High Pressure Carbon Polymers from Impact Melt Rock of the Giant Popigai Astrobleme (Siberia, Russia)

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Abstract. The Popigai astrobleme is a unique geological object with huge storages of impact diamonds of high hardness quality being perspective as an abrasive material. In spite on very well-known after-graphitic nature of the Popigai diamonds, it was predicted that a part of them might have non-graphitic precursor as the target of the meteorite crater partly consist of sedimentary rocks with coals and bitumens. In this study by use of a complex of modern methods we have analyzed unusual carbon particles from impact melt rocks of the Popigai astrobleme. The studied carbons according to the provided Raman studies belong to high pressure polymer with hydrogenated carbons - hydrogenated amorphous tetrahedral diamond-like carbon (ta-C:H) and rare polymeric a-C:H. A list of typomorphic features of the high pressure non-crystalline carbons are described in the paper on the basis of UV Raman spectroscopy, scanning electron microscopy, microprobe and δ13C isotopic composition analysis.

1. Introduction

Carbons under intensive shock treatment can provide a number of carbon phases including impact diamonds [1-5 et al.], new-formed graphite, lonsdaleite, high pressure glassy carbon and carbyne (probably) [6-10]. Among the impact carbons the impact diamonds look the most impressive by present. But, the impact high pressure carbon polymers may be interesting too as a solid low ordered/amorphous matter formed under extremely high pressure and temperature. The carbon polymers were found at the Kara astrobleme impactites [6, 8, 9]. The distribution in the impact objects and physical properties of the high pressure carbon polymers (HPCP) and correspondently their application potential are not clear and require special studies.

Among the impact objects there are 190 proven meteorite craters. The Popigai astrobleme was detail studied in 70s-80s years of the XX century with widest works on diamond prospecting. It was found that it is the largest diamondiferous objects in the nature [1, 10]. The astrobleme has about 100 km diameter and well known by huge storages of impact diamonds at the concentrations in the deposits about 10-14 carat/ton (average for rich impactites) on the wide square – 46 km2 for diamond rich impact melt rocks and 38 km2 for suevites; and about 1000 km2 for impactites with lower diamond concentrations [10]. The Popigai diamonds have high hardness quality being perspective as an abrasive material [1, 10]. In spite on very well-known after-graphitic nature of the Popigai diamonds [1, 3, 11], recently it was predicted that a part of them might have non-graphitic precursor [6, 7] as the target of...
the meteorite crater partly consist of sedimentary rocks with coals and bitumens [1]. In this study we have analyzed unusual carbon particles from impact melt rocks of the astrobleme.

2. Object and Methods
The sampling was provided by N. V. Vladykin from melt rocks at the Skal’ny deposit of the Popigai meteorite crater (Siberia, Russia). The analyzed carbon particles had been enriched by chemical dissolution of the host melt rock by HF treatment. The undissolved material had been analyzed under an optical binocular for selection of the carbon particles. The selected particles were studied by a complex of methods at the Center for Collective Use “Geonauka” (IG FRC Komi SC UB RAS, Syktyvkar, Russia) including microscopic, structural and spectroscopic observations such as optical microscopy observations (POLAM-312, LOMO), scanning electron microscope (SEM) (VEGA 3 TESCAN SEM with VEGA 3LMN, INCA ENERGY 450 energy dispersive detector, Tescan, Czech Republic), visible Raman spectroscopy (LabRam HR800, Horiba Jobin Yvon, France) and isotopic analysis. Also, we have analyzed the carbon matter by UV Raman spectroscopy measurements which have been provided at the SSC FSUE Keldysh Research Centre (Moscow, Russia) with a Raman spectrometer T64000 (Horiba Jobin Yvon, Japan) at 244 nm laser excitation.

The isotopic study has been provided for individual carbon grains, every single carbon grain has been selected under microscope and set by a needle into its own individual Sn box for analysis. The $\delta^{13}$C isotopic measurements have been produced with a mass-spectrometry complex DELTA V Advantage (ThermoFisher Scientific, Germany) with a GasBench II system. Accuracy measurements of $\delta^{13}$C is $\pm 0.1 \%$ relatively to a PDB standard.

3. Results
3.1. SEM study and microprobe analysis
First of all, we would like to take attention to morphological features of the studied carbons. Following to optical microscopy observations and scanning electron microscopy studies we divided the extracted particles for 3 groups – angular fragments with glance surface; irregular particles with bubble texture and particles with pumice texture (Figures 1–3). The carbons have black color and greasy luster. No any presence of layer texture has been found in contrast to crystalline graphitic matter that usually has layered texture evidently seen under SEM observations. In our case the surface was very smooth.

