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OF THE REPUBLIC OF KAZAKHSTAN

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**CARBONACEOUS CONNECTIONS AND OXIDE OF SILICON
IN NANOWORLD**

Abstract. The compounds of CmHn and SimOn types are the steady and widespread massive material in normal conditions. In terms of carbon particles selected in Kazakhstan deposits, it was established, that all types of particles identified by the classification of nanoforms during synthesis exist in natural conditions in the deposits. In many cases the formation of nanosize particles associated with "capture" of inclusions. Assumptions about dimensions of inclusions were made.

Example of reconnaissance – surveyed systematization of twenty – five objects for the identification of promising deposits are given. The areas, perspective for extraction of formed forms are not those for the formed graphites. The probable model of carbon behavior in the nature was described.

Carbonaceous matter (oxide of silicon) and its composites are capable to become a natural raw material.

Key words: nanosize, carbonaceous particles, inclusions, deposits.

Introduction. The world has already entered into the nanoera and it is difficult to find the sphere of human activity wherever nanosized particles are not used. Now it is time when unusual properties of nanomaterials were already discovered. The world has passed to a directed study of the properties of specific materials involving nanoscale formations. Moreover, many composite materials will be obtained in several stages. Hard core of nanowaves are obtained by physical chemistry methods, but because of small quantities of the product it does not satisfy the demand of the industry. We are faced with the task of finding the sources of nanosubstances in nature. It will be a new raw material. Based on knowledge of nanoparticles, data on synthesis processes and geological conditions of genesis [1, 2], we can predict the occurrence of these particles in known (analytically studied) deposits. For the initial studies, the most common carbon and siliceous components of rocks and ore materials are selected. Carbon shales are considered promising in research for carbon. A reconnaissance survey for the content of natural substance nanoforms are carried out for more than 25 developing processes. Fields of primary research have been identified, nanoforms isolated by chemists have been found.

Combinations of CmHn and SimOn. Carbon combinations and silica (oxide of silicon) are one of the most common minerals on Earth. Therefore, we began to study nanoscale rocks from them. Carbon and silicon are elements of group 4, 2 and 3 periods of the periodic table. They can both give and receive electrons, attaching other elements. The combinations formed in most cases of the type CmHn and SimOn (for example, CH₄ and SiO₂) were considered. When formed from the galactic cloud of hydrogen – they are formed among the first and are sufficiently stable in terrestrial conditions. Moreover, if compounds of CmHn type can be found in gaseous (gas), solid (carbon, shales) and in the liquid state (oil), then compounds of the SimOn type are found mainly in the form of solid compounds (quartz). Carbon and its compounds have different forms (CH₄, C₂H₂ ..., CO ...). But they all turn into carbon (C) at low temperatures. SimOn compounds are stable under the same and higher temperature conditions and do not convert to silicon (Si).

The substance formed in natural conditions has a mass of inclusions, which complicates its diagnosis. At the same time, the same substance synthesized from a finite number of certain atoms, under given

conditions, has practically no foreign impurities, it is "pure", and can be diagnosed [3-6]. There are many works devoted to the study of the characteristics of synthesized substances and their application. This became the basis for research and comparison of substances obtained from two methods – synthesized and found in deposits.

Due to the formation of the substance occurs at a nanoscale level, not individual chemical elements, but the forming substances were investigated. Sample preparation and research were conducted under the same conditions. Visualization of objects was carried out with the help of a transmission electron microscope [7, 8]. According to the previously made classification of morphostructures of synthesized objects, their formation in nature was predicted (formation in a nanozone, hierarchical scheme). Then, according to the received data, natural objects were investigated.

Types of particles. More than 25 deposits/developing process were analyzed for the presence of nanoparticles analogous to synthesized ones. To find the nanoforms in their material, the deposits were selected along the known synthesis conditions. With a possible coincidence of the conditions of synthesis and natural conditions all forms of particles of nanosubstance predicted by chemical science were found [9-11]. However, in nature, due to the influence of environmental conditions, non-standardized contribution of catalysts, the presence of a more complex environment, etc., the morphology of some nanoparticles is slightly different from the synthetic (initial – reference) nanoscale particles (Table). For example, in the presence of tubular particles of big diameter the "sagging" individual parts is possible. The uncontrolled surface of the tube can form a structure resembling a launder (Bekenov's new mineral [12]). In the synthesis processes, giant nanotubes are observed. Their walls contain graphite compounds and, therefore, do not bend under their own weight.

