

GOLD MINERALIZATION IN OIL FIELDS OF THE SOUTH CASPIAN BASIN*

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Summary. The basis of idea of the gold content of the South Caspian oil-and-gas bearing basin is the notion regarding the forming of gold-bearing catagenic solutions by the oil-gas generating Paleogene – Lower Miocene sediments which within the zone Volga-Don-Pre-Caucasus–Trans Caspian enclose the complex sulphide-phosphatic-rare metal-uranium deposits. In iron sulphides there are constant gold, cobalt, nickel, molybdenum, rhenium, rare copper, zinc, plumbum and arsenic, but in pyritiferous horizons of some regions there are often inclusions of native minerals – gold, bismuth, tin and copper.

The detail geologic-geophysical and isotopic-geochemical studies have showed that in the South-Caspian sedimentary basin in “oil-gas window” the catagenic aqueous solutions enriched with ore components were intensively generated along with formation of liquid and gaseous hydrocarbons. It is proved by high content and constant presence of gold, silver, copper, molybdenum, zinc, arsenic and other metals in oils, bitumens and formation waters. This stimulated the study of possibility of ore accumulations forming in the paleo-sources of the fluids’ catagenic discharge and confirmed our predictions regarding the noble metal and oil paragenesis in the South Caspian sedimentary basin.

The top-cut concentrations of gold and palladium as well as the indicators of the epithermal mineralization of gold of the Carlin-type – arsenic and barium – were revealed within the zone.

Such study for gold exploration within the South Caspian basin was performed for the first time. The obtained results open the basin’s prospects as the gold-oil-bearing one. The revealed gold-ore mineralization represents a discovery of a new genetic type of gold-ore mineralization in Azerbaijan also known worldwide as stratiform Carlin-type with microdisseminated, low content and significant reserves of gold.

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Introduction

Our interest to gold mineralization in hydrocarbon-bearing sedimentary basins is stipulated by the following circumstances:

1. Oil-bearing Carline-type gold deposits of west-central Nevada, US (Gold Point electrum deposits and the Carlin-type gold ore bodies of Yankee basin in the Alligator Ridge mining district) appear as the best example of low temperature gold mineralization.

2. The recently discovery of micro-disseminated gold and gold-base metal alloys in sedimentary rocks of the Western Canada Sedimentary Basin (WCSB) (nearby Athabasca tar mining) has led to the recognition of a new and potentially important occurrence of low temperature sedimentary-hosted gold mineralization named as Prairie-type.

The primary objective of our study was to understand: are these gold deposits types unique or can we find them in other localities in the world including the

South Caspian basin and if so, are they similar to **Prairie-type sedimentary Au, Carlin-type Au** or in a class of their own? We need to understand them so that we can be more effective in our exploration for them.

Preliminary integrated investigations carried out in South Caspian basin manifested the intensive mineralization and Au-Pd anomaly that caused the selection of some fields as the object for this study.

We expect that this paper considerably improves our understanding of the industrial gold deposits formation in paragenesis with hydrocarbons in the South Caspian sedimentary basin, which is a new direction for mineral deposits discovering in this oil reach province. This will contribute much to the strategy of noble metals exploration in the South Caspian region as well as other similar hydrocarbon basins all over the world.

Idea justification

Gold mineralization in the Western Canada Sedimentary Basin (WCSB) at Fort MacKay, northeastern Alberta, nearby Athabasca tar sands mining

* Discussion paper

(Prairie formation) occurs as <5 micron-sized grains associated with bitumen in silicified limestone and calcareous sediments within pipe-shaped solution chimneys interpreted to represent focused, paleobrine discharge sites. Micro-disseminated mineralization is proposed to have occurred by mobilization (scavenge) and transport of gold and other metals in oxidizing, halide-rich brines derived from the halite-bearing Prairie formation at a maximum paleotemperature of about 90°C. Metal deposition was related to changes in redox potential along the flow path and, in part, to the presence of hydrocarbons.

The oil-gold paragenesis is in the best way represented in the Carlin-type gold deposits. Because of abundant oil-saturation some of them have been named oil-bearing Carline-type gold deposits as for instance the Gold Point electrum deposits near Railroad Valley and the Carlin-type gold ore bodies of Yankee basin in the Alligator Ridge mining district, west-central Nevada, US. (Hulen and Collister, 1999).

Carbon and oxygen isotopic systematics of the gold-oil-bearing calcite of the Yankee group deposits show that it is of hydrothermal rather than diagenetic origin; it is quite similar to ore-stage calcite at the Carlin deposit itself located about 100 km to the north. The Yankee fluid-inclusion and fracture-filling "free" oils were clearly involved in the gold-mineralizing hydrothermal system but were not thermally degraded to pyrobitumen, the analogous solid hydrocarbon characteristic of Carlin-type gold deposits. The oil-bearing fluid inclusions all have homogenization temperatures less than 120°C. Temperature-sensitive biomarker transformation ratios both in the fluid-inclusion oils and in the "free" oils, expressed as equivalent vitrinite reflectance (R_o ; 0.75–0.95%), suggest peak paleotemperatures no higher than about 145°C (Hulen and Collister, 1999). Thus the Yankee system was cooler than the 175° to 250°C widely cited as typical for Carline-type mineralization. It is very important to note that stable isotopic systematics coupled with fluid-inclusion microthermometry reveal that the Gold Point and the region's premier Grant Canyon oil field thermal waters were otherwise identical in composition and temperature (Hulen et al., 1998). Origin of Carlin-type deposits is enigmatic. Basically recent studies indicate the formation of Carlin-type deposits from relatively low pH, and low-to moderately-saline convective circulated fluids of mixed meteoric and magmatic or metamorphic origin, which leached gold from deep metamorphic or sedimentary rocks (Kuehn and Rose, 1995; Seedorff and Barton, 2004; Ilchik and Barton, 1997).

Carlin-type deposits are large, disseminated, carbonate (calcareous) sediment-hosted gold ore bodies characterized by relatively high Au/Ag, en-

richment in As, Sb, Hg, and Tl, and by the dominance of "invisible gold" as ions or submicron-sized particles in iron sulfide. The deposits are under strong structural control of faults and folds (Radtke, 1985; Hofstra and Cline, 2000). In the Carlin systems the physical properties of the host environment place major constraints on ore formation. High porosity host rocks are capped by structural or stratigraphic closures which trap the ore fluid similar to oil accumulation process (Burton et al., 1985).

In addition, Ge X. and colleagues studied the spatial association of hydrocarbons with a Carlin-type gold deposit in detail in Nanpanjiang Basin, South China (Ge X. et al., 2022). Based on complex studies using high-resolution transmission electron microscopy, electron probe microanalysis, and in-situ sulfur isotope analysis of both pyrobitumen and gold-bearing pyrite, they established that liquid hydrocarbons are responsible for the precipitation of metallic gold and could have acted as gold carrier before metal precipitation.

Carlin-type gold deposits are of major economic interest to mining companies because they represent low-cost, bulk-mineable targets. Low grade of gold in the ore is compensated by large size of deposits. For example, Newmont's Gold Quarry deposit is the largest currently known deposit along the Carlin Trend in Nevada, containing 198 million tons grading 1.19 gram/gold per ton, or 259.375 contained tons of gold.

