

1 **Petrological and geochemical characteristics of xylites and associated lipids from the First**
2 **Lusatian lignite seam (Konin Basin, Poland): implications for floral sources, decomposition and**
3 **environmental conditions**

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16
17 **Abstract**

18 Single pieces of fossil wood fragments (xylites) were collected from the middle Miocene First
19 Lusatian lignite seam at the Adamów, Józwin IIB and Tomisławice opencast mines and are
20 characterized by maceral variety, cellulose contents and their molecular and isotopic composition.
21 Biomarker composition of xylites and $\delta^{13}\text{C}$ of their total organic matter, lipids and cellulose are used to
22 provide insights into woody plant community and the effects of wood decomposition.

23 The investigated xylites represent fragments of fossil wood from conifers, most likely species of
24 Cupressaceae, indicated by terpenoid biomarkers characteristic for conifers and by the $\delta^{13}\text{C}$ values of
25 the extracted cellulose. This conclusion is confirmed by paleobotanical data highlighting *Taxodium*
26 and *Nyssa* as the main elements of the wet forest swamps. Due to the wet swamp habitat and the

higher-decay resistance exclusively wood fragments of conifers are found in the lignite seam. Minor abundances of angiosperm-derived triterpenoids in the xylites are explained by impurities from inherent detritic lignite.

The xylites are characterized by minor to moderate extents of gelification, but elevated to high cellulose decomposition. The relationship between $\delta^{13}\text{C}$ values of xylites and their cellulose contents reflects wood decomposition removing preferentially the ^{13}C -enriched compounds, but decomposition did not affect the $\delta^{13}\text{C}$ of cellulose. Despite of similar $\delta^{13}\text{C}$ of xylites and detritic lignite, differences in isotopic composition of hopanoids argue for slightly different microbial communities involved in the decomposition of the respective OM. Thus, we conclude that wood decomposition proceeded in a freshwater environment under acidic conditions by fungi and bacteria.

Variations in water availability during growth periods of the conifers are suggested as the most probable cause for the observed minor variations in isotopic composition of plant lipids. The positive relationship found between $\delta^2\text{H}$ and $\delta^{13}\text{C}$ of plant biomarkers, and cellulose of xylites can be explained by the ability of vascular plants to minimize evapotranspiration during dryer phases resulting in plant OM enriched in ^{13}C and ^2H . The significant differences in $\delta^2\text{H}$ between diterpenoids of different structural types and *n*-alkanes are most likely caused by differences in isotopic fractionation during lipid biosynthesis.

Keywords: Biomarkers; Cellulose; Fossil wood; Paleovegetation; Stable isotopes; Terpenoids

1. Introduction

Information about environmental changes over Earth's history (e.g., air temperature, humidity, pCO_2 , $\delta^{13}\text{C}$ of atmospheric CO_2) have been obtained from the stable isotope composition of cellulose extracted from single tree rings and wood fragments (Feng and Epstein, 1995; Schleser, 1995; Arens et al., 2000). However, their interpretation with respect to climate change is complicated by interfering processes like inter-species and intra-species variations in $\delta^{13}\text{C}$ and postdepositional changes due to

53 different decay resistance of macromolecules (Benner et al., 1987; Lücke et al, 1999; van Bergen and
54 Poole, 2002; Marynowski et al., 2007). The combination of biomarker and stable isotope analyses has
55 been successfully applied to reconstruct changes in vegetation and the environment of lignite
56 deposition (van Bergen and Poole, 2002; Poole et al., 2006; Bechtel et al., 2008), as well as in carbon
57 cycling and isotope fractionation processes (Bechtel et al., 2008; Jahren and Sternberg, 2008).

58 The $\delta^{13}\text{C}$ values of individual lipids are frequently used to identify their biological sources and
59 biosynthetic pathways during synthesis (Pancost et al., 2007; Đoković et al., 2018). In a recently
60 published database from peats, biomarkers were related to climate and changes in vegetation (Naafs et
61 al., 2019). Vascular plants adjust stomatal aperture to minimize water loss during warm and dry
62 periods (van Bergen and Poole, 2002; Jahren and Sternberg, 2008; Bechtel et al., 2008) which also
63 affects the isotopic composition of newly formed biomolecules. Therefore, ^{13}C -enriched OM (i.e.,
64 cellulose, *n*-alkanes, and diterpenoids) of xylites may indicate dryer conditions during wood formation
65 (and vice versa). The additional influences of environmental and vegetational changes on the
66 molecular and isotopic systematics of modern plants and plant-derived lipids were addressed by
67 Diefendorf and Freimuth (2017) and Diefendorf et al. (2019). Further postdepositional effects like the
68 effect of increasing maturation on the isotopic composition of lignin (Lee et al., 2019) have also to be
69 considered.

70 Hydrogen isotope analyses on lipids have been shown to shed light on influences of climatic
71 factors on $\delta^{13}\text{C}$ of plant biomarkers. The hydrogen isotopic composition of water in the environment
72 mainly depends on temperature, evaporation and precipitation. The $\delta^2\text{H}$ values of individual lipids
73 have been shown to reflect the isotopic composition of the source water modified by isotopic
74 fractionation during the biogeochemical pathway (Sessions et al., 1999). Previous studies by Yang and
75 Huang (2003) revealed a similar difference between $\delta^2\text{H}$ values of alkanes from angiosperm leaves
76 from the Miocene Clarkia deposit (USA) and sediment water (apparent fractionation) as observed in
77 modern species (123‰; Sachse et al., 2004, 2006). Therefore, hydrogen isotope ratios of leaf wax-
78 derived *n*-alkanes are frequently used in paleohydrology and climate research (Sachse et al., 2012).

Our study is focused on the fossil wood remains (xylites) collected from the First Lusatian lignite seam of the Konin Basin in Poland, deposited during the mid-Miocene Climatic Optimum. Based on the results of previous investigations, grasses and herbs were suggested as the peat-forming vegetation of detritic lignites, whereas xylitic lignites showed geochemical characteristics typical of woody conifers (Fabiańska and Kurkiewicz, 2013). This interpretation was supported by biomarker and $\delta^{13}\text{C}$ data from xylites of the Lubstów mine within the Konin Basin (Bechtel et al., 2007). Changes in biomarker composition and $\delta^{13}\text{C}$ of xylite from the Lubstów mine, related to gelification and cellulose decomposition of wood remains, have also been found (Bechtel et al., 2007).

Palynomorphs of taxa representing a swamp forest environment (*Taxodium*, *Nyssa*, *Alnus* and *Liquidambar*) as well as of shrubs from peat bogs have been found within the lignite seams of the Konin Basin. Pollen elements of the coniferous (e.g., *Sequoia*, *Pinus*) and deciduous forest (e.g., *Betula*, *Fagus*, *Quercus* and *Ulmus*) indicated the presence of dryer habitats within the mire (Sadowska and Giża, 1991; Piwocki and Ziemińska-Tworzydło, 1997; Kasiński and Słodkowska, 2016; Worobiec et al., 2020). In a previous study, detritic lignite samples from identical sampling locations as the xylites, studied here, (i.e., three opencast deposits within the Konin Basin) have been investigated by Bechtel et al. (2019). The discussion of the lipid composition and carbon isotope data of detritic lignite in combination with the results of paleobotanical studies highlighted the varying contribution of gymnosperms vs. angiosperms to the peat-forming vegetation. Furthermore, the possible contribution of biomarker data to gain information on climate and implications about the effects of changes in vegetation and carbon cycling on $\delta^{13}\text{C}$ of lignite samples within the peat have been addressed.

