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Composition And Morphology Of Metal Microparticles In Paleozoic Sediments Of Caspian Depression

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Abstract- Using the microprobe analysis 18 samples of metallic micro-particles were studied (spheres, plates, coils, wire) from Paleozoic deposits of the Caspian basin. The morphology of the microparticles and their chemical composition showed that the microparticles have different origins. The formation of spiral and wire type forms is associated with volcanic activity, and magnetite microspheres were formed in the Earth atmosphere during the flight and meteorite ablation. It is determined that Mn (0.8-2%), rarely Cr is uniformly distributed in magnetite microspheres. In the interstices of magnetite tablets the releases of native nickel, nickel oxides, the awaruite of Ni3Fe are met rarely. Among the spiral formations the intermetallic compositions of Fe-Cr-Mn and Fe-Cr-Ni are met and the mechanism of their formation in the development of subvolcanic chamber is proposed. The diagrams lg (Cr/Ni) - lg (Cr/Mn) and lg (Fe/Cr) - lg (Fe/Ni) allow to reveal the geochemical differences of metallic microparticles of volcanic and cosmic origin. The metallic microparticles discovered in sedimentary rocks, may be an additional tool for regional parallelization of multipartite cuts, may lead to the revision of biotic process models, the assessment of terrestrial and cosmic processes impact on them, help in the search for hydrocarbon deposits and stratified deposits of solid minerals.

Keywords: sedimentary rocks, the Caspian basin, microspheres, spiral formations, intermetallic compounds.

1. INTRODUCTION

During recent years the increased interest of geologists to the survey of exotic metal microparticles (up to 1 mm), contained in sedimentary rocks [1; 2; 3; 4], is conditioned by several reasons. Firstly, such objects may help in the study of the earth (in the case of their endogenous origin) and space processes degree on the biotic crises in the Phanerozoic history of the Earth. Second, they are related with the prospects of ultraprecise stratigraphic correlations performance of different scale [5; 6; 7; 8; 9; 10].

The metallic microparticles are formed by various processes: space [2; 5], technological and endogenous ones. The latter may be associated with volcanic activity, hydrothermal and fluid emanations in sedimentary layers [3; 11; 12]. In order to cognize the history of the Earth and stratigraphic correlation the greatest interest is presented by the microparticles of space and of volcanic origin, as they carry the information about the short-term (often catastrophic) processes which take place in the geological past. The space metallic formations are probably the particles of meteorite dust formed as a result of the of the Earth surface bombing by celestial bodies and are often confined to the stratigraphic boundaries of different ranks [5]. The amount of substance which drops down on Earth each year from outer space in the form of meteor dust makes no less than 4 million kg. [13; 14; 15]. The formation of magmatic microparticles could occur at the moment of volcanic ash release into the atmosphere, and during undersea eruptions. The metal particles may be of various origins may be quite identical by shape [3]. Therefore, in order to establish the nature of metal particle origin the simple description of their external form is not enough. In addition to morphological studies, the knowledge about the chemical composition of these objects is required that will allow to develop more precise geochemical criteria by which the genetic conclusions will be possible.

2. SUBJECT AND METHODS OF RESEARCH

The object of the study were the metal microparticles, extracted from the upper Paleozoic sediments of the Caspian Basin (north-eastern part of the Caspian Sea). The material was selected from the powder of micropaleontological samples and was analyzed by microprobe in the laboratory of the scanning electron microscopy of the interdisciplinary center "Analytical Microscopy" of Kazan Federal University using the automated system of mineralogy «QEMSCAN» and a field emission scanning electron microscope "MERLIN" Sarl Zeiss, equipped with energy dispersive spectrometer «AZTEC» X-MAX Oxsford Instruments (the accelerating voltage of 20-25 kV, the working section of 10-24 mm, the sensing locality of 1 micron, the accuracy of chemical element measurement makes 0.1-1%).

The upper Paleozoic deposits in the Caspian basin lie at great depths (up to 4.5 km), which allowed us not to consider the hypothesis of a man-made origin of microparticles in this work. The occurred metal formations (microspheres, plates, spirals, wire) have the size from 10-20 microns to 1 mm, and are combined in two groups. The first group included magnetite microspheres supposedly of cosmic origin; the second one is presented by mretallic particles of volcanic (?) origin various by form and composition.

