

# Oxygen, carbon, and strontium isotope geochemistry of diamond-bearing carbonate rocks from Kumdy-Kol, Kokchetav Massif, Kazakhstan

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## Abstract

Diamond-bearing carbonate rocks from Kumdy-Kol, Kokchetav massif, Kazakhstan, were strongly altered by fluids flowing through fractures and infiltrating along grain boundaries during exhumation. Alteration includes retrogradation of high-grade silicate assemblages by hydrous minerals, replacement of diamond by graphite and of dolomite by calcite. Diamond-bearing carbonate rocks are among the most intensely altered isotopically with  $\delta^{18}\text{O}_{\text{VSMOW}}$  values as low as +9‰,  $\delta^{13}\text{C}_{\text{VPDB}} = -9\text{‰}$ , and  $^{87}\text{Sr}/^{86}\text{Sr}$  as high as 0.8050. Evidence of isotopic equilibration between coexisting dolomite and high-Mg calcite during ultrahigh-pressure metamorphism (UHPM) is preserved only rarely in samples isolated from infiltrating fluids by distance from fractures. Isotopic heterogeneity and isotopic disequilibrium are widespread on a hand-specimen scale. Because of this lack of homogeneity, bulk analyses cannot provide definitive measurements of  $^{13}\text{C}/^{12}\text{C}$  fractionation between coexisting diamond and carbonate. Our study adequately documents alteration on a scale commensurate with observed vein structures. But, testing the hypothesis of metamorphic origin of microdiamonds has not fully succeeded because our analytical spatial resolution, limited to 0.5 mm, is not small enough to measure individual dolomite inclusions or individual diamond crystals.

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**Keywords:** Diamond–eclogite facies; Oxygen isotopes; Carbon isotopes; Strontium isotopes; Exhumation; Continental collision

## 1. Introduction

Diamond- and coesite-bearing crustal rocks outcrop over an area measuring  $100 \times 10$  km in the Kokchetav massif, Kazakhstan (Sobolev and Shatsky, 1990; Shatsky et al., 1995; Dobretsov et al., 1995; Ernst et al., 1995; Kaneko et al., 2000; Maruyama and Parkinson 2000; Theunissen et al., 2000; Katayama et

al., 2000). Sobolev and Shatsky (1990) reported the occurrence of microdiamonds ( $<20$   $\mu\text{m}$  average diameter) in garnet–pyroxene and pyroxene–carbonate–garnet rocks, biotite gneisses and schists from the Kumdy-Kol locality (Fig. 1). The diamonds are preserved as inclusions in metamorphic porphyroblasts despite extensive retrograde metamorphism. Because of their persistence in minerals of metamorphic origin, e.g. garnet, clinopyroxene, and zircon, the diamonds were interpreted to have formed in situ during an episode of ultrahigh-pressure metamorphism (UHPM)

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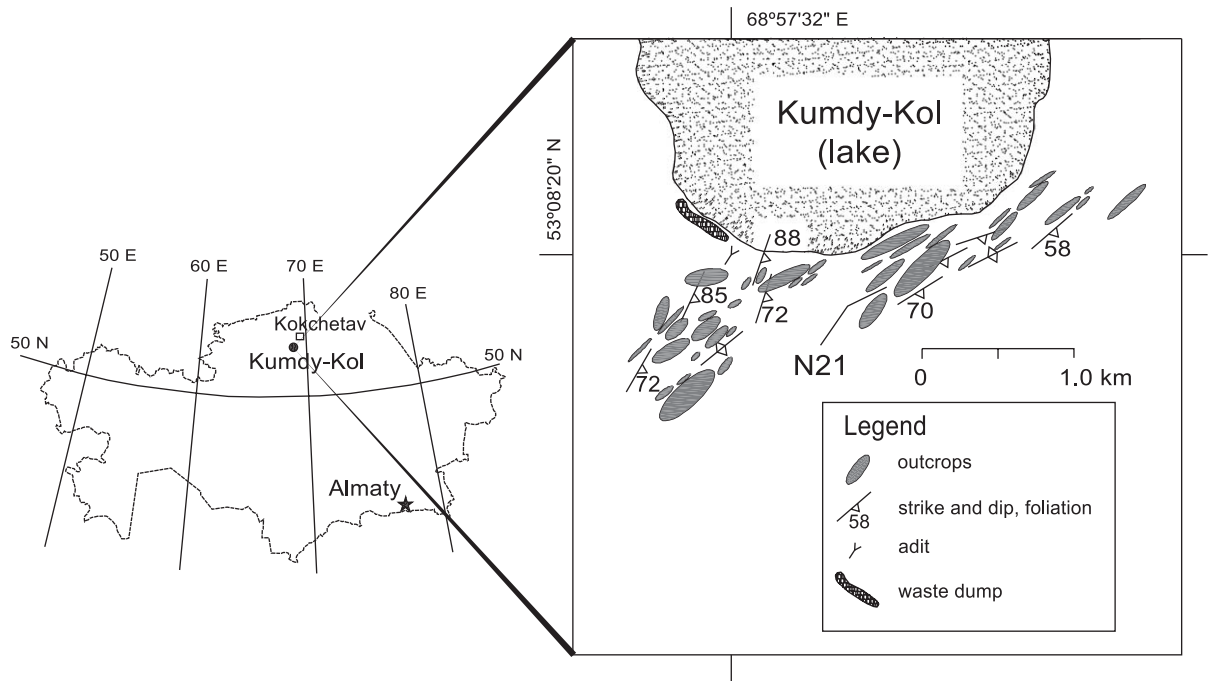


Fig. 1. Geologic map and sample locations of Kumdy-Kol, Kokchetav massif, Kazakhstan. Outcrops include eclogite, amphibolite, schist, gneiss, and carbonate (Kaneko et al., 2000, Fig. 5, pp. 270).

(Sobolev and Shatsky, 1990; Shatsky et al., 1995). The hypothesis of UHPM origin is an important one, not only for its implication of subduction and exhumation to and from unprecedented depths in the mantle, but also because of the increasing number of discoveries of microdiamond occurrences in metamorphosed crustal rocks (Xu et al., 1992; Dobrzhinetskaya et al., 1995; Massonne, 1998).

Not surprisingly, the proposal of diamond origin in UHP metamorphism has been subjected to evaluation. Petrologic study has shown that metamorphic  $P$ – $T$  conditions estimated from mineral assemblages of rocks in contact with diamond-bearing lithologies are within the stability field of diamond (Shatsky et al., 1995; Zhang et al., 1997; Okamoto et al., 2000). Kokchetav microdiamonds define a unique population in relation to other diamonds in their distinctive water and carbonate inclusions, nitrogen content,  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  values, and textural habits (De Corte et al., 1998, 2000; Cartigny et al., 2001). The presence or absence of diamond from adjacent rock types has been explained by local differences in fluid composition

(Ogasawara et al., 2000). It may be seen that diamond parageneses share much in common with other metamorphic minerals:  $P$ ,  $T$ , fluid composition as well as bulk rock chemical composition are seen as controlling factors. Nevertheless, these observations constitute a permissive test of consistency but not a definitive validation of an in situ UHP metamorphic origin for Kokchetav microdiamonds.

