JAHRBUCH DER GEOLOGISCHEN BUNDESANSTALT
Jb. Geol. B.-A. | ISSN 0016–7800 | Band 140 | Heft 4 | S. 441–445 | Wien, Juni 1998
The Early Miocene Lignite Deposit of Oberdorf N Voitsberg (Styria, Austria) | Editor: F.F. Steininger

Chemofossils (“Biological Markers”) from the Early Miocene Lignite Opencast Mine Oberdorf (N Voitsberg, Styria, Austria)

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Styria
Pannonian Basin
Styrian Basin
Lignite
Early Miocene
Chemofossils
Resin
Wood
Liquid Gas Chromatography
Mass Spectroscopy

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Zusammenfassung

In einigen Proben (Harz, fossiles Holz, Braunkohle) aus dem Köflach-Voitsberger Kohlerevier wurden einige Chemofossilien – Phyllocladan, Isophyllocladen, Norpimaran und Simonellit – mittels kombinierter Gaschromatographie/Massenspektroskopie identifiziert; ihr möglicher botanischer Aussagewert sowie eine mögliche Bedeutung als Indikatoren für das Ausmaß der Diagenese organischer Substanzen werden diskutiert.

Abstract

In some samples (resin, wood, lignites) from the Köflach-Voitsberg lignite mining district a few biological markers (“chemofossils”) – phyllocladane, isophyllocladene, norpimarane and simonellite – have been identified by means of combined gas liquid chromatography/mass spectroscopy; their possible botanical affinities and their possible usefulness as indicators for the extent of diagenesis of organic substances is discussed.

1. Introduction

The Köflach-Voitsberg lignite mining district is known to specialists studying organic minerals for the occurrence of hartite (= α-phyllocladane, occurring at this locality in rather large ideomorphic crystals) and koeflachite, having been described by DOELTER (1878) as some sort of fossil resin.

As far as hartite is concerned already ROLLE (1856) had realized that this was a crystallized hydrocarbon, nevertheless it lasted rather long (BRIGGS, 1937) until the exact chemical structure had been determined: α-dihydrophyllocladene (= α-phyllocladane).

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Streibl & Herout (1969) emphasized that this was a rather common mineral in various coal mines; a number of other organic minerals have been recognized as junior synonyms: iosen, josen, bombiccite, hofmannite and branchite (e.g. Hintze, 1933). As far as the Köflach-Voitsberg area is concerned the detailed studies published by Soltys (1929) and the crystallographical descriptions by Machatschki (1924) must be mentioned. The possibility to isolate "josen" (see above) by extraction of lignite from the Köflach coal mining district (using carbon disulfide as solvent) has been reported already by F. Machatschki, too.

The second important organic mineral from the Köflach area is the so-called "köflachite", which has recently been restudied and shown to be – mainly at least – a mixture of different hydrocarbons (phyllocladane, eudesmane, sandaracopimarane, dehydroabietane, norpimarane, retene, and simonellite [Vávra, 1993]). In respect to these results there exists one problem however: the redescription mentioned could not include the type material published and studied by C. Doelter – it has not been possible to locate his material in any collection indeed. There seems to have been a greater variety of fossil resins in the Köflach area (e.g. Rumpf, 1870) and one can only hope that the "köflachite" having been studied (Vávra, 1993) corresponds to the (lost ?) type material as described by C. Doelter.

The various reports on organic minerals from the Köflach-Voitsberg lignite mining district have been the reason to include the search for possible biological markers ("chemofossils") in the current study.

2. Samples and Methodology

Various samples from the open cast mine of the Köflach-Voitsberg lignite mining district have been treated with solvents and the extracts searched for biological markers by means of gas liquid chromatography/mass spectroscopy. Most satisfying results have been yielded by using fresh samples; paleobotanical macrofossils have been studied too – in these samples unfortunately no chemofossils could be detected however. In the following description, results concerning four samples shall be given in some detail.

Table 1.
Numbers, descriptions and file names of the samples studied.

Sample Nr.	Sample	File Name
OB 10, northern margin	Resin	KV249
OB 10, northern margin	Wood	KV250
KV-1	open cast mine Bärnbach, lower seam 6264, lignite	KV279
KV-2	open cast mine Bärnbach, lower seam 6264, lignite	KV280

For the extraction of the samples a mixture of methylene chloride and methanol (1:1) has been used: refluxing and ultrasonics proved successful. The solutions have then been used for computer-aided, combined gas liquid chromatography/mass spectroscopy without any further separation. The gas chromatograms (more correct: "total ion chromatograms") yielded satisfying separation of the single compounds. Identification was achieved by comparisons with the mass spectra published by Philp (1985) as well as by means of a library of our own containing mass spectra of components of fossil resins and similar samples. For closer details see experimental part.

