ELSEVIER

Chemical Geology 176 (2001) 265–281

CHEMICAL GEOLOGY
INCLUDING
ISOTOPE GEOSCIENCE

www.elsevier.com/locate/chemgeo

The origin and formation of metamorphic microdiamonds from the Kokchetav massif, Kazakhstan: a nitrogen and carbon isotopic study

Pierre Cartigny [a,b,*], Katrien De Corte [c,d], Vladislav S. Shatsky [e], Magali Ader [a], Paul De Paepe [c], Nikolay V. Sobolev [e], Marc Javoy [a]

[a] *Laboratoire de Géochimie des Isotopes Stables, Université Paris 7 et Institut de Physique du Globe, Place Jussieu 2, F-75251 Paris, Cedex 05, France*

[b] *Geochemisches Institut der Universität Göttingen, Goldschmidtstraße 1, D-37077 Göttingen, Germany*

[c] *Department of Geology and Soil Science, University of Ghent, Krijgslaan 281, S8, B-9000 Ghent, Belgium*

[d] *Department of Geology and Mineralogy, Royal Museum for Central Africa, Leuvensesteenweg 13, B-3080 Tervuren, Belgium*

[e] *Institute of Mineralogy and Petrography, Novosibirsk 630090, Russia*

Received 1 October 1999; accepted 25 September 2000

Abstract

This study reports $\delta^{13}C$, $\delta^{15}N$ and N-content values for microdiamonds from ultrahigh-pressure metamorphic rocks of the Kokchetav massif in Kazakhstan. Both alluvial diamonds and in-situ diamonds from a garnet–clinopyroxene rock and a marble (i.e. a garnet–pyroxene dolomitic rock) were investigated. In-situ diamonds were analysed in batches, because of their small size (average 40 μm), whereas the larger alluvial diamonds were analysed individually. The latter group has $\delta^{13}C$-values ranging from −15.92‰ to −10.57‰, $\delta^{15}N$ from −1.8‰ to +1.1‰ and N-contents from 2300 to 3650 ppm. Diamonds from the garnet–clinopyroxene rock yield mean values of −10.50‰ for $\delta^{13}C$, +5.9‰ for $\delta^{15}N$ and a high average nitrogen content of 11,150 ppm. Values for diamonds in marble are −10.19‰, +8.5‰ and 2650 ppm, respectively.

For diamonds from garnet–clinopyroxene rock and marble, there is more nitrogen released by bulk combustion than estimated by infrared (IR) spectroscopy, the differences being of about 7000 and 1500 ppm, respectively. These differences suggest that a significant quantity of nitrogen is IR-inactive and may be present as fluid inclusions. Their carbon and nitrogen isotopic compositions are compatible with an in-situ crystallisation of diamond from dominantly metasedimentary sources, suggesting that sedimentary nitrogen can be subducted to very high pressures. Carbon isotopic fractionation between coexisting carbonate and diamond suggests crystallisation temperatures before the peak of metamorphism at temperatures probably below 700°C and deduced pressures of 3 GPa. Relative to the isotopic data reported for sediments,

* Corresponding author. Laboratoire de Géochimie des Isotopes, Université Paris 7, Institut de Physique du Globe, Place Jussieu 2, 75251 Paris, Cedex 05, France. Fax: +33-1-44-27-28-30.

E-mail address: cartigny@ipgp.jussieu.fr (P. Cartigny).

PII: S0009-2541(00)00407-1

metasediments and in-situ diamonds, the slightly ^{15}N-depleted compositions of alluvial diamonds is striking. These values suggest that the contribution of any metasedimentary source is unlikely and may point toward a mafic/ultramafic protolith.

Keywords: Metamorphic microdiamond; Nitrogen; Carbon

1. Introduction

Geological environments for microdiamond (< 1mm) occurrences are increasingly recognized on Earth. They include kimberlites, lamproites and placer deposits (e.g. Harris, 1992 for review), in meteorites and impact craters (e.g. Hough et al., 1995), in lamprophyre dike (MacRae et al., 1995), volcaniclastic komatiites (Capdevilla et al., 1999), K–T boundary sites (e.g. Carlisle and Braman, 1991) and ultrahigh-pressure metamorphic rocks (e.g. Sobolev and Schatsky, 1990). Microdiamonds in the last context occur in metamorphic rocks from the Kokchetav massif in Kazakhstan (Sobolev and Schatsky, 1990), in Dabie Shan, China (Xu et al., 1992), in the Western Gneiss region of Norway (Dobrzhinetskaya et al., 1995) and in the Saxonian Erzgebirge, Germany (Massonne, 1999). However, abundant crystals are found only in the Kokchetav massif. In Kazakhstan, previous studies strongly suggest that diamonds were not incorporated in the sediments before subduction, deriving, for example, from an eroded kimberlite but have crystallised in-situ within their stability field and therefore have formed in a paleo ultrahigh-pressure metamorphic event (Shatsky et al., 1989; De Corte et al., 1998).

Despite the small size of in-situ Kokchetav diamonds (average size is 15 μm; Shatsky et al., 1989), their morphology and Fourier Transform InfraRed (FTIR) spectroscopy data compared to larger alluvial diamonds demonstrate that diamond characteristics vary as a function of the host-rock, supporting the presence of distinct diamond populations (De Corte et al., 1998, 1999). For example, diamonds with octahedral habit are observed only in zoisite gneisses devoid of symplectitic zoisite. Cubo-octahedral crystals are predominant in biotite gneisses and are characteristic also of diamonds found in the alluvials derived from the massif. Garnet–clinopyroxene–dolomitic rocks (i.e. impure marbles), zoisite gneisses rich in symplectitic zoisite and garnet–clinopyroxene rock typically contain cuboidal diamonds. Similarities of morphology and real structure for microdiamonds from kimberlites and metamorphic rocks have recently been discussed by Shatsky et al. (1998).

Previous work (Finnie et al., 1994; Taylor et al., 1996; De Corte et al., 1998, 1999) has also shown that the degree of substitution of carbon by nitrogen within the crystal structure as detected by FTIR microspectroscopy is the most pronounced for alluvial diamonds (up to 5200 ppm N; $n = 20$). Diamonds from garnet–clinopyroxene rocks form an intermediate group (1050–2800 ppm N; $n = 18$), followed by diamonds from marble (less than 580 ppm N; $n = 6$). The idea of distinct diamond populations is also supported by the evidence that diamonds from garnet–clinopyroxene, zoisite gneiss with symplectitic zoisite and marbles typically contain water and carbonate inclusions. In contrast, alluvial diamonds do not contain carbonate inclusions or water (or only a minor amount).

The finding of carbonate and water inclusions in metamorphic microdiamonds from garnet–clinopyroxenite and marble implies diamond growth from a C–O–H rich fluid (De Corte et al., 1998, 1999). The source(s) of these fluids however remains unclear. In an attempt to better constrain the source(s) of carbon and nitrogen of these microdiamonds, carbon and nitrogen isotopic compositions together with nitrogen contents have been determined on a series of well-characterised samples. The study of microdiamonds is also simplified and significant relative to other (e.g. silicate) minerals since they record only ultra-high pressure metamorphic conditions and did not reequilibrate during retrograde metamorphism outside their stability field; otherwise, they would have been graphitised. The study of microdiamonds may thus provide an insight into the conditions

prevailing under ultra high-pressure metamorphism and probably at the time of their crystallisation.

2. Sample description

In the present study, three well characterised sample types were considered: (1) alluvial diamonds from Tertiary sands located between 100 and 200 km north of the Kokchetav massif; (2) diamonds extracted from a garnet–clinopyroxene rock (sample 2-4i); and (3) diamonds isolated from a garnet–clinopyroxene dolomitic rock, also referred to as marble (sample K92-99i). Diamonds from groups (2) and (3) are described in the text as "in-situ diamonds".

Alluvial diamonds range in size between 100 and 300 μm. In contrast, in-situ diamonds are rarely larger than 135 μm. They were isolated by a thermochemical extraction process described by De Corte (2000). Both in-situ diamonds larger than 60 μm in size and all alluvial diamonds have been previously analysed by FTIR spectroscopy ($n = 9$ for sample 2-4i; $n = 3$ for sample K92-99i; De Corte et al., 1998, 1999).

In addition, we determined carbonate contents and carbon isotopic compositions of the garnet–clinopyroxene rock 2-4 and the marble K92-99.

3. Analytical techniques

Alluvial and in-situ microdiamonds were wrapped in platinum foil and cleaned at 600°C in air to remove any organic contamination. Due to the small diamond size and thus a high surface to volume ratio (to be degassed), special care was taken to remove any gas absorbed on the sample surface. Samples were therefore kept under vacuum ($\approx 10^{-7}$ Torr) for 12 h and afterwards were degassed for 1 h by pyrolysis under higher vacuum ($\approx 10^{-8}$ Torr) at 1100°C before combustion. To demonstrate the absence of any air-contribution, ^{40}Ar (i.e. $m/z = 40$) was also monitored in the mass spectrometer. The amount of ^{40}Ar recovered from sample and blank analyses being identical within experimental error, it shows that atmospheric nitrogen contamination was indeed avoided.