The presence of bubble and pumice texture of the analyzed carbon matter point to initial presence of fluid phase in the precursor. The elements of fluidal morphology (Figure 3 c, d) allow to think that the precursor was in the state of moving (in plastic/melt state) before its solidification. The both characteristics point to non-graphitic state of the precursor. The chemical composition of the analyzed particles (Table 1) is characterized with quite high quantity of impurities that could belong to “ash elements”, at the same time high content of oxygen can belong to relict impurity of the origin organic matter. In rare cases nitrogen has been seen within the analyzed matter.

3.2. Isotopic study
The impressive data have been produced by isotopic study. According to the provided measurements of the $\delta^{13}$C isotopic composition of the organic carbon of the high pressure carbon polymer by individual particles (Table 2) we have found that it has the narrow range of the data – from -21.26 to -25.58 \% (with the overage value -23.15\% at the accuracy measurements $\pm 0.1 \%$ relative to a PDB standard). The measured isotopic composition of the polymer carbon is essentially different from the published data on the Popigai gneiss graphite which has average content -15 \(\div\) -17 \% with the range limits -21 \(\div\) -7 \% [1]. At the same time earlier it was presented that the close isotopic characteristic (from -21\% to -32\%) is the typomorphic feature of the after-coal matter and carbonado [6, 7, 9, 12, 13]. Also, it is interestingly that a part of the newly formed graphite can have specific $\delta^{13}$Corg isotopic composition belonging similarly to sedimentary carbon of coal -24.12 \% (Table 2).
Figure 1. SEM images of carbon particles of angular shape fragments. The particles have generally massive texture, rare with fibril texture (c). This variety is characterized by black color, bright luster, by absence of porous structural elements and fluidal morphology.
Figure 2. SEM images of carbon particles with bubble texture. The particles of the group have numerous pores of different sizes – up to 100 µm. Generally, they have smooth surface, irregular (sometimes rounded rounded (c) shape. The pores can be distributed irregularly through a particle.
Figure 3. SEM images of carbon particles with pumice texture. The variety of the carbon particles has highly porous texture with thin jumpers forming pumice. Sometimes they preserve fluidal-like texture and shape (c). The particles have black color, do not have clearly-recognized luster by the reason of highly differences of a relief.
Table 1. Chemical composition of the Popigai high pressure carbon polymers for different individual particles.

| Component content, wt % | Total* |
|-------------------------|--------|
| C  | 87.63 | 1.36  | 5.01 | 0.15 | 3.85 | 0.48 | 0.64 | 0.29 | 0.41 | 0.17 | 100.00 |
| N  | 93.07 | 3.78  | 2.34 | 0.08 | 0.12 | 0.32 | 0.12 | 0.09 | 0.1 | 100.00 |
| O  | 95.74 | 2.27  | 1.13 | 0.27 | 0.49 | 0.49 | 0.09 | 0.25 | 0.17 | 100.00 |
| F  | 86.43 | 8.6   | 4.57 | 0.07 | 0.07 | 0.25 | 0.17 | 0.09 | 0.08 | 100.00 |
| Na | 91.98 | 4.32  | 1.41 | 0.25 | 0.17 | 0.7 | 0.09 | 1.09 | 0.19 | 100.00 |
| Al | 85.73 | 11.32 | 0.23 | 2.5 | 0.04 | 0.09 | 0.08 | 0.08 | 0.10 | 100.00 |
| Si | 89.01 | 7.97  | 0.21 | 2.56 | 0.07 | 0.09 | 0.08 | 0.08 | 0.10 | 100.00 |
| S  | 85.29 | 12.21 | 1.5 | 0.26 | 0.06 | 0.42 | 0.17 | 0.24 | 0.09 | 100.00 |
| Cl | 89.95 | 6.02  | 0.37 | 2.1 | 0.26 | 0.41 | 0.06 | 0.42 | 0.17 | 0.24 | 100.00 |

*Note: the microprobe data have been normalised to 100% by a technical reason of carboniferous matter analysis by microprobe measurements by the used equipment and the corresponding analytical program support.

