydrothermal influence. In the Cretaceous zone, the metal content of Gobustan is lower than in Absheron, however, around the Solakhay-deep and Shamakhi-Gobustan volcanoes, possible channels for the supply of HREE-enriched brines into the upper complexes through volcanic apparatuses are observed.

Lower Kura Region

This region on the map, primarily represented by blue and green fields of 1–3 and 3–10 g/L, is a zone of infiltration water exchange. REE anomalies are few and associated with the Bahar, Khara-Zira, and Kursangi volcanoes, where mixing with more saline waters occurs. Precious metals are shown sporadically within the Garabaghly, Bahar, and Duvanny-Deniz fields, consistent with refining data for ferruginous oil.

In the Maikop series (fig. 2b), mineralization increases

to yellow fields of 10–30 g/L toward the mouth of the Kura River; REEs here may reflect secondary concentration in the presence of hydrogen sulfide and ammonium.

In the Cretaceous deposits (fig. 2c), the formation of deep Br–I–Li brines is presumed to have occurred beneath the Lower Kura zone. Au, Ag, and REE deposits near the

Kursangi–Glubinny and Muradkhanly volcanoes indicate a potential resource for direct REE extraction, similar to iodine plant technologies.

The metal contents of groundwater on the western edge of the South Caspian Basin are shown in tables 3 and 4.

Studies of the relationship between the hydrocarbons and

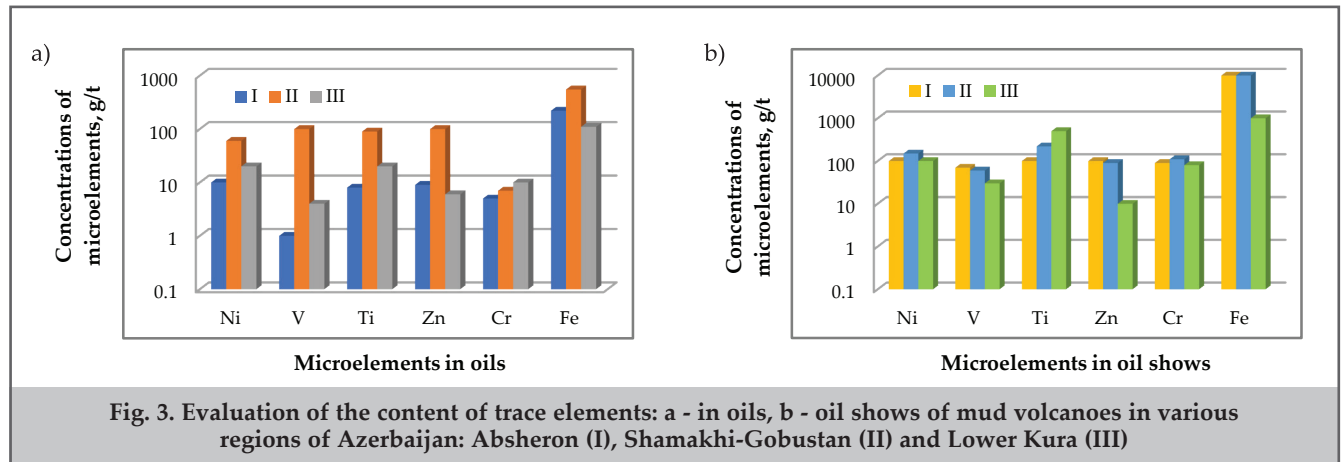


Fig. 3. Evaluation of the content of trace elements: a - in oils, b - oil shows of mud volcanoes in various regions of Azerbaijan: Absheron (I), Shamakhi-Gobustan (II) and Lower Kura (III)

