Research Open

Geology, Earth and Marine Sciences

Volume 6 Issue 7

Research Paper

^{13}C-rich Diamond in a Pegmatite from Rønne, Bornholm Island: Proofs for the Interaction Between Mantle and Crust

Rainer Thomas*

Im Waldwinkel 8, D-14662 Friesack, Germany

***Corresponding author:** Rainer Thomas, Im Waldwinkel 8, D-14662 Friesack, Germany

Received: October 23, 2024; **Accepted:** October 29, 2024; **Published:** November 02, 2024

Abstract

In this contribution, we show for the first time ^{13}C-rich diamonds in a pegmatite of the 1,400 Ma old Rønne granite. The position of the first-order diamond line depends on the laser excitation energy in the case of deep (55μm) diamond crystals. The best values can be obtained at energies lower than 1mW. The value of 1309 cm^{-1} corresponds to 55% ^{13}C-diamond, a pressure of ~7 GPa, and a depth of ~210 km. Diamond crystals about 20 μm under the sample surface show no such dependence. Diamonds in a pegmatite sample are unusual and are an essential hint for the involvement of supercritical fluids in the pegmatite formation.

Keywords: *^{13}C-rich diamond, Raman spectroscopy, Pegmatite, Supercritical fluid, Bornholm island*

Introduction

During the work on deuterium and $^{13}CO_2$-rich fluid inclusion in pegmatite quartz from the Rønne pegmatite from Bornholm Island, Denmark [1], we found as a surprise ^{13}C-rich diamond inclusion. The G-band of graphite is completely missing. Diamonds in a more crustal rock are entirely out of place. In a couple of papers, the author and the co-authors [1-5] and references in there) have shown that supercritical fluid comes fast from the Earth's mantle into the crustal region together with its load (diamond and other high-pressure minerals). In the crust region, the supercritical fluid changes into critical and under-critical fluid. In this state, chemical and physical processes that are nearly unknown happen.

Sample Material and Early Results

The about 1,400 Ma old granite from the Klippelokke quarry, 3 km ENE of Rønne (Bornholm Island, Denmark), contains an uncomplicated quartz-feldspar pegmatite veins (subhorizontal or vertical) with a conspicuous graphic texture and only minor amounts of mica. The potassium felspar is flesh-red (called "red admirals"), and the quartz glyphs are smoky-colored [3]. The quartz contains mainly fluid inclusions of secondary origin. However, a small number of quartz grains contain a very high number of carbonate-CO_2 inclusions. Some inclusions also contain significant amounts of zabuyelite [Li_2CO_3] [3]. In such quartz grains, secondary fluid inclusions are rare. Figure 1 shows a typical ^{13}C-rich diamond-calcite aggregate, which is 55 μm deep under the surface, demonstrating that such diamonds are not contaminations from the preparation [6]. The up to now found largest area with some graphite and ^{13}C-rich diamond is 660 x 600 μm^2 (like Figure 2). That means that in the Rønne pegmatite sample, diamond is not a rare phase. In quartz grains often related to graphite, there are also smooth spherical inclusions of different minerals (for example, coesite remnants and ^{13}C-rich graphite). Generally, we used for our studies cleaned and, on both sides polished thick sections with a thickness of 500 μm.

