This is the peer-reviewed, final accepted version for American Mineralogist, published by the Mineralogical Society of America.
The published version is subject to change. Cite as Authors (Year) Title. American Mineralogist, in press.
DOI: https://doi.org/10.2138/am-2020-7513. http://www.minsocam.org/

Revision 1, May 8, 2020

Origin, properties and structure of breyite: the second most abundant mineral inclusion in super-deep diamonds

Word Count 5753

FRANK E. BRENKER[1], FABRIZIO NESTOLA[2,1], LION BRENKER[1], LUCA PERUZZO[3], JEFFREY W. HARRIS[4]

[1]Geoscience Institute, Goethe University Frankfurt, Altenhoeferallee 1, 60438, Frankfurt am Main, Germany
[2]Dipartimento di Geoscienze, Università di Padova, Via Gradenigo, 6, 35131 Padova, Italy
[3]CNR-IGG, Padova, Via Gradenigo, 6, I-35131 Padova, Italy
[4]School of Geographical and Earth Sciences, University of Glasgow, G12 8QQ, Glasgow, United Kingdom

*Corresponding Author: f.brenker@em.uni-frankfurt.de

ABSTRACT

Earth´s lower mantle most likely mainly consists of ferropericlase, bridgmanite and a $CaSiO_3$-phase in perovskite structure. If separately trapped in diamonds these phases can be transported to Earth´s surface without reacting with the surrounding mantle. Although all inclusions will remain chemically pristine, only ferropericlase will stay in its original crystal structure, whereas in almost all cases bridgmanite and $CaSiO_3$-perovskite will transform to their lower pressure polymorphs. In the case of perovskite structured $CaSiO_3$ the new structure that is formed is closely related to that of walstromite. This mineral is now approved by the IMA commission on new minerals and named breyite. The crystal structure is triclinic (space group: *P*-1) with lattice parameters a_0 = 6.6970(4) Å, b_0 = 9.2986(7) Å, c_0 = 6.6501(4) Å, α = 83.458(6)°, β =

76.226(6)°, γ = 69.581(7)°, V = 376.72(4) Å. The major element composition found for the studied breyite is $Ca_{3.01(2)}Si_{2.98(2)}O_9$. Breyite is the second most abundant mineral inclusion after ferropericlase in diamonds of super-deep origin. The occurrence of breyite has been widely presumed to be a strong indication of lower mantle (> 670km depth) or at least lower transition zone (> 520km depth) origin of both the host diamond and the inclusion suite.

In this work, we demonstrate through different formation scenarios that the finding of breyite alone in a diamond is not a reliable indicator of the formation depth in the transition zone or in the lower mantle and that accompanying paragenetic phases such as ferropericlase together with $MgSiO_3$ are needed.

Keywords: breyite, diamonds, super-deep diamonds, Earth´s mantle, transition zone, lower mantle, walstromite, $CaSiO_3$

INTRODUCTION

Breyite is the analogue of what is typically called "$CaSiO_3$-walstromite" in diamond research due to its composition and similar crystal structure to walstromite ($Ca_2BaSi_3O_9$). In nature this mineral is only found in the so-called super-deep diamonds (Joswig et al. 1999; Stachel et al. 2000; Brenker et al. 2002, 2005; Stachel et al. 2005; Anzolini et al. 2016, 2018; Smith et al. 2018). These are a rare category of diamonds (about 1% of the entire population, Stachel and Harris 2008), which crystallize between about 300 km and even 800 km depth (Harte 2010) and are well distinguishable from "lithospheric diamonds", which crystallize at shallower depths between about 120 and 220 km in the mantle.

Breyite is considered one of most abundant minerals in super-deep diamonds, likely to be second after ferropericlase, (Mg,Fe)O, and one of the most important markers to detect such diamonds (i.e. ferropericlase is stable over the entire Earth's lower-upper mantle and thus cannot be considered an actual depth marker). Here we report the structure, properties and origin of this important mineral in diamond research and mantle petrology.

Breyite studied in this work was approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association under the code IMA 2018-062. The holotype of breyite is deposited at the Museum of Mineralogy of the University of Padova under the catalogue number MMP 20371.

The new mineral honours the German mineralogist, petrologist and geochemist Gerhard P. Brey (born 1947). He was a Professor of Mineralogy at the Institute of Geosciences, Goethe University Frankfurt, Germany, from 1994 until his retirement in 2014. Brey was a pioneer in experimental petrology at high pressure conditions and well known for his development of a comprehensive set of thermobarometers for lherzolites and related rocks.

RESULTS AND DISCUSSION

Occurrence and mineral association

In general and apart from ferropericlase, breyite is found associated within diamonds mainly with inclusions of $CaTiO_3$ perovskite, β-Ca_2SiO_4 larnite, titanite-structured $CaSi_2O_5$ (a further new phase within diamonds not officially named yet) (Brenker et al. 2005; Anzolini et al. 2016) and in one case with ringwoodite (the high-pressure polymorph of olivine found in the mantle transition zone between 520 and 660 km depth, Pearson et al. 2014).

Breyite studied in this work was found within a diamond from the Sao Luiz placer deposits (Juina area, Mato Grosso State, Brazil) and was intimately associated with $CaTiO_3$ perovskite (see Fig. 1), with a composition particularly rich in Si and Al being $Ca_{0.98}Ti_{0.83}Si_{0.13}Al_{0.06}O_3$ (obtained on the grain in Fig. 1 by semiquantitative EDS analysis)

Appearance and physical properties

Breyite is transparent, colorless, has a vitreous lustre and is non-fluorescent. Cleavage and parting were not observed. The size of the studied crystal was approximately 140 x 150 x 100 microns. Physical and optical properties were determined whilst the inclusion was still partially in the diamond. The density, $\rho = 3.072$ g/cm^3 was calculated on the basis of the unit-cell volume obtained by X-ray diffraction. Attempts to determine Mohs hardness failed principally because of the inclusion size and the size factor prevented other direct optical or physical properties from being reliably determined.

