



HAL
open science

Fourier transform infrared spectroscopy data and carbon isotope characteristics of the ophiolite-hosted diamonds from the Luobusa ophiolite, Tibet, and Ray-Iz ophiolite, Polar Urals

Xiangzhen Xu, Pierre Cartigny, Jingsui Yang, Yildirim Dilek, Fahui Xiong,
Guolin Guo

► To cite this version:

Xiangzhen Xu, Pierre Cartigny, Jingsui Yang, Yildirim Dilek, Fahui Xiong, et al.. Fourier transform infrared spectroscopy data and carbon isotope characteristics of the ophiolite-hosted diamonds from the Luobusa ophiolite, Tibet, and Ray-Iz ophiolite, Polar Urals. *Lithosphere*, 2017, 10 (1), pp.156-169. 10.1130/L625.1 . insu-01859804

HAL Id: insu-01859804

<https://insu.hal.science/insu-01859804>

Submitted on 22 Aug 2018

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Fourier transform infrared spectroscopy data and carbon isotope characteristics of the ophiolite-hosted diamonds from the Luobusa ophiolite, Tibet, and Ray-Iz ophiolite, Polar Urals

Xiangzhen Xu^{1,*}, Pierre Cartigny², Jingsui Yang¹, Yildirim Dilek³, Fahui Xiong¹, and Guolin Guo⁴

¹CARMA (CENTER FOR ADVANCED RESEARCH ON MANTLE), CENTER OF CONTINENTAL DYNAMICS, INSTITUTE OF GEOLOGY, CHINESE ACADEMY OF GEOLOGICAL SCIENCES, 26 BAIWANZHANG ROAD, BEIJING 100037, CHINA

²LABORATOIRE DE GÉOCHIMIE DES ISOTOPES STABLES, INSTITUT DE PHYSIQUE DU GLOBE DE PARIS, SORBONNE PARIS CITÉ, UNIVERSITÉ PARIS DIDEROT, UMR (UNITÉ MIXTE DE RECHERCHE) 7154 CNRS (CENTRE NATIONAL DE LA RECHERCHE SCIENTIFIQUE), 75005 PARIS, FRANCE

³DEPARTMENT OF GEOLOGY AND ENVIRONMENTAL EARTH SCIENCE, MIAMI UNIVERSITY, 118 SHIDELER HALL, 250 S. PATTERSON AVENUE, OXFORD, OHIO 45056, USA

⁴STATE KEY LABORATORY BREEDING BASE OF NUCLEAR RESOURCES AND ENVIRONMENT, EAST CHINA INSTITUTE OF TECHNOLOGY, 418 GUANGLAN AVENUE, NANCHANG 330013, CHINA

ABSTRACT

We report new $\delta^{13}\text{C}$ data and N content and aggregation state values for microdiamonds recovered from peridotites and chromitites of the Luobusa ophiolite (Tibet) and chromitites of the Ray-Iz ophiolite in the Polar Urals (Russia). All analyzed microdiamonds contain significant nitrogen contents (from 108 to 589 atomic ppm \pm 20%) with a consistently low aggregation state and show identical infrared spectra dominated by strong absorption between 1130 cm^{-1} and 1344 cm^{-1} , and therefore characterize type Ib diamond. Microdiamonds from the Luobusa peridotites have $\delta^{13}\text{C}$ (PDB) values ranging from -28.7‰ to -16.9‰ , and N contents from 151 to 589 atomic ppm. The $\delta^{13}\text{C}$ and N content values for diamonds from the Luobusa chromitites are -29‰ to -15.5‰ and 152–428 atomic ppm, respectively. Microdiamonds from the Ray-Iz chromitites show $\delta^{13}\text{C}$ values varying from -27.6‰ to -21.6‰ and N contents from 108 to 499 atomic ppm. The carbon isotopes values have features similar to previously analyzed metamorphic diamonds from other worldwide localities, but the samples are characterized by lower N contents. In every respect, they are different from diamonds occurring in kimberlites and impact craters. Our samples also differ from the few synthetic diamonds we analyzed, in that they show enhanced $\delta^{13}\text{C}$ variability and less advanced aggregation state than synthetic diamonds. Our newly obtained N aggregation state and N content data are consistent with diamond formation over a narrow and rather cold temperature range (i.e., $<950\text{ °C}$), and in a short residence time (i.e., within several million years) at high temperatures in the deep mantle.

LITHOSPHERE, v. 10; no. 1; p. 156–169; GSA Data Repository Item 2017288 | Published online 27 July 2017

<https://doi.org/10.1130/L625.1>

INTRODUCTION

Studies of diamonds are significant because the understanding of the occurrence of natural diamonds reveals critical information about the deep Earth geological processes in the continents and in the mantle, and about the scale of and the nature of carbon cycle in the Earth. Diamonds can also form due to metamorphism at sufficiently high pressures (>35 kbar) and temperatures ($>900\text{ °C}$) to cross the graphite-diamond transition. Following the original report of metamorphic diamond occurrence in the Kokchetav massif in Kazakhstan (Sobolev and Shatsky, 1990), metamorphic diamonds have been described in garnets from the Dabie Shan ultrahigh-pressure (UHP) complex in China (Xu et al., 1992), the Western Gneiss region in Norway (Dobrzhinetskaya et al., 1995), the Erzgebirge massif in Germany (Massonne, 1999, 2003), gneissic samples of the Maksyutov complex in Russia (Bostick et al., 2003), the ophiolitic UHP unit in the Italian Western Alps (Frezzotti et al., 2011), and the Variscan granulites of the Bohemian Massif in the Czech Republic

(Kotkova et al., 2011; Naemura et al., 2011). The identification of diamond in situ, e.g., using Raman spectroscopy, is usually taken as strong evidence that diamond formed within the host rock (but see Menneken et al., 2007; Dobrzhinetskaya et al., 2014), as opposed to physical and chemical extractions from the heaviest samples of rocks for which the lack of contamination cannot be demonstrated.

Over the past 30 yr there have been several reports of diamond occurrences in ultramafic rocks of ophiolites in southern Tibet (Institute of Geology, Chinese Academy of Geological Sciences, 1981; Bai et al., 1993). These findings from ophiolite-hosted peridotites were initially received with caution and skepticism, due to the lack of in situ diamond occurrences as well as the strong resemblance of cuboctahedra crystal habit of both synthetic and ophiolite-hosted diamonds (Taylor et al., 1995). However, a much larger number (i.e., >100) of diamonds have been recovered from different ophiolites in different orogenic belts in recent years. Diamond was discovered in the Kangjinla chromite deposit in the Luobusa ophiolite (Tibet; Xu et al., 2009), and a diamond inclusion in an Os-Ir alloy of chromitite from the same ophiolite, associated with other high-pressure minerals, including coesite and kyanite, was reported in Yang et al. (2007).

*Corresponding author: xuxiangzhensj@aliyun.com

Very reducing conditions were deduced from the occurrence of osbornite (TiN), cubic boron nitride (cBN), TiO₂-II, moissanite (SiC), and zangboite (FeTiSi₂) (Li et al., 2009; Dobrzhinetskaya et al., 2009), and these reduced conditions were seen as consistent with diamond stability at depth and preservation from oxidation during uplift. More recent studies discovered the existence of abundant diamonds in peridotites and chromitites of ophiolites in China, Myanmar, Russia, and Turkey (Xu et al., 2015; Yang et al., 2014a, 2014b, 2015; Lian et al., 2017), and in metamorphic peridotites and chromitites. The occurrence of six in situ diamonds in the chromitites from both Luobusa and Ray-Iz ophiolites was confirmed (Yang et al., 2014a, 2015). Consequently, ophiolitic peridotites and chromitites have been identified as a new and significant environment for natural diamond occurrence (Yang et al., 2015). Nevertheless, the source of carbon for ophiolite-hosted diamonds and the formation and the mode of integration of microdiamonds into ophiolitic chromitites are still not well known, and are debated (Liou et al., 2014).

In this paper we evaluate and discuss the origin and formation of ophiolite-hosted diamonds by utilizing N contents, N aggregation states, and carbon isotope ratios of natural microdiamonds recovered from the peridotites and chromitites of different ophiolites. Nitrogen is the most abundant impurity in natural diamonds and is present in many combinations of nitrogen-vacancy centers, as can be detected with Fourier transform infrared spectroscopy (FTIR) (e.g., Mendelsohn and Milledge, 1995). The significance of nitrogen in diamond studies is that the N aggregation characteristics can be utilized to constrain diamond residence time and temperatures in the mantle. Carbon isotopic composition in diamonds varies considerably, depending on the diamond type and the petrogenetic processes in different physical conditions. Thus, the combined N and C isotope data from ophiolite-hosted diamonds help us better constrain their C source and formation in oceanic mantle peridotites. We first briefly discuss the crystal morphology in different diamond types and establish the natural occurrence of diamonds in fossil oceanic peridotites, then discuss various mineral inclusions found in these natural diamonds and present our N and C isotope data. We show that the analyzed microdiamonds likely formed from light, recycled surface carbon in a narrow range of temperatures, in highly reducing conditions in the mantle, and that they had relatively short residence time (several million years). In our categorization of ophiolite-hosted diamonds we use the classification scheme based on infrared characteristics of diamonds.

GEOLOGICAL SETTING AND SAMPLE DESCRIPTION

Our microdiamond samples come from a larger sample set of several thousand of diamond grains recovered from the peridotites and chromitites of the Kangjinla chromite deposit in the Luobusa ophiolite (Tibet) and from chromitites of the Ray-Iz ophiolite (Russia). The Luobusa ophiolite at the eastern end of the Yarlung-Zangbo suture zone (YZSZ) (Fig. 1) consists mainly of harzburgite, lherzolite, and dunite, with minor crustal gabbro and basalt (Yang et al., 2014a; Fig. 1A). It hosts economically significant podiform chromitites with lenticular-tabular masses of high-Cr magnesiochromite (Fig. 1B) (Zhou et al., 1996). These podiform chromite deposits are estimated to contain $\sim 5 \times 10^6$ t of chromite reserves (Zhang et al., 1996).

The Ray-Iz ophiolite in the Polar Urals consists mainly of depleted harzburgite-dunite, and contains podiform chromitites similar to those in Luobusa (Fig. 2; Savelieva et al., 2007). The central chromite deposit (CCD; Fig. 2B) is the largest of the more than 200 ore bodies in the massif. The W214 orebody is ~ 100 m long and 5 m wide, extending to >100 m at depth, and is partly surrounded by a thin dunite envelope and locally in direct contact with a coarse-grained, weakly serpentinized harzburgite. It is estimated to contain $\sim 10 \times 10^6$ t of chromite ore.

All studied microdiamonds were processed at the Institute of Multipurpose Utilization of Mineral Resources, Chinese Academy of Geological Sciences, Zhengzhou, by a combination of gravity, magnetic, and electrostatic techniques. Details of the mineral separation procedures were given in Xu et al. (2009). Our microdiamond samples belong to four well characterized types: (1) Kangjinla chromite (Luobusa ophiolite), herein referred to as KCr (Fig. 1); (2) mantle peridotite of the Kangjinla chromite deposit, herein referred to as Ky (Fig. 1); (3) chromite of the CCD from the Ray-Iz ophiolite, herein referred to as WR (Fig. 2); and (4) chromite of the W214 from the Ray-Iz ophiolite, herein referred to as WP (Fig. 2).

The separated diamonds are all pale yellow to colorless, euhedral to subhedral crystals, 100–500 μm across, with octahedral, cuboctahedral, hexoctahedral, and dodecahedral morphologies (Fig. 3; Appendixes 1–4 in the GSA Data Repository¹). Some grains are single crystals, whereas others are polycrystalline or skeletal. We also analyzed a series of synthetic diamonds for comparison. These synthetic diamonds were purchased from HuangHe Whirl Wind Limited Company, Henan, under the reference type HSD80+; they are the typical yellow, regular crystal with hexoctahedron structure, with strong thermal stability and almost no impurities (Appendix 5 in the GSA Data Repository).

ANALYTICAL TECHNIQUES

We selected clean, large, transparent, and flat diamond grains from the chromitites and mantle peridotites of the Luobusa ophiolite and from the chromitites of the Ray-Iz ophiolite. The grain sizes of these diamonds range between 100 and 300 μm .

Nitrogen contents and aggregation states of representative diamonds were determined by transmission infrared (IR) spectroscopy at the Laboratoire de Géochimie des Isotopes Stables, Institut de Physique du Globe de Paris, using an IR-Plan microscope (Spectratech) equipped with a MCT-A (mercury cadmium telluride–narrow band) detector following the procedure described by De Corte et al. (1998). The microscope was coupled with a Nicolet 6700 Magna IR FTIR spectrometer, and spectra between 4000 and 850 cm^{-1} were recorded at a resolution of 8 cm^{-1} . Diamonds were mounted on an ~ 300 - μm -thick BaF₂ plate and the best results were obtained using 1400 scans of crystals of <200 μm and 300 scans of larger samples. The use of BaF₂ as holder made it possible to obtain spectra of acceptable low signal/noise ratio in the region above 850 cm^{-1} . In order to reduce scattered IR radiation, the diameter of the IR beam was adjusted to fit the size of the diamond grains by masking with variable apertures. To examine the homogeneity of the diamonds and the overall reproducibility of the procedure, three spectra at different faces for each crystal were collected.

