

Synchrotron infrared and Raman spectroscopy of microdiamonds from Erzgebirge, Germany

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Abstract

Metamorphic diamonds from the Erzgebirge, Germany have been investigated using synchrotron infrared absorption, Raman scattering, and fluorescence spectroscopy. Infrared absorption features associated with C–C, C–H bonds, molecular H₂O, OH[−] and CO₃^{2−} radicals, and N-impurities were observed. The results suggest that a carbon–oxygen–hydrogen (COH) supercritical fluid is the most probable concept to explain the origin of diamonds from ultrahigh-pressure metamorphic terranes (UHPM). Investigation of the nitrogen impurities suggests that the Erzgebirge diamonds belong to the Type 1b-1aA, which is similar to metamorphic diamonds from the Kokchetav massif of Kazakhstan and the Western Gneiss Region of Norway, and differentiates them from other nitrogen-bearing diamonds from kimberlitic sources (Type 1aAB). The occurrence of nitrogen impurities as single atoms in the crystal lattice implies that the Erzgebirge diamonds had a short residence at high-pressure and high-temperature, which therefore suggests a possibility for very fast exhumation. Both infrared and previous studies of nanoinclusions using a transmission electron microscope support a concept of diamond crystallization from a COH rich supercritical fluid.

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1. Introduction

Over the last decade, microdiamonds of 1- to 300- μm size have been found in ultrahigh-pressure metamorphic (UHPM) rocks with crustal affinities within the Paleozoic–Mesozoic collisional orogenic belts of Kazakhstan (Kokchetav massif), China (Dabie and

Qiadam territories), Norway (Western Gneiss Region), Germany (Erzgebirge massif), Greece (Rhodope), and Russia (Ural Mountains) [1–12]. The microdiamonds in all of these areas, except for a pseudomorphic cubic graphite replacing diamond and microcrystalline diamonds in the Ural Mountains [12], have been repeatedly confirmed and unconditionally accepted.

The largest diamond deposits are located in the Kokchetav massif, with the average diamond containing ~20–30 carats/ton in felsic gneisses and up to

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~2700 carats/ton in marbles [13]. The Erzgebirge massif in Saxonia, Germany is another site with a high diamond concentration similar to that of Kazakhstan. In both localities, the diamonds are well preserved, although some of them are graphitized or completely transformed to graphite. In contrast, only a few diamond crystals have been found in other UHPM terranes. Geologists believe that the rarity of diamonds in some ultrahigh-pressure rocks is due to a complete diamond-to-graphite transformation accompanied by intensive recrystallization of rock-forming minerals at low temperatures and low pressures or a very low concentration of CO₂ ($X_{\text{CO}_2} < 0.01$) that would not lead to a significant diamond crystallization, or both [14,15].

The size of microdiamonds is an important parameter because it may cast light on the history of the diamonds' formation. In the Kokchetav massif of Kazakhstan, the microdiamonds range in size from 1 to 300 μm; smaller diamonds of a size ~1–50 μm are abundant within Si-rich rocks (quartzo-feldspathic gneisses), whereas diamonds of larger size (~50–300 μm) occur mostly within garnet pyroxenites and marbles. The larger Kokchetav diamonds (100–300 μm) were intensively studied with conventional infrared (IR) spectroscopy [16–18], which revealed that the diamonds contain molecular H₂O, CO₂²⁻ and OH⁻ radicals, and nitrogen; the latter exists in a low aggregation state (Type 1b-1aA). The IR data are consistent with direct observations of nanometric fluid and carbonate and OH-bearing crystalline inclusions in these microdiamonds [19–22]. Two concepts of diamond origin are under discussion: (1) crystallization from a supercritical carbon–oxygen–hydrogen (COH) or COH-multicomponent fluid [13,17–23], or (2) from a silicate or carbonate melt [24,25]; it has also been proposed that diamonds from the Kumdikol area of the Kokchetav massif were crystallized during two episodes [13]. The uncertainties in interpretation of diamond origins and the evidence of two stages of diamond crystallization suggest that IR studies with a better resolution, including those utilizing advanced microspectroscopy techniques, are needed to investigate smaller diamonds and their zoning, because the smaller and larger crystals may be formed by different mechanisms. It is also possible that diamonds of different sizes may originate from different carbon sources [13].

In contrast to the Kokchetav massif, the Erzgebirge diamonds are hosted by quartzo-feldspathic gneisses, with no evidence of any carbonate rocks that would associate with the diamond-bearing lithologies. Moreover, the Erzgebirge diamonds are represented only by small crystals of ~1–50 μm in size. There is a need for

characterizations of diamonds from UHPM terranes using state-of-the-art microspectroscopy techniques. This paper presents first IR absorption, Raman scattering and fluorescence spectroscopy studies of loose diamonds extracted from garnet–phengite–quartzo-feldspathic gneisses collected from the Erzgebirge massif in Germany.

