

Mode of occurrence, textural settings and nitrogen-isotopic compositions of in situ diamonds and other carbon phases in the Bencubbin meteorite

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Abstract

Investigations on a polished thin section (PTS) by reflected-light microscopy, laser micro-Raman spectroscopy, and cathodoluminescence of the Bencubbin meteorite revealed the presence of diamond grains ranging in size from 200 nm to 1 μm in Fe–Ni metal, silicates, and at metal–silicate interfaces. Most of the diamonds are associated with poorly graphitized carbon (PGC). Nitrogen isotopic measurements with the new generation NanoSIMS 50 ion microprobe indicate the presence of two isotopically distinct types of nitrogen carriers: One carrier type consists of diamonds, their associated PGCs, and diamond-free PGCs (called group-B). It is N-poor and has isotopically close to normal N. The other carrier type consists only of diamond-free PGCs (called group-A), is N-rich and heavily enriched in ^{15}N ($\delta^{15}\text{N}_{\text{max}} \sim 1000\text{‰}$). The petrographic and Raman characteristics of the diamonds are indicative of formation by shock. The difference in the N-isotopic compositions of diamonds and the associated group-B PGCs on the one hand, and the group-A diamond-free PGCs on the other, suggests that a ^{15}N -rich component was probably incorporated into the Bencubbin parent body in an episode subsequent to the shock event that induced carbon–diamond phase transformation from the pristine PGCs with isotopically normal nitrogen. In the second episode, presumably in a milder shock event, significant amounts of N were delivered and redistributed among different phases. The isotopically heavy N signature is hence not pristine to the Bencubbin parent body, but was brought in by a second impactor.

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1. Introduction

For a long time, the Bencubbin meteorite has

been known to contain isotopically highly anomalous nitrogen, with bulk $^{15}\text{N}/^{14}\text{N}$ up to two times the normal (air) ratio of 3.68×10^{-3} , i.e. $\delta^{15}\text{N}_{\text{Air}}$ ($= [({}^{15}\text{N}/{}^{14}\text{N})_{\text{Sample}}/({}^{15}\text{N}/{}^{14}\text{N})_{\text{Air}} - 1] \times 1000$) of up to 1000‰ [1,2]. Recently, different types of nitrogen carriers with $^{15}\text{N}/^{14}\text{N}$ ratios comparable to that of the bulk nitrogen in Bencubbin were found in an acid-resistant residue [3] and in situ

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[4]. It has been suggested that the enrichments in ^{15}N are of interstellar origin [1–4]. However, since Bencubbin experienced severe shock melting, several authors argued that the original carriers of heavy nitrogen (assumed to be organic) have been completely destroyed in the shock event and that the heavy nitrogen was redistributed among several phases [4,5]. Whether the shock event did occur at the same time when ^{15}N -rich matter was acquired by the Bencubbin parent asteroid remained unresolved. In this paper, we report the discovery of in situ diamonds in Bencubbin. These diamonds and other carbon phases were studied for N-isotopic compositions, which, together with their petrographic settings, provide important information on the complex formation-history of this differentiated and shock-melted meteorite.

2. Experimental techniques

Diamonds and graphite were searched for in a polished thin section (PTS) of the Bencubbin meteorite by reflected-light optical microscopy and a LEO 1530 high resolution field emission scanning electron microscope (FESEM). With its energy dispersive X-ray (EDX) system, it was possible to identify graphites with sizes as small as a few tens of nanometers in the FESEM. Also, cathodoluminescence (CL) images were acquired in order to determine CL characteristic bands of diamonds and to identify additional small diamonds.

Laser micro-Raman spectra of the diamond and graphite in Bencubbin, as well as a diamond powder used for polishing, were recorded with a Dilor[®] XY spectrometer equipped with confocal optics and a nitrogen-cooled CCD detector. A microscope is used to focus the excitation laser beam (488 nm exciting line of a Spectra Physics[®] Ar⁺ laser) to a 2 μm spot and to collect the back-scattered Raman signal. Integration times ranged from 120 to 300 s, with laser power on the sample between 2 and 50 mW.

N-isotopic compositions of the Bencubbin diamonds and graphites were measured with the Cameca NanoSIMS 50, a new generation ion microprobe, which was recently installed at the

Max-Planck-Institute for Chemistry. This instrument is characterized by a high spatial resolution, high sensitivity, and simultaneous detection of up to six isotopes. A focused primary beam of Cs^+ ions with a diameter ≈ 50 nm was rastered over areas $5 \times 5 \mu\text{m}^2$ around the diamonds and graphites. Secondary ion images of $^{12}\text{C}^-$, $^{16}\text{O}^-$, $^{12}\text{C}^{14}\text{N}^-$, $^{12}\text{C}^{15}\text{N}^-$, and $^{28}\text{Si}^-$ were acquired at a mass resolving power of ≈ 6000 ($^{12}\text{C}^{15}\text{N}^-$) and ≈ 3000 (the other species), respectively, to locate grains of interest. Elemental and isotopic ratios were subsequently obtained by spot measurements with a static and focused primary beam of ≈ 1 pA. Total integration times varied between 3.5 and 7 min. The number of counts of ^{12}C cumulated during a measurement is usually between 10^5 and 10^6 . The N-isotopic ratios of the diamonds and graphites were normalized to those obtained for the 1-hydroxy-benzotriazole hydrate ($\text{C}_6\text{H}_5\text{N}_3\text{O}\cdot\text{H}_2\text{O}$) standard ($\delta^{15}\text{N}_{\text{Air}} = -1\text{‰}$). This standard gives $^{12}\text{C}^{14}\text{N}^-$ intensity about 2.2 higher than the $^{12}\text{C}^-$ intensity. The instrumental mass fractionation for $^{12}\text{C}^{15}\text{N}^-/^{12}\text{C}^{14}\text{N}^-$ obtained from nine measurements of the 1-hydroxy-benzotriazole hydrate standard is $-8\text{‰}/\text{amu}$. Analyses of the epoxy in which the Bencubbin sample is mounted yield normal N-isotopic ratio with a weighted mean from 10 measurements of $\delta^{15}\text{N} = -6 \pm 6(1\sigma)\text{‰}$. We are thus confident that the differences in the instrumental mass fractionation of N-isotopic ratios of different matrices are small.

