Pergamon

PII S0016-7037(98)00266-X

Evidence of fluid inclusions in metamorphic microdiamonds from the Kokchetav massif, northern Kazakhstan

K. De Corte,*[1,2] P. Cartigny,[3] V. S. Shatsky,[4] N. V. Sobolev,[4] and M. Javoy[3]

[1]Department of Geology and Soil Science, University of Ghent, Krijgslaan 281 S8, B-9000 Ghent, Belgium
[2]Department of Geology and Mineralogy, Royal Museum for Central Africa, Leuvensesteenweg 13, B-3080 Tervuren, Belgium
[3]Laboratoire de Géochimie des Isotopes Stables, Université de Paris 7 et Institut de Physique du Globe,
Place Jussieu 2, F-75251 Paris Cedex 05, France
[4]Institute of Mineralogy and Petrography, Novosibirsk 630090, Russia

Abstract—Microdiamonds from garnet clinopyroxenites of the Kokchetav massif (northern Kazakhstan) and associated alluvial diamonds have been investigated using infrared spectroscopy. All diamonds have high nitrogen contents (from 747 up to 4488 ± 20% at. ppm) and are of type Ib-IaA. Nitrogen data are consistent with a diamond formation over a narrow temperature range. Microdiamonds from garnet clinopyroxenites are characterized by water and carbonate inclusions, similar to those occurring in fibrous coated diamonds from kimberlite, which suggest that diamonds grew from a C-H-O fluid. In contrast, alluvial microdiamonds do not contain any carbonate inclusions and H_2O is absent or present in only minor amounts. Alluvial diamonds are considerably more N-rich but have a similar range of nitrogen aggregation states. It is suggested that alluvial diamonds belong to a separate diamond population compared with the microdiamonds from garnet clinopyroxenites.

The Kokchetav microdiamonds are distinct from kimberlitic fibrous diamonds in that they contain abundant Ib centres, have high nitrogen contents and show different populations depending on host rock type. These characteristics support a metamorphic origin for the microdiamonds from the UHPM rocks of the Kokchetav massif. *Copyright © 1998 Elsevier Science Ltd*

1. INTRODUCTION

In 1990 microdiamonds (<1 mm) were discovered in situ in ultra-high pressure metamorphic (UHPM) rocks from the Kokchetav massif, northern Kazakhstan (Sobolev and Shatsky, 1990). It was suggested that the UHPM environment represents a new geological context for diamond formation. However, although considerable research on the matter was carried out during the last decade, a consensus about the formation of the Kokchetav diamonds has not yet been reached. Three fundamentally different models have been formulated.

1. The pre-metamorphic relict model suggests that diamonds are of kimberlitic origin (Marakushev et al., 1995). Diamonds of mantle origin were deposited in crustal sediments which later were metamorphosed.
2. The metastable growth model states that diamonds grew metastably below the diamond equilibrium pressure during a metamorphic event (Dobrzhinetskaya et al., 1994).
3. The UHPM model contends that diamonds grew stably within the equilibrium stability field during a metamorphic event (Sobolev and Shatsky, 1990).

To assess each of these models, the Kokchetav diamonds have been studied by infrared absorption spectroscopy. Fourier transform infrared spectroscopy (FTIR) is of special interest since, in a nondestructive way, it provides information on the nature of volatile and substitutional impurities (e.g., Chrenko et al., 1967; Navon et al., 1988), in particular nitrogen (see Harris,

1992, for review). Nitrogen is the most important lattice impurity in diamond (Kaiser and Bond, 1959). Diamonds may be classified either as type I, containing more than ~20 ppm of substitutional nitrogen (the detection limit of FTIR), or as type II (essentially nitrogen free). On the basis of the dominant nitrogen defect centre present, type I diamonds are subdivided into three major types: Ib (single nitrogen atoms substitution for carbon atoms), IaA (nitrogen pairs) and IaB (probably four nitrogen atoms plus a vacancy) (see Davies, 1976; Chrenko et al., 1977; Evans and Qi, 1982; Woods, 1986; Jones et al., 1992). Natural diamonds may be of mixed type Ib-IaA or type IaA-IaB affinity. It is generally accepted that diamonds incorporate nitrogen as a 1:1 substitution for carbon (type Ib) and that single nitrogen atoms tend to aggregate by a second order kinetic process to form IaA and IaB type diamonds. In accordance with standard theory, once the nitrogen is incorporated into the diamond lattice, its degree of aggregation (the nitrogen aggregation state) depends mainly on the initial nitrogen content, the prevailing temperature (T) during aggregation and the time (t) spent at this temperature (Chrenko et al., 1977; Evans and Qi, 1982; Taylor et al., 1996). Consequently, peak temperatures, residence times, and exhumation rates can theoretically be constrained by using the nitrogen aggregation state in diamond.

Prior to this investigation, FTIR spectroscopy was conducted on four large crystals (up to 500 μm) from alluvial deposits associated with the Kokchetav massif (Finnie et al., 1994; Dobrzhinetskaya et al., 1995; Taylor et al., 1996). The present study includes, for the first time, infrared absorption spectra of in situ microdiamonds from two garnet clinopyroxenites (sample K76-94 and sample 2-4) of the Kumdy-Kol deposit. For

---

*Author to whom correspondence should be addressed (kdecorte @africamuseum.be).

Kumdy-Kol, recognized as the type locality of microdiamonds in UHPM rocks of the Kokchetav massif, in situ diamonds have been described in several rocks, including garnet-pyroxene dolomitic rocks, garnet clinopyroxenites, garnet-biotite gneisses, and schists (Sobolev and Shatsky, 1990), as well as in cataclastic garnet-pyroxene-quartz and garnet-biotite-quartz rocks. Diamonds are distributed heterogeneously within these rocks where their size varies from 2 up to 400 μm (average size 15 μm). Diamond crystals occur as inclusions in zircon, garnet, clinopyroxene, secondary mineral aggregates replacing garnet and clinopyroxene (Sobolev and Shatsky, 1990; Shatsky et al., 1995), as well as in kyanite, biotite, and rarely in secondary quartz inclusions. The age of metamorphism is dated at 535 Ma (Claoué-Long et al., 1991). For comparison, thirteen alluvial diamonds (200–380 μm) from the northern part of the Kokchetav massif were also examined in this study. They are derived from Tertiary sands located ca. 200 km north of Kumdy-Kol and were taken from the same locality as those studied by Finnie et al. (1994). Reconstruction of drainage patterns indicates that these sands originate from rocks of the Kokchetav massif.