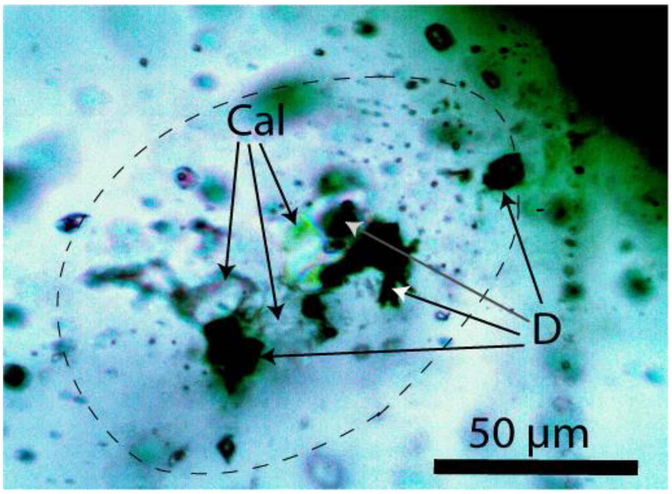

Figure 1: Detail of the pegmatite quartz from Bornholm Island. The dashed line shows the inclusion of a ^{13}C-rich diamond in quartz. The inclusion is not easy to see in the quartz material (only in polarized light). D – diamond, Cal – calcite. The diamonds are about 55 μm deep. Note the semicircular patterns of tiny diamonds right above.

Methodology

For our studies here, we used only microscopic and Raman spectroscopic technics.

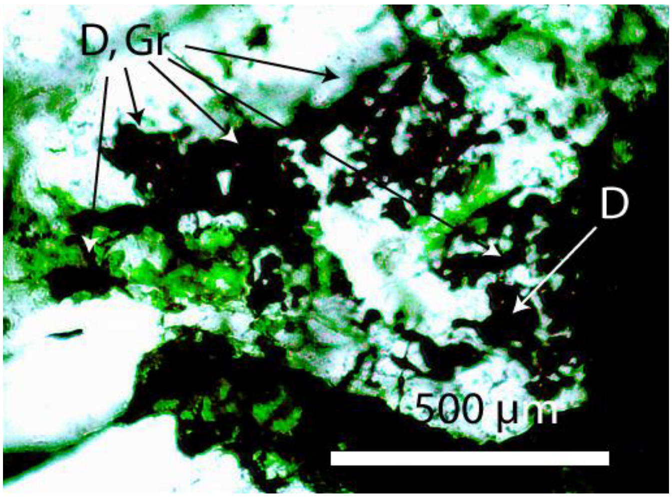

Figure 2: Large area with many ^{13}C-rich graphite (Gr) and ^{13}C-rich diamond (D) crystals. The quartz in-between is characterized by very strong Raman bands (as high as the main quartz band at 464 cm^{-1} in the region (80 – 300 cm^{-1}). The diamond-bearing area is about 20 µm deep.

Raman Spectroscopy

We have performed all microscopic and Raman spectroscopic studies with a petrographic polarization microscope with a rotating stage coupled with the EnSpectr Raman spectrometer R532. The Raman spectra were recorded in the spectral range of 0–4000 cm^{-1} using an up to 50 mW single-mode 532 nm laser, an entrance aperture of 20 µm, a holographic grating of 1800 g/mm, and a spectral resolution ranging from 4–6 cm^{-1}. Generally, we used an objective lens with a magnification of 100x – the Olympus long-distance LMPLFLN100x objective. The laser power on the sample is adjustable down to 0.02 mW. The Raman band positions were calibrated before and after each series of measurements using the Si band of a semiconductor-grade silicon single-crystal. The run-to-run repeatability of the line position (based on 20 measurements each) is ± 0.3 cm^{-1} for Si (520.4 ± 0.3 cm^{-1}) and 0.5 cm^{-1} for diamond (1332.7 ± 0.4 cm^{-1} over the range of 80–2000 cm^{-1}). The FWHM = 4.26 ± 0.42 cm^{-1}. FWHM is the Full-Width at Half Maximum. We used a water-clear natural gem-type diamond crystal (Mining Academy Freiberg: 2453/37 from Brasil) as a diamond reference (for more information, see Thomas et al. 2022 [4]. Other references are small diamond grains in pegmatite quartz left by the preparation [6]: Mean from 10 grains (Lorentz-fitting): 1332.7 ± 0.39 cm^{-1} and FWHM = 4.26 ± 0.42 cm^{-1}.

