Depth of formation of super-deep diamonds: Raman barometry of CaSiO3-walstromite inclusions

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Depth of formation of super-deep diamonds: Raman barometry of $CaSiO_3$-walstromite inclusions

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Abstract

"Super-deep" diamonds are thought to have a sub-lithospheric origin (i.e., below ~300 km depth) because some of the mineral phases entrapped within them as inclusions are considered to be the products of retrograde transformation from lower-mantle or transition-zone precursors. $CaSiO_3$-walstromite, the most abundant Ca-bearing mineral inclusion found in super-deep diamonds, is believed to derive from $CaSiO_3$-perovskite, which is stable only below ~600 km depth, although its real depth of origin is controversial. The remnant pressure (P_{inc}) retained by an inclusion, combined with the thermoelastic parameters of the mineral inclusion and the diamond host, allows calculation of the entrapment pressure of the diamond-inclusion pair. Raman spectroscopy, together with X-ray diffraction, is the most commonly used method for measuring the P_{inc} without damaging the diamond host.

In the present study we provide, for the first time, a calibration curve to determine the P_{inc} of a $CaSiO_3$-walstromite inclusion by means of Raman spectroscopy without breaking the diamond. To do so, we performed high-pressure micro-Raman investigations on a $CaSiO_3$-walstromite crystal under hydrostatic stress conditions within a diamond-anvil cell. We additionally calculated the Raman spectrum of $CaSiO_3$-walstromite by ab initio methods both under hydrostatic and non-hydrostatic stress conditions to avoid misinterpretation of the results caused by the possible presence of deviatoric stresses causing anomalous shift of $CaSiO_3$-walstromite Raman peaks. Last, we applied single-inclusion elastic barometry to estimate the minimum entrapment pressure of a $CaSiO_3$-walstromite inclusion trapped in a natural diamond, which is ~9 GPa (~260 km) at 1800 K. These results suggest that the diamond investigated is certainly sub-lithospheric and endorse the hypothesis that the presence of $CaSiO_3$-walstromite is a strong indication of super-deep origin.

Keywords: Diamond, inclusion, $CaSiO_3$-walstromite, micro-Raman spectroscopy, ab initio methods, elastic geobarometry

Introduction

Diamonds and the mineral inclusions that they trap during growth provide a unique window on the deep Earth. A small portion (~6%) of diamonds (Stachel and Harris 2008) are interpreted to crystallize between 300 and 800 km depth (Harte 2010) because some of the inclusions entrapped are considered to be the products of retrograde transformation from lower-mantle or transition-zone precursors. However, in many cases undisputed evidence of these purported high-pressure precursors as inclusions in diamonds is lacking, and, consequently, their real depth of origin has been proven only in rare cases (e.g., Brenker et al. 2002; Pearson et al. 2014). Most so-called "super-deep diamonds" contain mainly walstromite-structured $CaSiO_3$ (hereafter $CaSiO_3$-walstromite), ferropericlase ([(Fe,Mg)O)], enstatite ($MgSiO_3$), and jeffbenite [$(Mg,Fe)_3Al_2Si_3O_{12}$], a tetragonal phase with garnet-like stoichiometry previously known by the acronym TAPP (see Nestola et al. 2016), and it is through the study of these mineral phases that the depth of formation of super-deep diamonds can be retrieved.

$CaSiO_3$-walstromite is the dominant Ca-bearing phase in super-deep diamonds (Joswig et al. 1999), and in almost all cases it is considered the product of back transformation from $CaSiO_3$-perovskite, which is stable only below ~600 km depth within the regular high-pressure assemblage of peridotitic/eclogitic mantle rocks (Frost 2008; Kaminsky 2012). However, there is compelling evidence that at least some $CaSiO_3$-walstromite originate within the upper mantle (Brenker et al. 2005; Anzolini et al. 2016), although this would require a substantial change in the source rock chemistry. Assuming peridotitic/eclogitic mantle chemistries, $CaSiO_3$-perovskite is the main Ca-host in the lower mantle (Ringwood 1991), but is also present in the

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lowermost transition zone, where it exsolves from majoritic garnet at pressures greater than 20 GPa (Irifune and Ringwood 1987). Nevertheless, there are currently no reliable literature data on the exact pressure at which $CaSiO_3$ inclusions originally crystallize and therefore no valid evidence whether or not each $CaSiO_3$-walstromite derives from $CaSiO_3$-perovskite.

