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$NaHCO_3$-$NaDCO_3$ and $^{13}CO_2$-Rich Fluid Inclusion in Pegmatite Quartz from Bornholm Island/Denmark

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Abstract

In this short contribution, we present Raman data for the main lines of the synthetic system $NaHCO_3$-$NaDCO_3$. Furthermore, we show that some CO_2-rich fluid inclusions in pegmatite quartz in the 1,400 Ma old Rønne granite from Bornholm Island contain D-rich nahcolite. Moreover, we also found ^{13}C-rich CO_2 in some fluid inclusions, as well as coronene [$C_{24}H_{12}$], a highly condensed six-ring polycyclic aromatic hydrocarbon. The occurrence of ^{13}C-rich diamonds in a granite-pegmatite system forces the acceptance of supercritical fluids coming fast from the old mantle region. Maybe supercritical fluids are generally responsible for pegmatite formation.

Keywords: *Raman spectroscopy, $NaHCO_3$-$NaDCO_3$-rich CO_2 inclusions, $^{13}CO_2$-rich inclusions, 13C-rich diamond, Pegmatites, Bornholm Island*

Introduction

During the study of nahcolite-rich [$NaHCO_3$] inclusions in pegmatite quartz from Bornholm [1], we found carbonates that could not identified with Raman spectroscopy because of missing reference spectra. Other with Raman determined carbonates and bicarbonates are calcite, zabuyelite [Li_2CO_3], rare amounts of natrite [Na_2CO_3], gregoryite [K_2CO_3], kalicinite [$KHCO_3$], and dawsonite [$NaAl(CO_3)(OH)_2$]. Also, graphite is present. A list of carbonate species is in Table 1, given in Thomas et al. 2011 [1]. Because most inclusions are composed of solid carbonates in CO_2 only and there are a small couple of silicate melt inclusions, we can assume that the trapping temperature must be about 700°C or higher. After our studies [2,3] about supercritical fluids coming from mantle deeps, unusual mineral phases are possible. We think here on deuterium-bearing carbonates. No Raman spectra are available for deuterium-bearing nahcolite; therefore, we have synthesized such phases in the $NaHCO_3$ – $NaDCO_3$ system. Furthermore, we observed exceptional $^{13}CO_2$-rich fluid inclusions, which can traced back to the reaction of the supercritical fluid with ^{13}C-rich diamond present in the pegmatite quartz from Bornholm Island.

Table 1: Results of the Raman measurements on pure $NaHCO_3$ and $NaDCO_3$ and mixed $Na(HD)CO_3$.

Compound	Origin	Mean (cm^{-1})	FWHM (cm^{-1})	n
$NaHCO_3$	RRUFF R070237	1045.3	4.82	1
$NaHCO_3$	This work	1045.1 ± 0.9	5.41 ± 0.13	12
On Si				
$NaHCO_3$	This work	1044.1 ± 0.3	7.14 ± 0.23	6
$Na(H_{0.18}D_{0.82})CO_3$	This work	1064.4 ± 1.8	13.71 ± 4.39	12
$NaDCO_3$	This work	**1069.1 ± 0.2**	5.91 ± 0.33	13
On glass				
$Na(H_{0.02}D_{0.98}CO_3$	This work	1068.3 ± 0.4	6.10 ± 1.17	10
$NaDCO_3$	This work	**1069.3 ± 0.6**	5.45 ± 1.18	11

Sample Material

The about 1,400 Ma old granite from the Klippelokke quarry, 3 km ENE of Rønne (Bornholm Island, Denmark), contain 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 (see Thomas et al. 2011) [1]. 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] (see Thomas et al. 2011) [1]. In such grains, secondary fluid inclusions are rare. Figure 1 show typical nahcolite-bearing CO_2 inclusions.

Because there are no Raman spectra of deuterium-bearing nahcolite present as a reference in the literature, we have prepared such crystals by reaction of analytical poor $NaHCO_3$ and D_2O (heavy water).

