

History of Natural Diamond Formation Based on Defect Characteristics Detected by Spectroscopic Methods

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Introduction

The history of natural gem diamond formation that genetically related with impact events followed by shock, progressive and regressive metamorphism of target rock areas has been deduced by data obtained by complex nondestructive spectroscopic methods: Raman spectroscopy, PLS, CLS, IRS and also mineralogical and literature data. About 200 representative natural gem diamonds have been picked out from investigated thousands samples: colorless, yellow, brown colors, 0.03 – 1.60 carat weight, zoning with cubic internal morphology of crystal centers graduated to cubo-octahedral and octahedral forward to intermediate and rim zones, mineral inclusions in central zones were represented by tiny inclusions of graphite, α -Fe, Ni-Fe, sulfides etc., intermediate – by peridotitic, eclogitic and UHP minerals, often surrounded by discoid fractures and melt inclusions; rim zones – association of secondary minerals and gas/fluid inclusions. Diamond zones were differentiated by C and N isotopic compositions and also N content and N aggregation state. All diamond crystals had dislocations, plastic deformation, discoid fractures around inclusions and birefringence.

UHP-HT features of natural diamonds

1. The presence of $sp^1 \rightarrow sp^2 \leftrightarrow sp^3$ carbon phase transformations (Fig.1), including diamond \leftrightarrow lonsdaleite transformation that has been completed in nanoseconds under a shock wave compression of cubic diamond [He, 2002]. Lonsdaleite line maximum in Raman spectra is the 1324.4 cm^{-1} (552.2 nm).

