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Discussion

Comment on “Diamond, former coesite and supersilicic garnet in metasedimentary rocks from the Greek Rhodope: a new ultrahigh-pressure metamorphic province established”

by E.D. Mposkos and D.K. Kostopoulos
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The documentation of diamond in metamorphic crustal rocks from collision zones is evidence for continental subduction at mantle depths exceeding 100 km. The occurrence of such metamorphic microdiamonds is well established and was characterized in situ in the Kokchetav Massif of Kazakhstan [1] and in the Erzgebirge of Germany [2]. An isolated report from the Western Gneiss Region, Norway [3] was recently confirmed by in situ findings [4] and, whereas the report of a few larger metamorphic diamonds in the Dabie Shan-Sulu terrain, eastern China [5] has not yet been independently duplicated, it is lent credence by the discovery of in situ metamorphic microdiamonds in Central China [Jingsui Yang et al., submitted]. In a recent paper, Mposkos and Kostopoulos ([6], MK in the following) report the discovery of ultrahigh pressure (UHP) mineral in-

dicators from the Rhodope metamorphic province, northern Greece. Among these, the identification of microdiamonds as inclusions in eclogite-facies garnet constitutes the most definite evidence for UHP metamorphism. However, we suggest that the data reported in this paper do not lend unambiguous support to this identification.

Because of the major consequences for geological history, it is vital that the origin of diamond in such study is established beyond doubt. Diamond can actually be an artifact of thin-section preparation, for instance, as residual particles from the diamond saw or the polishing material. To eliminate such doubt, the best method is probably to check for the presence of diamond inclusions *within* the section by focusing at various depths [2], and not restrict the analysis to the two polished sides of the rock slice. In this respect, the scanning electron microscope (SEM) (therefore surface) images proposed by MK are ambiguous. The reported octahedral shape of diamonds is not easy to recognize in their figure 2C,D. More surprising is the interpretation of their figure 2E, which is supposed to illustrate

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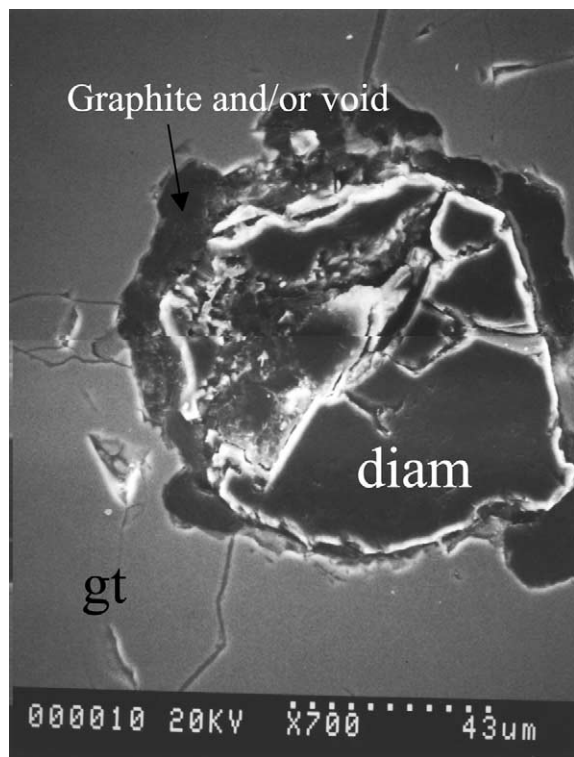


Fig. 1. Secondary electron image of a diamond inclusion within garnet (gt) in garnet–diopside rock (Kokchetav Massif, Kazakhstan). Sample #25018 Ruhr-Universität Bochum, courtesy H.-P. Schertl. Hitachi 2500 microscope, 20 kV (ENS Géologie, Paris).

an octahedral diamond inclusion within garnet. In our opinion, this image resembles more closely a void within garnet, probably due to the extraction of the inclusion (diamond?) itself. For comparison, the SEM image of a diamond inclusion in garnet from the Kokchetav Massif is shown in Fig. 1: the diamond crystal can easily be recognized. The transmitted-light micrograph presented by MK (their figure 2B) does indeed leave the possibility that the inclusions, whatever they are, occur at various depths within the garnet section and therefore can be characterized.