The C, O, and Sr isotopic study reported herein was undertaken as part of an ongoing study of UHPM carbonate rocks from Kumdy-Kol (Ogasawara et al., 1995, 1997, 2000, 2002). Samples and sample numbers are the same as those investigated by Ogasawara et al. (2000) and Katayama et al. (2000b). A complete isotope data set is archived in the MS thesis of M. Ohta, Waseda University, Tokyo, Japan. The isotopic results of this study, together with observations of mineralogical, textural, and structural retrograde metamorphic features, provide a detailed documentation of the intensity of retrograde metamorphism and isotopic metasomatism that followed UHP metamorphism.

## 2. Geologic occurrence of diamond-bearing carbonate rocks

The Kokchetav massif consists of metamorphosed Proterozoic protoliths encircled by the Ural–Mongolian fold belt of Caledonian rocks (Dobretsov et al., 1995). Calculated Nd model ages of massif rocks are as young as 800 Ma but are mostly in the range 1800–2700 Ma (Shatsky et al., 1999). The superjacent stratigraphic succession includes the Upper Proterozoic passive margin, platform sediments covered by Ordovician–Devonian island arc volcanics and sediments (Dobretsov et al., 1995). Rocks of the Kokchetav massif were subducted and metamorphosed in the upper mantle during a Cambrian collision of microcontinental and continental plates with the Siberian Craton. A detailed investigation of zircons from diamond-bearing biotite gneiss gave concordant U–Pb ages at 530 ( $\pm 7$ ) Ma, and this is interpreted as the age of coesite–eclogite and diamond–eclogite facies metamorphism (Claoue-Long et al., 1991). Spot analyses of zircons with a SHRIMP ion probe show U–Pb ages of 537 ( $\pm 9$ ) Ma (Katayama et al., 2001). Mineral isochrons of Sm–Nd measured on UHP metamorphic rocks record a metamorphic age of 524–535 Ma (Shatsky et al., 1999). Exhumation from mantle to crustal depths was evidently rapid because Ar–Ar ages of biotite and muscovite from diamond-bearing rocks are 517 ( $\pm 5$ ) Ma (Shatsky et al., 1999; cf. Hermann et al., 2001).

Pressure–temperature conditions at peak metamorphism of Kokchetav rocks are estimated to be within the stability field of diamond at 800–1000 °C and 40–60 kbars (Shatsky et al., 1995; Katayama et al., 2000a,b; Zhang et al., 1997; Okamoto et al., 2000; Ota et al., 2000). Recently, a minimum pressure of 60 kbars was proposed on the basis of excess Si in titanate (Ogasawara et al., 2002). Evidence of ultrahigh-pressure metamorphic conditions includes not only the presence of diamond but also coesite as inclusions in garnet, diopside, and zircon (Shatsky et al., 1995; Katayama et al., 2000a). A variety of petrological indicators including solid solution of K in diopside, Al in titanite, Na in garnet, coesite needles in titanite, and quartz exsolution from supersilicic clinopyroxene also suggest UHP conditions (Shatsky et al.,

1995; Zhang et al., 1997; Katayama et al., 2000b; Ogasawara et al., 2002).

There are two current tectonic interpretations of the Kokchetav massif. The tectonic mega-mélange model of Dobretsov et al. (1995) appeals to post-metamorphic deformation to account for a jumble of fault-bounded blocks carrying rocks of UHP and non-UHP metamorphic facies in close proximity. Diamond-bearing rocks are assigned to Unit I of the pre-metamorphic Zerenda series of Dobretsov et al. (1995). In a contrasting interpretation, a wedge-extrusion mechanism is held responsible for a stack of thin nappes resulting in such anomalous juxtapositions as andalusite–sillimanite pelites of the Dault series structurally underlying diamond- and coesite-bearing UHP rocks (Kaneko et al., 2000; Maruyama and Parkinson, 2000). Diamond-bearing rocks outcrop in Unit II of Kaneko et al. (2000). The data of this paper do not give a strong test of the competing tectonic hypotheses. The evidence of pervasive chemical, mineralogical, and isotopic alteration of diamond-bearing carbonates presented below is consistent with a UHP nappe overriding actively metamorphosing, actively dehydrating sediments during exhumation.

## 3. Methods of study

Most of the samples of diamond-bearing carbonate rocks were collected from mining dumps surrounding the mouth of an abandoned and sealed adit that was driven during an active phase of mineral exploration at Kumdy-Kol during the 1980s (Fig. 1). The disused adit was briefly opened and lighted to a depth of 300 m for the benefit of participants in the Fourth International Eclogite Field Symposium in 1999. This unique opportunity to sample in situ provided an important validation of the results of sampling in the waste dumps.

The Borovoye dolostones were collected 90 km east of Kumdy-Kol. The Borovoye data are included as examples of low-grade metamorphic carbonates for comparison to the diamond–eclogite carbonates of Kumdy-Kol (Table 1). The dolostones are assigned to Unit V of the pre-metamorphic Zerenda series of Dobretsov et al. (1995), a succession of low-grade metamorphosed quartzites, black shales, and dolomitic

Table 1  
Isotopic composition of samples

Locality/ rock type	Sample number	Mineral	$\delta^{18}\text{O}$ (VSMOW)	$\delta^{13}\text{C}$ (VPDB)	$^{87}\text{Sr}/^{86}\text{Sr}$
<i>Kumdy-Kol locality: diamond– and coesite–eclogite facies</i>					
<i>Dolomite marble I (+ garnet + diopside + diamond)</i>					
Waste dump	C 43	Dol	13.8	– 6.0	
		Cc	10.8	– 6.1	
		Cc	10.1	– 6.6	
		Dol	14.2	– 6.1	0.802553
Waste dump	C 45	Dol	14.4	– 4.3	
		Dol			0.771826
From adit	KK-4A	Cc	10.8	– 5.5	
From adit	KK-4B	Cc	9.4	– 3.6	
		Cc	9.1	– 3.6	0.751476
Waste dump	KK-4G	Cc	9.7	– 9.4	
Waste dump	KK-4H	Dol	13.1	– 7.0	
Waste dump	KK-4I	Dol	13.6	– 6.8	
Waste dump	KK-4J	Dol	13.3	– 4.0	
		Dol	13.0	– 4.0	
		Dol	12.7	– 3.9	
		Cc	10.7	– 6.1	
		Cc	11.1	– 6.3	
		Cc	11.1	– 5.5	
		Dol			0.774074
Waste dump	XX01j	Dol	13.9	– 4.4	
		Dol	13.9	– 4.4	
		Dol	14.7	– 4.3	
		Dol	14.7	– 4.0	
		Dol	14.7	– 4.1	
		Dol	14.8	– 3.9	
		Dol	15.2	– 4.0	
		Dol	15.4	– 4.3	
		Dol	15.1	– 4.3	
		Dol	14.3	– 3.9	
		Dol	14.1	– 4.3	
		Dol	13.8	– 4.4	
		Dol	14.0	– 4.3	
Waste dump	XX01k	Dol	15.3	– 4.4	
		Dol	14.8	– 4.3	
		Dol	14.6	– 4.2	
Waste dump	ZW 18	Cc	11.5	– 5.2	
		Cc	11.2	– 5.6	
		Cc			0.758362
From adit	ZW 20	Cc	11.0	– 5.3	
		Cc	11.0	– 5.3	
		Dol	13.9	– 5.3	

