

Research Paper

# Monocrystalline lonsdaleite in REE-Rich Fluorite from Sadisdorf and Zinnwald/E-Erzgebirge, Germany

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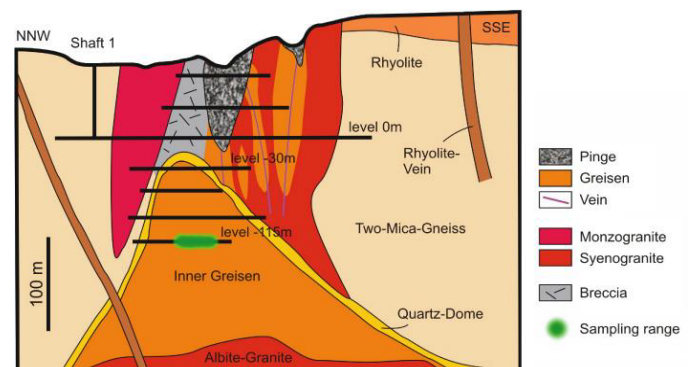
## Abstract

We present the results of our Raman studies on natural lonsdaleite crystals in fluorite of the two tin deposits Sadisdorf and Zinnwald in the E-Erzgebirge/Germany. The Raman spectra, especially from Zinnwald, can be deconvoluted into three Raman-active vibrational modes:  $E_{2g}$ ,  $A_{1g}$ , and  $E_{1g}$ . For the origin, transport via supercritical fluid or melting from the mantle region into the crust is necessary.

**Keywords:** Lonsdaleite, REE-rich fluorite, Raman spectroscopy, Sadisdorf and Zinnwald tin-tungsten deposits, Supercritical fluid

## Introduction

The Variscan Erzgebirge (German side) and Krušné hory (Czech side) contain many tin-tungsten deposits of vein and greisen type. Famous deposits are that from Zinnwald, Cinnovec, Krupka, Sadisdorf, Ehrenfriedersdorf, and Geyer. For the regional geology and description of single deposits, extensive literature is present [1-5] and references in these). From a repetition of that, we will abstain because our described observations are new and do not fit into the old genetic view, forcing us to adopt a new approach for the whole region. In the abandoned Sadisdorf Sn-W-(Cu) deposits, there are vein and greisen-type mineralizations (Figures 1a and 1b).



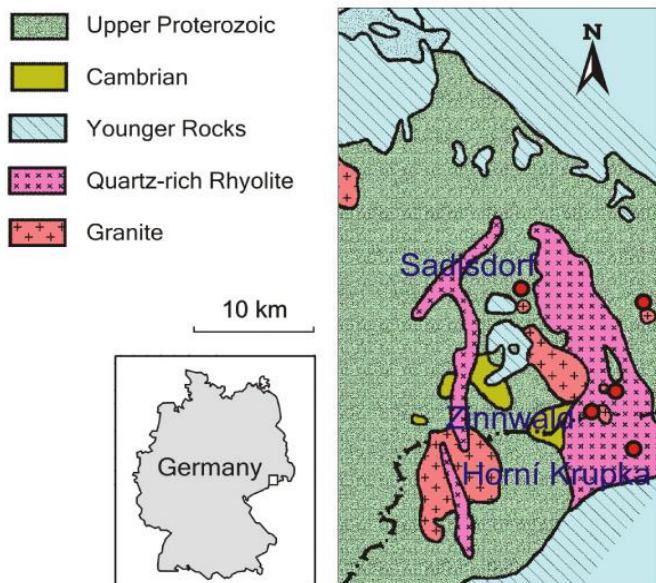
**Figure 1b:** Schematic cross-section through the Sadisdorf deposit with the approximate origin place of the studied sample. The green color marks the origin of the Sadisdorf sample.

The frequently present breccia pipes here are analogous to the famous Schneckenstein breccia in the W-Erzgebirge, which is very characteristic of this mineralization type [6]. During the study of thin sections from the Sadisdorf deposit, peculiar violet fluorite aggregates attract attention. These aggregates contain many black, sometimes bent needles, as well as also spherical to elliptical carbon solids. A similarity to the other described new findings of spheric high-pressure minerals is very obvious (see, for example, Thomas et al., 2023) [7]. This publication also contains a schematic geological map of the Erzgebirge-Vogland Zone with the Variscan granites, etc.