The magnetite microspheres of the Caspian depression are almost perfectly spherical formations with the diameter of 170-950 microns at an average value of 425 mm (Fig. 1). They exceed similar object 5-10 or more by size in comparison with the similar objects from other regions [2; 5, etc.]. They have a steel-gray color, metallic luster and a various relief surface ("takyrs", tablets, projections, triangular depressions, etc..). This difference in size may be related to different technology of sample preparation. We used a dissecting needle and a permanent magnet, and in the cited studies the allocation of microspheres occurred in an aqueous medium by the means of a powerful neodymium magnet. An ideal spherical shape of these facilities, along with a textured surface, is one of the evidences of their cosmic origin [1; 2].

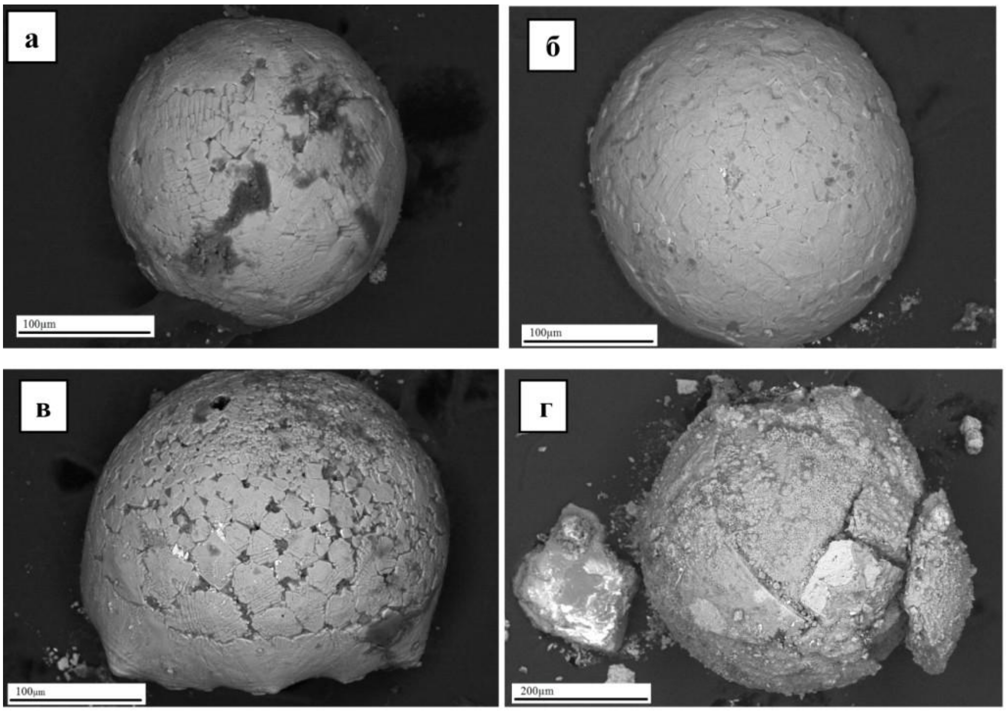


Fig. 1. Magnetite microspheres of Caspian depression
а - sample 1, б - sample 2, в - sample 3 г - sample 4. The composition - see Table 1.

3. RESULTS AND ITS DISCUSSION

The analysis of the microspheres elemental composition shows (Table 1) that they consist of a polycrystalline aggregate of magnetite (Fe_3O_4) and wustite (FeO); perhaps there is a small proportion of native iron in the form of separate tiny particles magnetized to microspheres. This mineral composition is characteristic of the stony meteorite metal part [1] and confirms the conclusion that the meteorites contain a very small number of mineral-forming elements (less than 4), compared with terrestrial minerals - more than 4. The iron oxides of microspheres has an evenly distributed manganese (0.8-2 %), and in rare cases it has chrome. Titanium is absent in microspheres, and Si, Al, Ca, K is present in small quantities (see Table 1). The nickel inclusions are found in the interstices of magnetite tablets: native nickel, nickel oxides, awaruite (Ni_3Fe). According to all these parameters the microspheres of Caspian depression may be attributed to the objects of cosmic origin [1; 6].

