

Research Article

Orthorhombic Cassiterite and ^{13}C -rich Diamond in a Sample from the Land's End Granite, SW England, and Some Remarks on the Origin of the ^{13}C -rich Diamond and Graphite

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Abstract

A cassiterite sample from Land's End granite, SW England, contains cassiterite crystals rich in orthorhombic phases. A precise classification is not possible by mixing remnants of different polytypes. Obviously, the main phase is the polymorph type Pbcn (PbO_2 -type), which forms around 30 GPa. The possibility of the formation of polytypes of cassiterite at such high pressures is indicated by the proof of the presence of diamond. Some diamonds and graphite are rich in ^{13}C , 28% and 11.45% respectively. Such a high concentration of ^{13}C in diamond is only possible by effective isotope fractionation in a supercritical fluid. Significant higher ^{13}C values, up to 95%, were found by the author.

Keywords: Land's End Granite, Raman spectroscopy, Orthorhombic cassiterite, ^{13}C -rich diamond and graphite, Supercritical fluid

Introduction

The naturally occurring form of cassiterite is usually tetragonal and crystallizes in the rutile-type structure. However, Thomas (2023a) has shown that cassiterite can also crystallize as an orthorhombic polytype and is widespread in the Erzgebirge and Schlaggenwald (Horní Slavkov, Czech Republic). Last time, a couple of experimental works on the different polytypes of cassiterites were performed [1-5]. From these experiments, it follows that the orthorhombic cassiterite types formed under high pressure and high temperature. Because the orthorhombic cassiterite of the Variscan tin deposits in the Erzgebirge region is part of the tetragonal cassiterite formed in the upper crustal region, it is, therefore, formally a low-pressure formation. The appearance of orthorhombic cassiterite here needs, thus, a plausible explanation [6,7]. Essential indicators for the occurrence of the high-pressure cassiterite polytypes are the paragenetic high-pressure minerals diamond, lonsdaleite, and others, which came from the mantle region via supercritical fluid, as well as the Lorenzian distribution of some trace and main elements [8]. Proofs for such new transport mechanisms are in Thomas et al. (2023a) [1]. In this contribution, we will show that orthorhombic cassiterite and diamond are not only related to the vast Variscan Erzgebirge region but also to the Cornubian Batholite and other places. Furthermore, we will give a further example of the diamond of the Land's End granite batholite, England, which is exceptionally rich in ^{13}C . Such strong isotope fractionation of carbon needs an explanation.

Sample Material and Raman Spectroscopy: Methodology

Sample Material

A concise description of the Land's End Granite, their geology, mineralogy, and geochemistry was given by Drivenes (2022) [9]. We use an uncovered microprobe sample von Kristian Drivenes for the Raman spectroscopic studies. Before our studies, the owner removed the carbon coating from the sample with diamond paste. The main minerals are cassiterite, tourmaline (dravite, uvite, and olenite), quartz, rutile, and apatite (all determined with Raman spectroscopy). According to Drivenes (2022) [9], tourmalines contain Sn in relatively high concentrations, up to 2.53%. The owner of the sample has significant problems with the new findings.

Microscopy and Raman Spectroscopy

We performed all microscopic and Raman spectroscopic studies with a petrographic polarization microscope (BX 43) with a rotating stage coupled with the EnSpectr Raman spectrometer R532 (Enhanced Spectrometry, Inc., Mountain View, CA, USA) in reflection and transmission. 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 spectral resolution ranging of 4 cm^{-1} . Generally, we used an objective lens with a magnification of 100x: the Olympus long-distance LMPLFLN100x objective (Olympus, Tokyo, Japan). 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 (for the studies on cassiterite) and a water-clear diamond crystal (Mining Academy Freiberg: 2453/37 from Brazil) for the Raman studies on diamond. The run-to-run repeatability of the line position (based on 20 measurements each) is $\pm 0.3 \text{ cm}^{-1}$ for Si ($520.4 \pm 0.3 \text{ cm}^{-1}$) and 0.4 cm^{-1} for diamond ($1332.7 \text{ cm}^{-1} \pm 0.4 \text{ cm}^{-1}$ over the range of 0–2000 cm^{-1}). The FWHM = $4.26 \pm 0.42 \text{ cm}^{-1}$. FWHM is the Full-Width at Half Maximum. We also routinely determined the zero point of the Raman spectrometer for the first-order band position of the ¹³C-rich diamond.