In this study, single pieces from larger xylites were selected from the middle Miocene First Lusatian lignite seam at approximately equal distances along profiles from the same opencast mines within the Konin Basin as investigated for detritic lignite samples in our previous study (Bechtel et al., 2019). The aim of the study is to reveal information about the effects of wood decomposition and environmental conditions on stable isotope composition of woody plant OM. Carbon and hydrogen isotope ratios of cellulose, plant wax and resinous lipids are reported, and are discussed for their

106 suitability as environmental proxies. Finally, we aim for an improved understanding of
107 palaeoenvironmental changes during peat accumulation from our combined application of molecular
108 and isotopic proxies.

109

110 **2. Geological setting and samples**

111 Cenozoic sediments were deposited within fault-bounded, relatively shallow tectonic, graben-like
112 depressions located in the Konin vicinity in central Poland ([Fig 1a](#)). The Cretaceous bedrock of these
113 grabens is built of marls and sandstones with carbonate cement. The Paleogene and Neogene deposits
114 are characterized by stratigraphic gaps in the territories of the Adamów, Józwin IIB and Tomisławice
115 opencasts ([Fig. 1](#)). Almost the entire Paleocene, Eocene and upper Oligocene sediments are missing in
116 the record. Therefore, the oldest Paleogene sediments are of early Oligocene age in the Adamów and
117 Tomisławice. They are of marine origin including glauconitic sands and occasionally gravels ([Widera,](#)
118 [2010, 2016](#)). It is worth noting that the Paleogene sediments in the area of the Józwin IIB opencast
119 have not been documented until now ([Chomiak et al., 2019; Widera et al., 2019](#)).

120 The Koźmin and Poznań formations are the two main Neogene lithostratigraphic units in central
121 Poland. They were deposited after regional uplift of the study area that took place in the late
122 Oligocene. The lower Koźmin Formation is made up of fluvial sands with coaly interbeddings of
123 early- to mid-Miocene age. The upper Poznań Formation, which age covers the time interval from
124 mid-Miocene to early Pliocene, is divided into the Grey Clays and Wielkopolska members (e.g.,
125 [Piwocki and Ziemińska-Tworzydło, 1997; Widera, 2013; Chomiak et al., 2019; Widera et al., 2019](#)).

126 The Grey Clays Member consists primarily of the First Lusatian lignite seam, which is currently
127 being exploited in all opencasts belonging to the Konin Basin. This seam is up to several meters thick
128 (on average below 10 m) ([Fig. 1b-d](#)) and has been deposited during the final phase of the mid-Miocene
129 Climatic Optimum ([Zachos et al., 2001; Bruch et al., 2007; Kasiński and Słodkowska, 2016; Widera,](#)
130 [2016](#)). The age of the studied seam was estimated at 15 +/- 1.5 Ma on the basis of radiometric dating
131 of tuff layers from various regions of Poland, including the Konin area ([Wagner, 1984; Matl and](#)
132 [Wagner, 1985](#)). Additionally, this lignite seam is correlated palynologically both throughout the Polish

133 and European lowlands territory (e.g., Sadowska and Giża, 1991; Kasiński and Słodkowska, 2016;
134 Worobiec et al., 2020). The First Lusatian lignite seam evolved from low-lying mires (backswamps) in
135 the extra-channel area of a mid-Miocene fluvial system (Widera, 2016; Chomiak et al., 2019).

136 The examined lignite seam (i.e., the First Lusatian one) belongs to humic ortholignite. It is
137 characterized by low-coal rank (mean reflectance (R_r^o) < 0.3%) and low carbon content ($60\% < C^{daf} <$
138 70%) (Kwiecińska and Wagner, 2001). Moreover, a relatively high ash yield ($A^d \sim 20$ wt% average)
139 and low average sulfur content (< 1 wt%) are typical of the First Lusatian lignite seam in the Konin
140 Basin and in the remaining part of central Poland (e.g., Piwocki, 1987; Kwiecińska and Wagner,
141 1997). Twenty-seven samples of large pieces of xylite, carefully separated from the detritic lignite,
142 were taken along three profiles at the Adamów, Józwin IIB and Tomisławice opencasts (Fig. 1). The
143 location of sampling is shown in Fig. 1b-d.

145 3. Analytical methods

146 3.1. Micropetrography

147 Twelve xylite samples from different parts of the three profiles have been selected for microscopic
148 inspection based on varying cellulose yields. Pieces from homogenised xylite samples were embedded
149 into epoxy resin and polished to obtain a smooth surface. The samples were investigated by a Leica
150 DM 4P microscope using reflected white and fluorescent light.

152 3.2. Ash yield, carbon, and total sulfur analyses

153 The total carbon (TC), and total sulfur (TS) contents were determined by Elemental Analysis
154 (Eltra Helios CS analyser). Total organic carbon (TOC) was measured with the same instrument on
155 samples pre-treated with half-concentrated phosphoric acid. The total inorganic carbon (TIC) was
156 calculated as $TIC [wt\%] = TC - TOC$. Ash content was determined via combustion of dried and
157 homogenized samples at 550°C for 4 h.

159 3.3. Pretreatment and cellulose extraction

Pieces of fossil wood were freeze-dried and milled for homogenization. An aliquot of the sample was decalcified in a water bath (5% HCl, 50°C) for two hours to remove inorganic carbonates prior to the analyses of $\delta^{13}\text{C}$ of fossil wood. Cellulose extraction followed the CUAM-protocol (Wissel et al., 2008) with slight adaptations for the specific samples.

164

3.4. Stable carbon isotope analyses

For $\delta^{13}\text{C}$ analyses of fossil wood and cellulose, a sample amount of about 200–300 μg ($\sim 100 \mu\text{g}$ carbon) was weighed into tin foil capsules. Samples were combusted at 1050°C with excess oxygen in an elemental analyser (EuroEA, Eurovector) and measured online with a coupled isotope ratio mass spectrometer (IsoPrime, GV-Instruments). Carbon content was determined by peak integration (m/z 44 and 45) and calibrated against a certified elemental standard.

Isotope ratios are given as δ -values in per mil (‰), where $\delta = (R_{\text{sample}}/R_{\text{standard}} - 1) \times 1000$, with R_{sample} and R_{standard} as isotope ratios ($^{13}\text{C}/^{12}\text{C}$) of sample and standard, respectively. Samples were measured together with laboratory standards calibrated against international carbon isotope standards and are reported scale-normalized to the VPDB scale. The overall precision of replicate analyses was better than $\pm 0.1\text{‰}$. Preparation of cellulose and carbon isotope measurements on fossil wood and cellulose were carried out at the Institute of Bio- and Geoscience, Agrosphere, Forschungszentrum Jülich GmbH (Germany).

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3.5. Molecular composition of lipids

After extraction of aliquots (5 g) of dry lignite samples by a mixture (9:1) of dichloromethane (DCM) and methanol (MeOH) in a Dionex ASE 200 accelerated solvent extractor (75°C, 100 bar, 1 h), the extracts were saponified at 80°C for 3 h using a 6% potassium hydroxide (KOH) solution in MeOH. The neutral lipids were recovered by extracting the KOH/MeOH with 3 x 1 ml *n*-hexane, whereas fatty acids were subsequently recovered after addition of concentrated HCl at pH=1. The neutral lipids were then separated using Supelco silica columns (LC-SI, 6 ml, 500 mg sorbent) into 3 fractions of various polarity using 4 mL of the following eluents: 1) 100% *n*-hexane; 2) *n*-hexane:

187 DCM mixture (1:1 v/v) and 3) DCM:MeOH mixture (95:5 v/v). The first fraction (F1) contains
188 hydrocarbons, the second ones (F2) ketones plus polycyclic aromatic hydrocarbons, and the third
189 fraction (F3) contains the alcohols. Fatty acids (FAs) and fractions F3 were derivatised with BSTFA
190 (N,O-bis(trimethylsilyl)trifluoroacetamide) for 1 h at 80°C to form trimethylsilyl (TMS) esters and
191 ethers, respectively.

