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Syngenesi s or Protogenesi s? New constraints on diamond formation from olivine inclusions

Fabrizio Nestola^{1,*}, Paolo Nimis¹, Ross J. Angel¹, Sula Milani¹, Marco Bruno², Mauro Prencipe², Jeffrey W. Harris³

¹Dipartimento di Geoscienze, Università di Padova, via Gradenigo 6, I-35131 Padova, Italy, ²Dipartimento di Scienze della Terra, University of Torino, via Valperga Caluso 35, I-10125, ³School of Geographical and Earth Sciences, University of Glasgow, Glasgow, UK. *e-mail: fabrizio.nestola@unipd.it.

Diamond is almost chemically pure carbon and extremely chemically inert. Therefore, unlike silicate minerals, the structure and chemistry of diamond reveals very little about its conditions of formation. Much of what is believed about the genesis and distribution of diamond in the Earth's mantle has therefore been deduced indirectly from the characterisation of its mineral inclusions. It is often assumed that the inclusions were formed at the same time as the host diamond (that they are *syngenetic*), and do not represent pre-existing material that was passively incorporated into the growing diamond (*protogenetic* inclusions) or late material that formed within a pre-existing diamond (*epigenetic* inclusions). However, the widespread assumption that many or most inclusions in diamonds are syngenetic is based on very few direct measurements. Therefore we have determined the crystallographic orientations of forty-seven olivine inclusions with diamond-imposed morphology, a feature generally interpreted to indicate syngenesi s, in twenty-one diamonds from the Udachnaya kimberlite (Siberia). Our unprecedented large dataset indicates no overall preferred orientation of olivines in diamond. Nonetheless, multiple inclusions within a single diamond frequently exhibit similar orientations implying that they are derived from single original monocrystals. Carbon precipitation in a pre-existing olivine-rich matrix thus appears to be the most likely mechanism of formation of these peridotitic diamonds at Udachnaya. The olivine inclusions would thus pre-date the diamond growth and are therefore *protogenetic*, throwing the real significance of the many inclusions in diamonds claimed to be “syngenetic” into doubt.

Diamond – Olivine – Protogenesi s/Syngenesi s – Crystallographic orientation

The identification of syngenetic inclusions has long been of paramount importance in diamond studies. Since diamond behaves as an inert container, any geological information extracted from a syngenetic inclusion, such as pressure and temperature of formation, age, and geochemistry of the parent medium, should also unequivocally apply to its host diamond. The most commonly used “proof” of syngenesi s is the imposition of the morphology of the diamond on the inclusion (e.g. 1,2). This traditional criterion is based on the belief that diamond can impose its morphology upon the inclusion only during mutual growth, owing to its much greater “form energy” (3). This view

was challenged by the recognition of inclusions of harzburgitic garnets with diamond-imposed morphology and sinusoidal chondrite-normalised Rare Earth Element (REE) patterns. Sinusoidal REE patterns are typical of garnets that underwent a multi-stage geochemical evolution, which would imply protogenesis (4). But syngenesism cannot be completely excluded because the REE patterns could be generated if the garnet crystallized directly from a melt that was modified by chromatographic exchange reactions with refractory garnet peridotites (5) or via reactions between mantle peridotite and diamond-forming fluids (6). It was suggested that an epitactic relationship between the inclusion and its host would represent a more robust proof of syngenesism (2, 3, 7, 8), but a systematic survey of these relationships for the different mineral species is lacking or has been restricted to limited sets of samples. In pioneering work on olivine, the most commonly-included silicate, Mitchell and Giardini (9) showed that two elongated inclusions in two diamonds had an orientation $((010)_{\text{olivine}} // (111)_{\text{diamond}}$ and $[101]_{\text{olivine}} // [101]_{\text{diamond}}$) that has been interpreted as reflecting an epitactic relationship (10). Although similar (but usually not exact) orientations were occasionally reported for other olivines (3, 10), doubts remain as to their actual statistical significance. The problem is quite simply that the orientations of only a handful of olivine inclusions have been measured and reported. Therefore, in order to provide statistically significant data on the relative crystallographic orientations of olivine inclusions in diamond, and thus to provide new constraints on the mechanisms of formation of diamond, we have determined the orientations of approximately 50 olivine inclusions in diamond. The study was performed by single-crystal X-ray diffraction on inclusions still trapped in diamonds from Udachnaya, Siberia (Russia).

