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Paragenesis of Micro - and Nanominerals as Indicators of Fluid-Dynamic Conditions of Soil Formation in Oil and Gas - Bearing Intermountain Mud-Volcanic Depressions of the Baikal Region

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Abstract: ***It is shown that the soil is a mineral petrographic facie of endogenous-exogenous oil and gas bearing lithocomplexes of mud volcanoes in the South Siberian region, which belong to the fluid-dynamic systems of modern Earth degassing pipes. The fluid-dynamic regime of the latter determines wide variations of thermodynamic, physic-chemical, and geochemical conditions of soil formation. It has been established that mineral associations are formed thousand can be used as soil-genetic indicators. A number of the mineral parageneses of soil formation fluid-dynamic conditions is identified: fluid-pyrometamorphic one, appeared during recovered gases strong oxidation and natural cracking of liquid oil; fumarolesteam gasous one; heterogenization products of hot springs hydrotherm; hydrothermal-sedimentary chemogenic one involving bacterial communities.***

Keywords: parageneses, minerals, fluid-dynamic, soil

1. Introduction

The Baikal region belongs to the oil and gas-bearing provinces according to the fluid-dynamic characteristics represented by the ecological and geological system of the Earth degassing hydrocarbon branch [11], which has specific features that are of great importance for the soil covers formation.

In the 40-60 years of the XX century, through collaborative research of Soil Institute oil geologists and researchers (the USSR Academy of Sciences)it was first time established [1] "... a new important phenomenon, about the existence of which in the past only a few geochemists and soil scientists guessed as the powerful influence of oil and gas deposits on the soil, geochemical and biological processes course in the earth's crust near - surface soils and, in particular, the soil envelope". It was found that hydrocarbon flows interacting with early soil minerals associations lead to the new parageneses formation in the thickness of soil horizons. Most often, water and oil-gas fluids income to the daytime surface passes through the modern degassing channels (pipes), mainly represented by discontinuous faults, various structures of mud volcanoes, including mineral thermal and freshwater cold water sources [8, 9, 11].

During the period under review, an important mineralogical indicator of the correlation between the soil cover and the deep oil - gas deposit was established. Its essence lies in the fact that the soil is covered with a clay-carbonate forest-calcareous "cap", the boundaries of which coincide with the contour of the oil deposit. The interrelation of mineral formation processes with the activity of mud volcanoes, which periodically supply pulp, rich with water-gas-oil fluid to the forming soils was revealed.

The electron microscopic and x-ray structural investigation results of the of oil-bituminous soil clay-carbonate "caps" material composition and mud-volcanic pulp sand-clay deposits laid to the basis for a new direction in mineralogy created by I. D. Sedletsky, called as colloid-dispersed mineralogy [7].

The last decades of the past century and the beginning of the twenty-first century are marked by significant interest in the component composition study, transformation and behavior of petroleum hydrocarbons in soils. The main attention with thisis paid to the geochemical and ecological aspects of the gas-oil fluids behavior and transformation under the conditions of the generally accepted hypergene genetic model of soil cover formation. With rare exceptions, the soils formation and transformation deep endogenous factor as a result of the lithosphere cold degassing occurrence, primarily the functioning of mud volcanoes and water sources that transport oil hydrocarbons to the soil formation zones, is not considered. In light of the stated above, the continuation of interrupted for a long time started in the 40-60 years of the twentieth century specialized mineralogical studies of soil covers in Russia oil and gas areas and other countries, it seems to be a very urgent problems. A particularly important issue is the study of mineralogical indicators of the mud volcanism various forms influence on the soil formation processes. The results proposed for publication are the first step in systematic research of the Baikal region, which aims to create an endogenous-exogenous genetic concept of soil formation in the future.

2. Theoretical and methodological approaches to research of mineralogical indicators of soil formation fluid-dynamic endogenous signs

The results of joint research obtained in recent years by geologists and biologists of the Buryat scientific center of the SB RAS, as well as the discovery by soil scientists in the Barguzin depression of unusual sections in structure and material composition of bituminous soil formations that

arose on domed and crater mud-volcanic morphostructures, allowed us to propose new theoretical and methodological approaches to the study of soil formation processes.