192 For gas chromatographic analysis 2 µl of the fractions was injected slitless (injector temperature
193 275°C) onto a 60 m DB-5MS fused silica column (i.d., 0.25 mm; 0.25 mm film thickness). The gas
194 chromatograph (GC) was coupled to a ThermoFisher ISQ quadrupole mass spectrometer (GC–MS
195 system). The instrumental parameters during analyses were identical to that outlined in our previous
196 article ([Bechtel et al., 2019](#)). Data were processed using an Xcalibur data system. Individual
197 compounds were identified on the basis of retention time and by comparison of the mass spectra with
198 published data. Concentrations of different compounds were calculated using peak areas in the total
199 ion current chromatograms in relation to those of internal standards added in known concentrations
200 (squalane to F1, 1,1'-binaphthyl to F2, 1-nonadecanol to F3, and nonadecanoic acid to FA fractions,
201 respectively). The concentrations are given relative to the TOC contents of the xylites.

202 203 3.6. Compound-specific isotope analyses

204 The $\delta^{13}\text{C}$ and $\delta^2\text{H}$ of *n*-alkanes and terpenoids were measured in duplicate, using a Trace GC-Ultra
205 gas chromatograph attached to a Thermo Fischer Delta-V isotope ratio mass spectrometer (irMS) via a
206 combustion and high temperature reduction interface, respectively (GC Isolink, Thermo Fischer). The
207 GC was equipped with a 30 m DB-5MS fused silica capillary column (i.d., 0.25 mm; 0.25 µm film
208 thickness). The GC operational parameters were identical to that described by [Bechtel et al. \(2019\)](#).
209 Raw isotope values were initially converted to the VPDB and VSMOW scale, respectively, using
210 Thermo Isodat 3.0 software and pulses of a monitoring gas measured at the beginning and end of each
211 analysis. Analytical precision (between ± 0.2 and 0.3‰ for C; below $\pm 3\text{‰}$ for H) was controlled by
212 repeated measurements (after every 10 sample injections) of the C3 *n*-alkane standard mix from Arndt
213 Schimmelmann (Indiana University).

214

215 **4. Results**

216 *4.1. Micropetrography and bulk geochemical data*

217 Microscopic inspection of selected xylites was performed to evaluate the purity of the
218 macrofossils and their degree of gelification. The samples contain mainly textinite, textoulminite, and
219 phlobaphinite in various proportions. Inside the cells of textinite, crystalline inorganic phases (Fig. 2a)
220 are observed in several samples. Increased extents of gelification are reflected by higher textoulminite
221 and lower textinite abundances (Table 1). Textinite is the predominant maceral in ungelified samples
222 (Fig. 2a–d), whereas gelified samples contain textoulminite plus rare ulminite (Fig. 2e, f). Lower
223 fluorescence intensities of huminite (dark brownish to greenish) are observed in gelified xylites (Table
224 1; Fig. 2). Generally, xylites from the Józwin IIB mine are characterized by higher extents of
225 gelification (Table 1). Resinite is present in minor amounts in all xylites (Fig. 2a, b).

226 The TOC contents of fossil wood remains are in the range of 32.5 to 53.6 wt% (Table 1). The
227 TOC values are lower than previously obtained from the xylites of the Lubstów deposit, despite of
228 comparable extents of gelification (Bechtel et al., 2007). Low TOC contents (< 40 wt%) were obtained
229 from the lowermost sample taken from the Tomisławice mine, in sample JX-02 from the Józwin IIB
230 mine and from several xylites of the Adamów mine (Fig. 3a). Ash yields of several of the woody
231 macrofossils are exceeding 5 wt% (Table 1; Fig. 3a), arguing for impurities due to inherent detritic
232 lignite, as wood from temperate zones yielded less than 1 wt% ash (Misra et al., 1993). Ash yields up
233 to 5 wt% are reported from tropical wood (Fengel and Wegener, 1984). The TOC of woody
234 macrofossils is controlled by interfering parameters, including mineral matter contents from inherent
235 detritic lignite, its TOC content, and cellulose decomposition. Therefore, no relationship exists
236 between ash yields and TOC of xylite.

237 The TIC contents vary between 0.0 and 3.8 wt% (Table 1; Fig. 3b) and are generally higher as
238 measured within samples of detritic lignite (Bechtel et al., 2019). The results argue for mineralization
239 of wood by calcium carbonate within the mire. Based on the results obtained during experimental

240 treatments of wood with electrolyte solutions (Merk et al., 2016), the crystalline phases inside the
241 cellular structure of wood (Fig. 2a) consist most likely of CaCO₃ polymorphs.

242 Total sulfur contents below 2 wt% argue for deposition in a freshwater environment (Casagrande,
243 1987). Elevated sulfur contents are obtained from xylites from the upper part of the Adamów mine,
244 xylites from the Józwin IIB mine and the lowermost sample from the seam in the Tomisławice mine
245 (Fig. 3b).

246 Cellulose yields of fossil wood remains ranged between 1.6 and 24.2% (dry wt.; Table 1; Fig. 3a),
247 but seem to be unrelated to the varying gelification extent of selected samples (Table 1). Highest
248 cellulose yields were measured in xylites of the Tomisławice mine (Fig. 3a). With an approximate
249 original cellulose content of 40 to 50%, (Pettersen, 1984), the data indicate advanced to high extent of
250 cellulose decomposition. However, impurities due to inherent detritic lignite certainly also reduced
251 cellulose yields.

252 Extractable organic matter yields (EOM) vary from 18.3–64.6 mg/g TOC (Table 1). A negative
253 relationship exists between EOM and cellulose yields (Fig. 4), suggesting biogeochemical formation of
254 lipids in the wood during gelification and cellulose decomposition by bacteria and fungi. However, the
255 relative enrichment of EOM due to the depletion of fossil wood in cellulose and (partly) lignin cannot
256 be excluded. Hydrocarbons plus ketones contribute between 5 and 16% to the EOM, consistent with
257 the low maturity of organic matter. Relative proportions of alcohols (6–15%) and carboxylic acids (9–
258 22% of EOM) vary in comparable ranges. Polar macromolecular compounds (i.e., resins; Table 2) are
259 present in highest proportions (> 50%).

260

261 4.2. Molecular composition of wood and associated lipids

262 As the presence of inherent detritic lignite is indicated based on ash yields, plant-wax lipids,
263 steroids and hopanoids may partly originate from detritic OM, and are only briefly discussed in this
264 paper. A detailed overview of the results from detritic lignite at identical sampling sites within the
265 seam is given by Bechtel et al. (2019). However, the isotopic compositions of *n*-alkanes are expected
266 to provide important supplementary information about the determining role of environmental factors

on $\delta^{13}\text{C}$ and $\delta^2\text{H}$ of lipids from land plants, as plant-wax alkanes have been most extensively studied for the reconstruction of climatic changes (Sachse et al., 2012). They are, therefore, discussed together with the results from resinous compounds and cellulose. Hopanoids are included as they may provide additional information about the environment of wood decomposition and the bacterial communities.