Single-inclusion elastic barometry, a method recently improved by Angel et al. (2014a, 2014b, 2015a, 2015b), allows us to estimate the pressure and temperature conditions of entrapment for an inclusion within a diamond by knowing its residual pressure (P_{inc}), measured while the host is at ambient conditions, and the thermoelastic parameters of the mineral inclusion and the diamond host. In principle, the P_{inc} sustained by an inclusion while still entrapped within a diamond can be determined mainly in two ways: (1) by comparing the unit-cell volume of the inclusion before and after release from its host; (2) by comparing the Raman spectrum of the inclusion still trapped within the diamond and the Raman spectrum of the same mineral phase at room pressure. The first method requires inclusions large enough to be analyzed by single-crystal X-ray diffraction, but large inclusions are more likely to fracture the surrounding host during exhumation (Van der Molen and Van Roermund 1986; Artioli et al. 2008), and therefore their internal pressure is largely released. The second method allows to analyze tiny inclusions, which commonly preserve higher internal pressures, and, on the other hand, to prevent the host-inclusion system from destruction or damages. The host-inclusion system integrity preserves information about both the pressure exerted by the diamond on the inclusion and the relationships between the two, which may provide further details on the diamond-inclusion growth mechanisms (e.g., crystallographic orientation relationships, CORs; Nestola et al. 2014, 2017; Angel et al. 2015b; Milani et al. 2016).

In this light, we have determined experimentally the pressure-induced shift of Raman peaks for a synthetic $CaSiO_3$-walstromite up to 7.5 GPa under hydrostatic conditions to obtain a calibration system that enables us to determine the P_{inc} of a $CaSiO_3$-walstromite inclusion without breaking the diamond host. However, the effect of the elastic anisotropy of the host and the inclusion and the effect of a deviatoric stress field on the stress state of the inclusion arising from the absence of fluids at the interface between diamond and inclusion (see Nimis et al. 2016) are still unknown. Therefore, to prevent any misinterpretation of our results in terms of Raman peak shifts we calculated the Raman spectrum of $CaSiO_3$-walstromite by ab initio methods both under hydrostatic and non-hydrostatic conditions. Last, we estimated the entrapment pressure of a $CaSiO_3$-walstromite inclusion found in a diamond by single-inclusion elastic barometry.

Experimental methods

Samples

The single $CaSiO_3$-walstromite crystal, whose longest dimension is 40 μm, used for the high-pressure Raman investigations came from the experimental batch of Gasparik et al. (1994), synthesized at 2000 K and 9 GPa.

The diamond investigated in this study (Fig. 1a) was a 2.70-carat oval cut Type-II diamond. The inclusion investigated (Fig. 1b) was a $CaSiO_3$-walstromite, identified by comparison with Raman spectra reported by Nasdala et al. (2003) and Brenker et al. (2005, 2007).

Experimental in situ calibration of $CaSiO_3$-walstromite Raman spectra at high pressure

The ambient-pressure Raman spectrum of the synthetic single crystal of $CaSiO_3$-walstromite was collected with a Thermo-Scientific DXR Raman Microscope using a green solid-state laser (532 nm) as excitation source at the Department of Geosciences, University of Padova. The analyses were performed using a 50× long working distance (LWD) objective with ~2.5 cm^{-1} spectral resolution and 1 μm spatial resolution at 10 mW of power. The Raman system was set with 900 lines/mm grating and a 25 μm pinhole. Spectra were recorded in the frequency range extending from 100 to 3500 cm^{-1}; to maximize the signal-to-noise ratio, each spectrum was collected 10 times using an exposure time of 20 s, and then merged together at the end of the acquisition. The instrument was calibrated by using the calibration tool provided by Thermo-Scientific.

