Low-temperature microdiamond aggregates in the Maksyutov Metamorphic Complex, South Ural Mountains, Russia

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ABSTRACT

The Middle Paleozoic Maksyutov Complex is an important component of the Eurasian collisional orogeny. It consists of dominant mica-rich garnet schist and mica-poor quartzofeldspathic gneiss enclosing minor mafic eclogite boudins (unit no. 1). Employing Raman spectroscopy, we identified three cuboidal microdiamond inclusions (~2–3 micrometers in diameter) in garnet hosts from two different mica-poor gneissic samples. Broad spectral bands and high magnification SEM images suggest that the cuboids are fine-grained nanocrystalline diamond aggregates characterized by limited long-range ordering. Their poor crystallinity is compatible with relatively low-temperature, solid-state growth in the absence of both melt and a C-O-H-N fluid. Poor crystallinity, and small grain size suggest that such aggregates may represent the lowest temperature microdiamonds yet identified in nature. Their formation required ultrahigh-pressures (UHP) at a minimum of 3.2 GPa, and a metamorphic temperature of ~650 °C. Blocky graphite up to 10+ mm across in the matrix of mica-rich carbonaceous garnet schist may represent pseudomorphs after much larger neoblastic diamonds. Thermobarometric calculations for analyzed coexisting garnet + omphacite + phengite from six Maksyutov unit no. 1 mafic eclogites indicate retrograde physical conditions of 610–680 °C, 1.7–2.6 GPa, slightly lower-pressure conditions than the coesite stability field. Complete conversion of diamond to blocky graphite in the mica-rich schists, and recrystallization of coesite to quartz in the schists, quartzofeldspathic gneisses, and eclogite pods reflect relatively slow exhumation from ~110 km depth to upper crustal levels over 60–90 m.y. Phengite inclusions in zircon and garnet hint at modest activity of H_2O during prograde UHP metamorphism of the eclogites and mica-poor gneisses. The latter have retained rare, tiny microdiamond inclusions in garnet on decompression. Abundant white mica in the carbonaceous garnet schists probably reflects a C-O-H-N fluid-mediated, kinetically enhanced prograde production of diamond, and efficient obliteration of this phase accompanying leisurely ascent of the subduction complex. In contrast, associated mica-poor gneisses and eclogites were relatively dry during exhumation, so retained rare nanocrystalline microdiamond inclusions in garnet.

INTRODUCTION

Crustal rocks recrystallized at confining pressures characterized by stabilities of the dense phases coesite and/or diamond are defined as ultrahigh-pressure (UHP) metamorphic rocks. *P-T* conditions required for the production of these polymorphs, as well as other UHP phase assemblages such as K-rich and/or supersilicic clinopyroxene and majoritic garnets, involve pressures of at least 2.7–3.2 GPa (Liou et al. 1988). Such minerals and assemblages indicate that lithologic materials initially formed near the surface of the Earth have been subducted to great depths, recrystallized under extreme conditions, and then exhumed through a process such as buoyancy-driven tectonic regurgitation (Ernst et al. 1997).

In the first reported occurrence in the world of UHP crustal rocks, Chesnokov and Popov (1965) described quartz textures that they interpreted as pseudomorphs after coesite in metabasaltic eclogite lenses from the Middle Paleozoic Maksyutov Complex in the Shubino area of the South Ural Mountains. Their conclusion was based on the presence of cracks radiating from SiO_2 inclusions in host garnets. Dobretsov and Dobretsova (1988) reported petrographic evidence of relict coesite in a jadeitic quartzite from the Karayanova area (Sakmara River), 35 km north of Shubino. However, later petrologic and structural studies (Matte et al. 1993; Beane et al. 1995; Lennykh et al. 1995) failed to identify the presence of UHP minerals in the Maksyutov Complex; these workers documented minimum physical conditions of metamorphism of 1.5–1.7 GPa and ~650 °C, derived by thermobarometric methods. Subsequently, Leech and Ernst (1998, 2000) described mm-to-cm-scale blocky graphite surrounded by quartz + mica pressure shadows in micaceous, carbonaceous metasedimentary units at Karayanova. The penetrative foliation of the mica schist wraps around the blocky graphite as if it had behaved as a hard, resistant phase during deformation. Leech and Ernst opined

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that the precursor mineral was probably neoblastic diamond, and because the C was inferred to have been biogenically produced ($\delta^{13}C = -33 \pm 9$, Leech and Erust 1998), a crustal portion of the Maksyutov Complex was postulated to have been subducted to great depth during putative UHP metamorphism. We speculate that the coarse grain size of the blocky C crystals may have been kinetically favored by prograde evolution of a C-O-H-N fluid in the mica-rich metasedimentary units. De Corte et al. (2000), Dobrzhinetskaya et al. (2001), and Imamura et al. (2002) have documented such a fluid composition as responsible for production of the richly diamondiferous metasedimentary rocks of the Kokchetav Massif, Northern Kazakhstan.

Employing thermotectonic modeling, Leech and Willingshofer (2001) demonstrated the possibility of these UHP conditions, based on available heat-flow and geochronologic data. Although it is plausible that the blocky graphite aggregates are pseudomorphs after diamond, based on somewhat similar morphologies in the Ronda and Beni Bousera peridotite massifs (Pearson et al. 1989; Davies et al. 1993), this interpretation has remained highly controversial due to the failure to identify any surviving UHP minerals. Moreover, based on petrologic and geochronologic study of several isotopic systems including new Rb−Sr data, Glodny et al. (2002) recently concluded that Maksyutov mafic eclogites and associated micaceous garnet schists were never subjected to UHP conditions.

