

Crystallization environment of Kazakhstan microdiamond: evidence from nanometric inclusions and mineral associations

L. F. DOBRZHINetskAYA¹, H. W. GREEN^{1,2}, K. N. BOZHILov^{1,2}, T. E. MITCHELL³
AND R. M. DICKERSON³

¹Department of Earth Sciences, ²Institute of Geophysics and Planetary Physics, University of California, Riverside, CA, 92521, USA (Larissa@ucr.ac1.ucr.edu)

³Science and Technology Division, Los Alamos National Laboratory, Los Alamos, NM, 87545, USA

ABSTRACT Nanometric solid inclusions in diamond incorporated in garnet and zircon from felsic gneiss of the Kokchetav massif, Kazakhstan, have been examined utilizing electron microscopy and focused ion beam techniques. Host garnet and zircon contain numerous pockets of multiple inclusions, which consist of 1–3 diamond crystals intergrown with quartz, phengite, phlogopite, albite, K-feldspar, rutile, apatite, titanite, biotite, chlorite and graphite in various combinations. Recalculation of the average chemical composition of the entrapped fluid represented by multiple inclusion pockets indicates that such fluid contained a low wt% of SiO₂, suggesting a relatively low-temperature fluid rather than a melt. Transmission electron microscopy revealed that the diamond contains abundant nanocrystalline inclusions of oxides, rare carbonates and silicates. Within the 15 diamond crystals studied, abundant inclusions were found of SiO₂, TiO₂, Fe_xO_y, Cr₂O₃, ZrSiO₄, and single grains of Th_xO_y, BaSO₄, MgCO₃, FeCr₂O₄ and a stoichiometric Fe-rich pyroxene. The diversity of trace elements within inclusions of essentially the same stoichiometry suggests that the Kokchetav diamond crystallized from a fluid containing variable amounts of Si, Fe, Ti, Cr, Zr, Ba, Mg and Th and other minor components such as K, Na, P, S, Pb, Zn, Nb, Al, Ca, Cl. Most of the components in crystals included in diamond appear to have their origin in the subducted metasediments, but some of them probably originate from the mantle. It is concluded that Kokchetav diamond most likely crystallized from a COH-rich multicomponent supercritical fluid at a relatively low temperature (hence the apparently low content of rock-forming elements), and that the diversity of major and minor components suggests interactions between subducted metasediments and mantle components.

Key words: COH-fluid; Kazakhstan microdiamond; nanoinclusions; oxides; subduction.

INTRODUCTION

Metamorphic diamond is testimony to exhumation of rocks from depths in excess of about 120 km, and the inclusions within them are pristine witnesses to the chemical environment of the medium from which the diamond crystallized. Diamond is the strongest mineral and is essentially inert in rocks, hence it resists chemical reaction with its host or included minerals both during residence at depth within the diamond stability field and during ascent to the Earth's surface. Therefore, diamond is the most reliable sampling container for transporting fluid and solid crystalline material from depth within the Earth to the surface (e.g. Moore & Gurney, 1985; Navon *et al.*, 1988; Navon, 1991; Harte & Harris, 1994; Joswig *et al.*, 1999; Gillet *et al.*, 2002). Zircon is less strong than diamond, allowing cracking and interaction of inclusions with subsequent environments, but it, too, is chemically inert and therefore an excellent container for diamond and other associated inclusions. In contrast, garnet is not an inert container because it may

react readily with silicates included along with diamond and/or with trapped droplets of fluid or melt, to produce a diversity of multiphase silicate and oxide inclusions during the entire metamorphic history of the rocks (e.g. Dobrzhinetskaya *et al.*, 2001a; Stöckhert *et al.*, 2001).

Microdiamonds from ultra-high pressure terranes are usually reported as inclusions only in refractory minerals such as garnet and zircon (also kyanite). However, diamond from the Kokchetav massif is also found as inclusions in diopside, biotite after phengite, quartz, and at grain boundaries (Dobrzhinetskaya *et al.*, 1994). The latter microstructural locations clearly indicate that diamond can be preserved through retrogressive amphibolite-grade metamorphism. Whereas preservation of microdiamond attests to the mineral's robust nature, discussion continues over the type of crystallization medium for microdiamond in Kokchetav. This problem is of great importance because it may cast light on the origin of all microdiamond formation related to deep subduction and exhumation of continental material during continental

collision. Ten years ago, the Kokchetav massif was the only site where microdiamonds had been found (Sobolev & Shatsky, 1990). However, now microdiamonds are known from five additional ultra-high pressure metamorphic (UHPM) terranes: Dabie, China (Xu *et al.*, 1992), Western Gneiss Region, Norway (Dobrzhinetskaya *et al.*, 1995; Van Roermund *et al.*, 2002), Erzgebirge, Germany (Massonne, 1999), Sulawesi, Indonesia (Parkinson & Katayama, 1999) and Greek Rodope (Mposko & Kostopoulos, 2001), but are abundant only in Kazakhstan and Germany. The rare occurrence of microdiamonds in the other localities may be due to more intense retrograde reaction of diamond to graphite (Dobrzhinetskaya *et al.*, 2001a).

Dobrzhinetskaya *et al.* (2001a) have earlier reported on the discovery of nanometric inclusions of oxides, MgCO₃ and BaSO₄ in diamond from garnet–biotite gneiss from the Lake Kumdikol locality of the Kokchetav massif, Kazakhstan. Here further results on these nanometric crystalline inclusions are presented, along with observations of both diamond-bearing and diamond-free multiple inclusion pockets in garnet and zircon from feldspathic gneiss. A large number of diamond crystals has been extracted for transmission electron microscope (TEM) analysis utilizing conventional argon ion milling and also employing the new technique of Focused Ion Beam (FIB). The latter technique involves choosing a specific grain (diamond or otherwise) in a polished surface viewed in the scanning electron microscope (SEM) followed by excavation of a foil oriented normal to the polished surface using a focused beam of Ga ions. This technique is particularly useful for TEM research on microdiamonds because of their small size and hardness, greatly facilitating discovery and analysis of nanometric inclusions within them.

Previous studies of the Kokchetav diamond-bearing lithologies have suggested several different origins of microdiamonds, namely (i) crystallization from CH₄-rich fluid (Sobolev & Shatsky, 1990), (ii) COH-rich fluid (De Corte *et al.*, 1998; Ogasawara, 2001), or (iii) from a COH-rich multicomponent fluid (Dobrzhinetskaya *et al.*, 2001a, Dobrzhinetskaya & Green, 2001b). Experimental results were also used to suggest diamond crystallization from an alkaline-carbonate/carbonate melt (Hermann & Green, 2001; Shatsky *et al.*, 2001; Pal'yanov *et al.*, 2002) or from a COH-supercritical fluid (e.g. Akaishi & Yamaoka, 2000; Dobrzhinetskaya *et al.*, 2001c; Sokol *et al.*, 2001). Determination of which of these processes was active during diamond crystallization in the Kokchetav rocks can place important constraints on the oxygen fugacity and the temperature of the fluid. The new observations reported here, both from the nanometric inclusion suite and from comparison of the chemical compositions and morphologies of minerals entrapped together with diamond inside garnet and zircon cast additional light on this debate.

GEOLOGICAL BACKGROUND

The Kokchetav massif is an ultra-high pressure metamorphic terrane in Kazakhstan, formed during a Palaeozoic continental collision. The diamond ore bodies of economic concentrations are located near Lakes Kumdikol and Barchikol, within metasedimentary lithologies of continental affinity intercalated with metavolcanic rocks (Dobrzhinetskaya *et al.*, 1994; Dobretsov *et al.*, 1995; Maruyama & Parkinson, 2000; Kaneko *et al.*, 2000). Diamond-bearing rocks have a crustal protolith of Precambrian age (2500–2000 Ma) which later, during continental collision at *c.* 520–540 Ma, were metamorphosed at a pressure of at least 4–6 GPa and a temperature of 900–1100 °C (Ekimova *et al.*, 1992; Sobolev & Shatsky, 1990; Clauue-Long *et al.*, 1991; Zhang *et al.*, 1997; Katayama *et al.*, 2000a,b, 2001; Ogasawara *et al.*, 2001). Recent studies suggest pressures as high as 7 GPa (Okamoto *et al.*, 2000; Zhu & Ogasawara, 2002).