## Sample Material

### Sadisdorf

The rock material is from the endocontact of the tin-tungsten-copper deposit Sadisdorf in eastern Erzgebirge/Germany [1,8]. The sample thin section (SD-H01B) is from a fine-granular white quartz-topaz rock with violet fluorite, taken during the exploration



**Figure 1a:** Location and simplified geological map of the Sadisdorf and Zinnwald deposit/ E-Erzgebirge.

campaign Sc-ore 2012/2013 - the violet fluorite is, according to Raman spectroscopy, very REE-rich. Besides the primary mineral quartz and rarer topaz, there are many small, mostly opaque mineral grains of wolframite, cassiterite, columbite, and others. The large fluorite aggregates are not isomorphic but more in tube or irregular form. Smaller fluorite crystals are isometrically. These large tubular fluorite aggregates contain many black and transparent needles, grains, and curved crystals (Figure 2) and are generally fluid inclusion-free. If present, then they are secondary late formations.

The curved black crystal (Figure 2) contains many nano-diamonds. The straight black needles are prevailing graphite-like material. Graphite is very often present in the Variscan tin mineralization, and it is also often present in cassiterite. Graphite has mostly not been paid attention to in the past.

### Zinnwald

For comparison, we used fluorite grains included in tabular zinnwaldite crystals from the Zinnwald deposit (deep Bünau gallery) in the E-Erzgebirge/Germany, which is not far from the Sadisdorf deposit (taken by the first author in 1984). This violet fluorite sample contains numerous sharp black disk-like bodies of lonsdaleite-diamond-graphite (Figure 3). Some of these form half-moon-like bodies (Figure 4) where the sharp edges lie parallel to the crystallographic{100} planes.

It follows from Figures 3 and 4 that the black bodies obviously form hemispheres on the fluorite surfaces. The general impression is that this fluorite is an early formation and has a more plastic behavior at the formation time. That spoke for a high-temperature and high-pressure formation from a fluorine-rich melt containing such C-aggregates.

### Methodology: Microscopy and Raman Spectroscopy

For the study of the lonsdaleite-diamond-graphite-bearing samples and their paragenetic main minerals, we use the Zeiss JENALAB pol as well as the Raman spectrometer EnSpectr R532 combined with the Olympus BX43 microscope both for transmitted and reflected light



Figure 2: Curved graphite aggregate with nano-diamonds in REE-rich fluorite. All black points are graphite-like stuff and contain nano-diamonds.

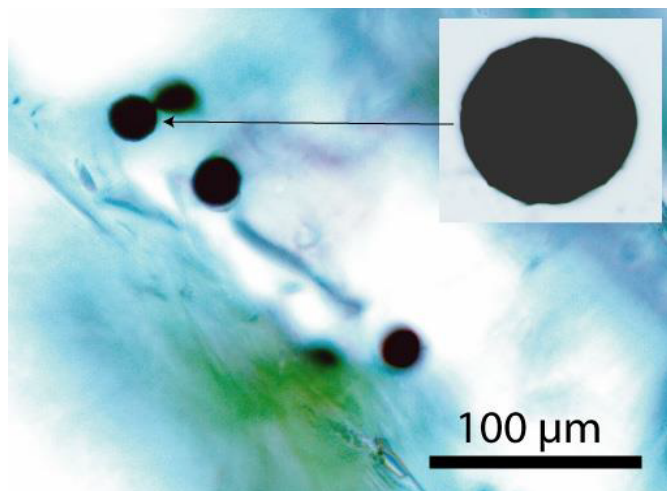


Figure 3: Small disk-like bodies of lonsdaleite in fluorite from Zinnwald/E-Erzgebirge (top view).

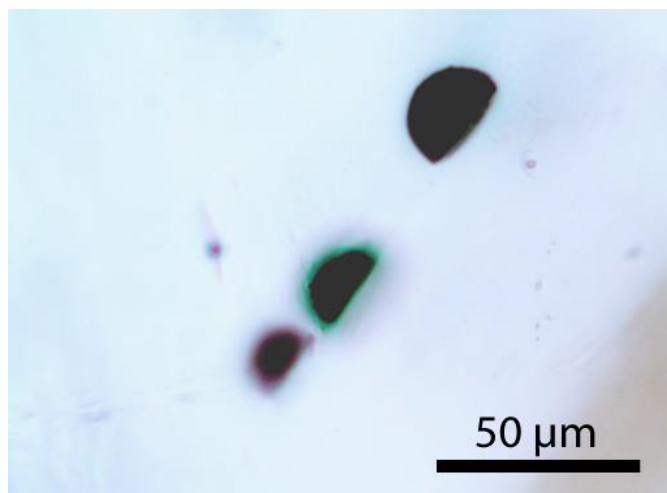


Figure 4: Side view of such bodies, as shown in Figure 3, arranged to the growth zones of the fluorite host.