Table 1 (continued)

Locality/ rock type	Sample number	Mineral	$\delta^{18}\text{O}$ (VSMOW)	$\delta^{13}\text{C}$ (VPDB)	$^{87}\text{Sr}/^{86}\text{Sr}$
<i>Kumdy-Kol locality: diamond– and coesite–eclogite facies</i>					
<i>Dolomite marble I (+ garnet + diopside + diamond)</i>					
From adit	ZW 20	Dol	13.9	– 5.3	
		Dol			0.769999
		Cc			0.770420
From adit	ZW 21	Dol	9.8	– 5.2	
		Cc	11.1	– 5.3	
		Cc	11.3	– 6.0	
		Dol	9.6	– 5.5	
		Dol	9.6	– 5.4	
		Cc	11.0	– 5.4	
		Cc			0.753723
		Dol			0.751473
Waste dump	ZW 45	Dol	14.1	– 6.2	
		Dol	13.9	– 6.3	
		Cc	10.6	– 6.6	
		Cc	10.8	– 6.6	
		Dol			0.790403
		Cc			0.768389
Waste dump	ZW 46	Dol	13.9	– 5.1	
		Dol	14.2	– 5.0	
		Dol	14.3	– 4.8	
		Dol	13.7	– 4.6	
		Dol			0.775972
	ZW 47	Dol	14.0	– 4.4	
		Dol	14.6	– 4.1	
		Dol	14.2	– 4.0	
		Dol	14.2	– 4.8	
		Dol			0.775507
<i>Dolomite marble II (+ diopside + diamond)</i>					
Waste dump	C 46	Dol	18.0	– 1.4	
		Dol	18.2	– 1.5	
		Dol	17.1	– 1.6	
		Cc	14.8	– 1.8	
		Cc	15.1	– 1.8	
		Cc			0.774300
Waste dump	J 187	Dol	16.5	– 2.3	
		Cc	12.7	– 3.1	
		Cc	11.5	– 3.0	
		Dol	15.3	– 2.4	
		Dol	16.8	– 2.3	
		Cc	12.0	– 2.9	
		Dol			0.765496
		Cc			0.785009
Outcrop	N 21	Cc	14.6	– 2.5	
		Dol	18.6	– 1.5	
		Cc	14.4	– 2.5	
		Dol	18.2	– 1.5	
		Dol	18.2	– 1.9	

Table 1 (continued)

Locality/ rock type	Sample number	Mineral	$\delta^{18}\text{O}$ (VSMOW)	$\delta^{13}\text{C}$ (VPDB)	$^{87}\text{Sr}/^{86}\text{Sr}$
<i>Kumdy-Kol locality: diamond- and coesite-eclogite facies</i>					
<i>Dolomite marble II (+ diopside + diamond)</i>					
Outcrop	N 21	Cc	12.9	-2.8	
		Dol			0.777518
		Cc			0.772652
Waste dump	ZW 48	Dol	19.7	-2.2	
Waste dump	ZW 48-2	Dol	18.9	-2.4	
		Dol	19.7	-2.3	
		Cc	14.3	-1.1	
		Cc	13.6	-1.3	
		Dol	20.4	-1.0	
		Cc	13.0	-1.4	
		Dol	20.5	-1.5	
		Cc	13.6	-1.6	
		Dol			0.760648
		Cc			0.751491
<i>Dolomitic marble (+ diopside + forsterite + Mg - calcite)</i>					
Waste dump	KK-4M	Cc	13.3	-2.2	
Waste dump	Y 629	Dol	11.1	-2.0	
		Mg - cc	11.2	-1.9	
		Dol			0.726620
		Mg - cc			0.727265
Waste dump	Y 631	Mg - cc + dol	13.1	-1.8	
		Mg - cc + dol	12.4	-1.8	
		Mg - cc + dol	13.2	-1.6	
		Mg - cc + dol	12.2	-2.2	
		Cc	10.7	-5.9	
		Mg - cc + dol	12.9	-1.8	
		Mg - cc + dol	12.9	-1.7	
Waste dump	Y 647	Mg - cc + dol	13.0	-1.5	
		Mg - cc + dol	13.1	-1.5	
		Mg - cc + dol	12.3	-1.6	
		Mg - cc + dol	12.5	-1.8	
		Mg - cc + dol	12.6	-1.7	
Waste dump	Y 662	Mg - cc	10.7	-2.0	
		Mg - cc	10.7	-2.0	
		Dol	11.1	-1.9	
		Dol	10.6	-2.0	
Waste dump	Y 664	Mg - cc	11.3	-2.0	
		Dol	11.1	-2.0	
		Dol	11.4	-2.1	
Waste dump	Y 665	Mg - cc	11.3	-2.1	
		Dol	10.9	-1.6	
		Dol	11.9	-1.5	
		Mg - cc	12.9	-1.6	
		Dol	11.7	-1.6	
		Dol			0.789131
Waste dump	Y 676	Dol	11.1	-1.9	
		Dol	11.3	-1.8	

Table 1 (continued)

Locality/ rock type	Sample number	Mineral	$\delta^{18}\text{O}$ (VSMOW)	$\delta^{13}\text{C}$ (VPDB)	$^{87}\text{Sr}/^{86}\text{Sr}$
<i>Kumdy-Kol locality: diamond- and coesite-eclogite facies</i>					
<i>Dolomitic marble (+ diopside + forsterite + Mg - calcite)</i>					
Waste dump	Y 676	Mg - cc	11.3	-1.9	
		Mg - cc	11.3	-1.9	
		Dol			0.725952
		Mg - cc			0.727082
<i>Calcite marble (+ diopside + potassium feldspar)</i>					
Waste dump	J 76	Cc	11.0	-0.6	
		Cc	10.9	-0.7	
		Cc	11.1	-0.5	
		Cc	10.8	-0.8	
		Cc			0.719633
Waste dump	J 81	Cc	10.6	0.0	
		Cc	10.5	-0.1	
		Cc	10.6	-0.9	
		Cc			0.728213
<i>Burovoye locality: Late Proterozoic, low grade metasediments, 90 km East of Kumdy-Kol</i>					
<i>Dolostone</i>					
Outcrop	K 879	Dol	17.9	1.4	
		Dol	17.8	1.5	
		Dol			0.711923
Outcrop	K 882	Dol	24.4	3.1	
		Dol	24.6	3.2	
		Dol	25.5	2.9	
		Dol	24.8	3.3	
		Dol			0.709160
Outcrop	L 394	Dol	19.9	1.8	
		Dol	19.6	1.8	
		Dol	20.0	2.0	
		Dol	19.8	1.9	
		Dol			0.709540
Outcrop	L 396	Dol	17.7	0.1	
		Dol	20.6	4.7	
		Dol	19.8	4.7	
		Dol			0.711662
		Dol			0.711594
Outcrop	L 397	Cc (vein)	18.4	-3.6	
		Cc (vein)	16.7	-0.7	
		Dol	17.3	-1.7	
		Dol	17.0	0.2	
		Dol	17.1	0.5	
		Dol			0.712652

marbles of Neoproterozoic–Vendian age (Dobretsov et al., 1995).

