

Comment on “Discovery of davemaoite, CaSiO₃-perovskite, as a mineral from the lower mantle”

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Data used as evidence that diamond GRR-1507 formed in the lower mantle instead supports a much shallower origin in cold, sub-cratonic lithospheric mantle. X-ray diffraction data are well matched to phases common in micro-inclusion-bearing lithospheric diamonds. The calculated bulk inclusion composition is too imprecise to uniquely confirm CaSiO₃ 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, FTIR and LA-ICPMS data to argue that diamond GRR-1507 contains inclusions of an unusual alkali and chrome-rich variety of CaSiO₃ in the cubic perovskite structure. The apparent discovery of a natural perovskite-structured CaSiO₃ phase was accepted by the IMA 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 mono-crystals. The exterior coats contain numerous sub-micrometer fluid inclusions (*2, 3*) and classify as nitrogen-rich type IaA, consistent with growth in the lithosphere (*2*). The inclusions studied by (*1*) are from the mono-crystalline core of diamond GRR-1507. Based on the interpreted mineralogy of the inclusions, Tschauner et al. (*1*) 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 ~900-950 at.ppm N with 2-20% 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 ≤20 %B like GRR-1507. The subregular characteristics of the platelet peak at 1373 cm⁻¹ also supports 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 timescales. For a temperature of ~1700 °C at the top of the lower mantle the residence time is <100 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 timescale 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 CaSiO₃ 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 laser ablation 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 encountered. Accuracy and precision are highly dependent on appropriate standardization and background subtraction.

Examination of the raw data kindly provided by the authors 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 (1) is unlike any previously synthesized calcium silicate perovskite or any natural CaSiO_3 -rich inclusion reported in sub-lithospheric diamonds ($n=53$) (Fig. 1b) (7), possessing extraordinarily high K, Na, and Cr. In contrast, we observe that the calculated inclusion composition is generally consistent with fluid and solid micro-inclusion compositions measured in coated and cubic lithospheric diamonds, especially those from the GRR suite (Fig. 1b) (2, 8). While 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 (9).

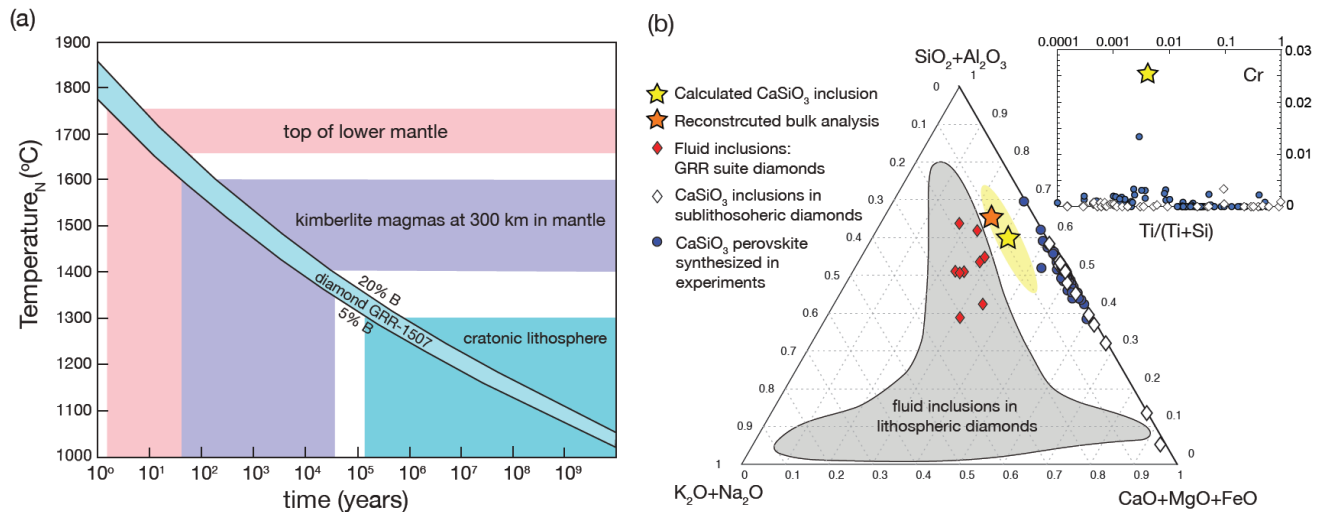


Figure 1. **(a)** Temperature versus time calculated for a N aggregation state in diamond ranging from 5% to 20% B centers, values that are consistent with the FTIR analysis of diamond GRR-1507. Also shown are estimated temperatures for the top of the lower mantle, for primary kimberlite magmas at ~300 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 CaSiO_3 inclusion (weight%) 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 (grey field) (9), fluid inclusions in GRR-suite diamonds (red triangles) (2), previously reported compositions of CaSiO_3 inclusions in sublithospheric diamonds and experimentally synthesized CaSiO_3 perovskites in peridotitic and basaltic bulk compositions (7). The figure at right shows the Cr content of the calculated CaSiO_3 inclusion (yellow star) relative to CaSiO_3 inclusions and CaSiO_3 perovskites in experiments (elemental abundances are per formula unit).