Results

Raman measurements on four different diamond crystals in pegmatite quartz from Bornholm Island (Table 1) gave for the first-order Raman line a mean of 1313.52 ± 3.06 cm^{-1} (53 measurements; crystals: I-IV) and FWHM = 64.47 ± 3.61 cm^{-1}. Opposite to gem diamond crystals, the FWHM value is enormous. This results from the long way from the mantle region at high temperatures and an extended stay at about 700°C in the intrusion level. The group with the lowest value for the first-order diamond line is 1309 ± 0.93 cm^{-1}. They result in long-time measurements at low laser energy (≤1 mW), however, at long time (2000 s).

Table 1: Results of the measured data on the ^{13}C-rich diamond from the Bornholm pegmatite. Crystals I-IV: 55 µm deep under the surface; crystal V: 20 µm deep.

Crystal	Laser energy (mW)	Mean (cm^{-1})	±1s	FWHM (cm^{-1})	±1s	n
I	50.0 mW	1318.24	-	62.16	-	2
I	29.1 mW	1315.33	1.78	65.82	10.59	20
I	22.1 mW	1311.64	-	69.40	-	1
I	4.33 mW	1309.30	-	61.45	-	1
I	0.92 mW	1308.60	-	60.28	-	2
I	0.15 mW	1309.00	0.93	56.65	4.00	6
II	0.92 mW	1311.11	0.40	69.09	-	4
III*	29.1 mW	1315.80	0.89	63.32	2.40	10
IV	9.1 mW	1313.16	0.18	68.70	3.20	6
IV	0.92 mW	1309.00	-	63.00	-	1
V**	9.1 mW	1304.40	2.78	85.78	5.98	10

*Crystal III is a small, maybe different ^{13}C-rich diamond -see Figure 1.

**Crystal V is from the large area near the surface (20 µm deep) – see Figure 2.

Refrain from crystal III in Table 1; there is a passable correlation between the used laser energy (mW) for the 532 nm excitation) and the position of the first-order Raman line (P) of the studied ^{13}C-rich diamond:

$$P = 1308.56\ \text{cm}^{-1} + 0.1976 * (\text{mW}).\quad (r^2 = 0.928) \qquad (1)$$

The scatter is the result of minor variations of the laser focus on the diamond sample, about 55 µm deep, from the sample surface. Such variations with the laser energy are not observed for diamonds in Figure 2.

Figures 3 and 4 show exemplarily typical Raman spectra of ^{13}C-rich diamonds taken at different laser powers on the sample (taken with 29.1 and 0,91 mW on the sample, respectively).

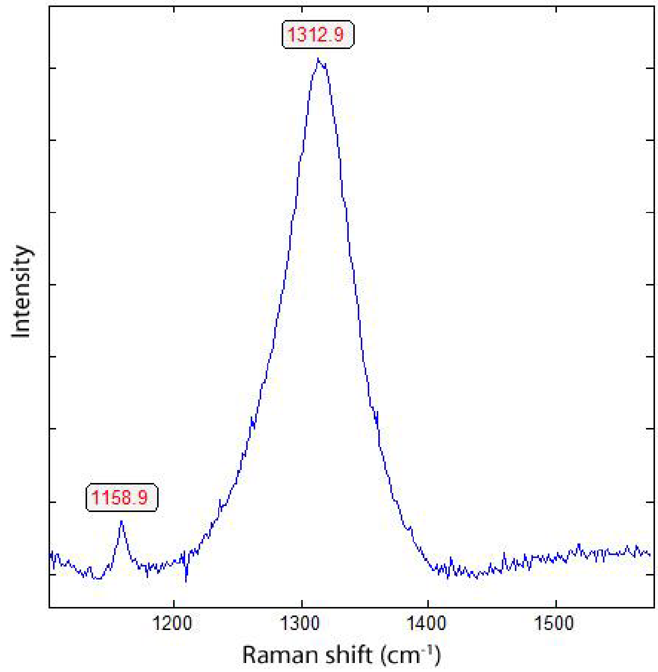

Figure 3: Raman spectrum of the first-order Raman line (29.1 mW on the sample) of ^{13}C-rich diamond from pegmatite quartz from Bornholm Island (exposition 50 s). The line at 1158.9 is from the quartz of the matrix.