Samples were analysed using the procedure described by Boyd et al. (1995) for conventional macrodiamonds with a combustion apparatus slightly modified for these samples. Compared to the on-line combustion of Boyd et al. (1995), the reaction vessel in these analyses was made of a quartz tube (OD 6/ID 4 mm) crimped in the middle to receive the sample (see Fig. 1).

Diamonds were combusted online in an oxygen atmosphere and carbon converted into CO_2. Nitrogen was separated from carbon dioxide and any nitrogen oxide reduced to N_2 using a CaO–Cu furnace. Nitrogen concentrations were measured with an accuracy better than 5% using a capacitance manometer. Nitrogen isotopic composition was analysed with a triple collector static vacuum mass spectrometer connected directly to the extraction line. An accuracy of 0.5‰ for δ^{15}N was established on the basis of the analyses of international standards. CO_2 was quantified with a precision better than 1% using a piezoresistive gauge. Values for δ^{13}C were determined with an accuracy of 0.1‰ using a conventional gas isotope ratio mass spectrometer (for more details concerning this paragraph, see Boyd et al., 1995 and references therein).

The relatively large size of alluvial diamonds allowed single stones to be analysed, whereas in-situ

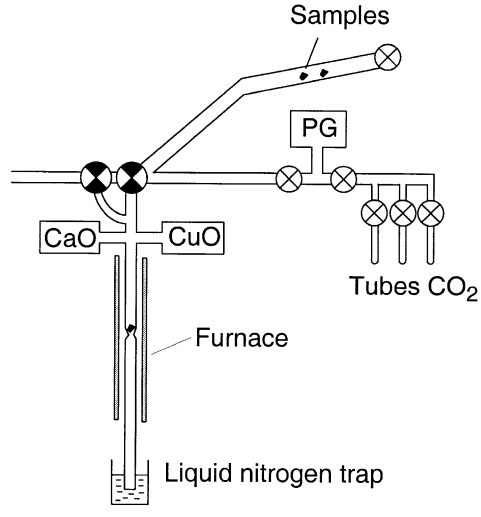

Fig. 1. Schematic outline of the carbon and nitrogen extraction line. See text and also Boyd et al. (1995) for details. PG = piezoresistive gauge.

Table 1
$\delta^{13}C-\delta^{15}N$ and N contents of microdiamonds found in alluvials and deriving from ultrahigh-pressure rocks of Kokchetav

Name	Weight (mg)	$\delta^{13}C$ (‰)	$\delta^{15}N$ (‰)	N (ppm)	N (ppm) FTIR[a]
T86-4	0.0896	−11.95	$-0.3^{-0.7}_{+0.7}$	2352	2360–2713
T86-5	0.0517	−12.60	$-0.3^{-0.8}_{+0.8}$	2923	2696–3550
T86-8	0.0417	−12.29	$+1.1^{-0.9}_{+1.0}$	2735	2477–5076
T86-10	0.0535	−15.76	$-1.1^{-0.9}_{+0.8}$	2681	2498–2758
T86-11	0.0407	−12.80	$+0.1^{-1.0}_{+1.0}$	2361	2709–3109
T86-13	0.0438	−15.92	$+0.0^{-0.8}_{+0.8}$	3643	2128–2588
T86-14	0.0661	−10.57	$-1.4^{-0.8}_{+0.7}$	3164	2695–2840
T86-15	0.0574	−13.36	$-1.8^{-0.9}_{+0.8}$	2324	3814–5236
T86-16	0.0315	−12.29	$-0.8^{-1.1}_{+1.0}$	2860	2519–3367

[a]Nitrogen contents obtained using infrared microspectroscopy (DeCorte et al., 1998, 1999) are shown for comparison.

diamonds needed to be grouped prior to analysis. With a mean diamond size of ca. 30 μm (computed from the 2-4 sample), a 1-mg sample is composed of more than 25,000 microdiamonds. Analyses of alluvial diamonds allow the variability between single samples to be investigated whereas analyses of in-situ diamonds yield average $\delta^{13}C-\delta^{15}N$–N-values.

A further technical problem was the presence of remaining zircons in the in-situ diamond mixture. Even after copious and very careful handpicking, about 10 ± 5% of this mineral remained. However, a complete combustion (better than 99.9%) of diamonds is readily obtained under our experimental conditions whereas zircons are absolutely undisturbed under these conditions. Hence, nitrogen contents of in-situ microdiamonds were calculated using the amount of carbon released by diamond combustions, as quantified by the piezoresistive gauge. Using this method, nitrogen contents of in-situ microdiamonds, (see sample 2-4, Table 2) are reproducible. No correlation between carbon yields and calculated nitrogen contents was observed which confirms that zircons did not contribute to the nitrogen recovered from the combustion.

Carbonate and total reduced carbon contents and associated carbon isotopic compositions were determined for the garnet–clinopyroxene rock (sample 2-4-i) and for the marble (sample K92-99-i) using a step-heating procedure. The apparatus used is exactly the same as the one described by Pineau and Javoy (1994); the temperature and the oxygen fugacity conditions of the steps changed and were given below. The gases were sequentially extracted from the sample in three temperature steps of 1 h each. The first step at 500°C with 12 mm Hg oxygen pressure removed any organic carbon contamination. The second step at 800°C under vacuum decarbonated the sample, and the CO_2 extracted allows the determination of the carbonate content and C-isotopic composition. The third step at 1350°C with 12 mm Hg oxygen pressure combusted the total reduced carbon (graphite + diamond) and the resulting CO_2 allows the determination of the reduced carbon content and isotopic composition. In the case of the marble, a good separation of the CO_2 from the total reduced carbon was impossible by this technique since carbonate minerals were too abundant and were present as inclusions in more refractory minerals. In this case, the CO_2 recovered from the last step contains a mixture of CO_2 coming from the decarbonation of residual carbonate and from the oxidation of reduced carbon. Consequently, this step gives a maximum value for the reduced carbon content (sample 92-99-i).

4. Results

The results for the alluvial diamonds are reported in Table 1. They have $\delta^{13}C$-values ranging from −15.92‰ to −10.57‰ (mean = −13.06‰),

Table 2
$\delta^{13}C-\delta^{15}N$ and N contents of microdiamonds from garnet–clinopyroxene rock (sample 2-4-i) and marble (i.e. garnet–pyroxene dolomitic, sample 92-99-i) from the ultrahigh-pressure massif of Kokchetav

Name	Weight (mg)	$\delta^{13}C$ (‰)	$\delta^{15}N$ (‰)	N (ppm)	N (ppm) FTIR[a]
2-4-i	1.5324	−10.71	$+5.6^{-0.5}_{+0.6}$	11,340	1050–2800
2-4-i	0.7893	−10.65	$+6.6^{-0.5}_{+0.6}$	11,385	1050–2800
2-4-i	0.6206	−10.34	$+6.1^{-0.5}_{+0.6}$	10,872	1050–2800
2-4-i	1.6789	−10.50	$+5.8^{-0.5}_{+0.5}$	11,237	1050–2800
2-4-i	0.5990	−10.32	$+5.3^{-0.5}_{+0.6}$	10,879	1050–2800
92-99-i	0.1181	−10.22	$+8.0^{-0.5}_{+0.5}$	2620	< 580
92-99-i	0.2197	−10.21	$+8.9^{-0.5}_{+1.4}$	2762	< 580

[a]Nitrogen contents obtained using infrared microspectroscopy (DeCorte et al., 1998, 1999) are shown for comparison ($n = 9$ and $n = 3$ for sample 2-4-i and 92-99-i, respectively).

Table 3
Carbon isotopic composition and content of carbonate and total reduced carbon of diamond-bearing garnet–clinopyroxene rock and marble

Name	Carbonate		Reduced carbon	
	C (ppm)	δ^{13}C (‰)	C (ppm)	δ^{13}C (‰)
2-4-i	480	-5.9 ± 0.3	490	-10.4 ± 0.2
92-99-i	88,200	-4.3 ± 0.1	< 2680	n.d.

δ^{15}N-values close to the atmospheric value, from −1.8‰ to +1.1‰ (mean = −0.5‰) and high N-contents, from ≈2300 to 3650 ppm. Results for in-situ diamonds are reported in Table 2. Five batches of diamonds from a garnet–clinopyroxene rock (sample 2-4) were analysed. Results are consistent, yielding a mean δ^{13}C-value of −10.50‰, a mean δ^{15}N-value of +5.9‰ and high average N contents of 11,150 ppm. Two batches of diamonds (92-99i, Table 2) from the marble give a mean δ^{13}C-value of −10.22‰, with a mean δ^{15}N-value of +8.5‰ and an average N content of 2650 ppm. Measured carbon isotopic compositions (Tables 1 and 2) are similar to the values reported by Pechnikov et al. (1993) for diamonds from a pyroxene–carbonate rock (−12.4‰ to −10.6‰) from the Kokchetav massif. Carbonate contents and carbon isotopic compositions from both the garnet–clinopyroxene rock and the marble are reported in Table 3; carbonate carbon contents being about 480 ppm and 8.82 wt.%C with δ^{13}C-values of −5.9‰ and −4.3‰, respectively. The total reduced carbon (graphite + diamond) content of the marble is below 2680 ppm. The total reduced carbon in garnet–clinopyroxene rock is 490 ppm, very similar to carbonate contents, with a δ^{13}C-value of -10.4 ± 0.2‰, very similar to the mean diamond δ^{13}C-value (see Table 2).

