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Evidence for two blue (type IIb) diamond populations

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Blue type IIb diamonds owe their colour to the presence of low concentrations (about 0.01–10 parts per million)[1] of boron. It has been argued, on the basis of their inclusions, that these rare stones are all derived from the lower mantle (at depths of about 600 km)[1]. Limited new carbon-isotopic data presented by ref. [1] were interpreted to complement earlier analyses of blue type II diamonds, collectively reflecting a range of light-to-heavy carbon-isotopic signatures. Our analysis indicates that type IIb diamonds instead represent two isotopically distinct parageneses with contrasting inclusions, one indeed derived from the lower mantle, and the other linked to the websteritic suite, and therefore of lithospheric provenance.

The mineral assemblages recognized in the type IIb stones[1] can be divided into a number of groups. An inferred basaltic assemblage, including coesite and jeffbenite, and phases interpreted to represent inverted bridgmanite, constitute relatively Mg-rich (basic–ultrabasic) associations. However, the most common inclusion (in 31 of 46 of the type IIb diamonds studied by ref. [1] is breyite (formerly referred to as $CaSiO_3$-walstromite), which is usually associated with larnite[1]. These two Ca-bearing minerals may be accompanied by ferropericlase and Mg-silicates, although these latter phases are often absent.

The presence of contrasting Mg-rich and Ca-rich associations in the blue diamonds studied suggests a bimodal population. This is strongly supported by the size frequency distribution of the Mg- and Ca-rich associations, illustrated in Fig. 1. It is pertinent to note that ferropericlase and breyite do not provide unequivocal evidence for a lower-mantle origin of the host diamond because both phases can also form at lithospheric pressures in a Ca-rich environment[2–4]. Diamonds with inclusions of breyite and ferropericlase, with or without larnite, but lacking Mg-silicates, are therefore shown as a separate class, as are diamonds containing only ferropericlase (that is, lacking Mg-silicates).

The two basic–ultrabasic subsuites are strongly biased to small sizes, with all stones less than 2.5 carats, and 17 of the 19 stones less than 1 carat, of which 13 are less than 0.5 carat. The breyite-larnite association forms a small proportion (6 of 18) of the stones less than 1 carat. All but one of the stones larger than 2 carats (17 of 18 diamonds) belong to the Ca-rich–ferropericlase suites. The available data thus indicate that the large blue diamonds are derived from the Ca-rich–ferropericlase suites, whereas the lower-mantle (superdeep) association is characterized by small sizes.

This size–composition dichotomy is supported by the small number of C-isotopic analyses reported for type IIb stones by Smith et al.[1]. One breyite-bearing diamond (sample number DVBT)), with $\delta^{13}C = -13.4‰$, falls at the edge of the carbon-isotopic range of large irregular type IIa diamonds from the Cullinan (formerly known as Premier) kimberlite. The acronym CLIPPIR[5] has been proposed for this type II population. Two further diamonds, from the basic–ultrabasic suite, (Sano's samples 110208245245 and 110208425476) have $\delta^{13}C$ signatures of $-3.4‰$ and $-1.8‰$, respectively. These fall well outside the range of the majority of the Cullinan CLIPPIR stones, but within the field of sublithospheric diamonds from this locality[6] (Fig. 2), which include the first confirmed inclusion of $CaSiO_3$-perovskite[7]. Rather than being complementary to earlier isotopic data for blue diamonds, the limited new carbon-isotopic data[1] underline a contrast between the smaller type IIb stones with basic–ultrabasic sublithospheric inclusion assemblages, and stones comprising the large, irregular gem-quality Cullinan blue diamond population. Collectively, the evidence suggests the occurrence of two distinct type IIb populations, distinguished by size, inclusion association and carbon-isotopic signatures.

The majority of CLIPPIR type IIa diamonds from the Cullinan kimberlite are characterized by light carbon isotopes ($\delta^{13}C < -14‰$) and lack a dominant 'mantle' peak at about $-5‰$ (Fig. 2). This, in turn, closely matches the very distinctive signature of websteritic diamonds[8], pointing to a lithospheric provenance. CLIPPIR diamonds from the Letseng kimberlite (Lesotho) show a similar websteritic signature, with the majority of stones having $\delta^{13}C < -13‰$ (ref. [9]).