Anzolini et al. (2016) determined the isothermal bulk modulus and thermal expansivity, of a synthetic breyite by X-ray diffraction whilst at high pressures and high temperatures. The pressure-volume data gave a bulk modulus value of K_{T0} = 78.6(1.6) GPa for a first-pressure derivative fixed to 4, whilst the temperature-volume data fitted to a thermal pressure equation of state, provided a coefficient of thermal expansivity $\alpha_0 = 2.55(9)\times10^{-5}$ K^{-1} at 298 K. Such thermoelastic data are useful to apply elastic geobarometry for the breyite-diamond pair in order to retrieve the depth of formation (see Anzolini et al. 2016, 2018). However, in this work it was not possible to apply this approach even before exposing the inclusion because its spatial position was already too close to the surface of the diamond host and this precludes any attempts to obtain a reliable value of the depth of formation (Mazzucchelli et al. 2018).

Composition of breyite

In order to confirm the composition, the inclusion was partially exposed (see Figure 1) by drilling the diamond host with an unshielded argon beam using a JEOL cross section polisher enabled to work at low temperature at the Geoscience Institute, University of Frankfurt. Electron backscattered images and EDS chemical semiquantitative analyses were obtained by a CamScan MX3000 electron microscope equipped with a LaB_6 source and an EDAX system installed at Department of Geosciences, University of Padova. Chemical analyses were performed (25 kV and ~ 25 mm working distance) on small relatively flat surface areas resulting from the cross section polisher and using a well characterized nearly pure diopside (in turn measured by WDS in the same Department) as a reference for calibration (Pandolfo et al. 2015). As expected from previous work (e.g. Bulanova et al. 2010), our EDS analyses did not show any elements other than Ca and Si above the minor element level (Fig. 2 and Table 1). The empirical formula (based on 9 oxygens per formula unit) is $Ca_{3.01(2)}Si_{2.98(2)}O_9$; the simplified formula being $Ca_3Si_3O_{12}$, corresponding to 48.28 wt% CaO and 51.72 wt% SiO_2 (normalized to 100 %). Just for comparison, Bulanova et al. (2010) on the $CaSiO_3$-walstromite (previous known name of breyite) beyond Ca and Si reported only Fe as main impurity with FeO = 1.87 wt%. However, for our breyite no counts were measured above the background in the 6.4 keV region (Fe Kα), even after long acquisitions.

Crystal structure of breyite

Complete intensity X-ray diffraction data were collected on the inclusion still within its diamond host. Indeed, the slight exposure (Figure 1) of the inclusion made centering the mineral easier in the X-ray beam. However, the extremely large size of the diamond host with respect to the inclusion was the main problem to face in collecting intensity X-ray diffraction data. The X-ray data were collected using a Rigaku-Oxford Diffraction Supernova goniometer equipped with an X-ray micro-source assembled with a high intensity and no noise Pilatus 200K Dectris detector installed at the Department of Geosciences, University of Padova. The Mo*K*α micro-X-ray source works at 50 kV and 0.8 mA, with a sample to detector distance of 68 mm. The micro source ensures a brilliance at least ten times higher than conventional sealed X-ray tubes and a beam spot of about 0.120 mm. Before carrying out a complete data collection, several scans were performed to verify the proper crystal centering under the X-ray beam. Such a procedure generates data with similar quality to that of a routine measurement on a crystal in air.

The size of the inclusion was 0.060×0.020×0.015 mm^3 the thickness being 0.015mm estimated by micro-Raman spectroscopy. A total of 9351 reflections, down to a resolution of 0.71 Å and a redundancy equal to 4, were collected giving an $F^2/sig(F^2)$ = 13.7. Data completeness was 99.8%, but the R_{int} for *P*-1 was poor (0.129) likely due to a series of non-trivial overlaps with the reflections of the diamond host. Data reduction was performed using Crysalis Pro software (Rigaku-Oxford Diffraction), which corrects for the Lorentz-polarization effect and absorption. Intensity data collection and crystal structure refinement (using neutral scattering curves and anisotropy for all atoms) information were performed using Shelx-97 (Sheldrick 2008) starting from the model by Joswig et al. (2003). A list of 15 calculated *d* spacings from the crystal structure are reported in Table 2, whereas the complete dataset of the structure can be found in the deposited CIF file. In terms of refinement strategy, we performed the refinement leaving free

to refine the occupancy factors of the three crystallographic Ca sites and not refining the occupancies of Si and O atoms. Such refinement provided a structural formula of $Ca_{0.99(1)}SiO_3$, which is in perfect agreement with the chemical formula obtained by the EDS measurements and demonstrating that any possible impurity could be present only in traces.

The first crystallographic report for breyite was published as $CaSiO_3$-walstromite by Joswig et al. (2003). Here we report an identical crystal structure (respecting the same nomenclature) to that of Joswig et al. (2003). Breyite is a ring silicate according to the Liebau classification. The crystal structure is illustrated in Figure 3 viewed down the c axis. The three sites for Ca are of 6, 7, and 8- coordinated polyhedra with average distances between <Ca-O> of 2.362, 2.534 and 2.517 Å, respectively. The three tetrahedrally coordinated distances for $(Si1O)_4$, $(Si2O)_4$ and $(Si3O)_4$ are similar having <Si-O> of 1.635, 1.637 and 1.630 Å, respectively.

The three Si-O-Si angles for the silicate rings are also very similar, differences being within about 2.6° of each other as follows:

Si1-O3-Si2 = 124.46°; Si2-O6-Si3 = 121.82°; Si3-O9-Si1 = 122.85°

The three O-T-O angles show very slightly larger differences (up to 3°) and are:

O3-Si2-O6 = 100.96°; O6-Si3-O9 = 103.99°; O9-Si1-O3 = 103.17°

Bridging oxygen distances are also very similar being: O3-O6 = 2.589 Å, O3-O9 = 2.610 Å and O6-O9 = 2.612 Å.