Table 2. Data of \( \delta^{13}C_{org} \) isotopic composition of the Popigai high pressure carbon polymers for individual particles.

| Particle description                          | \( \delta^{13}C \) | Carbon phase                  |
|----------------------------------------------|-------------------|-------------------------------|
| 1 Black angular particle with shagreen surface | -24.12            | After-coal graphite           |
| 2 Black angular particle with glance surface  | -25.58            | After-coal glass-like carbon  |
| 3 -.                                          | -21.26            | -.                            |
| 4 -.                                          | -22.96            | -.                            |
| 5 -.                                          | -22.30            | -.                            |
| 6 -.                                          | -22.79            | -.                            |
| 7 -.                                          | -24.01            | -.                            |
| Overage                                       | -23.15            | After-coal glass-like carbon  |

3.3. Raman spectroscopy
The typical Raman UV spectra of the UHPCP is presented with several bands – 1200 cm\(^{-1}\), D and G bands. The most intensive is the G band which is posited at 1608 cm\(^{-1}\) and presents sp\(^2\) carbon state. At the left side of the G band the D band is evidently seen which is usually absent in crystalline graphitic substances. But, the D band under UV laser excitation can exist if the carbon matter is presented with disordered rings then the D peak survive in UV [14, 15].

Also, in the typical UV Raman spectra we evidently observe the presence of the wide band centered at 1200 cm\(^{-1}\) that rather can correspond to sub-nanocrystalline diamond probably up to amorphous tetrahedral diamond-like carbon (ta-C) [14-18].

The observed UV Raman spectra with the distinguished 1200 cm\(^{-1}\), D and G bands by the whole spectral profile can be assigned to hydrogenated ta-carbon (ta-C:H) which UV Raman characteristics had been described in detail in works [14, 15]. The rare spectra (Figure 4, upper spectrum) with D-like peak at 1400 cm\(^{-1}\) can be attributed to polymeric amorphous carbon – a-C:H [14]. We think that more detail study by high resolution transmission electron microscopy and electron energy loss spectroscopy
can give a detail information about features the carbon atoms state and polymers structure at the atomic resolution level.

![Figure 4](image)

**Figure 4.** Raman spectra of high pressure carbon polymers: bottom grope spectra - polymeric a-C:H; top spectrum - ta-C:H (hydrogenated diamond-like carbon). Additional lines detected by UV laser radiation: artifact lines from a Raman spectrometer optical system – SiO$_2$ glass – 465, 797, 1064 cm$^{-1}$; artifact lines from room air – O$_2$ – 1555 cm$^{-1}$; N$_2$ – 2330 cm$^{-1}$.

4. Discussion and conclusions
The carboniferous matter have specific morphology with abounding bubbles presence up to forming of purmice texture. Sometimes carbon particles have stream-like/fluidal texture. According to the provided analysis we have found that the extracted carbon particles are presented with glass-like carbons presented with amorphous hydrogen-containing matter (bitumen-like composition). The complex data point to nongraphitic initial nature of the studied carbons from the melt impactites. The analyzed matter is rather presented with high pressure product of impacted coal matter (bitumen substance). It is known [1] that the Popigai target is partly composed of 5 stratigraphic levels of sedimentary rocks enriched in coals and bitumenes of Proterozoic-Cretaceous and Pliocene-Quarternary ages. Our find of “after-coal” products within the melt rock can allow to suppose that the coal could be a source for a part of the impact diamonds formation within the Popigai structure.

The isotopic measurements are in a good correspondence with the proposed idea of after-coal nature of the analyzed carbon material. Following to the provided here isotopic study we evidently see that for isotopic data interpretation it would be more correctly to measure and analyze isotopic data by curtain particles selected from concrete parts of melt rocks and suevitic components (from melt zones, relict rock fragments and minerals) independently. The different initial origin of the carboniferous matter is the reason of the wide range of the isotopic composition -9.9 $\div$ -31.5 $\%_0$ of the Popigai impact diamonds described earlier [1] that cover after-graphite and after-coal impact diamonds.

According to the presented here UV Raman spectroscopy studies the analyzed noncrystalline carbon impact products can be assumed generally as high-pressure variety of hydrogenated amorphous
tetrahedral diamond-like carbon (ta-C:H) and rare as polymeric a-C:H. In the future, the described high pressure non-crystalline carbon matter can be interesting for determination of the details of their proven state, polymeric structure and physical properties. The high pressure non-crystalline carbons can be interesting as possible new materials.

By this work we prove the partial preservation of the sedimentary carboniferous matter (coal/bitumens state) of the sedimentary part of the Popigai target sequence transformed into high pressure carbon polymorphs. Thus, in the impact process for the shock high level PT-conditions up to impact melting the typomorphic features of the noncrystalline matter such as observed ta-C:H probably can be used. At the same time, we see in the future the need of high resolution studies that can give more detail information about typomorphism of the high pressure non-crystalline impact carbons.

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