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Comment on “Discovery of davemaoite, CaSiO_3 -perovskite, as a mineral from the lower mantle”

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Tschauner *et al.* (Reports, 11 November 2021, p. 891) present evidence that diamond GRR-1507 formed in the lower mantle. Instead, the data support a much shallower origin in cold, subcratonic lithospheric mantle. X-ray diffraction data are well matched to phases common in microinclusion-bearing lithospheric diamonds. The calculated bulk inclusion composition is too imprecise to uniquely confirm CaSiO_3 stoichiometry and is equally consistent with inclusions observed in other lithospheric diamonds.

Tschauner *et al.* (1) use a combination of micro-x-ray diffraction and fluorescence, Fourier-transform infrared spectroscopy (FTIR), and laser ablation inductively coupled plasma mass spectrometry (LA-ICPMS) data to argue that diamond GRR-1507 contains inclusions of an unusual alkali- and chrome-rich variety of CaSiO_3 in the cubic perovskite structure. The apparent discovery of a natural perovskite-structured CaSiO_3 phase was accepted by the International Mineralogical Association as a new mineral, davemaoite.

Diamond GRR-1507 belongs to a suite of diamonds previously studied by Navon *et al.* (2). The suite includes both cubic and coated octahedral diamonds whose cores are typically monocrystals. The exterior coats contain numerous submicrometer fluid inclusions (2, 3) and classify as nitrogen-rich type IaA, consistent with growth in the lithosphere (2). The inclusions studied by Tschauner *et al.* are from the monocrystalline core of diamond GRR-1507. On the basis of the interpreted mineralogy of the inclusions, Tschauner *et al.* posit that this core grew in the lower mantle. We demonstrate that the data presented in (1) do not support this interpretation.

We fitted the published FTIR spectra for the monocrystalline core (1) to calculate the abundance and aggregation state of N. Saturation of the reported absorbance spectra around 1280 cm^{-1} yields minimum estimates of total N abundance and maximum estimates of the relative proportion of nitrogen in B centers (% B). We obtain ~900 to 950 at.ppm N with 2 to 20% in B centers for the monocrystalline core. High concentrations of poorly aggregated

nitrogen are grossly inconsistent with a lower-mantle origin for the core. Sublithospheric diamonds are overwhelmingly very low in N (72% are type II and 94% have N < 100 at.ppm) that is dominated by B centers (87% have >50% B), consistent with residence at high temperature (4, 5). Only <2% of lower-mantle diamonds are N-rich (>300 at.ppm) and none has $\leq 20\%$ B like GRR-1507. The subregular characteristics of the platelet peak at 1373 cm^{-1} also support a low-temperature mantle environment (6).

The N data show that if the core of diamond GRR-1507 originated in the lower mantle, it cannot have experienced mantle or magmatic temperatures for geologically appreciable time scales. For a temperature of ~1700°C at the top of the lower mantle, the residence time is <10 years (Fig. 1A). We know of no geological process of transport from the lower mantle to the lithosphere that can occur at temperatures low enough and over a time scale short enough to prevent extensive aggregation of N into B centers. The N data are best explained by formation of the GRR-1507 diamond core at lithospheric temperatures (e.g., <1300°C) with long-duration storage (Fig. 1A).

The inclusions reported as perovskite-structured CaSiO_3 were not exposed for accurate compositional analysis. Instead, the composition of the inclusion was calculated by (1) through mass balance using phase proportions determined by x-ray diffraction and a bulk LA-ICPMS compositional measurement that incorporates diamond plus all included material. This technique requires assumptions about the precise origin of the signal as the ~100- μm laser beam ablates through the diamond, sampling all inclusions

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encountered. Accuracy and precision are highly dependent on appropriate standardization and background subtraction.

Examination of the raw data shows that the background correction, calibration, and assumptions about the source of the signal lead to gross uncertainties in the measurement that are at least an order of magnitude larger than reported. We calculate a minimum single standard deviation of $\pm 65\%$ relative for the background-corrected Si signal, discounting one integration where no background-corrected signal was observed. As Si is used as the internal standard, its analytical uncertainty should be, but was not, propagated into uncertainties for the other elements; we calculate minimum relative standard deviations for Ca and K of $\pm 30\%$. These uncertainties preclude accurate determination of the bulk composition or stoichiometry of individual inclusion phases. There are also significant temporal mismatches in the timing of the peak signals for K and Ca, which arrive early relative to Si, making it impossible to establish whether the undetermined origin of the Si signal spatially correlates with other elements.

The calculated CaSiO_3 inclusion composition (*I*) is unlike any previously synthesized calcium silicate perovskite or any natural CaSiO_3 -rich inclusion reported in sublithospheric diamonds ($n = 53$) (Fig. 1B), possessing extraordinarily high K, Na, and Cr. In contrast, we observe that the calculated inclusion composition is generally consistent with fluid and solid microinclusion compositions measured in coated and cubic lithospheric diamonds, especially those from the GRR suite (Fig. 1B) (2, 7). Although abundant fluid inclusions are uncommon in the cores of coated diamonds, examples have been observed with compositions similar to those found in the coated portion, and with K, Ca, and Si as prominent components (8).