and equipped with a rotating stage. Note here that the incident laser light is always polarized – in our case, N – S (see Tuschel, 2012) [9]. Generally, we used an Olympus long-distance LMPLFL100x objective lens. For the identification of different minerals, we used the RRUFF and the Hurai et al. Raman mineral databases [10,11]. As references, we applied a water-clear diamond crystal from Brazil ( $1331.63 \pm 0.60 \text{ cm}^{-1}$ ) and a semiconductor-grade silicon single-crystal ( $520.70 \pm 0.15 \text{ cm}^{-1}$ ). For this study, we used laser energies from 0.9 to 50 mW on the sample. Because the minerals lonsdaleite, diamond, and nano-diamond contain black graphite particles and are metastable in the new upper crust surrounding, heating by the laser energy can partially destroy these minerals in the extreme case or shift the characteristic peak position of Raman bands [12,13] to lower values.

## Results

### Sadisdorf

The sizeable bent carbon crystal (Figure 2) contains many small nano-diamonds. The diamond main band lies at  $1331.8 \pm \text{cm}^{-1}$  (11

different crystals). The FWHM (Full Width at Half Maximum) is  $83.1 \pm 13.9 \text{ cm}^{-1}$ . Needle-formed diamonds, generally black, give the prominent diamond peak a value of  $1333.6 \pm 5 \text{ cm}^{-1}$  (5 needles). In violet REE-rich fluorite of the rock, there are a lot of black needles and spheric or elliptic crystals. Some needles are twisted or bent. Most of them contain graphite or carbonaceous material (see Beyssac et al., 2002) as well as nano-diamonds. There are also whisker-like transparent and some thick, short, transparent prismatic crystals. As a total surprise, the rare whiskers and these short prismatic crystals are, according to Raman spectroscopy, lonsdaleite (Lon). Such crystals are present exclusively only in fluorite. Figure 5 shows two such prismatic lonsdaleite crystals, and Figure 6 depicts a lonsdaleite whisker. The lonsdaleite crystal (Lon) in the center of Figure 5 is  $14 \times 2 \text{ }\mu\text{m}$  large.

By the Raman spectrum (band at  $1325 \text{ cm}^{-1}$ ), these transparent crystals are monocrystalline lonsdaleite (see Shumilova et al., 2011) [14] and, according to Bhargava et al. (1995) [15], hexagonal diamond. By the form (long-prismatic), the hexagonal diamond has a high probability of being lonsdaleite (Figure 6).

With Raman spectroscopy, we obtained the following data for the five lonsdaleite crystals:  $1318 \pm 3.8 \text{ cm}^{-1}$ . Opposite to fluorite, the black points (mainly carbon) in quartz are ore minerals like wolframite, columbite, and different sulfides. Obviously, bulk rocks (quartz and topaz) are the result of varying evolutions. Fluorite looks like remnants of a high-temperature melt. According to Seiranian et al. (1974), the eutectic points in the  $\text{CaF}_2$ - $\text{YF}_3$  system occur at 60 and 91 % (mol/mol) and 1120 and 1106 °C. Similar systems ( $\text{CaF}_2$ - $\text{BaF}_2$ ) have analog high temperatures (Figure 8) [16].

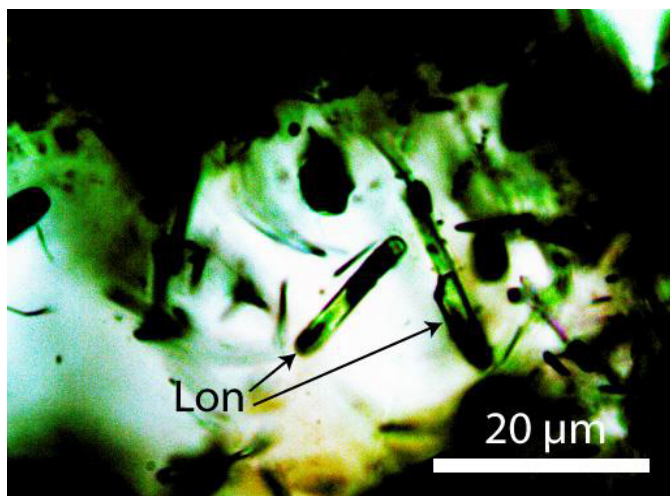


Figure 5: Lonsdaleite (Lon) crystals in REE-rich fluorite.