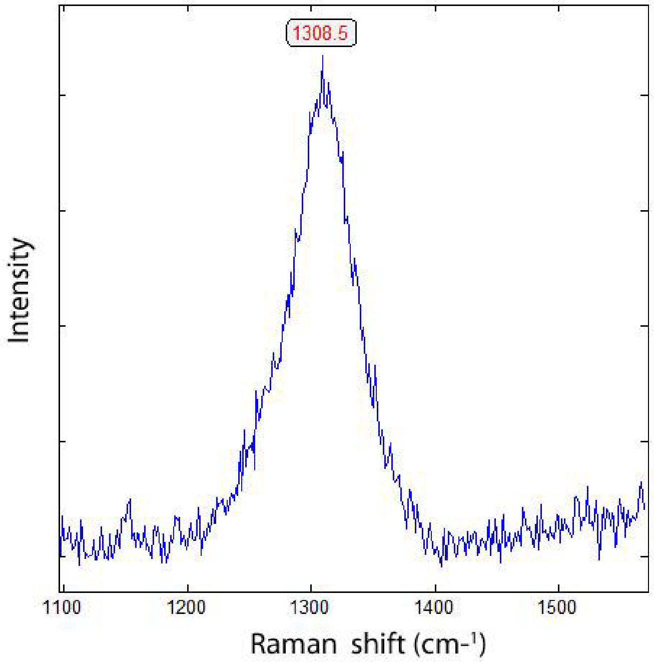

Figure 4: Raman spectrum of the first-order Raman line (0.91 mW on the sample) of ^{13}C-rich diamond from pegmatite quartz from Bornholm Island (exposition 2000 s).

The lowest value for the first-order diamond line is 1303.4 cm$^{-1,}$ obtained from the largest diamond-graphite area (660 x 600 µm^2; see above). The large FWHM values for all measured diamond grains are the result of stress in an extraneous surrounding (upper crust), by a large dislocation density and ^{13}C/^{12}C disorder [6].

Interpretation

We have found in pegmatite quartz from Bornholm Island (Rønne granite) diamonds rich in ^{13}C. Because there is a relatively good correlation between the used excitation energy and the ^{13}C content in the diamond, we can accept that the data for the low energy represents the best Raman values for the ^{13}C-rich diamond (1308.9 ± 0.16 cm^{-1}, n = 9) because at high excitation and the dark color heating and Raman shift to higher values is inevitable. According to Schiferl (1997) [7] and Akaishi et al. (2000) [8], the results correspond to a hydrostatic pressure of about 7 GPa (~210 km depth), and according to Anthony and Banholzer (1992) [9] to 55% ^{13}C in the studied diamond (see also Thomas et al. 2021) [10]. ^{13}C-rich graphite has a D band at 1338 cm^{-1} and a G band at 1555 cm^{-1} [11]. The D band for the ^{12}C implanted graphite is 1358 cm$^{-1,}$ and the G band is at 1581 cm^{-1}. From the graphite with the typical very weak D and very strong G bands, the values are given in Table 2.

Table 2: Data for the Raman G band of graphite (Gr) – laser wavelength 532 nm.

Gr-Crystal	Laser energy (mW)	Mean (cm^{-1})	± 1s	FWHM (cm^{-1})	± 1s	n
^{13}C-rich Gr	29.1 mW	1562.56	10.82	76.02	6.02	10
^{12}C-rich Gr*	29.1 mW	1581.5	-	13.50	-	1
Gutierrez et al. (2014)						
^{12}C Gr	-	1581	-	-	-	-
^{13}C Gr	-	1555	-	-	-	-

*See Thomas et al. (2021) – [10].