The simple reaction is $NaHCO_3 + D_2O \rightarrow NaDCO_3 + HDO$ (D_2O in excess). (1)

By the further reaction of $NaDCO_3$ with the produced HDO, we obtain, according to the following equation, the stable compound $Na_2HD(CO_3)_2$:

$$2\,NaDCO_3 + HDO \rightarrow Na_2HD(CO_3)_2 + D_2O\uparrow \quad (2)$$

The pure $NaDCO_3$ compound is rare after the reactions (1) because

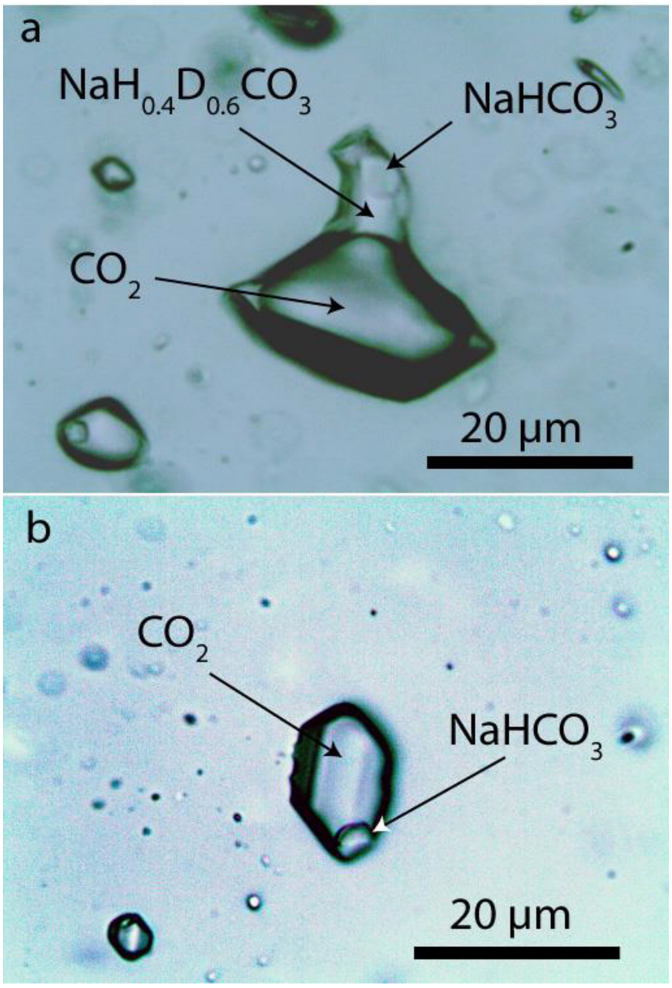

Figure 1: Typical nahcolite+D and CO_2-bearing inclusion in pegmatite quartz from Bornholm Island.

the DHO concentration increases steadily. The pure $NaDCO_3$ phase forms during fractionated crystallization under the microscope as tiny crystals (Figures 2 and 3). X-ray studies about the last compound must follow.

Methodology

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

Raman Spectroscopy

We have performed all microscopic and Raman spectroscopic studies with a petrographic polarization microscope with a rotating stage coupled with the En*S*pectr 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-

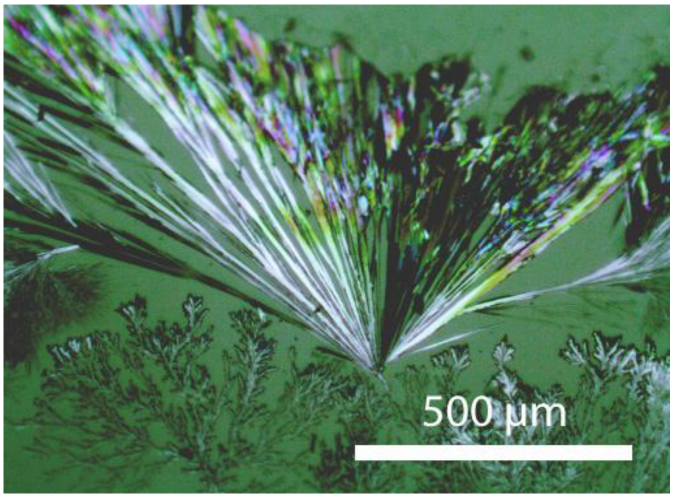

Figure 2: $NaDCO_3$ crystals grown from a concentrated $NaDCO_3$ solution under the microscope (in transmitted light).