The high-pressure Raman spectra were collected at the Department of Sciences, University of Roma Tre, with a Horiba LabRam HR micro-Raman spectrometer equipped with a green solid-state laser (532 nm) focused through a 20× LWD objective. A ETH diamond-anvil cell with 600 μm size culets was loaded with the crystal of $CaSiO_3$-walstromite and a 4:1 mixture of methanol:ethanol as pressure-transmitting medium. Pressure was determined by the calibrated shift of the R_1 ruby fluorescence band (Mao et al. 1986). The spatial resolution was ~1 μm and the spectral resolution was 0.3 cm^{-1}. For the ruby, optical filters were employed to achieve ~1 mW at the sample surface; the Raman system was set with 1800 lines/mm grating, exposure time 1 s (3 times), confocal hole of 300 μm and slit of 200 μm. For the $CaSiO_3$-walstromite, optical filters were employed to achieve ~50 mW at the sample surface; the Raman system was set with 1800 lines/mm grating, exposure time 60 s (3 times), confocal hole of 100 μm and slit of 100 μm. The calibration was done using the main Raman line (520.5 cm^{-1}) of a silicon standard.

The Raman spectrum of the $CaSiO_3$-walstromite inclusion was collected at the Gemological Institute of America with a Renishaw inVia Raman microscope using the 514.5 nm output wavelength of a 150 mW argon-ion laser, at 100% output power. The analyses were performed using 50× LWD lens with a 0.55 numerical aperture and the system was set with 1800 lines/mm grating. Spectra were recorded in the frequency range extending from 100 to 1200 cm^{-1}; to maximize the signal-to-noise ratio, each spectrum was collected four times using an exposure time of 60 s, and then merged together at the end of the acquisition. The calibration was done using an internal silicon standard (inside the instrument) using its main Raman line (520.5 cm^{-1}).

The baseline subtraction with a quadratic function and the Lorentzian fitting were carried out using the Thermo-Scientific OMNIC Spectra Software.

Ab initio calibration of $CaSiO_3$-walstromite Raman spectra at high pressure

The ab initio calculation of the vibrational frequencies and intensities of the Raman-active modes was performed by using the CRYSTAL14 software (Dovesi et al. 2014). A hybrid HF/DFT Hamiltonian was used (WC1LYP) that employs the Wu-Cohen DFT exchange functional (Wu and Cohen 2006) corrected with a fraction (20%) of the exact non-local Hartree-Fock exchange, and the Lee-Young-Parr DFT correlation functional (Lee et al. 1988). The grid for the evaluation of the DFT exchange–correlation functionals was chosen by the keyword XLGRID of the CRYSTAL14 user manual (Dovesi et al. 2014) and corresponds to a total of 345 185 points in the unit cell. A measure of the excellent numerical accuracy

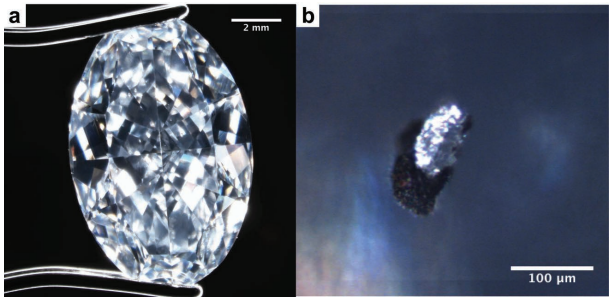

Figure 1. (**a**) Expanded view of the inclusion-bearing diamond studied in this work. (**b**) Close-up of the $CaSiO_3$-walstromite inclusion investigated. The black halo around the inclusion indicates the presence of graphitization inside a fracture. (Color online.)

