Freitalite, C\textsubscript{14}H\textsubscript{10}, a new aromatic hydrocarbon mineral from Freital, Saxony, Germany

Thomas Witzke\textsuperscript{1}, Martin Schreyer\textsuperscript{1}, Benjamin Brandes\textsuperscript{2}, René Csuk\textsuperscript{2}, and Herbert Pöllmann\textsuperscript{3}

\textsuperscript{1}Malvern Panalytical, Application Laboratory, Lelyweg 1, 7602EA Almelo, the Netherlands
\textsuperscript{2}Organic Chemistry, Martin-Luther-Universität Halle-Wittenberg, Kurt-Mothes-Str. 2, 06120 Halle (Saale), Germany
\textsuperscript{3}Institute of Geosciences and Geography, Department Mineralogy/Geochemistry, Martin-Luther-Universität Halle-Wittenberg, Von Seckendorff-Platz 3, 06110 Halle (Saale), Germany

Correspondence: Thomas Witzke (thomas.witzke@panalytical.com)

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Abstract. The new mineral species freitalite, C\textsubscript{14}H\textsubscript{10}, corresponding to the aromatic hydrocarbon anthracene, has been discovered on the mine dump of the Königin Carola shaft (also named Paul Berndt Mine), Freital, near Dresden, Saxony, Germany. The mineral forms thin blades or flakes of irregular shape up to a few millimetres in size and shows an intense violet or whitish-violet to white colour. Freitalite is a product of pyrolysis of coal at low oxygen fugacity and was formed by sublimation from a gas phase. The mineral is associated with sulfur and hoelite. Elemental analysis gave (in wt. %, average of three analyses) C 94.07, H 5.571 and total 99.641. The empirical formula is C\textsubscript{14.00}H\textsubscript{9.88} (calculated for C = 14). The identity with anthracene was confirmed by infrared and Raman spectroscopy, high-performance liquid chromatography, gas chromatography with mass spectrometry, \textsuperscript{1}H and \textsuperscript{13}C NMR spectrometry, and X-ray powder diffraction. Freitalite is monoclinic, \textit{P}2\textsubscript{1}/\textit{a}, with lattice parameters \textit{a} = 8.5572(9), \textit{b} = 6.0220(5), \textit{c} = 11.173(1) A, \textit{β} = 124.174(1)° and \textit{V} = 476.34(3)Å\textsuperscript{3} refined from powder data. The calculated density of 1.242 g cm\textsuperscript{-3} (for \textit{Z} = 2) is very close to the measured density of 1.240 g cm\textsuperscript{-3}. Freitalite was accepted as a new mineral by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (IMA 2019-116).

1 Introduction

The mineral was found in 1987 and 1988 on the mine dump of the coal mine Königin Carola shaft (also named Paul Berndt Mine), Freital, Döhlen basin, near Dresden, Saxony, Germany, by one of the authors (Thomas Witzke). Further studies showed that it corresponds to the organic compound anthracene, C\textsubscript{14}H\textsubscript{10} (Witzke, 1990).

The aromatic hydrocarbon compound C\textsubscript{14}H\textsubscript{10} is known with two isomers: anthracene and phenanthrene. The latter was described as the mineral ravatite (IMA 1992-019) from a burning coal seam near Ravat, Tajikistan (Nasdala and Pekov, 1993). The submission of anthracene as a new mineral was prevented for decades because of its formation on a burning mine dump.

Since the beginning of the 1990s, phases formed on burning mine dumps were not accepted as minerals anymore (Ernest H. Nickel, personal communication, 1991). The formal decision of the International Mineralogical Association (IMA) Commission on New Minerals and Mineral Names that “as a general rule, products of combustion are not to be considered minerals in the future” was published by Nickel and Grice (1998). One of the reasons given was that the possibility of human intervention in originating a fire could not be excluded.