The key unsolvable question for soil scientists today is what is considered soil and what is considered rock. As B. G. Rozanov emphasizes [5]: «Great difficulties are usually caused by determining the lower limit of the soil profile, which the soil scientist often does not even try to set, this is so debatable." As examples of such boundaries, he cites peatlands, stratified tertiary clays in the Kharga depression (Egypt), and saline soils ("Shors") of the Pre Caspian lowland, the desert salt crust, weathering crust. This situation is associated with a number of outdated erroneous geological concepts that do not allow soil scientists to reliably interpret the spatial and genetic relationships that exist between soils and associated rocks. Below there are some of them thatwe or with our participation have set in recent years:

1) Geological data clearly indicate the dominantrole ofmud volcanoes in the deserts formation. Mud volcanoes of the gas-water-lithoclastic type sporadically emit large masses of Gryphon silt-sand material to the earth's surface, which then undergoes Aeolian transport and wide area distribution [9, 11];
2) For weathering crusts, the blanket like not lithiated loose tectonomixtites referred to the dynamometamorphite group of the kakiritefacies are not rarely taken [14];
3) Temperature dualism of the cold degassing occurrence gas form [11] (gas-explosive stage of mud volcano lithocomplexes formation) [9]. It is expressed in the fact that in some cases there is a thermal effect on certain areas of land, and in others – degassing pipes, working on the principle of a refrigerator, form glaciation and permafrost areas and sections;
4) on the example of the Barguzin basin a hydrothermal origin of saline soils is set due to discharge of Kucheger thermal mineral waters source [16], which corresponds to hydrothermal-sedimentary chemogenic, with the microorganisms participation, genetic group of mud volcanoes mineral assemblages [9].

2.1 Soil - mineralogical and petrographic facie of endogenous-exogenous lithcomplexes of mud volcanic origin

Created in the mid-twentieth century, colloid-dispersed mineralogy is largely based on the investigation results of the soil formations material composition in mud-volcanic regions that are part of the gas-oil bearing provinces located in the southern part of the USSR. Their characteristic features are:

- Micro-and nano-sized individuals of dispersed particles;
- Combination in the dispersed particles composition of cryptocrystalline and amorphous phases of the same or similar chemical composition;
- The presence of visually different organic matter macromatrices of endogenous oil-gas and exogenous bacterial origin (humus), as well as hydrothermal amorphous-crystalline new formations consisting of aggregates.

All these characteristics allow us to consider soil formations as a specific mineralogical-petrographic facies of mud volcanoes endogenous-exogenous lithocomplexes in the South Siberian region mud volcanism [9], the formation of which occurs in near-surface and surface conditions of hydrothermal-sedimentary fluid-clastogenic-sedimentary lithogenesis with the leading role of chemogenic and biogenic (bacterial) mineral formation mechanisms.

2.2 Morphostructures of the soil covers and sections - coherent fluid-dynamic structures of the Earth cold degassing pipes

Natural phenomena and processes included in the concept of the Earth cold degassing are united by a number of features [11]: 1) short-term and impulsive (quasi-periodic) manifestations; 2) mainly local functioning of the model main structural element – degassing pipes (gas and gas-water-lithoclastic mud volcanoes, decompression zones, tectonic and seismotectonic disturbances, water sources, hydrocarbon deposits), which have very wide dimensions (diameter) in plan (from the first centimeters to giant ones at the Earth's poles) and to a depth (from tens of centimeters to the level of the upper mantle and below); 3) the degassing pipes confinedness not only to seismically active oceanic and continental rift zones with strong earthquakes, but also to areas with trigger seismicity characterized by weak earthquakes and short-term activation of neotectonic faults individual segments. These areas, where earthquakes with a magnitude > 3 rarely occur, are usually characteristic of platform territories; 4) mostly latent, rarely directly observed processes and morphostructures of degassing pipes active operation. We add to this that the degassing pipe is a classic example of synenergetic fractal dissipative structures in nonlinear dynamics.