The South Caspian sedimentary basin (SCSB) is generally accepted as one of the richest petroleum province in the world. High-productive oil and gas deposits in the SCSB are concentrated in the Lower Pliocene deposits so called Productive Series (PS) accumulated in the Absheron peninsula, South-East Gobustan, Lower Kura depression, Baku and Absheron archipelagos (Fig. 1). Isotopic-geochemical (biomarker) investigations of oils and organic matter (OM) as well as correlation "oil-oil", "rock-oil" demonstrate that oils in the PS are derivatives of the Paleogene-Lower Miocene (Maykopian) and Middle-Upper Miocene (Diatomic) oil-generating complexes (Guliyev et al., 2000, 2001; Гулиев и др., 1999; Feyzullayev et al., 2001). In Volga-Don-Pre-Caucasus-Trans-Caspian region the Paleogene-Lower Miocene sedimentary complex is characterized by exclusively high ore-content which is expressed by sheet-like deposits of metalliferous bone detritus of fish and sulfides extending for many kilometers. These sheet deposits are complex sulfide-phosphate-rare metal-uranium deposits of a sedimentary type. In iron sulphides there constantly occur gold, cobalt, nickel, molybdenum, rhenium and rarely, copper, zinc, lead and arsenic. There often occur inclusions of native metals – gold, bismuth, tin and copper in pyritaceous horizons in some regions.

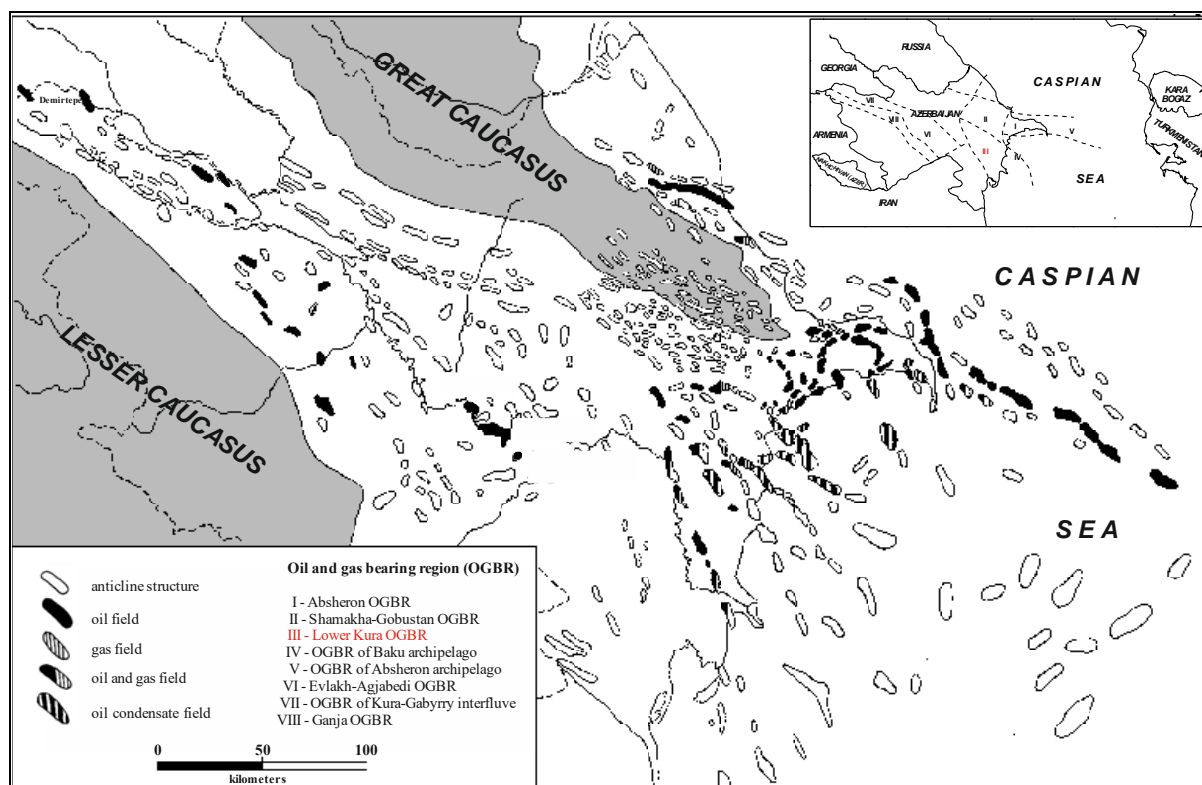


Fig. 1. Location map of oil-gas bearing regions and structures in the South Caspian sedimentary basin

This circumstance initiated investigations of generation of metalliferous catagenic solutions by the Paleogene-Lower Miocene oil-generating series in the SCB and possible formation of the ore-accumulations in zones of fluids' catagenic discharge.

Which data or criteria stipulate successful result?

Isotopic-geochemical (genetic) criteria

A peculiar feature of the oil-generating Paleogene-Miocene deposits in the SCSB is abundance of jarosite in the bedding surfaces of pyrobituminiferous shales with fish remnants. Formation of jarosite (natrojarosite) is, no doubt, associated with the destruction of primary accumulations of iron sulfides during the migration of catagenic heated carbon-dioxide-sodium-chloride solutions through the inter-laminar spaces of shales. Process of jarotization is a quite favorable factor for the saturation of water solutions by metals of the decomposing sulfides. For this reason, of a great importance are paleo- and recent centers of gas-water-oil fluids catagenic discharge. In favorable structural-lithological and geochemical environments, accumulations of the ore matter are confined to them. From this point of view of a special interest are zones of tectonic dislocations which control formation of oil-gas anticlinal structures.

The above-mentioned is regularly reflected in the concentration of metals in formation waters of oil-gas bearing fields of the studied region. Investigation of

distribution of ore-forming elements (Ag, Cu, Mn, Fe, As, Cd, Mo, Sr, Ba, U, Ra, Th, Ga, Tl, Ge, Zn, Pb, Bi) in formation and pore waters of the Tertiary complex of the South Caspian basin, as well as the comparison of formation waters with the mineral-forming solutions of areas of the recent ore-deposition such as the depressions Discovery and Atlantic II (Red Sea rift), Cheleken peninsula (Turkmenia), active volcanic zone Taupou (New Zealand) show that formation waters of the west flank of the South Caspian basin independently on low mineralization (14-147 g/l) according to metal content are comparable with ore-forming solutions (250-320 g/l) of the above-mentioned areas of the recent ore-formation (Багирзаде и др., 1988; Ахундов и Саппо, 1960; Агаларов и др., 1980; Богашова, 2007; Лебедев и Никитина, 1983; Пушкина, 1965; Эмери и др., 1974; Юшко-Захарова и др., 1986). Comparative analysis is given in Table 1.

The permanent presence and highly concentrations of gold, silver, copper, molybdenum, zinc, arsenic and other metals in the different-facial deposits as well as in oils and bitumens of the South Caspian oil-gas bearing basin (Мирзоев и Харитонов, 1982; Раковский и др., 1985; Бабаев, 1984; Мехтиев и др., 1986; Израэлян, 1959, 1964; Израэлян и др., 1975; Багирзаде и др., 1988; Huseynov, 2002) also reflect the metallogenic specialization of the East-Caucasian area of the Paratethys paleobasin in the Paleogene-Miocene time (Table 2).