SAMPLES AND METHODS

Nine of the largest diamond crystals from the garnet clinopyroxenite sample K76-94 and nine large microdiamonds from the garnet clinopyroxenite 2–4 were selected after isolating diamonds of ca. 200 g rock by thermochemical extraction. All crystals are yellow, translucent cuboids with a complex surface morphology. The size of the investigated crystals ranges from 80 to 139 μm (Table 1). The size of the sixteen analysed alluvial diamonds, possessing a cubo-octahedral morphology, is significantly larger and varies from 200 to 380 μm (Table 2). All crystals were cleaned with conc. H_2SO_4 and H_2O. Shortly before the analysis they were put in a muffle-furnace at 600°C for a final cleaning.

Nitrogen contents and aggregation states were determined by transmission IR spectroscopy at the Laboratoire de Géochimie des Isotopes Stables, Paris, using an IR-Plan microscope (Spectratech) equipped with a MCTA detector. The microscope was coupled with a Nicolet 550 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 a ca. 1 mm thick BaF_2 plate and the best results were obtained using 1400 scans of crystals of <200 μm and 300 scans of larger samples. The use of BaF_2 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 by masking with variable apertures. To examine the homogeneity of the diamonds, at least two spectra at different depths of focus for each crystal were collected, where possible, on different faces.

The measured spectra were baseline corrected and normalized to a constant pathlength of 1 mm. The absorption at 1995 cm^{-1} was set to 1.194 (Fischer, pers. commun., 1995). Nitrogen abundances and aggregation states were estimated by deconvolution the IR spectra in the 1400–1000 cm^{-1} region using a 120 point least square regression fit and the IR absorption coefficients of 250 atomic ppm/mm for Ib nitrogen and 160 atomic ppm/mm for IaA nitrogen (Kiflawi et al., 1994; Boyd et al., 1994). Notwithstanding the rather small size of the investigated diamonds, a precision of 20% for the total nitrogen content and between 5 to 18% for the degree of nitrogen aggregation was achieved (Tables 1 and 2).

3. RESULTS

All of the sampled diamonds from garnet clinopyroxenites and alluvial diamonds show absorption bands due to nitrogen, and the nitrogen data are listed in Tables 1 and 2. The aggre-

gation state is invariably low. Mixed type Ib-IaA spectra are indicated by IR absorption bands at 1132 cm^{-1} and 1282 cm^{-1} with a weaker band at 1200 cm^{-1}. No further aggregation of nitrogen IaB has been observed and there is no development of platelets as indicated by the absence of a platelet peak at ~1370 cm^{-1}. For the in situ microdiamond sample set, the aggregation state varies from 48 (+5) to 72 (±8)% of IaA centers, and from 36 (+5) up to 82 (+15)% for alluvial diamonds. Nitrogen aggregation states for the two diamond types are similar although alluvial diamonds display the lowest values (Fig. 1). Significant differences in aggregation state between different diamonds of one sample set and even within a single sample have been demonstrated. Zonation in nitrogen content and variation in aggregation state within single diamonds were determined by varying focussing depth during individual analyses. The nitrogen content of diamonds from garnet clinopyroxenites varies from 747 to 2370 (±20%) at. ppm nitrogen (Table 1). As shown by Fig. 1 and Table 2, alluvial diamonds display higher nitrogen abundances (1416–4488 ± 20% at. ppm nitrogen). One diamond (JH01-3) studied by Finnie et al. (1994) demonstrates a nitrogen content of 1218–1198 at. ppm., outside the field determined for alluvial diamonds in the present investigation. In comparison, other diamonds occupy the same range as alluvial diamonds, but towards lower values (Finnie et al., 1994; Dobrzhinetskaya et al., 1995). Nitrogen abundances and aggregation states vary within single crystals in some cases in a nonsympathetic manner with respect to the expected aggregation kinetics (e.g., in Fig. 1 the aggregation state remains the same for different nitrogen contents). Over the sample set there is no correlation between diamond nitrogen aggregation state and nitrogen content (Fig.1).

Infrared spectra of diamonds from garnet clinopyroxenites also exhibit absorption bands characteristic of impurities other than nitrogen (Fig. 2). The small peak at 3107 cm^{-1} (and the associated 1405 cm^{-1} line) is due to hydrogen occurring in the diamond matrix (Woods and Collins, 1983). The band at 1430 cm^{-1} is one of the two characteristic carbonate bands (the other absorption at 876 cm^{-1} lies too close to the lower spectral limit to be easily detected), and the strong bands at 1630 and 3420 cm^{-1} are the result of H-O-H bonding and O-H stretching, respectively (Chrenko et al., 1967; Navon et al., 1988). The absence of sharp narrow peaks near 3600 cm^{-1} (typical of hydroxyl groups), the relative height of the H-O-H band, and the good correlation between the intensities of the OH and H_2O-bands, suggest that water is present as H_2O molecules (see also Chrenko et al., 1967, and Navon et al., 1988). So far, no molecular CO_2 peaks (at 2350 cm^{-1}) nor distinct silicate peaks (1000 and 1100 cm^{-1}) (Navon et al., 1988; Navon, 1991; Schrauder and Navon, 1994) have been detected. All investigated in situ microdiamonds exhibit similar absorption bands in the inclusion-bearing zones between 4000 and 1000 cm^{-1}; however, as shown by Fig.5, variations in intensity between carbonate, water, and nitrogen absorptions from one sample to another occur.