Note that modern degassing pipes differ in the parameters of fluid-dynamic systems (seismicity, electrically conductive layers, geothermal characteristics, hydrogeological conditions, gas fluids composition), which they generate. Accordingly- the scale of soil formation. But at the same time they are characterized by equal or close to the landscape and geomorphological features. Thus, the central region of the Russian platform with trigger seismicity and the development of black soils on a flat terrain has now undergone hydrogen degassing with the morpho structures formation of various sizes degassing pipes, which changed the flat terrain and negatively affected the early black soil cover [4]. The largest crater like mud-volcanic structures with a diameter of 2.5-3 km and a depth of 2.5-3m quickly swamp. Their drilling showed a complete absence of black organic matter in the underlying soils. At the same time, it is noted that smaller saucer shaped modern crater morphostructures with a diameter of 50-150m are laid on Cretaceous sands. If within the mud-volcanic structures of large-scale hydrogen degassing, forest and forest plantations die, grass stops growing in places, then many hundreds of small-sized saucer-shaped depressions in the Cretaceous sands are overgrown with shrubs and forest [4]. From this, we can conclude that hydrogen degassing pipes play a constructive role in soil formation, similar to degassing pipes with other characteristics of the fluid dynamic functioning mode. In this regard, let’s consider an example

of the Baley degassing pipe, the unique in time duration functioning interval, which started 140 million years ago and has not continued to this day, confined to the Unda-Dayadepression of the Transbaikal territory, identified by our research [10]. This structure is notable for the fact that in a vertical section with a thickness of about 450 m of the lower Cretaceous mud-volcanic lithocomplexes, according to the drilling data 9 paleosoilshorizons were revealed and fixed by the presence of burned organic wood vegetation accumulations in the core, similar to what is currently happening during hydrogen degassing on the Russian platform [5].The fluidodynamic system of the Baley degassing pipe has the following main characteristics: 1) the depth of the hearth is 6-7 km with a heat flow of 60 mW/m2 and the hearth zone temperature is 100-120° C; 2) PT formation conditions: P 3300-15 bar, T^0 ≥1000 – 70^{0}C; 3) variability of the C – O – H – N – S fluid system from restored to highly oxidized one; 4) wide distribution of carbonaceous matter in mud-volcanic lithocomplexes and their constituent minerals in solid (according to Romanov spectroscopy, a graphite-like substance that arose from the fluid phase, tectononaphtoid close to shungite), liquid and gaseous forms. From the point of view of nonlinear dynamics, 9 paleosoil plant horizons form a subharmonic bifurcation morphostructure close to the periodic one, which fixes 9 cycles of the degassing pipe lithocomplexes formation with the final coherent soil-plant formations.

3. Methodology of mineralogical investigations

Given above in section 2 theoretical and methodological ideas have been the basis for the soil study as a bio-inert lithologic-petrographic facie of mud volcanic lithpocomplexes and fluid-dynamic component of ecological-geological system model of the Earth cold degassing in Transbaikalia. Inland riftogenesis

Table 1: Baley degassing pipe characteristics

Lower Cretaceous morphostructures	Dimensions in plan, (depth)	Gas fluid[3] composition (%) and lithocomplexes	Depth marks (m) of detritus accumulation in core [2]
Dome one Baley Dome one Taseevo	1.1 x 1 km (180m) 1.9x1.6 km (180m)	$N_2$24-75, $H_2$11-52 (CO_2 + H_2S) 12-22 Geyserites and pelito-siltstone psammitic rocks	55 107.9
Deep crater-type morphostructure	Estimated sizes more than 3x2.7 km (180-600m)	N_2 39-47, H_2 25-36 (CO_2 +H_2S) 19-27, Hydrocarbon gases with CH_4 1.3-4.3 Carbonated psammitic psephite and brecciated rocks	201.7 308.6 349.3-542.3 355.4 402.3 416.5-411.3 448.6-447

When considering soil formations as specific rock lithocomplexes of mud volcanoes, the same material composition investigation method of both was used. It differed somewhat in the samples preparation for the study of loose sediments, including humus, and massive rocks , among others those contained in the form of relatively large fragments in a loose binding mass.

