

CO₂ nanoinclusions in diamonds

Oded Navon¹, Yael Kempe¹, Sergei Remennik¹, Yitshak Avigad¹,
Janina Czas¹ and Yaakov Weiss¹

¹ The Hebrew University of Jerusalem, Israel, yakov.weiss@mail.huji.ac.il

Introduction

Thirty years after finding solid CO₂ inclusions in a diamond of unknown origin (Schrauder and Navon, 1993), we still face serious gaps in our understanding of the source and nature of such inclusions. The best-known sources of CO₂-bearing diamonds are the George Creek and Sloan kimberlites in Colorado, USA (Chinn, 1995), but the characteristic IR absorption was also identified in diamonds from Jagersfontein (Chinn, 1995) and Voorspoed in South Africa (this study), and in other undocumented localities (Chinn, 1995). They are also encountered in the general diamond production (Barannik et al., 2021).

The diamonds

We report a new FTIR and TEM study of a set of diamonds from George Creek and a single diamond from Voorspoed. The diamonds were selected from the collection of Malcolm A. McCallum based on their color and most are zoned, with brown yellow and clear parts. IR spectra reveal the presence of CO₂ in the diamonds, but no correlation was found between color and CO₂ absorption (i.e. CO₂ was detected in clear zones as well; see also Barannik et al., 2021). The common absorption bands due to nitrogen in A-, B- or C-centers are only seen in some of the colorless zones. In the CO₂-bearing parts, a complex and variable spectrum with multiple bands occupies the 800-1400 cm⁻¹ spectral range. A few diamonds also show the presence of a weak N3HV-center peak at 3107 cm⁻¹.

The inclusions

Four diamonds with clear CO₂ IR bands, one from Voorspoed and three from George Creek, were selected and foils were cut by FIB at their CO₂-rich zones. Octahedral, nanometric inclusions, 2-20 nm in size (median = 4 nm) were found in the foil of diamond ON-GCR-28602 (Fig. 1a,b). The number density of inclusions reached ~40000/μm³ (Fig. 1b and 6 other images), corresponding to ~500 ppm (by weight) of carbon dioxide in the diamond. In the other two foils, most inclusions were of similar size (~2-5 nm), but no larger ones were detected.

TEM-EDS of ON-GCR-28602 reveals only carbon, oxygen, nitrogen and sulfur. In one large inclusion oxygen and nitrogen are distributed in the bulk, while sulfur is concentrated (and oxygen is lower) near the apexes of the inclusion (Fig. 1c-e). Analysis of 6 nanoinclusions in this foil yielded a weighted average content of 77% oxygen, 17% nitrogen and 6% sulfur. Oxygen and sulfur were also detected in the other two diamonds. In one, no accurate analysis was possible. In the other, an average of 7 inclusions yielded 80% oxygen and 20% sulfur, with nitrogen below detection. Shiryayev et al. (2023) also reported oxygen-bearing nanoinclusions, but no sulfur or nitrogen.

In the Voorspoed diamond, ON-VRS-664, we found many N₂-rich nanoinclusions of similar size, but no oxygen-rich ones. So the CO₂ must reside in other sites. This diamond also carries microinclusions (800-1000 nm in size) that contain gaspeite (Ni,Fe)CO₃ together with a void. As both carbonate and CO₂ were detected by IR spectroscopy, we propose that the CO₂ resided in the voids and escaped during the milling of the foil to ~120 nm.