Results

Orthorhombic Cassiterite

Usually, cassiterite in the classic Variscan tin deposits grows in the tetragonal rutile form (Figure 1). So, the occurrence and the proof of orthorhombic cassiterite in the upper crust raises a lot of questions regarding the formation processes. Explanations are in Thomas 2023a [1,6-8]. A Raman spectrum of typical tetragonal cassiterite from the Tannenberg mine near Mühlleiten/ Vogtland, Germany is shown in Figure 1.

Five Raman lines are characteristic of the Raman spectrum of the tetragonal cassiterite (Figure 1): 777.1 cm^{-1} (medium), 634.1 cm^{-1} (very strong), 471.7 cm^{-1} (weak), 257.3 cm^{-1} (very weak), and 75 cm^{-1} (strong). The main line at 634.1 cm^{-1} has a FWHM of 12.6 cm^{-1} . According to Chukanov and Viggasina (2020) [10], using a 633 nm He-Ne laser, four lines are typical for tetragonal cassiterite: 842 , 776 , 635 , and 475 cm^{-1} . Bands at lower Raman shift values (between 100 and 200 cm^{-1}) are mostly not given (for example, in the RRUFF database [11]).

Figure 2 shows a typical Raman spectrum of the orthorhombic cassiterite from Land's End Granite, characterized by very strong bands in the low-frequency range.

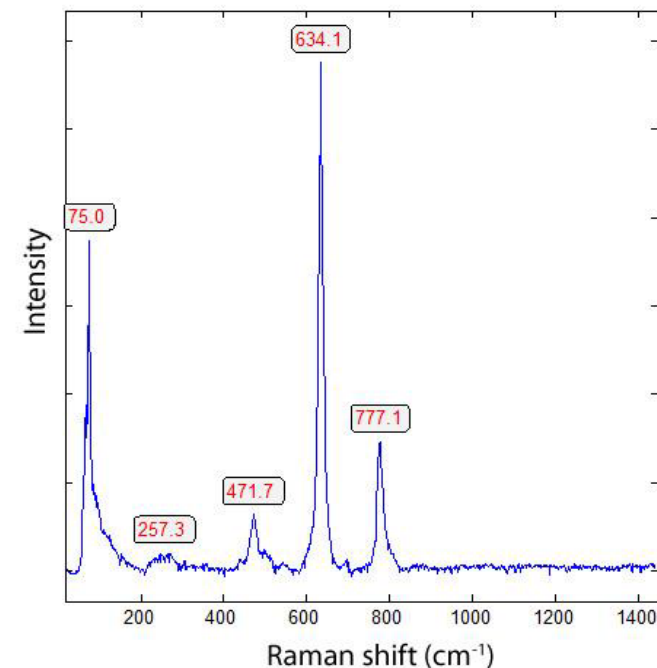


Figure 1: Typical Raman spectrum of a tetragonal cassiterite crystal (Tannenberg mine near Mühlleiten/Vogtland, Germany). A high tourmaline content characterizes this deposit.

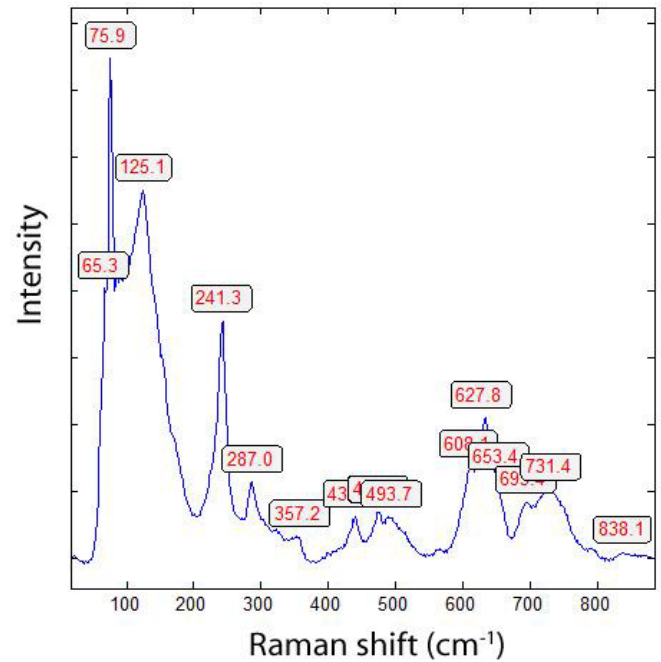


Figure 2: Raman spectrum of orthorhombic cassiterite from Land's End's Granite. The strong Raman bands at 75.9 and 125.1 are typical for the polymorph cassiterite Pbcn type (PbO_2 -type).

