

# Diamonds from the Popigai impact structure, Russia

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## ABSTRACT

**Diamonds were found in impact melt rocks and breccias at the Popigai impact structure in Siberia. The diamonds preserve the crystallographic habit and twinning of graphites in the preimpact target rocks, from which they formed by shock transformation. Secondary and transmission electron microscopy indicate that the samples are polycrystalline and contain abundant very thin lamellae, which could represent stacking faults, with local hexagonal symmetry, or microtwins. Microcrystalline units are  $\leq 1 \mu\text{m}$ . Infrared spectroscopy indicates the presence of solid  $\text{CO}_2$  and water in microinclusions in the diamonds,  $\text{CO}_2$  being under a pressure greater than 5 GPa (at room temperature). Trace element and isotopic compositions confirm the derivation from graphite precursors.**

## INTRODUCTION

Diamonds in terrestrial impact craters have been studied in Russia and the Ukraine (e.g., Masaitis, 1993; Masaitis et al., 1972, 1990; Vishnevsky and Palchik, 1975; Gurov et al., 1995), at the Ries crater (Rost et al., 1978) and have generated interest elsewhere (e.g., Koeberl, 1995; Hough et al., 1995, 1997). Impact diamonds as much as 1 cm (not single crystals) have been found in impact breccias at the 100-km-diameter Popigai crater in Russia (Masaitis et al., 1972). The Popigai impact structure, centered at lat  $71^\circ 38' \text{N}$  and long  $111^\circ 11' \text{E}$ , at the northeast slope of the Anabar shield in northern Siberia, dates to about 35.7 Ma (Bottomley et al., 1997). The target rocks consist of Archean crystalline rocks and an overlying sequence of up to 1 km of northward-dipping Proterozoic and Cambrian quartzites, dolomites, limestones, and Permian sandstones and argillites, invaded by Triassic dolerite sills and dikes.

Suevites (melt-fragment-bearing impact breccias) overlie allogenic (melt-free) polymict breccia and form a continuous cover more than 1 km thick in the central part of the structure; suevites also occur as lenses or irregular bodies within the allogenic breccia. Impact melt rocks (tagamites; Masaitis, 1994) crop out mostly in the western part of the structure as sheet-like bodies as thick as 600 m, and as smaller irregular bodies within suevites (Masaitis, 1994). Diamonds were found in strongly shocked gneiss clasts within impact melt rocks and suevites (Masaitis, 1993; Masaitis et al., 1972) and can be extracted by acid digestion of the whole rocks. The distribution of impact diamonds in impact breccias is a function of the initial distribution of graphite-bearing rocks among the target rocks, as well as the shock zonation. No impact diamonds were formed in the central part of the crater, because residual temperatures in the melt rocks were too high and led to secondary graphitization. However, in the zone immediately outside the central part, the pressures were high enough and the temperatures low enough to form and preserve abundant impact diamonds (Masaitis, 1993).

## MINERALOGY OF IMPACT DIAMONDS

The gneissic target rocks at Popigai contain graphite flakes, crystals, and aggregates 20  $\mu\text{m}$  to  $\geq 10 \text{ mm}$ . Well-shaped tabular graphite crystals are usually 0.1–1 mm long and are elongated parallel to the gneissic fabric. Diamonds, which are also found in situ in shocked crystalline rocks (Fig. 1A), commonly show tabular or isometric shapes, indicating that they preserve the crystal habit of the precursor graphite crystals and are thus paramorphs after graphite (paracrystals, cf. Masaitis et al., 1990). Goniometric examinations of the diamond paracrystals show occasional deviations of the vertical prismatic crystal angles from the  $60^\circ$  present in graphite.