Carbonate rocks were cut into 5 × 8 cm (approximately) slabs, polished, and stained with Alizarin Red S and potassium ferricyanide to distinguish dolomite

from calcite. The grain size of the carbonate minerals is sufficiently large (1 mm) that individual crystals could be sampled with a dentist's drill. Thus we obtained spatially resolved, mineral-specific analyses of individual layers and veins for most of the samples.

Powdered calcite and dolomite samples obtained by drilling stained slabs were reacted at 100 °C with 100% phosphoric acid. The acid fractionation factor of Swart et al. (1991) was used for calcite and that of Rosenbaum and Sheppard (1986) for dolomite. Analysis of standard reference materials gave for NBS-18,  $\delta^{18}\text{O}_{\text{VSMOW}} = +6.89\text{‰}$  and  $\delta^{13}\text{C}_{\text{VPDB}} = -5.17\text{‰}$ , and for NBS-19,  $\delta^{18}\text{O}_{\text{VSMOW}} = +28.50\text{‰}$  and  $\delta^{13}\text{C}_{\text{VPDB}} = +1.89\text{‰}$ . Recommended values for NBS-18 are  $\delta^{18}\text{O}_{\text{VSMOW}} = +7.35\text{‰}$  and  $\delta^{13}\text{C}_{\text{VPDB}} = -4.9\text{‰}$ , and for NBS-19,  $\delta^{18}\text{O}_{\text{VSMOW}} = +28.6\text{‰}$  and  $\delta^{13}\text{C}_{\text{VPDB}} = +1.95\text{‰}$  (Gonfiantini et al., 1995). The average and standard deviation for 28 analyses of a local working standard of calcite over the time interval during which the analyses were undertaken is  $\delta^{18}\text{O}_{\text{VSMOW}} = +18.9\text{‰}$  ( $\pm 0.2$ ) and  $\delta^{13}\text{C}_{\text{VPDB}} = -8.0$  ( $\pm 0.1$ ).

Powdered calcite and dolomite samples for Sr-isotope analysis were obtained by drilling and 3–5

mg were dissolved in 3 N  $\text{HNO}_3$ . Chemical separation of the strontium isotopes was achieved by elution through columns using Sr-Spec resin. The samples were re-dissolved in 0.5 N  $\text{HNO}_3$  and analyzed on the Plasma 54 Multicollector ICP-MS in static mode. Isotopic ratios were corrected for fractionation using  $^{86}\text{Sr}/^{88}\text{Sr} = 0.1194$  and an exponential fractionation law. Corrections were also made for Kr and Rb interferences using  $^{83}\text{Kr}$  and  $^{85}\text{Rb}$ . The average of four standards of the NIST strontium standard NBS 987 gave a value of  $^{87}\text{Sr}/^{86}\text{Sr} = 0.710238 \pm 0.000017$ .

#### 4. Field relations of diamond-bearing rocks

It is important to remember that the structural relations of most of the diamond-bearing carbonate samples are unknown because they were collected from waste dumps remaining after exploratory mining. Despite diligent searching, natural outcrops of diamond-bearing rocks were rarely found. Sample N21 (Figs. 1 and 2, Dolomite Marble II) is the only specimen in this study collected from a natural outcrop (Ogasawara et al., 2000; Katayama et al., 2000b). The adit, briefly re-opened in 1999, revealed the presence

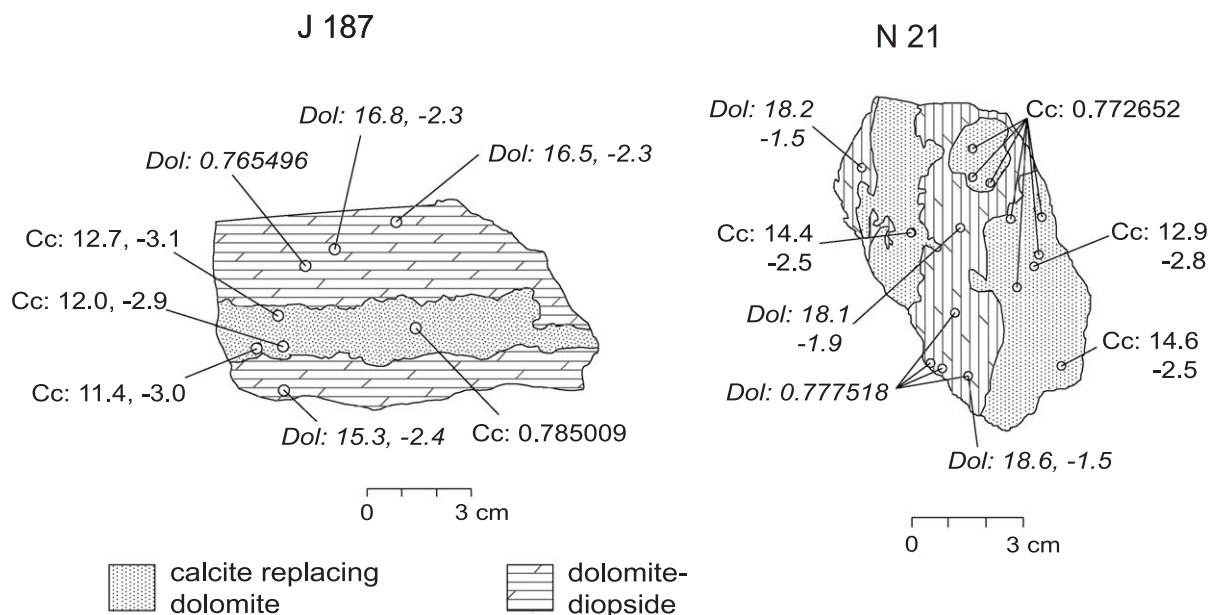


Fig. 2. Distribution of  $\delta^{18}\text{O}$ ,  $\delta^{13}\text{C}$ , and  $^{87}\text{Sr}/^{86}\text{Sr}$  in polished slabs of diamondiferous Dolomite Marble II (dolomite–diopside) from Kumdy-Kol.