The forms of nanoparticles found in nature

1	Roundshape	Gold grain, V. Matvienko; opals, sintered and «adherent» particles (TEM, IGS)
2	Tubes	Fiber rocks; «graphite structures»; new mineral, G. Bekenova (TEM, IGS)
3	Fibres	Copper-palladium mesh (TEM, IGS)
4	Films и covers	Graphite, carbon (TEM, IGS)
5	Cloud particles	In all natural samples (TEM, IGS)
6	Active particles	Particle edges
7	Particles with regular crystallographic projections	Nanodiamonds from Yakutia and Bakyrchik (TEM, IGS)

Table shows the observed nanoforms of particles, analogs to synthesized particles (the second column), mineral species, research authors, instrument and place where images of nanforms were obtained (third column).

The table is agreed with numerous reports carried out at the Institute of Geology works.

Inclusions. Under formation of nanoparticles in nature, carbon compounds (and silica) should release inclusions. Inclusions – impurities (including ore) may differ in location in the carbon-bearing matter [13] (Figure).

An ionic level of inclusions is possible (Figure, a). It is formed by inclusions in a lattice constructed of atoms. For layered minerals, for example graphites, this is an occurrence in layers of graphs/graphenes (entry into their crystal lattice, according to the hierarchical scheme this corresponds to the first level). In this case uncharacteristic minerals are formed. The average (stoichiometric) composition of these phases can correspond to one of a number of compounds. The final members of the series are pure (with unbroken stoichiometry of allotropic compounds - simple in the crystallographic formula) minerals.

Inclusions can be at the atomic-molecular level (Figure, b), which is typical for a mixture of individual molecular forms (minerals). For carbon, this level is formed from individuals (impurities) entering the layered structures (as in the formation of graphite layers).

Inclusions can be in cluster form (Figure, c), which is obtained by closing the connections inside the substance/impurity. Such formations are distinguished in placers in the form of "rounded-sintered" nuggets. According to the hierarchical scheme – this phenomenon corresponds to the second and higher levels of nanosubstance formation.



Occurrence of an impurity in layers of graphite:
a – the layers forming graphite; b, c – impurities.

Probably, the levels of composite compounds should correspond to the same levels (ionic, molecular and cluster compositional compounds).

The dispersed carbons themselves can also have chemically unconnected (independent) clusters – nurnazenes (similar to small fullerenes).

The formation of monocrystals of diamonds and quartz, probably goes on a different way. Carbon in a hierarchical scheme can form compounds of the first stage, on the basis of atom. Silica belongs to the second stage, that means, compositions based on the SiO_2 molecule are dominated (octahedral or tetrahedral crystallographic forms). The formation of quartz, as described by N. Shabanova, [14], is derived from unsaturated solutions.

The morphostructures of synthesized nanosized particles are much richer than natural formations. Probably, it is due to the "limit" effect of the elements diversity involved in the formation of matter in natural nanozones.

In natural phenomenon was established the prevalence of cloudy-film structures of carbonaceous matter. The matter is able to form the unique shells on the boundaries of the mineral matrix particles, thus forming composite compounds [15]. Composite materials are also in demand in the industry.

From theoretical research follows practical conclusions. Where the extracted phase and dimensions of the ore body can be formed, dimension (the size of the dispersion to which the rock is to be crushed) and extraction technology (including the extracted element). All this determines the complex of technological problems of using minerals and, so far not taken into account, new properties of mineral raw materials.

Classification of objects. Reconnaissance studies have allowed us to classify objects according to certain parameters (DTA, XRF, TEM) in turns of research.

There are the most promising deposits for the searching a nanostructures Maykol deposit, Siyakezen, Akzhaylau-2, and Karaganda coal basin. The Maikol deposit contains bulk particles of graphites and prospective generating graphene/grafan. Siyakezen's deposit contains bulk particles of graphite, and in intermountain valleys, there are particles formed during local ignition of "fluids" - gases. The occurrence of Akzhaylau-2 may contain diamond-like forms, the formation of which may also be associated with the release of gas fluids. Deposits of Karaganda coal basin contains bulk particles of graphite and can contain diamond-like forms, the formation of which can also be associated with the release of gas fluids.

Then there are the deposits of the second stage: Karasai, Koksui, Oikaragai, "Ayuly", Tekeli, etc.