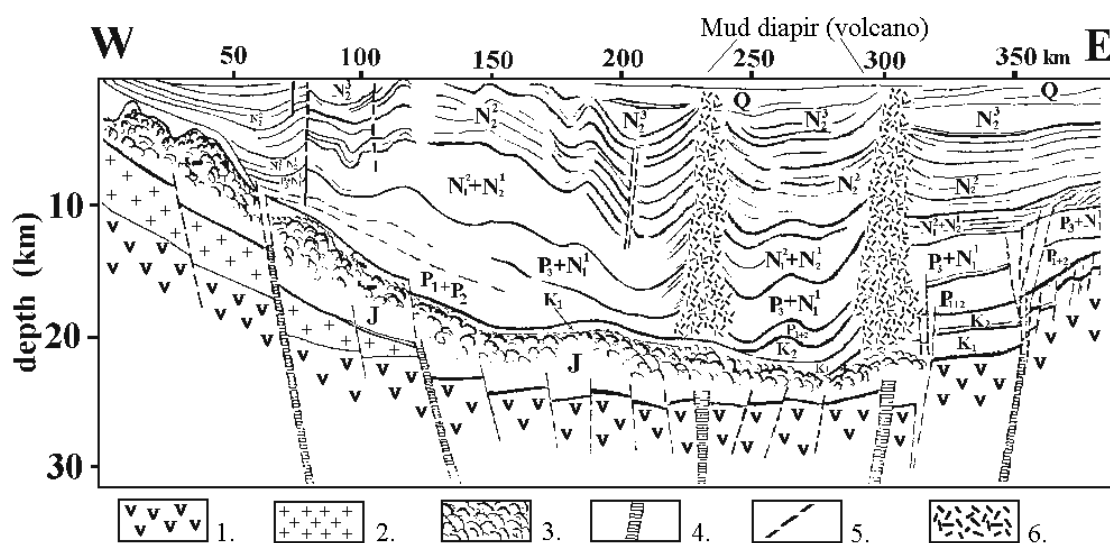


Fig. 2. 12th sec. regional seismic profile cross South Caspian basin (Ализаде и др., 2018). 1 – basaltic layer; 2 – granitic layer; 3 – Mesozoic igneous rock; 4 – crustal faults; 5 – faults; 6 – zone of no seismic information, presumably mud diapir

Results of the conducted studies allow confirming that the southern water area of the Paratethys (within the recent borders of the South Caspian basin) in the Paleogene-Miocene time is also characterized by high metallogenic specialization for some precious, rare and non-ferrous metals and intensive forming of gold-sulphide-rare metal formations in oil-generating complexes.

While choosing the object of investigations, we adhered to the main term that the hydrocarbonaceous fluids have been generated by the Paleogene-Lower Miocene (Maykopian) regional gold-hydrocarbon producing complex.

Isotopic-geochemical investigations of oils in the SCSB and correlation “oil-source rock” and “oil-oil” demonstrate that a share of fluid-generating complexes of different ages in the reservoirs infill is not equal in different oil-gas regions and even in the fields (Гулиев и др., 1999; Guliyev et al., 2001; Huseynov, 2000; Feyzullayev et al., 2004; Фейзуллаев и др., 2022). The highest contribution of the Maykopian complex to the generation of isotopic-light oils was recorded in some regions, and the reservoirs of the individual oil field are infilled with Maykopian fluids in a maximal degree.

Isotopic biomarker criteria (thermal maturity of fluids)

Oils in the selected oil field according to biomarker features (isomerization of normal sterane C29, correlation of monoaromatic and triaromatic steranes etc.) are the most matured (Ro% – up to 0.75) (Guliyev et al., 2000; Guliyev et al., 2001) which corresponds to paleotemperature of trans-

formation of the OM in the Maykopian complex in the interval (T°C) 125-135°C. Thermal maturity of hydrocarbonaceous gases calculated on the base of isotopic composition of ethane according to the correlation $\delta^{13}C(C_2H_6)(\text{‰})=22.6lgRo(\text{‰})-32.2$ (Faber, 1987) varies in the interval Ro% 0.95-1.1. This corresponds to paleotemperature transformation of the OM 145°-150°C. These temperatures are quite favorable for the transformation of montmorillonite into hydromica and release of the interlayer water as well as for the dissolution of the ore minerals there and for their saturation with the ore elements, i.e. for the formation of typical ore hydrotherms.

Structural criteria

Most of the oil-gas structures in the South Caspian basin are controlled by zones of deep regional faults and some oil deposits are tectonically-shielded. Zones of tectonic dislocations are characterized by high fluid activity, mud volcanoes development, gas-oil manifestations and discharge of dehydrated and mineralized elision waters (Guliyev and Huseynov, 2015; Aliyev et al., 2024). Thickness of the Paleogene-Lower Miocene fluid-generating deposits is up to 1500-3000 m from deep seismic data (Fig. 2). Scale of oil-gas content demonstrates the focused fluid flow and high fluid-generating potential of the Paleogene-Lower Miocene complex of the basin. It should be emphasized that the SCB is characterized by a very high elision regime and abnormally high formation pressures in the Paleogene-Pliocene hydrodynamic system.

Table 1

Oreforming elements content in the formation water of the South Caspian oil-gas fields and natural hydrotherms (mg/l)