Nitrogen concentrations in Bencubbin graphites and diamonds were estimated from the average CN^-/C^- sensitivity factor given by [6] within a factor of 2 for different standards. The sensitivity factor measured on the 1-hydroxy-benzotriazole hydrate standard in this study is compatible with that reported by [6] for the same standard. Since large matrix effects were observed by [6], the estimated N concentrations lower than 2 wt% can be considered accurate only within a factor of 2–3. For higher concentrations, the estimated values are overestimated [7].

Terrestrial contamination from outgassed sample or sample housing is generally low considering the amounts of nitrogen measured in the carbon phases. The lowest N we measured in a Bencubbin graphite is about 100 ppm. If this concentra-

tion is taken as upper limit for contaminating N, it would represent < 10% of N concentrations in diamond and PGCs, thus changing intrinsic N-isotopic signatures only marginally.

3. Results

3.1. Petrography

Previous detailed petrographic studies of the Bencubbin meteorite showed that it is a heterogeneous breccia that contains clasts of different types of meteoritic components including metal, silicates, shock-melted matrix, and rare ordinary and carbonaceous chondrite fragments [8–11]. The polished thin section (PTS) we used for this study is texturally similar to those studied by Newsom and Drake [9]. It mostly consists of large (up to mm-sized) slugs of metal and silicate clasts almost evenly distributed throughout the section and cemented by a small amount of shock-melted silicate materials and metal droplets. Our section contains no ordinary or carbonaceous chondrite clasts.

Our reflected-light optical microscopy and SEM study of the Bencubbin section revealed the presence of diamonds in 17 locations. The diamonds range in size from 200 nm to 1 μm , and are located in Fe–Ni metal, silicates, and at metal–silicate interfaces (Fig. 1). The even spatial distribution of diamond among all constituents of the sample suggests that diamond is not localized in a specific region. Also, it appears that there is no preferential setting of the diamonds (i.e. in metal or in silicates), but this cannot be considered conclusive at this time because we only sampled 17 locations.

Most of the diamonds are associated with graphitic carbon. A few others were found as isolated grains in metal and silicates. Fig. 1A,B shows some diamonds sited in pockets of fine-grained ($\ll 1 \mu\text{m}$) graphitic carbon matrices. These pockets are located between metal and silicates, and in one case only in the metal. Fig. 1C,D depicts another example of three diamond grains sited in graphitic carbon in a metal grain. The diamonds are clearly distinguished by their

active cathodoluminescence signal (Fig. 1D). Not far from this diamond–graphite mixture, a 500 nm isolated grain of diamond (not shown in the figure) was also found in the same metal. In another area, a 200 nm sized diamond grain was found in metal present in a shock melt vein (Fig. 1E,F). In addition to diamonds and associated phases, we also found isolated, diamond-free graphitic carbon grains in metal. Their abundance is difficult to estimate because they are not homogeneously distributed, but they are clearly much more common than the diamonds and their associated graphites. As for silicates, we did not spend much effort on searching for isolated graphitic carbons there. However, a mistakenly taken Raman spectrum from an area of a diamond-free olivine grain confirmed the characteristic bands of graphite, indicating its presence.

3.2. Cathodoluminescence and Raman characterizations

The presence of diamond in Bencubbin was also confirmed by cathodoluminescence (CL) and laser micro-Raman spectroscopy. CL images of five diamonds were obtained by scanning the respective regions, and the record of a CL spectrum (Fig. 2A) of one of the diamonds showed a dominant band at 435 nm, as expected [12]. Nine of the Bencubbin diamond grains were studied by laser micro-Raman spectroscopy and all exhibit the characteristic Raman one-phonon band near 1332 cm^{-1} (Fig. 2B). Because the Bencubbin thin section was polished with diamond powder, individual grains of the latter were also analyzed by laser micro-Raman for comparison. Their Raman spectra are clearly distinct from those of the Bencubbin diamonds. Compared to the polishing diamonds, the Raman bands of the Bencubbin diamonds are shifted towards lower wavenumbers (Fig. 2B), a feature characteristic of polycrystalline impact-induced nanodiamond (see discussion below). The Bencubbin diamonds show shifting of the one-phonon band position at maximum intensity from 1331.5 cm^{-1} to 1325.6 cm^{-1} . We found the degree of shift of the one-phonon band position to depend on the intensity of the laser beam; the higher the power of the laser, the lower the