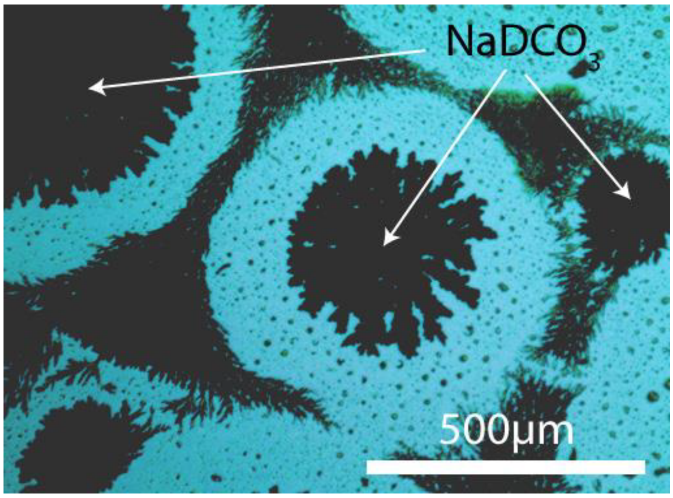

Figure 3: $NaDCO_3$ crystals on silicon grown from a concentrated $NaDCO_3$ solution under the microscope (in reflected light). The arrows show the pure $NaDCO_3$ crystals.

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 diamond crystal (Mining Academy Freiberg: 2453/37 from Brasil) as a diamond reference (for more information, see Thomas et al. 2022 [3].

Calibration Curve for the Determination of $NaDCO_3$

For the construction of a provisional calibration curve between $NaHCO_3$ and $NaDCO_3$, we solved a small amount of analytical pure $NaHCO_3$ in D_2O 99.9% from PelementSamples, Belchertown, MA/USA. We converted it into a significant excess of pure heavy water [D_2O] into $NaDCO_3$ according to reaction (1). We gave a droplet of this solution on a microscope glass slide with a hollow or semiconductor-grade silicon wafer (Figure 3 and Figure 4).

As described above, we produced $NaDCO_3$-rich phases by reaction of $NaHCO_3$ and heavy water (D_2O) according to the equation (1) and (2). Richardson and Hood (1937) [4] wrote that the concentration of

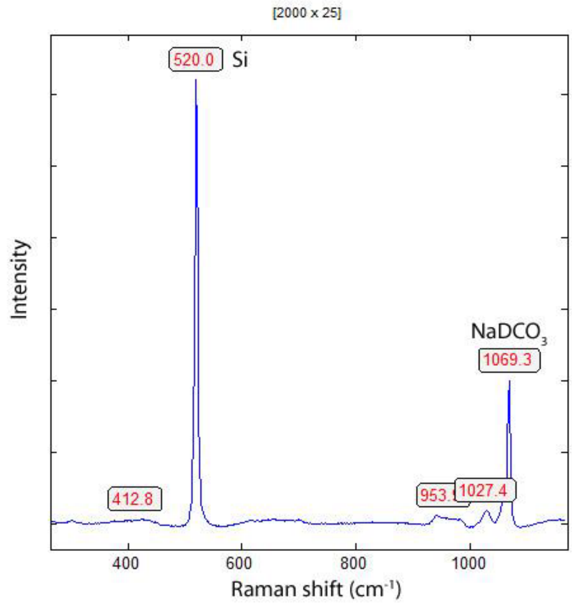

Figure 4: Raman spectrum of $NaDCO_3$ on a Si wafer (520 cm^{-1} reference).