5. Discussion

5.1. Nitrogen as fluid inclusions: new evidence for diamond crystallisation from a fluid phase

In contrast to alluvial diamonds for which there is a reasonable agreement between nitrogen contents determined by combustion and by FTIR spectroscopy (Table 1), the two methods give very significant differences for in-situ diamonds (Table 2). For diamonds from the garnet–clinopyroxene rock (sample 2-4i) and the marble (92-99i), there is more nitrogen released by bulk combustion than estimated by infrared (IR) spectroscopy. For diamonds from the garnet–clinopyroxene rock (sample 2-4i), the amount of nitrogen can reach more than 7000 ppm. Diamonds from this rock may therefore contain at least 7000 ppm of an infrared inactive form. FTIR spectroscopy of diamonds from marble is not precisely constrained as a consequence of poor quality infrared spectra, but the reliable data obtained on two crystals suggest a maximum nitrogen content of 580 ppm (De Corte et al., 1999; Table 2). If this value is increased to 1100 ppm, in order to account for a possible higher mean N-content over this diamond population, an excess of ≈1500 ppm of infrared-inactive nitrogen must be present also in these diamonds. Such a difference between FTIR spectroscopy and bulk combustions has, to our knowledge, not been previously reported among mantle-derived diamonds and may be symptomatic of (some) metamorphic diamonds.

Within the diamond crystal lattice, nitrogen occurs in a variety of defects, most giving rise to characteristic IR absorptions. It is well established that there exists four main nitrogen-bearing defects; A (IaA diamond, N-pairs), B (IaB, probably four N atoms plus a vacancy), C (Ib, isolated N) and D (unknown structure) (see Davies, 1976; Woods, 1986; Sobolev, 1991; Jones et al., 1992). These four types of defects are linked by a diffusion process, following a second order kinetic, resulting in conversion of C to A centres and, when C is no longer present, to B and D defect centres (e.g. Chrenko et al., 1977; Evans and Qi, 1982). The aggregation sequence can be extended if platelet (i.e. bearing D-defects) degradation leads to the formation of voidites (e.g. Evans et al., 1995) which are not detectable by FTIR (e.g. Woods, 1994). In diamonds characterised by an advanced nitrogen aggregation state, it has been shown that IR inactive nitrogen may be present within voidites (e.g. Woods, 1994 and references therein).

Metamorphic microdiamonds have low nitrogen aggregation states, yet very high nitrogen contents. All the diamonds studied so far only contain nitrogen C- and A-defects (Type Ib-IaA diamonds; Finnie et

al., 1994; Taylor et al., 1996; De Corte et al., 1998, 1999) and thus neither B- or D-defects. The missing nitrogen therefore is unlikely to be within the crystal structure initially in some form of substitution for carbon, but rather outside.

The most likely explanation is that excess nitrogen is present as fluid inclusions. This suggestion is supported by two observations. First, a C–O–H rich fluid trapped within in-situ diamonds from both the marble and garnet–pyroxene rocks has been identified by FTIR spectroscopy. Secondly, in the mean time, alluvial diamonds do not show any excess nitrogen together with no (or very minor) amount of water or carbonate (De Corte et al., 1998, 1999). This observation links the presence/absence of excess nitrogen to the presence/absence of trapped fluid(s). The likely presence of fluid inclusions within the microdiamonds may also explain the relatively high concentration of noble gases observed by Verchovsky and Begeman (1993) during step-heating combustion.

Because part of the nitrogen from in-situ diamonds is present within two phases (diamond and probably fluid inclusions), the measured δ^{15}N-value will represent a mixture of substitutional and nonsubstitutional nitrogen. This is clear that nitrogen present under a substitutional form (i.e. trapped within the diamond lattice) was initially present in the C–O–H rich fluid from which the diamond crystallised. In the same way, nitrogen under a nonsubstitutional form was trapped during growth, within the fibrous texture of the diamond (Shatsky et al., 1998; De Corte et al., 1998) and is originating from the same fluid from which diamond crystallised. The diamond δ^{15}N-value is therefore likely to be representative of the δ^{15}N of the growth medium from which metamorphic diamond crystallised. In fact, the measured δ^{15}N-value could be difficult to interpret only if diamond growth was associated with a strong fractionation of N-isotopes. There is however no relationship between the measured δ^{15}N-value and the relative amount of nitrogen under substitutional and nonsubstitutional form (i.e. from about 0% up to 80% nonsubstitutional-N for diamonds from alluvials and garnet–clinopyroxene rock, respectively). This does not allow to suggest a strong kinetic fractionation of N-isotopes between N_2 and N in diamond during crystal growth. The δ^{15}N-value, therefore, is considered as significantly representative of the growth medium.

5.2. Source of carbon and nitrogen within in-situ diamonds and growth scenario

The origin and formation of metamorphic microdiamonds from the Kokchetav massif has been addressed by several groups. It has been either argued that metamorphic diamonds grew within their host-rocks (Sobolev and Schatsky, 1990) or were detrital minerals incorported in the sediments which were later metamorphosed (Marakushev et al., 1998). Further work demonstrated a strong dependence between the physical characteristics (e.g. shape, size, color, substitutional nitrogen content) and abundance of in-situ diamonds between the different host rocks (De Corte et al., 1999). Such evidence is seen as incompatible with a detrital origin of the diamonds and supports an in-situ crystallisation of the diamonds. The present results show that there exists also a strong difference between δ^{15}N-values, bulk N-contents and the proportion of nonsubstitutional nitrogen for the diamonds from the different host-rocks analysed. Although covering a quite narrow range of δ^{13}C-values, it could also be that mean diamond δ^{13}C-values (i.e. -13.06, -10.50 and -10.22 for diamonds from the alluvials, garnet–clinopyroxene rock and marble rock, respectively) would show slight but significant differences and be characteristics of their host rock. Taken together, the present results support the idea of a formation of diamonds within their host rock, a conclusion in agreement with previous conclusions summarised above. Moreover, in-situ diamonds have unusually high nitrogen content relative to kimberlitic diamonds (Fig. 2). This observation is not compatible with a model suggesting that the diamonds would derive from a kimberlite and were incorporated in the sediments prior to subduction (Marakushev et al., 1998). Accordingly, the most plausible explanation is that sources for C and N derived from the metamorphic rocks.

Phanerozoic organic matter is characterised mostly by positive δ^{15}N-values, typically from 0‰ to $+5$‰ (e.g. Rau et al., 1987; Peters et al., 1978; Fig. 3). Through diagenesis and metamorphism, organic matter undergoes a strong loss of nitrogen but no major

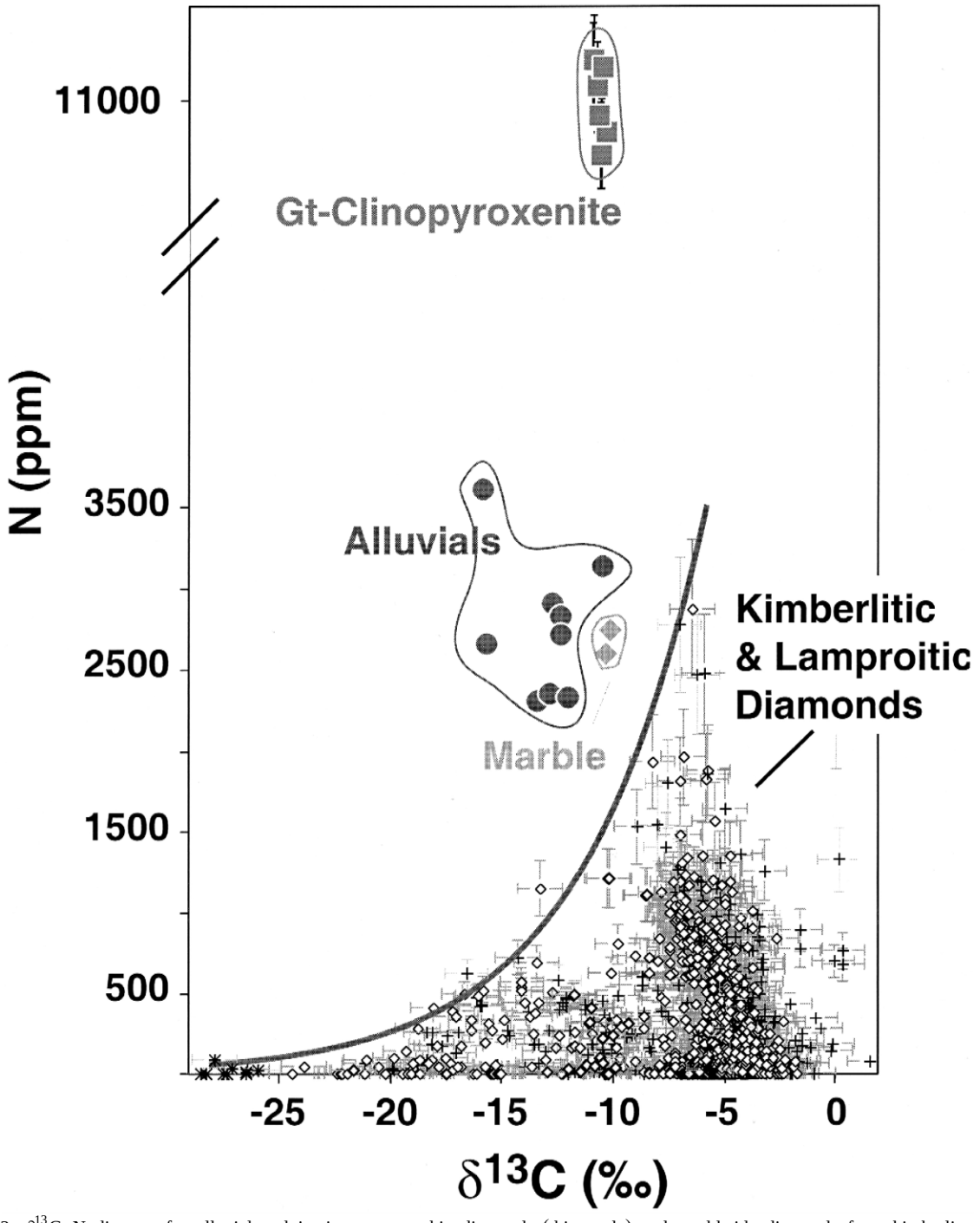

Fig. 2. δ^{13}C–N diagram for alluvial and in-situ metamorphic diamonds (this study) and worldwide diamonds from kimberlites and lamproites (adapted from Cartigny et al., 1999).