2. Geological setting and sampling

The Late Paleozoic crystalline massif of the Erzgebirge is located in Saxony, Germany and continues to the northern part of the Czech Republic. The central part of the massif is composed by ortho- and paragneisses that contain numerous lenses of eclogite and a few lenses of garnet peridotite [25–27]. Diamonds occur in quartzo-feldspathic gneisses as inclusions in garnet, kyanite, and zircon [7,8]. Relics of TiO₂ with α-PbO₂ structure [28] and conventional geothermometry data suggest that felsic rocks were metamorphosed at $T=1200$ °C and $P\sim 8$ GPa in a course of deep subduction [27]. During exhumation process, the diamond-bearing rocks were partly recrystallized at lower pressures and temperatures, although many diamond crystals still remain well-preserved in these rocks [14,25].

We collected diamond-bearing garnet–phengite–quartzo-feldspathic gneisses in small outcrops at the eastern shore of the Saldenbach Water Reservoir, about 1.5 km northwest of the village of Forchheim, Saxonian Erzgebirge, Germany. We found abundant microdiamonds of 3–20 μm size as inclusions in garnets, kyanites, and zircons during studies of the polished thin sections with the aid of an optic microscope. Several diamond grains were extracted from the rock specimens for synchrotron micro-IR studies, which require a single crystal sample.

3. Diamond extraction from the rock

The separation of diamonds from their host rocks by NaOH fusion is a well-established technique in the kimberlitic diamond exploration industry, but the procedure is not applicable to the extraction of microdiamonds from UHPM rocks due to their very small size and fragility. A special method of thermochemical digestion of diamond-bearing, ultrahigh-pressure rocks was developed in Russian institutions in the 1980s during the period of Kokchetav diamond prospecting and exploration [29]. This method combines elements of the traditional chemical digestion of rock-forming minerals such as quartz, feldspars, garnet

and micas, followed by dissolving in strong acids (HF and/or HNO₃, HCl), step by step, to eliminate all solid remains of refractory minerals such as zircon, kyanite, and titanate. The diamond, due to its chemical inertness, remains as a solid residual at the bottom of the chemical dish. We have modified this method by carefully choosing suitable concentrations and proportions of chemical reagents, as well as the temperature and time of reactions, so as to remove undesirable components of the rock while keeping the diamonds protected from chemical digestion and “burning”. Such a modification was obtained through a series of chemical experiments on powdered “blank” rocks containing no diamonds, on diamond-bearing gneisses with a higher and a lower content of diamonds, and on garnet and zircon separates containing diamond inclusions. The most successful procedure is the following:

- Step 1 (oxidation) After standard electromagnetic separation, 5 mg of garnet concentrate powdered to 70–50 μm was mixed with 0.5 ml of 0.1% KNO₃ and kept at room temperature until oxidation reactions were completed and the solid residuum was completely dried.
- Step 2 (fusion) The resulting residuum was mixed with 1.2–1.4 g of granular NaOH and kept at 470 °C at atmospheric pressure in the electrical furnace (Cress MFG Co) during 20 min. We have established during several experiments that the upper limit of temperature is 450–500 °C for which diamonds retain their delicate, intricate, shapes, and, at the same time, all of the surrounding silicate minerals have been completely dissolved.
- Step 3 (rinsing) This step involved rinsing of the alkali-fused residuum, first with water and then with concentrated HCl acid until full neutralization. Both processes were performed several times, using careful filtration, until only a small amount of other solids remained. The residuum obtained after rinsing and neutralization was dried at room conditions and examined with aid of an optical microscope. Such residua usually consist of fused or strongly leached pieces of garnet,

and undamaged crystals of diamond. The amount of diamond found in the residuum depends on the original diamond concentration in the sample. The procedure of oxidation, fusion and rinsing may require repetition several times to gradually minimize the amount of the residuum until the diamond crystals can be found.

Although we provide here the exact procedure, we warn those who would like to reconstruct the method that successful microdiamond extraction highly depends on the chemical composition of the host garnets, the volume of mechanical defects introduced during powdering, and alteration products within the garnets and at the diamond–garnet boundaries. Therefore, the main stages of the procedure must be creatively “tailored” to the chosen host-rock/mineral compositions by changing proportion and concentration of KNO₃ needed for oxidation, and increasing or shortening the time of fusion of the residuum with NaOH.