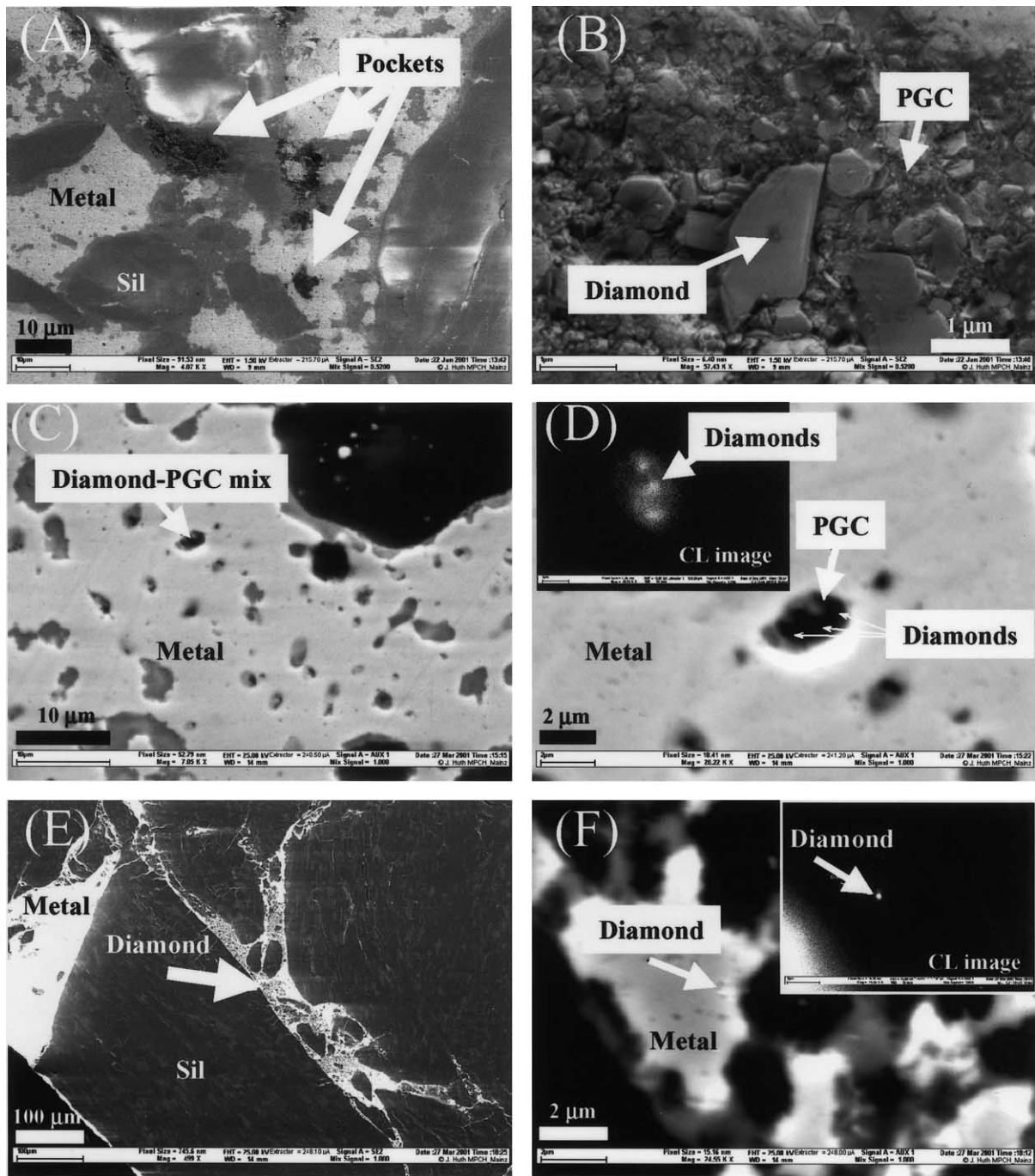


Fig. 1. (A) SEM backscattered electron (BSE) image of a metal–silicate region in the Bencubbin meteorite. Diamond–PGC mixtures are located in pockets. (B) Detailed image of one of the diamond–PGC pockets indicated by an arrow in A. (C) A 2 μm sized diamond–PGC mixture inside a metal grain. (D) Detailed image of diamond–PGC mixture shown in C. Three diamond grains embedded in PGC are easily recognized in the cathodoluminescence image (upper view) by the bright luminescent spots. (E) A shock vein in Bencubbin in which diamond has been found. (F) A high magnification image of a 200 nm sized diamond grain inside a metal grain from the shock vein. The diamond is easily recognized in the CL image (upper view) by the bright spot.

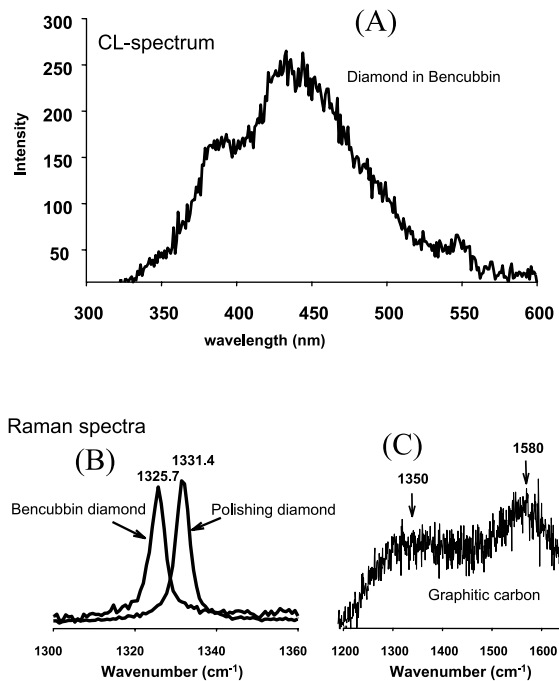


Fig. 2. (A) Cathodoluminescence spectrum of a diamond grain in Bencubbin. The emission peak near 435 nm is characteristic of diamond. The origin of the emission peak near 385 nm is unknown. (B) First-order Raman spectra of Bencubbin diamond and polishing diamond (the intensity for Bencubbin diamond was enhanced to underline the difference in Raman shifts). The spectra are distinct, suggesting Bencubbin diamond is intrinsic and not contamination from polishing. (C) First-order Raman spectrum of graphitic carbon associated with diamond. The width and the comparable heights of the bands near 1350 cm^{-1} and 1580 cm^{-1} are characteristics of a poorly graphitized carbon (PGC).

band position. This shift in band position is reversible through change in the laser power. In contrast, the polishing diamonds have band positions close to 1331.5 cm^{-1} regardless of the intensity of the incident laser beam (Table 1). Moreover, the Raman signal of the polishing diamonds is several times as intense as that of the Bencubbin diamonds. This clearly demonstrates that the Bencubbin diamonds are structurally different from polishing diamonds.