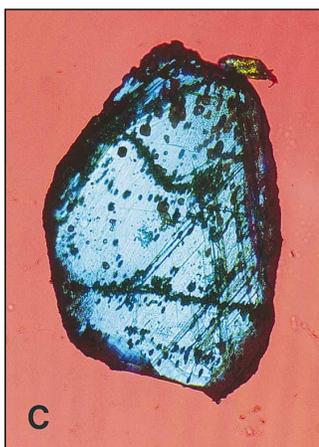
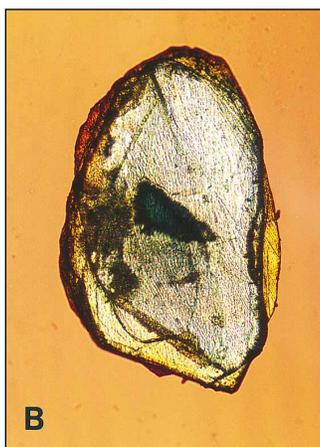
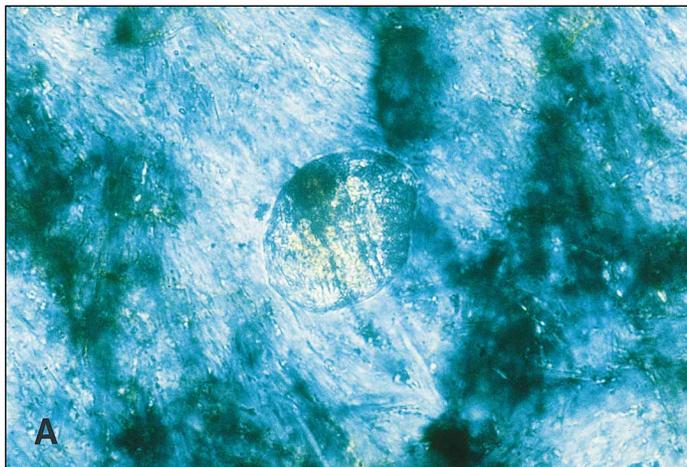
The diamonds vary from black, gray, and brown, to yellowish-white and translucent, and show strong birefringence (up to 0.025). The origin of the color variation is unknown. They commonly display a layered texture (in some cases with slight rotation between connected layers), twinning, and striations (Fig. 1, B and C). The diamonds often show dense, narrowly spaced lamellae (Fig. 1B), which are interpreted to be the result of the shock transformation of the graphite to diamond. They also inherit one or two intersecting sets of more widely spaced twinning striations of the initial graphite (h.h. $\bar{2}$ h.l) (Fig. 1C), which may have formed in graphite by shock compression before transformation to diamond (cf. Masaitis et al., 1990).

## SAMPLES AND TECHNIQUES

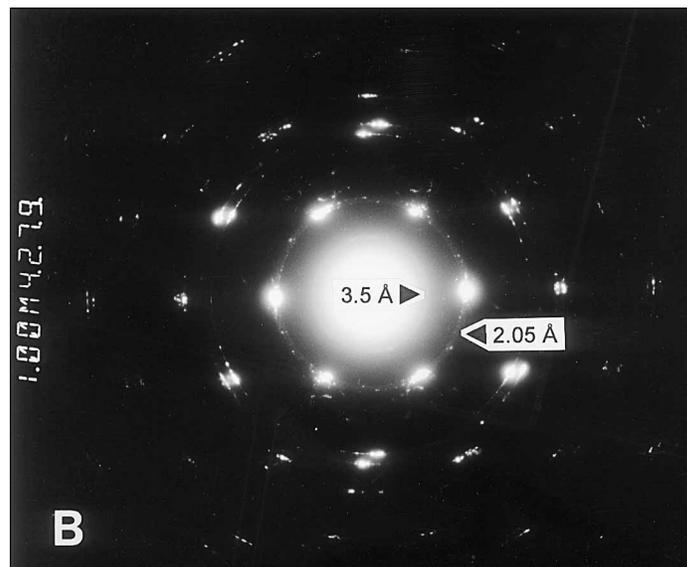
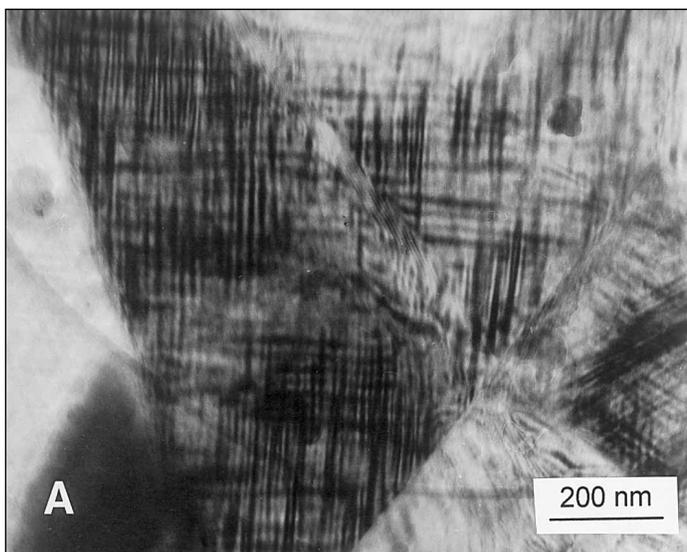
We performed a detailed study of impact diamonds as large as 2 mm (three yellowish—PY-1 to PY-3; three black—PB-4 to PB-6) by a variety of techniques, starting with scanning electron microscopy (SEM) and infrared absorption (IR) measurements. The IR spectra were obtained on uncut samples to avoid alteration during polishing when the samples' temperatures are as high as 1000  $^\circ\text{C}$ . The three black samples were too opaque to obtain IR spectra. Spectra were collected on the three yellowish samples (PY1-3), and on one smaller black Popigai diamond (MSPOPI), using a Nicolet 740 Fourier-transformed infrared (FTIR) spectrometer (see Schrauder and Navon [1993] for details). Subsequently, the samples were cut or broken into several pieces for transmission electron microscopy (TEM), instrumental neutron activation analysis (INAA), X-ray, isotopic,