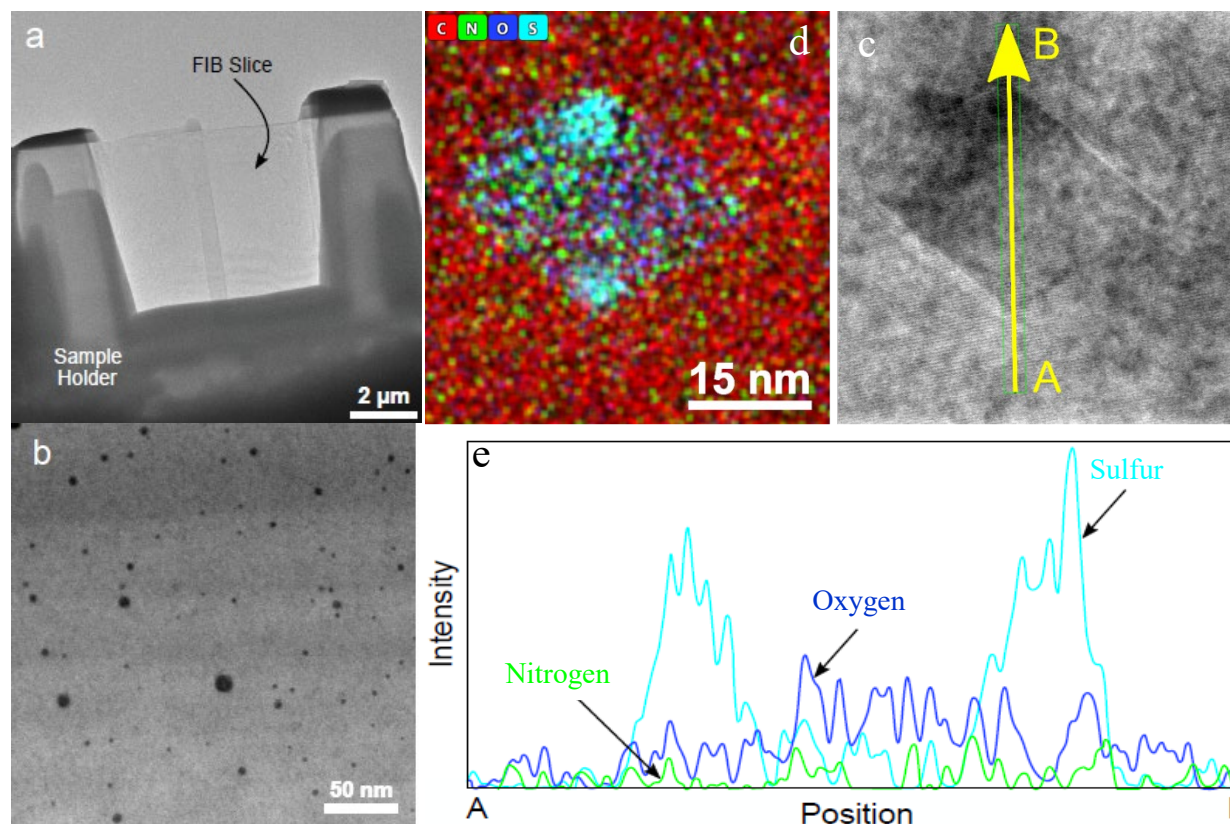


Figure 1: The lamella cut from diamond ON-GCR-28602. a. The foil (BF STEM). b. Most inclusions are scattered randomly (BF STEM). c and d. A closeup of an inclusion and an EDS map of its composition. e. X-ray intensity profile across the inclusion in c. (yellow arrow in c) showing the concentration of sulfur in the apexes of the inclusion.

Infrared absorption by CO₂

IR transmission spectra on polished plates cut from the George Creek diamonds reveal bands centered at ~ 640 - 660 , 2345 - 2425 , 3630 and 3750 cm^{-1} , corresponding to the ν_2 , ν_3 , $\nu_3+2\nu_2$, and $\nu_3+\nu_1$ vibrations of solid CO₂-I phase under pressure (Schrauder and Navon, 1993; Chinn et al., 1995; Barannik et al., 2021). The band positions vary between diamonds and, in many cases, also between different zones in a single plate Fig. 2a,b). The intensity of some bands in single diamonds correlate positively, but others anticorrelate or show no correlation (cf. the bands at 2370 and 2420 cm^{-1} in Barannik et al., 2021).

Pressure alone cannot explain the variety of the observed bands or the multiple peaks at 2300 - 2450 cm^{-1} in individual diamonds (Chinn, 1995, Barannik et al., 2021). TEM-EDS suggest a role for sulfur compounds. SO₂ may explain some of the bands at 900 - 1350 cm^{-1} , but it is rich in oxygen and we observe only little oxygen together with the sulfur (Fig. 1e). H₂S absorbs at ~ 1260 cm^{-1} and may be present in the inclusions, but cannot explain the multiple peaks at ~ 2350 - 2420 cm^{-1} . The correlation we observe between the peaks at ~ 2885 cm^{-1} (typical of C-H bonds) and the CO₂ peaks (Fig. 2c) suggests the presence of organic matter in the inclusions. Hence, a possible explanation is that in such small inclusions, the absorption by molecules on the interface between the CO₂ crystal, the sulfur phase, organic matter, or the inclusion walls is important and leads to a shift of the CO₂ bands (e.g., Kaufman et al, 2011). The excellent correlation between the intensities of the carbonate and the CO₂ bands (Fig. 2d) strongly suggests that both phases reside together in the microinclusions. Thus the nature of the CO₂ in ON-VRS-664 is different than that in the George Creek diamonds. The presence of the CO₂ as a large crystal gives more confidence in using the position of the 2390 cm^{-1} band for pressure estimation of ~ 8 GPa at room temperature (based on the blueshift of that band). Indeed, the result agrees with other pressure indicators in this diamond.