Identification of a CaSiO_3 -structured perovskite phase relies on x-ray diffraction (*I*). The intensity versus 2θ diffraction pattern reported in (*I*) is fit with a combination of bcc (body-centered cubic) iron ($Im\bar{3}m$), cubic (Mg,Fe)O oxide ($Fm\bar{3}m$), and another phase with cubic space group $Pm\bar{3}m$ (Fig. 2A) that is assigned to a perovskite-structured phase. This interpretation is non-unique. For example, B2-KCl (also $Pm\bar{3}m$), which is stable at pressures above ~ 2 GPa at 300 K (9), fits the observed diffraction peaks equally well with a geologically reasonable remnant pressure of ~ 5 GPa at 300 K. A combination of KCl (B2), chromite (accounting for the high measured Cr), and iron can fit the published diffraction pattern equally well (Fig. 2B). All of these minerals are previously reported as microinclusions in coated and monocrystalline lithospheric diamonds (10, 11).

Raw diffraction images of all phases except iron metal

are spotty, not powder diffraction rings, rendering peak intensities unreliable for phase identification, and phase proportions cannot be accurately determined using Rietveld refinement. Further, the raw diffraction data collected in a two-dimensional grid over the inclusion's area reveals the presence of additional phases unreported in (*I*). These phases include calcite, and possibly lizardite, within ~ 10 μm laterally of the reported inclusion location and were likely incorporated in the bulk LA-ICPMS analysis.

Our reappraisal of the data presented by Tschauner *et al.* is overwhelmingly indicative of diamond formation in cold lithospheric mantle, especially when set in the context of observations from previous investigations of coated lithospheric diamonds, including the GRR suite. We found no compelling evidence for the presence of a phase with CaSiO_3 stoichiometry having the perovskite structure in this diamond.

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SUPPLEMENTARY MATERIALS
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 Data S1 to S3

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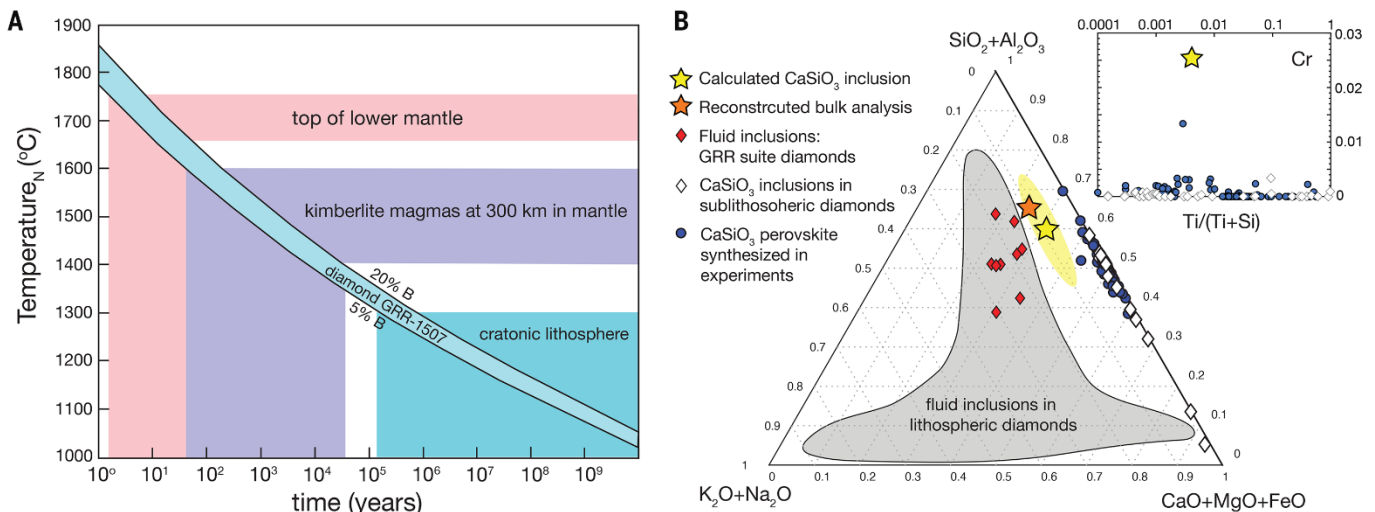