Table 1: Results of the Raman measurements on different cassiterite crystals (orthorhombic Pbcn type) from Land's End, Cornwall, SW England.

Band (cm^{-1})	Intensity (rel.)	Raman mode	n
76.6 ± 2.5	vs	A_g	22
119.5 ± 2.3	vs	B_{2g}	13
236.9 ± 5.3	s	A_g	25
439.0 ± 2.3	s - m	B_{2g}	15
$608.7 \pm 3.5^*$	m - w	B_{2g}	26
631.1 ± 1.8	vs - m	B_{1g}, B_{2g}	22
$835.9 \pm 2.9^{**}$	w - vw	B_{2g}	19

vs - very strong, s - strong, m - medium, w - weak, vw - very weak; n - measured crystals

Some Raman lines are not stable under the 532 nm laser (50 mW on the sample). The best data are obtainable with a low laser power of 4 mW on the sample at a long measuring time of 2000 or 4000 s.

* This Raman band is a shoulder of the 631.1 band and can be a remnant of the Pnma-I (cotunnite) cassiterite type.

** This Raman band is not present in the computed Raman modes (Balakrishnan et al., 2022) [5]. According to Hellwig et al. (2003) [2], that band is a high-pressure remnant of the Pnmm CaCl_2 type of cassiterite (14.8 GPa).

Typical for this Raman spectrum is the strong band at about 125.1 cm^{-1} and the medium bands at 627.8 cm^{-1} and 241.3 cm^{-1} , characteristic for the orthorhombic Pbcn polymorph of cassiterite [5]. Table 1 shows the mean and the standard deviation for measured Raman bands of the Pbcn cassiterite type.

The data in Table 1 are representative of orthorhombic cassiterite of the Pbcn polytype (PbO_2 -type). After Shieh et al. (2006) [3], the transition of polymorphs is sluggish. Therefore, we find that besides the Pbcn-type, remnants of the cotunnite and CaCl_2 -type. Generally, the tetragonal cassiterites ($P4_2/mnm$) containing orthorhombic cassiterite phases also include the orthorhombic cassiterite polytypes:

Pnnm (CaCl_2), Pbcn (PbO_2), Pbcn (ZrO_2), and Pnma-I. The Pbcn and Pbcn polytypes are metastable phases converted into more stable polymorphs under certain experimental conditions [5]. Nevertheless, we find these phases efficiently with the help of Raman spectroscopy. According to Girao (2018) [4], the essential phase transformations of tetragonal cassiterite happen at 14.8 GPa to the CaCl_2 -type (Pnnm) and at 30 GPa to the PbO_2 -type (Pbcn).

^{13}C -Rich Diamond

During the study of the sample, blue tourmaline crystals are striking. In the black cores of some blue tourmaline crystals, we found ^{13}C -rich diamonds. The Raman spectrum is shown in Figure 3. That ^{13}C -rich diamond was used for deleting the microprobe carbon film is improbable. The effort to produce ^{13}C -rich diamond for sample preparation is enormous and is therefore highly unlikely.

As a first approximation, according to Enkovich et al. (2016) [12], results in a ^{13}C concentration for the diamond of 28% and the graphite of 11.45%. That is an unusually high ^{13}C value. Because the sample is repeatedly cleaned with diamond paste, remnants of diamond are possible. Therefore, a comparison with a similar diamond paste was necessary. Figure 4 shows a Raman spectrum of such a diamond from the paste used. The graphite band is nearby, wholly missing.