Most (>90%) of the diamond ore bodies in both deposits are represented by feldspathic gneisses and quartz-rich rocks intercalated with calc-silicate rocks, marbles, and layered garnet pyroxenites with enclosed lenses of eclogite. Diamond occurs mainly in garnet–biotite gneiss, garnet–two-mica gneiss, zoisite gneiss, garnet–kyanite schist, garnet pyroxenite, calc-silicate rocks, marble, and quartzite. Diamond crystals (from 1 to >80 µm diameter) are included in virtually all minerals: garnet, quartz, biotite, phlogopite, clinopyroxene, kyanite and zircon, even though some of these minerals are unstable under conditions of diamond formation. Diamond of 10–20 µm in diameter also are present at garnet–biotite grain boundaries (Dobrzhinetskaya *et al.*, 1994), suggesting their possible growth at the interphase boundaries of former garnet–phengite assemblages stable during diamond crystallization.

SAMPLES, TECHNIQUES AND INSTRUMENTATION

Samples of garnet–biotite gneiss (K182-2 and K123/93) were collected from the diamond ore body on the south-west shore of Lake Kumdikol. The rock consists of plagioclase (40 vol.%), garnet (20 vol.%), quartz (25 vol.%), phengite + biotite + muscovite + sericite (10 vol.%), chlorite (<4 vol.%) and graphite (<1 vol.%), with accessory diamond, apatite, zircon, titanite, rutile, and tourmaline.

Several polished thin sections were cut parallel to each other from both samples K123-93 and K182-2. More than 30 garnet crystals and about 20 zircon crystals containing diamond-bearing and diamond-free multiple inclusion pockets were studied in detail by optical microscopy. For optical microscopy and for SEM, the thin sections were polished with a series of abrasives of Al₂O₃ finishing with an EXTEC colloidal silica suspension (0.06 µm size of particles) for 24 h. This technique avoids potential contamination and leaves the diamonds standing in relief, surrounded by flat surfaces of the other phases and the host mineral, thereby providing an opportunity to observe grain boundaries and clear spatial relationships within the pockets. The most illustrative and representative four grains of garnet and five of zircon from these thin sections were further studied using Philips XL30 FEG SEM at the University of California at Riverside (UCR), operating at 15 and 20 kV. The EDAX micro-analytical system of this microscope consists of an energy dispersive X-ray spectrometer (EDS) equipped with a Si detector with a super-ultra-thin window and a resolution of 137 eV MnK_α. The spectral data were acquired at 1500–2000 counts per second with dead time below 25%, beam current of about 1 nA, and effective spot size of about 1.5 µm.

For TEM, diamonds extracted from both garnet separates and powdered rock were used. A procedure similar to that reported by Dobrzhinetskaya *et al.* (2001a) was used. Thin foils for TEM were prepared using a special grain mounting technique (see Alani *et al.*, 1997) utilizing conventional argon ion milling with a PIPS of Gatan Inc. and FIB of gallium ions at Fibics Inc. A Vacuum Generators HB 601 scanning transmission electron microscope (STEM) was used at Los Alamos National Laboratory (LANL) to obtain analytical data from inclusions incorporated in diamond and for image acquisition. The STEM was operated at an accelerating voltage of 100 kV and is

equipped with both a Link energy-dispersive X-ray spectrometer (EDS) and a parallel electron energy-loss spectrometer (PEELS, Gatan, Inc.). The minimum size of the electron probe beam is about 0.2 nm. Some samples were also studied at UCR using a Philips CM300 analytical TEM with a twin lens and LaB6 filament, operated at 200 and 300 kV. This TEM is equipped with an EDAX system for acquisition and processing of energy dispersive X-ray spectra, a Si detector with resolution of 135 eV at MnK_α, an ultra-thin window and MX-TEM software. The minimum size of the electron probe beam is about 0.2 nm (for details see Dobrzhinetskaya *et al.*, 2000). Crystallographic and structural features of the diamonds and some inclusions were also studied at LANL using a JEOL 3000F high-resolution transmission electron microscope (HRTEM) equipped with a parallel electron energy loss spectrometer (PEELS), and a Gatan Multiscan CCD camera for digital image acquisition. The JEOL HRTEM is operated at accelerating voltages up to 300 kV with point to point resolution of 1.7 Å.

SEM STUDIES OF GARNET AND ZIRCON IN SITU

Inclusions in garnet

Diamond-bearing multiple inclusion pockets (Fig. 1) are mostly represented by one to three diamond crystals intergrown with quartz and with phengite of low paragonite component (Fig. 1a,b) and are associated

with chlorite developed at garnet–phengite interfaces (Fig. 1b). The pockets may also consist of a single diamond plus albite and quartz (Fig. 1c) that probably are a decomposition product of jadeite + coesite. Within the pockets there are also the following combinations: diamond plus apatite (Fig. 1d) or apatite plus phlogopite (partly replaced by chlorite and biotite); diamond plus rutile, quartz and titanite; diamond plus quartz and K-feldspar. In all multiple inclusion pockets, a single diamond crystal usually occupies > 50–70% of the volume, suggesting that the fluid or melt trapped by garnet consisted mostly of CO₂ and SiO₂, with a small amount of alkalis, P, Ti, Al, Mg, Fe and Ca. The volume fraction of diamond in such polyphase pockets is much higher than that observed by Stöckhert *et al.*, 2001) in similar diamond-bearing pockets from Erzgebirge garnet-phengite felsic gneisses of eastern Germany. Diamond-free multiple inclusions within the same garnet consist of rutile, apatite and high-Al titanite, in many cases intergrown with phengite or, rarely, with phlogopite. One pocket was found to contain rutile, titanite, phengite with high paragonite component, and Mn-rich titanite-magnetite.