We have extracted nine diamond crystals from 4 mg of Erzgebirge garnet concentrates; dozens of others were lost during processing as we developed the right procedure. Seven of the recovered diamonds ranged 3–15 μm in size, and two of them were ~30 and ~50 μm in size. All diamonds were transparent and exhibited light honey-brownish or light-brown color that distinguished them from light-yellow, yellow-greenish, and colorless diamonds from the Kokchetav massif, Kazakhstan [29] and the light yellow-greenish diamonds from the island of Fjortoft, Norway [5]. The diamonds of ~30 and 50 μm size were chosen for studies.

4. Scanning electron microscope studies

Electron images of loose diamonds were obtained using a scanning electron microscope (SEM) (Philips XL30 FEG) at the Central Facility for Advanced Microscopy and Microanalysis of the University of California at Riverside. The EDAX microanalytical system of this microscope consists of an energy dispersive X-ray spectrometer (EDS) equipped with an Si detector with a super-ultrathin window and a resolution of 137 eV MnK_α. The spectral data were acquired at 1500–2000 counts per second with dead time below 25%, a beam current of approximately 1 nA, and an effective spot size of about 1.5 mm.

The diamonds were picked up under the binocular microscope by a thin needle and carefully placed on a standard SEM holder covered with a “carbon” tape, and no additional carbon coating was applied to the diamonds. Images of the diamonds were acquired in secondary electron mode at 15 and 20 kV with a working distance of 10 units. The first diamond ($\sim 35 \mu\text{m}$; Fig. 1a) is an imperfect crystal; its shape is characterized by a combination of cube and octahedral faces complicated with sharp corners, hillocks, and tiny channel-like cavities. The second diamond ($\sim 50 \mu\text{m}$; Fig. 1b) is a round-like crystal complicated with numerous tiny cube-like and octahedral faces. Along with the images of the loose diamonds, we provide the image of a diamond *in situ* (Fig. 2) specifically to

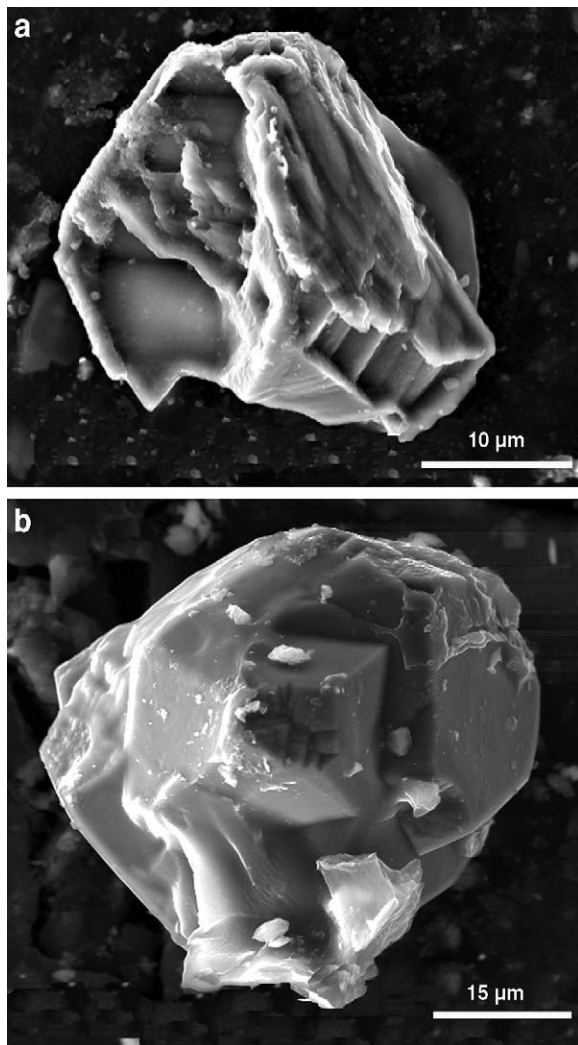


Fig. 1. SEM, secondary electron images (15 kV, spot size 3) of diamonds extracted from garnet–phengite–quartzo–feldspathic gneiss of the Erzgebirge massif, Germany: (a) diamond #1, (b) diamond #2.