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**Figure 1. A:** Authigenic Popigai impact diamond (diameter about 150  $\mu\text{m}$ ) in recrystallized plagioclase within strongly shocked biotite-garnet gneiss, which, in turn, is a clast within massive impact melt; crossed polarizers. **B:** Popigai diamond (long dimension 560  $\mu\text{m}$ ) showing fine lamellar structure due to shock metamorphism, and (dark zone at center) remnant of Wesselowski twin inherited from original graphite; circular polarization. **C:** Impact diamond (long dimension 570  $\mu\text{m}$ ) showing slight etching preferentially along twinning junctions and fissures, and flakes of secondary graphite; circular polarization.



**Figure 2. A:** Bright-field transmission electron microscope image showing lamellae (dark) that represent stacking faults in black impact diamond PB-5. **B:** Selected area electron diffraction pattern of sample area shown in A; 3.5  $\text{\AA}$  reflection corresponds to graphite, and 2.05  $\text{\AA}$  reflection corresponds to diamond.

and other studies. TEM was done with a Philips CM20-STEM at 200 kV on crushed and ion thinned diamonds.

### ELECTRON MICROSCOPY

All impact diamonds are polycrystalline. SEM and TEM studies show that the diamonds are partly covered by a thin amorphous film, which may be a result of their being briefly in a high-temperature environment. X-ray diffraction (XRD) analyses of fragments of our samples (using a Gandolfi camera) show that two of them may contain as much as 25 vol% lonsdaleite, but the others do not show evidence for the hexagonal diamond modification. The evaluation of the XRD spectra show distinct line broadening, which is most likely due to the small crystallite size of the polycrystalline aggregates.

The TEM investigations show an internal layered texture with thicknesses of a few micrometres, which may be inherited from the precursor graphite. Sizes of individual diamond microcrystals are on the order of 1  $\mu\text{m}$  or less. Figure 2A shows the intergrowth of the cubic diamond phase with a lamellar phase or defect. The nature of these lamellae could not be elucidated because of the limited resolution of the TEM (2.7  $\text{\AA}$ , whereas (111) lattice repeats correspond to 2.05  $\text{\AA}$ ; Fig. 2B). The lamellae could represent either stacking faults or microtwins. If multiple stacking faults occur, the lamellae could be interpreted to be lonsdaleite, the hexagonal diamond polymorph.