Challenged and puzzled by the provocative occurrence of blocky graphite at Karayanova, we initiated detailed petrographic, SEM, electron microprobe, and micro-Raman investigations of inclusions in abundant garnet and sparse zircon separates from Maksyutov mafic eclogites and quartzofeldspathic gneisses. Our objective was to determine whether or not portions of the terrain could be proven to have attained UHP conditions. We did not investigate the micaceous schists because such lithologies apparently have back-reacted thoroughly on exhumation. The present study reports the discovery and documentation of three tiny, poorly crystallized microdiamond inclusions in neoblastic garnets from two different mica-poor gneissic rocks, so at least portions of the Maksyutov Complex evidently sustained lithostatic pressures in excess of 3.2 GPa. Therefore, the belt should be included in the growing list of continental collisional orogens now recognized to have been subjected to extraordinarily deep subduction prior to decoupling from the downgoing plate and returning to upper levels of the sialic crust.

GEOLOGIC RELATIONSHIPS

The high-pressure (HP) to ultrahigh-pressure metamorphic Maksyutov Complex, South Ural Mountains, Russia, is part of the Paleozoic Ural-Mongolian fold system (Sengör et al. 1993; Berzin et al. 1996). It forms an elongate north-south collisional belt marking the junction between the Siberian platform and Kazakhstan-North Tienshan microcontinent on the east, and the East European platform on the west (Zonenshain et al. 1984, 1990; Puchkov 1993; Matte 1995; Scarrow et al. 2002). The metamorphic terrain is bounded to the east by the Main Uralian fault, juxtaposing it against feebly recrystallized Ordovician-Silurian ophiolites and associated flyschoid sedimentary units. General geologic relations are shown in Figure 1.

The Maksyutov Complex consists of three superimposed lithotectonic members that together constitute a composite slab about 6–12 km in maximum aggregate thickness, and more than 120 km in length (Lennykh 1977; Moscovchenko 1982; Valizer and Lennykh 1988). The lithotectonic entities are characterized by contrasting mineral parageneses (Beane et al. 1995; Lennykh et al. 1995): (1) The polymetamorphic eclogitic mica schist, unit no. 1, underwent HP-UHP metamorphism, overprinted by later, lower-pressure assemblages; (2) The metaophiolite, unit no. 2, was subjected to blueschist-, then greenschist-facies metamorphism; and (3) the intermediate-grade Yumaguzinskaya unit, dominated by quartzite + mica schist, and lacking eclogitic lithologies, was subjected to blueschist-facies recrystallization. Unit no. 1 probably represents a fragment of the Late Proterozoic East European platform (Dobretsov and Sobolev 1984; Dobretsov et al. 1996). It consists of supracrustal, mainly pelitic + mica-poor quartzofeldspathic paragneisses, with much less abundant graphitic garnet-mica schists and boudins + tectonic blocks of mafic and rare ultramafic compositions. The eclogitic phase assemblages formed and incipiently recrystallized during deep-seated stages of decompression at about 375–390 Ma, as indicated by Sm-Nd bulk-rock data (Shatsky et al. 1997), $^{40}Ar/^{39}Ar$ phengite and U-Pb rutile data (Beane and Connelly 2000), Rb-Sr mineral systematics (Glodny et al. 2002), and U-Pb zircon dating (Leech
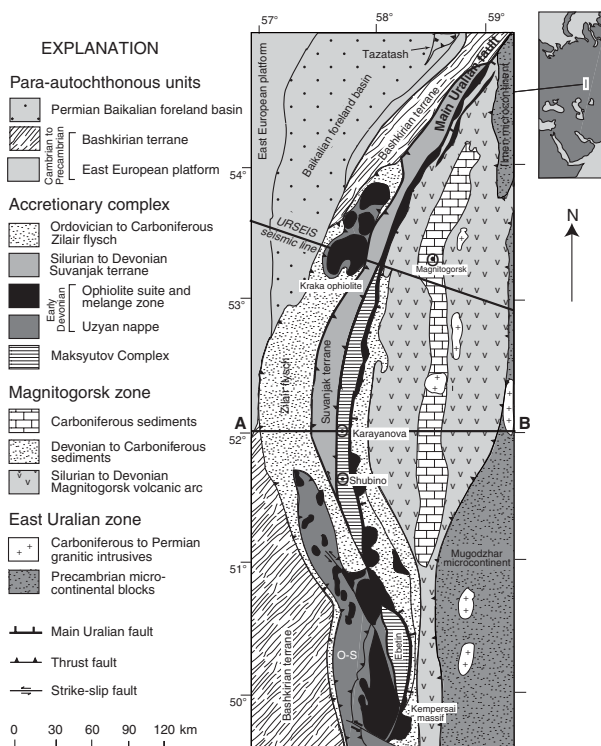

FIGURE 1. Geotectonic map of the South Ural Mountains, Russia, adapted from Leech and Stockli (2000). The Urals Reflection Seismic Experiment and Integrated Studies (URSEIS) transect, providing important depth control, and the geologic cross-section A-B of Figure 2 are indicated.

et al. 2002). Unit no. 2 consists of oceanic crust and associated sediments, and formed during Ordovician-Silurian seafloor spreading (Sm-Nd isochron obtained on oceanic greenstones; Edwards and Wasserburg 1985). The Yumaguzinskaya unit might represent Paleozoic subducted distal turbidites, but the origin of this entity is obscure.