In addition to microspheres the studied rocks revealed various metal particles of oxygen free alloys by shape and composition (intermetallic compounds): Fe-Cr-Mn and Fe-Cr-Ni (Fig. 2, 3, Tabl. 2, 3). In order to establish the geochemical differences of metal particle genesis, we compared their elemental composition with the composition of meteorites according to literature sources [16; 17; 18]. At that the logarithms of Fe, Cr, Mn, Ni concentration ratios are used. The obtained data are brought to the diagrams (Fig. 4, 5), where the average compositions of meteoric matter, ultrabasic and basic rocks are shown, as well as the composition of volcanic exhalations of Big Tolbachinsky eruption [18].

For the formation of the studied metallic microparticles one may propose a mechanism which is described below, and these processes are thoroughly described in [16]. Andesitic and basaltic volcanism is a dominating one in the world, and the source magmas are generated in the mantle at a partial (fractional) melting of its constituent rocks under the influence of hot ascending fluids that bring in the nucleus of magma formation not only heat, but also low-melting and incompatible mantle elements. Therefore a magmatic smelting is enriched by Fe, Cr, Mn, Ni, and often by Zn, Cu and other elements. Going up, such magma develops subvolcanic foci.

The subvolcanic outbreak has a fluid-magmatic differentiation of the melt, in which magma is enriched in top part of the chamber by fluid and fusible elements. At the same time the fluid pressure increases, which will significantly exceed the pre-explosive phase of a lithostatic pressure. Here, in the terms of gas fluid (with an increased pressure) containing hydrogen, a fluid-magmatic differentiation of melt with the isolation of metallic melt drops takes place, as shown in model experiment [16].

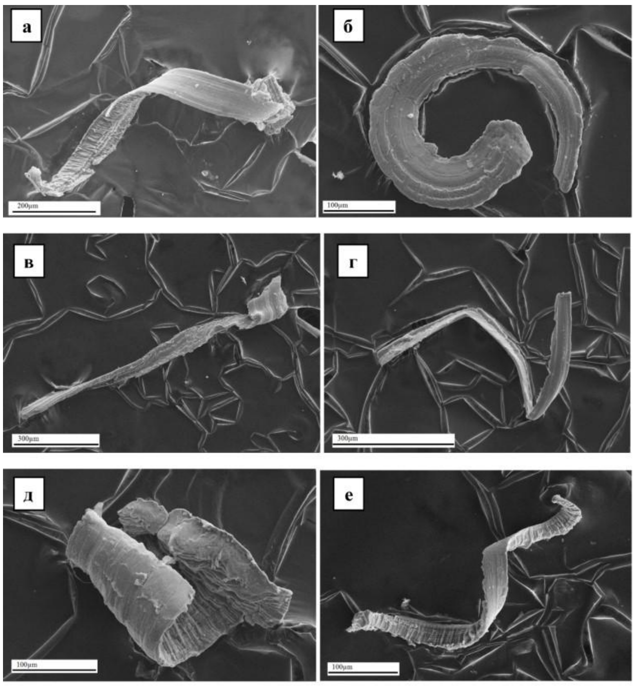


Fig. 2. Spiral intermetallic compounds of Caspian depression
a - sample 1, б - sample 2, в - sample 3, г - sample 4, д - sample 5, е - sample 6.
The composition of the sample, see. Table 2.

Table 1. Composition of magnetite microspheres, wt. %

Sample	Fe	O	Mn	Cr	Al	Si	Ca	K
1	68.26	23.49	0.57	0.20	0.06	0.82	2.27	1.14
2	71.08	23.89	0.44	н. о.	0.32	1.46	0.80	н. о.
3	75.56	22.59	н. о.[1]	н. о.	0.16	0.39	0.53	0.19
4	72.91	22.66	0.21	н. о.	н. о.	0.33	2.83	0.34
Average	71.95	23.16	0.31	0.05	0.14	0.75	1.61	0.42

