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Metal-sulfur-COH-silicate fluid mediated diamond nucleation in Kokchetav ultrahigh-pressure gneiss

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Abstract: Submicron metal sulfides, randomly oriented microdiamonds and phlogopite have been identified as multiphase inclusions in garnet of a garnet-clinopyroxene-quartz crustal rock from the Kokchetav Massif in Kazakhstan. Analytical electron microscopy shows that metal sulfides are entrapped among diamond aggregates away from infiltration cracks and do not exhibit any specific crystallographic relationship with associated microdiamonds, thus implying a possible syngenetic nucleation of microdiamonds from a precursive fluid containing dissolved metal sulfides. The diamonds increased in size via a spiral growth mechanism, as manifested by dislocations radiating from nuclei toward faceted surface outcrops.

Key-words: diamond, fluid, metal sulfides, inclusions in garnet, ultrahigh-pressure, metamorphism.

Introduction

Molten metal (Bovenkerk *et al.*, 1959) is much more effective in catalyzing the graphite-to-diamond transition in the diamond stability field, in comparison with other solvent-catalysts such as silicate melt of kimberlite composition (Arima *et al.*, 1993), carbonate fluid (Paly'anov *et al.*, 1999a and 1999b; Kumar *et al.*, 2000; Sokol *et al.*, 2000), and COH fluid having been proved experimentally to be effective at 7.7 GPa and 1300-2000°C (Akaishi & Yamaoka 2000; Kumar *et al.*, 2000). However, the catalytic role of molten metal is not evident for natural diamonds. The occurrence of metal sulfide inclusions in diamonds from kimberlite-type rocks, either peridotitic or eclogitic (Deines & Harris, 1995; Bulanova *et al.*, 1998), implies the possibility of their catalytic role in the crystallization of syngenetic diamonds in the Earth's mantle, although it is not clear whether diamond nucleates epitaxially on such "seeds" specifically (Orlov, 1977; Bulanova *et al.*, 1998). The same question remains unanswered for the crustal microdiamonds in ultrahigh-pressure (UHP) metamorphosed gneisses and dolomitic marbles from the Kokchetav Massif in Kazakhstan (De Corte *et al.*, 1998 and 2000; Ishida & Ogasawara, 2000; Sobolev & Shatsky, 1990; Dobrzhinetskaya *et al.*, 2001) and gneisses from Saxonian Erzgebirge in Germany (Massonne, 1998; Stöckhert *et al.*, 2001). It has recently been found that the microdiamonds are associated with submicron-size metal sulfides from the latter UHP gneiss (Hwang *et al.*, 2001). Such tiny metal sulfide inclusions trapped in diamond aggregates are accessible by analytical electron microscopy (AEM) but not by electron probe microanalyzer (EPMA) or vibrational spectroscopic techniques. This discovery has led us to consider whether the diamond/metal sulfides association is common also to the Kokchetav UHP gneisses, and whether the metal sulfides have a specific crystal structure in the diamond stability field from the viewpoints of crystal chemistry, physics and thermodynamics (Vaughan & Craig, 1976; Kostov & Minčeva-Stefanova, 1982). It is also of paramount importance to determine the crystallographic relationship between diamond and metal sulfide in order to decide whether the genesis of crustal diamonds occurs by a metal-sulfur-COH-silicate fluid mediated synthesis, *i.e.* siderophile and/or chalcophile elements as solvent-catalysts, or by an epitaxial nucleation on crystalline metal sulfide seed.

Sample description and experimental procedures

The Kokchetav sample K12A studied here is a garnet-clinopyroxene-quartz rock with minor biotite and amphibole, which records a somewhat lower metamorphic temperature (740-780°C) than other diamondiferous gneisses in the mas-

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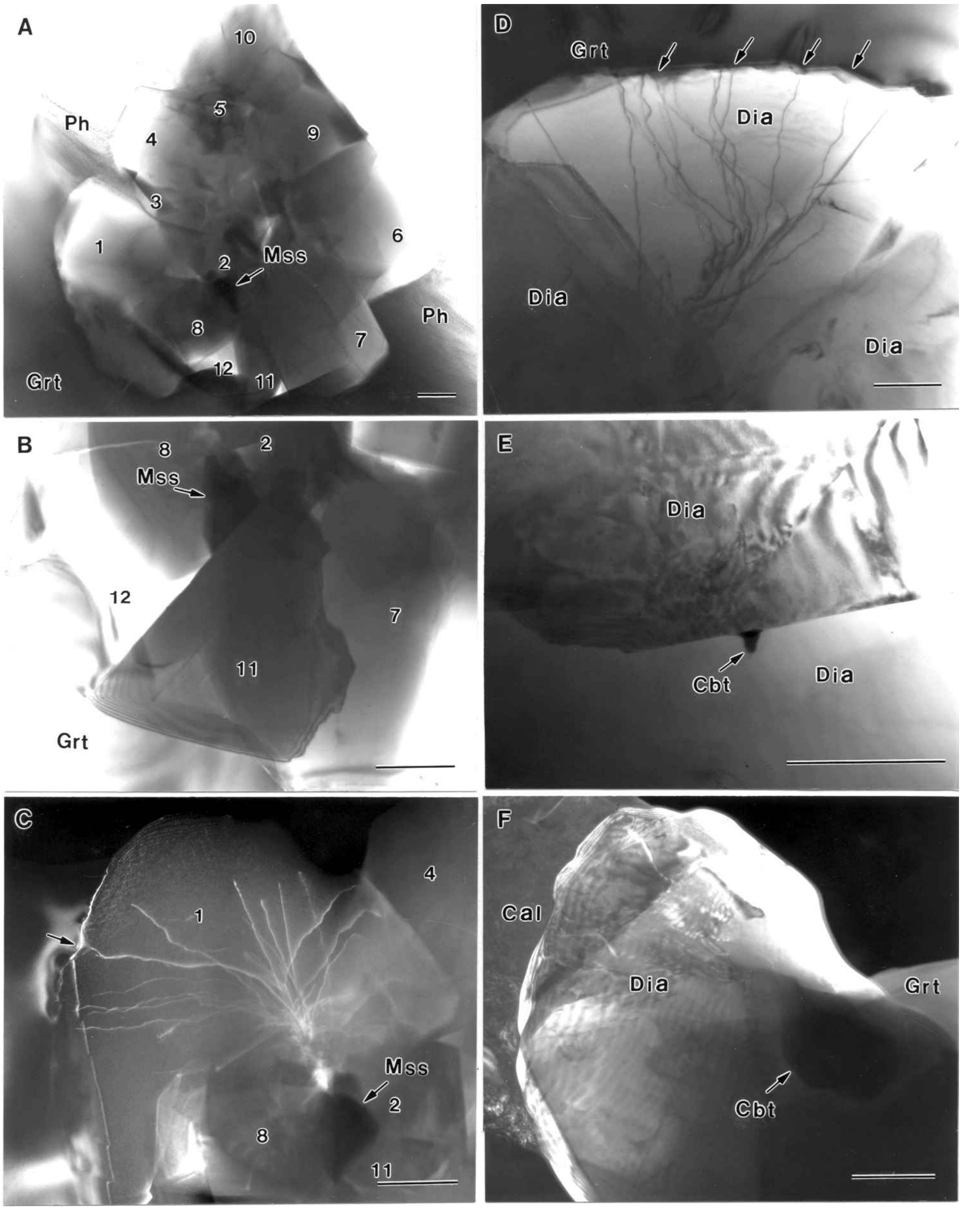