According to the new guideline of the Commission on New Minerals, Nomenclature and Classification (CNMNC) of the IMA (Parafiniuk and Hatert, 2020), phases forming on burning coal dumps with no human agency initiating the fire and no anthropogenic material deposited there should be treated as minerals. The mine dump of the Königin Carola shaft meets these criteria; there is no indication of human activities in initiating the fire or anthropogenic material de-
The type locality of freitalite is the mine dump of the Königin Carola shaft, Freital, near Dresden, Saxony, Germany (51.00277° N, 13.63827° E). The coal mine was active from 1872 to 1959. In 1948, the mine was renamed to Paul Berndt Mine, but the original name, usually in the short form Carola shaft, stayed very popular. Around 1960 the mine dump caught fire by the well-known process of spontaneous self-ignition. Self-heating and spontaneous combustion processes of coal and the influence of parameters like the iron sulfide content, coal lithology, and water and oxygen supply are described in numerous papers, e.g. Nelson and Chen (2007), Onifade and Genc (2018), Sýkorová et al. (2018), Stracher et al. (2010, 2015), and references therein. As a result of the combustion processes, a complex suite of gases like CO₂, SO₂, SO₃, NH₃, HCl, H₂S, H₂Se, different hydrocarbons and several other compounds can be emitted and lead to the formation of minerals by condensation, sublimation, chemical reaction of gases, leaching of rocks by acidic solutions and metasomatic reactions (Witzke et al., 2015; Sýkorová et al., 2018). The mine dump of the Königin Carola shaft consists of natural rocks surrounding the coal (shale, sandstone, conglomerate) and residual coal. The coal is generally rich in sulfidic sulfur, which promotes the spontaneous self-ignition. The sulfur content in the common coal was in the range of 2%–5% but could reach in some lithotypes up to 30% (27% sulfidic as pyrite). Very pyrite-rich coal shows strong oxidation effects already after a few days exposure to air (Reichel, 1984). The mine dump was renovated and recultivated in 2014 and the fire is extinguished.

Freitalite is associated with sulfur and rarely with hoelite (anthraquinone, C₁₄H₁₀O₂). The crystals are usually grown on sulfur and sometimes overgrown by sulfur. The minerals formed as a result of the combustion processes on the mine dump were described by Witzke (1990). The other C₁₄H₁₀O₂ isomer ravatite (phenanthrene) was found very rarely on the mine dump but not directly associated with freitalite (Witzke, 1995). Freitalite is a product of pyrolysis of the coal at low oxygen fugacity and was formed by sublimation from a gas phase. The mineral was found in fumaroles 5 to 40 cm below the surface in a temperature range of 20–70 °C. Some of the data obtained for freitalite were already published (Witzke, 1990; Thalheim et al., 1991; Nasdala et al., 1993). The formation of aromatic hydrocarbons as pyrolysis products and deposition at lower temperatures near the surface of burning dumps, including anthracene, is described by Akulov and Akulova (2020).

The mineral was also identified on a sample labelled “kratochvilite” from a burning coal mine dump at Libušín near Kladno, Bohemia, Czech Republic. Small violet blades from the burning mine dump of the Becker shaft, Hänichen near Dresden, Saxony, Germany, named “Anilinviolett” by Groth (1867), might be, according to the chemical tests and the given short description, identical with freitalite.

### 3 Mineral description and physical properties

Freitalite forms thin blades or flakes of irregular shape up to a few millimetres in size, rarely up to nearly 1 cm, with the dominant form [001] (Fig. 1). The larger flakes are usually composed of several crystals, intergrown parallel [001] in different orientations. The thickness of small blades (single crystals) is around 1 μm. The blades are often curved. The mineral shows an intense violet or whitish-violet to whitish, the lustre vitreous to pearly and the Mohs hardness is 1. The blades are flexible and malleable. Thin crystals are transparent and larger flakes translucent. Freitalite shows an intense bluish-white fluorescence in short- and long-wave ultraviolet light (254 and 365 nm).

![Figure 1. Violet flakes of freitalite on sulfur from the mine dump of the Königin Carola shaft, Freital, near Dresden, Saxony, Germany. Picture width is 9 cm.](https://example.com/freitalite_flakes_image)
4 Chemical data

Chemical data for freitalite were obtained by high-performance liquid chromatography (HPLC), gas chromatography (GC) with mass spectrometry (MS) and CHN elemental analysis.

HPLC was performed using LiChrosorb RP-8 columns and as reference materials synthetic anthracene (C_{14}H_{10}), synthetic phenanthrene (C_{14}H_{10}), synthetic fluorene (C_{13}H_{10}) and synthetic antraquinone (C_{14}H_{8}O_{2}). One of the co-type samples of freitalite from Freital, Germany, gave 98.3 % anthracene, 0.4 % phenanthrene, 0.1 % fluorene and 1.2 % not identified (possibly dianthracene). A sample labelled kratochvilit from Libušín near Kladno, Czech Republic, gave a very similar result: 97.1 % anthracene, 0.6 % phenanthrene and 1.8 % not identified (possibly dianthracene) and is therefore also freitalite. Sample no. 30345 from the National Museum, Prague, Czech Republic, labelled kratochvilit from Libušín near Kladno, was found by HPLC analysis to be a mixture of anthracene and phenanthrene in a ratio close to 1:1 with anthracene slightly dominant and only traces of fluorene (Witzke, 1990).

GC/MS investigation (electron ionization) of a material from a co-type sample of freitalite (Fig. 2) gave a spectrum corresponding completely to the spectrum of synthetic anthracene (NIST Chemistry WebBook, 2018a).