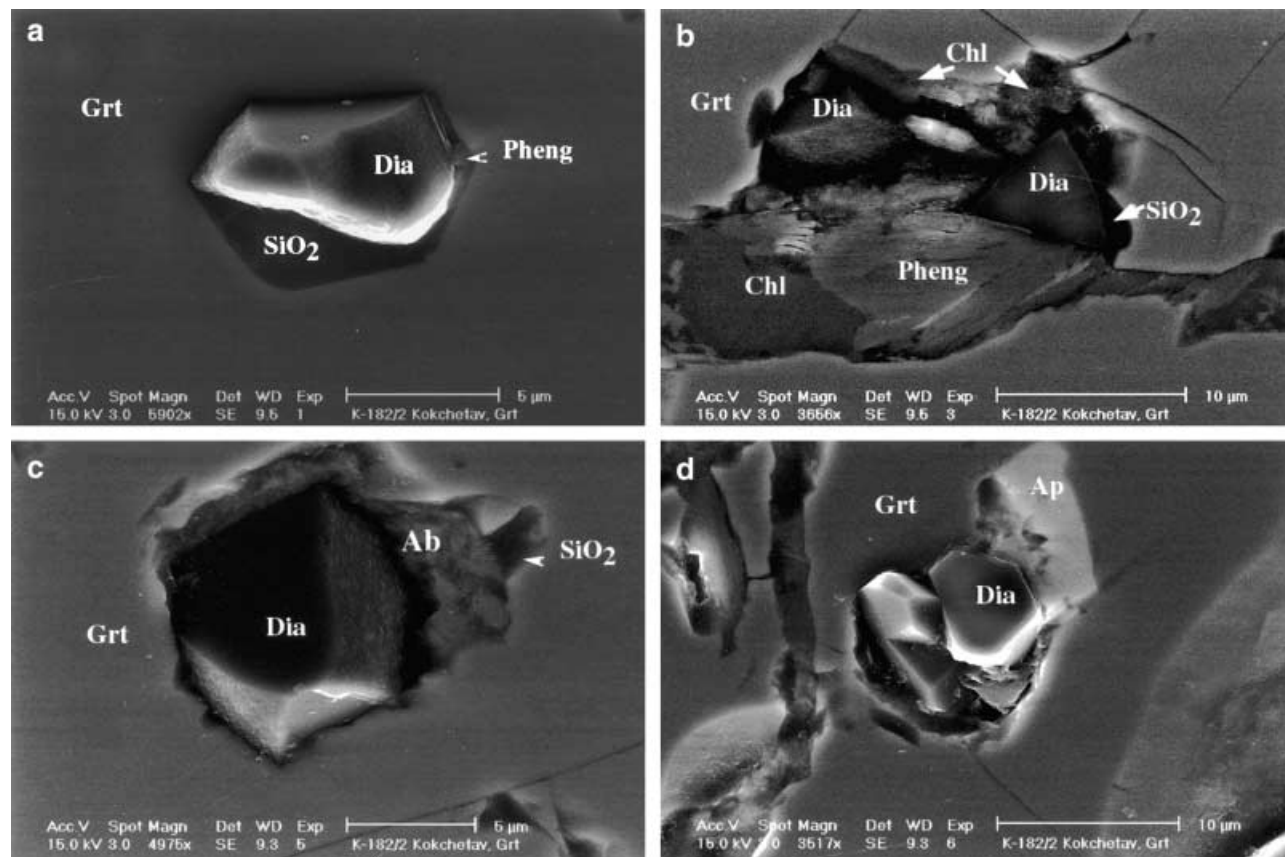


Fig. 1. SEM images obtained in secondary electron mode. Diamond-bearing multiple inclusion pockets in garnet from felsic gneiss (sample K-182/2), the Lake Kumdukol, Kokchetav massif, Kazakhstan. a – diamond-quartz-phengite pocket; b – strongly altered silicate inclusions containing phengite partly replaced by biotite and chlorite (probably after garnet and biotite), intergrown with quartz and two diamond crystals, of which the very tops are visible on the polished surface (two more diamond crystals have been noted in transmitted light); c – diamond-albite-quartz pocket; d – diamond-apatite pocket.

Single inclusions of graphite, quartz, titanite and rutile also have been observed.

Calculation of the silica content of a multiple-inclusion pocket

To address the fluid-vs.-melt question quantitatively, the average SiO₂ content of a multiple-inclusion pocket (pocket A) was calculated from sample K-182-2, which contains diamond, albite and quartz. A thick (60 μm) thin section was polished in several steps, with observations of the configuration of the minerals made at each step (one intermediate section/surface of this pocket is shown in Fig. 1c). In order to measure the volume of each mineral species in the pocket, the area of each mineral was measured in each of six serial sections of the pocket under study. The measurements were made using Adobe Photoshop on images obtained in reflected light with a Polaroid Digital Microscope Camera (DMC-1) on a Nikon photomicroscope. The result shows that diamond occupies 70% of the volume, albite 20 vol.% and SiO₂ 10 vol.%. The relative error of such measurement is estimated as ± 20%. Taking into account the specific gravity of the minerals ($\rho_{\text{Diamond}} = 3.51$; $\rho_{\text{Albite}} = 2.60$ and $\rho_{\text{SiO}_2(\text{quartz})} = 2.65$; Klein & Hurlbut, 1993) and the measured composition of albite (SiO₂ = 66.94; Al₂O₃ = 18.64; CaO = 3.07; FeO = 4.81; Na₂O = 6.55; all in wt.%), an average SiO₂ content of *c.* 19 wt% was calculated for the whole volume.

Inclusions in zircon

Zoned prismatic and rounded zircon contains single inclusions of diamond as well as diamond-bearing polyphase inclusions containing phengite, albite + quartz and graphite. Most of them are situated closer to the rim zones than to the core. Figure 2(a) shows a zircon containing several diamond situated close to the core and a single diamond intergrown with phengite located in the rim (phengite composition is given in Fig. 2b). Many pure carbon inclusions consisting of diamond partly replaced by graphite (Fig. 2c) and several inclusions of SiO₂ with 'fluid-pocket structure' (Fig. 2d) were also found in the central parts of elongated and rounded zircon grains. Single inclusions of phengite, plagioclase and graphite were also observed in different combinations in almost all studied zircon, similar to those described in detail by Katayama *et al.* (2000a).

In addition, many diamond-bearing inclusions in zircon have chlorite between the diamond and the zircon, with chlorite-filled microcracks extending away from the inclusion. The curvilinear, often tortuous, morphology of chlorite-zircon boundaries suggests that part of the diamond has been dissolved ('etched out') by the fluid that originally filled the microcracks and replaced by chlorite. This probably happened during exhumation, outside of the diamond stability

field, but chlorite stability extends to pressures well within the diamond field (Ulmer & Trommsdorff, 1999), so we cannot be certain of that.

Alteration of diamond to graphite also is observed in the rim zones of zircon crystals. This contrasts with the observation of Katayama *et al.* (2000a) that low-grade metamorphic minerals occupy the zircon cores, whereas the rim zones contain only high-pressure and ultra-high-pressure minerals such as diamond, coesite, jadeite and garnet. Here, it appears that a partial record of decompression reactions is preserved following UHP metamorphism. Polyphase pockets including one or two diamond crystals intergrown with phlogopite plus SiO₂, or with phengite of high paragonite content associated with titanite also have been found in zircon. The volumetric ratio of diamond to silicate and other phases in these pockets is estimated to be from 80 : 20 to 90 : 10. Thus, although there are many pockets consisting of only silicates, even pure silica, the SiO₂ content of diamond-bearing inclusion pockets in zircon appears to be even smaller than in similar pockets in garnet rarely as much as 20 vol.%.

TEM STUDIES OF INCLUSIONS IN DIAMOND

Solid nanometric crystalline inclusions from 15 diamond crystals were analyzed (see Table 1). All studied inclusions are interpreted as being syngenetic with the diamond (e.g. Harris, 1968) because they are totally enclosed within them and neither open nor healed cracks leading to them have been observed. A total of 65 nanometric inclusions were found and examined by EDS. Titanium oxide and silica are the most abundant inclusions (Fig. 3) overall and were identified in most of the 15 diamonds investigated.

At least four types of Ti-oxide compositions (e.g. Fig. 4a–d) were noted and distinguished from each other by various amounts of different impurities (Nb, Fe, Cr, Zn, K, S, P, Pb, Ca and Si). Silica inclusions are also characterized by diverse minor components (Table 1) such as Al, Fe, Cr, K, S, and Ca (Fig. 5). However, structural evidence is not yet available to determine whether these crystals are quartz, coesite, or stishovite. Chromium-oxide inclusions have been found in 3 of 15 investigated diamond. They are also enriched in minor components such as Fe, Al, Ti, K, P, Ni and Si in varying proportions (e.g. Fig. 6 and also see figs 3D, H in Dobrzhinetskaya *et al.*, 2001a). Generally, Cr₂O₃ inclusions are found together with TiO₂ inclusions. For example, in diamond A (foil a) separated from garnet LD93-A (see Table 1), a Cr₂O₃ inclusion containing minor amounts of Fe and Ti occurs in association with three TiO₂ inclusions and one inclusion of stoichiometric Fe-rich pyroxene. Among the three Ti-oxide inclusions – one is pure TiO₂, the second contains a few minor components (P, S, Si, Fe), and the third is characterized by diverse minor components; P, S, Si, Nb, Cr, Fe, K and Ca are detected (Table 1). In diamond B (LD92-B), one