of a 2-m-thick lens of Dolomite Marble I (defined below) with distinctive garnet porphyroblasts (samples KK-4A, ZW 20 (Fig. 3), and ZW 21, distance from tunnel mouth 302 m) in contact with garnet–biotite gneiss at the end of the cleared portion of the tunnel. This validates the origin of the waste dump samples of Dolomite Marble I. Other rock types and their observed thicknesses in the tunnel are garnet–biotite gneiss (30 m), muscovite–chlorite–actinolite–tourmaline–quartz rock (35 m), eclogite (2 m), and pyroxene–garnet–quartz rock (3 m) (descriptions and thicknesses courtesy of Shatsky and Sobolev). Microdiamonds occur in all of these rock types over a continuously exposed interval of 72 m in the tunnel walls (Shatsky and Sobolev, personal communication). Samples ZW 20 (Fig. 2) and ZW 21 have diamond inclusions in garnet confirmed by micro-Raman anal-

ysis. Tectonic contacts between rock types are evident in tunnel walls. Secondary calcite is found in a calcite-cemented vein breccia collected 240 m from the tunnel mouth (KK-4B).

Despite the difficulty of collecting diamond-bearing samples from outcrops and observing their relationships to other rock types and structures, a basic understanding of their field relations is provided by study of hand specimens. Evidences of mechanisms of mineralogical alteration are visible to the naked eye and widely prevalent. Two types of alteration processes operated in Kumdly-Kol rocks: (1) fluid flow in fractures as recorded by mineral vein fillings; and (2) fluid infiltration through permeable rocks as recorded by the replacement of dolomite by calcite. Sample KK-4J (Fig. 3) is an example of fracture-controlled fluid flow with accompanying infiltration. In KK-4J, a

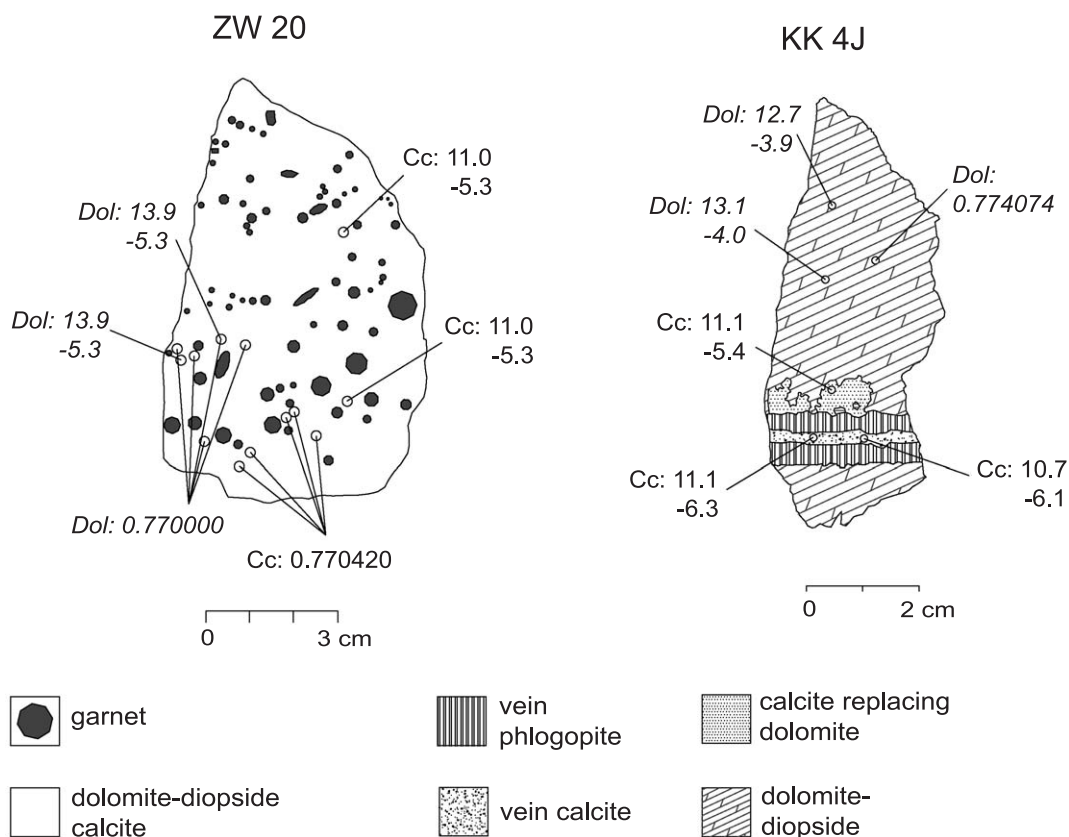


Fig. 3. Distribution of  $\delta^{18}\text{O}$ ,  $\delta^{13}\text{C}$ , and  $^{87}\text{Sr}/^{86}\text{Sr}$  in polished slabs of diamondiferous Dolomite Marble I (dolomite–garnet–diopside) from Kumdly-Kol.

mineralogically zoned calcite–phlogopite vein cross-cuts dolomite. Vein fluids broke out of the fracture, infiltrated wall rocks, and replaced dolomite with calcite (Fig. 3). Additional evidence of fluid flow in fractures was found outcropping in the wall of the adit in the form of a calcite-cemented vein breccia (sample KK-4B, depth 240 m). A mineralogical record of fluid infiltration along permeable layers is seen in samples J187 and N21 where calcite has preferentially replaced dolomite in layers resembling centimeter-thick bedding (Fig. 2).

## 5. Petrography of carbonate rocks

The diamond-bearing rocks of Kumdy-Kol have been assigned to Unit II of Kaneko et al. (2000). Carbonate rocks from the diamond locality at Kumdy-Kol were classified into four groups based on their petrographic features prior to carrying out isotopic analyses. As will become evident below, the four

groups of carbonate rocks, Dolomite Marble I, Dolomite Marble II, Dolomitic Marble, and Calcite Marble, define separate fields of data distribution when graphed on cross plots of  $\delta^{18}\text{O}$  vs.  $\delta^{13}\text{C}$ ,  $\delta^{18}\text{O}$  vs.  $^{87}\text{Sr}/^{86}\text{Sr}$ , and  $\delta^{13}\text{C}$  vs.  $^{87}\text{Sr}/^{86}\text{Sr}$  (Figs. 4 and 5). Note that the hand specimen evidence of alteration by fluid flow in fractures and along permeable layers described above is manifested in a thin section as replacement of primary assemblages of garnet, diopside, dolomite, and diamond by secondary phlogopite, tremolite, calcite, and graphite.