Model. Probably, "carbon cycle in nature" is as follows. In parent rocks, all carbon is in compounds. After the expiration of the time, the rocks are transformed, and the carbonaceous masses begin to separate, ... including carbonaceous shales (in these thermodynamic conditions, the carbon in the shales forms a layered system). The formed schistose structures are probably related to the penetration of carbonaceous substances through the schistosity of the rocks. Schistosity is accompanied by the formation of graphene/graphane and graphite. Next comes the release of carbon gas from the original ground. There is a decrease in the length of the crystal structures. In natural objects discoloration of carbonaceous matter is observed. The "washout" of dispersed (nano-sized) carbon leads to the appearance of structures released from the «original ground» that are similar to Raskelite. "Nonvolatile" fine dispersed nanosized carbonaceous substance, getting into the soil, turns into a suspension (amorphized) and colloid, and washed out by atmospheric and ground water. It is possible the formation of secondary forms. As for the siliceous compounds, they obviously undergo the same transformations. But unlike carbon, which can form structures of atoms (beginning with the first level in a hierarchical scheme made by chemists), the formation of SimOn structures occurs from the second – molecular level.

The probable presence of "graphite" structures may lead to the appearance of graphite degree of order in general non-graphite layered structure [16]. In the weathering zone massing the formed graphites and the products of their decay/growth. Together with the amorphous particles there are two-three-dimensional structured particles and various graphites – well-structured formations.

Conclusion. There is always a risk that, it is necessary to determine the priority of the investigation of deposits/manifestations according to another principle. The exhalation of natural nanoforms, similar to those synthesized, may not be in the first place. But studies of developed structures exclude the priority of studying deposits, where graphene or composites based on shell structures (capsules) of carbon and silica are expected. The extraction of the found substance (carbon particles and silica) is not immediately profitable, as it requires new technologies for extraction, transportation and processing. It is also necessary to clarify the existence in nature of nurnazenes, with prospective application.

Carbonaceous matter (silica) and its composites can and should become a natural mined raw material.

The science of nanosubstance is at the beginning, but it is stimulated by nanotechnologies, which requires new materials for obtaining new, more profitable goods. And this explains the lack of a systematic approach to research. But only systematic research can lead society to the desired result. There is a research at the nanoscale level of the phases - inclusions (including ore) in all rock-forming minerals. There is a selection of material on the phases of available chemical and other data with mathematical confirmation of frequency.

Probably, soon it will be possible not only to distinguish the impurities entering into the graphene structure and between the layers of graphene, in the graphite structure and between the packing of graphites, but also purposefully to extract this phase. Then, ore mining technologies in carbonaceous shales will become non-waste, and synthesis in limited amount will be changed by extraction in applied volume.

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НАНОМИРДЕГІ КАРБОН КОМПОНЕНТТЕРІ МЕН КРЕМНЕЗЕМ

Аннотация. CmHn және SimOn типіндегі қосылыстар осы геосфералық жағдайда тұрақты және кен таралған тастар болып табылады. Қазақстандық кен орындарында таңдап алынған көміртекті бөлшектердің мысалында синтез кезінде нано түрлердің жіктелуімен анықталған бөлшектердің барлық түрлері кен орындарындағы табиғи жағдайларда бар екендігі анықталды. Көптеген жағдайларда наноөлшемді бөлшектердің қалыптасуы инклюзиялардың «басып алынуына» байланысты. Инклюзияның өлшемдері туралы болжамдар қабылданады.

Келешегі бар кен орындарын анықтау үшін барлау-іздістіруге алынған жиырма бес объектіні жүйелендіруге мысал келтірілген. Алынған нысандарды алу үшін перспективалы болып табылатын облыстар қалыптасқан графиттерге ұқсас емес. Табиғаттағы көміртекті мінез-құлықтың ықтимал моделі сипатталған.

Көміртекті заттар (кремнезём) және оның композиттері табиғи минералды шикізат болуы мүмкін.

Түйін сөздер: нанокұрылымды, көміртекті бөлшектер, қосындылар, кендер.

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УГЛЕРОДИСТЫЕ СОЕДИНЕНИЯ И КРЕМНЕЗЁМ В НАНОМИРЕ

Аннотация. Соединения типа CmHn и SimOn являются устойчивыми и распространенными породами в нормальных условиях. На примере углеродных частиц, отобранных в Казахстанских месторождениях установлено, что все виды частиц, выделенные классификацией наночастиц при синтезе, существуют в природных условиях в месторождениях. Во многих случаях в образование наноразмерных частиц сопряжено с «захватом» включений. Сделаны предположения о размерностях включений.

Приведен пример систематизации рекогносцировочно-обследованных двадцати пяти объектов для выделения перспективных месторождений. Площади, перспективные для добычи образующихся форм, не являются таковыми для сформированных графитов. Описана вероятная модель поведения углерода в природе.

Углеродистое вещество (кремнезём) и его композиты могут стать природным добываемым сырьем.

Ключевые слова: наноразмеры, углеродистые частицы, включения, месторождения.

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