None of the analysed alluvial diamonds display clear absorption bands due to carbonates or O-H (Fig. 3). Neither the 1374 nor the 1353 cm^{-1} absorption bands were found, a result contrasting with that of Finnie et al. (1994). Their significantly less noisy spectra (related to their bigger size) exhibit however, next to nitrogen bands, clear absorption bands in the wavenum-

Table 1. Experimental data of diamonds from garnet clinopyroxenites

Sample	Size (μm)	Analysis	Type	N_{tot} (at. ppm)	% IaA formed	Error on % IaA
			Microdiamonds from garnet clinopyroxenites			
K76-94/3	139	3t1	Ib-IaA	Nd	Nd	—
		3t2	Ib-IaA	Nd	Nd	—
		3t3	Ib-IaA	Nd	Nd	—
K76-94/5	90	5m1	Ib-IaA	1165	63	10
		5m2	Ib-IaA	1387	68	10
		5m3	Ib-IaA	1239	69	10
K76-94/6	85	6t1	Ib-IaA	Nd	Nd	—
		6t2	Ib-IaA	Nd	Nd	—
K76-94/7	90	7t1bis	Ib-IaA	966	59	15
		7t3bis	Ib-IaA	1101	56	10
K76-94/8	80	8t1	Ib-IaA	1465	60	5
		8t2	Ib-IaA	1070	66	10
		8t3	Ib-IaA	2084	54	7
K76-94/9	(fragment) 104	9t1	Ib-IaA	Nd	Nd	—
		9t3	Ib-IaA	Nd	Nd	—
K76-94/10	96	10m1	Ib-IaA	831	72	8
		10m2	Ib-IaA	1395	48	5
		10m4	Ib-IaA	1009	59	8
		10m5	Ib-IaA	747	49	8
K76-94/11	90	11t1	Ib-IaA	1921	74	15
		11t3	Ib-IaA	2189	74	15
K76-94/12	(fragment) 120	12t1	Ib-IaA	Nd	Nd	—
		12t2	Ib-IaA	Nd	Nd	—
		12t4	Ib-IaA	Nd	Nd	—
2-4/1	85	1m2	Ib-IaA	2370	59	6
		1m3	Ib-IaA	1684	68	15
2-4/2*	110	2m1	Ib-IaA	1379	63	10
		2m2	Ib-IaA	1108	62	10
2-4/3	105	3t1	Ib-IaA	1240	61	10
		3t2	Ib-IaA	1306	61	10
2-4/4	90	4t1	Ib-IaA	1303	62	10
		4t2	Ib-IaA	1366	61	10
		4t3	Ib-IaA	1602	59	7
2-4/5	94	5t1	Ib-IaA	1011	70	18
		5t2	Ib-IaA	1253	61	10
2-4/6	96	6t1	Ib-IaA	1380	54	5
		6t2	Ib-IaA	1315	58	8
		6t3	Ib-IaA	1303	60	7
		6t4	Ib-IaA	1192	67	12
2-4/7	104	7t1	Ib-IaA	1302	63	12
		7t2	Ib-IaA	896	65	12
2-4/8	125	8t1	Ib-IaA	1084	60	10
		8t2	Ib-IaA	1096	57	10
		8t3	Ib-IaA	898	69	15
2-4/9	110	9t1	Ib-IaA	1962	59	5
		9t2	Ib-IaA	1986	62	5

Nd: not detectable; *: 2 intergrown cuboid crystals (75 and 69 μm)

ber range 3400 cm^{-1} to 2750 cm^{-1} due to hydrogen complexes (Woods and Collins, 1983). Four analysed alluvial diamonds show a weak absorption at 1630 cm^{-1} caused by molecular H_2O.

4. DISCUSSION

4.1. Crystallization from a C-O-H bearing Fluid

The presence of nitrogen, carbonate, and water within microdiamonds from garnet clinopyroxenites suggest a volatile C-O-H enriched phase was trapped during diamond precipitation. The importance of "fluids" for the Kokchetav diamonds was already highlighted by Shatsky et al. (1989), who argue for changing growth conditions in order to explain the different diamond morphologies. Subsequent X-ray topography work on cuboid microdiamonds from the same garnet clinopyroxenites and on alluvial diamonds (Martovitskiy et al., 1987; Shatsky et al., 1998a) supported this statement and revealed the presence of a core surrounded by a polycrystalline zone of fibres (Fig. 4). Fibrous textures represent rapid growth and they are characterized by abundant micro-inclusions (Kamiya and Lang, 1965; Moore and Lang, 1972; Navon et al., 1988). The bulk of nitrogen content and inclusions is therefore believed to reside in the fibrous texture of the diamonds.

The present FTIR data give a direct proof of diamond formation from a fluid and extend diamond genesis from a fluid

Table 2. Experimental data of alluvial diamonds

			Alluvial diamonds			
Sample	Size (μm)	Analysis	Type	N_{tot} (ppm)	% IaA formed	Error on % IaA
T-86-1	248	T-86-1m1	Ib-IaA	1910	62	15
		T-86-1m2	Ib-IaA	1706	77	15
T-86-2	320	T-86-2m1	Ib-IaA	2275	65	15
		T-86-2m2	Ib-IaA	1842	62	15
T-86-3	272	T-86-3m2	Ib-IaA	2385	78	15
		T-86-3m3	Ib-IaA	2209	60	15
T-86-4	310	T-86-4t2	Ib-IaA	2325	45	5
		T-86-4t3	Ib-IaA	2023	53	5
T-86-5	290	T-86-5t1	Ib-IaA	2311	58	5
		T-86-5t2	Ib-IaA	2856	59	5
		T-86-5t3	Ib-IaA	2494	64	5
		T-86-5t4	Ib-IaA	3043	60	5
T-86-6	200	T-86-6t1	Ib-IaA	2103	47	5
		T-86-6t2	Ib-IaA	2427	48	5
		T-86-6t3	Ib-IaA	2078	45	5
T-86-7	380	T-86-7t2	Ib-IaA	1642	38	5
		T-86-7t3	Ib-IaA	1727	48	5
		T-86-7t4	Ib-IaA	2554	44	5
		T-86-7t5	Ib-IaA	1992	44	5
		T-86-7t6	Ib-IaA	1994	41	5
T-86-8	225	T-86-8t1B	Ib-IaA	4351	82	15
		T-86-8t2	Ib-IaA	3217	74	5
		T-86-8t3	Ib-IaA	2420	76	15
		T-86-8t4	Ib-IaA	3076	70	15
		T-86-8t5	Ib-IaA	2123	59	10
T-86-9	165	T-86-9t1	Ib-IaA	3310	57	10
		T-86-9t2	Ib-IaA	3039	68	12
T-86-10	210	T-86-10t1	Ib-IaA	2141	68	10
		T-86-10t2	Ib-IaA	2155	59	10
		T-86-10t3	Ib-IaA	2364	64	10
T-86-11	200	T-86-11t1	Ib-IaA	2665	57	5
		T-86-11t2	Ib-IaA	2522	58	5
		T-86-11t3	Ib-IaA	2419	54	5
		T-86-11t4	Ib-IaA	2322	56	5
T-86-12	245	T-86-12t1	Ib-IaA	2260	51	5
		T-86-12t2	Ib-IaA	1416	50	10
		T-86-12t4	Ib-IaA	1796	45	5
T-86-13	245	T-86-13t3	Ib-IaA	1824	55	10
		T-86-13t4	Ib-IaA	2218	49	5
T-86-14	280	T-86-14t1	Ib-IaA	2310	39	5
		T-86-14t2	Ib-IaA	2434	36	5
T-86-15	255	T-86-15t1	Ib-IaA	4488	68	8
		T-86-15t2	Ib-IaA	3753	74	9
		T-86-15t3	Ib-IaA	3269	71	10
T-86-16	200	T-86-16t1	Ib-IaA	2886	54	5
		T-86-16t2	Ib-IaA	2214	61	5
		T-86-16t3	Ib-IaA	2159	59	5
		T-86-16t4	Ib-IaA	2729	70	7