The shifts in the Raman bands of Bencubbin diamonds are similar to those observed in impact diamonds from the Ries Crater [13]. The shifts can be understood in terms of a comparatively small size of the diamond crystallites. With com-

paratively higher wavenumbers, the full width at half maximum (FWHM) of the Raman bands of the Bencubbin diamonds becomes smaller and the bands become slightly asymmetric, a phenomenon also observed in the Ries impact diamonds. This indicates that the Bencubbin diamonds formed by shock.

The graphitic carbons show two Raman bands, an ‘order’ (O) band at 1580 cm^{-1} and a ‘disorder’ (D) band at 1350 cm^{-1} (Fig. 2C). The position of these bands (the -D,-O bands in Table 1), their large widths and comparable heights are characteristic of highly disordered graphite [14]. Some isolated graphitic grains were quickly consumed under the laser beam and could not be analyzed. They are very similar to the fluffy phase in acid-resistant residues from Bencubbin, of which we were able to analyze only one. The Raman spectrum of the analyzed grain (unpublished) shows disorder and a strong background suggesting fluorescence. The graphitic carbons in Bencubbin do not have the ordered structure of graphite *sensu stricto*, and hence we preferably call them poorly graphitized carbons (hereafter PGCs).

3.3. N-isotopic compositions

A total of 24 PGCs, eight diamonds, and one diamond-PGC mixture was measured for N-isotopic compositions. In a first step the locations around the grains of interest were studied by ion imaging with the NanoSIMS (Table 2, Fig. 3). Subsequently, 21 isolated PGCs and two diamond grains (i.e. without visible association with other carbon phase), three diamond-associated PGCs, and six PGC-associated diamonds were analyzed individually (i.e. without contribution from the surrounding phase). The ion images of the diamond-PGC mixture show no clear isotopic distinction between the diamonds and PGCs. As a result, we were not able to analyze them separately but measured 10 different locations of the same diamond-PGC mixture.

The N-isotopic compositions of the Bencubbin diamonds and PGCs are summarized in Table 2 and plotted in Fig. 4. The diamonds, diamond-associated PGCs, and the diamond-PGC mixture show comparatively similar $^{15}\text{N}/^{14}\text{N}$ ratios which

Table 1

The characteristic Raman bands of the Bencubbin diamond and PGCs, and polishing diamond

| Sample | Phase | Diamond one-phonon band (cm ⁻¹) | Intensity | Graphite-D,-O bands (cm ⁻¹) | Intensity |
|-------------------|------------------|---|-----------|---|----------------|
| Bencubbin (SPA) | Diamond+graphite | 1325.6 | 1390 | bump (~1350, ~1580) | (~1400, ~1500) |
| | Diamond | 1325.6 | 8396 | | |
| | Diamond | 1325.7 | 2537 | | |
| | Diamond+graphite | 1326.3 | 2078 | bump (~1350, ~1580) | (~1450, ~1300) |
| | Diamond+graphite | ~1328.5 | ~492 | ~1556 | ~492 |
| | Diamond+graphite | ~1330.5 | ~589 | ~1555 | ~578 |
| | Diamond+graphite | 1329 | 1588 | ~1580 | ~1400 |
| | Diamond+graphite | 1330 | 537 | ~1560 | ~460 |
| | Diamond+graphite | ~1331.5 | 4372 | ~1360, ~1600 | ~3100, ~3530 |
| | Graphite | | | ~1356, ~1594 | ~2848, ~2614 |
| Polishing diamond | Graphite | | | ~1356, 1587 | ~3575, 38.49 |
| | Diamond | 1331.4 | 10966 | | |
| | Diamond | 1331.5 | 40704 | | |
| | Diamond | 1331.5 | 33944 | | |
| | Diamond | 1331.5 | 40573 | | |

are close to normal (i.e. not much different from the terrestrial $^{15}\text{N}/^{14}\text{N}$ ratio of 3.68×10^{-3}). The $\delta^{15}\text{N}$ values show some variability, ranging from -196 ± 129 to 58 ± 46 ‰ ($\delta^{15}\text{N}_{\text{mean}} = -33 \pm 28$ ‰). In three PGC-associated diamonds, ^{15}N is clearly depleted, with $\delta^{15}\text{N}$ values of down to -151 ± 16 ‰. Although the values are not very extreme, they add support to the conclusion that the diamonds are intrinsic to the meteorite and not contamination from the polishing diamond powder, which is expected to have $\delta^{15}\text{N}$ close to zero. The CN^-/C^- ratios in diamonds, diamond-associated PGCs, and the diamond–PGC mixture cover a wide range of values with a systematic increase from isolated diamonds (mean $\text{CN}^-/\text{C}^- = 0.005$) through the PGC–diamond mixture and PGC-associated diamonds (0.024 and 0.05, respectively) to diamond-associated PGCs (0.76). In terms of N concentrations, isolated diamonds have a few hundred ppm nitrogen, which is on average $\sim 10\times$ and $\sim 150\times$ less than that in PGC-associated diamonds and in diamond-associated PGCs, respectively.