Fig. 1. (A) Transmission electron micrograph (bright-field image) of a micro-inclusion assemblage: diamonds (labeled as 1 to 12), phlogopite (Ph), metal sulfide solid solution (Mss) in garnet (Grt) host; (B) Transmission electron micrograph (bright-field image) of the same area as (A) showing diamond 11 with edge-on {111} faces at an intersecting angle of 71.5° when adjoined with garnet and diamond 12, but corrugated at contact with inner diamond 7; (C) Transmission electron micrograph (dark-field image) of diamond 1 with dislocations radiating from entrapped Mss to surface outcrops (arrows); (D) as the case of (C) but from other diamond aggregates (denoted as Dia) showing better the faceted outcrops (arrows) linked to dislocations; (E) and (F) Transmission electron micrograph of cobaltite (denoted as Cbt) at diamond grain junction and diamond/garnet boundary, respectively. Scale bars = 500 nm.

sif, typically at pressures ≥ 4 GPa and temperatures of 900-1000°C (Zhang *et al.*, 1997). Details of petrologic studies on this sample have been reported by Zhang *et al.* (1997). The microdiamond inclusions present in almandine-rich garnet are frequently surrounded by phlogopite or white mica (Zhang *et al.*, 1997). In the present study, to ensure that diamond aggregates were thinned, yet preserved for AEM observations, petrographic thin sections of the sample were argon-ion milled with extreme care by a precision ion polishing system. We used a JEOL 3010 instrument at 300 kV for imaging, selected area electron diffraction (SAED), and point-count energy dispersive x-ray (EDX) analysis of the milled thin foils, which were supported by a copper ring. Representative AEM observations were done in seven diamond-inclusion pockets and six graphite-inclusion pockets in four garnet crystals, as follows.

AEM observations

Both diamond-inclusion pockets and graphite-inclusion pockets were randomly distributed and not associated with one another in each of the garnet crystal studied. There is no appreciable zonal structure in the garnets except near Ca-infiltrated cracks exhibiting a higher grossular component.

In the diamond-inclusion pockets, microdiamond aggregates are always associated with phlogopite in faceted pockets following {110} garnet as represented in Fig. 1A. Point count EDX analysis indicated that the Mg/(Mg+Fe) atomic ratio of the phlogopite is ~0.80 (Fig. 3A), higher than the ratio of ~0.6 in matrix biotite. This composition is consistent with the occurrence in lamproite, as supported also by phlogopite with a similar composition co-existing with diamonds in kimberlite-related rocks (Atkinson *et al.*, 1984)

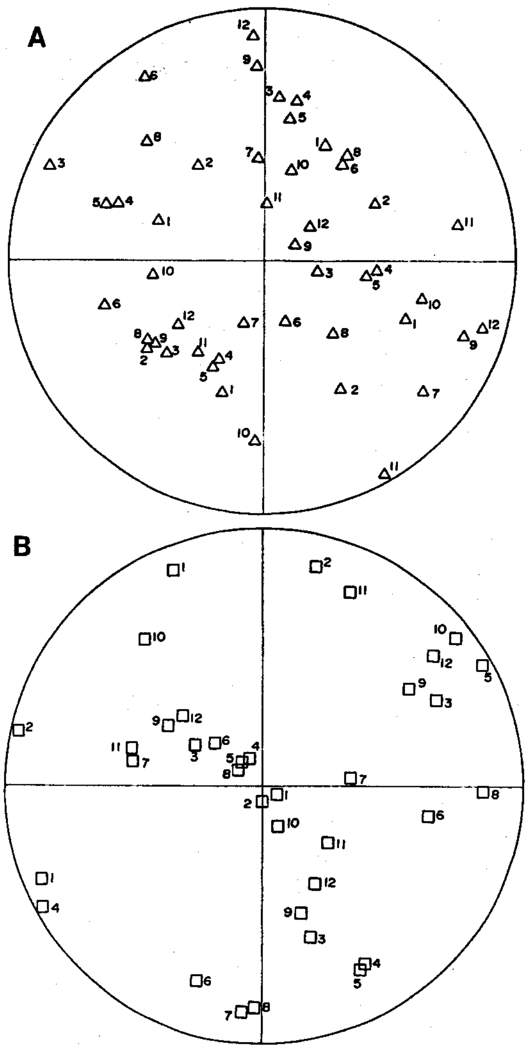

Fig. 2. (A) and (B) Stereographic projection of the {111} and {100} pole, respectively, of 12 diamond crystals numbered in Fig. 1A.

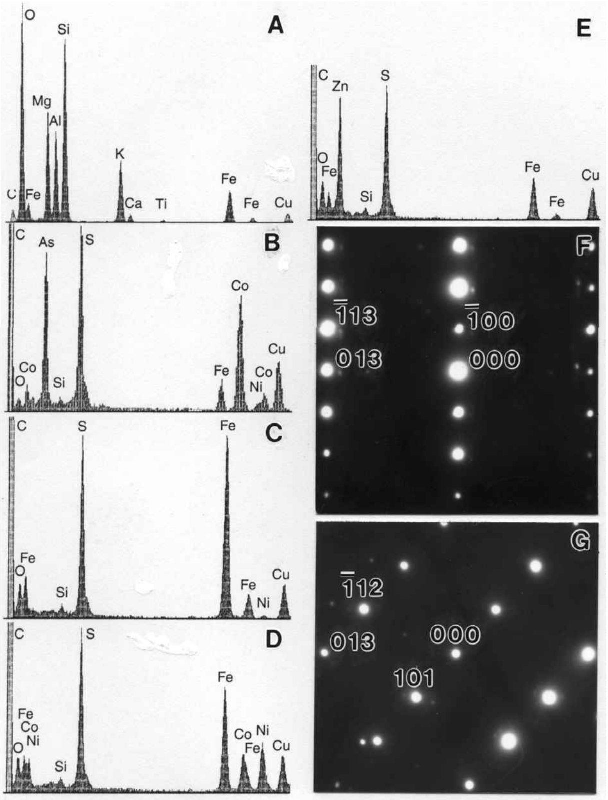

Fig. 3. (A) to (E) EDX spectra of phlogopite, cobaltite, nearly $Fe_{1-x}S$ with minor Ni, $(Fe,Ni,Co)_9S_8$ and $(Zn_{0.66}Fe_{0.33})S$ particles, respectively. Minor Cu, Si, and O counts are from the Cu ring and garnet matrix. (F) and (G) SAED patterns in [03$\bar{1}$] and [13$\bar{1}$] zone axis respectively, taken from cobaltite particle in Fig. 1F. The $\bar{1}00$ and 101 are caused by the As-S ordering. The 013 is double diffraction spot.

and Saxonian UHP gneiss (Hwang *et al.*, 2001). The phlogopite basal layers tend to be parallel or near parallel to the surrounding garnet wall, suggesting a topotectical deposition of phlogopite.