4.2.1. Plant wax derived lipids

The *n*-alkanes contents of the xylite samples vary from 75 to 440 $\mu\text{g/g}$ TOC (Table 2; Fig 3c). The *n*-alkane concentrations of woody macrofossils are unrelated to differences in lithotype within the lignite sections (Fig. 3). Long-chain *n*-alkanes ($>n\text{-C}_{27}$; Fig. 5a) with a marked predominance of odd carbon numbered homologues are present in highest abundances, consistent with their origin from plant-wax OM and the immature character of OM (Eglinton and Hamilton, 1967; Cranwell, 1977).

The long-chain ($> \text{C}_{23}$) odd-numbered *n*-alkan-2-ones are relatively abundant in the ketones fractions (F2) and occur together with polycyclic aromatic and polar terpenoids (Fig. 5b). The 6,10,14-trimethyl-pentadecan-2-one is present in high abundances and is suggested to represent a degradation product of phytol (Fig. 5b).

The alcohol fractions (F3) of the samples are dominated by *n*-alkanols in the $\text{C}_{14}\text{--C}_{30}$ carbon number range (Fig. 5c). Predominant are the even-numbered long-chain *n*-alkanols ($> \text{C}_{22}$), originating from plant cuticular waxes (Püttmann and Bracke, 1995; Ficken et al., 2000).

Even-numbered saturated fatty acids (*n*-FAs) with maxima at C_{24} and C_{26} , respectively, predominate in all xylite samples (Fig. 5d). They are characteristic constituents of leaf epicuticular waxes (Eglinton and Hamilton, 1967). Beside of hopanoids, microbial activity during gelification of the woody macrofossils is reflected by low relative abundances of branched-chain FAs ($\text{C}_{16:1}$ and $\text{C}_{18:1}$; Fig. 5d) (Volkman et al., 1980; Kaneda, 1991).

4.2.2. Steroids, hopanoids

The C_{29} (Δ^4 , Δ^5)-sterenes and C_{29} diaster-13(17)-enes were found in low concentrations (4.1–48.9 $\mu\text{g/g}$ TOC, Table 2). In contrast, β -sitosterol, campesterol, stigmastanol (Fig. 5c), and minor cholesterol (all

as TMS ethers) are present in the alcohol fractions (F3) of several xylites in high abundances (sum of sterols plus stanols > 100 µg/g TOC; Table 2; Fig. 3c). The predominance of C₂₉ steroids in the lipids is consistent with their origin from land plant OM (Volkman, 1986).

Hopanoids are found in elevated concentrations in the extracts of the xylites (Table 2; Fig. 3c). The 17 α ,21 β (H)- and 17 β ,21 β (H)-type hopanes from C₂₇ to C₃₁ were identified. The C₂₈ hopanes are missing, and the 17 α ,21 β (H)-C₃₁ hopane (22R) predominates by far (Fig. 5a). In addition to the hopanes, the C₂₇ and C₃₀ hop-17(21)-enes are present. All samples show low $\beta\beta/(\alpha\beta + \beta\beta)$ ratios (0.06–0.22) of the C₃₁ hopanes (Table 2; Fig. 5a). The D-ring monoaromatic hopanoid occurs in all xylite samples (Philp, 1985). The C₃₂ $\beta\beta$ -hopanol (TMS) is present in the alcohol fractions, and C₃₁ to C₃₂ $\beta\beta$ - and $\alpha\beta$ -hopanoic acids (TMS) were identified in the carboxylic acid fractions (FA) in variable abundances (8.8–83.2 µg/g TOC; Figs. 5c, d). Highest concentrations of hopanoids (> 100 µg/g TOC) were found in xylites from the Józwini IIB mine (Table 2; Fig. 3c).

306

4.2.3. Sesquiterpenoids, diterpenoids, non-hopanoid triterpenoids

The sesquiterpenoids consist of cadinenes, curcumene, cuparene and cadalene (3.4–91.5 µg/g TOC) in the hydrocarbon fractions (Grantham and Douglas, 1980; Simoneit and Mazurek, 1982). Cadaleane predominates by far (Fig. 5a). Major constituents of the hydrocarbons are abietane, isopimarane, pimarane, and phyllocladane type diterpenoids. Saturated diterpenoids include, isonorpimarane, norpimarane, norabietane, pimarane, abietane, and 16 α (H)-phyllocladane (Hagemann and Hollerbach, 1979; Noble et al., 1985; Philp, 1985; Fig. 5a). Pimarane, isonorpimarane, and norpimarane are present in highest abundances in most samples. Aromatic diterpenoids (e.g., dehydroabietane, 18-norabietatriene, tetrahydroretene, simonellite, and retene; Philp, 1985) were identified in the hydrocarbons (F1) and partly the ketones (F2) fractions (Figs. 5a, b). Ferruginol and dehydroferruginol (Otto et al., 1997) are present in the ketones fractions (Fig. 5b) of all samples. Furthermore, labdan-15-oic, isopimaric, and abietic acids (as TMS esters; Otto and Simoneit, 2002) were identified in the carboxylic acids fractions (Fig. 5d). Total concentrations of diterpenoids vary

320 between 148 and 1698 $\mu\text{g/g}$ TOC (Table 2). High concentrations of diterpenoids indicate abundant
321 resinous organic matter in the fossil wood fragments (Fig. 3d).

322 In most xylites, the following oleanane, ursane, and lupane type triterpenoids were identified in
323 the hydrocarbon fractions of xylites: *des*-A-oleanenes, *des*-A-lupane, olean-12-ene, olean-13(18)-ene,
324 and urs-12-ene. They are present in very low concentrations between 3.1 and 24.7 $\mu\text{g/g}$ TOC (ten
325 Haven et al., 1992; Logan and Eglinton, 1994; Philp, 1985; Rullkötter et al., 1994). The aromatic
326 triterpenoid hydrocarbons contain of 24,25-dinoroleana-1,3,5(10),12-tetraene (Fig. 5a), 24,25-
327 dinoroleana-1,3,5(10)-triene, 24,25-dinorlupa-1,3,5(10)-triene (Spyckerelle et al., 1977; Wakeham et
328 al., 1980; Wolff et al., 1989), as well as tetramethyl-octahydro-picenes (Fig. 5b) and trimethyl-
329 tetrahydro-picenes (LaFlamme and Hites, 1979; Wakeham et al., 1980). In the ketones (F2) and
330 alcohol fractions (F3), respectively, friedelin, β - and α -amyrin, as well as lupeol were identified, (Fig.
331 5b, c). Total concentrations of non-hopanoid triterpenoids (17–106 $\mu\text{g/g}$ TOC) are low compared to
332 the contents of diterpenoids (Table 2; Fig., 3d).

333

334 4.3. Stable isotope composition of xylites and lipids

335 The $\delta^{13}\text{C}$ values of the xylites (TOC) vary between -23.7 and -26.6‰ (Table 1; Fig. 6a). The
336 average carbon isotopic composition ($\delta^{13}\text{C} = -25.0\text{‰}$) is nearly identical as reported for xylites of the
337 Lubstów deposit (mean $\delta^{13}\text{C}$ of -24.5‰ ; Bechtel et al., 2007). The carbon isotopic composition also
338 varies in comparable ranges as obtained from detritic lignite samples from identical sections of the
339 First Lusatian seam in the Konin Basin (-24.9 to -26.2‰ ; Bechtel et al., 2019). Carbon isotope ratios
340 of extracted cellulose are in the range from -19.9 to -22.7‰ (Table 1; Fig 6a). On average $\delta^{13}\text{C}$
341 cellulose is enriched by about 3.6‰ with respect to $\delta^{13}\text{C}$ of xylites.