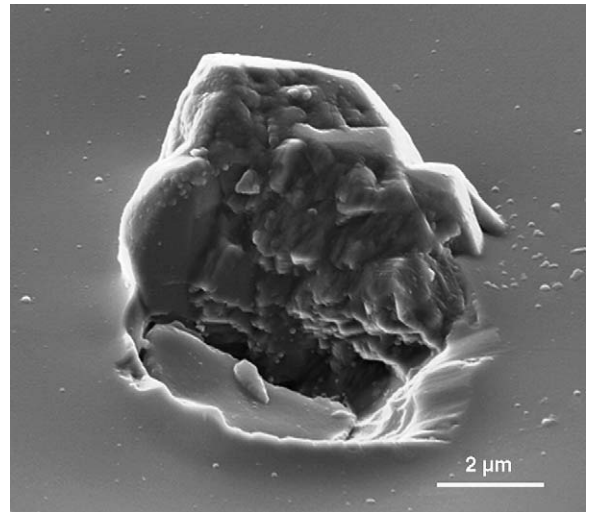


Fig. 2. SEM, secondary electron image (at 5 kV, spot size 3) of Erzgebirge diamond included in zircon [18].

emphasize the similarity of their morphologies. Fig. 2 shows the secondary electron SEM image of a typical Erzgebirge diamond *in situ*, which stands out above the flat surface of its host mineral zircon [22]. Half of this diamond crystal is still contained within the zircon host grain. With a final polishing using the SiO_2 colloidal system of $0.06 \mu\text{m}$, we were able to polish out an $\sim 2.5\text{-}\mu\text{m}$ -thick layer of host zircon to let the denser diamond stand out above the zircon surface. A comparison of diamonds extracted from their host rock with those “*in situ*” showed that the morphology of the Erzgebirge diamonds is uniform.

5. Synchrotron IR and Raman measurements

5.1. Technical background on the synchrotron experiments

Synchrotron radiation, a bright source of infrared photons, was first exploited in microspectroscopy to probe organic and non-organic materials with sizes close to the diffraction limit [30–33]. This provides IR spectra with high signal-to-noise ratios at spatial resolutions as fine as $3\text{--}10 \mu\text{m}$. Mid-IR photons are too low in energy ($0.05\text{--}0.5 \text{ eV}$) to either break the chemical bonds or cause ionization; they also produce a minimal heating of samples. Synchrotron microspectroscopy is a well-established method that over a decade was successfully applied to studies of biological tissues and cells, semiconductors, geological materials, interplanetary dust particles, forensics, the corrosion of metals, structural composites, and polymer laminates.

We performed infrared measurements of the Erzgebirge diamonds at the U2A beam line of the National Synchrotron Light Source (NSLS) at the Brookhaven National Laboratory (BNL) in Brookhaven, USA. The optical layout of the beam line facility was described in detail elsewhere [31]. The diamond IR spectra were collected with a Bruker IFS 66v/ S vacuum Fourier transform interferometer interfaced with the synchrotron source and a modified Bruker IRscope-II microscope equipped with an HgCdTe type-A detector. The top aperture/field stop was set to $10 \times 10 \mu\text{m}^2$, and the spectra were acquired in the range of $600\text{--}4000 \text{ cm}^{-1}$ with a KBr beam splitter. The optical bench was evacuated, and the microscope was purged with dry nitrogen gas during the measurements to reduce or eliminate water vapor absorption. A spectral resolution of 4 cm^{-1} was applied to all spectra. In addition, the Raman scattering and fluorescence spectra of diamonds were obtained in backscattering mode with a Jobin Yvon H-460 spectrograph equipped with a charge-coupled device (CCD) detector. The excitation source was an Ar^+ laser operated at 514.5 nm . A laser beam a few micrometers in diameter was focused onto the diamond crystals. Diamonds of interest were cleaned in low-concentrated H_2SO_4 , and dried in a vacuum oven at $120 \text{ }^\circ\text{C}$ for 72 h before the synchrotron experiment.

Both synchrotron IR absorption spectra (Fig. 3) collected from diamond #1, (Fig. 1a) and diamond #2 (Fig. 1b) contain additional fringes (“noise”), which are a result of a beam-scattering effect caused by non-flattened surfaces of raw crystals. Both spectra show presence of nitrogen impurities, OH stretching mode, molecular H_2O , CO_3^{2-} radical, and C–C diamond phonon absorption bonds.