Metal content of groundwater on the western side of the South Caspian Basin			Table 3
Volcano / area	Predominant type of water (according to Sulin)	Expected metal association	
Lokbatan (Apsheron)	GKN → CC when mixed	LREE (La, Ce, Nd), Au–Ag, U; V–Ni in ash	
Dashgil (Gobustan)	GKN, moderate 3–10 g/l	LREE, negative Ce anomaly; point Au	
Pirallahi (Absheron)	Alkaline GKN 8–30 g/l	Au, Ag, Sm–Eu, possible endogenous input	
Kalmas (Gobustan)	MC/mixed	Medium REE, S-linked complexes	
Airantekan (Gobustan)	GKN sulfide	Ce≈0, Eu positive; HREE focal	
Bozdag-Gobu (Absheron)	CC 10–37 g/l	HREE (Gd, Yb), Eu ²⁺ , Li, Br, I	
Girmaki (Gobustan)	Transition to CC	Diagenetic REE concentration, Ca–Mg	
Kursangi (Lower Kura)	GKN ↔ CC	Au–Ag point, Fe–oil; Li+REE prospect	
Bahar (Lower Kura)	Recovery CC	Br–I–Li, REE in solutions	
Shikhzagirli	Deep HC >30 g/l	Maximum REE+Au+U; V/Ni>1	
Binagadi (Absheron)	SC/GKN	Hypergenic LREE, weak Au	
Gushchu (Apsheron)	CC	HREE, Positive. Eu, Li–Rb	

Legend: GKN – sodium bicarbonate; SC – sodium chloride; MC – magnesium chloride; CC – calcium chloride; LREE – light rare earth elements; HREE – heavy rare earth elements

Metal content of groundwater at deposits on the western side of the South Caspian Basin						Table 4
SOCAR field	Water type	I mg/l	Br mg/l	Li mg/l	Expected metals	
Neftchala	CC recovery	60	450	25	REE+Li, Br, I	
Shah Deniz	CC >30	40	300	18	HREE, Eu, U, Au	
Azeri–Chirag–Gunashli	GKN/CC	55	420	22	LREE, Au–Ag	
Sangachal–Deniz	CC 10–37	50	380	20	Au, Ag, REE	
Muradkhanly-old fund	CC >30	65	500	28	HREE, Li, U	
Mishovdagh (mothballed)	GKN 3–10 g/l	LREE, Fe, dotted Au				
Kurovdagh	SC/GKN	Ni–V, Au–Ag				
Garabaghly	CC 10–37	Au–Ag+REE				
Muradkhanly	CC >30	HREE, Eu, Li				
Bahar (mothballed)	CC recovery	Br–I–Li, REE				
Oil Rocks (reference)	CC	Au, U in ash				

REE composition of oil from various regions of the South Caspian oil and gas basin have revealed key patterns in their distribution across the region's cross-section and area. These patterns have been found to be associated with host rocks and to be indicators of the type of initial organic matter (OM), the redox conditions of its burial, and secondary oil transformation processes in reservoirs. For their generalizations, the authors used a wide range of trace elements identified in the oil by various methods (chemical, spectral, neutron activation): Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Be, Zn, Sr, Zr, Mo, Sn, Ba, and Pb [9].

Up to 40 different chemical elements were detected in the studied oil. The main components of the ash from Azerbaijani oil were found to be Ni, Fe, V, Co, Cr, and Cu, which are present in whole and tenths of a percent (on an ash basis) [6]. According to averaged data, iron group elements found in oil form the following concentration ranges (table 5).

These data show that the composition of oil from various Azerbaijani fields is largely similar in terms of trace element content, indicating common geochemical conditions of their formation. Two types of oil are distinguished based on the predominance of Ni or Fe among the chemical elements: nickel-rich and ferrous. This difference in oil concentrations is likely due to the paleofacies conditions of burial of the original organic matter, which are more oxidized for ferrous oil. The V/Ni ratio, like the V/Fe ratio, is less than 1, which is typical for most Cenozoic oil from other regions.

Thus, regardless of the geological and tectonic structure of the region, the distribution of REEs in oil is significantly differentiated and indicates an endogenous component. It is noted that immature oil from Azerbaijan and nearby regions of Western Turkmenistan, Georgia, and the Western Ciscaucasia are quite similar in their trace element composition, forming a single fluid type genetically linked to the characteristics of the original organic matter and the conditions of its burial. They are characterized as oil depleted in trace elements, particularly in the main, well-studied elements of oil ash—V and Ni. The contents of these elements are below 10 ppm. Fe and Ni are characteristically predominant over V.

A genetic indicator—a V/Ni ratio of less than 1—refers to the oil type being ferrous or nickel-rich. Based on the provided trace element characteristics, the early-generation oil under consideration differ significantly from oil of other genesis with similar physicochemical properties. It is known that V and Ni, like many other iron group elements, are concentrated in the resinous-asphaltene fractions of crude oil, and their high concentrations are typically characteristic of heavy oil. For comparison, heavy oil from some fields in the Volga-Ural region contain up to 500 g/t V and up to 190 g/t Ni, while those from the Timan-Pechora region contain up to 240 g/t V and up to 170 g/t Ni [10-13].