342 The odd numbered C_{27} to C_{31} *n*-alkanes yielded $\delta^{13}\text{C}$ values between -29.0 and -31.5‰ (Table 3)
343 as usually obtained from C_3 plants (O'Leary, 1981). As previously found in several lignite and coal
344 samples (e.g., Collister et al., 1994; Huang et al., 1995), a general trend of slightly decreasing $\delta^{13}\text{C}$

values with increasing carbon number is observed (Fig. 6b). The hydrogen isotopic compositions of these *n*-alkanes are in the range of −162 to −174‰ (Table 4; Fig. 6d).

The $\delta^{13}\text{C}$ values of norabietane, pimarane and 16 α (H)-phyllocladane vary between −24.2 and −26.5‰, and are about 4 to 5‰ heavier than those of the *n*-alkanes (Table 3; Fig. 6c). Comparable data have been reported for coals from the Liaohe Basin, China (Tuo et al., 2003). Aromatic diterpenoids (e.g., dehydroabietane, simonellite) show up to 1‰ higher $\delta^{13}\text{C}$ (−23.8 to −25.1‰) as saturated diterpenoids (Table 3), in agreement with the results of previous studies (Đoković et al., 2018). Gymnosperm-derived diterpenoids are depleted in ^2H compared to long-chain *n*-alkanes (−231 to −294 ‰; Table 4; Fig. 6e). Pimarane-type diterpenoids are characterised by lowest $\delta^2\text{H}$ values (Table 5).

The isotopic composition ($\delta^{13}\text{C}$) of the $\alpha\beta$ -C₃₁ hopane (22R) fall within the range of −25.6 to −27.9‰; Table 3). Slightly lower $\delta^{13}\text{C}$ (−26.6 to −28.6‰) have been obtained from the $\beta\beta$ -C₃₁ hopane. In contrast, the $\delta^{13}\text{C}$ values of the hop-17(21)-ene vary between −29.3 and −34.4‰ (Table 3).

5. Discussion

5.1. Chemotaxonomy of xylites

Swamp forest taxa in the Konin lignite include *Taxodium*, *Glyptostrobus*, and *Nyssa*, whereas pollen elements of *Pinus*, *Sequoia*, *Betula*, *Fagus*, *Quercus* and *Ulmus* are considered as are derived from dry forest surrounding the swamps (Sadowska and Giza, 1991; Piwocki and Ziemińska-Tworzydło, 1997; Kasiński and Słodkowska, 2016; Worobiec et al., 2020).

The frequency abundances of different compound classes of terpenoids in the xylite extracts are shown in Fig. 7. Pimarane, abietane and phyllocladane type diterpenoids predominate by far. Ferruginol and dehydroferruginol are present in variable abundances in the xylites (Fig. 7). While diterpenoids have been considered as markers for gymnosperms (i.e., conifers; Otto and Wilde, 2001), oleanane, ursane and lupane type triterpenoids have been reported to occur in angiosperms (Karrer et al., 1977; Sukh Dev, 1989). The percentages of the summed diterpenoids relative to total terpenoids range from 74–99% ((di-/(di- + tri-)terpenoid ratios > 0.73; ratios are based on the sum of

372 concentrations of non-polar and polar compounds) and, thus, argue for gymnosperms (i.e., conifers) as
373 sources of our sampled wood fragments (Table 2; Fig. 3e). This is consistent with previous data of
374 terpenoid hydrocarbon ratios from xylites of the Second Lusatian lignite seam (Bechtel et al., 2007;
375 Fabiańska and Kurkiewicz, 2013).

376 As only pieces from single larger xylites have been collected, they should contain the lipids
377 characteristic for either gymnosperm or angiosperm wood. However, impurities from inherent detritic
378 lignite are most likely responsible for the contribution of triterpenoids, as indicated by a negative
379 relationship between ash yields and di-/((di- + tri-)terpenoid ratios (Fig. 8). This implies that the non-
380 specific lipids (plant-wax constituents, steroids, hopanoids) may reflect mixtures from various sources
381 (i.e., wood and detritic lignite).

382 The relative abundances of terpenoid biomarkers from xylites and detritic lignite differ
383 significantly (Fig. 7; Fig. 8 in Bechtel et al., 2019). The detritus samples contain high amounts of
384 triterpenoids of angiosperm origin, while diterpenoids predominate by far in the extracts from xylites.
385 The results imply different floral assemblages contributing to detritic lignite and the sole occurrence of
386 conifer wood in xylites, respectively. The data argue for the selective preservation of conifer wood in
387 the mires.

388 The phenolic abietane ferruginol is present in the extracts of most conifer families, especially in
389 species of Cupressaceae, and Podocarpaceae, but seems to be absent in Pinaceae (Otto and Wilde,
390 2001). Phyllocladanes have been also described to occur in different conifer families; only in Pinaceae,
391 phyllocladanes have not been found. Abietane type diterpenoids in the geosphere are considered to be
392 derived from abietic acid, preferably found in Pinaceae, or from phenolic derivatives (i.e., ferruginol;
393 Otto et al., 1997). Based on palynological and biomarker data from Pliocene lignite deposits of the
394 Yunnan Province (China), abietane, pimarane, and isopimarane have been suggested as markers for
395 Pinaceae (Liu et al., 2018). Considering the age of the Polish lignite, the paleobotanical data from
396 lignites of the Konin Basin, and the terpenoids discussed above, xylites could, thus, more specifically
397 be interpreted as wood remains of species of the coniferales families Cupressaceae, and/or Pinaceae

398 (Otto and Wilde, 2001; Stefanova et al., 2002). Again, this is in accordance with our previous study on
399 xylites from the Lubstów deposit (Bechtel et al., 2007).

400 Diterpenoid composition of detritic lignite (Fig. 8, Bechtel et al., 2019) and xylites (Fig. 7) are
401 comparable showing varying abundances of phyllocladane-, abietane-, pimarane-type diterpenoids and
402 ferruginol plus dehydroferruginol, arguing for their origin from species of Cupressaceae and Pinaceae
403 families. However, the presence of phyllocladane type diterpenoids, ferruginol and cuparene in all
404 samples taken from individual xylites argue against Pinaceae and for Cupressaceae as precursor plants
405 of fossil wood remains (Grantham and Douglas, 1980; Otto and Wilde, 2001). The sole presence of
406 woody fragments from conifers (most probably Cupressaceae) may also be due to their higher-decay
407 resistance compared to angiosperms (Bechtel et al., 2008). Fossil wood from Pinaceae may have not
408 been found due to their occurrence in dryer habitats (Kasiński and Słodkowska, 2016; Worobiec et al.,
409 2020). Selective alteration and degradation of terpenoids during diagenesis must be considered
410 (Diefendorf et al., 2015), but seem to be of minor importance based on low to moderate extent of
411 gelification of xylites and the low maturity of OM.

412

413 5.2. Environment and mechanisms of wood decomposition

414 Based on low sulfur contents (< 2 wt%) of the detritic lignite samples (Bechtel et al., 2019) and
415 the investigated xylites (Table 1), an evolution of the lignite seam under freshwater conditions is
416 suggested. Previous palynological and sedimentological analyses provided further evidence for peat
417 formation in the overbank depositional environment typical of backswamp areas (Sadowska and Giża,
418 1991; Piwocki and Ziemińska-Tworzydło, 1997; Widera, 2016).