Micro-Raman spectroscopy

Micro-Raman spectra of breyite were obtained using a ThermoScientific DXR Raman microscope installed at Department of Chemistry Sciences, University of Padova. A 532 nm laser caused the excitation. The laser power was 10 mW and the Raman spectrum was collected

for about 900 seconds. Using a 50× objective the spatial resolution was 1 μm whereas the spectral resolution was about 2.5 cm^{-1}. The five main peaks, in order of decreasing intensity, are: 659, 980, 127, 1040 and 159 cm^{-1}. The Raman spectrum of breyite is shown in Figure 4 and also shown for a comparison is the breyite published in Smith et al. (2018) whilst still within a blue super-deep diamond (see their Figure 1). As the latter breyite is under a residual pressure, the Raman band shift toward higher wavenumbers, but both spectra are comparable. In terms of band assignment, based on previous Raman works on Ca-silicates (e.g., Richet et al. 1998), all vibrational modes above 900 cm^{-1} are represented by Si-O stretching vibrations with non-bridging (peaks between 950 and 1000 cm^{-1}) and bridging oxygens (the peak at 1040 cm^{-1}); at intermediate frequencies between about 430-450 and at 745 cm^{-1} the possible vibrational modes belong to the Si-O-Si stretching and bending bridging bonds; finally, the region at lower frequencies between about 130 and 430 cm^{-1} is most likely represented by the silicate network along with Ca-O stretching vibrations. As breyite has quite a variable crystal size from large 200 μm (Anzolini et al. 2016) down to 1-2 μm (Smith et al. 2018), it is evident that micro-Raman spectroscopy is perhaps the best technique to identify breyite.

ORIGIN OF BREYITE: IMPLICATIONS FOR THE DEPTH OF FORMATION OF SUPER-DEEP DIAMONDS

Experimental studies at high pressure with a large variety of rock compositions suggest that a separate Ca-Si-O phase in the Earth´s mantle exists only from the deep transition zone (from about 520 km depth) into the lower mantle to beyond 1000 km depth (e.g. Irifune et al. 1994; Irifune and Ringwood 1993; Wu et al. 2009). The stable phase of $CaSiO_3$ under these conditions is a cubic perovskite structure with space group *Pm*-3*m*. The cubic polymorph

transforms to a tetragonal *I*4/*mcm* perovskite at about 12 GPa (e.g., Thomson et al. 2019). However, the only natural $CaSiO_3$-perovskite found still preserved within a diamond does not show a cubic symmetry and appears to be orthorhombic *Pbnm* like the isostructural $CaTiO_3$ (Nestola et al. 2018).

Whether the precursor of breyite is cubic, tetragonal or orthorhombic perovskite needs to be settled by experimental petrology, which to our knowledge has not yet been completed.

Based on this information, regardless if the higher pressure precursor is cubic or not, the widely accepted interpretation about the origin of breyite is that it was entrapped as $CaSiO_3$-perovskite during diamond growth in the deeper transition zone or the lower mantle (e.g. Joswig et al. 1999 and Stachel et al. 2005 for a general review). During uplift of the diamond host to the upper mantle, the $CaSiO_3$ perovskite transformed to its lower pressure polymorph breyite. The exact depth of this transformation is not well defined, due to residual pressures in the inclusion, ambient mantle temperature and possible effects of minor and trace elements on the stability field of breyite.

If we take into account the pressure-temperature stability field of $CaSiO_3$ in the pure system defined experimentally (Gasparik et al. 1994; Akaogi et al. 2004, Sueda et al. 2006), depths no deeper than about 270-300 km for the transformation are proposed. Anzolini et al. (2019) argued that at these depths, diamond is in its elastic regime (Anzolini et al. 2019) and due to its very high bulk modulus (i.e. K_{T0} = 444 GPa, Prencipe et al. 2014) it would be difficult for diamond to accommodate the volume change necessary to transform $CaSiO_3$-perovskite to breyite and the fully elastic paths would provide a too low pressure; indeed such volume change should only be allowed if diamond would show significant fractures at the diamond-host interface. However, our own TEM studies around super-deep inclusions show a high dislocation

density which indicates that plastic deformation indeed occurred in the diamond host. Based on thermodynamic calculations and available thermoelastic data, Anzolini et al. (2016) demonstrated that the $CaSiO_3$-perovskite to breyite transformation would require a volume change of about 28%. Such a high volume change can be accommodated by diamond only within its plastic deformation regime, which might require a depth of transformation larger than 450 km (i.e. about 15 GPa) (Anzolini et al. 2016).

A detailed chemical tomography of several Ca-Si-O inclusions in a diamond from Kankan applying synchrotron XRF techniques, have shown that the Ca to Si ratio of most inclusions deviates from the expected unity of both elements, if a pure $CaSiO_3$-perovskite is assumed as entrapped phase (Brenker et al. 2005). From experimental work it would be possible to have the Ca:Si ratio less than 1, if an SiO_2-polymorph (e.g. stishovite) is entrapped together with the $CaSiO_3$-perovskite. Brenker et al. (2005) have demonstrated that some of the inclusions show values of the Ca:Si ratio of more than 1.6 and concluded that this would be possible only if we consider the existence of a Ca-rich lithology within Earth´s upper mantle in a depth range enabling the coexistence of Ca_2SiO_4-larnite either with $CaSiO_3$ ($CaSiO_3$-perovskite or breyite) or with $CaSi_2O_5$-titanite. In this case, it is no longer necessary to start with the entrapment of a $CaSiO_3$-perovskite which would eliminate the transformation volume enigma.

A compositional argument against a precursor $CaSiO_3$-perovskite was raised by Walter et al. (2008) due to the low Mg-content measured in several breyite inclusions, which contradicts experimental data and questions that a $CaSiO_3$-perovskite precursor phase was ever in contact with bridgmanite or majorite under deep mantle conditions.