Isolated, diamond-free PGCs show much more variable N-isotopic and CN^-/C^- ratios (Fig. 4). They seem to be separated into two groups: one anomalously enriched in ^{15}N with high CN^-/C^- ratios (hereafter called group-A), and another with $\delta^{15}\text{N}$ and CN^-/C^- values close to those in diamonds and diamond-associated PGCs (group-

B). In group-A, a maximum $^{15}\text{N}/^{14}\text{N}$ ratio of $2\times$ terrestrial (i.e. $\delta^{15}\text{N} \approx 1000$ ‰) is encountered. This N-isotopic ratio is consistent with the ratio found in bulk Bencubbin [1,2]. It is also comparable to the maximum $^{15}\text{N}/^{14}\text{N}$ ratio of the fluffy carbon phase previously encountered in an acid-resistant residue from Bencubbin [3]. In addition, while group-B PGCs have CN^-/C^- ratios not higher than 0.2, all but one of the group-A PGCs have CN^-/C^- ratios between 0.4 and 9, suggestive of distinctly higher nitrogen concentrations. The N contents of group-A PGCs are estimated to be on the order of several wt%. This is also comparable to the CN^-/C^- ratios in the fluffy carbon found in the Bencubbin residue [3], indicating that the group-A PGCs may represent the fluffy phase. Illustrative ion images of this ^{15}N -rich PGC type are shown in Fig. 3C,D. The displayed grain has a low C^- signal but high CN^-/C^- ratio of ~ 9 , which is comparable to the high CN^-/C^- ratios of organic standards [6,15]. It is remarkable that the ^{15}N -rich PGC grain is just a few micrometers away from a diamond grain having much lower CN^-/C^- ratio and normal N-isotopic signature (Fig. 3C,D).

4. Discussion

Our finding of in situ sub-micrometer-sized dia-

Table 2
Isotopic composition of diamonds and PGCs in Bencubbin

| Region | Phase | Association | Grain | Meas. # | $\delta^{15}\text{N}$ | Error | CN ⁻ /C ⁻ | Error | N ^a (wt%) |
|--------|---------------|-------------|-------|---------|-----------------------|-------|---------------------------------|---------|-------------------------|
| C01 | PGC | isolated | 2 | 3 | -75 | 74 | 0.002 | 0.0001 | 0.01 |
| C01 | PGC | isolated | 3 | 2 | 20 | 92 | 0.002 | 0.0002 | 0.01 |
| A01-03 | PGC | isolated | 1 | 1 | 891 | 50 | 0.647 | 0.065 | < 4 |
| A01-03 | PGC | isolated | 2 | 1 | 870 | 161 | 1.08 | 0.366 | < 7 |
| A01-03 | PGC | isolated | 3 | 1 | 893 | 60 | 1.1 | 0.085 | < 8 |
| A01-03 | PGC | isolated | 4 | 1 | 960 | 105 | 0.411 | 0.064 | < 3 |
| A1-04 | PGC | isolated | 1 | 1 | 842 | 59 | 1.62 | 0.117 | < 11 |
| A1-04 | PGC | isolated | 2 | 1 | 933 | 112 | 0.678 | 0.098 | < 5 |
| A1-04 | PGC | isolated | 3 | 1 | 341 | 135 | 0.148 | 0.02 | 1 |
| A1-04 | PGC | isolated | 4 | 1 | 787 | 207 | 0.011 | 0.004 | 0.08 |
| A1-04 | PGC | isolated | 5 | 1 | 180 | 151 | 0.002 | 0.0004 | 0.01 |
| A1-04 | PGC | isolated | 6 | 1 | 865 | 57 | 0.689 | 0.13 | < 5 |
| A1-04 | PGC | isolated | 7 | 1 | 950 | 40 | 2.06 | 0.434 | < 14 |
| A1-04 | PGC | isolated | 8 | 1 | 132 | 268 | 0.017 | 0.001 | 0.1 |
| B01 | PGC | isolated | 2 | 1 | 862 | 59 | 9.04 | 0.734 | < 63 |
| B01 | PGC | isolated | 3 | 1 | 267 | 163 | 0.165 | 0.036 | 1 |
| B01 | PGC | isolated | 4 | 1 | 844 | 67 | 5.65 | 0.35 | < 40 |
| C02 | PGC | isolated | 1 | 1 | 66 | 239 | 0.001 | 0.0001 | 0.01 |
| C02 | PGC | isolated | 2 | 1 | 881 | 97 | 1.09 | 0.092 | < 8 |
| C02 | PGC | isolated | 3 | 1 | 307 | 244 | 0.121 | 0.003 | 0.8 |
| C02 | PGC | isolated | 4 | 1 | -181 | 139 | 0.11 | 0.002 | 0.8 |
| A02 | PGC | D | 1 | | -135 | 50 | 0.171 | 0.017 | 1 |
| A01-01 | PGC | D | 5 | 1 | 41 | 69 | 0.481 | 0.042 | < 3 |
| A01-01 | PGC | D | 6 | 1 | 58 | 46 | 1.63 | 0.130 | < 11 |
| B01 | D | isolated | 1 | 3 | 39 | 92 | 0.002 | 0.00003 | 0.01 |
| C01 | D | isolated | 1 | 3 | 38 | 43 | 0.007 | 0.0001 | 0.05 |
| A01-01 | D | PGC | 1 | 3 | -87 | 22 | 0.032 | 0.001 | 0.2 |
| A01-01 | D | PGC | 2 | 2 | -151 | 16 | 0.080 | 0.004 | 0.6 |
| A01-01 | D | PGC | 3 | 2 | -99 | 48 | 0.008 | 0.0003 | 0.06 |
| A01-01 | D | PGC | 4 | 1 | 17 | 48 | 0.158 | 0.027 | 1 |
| A02 | D | PGC | 2 | 1 | -37 | 32 | 0.017 | 0.0005 | 0.1 |
| A02 | D | PGC | 3 | 1 | -6 | 35 | 0.010 | 0.001 | 0.07 |
| B02 | PGC-D mixture | | 1 | 1 | -87 | 41 | 0.015 | 0.003 | 0.1 |
| B02 | PGC-D mixture | | 2 | 1 | -7 | 34 | 0.069 | 0.013 | 0.5 |
| B02 | PGC-D mixture | | 3 | 1 | 10 | 83 | 0.005 | 0.0002 | 0.03 |
| B02 | PGC-D mixture | | 4 | 1 | -72 | 93 | 0.003 | 0.0002 | 0.02 |
| B02 | PGC-D mixture | | 5 | 1 | 8 | 32 | 0.036 | 0.006 | 0.3 |
| B02 | PGC-D mixture | | 6 | 1 | -14 | 39 | 0.017 | 0.001 | 0.1 |
| B02 | PGC-D mixture | | 7 | 1 | -44 | 31 | 0.024 | 0.003 | 0.2 |
| B02 | PGC-D mixture | | 8 | 1 | -196 | 129 | 0.004 | 0.0002 | 0.03 |
| B02 | PGC-D mixture | | 9 | 1 | 25 | 32 | 0.041 | 0.007 | 0.3 |
| B02 | PGC-D mixture | | 10 | 1 | 2 | 40 | 0.027 | 0.004 | 0.2 |