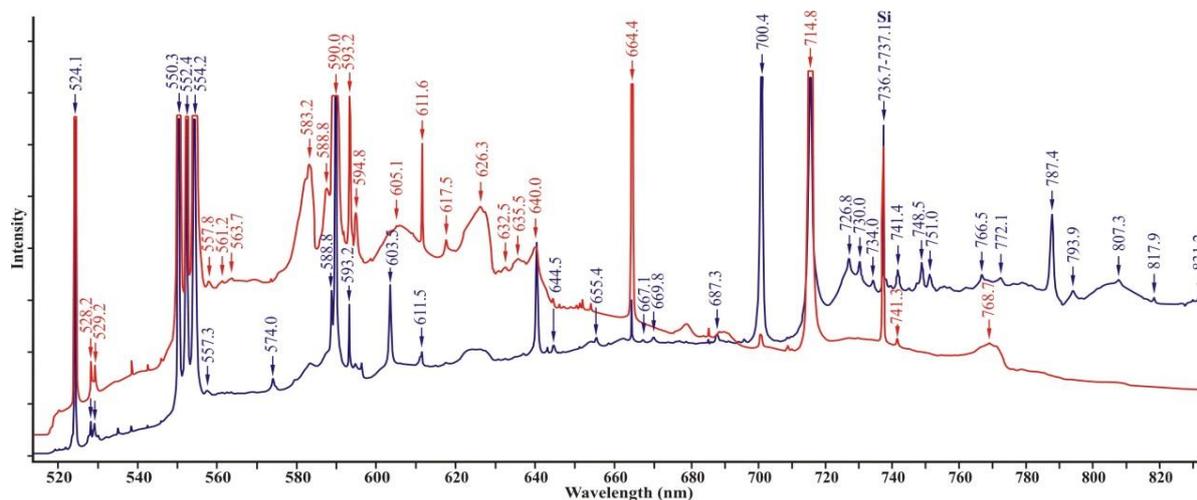


Fig. 1. PLS (λ_{exc} 514.5 nm) IaAB (regular) diamond. Strong lines in range 550.3-552.4 nm – $sp^2 \leftrightarrow sp^3$ carbon phase transformations [Zaitsev, 2001]; 554.2-554.7 nm – $sp^1 \rightarrow sp^2 \rightarrow sp^3$ primary carbon matter transformations by shock wave [Miyamoto, 1993]; 583.2-594.8 nm – superposition of II order Raman lines and radiation defects; 524.1, 664.4, 714.8 nm lines identified radiation damage [Zaitsev, 2001]; 605.1- 640-700.4, 787.4, 793.9 nm - Ni-N defects, 669.8 - Co-N defect [Yelissev., Kanda, 2007]; 528.2 nm – Si--defects, 736.7-737.1 – [Si—V]– defect [Clark et al., 1995]. These defects formed at different PT conditions and preserved in natural diamonds have different temperature formations: $sp^1 \rightarrow sp^2 \rightarrow sp^3$ carbon phase transformations >2500 K, Ni-N ~2500–1600 K, Co-N ~1850–1750 K, [Si-V]– ~2200 –1200–800 K, and radiation damage ~1000 - 800 K.

2. Raman line in studied natural diamonds represented intensive positive or negative asymmetric line with maximum 1332.5 cm^{-1} , and FWHM in the range 3.2 cm^{-1} to 9 cm^{-1} (as a result of HPHT environment conditions) and $\gg 4.5 \text{ cm}^{-1}$ to very large width (HPHT + radiation damage conditions).
3. UHP mineral inclusions in diamonds: diamond \leftrightarrow lonsdaleite, coesite, SiC and its various modifications, majorite, ringwoodite, TAPP, perovskite and etc. Protogenetic central nano-inclusions, appeared to be diamond seeds, its mineral compositions are carbon phases with He, Ar, Ne, Xe, H₂, N₂, CO₂, CO, H₂O, CH₄ gases, REEs, Fe, Cu, Cr, Au, Ag and etc.; Ni, Fe, Co, Cu, Zn sulfides etc.; Fe-Cr, Fe-Cr-Ti, Fe-Cr-Ni, FeC, oxides Mg, Ti, Pb, Ba. All nano-inclusions are minerals extraterrestrial origin [Rubin, 1997].
4. Variety of crystal structure defects, dislocations, plastic deformations, discoid fractures around inclusions, birefringence, mosaic structures.

Carbon, nitrogen, hydrogen, noble gas sources in natural diamonds

Nano-diamonds from chondritic meteorites, micro-meteorites, IDPs indicating that they formed outside our solar system and reflecting the conditions in interstellar space, solar nebula and host meteorites [Huss, 2005]. They were the sources of carbon, nitrogen, hydrogen, noble gases in earth's diamonds. ^{13}C value in kimberlitic diamond varied in the range (-41% to $+5.0\%$) [Cartigny, 2005]. Value $\delta^{13}\text{C}$ eclogitic and micro-diamonds are nearly to value $\delta^{13}\text{C}$ (-31 to -38%) similar to extraterrestrial nano-diamonds. Variety of C modifications and its isotope compositions allow to assume a derivation of different diamond groups from various or mixed carbon sources reflected host rocks (target + impactor) composition. Most part C- and N- containing phases in carbonaceous chondrites are organic matter, which is characterized by high D/H ratio, value δD ($+300$ to $+1600\%$) [Remusat, 2015].

Dawson (1980) wrote: "Nitrogen exists in platelets and segregated nodes within diamond which is the only site of upper-mantle nitrogen known at present. Whereas some evidence, albeit scanty, exists for a source of carbon and phosphorus, the initial source of the nitrogen and other rare gases within diamond must remain an enigma". There is only one answer of this enigma: C, N, H, noble gases have extraterrestrial nature. N is widely distributed in Universe and present in diamonds and matrix of chondritic meteorites, micro-meteorites, IDPs, asteroids, comets as variety molecules, including organic. Interstellar organic matter has anomalies of H and N isotope, that suggesting of its derivation in presolar molecular clouds or protoplanet disk. [Remusat, 2015]. Values $\delta^{15}\text{N}$ (-25 to $+20\%$) are in kimberlite diamonds and $\delta^{15}\text{N}$ ($+5.3$ to $+25\%$) in micro-diamonds from Kumdyy-Kol deposit.