The measured spectra were baseline corrected and normalized to a thickness of 1 mm assuming an absorption coefficient of 11.94 absorption unit/ cm^{-1} at 1995 cm^{-1} . Nitrogen abundances and aggregation states were estimated by deconvolution of the IR spectra in the 1400–900 cm^{-1} region using a 23 point least-square regression fit. As described in the following, we did not find any evidence for any significant advanced aggregation of nitrogen, i.e., no IaB component, only Ib, possibly Ib-IaA. The spectra were thus deconvoluted using a two-component linear least-squares

¹GSA Data Repository Item 2017288, Appendix 1: Topography of microdiamonds from chromite of the Luobusa ophiolite, Tibet; Appendix 2: Topography of microdiamonds from mantle peridotite of the Luobusa ophiolite, Tibet; Appendix 3: Topography of microdiamonds from chromite (WR) of the Ray-Iz ophiolite, Polar Urals; Appendix 4: Topography of microdiamonds from chromite (WP) of the Ray-Iz ophiolite, Polar Urals; Appendix 5: Topography of the synthetic diamonds, is available at <http://www.geosociety.org/datarepository/2017>, or on request from editing@geosociety.org.

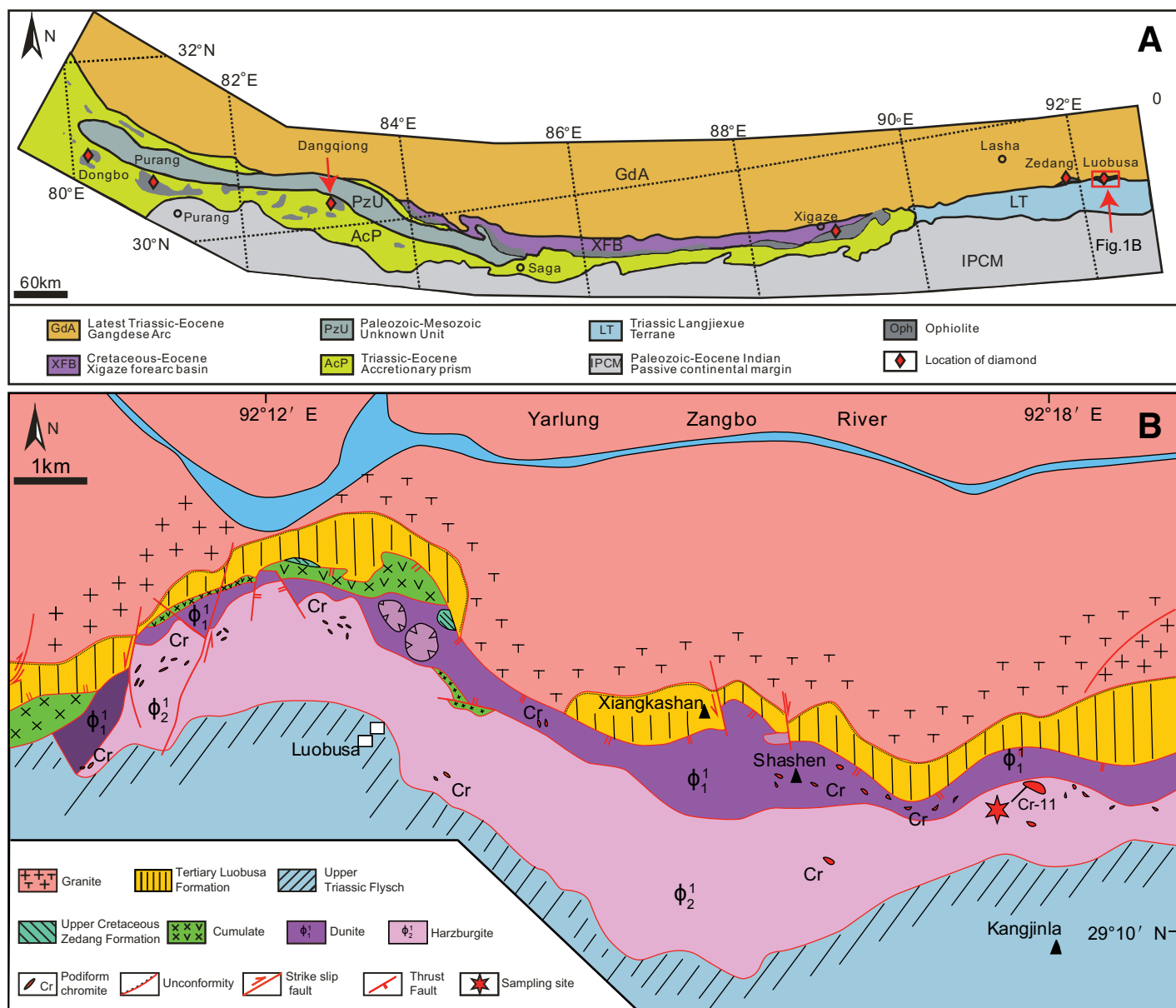


Figure 1. (A) Index map showing the location of the Yarlung-Zangbo suture zone (revised after Xiong et al., 2016). (B) Simplified geological map of the Luobusa ophiolite, Tibet (revised after Zhou et al., 1996).

regression program that determines the optimum percentage aggregation from Ib (the C component) to IaA (the A component) (Finnie et al., 1994), and N content and N aggregation state were determined using IR absorption coefficients of 250 atomic ppm/cm⁻¹ and 162 atomic ppm/cm⁻¹ (Kiflawi et al., 1994; Boyd et al., 1994) for single (Ib diamond) and N pairs (IaA diamond), respectively. In the literature, analytical precision associated with N content and N aggregation determinations are typically 20% and 5%, respectively (Field, 1992; Finnie et al., 1994). In this study where diamonds were both N poor and small, the multiple deconvolution of a same spectra could result in error of as much as 15% in N aggregation determination. The N content determination, which relies critically on both the thickness estimation of diamond (i.e., where the baseline correction in the 2000–2600 cm⁻¹ region is critical) and the deconvolution of the two N-bearing spectra (i.e., where the baseline correction in the

850–1500 cm⁻¹ region is critical) could not be determined with reproducibilities better than 20% (Tables 1–4).

Once N concentrations and N aggregation values of diamonds were determined, diamonds were weighed, wrapped in platinum foil, cleaned at 500 °C in air to remove any organic contamination, and combusted in O₂ atmosphere; the procedure was described by Boyd et al. (1995) for conventional macrodiamonds with a combustion apparatus slightly modified for these samples (Cartigny et al., 2001).

Released CO₂ was quantified with a precision better than 1% using a piezoresistive gauge, and δ¹³C (PDB, Peedee belemnite) [where δ¹³C_{sample} = (13C/12C_{sample} / 13C/12C_{PDB}) - 1 × 1000] was determined with an accuracy better than 0.1‰ using a gas-source isotope ratio mass spectrometer ThermoFischer Delta +XP equipped with a micro-volume device. The carbon isotope analyses of diamond grains from the Tibet and Ray-Iz ophiolite

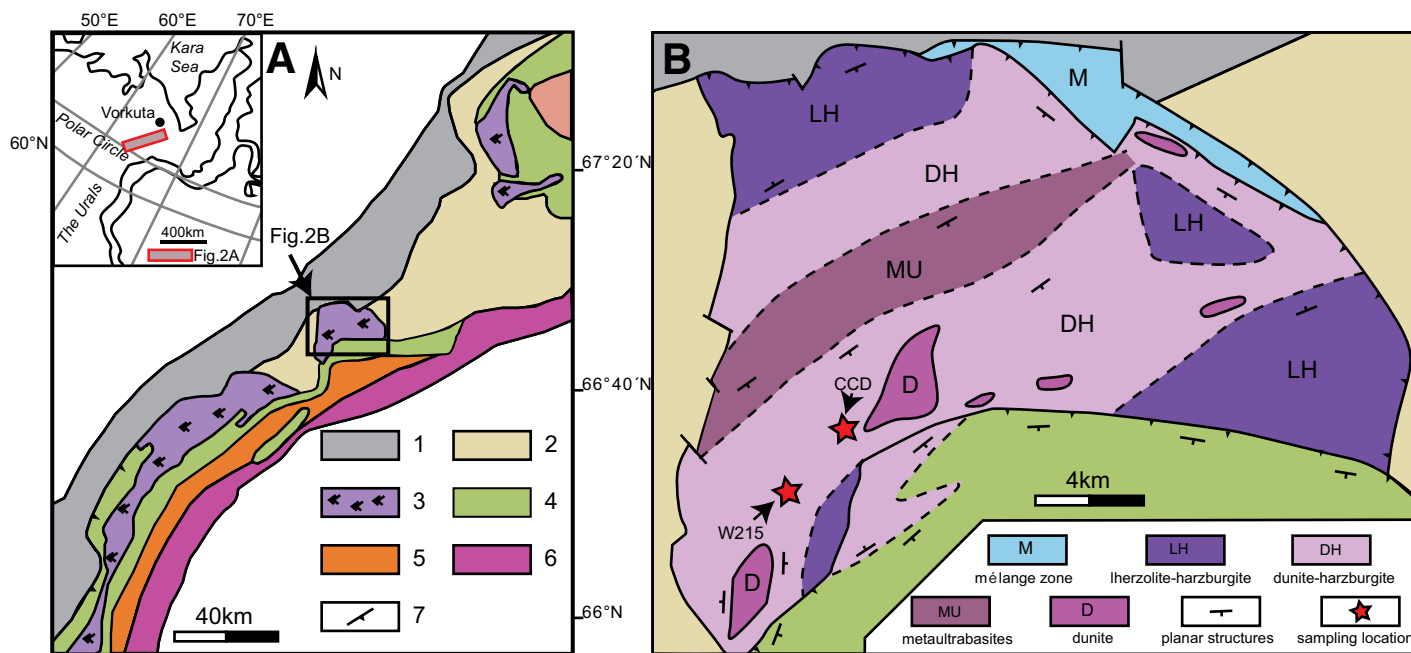


Figure 2. Simplified geological maps of the Vorkuta ophiolite belt in the Polar Urals and the Ray-iz ophiolite (revised after Yang et al., 2015). (A) Index map of the northern Ural Mountains. 1—Allocthonous Paleozoic sedimentary assemblages of the continental shelf and slope, volcanic units (Lemva Zone), and pre-Ordovician bimodal volcanic series (Uraltau Zone). 2—Precambrian and pre-Paleozoic volcanic and sedimentary complexes of the crystalline basement of the East European platform. 3—Ultramafic rocks, mainly harzburgite and dunite with minor lherzolite. 4—Metamorphosed gabbro, olivine gabbro, and minor troctolite and pyroxenite. 5—Early Devonian tonalite and granodiorite and Middle Devonian diorite and monzodiorite. 6—Island-arc complex. 7—Major thrust faults and fault systems. (B) Geologic map of the Ray-iz ophiolite.

were performed by secondary ion mass spectrometry at the GeoForschungsZentrum (GFZ; Potsdam, Germany) and by ion microprobe at the University of Western Australia (Yang et al., 2014a, 2014b).

CRYSTAL MORPHOLOGY IN DIFFERENT DIAMOND TYPES

Commercially, most synthetic diamonds are grown from graphite in the presence of solvent and/or catalyst metals such as iron, cobalt, and nickel alloys, at temperatures and pressures of 1550–1600 °C and 5–6 GPa, respectively, and develop different morphologies due to the variations in internal cell pressure and temperature (Burns and Davies, 1992). There are no available results of a systematic study of synthetic diamonds, and we therefore use and discuss the extant data with appropriate caution.

Ophiolite-hosted diamonds exhibit cubes with small octahedral faces through cuboctahedra to octahedral with small cube faces (Fig. 3; see also Howell et al., 2015). Previous studies have shown that the cubic {100} face may occur extremely rarely among kimberlitic diamonds, whereas it is ubiquitous among synthetic diamonds (e.g., Pearson et al. 1995). This obvious similarity in morphologies (i.e., both are in the cuboctahedron spectrum) between the ophiolitic and synthetic diamonds make the ophiolite-hosted diamonds look like synthetic diamonds. Note that this statement is valid for kimberlitic macrodiamonds and that additional morphologies have been described in microdiamonds from metamorphic massifs (De Corte et al., 1998, 1999) and from kimberlites (Kvasnitsa et al., 1999; Kvasnytsya, 2013). In particular, cuboctahedra have been reported among diamonds. The ophiolitic diamonds are all pale yellow to colorless, euhedral to subhedral crystals, with octahedral, cuboctahedral, and dodecahedral morphologies (Xu et al., 2015). One major difference is that the common rounded rhombic dodecahedron in natural diamond is not normally observed among synthetic diamonds (Field, 1992). Moore

and Lang (1974) concluded that this habit in natural diamonds stems from dissolution from the octahedral form and is not a growth feature.

It has been shown that, with increasing pressures and temperatures, the morphology of synthetic diamond changes progressively from cube to cuboctahedron to octahedron. However, with an increase in water concentration in the metal melt, the dominant growth form of diamond evolves from octahedron, which is stable at a C_{H_2O} ranging from 0 to 0.2 wt%, to rhombic dodecahedron that is stable at C_{H_2O} from 0.22 to 0.4 wt% (Palyanov et al., 2012). In other words, if ophiolitic diamonds resulted from contamination, some would need to be specifically grown from a high-water system; we are not aware of any commercial synthetic diamonds to be grown from such compositions.

NATURAL VERSUS EXTERNAL ORIGIN OF OPHIOLITE-HOSTED DIAMONDS

The occurrence of natural diamonds in oceanic peridotites and chromitites has been questioned before, and some have even suggested that diamond separates reported from ophiolitic peridotites and chromitites may have been externally introduced due to potential contamination in rock processing. Here we briefly discuss this issue and present new arguments in support of the natural origin of microdiamonds in ophiolitic upper mantle peridotites.