Results and discussion

The crystallographic orientations, relative to their host diamonds, of the forty-seven olivine inclusions that we have measured are shown in Figure 1a. As a whole, the data show no statistical preference for any specific orientation. Only three olivines show an orientation comparable to that found by Mitchell and Giardini (9) (Fig. 1b). The absence of any clustering around this specific

orientation suggests that the three observed cases are the result of chance. On a statistical basis, such an orientation does not appear to be typical of olivines in diamond. The absence of a preferred orientation relationship indicates a lack of interfacial energy control during the formation of the inclusion–host pairs, which excludes epitaxy for most, if not all, olivines. Lack of epitaxy alone does not, however, rule out syngenesity. Although it is not known how the interfacial energy varies with orientation of the olivine, the variation could be too small to impose a specific orientation even if olivine and diamond grew together.

Although the overall distribution of olivine orientations appears to be random, multiple inclusions within the same diamond often show very similar orientations (within 8 to 18°) (Fig. 2). Up to three distinct sets of such similarly-oriented inclusions have been found within a single diamond. None of these sets has an orientation similar to that found by Mitchell and Giardini (9). Different olivines, or different sets of similarly-oriented olivines, within the same diamond may share a similar orientation for either $[100]_{\text{olivine}}$ or $[010]_{\text{olivine}}$ (within 10 to 12°; see diamonds 6, 14 and 21 in Fig. 2), but with the other axes oriented in completely different directions.

The clustering of the orientation of multiple inclusions in the same diamond is the most intriguing and unexpected result of our study. It indicates that a specific control must have operated on the relative orientations of these groups of olivine inclusions. However, given that the overall pattern of olivine orientations is random (Fig. 1a) and that the different sets of similarly-oriented olivines do not have the same orientation with respect to their respective diamonds (Fig. 2), such control cannot be related to interfacial processes. Given that epitaxy is not a possible control, we suggest that the only possible explanation is that each group of similarly-oriented olivines are remnant parts of one original monocrystal. This conclusion implies that the olivines existed prior to the diamond and are therefore protogenetic.

In principle, two mechanisms can be envisaged by which a protogenetic olivine can achieve a diamond-imposed morphology, namely (i) modification of the inclusion's shape after encapsulation, and (ii) selective partial dissolution of olivine during diamond growth. Mechanism (i) could take place by, for example, diffusion creep through the crystal lattice (Nabarro-Herring creep) or along the inclusion-host interface (Coble creep). We would expect this process to leave some features in the diamond just around the inclusions which would be revealed by cathodoluminescence (CL) studies. Inclusions in CL-zoned diamonds are often surrounded by μm - to $10\ \mu\text{m}$ -scale zones without zonation (11, 12), but these CL "dead zones" rarely have the breadth and morphology that one would expect if they were ghosts of pre-existing included material, and may rather be a consequence of strain around the inclusion (13). Although the energies required by diffusion creep in a diamond–olivine pair are unknown they are probably very large, given the absence of free fluid and the very low self-diffusivity of carbon in diamond (14). Therefore, it appears highly unlikely that the commonly observed diamond-imposed morphology is the result of post-entrapment processes.

Mechanism (ii) appears to be a more viable process. If diamond grows from a fluid or melt percolating through and reacting with an olivine-rich mantle rock, it may force selective dissolution of an adjacent olivine and, if required by mass-balance constraints, its re-precipitation elsewhere, so as to allow diamond to develop its energetically-favoured faceting. In some rare cases, one or more portions of the olivine itself may eventually remain entrapped in the growing diamond. During the incorporation process, the diamond–olivine interface is adjusted by means of interface diffusion. In this way, the interface strain energy is minimized and the inclusion achieves a diamond negative-crystal morphology (Fig. 4). In this case, the energies required to shape the inclusion would be much smaller than for mechanism (i), owing to the presence of a fluid medium.

If two or more portions of an original olivine monocrystal are incorporated, groups of similarly-oriented inclusions will be formed. Based on the size and spacing of the inclusions, the minimum required size of the original monocrystals (1 to 1.2 mm) would be compatible with the typical grain size of olivine in Udachnaya mantle rocks (from <0.1 mm to >1 cm, 15). Deformation of the original olivine monocrystal prior to diamond growth and/or limited rotations of olivine fragments during their incorporation in diamond would explain the small degree of mis-orientation observed within some of the inclusion sets (Fig. 2). Incorporation of portions of different original monocrystals would explain the occurrence of distinct sets of similarly-oriented inclusions within a single diamond (Fig. 2). A similar orientation for either $[100]_{\text{olivine}}$ or $[010]_{\text{olivine}}$ between the distinct sets of similarly-oriented inclusions within a single diamond (Fig. 2) would be consistent with the strong preferred orientation of $[100]_{\text{olivine}}$ and of $[010]_{\text{olivine}}$ in coarse and, respectively, porphyroclastic mantle peridotites from Udachnaya (16).