provided by such a grid is the evaluation of the total number of electrons in the unit cell, by the numerical integration of the electron density over the cell volume: 348.000013 electrons out of 348. The atomic basis sets employed were from the CRYSTAL online library at the address www.crystal.unito.it/basis-sets.php. More precisely, they were 86-511G(2d) for Ca, 86-311G(1d) for Si, and 8-411G(2d) for O, where the symbols 1d and 2d stand for the presence of one and two polarization functions, respectively. The thresholds controlling the accuracy of the calculation of Coulomb and exchange integrals were set to 8 (ITOL1 to ITOL4) and 18 (Dovesi et al. 2014). The diagonalization of the Hamiltonian matrix was performed at 8 independent *k* vectors in the reciprocal space (Monkhorst net; Monkhorst and Pack 1976) by setting to 2 the shrinking factor IS (Dovesi et al. 2014). Cell parameters and fractional coordinates were optimized by analytical gradient methods, as implemented in CRYSTAL14 (Civalleri et al. 2001; Dovesi et al. 2014). Geometry optimization was considered converged when each component of the gradient (TOLDEG parameter in CRYSTAL14) was smaller than 0.00003 hartree/bohr and displacements (TOLDEX) were smaller than 0.00012 bohr with respect to the previous step. Lattice parameters and fractional coordinates were optimized at the WC1LYP level (static values: no zero point and thermal effects included), at the static pressures of 0 and 4 GPa, and at 4 other *non-hydrostatic* stress conditions specified by matrices representing the stress tensor in a Cartesian frame (with e_1, e_2, e_3 basis vectors), where the e_2 vector is parallel to the *b* lattice vector; the e_1 and e_3 vectors are, respectively, subparallel to the *a* and *c* lattice vectors, derived from a standard orthogonalization of the lattice basis. The chosen 4 stress matrices corresponded to a hydrostatic component of 4 GPa plus deviatoric stresses (pure shear, traceless stress matrices) having eigenvalues 1, –0.5, and –0.5 GPa, and directions of maximum compression (eigenvalue 1 GPa), respectively, along e_1, e_2, e_3, and the softest direction [1$\bar{1}$2] (the latter one is given with reference to the crystal lattice basis). Vibrational frequencies were calculated at 0 and 4 GPa and at the four non-hydrostatic stress conditions, as the eigenvalues of the matrix of the second derivatives of the full potential of the crystal with respect the mass-weighted nuclear displacements (Hessian matrix; Pascale et al. 2004). Relative intensities of the Raman signals are computed using a fully analytical approach formulated and implemented in the CRYSTAL14 program (Maschio et al. 2012, 2013).

RESULTS

Raman spectrum at ambient pressure

Before performing the high-pressure Raman measurements, we examined the Raman spectrum of the synthetic $CaSiO_3$-walstromite at ambient conditions (Fig. 2). The three main Raman peaks, in order of decreasing intensity, were observed at 656, 977, and 1037 cm^{-1} (hereafter called Peak 1, 2, and 3, respectively). The raw spectrum (Supplemental[1] Fig. S1) shows also lower intensity peaks in the 200–590 cm^{-1} region (the main ones at 301, 328, 349, 396, and 512 cm^{-1}) and in the 810–950 cm^{-1} region (the main ones at 813, 838, 857, and 950 cm^{-1}); another peak is centered at 1055 cm^{-1}. Our ambient Raman frequencies agree with those reported in previous studies within the experimental uncertainty (Nasdala et al. 2003; Brenker et al. 2005, 2007).

Effect of hydrostatic pressure on the Raman frequencies: Comparison between experiment and simulation

In situ Raman spectra of the three main peaks (656, 977, and 1037 cm^{-1}) of crystalline $CaSiO_3$-walstromite, measured as a function of pressure up to 7.5 GPa, are shown in Figure 2. Data analysis of the spectra was carried out using Thermo-Scientific OMNIC Spectra Software with Gaussian function. The measured frequencies are reported in Supplemental[1] Table 1.

It is evident that all Raman peaks shift continuously toward higher wavenumbers with increasing pressure throughout the pressure range. In particular, Peaks 1 and 2 show an almost linear trend. The pressure-dependence of the three main Raman bands was fitted with a weighted linear regression and the resulting pressure coefficients were: dν/dP = 3.22(±0.05) cm^{-1} GPa^{-1} for Peak 1, dν/dP = 5.16(±0.09) cm^{-1} GPa^{-1} for Peak 2, and dν/dP = 6.5(±0.1) cm^{-1} GPa^{-1} for Peak 3 (Fig. 3a). Minor peaks were too weak to be fitted accurately at high pressure; therefore they were not considered for the calculation of the pressure coefficients.