Perraki et al. (2009) presented four valuable microscopic and spectroscopic criteria to distinguish natural metamorphic microdiamonds from externally introduced diamond (in a thin section) as residual particles from the diamond saw or the polishing material. The diamonds we have examined in our study are free of the sample preparation material. Moreover, the diamond size (generally several hundreds of micrometers) is much larger than that of the largest polishing diamond material used (0.2–5

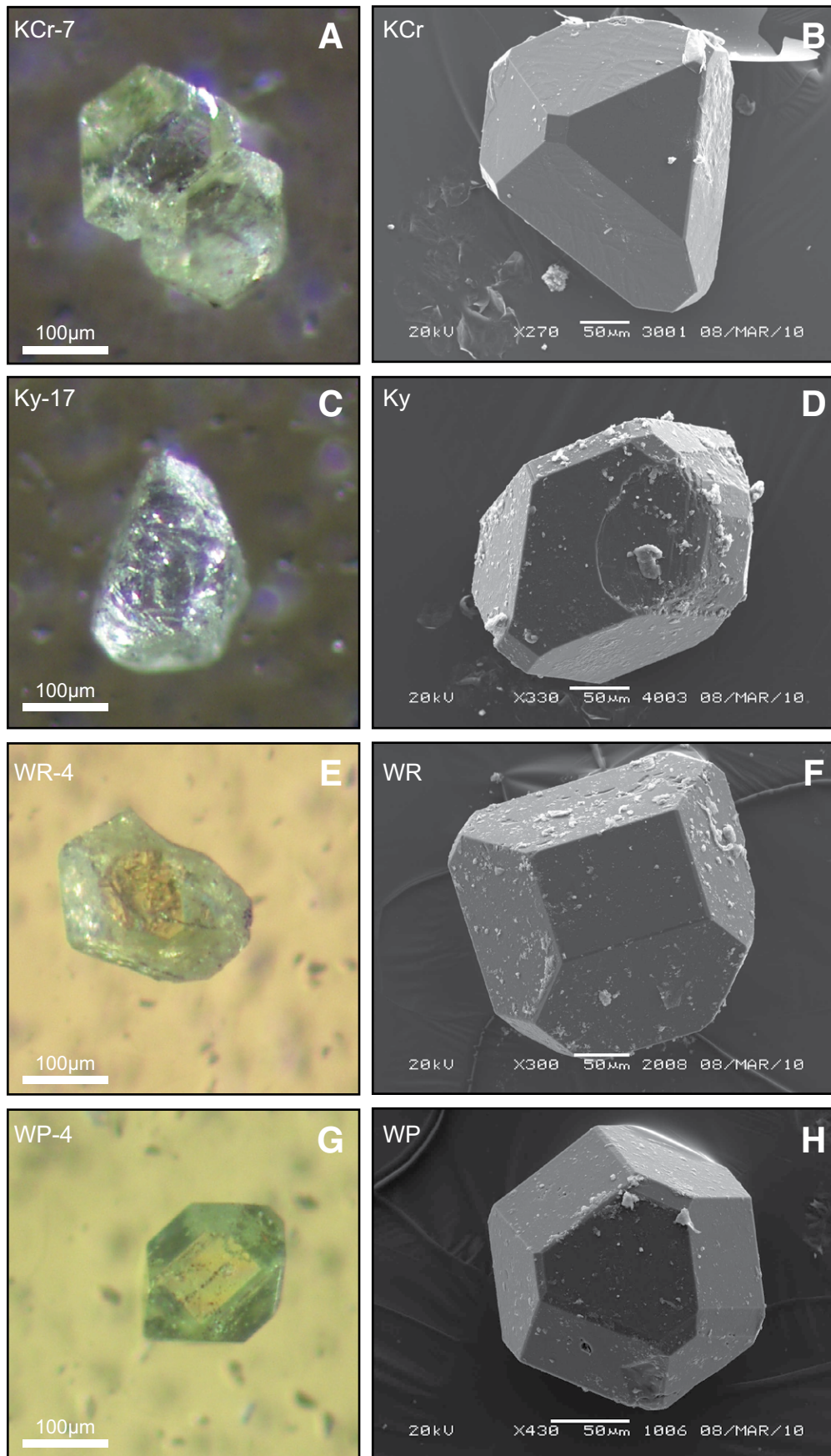


Figure 3. Topography of microdiamonds from chromitites and mantle peridotites. (A) Polycrystalline diamond from chromitite (Luobusa ophiolite, Tibet) exhibits cuboctahedral morphology and in light yellow color under a binocular microscope. (B) Scanning electron microscope (SEM) image of diamond from chromitite (Luobusa ophiolite, Tibet) displaying octahedral-dominated cuboctahedron crystal habit. (C) Colorless diamond from mantle peridotite (Luobusa ophiolite, Tibet) showing cuboctahedral morphology under a binocular microscope. (D) SEM image of diamond from mantle peridotite (Luobusa ophiolite, Tibet) displaying hexoctahedron crystal morphology. (E) Diamond from chromitite of the Ray-Iz ophiolite (Polar Urals, Russia) showing hexoctahedral morphology and strong yellow color under binocular microscope. (F) SEM image of diamond from chromitite of the Ray-Iz ophiolite (Polar Urals, Russia) showing hexoctahedron crystal morphology. (G) Diamond from chromitite of the Ray-Iz ophiolite (Polar Urals, Russia) showing hexoctahedral morphology and strong yellow color under binocular microscope. (H) SEM image of diamond from chromitite of the Ray-Iz ophiolite (Polar Urals, Russia) with a cuboctahedron morphology.

TABLE 1. $\delta^{13}\text{C}$ AND N CONTENTS OF MICRODIAMONDS RECOVERED FROM THE CHROMITITE OF THE LUOBUSA OPHIOLITE, TIBET

Sample	Weight (mg)	$\delta^{13}\text{C}$ (‰)	N (at. ppm, $\pm 20\%$)	%IaA formed ($\pm 5\%$)
KCr-1	0.0101	-25.908	310	0
KCr-2	0.0112	-26.175	368	0
KCr-3	0.0093	-15.539	271	0
KCr-4	Nd	Nd	203	0
KCr-5	Nd	Nd	203	9
KCr-7	0.017	-17.13	248	0
KCr-9	0.0086	-27.172	251	0
KCr-10	0.0116	-16.761	Nd	Nd
KCr-11	0.0146	-26.174	194	14
KCr-13	Nd	Nd	410	13
KCr-14	0.0105	-25.195	374	0
KCr-15	0.0129	Nd	161	11
KCr-16	0.017	-29.039	208	11
KCr-18	0.0087	-18.713	401	7
KCr-19	Nd	Nd	152	15
KCr-20	0.0084	-26.617	255	0
KCr-21	0.01	-28.329	383	0
KCr-22	0.0096	-25.478	321	0
KCr-23	0.0295	-24.907	215	13
KCr-24	0.0161	-26.681	180	0
KCr-25	0.0147	-17.228	428	0

Note: Nd—not detectable.

TABLE 2. $\delta^{13}\text{C}$ AND N CONTENTS OF MICRODIAMONDS RECOVERED FROM THE MANTLE PERIDOTITE OF THE LUOBUSA OPHIOLITE, TIBET

Sample	Weight (mg)	$\delta^{13}\text{C}$ (‰)	N (at. ppm, $\pm 20\%$)	%IaA formed ($\pm 5\%$)
Ky-1	0.0092	-25.216	Nd	Nd
Ky-2	Nd	Nd	152	0
Ky-3	Nd	Nd	459	0
Ky-4	Nd	Nd	420	0
Ky-5	0.0223	-24.68	Nd	Nd
Ky-6	0.0105	-26.218	324	0
Ky-7	Nd	Nd	191	3
Ky-8	0.0096	-27.174	Nd	Nd
Ky-9	Nd	Nd	472	0
Ky-10	0.0139	-25.993	342	4
Ky-11	Nd	Nd	589	0
Ky-12	Nd	Nd	434	0
Ky-13	0.0189	-28.741	Nd	Nd
Ky-14	0.0207	-25.727	Nd	Nd
Ky-15	0.0143	-25.42	209	0
Ky-16	0.0117	-25.913	203	0
Ky-17	0.0107	-26.458	345	1
Ky-18	0.0082	-21.527	318	7
Ky-19	0.0121	-16.866	Nd	Nd
Ky-20	0.013	-17.797	364	0
Ky-21	0.012	-26.612	385	0
Ky-22	Nd	Nd	274	0
Ky-23	0.0087	-26.105	155	0
Ky-24	0.0142	-27.153	331	0

Note: Nd—not detectable.

TABLE 3. $\delta^{13}\text{C}$ AND N CONTENTS OF MICRODIAMONDS RECOVERED FROM THE CHROMITITE OF THE RAY-IZ OPHIOLITE IN THE POLAR URALS

Sample	Weight (mg)	$\delta^{13}\text{C}$ (‰)	N (at. ppm, $\pm 20\%$)	%IaA formed ($\pm 5\%$)
WR-2	0.0372	-26.575	108	0
WR-4	Nd	Nd	287	0
WR-5	Nd	Nd	235	0
WR-6	Nd	Nd	260	0
WR-7	Nd	Nd	229	0
WR-8	0.0258	-25.842	210	0
WR-9	0.0236	-26.07	291	0
WR-10	0.0205	-27.387	236	0
WR-11	Nd	Nd	226	0
WR-13	Nd	Nd	265	0
WR-15	Nd	Nd	309	0
WR-17	Nd	Nd	169	0
WR-18	0.0211	-26.276	227	0
WR-19	0.0098	-26.48	307	8
WR-20	Nd	Nd	330	0
WR-21	0.0156	-26.836	182	0
WR-22	0.0232	-26.192	276	0
WR-24	Nd	Nd	192	0
WR-25	0.0113	-26.607	198	0
WR-26	0.0176	-26.834	250	0
WR-27	Nd	Nd	140	0
WR-29	Nd	Nd	221	0
WR-30	0.0113	-21.62	499	0
WR-31	0.0387	-27.581	289	0
WR-32	0.0125	-26.944	363	0
WP-1	0.008	-29.361	Nd	Nd
WP-2	Nd	Nd	493	0
WP-3	0.0112	-23.016	362	0
WP-4	Nd	Nd	339	0
WP-5	Nd	Nd	230	0
WP-6	0.0134	-26.016	217	0
WP-7	Nd	Nd	188	0
WP-8	0.0135	-26.058	Nd	Nd
WP-10	0.0109	-25.749	Nd	Nd
WP-11	0.0063	-27.192	456	0
WP-12	0.0044		324	0
WP-13	0.0092	-24.944	268	0
WP-14	0.0081	-25.899	Nd	Nd
WP-15	0.0125	-26.019	Nd	Nd
WP-16	0.0096	-27.294	358	0
WP-18	0.0212	-26.92	Nd	Nd
WP-19	0.0092	-27.495	261	0
WP-21	Nd	Nd	170	12
WP-23	0.0085	-25.552	202	0
WP-24	Nd	Nd	307	0
WP-25	0.0114	-25.839	255	0
WP-26	Nd	Nd	400	0

Note: Nd—not detectable.

TABLE 4. $\delta^{13}\text{C}$ AND N CONTENTS OF SYNTHETIC MICRODIAMONDS

Sample	Weight (mg)	$\delta^{13}\text{C}$ (‰)	N (at. ppm, $\pm 20\%$)	%IaA formed ($\pm 5\%$)
SYNc-1	1.502	-20.841	104	8
SYNc-2	1.817	-21.171	95	10
SYNc-3	1.983	-21.385	100	10
SYNc-4	Nd	Nd	74	12
SYNc-5	1.535	-21.611	146	7
SYNc-6	1.599	Nd	152	11
SYNc-7	1.992	Nd	111	12
SYNc-8	1.832	Nd	120	11
SYNc-9	1.852	-21.098	113	13
SYNc-10	1.684	-21.459	125	8
SYNc-11	1.454	-20.596	132	10
SYNc-12	Nd	Nd	101	11
SYNc-13	1.5113	-20.568	120	12
SYNc-14	1.7828	Nd	176	6
SYNc-15	1.8168	-21.452	126	11
SYNc-16	1.4596	-21.197	138	9
SYNc-17	1.7216	-20.518	125	13

Note: Nd—not detectable.

µm). Therefore, we confirm that the microdiamonds we studied did not originate from external residual particles.

Additional evidence further supports the idea that ophiolitic diamonds are natural. This includes higher concentration of trace elements in the Tibetan diamonds, and the predominance of Ni-Mn-Co alloy inclusions, manganese-rich spinel, manganese-rich olivine and manganese-rich garnet, graphite, fluid inclusions, CaCO₃, CaSO₄, and occasional rare earth element (REE) rich inclusions (Yang et al., 2015; Howell et al., 2015); all these phases are not expected among synthetic diamonds. For example, even alloy inclusions in synthetic diamonds are distinct in that they are Fe-Ni alloys (Field, 1992). The report of two diamonds in situ is further evidence that these diamonds are natural.