Mineral parageneses for HP-UHP metamorphosed rocks of unit no. 1 described by Dobretsov et al. (1996) include: (1) coesite (chiefly pseudomorphs) + garnet + omphacite + rutile + zoisite; (2) jadeite + quartz + garnet + kyanite + paragonite; (3) garnet + omphacite + barroisite; and (4), garnet + glaucophane + lawsonite. Retrogression of unit no. 1, involving production of garnet + glaucophane schists, then greenschists, indicates a clockwise P-T trajectory (Beane et al. 1995). Ophiolitic unit no. 2 is characterized by serpentinite mélange containing lawsonite-bearing metarodingite and gabbroic amphibolite. Tabular lawsonite porphyroblasts have been replaced pseudomorphically by clinozoisite. Metamélanges contain blocks of ultramafic lithology, metabasaltic blueschists, and metasedimentary quartz-jadeite rocks.

The Ordovician-Silurian generation of Maksyutov unit no. 2 ophiolites, the deep subduction of unit no. 1, the mutual suturing of the Yumaguzinskaya, units no. 1 and no. 2, and the exhumation of this composite terrain from beneath the more easterly Devonian Magnitogorsk island arc were progressively younger Paleozoic events. UHP recrystallization in both Maksyutov and Kokchetav terrains probably reflects Early and Middle Paleozoic collisions of the East European platform along its eastern, passive margin with the Siberian platform and a salient of the more southerly Kazakhstan-North Tienshan microcontinental assembly (Shatsky et al. 1997; see also Friberg et al. 2002). The last stages of penetrative deformation and blueschist-facies metamorphism of the terrain amalgam at approximately 355 Ma (^{40}Ar/^{39}Ar mica data of: Matte et al. 1993; Beane and Connelly 2000) evidently were contemporaneous with continued subduction and accretion of in-
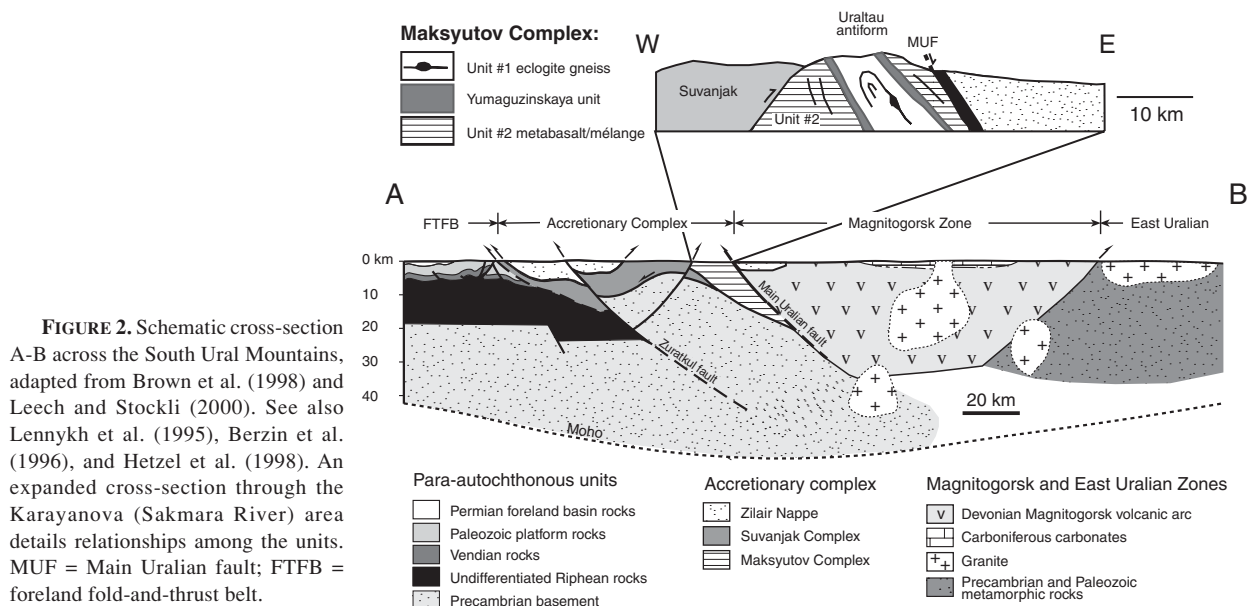
tervening intracontinental ocean crust as young as Late Silurian. This date provides only a younger age limit for the time of partial exhumation of the HP-UHP Maksyutov Complex; however, greenschist-facies metamorphism took place at about 335 Ma (Beane and Connelly 2000), by which time the complex was sequestered at mid-continental crustal levels. Continued exhumation to shallow depths at temperatures of ~110 °C (3–4 km), as determined by apatite fission-track data (Leech and Stockli 2000), occurred by about 300–315 Ma.

Dobretsov et al. (1996) conjectured that continuing deformation of the Maksyutov Complex was related to Early Permian sinistral strike slip along the Main Uralian fault. This transcurrent motion would reflect an important change in lithospheric plate kinematics, and might have been partly responsible for the gradual exhumation and surface exposure of subducted but buoyant, retrograde metamorphosed Maksyutov HP-UHP quartzofeldspathic rocks (Leech 2001). A cross-section utilizing both petrologic and seismic profiling data is presented as Figure 2. From the geologic mapping by Lennykh et al. (1995) and Brown et al. (1998), unit no. 1 appears to be no more than 2–3 km thick; thermotectonic modeling by Leech and Willingshofer (2001) suggests a possible 5 km maximum thickness for unit no. 1.