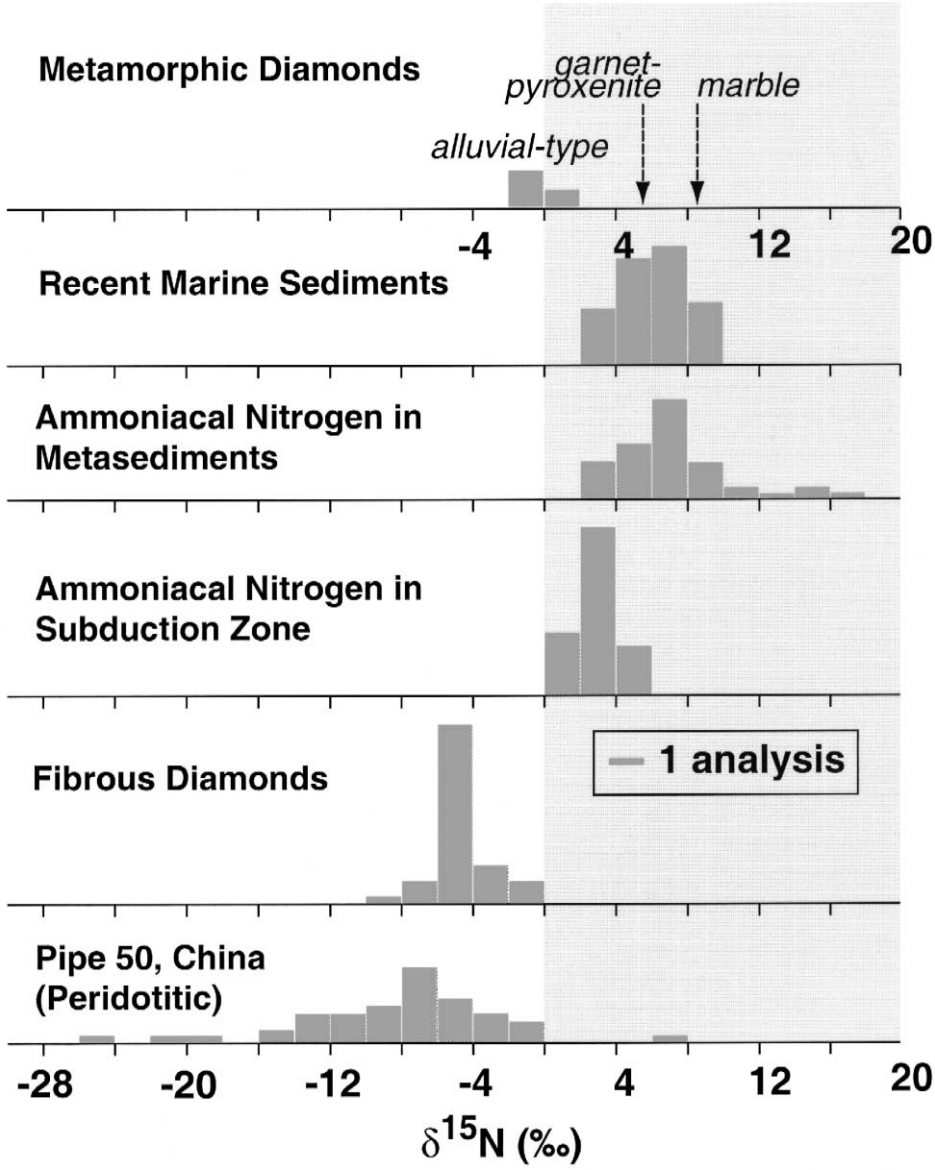

Fig. 3. δ^{15}N-values for alluvial and in-situ metamorphic diamonds (this study) and for recent marine sediments (Peters et al., 1978), ammoniacal nitrogen in metasediments (Haendel et al., 1986), ammoniacal nitrogen in subduction zones (Bebout and Fogel, 1992), worldwide fibrous diamonds and peridotitic diamonds from China (Cartigny et al., 1997 and references therein).

variations of its δ^{15}N-value (Ader et al., 1998). With increasing metamorphism, nitrogen can be fixed as fluid inclusions (Andersen et al., 1989) or as ammonium substituting for potassium within potassic minerals such as clay minerals (e.g. Williams and Ferrell, 1991), micas and feldspars (e.g. Honma and Itihara, 1981). It is well documented that devolatilisation processes occur during prograde metamorphism and lead to further loss of nitrogen and to an increase in δ^{15}N-values of the residual ammoniacal nitrogen; from $+5‰$ up to $+16‰$ (Haendel et al., 1986; Bebout and Fogel, 1992; Fig. 3). As symbol-

ised by arrows in Fig. 4, previous data for metasediments (up to 18 kbar) demonstrate that increasing metamorphism is not only associated with an enrichment in ^{15}N of ammoniacal nitrogen but also with an enrichment in ^{13}C of the reduced carbon, the latter due to the loss of ^{12}C depleted-material (e.g. CH_4) and/or partial reequilibration with carbonates (e.g. Bebout, 1995).

Microdiamonds from garnet–clinopyroxene rock and marble from Kokchetav clearly display positive $\delta^{15}N$-values (Fig. 3; Table 2). Nitrogen isotopic data are therefore in agreement with a metasedimentary origin for the nitrogen. On Fig. 4, microdiamonds $\delta^{13}C$- and $\delta^{15}N$-values (Tables 1 and 2) are plotted together with those of Bebout (1995). Fig. 4 includes data obtained on microdiamonds formed from a fluid whereas other data represent residual ammoniacal nitrogen. In-situ diamonds indeed precipitated from a C–O–H fluid-phase, and therefore represent nitrogen trapped from a devolatilised phase whereas lower metamorphic grade sediments represents residual ammoniacal nitrogen (Bebout, 1995). Considering the nitrogen isotopic fractionation, $\Delta_{rock\text{-}fluid}$-values for nitrogen bearing-species, in particular between NH_4^+ and N_2, isotopic fractionation values are likely to be below 2‰ at 700°C (Hanschmann, 1981; Richet et al., 1977; Bebout and Fogel, 1992). From Fig. 4, in-situ metamorphic microdiamonds fall on the extrapolated metamorphic trend and one can estimate that ammoniacal nitrogen within potassic phases had $\delta^{15}N$-values about 8‰ and 10‰.

In the present study, it is most probable that in-situ diamond $\delta^{13}C$-values reflect the strong influence of partial reequilibration with carbonates (see

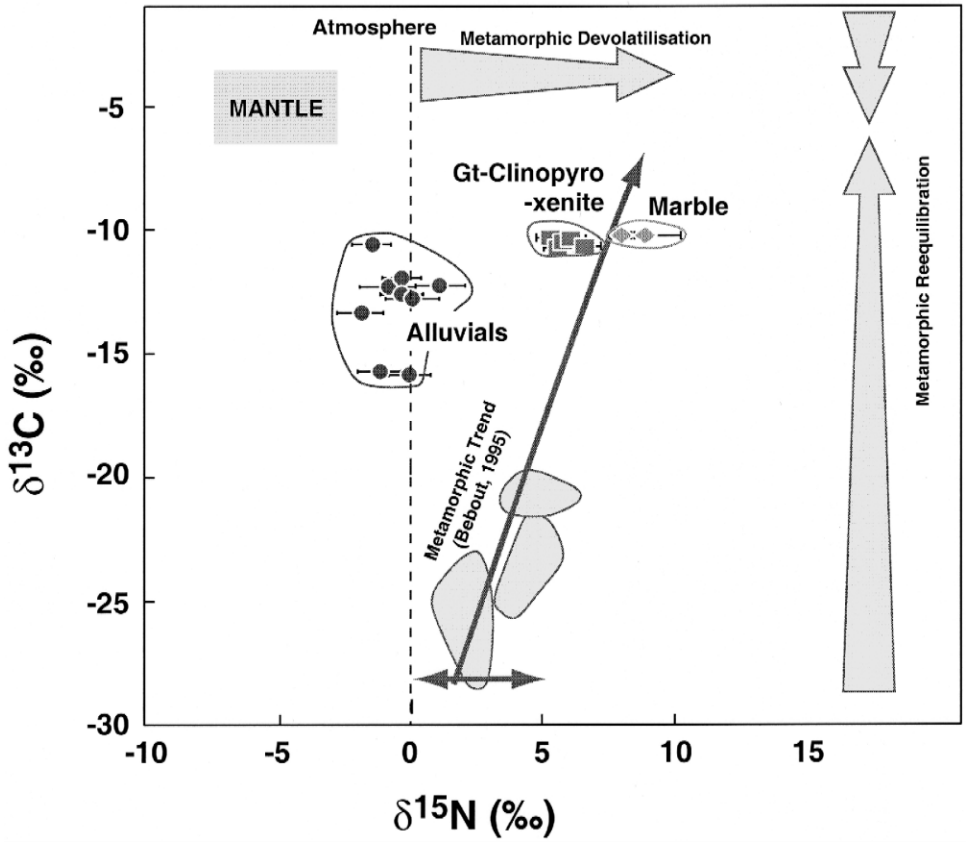

Fig. 4. Carbon and nitrogen isotopic compositions of microdiamonds from the Kokchetav massif and data for ammoniacal nitrogen in metamorphic rocks from Catalina (Bebout, 1995).