The FTIR and C isotope characteristics of microdiamonds can be also used to discuss their natural versus external origin. The nitrogen characteristics of high pressure–high temperature synthetic diamonds are well documented, although published N content and N aggregation state data from synthetic diamonds are scarce in the literature. Synthetic diamonds contain mainly single-substitutional nitrogen and N pairs, typically to a lesser extent (e.g., most <20%) in comparison to natural diamonds, i.e., Ib-IaA diamonds with concentrations typically ~200 atomic ppm N (Collins, 2000). The occurrence of unaggregated nitrogen (type Ib) state reflects their short residence frames (from several minutes to weeks) at high temperatures (Finnie et al., 1994; De Corte et al., 1998; Cartigny, 2010; Howell et al., 2015; Smith et al., 2016). Because single N defects are responsible for the absorption of light that gives high pressure–high temperature synthetic diamonds their characteristic yellow color, as are the ophiolitic diamonds, being smaller than the currently investigated synthetic diamonds, i.e., from 100 to 500 µm, their colors are only pale yellow to colorless and the general observation is that their N content and N aggregation state are overall similar. The range of nitrogen concentrations and the lack of aggregation can also account for the range of colors observed in the ophiolitic diamonds. Carbon centers create yellow color and the range of concentrations of ~10 to >400 ppm produces a wide spectrum from nearly colorless to intense yellow.

It is well accepted that the N aggregation in diamond is a secondary process (Strong and Chrenko, 1971; Evans and Qi, 1982; Lu et al., 2001), and that higher N content leads to more advanced aggregation for a given temperature and residence time. It is, therefore, important to notice that the synthetic diamonds we have analyzed are overall poorer in N but have a comparatively higher N aggregation state (Table 4). So, if ophiolite-hosted microdiamonds were a result of contamination, they would have needed to grow at lower temperatures and/or shorter time scales to preserve their pure Ib nature; however, this is not the case.

MINERAL INCLUSIONS IN OPHIOLITE-HOSTED DIAMONDS

We performed focused ion beam analyses (at the GFZ) combined with transmission electron microscopy on mineral inclusions in microdiamonds from the Luobusa peridotites and chromitites. During the course of these analyses we observed a unique stacking fault in one diamond and detected some special inclusions, such as Co-Mn-Ni alloys, Mn-contained minerals (manganese spinel, manganese olivine, and manganese garnet), graphite, fluid inclusions, CaCO₃, CaSO₄, and a rare earth phase (Yang et al., 2015). Although we did not find these inclusions by IR data, the stacking fault in the Luobusa diamond may be attributed to its rapid growth.

Ophiolite-hosted microdiamonds also contain Ni-Mn-Co alloys, and this is another different feature between ophiolitic and synthetic diamonds grown from Fe alloys. The occurrence of abundant fluid and mineral microinclusions, such as nanometer-sized Ni-Mn-Co alloys associated with graphite, galaxias, coesite, tephroite, spessartine, Mn-oxide, native

Mn, and fluid inclusions containing REEs, carbonates, chromite, and moissanite (Yang et al., 2015; Howell et al., 2015), are significant features that do not occur in synthetic diamonds. In addition, stacking faults on some diamond faces are indicative of a natural origin.

DIAMOND CLASSIFICATION BASED ON NITROGEN CONTENTS

Diamonds are grouped into type I and type II (Robertson et al., 1934). On the basis of the ultraviolet transparency and absorption in the infrared (IR) spectra, type I diamond contains nitrogen in a number of different forms, whereas type II diamond is considered a nitrogen-free variety (i.e., containing <20 ppm nitrogen, the detection limit by most FTIR studies). Depending on the speciation of nitrogen, type I diamonds were further subdivided into type IaA (main absorption at 1282 cm⁻¹), IaB (1175 cm⁻¹), and Ib (1130 cm⁻¹) (Field, 1992). These correspond to the three distinct N-bearing defects: N pairs, cluster of 4 N atoms around a vacancy and single N defect for IaA, IaB, and Ib diamonds, respectively. Initially, nitrogen singly substitutes for carbon (type Ib diamond) and subsequently these N atoms migrate to form pairs (type IaA) and clusters to four atoms and a vacancy (type IaB) (Woods, 1986). According to the diffusion process, mixtures of Ib-IaA and IaA-IaB diamonds are commonly described. Theoretically, experimental activation energies can be used to obtain mantle residence time for a given temperature, or to calculate temperatures for a given residence time assuming that the aggregation is a secondary process (Lu et al., 2001). The transformation of diamond is consistent with the second-order kinetics obeying the rate equation (Evans and Harris, 1989; Evans and Qi, 1982; Taylor et al., 1990).

NITROGEN AND CARBON ISOTOPE CHARACTERIZATION OF OPHIOLITE-HOSTED DIAMONDS

We obtained FTIR data for 25 diamonds from the chromitites and 24 diamonds from the mantle peridotites of Luobusa, and for 32 diamonds from the chromitite WR and 26 diamonds from the chromitite WP in Ray-Iz. We obtained reliable quantitative deconvolution (typical examples are shown in Fig. 4) for a total of 21 diamonds from the chromitites and 18 diamonds from the mantle peridotites of Luobusa, for 25 diamonds from the chromitite WR, and 16 diamonds from the chromitite WP of Ray-Iz (Tables 1–3). For others, the baseline was too complex to get good fit of the data. The aggregation state is invariably low. All IR spectra are virtually identical, and are dominated by strong absorption between 1130 cm⁻¹ and 1344 cm⁻¹ (Fig. 4) with no significant peak either at 1282 cm⁻¹ (typical of A centers) or 1170 cm⁻¹ (typical of B centers), making the diamonds type Ib, with virtually no IaA component. The only deconvolutions of spectra that yielded significant IaA (e.g., KCr-19) were generally associated with a significant residual spectrum.

The calculated results of N in diamond from the Kangjinla chromitite (Luobusa) are 152–428 atomic ppm N, with 0%–15% of IaA. The nitrogen concentrations in the mantle peridotite are 151–589 atomic ppm N, with 0%–7% of IaA (Tables 1 and 2). The nitrogen contents in the chromitite (WR) for the Ray-Iz samples are 108–499 atomic ppm N, the highest value of IaA content is to 8%, whereas in the chromitite (WP) it is 170–493 atomic ppm N; the highest data value for IaA content is 12% (Table 3). The diamonds from the Luobusa peridotites and chromitites are similar to the diamonds from the chromitite in the Ray-Iz ophiolite in terms of their similar nitrogen abundance (151–589 atomic ppm N; Tables 1–3; Fig. 5).

We analyzed 59 diamonds from Luobusa and Ray-Iz for carbon isotopes (16 Ky, 16 KCr, 13 WR, and 14 WP). Diamonds from the Luobusa mantle peridotites have δ¹³C values ranging from –28.7‰ to –16.9‰, with an average value of –24.9‰. Values for diamonds from the Luobusa

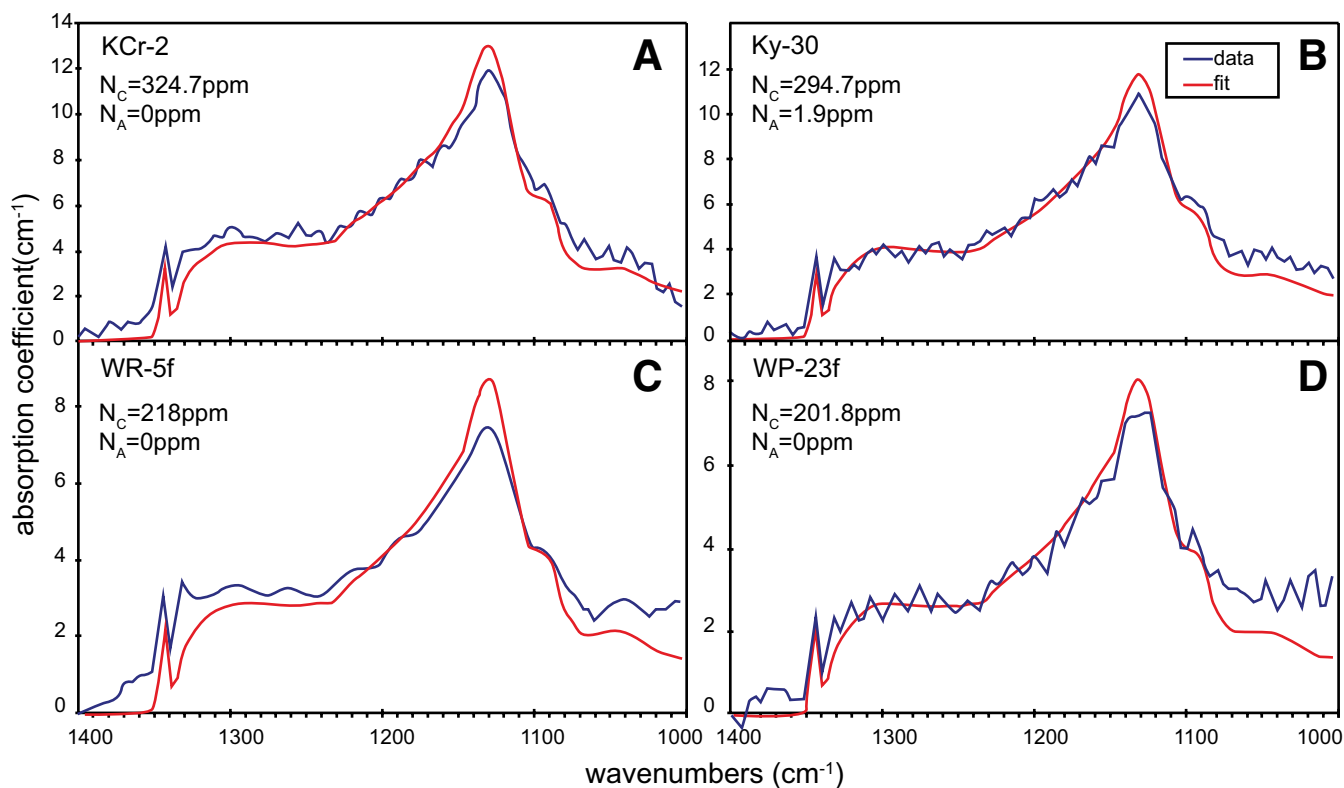


Figure 4. Infrared spectrum for diamond crystals recovered from the Luobusa chromitite and mantle peridotites, and from the Ray-Iz chromitite. (A) Infrared spectrum for diamonds recovered from the Luobusa chromitites. (B) Infrared spectrum for diamonds recovered from the Luobusa mantle peridotites. (C, D) Infrared spectrum for diamonds recovered from the Ray-Iz chromitite.

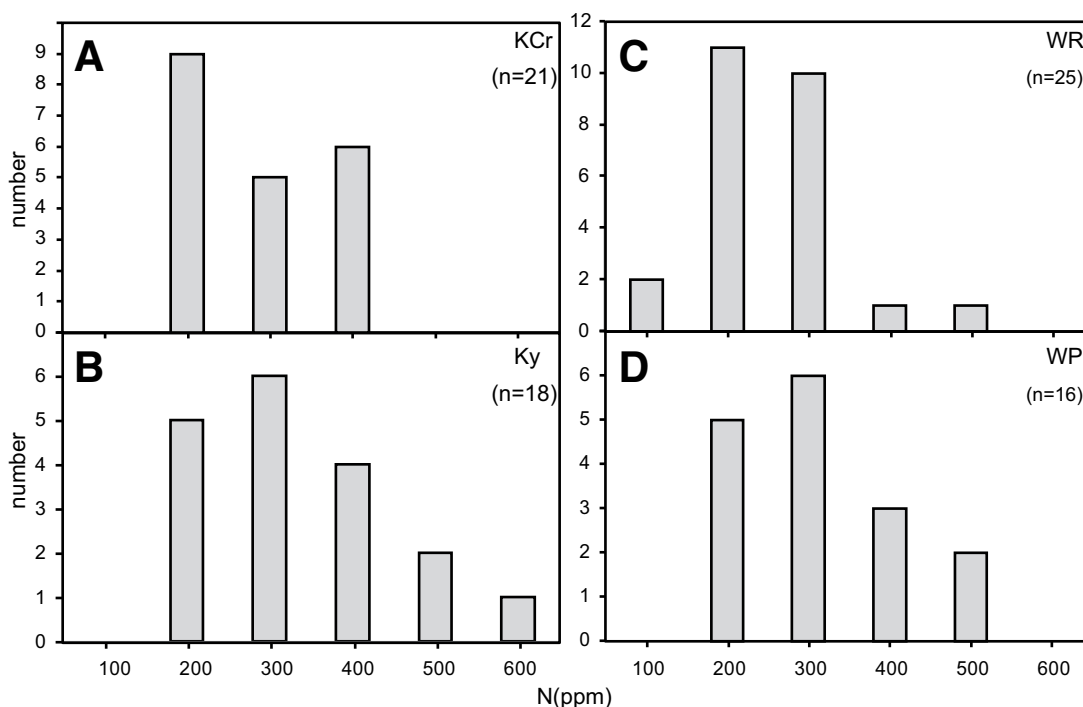


Figure 5. Comparison of nitrogen content for diamonds recovered from the Luobusa chromitites and mantle peridotites, and from the Ray-Iz chromitites. (A) Nitrogen content for diamonds recovered from the Luobusa chromitite. (B) Nitrogen content for diamonds recovered from the Luobusa mantle peridotite. (C, D) Nitrogen content for diamonds recovered from the Ray-Iz chromitite.

chromitites are from -29% to -15.5% with an average value of -23.6% . Diamonds from the Ray-Iz chromitites have $\delta^{13}\text{C}$ values varying from -29.4% to -21.6% . The $\delta^{13}\text{C}$ values of WP and WR do not vary much; most (26 of 27) are between 25.5% and 27.5% , and one sample from WR was -21.6% . The average $\delta^{13}\text{C}$ value of both WR and WP samples is -26.2% (Table 3). Overall, diamond $\delta^{13}\text{C}$ values are whatever their host rock values are (from -15% to -30%), but have similar average values of $\sim -25\%$ (Fig. 6).

