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Nanostructured ordering in natural fullerene-like carbon

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Study of the noncrystalline solid carbon, which is responsible for the most essential properties of Precambrian shungite rocks (shungite occurrences in the north-western part of the lake Onega, Karelia, Russia), is of interest because of a number of its physico-chemical properties underlying its many perspective applications [1]. Shungite carbon has graphite-like structure at the atomic level, but high-temperature treatment of the carbon does not lead to its graphitization. Basic structural element is globule. Shungite globule is a spherical or ellipsoidal multi-layer carbon formation, about 10 nm in size. Nature of these globules is supposed to be fullerene-like.

Due to appeared to the present time to high-resolution scanning probe microscopic methods difficulties with visualization nanometrical structural elements of metastable natural substances are removed [1, 2]. We applied scanning tunneling (STM) and atomic force (AFM) microscopes.

for study highly-carbonaceous (to 98%) shungite carbon from various deposits, which different pressure - temperature of formation are characterized [1].

The supermolecular globular structure is concerned with to genetic features of substances, first of all with pressure - temperature and features of material composition of mineral formation environments. As one of the basic regulation of the supermolecular constitution of the investigated substances logarithmically normal distributions of structural elements on the sizes can be distinguished. Such character of distribution can speak that visualized supermolecular elements are aggregates of colloidal particles. The following step in research of supermolecular constitution is the structural-morphological analysis of images to reveal elementary form of the ordering expressing in a periodic arrangement of structural elements. As a whole it reveals diffraction analysis the analogue of which is Fourier-analysis in our case. Fourier Transformation has confirmed visually observed absence of a regularity in a relative location of elements of supermolecular structures, however has allowed to reveal the presence morphological analysis of researched substances in a number of samples statistically noted directions it testifies to occurrence presence of original superstructures ordering.

Possible mechanisms of aggregations of shungites globules were analyzed.

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The transition from alluaudite- to wyllieite-type phosphates: which is the role really played by aluminium?

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The wyllieite group of minerals consists of Na-Mn-Fe-Al-bearing phosphates which exhibit a crystal structure topologically similar to the alluaudite structure. However, the ordering of cations in the wyllieite structure induces a splitting of the M(2) and X(1) sites of alluaudite into the M(2a) M(2b) and X(1a) X(1b) positions. Consequently, the $C2/c$ space group of alluaudite transforms into $P2_1/n$ in wyllieite, with no significant change of the unit-cell parameters, and with a structural formula which corresponds to $X(2)X(1a)X(1b)M(1)M(2a)M(2b)(PO_4)_3$ [1]. Recently, the description of the new mineral species ferrosemaryite, $NaFe^{2+}Fe^{3+}Al(PO_4)_3$, in the Rubindi pegmatite, Rwanda, initiated a detailed mineralogical study of the wyllieite group of minerals [2, 3]. This study indicates that aluminium is localized on the M(2a) site of rosemaryite and ferrosemaryite, not on the M(2b) site as observed in ferrowyllieite [1]. Because aluminium is considered by Moore & Molin-Case [1] as responsible for the splitting of the M(2) site into M(2a)-M(2b), it is essential to understand the role played by this cation in the alluaudite and wyllieite structures. In the present study, Al-rich phosphates with a nominal composition $Na_2Mn_2Al(PO_4)_3$ were hydrothermally synthesized at 300-800°C and 1-5 kbar [4], in order to obtain wyllieite-type phosphates. Between 300 and 600°C, white powders without visible crystals were obtained, and the powder X-ray diffraction patterns correspond to those of alluaudite-type phosphates, without any supplementary reflection typical of the $P2_1/n$ wyllieite space group. As discussed by Hatert *et al.* [2], however, the identification of actual wyllieite-type phosphates can only be confirmed by single-crystal X-ray diffraction techniques. At 700°C/3.5 kbar and 800°C/1 kbar, tiny acicular crystals were obtained and single-crystal structure refinements indicated an alluaudite-type structure [5]. Consequently, it appears that the presence of significant amounts of aluminum into the alluaudite structure is not the only parameter which provokes the splitting of the M(2) site and the crystallization of wyllieite. This conclusion is confirmed by the synthesis of the wyllieite-type phosphate $Na_{1.265}Mn^{2+}_{2.690}Mn^{3+}_{0.785}(PO_4)_3$, at 400°C and 0.1 kbar [6], which also indicates that wyllieite-type phosphates crystallize at lower temperatures than alluaudites. Further experimental investigations, starting from the $Na_2Mn_2Al(PO_4)_3$ composition, are absolutely necessary to obtain single-crystal data below 700°C and to eventually detect the presence of wyllieite-type phosphates.

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