Depth of formation of super-deep diamonds

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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 $CaSiO_3$ ($CaSiO_3$-walstromite), ferropericlase ((Fe,Mg)O)), enstatite ($MgSiO_3$) and jeffbenite (($Mg,Fe)_3Al_2Si_3O_{12}$), 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 a dominant Ca-bearing phase in super-deep diamonds (Joswig et al. 1999) and it has been suggested that it is the product of back transformation from $CaSiO_3$- perovskite, which is stable only below ~600 km depth. Nevertheless, its real depth of origin is controversial. Single-inclusion elastic barometry, a method recently improved by Angel et al. (2014, 2015), 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 at ambient conditions, and the thermoelastic parameters of the mineral inclusion and the diamond host. The P_{inc} sustained by an inclusion 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 and therefore their internal pressure is largely released. The second method allows the analysis of tiny inclusions with no fractures in the diamond host, which commonly preserve higher internal pressures, and, at the same time, the original integrity of the host-inclusion system is maintained.

This work aims to obtain the depths of formation of diamonds containing $CaSiO_3$-walstromite inclusions by non-destructive methods. At present, we have studied 6 super-deep diamonds by a combination of in situ single-crystal X-ray diffraction and micro-Raman spectroscopy. High-pressure micro-Raman investigations were carried out to obtain a calibration curve to determine the P_{inc} of a $CaSiO_3$-walstromite inclusion by means of Raman spectroscopy without breaking the diamond. 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. Lastly, we applied single-inclusion elastic barometry to estimate the entrapment pressure of a $CaSiO_3$-walstromite-diamond pair.

Experimental Methods

X-ray data were collected in situ on the inclusions using a a Rigaku Oxford Diffraction *SuperNova* goniometer, equipped with a Dectris *Pilatus 200 K* area detector and with a *Mova* X-ray microsource. A Mo$K\alpha$ radiation was operated at 50 kV and 0.8 mA.The sample to detector distance was 68 mm. Data reduction was performed using CrysAlis software (Rigaku Oxford Diffraction), which corrected for Lp

effects and absorption. Raman measurements were carried out in situ with a Thermo Scientific™ DXR Raman Microscope using a green argon ion laser (532 nm) as excitation source at the Department of Geosciences, University of Padova. The analyses were performed using a 50× objective with ~2.5 cm⁻¹ spectral resolution and 1.1 μm spatial resolution at 10 mW of power. The synthetic $CaSiO_3$-walstromite crystal selected for the Raman investigation was synthesized at 9 GPa and 2000 K in a multi-anvil press. First, a Raman spectrum was collected at room conditions; for the high-pressure measurements a diamond-anvil cell was loaded with the crystal of $CaSiO_3$-walstromite, a piece of ruby as internal pressure standard and a 4:1 mixture of methanol:ethanol as pressure- transmitting medium. The Raman spectra were collected at the University of Roma Tre with a micro-Raman spectrometer equipped with a green argon ion laser (532 nm) focused through a 20× LWD objective. The spatial resolution of the sample surface was ~1 μm and the spectral resolution was 0.3 cm⁻¹. Spectral fitting was carried out using the Thermo Scientific™ OMNIC™ Spectra Software. 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. 2013).

Analytical Results

At ambient pressure the main Raman peaks of $CaSiO_3$-walstromite were observed at 656, 977 and 1037 cm⁻¹ (hereafter called Peak 1, 2 and 3, respectively). With increasing pressure, all Raman peaks shifted continuously toward higher wavenumbers. In particular, Peaks 1 and 2 showed almost linear trends. The pressure-dependence of the three main Raman bands was fitted with a weighted linear regression and the resulting pressure coefficients were: dv/dP = 3.22(5) cm⁻¹ GPa⁻¹ for Peak 1, dv/dP = 5.16(9) cm⁻¹ GPa⁻¹ for Peak 2 and dv/dP = 6.5(1) cm⁻¹ GPa⁻¹ for Peak 3 (Figure 1a). Our calculated Raman spectra under hydrostatic stress are comparable with the experimental frequencies. Again, 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: dv/dP = 3.32 cm⁻¹ GPa⁻¹ for Peak 1, dv/dP = 4.68 cm⁻¹ GPa⁻¹ for Peak 2 and dv/dP = 5.89 cm⁻¹ GPa⁻¹ for Peak 3 (Figure 1b). The ab initio calculated peak shifts under non-hydrostatic stresses show patterns similar to those under hydrostatic pressure. Also, the pressure-dependencies of the three main peaks under non-hydrostatic stresses are comparable to those calculated under hydrostatic pressure. However, 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.Therefore, we used its pressure coefficient to calculate the P_{inc} of an inclusion still trapped within a diamond which shows the highest Raman peak shifts ever reported in the literature (main Raman peaks at 669, 999 and 1061 cm⁻¹) and we obtained a value of 4.26(7) GPa.
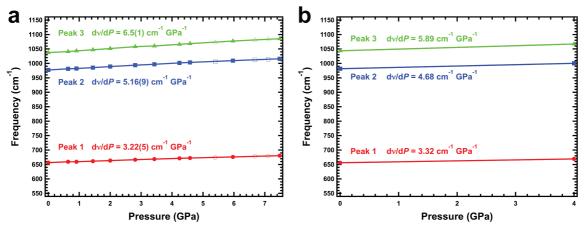

Figure 1: a) Experimental and b) calculated pressure dependencies of the main Raman peaks of $CaSiO_3$-walstromite under hydrostatic conditions. In a) compression and decompression are represented by solid and open symbols, respectively. The error bars lie within the symbols.

Ten CaSiO$_3$-walstromite inclusions were individually investigated by single-crystal X-ray diffraction. All of the inclusions have unit-cell volumes less than the room pressure volume of CaSiO$_3$-walstromite (~376 Å^3), confirming the Raman results that these inclusions retain a remnant pressure. We have determined their residual pressures, which range from ~ 0.17 to ~ 1.8 GPa, by using the thermoelastic parameters for CaSiO$_3$-walstromite reported in Anzolini et al. (2016). The presence of fractures around these inclusions explains why they exhibit lower pressure than the residual pressure of 4.26(7) GPa obtained previously by using the Raman calibration curve.

The calculation of the pressure of formation for the CaSiO$_3$-walstromite – diamond pair was performed with the software EoSFit7c. 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. (2015) and the residual pressure of 4.26(7) GPa. Assuming a temperature range between 1200 K and 2000 K for C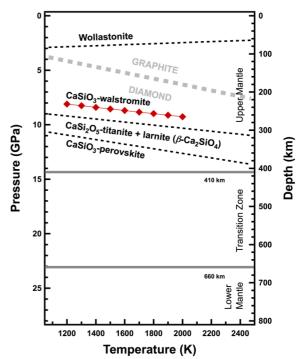aSiO$_3$-walstromite formation, we obtained entrapment pressures ranging from 8.10 to 9.27 GPa, corresponding to 240-280 km depth (Figure 2, from Anzolini et al. 2017).

Figure 2: Phase diagram of the CaSiO$_3$ system. Entrapment pressures from which our sample may have originated are represented with red symbols.

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