Element	OIL AND GAS BEARING REGION						OREFORMING SYSTEM									
	Shamakha-Gobustan		Absheron		Low Kura		Pricaspian		Red sea rift Atlantis II Discovery M 25-28 %		Cheleken		Active volc.zone Taupo, New Zealand		World Ocean water M 3.5 %	
Water type Mineralizat.	Maykop Hydrocarb-at. M 1.39 %	PS Porous solution M 7.8 - 12.5 %	PS ₁ Hydrocarbonat. M 1.65-2.86 %	PS ₂ Cl-Ca M 5.4-14.7 %	PS ₂ Cl-Ca M 12-18 %	Maykop Cl-Ca M 3.2-3.7 %	Atlantis II Discovery M 25-28 %	Cl-Ca M 23.08 %	H ₂ S M 25.37 %	Cl-Ca M 23.08 %	H ₂ S M 25.37 %	Atlantis II Discovery M 25-28 %	Cl-Ca M 23.08 %	H ₂ S M 25.37 %	Cl-Ca M 23.08 %	H ₂ S M 25.37 %
Ag	0.014-0.126 0.183-1.647	0.416-3.266 5.47-42.97	0.066 0.868	1.5 0.000126	1.5 0.000126	0.036-0.328 0.48-n.n	0.3 0.0064	0.036-0.328 0.48-n.n	0.036-0.328 0.48-n.n	0.036-0.328 0.48-n.n	0.036-0.328 0.48-n.n	0.3 0.0064	0.036-0.328 0.48-n.n	0.036-0.328 0.48-n.n	0.036-0.328 0.48-n.n	0.036-0.328 0.48-n.n
Cu	0.832 0.00177	2.84-25.15 0.006-0.054	1.15 0.0036	2.59 0.0055	2.59 0.0055	0.221 0.0047	0.3 0.0064	0.221 0.0047	0.221 0.0047	0.221 0.0047	0.221 0.0047	0.3 0.0064	0.221 0.0047	0.221 0.0047	0.221 0.0047	0.221 0.0047
Mn	0.41 0.00041		0.126 0.000126	1.5 0.000126	1.5 0.000126	1.1 0.0011		1.1 0.0011	1.1 0.0011	1.1 0.0011	1.1 0.0011		1.1 0.0011	1.1 0.0011	1.1 0.0011	1.1 0.0011
Fe	5.04 0.00012			1.26-84 0.00003-0.002	1.26-84 0.00003-0.002	13.02 0.00031		13.02 0.00031	13.02 0.00031	13.02 0.00031	13.02 0.00031		13.02 0.00031	13.02 0.00031	13.02 0.00031	13.02 0.00031
As																
Cd																
Mo	0.0693 0.063	0.78-1.25 0.71-1.14				0.185 0.168		0.185 0.168	0.185 0.168	0.185 0.168	0.185 0.168		0.185 0.168	0.185 0.168	0.185 0.168	0.185 0.168
Sr	1.292 0.038		1.04 0.0041	1.53 0.45	1.53 0.45	34 0.1		34 0.1	34 0.1	34 0.1	34 0.1		34 0.1	34 0.1	34 0.1	34 0.1
Ba	3.45 0.0053		0.48 0.00074	1.17 0.18	1.17 0.18	9.1 0.014		9.1 0.014	9.1 0.014	9.1 0.014	9.1 0.014		9.1 0.014	9.1 0.014	9.1 0.014	9.1 0.014
U	0.0038 0.0015		0.0045 0.0018	0.0004 0.00016	0.0004 0.00016	0.00063 0.00025		0.00063 0.00025	0.00063 0.00025	0.00063 0.00025	0.00063 0.00025		0.00063 0.00025	0.00063 0.00025	0.00063 0.00025	0.00063 0.00025
Ra	3.2 x 10 ⁻⁸ 0.032		9.6 x 10 ⁻⁸ 0.096	1.2 x 10 ⁻⁷ 0.12	1.2 x 10 ⁻⁷ 0.12	4.9 x 10 ⁻⁷ 0.49		4.9 x 10 ⁻⁷ 0.49	4.9 x 10 ⁻⁷ 0.49	4.9 x 10 ⁻⁷ 0.49	4.9 x 10 ⁻⁷ 0.49		4.9 x 10 ⁻⁷ 0.49	4.9 x 10 ⁻⁷ 0.49	4.9 x 10 ⁻⁷ 0.49	4.9 x 10 ⁻⁷ 0.49
Th			0.00083 0.000063			0.00049 0.000037		0.00049 0.000037	0.00049 0.000037	0.00049 0.000037	0.00049 0.000037		0.00049 0.000037	0.00049 0.000037	0.00049 0.000037	0.00049 0.000037
Ga			0.0034 0.00018	0.0012 0.000065	0.0012 0.000065											
Tl			0.0021 0.0021	0.00067 0.00067	0.00067 0.00067											
Ge			0.0042 0.003	0.0034 0.0024	0.0034 0.0024											
Zn																
Pb			0.29-0.58 0.018-0.036			4.98 0.06		4.98 0.06	4.98 0.06	4.98 0.06	4.98 0.06		4.98 0.06	4.98 0.06	4.98 0.06	4.98 0.06
Bi			0.56-10.69 62.22-187.7			0.60 0.0376		0.60 0.0376	0.60 0.0376	0.60 0.0376	0.60 0.0376		0.60 0.0376	0.60 0.0376	0.60 0.0376	0.60 0.0376

The note: in numerator – contents in water (mg/l); in a denominator – clarke of concentration

Table 2

Distribution of oreforming elements in the South Caspian oils

Element	Clarke	Maykop oils	PS oils
Cu	5.7×10^{-3}	$1.55 \times 10^{-4} - 2.2 \times 10^{-4}$	$1.3 \times 10^{-5} - 4 \times 10^{-5}$
U	3.2×10^{-4}	2.2×10^{-6}	1.7×10^{-6} PS ₂ 2.2×10^{-7} PS ₁
Ra		1.1×10^{-13}	$1.16 \times 10^{-13} - 1.9 \times 10^{-13}$
Ga	3.0×10^{-3}	Undetermined	12.85×10^{-7} PS ₂ 5.85×10^{-7} PS ₁
Tl	1.0×10^{-4}	Undetermined	9.4×10^{-7} PS ₂ 3.7×10^{-7} PS ₁
Ge	2.0×10^{-4}	Undetermined	8.82×10^{-7} PS ₂ 4.23×10^{-7} PS ₁
Pb	2.0×10^{-3}	9×10^{-6}	6.72×10^{-6}
Zn	8.0×10^{-3}	$0.0 - 5.3 \times 10^{-5}$	9.3×10^{-5}
Mo	2.0×10^{-4}	6×10^{-6}	$3.0 \times 10^{-7} - 5.1 \times 10^{-6}$
Cr	1.0×10^2	$1.8 \times 10^{-5} - 1.1 \times 10^{-4}$	7.8×10^{-6}
Ag	1.0×10^{-5}	4.0×10^{-6}	$4.7 \times 10^{-7} - 2.0 \times 10^{-6}$
Au	1.1×10^{-7}	4.3×10^{-7}	4.4×10^{-7}

Lithological criteria

The Lower Pliocene deltaic and fluvial oil deposits are successively overlapped by deposits of all stratigraphic units of the Lower, Middle and the Upper Pleistocene (Absheron – 1700-800 Ka, Tyurkyan – 800-700 Ka, Baku – 700-350 Ka, Khazar – 350-75 Ka and Khvalyn – 75-10 Ka horizons). The Pleistocene deposits have been accumulated in isolated basin environment, which was temporarily connected with Evksin (Black Sea). Lithologically the Pleistocene succession is represented by alternative carbonaceous sandy-silty-clayey deposits, marls, detritus limestones, coquina. The thickness of Pleistocene deposits in some place (especially in the near-crust area along the deep faults) is up to 1000 m. Lithologically these deposits are quite favorable for the accumulation of gold (they are carbonaceous geochemical and sorption-mechanical barrier) and are the same type as some oil and gold fields – the Gold Point electrum deposits near Railroad Valley, the Carlin-type gold deposits of the Yankee basin in the southern Alligator Ridge mining district (Nevada, USA) and the “Prairie” type micro-disseminated gold mineralization of the Western Canada Sedimentary Basin at Fort MacKay (northeastern Alberta) in Canada (Hulen and Collister, 1999; Abercrombie, 1997; Fedikow et al., 1996; Fedikow et al., 1997).

Detailed geological-geophysical and isotopic-geochemical investigations demonstrated that there

occurred intensive generation of catagenic water solutions saturated by ore components in the SCSB in “oil-gas window” alongside with formation of liquid and gaseous hydrocarbons (Huseynov, 2002; Guliyev et al., 2004).