5.2. Nitrogen aggregation in diamonds: background

Almost all natural diamonds contain substitutional nitrogen impurities in amounts ranging from a few to several thousand atomic parts per million (ppm) [34–38]. In diamond, nitrogen occurs as four main point defects (A, B, C, and D defects or centers) [34–38], which give a rise to the specific absorption corresponding to $1400\text{--}900 \text{ cm}^{-1}$ wavelength numbers. Experimental studies have shown that these defects in diamond structure are linked by a diffusion process following a second-order kinetics, higher temperatures, higher nitrogen content, and/or longer residence times that promote nitrogen aggregation. The process includes the incorporation of the singly substituted N atoms, named C-defects (Type Ib diamonds), which easily occur at respectively lower temperatures. With time, single N

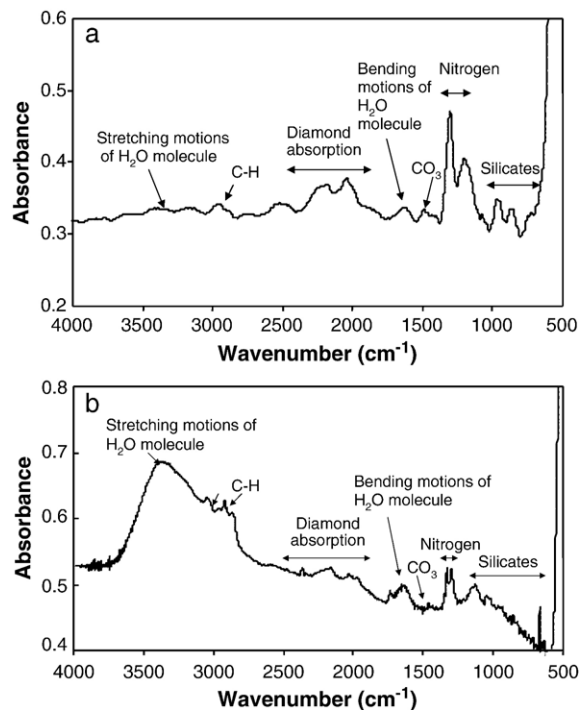


Fig. 3. Synchrotron IR spectra (beam line U2A, Brookhaven National Laboratory) obtained from Erzgebirge diamond #1 (a) and diamond #2 (b).

atoms join together to form pairs called A centers (Type IaA diamonds) [34,35]. Further diffusion and aggregation of the nitrogen forms four N atoms plus a vacancy (Type IaB diamonds). According to such a classification, most kimberlitic diamonds containing nitrogen belong to Type IaA–IaB, whereas diamonds from UHPM terranes (Kokchetav massif, Kazakhstan, and Fjortoft Island of Norway) belong to mixed Type Ib–IaA. The concept of nitrogen aggregation in diamond structure is widely used in the geosciences for calculations of the temperature at which diamonds were crystallized if the residence time and the activation energy required for the transition of C to A defects are known [18,36–39]. However, available publications show that there is no good agreement between calculations provided by different authors for the Kokchetav diamonds; for example, one group of researchers suggests a temperature of $\sim 700 \text{ }^\circ\text{C}$ [16,18], whereas another group proposes $\sim 900 \text{ }^\circ\text{C}$ [17,37] (both temperature estimates assume the same geological residence time of 5 m.y.). The critical discussion of this issue [37] established that the result depends upon the choice of the activation energy (e) values, which usually derive from experimental works. Experiments [37] have confirmed that $e=4.4 \text{ eV}$

provides the best estimate of temperature for octahedral growth sectors of diamonds, while $e=6.0$ eV fits better for cube growth sectors of diamond. The temperature of 900 °C calculated by Taylor et al. [17,37], using the $e=6.0$ eV parameter and therefore assuming that almost all Kokchetav diamonds are represented by cuboidal crystals, fits better with the range of temperatures derived from a conventional geothermobarometry (920–1250 °C) applied for natural diamond-bearing rocks [40–42].

5.3. Erzgebirge diamonds: IR microspectroscopy

Both studied diamonds exhibit the characteristic C–C diamond phonon absorption bands in the region of 2600–2000 cm^{-1} . Diamond #1 is characterized by clear nitrogen-related absorptions, with a strong peak at 1282 cm^{-1} testifying for the presence of nitrogen aggregated as N-pairs (A defects). There are also weak but significant nitrogen absorption bands at 1130 cm^{-1} (as detected by software) and around 1344 cm^{-1} (Fig. 3a), which are characteristics of C defects. Given that nitrogen forms C defects which then aggregate to A defects, and further from A to B defects, the absence of absorptions typical of B defects (e.g. at 1175 cm^{-1}) is considered as a confirmation that this diamond belongs to Type Ib-IaA.

Deconvolution of the collected IR spectra was performed by both the hand method and using a homemade computational program. In both cases, the calculated amount of nitrogen in diamond #1 was ~ 1630 ppm ($\pm 20\%$) with $70\% \pm 10\%$ of IaA. The latter error is quite large, and it mostly depends on the uncertainty associated with baseline correction in the region of wavelength numbers below 1000 cm^{-1} .