The first-order diamond band of the DP diamond paste B is at $1331.9 \pm 0.22 \text{ cm}^{-1}$, and the FWHM is $5.4 \pm 0.2 \text{ cm}^{-1}$. Thomas et al. (2023a) [13] listed the Raman spectroscopic result for technical diamonds used for geological sample preparation. Such a substantial shift from 1332.7 cm^{-1} to 1318.8 cm^{-1} could not be observed. To be sure, we scrutinized the zero point of the Raman spectrometer steadily. Besides this, for the sample's extreme ^{13}C values, there are also ^{12}C -rich nano-diamonds (mostly in cassiterite) present. From 10 different

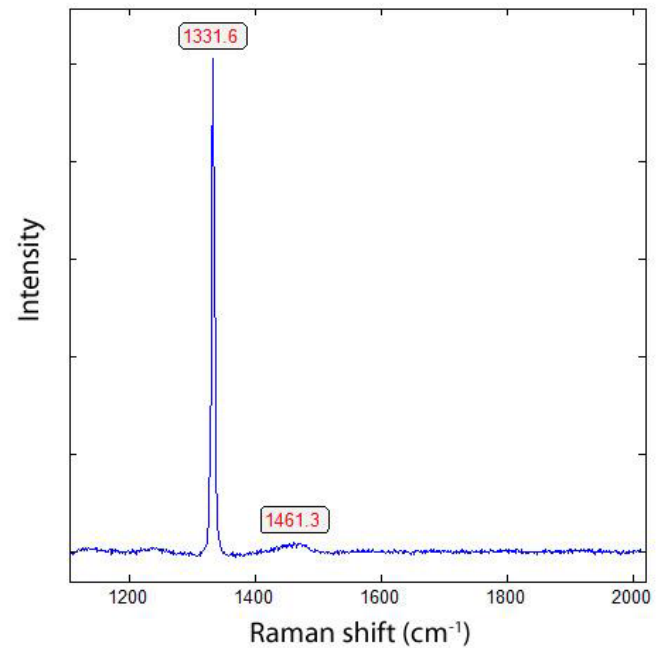


Figure 4: First order Raman spectrum of diamond of a DP diamond paste B from H. Struers, Chemiske Laboratorium, Copenhagen, Denmark. [2.2% ^{13}C].

crystals, a mean of $1328.0 \pm 2.8 \text{ cm}^{-1}$ and a FWHM of $33.3 \pm 12.9 \text{ cm}^{-1}$ result. According to the mean comparison (0.999) between the ^{12}C -rich diamond in cassiterite and the diamond used for polishing, a significant difference results. The same holds for the FWHM values.

Interpretation

Usually, in upper-crust tin deposits, neither orthorhombic cassiterites nor diamonds are present. Explanations for those unusual observations are in Thomas (2023a) [1,8,9] and Thomas et al. (2023) regarding the different contributions to these problems. The strong ^{13}C isotope enrichment in diamond and graphite is a further challenge. The simplest explanation is the interaction between the Earth's mantle and the crust via supercritical fluids. Such fluids are brought from mantle depth not only water, CO_2 , and CH_4 but also solid mineral phases such as foreign substances like diamonds, lonsdaleite, high-pressure SiO_2 , cassiterite polymorphs, etc. Because supercritical fluids are characterized by high diffusion rates and extremely low viscosity, isotope fractionation should also be extensive.

Table 2 summarizes the current results of the measured ^{13}C -rich diamonds and graphite. The ^{13}C -values of the measured diamonds and related graphite are uncommonly high and are nowhere near the "classic" diamonds and graphite data [20].

Discussion

Thomas and coauthors show that in upper crust mineralizations, especially in the Variscan tin deposits of the Erzgebirge, however, also at other places (Bornholm pegmatite, Land's End Sn deposit, and Reinbolt Hills pegmatite), there are indications of the interaction between deep mantle and upper crust [19] via supercritical fluids. A huge problem is that most natural diamonds have low ^{13}C concentrations. According to Cartigny (2005) [20], the abundance for ^{12}C is about 98.9% and for ^{13}C 1.1%. Therefore, the ratios are expressed