Idea approbation and Results

The necessity of the investigation of gold-oil paragenesis in South Caspian basin has been proved by the preliminary data. We conducted reconnaissance field studies and geochemical testing of the fault zones within one oil field the thickness of which is more than 100 m. Preliminary testing of one of such zones within distance of 80 m across the strike of the fault showed hurricane concentrations of gold (0.3 to 0.9 g/t), palladium (0.2-0.7 g/t), corresponding to the lower boundary of commercial (cutoff grade) amounts, as well as indicators of the Carlin type epithermal gold mineralization: arsenic on average 1665 g/t, antimony – 30g/t and barium – 1794 g/t, which exceed the Clarke values by 1700, 250-1000 and 170 times respectively (Table 3). There have been also determined abnormally high, relative to the Clarke values, content of the following elements: iron – 10-15 times; manganese and nickel – up to 100 times, copper – 10 times. Zinc and lead exceed the Clarke values up to 2 times. Contrary to the above mentioned metals, silver and uranium contents in the investigated zone are tens times below the Clarke value.

Table 3

Distribution of ore elements in the mineralized zone of the fault

№	Fe	Mn	Ti	P	Sb	Cr	Ni	Cu	Zn	As	Zr	Ba	Pb	Au	Pd	Ag	U
	wt. %				g/t												
min	4.28	0.18	0.22	0.05	12	22	144	45	27	161	24	84	11	0,3	0,2	<1*10 ⁻⁴	<0.1
max	14.4	0.34	0.3	0.07	48	149	223	64	35	3230	62	3580	15	0,96	0,7	<1*10 ⁻⁴	<0.1
mean	9.39	0.29	0.26	0.06	25.7	29.4	188	53.2	31.3	1665	38.2	1794	12.7	0.57	0.35		
Clarkes by Turekian and Wedepohl, 1961																	
sand	0.98	0.00n	0.15	0.02	0.0n	35	2	n	16	1	220	n*10	7	0.00n	n.d.	0.0n	0.45
carbonate sediments	0.38	0.11	0.04	0.04	0.2	11	20	4	20	1	19	10	9	0.00n	n.d.	0.0n	2.2

* - Fe, Mn, Ti, P, V, Cr, Ni, Cu, Zn, As, Zr, Ba, Mn, Au, Pd, Pb, Ag – were determined by the atomic-absorbption analysis in the device Analyst-300 (Perki-n Elmer, USA).

** - U was determined in the device SARI-2 (limit of sensitivity $1 * 10^{-3} \%$)

As a result of correlation analysis, in the mineralized zone there have been determined three associations of elements: I – Fe-Cu-As-Ba-(Mn); II – Cr-Ti-Zr; III – Au-Pd-Pb. Elements from associations I and III negatively correlate with elements from association II and do not correlate absolutely or weakly with each other. This indicates that Fe, Cu, As, Ba, Mn, Au, Pd and Pb have been delivered to the fault zone and control the balance of Cr, Ti and Zr, which are components of stable in situ accessory minerals of the enclosing sandstones. Superimposed character of the mineralization is confirmed by microscopic investigations of samples from the fault zone.

It should be emphasized that we investigated and tested only the uppermost part of the fault zone which is an area of active circulation of oxygen-rich surficial-atmospheric waters. It is known well enough, that gold, palladium, lead and especially uranium and silver are active migrants in the waters of hypergenesis. For example, palladium is the only member of the PGE that is significantly mobile and dilute surface waters. It forms hydroxyl complexes Pd(OH)₂, Pd(OH)³⁻ and Pd(OH)₄²⁻. The results of the field and laboratory studies show that Pd is mobilized from the ore and is car-

ried in solution to be fixed with organic material in sediments, clay minerals and other sorbents (Cameron and Hattori, 2003; Olivo et al., 2001). One can suppose that absence of uranium and silver in the upper near-surface area of the fault zone is a result of their complete leaching whereas the observed amounts of gold (0.3-0.96 g/t) and palladium (0.2-0.7 g/t) although are high but still much more lower than their initial concentrations. Optical microscopic investigations demonstrate that the main bulk of the ore mass mostly composed of aggregates of iron hydroxides formed on pyrite disseminations and phromboides. Pyritization is of a superimposed character (Fig. 3).

Fragmental grains of non-ore minerals are densely impregnated by dotted inclusions and veins of pyrite and in some places they are corroded by it. A visible gold has not been determined (Fig. 3). Absence of correlation of gold, palladium and lead (association III of elements remobilized from oxidation zone) with iron excludes their accumulation in iron hydroxides. At the same time, the strong correlation and high contents of elements association Fe-Cu-As-Ba-Mn are caused by their accumulation in the zone of hypergenesis and iron hydroxides (Fig. 4).

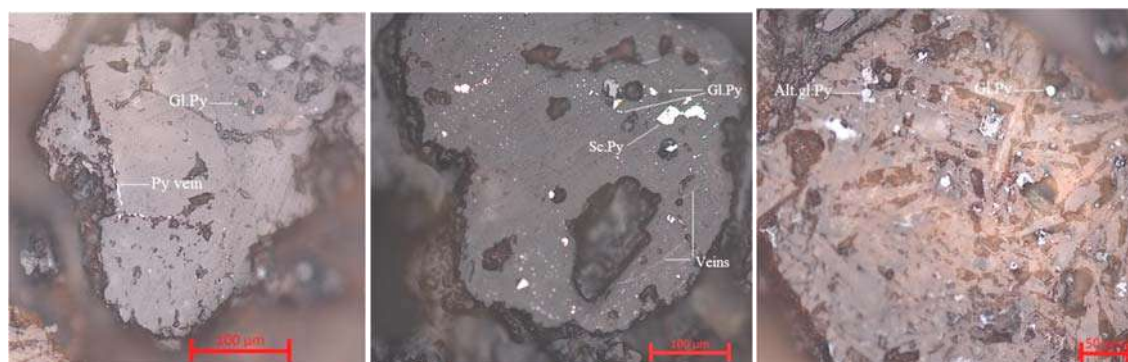


Fig. 3. Photo optical microscopic study of polished sections illustrate a superimposed character of pyritization. Pyrite aggregates: Py vein – vein, Gl.Py – globular, Sc.Py – secondary, Alt gl.Py – altered globular