We obtained FTIR data for 17 synthetic diamonds together with 11 C isotope measurements (Table 4). Their nitrogen contents vary significantly, and are on the lower side of metamorphic diamonds (from 73 to 176 ppm, average = 121 atomic ppm N). Their N aggregation is more advanced (Ib-IaA diamonds) in comparison to those obtained from natural diamonds. It is important to note that because of their larger size, the precision on N concentration and N aggregation state is much better than for the investigated natural samples, i.e., the occurrence of N pairs is significant. Synthetic diamonds have $\delta^{13}\text{C}$ values ranging from -21.6% to -20.5% , with an average value of -21.1% . Compared with other investigated diamonds, synthetic diamonds cover a more restricted range of $\delta^{13}\text{C}$ values and have lower N contents, yet more advanced aggregation states.

Carbon isotopes in synthetic diamonds are known to be depleted in the ^{13}C isotope, and these depleted values primarily reflect the isotopic composition of the starting material (e.g., graphite). Natural graphite displays a large range of C isotope composition with an average value of $-25\% \pm 5\%$, within the range shown by ophiolite-hosted and synthetic diamonds. However, one fundamental observation is critical. Synthetic diamonds show an intrinsic C isotope homogeneity that reflects a limited (typically a few per mille) C isotope fractionation during the growth of synthetic diamond (Reutsky et al., 2008a, 2008b, 2012). In most cases,

ophiolite-hosted diamonds show much more variable C isotope compositions in comparison to synthetic diamonds. The diamonds from the Ray-Iz chromitites range from -27.6% to -21.6% in $\delta^{13}\text{C}$ values, whereas the Luobusa peridotites and chromitites range from -28.7% to -16.9% and -29% to -15.5% , respectively. Only the WP samples show an isotope homogeneity that would be consistent with synthetic diamond. The similar average $\delta^{13}\text{C}$ values among all the investigated diamonds could be seen as an argument that the diamonds result from massive contamination, in this case most likely occurring in the laboratory during their separation and recovery, but the fact that Howell et al. (2015) found similar $\delta^{13}\text{C}$ values in diamonds extracted in a distinct laboratory make this possibility less likely.

Howell et al. (2015) reported on the shape, FTIR characteristics, and $\delta^{13}\text{C}$ - $\delta^{15}\text{N}$ -N contents of the Luobusa diamonds together with additional data on synthetic industrial diamonds. Overall, our results are consistent with those of Howell et al. (2015). For example, their $\delta^{13}\text{C}$ values ranged from -28.3% to -24.0% with an average value of 25.8% . Although they did not provide any data, Howell et al. (2015) indicated that they found pure Ib diamonds, a result consistent with our observations. Our data are also consistent with those in Yang et al. (2014a), i.e., $\delta^{13}\text{C}$ values ranging from -18% to -28% for diamonds from the chromitite, mantle peridotite of Luobusa, mantle peridotite of Dongbo, Purang, Dangqiong, Xigaze, and Zedang, located along the Yarlung-Zangbo suture zone, and ophiolite chromitite of the Polar Urals. The N isotope values for the Luobusa diamonds show far more variation than has been reported from synthetic diamonds. A second difference is the higher concentration of trace elements in the Luobusa diamonds, and the predominance of Ni-Mn-Co alloy inclusions and rare REE-rich inclusions, in contrast to the Fe-Ni alloys common in synthetic high pressure–high temperature diamonds.

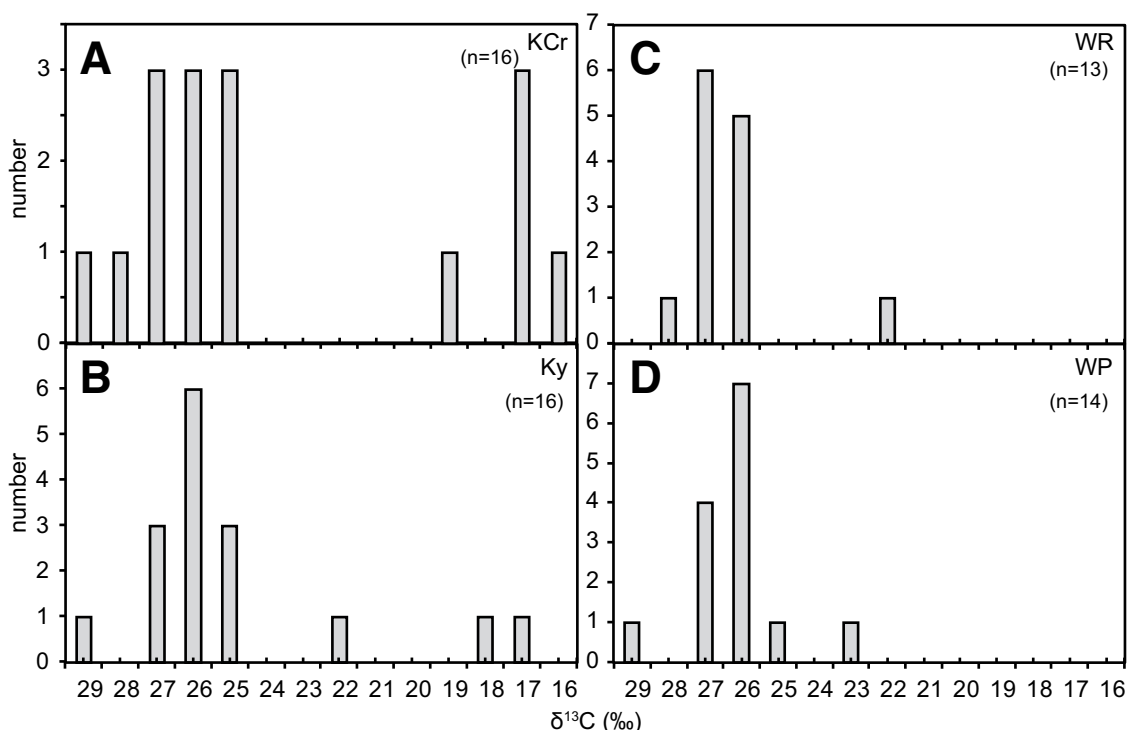


Figure 6. Carbon isotopic composition of diamonds from the Luobusa chromitites and peridotites, and from the Ray-Iz chromitites. (A) Carbon isotopic composition of diamonds recovered from the Luobusa chromitites. (B) Carbon isotopic composition of diamonds recovered from the Luobusa mantle peridotites. (C, D) Carbon isotopic composition of diamonds recovered from the Ray-Iz chromitite.

METAMORPHIC ORIGIN OF OPHIOLITE-HOSTED DIAMONDS

Natural diamonds commonly contain nitrogen in abundance varying from a few to several thousand atomic ppm N and show large variations in aggregation states (Boyd et al., 1994). Kimberlitic diamonds type Ib are very rare (<0.1%; reviewed in Cartigny et al., 2004; Nadolny et al., 2006; Hainschwang et al., 2013; Cartigny, 2010; Smit et al., 2016; Smith et al., 2016) and exhibit high nitrogen aggregation states and would plot on the right side of Figure 7 (IaAB diamonds, e.g., Javoy et al., 1984; Deines et al., 1997; Cartigny et al., 1997). This is because, in kimberlites and lamproites, most diamonds (>95%) are xenocrysts, which must have formed earlier when their host rocks equilibrated in the Earth's mantle (Richardson et al., 1984; Shirey et al., 2013, for review). Diamonds from ultrahigh-pressure metamorphic terranes all belong to the mixed type Ib-IaA (e.g., Dobretsov et al., 1995; De Corte et al., 1998, 1999; Dobrzhinetskaya et al., 2006; Cartigny et al., 2004; Finnie et al., 1994).

Our IR studies have shown that the ophiolitic diamonds have a strong absorption at 1130 cm^{-1} , making them type Ib. In this respect, they appear less aggregated (i.e., 0% IaA) than previously analyzed metamorphic diamonds (most between 20% and 80% IaA; Finnie et al., 1994; De

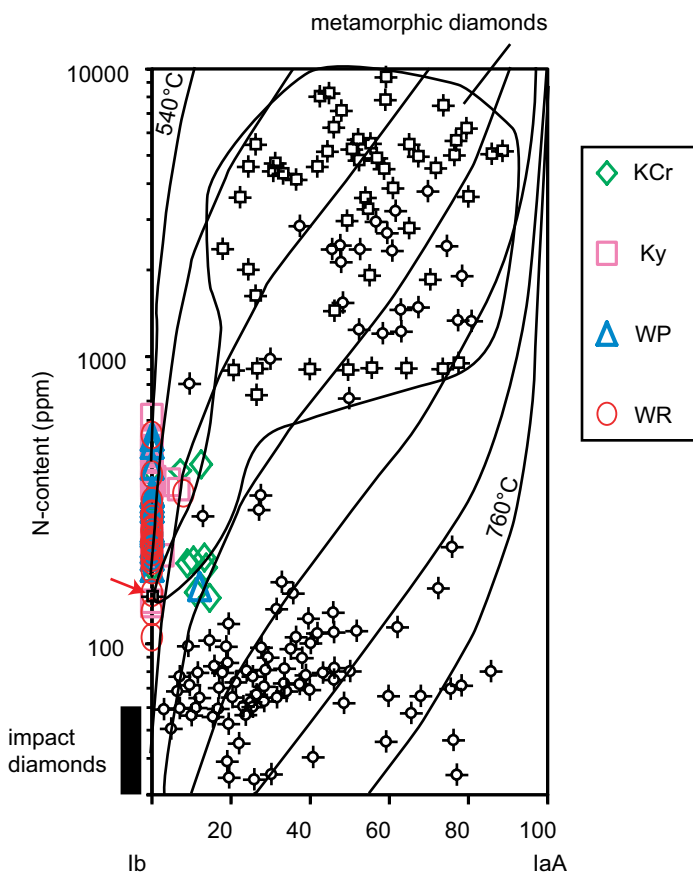


Figure 7. Nitrogen aggregation versus nitrogen content in ophiolite-hosted microdiamonds from the Luobusa ophiolite (Tibet) and the Ray-Iz ophiolite in the Polar Urals (Russia) (after Cartigny et al., 2004; Dobrzhinetskaya et al., 2006). Open circles with crossing lines are diamonds from the worldwide collection of kimberlites; open squares with crossing lines are from metamorphic diamonds. KCr—Kangjinla chromite (Luobusa ophiolite); Ky—mantle peridotite of the Kangjinla chromite deposit; WP—chromitite of the W214 from the Ray-Iz ophiolite; WR—chromitite of the CCD from the Ray-Iz ophiolite.

Corte et al., 1998, 1999; Cartigny et al., 2004; Dobrzhinetskaya et al., 2007); ophiolitic diamonds are the least aggregated samples reported so far. There is a large consensus that the preservation of the type Ib feature of diamonds can be preserved only through rapid (a few million years; Fig. 7) tectonic exhumation of the metamorphic diamonds after their formation at temperatures <1000 °C (for metamorphic diamonds, see Howell et al., 2015; Finnie et al., 1994; De Corte et al., 1998, 1999; for mantle diamonds see Cartigny, 2010; Smit et al., 2016; Smith et al., 2016). Their nitrogen concentrations range from 108% to $589\% \pm 20\%$ atomic ppm; these values are clearly higher than both mantle Ib-IaA diamonds and impact-related diamonds, respectively (Fig. 7); they are also lower by about one order of magnitude than previously studied metamorphic diamonds (see references above). However, note that there was one supposedly metamorphic diamond from Akluilák (Cartigny et al., 2004; red arrow in Fig. 7) plotting within the field of ophiolitic diamond. Because N aggregation depends on time, temperature, and nitrogen content (Evans and Qi, 1982), the lower N aggregation state and N content character of ophiolitic diamonds is actually consistent with a similar temperature-time history for previously studied metamorphic diamond. The isotherms illustrated in Figure 7 were calculated using constant temperature and an assumed residence time of 1 m.y.; Figure 7 clearly shows that ophiolitic diamonds and previously analyzed metamorphic diamonds differ in their average N contents, but have temperature-time histories that are broadly consistent. The isotherms illustrated in Figure 7 rely on a simplistic model, but that would not change our conclusion if a more complex model with changing temperature was considered.

Compared with mantle-derived rocks that typically contain a few parts per million of nitrogen, sediments are nitrogen rich (to 2000 ppm; see Busigny and Bebout, 2013, for review). This primarily results from the occurrence of organic matter that is characterized by high N/C ratios, the nitrogen being originally sourced from the atmosphere by primary producers such as cyanobacteria. Hydrothermal alteration would also lead to nitrogen enrichment, but to a lesser extent (~5–10 ppm; e.g., Busigny et al., 2005a, 2005b; Philippot et al., 2007); in this case, nitrogen mostly originates from N species dissolved in seawater. During subduction, dehydration reactions occur but significant amounts (typically 80%) remain within the rocks and are returned to the mantle (Busigny et al., 2011). The fact that ophiolitic diamonds are poorer in nitrogen than metamorphic diamonds is consistent with primary evidence that metaperidotites and metagabbros contain ~10 times less nitrogen than the metamorphic diamonds from metasediments (De Corte et al., 1998; Cartigny et al., 2001). The all but one positive $\delta^{15}\text{N}$ values measured among ophiolitic diamonds by Howell et al. (2015) are consistent with the positive $\delta^{15}\text{N}$ values measured among metasediments, metagabbros, and metaperidotites (Busigny and Bebout, 2013; Busigny et al., 2005b, 2011; Bebout and Fogel, 1992; Philippot et al., 2007).

