

CARBONADO AND YAKUTITE: PROPERTIES AND POSSIBLE GENESIS.

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Two types of carbonado are currently known, which are essentially different in composition, properties, the way of formation: it is common carbonado of Brazilian type, and yakutite. The latter was first encountered in the 60-s in placers of the Northern Yakutia and was called by the name of this region. It is represented by grains of flattened hexagonal form, not very large in size. Its main peculiarity is the presence of hexagonal carbon modification - lonsdaleite. It is characterised also by more heavier carbon isotopic composition as compared to carbonado, very low paramagnetic nitrogen content, and other peculiarities, which are generalized in Table:

Grain properties	Carbonado	Yakutite
Shape	irregular, isometric	flattened-hexagonal
Mass, carat	1-40 (up to 3167)	0.01-0.2 (up to 3)
Crystallite size, mkm	0.5-80 (usually 10-40)	0.1-1
Structure	not observed	10-90°
The presence of non-diamond carbon phases	none	lonsdaleite (up to 50%), chaoite also may be present
Photoluminescence spectra	N3, H3, H4, T1 systems	non-structural wide band
Paramagnetic nitrogen impurity (C-center, cm ⁻¹)	$4 \cdot 10^{18} - 3 \cdot 10^{19}$	absent (less than 10^{15})
Other paramagnetic centers, cm ⁻¹	$5.5 \cdot 10^{17} - 4.5 \cdot 10^{18}$	$2 \cdot 10^{18} - 1.2 \cdot 10^{19}$
Carbon isotope composition ($\delta^{13}\text{C}$, PDB, o/oo)	-23.2 - -30.6	-9.9 - -20.1
Hydrocarbon component impurity, %	up to 0.1	insignificant

A set of structural-compositional peculiarities of carbonado and yakutite allows to consider them as independent mineral varieties, which genetically differ from one another and from diamond.

Primary occurrences of yakutite were encountered in impact metamorphic rocks and also in stone and iron meteorites. Experimental conditions of obtaining of lonsdaleite-bearing

aggregates (momentary impact loading above 150 kb) and cry-stallographic study of yakutite show, that they are para-morphs after graphite, formed as a result of extremely high momentary loading explosive type.

The problem of genesis of carbonado of classical Bra-zilian type is more complicated, because it has been never encountered in primary occurrences. The absence of carbonado findings in kimberlites and lamproites in spite of more than a century of mining of primary deposits in Africa, Siberia, Australia, as well as the peculiarities of carbonado compo-sition permit us to draw a conclusion, that this mineral is associated neither with kimberlites nor lamproites, and it is most of all of non-plutonic origin. Based upon studies of carbonado structure L.F.Trueb and W.C.Butterman, and C.Jeynes suggested, that carbonado is an analogue of cera-mics and was formed as a result of high-temperature sintering when adsorbed impurities were eliminated and diamond particles were partially recrystallised. We could consider this mechanism of carbonado formation to be real, taking into account an experimental support for such sintering when producing of artificial carbonado.

However artificial carbonados greatly differ from natu-ral ones by essentially bigger crystallite size, the pre-sence of paramagnetic nitrogen, and other features. The most essential from genetic point of view is high density of dislocations in crystallites of natural carbonado, which have been studied by Y.Moriyoshi et al. Dislocations in cry-stallites are chaotically oriented and do not show polygoni-zation (as it takes place in balas crystallites). As dislo-cations are thermodynamically unstable element of crystalli-te structure and diffuse when heating, preliminary subjected to polygonization, the real pattern contradicts with hypo-thesis of high-temperature sintering with pressure. To ex-plain the genesis of natural carbonado we propose a hypothe-sis of crystallite formation without high pressure under lo-cal heating of carbon substrate. Small crystallite size is a decisive factor in this case.

When studying fine-dispersed metallic and other phases it was established, that surface energy in the smallest (1-100 nm) newly formed crystallites is an independent thermo-dynamic potential, which under certain conditions has an opposite direction as related to chemical potential. Due to this fact the parameters of phase transitions for small cry-stal particles depend on their sizes. This phenomenon was called as "phase dimension effect". If, besides pressure and temperature, we introduce into phase equilibrium calculation the third independent parameter "r", an effective crystalli-te radius, we obtain the following energy condition of sta-bility of crystallite diamond structure:

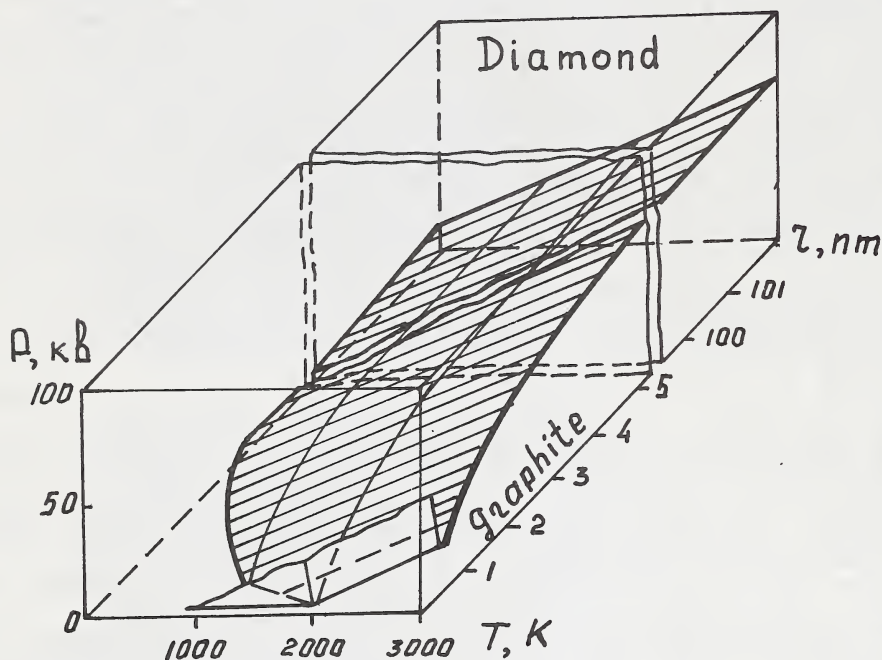
$$\Delta M^V - \left[(\epsilon_1 \epsilon - \epsilon_2 \frac{d}{a}) \frac{z}{a} - \frac{\epsilon_1 b}{2} \frac{d}{a} \right] \left[\epsilon \frac{z}{a} \left(\frac{z}{a} + b \right) \right]^{-1} < 0;$$

where ΔM^V - difference of volumetric chemical potentials of diamond and graphite,

ϵ_1, ϵ_2 - difference of energies of σ -bonding and π -bonding in graphite and diamond,

z, d, a, b, ϵ - geometric parameters of graphite and diamond crystallites.

A diagram of diamond phase equilibrium, calculated from this equation, is described as a surface in space with following coordinates: pressure - temperature - crystallite size:



If the second ("surface") member of the above equation is insignificant ($r \gg 100$ nm), then the diagram of graphite/diamond equilibrium does not differ from the known one. However as crystallite size decreases ($r \leq 10$ nm), the surface of phase equilibrium is noticeably deflected to the area of low pressures, while with the " r " ~ 1 nm diamond is stable even in the absence of external pressure in the temperature field up to 2000 K.

Based upon the above constructions we could suggest carbonado formation beyond high pressure field. In this case we could practically explain all the peculiarities of carbonado: degree and nature of dislocations in crystallites; essential impurities of polymerized hydrocarbon compounds; carbon isotopic composition, corresponding to organic matter; and inclusions of mineral phases uncommon for diamond.