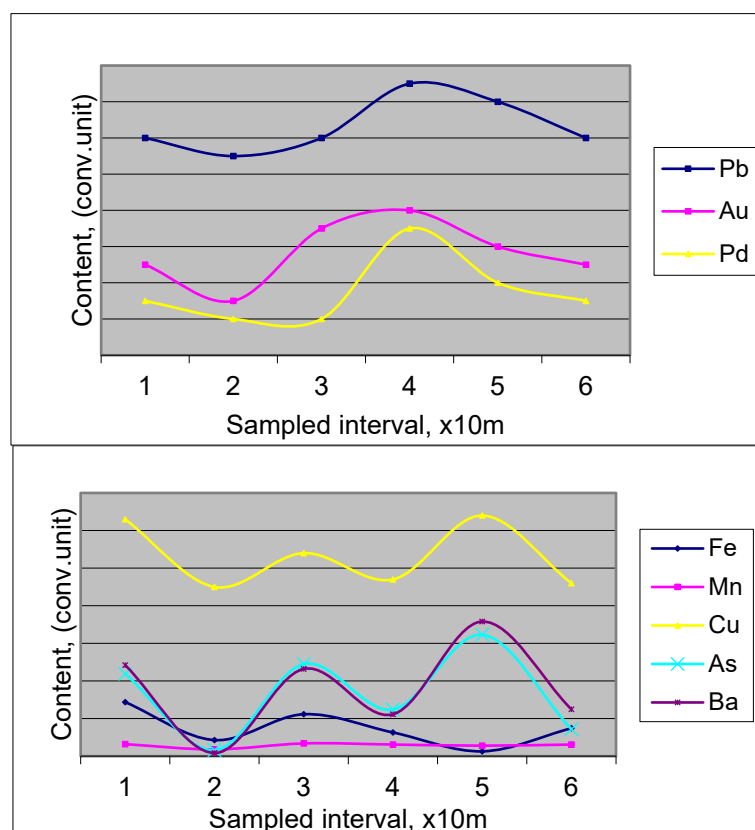


Fig. 4. Distribution and correlation of class I and III element's association within gold-bearing zone

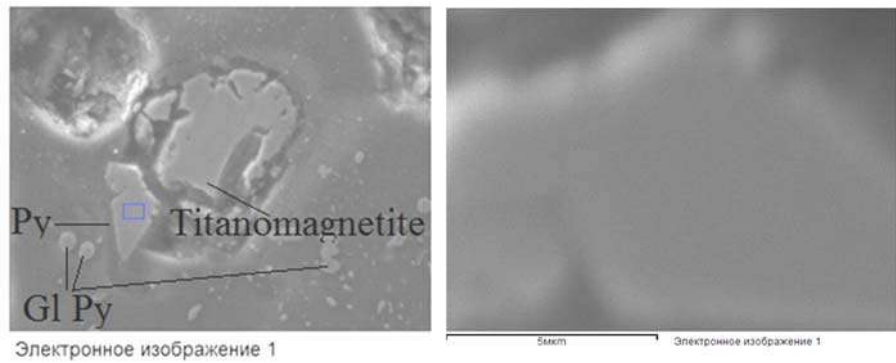
It is very important, that abnormally high amounts of gold and palladium were recorded in calcareous highly-porous sandstones with extremely low amounts of clayey minerals, OM and bitumen, which are the main sorbents, and concentrators of noble metals in stratiform deposits of the Carlin type. This enables to make a conclusion about the existence of commercial concentrations of gold and palladium in the deposits with a high amount of pelitic material and OM, such like clays, silts, silty sandstones, clayey sandstones which constitutes most of the Quaternary section in the studied oil field. At the same time by the analogy with gold epithermal deposits in Nevada and Alberta, one can make a conclusion about the initial concentration of gold in pyrite as well in the studied oil field in SCB. For example, pyrites in the Getchell field contain gold in amount of 2,400 ppm; in the Carlin field – 500 ppm (Cline, 2001; Togashi, 1992; Hausen, 1981; Radtke, 1985; Hausen et al., 1986; Cabri et al., 1989).

SEM analyses of rock samples (Fig. 5) from the mineralization zone of studied oil field show that gold in epigenetic impregnated (ingrained) and vein pyrite aggregates reaches hurricane concentration – from 17,500 ppm (1.75 wt.%) to 21,300 ppm (2.13 wt.%). It is 35-100 times higher than gold concentration in the Getchell's and Carline's pyrites. At magnifying for 10,000-12,000 times by SEM analyses

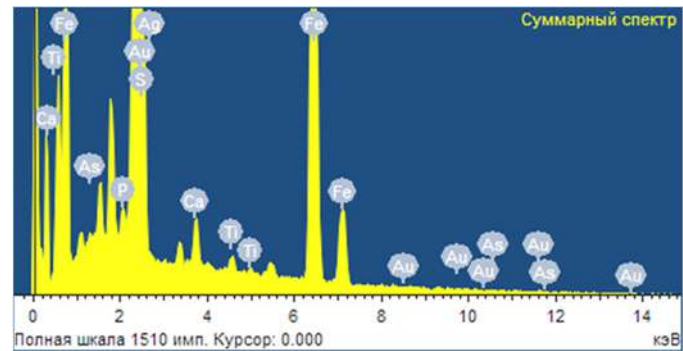
the mineral phase of gold in pyrite aggregates has not been detected (Fig. 6). Thus, one can come to conclusion that gold in pyrite aggregates is in the form of emulsion impregnation.

Chemical re-calculations demonstrate, that accumulation of such amount of iron hydroxides in the zone of oxidation in the investigated fault requires the decomposition of pyrite in amount from 8% to 29% in sediments (without the account of losses for the iron removed from the oxidation zone). This demonstrates intensive initial pyritization of this fragment of the fault and enables to make a supposition, that decomposing pyrites in the hypergenesis zone released significant amount of gold and other metals saturating by these metals the descending oxygen- and SO_4^{2-} containing sulphate waters. Thus, more high gold concentration in the lower horizons of the fault zones in the studied field is beyond all manner of doubt for the following reasons: 1) existence of thick horizons of high-permeable carbonates with high amount of clayey minerals and OM, i.e. favorable combination of carbonate and precipitating barriers; 2) abundance of gold-bearing sulfide disseminations; 3) redeposition in the reduction paleo-barrier of gold and palladium, leached out of the upper parts of the mineralized fault zone. Existence of such barrier is proved by the ascending hydrocarbon and hydrogen sulphide fluids.

Element	Weight %	Atomic %
P K	0.77	1.00
S K	54.05	67.35
Ca K	1.24	1.24
Ti K	0.56	0.46
Fe K	41.26	29.52
As L	0.00	0.00



Ag L	0.00	0.00
Au M	2.13	0.43
Total	100.00	



Element	Weight %	Atomic %
P K	0.88	1.14
S K	53.83	66.95
Ca K	1.68	1.67
Fe K	41.86	29.89
Co K	0.00	0.00
Ni K	0.00	0.00
As L	0.00	0.00
Ag L	0.00	0.00
Au M	1.75	0.35
Total	100.00	

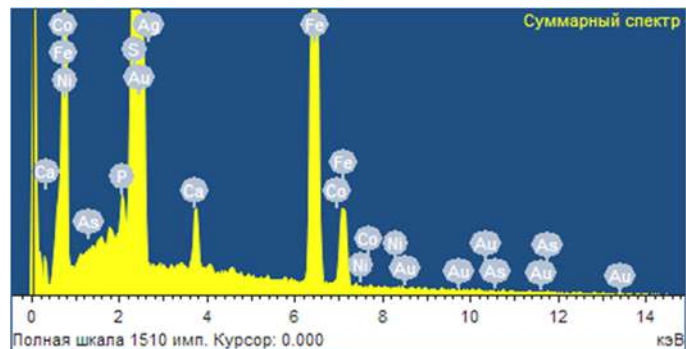
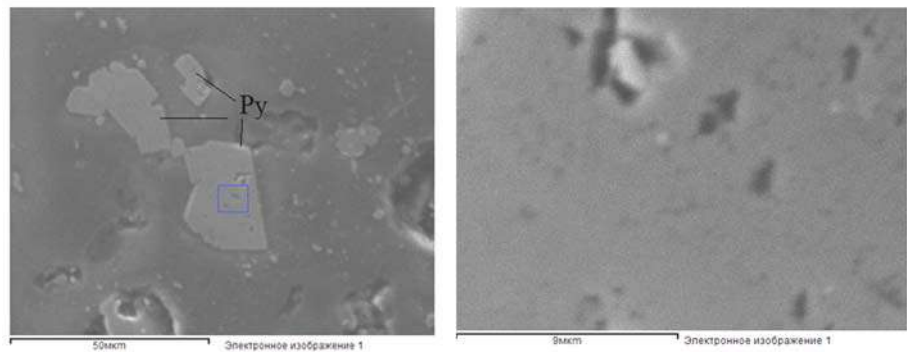