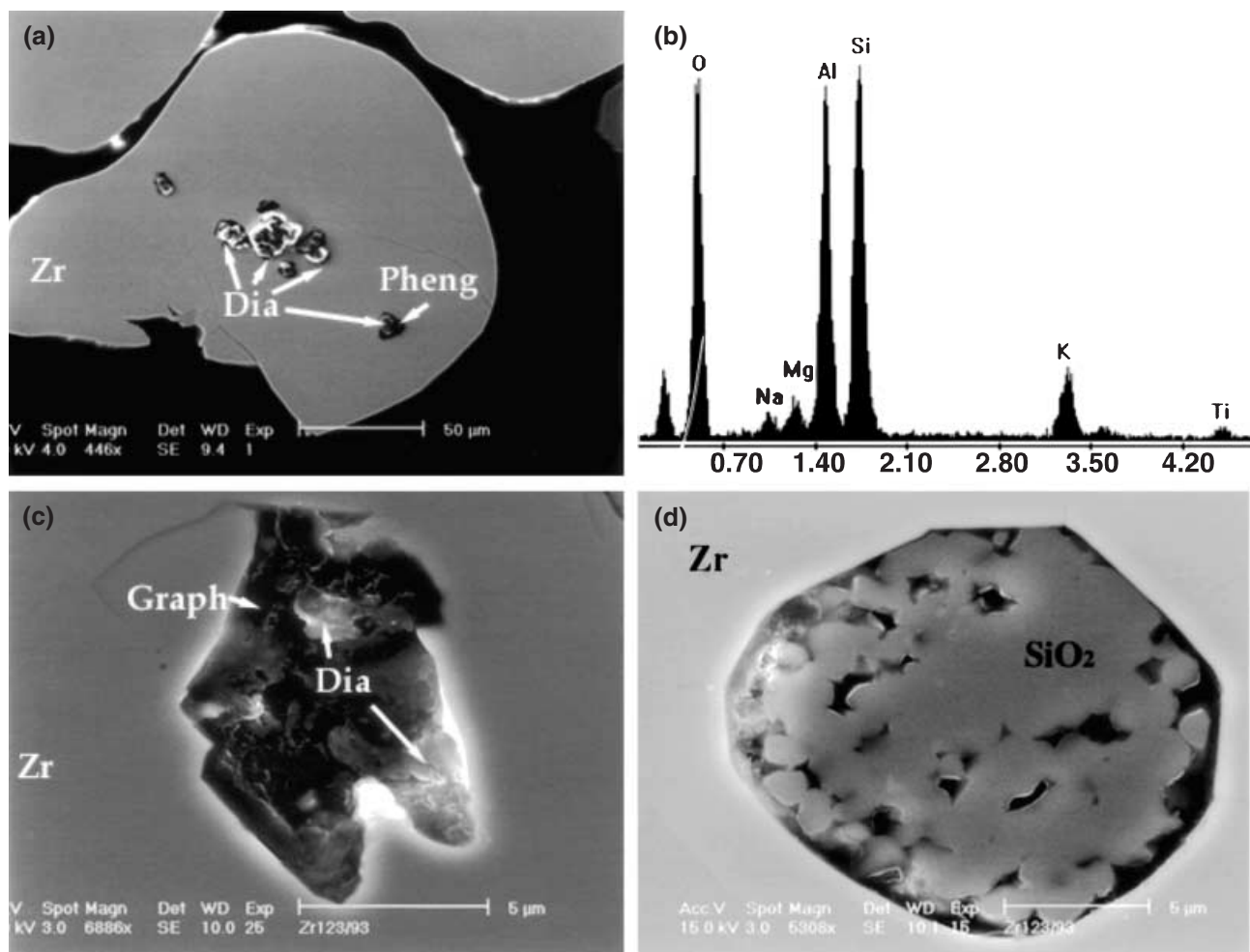


Fig. 2. SEM images obtained in secondary electron mode. Diamond-bearing inclusion: felsic gneiss, samples K-123/93 and K-182/2, the Lake Kumdukol, Kokchetav massif, Kazakhstan. (a) A general view of the polished zircon (Zr) grain with the multiple and single diamond-bearing and other inclusions standing out on its surface: note that diamond is situated close to its centre as well as the rim of the zircon. To the right of the zircon rim, a single diamond crystal is surrounded by phengite. The EDS spectrum of this phengite is shown in (b). (c) Imperfect single crystal of diamond partly replaced by graphite. (d) Polycrystalline quartz inclusion with 'fluid pocket' microstructural patterns: triangle or ameboid-like cavities were filled by liquid or gas which presumably escaped during polishing of the surface.

inclusion of Cr_2O_3 occurs together with two inclusions of TiO_2 and one inclusion of SiO_2 . In this assemblage the Cr_2O_3 contains a minor admixture of Fe and one of the two TiO_2 inclusions contains minor amounts of Nb and Fe while the second appears to be pure TiO_2 .

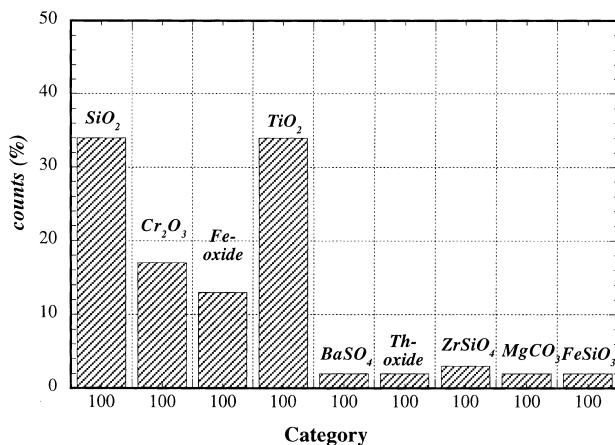
Because of their extremely small size and random orientations, thus far it has been very difficult to identify the phases present as inclusions beyond their chemical composition. One exception is esclaite that has been identified by selected area electron diffraction (SAED) of inclusions with a composition of Cr_2O_3 . Only out-of-zone-axis-orientation SAED patterns were obtained due to unfavourable orientation and thickness of the studied diamond foil containing the inclusion, but based on a limited number of d-spacing measurements and associated angles, the Cr_2O_3 inclusions are found to be structurally consistent with

esclaite. Very weak reflections at 2.96 \AA inconsistent with esclaite structure, were also observed in the SAED patterns. They were identified as belonging to (220) chromite spatially associated with the esclaite inclusions, an interpretation which is supported also by the presence of minor amounts of Fe and Ni in the EDS spectra or elemental mapping taken from the area of the esclaite inclusion (e.g. Fig. 6).

Two sets of Fe-oxide inclusions were detected. One is characterized by minor amounts of Al, K and Ca (Fig. 7a,b). The second type includes minor Si, Cl, S and Mg and occurs together with inclusions of Cr_2O_3 containing Al, Si, P, Ni and Fe. Zircon (ZrSiO_4) with trace Ti and Ca (Fig. 8a,b) was identified in one diamond that also contains nanometric inclusions of Fe- and Ti-oxides, and MgCO_3 . Zircon is a common accessory mineral in garnet-biotite gneisses of the

Table 1. Nanometric crystalline inclusions in Kokchetav microdiamonds separated from garnet (Grt) and from bulk rock of garnet-biotite gneiss. Trace elements are given in parentheses.