The diamond aggregates typically consist of euhedral microdiamonds with well-developed {111} faces in contact with either garnet or phlogopite (Fig. 1A, 1B), but in irregular contact with inner diamonds (Fig. 1B). Since some diamond crystals among the aggregates were removed during argon-ion milling, the “inner” diamonds may belong to the so-called core diamond according to the textural classification scheme of crustal microdiamonds for the Kokchetav Massif (Ishida *et al.*, 1999; Ogasawara *et al.*, 2000) (see Appendix). Stereographic projections of the {111} and {100} poles of 12 such diamond crystals (numbered in Fig. 1A) show that they have girdle patterns and no specific crystallographic orientation (Fig. 2A, 2B). Dislocations, but not twins, were found in each diamond crystal. Analogous to the occurrence in micrometer-size octahedral diamonds in kimberlite (Sunagawa *et al.*, 1984), these dislocations tend to radiate from a central point toward faceted outcrops (Fig. 1C, 1D). One of the diamonds in Fig. 1D was tilted to give a side view of growth pyramids and/or dissolution pits. There appeared to be a one-to-one correlation between the dislocation and the summit of growth pyramids and/or the end of dissolution pits. The g.R = 0 criterion at the two beam conditions (000, g) indicated that most dislocations outcropping at {111} surfaces are screw-type with Burgers vector 1/2<011>, the same as that reported by Sunagawa *et al.* (1984).

In diamond-containing pockets, submicron-size metal sulfide inclusions were observed at the diamond grain boundaries (Fig. 1A, 1B, 1C, 1E) and the diamond/garnet boundary (Fig. 1F), but not inside the diamond crystals. These metal sulfides are predominantly entrapped among diamond aggregates whose covering diamond crystals have been removed by ion milling, as shown representatively in Fig. 1A and 1B in which the relic diamonds are numbered 2, 7, 8, 11 and 12. In four such diamond-containing pockets, CoAsS particle with the EDX spectrum as shown representatively in Fig. 3B was identified by its SAED patterns (Fig. 3F, 3G) to be an ordered orthorhombic structure, *i.e.* cobaltite (space group $Pca2_1$), which was generally indexed as a pseudo-cubic ordered cell. Least-squares structure refinements based on 14 d-spacings measured on SAED patterns indicate a pseudo-cubic ordered cell with a = 0.5577 ±

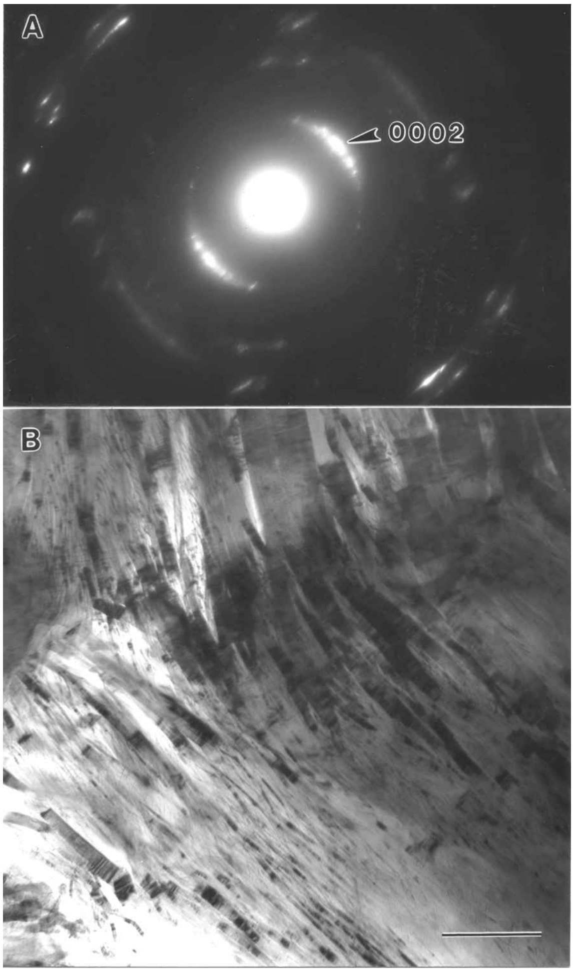

Fig. 4. (A) SAED pattern and (B) transmission electron micrograph (bright-field image) of graphite flakes with planar layers more or less parallel to each other. Scale bar = 200 nm.

0.0004 nm, in good agreement with that determined at ambient pressure for stoichiometric CoAsS (a = 0.5582 nm, JCPDS file 24-0048). There is no specific crystallographic relationship between cobaltite and adjacent microdiamonds. In three other pockets, metal sulfide solid solution was also identified compositionally in still thick diamond grain boundaries (Fig.1A, 1B, 1C), whose composition varied from nearly pyrrhotite $Fe_{1-x}S$ at center (Fig. 3C) to about pentlandite $(Fe,Ni,Co)_9S_8$ (Fig. 3D) and sphaleritic composition $(Zn_{0.66}Fe_{0.33})S$ at the edges (Fig. 3E).

In contrast, metal sulfides were not found in association with the graphite/phlogopite inclusions. In such inclusions, the graphite flakes are bifurcated and bended but not rolled, and generally less than 100 nm in thickness with the layer planes slightly rotated with respect to each other about the c-axis as indicated by the (0002) diffraction arc (Fig. 4). Lattice image (Fig. 5) indicated the graphite flake is highly defective and corrugated but not intergrown with other carbon structures such as diamond. The interplanar spacing (~0.344 nm) of the graphite is significantly larger than that of ideal graphite (0.334 nm) and can be classified as the so-called turbostratic type (Harris, 1999). The graphite flakes have no transformation twins and are not associated with diamonds in the pocket (Fig. 6A). There is no specific crystallographic relationship between graphite and phlogopite, although their basal planes may appear to be parallel (Fig. 6A). In some cases, phlogopite was replaced by chlorite overgrowth following parallel epitaxial relationship, which is due to fluid infiltration into the polyphase inclusions during retrograde metamorphism. Fluid infiltration was also found occasionally in one diamond-inclusion pocket containing calcite, chlorite, minute paragonite but not graphite (Fig. 6B). These retrograde minerals were only found in one of the seven diamond-inclusion pockets studied, suggesting that most diamond-inclusion pockets studied here have been in a closed system after their enclosure by the garnet matrix.