In the first case, schlich testing was carried out. At the initial stage of their preparation, they were elutriated in standing water, separated into a light clay fraction containing fragments of organic matter floating in the water (bacterial mats, bitumen). Then the schlich samples elutriated fraction was washed on a tray with the release of heavy (mainly ore minerals) and light fractions. A very useful operation is the phytoshlichs selection [13] in order to identify the mineralogical and geochemical features of the soils humus component inherited from the subjected to aging, destruction, and death woody vegetation that the humus was formed from. Phytoschlich samples were also washed in a tray with a selection of mineral substrate without division into light and heavy fractions. In the second case were selected and manually crushed mineralogical samples – rotolock (artificial concentrates), petrographic thin sections were made. Samples artificial heavy mineral concentrate was subjected to elutriation and washing in the same way as placer samples from unconsolidated lithocomplexes.

The washed material of schlich light and heavy fractions was subjected to magnetic and electromagnetic separation. For the minerals diagnosis the weighting material of schlich various fractions mentioned above and petrographic polish sections were used. A complex of methods was used, including traditional mineralogical and petrographic (optical with binoculars and polarizing microscopes, immersion, x-ray diffraction, quantitative chemical and spectral analyses) and modern microprobe, electron microscopic types of analysis, as well as Romanov spectroscopy. Data from microprobe and electron microscopic determinations of the elemental composition of organic mineral colloidal-crystalline micro-and nanoparticles extracted from schlich samples fractions detected in petrographic sections were calculated for standard mineral phases [9, 10, 12, 15]. In future researches, the authors also propose to use standard calculations based on the gross chemical composition of the schlich samples thin-elutriated light fraction using the NORMA computer program developed for studying soil horizons and sections in Northern Europe [6].

4. The Research Results

4.1. Soil forming morphostructures of mud volcanoes - model objects for mineralogical investigations

In the South Siberian mud volcanic region, the formation of modern positive relief microforms with soil "caps" is very

widespread, which is an activity consequence of mud microvolcans. These microforms form biaxial domed and stalagmite-like columnar structures [15] confined, respectively, to two different types of landscape-geomorphological settings that characterize the mud-volcanic relief of the Transbaikalia depressions: lake-swampy and dry-hill. Differences in the morphology, size, and material composition of dome and columnar microforms are mainly determined by the fluid-dynamic characteristics of mud volcanism occurrence and thedevelopment scale of bacterial communities correlated with them. Both varieties, positive with microstructures soils are covered with vegetation, eventually partially turning into phytogenic hummocks (figure 1.).

Figure 1: Soil and vegetation hummocky relief formed by domed structures of mud microvolcanism on the eastern coast of the gulf Proval near the Oymurvillage. Morphostructures appeared during the Baikal earthquake on August 29 – 30, 1959