419 Information about wood decomposition can be derived from hopanoid composition, gelification
420 extent and cellulose yield of the woody macrofossils. Cellulose yields of the xylites between 1.6 and
421 24.2 wt% argue for advanced to high degradation states. Cellulose decomposition has been attributed
422 to the activities of fungi (Benner et al., 1987) under oxic conditions. Nevertheless, bacterial
423 communities have been suggested to likewise contribute to wood decomposition under aerobic and
424 anaerobic conditions (Benner et al., 1984; Bechtel et al., 2007). The enhanced contents of hopanoids

obtained from xylites characterized by low cellulose yields confirm such a bacterial component for our samples (Figs. 3, 9). Larger contributions from impurities with larger decomposition state of the wood could result in a comparable relationship, but can be excluded based on the lack of relationship between hopanoid contents and ash yields. Likewise, increased impurities from detritic lignite, containing decomposed fragments from angiosperm wood, may result in the depletion of cellulose within the xylites. However, hopanoid contents of detritic lignite and xylites vary within comparable ranges (Bechtel et al., 2019) and would not explain the increased hopanoid contents in low cellulose xylites.

The hopane derivatives and hop-17(21)-ene found in the xylites are most likely derived from tetrafunctionalized bacteriohopanepolyols and diplopterol, respectively (Brassell et al., 1980; Ourisson et al., 1979; Rohmer et al., 1992; Inglis et al., 2018). These compounds have been identified in bacteria, as well as in some mosses, ferns, lichens and fungi (Bottari et al., 1972; Ourisson et al., 1979; Rohmer and Bisseret, 1994). The results of recent studies provided evidence that in peatlands $\alpha\beta$ -hopanoids are acid-catalyzed degradation products (Inglis et al., 2018). Therefore, the $\beta\beta/(\alpha\beta + \beta\beta)$ hopane ratio has been used to reconstruct the pH conditions in peat-forming environments. Very low $\beta\beta/(\alpha\beta + \beta\beta)$ ratios (0.06–0.22 $\mu\text{g/g}$ TOC ; Table 2) found in the extracts of the xylite fragments, their moderate hopanoid concentrations (34–111 $\mu\text{g/g}$ TOC) and low sulfur contents (average value of 1.2 wt%) point towards wood decomposition in the peat under acidic conditions (Casagrande, 1987; Inglis et al., 2018). The $\beta\beta/(\alpha\beta + \beta\beta)$ ratios are similar to the data obtained from detritic lignite samples (between 0.07 and 0.17 $\mu\text{g/g}$ TOC; Bechtel et al., 2019).

5.3. Factors influencing carbon isotopic composition of fossil wood and plant lipids

The positive relationship between cellulose content and $\delta^{13}\text{C}$ values of xylites (TOC; Table 1) indicates the progressive depletion of wood in ^{13}C during cellulose decomposition (Fig. 10a), as already reported from previous studies (Benner et al., 1987; Lücke et al., 1999; Bechtel et al., 2007). Our $\delta^{13}\text{C}$ data of xylite OM and cellulose (Table 1; Fig. 6a) are consistent with the suggested origin of

451 xylites from woody conifers, as cellulose from angiosperm wood has been reported to be ^{13}C depleted
452 relative to conifer wood (Lücke et al., 1999). This is also indicated by their terpenoid biomarker
453 composition.

454 Measurements during artificial maturation of modern wood indicated that during decomposition
455 cellulose is only slightly depleted in ^{13}C ($< 0.3\text{‰}$ relative to untreated wood) in contrast to the whole
456 wood (Schleser et al., 1999). Consistent with these observations, no significant relationship exists
457 between $\delta^{13}\text{C}$ of extracted cellulose from the xylite samples and cellulose yields (Fig. 10a). Our data
458 show varying differences in $\delta^{13}\text{C}$ of xylites and extracted cellulose between 2.3 and 4.3‰ ($\Delta\delta^{13}\text{C} =$
459 $\delta^{13}\text{C}_{\text{xylite}} - \delta^{13}\text{C}_{\text{cellulose}}$) along the expected negative relation between $\Delta\delta^{13}\text{C}$ and cellulose yield (Fig.
460 10b). These isotopic differences are in general agreement with that obtained for Miocene taxodioid
461 Cupressaceae (former Taxodiaceae) wood from the Garzweiler seam in Germany (3.8‰; Lücke et al.,
462 1999) and with isotopic data from fossil wood and extracted cellulose (differences in $\delta^{13}\text{C}$ of 3.0 to
463 4.6‰) from the Second Lusatian lignite seam at the Lubstów deposit (Bechtel et al., 2007).

464 The isotopic composition ($\delta^{13}\text{C}$) of the $\alpha\beta\text{-C}_{31}$ hopane (22R) was found to be slightly depleted in
465 $\delta^{13}\text{C}$ (-25.6 to -27.9‰ ; Table 3) relative to wood OM (mean $\delta^{13}\text{C}$ of TOC of xylites -25.0‰ ; Table 3;
466 Fig. 6a). The results argue for a heterotrophic bacterial population. The $\delta^{13}\text{C}$ values of the $\beta\beta\text{-C}_{31}$
467 hopane (-26.6 to -28.6‰) are on average 1.2‰ lower as the values obtained from $\alpha\beta\text{-C}_{31}$ hopane. In
468 contrast, the C_{30} hop-17(21)-enes show ^{13}C -depleted isotopic composition (average $\delta^{13}\text{C}$ of -32.2‰ ;
469 Table 3). Overall, the results imply the contribution of various bacterial communities in the
470 decomposition of wood within the peat (Pancost et al., 2000, 2007; Mitrović et al., 2016). Due to
471 impurities from detritic lignite, the hopanoids could reflect the microbial activities using OM of
472 detritic lignite as substrates. Despite of similar $\delta^{13}\text{C}$ values of TOC of xylites and detritic lignite (-25.0
473 and -25.6‰ , respectively), significantly lower $\delta^{13}\text{C}$ of $\beta\beta\text{-C}_{31}$ hopane (-32.2 to -36.7‰) in the lignite
474 samples at identical sampling positions as the xylites (Bechtel et al., 2019) argue against this
475 possibility. More likely, slightly different microbial communities were involved in the decomposition
476 of OM of xylites (compared to detritic lignite).

The $\delta^{13}\text{C}$ of extracted cellulose, plant wax *n*-alkanes (C_{27} , C_{29} , C_{31}), and diterpenoids show minor, but more or less parallel, fluctuations with depth in all 3 profiles (Fig. 6b, c). Because of similar sources of wood macrofossils from conifers (e.g., most likely from Cupressaceae) inter-species variations on $\delta^{13}\text{C}$ of cellulose and resinous compounds should be neglectible. The parallel tendencies in $\delta^{13}\text{C}$ with depth may argue for variations in $\delta^{13}\text{C}$ of CO_2 available to the plants as one of the possible causes. However, $\delta^{13}\text{C}$ variations of 2.5‰ are within the range of variability observed in the plants within a habitat, and can be explained without invoking variations in $\delta^{13}\text{C}$ of CO_2 (Diefendorf et al. 2019; Inglis et al., 2019). Furthermore, the Mid-Miocene Climatic Optimum is characterized by minor variations in $\delta^{13}\text{C}$ values of atmospheric CO_2 (around -5‰ ; Zachos et al., 2001; Tipple et al., 2010), Therefore, the obtained differences in $\delta^{13}\text{C}$ are interpreted to have been caused by water availability to the plants due to the adjustment of stomatal aperture to minimize water loss (van Bergen and Poole, 2002; Jahren and Sternberg, 2008; Bechtel et al., 2008; Diefendorf and Freimuth, 2017; Diefendorf et al., 2019).