In addition to nitrogen, the IR spectrum of diamond #1 also exhibits a clear absorption at 3107 cm^{-1} corresponding to C–H bonds in the diamond matrix. The sample also contains a small (but detectable) amount of water presented as absorption bands at 1630 cm^{-1} , which reflects bending motions of the H_2O molecule; absorption bands at 3420 cm^{-1} are identified as O–H stretches of the H_2O molecule. There is also a well-pronounced absorption band at 1430 cm^{-1} , corresponding to the carbonate radical CO_3^{2-} ; the latter might be incorporated in diamonds as carbonate microinclusions.

Diamond #2 is characterized by a minor amount of nitrogen because none of the major peaks typical of N-bearing defects can be identified (Fig. 3b). We infer that the N content in this sample is not higher than 160 ppm because above this value N content would lead to

resolvable IR absorption. The IR spectrum clearly shows the presence of bending motions of the H_2O molecule (absorption at 1630 cm^{-1}) and the OH region at 3420 cm^{-1} ; again, the latter reflects the stretching motions of the H_2O molecule. Peaks at 2870, 2925, and 3042 cm^{-1} correspond to the C–H stretching bands. In our case, as it was stated by a beam-scientist, they record a contamination of the beam with engine oil of the vacuum pumps that appeared in IR window at U2A beam line.

The Erzgebirge diamond #2 IR spectral characteristics are strikingly similar in both N content and C–H stretching bands to three microdiamonds from Akluilak minette dyke, Nunavut, Canada (see Fig. 1b in [39]) showing a possible correlation between C–H stretching bands and low N content. The recently discovered diamonds belong to a metamorphic diamond population (Type Ib-IaA), which, it is believed, were crystallized within deeply subducted sediments and later were

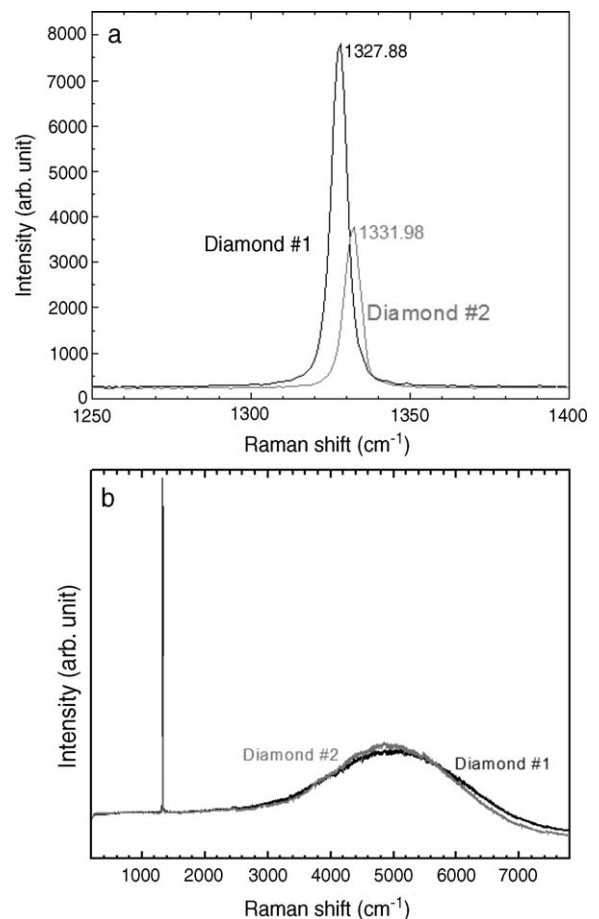


Fig. 4. Raman (a) and cathodoluminescence (b) spectra (beam line U2A, Brookhaven National Laboratory) of Erzgebirge diamonds #1 and #2.

“sampled” by the minette dyke and brought to the Earth’s surface [39].

5.4. The Erzgebirge diamonds: Raman scattering and fluorescence spectroscopy

Raman spectroscopy (Fig. 4a) revealed that diamond #1 is characterized by a sharp, high-intensity band at 1327.9 cm^{-1} , which deviates from the standard diamond peak at 1332 cm^{-1} , which reflects the first-order diamond lattice vibration of LO=TO phonon along the two-dimensional planes. The shift of the Raman band in diamonds to the lower- or higher-frequency regions may be interpreted as (1) deformation of the diamond lattice due to internal stress, (2) instrumental uncertainties, or (3) the presence of point defects or growth zoning defects in the diamond crystal [43–45]. Although we excluded any instrumental error, at this moment we are not able to provide any explanation of the Raman shift in diamond #1 to the lower-frequency region; for that, additional micro-X-ray studies would be necessary. Diamond #2 has a lower-intensity peak than diamond #1, but its Raman peak at 1331.98 cm^{-1} is similar to the diamond standard Raman band at 1332 cm^{-1} . The fact that the wide band occurred around 4900 cm^{-1} in the Raman spectra of both diamonds might be due to the presence of nitrogen impurities (Fig. 4b).