The Cullinan blue type IIb diamonds fall within the isotopic range of the associated CLIPPIR Type IIa stones from this locality[8,10], suggesting

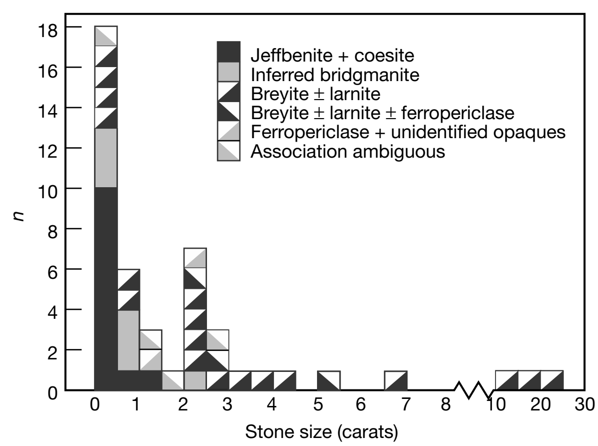

Fig. 1 | Size-class distribution of the different inclusion associations in the blue diamonds documented by Smith et al.[1] (see text for discussion). Total number of diamonds is 46; *n* is the number of diamonds in each size class. The black and grey squares together represent the Mg-rich (basic/ultrabasic) association. The remaining subgroups, dominated by the Ca-rich–ferropericlase suite but lacking Mg-silicates, are depicted by the grey and black triangles. Breyite was formerly referred to as $CaSiO_3$-walstromite. We note the change in scale above 10 carats. Although the diamonds studied were predominantly cut stones, it is assumed that these show a qualitative link to the relative sizes of the original raw diamonds.

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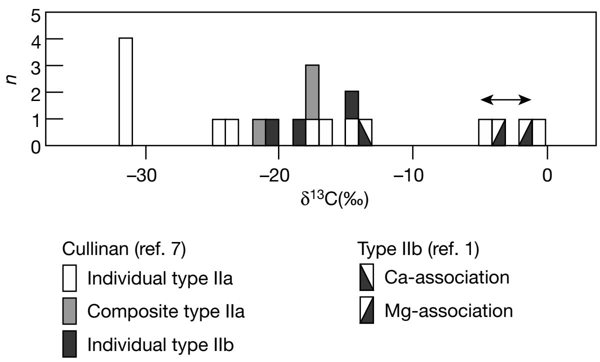

Fig. 2 | Comparison of carbon-isotopic signatures of Type IIa (CLIPPIR[5]) and blue IIb diamonds from Cullinan-documented[10] and type IIb stones of the Ca- and Mg-associations respectively, documented by Smith et al.[1]. Total number of samples analysed is 20; *n* is the number of diamonds in each isotopic class. We note that the three composite Cullinan samples represent aggregates of fragments from 30 individual stones[10]. The double-headed arrow indicates the carbon-isotopic range of sub-lithospheric diamonds at Cullinan[6].

a linked provenance. This is supported by the large sizes and irregular morphology of both the blue type IIb and type IIa (CLIPPIR) Cullinan stones. The limited carbon-isotopic data for the blue stones reported by Smith et al.[1] is consistent with a link between the Ca-association type IIb stones and the inferred websteritic suite, suggesting a lithospheric provenance.

Phase relations permit a lithospheric provenance of type IIb stones characterized by Ca-association inclusions. Larnite is not reported as a stable lower-mantle phase in basic and ultrabasic bulk-rock compositions[11,12], but can form by retrograde transformation of $CaSiO_3$-perovskite at pressures above the mantle transition zone in Ca-rich bulk compositions. However, the stability fields of $CaSiO_3$-perovskite and breyite are separated by a phase field with $CaSi_2O_5$-titanite and larnite[3]. The relatively common association of breyite and larnite in the blue diamonds is not readily explained in terms of retrograde inversion of $CaSiO_3$-perovskite in the complete absence of associated $CaSi_2O_5$-titanite inclusions. Further, in Ca-rich systems, breyite is a stable phase over a wide pressure range[3] (10–3 GPa, whereas wollastonite (the low-pressure polymorph of breyite), together with larnite, have been reported from the Oldoinya Lengai carbonatite[13], indicating the stability of these latter two silicates at crustal pressures in carbonatite-rich systems. The frequent association of breyite and larnite in blue diamonds could therefore be explained in terms of direct crystallization of these two phases in a carbonate/Ca-rich environment at pressures ranging between 10 GPa and 3 GPa (ref. [3]), which extend into the lithosphere.

The limited available data thus point to two contrasting parageneses for type IIb diamonds. One of these has a lower-mantle provenance[1], but the second shows affinities with websteritic diamonds, suggesting a much shallower source in the lithosphere. Thus, type IIb diamonds are poly-paragenetic, as has been demonstrated for type IIa stones from Cullinan[6].