Diamond	Inclusions	Number of inclusions
LD93-A (Grt), diamond A (TEM foil a)	Fe ₂ Si ₂ O ₆	1
	TiO ₂ (Nb, Cr, Fe, K, Ca, S, Si, P)	1
	TiO ₂ (P, S, Si and Fe)	2
	TiO ₂	4
LD93-A (Grt), diamond B (TEM foil b)	Cr ₂ O ₃ (Fe, Ti)	1
	Fe _x O _y	2
LD93-B (Grt)	SiO ₂	1
	SiO ₂	4
	TiO ₂	1
	TiO ₂ (Nb and Fe)	6
LD99-1 (Grt)	Cr ₂ O ₃ (Fe)	8
	SiO ₂ (Ca, Cr and Fe)	2
LD99-2 (Grt)	MgCO ₃ (Ca)	1
	Fe _x O _y	4
LD99-3 (Grt)	ZrSiO ₄ (Ti and Ca)	1
	TiO ₂ (Cr, Al and Fe)	1
	TiO ₂ (Cr)	1
	TiO ₂ (Fe)	1
	TiO ₂ (Fe)	1
	BaSO ₄	1
LD99-4 (Grt)	SiO ₂ (Al, Na and Fe)	1
	SiO ₂	3
LD99-5 (Grt)	Th _x O _y	1
	SiO ₂	3
LD99-6 (rock)	SiO ₂ (Cr, Al, S, K and Ca)	1
	TiO ₂ (Nb, Pb, Zn, Fe, Si and Ca)	1
LD99-7 (rock)	SiO ₂ (Cr, Al and Fe)	1
LD99-8 (rock)	Cr ₂ O ₃ (Al, Si, P, Ni and Fe)	2
	Fe _x O _y (Si, Cl, K, Mg)	1
LD99-9 (rock)	Fe _x O _y (Si, S, Cl)	2
LD99-10 (rock)	SiO ₂ (Al, Fe, Cr, K)	2
LD99-11 (rock)	SiO ₂ (K, Al)	3
	TiO ₂ (Nb, Zn, Cr, Fe)	2
LD99-12 (rock)	ZrSiO ₄	1

**Fig. 3.** Histogram showing the compositional abundance within the diversity of nanometric inclusions incorporated in microdiamond from diamond-bearing felsic gneiss.

Kokchetav massif. However, the composition of nanometric zircon included in diamond differs slightly from that of the larger zircon grains (1–2 mm in diameter) which incorporate diamonds as inclusions. The large zircon have nearly ideal stoichiometry, whereas the nanometric inclusions from diamond

contain significant amounts of Ca and Ti in addition to the ordinary zircon composition ($\text{SiO}_2 = 39.69 \text{ wt.}\%$, $\text{CaO} = 6.22 \text{ wt.}\%$, $\text{TiO}_2 = 8.16 \text{ wt.}\%$ and $\text{ZrO}_2 = 45.93 \text{ wt.}\%$). Single inclusions of BaSO_2 and Th_xO_y have been also detected (see Dobrzhinetskaya *et al.*, 2001a). One inclusion of an iron silicate has been defined. Quantification of the EDS spectrum by the Cliff-Lorimer method shows that its composition has stoichiometry corresponding to ferrosilite with a minor enstatite component ($\text{Fe}_{1.60}\text{Mg}_{0.14}\text{Ca}_{0.09}\text{Al}_{0.08}$)_{1.91}- $(\text{Si}_{1.93}\text{Al}_{0.07})_2\text{O}_6$.

EDS analyses suggest that almost all inclusions contain trace elements and that their abundances vary widely. Trace components such as Si, Cr, Fe, Ti, Mg, Ca, Al, K, Na, S, P, Nb, Cl, Zn and Ni (see Table 1) are abundant and two associated inclusions with the same basic chemistry may display distinctly different trace elements. We are quite confident that the trace elements are not scattered within the diamond itself because all of the EDS spectra gathered from diamond in which no inclusions are seen always show only pure carbon. On the other hand, it is not possible to rule out that these trace elements are contained in multiple crystals on a scale comparable to a few unit cells (unlikely, but not impossible) or that they lie in a film at the interface between the inclusions and host diamond.

DISCUSSION

Significance of mineral inclusions in diamonds and in multiple inclusion pockets from garnet and zircon

Our fundamental hypothesis is that the metamorphic environment from which metamorphic diamond crystallise can be inferred from the bulk chemical composition of diamond-bearing inclusion pockets in refractory hosts, coupled with the compositions of inclusions within the diamond themselves. These two environments, one external to the diamond and more directly related to crystallization processes, but also more prone to contamination during exhumation, and the other only indirectly related but arguably uncontaminated since formation, can, together, powerfully constrain the crystallization environment. The observations presented here represent three microstructural environments: (1) inclusions and polymineralic pockets in garnet which are most abundant but also most susceptible to contamination via cracking and/or retrograde reaction with the host; (2) similar inclusions and pockets in zircon which are immune to retrograde reaction with the host but also susceptible to cracking and alteration during exhumation; (3) nanometric inclusions within the diamond which are immune both to retrograde reaction with the host and to cracking, but which provide only indirect information about formation processes.

These results show that the first of these environments, diamond-bearing polymineralic pockets in

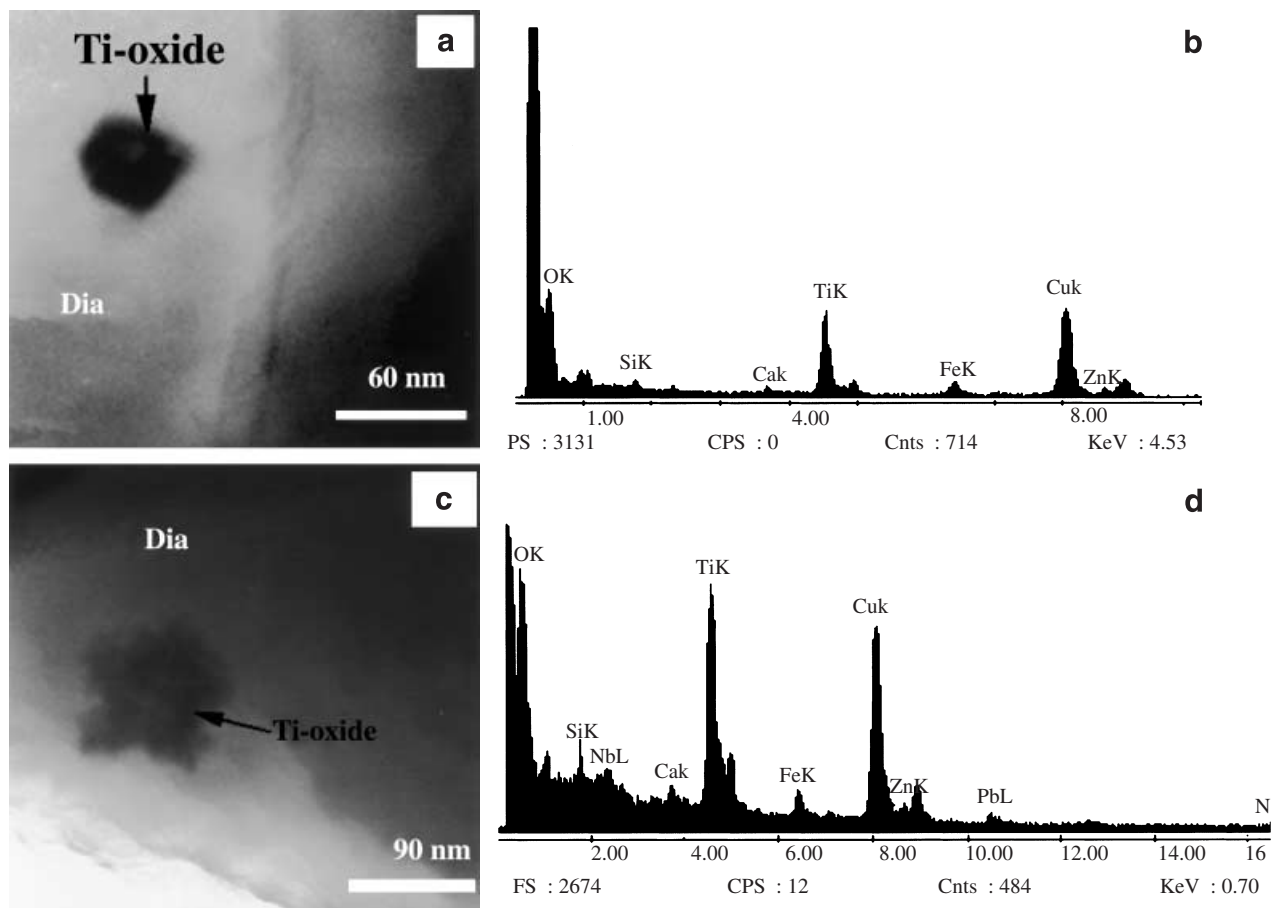


Fig. 4. Bright field TEM images (a, c) of diamond containing TiO_2 inclusions. EDS spectra (b, d) of the TiO_2 inclusions showing enrichment in Si, Ca, Fe and Zn (b) and in Nb, Si, Ca, Fe, Zn and Pb (d). Cu peaks are from supportive grid.