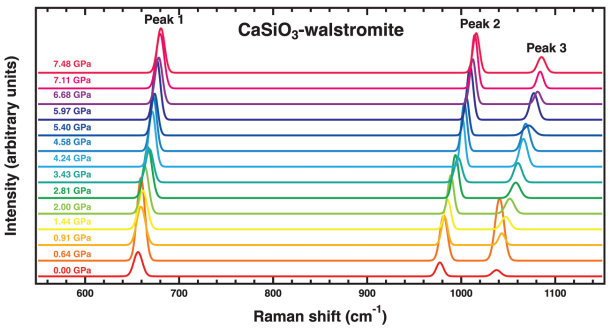

FIGURE 2. Raman spectra of synthetic $CaSiO_3$-walstromite up to 7.5 GPa. (Color online.)

Our calculated Raman spectra (Supplemental[1] Table 2) are comparable with the experimental frequencies reported in Supplemental[1] Table 1 within one or two standard deviations (σ). All Raman frequencies systematically increase with increasing pressure. The pressure dependence of the three main Raman bands was fitted with a weighted linear regression and the resulting pressure coefficients were: dν/dP = 3.33 cm^{-1} GPa^{-1} for Peak 1, dν/dP = 4.68 cm^{-1} GPa^{-1} for Peak 2, and dν/dP = 5.90 cm^{-1} GPa^{-1} for Peak 3 (Fig. 3b). These pressure dependencies match well with the experimental ones within one or two standard deviations (σ).

Effect of non-hydrostatic pressure on the Raman frequencies

The ab initio calculated peak shifts under non-hydrostatic stresses show patterns similar to those under hydrostatic pressure (Fig. 4). Also, the pressure dependencies of the three main peaks under non-hydrostatic stresses are comparable to those calculated under hydrostatic pressure, the differences being less than 2σ (Table 1). Relative to the values under hydrostatic pressure, Peak 1 and Peak 3 show negative shifts under any non-hydrostatic stress state: the mean differences of the Δν are –1.4 cm^{-1} for Peak 1 and –1.0 cm^{-1} for Peak 3, which correspond to a mean difference of the ΔP of –0.5 and –0.19 GPa, respectively. Conversely, Peak 2 shows a negative shift when the maximum compression is along e_1 (i.e., subparallel to the *a* lattice vector) and e_3 (i.e., subparallel to the *c* lattice vector), but a positive shift when the maximum compression is along e_2 (i.e., parallel to the *b* lattice vector) and [1$\bar{1}$2] (i.e., the softest direction, perpendicular to the layers): the mean difference of the Δν is –0.1 cm^{-1}, which corresponds to a mean difference of the ΔP of –0.02 GPa. This indicates that Peak 2 is the least sensitive to the application of differential stresses, and therefore it is the most reliable peak to be used as a calibrant to calculate the P_{inc} of a $CaSiO_3$-walstromite inclusion.

Inclusion residual pressure

The least sensitive peak to the deviatoric stress suffered by the $CaSiO_3$-walstromite inclusion enclosed in the diamond is