phase, as reported for fibrous (Navon et al., 1988; Schrauder et al., 1994) and octahedrally shaped diamonds of kimberlites (e.g., Harrison and Tolansky, 1964; Galimov, 1991; Bulanova, 1995; Cartigny et al., 1997) to microdiamonds from UHPM rocks from the Kokchetav massif.

The presence of water and especially carbonate inclusions can be explained by two ways.

1. Daughter phases of the trapped fluids. Fluids were initially homogeneous in composition, but during cooling by the uplift to the surface, they crystallized in a closed system.
2. Initially present as mineral grains. Carbonates were already

present in a solid state before being trapped by the growing diamond.

In the latter case the carbonates may induce fibrous growth, following the model of Kamiya and Lang (1965) and Moore and Lang (1972). These authors indeed state that particles adhering to the surface of the seeds inhibit continuous facetted growth when the new diamond growth proceeds, and this leads to series of independently nucleated fibres. Since no solid inclusions such as silicates have been identified, carbon must be present as carbonate grains for this model. To assess if carbonates crystallized before or after trapping, additional information is however required.
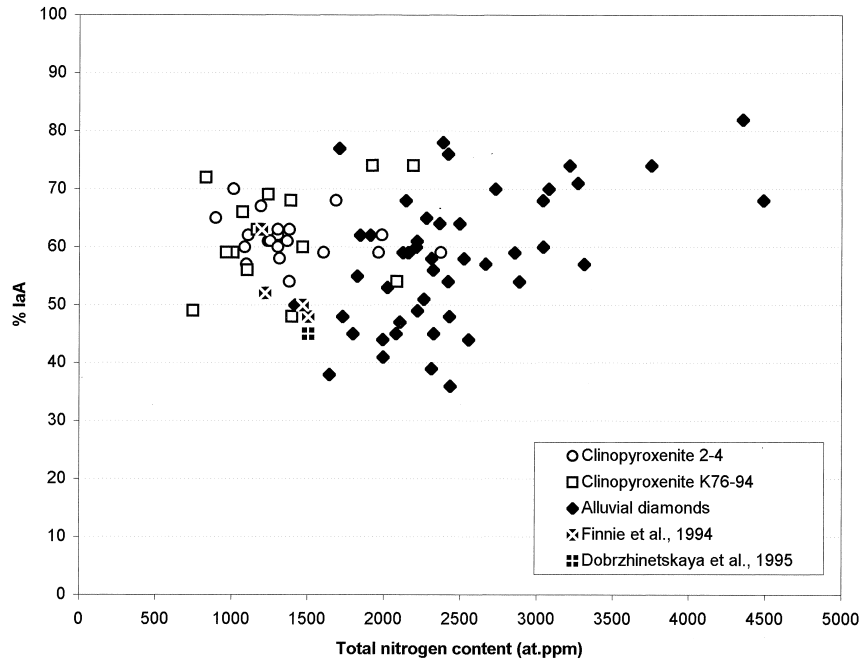
Fig. 1. The nitrogen abundances and aggregation states of diamonds from garnet clinopyroxenites K76-94 and 2-4 and of alluvial diamonds (Tables 1 and 2) are shown in addition to the data given by Finnie et al. (1994) and Dobrzhinetskaya et al. (1995).

4.2. Hydrous Fluids and/or Carbonatitic Melts?

A fundamental goal is now to characterize the composition of the C-O-H fluid. The available data of the diamonds from the