5.4. *H-isotopic composition of plant lipids and climate*

Paleobotanical data from the study area indicated humid conditions (mean annual precipitation in the range 820–1300 mm/year; Ivanow and Worobiec, 2017) and warm mean annual air temperatures (between 15.7–19.7 °C; Kasiński and Słodkowska, 2016; or between 15.7–18.0 °C; Worobiec et al., 2020) during the mid-Miocene Climatic Optimum. Following from this information we would expect only minor variations in the $\delta^2\text{H}$ values of meteoric water (Bowen, 2008) in the area of the Konin Basin during peat formation. Irrespective of that, variations in the extent of evapotranspiration, as well as biological factors, influence apparent fractionation and can lead to considerable fluctuations in $\delta^2\text{H}$ - of plant wax lipids (Sachse et al., 2006, 2012; Freimuth et al., 2017).

The $\delta^2\text{H}$ values of *n*-alkanes and diterpenoid biomarkers show variations up to 10‰ within the profiles (Table 4; Fig. 6d, e). Beside of the possible influence of minor climate variations, the low variability of $\delta^2\text{H}$ values of the *n*-alkanes from plant waxes and diterpenoids from wood resins could

also be caused by changes in water availability during the respective growth period of the trees, modifying apparent H-isotope fractionation through changes in stomatal aperture. This interpretation is supported by the positive relationships between $\delta^2\text{H}$ and $\delta^{13}\text{C}$ values of *n*-C₂₉, and between $\delta^2\text{H}$ of the *n*-C₂₉ alkane and $\delta^{13}\text{C}$ of extracted cellulose from the fossil wood fragments (Fig. 11a, b). The influence of different extents of degradation on the related isotopic patterns ($\delta^2\text{H}$ of *n*-C₂₉ and $\delta^{13}\text{C}$ of cellulose) can be neglected, as cellulose decomposition did not result in a significant shift in $\delta^{13}\text{C}$ of cellulose (see discussion in Chapter 5.3). Furthermore, $\delta^2\text{H}$ of plant-wax *n*-alkanes are considered to be only influenced during catagenesis over geological time scales (Schimmelmann et al., 2006).

Significant differences in $\delta^2\text{H}$ are seen between diterpenoids and *n*-alkanes, as well as between diterpenoids of different structural types (Table 4; Fig. 6d, e). This can be explained by differences in isotopic fractionation during lipid biosynthesis, as *n*-alkyl lipids associated with the acetogenic pathway were reported to be less depleted in ^2H as the diterpenoids derived from the non-mevalonic acid pathway (Chikaraishi et al., 2004). Further isotopic fractionation during lipid biosynthesis occurs during various biochemical reactions, such as decarboxylation of pyruvate to form acetate and hydrogenation with NADPH, respectively (Chikaraishi et al., 2004). However, pimarane-type diterpenoids are characterized by very low $\delta^2\text{H}$ values (around -280‰; Fig. 6e) compared to the abietane- and phyllocladane-type compounds. The results are in agreement with previous data (Tuo et al., 2006) and could be explained by different sources of hydrogen and/or different biosynthetic pathways during formation of pimarane-type diterpenoids.

6. Conclusions

Woody macrofossils (xylites) from the First Lusatian lignite seam are characterized by minor extents of gelification, but elevated to high cellulose decomposition. Based on terpenoid biomarker composition and $\delta^{13}\text{C}$ values of extracted cellulose, the xylites are indicated as fragments of fossil wood from conifers. Xylites most likely represent species of Cupressaceae, in agreement with available paleobotanical data. Impurities from inherent detritic lignite are responsible for minor

529 contributions of angiosperm-derived triterpenoids in the OM of xylites, as lipids from detritic lignite
530 have been found to contain triterpenoid biomarkers in high abundances. Similarly, plant-wax lipids,
531 steroids and hopanoids may be partly derived from OM of detritic lignite. The fact that only woody
532 fragments of conifers have been found is explained by their higher-decay resistance compared to
533 angiosperms. This interpretation is supported by the angiosperm-dominated terpenoid biomarker
534 composition found in detritic lignites from the same mines during a previous study (Bechtel et al.,
535 2019). Low $\beta\beta/(\beta\beta+\alpha\beta)$ hopane ratios and low sulfur contents imply freshwater conditions and
536 bacterial activity under acidic pH during wood decomposition within topogenous mires. As indicated
537 by different $\delta^{13}\text{C}$ values of $\beta\beta\text{-C}_{31}$ hopane (22R), slightly different microbial communities were
538 involved in decomposition of OM of fossil wood and detritic lignite respectively.

539 Advanced cellulose decomposition removing preferentially the ^{13}C -enriched compounds from
540 xylites is indicated to result in neglectable influence on $\delta^{13}\text{C}$ of cellulose, arguing for their applicability
541 in environmental reconstructions. The significant differences in $\delta^2\text{H}$ between diterpenoids and *n*-
542 alkanes, as well as between diterpenoids of different structural types are explained by differences in
543 isotopic fractionation during lipid biosynthesis. The positive relationships between $\delta^2\text{H}$ and $\delta^{13}\text{C}$ of *n*-
544 C_{29} , as well as between $\delta^2\text{H}$ of the C_{29} *n*-alkane and $\delta^{13}\text{C}$ of cellulose, imply variations in water
545 availability and, thus, stomatal aperture, as the most probable cause for the obtained minor variations
546 in isotopic composition of plant lipids and cellulose.

547 The results supplement the information obtained during our previous studies (Bechtel et al., 2007,
548 2019), as terpenoid biomarker composition in lignite is shown to be influenced by plant decomposition
549 and differences in ecology between the habitats. Stable isotope data of cellulose and plant biomarkers
550 of fossil wood are able to provide insights into environmental changes during peat accumulation.

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560

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798

800 **Captions of Figures**

801 **Fig. 1:** (a) Location of the studied lignite opencast mines in the Konin Basin (Poland); and lignite
 802 lithotypes, structural elements, and position of xylite samples in the profiles from the (b)
 803 Adamów, (c) Józwin IIB, and (d) Tomisławice opencast mines.

804 **Fig. 2:** Representative photomicrographs of wood fragments (reflected light; oil immersion): (a)
 805 Textinite in ungelified sample AX-01, (b) same field as in (a) (blue light irradiation), (c)
 806 textinite/textoulminite with a phlobaphinite (P) in weakly gelified sample TX-10, (d) same
 807 field as in (c) (blue light irradiation), (e) textoulminite/ulminite in sample JX-3 showing
 808 advanced gelification, (f) same field as in (c) (blue light irradiation).

809 **Fig. 3:** Sampling position and variation of concentrations and concentration ratios of lipids within the
 810 xylites from the First Lusatian lignite seam at the Adamów, the Józwin IIB, and the
 811 Tomisławice mines.

812 **Fig. 4:** Cross-correlation between extractable organic matter (EOM) and cellulose yields.

813 **Fig. 5:** Total ion current chromatograms of the (a) hydrocarbon fraction, (b) the ketone fraction, (c)
 814 the alcohol fraction, and (d) the carboxylic acids obtained from the xylite sample AX-09, Std.
 815 = Internal Standard (squalane (F1), 1,1'-binaphthyl (F2), 1-nonadecanol (F3), nonadecanoic
 816 acid (FA), respectively).

817 **Fig. 6:** Depth trends of carbon isotopic compositions of (a) TOC and cellulose , (b) C₂₇, C₂₉, and C₃₁
 818 *n*-alkanes, and (c) diterpenoids, and of hydrogen isotopic compositions of (d) C₂₇, C₂₉, and
 819 C₃₁ *n*-alkanes, and (e) diterpenoids within the studied profiles from the Adamów, Józwin IIB,
 820 and Tomisławice mines.