Opposite the Variscan diamonds and lonsdaleite in the Lusatian Mts, the Erzgebirge, and Thuringia, which consistently show a graphite G band, the Rønne diamond shows in the case of ^{13}C-rich diamond with no graphite band [12,13]. However, the pegmatite samples from Rønne contain very graphite-rich parties, too. The graphite is also ^{13}C-rich and is sometimes coupled with the rare 1332.3 ± 2.7 cm^{-1} nanodiamond. An important conclusion follows that the presence of ^{13}C-rich diamond is a further important hint that supercritical fluids often cause the formation of pegmatites by supercritical water with their load, which takes part in their formation.

Acknowledgment

The short paper is dedicated to my parents, Gerhard (1915-1994) and Anni (1920-1993) Thomas, who have prematurely promoted my strong interest in chemistry and Earth sciences.

References

1. Thomas R (2024) $NaHCO_3$-$NaDCO_3$ and $^{13}CO_2$-rich fluid inclusion in pegmatite quartz from Bornholm Island/Denmark. *Geol Earth Mar Sci* In preparation.
2. Thomas R, Rericha A (2024) Meaning of supercritical fluids in pegmatite Formation and critical-element redistribution. *Geol Earth Mar Sci* 6: 1-5.
3. Thomas R, Davidson P, Schmidt C (2011) Extreme alkali bicarbonate- and carbonate-rich fluid inclusions in granite pegmatite from the Precambrian Rønne granite, Bornholm Island, Denmark. *Contrib Mineral Petrol* 161: 315-329.
4. Thomas R, Davidson P, Rericha A, Recknagel U (2022) Water-rich coesite in prismatine-granulite from Waldheim/Saxony. *Veröffentlichungen Naturkunde Museum Chemnitz* 45: 67-80.
5. Thomas R, Davidson P, Rericha A, Recknagel U (2023) Ultra-high pressure mineral inclusions in the crustal rocks: Evidence for a novel trans-crustal transport mechanism. *Geoscience* 12: 1-12.
6. Keller DS, Ague JJ (2022) Possibilities for misidentification of natural diamond and coesite in metamorphic rocks. *Neues Jb - Mineral Abh* 197: 1276-1293.
7. Schiferl D, Malcolm N, Zaug JM, Sharma SK, Cooney TF, et al. (1997) The diamond 13C/12C isotope Raman pressure sensor system for high-temperature/pressure diamond-anvil cells with reactive samples. J. *Appl Phys* 82: 3256-3265.
8. Akaishi M, Kumar MDS, Kanda H, Yamaoka (2000) Formation process of diamond from supercritical H_2O-CO_2 fluid under high pressure and high temperature conditions. *Diamond and Related Materials* 9: 1945-1950.
9. Anthony TR, Banholzer WF (1992) Properties of diamond with varying isotope composition. *Diamond and Related Materials* 1: 717-726.
10. Thomas R, Rericha A, Davidson P, Beurlen H (2021) An unusual paragenesis of diamond, graphite, and calcite: A Raman spectroscopic study. *Estudos Geologicos* 31: 3-15.
11. Gutierrez G, Le Normand F, Aweke F, Muller D, Speisser C, et al. (2014) Mechanism of thin layers graphite formation by ^{13}C implantation and annealing. *Appl Sci* 4: 180-194.
12. Thomas R, Trinkler M (2024) Monocrystalline lonsdaleite in REE-rich fluorite from Sadisdorf and Zinnwald/E-Erzgebirge, Germany. *Geol Earth Mar Sci* 6: 1-5.
13. Thomas R, Recknagel U (2024) Lonsdaleite, diamond, and graphite in a lamprophyre: Minette from East-Thuringia/Germany. *Geol Earph Mar Sci* 6: 1-4.

Citation:

Thomas R (2024) ^{13}C-rich Diamond in a Pegmatite from Rønne, Bornholm Island: Proofs for the Interaction Between Mantle and Crust. *Geol Earth Mar Sci* Volume 6(7): 1-3.