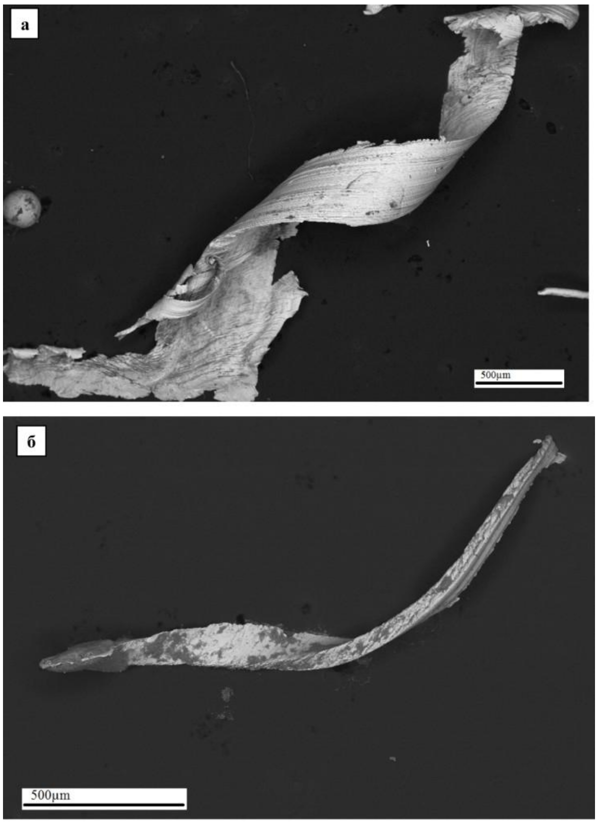


Fig. 3. Spiral compounds of Caspian depression

a – sample 1, б – sample 4. The composition of the sample, see Table 3.

[1] n. d. (here and then) – not determined

Table 2. Spiral particle composition of intermetallic compounds, wt. %

Sample	Fe	O	Cr	Ni	Si	Al	S	Mn	Other
1	53.21	6.18	10.83	0.85	4.31	2.11	н.о.	16.17	К -1.04 Ca-0.26 Na-3.01 Mg-1.35
2	57.89	0.58	17.59	1.88	0.64	н.о.	0.27	21.14	n. d.
3	61.19	1.08	17.77	3.04	0.76	0.22	0.27	15.69	n. d.
4	59.03	н.о.	17.48	1.77	0.49	0.06	0.25	20.92	n. d.
5	58.67	0.37	17.52	1.97	0.35	н.о.	0.19	20.94	n. d.
6	58.51	1.25	17.34	1.70	0.23	0.03	0.20	20.74	n. d.
Average	58.08	1.58	16.42	1.87	1.13	0.40	0.20	19.27	

The fluid starts to seep via rock cracks and pores with the latter clogging the mouth of the volcano, due to the high fluid pressure exceeding lithostatic one. During the infiltration and cooling the molten metal droplets give rise to the formation of metal plates, chip, spiral, wire formations and possibly spheroids. According to the composition the most part of these entities will correspond to metal alloys (intermetallides), native metals, and sometimes under favorable redox conditions to spinel-type metal oxides (magnetite, chrome spinel, etc.). The subsequent volcanic explosion, caused by increasing fluid pressure, throws into the atmosphere the metallic microparticles accumulated in the volcano crater in the form of volcanic ash. The molten metal droplets which were not solidified are ejected with ash, cooled in the atmosphere, form microspheres, preferably of magnetite composition. All these microparticles are deposited on the earth surface, they are buried in sediments and develop an exotic association of metal structures by its composition and form [3]. A similar mechanism of formation is offered by some researchers [11] for the metal particles of volcanic rocks within the seamounts in the Sea of Japan. The presence of metals in gas condensates exhalations of Big Tolbachinsky eruption (mg/l): Fe - 32, Cr – 0,39, Mn – 0,36, Ni – 0,36, Zn - 33, Cu – 6,4 may be confirmed by the possibility of metallic microparticles formation due to volcanic processes [17].