Discussion

Possible primary origin and stability field of metal sulfides/phlogopite

Diamond, phlogopite and metal sulfide are constantly present in the seven diamond-containing pockets studied. Calcite, chlorite and paragonite are additional minerals in only one pocket. These extra phases are low-pressure minerals and can be accounted for by retrograde fluid infiltrations. Secondary mineral/sulfide veins were not observed near other diamond-containing pockets in garnet. It is therefore conceivable that most diamond-containing pockets remain as a closed system since their formation, and the metal sulfides are most probably of primary origin. Note that metal sulfide nanocrystals are associated only with microdiamonds, but not with graphite inclusions including the one with retrograde fluid infiltration (Fig. 6A). These sulfide inclusions would most probably have precipitated and grown from a fluid that caused polycrystalline nucleation of diamond. (The sulfides at diamond grain boundaries can be rationalized by a relatively high nucleation rate than the growth rate of diamond.) Similar observations that submicron sphalerite (ZnS) and (Ni,Co)As associated with diamond/phlogopite inclusions in garnet of quartzofeldspathic rock from the Saxonian Erzgebirge, Germany (Hwang *et al.*, 2001) not only substantiate the scenario of a primary origin of metal sulfides but also suggest that sulfide-diamond association may not be uncommon for UHP metamorphic rocks.

A primary origin of metal sulfides trapped in microdiamond aggregates can also be substantiated by the fact that close-packed metal sulfides are stable from ambient pressure up to extreme pressure in the diamond stability field. In fact, static compression (Qadri *et al.*, 2001) and shock loading (Uchino *et al.*, 1999) experiments indicated a typical close-packed sulfide (sphalerite) is stable in the diamond stability field up to 16 GPa. Cobaltite, with close-packed anion or anion groups and metals in octahedral site as pyrite and cattierite CoS_2 (Vaughan & Craig, 1976; Kostov & Minčeva-Stefanova, 1982), is less compressible than sphalerite (Bridgman, 1925; Birch, 1966), and has a rather high melting point (ca. 1000°C) and ordering temperature (850°C) compared with other sulfides at ambient pressure (Vaughan & Craig, 1976; Kostov & Minčeva-Stefanova,

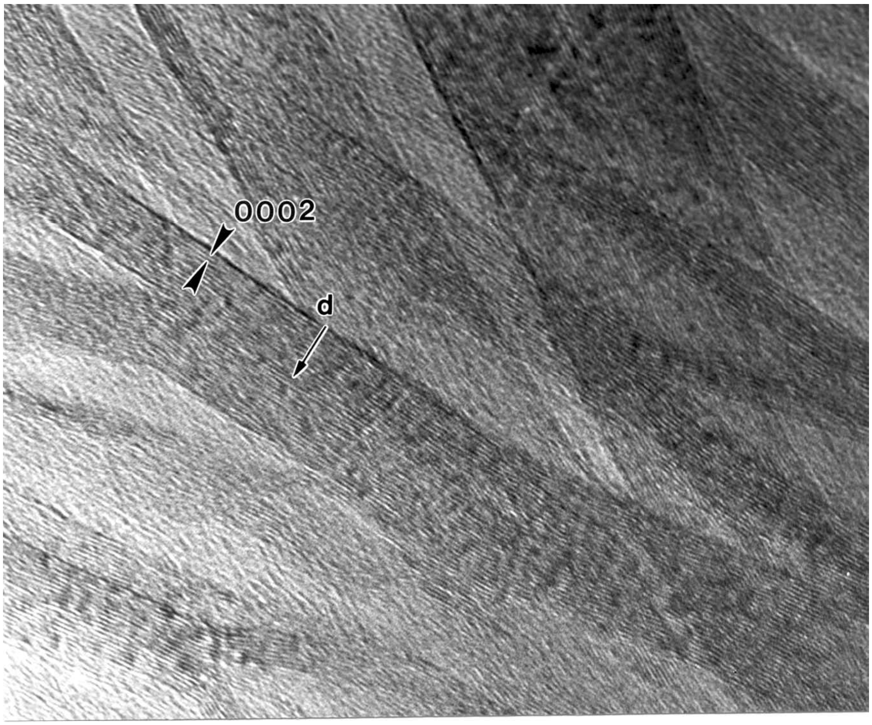

Fig. 5. Transmission electron micrograph (lattice image) of bifurcated and imperfect graphite flakes with (0002) interplanar spacing and dislocation (denoted as d) arrowed.

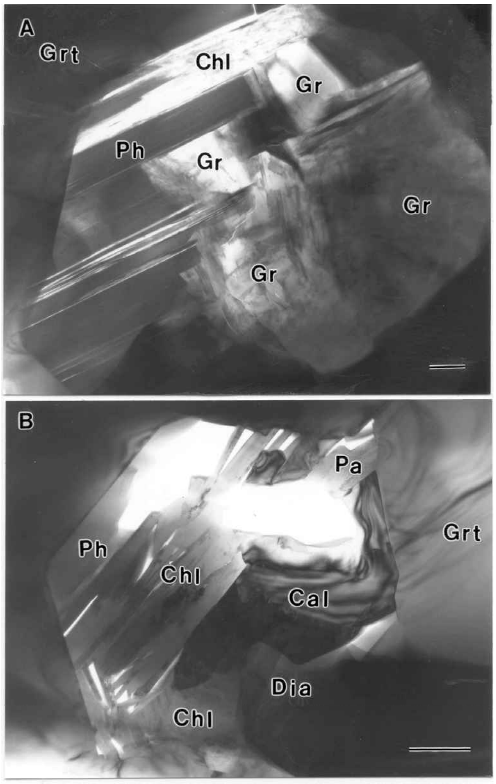

Fig. 6. (A) Transmission electron micrograph (bright-field image) of the inclusion assemblage: graphite (Gr) and phlogopite (Ph) with retrograde chlorite (Chl); and (B) bright-field image of the same diamond-containing inclusion assemblage as Fig. 1A with additional calcite (Cal), chlorite, and minor paragonite (Pa). Scale bars = 1 µm.

1982). Thus, cobaltite could also be stable in the diamond stability field.

Note that although the above discussion suggests that cobaltite or sphalerite could form in the diamond stability field, it does not exclude the possibility that these sulfide inclusions actually formed at lower P-T conditions, as in the case of some silicates in the Saxonian crustal diamond inclusions (Hwang *et al.*, 2001). Some metal sulfides in diamond-containing pockets show large compositional variations (see Fig. 3C, 3D and 3E) and are clearly not in chemical equilibrium. These sulfide inclusions might not have formed during the peak temperature conditions. It should be noted that the primary sulfide included during kimberlitic diamond growth is a monosulfide solid solution, from which subsequent subsolidus exsolution leads to the mineral sequence pyrite (FeS_2), pyrrhotite (FeS), pentlandite ($[Fe,Ni]_9S_8$), chalcopyrite ($CuFeS_2$), cubanite ($CuFe_2S_3$), and heazlewoodite (Ni_3S_2), as temperature decreases (Craig & Kullerud, 1969; Craig & Scott, 1976). The present metal sulfides with varied chemical compositions can be justified under the additional effect of chemical reaction with the included fluid.