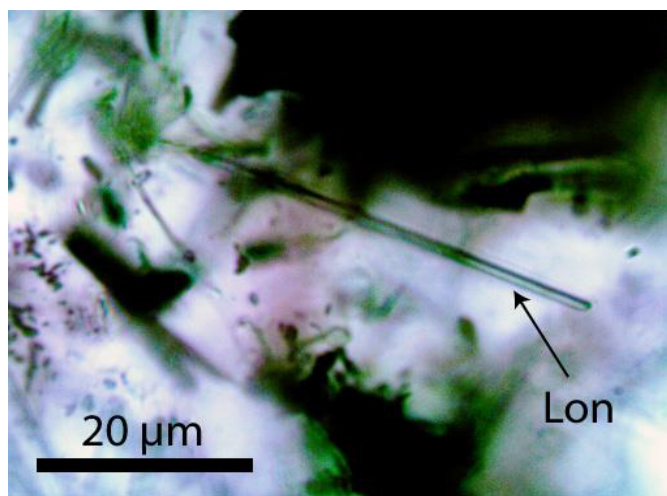


Figure 7: Lonsdaleite (Lon) whisker in fluorite. The whisker has a length of  $45 \text{ }\mu\text{m}$  and a thick of  $0.9 \text{ }\mu\text{m}$ .

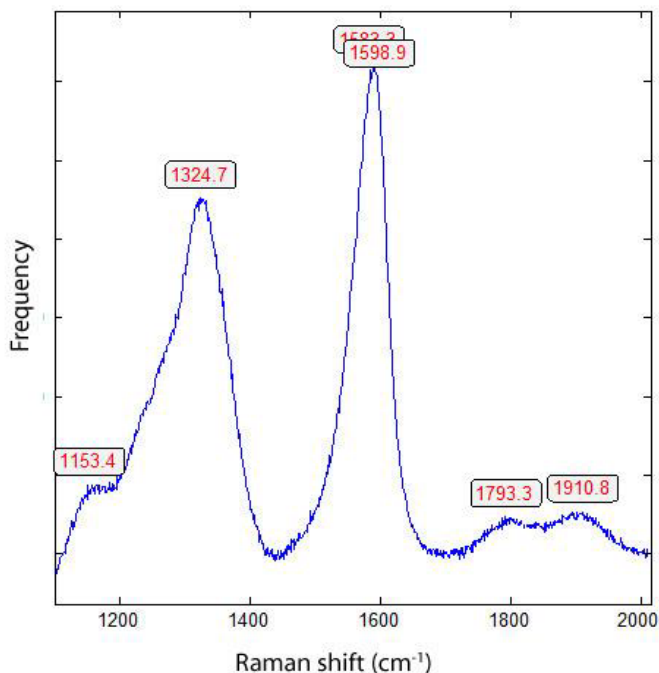


Figure 6: Raman spectrum of both lonsdaleite crystals in Figure 5. The broad Raman band at about  $1325 \text{ cm}^{-1}$  results from a small component of diamond (a two-phase crystal of lonsdaleite-diamond [14]).

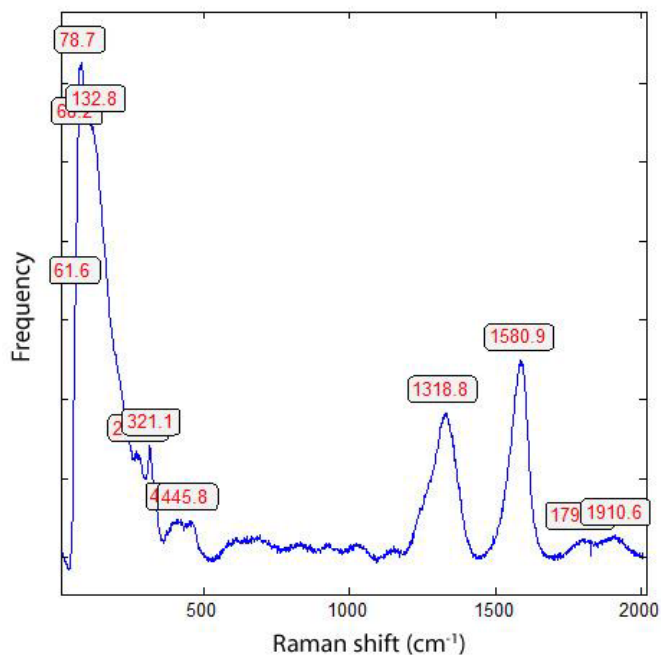


Figure 8: Raman spectrum of the whisker-like (Figure 7) monophase lonsdaleite crystal (characteristic band at  $1319 \text{ cm}^{-1}$ ). The bands at  $321 \text{ cm}^{-1}$  and lower values come from the matrix fluorite.