6. Discussion

Our synchrotron IR studies showed that the Erzgebirge diamonds contain nitrogen impurities, molecular H_2O , and OH^- and CO_3 radicals. The presence of both nitrogen C- and A defects classifies the studied diamonds as Type Ib–IaA, which is similar to other metamorphic diamonds from marbles and garnet–pyroxenites of the Kokchetav massif of Kazakhstan [16–18] and from the felsic gneisses on the island of Fjortoft in the Western Gneiss Region of Norway [5].

As we see from the diagram of nitrogen contents versus nitrogen aggregation values built up on the nitrogen measurements in the well-known kimberlitic diamonds and diamonds from UHPM terranes (Fig. 5), the Erzgebirge diamond plots are within the ranges of those from Kazakhstan and Norway, and they are clearly distinguished from diamonds from kimberlitic sources. The lowest concentration of nitrogen in the Erzgebirge diamonds ($\sim 160\text{ ppm}$) agrees with that of diamonds from Akluilak minette dyke, Nunavut, Canada [39], and it is close to the diamonds from Fjortoft, Norway [5].

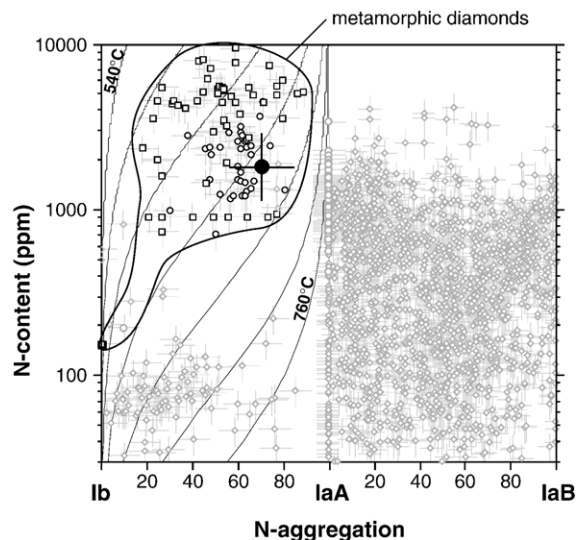


Fig. 5. Diagram of nitrogen aggregation versus nitrogen content in worldwide collected kimberlitic diamonds (gray patterns) and diamonds from ultrahigh pressure metamorphic terranes of the Kokchetav massive, Kazakhstan, and from the Western Gneiss Region, Norway (open circles) [18]. Black circles with crossing lines are diamonds from the Erzgebirge massif, Germany (this study).

Significant variability of nitrogen contents have been identified among microdiamonds from the same UHPM terrane (e.g., the Kokchetav massif: 150–10,000 ppm), between two diamonds recovered from the same sample (e.g., Erzgebirge: 160 and 1630 ppm), or even within a single sample, as has been shown for Kokchetav diamonds [16]. The origin of such variation remains unclear; it may reflect either the contribution of distinct or inhomogeneous fluids, fluid fractionation (e.g. by precipitating N-bearing minerals such as phengite), or kinetic fractionation of nitrogen related to diamond growth rate, or even different growth episodes from distinct fluids [13,46]. It also may be referred to the diamond growth from different fluids, or to the different rate of nitrogen incorporation into diamond structure during its crystallization. The nitrogen impurities characteristics suggest that the Erzgebirge diamonds belong to the Type Ib–IaA, which is similar to metamorphic diamonds from the Kokchetav massif of Kazakhstan and the Western Gneiss Region of Norway, and differentiates them from other nitrogen-bearing diamonds from kimberlitic sources (Type IaAB). According to the rather low activation energy ($\sim 4.4\text{ eV}$) for single N-atoms to aggregate into N-pairs, the occurrence of nitrogen impurities as single atoms in the crystal lattice implies that the Erzgebirge diamonds had a short residence time in a high-pressure and high-temperature environment (see related issue

developed for Kokchetav diamonds [16]). Indeed, any diamond with N-content higher than 100 ppm would be Type 1aA at a temperature of 700 °C within 1 m.y. Therefore, the detection of a 1b-component suggests the possibility for very fast exhumation (<1 m.y.). Though at this moment our limited data on nitrogen aggregation do not allow us to calculate a definite duration of exhumation of Erzgebirge diamond-bearing rocks, we refer to numerical modeling according to which exhumation from UHPM conditions occurred during 1–5 m.y. [47].