Of particular interest are the offshore and coastal fields of Azeri-Chirag-Gunashli, Shah-Deniz, and Sangachal-Deniz, which form a unified «deep reservoir - reservoir - formation water - process residue» system. Waters with a wide range of mineralization (8–60 g/l) with a predominance of sodium bicarbonate and calcium chloride types are recorded at the ACG blocks in the Surakhani and upper Maikop series intervals. These horizons coincide with areas where REE anomaly patterns are located on the maps (figs. 1a, b), suggesting elevated contents of light REE (La, Ce, Nd) and precious metals associated with oil asphaltene. The deep zone of the Shah Deniz field, which also produces Cretaceous reservoirs, is characterized by red fields >30 g/L (fig. 1c). These brines are predicted to be relatively enriched in heavy REE (Yb, Lu, Gd) and have a positive Eu anomaly, which is important for designing technologies for direct REE extraction from produced waters, similar to iodine-bromine production. The Sangachal-Deniz field and its onshore terminal complex form a natural accumulation hub for metals during the processing of nickel- and ferrous oil. The coincidence of the Au and Ag circles with this area on the maps emphasizes that it is here that it would be appropriate to create pilot plants for the extraction of REE from operational streams [14-16].

Modern interpretations of metal genesis processes consider three main mechanisms:

1. Deep-seated input (endogenous model). The main argument is the europium anomaly and the deviation of REE spectra from sedimentary standards. The proposed mechanism is mantle degassing and fluid influx through deep faults and mud volcanoes [7].

2. The influence of specific source rocks. The contribution of Eocene and Maikop shale strata (Oligocene-Miocene) cannot be ruled out; these shale strata may themselves be enriched in REEs due to hydrothermal activity.

3. Secondary processes. Biodegradation can lead to a relative enrichment of residual oil in heavy components and some REEs, but does not explain the europium anomaly. Hydrothermal fluids often carry anomalous concentrations of Eu^{2+} .

The obtained data are consistent with the hypothesis of a polygenic origin for trace elements in oil, where, along with a biogenic source (inherited from the original organic matter), endogenous input from deep zones of the Earth's crust plays a significant role. Possible mechanisms for the entry of REEs into oil include: mantle degassing and the influx of deep fluids through fault zones; the interaction of hydrocarbon systems with magmatic and hydrothermal formations; and secondary processes of supergene transformation of oil leading to the concentration of metals [7].

The oil of the South Caspian basin is a unique type in

Table 5
Concentration series of microelements
in Azerbaijani oil [6]

Field	A series of microelements (in descending order of concentration)
Oil stones	Ni > Fe > V > Co > Cu > Mn > Cr
Palchyg Pilpilyasi (Mud hill)	Ni > Fe > V > Co > Cu > Mn > Cr
Darwin Kyupesi	Ni > Fe > V > Co > Cu > Mn > Cr
Pirallahi-Deniz (Pirallahi Island)	Ni > Fe > V > Co > Cu > Mn > Cr
Gyurgany-Deniz	Ni > Fe > V > Co > Mn > Cu > Cr
Mishovdagh	Ni > Fe > Ti > V > Cr > Mn > Cu
Sangachal-Deniz	Fe > Ni > Cu > Co > Mn > V > Cr
Duvanny-Deniz	Fe > Ni > Cu > Mn > V > Co > Cr
Hum	Fe > Ni > Mn > Cu > Co > Cr > V
Bahar	Fe > Ni > Cu > Mn > Cr > Co > V
Kurovdagh	Fe > Ni > Cr > V > Mn > Ti > Cu
Kursangi	Fe > Ni > V > Cr > Mn > Ti > Cu
Garabaghly	Fe > Ni > V > Mn > Cr > Ti > Cu

Table 6

Key coefficients and their interpretation for SCB oil

Coefficient	Importance in South Caspian oil	Geochemical interpretation
$(La/Yb)_{N}$	8–15	Moderate enrichment of LREE relative to HREE may indicate mixing of sources
$(La/Sm)_{N}$	3–6	Fractionation within LREE is characteristic of fluid-magmatic systems
$(Gd/Yb)_{N}$	1.5–2.5	Minor HREE fractionation, typical for systems involving deep fluids
Eu/Eu*	1.2–2.0	A positive Eu anomaly is a marker of reducing conditions and the possible influence of hydrothermal/magmatic processes.

terms of its enrichment in gold (Au) and uranium (U) – this is an important aspect of its metallogenic specialization.