## Zinnwald

In the violet fluorite from Zinnwald, there are a lot of black bodies (Figures 3 and 4). Some are large enough to perform systematic Raman studies. In the beginning, we used 20 mW on the sample. The corresponding Raman spectrum (Figure 9) resembles the monophase lonsdaleite (Figure 3 in Shumilova et al., 2011) [14]. To prevent heating of the lonsdaleite sample by always presenting black carbon, we used low laser energy on the sample (0.9 mW of the 532 nm laser). The authors Goryainov et al., 2018 [17] used the excitation of a UV laser with a wavelength of 325 nm and low intensity of 1 mW on the sample.

## Interpretation

The synthesis of hexagonal lonsdaleite succeeded in 1966 by Bundy and Kasper (1967) – [18] at 1000°C and 130 kbar. In nature, lonsdaleite was found first (1967) in the Canyon Diablo meteorite by Frondel and Marvin (cited in Shumilova et al., 2011) [14] and in the Kumdykol diamond deposit (North Kazakhstan) by Shumilova et al., 2011) [14].

The Raman bands at 1318 to 1324  $\text{cm}^{-1}$  are evident and characteristic of the hexagonal diamond phase in the Sadisdorf material (see also Misra et al., 2006) [19]. Lonsdaleite in the fluorite shows a certain metastability due to laser irradiation, perceptible by the increase of the G bands at about 1580 to 1600  $\text{cm}^{-1}$  (Figures 6 and 8) and the black coloring of the nearly colorless lonsdaleite crystals during the Raman measuring. The metastability of high-pressure minerals coming from mantle deeps and staying at high temperatures for a long time in low-pressure regions (upper crust) is very characteristically [13,20-22]. One exception is moissanite here, which is very stable. Because lonsdaleite is a high-pressure and high-temperature mineral, its formation in the deposit level ( $\leq 3\text{km}$ ; see Thomas and Klemm, 1997) [23] is usually not possible. Therefore, the formation of the lonsdaleite-bearing fluorite occurred at significantly greater depths and came from mantle depths via supercritical fluids or melts into the crustal level. However, the formation of lonsdaleite whisker is, at the moment, a mystery.

## Discussion

According to Németh et al., 2014 [24] lonsdaleite does not exist as a discrete material. That is in contradiction to our observations. Figures 5 and 7 clearly show prismatic crystals with a Raman spectrum corresponding, according to Shumilova et al. (2011) [14], to natural lonsdaleite. Of course, the formation of lonsdaleite is unclear. However, this material is existent as prismatic crystals. The lonsdaleite whisker (Figure 7) shows the same Raman spectrum. Although it is well-known that cubic crystals can also form whiskers (for example, GaP-whiskers grown from a non-stoichiometric Sn-melt produced by the first author in 1970 (unpublished results). Shiell et al. (2016) [25] report the synthesis of almost pure nanocrystalline lonsdaleite in a diamond anvil cell at 100 GPa and 400°C from glassy carbon. That means lonsdaleite is, in contrast to Németh et al. (2014) [24], a discrete material. Our findings of macroscopic lonsdaleite in fluorite from Sadisdorf underline this statement. That means at least that at the formation of lonsdaleite, an enormous pressure has worked. Conceivable is the transport from mantle regions via supercritical fluids or melts or a tremendous pressure impact during the breccia formation. The lonsdaleite crystals in violet fluorite from Zinnwald/E-Erzgebirge are more frequent and more stable than the lonsdaleite from Sadisdorf. Therefore, we could perform more Raman measurements under different conditions. At the high intensity of the laser (about 20 mW on the sample), a very strong graphite line at 1581  $\text{cm}^{-1}$