below) since carbonates are obviously present in high abundances (Table 3). In sediments, carbon resides either as organic matter (i.e. reduced) or as carbonates (oxidised), having initial mean δ^{13}C-values around −25 (e.g. Craig, 1953; Schidlowski, 1983) and 0‰ (e.g. Craig, 1953; Veizer and Hoefs, 1976), respectively. It has also been shown that with increasing metamorphism, graphite–carbonate isotopic equilibrium can be reached during graphite crystallisation at temperatures as low as 500°C and is almost always reached for temperatures above 600°C (see particularly Figs. 3 and 4 in Dunn and Valley, 1992; and also Hahn-Weinheimer, 1965; Sheppard and Schwarz, 1970; Pineau et al., 1976; Valley and O'Neill, 1981; Wada and Suzuki, 1983; Scheele and Hoefs, 1992; Hoffbauer and Spiering, 1994 and references therein). Despite there being no experimental data involving diamond, theoretical work suggests that the fractionation for carbon isotopic equilibrium between graphite and diamond is likely to be smaller than 0.5‰ at temperatures above 700°C (Bottinga, 1969; Polyakov and Kharlashina, 1995). Therefore, under equilibrium conditions, fractionations in the diamond–carbonate system can be estimated. We neglect the carbon isotopic fractionation between diamond and graphite. Taking it into account would yield even lower carbon isotopic temperatures. The different fractionation curves between graphite and carbonate, as a function of temperature, are represented on Fig. 5. For samples 2-4i and 92-99i, carbon isotopic fractionations between graphite and carbonate are calculated from the data in Tables 2 and 3 and represented on Fig. 5. Considering the whole set of fractionation curves yields a range of equilibrium isotopic temperatures between ≈470°C and 680°C. Considering the most consistent fractionation curves yields temperatures between ≈540°C and 640°C (Fig. 5). These temperatures are clearly

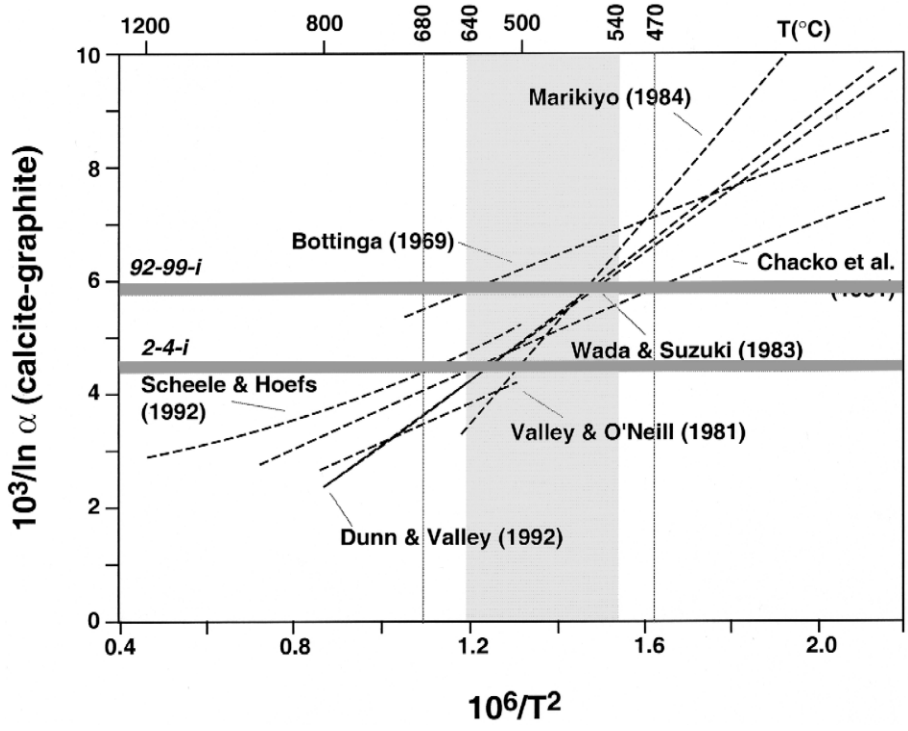

Fig. 5. Carbon isotopic thermometry of carbonate–diamond-bearing rocks according to theoretical, experimental and empirical determined carbon isotopic fractionation between calcite and graphite. Empirical or experimental carbon isotopic fractionation between graphite and diamond are lacking but theoretical work suggests fractionations below ≈0.5‰ for the deduced crystallisation temperatures (adapted from Scheele and Hoefs, 1992).

below the 900–1000°C envisaged for the peak of metamorphism in the Kokchetav massif (Chopin and Sobolev, 1995; Shatsky et al., 1999).

From Fig. 6 where the graphite/diamond transition is represented and the estimated temperatures, a pressure of crystallisation between 3.0 and 3.5 GPa can be inferred. On Fig. 6 is also represented the P–T evolution of the massif as reviewed by Zhang et al. (1997). From this figure, one can first notice that the deduced temperature–pressure window is compatible with the P–T evolution recorded by metamorphic rocks of the massif. Second, diamond growth has to take place during prograde metamorphism. We conclude that these isotopic temperatures are crystallisation temperatures. This implies that diamond records a crystallisation temperature, a situation contrasting with graphite, which usually records peak metamorphism temperatures (Dunn and Valley, 1992; Satish-Kumar and Wada, 1998).

The isotopic temperature proposed above are based on the assumption that isotopic equilibrium between carbonate and diamond was reached and that no other process affect the carbon isotopic composition of diamond or carbonate. There are however several factors that could affect slightly, or even strongly, the accuracy of isotopic temperatures. The

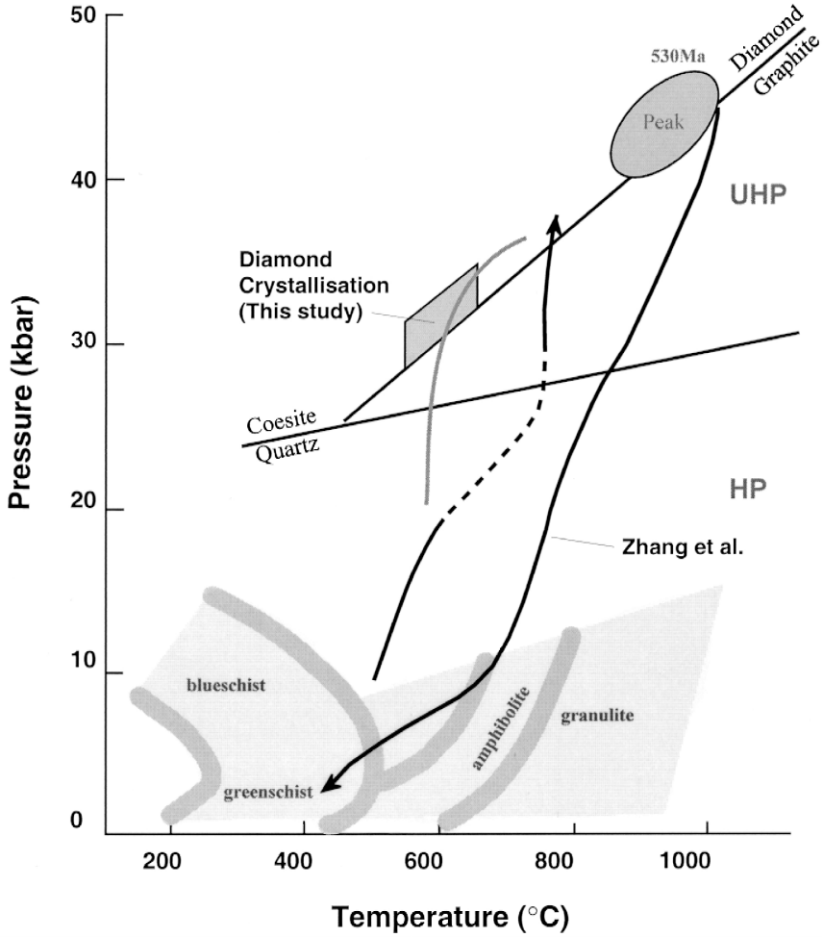

Fig. 6. The proposed P–T conditions for diamond crystallisation are compared with the P–T evolution of the Kokchetav massif as reviewed by Zhang et al. (1997).