### 5.1. Dolomite Marble I (Fig. 3)

Dolomite Marble I is granoblastic with an average grain size of 1 mm and consists of dolomite (60% by volume), diopside (15%, 4-mm porphyroblasts), garnet (<10%, 6-mm porphyroblasts; grossular–pyrope dominant components), phlogopite (10%), and talc (<10%) (sample ZW 20, Fig. 3). There are small amounts of low-Mg calcite, microdiamond, and

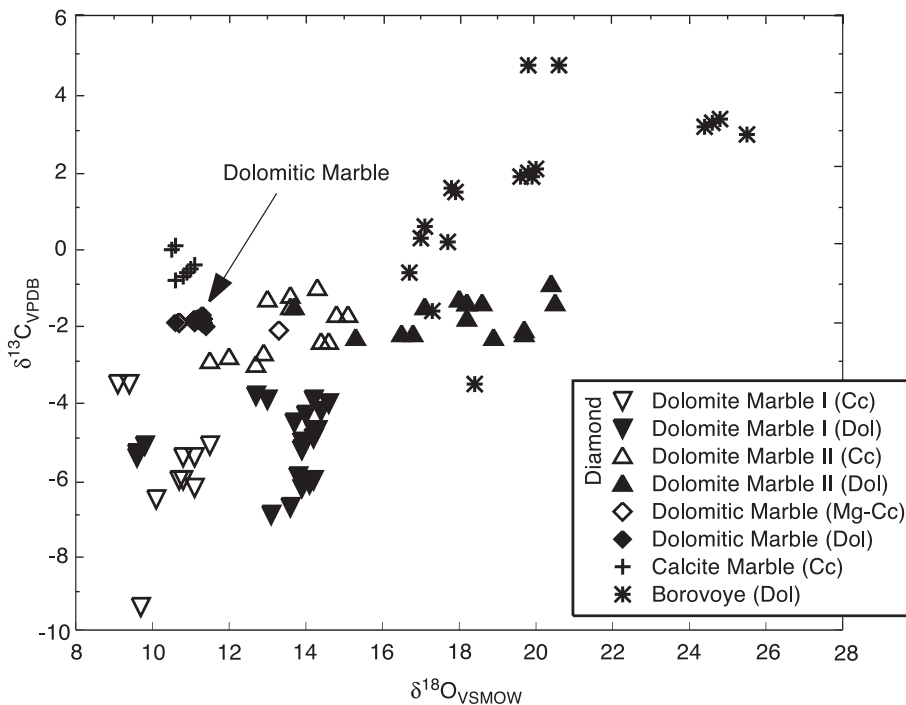


Fig. 4. Covariation of  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  in calcite and dolomite from Kumdy-Kol and Borovoye, Kokchetav massif, Kazakhstan. Borovoye samples are Neoproterozoic, low metamorphic grade dolostones outcropping 90 km east of Kumdy-Kol. The Borovoye data show distribution patterns typical of low-grade carbonates for comparison to the diamond–eclogite facies rocks of Kumdy-Kol.



graphite. Diamond is heterogeneously included in silicate porphyroblasts. A single garnet porphyroblast in sample ZW 46 contains over 1000 microdiamonds (Yoshioka et al., 2001). Hand specimens are massive to weakly banded. The UHP metamorphic assemblage is inferred to be dolomite–(aragonite)–diopside–garnet–diamond (Ogasawara et al., 2000). The former presence of aragonite–dolomite assemblages is suggested by inclusions of both dolomite and low-Mg calcite in diopside (Ogasawara et al., 2000). A calcite-cemented vein breccia (KK-4B) was found in the adit cross-cutting massive Dolomite Marble I (KK-4A). Phlogopite, tremolite, and calcite replace diopside, garnet, and dolomite. Diamond rimmed by graphite and graphite pseudomorphs after diamond are relatively abundant as inclusions in garnet but less prevalent in diopside.

### 5.2. Dolomite Marble II (Fig. 2)

Dolomite Marble II is a gneissic, layered rock lacking garnet, with a grain size of 1 mm. Representative layers consist of (A) dolomite (60%), diopside (30%, 4-mm porphyroblasts), and phlogopite (<10%), tremolite (<10%), or calcite (<10%) or (B) diopside (60%), calcite (20%), tremolite (10%), and phlogopite (10%). Calcite and tremolite are in reaction rims surrounding diopside. Microdiamond and graphite inclusions occur in diopside (Ogasawara et al., 2000).

### 5.3. Dolomitic Marble

Dolomitic Marble is massive, lacking both the weak foliation of Dolomite Marble I and the prominent layering of Dolomite Marble II. Its texture is granoblastic with a 1-mm grain size. Constituent minerals are Mg calcite (30%), dolomite (20%), forsterite (15%), diopside (<10%), Ti-clinohumite (<10%), a symplectite (10%) of diopside, spinel, and Mg calcite replacing garnet, and minor pyrrhotite, pyrite, and chalcocopyrite. Mg calcite inclusions in diopside have high MgCO<sub>3</sub> contents of 21.7 mol% (Ogasawara et al., 2000).

### 5.4. Calcite Marble

Calcite Marble is massive and granoblastic with 0.5–1.0-mm grain size. It consists of calcite (40%),

K-feldspar (30%), diopside (20%), a symplectite (<10%) of diopside and epidote, and minor quartz, phengite, and pyrrhotite.

## 6. Isotopic results

Samples of carbonate rocks for isotopic analysis were obtained by drilling, as described above, with the aim of acquiring data pertinent to the alteration history visible in hand specimen and in thin section. The use of chemical staining to distinguish between primary dolomite and secondary calcite made it possible to analyze them separately and to assess the degree to which isotopic equilibrium had been achieved between different generations of carbonate minerals. The isotopic data are discussed in relation to the petrographic classification of Kumdy-Kol carbonate rocks given in the previous section.

### 6.1. Dolomite Marble I

Dolomite Marble I has the lowest measured  $\delta^{13}\text{C}$  values found in Kumdy-Kol samples. The  $\delta^{13}\text{C}$  values range from  $-9.4\text{‰}$  (sample KK-4G) to  $-4\text{‰}$  (KK-4J and others). Fractionation of  $^{13}\text{C}/^{12}\text{C}$  between calcite and dolomite from the same hand specimen is irregular. In ZW 20 (Table 1; Fig. 4), calcite and dolomite both have  $\delta^{13}\text{C} = -5.3\text{‰}$ . Sample KK-4J has vein calcite with  $\delta^{13}\text{C} = -6.2\text{‰}$  and wall rock dolomite with  $\delta^{13}\text{C} = -4.0\text{‰}$ . Replacement calcite, infiltrating the wall rock from the vein, has an intermediate  $\delta^{13}\text{C}$  value of  $-5.4\text{‰}$  (KK-4J). Calcite from a vein breccia cross-cutting gneiss in the adit has  $\delta^{13}\text{C} = -3.6\text{‰}$  (KK-4B).