ANALYTICAL INVESTIGATIONS

Petrographic studies

Individual zircon and garnet mineral separations were made employing conventional physical separation techniques in order to search for micro-inclusions of coesite and/or diamond in these common "container" minerals. Parent eclogites, garnet-mica schists, and gneisses were not cut with a diamond-impregnated saw, but instead were mechanically crushed and sieved; powders were subjected to repeated magnetic and heavy-liquid separations until ~98% zircon and garnet concentrates were produced for analytical study. In all, only a few small zircon crystals were obtained from seven eclogite-facies rocks, but abundant garnet grains were concentrated from 26 samples. Monomineralic grain mounts were polished using Al$_2$O$_3$. At no stage were diamondiferous abrasives employed in treatment of the samples. Thus diamonds identified in these ex-

FIGURE 2. Schematic cross-section A-B across the South Ural Mountains, adapted from Brown et al. (1998) and Leech and Stockli (2000). See also Lennykh et al. (1995), Berzin et al. (1996), and Hetzel et al. (1998). An expanded cross-section through the Karayanova (Sakmara River) area details relationships among the units. MUF = Main Uralian fault; FTFB = foreland fold-and-thrust belt.

periments were derived from the host rock garnets. Furthermore, only inclusions that appeared to have smooth, continuous grain boundaries and no surface relief were chosen for further study.

The zircon samples include rare (<10) euhedral prisms, except for two samples containing ~50–100 crystals each. All grains exhibit sparse graphite inclusions and many fewer birefringent silicate inclusions. The latter are chiefly clinopyroxene, white mica, and quartz, with lesser amounts of rutile ± feldspar(s). No radial fractures in the host zircon prisms were observed in transmitted or reflected light.

Purified garnet grain mounts contain very abundant (50–200) sub- to euhedral crystals. Many birefringent silicate inclusions as well as a modest number of graphite inclusions are present; included mineral species are similar to those in the zircon prisms. Inclusions are especially abundant in small, sieve-textured garnet grains; fewer but larger inclusions characterize coarse-grained garnet euhedra. Peripheral fractures typify some of the garnets, but radial fractures are lacking, judging by both transmitted and reflected light observations.

SEM and electron microprobe studies

Zircon and garnet grain mounts previously studied petrographically were investigated using an electron microprobe, and a scanning electron microscope (SEM) equipped with an energy dispersive detector. Most secondary electron images were obtained using a JEOL JSM-5600, with an accelerating voltage of 15 kV. Select higher magnification images were obtained using an FEI model Serion instrument with an accelerating voltage of 5 kV. Microprobe and SEM techniques demonstrated the presence of a wide range of silicate and carbonaceous inclusions, especially in the sieve-textured garnets. Most abundant among the silicates were omphacitic clinopyroxene, quartz, phengitic mica, and feldspar(s). SEM also corroborated the conclusion made during reflected-light petrographic examination that radial cracks are essentially absent in the examined minerals; the fractures that are present do not emanate from the C or SiO_2 inclusions (Fig. 3). SEM study did, however, result in the identification of several small, cuboidal inclusions of C in garnets that required further investigation using Raman spectroscopy (Fig. 4). Although SEM alone could not provide crystal structure identification of C and SiO_2 polymorphs, three identified C inclusions represent poorly crystallized microdiamond, as described below.

RAMAN MICROPROBE STUDIES

Raman spectra of inclusions within the separated zircon and garnet grains were collected utilizing a Kaiser Hololab 5000 Raman microscope equipped with a 785 nm diode laser source. The spot size was 1 µm and the average incident intensity was approximately 30 mW at the sample, permitting rapid screening of carbonaceous inclusions. This spot size was sufficiently small that the spectra of inclusions were largely free of signal from the surrounding matrix of garnet. In all cases, the garnet Raman bands has maximum intensities less than 5–10% of the C peaks. However, for selected samples, the matrix signal was subtracted to facilitate spectral comparison. Laser power was reduced to <1 mW for some analyses to minimize sample degradation of some non-carbonaceous samples. This laser power is sufficiently low that polymorph transformation (which may occur for SiO_2 polymorphs) was not observed for any minerals. Spectra were collected with total integration times of about 200 seconds per point. Data were collected at approximately 1 cm^{-1} intervals and 4 cm^{-1} resolution.

The identities of selected micro-inclusions in host garnet and zircon concentrates were determined using a Raman microprobe by comparison with reference spectra. These surveys identified inclusions of graphite, quartz, monazite, feldspar(s), and muscovite; however, their large numbers made it necessary to screen the inclusions prior to analysis by Raman spectroscopy. Therefore, C inclusions of approximately cuboidal morphology were identified for further study using SEM methods. Nearly all of these carbonaceous inclusions were identi-
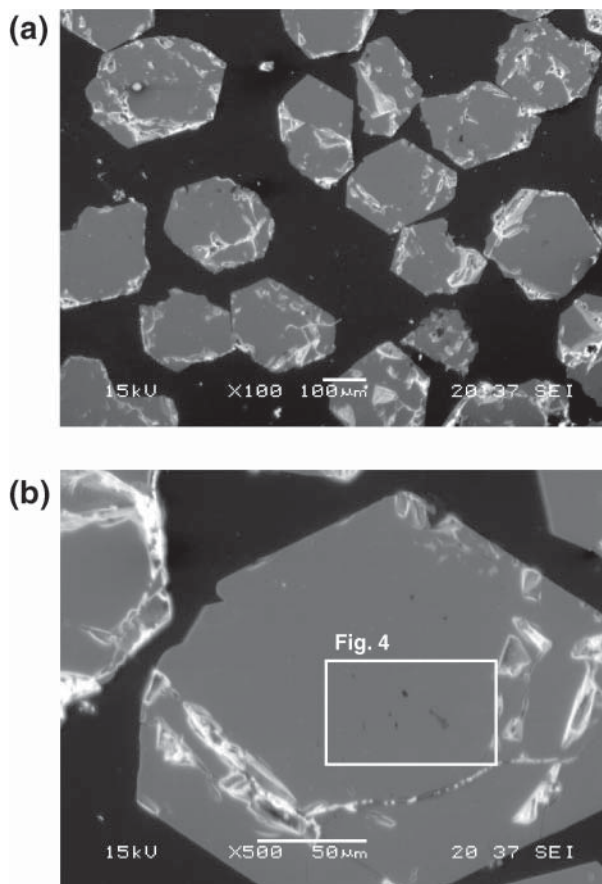