Kokchetav massif make it difficult to discuss the composition of the fluid phase from which the diamonds grew in any great detail unless further information is obtained. The present study provides however the following constraints.
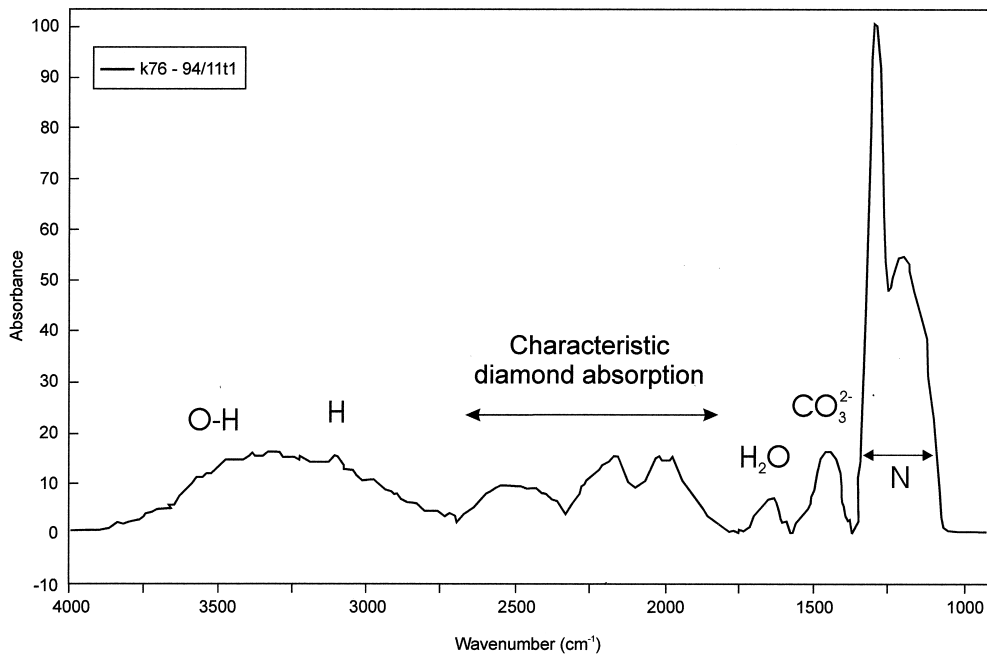
Fig. 2. Infrared absorption spectra of diamond sample K76-94/11 (analysis 11t1) from garnet clinopyroxenite K76-94.
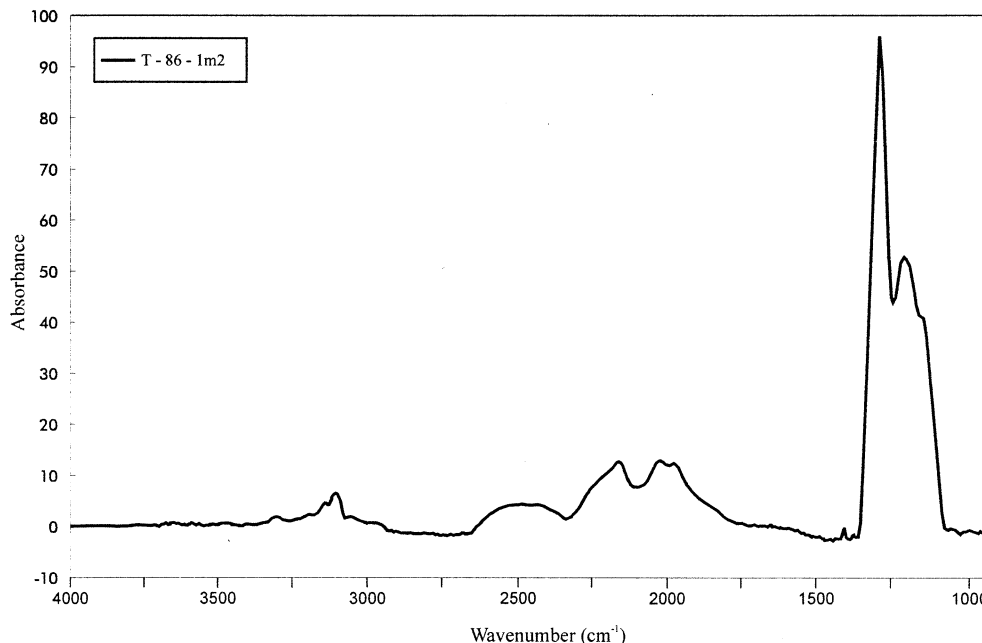
Fig. 3. Infrared absorption spectra obtained for alluvial diamond T-86-1 (analysis T-86-1m2) from the northern part of the Kokchetav massif.

Only oxidized species (carbonate-water) were recorded in microdiamonds from garnet pyroxenites of the Kokchetav massif, indicating relatively high oxygen fugacities of the diamond-forming medium. CH_4 and other reduced species are therefore not probable as dominating phases of the volatile assemblage.

Microdiamonds from garnet clinopyroxenites and kimberlitic fibrous diamonds contrast in size, aggregation state, and

Fig. 4.X-ray topography study of alluvial diamond OP-1 (size 100 m) shows the presence of a core surrounded by a fibrous texture (Photo by Rylov GM). Detailed investigations of the internal structure of diamond crystals have been published by Shatsky et al. (1998a).

geological setting, but they possess a similar internal morphology and inclusion content (Fig. 5) although neither silicates nor clear CO_2 peaks have yet been observed in diamonds from the first group (Chrenko et al., 1967; Navon et al., 1988; Navon, 1991; Boyd et al., 1992; Schrauder and Navon, 1994; Schrauder et al., 1994; this study). Based on the study of major and trace elements in fibrous kimberlitic diamonds, Schrauder and Navon (1994) and Schrauder et al. (1994) recognized the presence of hydrous and carbonatitic fluids in fibrous kimberlitic diamonds. The fluid compositions vary between these two endmembers. As a rule diamonds crystallized from a more carbonatite-rich medium bear low silicate contents, in contrast to those formed from more hydrous fluids. Extending these data to the diamonds of the Kokchetav massif, the absence of silicate absorptions and the strong carbonate absorptions in the diamonds from garnet clinopyroxenites would suggest the diamond-forming fluid to be more carbonatite like. In the case of the alluvial diamonds (without carbonate inclusions), a more important hydrous component of the fluid should perhaps be favoured.
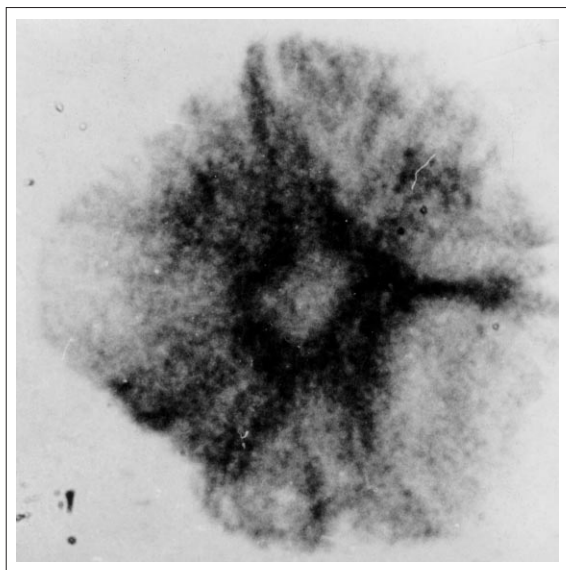
4.3. T-t Paths