Fig. 5. SEM analyses of pyrite aggregates from gold bearing zone in the SCB and spectrograms of distribution gold and other elements (instrument: JEOL 6610-LV)

Existence of a thick (up to 80 m) mineralized fragment composed of gold-palladium-bearing calcareous sandstones and characterized by the intensive hydrothermal activity within regional fault zone in studied oil field enables by analogy with the north Nevada to highly evaluate the potential epithermal gold content of the Carlin type in the great part of area under study.

As a result of this study we expect to estimate the gold and other noble metals potential in studied oil field. It will enable us to assess the gold potential of other hydrocarbon fields in the South Caspian basin, which will give us an unique chance to begin a new era in exploration of mineral resources in the basin which has more than 150 years history as an oil basin.

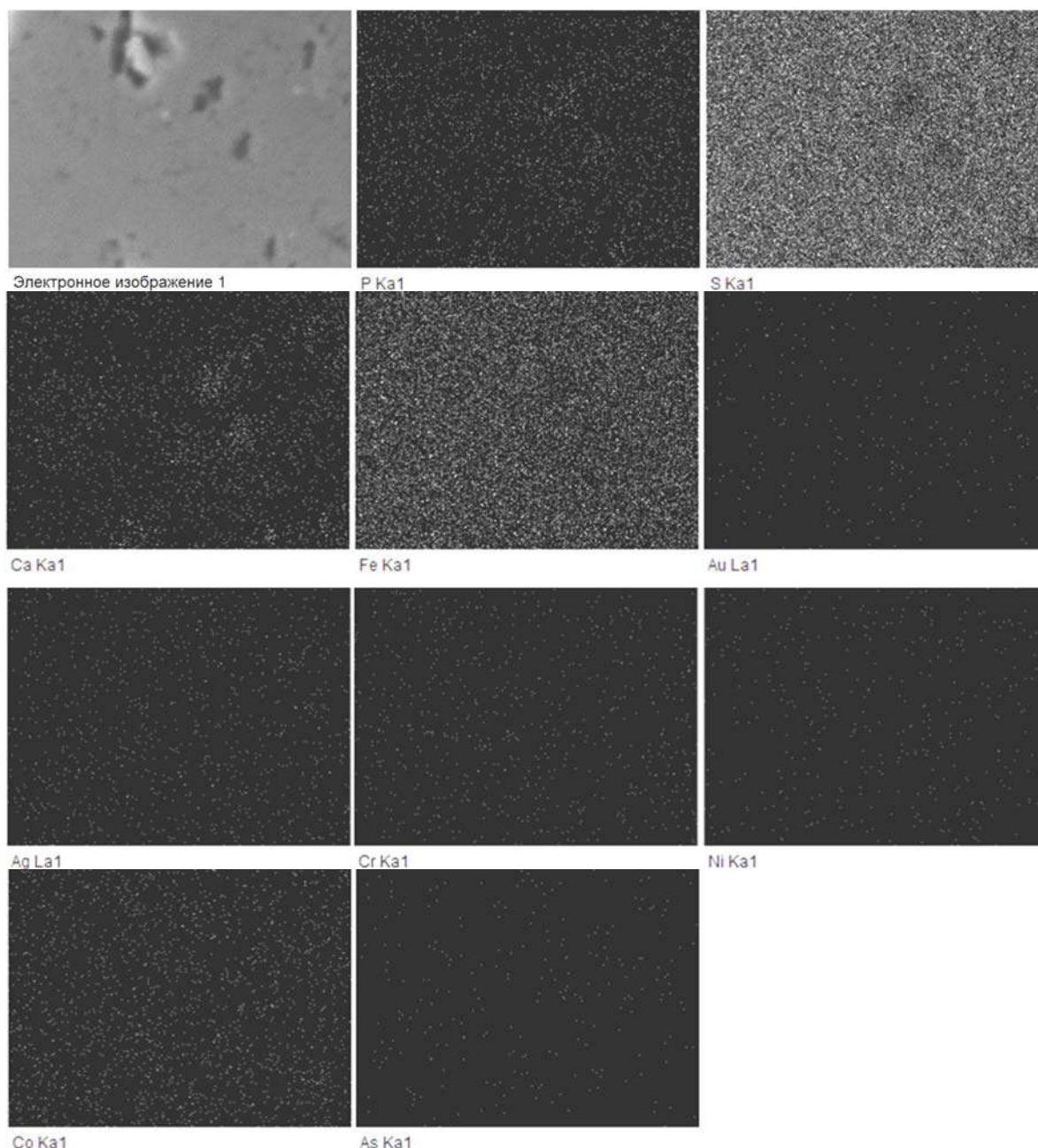


Fig. 6. SEM images of distribution mineral phase in the pyrite aggregate from gold bearing zone in the SCB (instrument: JEOL 6610-LV)

We also expect that this research will give us an opportunity to contribute much in ore industry of Azerbaijan, which is an important step in economic development of our country. The results that we are planning to receive and methodology, which we'll use, might be also applied to other analogous basins in the world.

As a next step, the following studies should be carried out in the study area:

- Determination of linear parameters, occurrence and morphology of mineralized fault zone and its geochemical halo. This should be performed by integration of different geophysical methods – gravimetric, magnetic and radiometric survey.

- Sedimentological investigations based on the integration of field works and data of log diagrams interpretation and aimed to determine facial types of rocks favorable for the ore- mineralization and to trace them in the area and in the vertical section.

- Geochemical testing and mapping aimed to determine Au, Pd contents and accompanying elements and intensity of geochemical anomaly.

- Petrographic investigations of ore-enclosing deposits to determine character of hydrothermal change and degree of mineralization of rocks.

- Mineralogic investigations including microprobe, X-ray spectral, X-ray diffractometric and SEM analyses.

- Isotopic and biomarker analyses to determine the gold-bearing fluid sources.
- 3D modeling of geometry of gold-bearing complexes and estimation of mineralization volume.