Signatures of noble gases He, Ne, Ar, Kr, Xe in meteoritic and comet matter preserved in natural diamonds. ^3He is original galactic component have been trapped outside our Solar System [Huss, 2005]. Value $^3\text{He}/^4\text{He}$ in natural diamonds varied in the range (7×10^{-1} – $8 \times 10^{-9}\%$) [Shukoljukov et al., 1996]. ^4He , Ne, Ar и Xe have radiogenic origin, ^{40}Ar and ^{21}Ne joined to diamond seeds during their formation in the space. Noble gases can identify by PL spectra: He $\sim 523, 536.6, \sim 562$, Ne⁺ – 716, 719.5 Xe⁺ – 811.6, 793.3, D (H⁺) – 555.0 nm lines [Zaitsev, 2001].

Transition metals - Ni, Co, Cr, Ti, Fe - and Si in natural diamonds

Transition metal defects were observed by PLS in studied diamonds mixed type 1b + IaAB (regular and irregular) with various N and H concentrations:

(Co-N) – the 519.7–521.1–523.4, 542.5, 544.1, 623.5 nm and Co-C – 669.4 nm systems [Tretiakova 2010] Temperature formation of these defects in the range ~ 1850 – 1750 K.

(Ni-N) defects – the S1, S2, S3, 535.2, 694.3–692.4, 603.6, 640.5, 700.6, 787.6, 795.3 nm are complex interstitial defects with various number N atoms [Yelisseyev, Kanda, 2007] were formed at temperature range ~ 2200 до ~ 1600 K.

Cr³⁺ center characterized of R₁ 693.7 nm and R₂ 692.2 nm lines in PLS.

Ti-defects the 973.2 and 991.8–1014 (replica) nm, the 991.8 nm center (Ti-Ti bonds) were observed in natural IIa type diamonds in PLS at first time by authors. Formations temperature of the 973.2 and 993.2–1014.1 nm defects ~ 1900 – 1800 K and 1600 K, respectively.

Fe. Most of natural diamonds are magnetic susceptibility, that due iron presence as Fe-magnetic impurity in nano- and submicron diamonds and fluid inclusions, which size \sim equal or less λ_{light} , doing them invisible under optic research; α -Fe, Fe₃C и Fe_xN phases/inclusions are known in meteorites and “central inclusions” in natural diamonds.

Si-defects – 528.2 nm, [Si-V]⁰⁻ – ~ 946–948 nm, and [Si-V]⁻ = 736.7–737.1 nm that formed at ~2200 – 1200–800 K.

Conclusion

All of above are evidences of impact events that were provoked diamond generation from carbon matter, delivered by meteoroids and followed diamond growth at shifting HPHT (sharp drop pressure and gradually decreased temperature) conditions corresponding of shock, progressive and regressive metamorphism with metasomatic alterations of impact area rocks.

So, natural diamonds generated and grown in solution-melts due to collision any meteoroid and the Earth followed by shock, progressive and regressive metamorphism in target rock areas. Protogenetic central inclusions in diamond represented by meteoritic minerals and appear to be diamond seeds, early diamond growth started at HPHT conditions by growth scheme HPHT synthetic diamonds; subsequent growth under lower PT conditions came by CVD growth scheme. Sources of C, N, H, noble gases had cosmic origin.

Simultaneous presence in PLS of single natural diamond (Fig.1) defects, formed and preserved at different PT conditions, demonstrate their different temperature formations $sp^1 \rightarrow sp^2 \rightarrow sp^3$ carbon phase transformations >2500 K, Ni-N ~2500–1600 K, Co-N ~1850–1750 K, Si ~2200 – 1200–800 K, radiation damage ~1000 - 800 K defects and suggest long diamond history during gradually changing HPHT conditions.

Diamond varieties (from gem stones to carbonado) occurred in one diamond deposit due conditions that took place during these events. Kimberlite pipes and dykes were formed under closer to vertical diamondiferous asteroid impacts to the Earth [Lyukhin, 2008]. At oblique impact diamondiferous asteroid, diamond dispersed on extended territories and later concentrated in placers. Deposits of “metamorphic” diamonds formed under oblique impacts as well. Every kimberlite pipe, every placer and metamorphic deposit of natural diamonds are especially individual under all its parameters.

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