### INFRARED SPECTROMETRY

The IR spectra of all diamonds examined exhibit the intrinsic diamond absorption bands. In addition, two of the transparent diamonds (PY-1, PY-3) show strong bands at around 655 and 2385  $\text{cm}^{-1}$ , which are identified as the  $\nu_2$  and  $\nu_3$  bands of  $\text{CO}_2$ , respectively (Fig. 3). These spectra also show the combination bands ( $\nu_3 + 2\nu_2$  and  $\nu_3 + \nu_1$ ) of  $\text{CO}_2$ . All four absorption bands are shifted from their 1 atm positions. Comparison with high-pressure spectra of solid  $\text{CO}_2$  (dry ice; Hanson and Jones, 1981) reveals that the positions of these peaks in the spectra of two samples fit the spectrum of solid  $\text{CO}_2$  at a pressure  $>5$  GPa. The spectra are similar to those of  $\text{CO}_2$ -bearing kimberlite diamonds reported by Schrauder and Navon (1993).

The two  $\text{CO}_2$ -bearing samples also show absorption bands at 1645 and 3420  $\text{cm}^{-1}$ , which are due to the presence of water. Because the bands are very broad and the peak positions cannot be determined exactly, the pressure for the trapped water cannot be constrained. Water concentrations were estimated from the peak heights of their main absorption bands at 3420  $\text{cm}^{-1}$ , using the 1 atm absorption coefficient of pure water, as given in Navon et al. (1988). For the samples PY1 and PY3, water contents of about 64 ppm were estimated

(the smaller MSPOPI sample contains about 250 ppm H<sub>2</sub>O). All samples also show bands at 480, 1222, and 1108 cm<sup>-1</sup>, which are probably due to silicates. The spectra of the impact diamonds clearly differ from those of mantle-derived diamonds (cf. Schrauder and Navon [1993] and references therein). Comparison of the Popigai diamonds with microdiamonds recovered from high-grade metamorphic rocks (e.g., Dobrzhinetskaya et al., 1995) shows significant differences: the impact diamonds are devoid of nitrogen, and no water- or CO<sub>2</sub>-absorption lines are present in the metamorphic diamonds. The sharp absorption lines at 3107 cm<sup>-1</sup>, which are attributed to hydrogen impurities (Davies et al., 1984), are also absent in the impact diamonds.

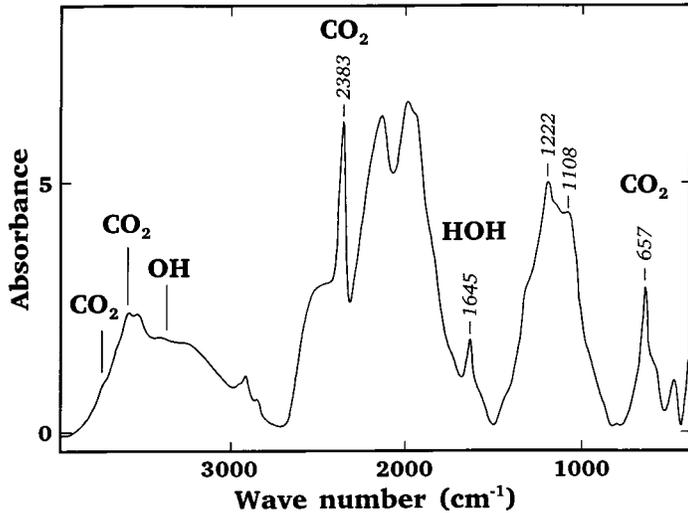


Figure 3. Infrared absorption spectrum of impact diamond PY-1. In addition to intrinsic diamond modes (double feature around 2000 cm<sup>-1</sup>), four CO<sub>2</sub> peaks are visible. Positions of all CO<sub>2</sub> bands are shifted compared to their room temperature and pressure values. Stretching and bending absorption modes of water are indicated at 1645 and 3420 cm<sup>-1</sup>. Absorptions at ~1222 and 1108 cm<sup>-1</sup> can be due to either nitrogen or silicate minerals.