garnet of feldspathic gneiss, while clearly showing evidence of cracking and retrograde reaction, nevertheless exhibit a bulk chemistry unlike that to be expected of a silicate melt. Similar pockets in zircon from the same rocks (environment 2) show less evidence of contamination and a bulk composition even more unlike that of a silicate melt. The sum of these observations suggests that the environment of diamond crystallization cannot have been that of trapped silicate melt that subsequently crystallized, but we probably cannot rule out the possibility of precipitation from a moving melt that deposited diamonds and silicates selectively.

The inclusions within the microdiamonds themselves, however, suggest a very different picture. Except for SiO_2 , none of the rock-forming minerals commonly coexisting with diamond on the larger scale are found as inclusions. In their place there is a bewildering variety of relatively rare mineral compositions, often exhibiting significant concentrations of rare trace elements such as Nb, Ba, Zn, Pb and Th. Even two crystals of apparently the same mineral in close proximity to each other frequently have distinctly different amounts of these trace elements. In

particular, oxides dominate the assemblage; silicates are virtually absent. Two conclusions are drawn directly from these observations: (i) the inclusions in diamond do not reflect phases simply incorporated from a static, fluid-absent environment as they grew; (ii) the oxygen fugacity during diamond growth was in the upper part of the range compatible with diamond growth.

The implication of disparate inclusion compositions observed in individual diamond seems to be that individual nanometric crystals or groups of crystals have grown in isolation from one another and from the larger-scale environment. Most clearly, none of the nanometric chambers in which these nanocrystals grew reflects a composition anything similar to a silicate melt or what might be expected from a hydrous fluid at high P - T saturated with the rock-forming components.

What environment might be capable of yielding such features in these diamonds? It is suggested that the most likely environment is that of a COH-fluid at high pressure and relatively low temperatures. De Corte *et al.* (1998) reported molecular H_2O and carbonate radical in Kokchetav diamonds and Dobrzhetinskaya

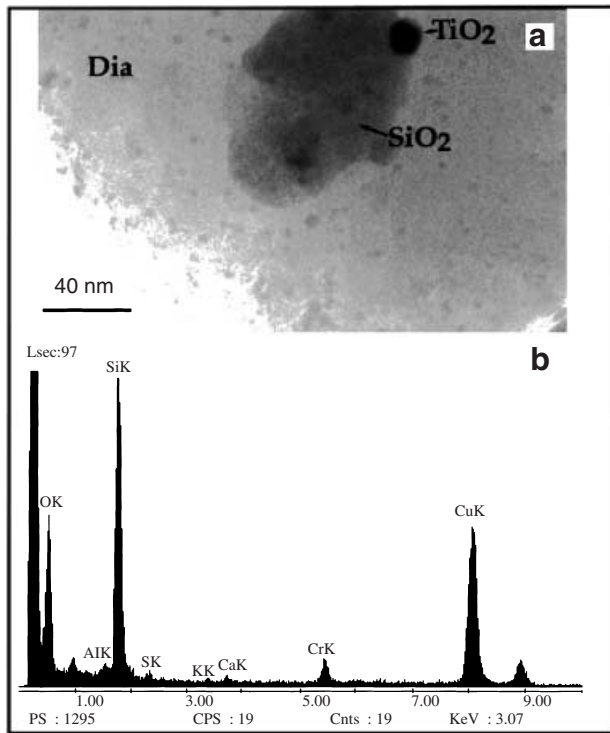


Fig. 5. Bright field TEM image (a) of diamond containing SiO_2 and TiO_2 inclusions. EDS spectrum (b) of SiO_2 inclusion enriched in Al, S, K, Ca and Cr. Cu peaks are from supportive grid.

et al. (2001a) imaged what appeared to be voids but which could be fluid inclusions containing only light elements not detectable by EDS analysis.

Source of components of the diamond-forming fluid: evidence of sediment–mantle interaction

Both quantitatively and qualitatively, the mineral compositions included in Kokchetav microdiamonds provide indications of the provenance of the fluid from which the diamond grew. SiO_2 , TiO_2 , Cr_2O_3 and Fe_xO_y (see Fig. 3) are the most abundant components incorporated into diamond. There can be little doubt that the abundance of SiO_2 is related to the crustal source of this component. It is known also that diamond-bearing metasedimentary rocks of the Kokchetav massif are enriched in TiO_2 in comparison with the sediments of the fore-arc, back-arc, leading- and trailing-edge settings (e.g. Dobrzhinetskaya & Mironova, 1996), and that this enrichment is indicated by wide-spread occurrences of titanite in all lithologies, be they felsic or carbonate metasediments, or eclogite with basalt bulk chemistry.

Although such an observation is not by itself proof of metasomatism, Ti enrichment is known to be a common signature of mantle metasomatism (e.g. Harte, 1987; Haggerty, 1991; Bodinier *et al.*, 1996). If this is the case here, then the source of Ti is the mantle (probably the subducting mantle lithosphere), but