The recognition of the protogenetic nature of olivine in diamond has interesting implications. Much experimental work has been devoted to reproducing diamond-bearing mineral assemblages containing the same minerals found as inclusions believed to be syngenetic with diamond, olivine being one of these (e.g., 17, 18). The ability of a model growth medium to precipitate such syngenetic associations is believed to be evidence for its relevance in natural diamond-forming processes (17, 18). That many, perhaps most, olivine inclusions are in fact protogenetic instead suggests that beneath Udachnaya, olivine was not a major co-product of the diamond-forming processes. Thus diamond-forming reactions of the type $\text{MgCO}_3 + \text{MgSiO}_3 = \text{Mg}_2\text{SiO}_4 + \text{C} + \text{O}_2$ (e.g., 19), or direct segregation of diamond from migrating peridotite–carbonate melts (e.g., 17), which would typically involve co-precipitation of diamond and olivine, are not supported by our data.

Our results for olivine cast doubts on the true significance of many other reported “syngenetic” inclusions. In the absence of unequivocal evidence for syngeneses (e.g., epitactic relationship of diamond with inclusions sitting parallel to diamond growth zones, away from its nucleation core; cf. 12), any inclusion with diamond-imposed morphology could well be protogenetic. Considering the potentially very fast growth rate of diamond (e.g. up to several mm per minute in experiments with carbonatitic melts; 20), such protogenetic inclusions may not re-equilibrate completely during diamond growth. Protogenicity and incomplete chemical resetting might account for part of the scatter in some isochrons obtained from inclusions (21). Similarly, the occurrence of several “cold” inclusions in diamonds recording P-T conditions similar to those of the ambient conductive mantle (22) might reflect protogenicity and lack of re-equilibration during rapid diamond growth rather than precipitation from diamond-forming fluids that were thermally equilibrated with the ambient mantle.

Conclusions

Our data demonstrate that (1) many olivine inclusions in diamonds are protogenetic and (2) a diamond-imposed morphology cannot be considered as a proof of syngenicity of mineral inclusions in diamonds. Point (1) supports a mechanism of diamond growth by metasomatism of pre-existing mantle rocks. Point (2) implies that many mineral inclusions in diamonds claimed to be syngenetic on the basis of shape alone, may actually be protogenetic. Potential incomplete re-equilibration of these inclusions during episodes of rapid diamond growth should therefore be considered when interpreting geochemical, geochronological and thermobarometric data based on inclusions in diamonds. Whether or not the inclusions reflect the conditions at the time of diamond growth will depend on the relative rates of diamond growth against the rates of chemical and isotopic re-equilibration within the inclusion phases. If diamond growth is sufficiently slow for chemical re-equilibration to take place, then a protogenetic inclusion would give the same information as a

syngenetic inclusion. Further systematic work is required to verify the protogenetic vs. syngenetic nature of inclusions of minerals other than olivine on a similarly statistically robust basis.

Materials and Methods

The sample suite studied in this work was comprised of twenty-one gem-quality diamonds ranging from 2 to 3.5 mm in overall size. They generally exhibit an octahedral habit and contain one to eleven optically visible olivine inclusions ranging from 40 to 520 μm in size. One diamond (named Diamond-3) among those studied is shown in Figure 3 to provide a better idea of the type of diamonds investigated in this work. The inclusions have flattened or elongated diamond-imposed cubo-octahedral shapes. Just one single inclusion shows a strongly elongated morphology and a distorted curvilinear outline, but with observable diamond-imposed faceting at least at one end. Up to four unambiguously distinguished inclusions ($\geq 160 \mu\text{m}$ in size) could be measured in a single diamond.