## TRACE ELEMENT AND ISOTOPIC COMPOSITION

The abundances of 31 minor and trace elements were determined by INAA in all bulk samples. The abundances are low, mostly in the parts per billion range; a few elements—Fe, Na, Zn, Ni—reach lower parts per million concentrations (Table 1). The contents of the siderophile elements Ni, Co, and Ir are enriched (up to 4.3 ppm, 0.9 ppm, and 0.2 ppb, respectively) compared to the abundances of lithophile elements in the diamonds (Table 1) and may indicate the presence of a minor meteoritic component (maybe introduced by hot vapor), similar to that observed in the impact melt rocks (cf. Masaitis, 1994). The rare earth elements show distribution patterns (Fig. 4) that are similar to those of the target rocks with negative Eu anomalies (Masaitis, 1994) and may reflect minor mineral inclusions from the precursor graphite.

Carbon isotope data for the Popigai diamond and graphite samples are shown in Figure 5, together with comparison data for kimberlitic (octahedral) diamonds and impact diamonds derived from the Chicxulub and Ries craters. The δ<sup>13</sup>C values for Popigai diamonds range from -20‰ to -8‰, and the two graphite samples (from Popigai) are also in

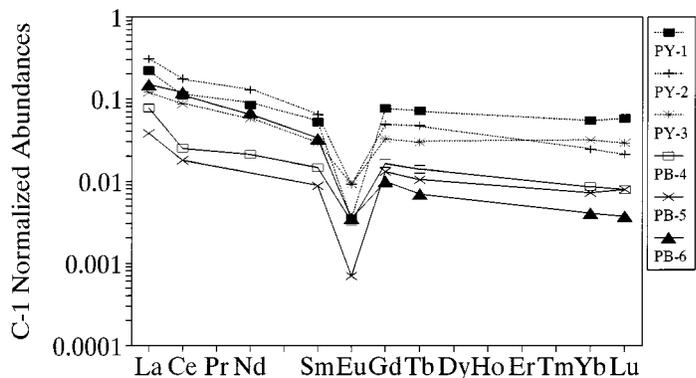


Figure 4. Chondrite-normalized rare earth element patterns of six Popigai impact diamonds, determined by INAA (for methods and normalization factors, see Schrauder et al., 1996).

TABLE 1. TRACE ELEMENT CONTENT OF POPIGAI DIAMONDS

	PY-1	PY-2	PY-3	PB-4	PB-5	PB-6
weight (mg)	0.95	0.89	2.77	3.13	4.85	8.55
Fe (ppm)	27	39.2	34.6	506	231	102
Na (ppm)	35.6	29.3	15.1	13.5	11.1	16.1
K (ppm)	46.3	52.3	16.5	6.63	8.8	53.6
Sc	30.9	12.8	77.9	1.7	3.17	17.3
Cr	355	457	208	381	191	226
Co	192	203	73	906	298	291
Ni	528	659	1400	4300	1600	1700
Zn	1170	2620	274	1070	716	323
As	21.7	14.8	12.7	20.3	62.5	45.1
Br	86.4	420	17	60	960	37.6
Rb	<100	<100	30	25	27	435
Sr	<3200	<3200	<1500	1300	200	<615
Zr	<1000	<1000	<200	80	60	150
Sb	<25	13.7	0.1	5	6.6	0.4
Cs	7.2	7.5	2.1	1.9	1.5	21.2
Ba	<3200	1880	1270	500	506	412
La	81	112	44	28.4	14	54
Ce	106	168	81	24	17	115
Nd	60	90	41	15	<20	48
Sm	12	14.6	6.8	3.3	2	7.5
Eu	0.3	0.8	0.8	0.28	0.06	0.3
Gd	<15	15	10	5	4	3
Tb	4.1	2.7	1.7	0.8	0.6	0.4
Yb	13.4	6	7.8	2.1	1.8	1
Lu	2.2	0.8	1.1	0.3	0.3	0.14
Hf	2.8	7.1	3.7	1.5	8.1	3.8
Ta	3.7	1.2	1.3	0.5	0.4	9
Ir	0.1	0.04	0.04	0.2	0.08	0.08
Au	0.2	0.3	0.02	0.09	0.2	0.06
Th	30	44	98	9.4	5.4	55
U	2	<30	2	1	2	1

Note: All data in ppb, except as indicated.