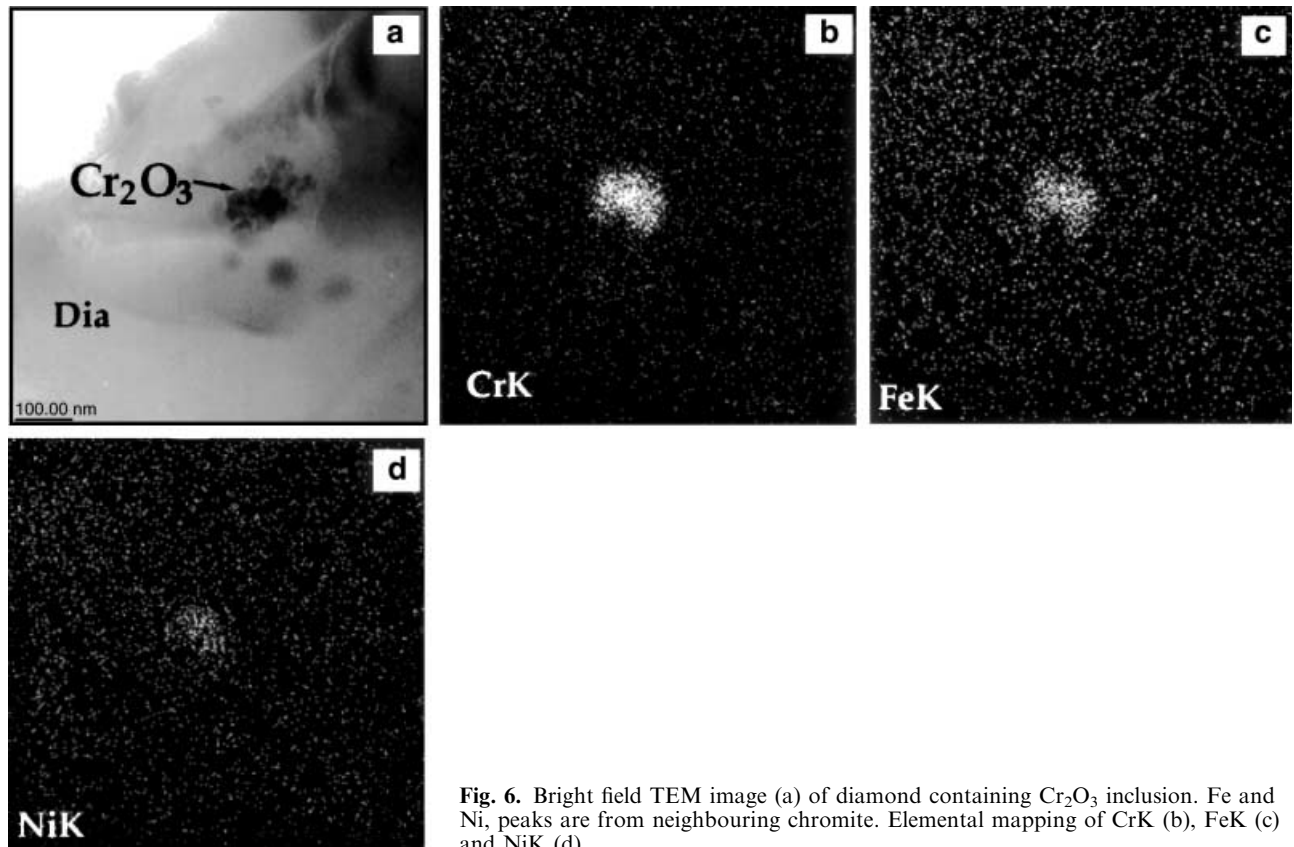


Fig. 6. Bright field TEM image (a) of diamond containing Cr_2O_3 inclusion. Fe and Ni peaks are from neighbouring chromite. Elemental mapping of CrK (b), FeK (c) and NiK (d).

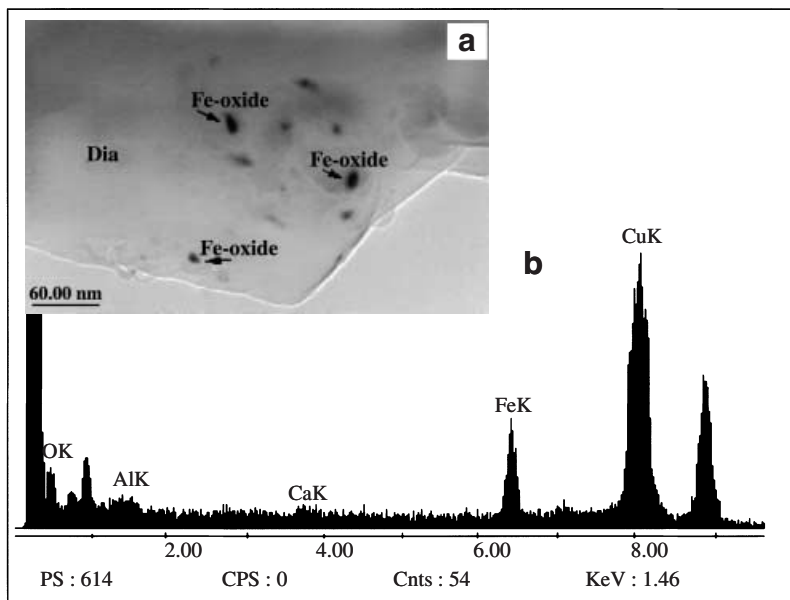


Fig. 7. Bright field TEM image (a) of diamond containing Fe-oxide inclusions. EDS spectrum of one of the Fe_xO_y inclusion enriched in Al and Ca. Cu peaks are from supportive grid.

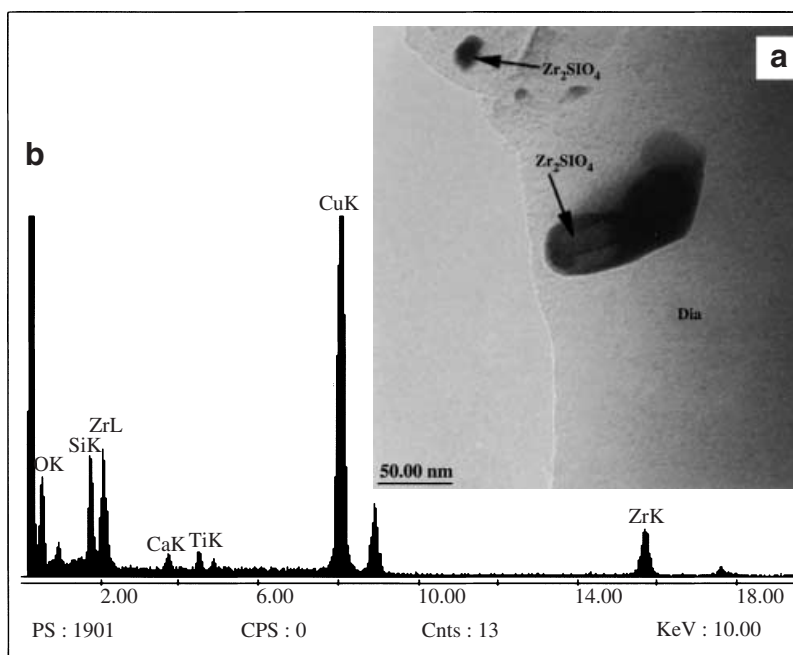


Fig. 8. Bright field TEM image (a) of diamond containing two zircon inclusions of similar composition. EDS spectrum (b) of the smaller inclusion enriched in Ca and Ti. Cu peaks are from supportive grid.

whether it was provided at the time of diamond growth or prior to diamond growth is not clear. Fe is abundant both in the crustal protoliths and the mantle, hence it is of little diagnostic value for fluid provenance. In contrast, Cr is extremely deficient in the Kokchetav metamorphic sequences (to the point of being undetectable in garnet by electron microprobe analysis), whereas it is a common component of mantle lithologies. As a consequence, the abundance of Cr_2O_3 inclusions suggests a mantle source. Amongst the rarer compounds, Th_xO_y and BaSO_4 most probably are

derived from the metasediments. Phosphates and carbonates are ambiguous. The crustal source of carbon has been confirmed by many researchers from carbon isotope studies on the Kokchetav diamond (Ekimova *et al.*, 1992; De Corte *et al.*, 1998; Cartigny *et al.*, 2001).

Based on these results we conclude that the mutual subduction of the felsic and carbonate rocks to the diamond stability region might have provided a fluid migration path between pelitic and carbonate rocks that caused decarbonation and, as a result, a source of

C, Si, Na, K, Ti, Ca, Mg and P, and other minor components. The interaction of this fluid with the ultramafic rock, of the mantle wedge or subducting lithosphere probably provided additional fluid components such as Cr and possibly Ti and Fe.

Nature of the diamond-forming medium

Previous studies of the Kokchetav diamond-bearing metamorphic rocks and diamond have suggested that diamond crystallized from (i) a CH₄-rich fluid (Sobolev & Shatsky, 1990; Shatsky *et al.*, 1995), or (ii) a COH-rich fluid (de Corte *et al.*, 1998), with the latter generalized to a COH-rich multicomponent supercritical fluid after discovery of abundant inclusions within the diamond (Dobrzhinetskaya *et al.*, 2001a). Recent experimental data on alkali/carbonate (or carbonate/granitoid) materials suggest diamond crystallization from alkali-carbonate/carbonate melt (Shatsky *et al.*, 2001; Hermann & Green, 2001; Pal'yanov *et al.*, 2002), while experiments on graphite or graphite and coal in the presence of H₂O support diamond crystallization from a COH- supercritical fluid (Akaishi & Yamaoka, 2000; Dobrzhinetskaya *et al.*, 2001c, 2002; Sokol *et al.*, 2001).