FIGURE 3. Scanning electron microscope image of surfaces of garnet crystals from specimen UM-5b, showing: (**a**) lack of radial fractures in several host garnets; and (**b**) garnet containing cuboidal carbon inclusion(s).
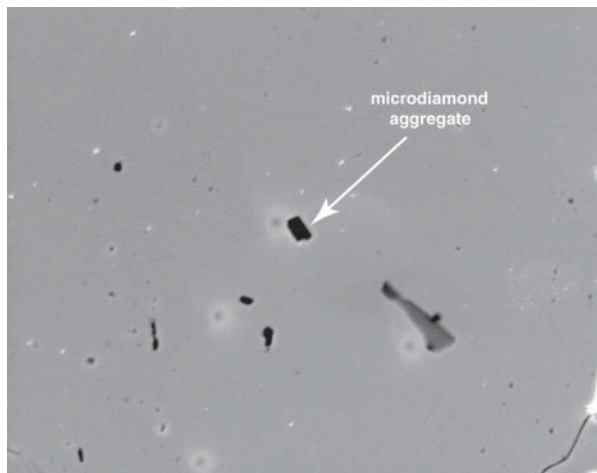

FIGURE 4. Scanning electron microscope image of a micrometer-scale cuboidal carbon inclusion in garnet from specimen UM-5b (see Fig. 3b). The Raman spectrum of this inclusion is shown in Figure 5.

fied as graphite using Raman spectroscopy. However, three 2–3 micrometer diameter C inclusions in three garnet grains examined by SEM techniques from two different eclogite-facies, mica-poor gneisses (samples UM-2a, and UM-5b; see Fig. 4) were identified as microcrystalline diamonds, based on the similarity of their spectra with those of other diamonds of extremely fine particle size. Sample Raman spectra of these cuboidal C inclusions are presented in Figure 5.

The spectra of these microcrystalline diamonds can be differentiated from those of other C phases based on the energy of their vibrations, with diamond scattering at about 1332 cm^{-1}, the single Raman band being attributed to the C-C bonding of sp^3-hybridized C. In contrast, well-crystallized graphite contains multiple spectral features, the largest of which is at 1581 cm^{-1} (the G-peak), with poorly ordered carbon (sp^2-hybridized) also scattering at about 1350 cm^{-1} (referred to as the D-peak; Wopenka and Pasteris 1993). The precise wavenumber of the D-peak is variable, depending on the laser wavelength (Pocsik et al. 1998; Matthews et al. 1999; Ferrari 2002). The micrometer-scale Maksyutov cuboidal inclusions exhibit a single spectral feature near 1350 cm^{-1} (1326, 1361, and 1370 cm^{-1}), and lack any sign of a G-peak. Although the band assignments vary somewhat from the standard due to limited crystallinity or other factors, these spectra can easily be differentiated from that of graphitic C (either amorphous or crystalline), which has multiple spectra bands, and a large spectral feature at about 1580 cm^{-1} that is absent entirely from these spectra (Fig. 5). In fact, the Raman shift observed in these spectra differs by about 20 cm^{-1} on average from that of diamond, but differs by over 200 cm^{-1} from that of the major spectral feature of graphite. Thus, these C inclusions are identified as microcrystalline diamond.

The spectral lines of these microcrystalline diamonds are markedly broadened and shifted relative to those of well-crystallized diamonds, due in part to the large contribution of surface states and disorder to the vibrational spectrum (Namba et al. 1992; Yoshikawa et al. 1993; Lipp et al. 1997; Prawer et al. 2000). Its extremely small grain size may account for the similarity of the spectrum of sample UM-2a to that of nanocrystalline diamond (Fig. 5). Although principally a function of the bonding and crystal structure, the position and the peak height/width ratio of the Raman spectrum is, to a lesser extent, related to the laser power and grain size of the target crystallites (Zhao et al. 1998; El Gorsey et al. 2001). For longer wavelength lasers such as that used in these experiments, the intensity of the G-peak decreases appreciably, and the position of the D-peak shifts to higher wavenumbers, in accordance with the trends observed in these spectra (Matthews et al. 1999). Elevated confining pressure may also cause a shift of the diamond line to higher wavenumbers (Xu and Mao 2000), partially accounting for the offset of the spectral feature from 1332 cm^{-1}. However, this pressure effect is unlikely to explain the observed Raman shifts for sample UM-5b, inasmuch as the present confining pressure would have to approach 10 GPa; the cuboids are at the surface of the host garnets, so such pressures would be totally unsustainable.

High-magnification SEM was used to examine the microstructure of microdiamond inclusions previously identified using Raman spectroscopy. Such observations (Figs. 6a and 6b) indicate that the inclusions are actually aggregates composed of much smaller crystallites or aggregates. The diameter of individual grains making up these aggregates is on the order of a few nanometers, consistent with the spectral broadening observed in the Raman spectra. Some aggregates appear to be cuboidal or even euhedral; such morphologies are also suggestive of diamond (or graphitic particles formed during retrograde metamorphism). Graphitic inclusions (Fig. 6c) typically have irregular borders, but are also aggregates of smaller crystallites. Some of these graphitic inclusions may have formed through retrograde metamorphism of microdiamond inclusions; unfortunately, we do not have sufficient data to determine whether this has occurred. These high-resolution SEM images support the conclusion drawn from Raman results that the inclusions consist of nanocrystalline diamond aggregates rather than representing a single, well-crystallized phase.