Identification of a CaSiO_3 -structured perovskite phase relies on X-ray diffraction (1). The intensity versus 2-theta diffraction pattern reported in (1) is fit with a combination of bcc iron ($Im\bar{3}m$), cubic $(\text{Mg,Fe})\text{O}$ 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 300K (10), 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 micro-inclusions in coated and mono-crystalline lithospheric diamonds (11, 12).

Raw diffraction images (kindly provided by the authors) 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 2-dimensional grid over the inclusion's area reveals the presence of additional phases unreported by (1). These phases include calcite, and possibly lizardite, within $\sim 10 \mu\text{m}$ laterally of the reported inclusion location and were likely incorporated in the bulk LA-ICPMS analysis.

Our re-appraisal of the data presented by (1) 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. There is no compelling evidence for the presence of a phase with CaSiO_3 stoichiometry having the perovskite structure in this diamond.

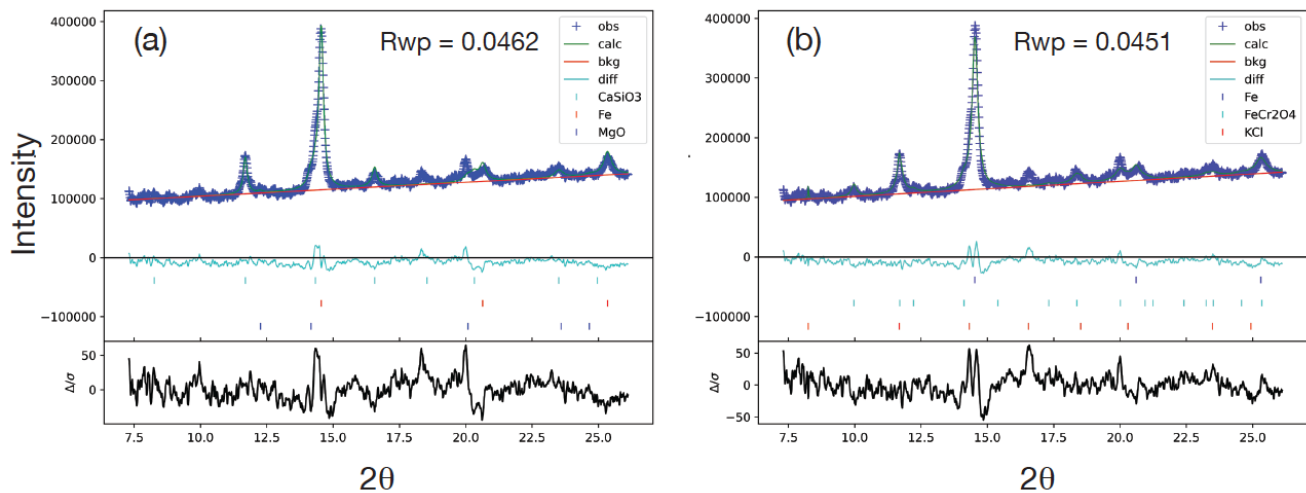


Figure 2. Full profile Rietveld refinement of the 1-D diffraction data published in (1). (a) Reproduced fit of (1) using CaSiO_3 perovskite at -4.9 GPa ($Pm\bar{3}m$) (13), pure bcc iron at -3.9 GPa ($Im\bar{3}m$) and $(\text{Mg,Fe})\text{O}$ oxide ($Fm\bar{3}m$). The fit has a weighted profile R-factor (Rwp) 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 Rwp of 0.0451. Using magnetite ($Fd\bar{3}m$; -1.2 GPa) produces a similar but somewhat poorer fit (Rwd = 0.058) than chromite. We note that in both refinements the unit cell volume of pure iron is significantly larger than pure iron at 1 bar, 300 K, requiring an apparent pressure of -3.9 GPa (14). Tschauner et al. (1) attribute this cell expansion to substitution of C into the bcc lattice. However, C incorporation into bcc iron reduces the cell volume rather than expands it (15) so this explanation fails.

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