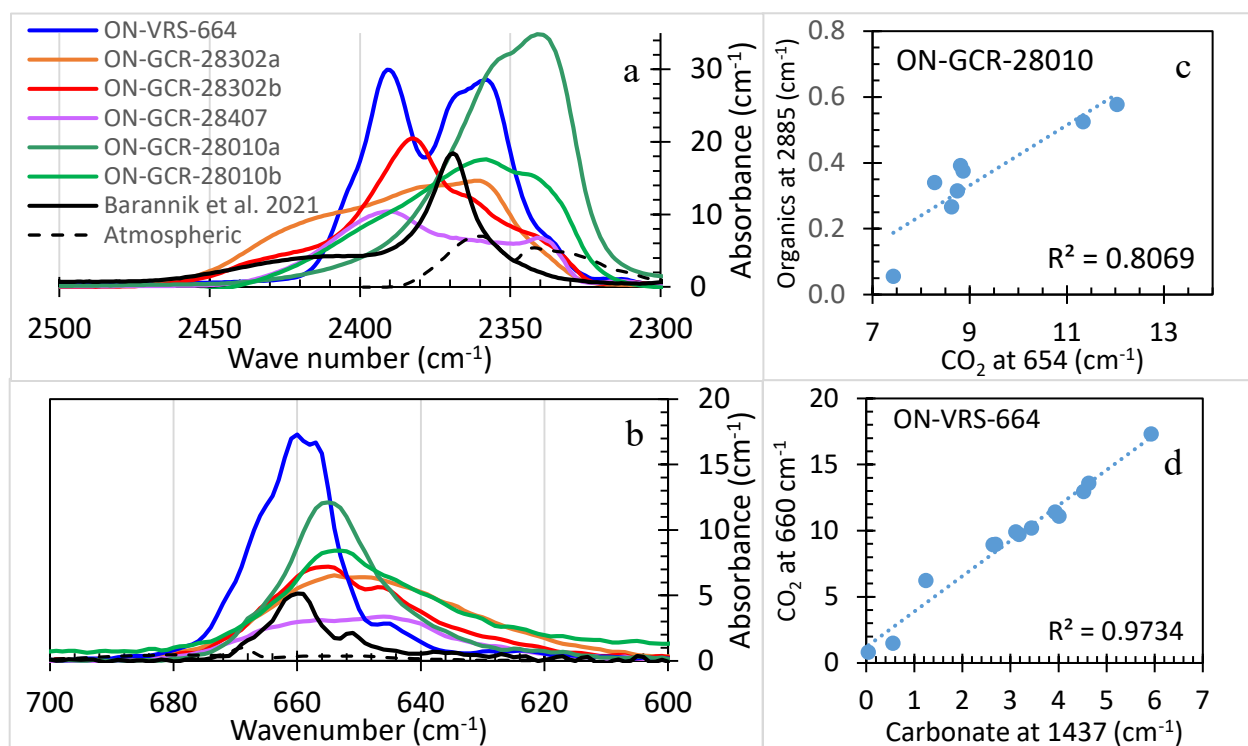


Figure 2: IR absorption of the ν_3 (a) and ν_2 (b) of $\text{CO}_2\text{-I}$ in a few diamonds. Many diamonds show multiple bands at $\sim 2350\text{ cm}^{-1}$. (c) The correlation of the intensity (absorbance per cm diamond thickness) of the band at $\sim 2885\text{ cm}^{-1}$ with the CO_2 peak at 654 cm^{-1} in different areas of a plate of diamond ON-GCR-28010 suggests the presence of organic matter in the nano-inclusions. (d) The excellent correlation between the intensity of carbonate at 1437 cm^{-1} and CO_2 at 660 cm^{-1} in various zones of diamond ON-VRS-664 suggests a close relation of the two phases (gaspeite and CO_2) that, most probably, reside together in the microinclusions.

Conclusions

The Voorspoed diamond contains CO_2 in microinclusions. In the George Creek diamonds, it resides in nano-inclusions, similar to those observed by Shiryayev et al. (2023), but together with sulfur. The nano-inclusions were formed, most probably, by exsolution of oxygen dissolved in the diamond next to trapped sulfur. The source of the sulfur, with no associated metal, is difficult to explain.

References

- Barannik EP, Shiryayev AA and Hainschwang T (2021) Shift of $\text{CO}_2\text{-I}$ absorption bands in diamond: a pressure or compositional effect? *Diamond and Related Materials*, 113, 108280
- Chinn IL (1995) A study of unusual diamonds from the George Creek K1 kimberlite dyke, Colorado. *PhD thesis*, The University of Capetown.
- Hanson RC and Jones LH (1984) Infrared and Raman studies of pressure effects on the vibrational modes of solid CO_2 . *Journals of Chemical Physics*, 75:1102-1112.
- Kauffman KL, Culp JT Goodman A and Matranga C (2011) FT-IR study of CO_2 adsorption in a dynamic Copper(II)-Benzoate-Pyrazine host. *Journal of Physical Chemistry*, 115:1857-1866.
- Schrauder M and Navon O (1993) Solid carbon dioxide in a natural diamond. *Nature*, 365:42-44.
- Shiryayev AA, Chesnokov Y, Vasiliev AL and Hainschwang T (2023) Exsolution of oxygen impurity from diamond lattice and formation of pressurized $\text{CO}_2\text{-I}$ precipitates. *Carbon Trends*, 11:100270.