Decades of study of kimberlitic diamonds also have suggested two primary avenues of their formation: COH-rich fluid (e.g. Melton & Giardini, 1981; Haggerty, 1986; Navon *et al.*, 1988; Schrauder & Navon, 1994) and silicate or sulphide melts (e.g. Sunagawa, 1993; Bulanova *et al.*, 1998). Part of this difference in interpretation has been the result of a gap between observations on natural diamonds and the way they have been produced in experimental conditions. For instance, since the 1950s, industrial experiments to grow synthetic diamonds at high pressure and high temperature have focused on reduced media using solvent metal-catalysts because those were the conditions first found to yield reasonable results (e.g. Bundy *et al.*, 1955). Growth of diamond from COH fluids was not successful until recently, when it was experimentally determined that H₂O appears to be an excellent catalyst promoting diamond crystallization from both amorphous carbon and crystalline graphite at high pressure and high temperature (e.g. Akaishi & Yamaoka, 2000; Dobrzhinetskaya *et al.*, 2001c, 2002; Sokol *et al.*, 2001).

The observations reported here on chemical composition and microstructure of nanometric solid inclusions in natural diamonds, coupled with the evidence of molecular H₂O and carbonates (De Corte *et al.*, 1998; Dobrzhinetskaya *et al.*, 2001a), are inconsistent with diamond crystallization from a highly reducing medium but are consistent with the concept of diamond crystallization from a COH fluid near the upper oxygen fugacity limit for diamond. The lack of detection of CH₄ by De Corte *et al.* (1998) suggests that the CH₄ content of the fluid was negligible. At about 5 GPa and 900–1000 °C, CH₄ becomes

negligible above fO_2 of $10^{-9.5}$ and diamond is stable up to fO_2 of 10^{-8} (Eggler & Baker, 1982), hence it is estimated the fO_2 during diamond growth to have been 10^{-8} – 10^{-9} .

One more important aspect in the diamond origin discussion in terms of fluid vs. melt is the morphology of the diamond themselves and the morphology of silicate and other inclusions occurring in diamond. The diamond crystals growing in a melt medium are often euhedral and therefore are characterized by planar growth layers on octahedral faces (e.g. McCallum *et al.*, 1979; Gurney, 1986). Essentially none of the diamond reported from the Kokchetav massif displays morphological features which would suggest their precipitation from a melt: the great majority are skeletal, rounded, rose-like, or cube-octahedral with some faces typical for hopper-crystals. Sobolev (1977) indicated that most inclusions in eclogitic diamonds from kimberlites are monomineralic and usually possess euhedral forms with octahedral morphology. He interpreted these features as evidence for their coprecipitation from a melt rather than crystallization from a fluid phase. None of the solid inclusions that we have observed within the Kokchetav diamonds display a euhedral form with octahedral morphology. As can be seen from our TEM images, all inclusions in diamond have more or less round configuration, sometimes showing very sharp oval boundaries but also often exhibiting a complicated 'zig-zag' or 'rose-like' configuration typical of skeletal and other imperfectly shaped diamond (e.g. Figs 4–7).

Experimental results (e.g. Ayers & Eggler, 1995; Ayers & Watson, 1993; Brenan *et al.*, 1995) and studies of fluid inclusions in eclogites (Philippot & Selverstone, 1991; Scambelluri *et al.*, 1997) show that silicate solubility in hydrous fluids increases with pressure, temperature and Cl concentration. Based on the evidence of molecular H₂O in Kokchetav diamonds (De Corte *et al.*, 1998) and our observations on the composition of nanometric inclusions in diamonds from felsic gneiss, it is concluded that diamond crystallized from a multicomponent COH-rich fluid.

The previous conclusions of Dobrzhinetskaya *et al.* (2001a,b) are strengthened by the additional data presented here and are also supported by new observations on the diamond-bearing, multiple inclusions in garnet from UHPM felsic rocks of the Saxonian Erzgebirge, Germany (Stöckhert *et al.*, 2001). These authors emphasized that Erzgebirge microdiamonds crystallized from a COH-fluid enriched in K, Na and SiO₂. Massonne (2001), however, preferred a melt model to that of a supercritical fluid. These results have shown that Kokchetav diamond contains abundant nanometric inclusions of ZrSiO₄, TiO₂ and Th_xO_y as well as other silicates and oxides enriched in Nb, Th, Zr, Ti, the solubility of which in hydrous fluid increases with increasing pressure and Cl concentration (e.g. Ayers & Watson, 1993; Brenan *et al.*, 1995). These data are compatible with the results of Philippot &

Selverstone (1991), who found brines rich in Fe, Ti, P, Ba, Ce, La and Th in eclogite veins from the Monviso ophiolitic complex in the Western Alps. All of these components except the rare earth elements are present in variable proportions in the nano-inclusions from Kokchetav microdiamond.

Finally, preliminary data obtained by Manning *et al.* (2001) on the mineral solubility in pure aqueous fluid at high pressures and temperatures indicate that, as a general rule, the solubility of many minerals (quartz, diaspore, corundum, calcite, forsterite, enstatite and the assemblages albite-paragonite-quartz) increases with increasing pressure at constant temperature. They also reported that in some cases solubility of minerals is three to four orders of magnitude higher at subduction zone conditions than in shallow crustal environments. These experiments are also compatible with our observations of a wide variety of components, which are dissolved in COH-rich fluid at high pressure and temperature as these conditions occur in the diamond stability region.

Ayers & Eggler (1995) indicated that at high pressure and high Cl concentration such fluid is analogous to a silicate melt. Recent experiments by Shen & Keppler (1997) and Bureau & Keppler (1999) unambiguously demonstrated that there is complete miscibility between silicate melt and water in most of the upper mantle, except at very shallow depth. It was also demonstrated that the hydrous melt and silicate-bearing vapour coexisting at low temperature merge compositionally to form a single-phase, supercritical, fluid stable at higher pressures (15–25 kbar). Stöckhert *et al.* (2001) emphasized that there is no criterion to distinguish alkali-silica-rich fluid from hydrous silicate melt at high pressure because the system is in the supercritical state.

Applying these data and concepts to subduction zones, whenever water is available, the solid material, be it part of the mantle wedge or the subducting slab, may be progressively dissolved in the supercritical fluid with increasing pressure and temperature. Given the high mobility of such fluids and high diffusivities within them, it should not be surprising to find evidence of both crustal and mantle components in their precipitation products, and in diamonds. This fluid moving through the subducted continental rocks may be trapped by any growing minerals such as garnet, kyanite, zircon, pyroxene, coesite and/or may precipitate some of its components at the grain boundaries. Diamond growth at the time of such metasomatism could, like the other minerals, include such precipitation products, or diamond growth within trapped pockets of this fluid could occur subsequently during UHP-metamorphism.

In summary, all of our observations and calculations suggest that diamond growth in UHP metamorphic rocks is consistent with the recently obtained experimental evidence for diamond crystallization directly from COH solution or from graphite in the

presence of H₂O as a catalyst (e.g. Akaishi & Yamaoka, 2000; Dobrzhinetskaya *et al.*, 2001c, 2002; Sokol *et al.*, 2001); attempting to distinguish between 'melt' and 'fluid' is more of a semantic exercise than a petrological one. Given the bulk chemical compositions in diamond-bearing pockets in garnet and zircon and within diamond themselves, the assemblages produced suggest that the fluid from which the inclusions grew was much more fluid-like than melt-like. We therefore suggest that the supercritical fluid from which the Kokchetav diamonds grew was at a temperature significantly below the dry solidus, reducing the melt components and enhancing the fluid components.

ACKNOWLEDGEMENTS

This project was supported by Los Alamos National Laboratory through Science and Technology Base Programs (grant 9949 to L.D) and partly by NSF grant EAR-0107118 to L.D and H.W.G). We appreciate perceptive and thoughtful reviews by E. Eide and B. Stöckhert that have led to substantial clarification and improvement of the paper. We thank Dr R. Alani, Gatan Inc. and Mr M. Phaneuf, Fibics Inc. for technical support in sample preparation.

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Received 13 June 2002; revision accepted 25 January 2003.