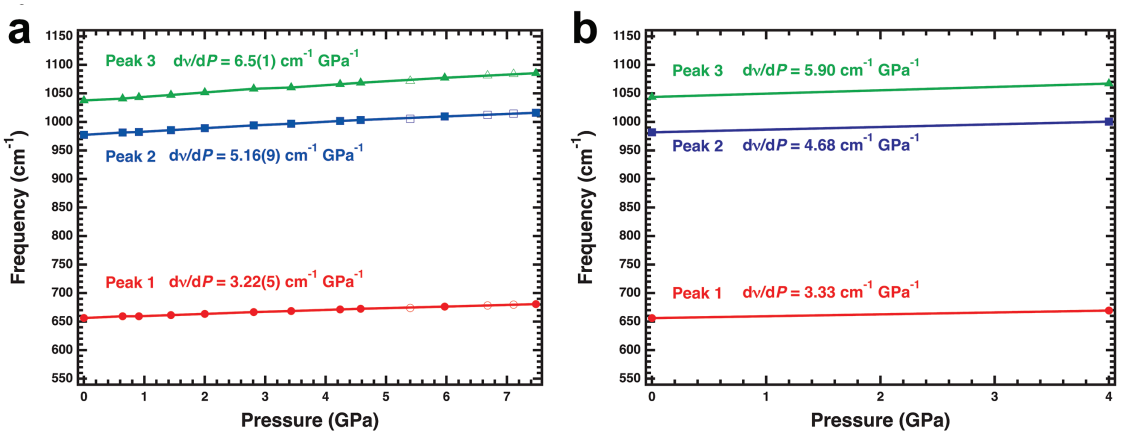

FIGURE 3. (**a**) Experimental and (**b**) calculated pressure-dependencies of the main Raman peaks of $CaSiO_3$-walstromite under hydrostatic conditions. In **a**, compression and decompression are represented by solid and open symbols, respectively. The error bars lie within the symbols. (Color online.)

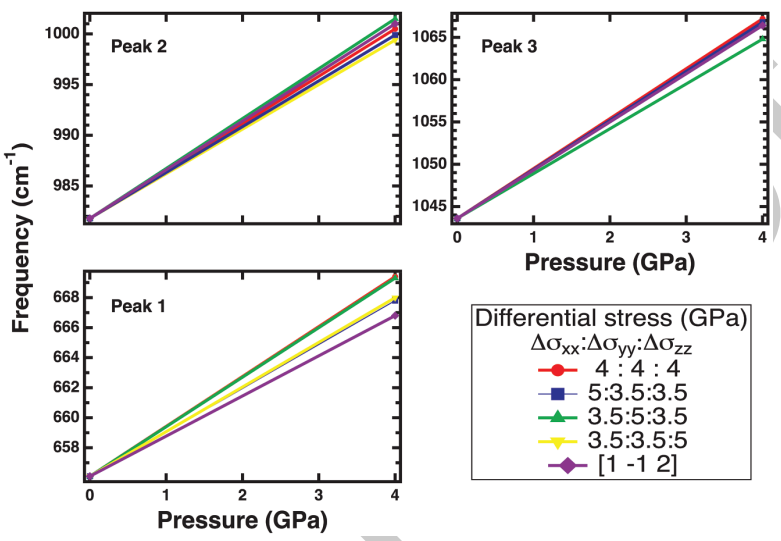

FIGURE 4. Calculated pressure dependencies of the three main Raman vibrational frequencies of $CaSiO_3$-walstromite at different stress states. (Color online.)

Peak 2, as explained in the previous paragraph. For this reason, we used the experimental pressure coefficient for Peak 2, which is 5.16(±0.09) cm^{-1} GPa^{-1}, to calculate the residual pressure (P_{inc}) retained by the $CaSiO_3$-walstromite inclusion found in the natural diamond (Fig. 1). The main Raman peaks of that inclusion were observed at 669, 999, and 1061 cm^{-1} (Fig. 5), which are the highest frequencies ever reported in literature for a $CaSiO_3$-walstromite still trapped within its diamond host. The calculation lead to the following residual pressure: 4.26(±0.07) GPa.

DISCUSSION

The Raman measurements show that the $CaSiO_3$-walstromite inclusion retains a residual pressure, as a consequence of the difference between the thermoelastic properties of the diamond host and those of the $CaSiO_3$-walstromite inclusion. This residual pressure, measured at ambient conditions, can be used to calculate the entrapment pressure and temperature conditions of the host-inclusion pair, provided that the equations of state of the mineral phase and the diamond are known and reliable. The basic concept behind this approach is that, at the moment of entrapment, the host fits the inclusion perfectly and the two are under the same P and T conditions (Izraeli et al. 1999; Howell et al. 2012; Nestola et al. 2012; Angel et al. 2014b, 2015b). However, this method relies on some assumptions: (1) the inclusion is spherical (Eshelby 1957, 1959; Mazzucchelli et al. 2017); (2) both the host and inclusion are elastically isotropic and homogeneous (Angel et al. 2014b); (3) at the moment of formation the inclusion perfectly fits in the diamond; and (4) deformation of