Additional considerations support the identification of microcrystalline diamond in these Maksyutov Complex rocks. Most importantly, the elemental analysis performed on the SEM restricts possible phases present to those containing C, or C and H (H cannot be detected directly by the SEM). There are three stable C phases, diamond, graphite, and fullerenes (e.g., C_{60}). Graphite and fullerenes are composed of sp^2-hybridized C, and have appreciably higher energy C-C bonds, with a bond order of 1.5, resulting in multiple Raman bands. This energy is much lower than for C-C single bonds for diamond spectra, or for the diamond inclusions identified in this study. Hydrocarbon inclusions also contain C-C single bonds, but can be disregarded based on Raman spectroscopy; the spectra of the three diamond micro-inclusions contain only a single feature, whereas hydrocarbons contain a variety of nonequivalent C-C bonds, and thus have multiple Raman spectral features. Consequently, the combination of SEM and Raman microanalysis supports the conclusion that these cuboids are very poorly ordered microdiamonds.

We also attempted to identify other UHP mineral inclusions (e.g., coesite) in these samples by Raman spectroscopy; however, we were unsuccessful. Although no other UHP polymorphs were identified, it is conceivable that they were present but not detected due to a limited sample size, or that they were not stable under the experimental conditions that were used. For example, coesite is rapidly converted to quartz under high laser power (>0.5 mW).

INTERPRETATION OF THE RAMAN SPECTRA

The broad bands in the Raman spectra obtained in this investigation indicate that the studied Maksyutov microdiamonds are poorly crystallized, very fine-grained, microcrystalline aggregates rather than single, well-ordered crystals (see also Fig. 6a). These microcrystalline aggregates may be the result of either: (1) the incomplete prograde UHP formation of diamonds typified by limited long-range ordering or (2) retrograde transformation of pre-existing well-crystallized diamonds during exhumation. Kinetic data suggest that the incomplete crystallization of diamonds from a carbonaceous substrate is most likely. An extremely high activation energy is required for the C polymorphic transition [148 kJ/mol to produce diamond (Solozhenko et al. 2002), vs. 22 kJ/mol for the dehydrogena-

tion of organic C (Dalla Torre et al. 1997)]. Consequently, the formation of microdiamonds from the original organic C would be very slow; moreover, a conjectured retrograde graphitization of well-ordered diamonds probably would not result in the preservation of relict, poorly crystalline microdiamonds.

The formation of microdiamonds characterized by limited long-range order would be plausible in the light of relatively low temperatures, and thus a sluggish rate of prograde transformation at Maksyutov. Kimberlitic diamonds (1100–1200 °C), as well as microdiamonds produced in the anatectic gneisses of the Kokchetav Massif (900–1000 °C) and most other microdiamond-bearing complexes, evidently formed in the presence of a melt or a highly charged fluid phase (Dobretsov et al. 1995; Shatsky et al. 1999) that facilitated diamond growth. For such upper mantle and UHP gneisses/granulites, C-O-H-N fluids associated with melts evidently were responsible for the transformation of graphite to well-ordered diamond (Larsen et al. 1995; Dobrzhinetskaya et al. 1995, 2001; Pal'yanov et al. 1999, 2002). In contrast, much lower thermobarometric *P-T* values suggest that Maksyutov eclogite-facies cuboids (both microcrystalline aggregates and large—now graphitic—blocky intergrowths) grew under subsolidus temperature conditions (Beane et al. 1995; Lennykh et al. 1995). Additionally, only very small amounts of an aqueous fluid accompanied UHP metamorphism of the mafic pods and mica-poor gneisses (Leech and Ernst 2000; Glodny et al. 2002); thus, at Karayanova, such fluids would not be widely available to catalyze diamond formation in the eclogites and mica-poor quartzofeldspathic gneisses, which produced only rare, tiny microcrystalline diamond aggregates. However, C-O-H-N fluids were undoubtedly abundant during prograde metamorphism of the richly micaceous graphitic metasedimentary lithologies—apparently favoring the growth of blocky diamonds in the garnet-mica schists—as well as their later total retrogression.

Retrograde transformation of diamonds into microdiamonds also may have occurred. There is some textural evidence for this hypothesis: the microdiamond inclusions identified by Raman spectroscopy have roughly cuboidal morphologies suggestive of a well-crystallized relict morphology. However, the cuboidal morphology is lacking for most inclusions, including graphitic inclusions, suggesting that the C in these samples was not uniformly crystalline, and that some poorly crystalline inclusions probably were still present prior to retrograde transformation. Additionally, the lack of a defined G-peak indicates that few of the microdiamond aggregates have been transformed to graphitic C. An alternative (but untested) possibility to explain the cuboidal morphology of the inclusions is that the microdiamonds can be packed into aggregates with regular morphology.
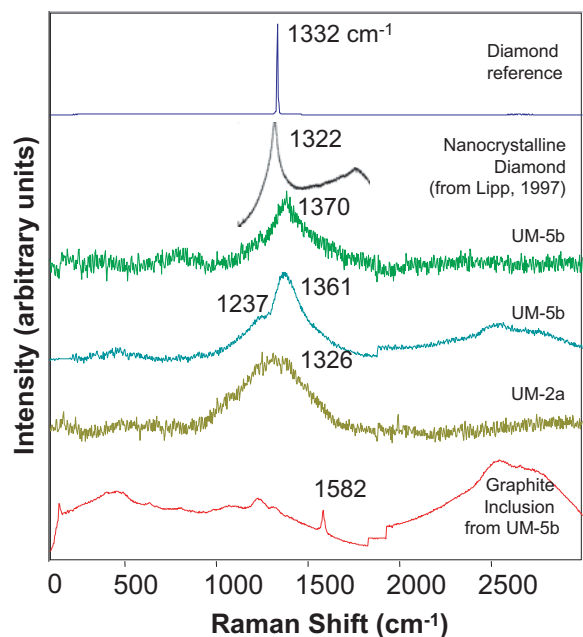