Because the relative concentrations of nitrogen in A centres is temperature (T) sensitive, the thermal history of a diamond can be deduced, if the residence time (t) and the activation energy for the transition of C to A centres is known (see section 1). Finnie et al. (1994) use the value of 4.4 eV for octahedral growth sectors, while Taylor et al. (1996) suggest the higher value of 6.0 eV is more appropriate for cube sectors. In the present study we started to calculate the aggregation temperatures (Fig. 6) for both values assuming a geological reasonable residence time of 5 Ma. It can be deduced from Fig. 6 that
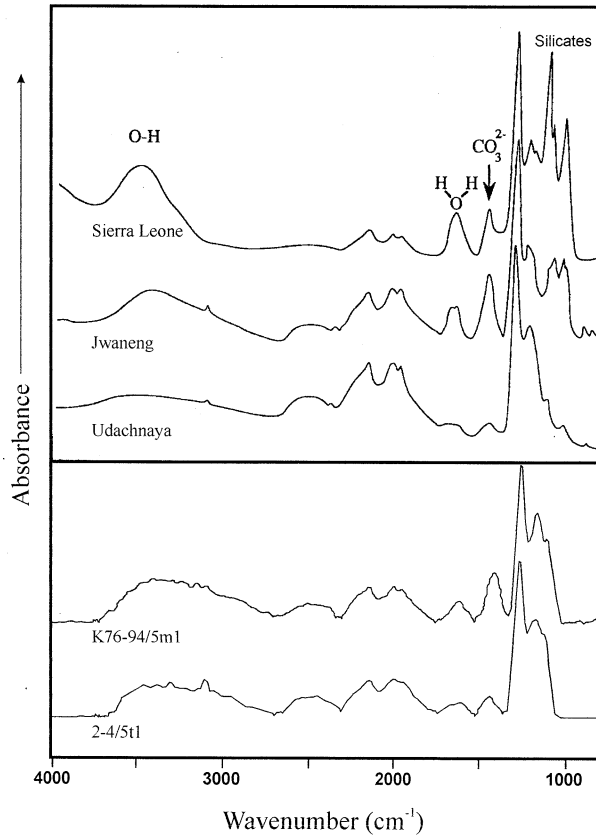
Fig. 5. Infrared absorption spectra of coats from Sierra Leone, Jwaneng, and Udachnaya (Boyd et al., 1992) and in situ diamonds from the Kokchetav massif.

resulted in an enhanced rate of aggregation and high concentrations of A centres. (2) Inclusions. Particular impurity element (concentrated in certain growth zones) could cause retardation or enhancement of the aggregation process in natural stones. (3) Growth layers of type II diamond. Probably related to very rapid changes in nitrogen concentration in the fluid reservoir from which the diamonds grew.

Kesson and Ringwood (1989) and Sobolev (1991) both suggest that A centres may be incorporated directly into the diamond lattice from N_2 which has been shown by Deines et al. (1989) to be an important species in oxidised fluids. W. R. Taylor (pers. commun., 1998), however, point out that this is not likely, for the following reason: the two nitrogen atoms in A centre are each bonded to three carbon atoms and only happen to be opposite one another as this eliminates the need to have a dangling bond on an adjacent carbon atom. To directly produce an A centre, an input of energy will be required to break the N=N bond of the N_2 present in the fluid.

4.4. The Metamorphic Origin Hypothesis

This study reveals differences between diamonds from garnet clinopyroxenites and alluvial diamonds. One may question from which rocks alluvial diamonds originate. Indeed, in contrast to diamonds from garnet clinopyroxenites, alluvial diamonds do not contain any carbonate inclusions and no or only minor amounts of H_2O. Moreover, their nitrogen contents plot at higher values and their aggregation state may be as low as 36% IaA. It is, however, clear that alluvial diamonds are derived from UHPM rocks of the Kokchetav massif. On one hand because of reconstruction of drainage pattern and on the other hand because of a nitrogen aggregation state which is similar to diamonds from garnet clinopyroxenites. Calculation of aggregation temperatures indicate similar thermal regimes for all investigated diamonds. Two hypotheses, or a combination of both, can be advanced to explain the differences: (1) Only diamonds from garnet clinopyroxenites without inclusions survived erosion and transportation. Diamonds containing carbonate inclusions and higher H_2O quantities would, by their more fragile character, have been broken or lost. (2) Alluvial diamonds and diamonds from garnet clinopyroxenite derived from two distinct rock types.

For several reasons hypothesis 2 is more likely. No diamond from garnet clinopyroxenite was found to be of the "alluvial type" and the morphology of the investigated alluvial diamonds does not correspond to the characteristic cuboid morphology of diamonds from garnet clinopyroxenites.

Accordingly, on the basis of the nitrogen characteristics and the inclusion content, at least two diamond populations may exist, probably linked to the host rock. If a relationship between diamond features and a rock type was established, the premetamorphic relict model for the microdiamond origin can be rejected. Moreover, the premetamorphic relict model contrasts with the overall preservation of isolated nitrogen centres (type Ib diamonds) in the Kokchetav diamonds (Finnie et al., 1994, Dobrzhinetskaya et al., 1995; Taylor et al., 1996; this study). Kimberlitic diamonds are very rarely of type Ib and rather exhibit high nitrogen aggregation states (e.g., Javoy et al., 1984; Deines et al., 1997; Cartigny et al., 1997, and references therein). As a rule fibrous kimberlitic diamonds are of type IaA.

whatever is the activation energy used, a narrow range (+50°C) of temperatures is obtained, suggesting a stable thermal regime during diamond formation. The 4.4 eV value gives however unrealistic temperatures for the residence time taken: indeed aggregation of nitrogen below 750°C is never reported. The activation energy of 6.0 eV is in concert with results from X-ray-topography; cubic growth sectors indeed dominate in the diamonds from the Kokchetav massif (Shatsky et al., 1998b).