Raman spectroscopy is the most appropriate tool to establish without any ambiguity the presence of microdiamonds in such rocks, as (1) it allows in situ measurements with a high spatial resolution and (2) it is possible to easily distinguish graphite from diamond because they have very different vibrational properties. The first-order Raman spectrum of a diamond inclusion within garnet from the Kokchetav massif is shown in Fig. 2a. For comparison, the first-order Raman spectrum of disordered graphite, probably a graphitized-diamond inclusion, from the same thin section is presented in Fig. 2b. The diamond is easily recognized by the very narrow peak at 1332 cm^{-1} corresponding to the F_{2g} mode of diamond. There is no possible confusion with the D1 defect band of graphite at 1350 cm^{-1} , as the band width of the latter is always at least one order of magnitude larger. The presence of diamond microcrystallites within a disordered graphite matrix

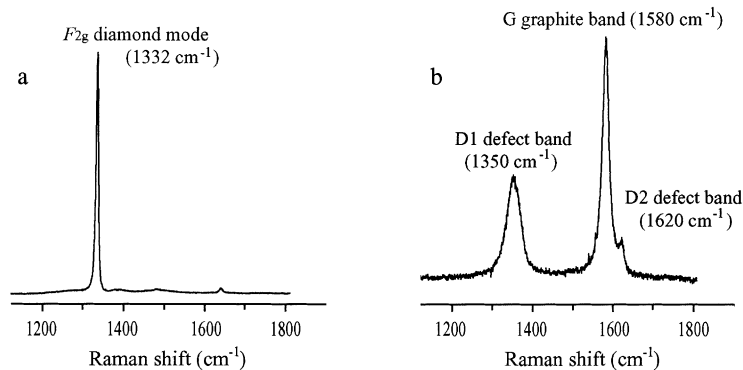


Fig. 2. (a) Raman spectrum from a diamond inclusion within garnet (Kokchetav Massif, Kazakhstan). (b) Raman spectrum from a graphitized diamond inclusion within garnet, same sample as in panel a. Sample courtesy R. Oberhänsli. Experimental conditions as given in [38].

is easily detected by the thin F_{2g} mode of diamond overlapping the broad graphite D1 band (e.g. figure 5 in [7]).

The comparison between the Raman spectrum published by MK (their figure 3) and the spectra presented here in Fig. 2 leads us to conclude that the former is representative of graphite, and not of diamond as suggested by MK. In our opinion, the band at 1334 cm^{-1} of this spectrum is too broad to be the F_{2g} mode of diamond and is instead the D1 defect band of graphite. MK explain the broadening of the alleged diamond band by the nanometric dimensions of the diamond domains, referring to Yoshikawa et al. [8]. First, it should be noted that the latter authors never used the term nano- in their paper as they studied micrometer-sized diamond particles. Second, these authors obtained a linewidth of 3.8 cm^{-1} for the smallest particles they studied, and this value is 10 times lower than the linewidth of the band at 1334 cm^{-1} observed by MK (ca. 40 cm^{-1}). Third, Yoshikawa et al. explain that it is nearly impossible to measure the Raman spectrum of diamonds less than 50 \AA in size. Nevertheless, referring to the studies of Chen et al. [9], MK estimate the size of the diamond crystallites at ca. 47 \AA , but apparently had no problem measuring the spectrum of such small crystallites. Chen et al. calculated the Raman spectra of a nanometric diamond powder using a phonon confinement model to compare with experimental data on the thermal annealing of diamond at atmospheric pressure. Considering the extraordinary complexity of the diamond–graphite transition in terms of kinetics, structural mechanisms, etc., the applicability of the correlation proposed by Chen et al. [9] to calculate crystallite dimensions with metamorphic diamond should at least be discussed by MK.

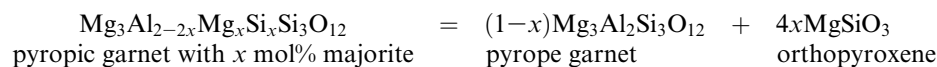
A clue to the interpretation of the MK spectrum is the presence of the shoulder at 1619 cm^{-1} on the graphite G band, which is correctly attributed by MK to disorder within graphite. This band at 1619 cm^{-1} is indeed classically ascribed to disorder within graphite, but is always associated with the presence of a main D1 defect band at 1350 cm^{-1} [10–12], a fact unaddressed by MK. The position of the D1 band is generally

situated at 1350 cm^{-1} when the Raman spectrum is obtained with an argon laser ($\lambda = 514.5\text{ nm}$). However, this defect D1 band has a strong dispersive character [13–15]. Mposkos and Kostopoulos used a HeNe laser with $\lambda = 632.8\text{ nm}$ (Kostopoulos, personal communication). If we calculate the position of the defect band of graphite with this wavelength, using the experimental correlation between the D1 band position and incident laser wavelength [14], we obtain a value in the range $1323\text{--}1334\text{ cm}^{-1}$. We conclude, therefore, that the 1334 cm^{-1} band in MK's figure 3 is the D1 defect band of graphite – an interpretation supported by the large width of this band, which, as shown above, precludes its interpretation as the F_{2g} mode of diamond. In summary, we interpret the Raman spectrum shown by MK in their figure 3 as that of a disordered graphite, with no evidence for the presence of diamond.