The constant mineral association in the diamond-containing pockets mentioned above also suggests that phlogopite is a primary phase. Phlogopite is known to decompose to garnet + liquid in the stability field of diamond in ultramafic systems (Giardini *et al.*, 1974). The decomposition temperature for biotite with the Fe/(Fe+Mg) ratio of 0.57-0.61 is about 1227°C at 5.5 GPa (Giardini *et al.*, 1974). Phlogopitic biotite appears to have approximately the same stability limit in the absence of H_2O (Kushiro *et al.*, 1967), but the limit is expected to shift to significantly lower temperatures in abundant H_2O (Giardini *et al.*, 1974). Phlogopite associated with microdiamond as inclusion in garnet from gneisses of the Kokchetav Massif has been suggested to form at UHP conditions (Sobolev & Shatsky, 1990; Zhang *et al.*, 1997). Such a mica mineral has a Si content of 2.8 to 2.9, similar to the biotite formed during the granulite facies overprint, implying unlikely an UHP phase for normal pelitic compositions (Hermann & Green, 2001a & b; Hermann, 2002). However, according to experimental results of the model system K_2O-CaO-MgO-Al_2O_3-SiO_2-H_2O (KCMASH), biotite persists up to ~3.7 GPa at 750°C with saturation of SiO_2, kyanite, and clinopyroxene (see Figure 2 of Hermann, 2002). In addition, as clearly shown by Hwang *et al.* (2001), the phlogopite flakes in diamond-inclusion pocket were enclosed by a diamond overgrowth layer, indicating that phlogopite is stable in the diamond stability field. Thus, phlogopitic biotite in diamond-containing pockets could be interpreted as a primary high-pressure phase in contrast to retrograde matrix biotite having a much lower Mg content.

Syngenetic nucleation of diamonds from fluid with dissolved catalysts

Sulfide inclusions, if found inside the diamonds, should give direct evidence of a diamond-sulfide connection as proposed for the formation of terrestrial diamond, for example those found in Mantle Xenoliths (Marx, 1972; Meyer, 1987). However, a nucleus with catalytic surface steps is allowed to cause polycrystalline diamonds as well. For example, the diamond crystallite that nucleates on the $\{111\}$-$\{001\}$ and $(\bar{1}11)$-$(1\bar{1}1)$ intersecting steps of the Si substrate shows perfect and partial epitaxial orientation, respectively (Lee *et al.*, 2000). In contrast, other sites lead to polycrystalline growth (Lee *et al.*, 2000). Given that metal sulfides could be stable in the diamond stability field yet are in crystallographically independent association with microdiamonds, all these phases were likely co-precipitated, *i.e.* syngenetic, from a fluid before and after enclosure in the garnet host, although the possibility that metal sulfides precipitated earlier cannot be completely excluded. However, some metal sulfides having variable chemical compositions forming at low temperatures may indicate that microdiamonds indeed formed from a fluid phase containing siderophile and chalcophile elements.

Fluid inclusions, such as brine (Izraeli *et al.*, 2001), have been reported in fibrous or cloudy diamonds, which give clues on mantle fluids from the depth of diamond stability field. Unfortunately fluids, in any form, were not directly observed in the present samples. Nevertheless, textural evidence as well as the need to transport carbon has been used to suggest that terrestrial diamonds generally grew from fluid (Sunagawa *et al.*, 1984; Izraeli *et al.*, 2001). In the present case, a one-to-one correlation between dislocation and the summit of growth pyramids together with the end of dissolution pits agrees with the spiral growth mechanism (Porter & Easterling, 1981; Sunagawa *et al.*, 1984) via a dissolution-precipitation process in a fluid/solution. It is also noteworthy that the radiating dislocation configurations are typical for solution-grown crystals (Tanner, 1976; Sunagawa *et al.*, 1984).

The association of microdiamonds with phlogopite and other phases as inclusions in garnets of quartzofeldspathic rocks from Saxonian Erzgebirge, implies precipitation from COH + silicate fluid (Stöckhert *et al.*, 2001) and/or a precedent melt (Hwang *et al.*, 2001). The diamond/mica association in the present study, as well as those reported in diamondiferous rocks from the Kokchetav Massif (Sobolev & Shatsky, 1990; Zhang *et al.*, 1997; Ishida & Ogasawara, 2000), therefore, suggests that the genesis of microdiamonds in equilibrium with a fluid and/or melt might be common for quartzofeldspathic crustal rocks subducted into the diamond stability field. (Note that at the diamond stability field, it might be hard to differentiate highly concentrated siliceous and alkaline fluids from melts (Scambelluri & Philippot, 2001).)

The solvent-catalyst effect is of concern to the diamond formation in metal-sulfur-COH-silicate fluid for diamondiferous rocks from both Saxonian Erzgebirge and Kokchetav Massif. Unfortunately there is no experimental data of this exact composition to compare with. The diamond growth experiments in pure sulfide melts may somehow shed light on this aspect. Aside from the possible compositional complexity and miscibility of the COH fluid and silicate melt, the catalytic nuclei in the liquid are most likely in the form of elements and/or atom clusters rather than crystalline state because there is no specific crystallographic relationships between diamonds and metal sulfides. If microdiamonds were nucleated on a crystalline seed, it would be hard to avoid epitaxial nucleation on some nucleation sites, as observed in the case of diamond deposition on a Si substrate (Lee *et al.*, 2000). This interpretation is in accordance with a number of elemental solvent-catalysts such as P (Akaishi *et al.*, 1993) and S (Sato & Katsura, 2001), which have been proved experimentally to facilitate diamond formation. The co-presence of Fe, Co, and Ni should further lower the limit of synthesis temperature of the present microdiamonds. For example, Fe and Ni, were found to be more effective in catalyzing diamond formation from carbon (graphite being most favorable) at P-T conditions as low as 5 GPa at 1400°C (Bovenkerk *et al.*, 1959). In general, the activation energies for solvent-catalyst assisted graphite to diamond transition vary inversely with the solubility of carbon in these solvents (Sung *et al.*, 1996). As a result of the easy dissolution of C and H, the melting points of these solvents are dramatically suppressed below their normal eutectic points, and the CH_4-like clusters can facilitate diamond formation in such a liquid phase. In view of these experimental and energetic considerations of catalytic effect, it is conceivable that siderophiles and chalcophiles in the precursive fluid of diamond-containing inclusions may control the crystallization of microdiamonds. A minute amount of these elements, as indicated by the submicron size of metal sulfides, could be adequate to make diamonds. This is substantiated by the fact that chalcophiles and siderophiles, in particular molten transition metals of group VIII of the periodic table, are used commercially as solvent/catalysts enhancing the mobility of carbon and mediating the precipitation of diamond at extreme pressures and temperatures (Burns & Davies, 1992; Haggerty, 1999). In fact, very small additions (as little as 1%) of conventional catalyst metals were found to be enough to provide a carbon solvent and promote diamond nucleation (Bundy, 1973). In addition, as commented by Chepurov *et al.* (1999), although it is accepted that most natural diamonds crystallized from silicate melts and the P-T conditions of their formation were estimated to be 900-1500°C and 50-60 kbar, no diamond have been synthesized at such low temperatures and pressures in silicate-carbon systems. Chepurov *et al.* (1999) has synthesized diamonds in fayalite+graphite and magnetite+ graphite mixtures by partial reduction of the samples with hydrogen and metallic titanium at 1300-1400° C and 50-55 kbar. Such experiments can be regarded as a simplified model of the formation of some types of natural diamonds during the interaction of reduced fluids with carbon bearing mantle rocks. It was found that the hydrogen caused local reduction of the samples with separation of metallic iron, which catalyzed the transformation of graphite into diamond. Iron reacted with other elements and was not found in the free state in the products of the experiments, again indicating also that a tiny amount of catalyst is adequate to produce diamond.