Ophiolitic diamonds are characterized by ^{13}C -depleted compositions from -29‰ to -15.5‰ (this study), a result consistent with previous reports (Yang et al., 2014a; Howell et al., 2015). The $\delta^{13}\text{C}$ distribution is different from those of typical kimberlitic diamonds (Fig. 8; see Cartigny et al., 2014, for review) with the noticeable exceptions of Dachine (French Guiana; Cartigny, 2010; Smith et al., 2016), and Jericho (northern Slave craton; De Stefano et al., 2009) both of which show some similarities with $\delta^{13}\text{C}$ modes at $\sim -26\text{‰}$ and $\sim -35\text{‰}$, respectively (not shown). The $\delta^{13}\text{C}$ distribution of ophiolitic diamonds is distinct from that of previously metamorphic diamonds, for which $\delta^{13}\text{C}$ values $\leq -20\text{‰}$ are rare (Fig. 8). The $\delta^{13}\text{C}$ values are overall similar to those measured on moissanite (natural SiC with $\delta^{13}\text{C}$ from -1‰ to -35‰ , $n = 36$; Fig. 8; data from Trumbull et al., 2009) from podiform chromitites of several ophiolite complexes, including the Luobusa and Dongqiao ophiolites in

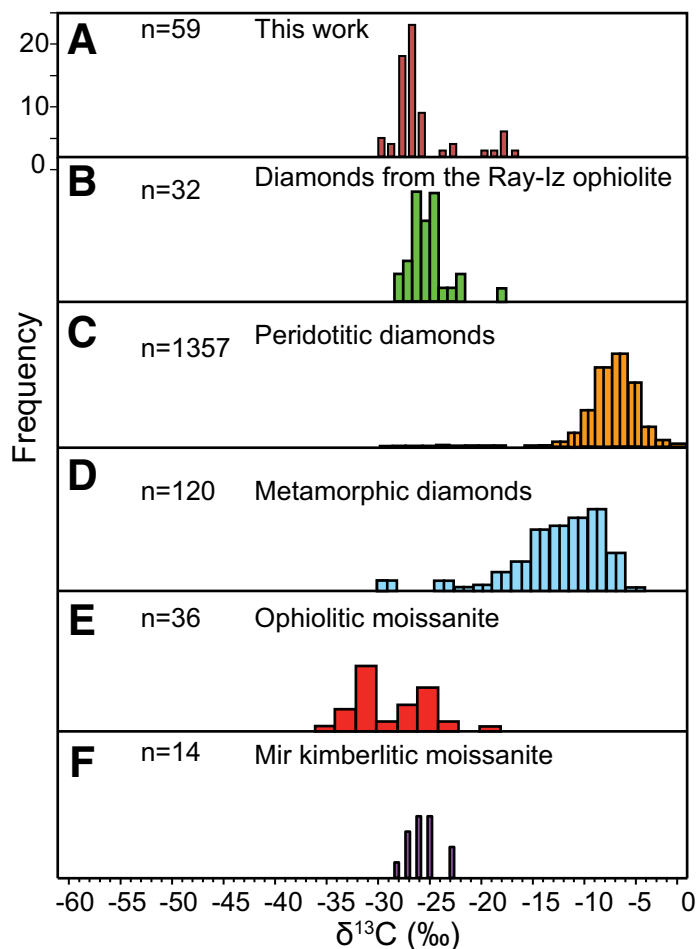


Figure 8. Histograms of $\delta^{13}\text{C}$ values for diamonds and moissanites from ophiolites and other occurrences in the Earth. (A) $\delta^{13}\text{C}$ value of Tibet and Ray-Iz diamond using a Thermo Finnigan MAT 253 mass spectrometer. (B) $\delta^{13}\text{C}$ value of Ray-Iz diamonds using secondary ion mass spectrometry (Yang et al., 2014a). (C) $\delta^{13}\text{C}$ value of peridotitic diamond in kimberlite (Cartigny, 2005). (D) $\delta^{13}\text{C}$ value of metamorphic diamonds in ultrahigh-pressure subduction zone (Cartigny, 2005). (E) $\delta^{13}\text{C}$ value of moissanites from ophiolites (Trumbull et al., 2009). (F) $\delta^{13}\text{C}$ value of moissanites from Mir kimberlite in Siberia (Mathez et al., 1995).

Tibet, the Semail ophiolite in Oman and the United Arab Emirates, the Ray-Iz ophiolite of the Polar Urals, Russia, and moissanite from the Mir kimberlite in Siberia (Trumbull et al., 2009; Mathez et al., 1995).

The very similar carbon isotope features of the ophiolite-hosted diamond and moissanite of the Tibet and Urals are consistent with a similar source. Diamond and carbide have not been described as coexisting within investigated samples from Luobusa and Ray-Iz; otherwise the strong stable isotope fractionation between these two phases (i.e., $\sim 8\text{‰}$ at $\sim 10,000\text{ °C}$; see Horita and Polyakov, 2015) would predict carbide to be significantly depleted in ^{13}C compared with diamond. The origins of carbide are still in debate, but their occurrence undoubtedly testifies that a range of reducing conditions existed, to provide conditions where metal (Fe, Fe-Ni, Ni-Mn-Co), carbides (SiC and Fe-C), and diamond could be formed.

The origin of such ^{13}C -depleted isotope compositions in deep-seated material is a long-standing question (for reviews, see Shirey et al., 2013; Cartigny et al., 2014), and one possibility is that they represent the isotope signature of subducted organic matter. The implicit consequence is that

the subducted material must be free of any carbonate. Having $\delta^{13}\text{C} \sim 0\text{‰}$, increasing metamorphism would lead to isotope equilibration between subducted organic matter and carbonate at temperatures $\sim 600\text{ °C}$ (Valley and O'Neil, 1981). No large compartments have been identified within the oceanic crust and lithosphere holding such negative bulk $\delta^{13}\text{C}$ values. Metaserpentines in particular are dominated by high $\delta^{13}\text{C}$ values (e.g., from -8‰ to -3‰ ; Vitale et al., 2017). The only compartment having such low $\delta^{13}\text{C}$ values is the altered oceanic crust, with $\delta^{13}\text{C}$ values from -14.9‰ to -26.6‰ (Shilobreeva et al., 2011). Carbon isotope compositions were interpreted as a mixing between organic compounds with $\delta^{13}\text{C} \sim -27\text{‰}$, and carbonates with $\delta^{13}\text{C} \sim 0\text{‰}$. The key question of virtually lacking carbonates in the studied altered oceanic crust and lithosphere remains.

ORIGIN OF OPHIOLITE-HOSTED DIAMONDS BASED ON NITROGEN AND CARBON ISOTOPE DATA

Significantly different activation energies have been calculated for aggregation in the octahedral and the cube sectors of high pressure–high temperature synthetic diamonds (Taylor et al., 1996). The higher activation energy of the cube sector (6eV, as opposed to 4.4eV in the octahedral sectors) has been attributed to vacancy-assisted nitrogen migration in the octahedral sectors. Assuming constant temperature, a diamond with N content higher than 100 ppm would aggregate its nitrogen into type IaA at a temperature of 700 °C within 1 m.y. (for similar calculations, see Finnie et al., 1994; De Corte et al., 1998; Cartigny, 2010; Howell et al., 2015; Smith et al., 2016). A time transfer of ophiolite-hosted diamonds has been calculated for a diamond having a nitrogen concentration of 500 ppm using an assumed formation temperature and depth, and a constant ascent rate (5 m.y.). We found that depths of 117 km with corresponding temperature of 950 °C for the cubic activation energy of Taylor et al. (1996) would result in a 10% IaA aggregation (values of 200 km and 1100 °C were found if the octahedral activation energy of Taylor et al., 1996, was used). This means that the estimated residence times within 1 m.y. represent maximums. From Figure 9, if we assume 4.4 eV, ophiolitic diamonds basically formed at shallow depths (117 km), just before leaving the diamond stability field.

Fluid inclusions (water, carbonate, hydrocarbon, silicate, and solid CO_2) and defects have been detected by FTIR spectra (Moe et al., 2017) and suggest that diamonds grew from an oxidized fluid introduced into the much reduced environments, i.e., as for previously studied metamorphic diamonds (e.g., De Corte et al., 1998). This raises the question of the carbon budget in these rocks, i.e., whether the carbon isotope composition of diamond reflects that of the fluid or a mixture between the subducted rocks and the percolating fluid. The origin of the fluid, i.e., whether it represent small-scale or large-scale mobility is also unknown. Providing the first $\delta^{13}\text{C}$ isotope data of the UHP microdiamonds ($\leq -8.7\text{‰}$), these metamorphic diamonds clearly show that their protolith was derived from recycled crustal material, such as extremely light and organic carbon and/or marine carbonates (Schertl and Sobolev, 2013).

Infrared absorption measurements show that diamond crystals synthesized in the metal-carbon melt contain 100–200 atomic ppm of nitrogen impurity in the form of single substitutional atoms (C centers) (Palyanov et al., 2013). Another possibility could be that the diamonds were produced under conditions of thermodynamic instability (Deryagin and Fedosayev, 1989). Diamond nanoparticles can form from a C-H-O fluid system under low pressure-temperature conditions, i.e., within the graphite stability field (Simakov et al., 2008; Simakov, 2010). Although such a model could account for the low aggregation state of nitrogen, our samples can be as large as several hundred microns, much larger than diamonds grown metastably, which we think makes this suggestion unlikely.

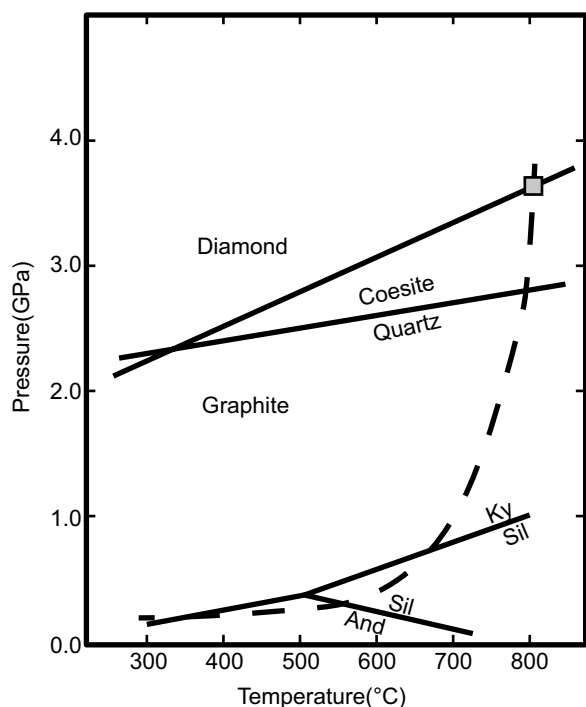


Figure 9. Temperature versus pressure calculated from the nitrogen aggregation relationship. Square represents the average formation depth (we assume activation energy of 4.4eV). Dashed line represents tendency to increase with temperature and pressure. Ky—kyanite; sil—sillimanite; and—andalusite.

CONCLUSIONS

Many similarities exist between ophiolitic and synthesized diamonds, including color, N aggregation state, and ^{13}C isotope compositions, but there are differences in the details, including their size, inclusions, and trace element concentrations; the independent confirmation from different research groups makes more reliable the conclusion that these ophiolitic diamonds are actually natural.

Rejecting anthropogenic contamination, ophiolitic diamonds are actually closer to previously studied metamorphic diamonds and very unlike diamonds formed in other contexts (e.g., impact craters, lithospheric mantle). However, ophiolitic diamonds have unique features suggesting that they may represent a new category of diamond formation on Earth. This is because ophiolitic diamonds are characterized by low N contents compared with previously studied metamorphic diamonds formed in metasedimentary rocks, and distinctive inclusions, among them Mn-rich minerals. All these features point to diamond formation in subducted ophiolites, i.e., within rocks from the oceanic mantle rocks.

The low aggregation state of ophiolitic diamonds (nearly pure Ib) implies an extremely short residence time (million year time scale) at high temperatures (<900 °C). To get a clear understanding of ophiolitic diamond formation, numerous questions remain, including the nature and formation of fluids leading to diamond formation, that require cross-disciplinary research.

ACKNOWLEDGMENTS

We thank Tatsuki Tsujimori and Hans-Peter Schertl for constructive and thorough reviews that helped us improve the paper. This research was funded by grants from the China Geological Survey (DD20160023-01), the National Science Foundation of China (grants 41672046, 41641015, 41202036), the Ministry of Science and Technology of China (201511022), and IGCP

(International Geoscience Programme) Project 649. We are grateful to Jeff Harris for discussions. We thank the Deep Carbon Observatory for funding our analytical work.