A striking feature of Dolomite Marble I is the strong oxygen isotope disequilibrium between coexisting dolomite and calcite (Table 1, Fig. 4). Dolomite is 3‰ enriched in  $\delta^{18}\text{O}$  in respect to calcite, in contrast to fractionations of 0.5‰, or less, measured in high grade metamorphic rocks (Sheppard and Schwarcz, 1970; Taylor and Bucher-Nurminen, 1986). A most extreme disequilibrium is observed in two samples collected in situ 301 m from the tunnel mouth at Kumdy-Kol (ZW 20 and ZW 21). Both of these samples have secondary calcite with similar  $\delta^{18}\text{O}$  values, but in ZW 20 (Fig. 4), dolomite

is enriched in  $^{18}\text{O}/^{16}\text{O}$  while in ZW 21 dolomite is depleted in  $\delta^{18}\text{O}$  relative to calcite.

The  $^{87}\text{Sr}/^{86}\text{Sr}$  values of dolomite and calcite from Dolomite Marble I rocks are the highest measured at Kumdy-Kol with values of 0.7500–0.8050; co-existing calcite–dolomite pairs differ by +0.0023 to –0.0220 in  $^{87}\text{Sr}/^{86}\text{Sr}$  (Fig. 5, Table 1).

## 6.2. Dolomite Marble II

Dolomite Marble II is higher in its  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values than Dolomite Marble I. Values of  $\delta^{13}\text{C}$  extend from –3 ‰ to –1 ‰ (Fig. 4, Table 1). The gneissic Dolomite Marble II rocks are the most heterogeneous in  $\delta^{18}\text{O}$  of all the diamond-bearing carbonates ranging from 11.5 to 20.5 (Table 1; Fig. 4). Oxygen isotopic disequilibrium between primary dolomite and secondary calcite is as strong or even stronger than in Dolomite Marble I. Dolomites from different layers differ in both  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  within the same hand specimen. The silicate-rich layers show more replacement calcite than silicate-poor layers, suggesting that infiltration was controlled by layering rather than

fractures. Sample N21 (Fig. 2) shows disequilibrium in  $\delta^{13}\text{C}$  between dolomite and calcite from contiguous layers, either reflecting pre-infiltration layer differences or implying that  $\delta^{13}\text{C}$  was fluid-dominated during infiltration.

Measured  $^{87}\text{Sr}/^{86}\text{Sr}$  values are 0.7515–0.7850 with calcite and dolomite from the same sample differing by +0.0195 to –0.0049 (Fig. 5; Table 1).

## 6.3. Dolomitic Marble

Dolomitic Marble has a limited range of variation in  $\delta^{13}\text{C}$ , –2.2 ‰ to –1.5 ‰, and in  $\delta^{18}\text{O}$ , +10.6 ‰ to +13.3 ‰ (Fig. 4; Table 1). The one exception, a single calcite analysis in Y631, resembles the vein calcite of KK-4J (see Dolomite Marble I) (Table 1). Dolomitic Marble is unusual in that four samples, Y 629, Y 662, Y 664, and Y 676, show virtually no fractionation of either  $^{18}\text{O}/^{16}\text{O}$  or  $^{13}\text{C}/^{12}\text{C}$  between coexisting dolomite and Mg calcite. Fractionations less than 0.5 are expected between coexisting carbonates at high temperature (Sheppard and Schwarz, 1970; Taylor and Bucher-Nurminen, 1986). Thus, Dolomitic Mar-

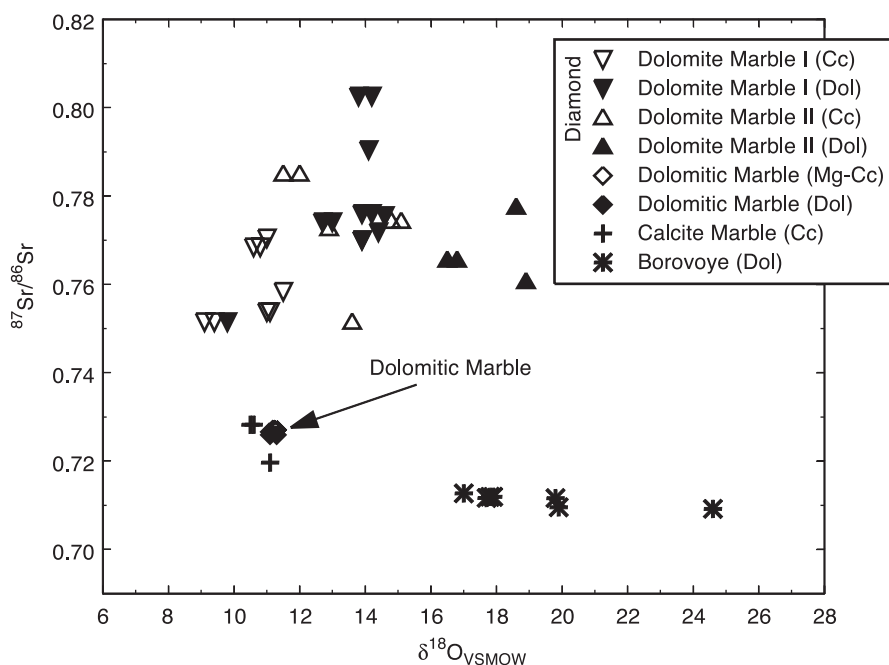


Fig. 5. Covariation of  $\delta^{18}\text{O}$  and  $^{87}\text{Sr}/^{86}\text{Sr}$  in calcite and dolomite from Kumdy-Kol and Borovoye, Kokchetav massif, Kazakhstan.

ble may preserve evidence of isotope equilibration at UHP metamorphic temperatures.

The  $^{87}\text{Sr}/^{86}\text{Sr}$  values, relatively homogeneous at 0.7259–0.7273, are lower than those of Dolomite Marble I and II. The low  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios correlate with a lack of secondary calcite (Fig. 5). Sample Y665 does not fully match the characteristics of the other samples and may represent incipient alteration, as may a single analysis of secondary calcite in Y 631.

#### 6.4. Calcite Marble

Calcite Marble resembles Dolomitic Marble in its  $\delta^{18}\text{O}$  and  $^{87}\text{Sr}/^{86}\text{Sr}$  but its  $\delta^{13}\text{C}$  values are 1 ‰ higher.

### 7. Discussion

The intensity of isotopic metasomatism affecting Kumdy-Kol rocks is high whether judged on the basis of C-, O-, or Sr-isotopes. Evidences visible in hand specimen and thin section suggest several controls on metasomatism. The presence of mineral-filled veins and associated wall-rock alteration demonstrates the important role played by fracture permeability in allowing access of externally derived fluids to the rocks following UHP metamorphism. Fluid infiltration along permeable layers is shown by the alteration of dolomite to calcite on a bed-by-bed basis in Dolomite Marble II rocks.