Following a second order kinetic reaction for the transition of Ib to IaA, one may expect a correlation between the nitrogen abundance and aggregation state over the sample set and within a single diamond. In the present study we, however, have shown nonsympathetic variations of nitrogen content and aggregation state within individual microdiamonds, and also an absence of correlation between the nitrogen abundance and aggregation state over the sample set (Fig. 1). Estimations of aggregation temperature based on the nitrogen aggregation make sense and point to diamond formation over a narrow range of time-temperature. There can be advanced three main reasons to explain the absence of correlation between the nitrogen content and the aggregation state: (1) Growth rate. For synthetic diamonds it has been documented that the growth process can be responsible for differences in aggregation state and nitrogen content. Kanda and Yamaoka (1993) suggested that fluctuations in growth rate led to the incorporation of excess defects in zones of rapid growth which subsequently
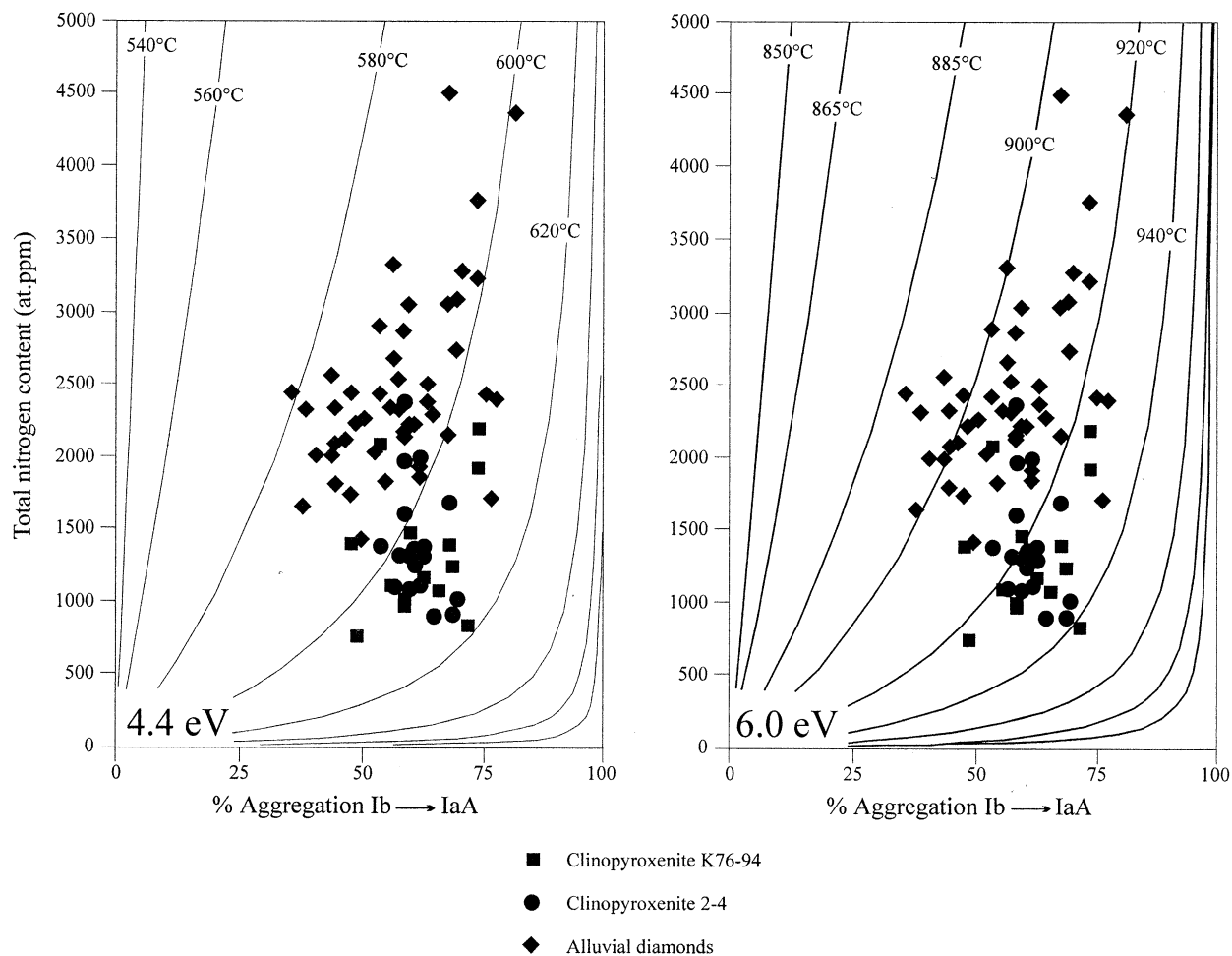
Fig. 6. Aggregation temperatures for an assumed residence time of 5 Ma. (a) activation energy = 4.4 eV, (b) activation energy = 6.0 eV.

For the reasons mentioned above, we favour the metamorphic origin for microdiamonds of the Kokchetav massif. FTIR data do not permit exclusion of the metastable or stable hypothesis, but, in addition to diamonds, the presence of coesite, high K content in clinopyroxene, high Al in sphene, high Si phengites, and grossular-pyrope garnets demonstrated UHP conditions. Equilibrium relations mark pressures above 40 kbar and minimum temperatures of 900°C (Sobolev and Shatsky, 1990; Shatsky et al., 1995). These P-T conditions fall within the stability field of diamond.

5. CONCLUSION

Microdiamonds of the Kokchetav massif are unique in that they have trapped relatively high concentrations of the medium from which it grew. The presence of water and carbonate inclusions in diamonds from garnet clinopyroxenites suggest they were formed from a C-O-H bearing fluid, consistent with their fibrous texture. The oxidized species make a hydrous/carbonatite- fluid the most probable.

Alluvial diamonds from the northern part of the Kokchetav massif do not contain carbonate inclusions, show less or no

H_2O absorption, and generally exhibit higher nitrogen contents compared to diamonds from clinopyroxenites. It is likely that alluvial diamonds derive from another host rock than clinopyroxenites, favouring the existence of different diamond populations.

Diamonds from clinopyroxenites and alluvial diamonds are all nitrogen-rich and of type Ib-IaA. Nitrogen data indicate diamond formation occurred in a narrow range of temperature, suggesting a stable thermal regime during diamond formation.

REFERENCES

Boyd S. R., Pillinger C. T., Milledge H. J., and Seal M. J. (1992) C and N isotopic composition and the infrared absorption spectra of coated diamonds: Evidence for the regional uniformity of CO_2-H_2O rich fluids in the lithospheric mantle. *Earth Planet. Sci. Lett.* **108,** 139–150.

Boyd S. R., Kiflawi I., and Woods G.S . (1994) The relationship between infrared absorption and the A defect concentration in diamond. *Phil. Mag. B.* **69,** 1149–1153.

Bulanova G. P. (1995) The formation of diamond. *J. Geochem. Expl.* **53,** 1–23.

Cartigny P., Boyd S. R., Harris J. W., and Javoy M. (1997) Diamonds and the isotopic composition of mantle nitrogen. *Terra Nova* **9,** 175–179.

Chrenko R. M., McDonald R. S., and Darrow K. A. (1967) Infra-red spectra of diamond coat. *Nature* **4,** 474–476.

Chrenko R. M., Tuft R. E., and Strong H. M. (1977) Transformation of the state of nitrogen in diamond. *Nature* **270,** 141–144.