REFERENCES CITED

- Bai, W., Zhou, M., and Robinson, P.T., 1993, Possibly diamond-bearing mantle peridotites and podiform chromitites in the Luobusa and Dongqiao ophiolites, Tibet: *Canadian Journal of Earth Sciences*, v. 30, p. 1650–1659.
- Bebout, G.E., and Fogel, M.L., 1992, Nitrogen-isotope compositions of metasedimentary rocks in the Catalina Schist, California: Implications for metamorphic devolatilization history: *Geochimica et Cosmochimica Acta*, v. 56, p. 2839–2849, doi:10.1016/0016-7037(92)90363-N.
- Bostick, B.C., Jones, R.E., Ernst, W.G., Chen, C., Leech, M.L., and Beane, R.J., 2003, Low temperature microdiamond aggregates in the Maksyutov complex, south Ural Mountains, Russia: *American Mineralogist*, v. 88, p. 1709–1717, doi:10.2138/am-2003-11-1211.
- Boyd, S.R., Pineau, F., and Javoy, M., 1994, Modelling the growth of natural diamonds: *Chemical Geology*, v. 116, p. 29–42, doi:10.1016/0009-2541(94)90156-2.
- Boyd, S.R., Re'jou-Michel, A., and Javoy, M., 1995, Improved techniques for the extraction, purification and quantification of nanomole quantities of nitrogen gas: The nitrogen content of a diamond: *Measurement Science & Technology*, v. 6, p. 297–305, doi:10.1088/0957-0233/6/3/007.
- Burns, R.C., and Davies, G.J., 1992, Growth of synthetic diamonds, *in* Field, J.E., ed., *The properties of natural and synthetic diamond*: London, Academic Press, p. 345–393.
- Busigny, V., and Bebout, G.E., 2013, Nitrogen in the silicate earth: Speciation and isotopic behavior during mineral-fluid interactions: *Elements*, v. 9, p. 353–358, doi:10.2113/gselements.9.5.353.
- Busigny, V., Ader, M., and Cartigny, P., 2005a, Quantification and isotopic analysis of nitrogen in rocks at the ppm level using sealed tube combustion technique: A prelude to the study of altered oceanic crust: *Chemical Geology*, v. 223, p. 249–258, doi:10.1016/j.chemgeo.2005.08.002.
- Busigny, V., Laverne, C., and Bonifacie, M., 2005b, Nitrogen content and isotopic composition of oceanic crust at a superfast spreading ridge: A profile in altered basalts from ODP Site 1256, Leg 206: *Geochemistry, Geophysics, Geosystems*, v. 6, Q12001, doi:10.1029/2005GC001020.
- Busigny, V., Cartigny, P., and Philippot, P., 2011, Nitrogen isotopes in ophiolitic metagabbros: A re-evaluation of modern nitrogen fluxes in subduction zones and implication for the early Earth atmosphere: *Geochimica et Cosmochimica Acta*, v. 75, p. 7502–7521, doi:10.1016/j.gca.2011.09.049.
- Cartigny, P., 2005, Stable isotopes and the origin of diamond: *Elements*, v. 1, p. 79–84, doi:10.2113/gselements.1.2.79.
- Cartigny, P., 2010, Mantle-related carbonados? Geochemical insights from diamonds from the Dachine komatiite (French Guiana): *Earth and Planetary Science Letters*, v. 296, p. 329–339, doi:10.1016/j.epsl.2010.05.015.
- Cartigny, P., Boyd, S., Harris, J., and Javoy, M., 1997, Nitrogen isotopes in peridotitic diamonds from Fuxian, China: The mantle signature: *Terra Nova*, v. 9, p. 175–179, doi:10.1046/j.1365-3121.1997.d01-26.x.
- Cartigny, P., De Corte, K., Shatsky, V.S., Ader, M., De Paepe, P., Sobolev, N.V., and Javoy, M., 2001, The origin and formation of metamorphic microdiamonds from the Kokchetav massif, Kazakhstan: A nitrogen and carbon isotopic study: *Chemical Geology*, v. 176, p. 265–281, doi:10.1016/S0009-2541(00)00407-1.
- Cartigny, P., Chinn, L., Viljoen, K.F., and Robinson, D., 2004, Early Proterozoic ultrahigh pressure metamorphism: Evidence from microdiamonds: *Science*, v. 304, p. 853–855, doi:10.1126/science.1094668.
- Cartigny, P., Palot, M., Thomassot, E., and Harris, J.W., 2014, Diamond formation: A stable isotope perspective: *Annual Review of Earth and Planetary Sciences*, v. 42, p. 699–732, doi:10.1146/annurev-earth-042711-105259.
- Collins, A.T., 2000, Spectroscopy of defects and transition metals in diamond: *Diamond and Related Materials*, v. 9, p. 417–423, doi:10.1016/S0925-9635(99)00314-3.
- De Corte, K., Cartigny, P., Shatsky, V.S., Sobolev, N.V., and Javoy, M., 1998, First evidence of fluid inclusions in metamorphic microdiamonds from the Kokchetav massif, northern Kazakhstan: *Geochimica et Cosmochimica Acta*, v. 62, p. 3765–3773, doi:10.1016/S0016-7037(98)00266-X.
- De Corte, K., Cartigny, P., Shatsky, V.S., De Paepe, P., Sobolev, N.V., and Javoy, M., 1999, Characteristics of microdiamonds from UHPM rocks of the Kokchetav massif, *in* Gurney, J.J., et al., eds., *Proceedings of the 7th International Kimberlite Conference*: Cape Town, South Africa, Red Roof Design, p. 174–182.
- Deines, P., Harris, J.W., and Gurney, J.J., 1997, Carbon isotope ratios, nitrogen content and aggregation state, and inclusion chemistry of diamonds from Jwaneng, Botswana: *Geochimica et Cosmochimica Acta*, v. 61, p. 3993–4005, doi:10.1016/S0016-7037(97)00199-3.
- Deryagina, B.V., and Fedosayev, D.V., 1989, The growth of diamond and graphite from gas phase: *Surface and Coatings Technology*, v. 38, p. 131–248, doi:10.1016/0257-8972(89)90129-1.
- De Stefano, A., Kopylova, M.G., Cartigny, P., and Afanasiev, V., 2009, Diamonds and eclogites of the Jericho kimberlite (northern Canada): *Contributions to Mineralogy and Petrology*, v. 158, p. 295–315, doi:10.1007/s00410-009-0384-7.
- Dobretsov, N.L., Sobolev, N.V., Shatsky, V.S., Goleman, R.G., and Ernst, W.G., 1995, Geotectonic evolution of diamondiferous paragneisses, Kokchetav complex, northern Kazakhstan: The geologic enigma of ultrahigh-pressure crustal rocks within a Paleozoic foldbelt: *The Island Arc*, v. 4, p. 267–279, doi:10.1111/j.1440-1738.1995.tb00149.x.
- Dobrzhinetskaya, L.F., Wirth, R., and Green, H.W., II, 2007, A look inside of diamond-forming media in deep subduction zones: *PNAS*, early edition, p. 1–5, doi:10.1073/pnas.06091611104.
- Dobrzhinetskaya, L.F., Eide, E.A., Larsen, R.B., Sturt, B.A., Tronnes, R.G., Smith, D.C., Taylor, W.R., and Posukhova, T.V., 1995, Microdiamond in high-grade metamorphic rocks of the Western Gneiss region, Norway: *Geology*, v. 23, p. 597–600, doi:10.1130/0091-7613(1995)023<0597:MIHGMGR>2.3.CO;2.