For the elemental analysis, a Foss Heraeus Vario EL (C-H-N-S) instrument was used. The average of three analyses and the measured range are given in Table 1. From the analyses, an empirical formula of C_{14}H_{9}O_{8} based on C = 14 could be calculated. This is very close to the ideal composition of anthracene, C_{14}H_{10}, which requires C 94.34, H 5.66 and total 100 wt. %.

5 Spectroscopic data

The infrared spectrum (measured in transmission mode, with KBr, NaCl and LiF prisms) was measured on material from a co-type sample from Freital, Germany (Witzke, 1990). The spectrum (Fig. 3) corresponds completely to the one from anthracene (NIST Chemistry WebBook, 2018b), except the shoulder at 1650 cm\(^{-1}\), which may be from a slight contamination. The spectrum can be easily distinguished from the spectrum of the isomer phenanthrene.

The Raman spectrum of a sample from Freital, measured with a GDM-1000 instrument (135° configuration, excitation line Ar* 5154 Å, 0.07 mW), corresponds to anthracene and can be easily distinguished from the spectrum of the isomer phenanthrene. The data were already published (Nasdala et al., 1993).

The \textsuperscript{1}H NMR spectrum in CDCl\(_3\) (Fig. 4) showed three major signals being centered at \(\delta = 8.44\) ppm (broad singlet, assigned to two hydrogens 1-H), \(\delta = 8.02\) ppm (multiplet, assigned to four hydrogens 3-H) and a multiplet at \(\delta = 7.48\) ppm (assigned to four hydrogens 4-H). The position

Table 1. Chemical composition of freitalite.

| Constituent | Average | Range          |
|-------------|---------|----------------|
| C           | 94.07   | 93.95–94.24    |
| H           | 5.571   | 5.375–5.688    |
| Total       | 99.64   |                |

Table 2. X-ray powder diffraction data (d in Å) for freitalite. Values in brackets are shoulders. Seven strongest lines are highlighted in bold.

| l meas | d meas | d calc | hkl | l meas | d meas | d calc | hkl |
|--------|--------|--------|-----|--------|--------|--------|-----|
| 98     | 9.252  | 9.248  | 0 01| < 1    | 2.293  | 2.294  | 220 |
| 9      | 5.048  | 5.047  | 011 | < 1    | 2.195  | 2.197  | 310 |
| 19     | 4.877  | 4.877  | 111 | 1      | 2.068  | 2.069  | 322 |
| 10     | (4.628)| 4.623  | 002 | 1      | 2.035 b| 2.041  | 224 |
| 100    | 4.587  | 4.588  | 110 |        |        |        |     |
| 22     | 4.181  | 4.183  | 201 |        |        |        |     |
| 7      | (4.152)| 4.155  | 202 | 2      | 1.999  | 2.000  | 321 |
| 2      | 4.084  | 4.083  | 112 | < 1    | 1.982  | 1.983  | 115 |
| 1      | 3.617  | 3.619  | 111 | 1      | 1.960  | 1.962  | 031 |
| 27     | 3.538  | 3.540  | 200 | 3      | 1.856  | 1.858  | 411 |
| 22     | 3.434  | 3.436  | 211 | 1      | 1.832  | 1.833  | 024 |
| 1      | 3.084  | 3.082  | 003 | < 1    | 1.810  | 1.815  | 231 |
| 20     | 3.050  | 3.052  | 210 |        |        |        |     |
| 2      | 3.010  | 3.011  | 020 | < 1    | 1.792  | 1.793  | 225 |
| 2      | 2.862  | 2.863  | 021 | 1      | 1.713  | 1.717  | 422 |
| < 1    | 2.828  | 2.831  | 121 |        | 1.710  | 1.712  | 424 |
| 2      | 2.770  | 2.771  | 120 | < 1    | 1.697  | 1.698  | 410 |
| 2      | 2.649  | 2.647  | 122 | < 1    | 1.652  | 1.653  | 116 |
| 2      | 2.520  | 2.522  | 214 | < 1    | 1.637  | 1.638  | 421 |
|        |        | 2.516  | 313 |        | 1.635  | 1.635  | 231 |
| 2      | (2.455)| 2.454  | 114 | < 1    | 1.652  | 1.653  | 116 |
| 2      | 2.442  | 2.445  | 311 | < 1    | 1.637  | 1.638  | 421 |
|        |        | 2.444  | 221 |        | 1.635  | 1.635  | 231 |
| 1      | 2.307  | 2.311  | 004 | < 1    | 1.602  | 1.602  | 515 |
|        |        | 2.304  | 314 |        |        |        |     |
of the signals, their multiplicity and the integrals correspond well with the signals observed for an authentic sample (anthracene, ReagentPlus, 99%, Merck, 141062) and data from the literature (Sharpless et al., 1974). The presence of small amounts of impurities was visible in the spectrum.