Claoué-Long J. C., Sobolev N. V., Shatsky V. S., and Sobolev A. V. (1991) Zircon response to diamond-pressure metamorphism in the Kokchetav massif, USSR. *Geology* **19,** 710–713.

Davies G. (1976) The A nitrogen aggregate in diamond-its symmetry and possible structure. *J. Phys. C, Solid State Phys.* **9,** L537–542.

Deines P., Harris J. W., Spear P. M., and Gurney J. J. (1989) Nitrogen and ^{13}C content of Finsch and Premier diamonds and their implications. *Geochim. Cosmochim. Acta* **53,** 1367–1378.

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. *Geochim. Cosmochim. Acta* **61,** 3993–4005.

Dobrzhinetskaya L. F., Braun T. V., Sheshkel G. G., and Podkuiko Y. A. (1994) Geology and structure of diamond-bearing rocks of the Kokchetav massif (Kazakhstan). *Tectonophysics* **233,** 293–313.

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* **23,** 597–600.

Evans T. and Qi Z. (1982) The kinetics of the aggregation of nitrogen atoms in diamond. *Proc. Royal Soc. London* **A381,** 159–178.

Finnie K. S., Fisher D., Griffin W.L ., Harris J. W., and Sobolev N. V. (1994) Nitrogen aggregation in metamorphic diamonds from Kazakhstan. *Geochim. Cosmochim. Acta* **58,** 5173–5177.

Galimov E. M. (1991) Isotope fractionation related to kimberlite magmatism and diamond formation. *Geochim. Cosmochim. Acta* **55,** 1697–1708.

Harris J. W. (1992) Diamond geology. In *The Properties of Natural and Synthetic Diamond* (ed. J. E. Field), Chap. 9, pp. 345–394. Academic Press.

Harrison E. R. and Tolansky S. (1964) Growth history of a natural diamond. *Proc. Royal Soc. London* **A279,** 490–496.

Javoy M., Pineau F., and Demaiffe D. (1984) Nitrogen and carbon composition in the diamonds of Mbuji Mayi (Zaïre). *Earth Planet. Sci. Lett.* **68,** 399–412.

Jones R., Briddon P. R., and Oeberg S. (1992) First-principles theory of nitrogen aggregates in diamond. *Phil. Mag. Lett.* **66,** 67–74.

Kaiser W. and Bond L. (1959) Nitrogen, a major impurity in common type I diamond. *Phys. Rev.* **115,** 857–863.

Kamiya Y. and Lang A. R. (1965) On the structure of coated diamonds. *Phil. Mag.* **11,** 347–356.

Kanda H. and Yamaoka S. (1993) Inhomogeneous distribution of nitrogen impurities in (111) growth sectors of high pressure synthetic diamond. *Diamond and Related Materials* **2,** 1420–1423.

Kesson S. E. and Ringwood A. E. (1989) Slab-mantle interactions, 2. The formation of diamonds. *Chem. Geol.* **78,** 97–118.

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. *Phil. Mag. B.* **69,** 1141–1147.

Marakushev A. A., Pertsev N. N., Zotov I. A., Paneyakch N. A., and Cherenkova A. F. (1995) Some petrological aspects of diamond genesis. *Geology of Ore Deposits* **37,** 105–121 (in Russian).

Martovitskiy V. P., Nadejdina E. D., and Ekimova T. E. (1987) Internal structure and morphology of non-kimberlitic diamonds. *Mineral. J.* **9,** 26–27.

Moore M. and Lang A. R. (1972) On the Internal Structure of Natural Diamonds of Cubic Habit. *Phil. Mag.* **26,** 1313–1325.

Navon O. (1991) High internal pressures in diamond fluid inclusions determined by infrared absorption. *Nature* **353,** 746–748.

Navon O., Hutcheon I. D., Rossman G. R., and Wasserburg G. J. (1988) Mantle-derived fluids in diamond micro-inclusions. *Nature* **335,** 784–789.

Schrauder M. and Navon O. (1994) Hydrous and carbonatitic mantle fluids in fibrous diamonds from Jwaneng, Botswana. *Geochim. Cosmochim. Acta* **58,** 761–771.

Schrauder M., Navon O., Szafranek D., Kaminsky F. V., and Galimov E. M. (1994) Fluids in Yakutian and Indian diamonds. *Mineral. Mag.* **58A,** 813–814.

Shatsky V. S., Sobolev N. V., and Yefimova E. S. (1989) Morphological features of accessory microdiamonds from metamorphic rocks of the Earth's crust. 28th Intl. Geological Congress, Workshop on diamonds, 94–95 (extended abstr.).

Shatsky V. S., Sobolev N. V., and Vavilov M. A. (1995) Diamond-bearing metamorphic rocks of the Kokchetav Massif (northern Kazakhstan). In *Ultrahigh Pressure Metamorphism* (ed. R. G. Coleman and X. Wang), Chap. 12, pp. 427–455. Cambridge Univ. Press.

Shatsky V. S., Rylov G. M., Yefimova E. S., De Corte K., and Sobolev N. V. (1998a) The morphology and real structure of microdiamonds from the Kokchetav massif metamorphic rocks, kimberlites, and alluvial placers. *Russian Geology and Geophysics* **39,** 942–955 (in Russian).

Shatsky V. S., Zedgenizov D. A., Yefimova E. S., Rylov G. M., De Corte K., and Sobolev N. V. (1998b) A comparison of morphology and physical properties of microdiamonds from the mantle and crustal environments. 7th Intl. Kimb. Conf., extended abstracts 797–799.

Sobolev E. V. (1991) The impurity centers and some problems of diamond genesis. 5th Int. Kimb. Conf., extended abstracts, 388–390.

Sobolev N. V. and Shatsky V. S. (1990) Diamond inclusions in garnets from metamorphic rocks: A new environment for diamond formation. *Nature* **343,** 742–746.

Taylor W. R., Canil D., and Milledge H. J. (1996) Kinetics of Ib to IaA nitrogen aggregation in diamond. *Geochim. Cosmochim. Acta* **60,** 4725–4733.

Woods G. S. (1986) Platelets and the infrared absorption of type Ia diamonds. *Proc. Royal Soc. London* **A407,** 219–238.

Woods G. S. and Collins A. T. (1983) Infrared absorption spectra of hydrogen complexes in type I diamonds. *J. Phys. Chem. Solids* **44,** 471–475.