- Dobrzhinetskaya, L.F., Liu, Z., Cartigny, P., Zhang, J., Tchkhetaia, N.N., Green, H.W., II, and Hemley, R.J., 2006, Synchrotron infrared and Raman spectroscopy of microdiamonds from Erzgebirge, Germany: *Earth and Planetary Science Letters*, v. 248, p. 340–349, doi:10.1016/j.epsl.2006.05.037.
- Dobrzhinetskaya, L.F., Wirth, R., Yang, J.S., Hutcheon, I.D., Weber, P.K., and Green, H.W., II, 2009, High-pressure highly reduced nitrides and oxides from chromitite of a Tibetan ophiolite: *Proceedings of the National Academy of Sciences of the United States of America*, v. 106, p. 19233–19238, doi:10.1073/pnas.0905514106.
- Dobrzhinetskaya, L.F., Wirth, R., and Green, H.W., II, 2014, Diamonds in Earth's oldest zircons from Jack Hills conglomerate, Australia, are contamination: *Earth and Planetary Science Letters*, v. 387, p. 212–218, doi:10.1016/j.epsl.2013.11.023.
- Evans, T., and Harris, J.W., 1989, Nitrogen aggregation, inclusion equilibration temperature and the age of diamonds, in Ross, J., ed., *Kimberlite and Related Rocks: Their composition, occurrence, origin and emplacement*: Geological Society of Australia Special Publication 14, p. 1001–1006.
- Evans, T., and Qi, Z., 1982, The kinetic of aggregation of nitrogen atoms in diamond: *Royal Society of London Proceedings*, ser. A, v. 381, p. 159–178, doi:10.1098/rspa.1982.0063.
- Field, J.E., ed., 1992, *The Properties of Natural and Synthetic Diamond*: London, Academic Press, 710 p.
- Finnie, K.S., Fisher, D., Griffin, W.L., Harris, J.W., and Sobolev, N.V., 1994, Nitrogen aggregation in metamorphic diamonds from Kazakhstan: *Geochimica et Cosmochimica Acta*, v. 58, p. 5173–5177, doi:10.1016/0016-7037(94)90302-6.
- Frezzotti, M.L., Selverstone, J., Sharp, Z.D., and Compagnoni, R., 2011, Carbonate dissolution during subduction revealed by diamond-bearing rocks from the Alps: *Nature Geoscience*, v. 4, p. 703–706, doi:10.1038/ngeo1246.
- Hainschwang, T., Fritsch, E., Notari, F., Rondeau, B., and Katruscha, A., 2013, The origin of colour in natural C center bearing diamonds: *Diamond and Related Materials*, v. 39, p. 27–40, doi:10.1016/j.diamond.2013.07.007.
- Horita, J., and Polyakov, V.B., 2015, Carbon-bearing iron phases and the carbon isotope composition of the deep Earth: *Proceedings of the National Academy of Sciences of the United States of America*, v. 112, p. 31–36, doi:10.1073/pnas.1401782112.
- Howell, D., et al., 2015, Diamonds in ophiolites: Contamination or a new diamond growth environment: *Earth and Planetary Science Letters*, v. 430, p. 284–295, doi:10.1016/j.epsl.2015.08.023.
- Institute of Geology, Chinese Academy of Geological Sciences, 1981, The discovery of alpine-type diamond bearing ultrabasic intrusions in Xizang (Tibet): *Geological Review*, v. 27, p. 445–447 (in Chinese with English abstract).
- Javoy, M., Pineau, F., and Demaiffe, D., 1984, Nitrogen and carbon composition in the diamonds of Mbuji Mayi (Zaire): *Earth and Planetary Science Letters*, v. 68, p. 399–412, doi:10.1016/0012-821X(84)90125-0.
- Kiflawi, I., Mayer, A.E., Spear, P.M., Van Wyk, J.A., and Woods, G.S., 1994, Infrared absorption by the single nitrogen and A defect centres in diamond: *Philosophical Magazine Part B*, v. 69, p. 1141–1147, doi:10.1080/01418639408240184.
- Kotkova, Y., O'Brien, P.J., and Ziemann, M.A., 2011, Diamond and coesite discovered in Saxony-type granulite: Solution to the Variscan garnet peridotite enigma: *Geology*, v. 39, p. 667–670, doi:10.1130/G31971.1.
- Kvasnitsa, V.N., Zinhouk, N.N., and Koptil, V.I., 1999, Typomorphism of diamond micro-crystals: *Moscow, Nedra*, 64 p.
- Kvasnitsya, V., 2013, Crystal forms of natural microdiamonds: *Diamond and Related Materials*, v. 39, p. 89–97, doi:10.1016/j.diamond.2013.08.005.
- Li, G., Fang, Q., Shi, N., Bai, W., Yang, J., Ming, X., Ma, Z., and He, R., 2009, Zangboite, TiFeSi_2 , a new mineral species from Luobusha, Tibet, China, and its crystal structure: *Canadian Mineralogist*, v. 47, p. 1265–1274, doi:10.3749/canmin.47.5.1265.
- Lian, D., Yang, J., Dilek, Y., Wu, W., Zhang, Z., Xiong, F., Fei, L., and Zhou, W., 2017, Diamond, moissanite and other unusual minerals in podiform chromitites from the Pozanti-Karsanti ophiolite, southern Turkey: Implications for the deep mantle origin and ultra-reducing conditions in podiform chromitite: *American Mineralogist*, doi:10.2138/am-2017-5850.
- Liou, J.G., Tsujimori, T., Yang, J.S., Zhang, R.Y., and Ernst, W.G., 2014, Recycling of crustal materials through study of ultrahigh-pressure minerals in collisional orogens, ophiolites, and mantle xenoliths: A review: *Journal of Asian Earth Sciences*, v. 96, p. 386–420, doi:10.1016/j.jseas.2014.09.011.
- Lu, F., Chen, M.H., Di, J.R., and Zheng, J., 2001, Nitrogen distribution in diamonds from the kimberlite pipe No.50 at Fuxian in Eastern China: A CL and FTIR study: *Physics and Chemistry of the Earth. Part A: Solid Earth and Geodesy*, v. 26, p. 773–780, doi:10.1016/S1464-1895(01)00126-0.
- Massonne, H.J., 1999, A new occurrence of microdiamonds in quartzofeldspathic rocks of the Saxonian Erzgebirge Germany and their metamorphic evolution, in Gurney, J.J., et al., eds., *Proceedings of the 7th International Kimberlite Conference*: Cape Town, South Africa, Red Roof Design, p. 533–539.
- Massonne, H.J., 2003, A comparison of the evolution of diamondiferous quartz-rich rocks from the Saxonian Erzgebirge and the Kokchetav Massif: Are so-called diamondiferous gneisses magmatic rocks?: *Earth and Planetary Science Letters*, v. 216, p. 347–364, doi:10.1016/S0012-821X(03)00512-0.
- Mathez, E.A., Fogel, R.A., Hutcheon, I.D., and Marshintsev, V.K., 1995, Carbon isotopic composition and origin of Sic from kimberlites of Yakutia, Russia: *Geochimica et Cosmochimica Acta*, v. 59, p. 781–791, doi:10.1016/0016-7037(95)00002-H.
- Mendelsohn, M.J., and Milledge, H.J., 1995, Geologically significant information from routine analysis of the mid-infrared spectra of diamonds: *International Geology Review*, v. 37, p. 95–110, doi:10.1080/00206819509465395.
- Menneken, M., Nemchin, A.A., Geisler, T., Pidgeon, R.T., and Wilde, S.A., 2007, Hadean diamonds in zircon from Jack Hills, Western Australia: *Nature*, v. 448, p. 917–920, doi:10.1038/nature06083.
- Moe, K.S., Yang, J.S., Johnson, P., Xu, X.Z., and Wang, W.Y., 2017, Spectroscopic analysis of microdiamonds in ophiolitic chromitite and peridotite: *Lithosphere*, doi:10.1130/L603.1 (in press).
- Moore, M., and Lang, A.R., 1974, On the origin of the rounded dodecahedral habit of natural diamond: *Journal of Crystal Growth*, v. 26, p. 133–139, doi:10.1016/0022-0248(74)90213-9.
- Nadolinny, V.A., Shatsky, V.S., Kozmenko, O.A., Stepanov, A.S., Palyanov, Y.N., and Kupriyanov, I.N., 2006, Study of local concentration of single substitutional nitrogen atoms in microdiamonds from the Kokchetav Massif: *European Journal of Mineralogy*, v. 18, p. 739–743, doi:10.1127/0935-1221/2006/0018-0739.
- Naemura, K., Ikuta, D., Kagi, H., Otake, S., Ueda, T., Ohi, S., Kobayashi, T., Svojtka, M., and Hirajima, T., 2011, Diamond and other possible ultradeep evidence discovered in the orogenic spinel-garnet peridotite from the Moldanubian Zone of the Bohemian Massif, Czech Republic, in Dobrzhinetskaya, L.F., et al., eds., *Ultrahigh-pressure metamorphism, 25 years after the discovery of coesite and diamond*: Amsterdam, Elsevier, p. 77–111, doi:10.1016/B978-0-12-385144-4.00002-3.
- Palyanov, Y.N., Borzdov, Y.M., Kupriyanov, I.N., and Khokhryakov, A.F., 2012, Effect of H_2O on diamond crystal growth in metal-carbon systems: *Crystal Growth & Design*, v. 12, p. 5571–5578, doi:10.1021/cg301111g.
- Palyanov, Y.N., Bataleva, Y.V., Sokol, A.G., Borzdov, Y.M., Kupriyanov, I.N., Reutsky, V.N., and Sobolev, N.V., 2013, Mantle-slab interaction and redox mechanism of diamond formation: *Proceedings of the National Academy of Sciences of the United States of America*, v. 110, p. 20408–20413, doi:10.1073/pnas.1313340110.
- Pearson, D.G., Davies, G.R., and Nixon, P.H., 1995, Orogenic ultramafic rocks of UHP (diamond facies) origin: Cambridge, U.K., Cambridge University Press, p. 456–510.
- Perraki, M., Korsako, A.V., Smith, D.C., and Mposkos, E., 2009, Raman spectroscopic and microscopic criteria for the distinction of microdiamonds in ultrahigh-pressure metamorphic rocks from diamonds in sample preparation materials: *American Mineralogist*, v. 94, p. 546–556, doi:10.2138/am.2009.2973.
- Philippot, P., Busigny, V., Scambelluri, M., and Cartigny, P., 2007, Oxygen and nitrogen isotopes as tracers of fluid activities in serpentinites and metasediments during subduction: *Mineralogy and Petrology*, v. 91, p. 11–24, doi:10.1007/s00710-007-0183-7.
- Reutsky, V.N., Borzdov, Y.M., and Palyanov, Y.N., 2008a, Carbon isotope fractionation associated with HPHT crystallization of diamond: *Diamond and Related Materials*, v. 17, p. 1986–1989, doi:10.1016/j.diamond.2008.06.003.
- Reutsky, V.N., Harte, B., Eimf, B., and Palyanov, Y.N., 2008b, Monitoring diamond crystal growth, a combined experimental and SIMS study: *European Journal of Mineralogy*, v. 20, p. 365–374, doi:10.1127/0935-1221/2008/0020-1816.
- Reutsky, V.N., Borzdov, Y.M., and Palyanov, Y.N., 2012, Effect of diamond growth rate on carbon isotope fractionation in Fe-Ni-C system: *Diamond and Related Materials*, v. 21, p. 7–10, doi:10.1016/j.diamond.2011.10.001.
- Richardson, S.H., Gurney, J.J., Erlank, A.J., and Harris, J., 1984, Origin of diamonds in old enriched mantle: *Nature*, v. 310, p. 198–202, doi:10.1038/310198a0.
- Robertson, R., Fox, J.J., and Martin, A.E., 1934, Two types of diamond: *Royal Society of London Philosophical Transactions*, ser. A, v. 232, p. 463–535, doi:10.1098/rsta.1934.0013.
- Savelieva, G.N., Suslov, P.V., and Larionov, A.N., 2007, Vendian tectono-magmatic events in mantle ophiolitic complexes of the Polar Urals: U-Pb dating of zircon from chromitite: *Geotectonics*, v. 41, p. 105–113, doi:10.1134/S0016852107020021.
- Schertl, H.P., and Sobolev, N.V., 2013, The Kokchetav Massif, Kazakhstan: "Type locality" of diamond-bearing UHP metamorphic rocks: *Journal of Asian Earth Sciences*, v. 63, p. 5–38, doi:10.1016/j.jseas.2012.10.032.
- Shilobreeva, S., Martinez, I., Busigny, V., Agrinier, P., and Laverne, C., 2011, Insights into C and H storage in the altered oceanic crust: results from ODP/IODP Hole 1256D: *Geochimica et Cosmochimica Acta*, v. 75, p. 2237–2255, doi:10.1016/j.gca.2010.11.027.
- Shirey, S.B., Cartigny, P., Frost, D.J., Keshav, S., Nestola, F., Nimis, P., Pearson, D.G., Sobolev, N.V., and Walter, M.J., 2013, Diamonds and the geology of mantle carbon: *Reviews in Mineralogy and Geochemistry*, v. 75, p. 355–421, doi:10.2138/rmg.2013.75.12.
- Simakov, S.K., 2010, Metastable nanosized diamond formation from a C-H-O fluid system: *Journal of Materials Research*, v. 25, p. 2336–2340, doi:10.1557/jmr.2010.0303.
- Simakov, S.K., Dubinchuk, V.T., Novikov, M.P., and Drozdova, I.A., 2008, Formation of diamond and diamond-type phases from the carbon-bearing fluid at PT parameters corresponding to processes in the Earth's crust: *Doklady Earth Sciences*, v. 421, p. 835–837, doi:10.1134/S1028334X08050280.
- Smit, K.V., Shirey, S.B., and Wang, W.Y., 2016, Type Ib diamond formation and preservation in the West African lithospheric mantle: Re-Os age constraints from sulphide inclusions in Zimmi diamonds: *Precambrian Research*, v. 286, p. 152–166, doi:10.1016/j.precamres.2016.09.022.
- Smith, C.B., Walter, M.J., Bulanova, G.P., Mikhail, S., Burnham, A.D., Gobbo, L., and Kohn, S.C., 2016, Diamonds from Dachine, French Guiana: A unique record of early Proterozoic subduction: *Lithos*, v. 265, p. 82–95, doi:10.1016/j.lithos.2016.09.026.
- Sobolev, N.V., and Shatsky, V.S., 1990, Diamond inclusions in garnet from metamorphic rocks: A new environment for diamond formation: *Nature*, v. 343, p. 742–746, doi:10.1038/343742a0.
- Strong, H.M., and Chrenko, R.M., 1971, Further studies on diamond growth rates and physical properties of laboratory-made diamond: *Journal of Physical Chemistry*, v. 75, p. 1838–1843, doi:10.1021/j100681a014.
- Taylor, W.R., Jaques, A.L., and Ridd, M., 1990, Nitrogen-defect aggregation characteristics of some Australasian diamonds: Time-temperature constraints on the source regions of pipe and alluvial diamonds: *American Mineralogist*, v. 75, p. 1290–1310.
- Taylor, W.R., Milledge, H.J., Griffin, B.J., Nixon, P.H., Kamperman, M., and Mathey, D.P., 1995, Characteristics of microdiamonds from ultramafic massifs in Tibet: Authentic ophiolitic diamonds or contamination?: 6th International Kimberlite Conference, Extended Abstracts: United Institute of Geology, Geophysics and Mineralogy, Siberian Branch of Russian Academy of Sciences, p. 623–624.

- Taylor, W.R., Canil, D., and Milledge, H.J., 1996, Kinetics of Ib to IaA nitrogen aggregation in diamond: *Geochimica et Cosmochimica Acta*, v. 60, p. 4725–4733, doi:10.1016/S0016-7037(96)00302-X.
- Trumbull, R.B., Yang, J., Robinson, P.T., Pierro, S.D., Vennemann, T., and Wiedenbeck, M., 2009, The carbon isotope composition of natural SiC (moissanite) from the Earth's mantle: New discoveries from ophiolites: *Lithos*, v. 113, p. 612–620, doi:10.1016/j.lithos.2009.06.033.
- Valley, J., and O'Neil, J.R., 1981, $^{13}\text{C}/^{12}\text{C}$ exchange between calcite and graphite: A possible thermometer in Grenville marbles: *Geochimica et Cosmochimica Acta*, v. 45, p. 411–419, doi:10.1016/0016-7037(81)90249-0.
- Vitale, B.A., Martinez, I., Elmaleh, A., Compagnoni, R., Chaduteau, C., Ferraris, C., and Esteve, I., 2017, Massive production of abiotic methane during subduction evidenced in metamorphosed ophicarbonates from the Italian Alps: *Nature Communications*, doi:10.1038/ncomms14134.
- Woods, G.S., 1986, Platelets and the infrared absorption of type Ia diamonds: *Royal Society of London Proceedings, ser. A*, v. 407, p. 219–238, doi:10.1098/rspa.1986.0094.
- Xiong, F., Yang, J., Robinson, P.T., Xu, X., Ba, D., Yuan, L., Zhang, Z., and He, R., 2016, Diamonds and other exotic minerals recovered from peridotites of the Dangqiong Ophiolite, western Yarlung-Zangbo suture zone, Tibet: *Acta Geologica Sinica*, v. 90, p. 425–439, doi:10.1111/1755-6724.12681.
- Xu, S., Okay, A.I., Ji, S., Sengor, A.M.C., Wen, S., Liu, Y., and Jiang, L., 1992, Diamond from the Dabie Shan metamorphic rocks and its implication for tectonic setting: *Science*, v. 256, p. 80–82, doi:10.1126/science.256.5053.80.
- Xu, X., Yang, J., Chen, S., Fang, Q., Bai, W., and Ba, D., 2009, An unusual mantle mineral group from chromitite orebody Cr-11 in the Luobusa ophiolite of the Yarlung-Zangbo suture zone, Tibet: *Journal of Earth Science*, v. 20, p. 284–302, doi:10.1007/s12583-009-0026-z.
- Xu, X., Yang, J., Robinson, P.T., Xiong, F., Ba, D., and Guo, G., 2015, Origin of ultrahigh pressure and highly reduced minerals in podiform, chromitites and associated mantle peridotites of the Luobusa ophiolite, Tibet: *Gondwana Research*, v. 27, p. 686–700, doi:10.1016/j.gr.2014.05.010.
- Yang, J., Dobrzynetskaia, L., Bai, W., Fang, Q., Robinson, P.T., Zhang, J., and Green, H.W., II, 2007, Diamond- and coesite-bearing chromitites from the Luobusa ophiolite, Tibet: *Geology*, v. 35, p. 875–878, doi:10.1130/G23766A.1.
- Yang, J., Robinson, P.T., and Dilek, Y., 2014a, Diamonds in ophiolites: A little-known diamond occurrence: *Elements*, v. 10, p. 127–130, doi:10.2113/gselements.10.2.127.
- Yang, J., Xu, X., Bai, W., Zhang, Z., and He, R., 2014b, Features of diamond in ophiolite: *Yanshi Xuebao*, v. 30, p. 2113–2124 (in Chinese with English abstract).
- Yang, J., Meng, F., Xu, X., Robinson, P.T., Dilek, Y., Makeyev, A.B., Wirth, R., Wiedenbeck, M., Griffin, W.L., and Cliff, J., 2015, Diamonds, native elements and metal alloys from chromitites of the Ray-Iz ophiolite of the Polar Urals: *Gondwana Research*, v. 27, p. 459–485, doi:10.1016/j.gr.2014.07.004.
- Zhang, H., Ba, D., Guo, T., Mo, X., Xue, J., Ruan, G., and Wang, Z., 1996, Study of Luobusa typical chromite ore deposit Qusong County, Tibet (Lhasa): Tibet, China, Xizang Peoples Press, 181 p. (in Chinese).
- Zhou, M., Robinson, P.T., Malpas, J., and Li, Z., 1996, Podiform chromitites in the Luobusa ophiolite (southern Tibet): Implications for melt-rock interaction and chromite segregation in the upper mantle: *Journal of Petrology*, v. 37, p. 3–21, doi:10.1093/ptrology/37.1.3.

MANUSCRIPT RECEIVED 8 OCTOBER 2016

REVISED MANUSCRIPT RECEIVED 7 APRIL 2017

MANUSCRIPT ACCEPTED 15 JUNE 2017