3. Results

A resin-like substance occurring in one of the samples studied (OB 10; northern margin, resin – see Table 1) yielded after extraction with methylene chloride and methanol a solution giving a total ion chromatogram with 17 peaks, a few of which could be identified by means of their mass spectra (Text-Fig. 1). Calculated in area-% these few peaks yield a total of 59 %. Most prominent of them is a peak (under conditions of chromatography as given below) at a retention time of 33.66 minutes (45 area-%): α-phyllocladane – as confirmed by its mass spectrum (Text-Fig. 1). An extremely small peak with a somewhat lower retention time could indicate a trace of -phyllocladane, but unfortunately did not yield a satisfying mass spectrum. Some other more outstanding peaks could be identified as: norpimarane (ret.time: 32.26, 7 area-%, Text-Fig. 2, 4), isophyllocladene (2 area-%, Text-Figs. 2, 3), and simonellite (3 area-%, Text-Fig. 2, 2). A peak at 20.07 minutes can be tentatively identified as a bicyclic sesquiterpene of molecular mass 194. For a short survey see Table 2.

Table 2.
Chemofossils from sample OB 10, northern margin, resin.

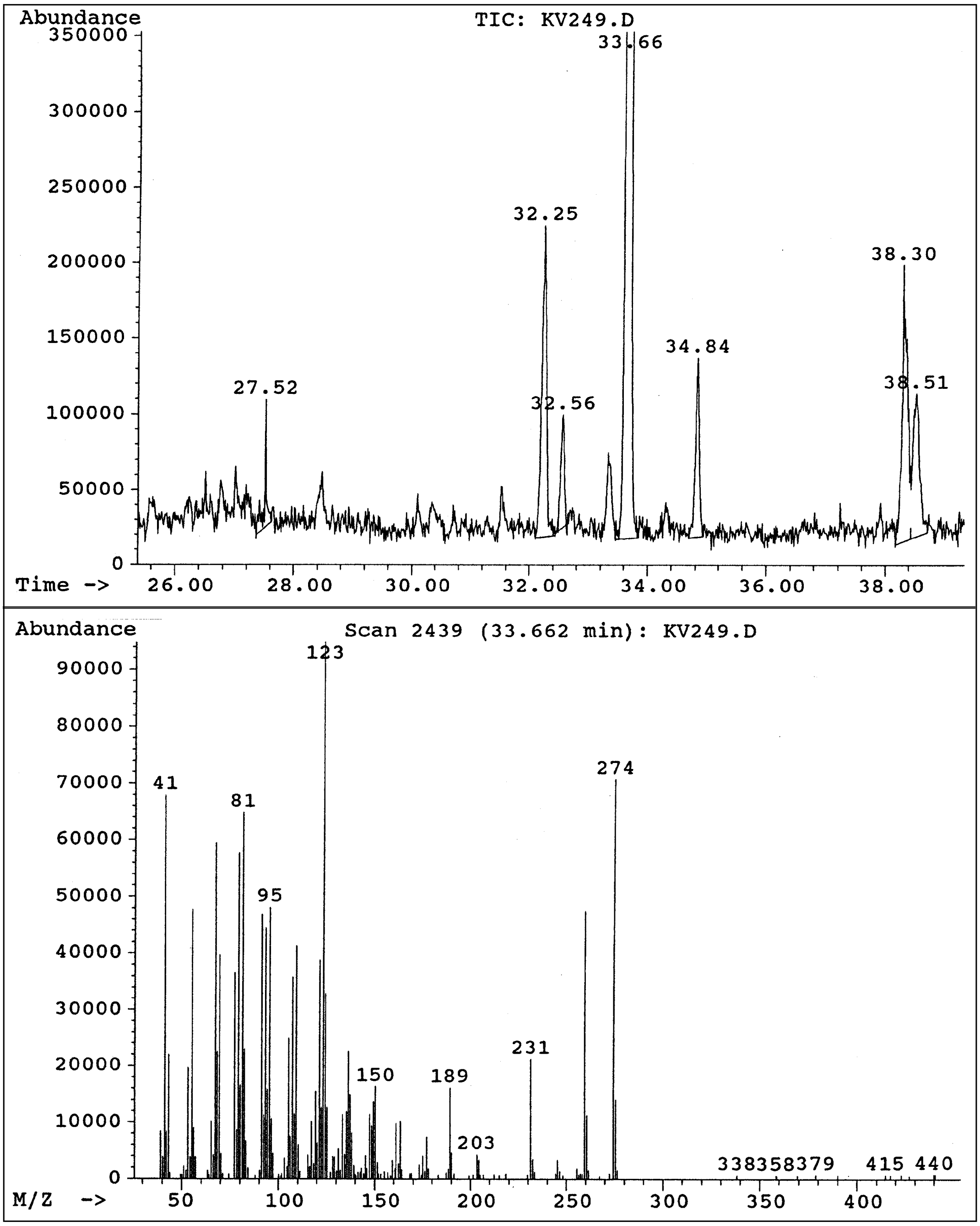
retention time	molec.mass	area %	identified as:
20,07	194	2	bicyclic sesquiterpene
32,26	262	7	norpimarane
32,55	272	2	isophyllocladene
33,66	274	45	phyllocladane
34,84	252	3	simonellite