TABLE 1. Calculated shifts of Raman frequencies under hydrostatic and non-hydrostatic stresses

State of stress	Peak 1				Peak 2				Peak 3			
	ν (cm^{-1})	Δν (cm^{-1})	dν/dP (cm^{-1}/GPa)	ΔP (GPa)	ν (cm^{-1})	Δν (cm^{-1})	dν/dP (cm^{-1}/GPa)	ΔP (GPa)	ν (cm^{-1})	Δν (cm^{-1})	dν/dP (cm^{-1}/GPa)	ΔP (GPa)
Hydrostatic	669.4	–	3.33	–	1000.5	–	4.68	–	1067.2	–	5.90	–
Non-hydrostatic along e_1	667.8	−1.6	2.93	−0.5	999.9	−0.6	4.53	−0.13	1066.8	−0.4	5.80	−0.07
Non-hydrostatic along e_2	669.3	−0.1	3.30	0.0	1001.5	1.0	4.93	0.21	1064.8	−2.4	5.30	−0.45
Non-hydrostatic along e_3	668.0	−1.4	2.98	−0.5	999.4	−1.1	4.40	−0.26	1066.5	−0.7	5.73	−0.11
Non-hydrostatic along [1$\bar{1}$2]	666.8	−2.6	2.68	−1.0	1001.0	0.5	4.80	0.10	1066.4	−0.7	5.70	−0.12
	Δ$\bar{\nu}$	−1.4	Δ$\bar{P}$	−0.5	Δ$\bar{\nu}$	−0.1	Δ$\bar{P}$	−0.02	Δ$\bar{\nu}$	−1.0	Δ$\bar{P}$	−0.19

Notes: Differences Δν and ΔP are with respect to the hydrostatic value. Positive values mean shift toward higher frequencies, negative values mean shift toward lower frequencies. Δ$\bar{\nu}$ and Δ$\bar{P}$ are the mean difference of the frequency and of the pressure, respectively, evaluated over the set of total numbers of peaks.

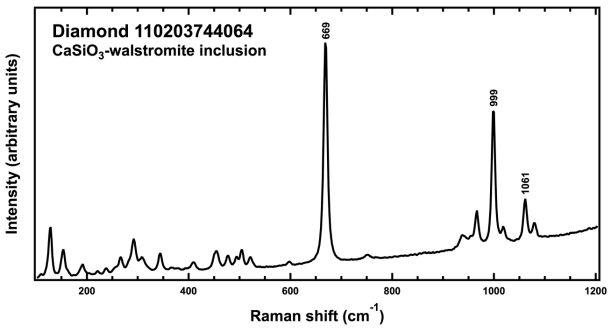

FIGURE 5. Raman spectrum of the $CaSiO_3$-wasltromite inclusion found in the natural diamond.

both the host and the inclusion is elastic and no brittle or plastic deformation has occurred. The assumption that both the host and the inclusion are elastically isotropic implies that the inclusion is under isotropic strains. But the stress state in an anisotropic inclusion subject to isotropic strains (e.g., there is no fluid at the interface, see Nimis et al. 2016) such as $CaSiO_3$-walstromite is never hydrostatic (Anzolini et al. 2016) and, therefore, its Raman shifts may potentially be affected by such non-isotropic deformation. Nevertheless, our results indicate that the second highest peak of $CaSiO_3$-walstromite, located at 977 cm^{-1}, is not very sensitive to non-hydrostatic stress, being the mean difference of the ΔP with respect to the hydrostatic value only –0.02 GPa (see Table 1), and thus it is suitable to estimate the remnant pressure of a $CaSiO_3$-walstromite inclusion within a negligible error.

The calculation of the pressure of formation (P_c) for the $CaSiO_3$-walstromite–diamond pair was performed with the software EoSFit7c (Angel et al. 2014a), by following the same method described in Angel et al. (2014b). We used thermal expansion and compressibility data for $CaSiO_3$-walstromite reported in Anzolini et al. (2016), thermoelastic properties for diamond from the review of Angel et al. (2015a) and the residual pressure obtained in this work, which is 4.26(±0.07) GPa.