FIGURE 5. Raman spectra of microdiamond aggregates in three different inclusion-bearing garnets, two host garnets from specimen UM-5b (the green spectrum is of the C inclusion pictured in Fig. 4), and one host garnet from specimen UM-2a. The broad feature near 1350 cm^{-1} is attributed to diamond (sp^3-hybridized C). For comparison, spectra of a well-crystallized reference diamond and that of a nanocrystalline diamond (Lipp et al. 1997) are also shown. A graphite inclusion from specimen UM-5b is also illustrated, with a typical sp^2-hybridized C-C stretch at 1582 cm^{-1} (G-peak).
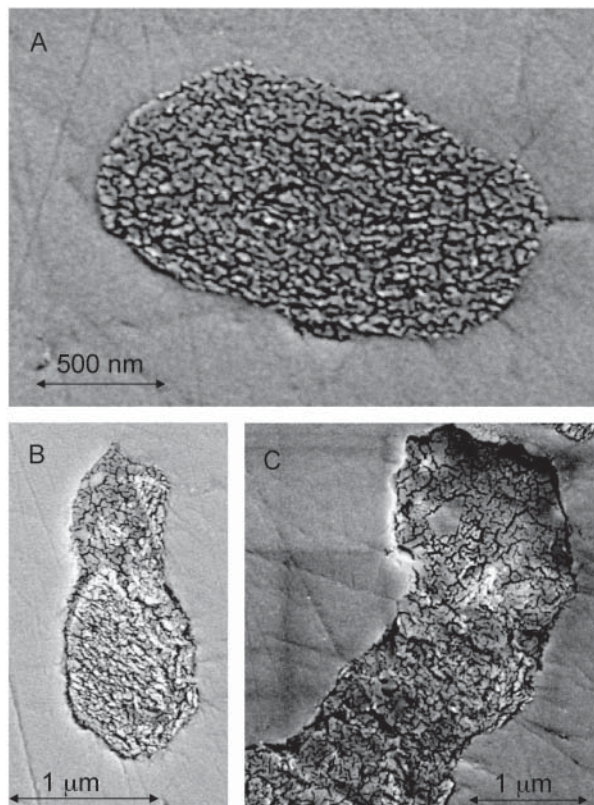

FIGURE 6. High magnification (30 000 × magnification) SEM images of microdiamond aggregates in UM-5b (A, B) and a graphitic C aggregate (C). The small crystallites that comprise the C inclusions are apparent in each image. Note the burn marks from the Raman microprobe for the graphite inclusion.

TABLE 1. Thermobarometric calculations for Maksyutov mafic eclogites employing the method of Carswell et al. (1997) and the garnet mixing model of Berman (1990)

Karayanova (Sakmara River locality)

UM-1a	610 °C,	2.37 GPa	garnet core, omphacite matrix
UM-3a	610 °C,	2.17 GPa	garnet core, omphacite inclusion
UM-3a	610 °C,	2.15 GPa	garnet rim, omphacite matrix
MC-98	610 °C,	1.87 GPa	garnet rim, omphacite matrix

Shubino (coesite pseudomorph locality of Chesnokov and Popov 1965)

UM-21	680 °C,	2.62 GPa	garnet core, omphacite inclusion
MC-161	610 °C,	1.71 GPa	garnet rim, omphacite matrix

Notes: Microprobe analyses of coexisting garnet + omphacite + phengite from Beane et al. (1995) and Leech and Ernst (2000).
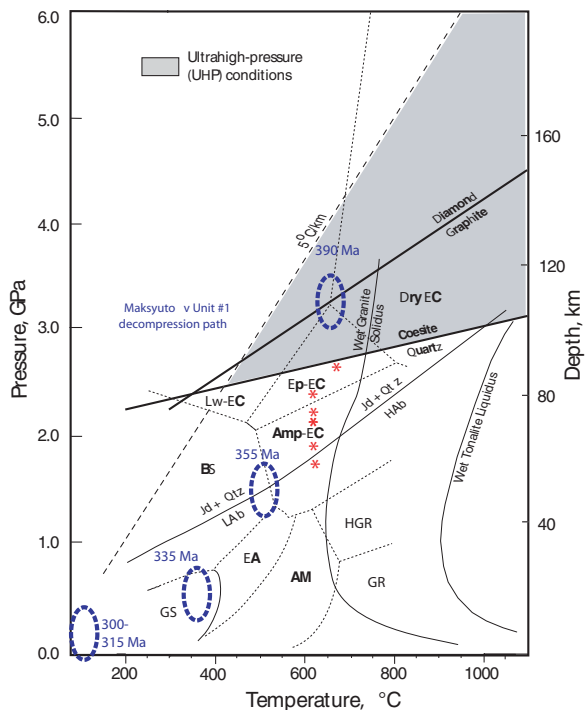

FIGURE 7. Petrogenetic grid for metabasaltic bulk-rock compositions (Liou et al. 1998; Okamoto and Maruyama 1999). A very low subduction-zone geothermal gradient of 5 °C/km is also shown. See Liou et al. (1998) for citations to experimental data for subsolidus phase transitions and the onset-of-melting curves. Metamorphic facies abbreviations are: AM = amphibolite; Amp-EC = amphibolite-eclogite; BS = blueschist; EA = epidote amphibolite; EC = eclogite; EP-EC = epidote-eclogite; GR = sillimanite-bearing granulite; GS = greenschist; HGR = kyanite-bearing granulite; P = prehnite; PA = pumpellyite-actinolite; PP = prehnite-pumpellyite; and ZE = zeolite. *P-T*-time stages in the metamorphism of the microdiamond-bearing Maksyutov Complex unit no. 1 rocks from the Shubino and Karayanova areas are indicated, based on geochronologic data of Shatsky et al. (1997), Beane and Connelly (2000), Leech and Stockli (2000), Glodny et al. (2002), and Leech et al. (2002). Asterisks indicate thermobarometric results from six garnet + omphacite + phengite-bearing eclogites (Table 1).