- **Gold (Au):** Average concentration in oil is ~0.50 g/t in ash (or ~0.0005 g/t in crude oil at 0.1% ash). The concentration ratio (Q_i^A) is 147.5, which means that gold is 150 times more enriched than average clay rocks. Gold is a typomorphic element for oil. It is probably present as ultrafine particles or as part of organometallic complexes with asphaltenes.
- **Uranium (U):** Average concentration in oil is ~20 g/t in ash (or ~0.02 g/t in crude oil). Degree of concentration (Q_i^A) is 4.8. Uranium is also included in the list of typomorphic elements for oil, probably associated with carboxylate or porphyrin complexes (table 6).

The sources of Au and U in the oil of the South Caspian are considered from the standpoint of polygenesis:

1. Biogenic (syngenetic) source: U may be inherited from marine plankton. Biogenic accumulation of Au is less obvious.

2. Deep (endogenous) source (most significant for the interpretation of anomalies): the work of the Gottich-Pisotsky school links the enrichment of oil with metals with deep fluids entering through faults.

3. Secondary (hypergene) source: biodegradation and oxidation processes can lead to residual concentration of Au; U can be introduced by infiltration waters.

A positive correlation is observed between Au and U and V, Ni, S, and asphaltene content. During oil refining, these elements can concentrate in process residues, forming man-made resources. Studying these elements is key to comprehensive development and environmental risk assessment.

Technologies for extracting rare earth elements from groundwater

The process of extracting REE from groundwater can be divided into key stages.

1. *Pre-treatment and concentration.* The goal is to remove the main macrocomponents (Ca^{2+} , Mg^{2+} , Na^+ , K^+ , SiO_2 , Fe, suspended matter) and increase the total concentration of REE. Methods used:

- Sedimentation/filtration: removal of iron, silica, carbonates.
- Membrane technologies: Nanofiltration (NF) is a key method for preconcentration. NF membranes retain multi-charged ions (including REE^{3+}) while allowing singly charged ions (Na^+ , K^+) to pass through. This allows for the removal of salts and increases the REE concentration by 10-100 times.
- Reverse Osmosis (RO): Used for further evaporation of water after NF or as the first stage.

2. Sorption extraction and separation (the most complex stage).

The goal is the selective extraction of REEs from a concentrated solution and their separation into individual elements or groups. The methods used are:

- Ion-exchange sorption: the use of special ion-exchange resins functionalized with groups (phosphonic, iminodiacetic) that chelate rare earth ions. Allows for the extraction of the entire rare earth group from the solution.
- Extraction (Solvent Extraction (SX): the «gold standard» for industrial REE separation (but from solid ores). For aqueous solutions, it requires pre-concentration. Organic extractants (e.g., di-2-ethylhexylphosphoric acid (D2EHP)) selectively extract REE from the aqueous phase into the organic phase, and then, by adjusting the acidity, they can be re-washed, separating them into groups (light, medium, and heavy).
- Membrane extraction: a modern hybrid method where extraction occurs through a porous membrane, which is safer and more effective.
- Specific sorbents: development of new materials (functionalized polymers, mesoporous silicates, MOFs) with increased affinity for certain REEs.

3. *Final purification and oxide production.* The goal is to obtain commercial oxides or salts of high purity (99.9% or higher). Methods used:

- Post-precipitation: addition of oxalates or carbonates to obtain poorly soluble REE precipitates.
- Calcination: calcination of oxalates or carbonates to produce pure oxides (RE_2O_3).
- Multiple extraction/sorption: to achieve «battery» purity.