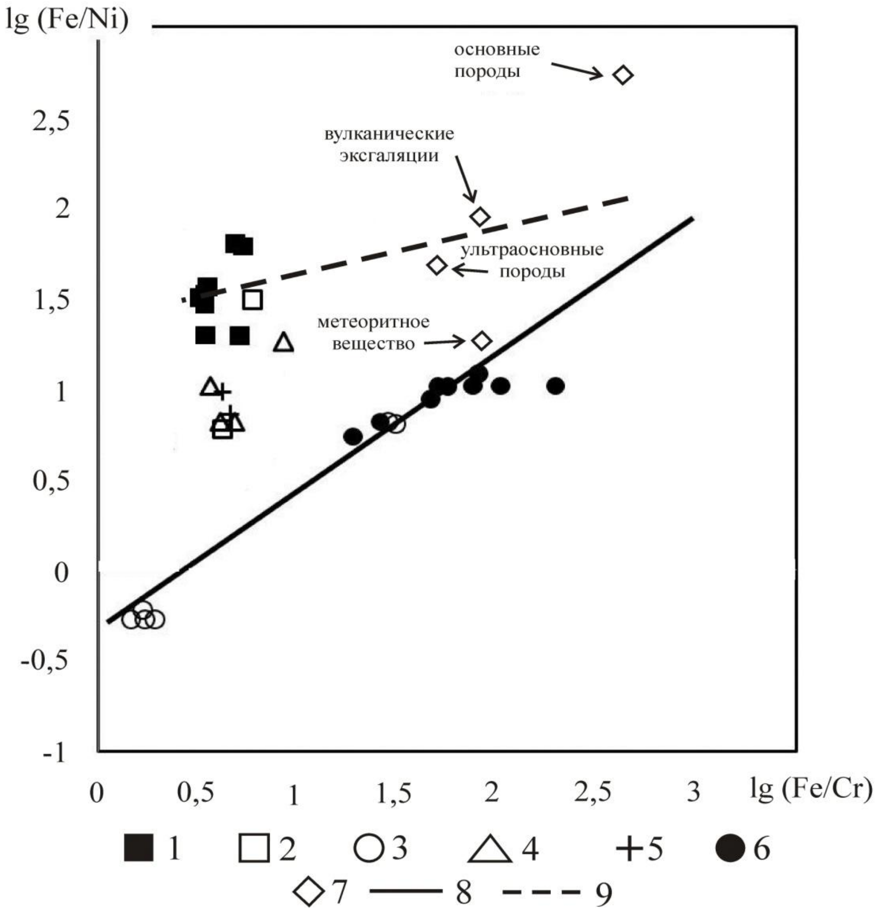
Table 3. The composition of metallic microparticles, wt. %

Sample	Fe	O	Cr	Ni	Si	Al	S	Mn	Other
Spiral formations									
1	42.93	24.91	14.87	1.40	0.58	0.14	0.14	14.21	K-0.13 Ca-0.36 Na-0.14 Mg-0.02 Cl-0.18
2	43.12	24.86	14.98	1.61	0.45	0.12	0.17	14.17	Ca-0.23 Na-0.17 Cl-0.12
3	41.31	25.43	14.19	1.25	0.84	0.17	0.30	13.21	K-0.27 P-0.11 Ca-1.83 Na-0.35 Mg-0.39 Cl-0.36
4	51.13	25.49	11.76	2.80	1.35	0.34	0.13	n. d.	Cu-1.83 Ca-4.15 Na-0.22 Mg-0.66 Cl-0.14
5	67.55	24.13	4.20	н.о.	0.94	0.27	0.21	1.07	P-0.27 Ca-0.73 Na-0.15 Mg-0.30 Cl-0.17
6	27.64	27.45	10.38	0.96	1.97	0.44	0.38	11.11	K-0.37 Ca-15.97 Na-0.90 Mg-1.93 Cl-0.50
Average	45.61	25.38	11.73	1.34	1.02	0.25	0.22	8.96	
Wire type formations									
7	52.62	24.37	14.47	6.85	0.29	n. d.	n. d.	1.34	Ca-0.05
8	51.81	24.44	13.70	5.58	0.43	n. d.	n. d.	1.11	Ca-0.29 K-0.17 Na-0.47 P-0.14 Cl-0.11 Cu-1,75
Average	52.22	24.41	14.09	6.22	0.36	n. d.	n. d.	1.23	

As can be seen, the composition of these precipitates is in a good agreement with the composition of the metallic microparticles that are considered in this and other studies [2; 3].

It is impossible to refer the spiral formations of 2 mm (Fig. 3) found by us to space objects, because these particles may melt and evaporate during a flight through the atmosphere. The highest temperatures during the passage of a micrometeoroid through the earth atmosphere are achieved at the speeds of 30 km/s, and make about 1800 °C that at the entrance angles less than 50° concerning the normal to the earth surface results in complete evaporation of particles. The high speed of fragment rotation ejected from the volcano crater, results in the appearance of helical structures. On the other hand, smaller coils may have a space origin as the rotational momentum may be obtained by the particles at the entrance to the atmosphere.