The considered spatially close structures create landscapes in the form of separate fields or peculiar covers of considerable size (figure 1), and they occur singly too. Some of these mud microvolcanism micro structures do not have a vegetation cover, since their formingis completed by the formation of carbonate-salt crusts.The structure and genetic model of the dome-shaped morphostructures formation are shown in figure 2, and their mineral composition is shown below[15]:1) biogenic macro – and trace minerals resulting from the participation of microorganisms: pyrite,magnetite, hematite, goethite, hydrocassiterite, diasporas, calcite, oligonite, pistomesite, sideroplesite, mesisite, the K-feldspar, albite, quartz, chlorite, chloritoid, muscovite, kaolinite, apatite, fluorapatite, xenotime, gypsum, anhydrite, barite;2) regulatory nanomineral of bacterial films: sphalerite, halite, sylvite, lawrencite, hydrophilite, chlormagnesite,molisite, goethite, calcite, siderite, dolomite, magnesite, witherite, calicinite, indigirite, nahcolite, albite, anortite, the K-feldspar, barium K-feldspar, sphene, tremolite, quartz, muscovite, kaolinite, pyrophillite,makatite, norbergite, ferripirofillite, paragonite, apatite, chlorapatite, strengite, bobierrite, anhydrite, gypsum, barite, szomolnokite, melanterite, jarosite, kiserite, mirabilite, tenardit, leonhardite, mercallite, alunite;3) microminerals,appeared with the active participation of mud-volcanic fluids gas components: Fe, Au, Cu-Zn, Al, Pb,anorthite, oligoclase, distene, wollastonite, olivine, enstatite, ferrosilite, pyrope-almandine garnet), cordierite; 4) the same standard nanominerals: Fe, Al, Si, carbides, (Fe-Si-Ti), hamrabaevite, cogenite, moissanite, rutile, ilmenite, arizonite, magnetite, magnesioferrite, hematite, iocite, spinel, hercynite, chromite, tugarinovite, baidellite, corundum, lime, periclase, anorthite, andesine, barium K-feldspar, quartz, ferrosilite, rhodonite, pyrope, tremolite. These lists of minerals partially include xenogenicsphene, feldspars, quartz, chlorite, chlorite, tremolite, magnetite, ilmenite, muscovite, corundum.

Figure 2: Model of a soil dome morphostructure formation on the example of the Baunt depression. Stages: A – the formation of gryphon seeps in the lumpy mud volcanic structures of fluid clastogenicpelito-psammitiematerial. Its covering is a black silt saturated with microorganisms; B – transformation of the pelito-psammitegryphon structure into a dome structure (growth in breadth and up) as a result of cyanobacterial mat active formation, intensive formation of bacterial organomineral aggregates in the structure surface part, under conditions of the gryphon water outpouring damping, blockage of the gryphon channel; B – conversion of a dome structure in a normal swamp soil-plant hummock associated with the soil microorganisms functioning.

4.2 Micro – and nanominerals parageneses- fluid dynamic conditions indicators of soil formation

As it was shown above, a characteristic feature of the modern degassing pipes functioning is a pulsed, short – term and locally manifested fluid dynamic regime that determines wide variations in thermodynamic, physico-chemical, and geochemical conditions for the formation of soil covers and sections. It has been established that at the same time mineral associations are formed that can be used as soil genetic indicators. The following mineral parageneses of fluid dynamic conditions of soil formation are distinguished:

- Fluid-pyrometamorphic, resulting from the oxidation of hydrocarbon gases, natural cracking of liquid oil: graphite, native Au, Pb, Fe, Cu, Si, Fe – Mn –Cr-Ni, Ni-Cu alloys, moissanite, cogenite, chromspinelide, ilmenite, iocite, lime, rutile, corundum, stavrolite, mullite, sillimanite (or disten, andalusite), topaz, plagioclase, pyroxene, garnet, amphibole.
- Fumarolic steam-gaseous: carbon black graphite, native sulfur, hematite, rutile, opal, chalcedony, anhydrite, gypsum, Na and Ca chlorides, lavrensite, bischofite, ammonia, analcime.
- Product of hydrothermal fluid (thermal waters) heterogenization with separation of water, gas and oil components: native Fe, Au, Ag, Pb, Cu-Zn intermetallides, goethite, hydrogoethite, psilomelane, Ni-cuprite, manganoilmenite, hematite, pyrite, marcasite, galenite, cinnabar, plagioclase, quartz, opal, chalcedony, chlorite, hydromicas, illite, smectite, kaolinite, boehmite, nahcolite, calicinite, calcite, siderite, dolomite, ankerite, cerussite, smithsonite, apatite, water phosphates, barite, anglesite, Fe sulfates, jarosite, gypsum.
- Hydrothermal-sedimentary chemogenic with the participation of microorganisms: native Pb, Ni, Zn, Cu,

Au, Ag, electrum, intermetallics Cr-Fe, Ni-Cu, Cu-Zn, Fe-La-Ce-Si, Ce-La-Nd-Pr, cogenite, magnetite, hematite, maghemite, povellit, scheelite, pyrite, sphalerite, argentite, cinnabar, metacinnabar, montroydite, massicot, uraninite, altait, quartz, opal, zeolites, chlorite, smectite, hydromica, calcite, aragonite, dolomite, lantanite, cutinite, thermonatrite, sylvite, halite, carnallite, bismoclite, glauberite, barite, gypsum, tenardit, jarosite, schairerite, phosphosiderite, lewnarkite, apatite, gorceixite, fluorite.