In Azerbaijan, the extraction of iodine and bromine from groundwater is a historically established, unique, and technologically advanced industry of global significance. Azerbaijan, along with Japan and Chile, has long been one of the world's leading iodine producers. Unlike many other regions, where iodine and bromine are extracted from seawater or associated brines, in Azerbaijan the source is natural, highly mineralized groundwater (brines), occurring in oil-bearing formations or separately [17-18]. These brines are characterized by high concentrations (I^- content reaches 40–120 mg/L, Br^- – 200–600 mg/L, which is thousands of times higher than in seawater) and a complex composition (in addition to iodides and bromides, they contain sodium, calcium, and magnesium chlorides, sulfates, often dissolved hydrocarbons, and hydrogen sulfide (H_2S)). [19].

The Azer-Yod plant in Neftchala is the largest iodine producer in the country. The plant develops the largest

iodine deposits in Europe. Azer-Yod is the fourth largest iodine producer after Chile, Japan, and the United States. The plant is located near the Hilli (18 km) and Neftchala (1 km) brine deposits, where the average iodine concentra-

tion is 42 mg/L. 120 industrial wells have been drilled at these deposits. Drilling additional wells and increasing the plant's capacity to 1000 tons per year are expected. Products are exported to countries such as Russia, Ukraine, India, China, and Poland [20-24].

Below are the stages of the technological scheme (fig. 4) for extracting iodine from natural brines/iodine-containing waters, on the basis of which iodine plants operate in Azerbaijan:

1. *Extraction and supply of raw materials:* Industrial brines or iodine-containing groundwater are extracted from specially drilled wells in brine deposits (iodine-bromine waters) and fed into the process line.

2. *Brine preparation:* Before chemical treatment, the solutions are purified from mechanical impurities (filtration). Acidity adjustment (acidification with sulfuric or other mineral acid) is often performed to stabilize iodide ions (I^-).

3. *Oxidation of iodides to elemental iodine (I_2):* An oxidizing agent, usually chlorine (Cl_2) or hypochlorite, is added to the brine, which oxidizes iodide ions to active elemental iodine ($I^- \rightarrow I_2$). This is the key chemical step.

4. *Desorption of iodine from solution:* After oxidation, iodine can be extracted from the solution in two main ways:

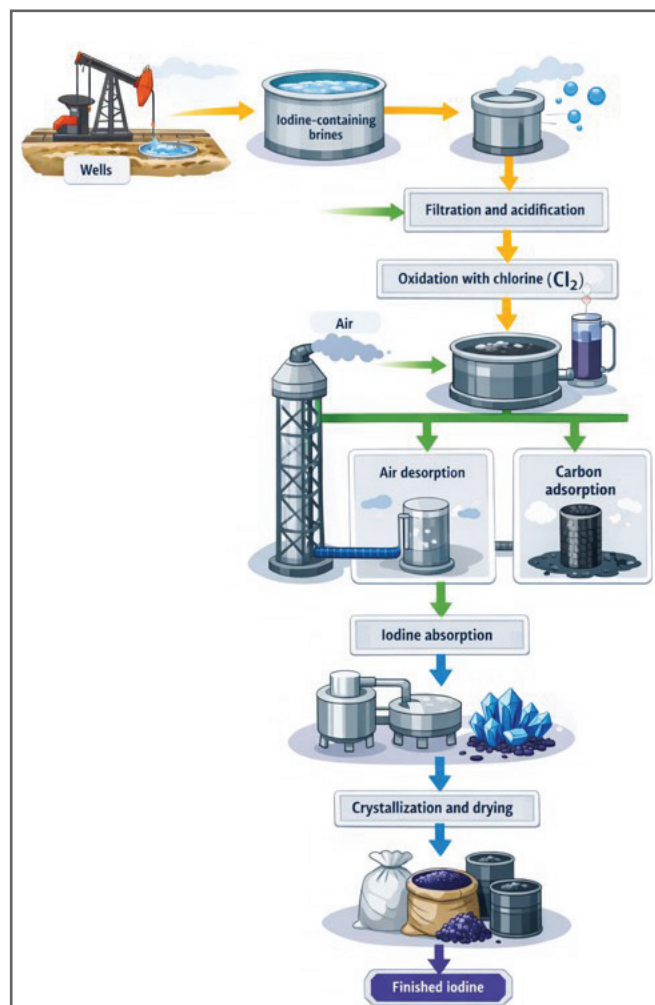
- Air desorption: Iodine is removed from the solution by forced air into the gas phase and transferred to the absorption column.
- Carbon adsorption method: Iodine is adsorbed on the surface of activated carbon and then desorbed by an alkaline solution or heating.