The orientations of the olivine inclusions in each diamond were determined by single-crystal X-ray diffraction on a four-circle STOE STADI IV diffractometer equipped with an Oxford Diffraction CCD area detector using $\text{MoK}\alpha$ radiation at 50 kV and 40 mA and a graphite crystal monochromator. The sample-to-detector distance was 60 mm. The diamonds were mounted as described in Nestola et al. (23). Each inclusion in each diamond was centered optically in the X-ray beam for diffraction measurements, and a series of diffraction images were recorded in ‘fixed-phi’ mode during which the sample was rotated about the omega axis of the diffractometer with the phi axis fixed at zero. The sets of resulting diffraction images (279 frames of 1 degree rotation each in omega) were processed by the CrysAlis software from Oxford Diffraction (now Agilent). The positions of the diffraction peaks from the inclusion(s) and diamond were indexed and used to determine the ‘orientation matrix’ which specifies the orientation of each crystal (inclusions or diamond) relative to the mount holding the sample. The indexing procedure results in the

unambiguous identification of which diffraction maxima in the dataset belong to which crystal, whether they are diamonds or inclusion crystals. Inspection of the intensities and a comparison of predicted spot positions with the observed intensities allows diffraction from inclusions not centered in the beam to be identified.

For a small crystal in air, well-centered on the diffractometer, the uncertainty in orientation determined in this way is significantly less than 0.1 degree. The relatively large size of the diamonds results in large diffraction spots, whose size may result in an uncertainty in orientation of the diamonds alone of up to 1.5 degree. Test measurements show that the uncertainties in the orientation of an inclusion introduced by the inclusion being off-centered by the radius of the X-ray beam are about 0.5 degree. The uncertainty in the relative orientation of an inclusion relative to its diamond host is therefore no more than 2 degree.

Because each orientation matrix defines the orientation of each crystal (inclusion or diamond) relative to the diffractometer, appropriate mathematical manipulation of the orientation matrices defines the *absolute* orientation of an olivine with respect to its host diamond (as in Figure 2). The angles between the crystallographic axes of the inclusion and its diamond host can then be determined (see Results and Discussion section).

For a comparison between the *relative* orientations of inclusions in different diamonds, it is necessary to take into account the ambiguity in indexing the diffraction patterns that arises from the symmetry of both the olivine and the diamonds. We eliminate the ambiguity by applying the appropriate symmetry operations to the orientation matrices of each inclusion and its host diamond, so as to bring a chosen axis of the olivine into a chosen crystallographic asymmetric unit of the diamond. The resulting *relative* orientations of all of the inclusions in their host diamonds is shown in Figure 1. Further technical details of the orientation calculations, the role of symmetry, and the plotting procedures are given in the Supporting Information.

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Figure captions

Figure 1. Inclusions of three different olivines contained in Diamond-3 investigated in this study.

Figure 2. Relative orientations of the olivine inclusions and their diamond hosts allowing for the point symmetry of both (for details see Supplementary Information). **a** The distribution of the olivine (100) and (001) planes is random, which excludes control by epitaxy. The apparent increase of point density close to the diamond (0 $\bar{1}$ 1) or (1 $\bar{1}$ 0) planes is largely due to a few sets of multiple inclusions in individual diamonds showing similar orientations relative to their respective hosts. If only one inclusion is considered for each of these sets of similarly oriented olivines, the density of the (010) normals in the projection sphere becomes more uniform. **b** Same plot as **a**, but highlighting those olivines for which the (010) plane lies within 10° of the (111) plane of the host diamond. Only three out of 47 olivines show an orientation comparable to that found by Mitchell and Giardini (9), i.e., they have both their (010) planes nearly parallel to (111)_{diamond} and their [101] axes nearly parallel to a diamond direction equivalent to [101]. In both **a** and **b**, the [UVW] labels refer to the host diamond.

Figure 3. Stereograms showing the absolute observed crystallographic orientation relationships of multiple inclusions that occur in single diamonds as determined by single-crystal diffraction (for details see Supporting Information).

Figure 4. Selective partial dissolution of olivine during diamond growth. The diamond is shown in grey, the remaining grains are differently oriented crystals of olivine. The solid lines inside the single crystals of olivine are not indicating any cleavage but want to indicate the original relative crystallographic orientations. At t_0 the diamond nucleates at an olivine grain boundary and grows. In t_2 the selective partial dissolution of olivine during diamond growth starts to operate; in t_3 two fragments of two different crystals of olivine are totally entrapped and show different crystallographic orientations. The process carries on reaching t_4 where multiple inclusions of olivines are encapsulated in the same large crystal of diamond. Such inclusions can show different orientations if belonging to different crystals of pre-existing olivines or show similar orientations if they are fragments of the same original crystal. Such scenario definitively match both the experimental observations we found in our work: (1) olivines can show different orientations in diamond; (2) multiple inclusions of olivine can show the same crystallographic orientations in one single diamond.