Assuming a temperature range between 1200 and 2000 K for $CaSiO_3$-walstromite formation (i.e., the same temperature range at which $CaSiO_3$-walstromite was successfully synthesized by Gasparik et al. 1994), we obtained entrapment pressures ranging from 8.10 to 9.27 GPa [P_{inc} = 4.26(±0.07) GPa] (Supplemental[1] Table 3), corresponding to 240–280 km depth (Fig. 6). Such pressure can be considered as a minimum estimate because of the presence of cracks around the inclusion (Fig. 1b), which would partly release the stress (see Mazzucchelli et al. 2016) and the effect of plastic deformation of diamond, which, if present, is not quantifiable yet. Taking this into consideration, the entrapment pressure could be set at higher values, at least on the boundary between $CaSiO_3$-walstromite and larnite + $CaSi_2O_5$-titanite. Considering instead Peak 1 or Peak 3 with the hydrostatic calibration, the arising error in the entrapment pressure would be ~0.5 and ~0.9 GPa, respectively, corresponding to an underestimation of the depth of about 10–20 km.

IMPLICATIONS

Our results on $CaSiO_3$-walstromite indicate that the main Raman peaks of $CaSiO_3$-walstromite are sensitive to deviatoric

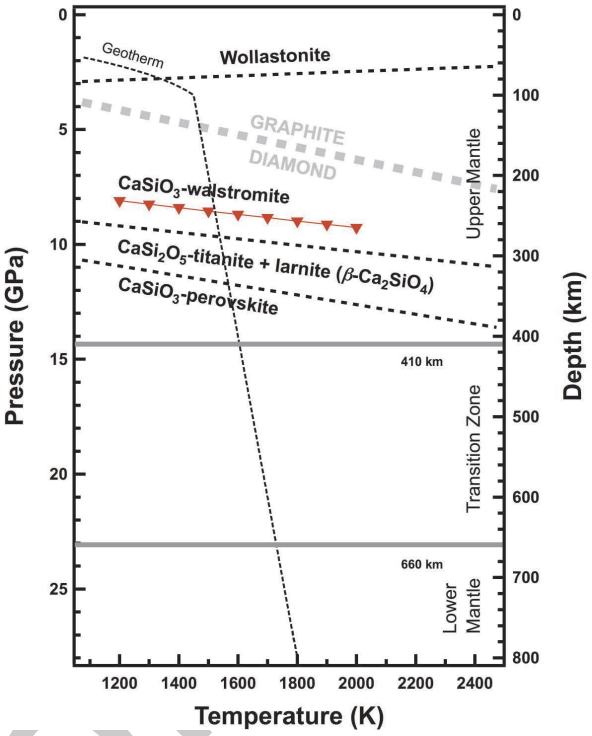

FIGURE 6. Phase diagram of the $CaSiO_3$ system, in which the phase boundaries are given as dotted lines (Essene 1974; Gasparik et al. 1994). The graphite-diamond phase boundary is shown as a gray dashed line (Day 2012). The geotherm is shown as a black dashed line (Turcotte and Schubert 2014). The 410 and 660 km discontinuities enclosing the transition zone are indicated by bold lines. Entrapment pressures from which our sample may have originated are represented with red symbols. (Color online.)

stress, with Peak 1 (656 cm^{-1}) and Peak 2 (977 cm^{-1}) showing the largest and smallest shifts, respectively. As a general rule, the use of these peaks is not ideal to retrieve reliable pressures from the Raman shifts. On the other hand, Peak 2, being the least sensitive to deviatoric stresses can be used, as in the present study, to calibrate the residual pressure retained by a $CaSiO_3$-walstromite inclusion still trapped in a diamond within a negligible error. Through this approach, we estimate the formation depth of a diamond–$CaSiO_3$-walstromite pair to be P = ~9 GPa (~260 km) if the temperature is 1800 K. This can be considered as a minimum value, as the presence of fractures at the diamond-inclusion interface would partly release the internal pressure of the inclusion. These results suggest that the diamond investigated is certainly sub-lithospheric and endorse the hypothesis that the presence of $CaSiO_3$-walstromite is a strong indication of super-deep origin.

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