Our analysis has a number of further important implications. (1) It underlines earlier studies[2,3] that stress that breyite, on its own, does not provide unambiguous evidence that the enclosing diamond has a lower-mantle provenance, because different polymorphs of $CaSiO_3$ can crystallize over a wide pressure range from Ca and carbonate-bearing systems. This observation is relevant for understanding the chemistry and mineralogy of the lower mantle. (2) The limited data[1] suggest that large irregular gem-quality type IIb blue diamonds like the Cullinan Dream have a lithospheric rather than lower-mantle provenance. (3) An important issue which must be addressed is the mode of formation of the websteritic type IIa (CLIPPIR)–IIb diamond suite. The carbon-isotopic signatures of these diamonds at Cullinan (Fig. 2)[10] contrasts strongly with the narrow range in $\delta^{13}C$ (−6‰ to −2‰ with a pronounced peak at −5‰) of the eclogitic type I and type II stones at the same locality[6,14]. This argues against a link between the CLIPPIRs and the eclogitic suite, as has been previously suggested[10].

Data availability

All data are from Smith et al.[1] and cited sources.

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Reply to: Evidence for two blue (type IIb) diamond populations

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In our earlier examination of boron-bearing (type IIb) diamonds[1] we reported inclusion assemblages comparable to those described previously in sublithospheric diamonds from transition-zone and lower-mantle depths[2–4], and ascribed them to subducted oceanic lithosphere. The boron that characterizes these unusual diamonds was proposed to come from seawater-serpentinized oceanic lithosphere. In the accompanying Comment[5], Moore and Helmstaedt reinterpret the data in our paper and propose that the type IIb diamonds actually constitute two distinct populations, one being sublithospheric as originally described and the other being a population of much shallower, lithospheric origin from websteritic host rocks. Although the observation that our largest diamonds contained only Ca-silicates (with or without ferropericlase) is interesting, we argue that this does not require the division of the type IIb samples into two populations. Even though such a division is conceivable, there is no evidence for a second, lithospheric type IIb diamond paragenesis. Instead, it remains more likely that those type IIb diamonds containing Ca-silicates alone are part of the firmly established sublithospheric type IIb diamond paragenesis, associated with deeply subducted slabs.

The most common inclusion observed in type IIb diamonds, Ca-silicate, is also recorded as being among the most common inclusion in all sublithospheric diamonds[2–4,6]. Ca-silicate inclusions were found in 31 of the 46 type IIb samples studied[1]. Some diamonds contained only these Ca-silicate inclusions, without additional minerals. The depth of origin for such individual samples with incomplete assemblages is ambiguous, but given the complete mineralogical overlap, these were interpreted to be part of the same population[1]. However, Moore and Helmstaedt[5] point out that the inclusion assemblage does not appear to be evenly distributed across the size range of the samples. Those containing only Ca-silicates (with or without ferropericlase), without the retrogressed Mg-bearing phases bridgmanite or majoritic garnet, are generally larger in size, accounting for the 17 largest of the 46 samples. On this basis, Moore and Helmstaedt[5] divide the samples into a 'Mg-rich' suite and a 'Ca-rich' suite, with generally smaller and larger sizes, respectively. They interpret their 'Ca-rich' suite to be from websteritic host rocks in the lithosphere.

The basis of the apparent relationship between inclusion budget and diamond size can be explained in other ways besides two distinct diamond populations. It may reflect choices made during cutting and polishing, or if it is a real phenomenon, it may indicate that the distribution of inclusions among the samples is not perfectly random. In sublithospheric diamonds, the inclusion content is as much a product of infiltrating low-degree melt as it is of the host rock mineral compositions[7]. The conditions leading to growth of larger diamonds, which could require larger supplies of carbon-bearing melt, could also influence the incorporated inclusion budget.

The predominance of Ca-silicate inclusions in sublithospheric diamonds has been interpreted, in part, as a product of diamond-forming processes[7,8]. Therefore, their apparent solitary occurrence among larger diamonds could arise from the larger supply of melt and from other conditions that provoke large crystal growth. We are not aware of studies examining the effect of diamond size on inclusion content. Larger diamonds might contain a slightly different inclusion budget than smaller diamonds from the same host rock. This effect could explain why the observed inclusions of former bridgmanite, stishovite, calcium ferrite (CF) structured phase and majoritic garnet are confined to the smaller type IIb diamond samples examined.

Even if those diamonds containing only Ca-silicates (with or without ferropericlase) were to be considered separately from other samples, there is strong evidence to suggest they have a sublithospheric origin. Although Ca-silicates, on their own, do not uniquely identify a sublithospheric origin in terms of depth, inclusions of $CaSiO_3$-walstromite (now named breyite) have never been recorded in a known lithospheric diamond, let alone as part of the websteritic suite. Furthermore, where ferropericlase is present, this assemblage is not stable under lithospheric conditions (breyite + ferropericlase react to form merwinite + olivine or clinopyroxene)[9]. Rather, Ca-silicates are common in known sublithospheric diamonds, being interpreted as an inversion product from the common high-pressure mantle phase $CaSiO_3$-perovskite trapped at depths[2,10–12] below about 360 km. The breyite-larnite assemblage ($CaSiO_3$ with or without Ca_2SiO_4) seen in several type IIb diamonds, apparently lacking complementary $CaSi_2O_5$ to balance the bulk Ca:Si ratio to 1, as expected for retrogressed pure $CaSiO_3$-perovskite, is a minor complication in this interpretation. However, this phenomenon has been well documented by X-ray fluorescence tomography in other