first would consist in a carbon isotopic disequilibrium between carbonates and diamond during diamond formation, diamonds having crystallised at higher temperatures than those recorded by the carbonate–diamond isotope thermometer. However, since isotopic equilibrium is almost always reached at temperatures of about 700°C (Sheppard and Schwarz, 1970; Pineau et al., 1976; Wada and Suzuki, 1983; Dunn and Valley, 1992; Scheele and Hoefs, 1992; Hoffbauer and Spiering, 1994), it would be very difficult to argue for the preservation of any C-isotope disequilibrium at temperatures in excess of 1000°C. Thus, if a slight isotopic disequilibrium cannot be ruled out from the present data, it would certainly not change the fact that diamond crystallisation did not occur at the peak of metamorphism. The second factor that could affect the accuracy of isotopic temperatures can be the crystallisation of graphite (from graphitised diamonds or retrograde C-bearing fluids) in isotopic equilibrium with carbonates during retrograde metamorphism. In that case, carbonate δ^{13}C-values may change (and increase in the closed system hypothesis) and accordingly affect the deduced isotopic temperature. Such hypothesis is however incompatible with the observed data. For marble, from a mass balance point of view, the high abundance of carbonate relative to total reduced carbon (Table 3) precludes any major changes of the carbonate δ^{13}C. The garnet–clinopyroxene rock displays similar carbon abundances in carbonate and reduced carbon (Table 3). In that case, the δ^{13}C-values measured for diamond and total reduced carbon are within experimental error (Tables 2 and 3). Therefore, the crystallisation of graphite from diamond is unlikely to affect the carbonate δ^{13}C-values since both graphite and diamond have nearly identical δ^{13}C-values. We conclude that the precipitation of graphite at equilibrium with carbonate is not indicated by the present observation. In fact, the present data rather suggest that graphite represent graphitised diamonds and that the amount of carbon brought in the rock during retrograde metamorphism is relatively small.

Another difficulty linked with low crystallisation temperatures exists in explaining how diamond nucleation can be reached at temperatures ≈ 700°C since in experiment, diamond cannot be synthesised at such low temperatures. In this particular case, we question whether (i.e. synthetic diamond) temperature constraints can be simply applied to natural diamonds. For example, graphite (as diamond) can hardly be synthesised at temperatures below 800°C, whereas in natural systems graphite crystals are already commonly formed at 500°C (e.g. Tagiri and Oba, 1986). Thus, although several factors could have affected the isotopic temperatures of diamond crystallisation, the hypothesis that diamonds crystallised at temperatures about 700°C during prograde path, as opposed to peak of metamorphism, is favored.

In summary, it is likely that, prior to diamond crystallisation, reduced carbon was present as graphite and that nitrogen was trapped within a potassium bearing phase, such as phengite (since it has been identified as intergrown with diamond, Shatsky et al., 1995) or one of its precursors. Diamonds may have crystallised at temperatures lower than 700°C during the prograde path, the different diamond morphologies reflecting variable driving force conditions. Metamorphic microdiamond crystallisation may show similarities with the experimental work of Tanigushi et al. (1996), Pal'yanov et al. (1998, 1999), Litvin (1998) and Litvin et al. (1998) in which synthetic diamonds are grown from alkaline carbonate–carbon melted mixtures (although in these experiments, synthetic diamonds are also grown under higher P–T conditions). The production of a carbonate-bearing fluid may catalyse the conversion of reduced carbon from graphite to diamond and/or the reduction of carbonate to diamond. In addition, the presence of carbonate in the fluid induces a decrease in the activity of NH_4^+ in silicate minerals, resulting in an increase of the fugacity of N_2 in the fluids (e.g. Moine et al., 1994). This can account for both the likely presence of N_2 in fluid inclusions and for the relatively high nitrogen contents of diamonds.

5.3. *Alluvial diamonds from the North of the Kokchetav massif*

On one hand, previous investigations by De Corte et al. (1998, 1999) outlined the strong similarity in the state of nitrogen aggregation between in-situ and alluvial diamonds, the latter deriving from the UHP massif and found in alluvial placers located ca. 200

km to the north of the Kokchetav massif. These results implied that the diamonds are likely to have undergone similar T–t evolution, in other words that they are all metamorphic (again see Fig. 6 of De Corte et al., 1998). On the other hand, this study revealed strong differences between the two diamond sets and alluvial diamonds. This observation has several implications. Firstly, alluvial diamonds may not be representative of the whole diamond deposit, and secondly, these alluvial diamonds may derive from a protolith (or protoliths) different from the diamond-bearing rocks under current investigation. Part of the present work was to further consider this possibility.

Indeed the present set of data further supports the existence of significant differences between alluvial and in-situ diamonds. For alluvial diamonds, there is a reasonable agreement between nitrogen contents determined by combustion and FTIR spectroscopy (Table 1). Those diamonds contain no water or carbonate inclusions (or only minor amounts) whereas this was not the case for in-situ diamonds (this study, see also Finnie et al., 1994; De Corte et al., 1998, 1999). In addition, alluvial and in-situ diamonds show strikingly different nitrogen isotopic compositions, the low δ^{15}N-values (i.e. -1.8‰ to $+1.1$‰; -0.5‰ mean) of alluvial diamonds, contrasting with positive δ^{15}N-values displayed by in-situ metamorphic diamonds ($\approx +5$‰ to $+8$‰). The present results further support the idea that alluvial and in-situ diamonds do not derive from the same protolith.

Moreover, it is of importance to notice that alluvial diamonds cover a narrow range of δ^{15}N-values. This suggests that alluvial diamonds are more likely to derive from a single protolith as opposed to a variety of protoliths. Their δ^{15}N-values (-1.8‰ to $+1.1$‰; mean -0.5‰) contrast with moderate to high δ^{15}N-values of sediments (≈ 0‰ to $+5$‰), metamorphosed crustal rocks (strictly positive δ^{15}N-values; Haendel et al., 1986; Bebout and Fogel, 1992; Fig. 3) and in-situ metamorphic diamonds specifically from this study. Accordingly, the absence of clearly positive δ^{15}N-values as those displayed by in-situ diamonds seems to exclude any metasedimentary nitrogen source. The absence of diamond with strictly positive δ^{15}N-values (e.g. $+5$‰ to $+8$‰ like in-situ diamonds) is at odds the fact that several metasedimentary diamond-bearing rocks (again with strictly positive δ^{15}N-values) have likely contributed to alluvial diamond deposit. We suggest that microdiamonds from, e.g. garnet–pyroxene or marble rocks eventually contributed to the so-called alluvial diamond deposit but were not sampled because of their generally smaller size or were destroyed during transport, their fibrous structure giving them a more fragile character. An investigation of small size (i.e. < 40 μm) alluvial diamonds would provide additional constraints.

Abdulkabirova and Zayachkovsky (1997) highlighted the presence of diamondiferous lamproites in and around the Kokchetav massif. There is no data available on diamond from these lamproites yet. Therefore, the relationship between the magmatic and the metamorphic unit(s) remains unknown. Namely, it is unknown whether the diamonds in the lamproites could be for example mantle-derived or inherited from digested metamorphic rocks and incorporated during emplacement. Nevertheless, considering published data on diamonds from other lamproites, several points can be drawn. In the present case, δ^{13}C- and δ^{15}N-values do not allow to discriminate lamproitic from alluvial diamonds since the field they define overlap (not shown). However, diamonds found within lamproites show rather high nitrogen aggregation state (i.e. IaA-IaB diamonds; Harris and Collins, 1985) relative to alluvial diamonds from the Kokchetav massif. These alluvial diamonds also show rather high nitrogen contents relative to kimberlitic/lamproitic diamonds (Fig. 2). From these two evidences, we conclude that alluvial diamonds are unlikely related to lamproites intruding the massif (Abdulkabirova and Zayachkovsky, 1997).

Considering that alluvial diamonds are metamorphic and derive from UHP rocks of the Kokchetav massif (as suggested on the basis of nitrogen aggregation state; De Corte et al., 1998), several hypotheses can be proposed to account for the rather low δ^{15}N-values. If one accepts that metamorphic devolatilisation identified for sediments leads to a ^{15}N enrichment of $+1$‰ to $+10$‰ in the residue (Haendel et al., 1986; Bebout and Fogel, 1992; Boyd and Philippot, 1998), then the pre-metamorphic protolith for alluvial diamonds requires a protolith with negative or very close to zero δ^{15}N. Such a low δ^{15}N-value would preclude any metasedimentary

source for the nitrogen (Haendel et al., 1986; Bebout and Fogel, 1992; Boyd and Philippot, 1998) and rather points towards to either (1) a mantle-derived source for nitrogen, as such a source is the only reservoir known to provide low δ^{15}N signatures (see Javoy et al., 1986; Cartigny et al., 1997) or (2) some atmospheric nitrogen. In this specific case, if atmospheric nitrogen was trapped as fluid inclusions (?) and subducted before alluvial diamond growth, the noble gase (in particular Ne) signatures should also be kept. The recognition of the protolith of alluvial diamonds is however difficult and, given the present state of knowledge, the interpretation of associated δ^{13}C-values would be hazardous. At least, the contribution of any metasedimentary source seems unlikely. The recognition of an olivine inclusion, typical of kimberlitic and lamproitic diamonds worldwide (Sobolev, Shatsky and Yefimova, unpublished data) within one alluvial diamond also points towards a mafic/ultramafic protolith.