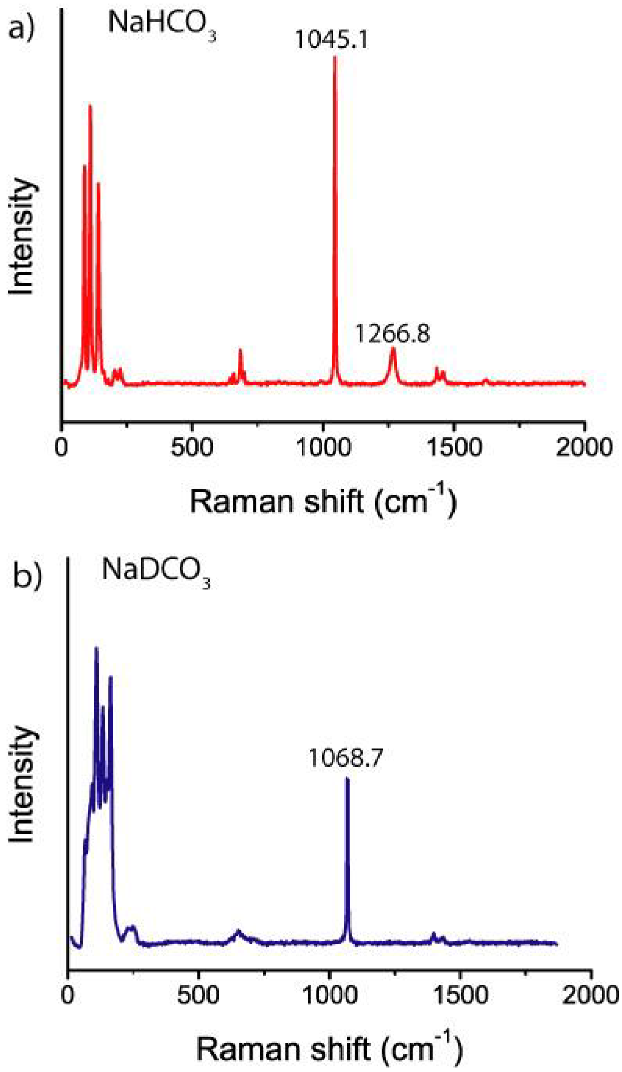

Figure 5: Raman spectra of $NaHCO_3$ (a) and very $NaDCO_3$-rich nahcolite (b) with D = 0.99.

$NaDCO_3$ is directly proportional to the amount of D_2O. That means pure $NaDCO_3$ crystals are rare (Figure 5).

The obtained Raman data are presented in Figure 6. For the first experiment, we used glass test tubes. The solution is strongly alkaline (pH ~ 11) and reacts readily with glass, forming K_2CO_3, $KHCO_3$, and other compounds. The formation of K_2CO_3 could proved by Raman spectroscopy (see also Conrad 2020) [5]. Therefore, for most experiments, we used later plastic vessels. In Table 1 are the results of the Raman determination listed.

From our observation under the microscope, we see for the reaction $NaHCO_3 + D_2O$ an order of:

$NaHCO_3 \rightarrow NaH_nD_{1-n}CO_3 \rightarrow NaDCO_3$ according to the equations (1) and (2).

Results

$NaDCO_3$-rich CO_2 Inclusion

In a small number of quartz grains in the Bornholm pegmatite, we found a high concentration of $NaHCO_3$-rich CO_2 inclusions. The amount of nahcolite [$NaHCO_3$] in these inclusions is a high variable. Figures 7 and 8 show that variability, from about 0 to more than 40% (in rare cases up to 100%).

$^{13}CO_2$-rich Vapor Phase in the $NaHCO_3$-$NaDCO_3$-Rich Fluid Inclusions

Some $NaHCO_3$-$NaDCO_3$-rich CO_2 inclusions contain also $^{13}CO_2$-rich phases. According to Vitkin et al. 2021 [6], there is a significant difference between the Raman position of pure $^{12}CO_2$ and $^{13}CO_2$, with 1388 cm^{-1} and 1370 cm^{-1} (Raman mode ν_1), respectively. From measurements at nine different inclusions, we obtained a mean of 1381.6 ± 1.44 cm^{-1} and a FWHM = 14.8 ± 4.7 cm^{-1} corresponding to 35.56 ± 8% $^{13}CO_2$. A natural reference with secondary CO_2 inclusion in quartz, taken at the same conditions, gave almost pure $^{12}CO_2$: 1387.94 ± 0.28 cm^{-1} (n = 11 different inclusions). Using a mean value comparison at a 0.999 statistical certainty results in a significant difference. A different method is used by Remingi et al. 2023 [7]. The $^{13}CO_2$-rich

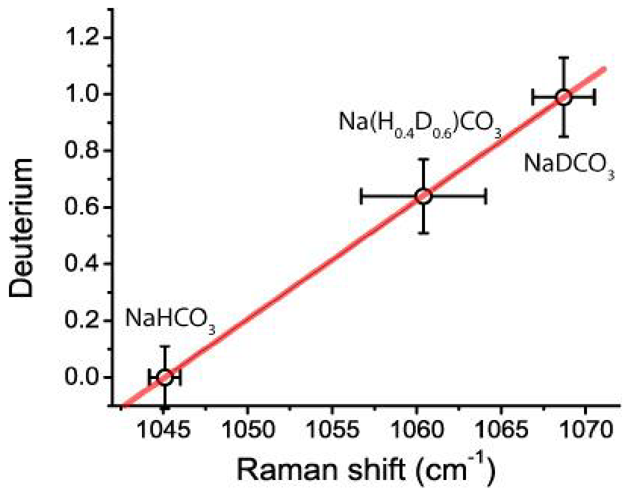

Figure 6: Calibration curve for the determination of the deuterium in mol fractions determined from the Raman shift.