It is noteworthy that metal sulfides in the form of negatively charged atom clusters associated with H_2O were known to undergo dehydration and then condensation to form sphalerite or wurtzite structure in aqueous and ambient conditions (Luther *et al.*, 1999). The formation of ZnS is such an example following the Ostwald step rule where nucleation of a more soluble phase is kinetically favored over that of a less soluble phase due to the lower solid solution interfacial tension of the more soluble phase. It is possible that the sulfate component (Dobrzhinetskaya *et al.,* 2001) or some cluster units of siderophiles and chalcophiles act as nucleation agent in the diamond stability field.

Since diamond formation requires a higher temperature and pressure for sulfur-carbon system (Sato & Katsura, 2001) than transition metals with carbon (Bovenkerk *et al.*, 1959; Sung *et al.*, 1996), the nucleation of diamonds from carbonaceous materials, including the most promising graphite, should be mediated mostly by molten metals (Bovenkerk *et al.*, 1959; Sung *et al.*, 1996) and under the effect of sulfur on the metal-carbon eutectic, besides the widely accepted role of COH + silicate fluid. Local concentration of 3-d transition metals in COH + silicate fluid is conceivable because these elements, in particular Fe, Co and Ni, have rather similar chemical affinities in terms of ionic radii *vs.* pH or electronegativity (Kostov & Minčeva-Stefanova, 1982). Intermediate reactivities of these transition metals have been suggested to be most effective in catalyzing the graphite to diamond transition in the diamond stability field (Sung & Tai, 1997). The metal-carbon eutectic melting line (Sung *et al.*, 1996) may thus give a fair P-T constraint for synthetic and natural diamond nucleation in the diamond stability field. This critical condition is further lowered by the cotectic melting line Fe+Ni+C (Fe+Co+C) (Kocherzhinskii *et al.*, 1993) and Fe+Ni+S+O (Urakawa & Kato, 1987) (Fig. 7) for crustal diamonds due to the co-presence of Fe, Ni, Co, S and hydrous-silicate components that led to the formation of phlogopite. This P-T condition is close to that determined by independent garnet-clinopyroxene thermobarometer, as mentioned, for this particular Kokchetav sample K12A (Zhang *et al.*, 1997).

The present study thus indicates that transition metal sulfides having a rather low melting temperature in the presence of carbon and being soluble in COH + silicate fluid may control diamond nucleation and paragenesis in a subducted continental crust. This may not be ignored in addition to a multicomponent COH fluid (Dobrzhinetskaya *et al.*, 2001; Stöckhert *et al.*, 2001) and a high CO_2 content (Ogasawara *et al.*, 2000) proposed to be required for the genesis of crustal diamonds.

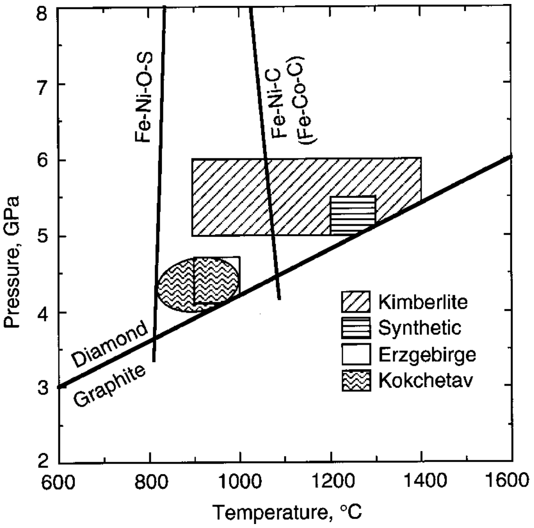

Fig. 7. The lower limits of pressure and temperature conditions for diamond formation from graphite and constrained by melting lines of Fe+Ni+C (Fe-Co-C) (Kocherzhinskii *et al.*, 1993) and Fe+Ni+S+O (Urakawa & Kato, 1987). Also shown in the figure are the graphite-diamond boundary (Sung *et al.*, 1996) and the formation T-P ranges for synthetic and kimberlite diamonds (Haggerty, 1999), crustal diamonds from Saxonian Erzgebirge (Massonne, 1998) and Kokchetav massif (Zhang, *et al.*, 1997; Katayama *et al.*, 2000).

Conclusions

Submicron metal sulfides in association with diamond inclusions in garnet were identified by AEM in a particular garnet-clinopyroxene-quartz rock K12A from the Kokchetav Massif. These metal sulfides have close-packed crystal structures and are not associated with graphite-containing pockets and/or infiltration cracks, suggesting a likely primary origin during diamond formation. The textural and phase assemblage evidences of diamond-containing pockets support the previous proposal of fluid-facilitated natural diamond genesis. It is noted however that the siderophile and chalcophile elements could be important solvent-catalysts in the fluid based on nonepitaxy relation of diamond/metal sulfides and reported synthesis P-T conditions. So far, the tiny metal sulfides in association with micrometer-size diamond inclusions in garnet were identified by AEM for the two specimens of UHP gneisses from the Kokchetav Massif and Saxony Erzgebirge. It is an open question whether AEM technique would reveal otherwise unrecognized solvent-catalysts for other natural diamond occurrences as well. Future petrologic and isotopic study is also important (Hermann *et al.,* 2001) in view of a better constraining of the liquid composition that would be stable at UHP conditions (Hermann & Green, 2001a & b).

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References

Akaishi, M. & Yamaoka, S. (2000): Crystallization of diamond from C-O-H fluids under high-pressure and high-temperature conditions. *J. Cryst. Growth,* **209**, 999-1003.

Akaishi, M., Kanda, H., Yamaoka, S. (1993): Phosphorus: an elemental catalyst for diamond synthesis and growth. *Science,* **259**, 1592-1593.

Arima, M., Nakayama, K., Akaishi, M., Yamaoka, S., Kanda, H. (1993): Crystallization of diamond from a silicate melt of kimberlite composition in high-pressure and high-temperature experiments. *Geology,* **21**, 968-970.

Atkinson, W.J., Hughes, F.E., Smith, C.R. (1984): Kimberlites and Related Rocks. Developments in Petrology. J. Kornprobst, ed., Elsevier, Amsterdam, v. 9, 195-225.

Birch, F. (1966): Compressibility; Elastic Constants. *in* "Handbook of Physical Constants – Revised Edition Memoir of the Geological Society of America", v. 97, 97-173.

Bovenkerk, H.P., Bundy, F.P., Hall, H.T., Strong, H.M., Wentorf Jr., R.H. (1959): Preparation of diamond. *Nature,* **184**, 1094-1098.