Conclusion

The Paleogene-Miocene complex of deposits of the South Caspian basin together with oil-generating potential has high ore (gold)-generating potential. In this connection paleo- and recent centers of katagenic discharging of gas-water-oil fluids have an important meaning. In favorable structural-lithological and geochemical conditions accumulations of ore matter are confined to them. From this viewpoint the mud volcanoes and zones of tectonic faults controlling their location have a special interest. According to geophysical and geochemical data on isotopic composition of oxygen, carbon and hydrogen of mud volcanoes waters and gases, the hearths of mud volcanoes are located on great depths – 10-12 km and their canals serve as the fluids' transportation ways (Fig. 2). Due to such great depth of fluid generation they are heated and saturated with metals.

Preliminary investigations of one of regional zones of tectonic dislocations within one of oil field confirmed our prediction about the possible formation of noble-metal (Au-Pd) and oil paragenesis in the SCB and the discovery of huge gold minerali-

zation within the oil fields. Gold is invisible and micro-disseminated in sulfides (mainly pyrite) and associates with carbonate and clay minerals.

Assessment of the gold potential of other hydrocarbon fields in the South Caspian basin will give us an unique chance to begin a new era in exploration of mineral resources in the basin which has more than 150 years history as an oil basin. We also expect that this research will give us an opportunity to contribute much in ore industry in Azerbaijan, which is an important step economic development of our country.

Investigation like this dealing the search for gold mineralization in the SCB conducted for the first time and result that we got allows us to transform oil-gas bearing basin to “gold-oil-gas bearing basin”.

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ЗОЛОТОРУДНЫЕ ПРОЯВЛЕНИЯ НА НЕФТЕНОСНЫХ ПЛОЩАДЯХ ЮЖНО-КАСПИЙСКОГО БАССЕЙНА*

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Резюме. В основу идеи золотоносности Южно-Каспийского нефтегазоносного бассейна положено представление о формировании золотоносных катагенных растворов нефтегазопроизводящими палеоген-нижнемиоценовыми отложениями, которые в полосе развития Волга-Дон-Предкавказье-Закавказье характеризуются исключительно высокой рудоносностью и вмещают комплексные сульфидно-фосфатно-редкометалльно-урановые месторождения осадочного типа. В сульфидах железа постоянно присутствуют золото, кобальт, никель, молибден, рений, реже медь, цинк, свинец и мышьяк, а в пиритовых горизонтах некоторых регионов часто обнаруживаются включения самородных металлов – золота, висмута, олова и меди.

Детальные геолого-геофизические и изотопно-геохимические исследования показали, что в Южно-Каспийском ОБ в "oil-gas window" наряду с формированием жидких и газообразных углеводородов интенсивно генерировались катагенные водные растворы, насыщенные рудными компонентами, что подтверждено высокими содержаниями и постоянным присутствием в нефтях, битумах и пластовых водах золота, серебра, меди, молибдена, цинка, мышьяка и других металлов. Это обстоятельство стимулировало изучение возможности формирования рудных скоплений в палеоочагах катагенной разгрузки флюидов. Изучение последних на одном из месторождений углеводородов подтвердило наши прогнозы о благородно-металльном и нефтяном парагенезисе в Южно-Каспийском осадочном бассейне.

В пределах зоны выявлены ураганные концентрации золота и палладия, а также индикаторов эпitherмального оруденения золота карлинского типа – мышьяка и бария. Выделений золота не обнаружено, оно невидимое, микродисперсное, ассоциирует с сульфидными минералами и рассеяно в породе.

Подобное исследование на предмет поиска золотого оруденения в Южно-Каспийском бассейне проведено впервые и полученные результаты открывают его новые перспективы как золото-нефтегазоносного. Выявленная золоторудная минерализация знаменует открытие нового генетического типа золотого оруденения в Азербайджане, известного в мире как стратиформный карлинский тип с дисперсным и низким содержанием золота, которое компенсируется большой протяженностью минерализованных зон и крупными запасами.

Ключевые слова: золото, нефтяное месторождение, минерализация, благородно-металльный и нефтяной парагенезис, центры разгрузки флюидов, геохимическая аномалия, стратиформные залежи

CƏNUBİ XƏZƏR HÖVZƏSİNİN NEFTDƏŞİYAN SAHƏLƏRİNDƏ QIZIL FİLİZİ TƏZAHÜRLƏRİ**

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Xülasə. Cənubi Xəzər neft-qaz hövzəsinin qızılı olma ideyasının əsasını neft-qaz istehsal edən Paleogen-Aşağı Miosen çöküntüləri ilə tərkibində qızıl olan katagen məhlullarının formalaşması təşkil edir. Volqa-Don-Zaqafqaziya-Xəzər yarı regionunun inkişaf zonasında Paleogen-Aşağı Miosen çöküntüləri kompleksi yüksək filiz tərkibi ilə səciyyələnir və mürəkkəb çöküntü tipli sulfid-fosfat-nadirmetal-uran yataqlarının olması ilə ifadə edilir. Dəmir sulfidlərin tərkibində qızıl, kobalt, nikel, molibden, renium, daha az mis, sink, qurğuşun və arsen bəzi regionların piritli horizontlarında isə çox vaxt xalis metallar – qızıl, vismut, qalay və mis aşkar olunur.

Geoloji-geofiziki və izotop-geokimyəvi tədqiqatlar göstərdi ki, Cənubi Xəzər hövzəsində neft-qaz pəncərəsində maye və qaz halında karbohidrogenlərin əmələ gəlməsi ilə yanaşı, filiz komponentləri ilə doymuş katagen sulu məhlulları da intensiv şəkildə əmələ gəlir və bu da neftlərdə, bitumda və lay sularında qızıl, gümüş, mis, molibden, sink, arsen və digər metalların yüksək tərkibi və daimi olması ilə təsdiq edilir. Bu hal flüidlərin katagen boşalmasının paleo-ocaqlarında filiz yığılmalarının əmələ gəlməsinin mümkünlüyünün öyrənilməsinə təkan verdi. Karbohidrogen yataqlarından birində sonuncunun tədqiqi Cənubi Xəzər çöküntü hövzəsində nəcib metal və neft paragenizi ilə bağlı proqnozlarımızı təsdiqlədi.

Zona daxilində qızıl və palladiumun qasırga konsentrasiyası, karlin tipli epitermal qızıl minerallaşmasının göstəriciləri – arsen və barium aşkar edilmişdir. Qızıl dənələri aşkar edilməmişdir, o, görünməzdir, mikrodispersdir, sulfid mineralları ilə assosiasiya olunur və süxurda səpələnmişdir.

İlk dəfədir ki, Cənubi Xəzər hövzəsində qızıl minerallaşmasının axtarışı üçün belə bir tədqiqat aparılır və əldə edilən nəticələr onun qızıl-neft-qazlı ərazi kimi yeni perspektivlər açır. Müəyyən edilmiş qızıl minerallaşması Azərbaycanda qızıl minerallaşmasının yeni genetik növünün aşkar edilməsini göstərir, dünyada dispers və aşağı qızıl tərkibinə malik stratiform karlin tipi kimi tanınan minerallaşmış zonaların genişliyi və böyük ehtiyatlarla kompensasiya olunur.

Açar sözlər: qızıl, neft yatağı, minerallaşma, nəcib metal və neft paragenizi, flüid axını mərkəzləri, geokimyəvi anomaliya, qatlı yataqlar

* Дискуссионная статья

** Müzakirə məqaləsi