In addition, MK take the presence of ‘new’ Raman bands with respect to standard graphite and diamond (at 1188 , 1450 , and 1537 cm^{-1}) as the most striking evidence of the phase transformation in diamond, and therefore justifying the presence of diamond. Similar bands (at 1189 , 1450 and 1544 cm^{-1}) were described by Gogotsi et al. [16] in the Raman spectrum of an indenter after transformation of diamond during diamond–diamond indentation experiments, at a pressure of several hundred GPa, and attributed to ‘a certain carbon structure’. In the spectrum obtained by MK the bands at 1188 and 1450 cm^{-1} are so weak that it is difficult to separate them from the background noise. The band at 1537 cm^{-1} is stronger, but both the origin and the analogy between this band and the band at 1544 cm^{-1} observed by Gogotsi et al. [16] should be discussed. Is that band systematically observed in all Raman spectra from Rhodope? In our opinion, it is again a shortcoming to compare the transformation of diamond during metamorphism (high temperature and high confining pressure, shear, geological timescale) to the experiment by Gogotsi et al., which represents an entirely different context (ambient temperature, low confining pressure, very high shear, short duration). Such a comparison is speculative, at best, as an explanation of the presence of ambiguous and weak fea-

tures in this Raman spectrum. It cannot be taken as evidence for the former presence of diamond.

As additional evidence for UHP, MK report the occurrence of apatite inclusions and crystallographically oriented inclusions of quartz and rutile in garnet, which they interpret as precipitates and evidence for a former majoritic garnet. Strictly speaking, the transformation of a majoritic garnet upon decompression leads to the exsolution of pyroxene, mostly orthopyroxene, according to a reaction of the type:



Such a reaction is documented from garnet in kimberlites [17] and from Alpine-type UHP garnet peridotite (W. Norway [18–20], eastern China [21]) and led to crystallographically oriented exsolution of ortho- and/or clinopyroxene. The occurrence of quartz, or rutile, or possibly apatite precipitates points to different reactions which may result from substitutions that are unrelated to the majoritic one, and so may have quite a different meaning in terms of P and T attained. The high phosphorus, titanium and sodium contents mentioned by MK can, for instance, be related to substitutions like $\text{MgSi}=\text{NaP}$ and $\text{MgAl}=\text{NaTi}$, which, although known in high-pressure and/or high-temperature garnets (e.g. [22–26]), do not bear the same implications of extreme pressures as the majoritic substitution. In any event, the presence in garnet of precipitates that do not involve pyroxene cannot be simply equated with a majoritic component in garnet. Furthermore, oriented inclusions should not be interpreted as precipitates without discussion, because crystallographically oriented quartz rods have been described in amphibolite-facies garnet where they are demonstrably epitaxial growth features, not exsolution [27–29]. Likewise, crystallographically oriented rutile needles in garnet also might not be exsolution features, but epitaxial intergrowths [30].

The best evidence presented by MK for possible UHP conditions is that obtained by the least sophisticated means: the thin-section photograph of their figure 2A indeed suggests a pseudomorph

after coesite, provided that the polycrystalline inclusion is made solely of quartz; that of their figure 2B is indeed reminiscent of variably graphitized microdiamond inclusions described from the Kokchetav massif [1,31] and the Erzgebirge [32]. However, if these inclusions are actually partly graphitized diamond, one should be able to show the unequivocal Raman signature of diamond in the relevant spectra (or to find preserved diamond included in zircon [33]). Interestingly, these dark ‘microdiamond’ inclusions in garnet

(figure 2B of MK) are aligned and show parallel faces, suggesting a crystallographic control by the host garnet. This is not a common feature of microdiamond inclusions (cf. [1,2]) but a quite common feature of primary fluid inclusions. Is this dark material [definitely graphite] a daughter mineral precipitated from a fluid inclusion, or does it replace diamond precipitated from a fluid or melt inclusion (cf. [34,35])? The Raman spectrum (MK’s figure 3) is very similar to that of graphite formed after diamond inclusions (Fig. 2b) but also to that obtained at the section surface on pristine graphite damaged by sample preparation [36,37].

In summary, clear evidence of diamond or majoritic garnet in Rhodope has not been presented by MK. The pieces of evidence provided by MK are a tantalizing indication of UHP, but are not compelling. They require a more rigorous discussion and further characterization, given the far-reaching implications of finding UHP relics. It may then eventually turn out that such relics are really present in the Rhodope rocks.

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