Bridgman, P.W. (1925): Linear compressibility of fourteen natural crystals: *Am. J. Sci.,* **10**, 483-498.

Bulanova, G.P., Griffin, W.L., Ryan, C.G. (1998): Nucleation environment of diamonds from Yakutian Kimberlites. *Mineral. Mag.,* **62**, 409-419.

Bundy, F.P. (1973): Diamond synthesis with non-conventional catalyst-solvents. *Nature,* **241**,116-118.

Burns, R.C. & Davies, G.J. (1992): Growth of Synthetic Diamond. *in* "The Properties of Natural and Synthetic Diamond", J.E. Field, ed., Academic Press, New York, 395-422.

Chepurov, A.I., Fedorov, I.I., Sonin, V.M., Bagryantsev, D.G., Osorgin, N.Y. (1999): Diamond formation during reduction of oxide- and silicate-carbon systems at high P-T conditions. *Eur. J. Mineral.,* **11**, 355-362.

Craig, J.R. & Kullerud, G. (1969): Phase relations in the Cu-Fe-Ni-S system and their application to magmatic ore deposits. *Econ. Geol. Mono.,* **4**, 344-358.

Craig, J.R. & Scott, S.D. (1976): Sulfide phase equilibria. In "Sulfide Mineralogy", P.H. Ribbe, ed., Min. Soc. Amer. CS1-CS100.

De Corte, K., Cartigny, P., Shatsky, V.S., Sobolev, N.Y., Javoy, M. (1998): Evidence of fluid inclusions in metamorphic microdiamonds from the Kokchetav massif, northern Kazakhstan. *Geochim. Cosmochim. Acta,* **62**, 3765-3773.

De Corte, K., Korsakov, A., Taylor, W.R., Cartigny, P., Ader, M., De Paepe, P. (2000): Diamond growth during ultrahigh-pressure metamorphism of the Kokchetav Massif, northern Kazakhstan. *The Island Arc,* **9**, 428-438.

Deines, P. & Harris, J.W. (1995): Sulfide inclusion chemistry and carbon isotopes of African diamonds. *Geochem. Cosmochim. Acta,* **59**, 3173-3188.

Dobrzhinetskaya, L.F., Green II, H.W., Mitchell, T.E., Dickerson, R.M. (2001): Metamorphic diamonds: mechanism of growth and inclusion of oxides. *Geology,* **29**, 263-266.

Giardini, A.A., Hurst, V.J., Melton, C.E., Stormer Jr., J.C. (1974): Biotite as a primary inclusion in diamond: its nature and significance. *Am. Mineral.,* **59**, 783-789.

Haggerty, S.E. (1999): A Diamond trilogy: superplumes, supercontinents, and supernovae. *Science,* **285**, 851-860.

Harris, P.J.F. (1999): Carbon nanotubes and related structures – new materials for the twenty-first century. Cambridge University Press, Cambridge, Ch. 3, 61-110

Hermann, J. (2002): Experimental constraints on phase relations in subducted continental crust. *Contrib. Mineral. Petrol.,* **143**, 219-235.

Hermann, J. & Green, D.H. (2001a): Experimental constraints on melt-carbonate interaction at UHP conditions: A clue for metamorphic diamond formation? Extended abstract for UHPM workshop 2001, Waseda University, Tokyo, Japan, 31-34.

–, – (2001b): Experimental constraints on high pressure melting in subducted crust. *Earth Planet. Sci. Lett.,* **188**, 149-168

Hermann, J., Rubatto, D., Korsakov, A., Shatsky V. (2001): Multiple zircon growth during fast exhumation of diamondiferous, deeply subducted continental crust (Kokchetav Massif, Kazakhstan). *Contrib. Mineral. Petrol.,* **141**, 66-82.

Hwang, S.L., Shen, P., Chu, H.T., Yui, T.F., Lin, C.C. (2001): Genesis of microdiamonds from melt and associated multiphase inclusions in garnet of ultrahigh-pressure gneiss from Erzgebirge, Germany. *Earth Planet. Sci. Lett.,* **188**, 9-15.

Ishida, H. & Ogasawara, Y. (2000): Diamond-phengite composite inclusion in garnet: Possible evidence of diamond stability under H_2O-bearing fluid in carbonate rock from the Kokchetav Massif.. *EOS Transactions AGU,* **81**, F1364.

Ishida, H., Ogasawara, Y., Ohta, M., Osumi, K. (1999): Microlaue X-ray diffraction study on microdiamonds from Kumdy-Kol in the Kokchetav UHP Terrane, Northern Kazakhstan. *EOS Transactions AGU,* **80**, F986.

Izraeli, E.S., Harris, J.W., Navon, O. (2001): Brine inclusions in diamonds: a new upper mantle fluid. *Earth Planet. Sci. Lett.,* **187**, 323-332.

Katayama, I., Zayachkovsky, A.A., Maruyama, S. (2000): Prograde pressure-temperature records from inclusions in zircons from ultrahigh-pressure-high-pressure rocks of the Kokchetav Massif, northern Kazakhstan. *The Island Arc,* **9**, 417-427.

Kocherzhinskii, Y.A., Kulik, O.G., Turkevich, V.Z. (1993): Phase equilibria in the Fe-Ni-C and Fe-Co-C systems under high temperatures and high pressures. *High Temp. – High Press.,* **25**, 113-116.

Kostov, I. & Minčeva-Stefanova, J. (1982): Sulphide Minerals – Crystal Chemistry, Paragenesis and Systematics. E. Schweizerbart'sche Verlagsbuchhandlung, Nägele u. Obermiller, Stuttgart, 1-212.

Kumar, M.D.S., Akaishi, M., Yamaoka, S. (2000): Formation of diamond from supercritical H_2O-CO_2 fluid at high pressure and high temperature. *J. Cryst. Growth,* **213**, 203-206.

Kushiro, I., Syono, Y., Akimoto, S. (1967): Stability of phlogopite at high pressures and possible presence of phlogopite in the earth's upper mantle. *Earth Planet. Sci. Lett.,* **4**, 197-203.

Lee, S.T., Peng, H.Y., Zhou, X.T., Wang, N., Lee, C.S., Bello, I., Lifshitz, Y. (2000): A nucleation site and mechanism leading to epitaxial growth of diamond films. *Science,* **287**, 104-106.

Luther, III G.W., Theberge, S.M., Rickard, D.T. (1999): Evidence for aqueous clusters as intermediates during zinc sulfide formation. *Geochim. Cosmochim. Acta,* **63**, 3159-3169.

Marx, P.C. (1972): Pyrrhotine and the origin of terrestrial diamonds. *Mineral. Mag.,* **38**, 636-638.

Massonne, H.J. (1998): A new occurrence of microdiamonds in Quartzofeldspathic rocks of the Saxonian Erzgebirge, Germany, and their metamorphic Evolution. *in* "Proc.7th Int. Kimberlite Conf.", J.J. Gurney, J.L. Gurney, M.D. Pascoe, S.H. Richardson, eds., Univ. Cape Town, P.H. Nixon Volume, v. 2, 533-539.