5. Discussion of results and main conclusions

The main endogenous factors in the formation of soil landscapes, morphostructures, costruction and material composition of sections are:

- Flow of deep water, oil, gases and fine rock material to the day surface in the soil formation zone;
- Paragenetic correlation between such main elements of the soil bio-inert systems as microorganisms – humus – petroleum bitumen – thermal water. However, since according to our ideas the soil is a near-surface, mineralogical-petrographic facie of mud volcanoes endogenous-exogenous lithocomplexes, a significant proportion of the mineral parageneses highlighted in section **4.2** belongs to bacterial minerals.

Thus, a comparison of the minerals species composition diagnosed in dried fragments of bacterial mats from deposits of gryphon waters and mud-volcanic depressions thermal springs [12] with a set of indicator minerals showed that more than 30% of the latter have bacterial genesis. It should be notedhere that the most important factor in the crystallization of micro and nanominerals in bacterial mats, in soils forming on the earth's surface is the evaporative geochemical barrier. We have shown above that during the formation of soil-forming positive morphostructural constructions as a result of mud microvolcanism, the number of bacterial mineral species can reach at least 50% of the total number of minerals in these formations. It is known that humus is formed during the destruction and transformation of biota residues by bacteria, primarily woody vegetation. At the same time, a very important but practically unexplored issue is the study of the mineralogical specificity of the protohumus wood substrate subjected to bacterial destruction and decay and its inheritance by humus. First attempt with the participation of this paper authors to resolve this issue was implemented in the investigation of the 12 kg phytoschlich sample mineral composition, from rotten heartwood of pine stump from the Mykert-Sanzheevka deposits (Pb, Zn, Ag, Au, PGE) soil and vegetation cover [14]. About 30 micro- andnanominerals, representatives of five different classes (native elements, sulfides, galenides, oxides, silicates, phosphates and carbonates) were diagnosed in the washed fraction of the phytoshlich sample. Including all the main ores minerals of the deposit (precious metals, quartz, calcite, dolomite, etc.) passed into the soil layer without changes, among them humus, but the other part (pyrite, pyrrhotite, galenite, sphalerite, magnetite) was transformed first into oxidized phases, then adding soil mineral associations.

A feature of Transbaikaliamud-volcanic soil-forming morphostructures is the gas-oil fluids participation in their formation, which often lead to the death, in particular, the combustion of bacterial clusters, and the transformation of their biomass into crystalline carbon. Specific micro-and nanomineral fluid - pyrometamorphic associations: native elements (Cr, Au, Ag, Cu, Pb, Zn, S, graphite), intermetallides (Fe-Cr-Ni, Ti-Fe-Cr, Ti-Cr, etc.), oxides (lime, corundum, cristabolite, etc.) are formed in the areas where bacterial mats intersect with microchannels through which gas-oil fluids enter, due to the temperature transformation of living matter, releasing from it, as well as the additional introduction of many chemical elements, dispersed amorphous and crystalline compounds by fluids

5.1 Conclusion

In the submitted article, the soils of oil and gas-bearing intermountain depressions of the Baikal region are considered as a bio-inert lithological-petrographic facie of mud-volcanic lithocomplexes and a fluid-dynamic component of the ecological-geological system model of the Earth cold degassing of intracontinental rift-genesis. Belonging to a single dispersed mineralogical-petrographic rock substance of mud-volcanic origin it characterizes the bifurcation stages of the biosphere-lithosphere interaction of nonlinear pulsation development of fluid-dynamic systems known to oil geologists as degassing pipes. The result of this interaction is reflected in the uniqueness of the mineral parageneses of endogenous-exogenous origin presented by the authors.

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