D: diamond, PGC: poorly graphitized carbon. The results for B02 are measurements done in different locations of the same diamond-PGC mixture. Errors are 2σ .

^a The N concentrations were calculated using the sensitivity factor given by [6]. N concentrations up to 2 wt% are considered to be accurate within a factor of 2–3. Concentrations > 2 wt% are probably overestimated [7].

monds and the distinct N-isotopic compositions in Bencubbin raises a number of new issues about the origin of diamond and PGCs and the origin and evolution of the N-isotopic anomaly in this

meteorite. The existence of carbon phases with two distinct N-isotopic signatures suggests the presence of at least two carriers of nitrogen with different isotopic signatures: one with ¹⁵N enrich-

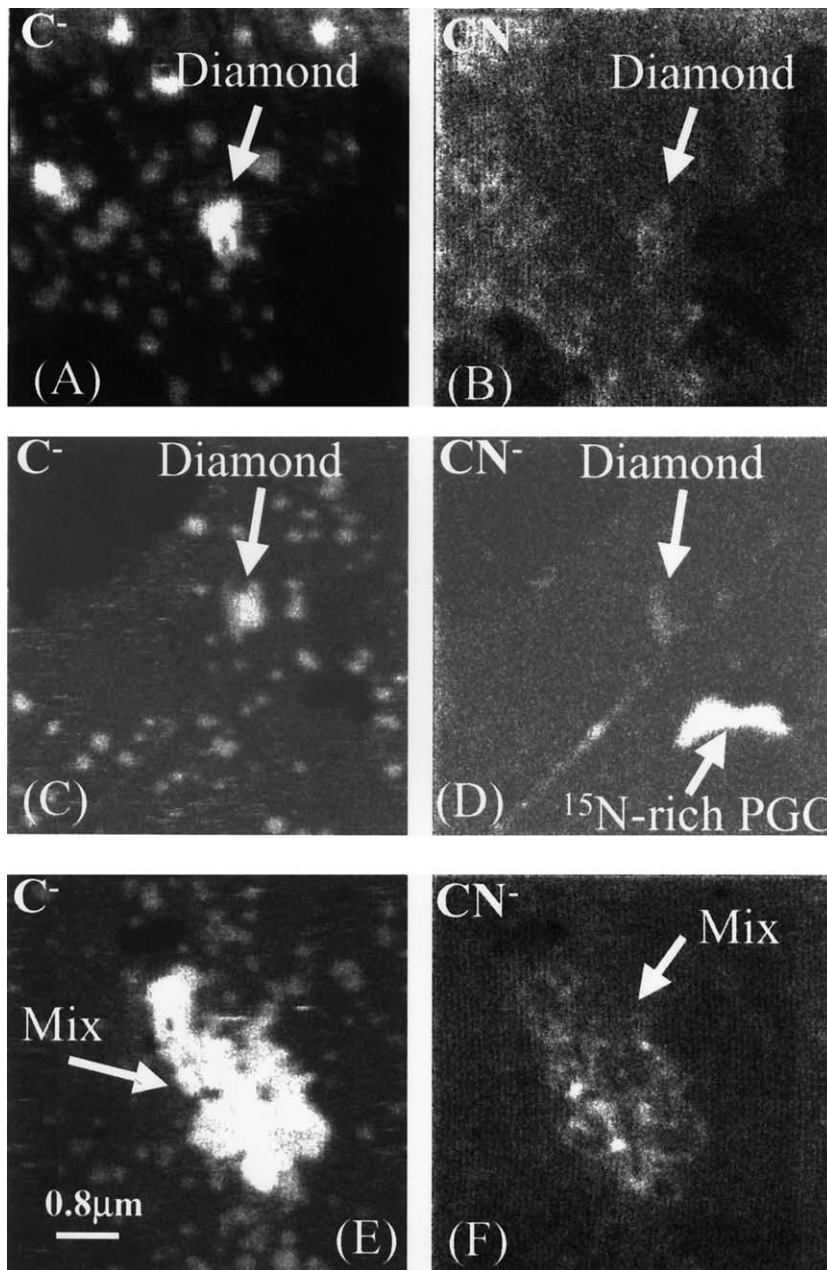


Fig. 3. C^- and CN^- ion images of diamond regions in Bencubbin acquired with the NanoSIMS 50 ion microprobe. Field of view is $5 \times 5 \mu m^2$. (A,B) A diamond grain with low N content in metal. (C,D) A diamond grain with close to normal N-isotopic composition and low N content near a PGC grain with high $^{15}N/^{14}N$ and high N concentration. (E,F) The diamond–PGC mixture of Fig. 1C.