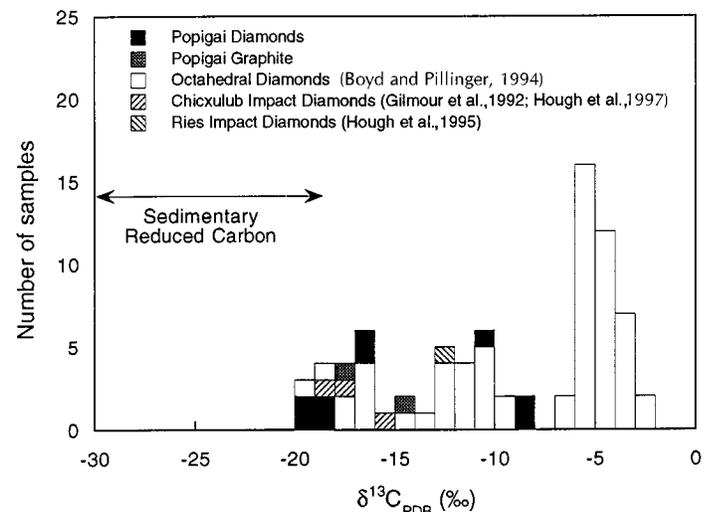


Figure 5. Carbon isotopic composition (PDB is Peedee belemnite) of Popigai impact diamonds and graphite compared to kimberlitic diamonds and diamonds derived from Chicxulub and Ries impact structures. Carbon isotope compositions of Popigai graphite and diamonds were determined by combustion of single crystals (<300 μg) at about 1000 °C for ≥2 h with excess CuO in sealed quartz tube, followed by gas purification and measurement on VG-SIRA 24 mass spectrometer to precision of ±0.1‰.

this range. Earlier analyses yielded a more restricted range of  $\delta^{13}\text{C}$ , from  $-12\%$  to  $-17\%$  (e.g., Vishnevsky and Palchik, 1975). The  $\delta^{13}\text{C}$  values are more depleted in  $^{13}\text{C}$  than the majority of mantle-derived kimberlitic diamonds, but more  $^{13}\text{C}$ -enriched than most biogenically derived carbon in sediments. The overlap in range for graphites and diamonds supports the conclusion that the Popigai diamonds are derived from graphitic precursors by shock metamorphism.

The nitrogen contents and isotopic ratios were also measured by mass spectrometry (cf. Gilmour et al., 1992) for some of our Popigai diamonds, but for most of them the concentrations were too low. The measured N contents ranged from 5 to 50 ppm, and the  $\delta^{15}\text{N}$  isotopic values range from  $-6\%$  to  $+2\%$ . The N abundances are very low, several orders of magnitude lower than those of kimberlitic diamonds. The isotopic composition and abundance of the Popigai diamonds are similar to the only previous measurement of these values in impact-derived diamonds, i.e., Cretaceous-Tertiary boundary nanodiamonds (Gilmour et al., 1992). The low N contents are expected if the diamonds are derived from nitrogen-poor graphite, but there are insufficient data on the nitrogen content of diamonds formed by chemical vapor deposition to eliminate that mechanism based on N content alone.

## SUMMARY AND CONCLUSIONS

The presence of large polycrystalline diamonds in impactites from the Popigai impact structure, Russia, have mineralogical and crystallographic characteristics that are very similar to those of graphites found in the graphite-bearing precursor gneisses, indicating that these diamonds have formed by shock-induced solid-state (martensitic) transformation of graphite to diamond. This transformation seems to have occurred between about 35 and 60 GPa (on the basis of petrographic observations of shock phenomena in the host rocks). The size of the individual crystallites is  $\leq 1\ \mu\text{m}$ , and TEM studies show the presence of abundant thin lamellae. It is surprising that the diamonds contain minor inclusions with  $\text{CO}_2$  at high pressure, which must have been included during the high-pressure shock transformation of graphite to diamond. This observation provides additional evidence against diamond formation by chemical vapor deposition processes. Trace element and carbon and nitrogen isotopic data, as well as the low N abundances, support the conclusion that the diamonds formed in situ by shock metamorphism.

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