The $^{13}$C NMR spectrum in CDCl$_3$ spectrum of freitalite is characterized by the presence of four signals at $\delta = 131.7$ ppm (assigned to the four carbons C-2), $\delta = 128.2$ ppm (assigned to four carbons C-3), $\delta = 126.2$ (assigned to two carbons C-1) and a signal at $\delta = 125.3$ ppm (assigned to four carbons C-4). The position of the signals corresponds very well with the observed signal positions of an authentic sample. Their assignment was based on spectra simulation (MestReNova calculation, vers. 14.01) as well as literature data (Caspar et al., 1975). The sample was not completely pure, as can be seen from the observed impurities.

6 Crystallographic data

X-ray powder diffraction data of freitalite were collected with an Empyrean diffractometer (Malvern Panalytical) using Cu Kα radiation. The instrument was equipped with a focusing mirror, 0.02 rad Soller slits and PIXcel$^{3D}$ detector. The powdered sample was measured in a 0.5 mm capillary. From the powder data (Table 2), the lattice parameter for a monoclinic cell with $a = 8.5572(9)$, $b = 6.0220(5)$, $c = 11.173(1)$ Å, $\beta = 124.174(1)^\circ$ and $V = 476.34(3)$ Å$^3$ were refined by a Pawley fit in the HighScore Plus 4.8 software (Malvern Panalytical). The calculated density of 1.242 g cm$^{-3}$ based on the empirical formula and the refined cell volume for $Z = 2$ is very close to the measured value.

The crystal structure of anthracene with the linear and planar arrangement of the benzene rings in the molecules was
first determined by Robertson (1933). He found a monoclinic cell, $P 2_1/a$, with $a = 8.58$, $b = 6.02$, $c = 11.18$ Å, $\beta = 125^\circ$ and $Z = 2$. Redeterminations and refinements were done by Mathieson et al. (1950), Sinclair et al. (1950), Cruickshank (1956) and Mason (1964). Studies at different temperatures and pressures were done by Ponomarev and Shilov (1983), Brock and Dunitz (1990), and Oehzelt et al. (2003). All the studies confirmed principally the data obtained by Robertson (1933). The unit cell is usually given as described by Robertson (1933) for better comparison with phenanthrene. Sometimes the cell is given in the standard setting in space group $P 2_1/c$, with $a = 9.463$, $b = 6.026$, $c = 8.550$ Å, $\beta = 103.57^\circ$, $V = 473.94$ Å³, $Z = 2$ (Wang, 1978), with the same cell volume as the one described in $P 2_1/a$.

A Rietveld refinement (Fig. 5) was performed using the powder diffraction data from the measurement in the capillary and the program HighScore Plus 4.8 (Malvern Panalytical). For the refinement, the data of the structure determi-
Figure 5. Rietveld refinement of the powder diffraction data of freitalite, using the structure data from Mason (1964). Atomic positions or occupation parameters were not refined. The hump in the scan is from the glass capillary. Glass contribution was modelled from an empty capillary.

Table 3. Crystallographic data of freitalite and ravatite.

|                      | Freitalite | Ravatite |
|----------------------|------------|----------|
| Formula              | C14H10     | C14H10   |
| Molecule             | ![Freitalite molecule](image1.png) | ![Ravatite molecule](image2.png) |
| Crystal system       | monoclinic | monoclinic|
| Space group          | P21/a      | P21      |
| a (Å)                | 8.5572     | 8.392    |
| b (Å)                | 6.0220     | 6.181    |
| c (Å)                | 11.173     | 9.558    |
| β (°)                | 124.174    | 98.48    |
| V (Å³)               | 476.34     | 490.4    |
| Z                    | 2          | 2        |
| D calc. (g cm⁻³)     | 1.242      | 1.207    |
| Reference            | this work  | Nasdala and Pekov (1993) |
nation of anthracene by Mason (1964) were used, converted to
the standard setting $P2_1/c$. Atomic positions or occupation
parameters were not refined. The contribution of the
glass was modelled from the measurement of an empty cap-
illary. In the Rietveld refinement of freitalite ($R$ exp. 1.375,
$R$ Profile 2.126, Weighted $R$ Profile 2.822, Goodness of
Fit 2.053, $R$ Bragg 0.46), the lattice parameters $a = 9.516,
b = 6.018, c = 8.557\,\text{Å}, \beta = 103.883^\circ$ and $V = 475.76\,\text{Å}^3$
were obtained, confirming the identification as anthracene.

The crystallographic data of the two $\text{C}_{14}\text{H}_{10}$ isomers frei-
talite and ravatite are compared in Table 3.

Data availability. XRD and Rietveld data are available in the Sup-
plement.

Supplement. The supplement related to this article is available on-
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