ment and one with close to normal $^{15}N/^{14}N$ ratio. This can be used to put constraints to unravel the complex thermal and metamorphic history of Bencubbin. The following questions are of central

interest: (1) What is the origin of the N-isotopic anomaly in Bencubbin? (2) Are the present ^{15}N -rich phases in Bencubbin pristine to the parent body (i.e. did they form in the same environment

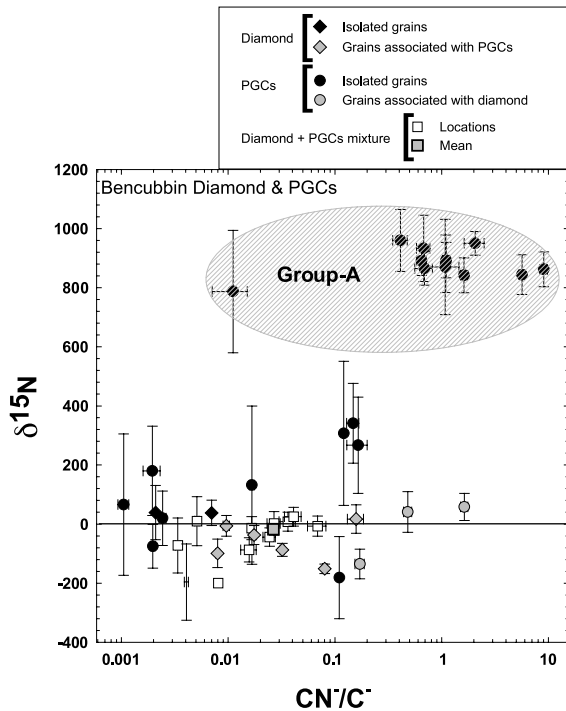


Fig. 4. $\delta^{15}\text{N}_{\text{Air}}$ vs. CN^-/C^- for diamond, associated PGCs, diamond–PGC mixtures, and isolated PGCs in Bencubbin. $\delta^{15}\text{N}_{\text{Air}}$ shows a bimodal distribution with peaks close to 0 and +1000‰, suggestive of two distinct N-isotopic reservoirs. The error bars are 2σ .

where the ^{15}N enrichment took place) or are they exogenic (i.e. induced in an impact event on the parent body)? (3) How did the diamonds and their associated PGCs form? (4) How did the group-A and group-B PGCs form and how is it possible that they coexist (in some cases even within the same metal grain just a few micrometers apart) in a so called differentiated and highly shocked meteorite? All these issues are addressed below.

4.1. Origin of the N-isotopic anomaly and its carrier phases in Bencubbin

The enrichment in ^{15}N by a factor of 2 is too large to be the result of fractionation processes in the solar system and an interstellar origin is favored instead [1–4]. There are four potential sources for ^{15}N enrichments in interstellar environments: (i) N-isotopic fractionation in interstellar

molecular clouds [16], (ii) explosive H burning nucleosynthesis in novae [17], (iii) explosive and neutrino-induced nucleosynthesis in Type II supernovae (SN) [18], and (iv) explosive He burning in Type Ia SN [19]. A nucleosynthetic origin of the ^{15}N enrichments would require the presence of grains from novae and/or SN at the Bencubbin formation site in the solar nebula. Grains with $^{15}\text{N}/^{14}\text{N}$ ratios up to $50\times$ terrestrial are indeed found in primitive meteorites [20,21]. However, their abundance is only ~ 0.1 ppm and much higher abundances would be required in order to account for the ^{15}N enrichments seen in bulk Bencubbin. Also, grains from novae and SN are expected to show large isotopic anomalies in other elements, e.g. carbon. Previous studies of carbon-bearing phases with ^{15}N enrichments in Bencubbin show close-to-normal C-isotopic ratios [3,4]. Hence, a circumstellar origin appears unlikely and a molecular-cloud origin of the ^{15}N -rich carriers is favored. For molecular-cloud material, also enrichments in deuterium are expected. At present, no H-isotopic data are available for Bencubbin, but studies of related bencubbinites showed large D enrichments with D/H ratios of up to 1×10^{-3} [4], which is $6.5\times$ the terrestrial D/H ratio.

While the ^{15}N enrichment in Bencubbin is likely to be of interstellar origin, this is probably not the case for all the phases that carry the enrichment. Among the ^{15}N -rich phases are graphitic carbon, silicates, metal, SiC, other unspecified carbides [1–4], and Cr–S (unpublished data). ^{15}N -rich gases were also recently reported in vesicles in silicates [5]. All these carriers and vesicles exhibit $^{15}\text{N}/^{14}\text{N}$ ratios not much different from the bulk $^{15}\text{N}/^{14}\text{N}$ ratio. This led several authors to conclude that the original ^{15}N carrier in Bencubbin was destroyed by metamorphic events [4,5].

4.2. Origin of diamond in Bencubbin

According to laboratory studies of diamond shock synthesis, a pressure of ~ 15 GPa (at 1000°C) is sufficient to produce diamond from graphite [22]. Bencubbin is a shocked polymict breccia and a shock pressure of a presumably much higher intensity has been proposed in order to explain the different petrographic textures [11].

Indeed, the presence of shock-induced diamonds in Bencubbin presents a strong evidence for shock. However, it may appear that chemical vapor deposition (CVD) could be responsible for the formation of diamond [23]. This process has been thought to be a possible mechanism to form diamonds in ureilites [24]. However, the significantly smaller wavenumbers of the Raman bands of the Bencubbin diamonds compared to those expected from CVD diamonds [25] suggest that a CVD origin is unlikely.