In summary, the present result definitely supports the idea that (1) Kokchetav alluvial diamonds are not derived from the most representative diamond-bearing rocks found in the UHP massif (i.e. garnet–clinopyroxene rock and marble) and (2) that these alluvial diamonds are not representative of the diamonds from the massif as a whole. This supports previous conclusions of De Corte et al. (1999). (3) The rather low δ^{15}N-values seem to reject the contribution of any metasedimentary nitrogen source.

6. Conclusions

The aim of this study has been to provide a first nitrogen and carbon isotopic systematic of microdiamonds as a function of their host-rock in order to better constrain their origin and formation. In conclusion, the following seven points are emphasised.

(1) A major proportion of the nitrogen present within diamonds recovered from a garnet–clinopyroxene rock and a marble, is likely present as fluid-inclusions. (2) For these diamonds, carbon and nitrogen stable isotopes strongly suggest a metasedimentrary origin. (3) Metamorphic microdiamonds may not have crystallised at the peak of metamorphism (i.e. 1000°C) but at temperatures $\approx$ 700°C.

(4) Diamonds of "alluvial" type appear to contain no significant amount of nitrogen as fluid inclusions, and (5) their nitrogen isotopic composition suggest that they may not derive from a metasedimentary protolith. An ultra-high pressure metamorphic rocks of mafic or ultramafic composition, i.e. different from the other investigated diamond-bearing rocks, is possible.

(6) When compared with diamonds from kimberlites and lamproites, metamorphic diamonds have unusually high concentrations of nitrogen.

(7) The present set of data shows that it is possible to subduct sedimentary nitrogen and carbon to great depths.

Acknowledgements

We express special thanks to J. Harris and W. Taylor for comments and strong improvements to the manuscript. Comments by J. Klerkx, J. Hoefs and N. Jendrzejewski are also greatly acknowledged. PC benefited from a grant by Naturalia and Biologia during acquisition of the results. KDC acknowledges receipt of a grant from the Flemish Institute for Support of Scientific and Technological Research in the Industry (IWT). The authors wish to thank W. Griffin, R. Burgess and the anonymous for very valuable comments and reviews. IPGP contribution 1720 and CNRS 249.

References

Abdulkabirova, M.A., Zayachkovsky, A.A., 1997. Diamond of Kazakhstan. In: Kazhegeldin, A.M., Abdulin, A.A., Bespaev, H.A., Votsalevsky, E.S., Daukeev, S.Z., Miroshnichenko, L.A. (Eds.), Almaty, Ministry of Geology and Preservation of Underground Resources. p. 83.

Ader, M., Boudou, J.P., Javoy, M., Goffé, B., Daniels, E., Vieth-Redemann, A., 1998. Isotope study of organic nitrogen of Westphalian anthracites from eastern Pennsylvania (USA) and from Bramsche Massif (Germany). Org. Geochem. 29, 315–323.

Andersen, T., Burke, E.A.J., Austraheim, H., 1989. Nitrogen bearing-aqueous fluid inclusions in some eclogites from Western Gneiss region of the Norwegian caledonides. Contrib. Mineral. Petrol. 103, 153–165.

Bebout, G.E., 1995. The impact of subduction-zone metamor-

phism on mantle-ocean chemical cycling. Chem. Geol. 126, 191–218.

Bebout, G.E., Fogel, M.L., 1992. Nitrogen-isotope compositions of metasedimentary rocks in the Catalina Schist, California: implications for metamorphic devolatilization history. Geochim. Cosmochim. Acta 56, 2839–2849.

Bottinga, Y., 1969. Carbon isotope fractionation between graphite, diamond and carbon dioxide. Earth Planet. Sci. Lett. 5, 301–307.

Boyd, S.R., Philippot, P., 1998. Precambrian ammonium biogeochemistry; a study of the Moine metasediments. Scotland Chem. Geol. 144, 257–268.

Boyd, S.R., Réjou-Michel, A., Javoy, M., 1995. Improved techniques for the extraction, purification and quantification of nanomole quantities of nitrogen gas: the nitrogen content of a diamond. Meas. Sci. Technol. 6, 297–305.

Capdevilla, R., Arndt, N., Letendre, J., Sanvage, J.F., 1999. Diamonds in volcaniclastic komatite from French Guiana. Nature 399, 456–458.

Carlisle, D.B., Braman, D.R., 1991. Nanometre-size diamonds in the Cretaceous/Tertiary boundary clay of Alberta. Nature 352, 708–709.

Cartigny, P., Boyd, S.R., Harris, J.W., Javoy, M., 1997. Nitrogen isotopes in peridotitic diamonds from Fuxian, China; the mantle signature. Terra Nova 4, 175–179.

Cartigny, P., Harris, J.W., Javoy, M., 1999. Diamond genesis, mantle fractionations and mantle nitrogen content: a study of δ^{13}C–N concentrations in diamonds. Earth Planet. Sci. Lett. submitted for publication (Oct. 1999).

Chopin, C., Sobolev, N.V., 1995. Principal indicators of UHP in crustal rocks. In: Coleman, R.G., Wang, X. (Eds.), Ultra-High Pressure Metamorphism. Cambridge Univ. Press, Cambridge, UK, pp. 96–131.

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

Craig, H., 1953. The geochemistry of the stable carbon isotopes. Geochim. Cosmochim. Acta 3, 53–92.

Davies, G., 1976. The A nitrogen aggregate in diamond—its symetry and possible structure. J. Phys. C: Solid State Phys. 9, L537–542.

De Corte, K., 2000. Study of microdiamonds from UHP metamorphic rocks of the Kokchetav massif (Northern Kazakhstan): characterization and genesis, PhD thesis, University of Ghent, Belgium, 173 pp.

De Corte, K., Cartigny, P., Shatsky, V.S., Sobolev, N.V., Javoy, M., 1998. First evidence of fluid inclusions in metamorphic microdiamonds from the Kokchetav massif, Northern Kazakhstan. Geochim. Cosmochim. Acta 62, 3765–3773.

De Corte, K., Cartigny, P., Shatsky, V.S., De Paepe, P., Sobolev, N.V., Javoy, M., 1999. Characteristics of microdiamonds from UHPM rocks of the Kokchetav massif. In: Gurney, J.J., Gurney, L.G., Pascoe, M.D., Richardson, S.H. (Eds.), Proceedings of the 7th International Kimberlite Conference, April 13–17, Cape Town, Red Roof Design cc, Goodwood, South-Africa. pp. 174–182.

Dobrzhinetskaya, L.F., Eide, E.A., Larsen, R.B., Sturt, B.A., Tronnes, R.G., Smith, D.C., Taylor, W.R., 1995. Microdiamond in high-grade metamorphic rocks of the Western Gneiss region, Norway. Geology 23, 597–600.

Dunn, S.R., Valley, J.W., 1992. Calcite–graphite isotope thermometry: a test for polymetamorphim in marble, Tudor gabbro aureole, Ontario, Canada. J. Metamorph. Geol. 10, 487–501.

Evans, T., Qi, Z., 1982. The kinetics of the aggregation of nitrogen atoms in diamond. Philos. Trans. R. Soc. London A381, 159–178.

Evans, T., Kiflawi, I., Luyten, W., Van Tendeloo, G., Woods, G.S., 1995. Conversion of platelets into dislocation loops and voidite formation in type IaB diamonds. Philos. Trans. R. Soc. London A449, 295–313.

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

Javoy, M., Pineau, F., Delorme, H., 1986. Carbon and nitrogen isotopes in the mantle. Chem. Geol. 68, 399–412.

Hahn-Weinheimer, V.P., 1965. Die isotopische Verteilung von Kohlenstoff und Schwefel in Marmor und anderen Metamorphiten. Sonderdruck aus der Geologischen Rundschau Band 55, 197–209.

Haendel, D., Mühle, K., Nitzsche, H., Stiehl, G., Wand, U., 1986. Isotopic variations of the fixed nitrogen in metamorphic rocks. Geochim. Cosmochim. Acta 50, 749–758.

Hanschmann, G., 1981. Berechnung von Isotopeeffeckten auf quantenchemischer grundlage am Beispiel stickstoffhaltiger Moleküle. ZfI-Mitt. 41, 19–39.

Harris, J.W., 1992. Diamond geology. In: Field, J.E (Ed.), The Properties of Natural and Synthetic Diamonds. pp. 345–393.

Harris, J.W., Collins, A.T., 1985. Studies of Argyle diamonds. Ind. Diamond Rev. 3, 128–130.

Hoffbauer, R., Spiering, B., 1994. Petrologic phase equilibria and stable isotope fractionation of carbonate–silicate parageneses from granulite-grade rocks of Sri Lanka. Precambrian Res. 66, 325–349.

Honma, H., Itihara, Y., 1981. Distribution of ammonium in minerals of metamorphic and granitic rocks. Geochim. Cosmochim. Acta 45, 983–988.