Fig. 1. Nitrogen defects and inclusion chemistry. (A) Temperature versus time calculated for a N aggregation state in diamond ranging from 5% to 20% B centers, values that are consistent with the FTIR analysis of diamond GRR-1507. Also shown are estimated temperatures for the top of the lower mantle, primary kimberlite magmas at ~300 km depth, and cratonic lithosphere. Note that melts at lower mantle depths will be hotter. Diamond GRR-1507 is inconsistent with residence in the lower mantle for more than ~100 years. (B) The composition of the calculated CaSiO₃ inclusion (wt%) reported by Tschauer *et al.* (1) (yellow star with 50% relative error envelope) and the reconstructed bulk analysis composition (orange star) plotted relative to coated and cubic lithospheric diamonds and their monocrystalline cores from the literature (gray field) (9), fluid inclusions in GRR-suite diamonds (red rhombuses) (2), and previously reported compositions of CaSiO₃ inclusions in sublithospheric diamonds and experimentally synthesized CaSiO₃ perovskites in peridotitic and basaltic bulk compositions (available at <https://doi.org/10.5683/SP3/LIVK1K>). The graph at right shows the Cr content of the calculated CaSiO₃ inclusion (yellow star) relative to CaSiO₃ inclusions and CaSiO₃ perovskites in experiments (elemental abundances are per formula unit).

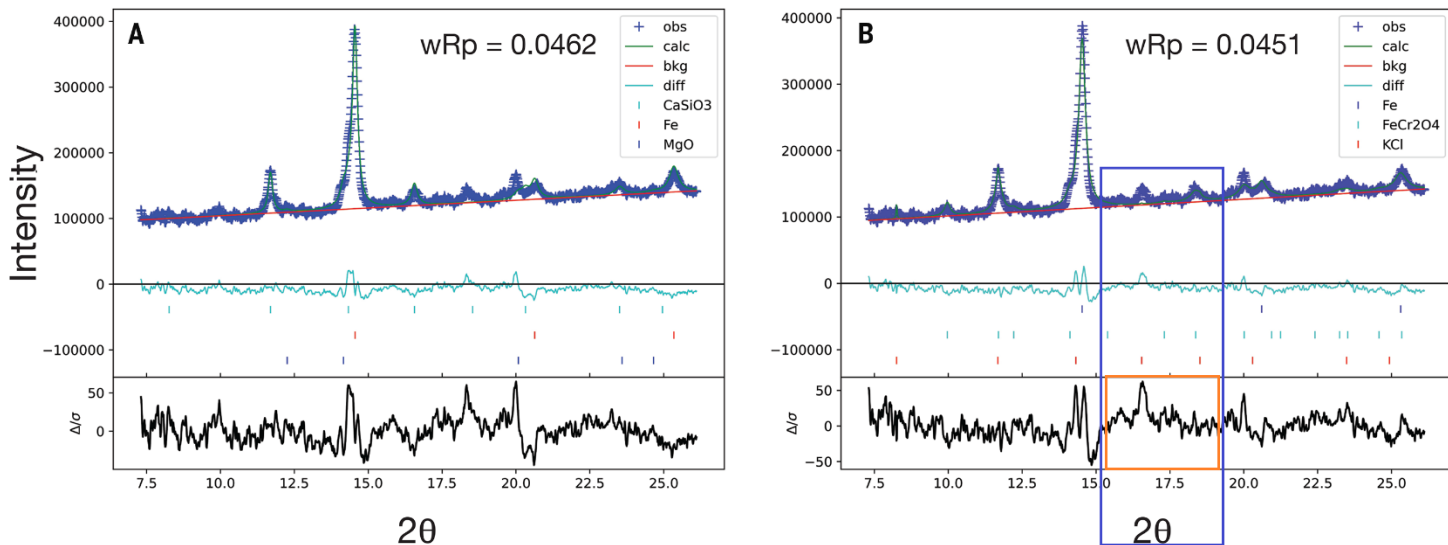


Fig. 2. Full profile Rietveld refinement of the one-dimensional diffraction data published in Tschauner *et al.* (A) Reproduced fit of (1) using CaSiO_3 perovskite at -4.9 GPa ($Pm\bar{3}m$) (12), pure bcc iron at -3.9 GPa ($Im\bar{3}m$), and (Mg,Fe)O oxide ($Fm\bar{3}m$). The fit has a weighted profile R-factor (wRp) of 0.0462, consistent with the fit reported in (1). (B) The fitted profile using B2-KCl ($Pm\bar{3}m$; 5 GPa), Fe (bcc; -3.9 GPa) and chromite ($Fd\bar{3}m$; -1.8 GPa) with a wRp of 0.0451. Using magnetite ($Fd\bar{3}m$; -1.2 GPa) produces a similar but somewhat poorer fit than chromite (wRp = 0.058). We note that in both refinements the unit cell volume of pure iron is significantly larger than that of pure iron at 1 bar, 300 K, requiring an apparent pressure of -3.9 GPa (13). Tschauner *et al.* attribute this cell expansion to substitution of carbon into the bcc lattice. However, carbon incorporation into bcc iron reduces the cell volume rather than expands it (14), so this explanation fails.

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