Including the information given above, we summarize possible formation scenarios of breyite and how to distinguish between them. Our primary subdivision will consider breyite as a

back transformation product from $CaSiO_3$-perovskite (1), as exsolution from $Ca(Si,Ti)O_3$-perovskite (2), as a direct reaction product from larnite (Ca_2SiO_4) plus titanite-structured $CaSi_2O_5$ (3), and finally by direct precipitation from an upper mantle Si-rich fluid percolating through a carbonaceous metasediment (4). Only option (1) requires the large depths indicated elsewhere, whereas options (2) to (4) allows breyite to form within the asthenospheric upper mantle as well.

(1) Breyite is a direct back-transformation product from $CaSiO_3$ perovskite. In this case, we reconsider the pressure-temperature stability field of breyite within the pure $CaSiO_3$-system (Gasparik et al. 1994; Akaogi et al. 2004, Sueda et al. 2006). A transformation to breyite would occur between 9 GPa and 13 GPa, for an mantle temperature between about 1100 (cold subduction zone, extrapolated from Abers et al. 2006) and about 2000 K (plume access T of 300 K, Nataf 2000), respectively. However, the entrapment pressure for the $CaSiO_3$-perovskite precursor must be much higher depending on the chosen composition of the experimental starting material. For example, using a pyrolytic composition, Zhang and Herzberg (1994) report that $CaSiO_3$-perovskite only appears between about 18 and 22 GPa, at temperatures between 1700 and 2500 K. Starting from a mid-oceanic ridge basalt (MORB) composition, Hirose and Fei (2002) showed that $CaSiO_3$-perovskite does not appear at pressures lower than 23 GPa at about 2000 K. The $CaSiO_3$ phase stability field does not change dramatically if endmember compositions of possible deep sea sediments are used as a starting composition (Irifune et al. 1994). Again the first occurrence of $CaSiO_3$-perovskite is at pressures corresponding to depths of the lower transition zone. Thus, all experimental results on likely mantle compositions indicate that the pressure-temperature stability field of $CaSiO_3$-perovskite is strongly influenced by the

starting composition, increasing minimum formation pressures by up to 10 GPa and placing formation at least in the lower part of the transition zone.

Reconsidering the large volume change needed to transform $CaSiO_3$-perovskite to breyite the scenario discussed seems unrealistic as long as diamond is within its elastic regime. However, several examples exist which clearly show that this transformation has taken place, which includes but is not limited to coexisting but separated inclusions of ringwoodite with breyite (Pearson et al. 2014). In general, any co-genetic Mg-rich inclusion (e.g. ferropericlase, enstatite or olivine) occurring together with breyite within the same diamond suggests an entrapment depth of more than 520 km. Only if pure Ca-Si-oozes or carbonatitic melts are involved a deviation from this formation depth is possible (Brenker at al. 2007).

(2) breyite is formed via exsolution from $CaSiO_3$-$CaTiO_3$-perovskite solid solution. Kubo et al. (1997) experimentally showed that at 9 GPa up to 40 mol% of $CaSiO_3$ can be dissolved into the perovskite structure of $CaTiO_3$ with complete solid solution at about 12.3 GPa. Thus breyite can be formed in the upper mantle as an exsolution product at pressures below 10 GPa (270-300 km depth) during uplift and ascent. Complex intergrowths between these two phases have been found (e.g. Bulanova et al. 2010, Zedgenizov et al. 2016). In conclusion, if $CaTiO_3$ is the main phase the depth of formation of breyite will be in the upper mantle. Based on the Si-content of the full assemblage a minimum pressure can be calculated. A lower mantle or deep transition zone origin is not required at the first place but cannot be excluded.

(3) Breyite is a reaction product of larnite (beta-Ca_2SiO_4) and titanite-structured $CaSi_2O_5$. Based on the stability fields in the pure $CaSiO_3$ system (Gasparik et al. 1994; Akaogi et al. 2004, Sueda et al. 2006), the finding of polyphase inclusions of breyite, larnite (beta-Ca_2SiO_4) and a $CaSi_2O_5$-titanite phase (Brenker et al. 2005), and elastic geobarometry calculations

(Anzolini et al. 2016, 2018), breyite formed as a product of a retrograde reaction between larnite and titanite-structured $CaSi_2O_5$ at pressures between 9 and 10 GPa in the upper mantle. Breyite appears as a relatively minor phase trapped between the other two more abundant phases and representing a reaction product of those phases, (Brenker et al. 2005). This suggests again that this super-deep diamond was formed at pressures between 9 and 14 GPa in the upper mantle still above transition zone depths (< 410km), breyite forming at depths not greater than 270-300 km.

(4) Breyite is a reaction product of carbonate and a Si-rich component (SiO_2 or Si-rich fluid). Observed high Sr, Y and Zr contents in Ca-silicate phases (including breyite itself) are typical of initial carbonaceous materials (e.g. Brenker et al. 2005). Thus breyite could possibly form from Ca(Mg)-carbonates reacting with a Si-rich component, like SiO_2 in subducted deep sea cherts, or simply as a Si-enriched fluid percolating through carbonaceous rocks. The simultaneous presence of breyite and primary carbonates (Brenker et al. 2007) would support this interpretation.

Fedoraeva et al. (2019) demonstrated that subduction of limestones and cherts on top of a hydrated basaltic crust could lead to the direct in-situ precipitation of $CaSiO_3$ in $CaCO_3$ marbles through the percolation of a high silica-rich hydrous fluid. The resulting assemblage of $CaSiO_3$ + $CaCO_3$ is able to survive subduction down to the diamond stability field where it melts and allows breyite + larnite + diamond to crystallize. This scenario would create breyite at very low pressures of about 6 GPa or even less (Fedoraeva et al. 2019). The authors further suggest that this might explain polyphase inclusions of breyite + larnite observed in super deep diamonds (Brenker et al. 2005, Anzolini et al. 2016). However, it fails to explain the coexistence of $CaSi_2O_5$-titanite with these phases, which requires at least 9 GPa in order to reach the two phase stability of larnite (Ca_2SiO_4) + $CaSi_2O_5$-titanite.