Shock metamorphism in the Bencubbin parent asteroid is thus the most plausible explanation for the origin of diamond. Supporting evidence for that is the presence of diamond in shock melt veins (see Fig. 1) and the shifts in the Raman bands to lower wavenumbers (Fig. 2) as observed for shock-induced diamonds from the Ries Crater [13]. The presence of diamonds together with associated PGCs in Bencubbin indicates incomplete solid state transformation (SST) of carbon, a feature typical of shock-induced graphite–diamond phase transformation [13]. In this case, the diamonds and their associated PGCs are expected to have similar N-isotopic composition (Fig. 4). These PGCs are probably remains of the primary carbon (i.e. the parental carbon of diamonds, [22]) and did not form by high-temperature post-shock back-transformation of diamond to secondary graphite, since such graphites show Raman spectra characteristic of highly ordered graphite (no ‘D’ band) [26]. Some group-B PGCs, especially those with N-isotopic signatures and CN^-/C^- ratios similar to those in diamonds and their associated PGCs, might also have been involved in the shock transformation process. The apparent absence of diamond in them can be an artifact due to the two-dimensional view of our samples. On the other hand, there is no evidence that group-A PGCs have experienced shock deformation or phase transition, and it is thus not surprising that none of our diamonds show the N-isotopic signatures and N concentrations of group-A PGCs.

4.3. A proposed scenario

We envisage from our results that at the time

the diamonds formed by shock, Bencubbin must have had a bulk N-isotopic composition similar to those of the diamonds and the associated PGCs (i.e. group-B), for the following reasons: From a chemical point of view, it is hardly conceivable to form the diamond by shock without inheriting the isotopic composition of the parental graphite. It is also hardly conceivable that the enrichment in ^{15}N would have been induced only in diamond-free PGCs, albeit both types of PGCs occur in close vicinity and in some cases in the same metal grain (see Fig. 3C,D). It is even more unlikely in view of the fact that group-A PGC grains are very N-rich (see Fig. 4). In addition, diamond grains enclosed inside metal grains have the same N-isotopic signature and N concentration as diamonds and associated PGCs between metal and silicates. A single-event shock-induced redistribution of N among all carbon phases would have revealed identical N concentrations and ^{15}N signatures in all PGC types and diamond. This demonstrates that the two signatures (represented by group-A and group-B populations) were produced in two different episodes. We argue that the diamonds were formed in the first episode, and the ^{15}N -rich component (group-A) must have been added in a later episode, possibly by an impact of an asteroid or a comet. The fluffy structure of the group-A PGCs as well as the high CN^-/C^- ratios in most of them suggest their original ^{15}N -rich precursor to have been organic. The Bencubbin parent body has thus witnessed at least two shock events, as has already been suggested by [11] based on metal records. Since the material from Bencubbin witnesses several successive heating events with a maximum temperature of at least 1000°C, capable to melt rocks [11] and to cause equilibration of N-isotopic ratios, we consider that any pervasive heating events must also have occurred prior to the time when the ^{15}N -rich impactor hit the Bencubbin parent asteroid.

In this event, nitrogen may have been induced and redistributed throughout the Bencubbin parent body. The group-A PGCs may have formed by nucleation and growth [27] from already dissolved carbon and from extraneous N-rich carbon delivered in the second event. The existence of some group-B PGCs with relatively higher $\delta^{15}N$

ratios can be explained by contribution from dissolved N-rich extraneous carbon. It may appear that the addition of ^{15}N -rich matter and subsequent redistribution of N could also have affected the $^{15}\text{N}/^{14}\text{N}$ ratios of the diamonds and their co-genetic PGCs. However, the diamonds and their associated PGCs are more compact than the fluffy diamond-free PGCs. This may have limited the extent of N dilution. Also, it is not surprising for meteoritic graphite to retain its N-isotopic signature during heating events, as two isotopically distinct graphitic carbons in Acapulco survived extended heating to solidus temperatures of $\approx 1200^\circ\text{C}$ [28] without becoming homogenized [29]. It is thus reasonable to assume that the original N-isotopic signature of the diamonds and their associated PGCs in Bencubbin was not changed significantly. Nevertheless, the original $^{15}\text{N}/^{14}\text{N}$ ratio may have been somewhat lower.

We note that group-A PGCs are not the only ^{15}N -rich phases in Bencubbin. Phases such as SiC and chromium-sulfide [3] have $\delta^{15}\text{N}$ values comparable to the 1000‰ of the bulk Bencubbin. If diamonds, their associated PGCs, and group-B PGCs were not significantly affected by the redistribution of ^{15}N -rich matter, this should also be the case for SiC, which is very refractory. Possibly, SiC was part of the isotopically anomalous impactor itself. At present we have no evidence for this, which, if correct, could constrain the nature of this isotopically anomalous impactor.

5. Conclusion

A detailed study of the Bencubbin meteorite revealed the presence of diamond and poorly graphitized carbon (PGC) in different locations (metal, silicates, metal–silicate boundaries). Isotopic signatures and CN^-/C^- ratios of these phases indicate two distinct groups: One group consists of diamonds, associated PGCs, and the group-B diamond-free PGCs, is N-poor and has isotopically close to normal N. The other group consists of the group-A diamond-free PGCs, is N-rich and anomalously enriched in ^{15}N ($\delta^{15}\text{N}_{\text{max}} \sim 1000\text{‰}$). The enrichment in ^{15}N in group-A PGCs is similar to those found in several

other phases in Bencubbin, and its origin is most likely interstellar. The absence of a specific carrier with extreme ^{15}N enrichment suggests that the original carrier was probably completely destroyed.

A scenario involving two shock events on the Bencubbin parent body is proposed in order to explain the two N-isotopic signatures in the various phases: An intense shock event with a peak-shock pressure exceeding 15 GPa that formed the diamonds via a solid state transformation (SST) of pre-existing carbon, and a later, less intense shock event that injected ^{15}N -rich ‘organic’ matter (carried by an asteroid or a comet) into the Bencubbin parent body, decomposed it, and redistributed N among different phases. Group-A ^{15}N -rich PGCs are formed during the second shock event.

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