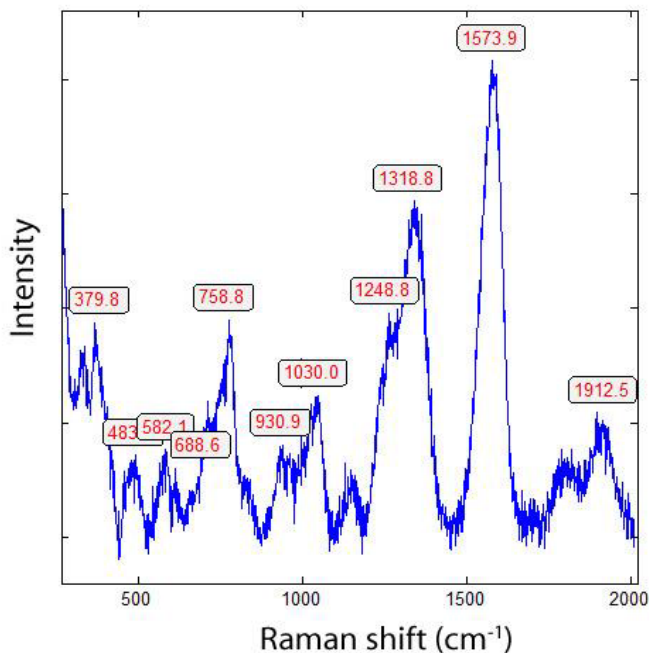


Figure 3: Raman spectrum of a ^{13}C -rich diamond crystal in blue tourmaline with the first-order diamond band at 1318.8 cm^{-1} . Also, the graphite G-band at 1573.9 cm^{-1} is relatively low. The FWHM are 48.8 and 60 cm^{-1} respectively.

Table 2: ¹³C-rich diamonds and ¹³C-rich graphite calculated according to Enkovich et al., 2016 [12] and Gutierrez et al., 2014 [14], from Raman measurements (means).

Diamond:

Origin	Raman band (cm ⁻¹)	¹³ C in diamond (%)	n	References
Land's End	1318.8	28.0	3	This work
Land's End	1328.0 ± 2.8	12.5	10	This work
Ehrenfriedersdorf	1286.7 ± 6.5	95.1	10	Thomas (2025) [8]
Bornholm	1311.1 ± 4.2	52.1	62	Thomas (2024c) [15]
Ehrenfriedersdorf, Beryl	1318.4 ± 6.1 1328.6 ± 5.6	36.0 10.9	19 14	Thomas et al. (2023b) [16]
Zinnwald	1313.9 ± 6.1	46.1	18	Thomas (2025) [8]
Reinbolt Hills	1312.1 ± 2.5	50.0	16	Thomas (2023c) [17]

Graphite:

Origin	Raman band (cm ⁻¹)	¹³ C in graphite (%)	n	References
Land's End	1573.9	11.45	3	This work
Land's End	-	-	-	This work
Bornholm	1562.6 ± 10.82	29.70	10	Thomas (2024c) [14]
Ehrenfriedersdorf	1518.1 ± 0.8	99.90	10	Thomas (2025) [8]
Ehrenfriedersdorf Beryl	1569.8 ± 5.2	18.1	13	Thomas et al. (2023b) [18]
Zinnwald	1521.5 ± 8.5	96.0	10	Thomas (2025) [19]
Reinbolt Hills	1575.3	9.2	1	Thomas (2023c) [17]

in parts per thousand relative to an internationally accepted standard. However, the finding of very high ¹³C values in natural diamond and graphite is a novum and needs an acceptable interpretation. Here, we interpret the formation of ¹³C-rich diamond and graphite as a result of a strong isotope fractionation of the species CO₂ and/or CH₄ in the supercritical fluid. Maybe the formation of this type of diamond and graphite happens directly at the upper crust during the transition from supercritical to the undercritical state. That is supported by the finding of SiC-whisker, diamond, and graphite in beryl [16,18]. The highest ¹³C concentration was found by the author in the cassiterite sample (Sn-70) from the Sauberg mine near Ehrenfriedersdorf [8], and high ¹³C values results also for diamond in cassiterite from Zinnwald (sample Sn-23). Using the data from Enkovich et al. (2016) [12], the results for ¹³C of the Sauberg-diamond is 99.9% and for the Zinnwald (sample Sn-23) 46.1%. More work is necessary to clear some open questions.

Conclusion

There are clear hints that some diamonds, together with SiC, grow at low pressure and moderate temperatures [18] via supercritical fluids. The transition from the supercritical to the under-critical state is a scientific challenge. The proof of the diamond formation at one-atmosphere pressure and relatively low temperatures (1025°C) by Gong et al. (2024) is a clear paradigm shift. Our results aim in the same direction.

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