A further experimentally confirmed reaction pathway is proposed by Woodland et al. (2020). In their work they showed that the melting temperature of an aragonite-coesite mixture under hydrous conditions will decrease down to 900°C forming a hydrous silicate melt. Reduction of this melt resulted in the crystallisation of graphite in equilibrium with breyite and titanite-structured $CaSi_2O_5$. They determined a maximum pressure of breyite formation of about 8 GPa due to the reaction $CaSiO_3$ + SiO_2 to $CaSi_2O_5$. Although this adds another interesting option to the upper mantle formation of breyite, inclusions in super-deep diamonds often show a Ca to Si ratio well above unity, which will contradict the Si-rich assemblage proposed by Woodland et al. (2020) and again it fails to explain the coexistence of $CaSi_2O_5$-titanite with larnite.

CONCLUSION

Breyite can be formed throughout the whole asthenospheric mantle, the transition zone and deep into the lower mantle. However, the different formation mechanisms indicate that being on its own as an inclusion in diamond is not a sufficient criteria to propose an origin in the lower mantle or deep transition zone (> 520 km depth). This conclusion is only valid if other inclusions such as Mg-rich co-genetic inclusions (ferropericlase, low-Ni enstatite (former $MgSiO_3$ perovskite), olivine polymorphs) are present. Furthermore, the intergrowth or coexistence within the same inclusions of breyite and $CaTiO_3$-perovskite indicate a former single phase of $Ca(Si,Ti)O_3$-perovskite which gave a lower limit of about 9 GPa or about 250 km for the depth of formation (Kubo et al., 1997). In contrast, if Ca-Si-O inclusions are detected which show a Ca/Si-ratio above 1, like in the case if larnite coexists with breyite in the same inclusion, a deep mantle origin is highly questionable. In this case it is by far much more likely that breyite was

formed in a depth range above 300 km, in order to allow either a formation within the two phase field of larnite plus $CaSi_2O_5$ or in the upper mantle by direct precipitation from a Si-rich fluid percolating through a carbonaceous metasediment. Subsequent melting and infiltration into the overlying reduced mantle will form the observed two phase assemblage and the diamond host (Fedoraeva et al. 2019).

IMPLICATIONS

The work presented here is the full description of the crystal structure of breyite, the second most abundant mineral found as inclusion in super-deep diamonds. Inclusions in this rare type of diamonds are the only direct mineral and rock samples from the asthenospheric mantle, the transition zone and even the lower mantle. The occurrence of breyite is used in numerous publications as strong indicator of an origin of at least 520km depths. In this work we discuss the different formation scenarios of this important mineral, which clearly show that the sole occurrence of breyite is not a sufficient indicator of its formation depth. Any published work about the composition and structure of the transition zone and lower mantle should be revisited and proof has to be given based on further criteria for its depth of origin.

ACKNOWLEDGEMENTS

FB acknowledge funding of the German Science Foundation DFG (project BR 2015 / 26-1 and BR 2015 / 31-1). The Diamond Trading Company (a member of the De Beers Group of Companies) is sincerely thanked for the donation of the studied diamonds.

REFERENCES CITED

Abers, G.A., van Keken, P.E., Kneller, E.A., Ferris, A. and Stachnik, J.C. (2006) The thermal structure of subduction zones constrained by seismic imaging: Implications for slab dehydration and wedge flow. Earth and Planetary Science Letters 241, 387-397.

Akaogi, M., Yano, M., Tejima, Y., Iijima, M. and H. Kojitani, H. (2004) High-pressure transitions of diopside and wollastonite: phase equilibria and thermochemistry of $CaMgSi_2O_6$, $CaSiO_3$ and $CaSi_2O_5$–$CaTiSiO_5$ system. Physics of the Earth and Planetary Interiors, 143, 145–156.

Anzolini, C., Angel, R.J., Merlini, M., Derzsi, M., Tokár, K., Milani, S., Krebs, M.Y., Brenker, F.E., Nestola, F., and Harris, J.W. (2016) Depth of formation of $CaSiO_3$-walstromite included in super-deep diamonds. Lithos, 265, 138–147.

Anzolini, C., Prencipe, M., Alvaro, M., Romano, C., Vona, A., Lorenzon, S., Smith, E.M., Brenker, F.E., Nestola, F. (2018) Depth of formation of super-deep diamonds: Raman barometry of $CaSiO_3$-walstromite inclusions. American Mineralogist, 103, 69-74.

Anzolini, C., Nestola, F., Mazzucchelli, M.L., Alvaro, M., Nimis, P., Gianese, A., Morganti, S., Marone, F., Campione, M., Hutchison, M.T., and Harris, J.W. (2019) Depth of diamond formation obtained from single periclase inclusions. Geology, 47, 219-222.

Brenker, F.E., Stachel, T., and Harris, J.W. (2002) Exhumation of lower mantle inclusions in diamond: ATEM investigation of retrograde phase transitions, reactions and exsolution. Earth and Planetary Science Letters, 198, 1-9.