The IR data are consistent with our previous studies of inclusions in the Erzgebirge diamonds performed with the aid of focused ion beam (FIB) and transmission electron microscopes (TEM) [22]. The studies demonstrate that Erzgebirge diamonds contain abundant nanometric solid crystalline inclusions of SiO₂ with an admixture of minor components such as K, P, Ti, Fe, or SiO₂-free crystalline inclusions of K, P, and O, or Pb_xO_y, and/or Pb₂CO₃, and Al₂SiO₅. We were unable to identify the structure of these nanometric phases by selected-area electron diffraction because they were not appropriately oriented for identification and tilting resulted in multiple patterns superimposed. Nevertheless, they yielded Bragg diffraction spots indicating that they were crystalline [22]. Hwang et al. [48] have reported that instead of crystalline inclusions they have observed phosphorous–potassium–silica (P–K–SiO₂) glass or Al–SiO₂ glass, which they interpreted to be a former melt hosted by Erzgebirge diamonds (their samples 25966 and M1). However, it is not clear to us whether Hwang et al. [48] have actually identified glass. They say (p. 98): “... careful EDX analyses in the present study revealed that these pockets are in fact P/K-rich silica glass...” We do not understand how one can identify glass by electron dispersive X-ray (EDX) analysis; to our understanding, diffraction is necessary. Hwang et al. [48] reported electron diffraction patterns only for host diamond, but not for nano-scale inclusions.

Our focused ion beam-assisted TEM studies showed that Erzgebirge diamonds also contain a considerable amount of nanometric-size euhedral cavities that are believed to represent decrepit fluid inclusions. Many of these cavities associate with dislocations of diamond growth. TEM researches have shown that the cavities are surrounded by amorphous film with average low atomic weight materials [22]. As we learned from IR, such cavities might present traces of former fluid inclusions containing CO₂, H₂O and potentially IR inactive species such as N₂, which were “burned” out due to sample treatment by ion (FIB) and electron (TEM) beams. The Raman spectroscopy also provides

some evidence that internal residual pressure probably still exists in diamond #1, which may therefore partly prevent a fluid from crystallizing. The synchrotron IR data, combined with observations of solid inclusions using TEM, suggest that the Erzgebirge diamonds crystallized in a media rich in volatile components such as CO₂, OH, and H₂O. Because no CH₄ (we know that the C–H absorption at 3107 cm⁻¹ is due to engine oil), or other reduced natural chemical species have been detected in the Erzgebirge diamonds, we assume that their crystallization occurred at relatively high oxygen fugacity ($fO_2 \sim 5\text{--}6$ log units), which was close to the upper limit of fO_2 for allowing diamond stabilization [49,50]. We emphasize that a concept of UHPM diamond crystallization from the COH fluid enriched in local components coherent with their host minerals or rock chemistry is unconditionally supported by direct observation of nanoinclusions using the TEM and IR data and observations on diamond-bearing pockets included in garnets [14,22,23]. Furthermore, extremely negative values of $\delta^{13}C$ in diamonds from Erzgebirge ($\delta^{13}C = -17\text{‰}$ to -27‰ [46]) and from Kazakhstan ($\delta^{13}C = -10\text{‰}$ to -17‰ [13,29]) does not fit with the diamond crystallization from a carbonate/carbonatite melt (average $\delta^{13}C = -0.22\text{‰}$ to -4.31‰ [51]) because such a strong isotopic fractionation between diamond and carbonate melt would not happen at high temperatures (i.e. the fractionation between calcite and diamond is below 5‰ at temperature above 800 °C [52]).

Finally, we would like to emphasize that sometimes discussions related to metamorphic diamond origin as being “fluid versus melt” reflect, simply, a semantic problem. Experiments have demonstrated that there is complete miscibility between silicate melt and water in most of the upper mantle, except at very shallow depths. Bureau and Keppler [53] showed that the hydrous melt and silicate-bearing vapor coexisting at low temperature merge compositionally to form a single-phase, supercritical fluid, stable at higher pressures (1.5–2.5 GPa). Therefore, above the supercritical point there is no difference in physical parameters between melt and fluid. Applying this concept to UHPM diamonds, whenever water is available in the subduction zone the solid material, including organic carbon matter, may be dissolved in the supercritical fluid with increasing pressure and temperature, and such a fluid becomes a media for diamond crystallization. Our interpretation of diamond origin is consistent with the recently obtained experimental evidence for diamond crystallization at high P and T directly from COH fluid or from graphite in the presence of H₂O [49,50]. This interpretation is also similar to that independently reached from

observations on diamond-bearing multiphase pockets included in garnet from Erzgebirge felsic gneisses [23].

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