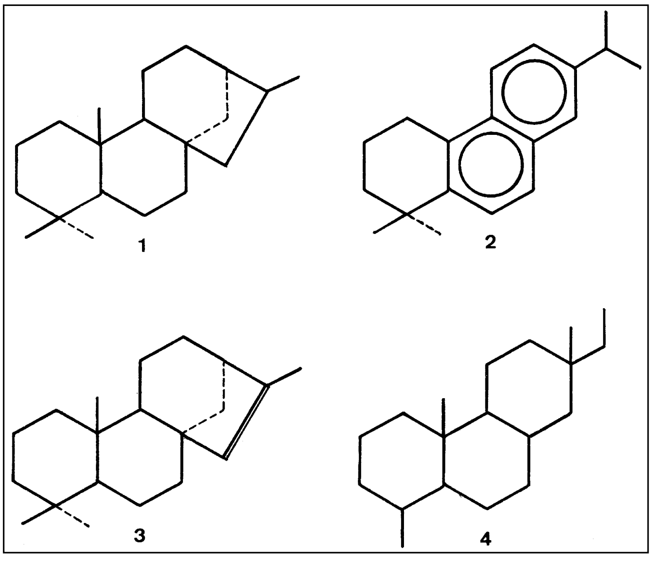
In an other sample of similar origin (OB 10, northern margin, "wood") only phyllocladane could be identified. Samples from the open cast mine Bärnbach (lower seam 6264) having been treated in the same way (methylene chloride and methanol [1:1], ultrasonics, refluxing) yielded a number of peaks, among which phyllocladane and simonellite could be identified, phyllocladane being again the main component. Perhaps it is of some interest to mention that the relation between simonellite and phyllocladane varies from sample to sample: whereas in both samples from the open cast mine Bärnbach (lower seam 6264) it has been rather high (0.377 resp. 0.251) it has been extremely low in the resin analyzed (0.075). The sample designated as "wood" yielded even no simonellite at all. As possible explanation a distinctly different degree of aromatization could be suggested.

4. Discussion of Results

Among the hydrocarbons identified by GC/MS after extraction of the samples as described above resp. below four are worth closer discussion. Phyllocladan – especially the alpha-isomer ($16\alpha(H)$-phyllocladane, Text-Fig. 2, 1) is well-known as a common biological marker in many lignites (e.g. Streibl & Herout, 1969). It may occur in such localities as a well-defined mineral species – which has been described under various names: hartite (type locality: Oberhart near Gloggnitz, Lower Austria), branchite (Tuscany, Italy), hofmannite (near Siena, Italy), bombiccite (Arno valley, Tuscany, Italy); for closer details see Dana (1892) and Hintze (1933). It has also been isolated from brown coals by extraction with carbon disulfide, followed by crystallization from ethanol or acetone (Streibl &

Text-Fig. 1.
Above: part of a total ion chromatogram (gas liquid chromatogram) of a resin (OB 10, northern margin) dissolved in methylene chloride/methanol; ion abundance versus retention time (in minutes).
32.25: norpimarane.
32.56: isophyllocladene.
33.66: α-phyllocladane.
34.84: simonellite.
Below: mass spectrum of phyllocladane, same sample.





Text-Fig. 2.
Formulas of hydrocarbons identified:
1 = α-phyllocladane; 2 = simonellite; 3 = isophyllocladene; 4 = norpimarane; the steric arrangement of atoms is (partly) indicated by stippled lines.

HEROUT, 1969; SOLTYS, 1929). Realizing that phyllocladane has been reported from the Köflach-Voitsberg lignite mining district already as mineral (hartite, see above) and that it is moreover also the main component of "köflachite" (VÁVRA, 1993) it is not surprising to detect it also as main constituent in the extracts used in this study.

During diagenesis of organic compounds α-phyllocladane is known to undergo very special changes: either there may take place a process of aromatization (after opening of the four-membered ring) or an isomerization via isophyllocladene, yielding finally β-phyllocladane. Such reaction schemes have been suggested resp. summarized and supported also by thermal degradation experiments by ALEXANDER et al. (1987) and discussed also by GRIMALT et al. (1990). Taking this into consideration the occurrence of isophyllocladene (Fig. 2, 3) and simonellite (Fig. 2, 2) together with α-phyllocladane in the above-mentioned samples from Styria can be easily understood: isophyllocladene is the necessary intermediate compound for the isomerization leading to the formation of β-phyllocladane; simonellite however is one of the stages of aromatization. Realizing that neither the last compound formed by aromatization processes (retene) nor β-phyllocladane could be detected in our samples, one can confirm in this way that our samples are still in a rather early state or in an intermediate state of diagenesis of organic compounds.