The developed diagrams (Fig. 4, 5) show that the composition of sediment microparticles in geochemical respect is significantly different from the composition of meteoritic material. They are closer to ultramain and main rocks and volcanic exhalations by composition. The metallic microparticles of volcanic origin develop a separate field separated from the cosmogenic microparticles. At that the cosmogenic particles have a common evolutionary trend (Fig. 4) or a single field (Fig. 5) with meteorites. The theoretical basis of these typomorphic geochemical differences is the different nature of space and volcanic material evolution. The composition of cosmic matter is determined by the composition of protosolar haziness material. The original composition of the volcanic material was determined by the composition of the substrate rocks, the degree of their fractional melting and fluid-magmatic interactions in the centers of magma formation within the progressive stage of the magmatic process development. Then, in the subvolcanic magma centers during the regressive stage of the magmatic process, a further fluid-magmatic differentiation of magma substance took place with the isolation of molten metal droplets. Different starting composition and different ways of volcanic and cosmogenic substance evolution and had to produce their distinctive geochemical features. Therefore, in order to identify the geochemical differences



основные породы - basic rocks / вулканические эксгаляции - volcanic exhalations / ультраосновные породы - ultrabasic rocks / метеоритное вещество - meteorite matter

Fig. 4. Diagram lg (Fe/Cr) – lg (Fe/Ni) of the metallic microparticles and meteorite composition

1 - our data concerning spiral microparticles; 2-5 - the particles from works: 2 - [11], 3 - [12], 4 - [2] 5 - [4]; 6 - meteorites according to [16; 17; 18], 7 - the average composition of meteoritic matter, magmatic rocks and volcanic exhalations according to the data of [17], 8 - meteor trend, 9 - volcanic trend.

of metallic microparticles of volcanic and cosmic origin we propose to use the method of diagram construction and analysis lg (Cr / Ni) - lg (Cr / Mn) and lg (Fe / Cr) - lg (Fe / Ni), tested in this paper.

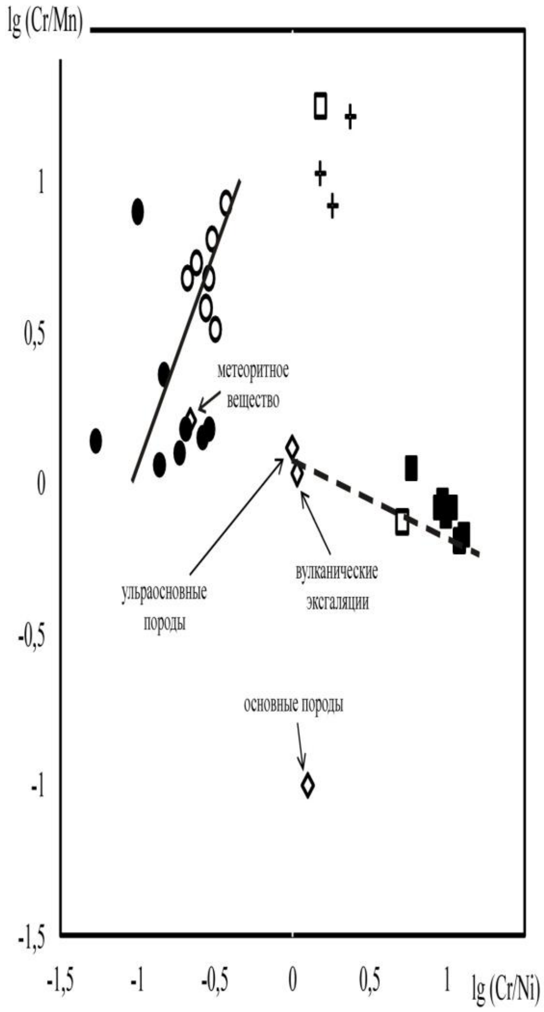


Fig. 5. Diagram lg (Cr / Ni) - lg (Cr / Mn) of metallic microparticles meteorite composition Designations, see fig. 4.

4. CONCLUSION

1. The data on the microstructure, chemical and mineral composition of metal microparticles may help to decode their genesis.

2. Using the microprobe studies and the construction of chemical diagrams the possibility of volcanic and cosmic samples separation was shown.

3. The mechanism of intermetallic compounds formation during the development of subvolcanic chamber was proposed.

4. Metal microparticles may act as an additional tool for stratigraphic correlation of layers with different facies.

Summing up the abovementioned things, we may conclude that the studied metal microparticles of Caspian depression have different origins. So the formation of spiral and wire forms is associated with volcanic activity, and magnetite microspheres were formed in the Earth atmosphere during the flight and ablation of meteorites. The mechanism of intermetallic compound formation at the development of spiral subvolcanic chamber is offered, which is confirmed by the data on modern volcanic eruptions. The metal microparticles discovered in sedimentary strata, irrespective of their origin, may be an additional tool for the regional parallelization of polyfacy cuts, may help in the search for hydrocarbon deposits and stratified deposits of solid minerals.