Brenker, F.E., Vincze, L., Vekemans, B., Nasdala, L., Stachel, T., Vollmer, C., Kersten, M., Somogyi, A., Adams, F., and Joswig, W. (2005) Detection of a Ca-rich lithology in the

374 Earth's deep (>300 km) convecting mantle. Earth and Planetary Science Letters, 236, 579–
375 587.
376 Brenker, F.E., Vollmer, C., Vincze, L., Vekemans, B., Szymanski, A., Janssens, K., Szaloki, I.,
377 Nasdala, L., Joswig, W., and Kaminsky, F. (2007) Carbonates from the lower part of
378 transition zone or even the lower mantle. Earth and Planetary Science Letters, 260, 1–9.
379 Bulanova, G.P., Smith, C.B., Blundy, J., Walter, M.J., Kohn, S.C., Gobbo, L. and Armstrong,
380 L.S. (2010) Mineral inclusions in sublithospheric diamonds from Collier 4 kimberlite pipe,
381 Juina, Brazil: subducted protoliths, carbonated melts and primary kimberlite magmatism.
382 Contribution to Mineralogy and Petrology, 160, 489–510.
383 Fedoraeva, A.S., Shatskiy, A., and Litasov, K.D. (2019) The join $CaCO_3$-$CaSiO_3$ at 6 GPa with
384 implication to Ca-rich lithologies trapped by kimberlitic diamonds. High Pressure
385 Research, doi: 10.1080/08957959.2019.1660325.
386 Gasparik, T., Wolf, K., and Smith, C.M. (1994) Experimental determination of phase relations in
387 the $CaSiO_3$ system from 8 to 15 GPa. American Mineralogist, 79, 1219–1222.
388 Harte, B. (2010) Diamond formation in the deep mantle: the record of mineral inclusions and
389 their distribution in relation to mantle dehydration zones. Mineralogical Magazine 74, 189–
390 215.
391 Hirose, K., and Fei, Y.W. (2002) Subsolidus and melting phase relations of basaltic composition
392 in the uppermost lower mantle. Geochimica et Cosmochimica Acta, 66, 2099-2108.
393 Irifune, T and Ringwood, A.E. (1993) Phase transformations in subducted oceanic crust and
394 buoyancy relationships at depths of 600-800 km in the mantle. Earth and Planetary Science
395 Letters, 117, 101-110.
396 Irifune, T., Ringwood, A.E., and Hibberson, W.O. (1994) Subduction of continental crust and

terrigenous and pelagic sediments: an experimental study. Earth and Planetary Science Letters 126, 351-368.

Joswig, W., Paulus, E.F., Winkler, B., and Milman, V. (2003) The crystal structure of $CaSiO_3$-walstromite, a special isomorph of wollastonite-II. Zeitschrift für Kristallographie, 218, 811–818.

Joswig,W., Stachel, T., Harris, J.W., Baur, W.H., and Brey, G.P. (1999) New Ca-silicate inclusions in diamonds – tracers from the lower mantle. Earth and Planetary Science Letters, 173, 1–6.

Kraus, W., and Nolze, G. (2000) PowderCell for Windows, version 2.4. Federal Institute for Materials Research and Testing. Berlin, Germany.

Kubo, A., Suzuki, T., Akaogi, M. (1997) High pressure phase equilibria in the $CaTiO_3$-$CaSiO_3$ system stability of perovskite solid solutions. Phys Chem Minerals 24, 488–494.

Mazzucchelli, M.L., Burnley, P., Angel, R.J., Morganti, S., Domeneghetti, M.C., Nestola, F., Alvaro, M. (2018) Elastic geothermobarometry: corrections for the geometry of the host-inclusion system. Geology, 3, 231-234.

Nataf, H.-C. (2000) Seismic imaging of mantle plumes. Annual Review of Earth and Planetary Sciences 28, 391-417.

Nestola, F., Korolev, N., Kopylova, M., Rotiroti, N., Pearson, D.G., Pamato, M.G., Alvaro, M., Peruzzo, L., Gurney, J.J., Moore, A.E., Davidson, J. (2018) $CaSiO_3$ perovskite in diamond indicates the recycling of oceanic crust into the lower mantle. Nature, 555, 237-241.

Pandolfo, F., Camara, F., Domeneghetti, M.C., Alvaro, M., Nestola, F., Karato, S.I., Amulele, G. (2015) Volume thermal expansion along the jadeite-diopside join. Physics and Chemistry of Minerals, 42, 1-14.

Pearson, D., Brenker, F., Nestola, F., McNeill, J., Nasdala, L., Hutchison, M., Matveev, S., Mather, K., Silversmit, G., and Schmitz, S. (2014) Hydrous mantle transition zone indicated by ringwoodite included within diamond. Nature, 507, 221–224.

Prencipe, M., Bruno, M., Nestola, F., De La Pierre, M., and Nimis, P. (2014) Toward an accurate ab initio estimation of compressibility and thermal expansion of diamond in the [0, 3000 K] temperature and [0, 30 GPa] pressures ranges, at the hybrid HF/DFT theoretical level. American Mineralogist, 99, 1147-1154.

Richet, P., Mysen, B.O., and Ingrin, J. (1998) High-temperature X-ray diffraction and Raman spectroscopy of diopside and pseudowollastonite. Physics and Chemistry of Minerals, 25, 401-414.

Sheldrick, G.M. (2008) A short history of SHELX. Acta Crystallographica, A64, 112-122.

Smith, E.M., Shirey, S.B., Richardson, S.H., Nestola, F., Bullocks, E.S., Wang, J.H., and Wang, W.Y. (2018) Blue boron-bearing diamonds from Earth's lower mantle. Nature, 560, 84-87.

Stachel, T., Brey, G.P., and Harris, J.W. (2005) Inclusions in sublithospheric diamonds: Glimpses of deep Earth. Elements, 1, 73-78.

Stachel, T., and Harris, J.W. (2008) The origin of cratonic diamonds — constraints from mineral inclusions. Ore Geology Reviews, 34, 5–32.

Stachel, T., Harris, J.W., Brey, G.P., and Joswig, W. (2000) Kankan diamonds (Guinea) II: lower mantle inclusion parageneses. Contributions to Mineralogy and Petrology, 140, 16–27.

Sueda, Y., Irifune, T., Yamada, A., Inoue, T., Liu, X. and Funakoshi, K.-i. (2006) The phase boundary between $CaSiO_3$ perovskite and Ca_2SiO_4 + $CaSi_2O_5$ determined by in situ X-ray observations. Geophysical Research Letters, 33, L10307, 1-4.