Hough, R.M., Gilmour, I., Pillinger, C.T., Arden, J.W., Gilkes, K.W.R., Yuan, J., Milledge, H.J., 1995. Diamond and silicon carbide in impact melt rock from the Ries impact crater. Nature 378, 41–44.

Jones, R., Briddon, P.R., Öberg, S., 1992. First-principles theory of nitrogen aggregates in diamond. Philos. Mag. Lett. 66, 67–74.

Litvin, Y.A., 1998. Hot spots of the mantle and experiment to 10 GPa: alkaline reactions, lithosphere carbonatization and new diamond-generating systems. Geol. Geofiz. 39, 1772–1779, (in Russian), English Translation: Russ. Geol. Geophys. 39, 1761–1767.

Litvin, Y.A., Chudinovskikh, L.T., Zharikov, V.A., 1998. Crystallisation of diamond in the $NaMg(CO_3)_2$–$K_2(CO_3)_2$–C system at 8–10 GPa. Dokl. Earth Sci. 359A, 433–435.

MacRae, N.D., Armitage, A.E., Jones, A.L., Miller, A.R., 1995. A

diamondiferous lamprophyre dike, Gibson Lake area, Northwest Territories. Intern. Geol. Rev. 37, 212–229.

Marakushev, A.A., Paneyakh, N.A., Zotov, I.A., 1998. The problem of mantle petrology. Geol. Geofiz. 39, 1750–1755 (in Russian), English Translation: Russ. Geol. Geophys. 39, 1740–1745.

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., Gurney, J.L., Pascoe, M.D., Richardson, S.H. (Eds.), Proceedings of the 7th International Kimberlite Conference, vol. 2. Red Roof Design, Cape Town, pp. 533–539.

Moine, B., Guillot, C., Gibert, F., 1994. Controls of the composition of nitrogen-rich fluids originating from reaction with graphite and ammonium-bearing biotite. Geochim. Cosmochim. Acta 58, 5503–5523.

Pal'yanov, Y.N., Sokol, A.G., Borzdov, Y.M., Khokhryakov, A.F., Sobolev, N.V., 1998. Diamond crystallisation in the systems $CaCO_3$–C, $MgCO_3$–C, and $CaMg(CO_3)_2$–C. Dokl. Earth Sci. 363, 1156–1159.

Pal'yanov, Yu.N., Sokol, A.G., Borzdov, Yu.M., Khokhryakov, A.F., Sobolev, N.V., 1999. Diamond formation from mantle carbonate fluids. Nature 400, 417–418.

Pechnikov, V.A., Bobrov, V.A., Podkuyko, Y.A., 1993. Isotopic compositions of diamond and accompanying graphite in North Kazakhstan metamorphic rocks. Geol. Int. 30, 153–157.

Peters, K.E., Sweeney, R.E., Kaplan, I.R., 1978. Correlation of carbon and nitrogen stable isotope ratios in sedimentary organic matter. Limnol. Oceanogr. 23, 598–604.

Pineau, F., Javoy, M., 1994. Strong degassing at ridge crests: the behavior of dissolved carbon and water in basalt glasses at 14°N, Mid-Atlantic Ridge. Earth Planet. Sci. Lett. 123, 179–198.

Pineau, F., Latouche, L., Javoy, M., 1976. L'origine du graphite et les fractionnements isotopiques du carbone dans les marbres métamorphiques des Gour Oumeladen (Ahaggar, Algérie), des Adirondacks (New Jersey, USA) et du Damara (Namibie, Sud-Ouest africain). Bull. Soc. Geol. Fr. 18, 1713–1723.

Polyakov, V.B., Kharlashina, N.N., 1995. The use of heat capacity data to calculate carbon isotope fractionation between graphite, diamond and carbon dioxide: a new approach. Geochim. Cosmochim. Acta 59, 2561–2572.

Rau, G.H., Arthur, M.A., Dean, W.E., 1987. $^{15}N/^{14}N$ variations in Cretaceous Atlantic sedimentary sequences: implication for past changes in marine nitrogen biogeochemistry. Earth Planet. Sci. Lett. 82, 269–279.

Richet, P., Bottinga, J., Javoy, M., 1977. A review of hydrogen, carbon, oxygen, sulphur and chlorine stable isotope fractionation among gaseous molecules. Annu. Rev. Earth Planet. Sci. 5, 65–110.

Satish-Kumar, M., Wada, H., 1998. Carbon isotope fractionation between calcite and graphite during high temperature metamorphism. Min. Mag. 62A, 1318–1319.

Scheele, N., Hoefs, J., 1992. Carbon isotope fractionation between calcite, graphite and CO_2: an experimental study. Contrib. Mineral. Petrol. 112, 35–45.

Shatsky, V.S., Sobolev, N.V., Yefimova, E.S., 1989. Morphological features of accessory microdiamonds from metamorphic rocks of the Earth's crust. In: Boyd, F.R., Meyer, H.O.A., Sobolev, N.V. (Eds.), Workshop on Diamonds. Extended Abstracts, Washington, DC, pp. 94–95.

Shatsky, V.S., Sobolev, N., Vavilov, V., 1995. Diamond-bearing metamorphic rocks of the Kokchetav massif, northern Kazakhstan. In: Coleman, R.G., Wang, X. (Eds.), Ultra-High Pressure Metamorphism. Cambridge Univ. Press, Cambridge, UK, pp. 427–455.

Shatsky, V.S., Rylov, G.M., Yefimova, E.S., De Corte, K., Sobolev, N.V., 1998. Morphology and real structure of microdiamonds from metamorphic rocks (Kokchetav Massif), kimberlites and alluvial placers. Geol. Geofiz. 39, 942–955 (in Russian), English Translation: Russ. Geol. Geophys. 39, 949–961.

Shatsky, V.S., Jagoutz, E., Sobolev, N.V., Kozmenko, O.A., Parkhomenko, V.S., Troesch, M., 1999. Geochemistry and age of ultrahigh pressure metamorphic rocks from Kokchetav massif (Northern Kazakhstan). Contrib. Mineral. Petrol. 137, 185–205.

Sheppard, S.M.F., Schwarz, H.P., 1970. Fractionation of carbon and oxygen isotopes and magnesium between between coexisting metamorphic calcite and graphite. Contrib. Mineral. Petrol. 26, 161–198.

Schidlowski, M., 1983. A 3800-million-year isotopic record of life from carbon in sedimentary rocks. Nature 333, 313–318.

Sobolev, E.V., 1991. The impurity centres and some problems of diamond genesis. Ext. Abstr. Vol., Fifth Intern. Kimb. Conf., Araxa, Brazil, 388–390.

Sobolev, N.V., Schatsky, V.S., 1990. Diamond inclusions in garnet from metamorphic rocks: a new environment for diamond formation. Nature 343, 742–745.

Tagiri, M., Oba, T., 1986. Hydrothermal syntheses of graphite from bituminous coal at 0.5–5 kbar water vapor pressure and 300–600°C. Jpn. Assoc. Mineral., J. Pet. Econ. Geol. 81, 260–271.

Tanigushi, T., Dobson, D., Jones, A.P., Rabe, R., Milledge, H.J., 1996. Synthesis of cubic diamond in the graphite–magnesium carbonate and graphite–$K_2Mg(CO_3)_2$ systems at high pressure of 9–10 GPa region. J. Mater. Res. 11, 2622–2633.

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

Valley, J.W., O'Neill, J.R., 1981. $^{13}C/^{12}C$ exchange between calcite and graphite: a possible thermometer in Grenville marbles. Geochim. Cosmochim. Acta 45, 411–419.

Veizer, J., Hoefs, J., 1976. The nature of $^{18}O/^{16}O$ and $^{13}C/^{12}C$ secular trends in sedimentary carbonate rocks. Geochim. Cosmochim. Acta 40, 1387–1395.

Verchovsky, A.B., Begemann, U.O., 1993. Implanted radiogenic and other noble gases in crustal diamonds from Northern Kazakhstan. Earth Planet. Sci. Lett. 120, 87–102.

Wada, H., Suzuki, K., 1983. Carbon isotopic thermometry calibrated by dolomite–calcite solvus temperatures. Geochim. Cosmochim. Acta 47, 697–706.

Williams, L.B., Ferrell, R.E., 1991. Ammonium substitution in illite during maturation of organic matter. Clays Clay Miner. 39, 400–408.

Woods, G.S., 1986. Platelets and the infrared absorption of type Ia diamonds. Philos. Trans. R. Soc. London A407, 219–238.

Woods, G.S., 1994. Voidites in diamonds. In: Davies, G. (Ed.), Properties and Growth of Diamond. Institution of Electrical Engineers, London, pp. 97–98.

Xu, S.T., Okay, A.I., Ji, S., Sengor, A.M.C., Su, W., Liu, Y., Jiang, L., 1992. Diamond from the Dabie Shan metamorphic rocks and its implication for tectonic setting. Science 256, 80–82.

Zhang, R.Y., Liou, J.G., Ernst, W.G., Coleman, R.G., Sobolev, N.V., Shatsky, V.S., 1997. Metamorphic evolution of diamond-bearing and associated rocks from the Kokchetav Massif, northern Kazakhstan. J. Metamorph. Geol. 13, 479–496.