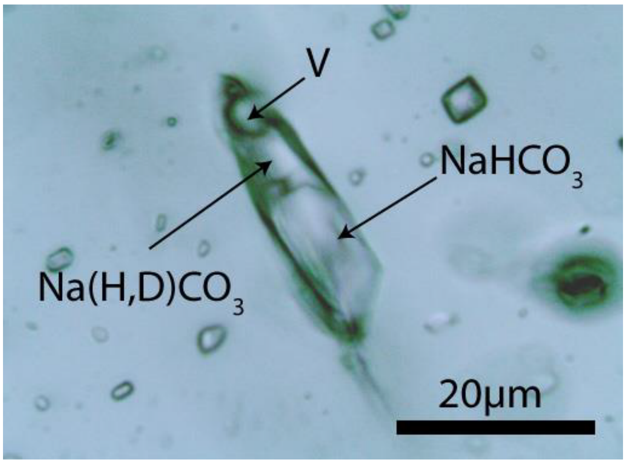

Figure 7: Complex $NaHCO_3$-Na(H, D)CO_3 inclusion in pegmatite quartz from Bornholm Island. V – CO_2-rich vapor phase.

Table 2: Results of the Raman measurements on pure $NaHCO_3$ and mixed Na(H, D)CO_3 in CO_2 inclusion in pegmatite quartz from Bornholm Island.

Compound	Origin	Mean (cm^{-1})	FWHM (cm^{-1})	n
$NaHCO_3$	RRUFF R070237	1045.3	4.82	1
$NaHCO_3$	This work	1045.2 ± 0.4	5.58 ± 0.89	15
$Na(H_{0.32}D_{0.68}CO_3$	This work	1061.3 ± 2.5	19.87 ± 6.58	21

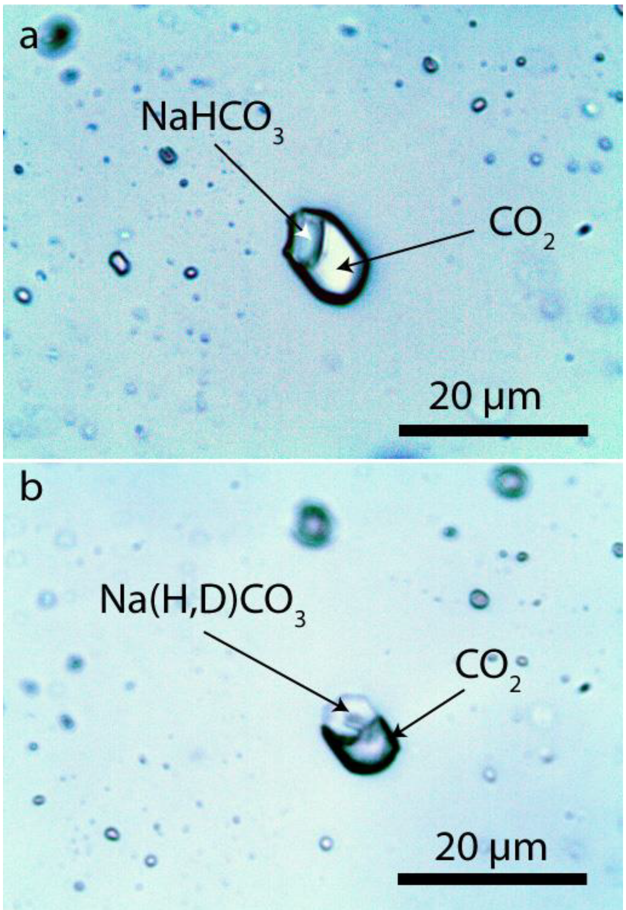

Figure 8: $NaHCO_3$-rich CO_2 inclusion in pegmatite quartz. a) The $NaHCO_3$ inclusion is composed of pure nahcolite. b) a deuterium-rich nahcolite inclusion in quartz. The volume of this solid phase is about 40%.

fluid phase is the result of the interaction between supercritical fluid and ^{13}C-rich diamond. Figure 9 shows an example of ^{13}C rich diamond beside calcite in pegmatite quartz from Bornholm Island.

From 10 different measuring points on the diamond (see Figure 10), a mean of 1316.11 ± 2.5 cm^{-1} and an FWHM = 60.54 ± 7.16 cm^{-1}, and according to Thomas et al. (2021) [6], this value corresponds to about 40% ^{13}C, which is relatively high. In the $^{13}CO_2$-rich inclusions, we have often observed coronene [$C_{24}H_{12}$] (~1351 cm^{-1}, FWHM = 9.9). Coronene is a highly condensed six-ring polycyclic aromatic hydrocarbon. For the formation, high temperatures are necessary.