Thomson, A.R., Crichton, W.A., Brodholt, J.P., Wood, I.G., Siersch, N.C., Muir, J.M.R., Dobson, D.P., Hunt, S.A. (2019) Seismic velocities of $CaSiO_3$ perovskite can explain LLSVPs in Earth's lower mantle. Nature, 572, 643-647.

Walter, M.J., Bulanova, G.P., Armstrong, L.S., Keshav, S., Blundy, J.D. Gudfinnsson, G., Lord, O.T., Lennie, A.R., Clark, S.M. Smith, C.B. & Gobbo, L. (2008) Primary carbonatite melt from deeply subducted oceanic crust. Nature, 454, 622-625.

Woodland, A.B., Girnis, A.V., Bulatov, V.K., Gerhard P. Brey, G.P., and Höfer, H.E. (2020) Breyite inclusions in diamond: experimental evidence for possible dual origin European Journal of Mineralogy, 32, 171–185.

Wu, Y., Fei, Y., Jin, Z., and Liu, X. (2009) The fate of subducted Upper Continental Crust: An experimental study. Earth and Planetary Science Letters 282, 275–284.

Zedgenizov, D.A., Ragozin, A.L., Kalinina, V.V., and Kagi, H. (2016) The mineralogy of Ca-rich inclusions in sublithospheric diamonds. Geochemistry International, 54, 890-900.

Zhang, J.Z., and Herzberg, C. (1994) Melting experiments on anhydrous peridotite KLB-1 from 5.0 to 22.5 GPa. Journal of Geophysical Research-Solid Earth, 99, 17729-17742.

FIGURE CAPTIONS

FIGURE 1. Electron backscattered image of breyite still kept within its diamond host (dark grey).

FIGURE 2. Representative EDS spectrum of breyite. The spectrum shows no other elements other than Ca and Si.

FIGURE 3. Crystal structure of breyite viewed down the c axis (a and b axes are shown on the left side of the Figure in red and green, respectively). All atoms are labelled and the unit

cell is shown in dotted line. Si1, Si2 and Si3 occupy the three semi-transparent tetrahedra coloured in yellow, blue and green, respectively.

FIGURE 4. Raman spectrum of breyite (in blue) between 120 and 1400 cm^{-1}. At 1333 cm^{-1} the main peak of the diamond host is shown. The overlapped spectrum in red is relative to breyite by Smith et al. (2018) for a crystal still within its diamond host and under a residual pressure, which causes a Raman band shift toward higher wavenumbers.

Table 1. Semiquantitative EDS analyses for breyite.

Oxide wt%	***Spot 1***	***Spot 2***	***Spot 3***	***Spot 4***	***Average***
SiO_2	53.00	50.87	52.17	51.79	51.96(0.89)
CaO	47.00	49.13	47.83	48.21	48.04(0.88)
Total	100	100	100	100	100

Table 2. Calculated X-ray powder diffraction data (in order of decreasing *d* spacing) for breyite obtained using the software PowderCell 2.4 (Kraus and Nolze 2000) based on the structural model from the CIF.

h k l	***Calculated d-spacings (Å)***	***Calculated relative intensity (%)***
0 1 0	8.71	12
1 0 1	5.01	32
-1 1 0	4.29	4
1 2 1	3.87	15

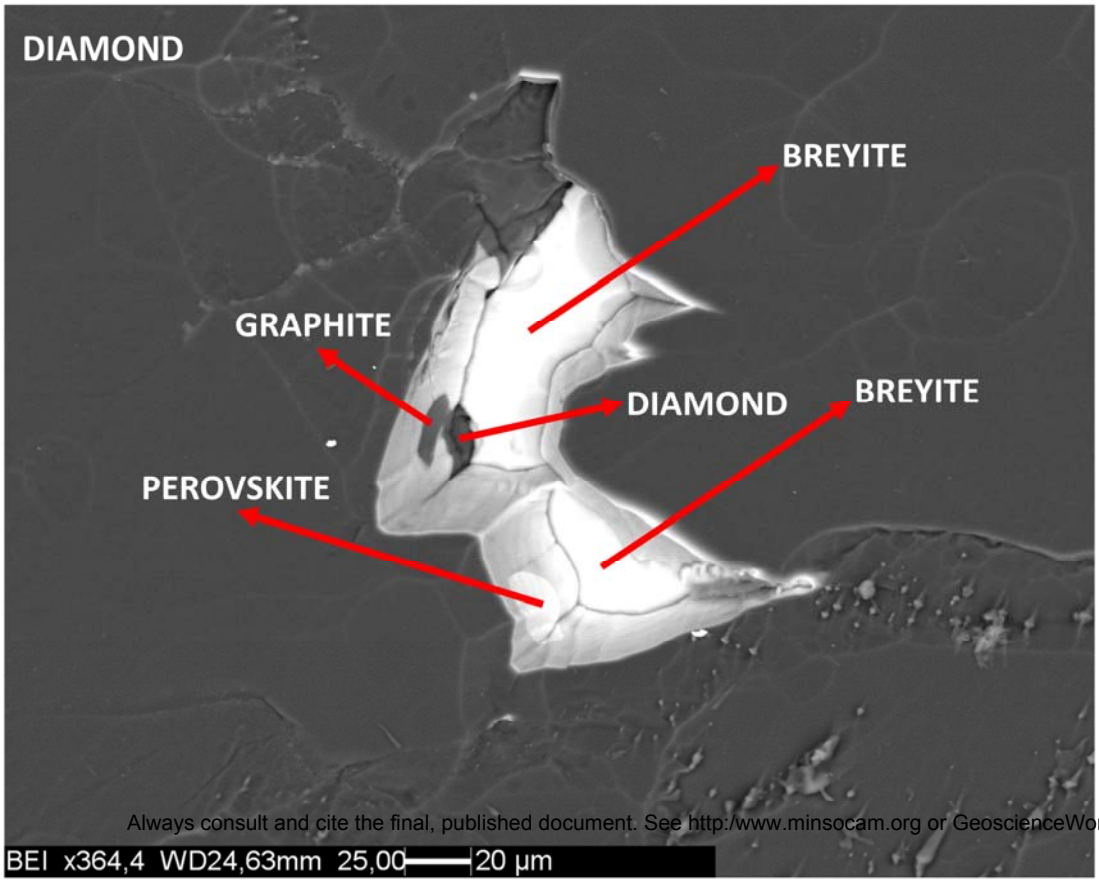
This is the peer-reviewed, final accepted version for American Mineralogist, published by the Mineralogical Society of America.
The published version is subject to change. Cite as Authors (Year) Title. American Mineralogist, in press.
DOI: https://doi.org/10.2138/am-2020-7513. http://www.minsocam.org/