Metamorphic minerals such as garnet, diopside, and forsterite in Kumdy-Kol carbonate rocks record metamorphic devolatilisation reactions (Ogasawara et al., 2000) that may have had a profound impact on  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  values (Rumble 1982). Considering the trajectories on  $\delta^{18}\text{O}$  vs.  $\delta^{13}\text{C}$  diagrams of typical carbonate rocks undergoing metamorphic decarbonation–dehydration reactions, it is seen that measured values at Kumdy-Kol of  $\delta^{18}\text{O} = +8.5$  ‰ to  $+14$  ‰ and of  $\delta^{13}\text{C} = -4$  ‰ to  $-9$  ‰ (Dolomite Marble I) may have been greatly depleted in relation to marine carbonates as a consequence of devolatilisation (Valley, 1986; Baumgartner and Valley, 2001). A comparison with low-grade, metamorphosed Proterozoic dolostones from Borovoye (Fig. 4, Table 1) shows a trajectory similar to those attributed to metamorphic devolatilisation reactions (Valley, 1986).

The presence of dolomite indicates a potential for strong isotopic metasomatism prior to metamorphism during the diagenetic formation of dolomite from calcite (Yao and Demicco, 1997). Additional ambiguity in interpreting  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  values is introduced by coupled depletions in these isotope ratios observed in unmetamorphosed Neoproterozoic carbonates (Jacobsen and Kaufman, 1999), a stratigraphic interval that may overlap in part the age of Kumdy-Kol protoliths (Dobretsov et al., 1995). In summary,  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  values of Kumdy-Kol carbonates record strong metasomatic alteration but whether isotopic depletion date from the time of protolith deposition, diagenesis, or UHP metamorphism is obscured by alteration that took place following metamorphism.

The intensity of Sr-isotope metasomatism may be understood by comparison to Sr isotope variations measured on samples screened on the basis of Mn/Sr, Rb/Sr,  $^{18}\text{O}/^{16}\text{O}$ , and  $^{13}\text{C}/^{12}\text{C}$ . Samples selected in this way are believed to be little affected by diagenetic or metamorphic alteration (Derry et al., 1989). The stratigraphic age range chosen for comparison is the Proterozoic, an interval that corresponds to the age of Kokchetav protoliths (Dobretsov et al., 1995). Values of  $^{87}\text{Sr}/^{86}\text{Sr}$  in marine carbonates rise throughout the Neoproterozoic from 0.7060 to 0.7090 at the base of the Cambrian (Jacobsen and Kaufman, 1999). The diamond-bearing rocks of Dolomite Marble I and II have the highest measured  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios, from 0.7500 to 0.8050, greatly in excess not only of Neoproterozoic but also of Phanerozoic unmetamorphosed carbonate sections.

The Dolomitic Marble samples are unusual in that they appear to have largely escaped the effects of isotopic alteration so evident in Dolomite Marble I and II. These rocks retain mineral assemblages of Mg calcite and dolomite with  $^{18}\text{O}/^{16}\text{O}$  and  $^{13}\text{C}/^{12}\text{C}$  fractionations between the minerals appropriate to high temperature metamorphic conditions. The rarity of secondary low-Mg calcite and the observed low  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios support the interpretation that Dolomitic Marbles may record UHP, diamond-forming metamorphic conditions. Samples of Dolomitic Marble are known only from the waste dump, thus, its outcrop relationships are unknown. It is proposed as a working hypothesis that the rocks were preserved from alteration during exhumation owing to their isolation by distance from fluid-filled fractures.

## 8. Diamond–carbonate $^{13}\text{C}/^{12}\text{C}$ fractionations

The apparent carbon isotopic disequilibrium between bulk diamond and bulk carbonate measured by Cartigny et al. (2001) must be addressed because it bears upon the vital question as to whether Kumdy-Kol microdiamonds are of metamorphic or detrital origin (cf. De Corte et al., 1998). Bulk analyses of microdiamonds give  $\delta^{13}\text{C}$  values of  $-10.5\text{‰}$  and  $-10.2\text{‰}$  from garnet–clinopyroxene and garnet–clinopyroxene–dolomite rocks, respectively. Bulk carbonate analyses of the same rocks are  $-5.9\text{‰}$  and  $-4.3\text{‰}$   $\delta^{13}\text{C}$  (no distinction between calcite and dolomite is made by Cartigny et al., 2001). The measured carbonate–diamond  $^{13}\text{C}/^{12}\text{C}$  fractionations, 4.6 and 5.9, are significantly larger than values (e.g. 3.8 or less) expected at the high temperatures recorded by mineral geothermometers at Kumdy-Kol (Cartigny et al., 2001).

It must first be recognized that our data showing hand specimen-scale inhomogeneity in carbon isotopes of dolomite and calcite in diamond-bearing rocks imply that bulk analyses would average over some range of heterogeneity and, in the absence of systematic sampling, may represent a biased analytical result. The carbonate  $\delta^{13}\text{C}$  values reported by Cartigny et al. (2001), i.e.  $-5.9\text{‰}$  and  $-4.3\text{‰}$ , fall within the range measured for Dolomite Marble I, a group with a range in  $\delta^{13}\text{C}$  of from  $-9\text{‰}$  to  $-4\text{‰}$  (Fig. 4). Furthermore, it is clearly inappropriate on textural grounds to regard calcite–diamond as a coeval equilibrium assemblage. Beyond these considerations, however, is the consistent picture that emerges from both textural observations and our isotopic data of extensive secondary mineralogical and isotopic alteration of diamond-bearing carbonate rocks. Diamond was locked inside either garnet or diopside, relatively invulnerable to alteration. Primary matrix dolomite, however, was exposed to direct contact with infiltrating fluids. The high  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios in dolomites of Dolomite Marble I rocks demonstrate its vulnerability to post-metamorphic isotopic alteration. Thus, the carbon isotope ratios of bulk carbonate measured by Cartigny et al. (2001) do not necessarily represent the composition of primary dolomite at the time of peak UHP metamorphism. In this context, it is unremarkable that their bulk analyses of diamond and carbonate show  $^{13}\text{C}/^{12}\text{C}$  fractionations

that are too large for UHP metamorphic conditions. A definitive test of diamond–dolomite carbon isotope equilibration has yet to be made owing to the difficulty of analyzing micron-size samples: in situ analysis of adjacent microdiamond and dolomite grains included in garnet or diopside or analyses of dolomite inclusions in diamond are needed.

## 9. Conclusions

The observed correlation between petrographically classified groups of rock samples and isotopic properties leads to the conclusion that pre-existing mineralogical and structural rock properties exerted a control over the course of alteration during exhumation. Perhaps the most surprising conclusion is that microdiamonds are preserved inside porphyroblasts in the most isotopically altered carbonate rocks found at the deposit. The present data, which have a spatial resolution dictated by the 0.5-mm diameter of the drills used to obtain samples of individual minerals, are inadequate to make a definitive test of whether the diamonds are in carbon isotopic equilibrium with primary dolomite. From an isotopic perspective, the question of whether Kumdy-Kol microdiamonds are of UHP metamorphic origin remains an open question.

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