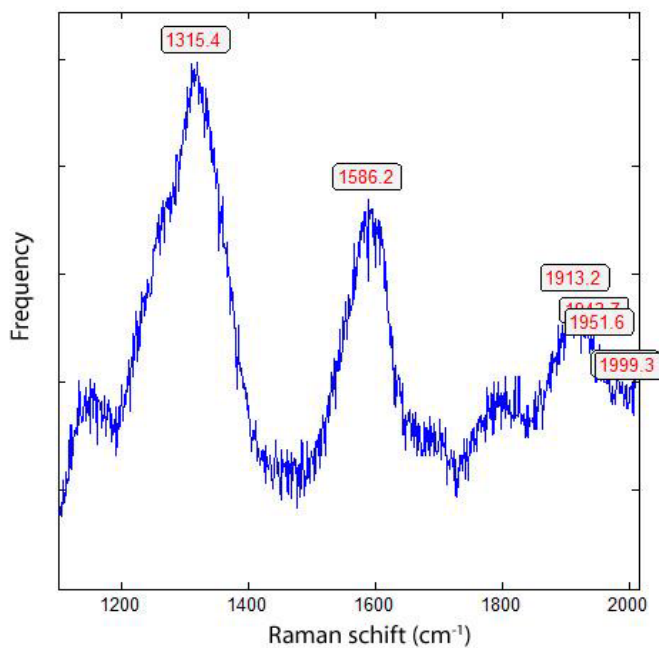


Figure 9: Raman spectrum of lonsdaleite in fluorite from Zinnwald/E-Erzgebirge taken at 20 mW on the sample.

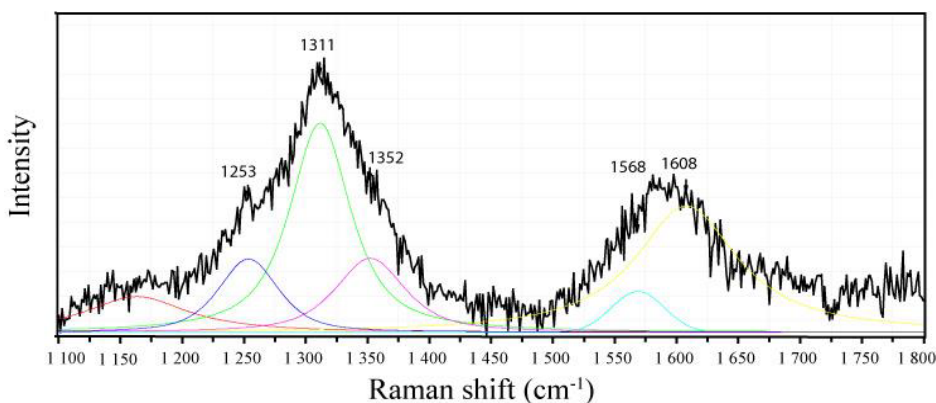


Figure 10: Raman spectrum of a lonsdaleite crystal (diameter ~ 24  $\mu\text{m}$ , thickness ~14  $\mu\text{m}$ ) in fluorite from Zinnwald/E-Erzgebirge, taken with 0.9 mW on the sample and a measuring time of 1000 s.

appears. The clear differentiation between diamond and lonsdaleite is uncertain (line at  $1328\text{ cm}^{-1}$ ). To avoid heating the lonsdaleite sample using the laser, we used a low-intensity laser excitation (0.9 mW on the sample) in analogy to Goryainov et al., 2018) [17], which used a 325 nm UV laser with 1 mW on the sample. Figure 10 shows the results of our measurements. We see clearly three Gaussian components at ( $1251.3 \pm 9.4\text{ cm}^{-1}$ ), ( $1310.6 \pm 3.9$ ), and ( $1350.4 \pm 9.9\text{ cm}^{-1}$ ), with the FWHMs of 57.4, 58.8, and  $67.0\text{ cm}^{-1}$ , respectively – 10 measurements each. These three experimental lines, according to Goryainov et al., 2018 [17], can be assigned to the theoretical Raman lines  $E_{2g}$ ,  $A_{1g}$ , and  $E_{1g}$  obtained through ab initio calculations [17]. Independent of the interpretation of our described carbon phases as lonsdaleite or hexagonal diamonds as inclusions in upper crustal minerals, transport via supercritical phases from the mantle region to the crust is necessary. Our here-presented results increase the number of high-pressure and high-temperature minerals (diamond, nano-diamonds, moissanite, stishovite, coesite, kumdykolite, beryl-II, cristobalite-II, cristobalite X-I, and  $\text{CaCl}_2$ -type cassiterite) in the Variscan granites and tin mineralizations in the crustal Erzgebirge region [26].

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