Discussion

The enrichment of D_2O can be explained by enrichment of D_2O by diffusion because the light water (H_2O) diffuses faster than the heavy water D_2O (Thomas and Davidson 2019) [8-11] in the supercritical fluid. The presence of ^{13}C-rich diamond (Figure 10) shows clearly that a supercritical fluid has transported diamonds via supercritical

Table 3: lists the main Raman lines of synthetic $NaHCO_3$, $NaDCO_3$, and mixed phases in inclusions in pegmatite quartz from Bornholm Island.

$NaHCO_3$ (synthetic)	Rel. Intensity	$NaDCO_3$ (synthetic)	Rel. Intensity	$NaDCO_3$-rich Bornholm	Rel. Intensity
88.7	s	75.1	s	70.0	m
110.5	vs	110.2	s	99.0	vs
141.4	s	150.3	m	153.8	s
		164.6	m		
203.8	w				
224.5	w			225.6	w
684.7	w	672.4	vw	695.2	vw
		701.3	vw		
1045.1	vs	1069.2	vs	1065.1	s
1266.7	m				
1434.5	vw			1428.3	vw

Relative intensities: vs: Very Strong, s: Strong, m: Medium, w: Weak, vw: Very Weak.
The mean for Bornholm is 1061.3 ± 2.5 cm^{-1} (21 different inclusions) and corresponds to D = 0.68 ± 0.11 and for 1065.1 cm^{-1} D = 0.84, the highest value.

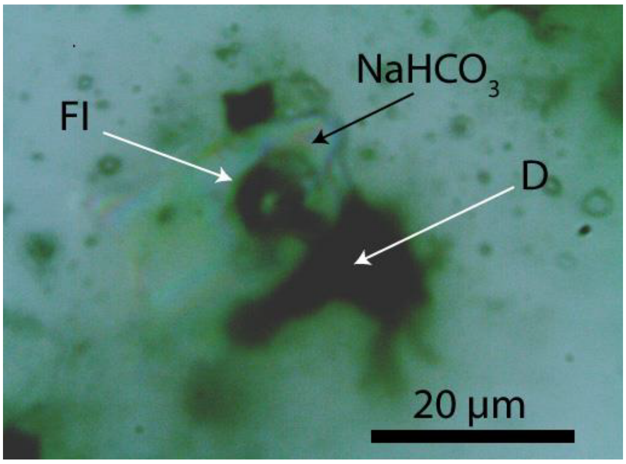

Figure 9: ^{13}C-rich diamond in a near spherical calcite inclusion in pegmatite quartz from Bornholm Island. The figure shows the diamond grain (D) in calcite. In the calcite is a CO_2-rich fluid inclusion (Fl).

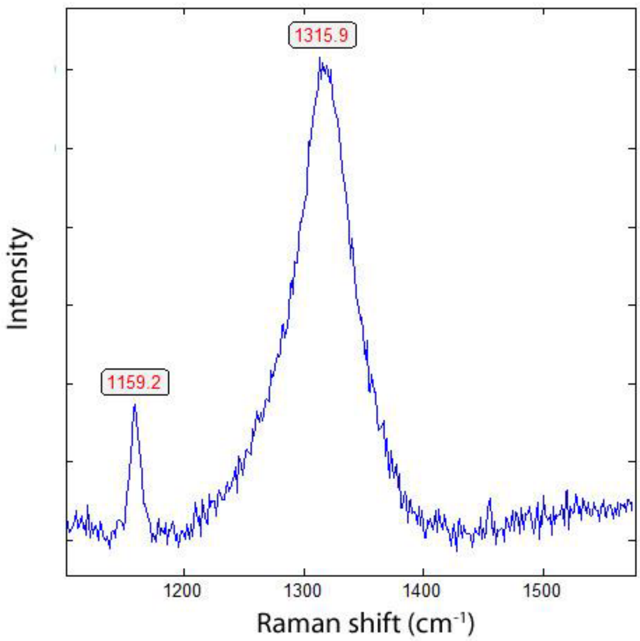

Figure 10: Raman spectrum of ^{13}C-rich diamond in pegmatite quartz from Bornholm Island.

fluid from mantle depths to the intrusion level of pegmatites. These findings force the idea that supercritical fluids are responsible for the formation of some pegmatites, as the author and coauthors have shown in many papers.

Acknowledgment

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