NEW THERMOBAROMETRIC COMPUTATIONS

In the absence of clear proof for the existence of UHP phases at Maksyutov, calculations of attending metamorphic conditions by Dobretsov and Dobretsova (1988), Beane et al. (1995),

Lennykh et al. (1995), and Leech and Ernst (2000) yielded similar minimum *P-T* values of 1.5–1.7 GPa, 600–650 °C. These workers emphasized that documentation of relict coesite and/ or diamond would require minimum pressures of 2.7–3.2 GPa. Our discovery of microdiamond inclusions in Maksyutov eclogite-facies garnets indicates that some of the mica-poor quartzofeldspathic gneisses within unit no. 1 must have been subducted to depths of at least 110 km. The presence of much larger blocky aggregates of graphite, occurring as a matrix phase in the carbonaceous, mica-rich garnet schists, suggests that metasedimentary members of unit no. 1 were subjected to the same conditions of deep underflow and metamorphism within the diamond *P-T* stability field (Leech and Ernst 1998), but at elevated aqueous fluid pressures.

As noted earlier, most of the investigated Maksyutov rocks have been pervasively back-reacted to lower-pressure phase assemblages. However, six phengite-bearing mafic eclogites appear to have been altered only slightly, hence we employed the thermobarometric program of Carswell et al. (1997) in conjunction with the garnet mixing model of Berman (1990) in order to determine the physical conditions of last re-equilibration. The Fe^{3+} content of the omphacitic clinopyroxene was estimated assuming that Fe^{3+} was equal to the excess of Na over Al. Table 1 presents computed *P-T* conditions. Pressures range from 1.7 to 2.6 GPa at temperatures of 610–680 °C (Beane et al. 1995; Lennykh et al. 1995; Leech and Ernst 2000). Assigned *P-T* values are shown on the petrogenetic grid of Figure 7. All eclogite samples lie in the high-pressure part of the graphite + quartz field except for specimen UM-21 from Shubino. This latter assemblage falls in the quartz field but adjacent to the coesite field boundary. This specimen involves a garnet core + clinopyroxene inclusion + phengite; clearly, retrogression was well underway for most analyzed assemblages—especially those involving garnet rims—but because of short diffusion paths, was not far advanced for core phases of UM-21, and, to a lesser extent, UM-1a and UM-3a.

PETROTECTONIC IMPLICATIONS

The Raman microprobe documentation of cuboidal microdiamond aggregates occurring as tiny inclusions in garnets indicates that mica-poor gneissic rocks (unit no. 1) from the Karayanova area of the Maksyutov Complex underwent UHP conditions during Middle Devonian subduction-zone metamorphism. This finding supports an earlier, controversial interpretation of neoblastic diamond pseudomorphs up to 10+ mm across in the matrix of mica-rich Karayanova schists enclosing mafic eclogite boudins (Leech and Ernst 1998). The hypothesized coarser grained diamonds are now represented by blocky graphite intergrowths. Garnet-clinopyroxene-phengite thermobarometry for eclogitic lithologies from both Shubino and Karayanova indicates physical conditions of 610–680 °C, 1.7–2.6 GPa, close to the coesite *P-T* field of stability (i.e., slightly retrogressed).

The rare preservation of microdiamond inclusions in refractory host garnets and the apparently total recrystallization of coesite to quartz reflect a lengthy period of decompression. Geochronologic evidence for intermediate stages of exhumation indicates that ascent from deep-seated to upper crustal lev-

els took place first more rapidly, then more slowly between 389–390 to 300–315 Ma (Matte et al. 1993; Shatsky et al. 1997; Beane and Connelly 2000; Leech and Stockli 2000; Leech and Willingshofer 2001; Glodny et al. 2002; Leech et al. 2002). This 75–90 m.y. ascent history, illustrated schematically in Figure 7, may reflect arrested development of the Uralian orogen, reflecting its thickened crustal root (Berzin et al. 1996; Brown et al. 1998; Knapp et al. 1998; Leech 2001; Scarrow 2002 et al.). It seems likely that the decompression-induced transformation of coesite to quartz proceeded much more rapidly than the conversion of diamond to graphite (Leech and Ernst 1998; Ernst et al. 1998).

The presence of phengite inclusions in the studied zircons and garnets implies at least a modest activity of H_2O during UHP metamorphism of the mafic eclogite and mica-poor quartzofeldspathic gneiss terrain. The associated carbonaceous, micaceous garnet schists would have generated a voluminous C-O-H-N fluid during prograde recrystallization/devolatilization; remaining aqueous fluid present during relatively slow decompression would be expected to catalyze the conversion of coarse groundmass diamond to graphite, and coesite to quartz (Rubie 1986, 1990; Mosenfelder and Bohlen 1997). The preservation of rare microdiamond inclusions in refractory (i.e., slow diffusion) garnets suggests that the mica-poor gneisses were virtually dry during their ascent to upper crustal levels.

Finally, limited long-range order and small grain size of the microdiamond aggregates suggest that these carbon cuboids may represent the lowest temperature microdiamonds yet identified in nature.

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