5. *Absorption and purification:* During air desorption, vaporized iodine is absorbed by a chemical absorbent (e.g., sulfite solution). The iodine is extracted from the absorbent, purified of impurities, and concentrated.

6. *Crystallization and drying:* The resulting iodine is converted from solution to solid form by crystallization (often using acids and cooling). The crystals are then dried and purified to the required quality (99%+ technical iodine).

7. *Storage and packaging:* Crystalline iodine is packaged and sent for sale or further processing.

Modern trends and developments in Azerbaijan are the improvement of technologies, the transition from «blowing» to ion exchange (sorption) and membrane technologies (electrodialysis, nanofiltration), as well as the use of ozone or hydrogen peroxide as cleaner oxidizers instead of chlorine («blue iodine method») [25-28].



The process includes brine extraction, preliminary treatment, acidification and oxidation of iodide ions to elemental iodine, subsequent separation of iodine from the solution by air desorption (or carbon adsorption), absorption, crystallization, drying, and production of high-purity commercial iodine

Fig. 4. Flow chart of the extraction of elemental iodine from iodine-containing brines, used at iodine plants in Azerbaijan

Conclusion

The study revealed that rare earth elements in oil from the South Caspian oil and gas basin have a complex, polygenic origin. Along with biogenic elements inherited from the original organic matter, deep-seated processes associated with mantle degassing and endogenous metal inputs play a significant role in shaping the trace element composition. The identified features of REE distribution can be used as geochemical indicators in assessing oil genesis, reservoir correlation, and forecasting petroleum potential in the region. REE distribution serves as a subtle indicator of water formation conditions. The most significant pattern is the relative increase in the proportion of heavy rare earth elements (HREE) in deep brines compared to light rare earth elements (LREE), which is associated with fractionation in high-salinity and high-temperature conditions. Ce and Eu anomalies help reconstruct the redox environment and temperature regime.

1. The hydrogeochemistry of the SCB is characterized by pronounced vertical zonation: from fresh infiltration waters at the periphery and upper part of the section to calcium-sodium chloride brines in the deeper parts of the basin. The spatial distribution of these waters is controlled by tectonics, lithology, and petroleum potential.

2. The study showed that rare earth elements in the oil of the South Caspian petroleum basin have a complex, polygenic origin. Along with biogenic elements inherited from the original organic matter, deep-seated processes associated with mantle degassing and endogenous metal input play a significant role in shaping the trace element composition. The most significant pattern is the relative increase in the proportion of heavy rare earth elements (HREE) in deep brines compared to light rare earth elements (LREE), which is associated with fractionation under high-salinity and high-temperature conditions. Oil from the South Caspian Basin are characterized by a unique REE distribution with a positive Eu anomaly, distinguishing them from oil from other basins. These data support a polygenic origin for trace elements with a significant role for deep-seated (endogenous) processes.
3. Oil from the South Caspian Basin, like oil worldwide, are anomalously enriched in gold and uranium relative to sedimentary rock clarkes. Au concentrations are ~0.1–1 ppm in ash, and U concentrations are ~1–20 ppm in ash. Elevated Au and U contents, especially in association with anomalous REEs, further support a polygenic model with a significant contribution from deep fluids.
4. Further study of rare earth elements in naphthides of the South Caspian Basin should be conducted using modern, high-precision analytical methods (ICP-MS, isotope analysis) in combination with integrated geological and geochemical modeling. Particular attention should be paid to identifying the spatiotemporal patterns of REE distribution in relation to tectonic activity and the deep structure of the region.
5. Azerbaijan has unique experience and natural resources for iodine and bromine extraction. The future of the industry lies in modernization: replacing the outdated «blowing» method with a combination of preliminary membrane concentration + selective ion-exchange sorption + «clean» oxidation.
6. Extraction of REEs from groundwater is a strategic direction for the future, especially for countries without rich ore deposits – it offers an opportunity to create a new high-tech industry based on existing oil and gas infrastructure. Key advantages include renewable energy, environmental friendliness, and synergy (simultaneous extraction of lithium, bromine, iodine, magnesium, and REEs).
7. The study of such complex, interdisciplinary technologies is the path to a promising future in resource economics, an area where geology, chemistry, materials science, and engineering intersect.

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