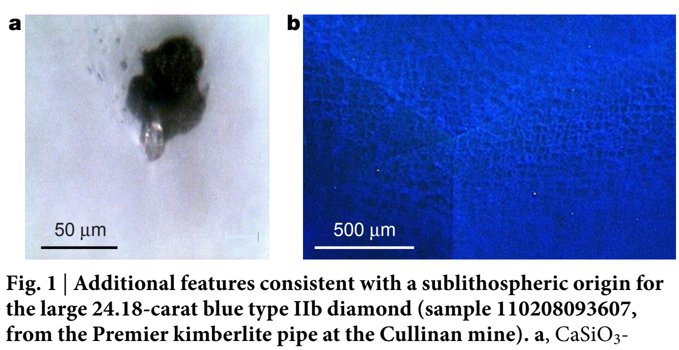

Fig. 1 | Additional features consistent with a sublithospheric origin for the large 24.18-carat blue type IIb diamond (sample 110208093607, from the Premier kimberlite pipe at the Cullinan mine). a, $CaSiO_3$-walstromite (breyite) inclusion with a lobate spray of small inclusions toward the upper left, plus a later-stage black graphitic fracture. **b**, Fine, weblike dislocation network seen with deep ultraviolet fluorescence imaging (also visible with cathodoluminescence). Straight lines are the facet edges.

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sublithospheric (that is, superdeep) diamonds[6] and may plausibly be attributed to diamond-forming reactions[8].

Elastic geobarometry supports the hypothesis that breyite inclusions are a strong indicator of superdeep origin[10]. The residual inclusion pressure was determined[1] for one of the medium-sized (2.70 carats) type IIb diamond samples containing only Ca-silicate inclusions. Even without inferring inversion from original perovskite structure, the physical pressure inside the breyite inclusion firmly constrains its origin to depths below about 260 km[1]. A similar geobarometry result was found for a ferropericlase inclusion in another type IIb sample, also argued by Moore and Helmstaedt[5] to be part of the Ca-rich lithospheric suite. Accounting for both elastic and plastic deformation in this inclusion–host pair indicates that its origin[1,13] is deeper than about 430 km or about 15 GPa. These depths are below the continental lithosphere.

The largest type IIb diamond studied[1], 24.18 carats (cut from a 122.52 carat rough diamond), also belongs to the Ca-rich group, containing only Ca-silicate inclusions. This diamond has textural features that match the known sublithospheric type IIb samples and that have not been documented in lithospheric diamonds. For example, the inclusions have lobate co-planar groups of smaller inclusions extending away from them, suggestive of extreme pressure release during their exhumation history (Fig. 1a). This is interpreted as expansion and proliferation of inclusion material into its own decompression crack, in line with the increase by approximately 30% in volume[11] expected for the inversion of $CaSiO_3$-perovskite to breyite during exhumation[1]. Another striking feature of this diamond that is consistent with a sublithospheric origin is its pronounced dislocation network (Fig. 1b). This texture is ubiquitous among type IIb diamonds, as well as among some other kinds of sublithospheric diamonds[14], requiring a history of deformation and considerable thermal annealing[15], and has yet to be documented in diamonds from the lithosphere[1].

Some type IIb diamonds are firmly established as sublithospheric, on the basis of inclusion assemblages and inclusion barometry. Other type IIb diamonds that contain only Ca-silicates (with or without ferropericlase) provide an incomplete and thus ambiguous mineral assemblage. However, the two groups postulated by Moore and Helmstaedt[5] (the Mg-rich and Ca-rich suites) are similar and there is no logical basis to conclude that they are two distinct populations. Likewise, the light carbon isotope measurements in some samples are not a valid means of assessing a lithospheric connection. In fact, Ca-silicate inclusions and a range in carbon isotope composition (including light carbon isotope values) are common features of superdeep diamonds in general. Moreover, there are only six different samples of type IIb diamond for which carbon isotopes have been measured to date[1,16], far too few to interpret a statistical distribution with multiple modes for specimens from possibly different kimberlite localities with a range of emplacement ages. We suggest that the proposed "two isotopically distinct parageneses"[5] simply reflect variations in subducted oceanic protolith or fluid composition within the same framework of sublithospheric diamond formation, as sampled by two or more kimberlites, for example, Premier (Cullinan) and Letseng.

In summary, there is no evidence to suggest that any of these diamonds formed at lithospheric depths. From our observations, all of the type IIb diamonds examined have consistent features and are best interpreted as representing a coherent sublithospheric paragenesis with a continuum of compositions.

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