Meyer, H.O.A. (1987): Inclusions in diamond. *in* "Mantle Xenoliths", P.H. Nixon, ed., John Wiley and Sons, New York, 501-522.

Ogasawara, Y., Ohta, M., Fukasawa, K., Katayama, I., Maruyama, S. (2000): Diamond-bearing and diamond-free metacarbonate rocks from Kumdy-Kol in the Kokchetav Massif, Northern Kazakhstan. *The Island Arc*, **9**, 400-416.

Orlov, Y.L. (1977): The Mineralogy of the Diamond. Wiley-Interscience, New York, 1-235.

Paly'anov, Y.N., Sokol, A.G., Borzdov, Y.M., Khokhryakov, A.F., Shatsky, A.F., Sobolev, N.V. (1999a): The diamond growth from Li_2CO_3, Na_2CO_3 and $CaCO_3$ solvent-catalysis at P= 7 GPa and T = 1700-1750°C. *Diam. Relat. Mater.*, **8**, 1118-1124.

Paly'anov, Y.N., Sokol, A.G., Borzdov, Y.M., Khokhryakov, A.F., Sobolev, N.V. (1999b): Diamond formation from mantle carbonate fluids. *Nature*, **400**, 417-418.

Porter, D.A. & Easterling, K.E. (1981): Phase transformations in metals and alloys. Van Nostrand, Reinhold, 198-203.

Qadri, S.B., Skelton, E.F., Dinsmore, A.D., Hu, J.Z., Kim, W.J., Nelson, C., Ratna, B.R. (2001): The effect of particle size on the structural transitions in zinc sulfide. *J. Appl. Phys.*, **89**, 115-119.

Sato, K. & Katsura, T. (2001): Sulfur: a new solvent-catalyst for diamond synthesis under high-pressure and high-temperature conditions. *J. Cryst. Growth.*, **223**, 189-194.

Scambelluri, M. & Philippot, P. (2001): Deep fluids in subduction zones. *Lithos*, **55**, 213-227.

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

Sokol, A.G., Tomilenko, A.A., Pal'yanov, Y.N., Borzdov, Y.M., Pal'yanova, G.A., Khokhryakov, A.F. (2000): Fluid regime of diamond crystallization in carbonate-carbon systems. *Eur. J. Mineral.*, **12**, 367-375.

Stöckhert, B., Duyster, J., Trepmann, C., Massonne, H.J. (2001): Microdiamond daughter crystal precipitated from supercritical COH + silicate fluids included in garnet, Erzgebirge, Germany. *Geology*, **29**, 391-394.

Sunagawa, I., Tsukamoto, K., Yasuda, T. (1984): Surface microtopographic study of octahedral crystals of natural diamond from Siberia, Materials Science of Earth's Interior. I. Sunagawa, ed., Terrapub, Tokyo, 331-349.

Sung, C.M. & Tai, M.F. (1997): Reactivities of transition metals with carbon: implications to the mechanism of diamond synthesis under high pressure. *Inter. J. Refract. Metals Hard Mater.*, **15**, 237-256.

Sung, C.M., Tai, M.F., Cheng, C.S., Huang, Q.S., Yao, Y.D. (1996): Kinetics of the graphite to diamond transition under high pressure. *High Temp. – High Press.*, **28**, 499-521.

Tanner, B.K. (1976): X-ray diffraction topography. Pergamon Press, London, 174 pp.

Uchino, M., Mashimo, T., Kodama, M., Kobayashi, T., Takasawa, E., Sekine, T., Noguchi, Y., Hikosaka, H., Fukuoka, K., Syono, Y., Kondo, T., Yagi, T. (1999): Phase transition and EOS of zinc sulfide (ZnS) under shock and static compressions up to 135 Gpa. *J. Phys. Chem. Solids*, **60**, 827-837.

Urakawa, S. & Kato, M. (1987): Experimental study on the phase relations in the system Fe-Ni-O-S up to 15 GPa. *in* "High-Pressure Research in Mineral Physics", M.H. Manghnani & Y. Syono, eds., Terra Scientific, Tokyo, 95-111.

Vaughan, D.J. & Craig, J.R. (1976): Mineral Chemistry of Metal Sulfides. Cambridge University Press, Cambridge, 1-493.

Zhang, R.Y., Liou, J.G., Ernst, W.G., Coleman, R.G., Sobolev, N.V., Shatsky, V.S. (1997): Metamorphic evolution of diamond-bearing and associated rocks from the Kokchetav Massif, Northern Kazakhstan. *J. Metamorph. Geol.*, **15**, 479-496.

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Appendix: Diamond/graphite classification scheme reported for Kokchetav massif

De Corte *et al.* (2000) and Ogasawara *et al.* (2000) described the coexistence of diamond and graphite in inclusions within garnets in gneiss and metacarbonate rocks from Kumdy-Kol in the Kokchetav Massif based on optical microscopy and laser Raman spectroscopy. Three subgroups were recognized by De Corte *et al.* (2000): (1) intergrowth of diamond and graphite; (2) separate graphite crystal, and (3) graphite forming a coating on diamond. In addition, Katayama *et al.* (2000) gave a report on the formation of microdiamond crystals from one graphite crystal using the evidence of graphite rimmed by diamonds as inclusions in zircon extracted from several Kokchetav UHP rocks. Moreover, the microdiamonds in diamondiferous dolomite marble were classified (Ishida *et al.*, 1999) as: (1) type-R (5-20 micron): rugged surface diamond, consisting mainly of core part with slight amount of surrounding parts, (2) type-S (5-20 microns): star-shaped form consisting of core and surrounding subhedral crystals, (3) type-T (1-7 microns): very fine grained transparent diamond without core. Based on micro-Laue diffraction, they further found that the cores of type-S and type-R are a single crystal, and core diamond and surrounding diamond grains of type-S have different crystal orientations.

In the present Kokchetav sample K12A, diamond inclusions in garnet, through detailed lattice imaging, were not found to co-exist with graphite. Some diamonds also survived from retrograde Ca-infiltration and chloritization-paragonitization without forming graphite (Fig. 6B). Since textural classification scheme may rely on specific analyzing techniques and/or rock types, future detailed study is required to see if the present diamond-containing and graphite-containing pockets, based on AEM observations as mentioned, fit the above scheme. In any case, the present microdiamond aggregates appear to better fit the type-S of the above classification of microdiamonds. The small inner or core diamond in the present aggregates can be interpreted as originally graphite or alternatively as a result of the effect due to assembling and sintering of microdiamonds, which nucleated rapidly from a precursive fluid. The graphite/phlogopite inclusions might be low-temperature minerals included in garnets or can be rationalized by the local shortage of catalysts, *i.e.*, siderophile and chalcophile elements which helped precipitation of diamond in the precedent fluid. Although the possibility of complete transformation of graphite to/from diamond cannot be completely excluded, the present observations may suggest that different occurrences of microdiamonds in UHP rocks may have different formation mechanisms.