Norpimarane (Fig. 2, 4) has nothing to do with the compounds of the phyllocladane-group however. Its formation by decarboxylation of sandaracopimaric acid during diagenesis offers a possible explanation how it may have been formed. Norpimarane has been reported to occur in (fossil) resins and lignites (PHILP, 1985); for chemotaxonomical purposes it is practically useless.

5. Significance of Phyllocladane for Chemotaxonomy

Realizing the rather unusual carbon skeleton occurring in phyllocladane and related compounds there is some temptation to discuss its possible significance as a biological marker in connection with chemotaxonomy. Substances with this carbon skeleton have been reported mainly from members of the Araucariaceae, Podocarpaceae and Taxodiaceae (e.g. HEGNAUER [1962] and references given there). In all these cases unsaturated compounds have been reported like phyllocladene (= “sciadopityene”) and its stereoisomers (kaurene = “podocarprene” and mirene). Isophyllocladene as well as its stereoisomer isokaurene (= “cryptomerene”) have been reported too. In respect to the formation of phyllocladane either these unsaturated hydrocarbons or/and a corresponding alcohol (phyllocladanol) must be regarded as only possible sources. The first step during diagenetic changes which such substances may undergo has obviously been a hydrogenation resp. a dehydration followed by hydrogenation – processes quite similar to those reported for the diagenesis of phytol (e.g. DIDYK et al., 1978). At any case the rather wide-spread occurrence of phyllocladane can be discussed in connection with chemotaxonomy. To find a really convincing or at least satisfying answer is not quite easy however. It seems reasonable perhaps at the present state of knowledge to suggest some genus of Taxodiaceae – like *Sciadopitys* and/or *Cryptomeria* – as possible source of material for the formation of phyllocladane. By reasons of biogeography of plants and paleobotanical data, other possible sources like Podocarpaceae and Araucariaceae can be excluded. Realizing however that *Sciadopitys* has been reported as a common constituent of European lignite floras (the grass-like needles are sometimes so common that a special variety of coal derives its name – “grass-coal” – from them) and realizing moreover that *Cryptomeria* has been confirmed for the European Tertiary too, the above-mentioned statement suggesting these two genera as possible sources of phyllocladane-prescursors may have some probability indeed. The fact that phyllocladane is also known to occur in coals from the Carboniferous and in Permian sediments (NOBLE et al., 1985; SCHULZE & MICHAELIS, 1990) shows possibly that already ancestral, Paleozoic conifers have been able to produce these compounds. At any case the discussion concerning the chemotaxonomy of phyllocladane compounds is obviously still in a preliminary stage. For details see OTT (1996) and the short summaries given by VÁVRA (1998, in print).

6. Experimental Details

❍ Samples
have been refluxed in solvent (methylene chloride/methanol = 1 : 1; ultrasonics) and used for gas liquid chromatography without any further separation.

❍ Gas liquid chromatography
Column: HP 1 (Crosslinked Methyl Silicone Gum), 25 m × 0,2 mm x 0,33 μm film thickness.
Carrier gas: helium (30 psi).
Injector: 250°C.
Oven: Initial temperature: 60°C.
Initial time: 2 minutes.
Increase of temperature: 6°C/min.
Final temperature: 250°C.

❍ Mass spectrometer
Transfer Line: 280°C.
Mass range: 35–520 daltons.
Sampling: 2.
Threshold: 400.

❍ Configuration of equipment (HEWLETT-PACKARD)
GC 5890, series II.
Automatic sampler: 7673.
MSD: 5971 A.

Acknowledgements

Financial support by the Fonds zur Förderung der wissenschaftlichen Forschung (FWF) within the project “Tagebau Oberdorf in Bärnbach bei Köflach” (P 10 337 GEO) is gratefully appreciated. The author owes sincerest thanks to Mr. B. BAUMGARTNER for laboratory work.

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Manuskript bei der Schriftleitung eingelangt am 19. Dezember 1997

Zeitschrift/Journal: Jahrbuch der Geologischen Bundesanstalt

Jahr/Year: 1997

Band/Volume: 140

Autor(en)/Author(s): Vávra Norbert

Artikel/Article: Chemofossils ("Biological Markers") from the Early Miocene Lignite Opencast Mine Oberdorf (N Voitsberg, Styria, Austria) 441-445