6. ACKNOWLEDGEMENTS

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REFERENCES

[1] Grachev A.F. The nature of cosmic dust in the sediments // The physics of Earth - 2010. - № 11. pp. 3-13.

[2] Korchagin O.A. The presence of metallic microspheres and microparticles in the early Cenomanian stage of Crimea - "the cosmic dust event" // Reports of the Academy of Sciences. - 2010. - V. 431, № 6. - pp. 783-787.

[3] Karpov G.A., Mokhov A.V. The microparticles of native metals, sulphides and oxides in andesitic volcanic ashes of Karymsky volcano // Volcanology and seismology. - 2010. - № 3. - pp. 19-35.

[4] Sungatullin A.D., Bakhtin A.I., Tsel'movich V.A., Sungatullina G.M., Glukhov M.S., Osin Yu. N., Vorobiev V.V. Nickel-iron microparticles in sedimentary rocks as the indicators of cosmic processes // Scientific notes of the Kazan University. Natural Sciences. - 2015b. - V. 157. - Book 3. - pp. 102-118.

[5] Grachev A.F., Korchagin O.A., Tsel'movich V.A., Kollmann H.A. Cosmic dust and micrometeorites in the transitional layer of clays at the Cretaceous-Paleogene boundary in the Gams section (Eastern Alps): morphology and composition // Physics of Earth - 2008. - № 7. - pp. 42-57.

[6] Sungatullin A.D., Sungatullina G.M., Osin Y.N., Trifonov A.A. Cosmic matter in the oil deposits of the Middle Caspian // Oil Industry. - 2014. - № 9. - pp. 77-79.

[7] Sungatullin A.D., Sungatullina G.M., Mikhail Glukhov, Osin Yu.N., Vorobiev V.V. The possibilities of space microspheres use when the correlation of oil and gas deposits takes place. // Oil Industry. - 2015a. - № 2. - pp. 16-19.

[8] Ebihara M., Miura T. Chemical characteristics of the Cretaceous-Tertiary boundary layer at Gubbio, Italy, Stevns Klint, copper, gold, dust, cerium // Geochimica et Cosmochimica Acta. – 1996. - V. 24. - P. 5133–5144.

[9] Miono S., Nakayama Y., Shoji M., Tsuji H., Nakanishi A. Origin of microspherules in Paleozoic-Mesozoic bedded chert estimated by PIXE analysis // Nuclear Instruments and Methods in Physics Research. - 1993. – V. 75. – P. 435–439.

[10] Schmitz B., Lindsröm M., Asaro F., Tassinari M. Geochemistry of meteorite-rich marine limestone strata and fossil meteorites from the lower Ordovician at Kinnekulle, Sweden // Earth and Planetary Science Letters. - 1996. – V. 145. - P. 31–48.

[11] Astakhova, N.V., Kolesnik O.N., Sedin V.T. Ore mineralization in volcanic rocks of seamounts of the Sea of Japan // Geochemistry. - 2014. - № 2. pp. 158-177.

[12] Goleva R.V., Lugovskaya I.G., Melnikov M.E. On the genesis of "space balls" in iron manganese ores of

the World ocean // Patriotic geology. - 2014. - № 1. - pp. 55-61.

[13] Barabanov V.F. Geochemistry. - L.: Nedra, 1985. - 423 p.

J., Muller R.A., Asaro F., Ram M., Stolz M.R. Extraterrestrial accretion from the GISP2 ice core // Geochimica et Cosmochimica Acta. - 2003. - V. 67. – P. 751–763.

[16] Marakushev A.A. Petrology. - M.: MSU, 1988. - 309 p.

[17] Handbook on geochemistry / G.V. Voitkevich, A.V. Kokin, A.E. Miroshnikov, V.G. Prokhorov. - M.: Nedra, 1990. - 480 p.

[18] Henderson P. Inorganic geochemistry. - M.: Mir, 1985. - 339 p.

[14] Sobotovich E.V. The cosmic substance in the earth crust. - M.: Atomizdat, 1976. - 159 p.

[15] Karner D.B., Levine