0 -2 1	3.55	7	493
1 1 2	3.15	40	494
2 2 0	3.03	58	495
0 3 0	2.90	100	496
-1 2 1	2.71	10	497
-2 1 0	2.63	24	498
0 -2 2	2.52	13	499
-1 -2 2	2.38	15	500
0 4 2	1.83	15	501
2 -3 1	1.79	18	502
-2 2 2	1.71	15	503
			504

505
506
507
508
509
510
511
512
513
514
515
516
517

518 **Figure 1**

519



This is the peer-reviewed, final accepted version for American Mineralogist, published by the Mineralogical Society of America.
The published version is subject to change. Cite as Authors (Year) Title. American Mineralogist, in press.
DOI: https://doi.org/10.2138/am-2020-7513. http://www.minsocam.org/

Figure 2

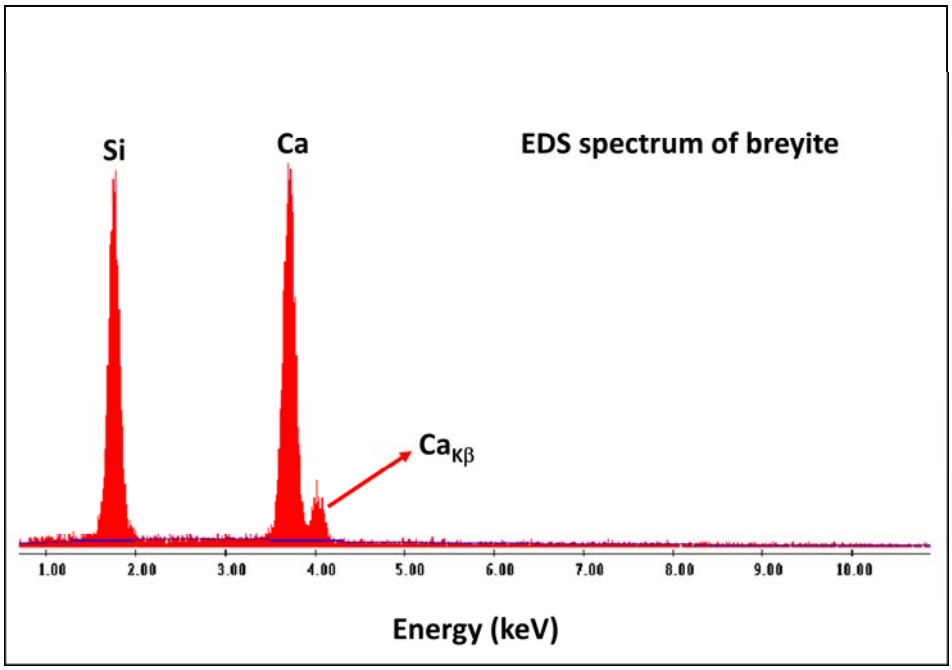


Figure 3

This is the peer-reviewed, final accepted version for American Mineralogist, published by the Mineralogical Society of America.
The published version is subject to change. Cite as Authors (Year) Title. American Mineralogist, in press.
DOI: https://doi.org/10.2138/am-2020-7513. http://www.minsocam.org/

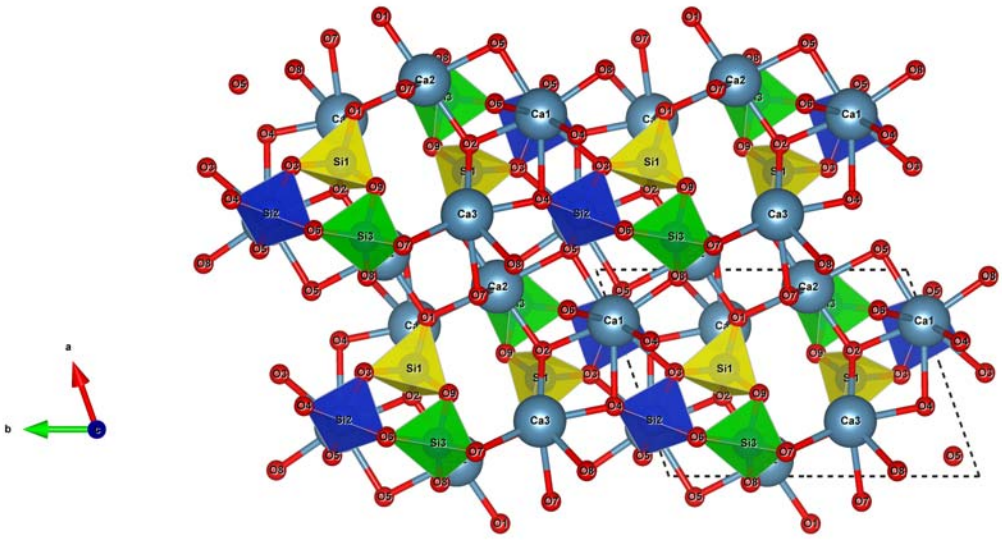


Figure 4