821 **Fig. 7:** Relative abundances of terpenoid biomarkers in the lipid fractions of the xylites.

822 **Fig. 8:** Cross-correlation between the di-/(di- + tri-)terpenoids ratios and ash yields.

823 **Fig. 9:** Relationship between the concentrations of hopanoids and the cellulose yields of the xylites.

824 **Fig. 10:** Correlations of (a) $\delta^{13}\text{C}$ of cellulose and TOC of xylites, respectively, versus cellulose yields,
825 and of (b) carbon isotope differences between cellulose and TOC of xylites versus cellulose
826 yields.

827 **Fig. 11:** Relationships between (a) $\delta^{13}\text{C}$ and $\delta^2\text{H}$ of the C_{29} *n*-alkanes, and between (b) $\delta^{13}\text{C}$ of
828 cellulose and $\delta^2\text{H}$ of *n*- C_{29} .

829

Research Highlights

- Xylites are affected by weak gelification and advanced cellulose decomposition
- $\delta^{13}\text{C}$ of xylites reflect the extent of cellulose decomposition
- Xylites represent wood remains of the same species of conifers in the lignite
- Fluctuating $\delta^{13}\text{C}$ and $\delta^2\text{H}$ of lipids within the seam are caused by water availability

Table 1: Sample locations, maceral variety and fluorescence of telohuminite, bulk geochemical parameters, and extractable organic matter yields

Deposit	Sample	Altitude (m a.s.l.) ^e	Maceral variety	Fluorescence intensity	Ash	TOC ^a	TIC ^b	S ^c	$\delta^{13}\text{C}$ TOC (‰ ₀₀ , VPDB)	$\delta^{13}\text{C}$ Cellulose (‰ ₀₀ , VPDB)	Cellulose yield (wt%)	EOM ^d (mg/g TOC)
						(wt%) ^f						
Adamów	AX-01	61.7	Textinite	High	3.2	38.4	3.5	0.28	-25.3	-21.6	6.8	46.2
Adamów	AX-02	62.3			2.8	41.0	2.7	0.32	-24.7	-20.9	6.2	39.9
Adamów	AX-03	63.0	Textinite	High	4.1	39.3	2.4	0.27	-24.0	-19.9	6.3	54.4
Adamów	AX-04	63.8			2.6	41.8	3.0	0.29	-24.6	-21.3	15.0	19.3
Adamów	AX-05	64.3	Textinite	High	3.0	42.7	0.5	0.26	-25.6	-21.9	10.6	29.0
Adamów	AX-06	64.7			3.5	40.5	2.1	0.30	-25.2	-21.7	7.4	61.5
Adamów	AX-07	65.5	Textinite/textoul. ^g	High/moderate	9.5	37.9	3.8	1.80	-26.2	-22.5	5.8	59.4
Adamów	AX-08	66.1			4.1	34.0	0.7	4.28	-24.9	-21.9	13.3	26.4
Adamów	AX-09	66.8			7.7	45.0	2.0	1.60	-26.0	-22.1	5.9	47.3
Adamów	AX-10	67.6			2.4	43.6	2.0	0.36	-26.1	-22.7	9.1	35.0
Józwin IIB	JX-01	41.5			11.0	41.5	2.5	1.57	-24.4	-21.4	5.7	42.8
Józwin IIB	JX-02	42.3			8.4	36.9	3.3	1.38	-26.6	-22.4	1.6	58.9
Józwin IIB	JX-03	43.2	Textoul./ulminite	Moderate/weak	2.7	52.8	n.d. ^h	1.44	-24.3	-22.0	18.2	21.8
Józwin IIB	JX-04	44.3			6.2	43.1	3.5	1.49	-25.4	-21.0	4.8	64.6
Józwin IIB	JX-05	44.8	Textoul.	Moderate/weak	4.1	44.8	3.8	2.06	-25.5	-21.5	5.2	39.9
Józwin IIB	JX-06	45.9			9.9	48.2	0.4	4.10	-25.5	-21.5	3.7	38.3
Józwin IIB	JX-07	46.1	Textoul.	Moderate	5.6	43.8	3.0	3.22	-25.5	-21.9	3.7	52.9
Tomisławice	TX-01	53.1			17.6	32.5	2.8	2.54	-24.6	-20.4	5.9	35.6
Tomisławice	TX-02	54.2	Textinite/textoul.	High/moderate	2.7	53.6	n.d.	0.35	-24.6	-21.9	21.8	26.4
Tomisławice	TX-03	55.0			3.0	53.2	n.d.	0.33	-24.4	-20.9	16.2	29.9
Tomisławice	TX-04	56.2			3.9	48.7	n.d.	0.30	-24.9	-20.6	7.4	43.6
Tomisławice	TX-05	57.3			5.5	45.9	2.5	0.26	-26.1	-21.9	4.1	49.6
Tomisławice	TX-06	58.2	Textinite	High	3.8	47.9	n.d.	0.36	-23.8	-20.3	24.2	18.3
Tomisławice	TX-07	59.2			3.7	48.8	0.7	0.57	-23.8	-20.6	19.4	20.1
Tomisławice	TX-08	60.4	Textinite	High	3.9	45.7	n.d.	0.60	-23.8	-20.2	13.5	35.6
Tomisławice	TX-09	61.3			4.1	45.2	n.d.	0.76	-25.3	-22.1	18.1	29.0
Tomisławice	TX-10	62.0	Textinite/textoul.	High/moderate	4.2	46.5	n.d.	1.23	-23.7	-20.6	19.3	23.8

^a Total organic carbon, ^b Total inorganic carbon content, ^c Total sulphur content, ^d Extractable organic matter, ^e Meter above sea level, ^f Weight percent, ^g Textoulminite,^h not detectable

Table 2: Proportions of hydrocarbons + ketones, carboxylic acids, alcohols, and macromolecular substances (i.e. resins) relative to EOM, and concentrations and concentration ratios of compounds and compound groups within the EOM of lignite samples

Deposit	Sample	HCs ^a + Ketones	Acids	Alcohols	Resins	<i>n</i> -Alkanes	Steroids	Hopanoids	Diter- penoids	Triter- ^b penoids	$\beta\beta/(\beta\beta + \alpha\beta)$ C ₃₁ Hopanes	Di-/(Di- + Tri-) terpenoids ^c
(wt%, EOM)						(µg/g TOC)						
Adamów	AX-01	15.8	15.2	17.0	52	94	373	67	1698	17	0.06	0.99
Adamów	AX-02	11.9	10.8	14.7	63	102	159	69	630	65	0.08	0.91
Adamów	AX-03	11.3	9.4	12.3	67	243	344	84	741	36	0.07	0.95
Adamów	AX-04	9.6	13.2	10.5	67	144	190	41	281	24	0.06	0.92
Adamów	AX-05	8.5	11.9	14.6	65	125	222	55	153	19	0.12	0.89
Adamów	AX-06	11.7	8.3	9.2	71	262	120	74	917	45	0.07	0.95
Adamów	AX-07	10.9	6.5	11.1	71	440	53	108	466	84	0.07	0.85
Adamów	AX-08	8.4	12.1	15.7	64	75	209	73	235	30	0.06	0.89
Adamów	AX-09	14.4	18.7	20.3	47	383	298	66	1468	201	0.08	0.88
Adamów	AX-10	9.8	10.4	17.9	62	250	137	84	329	32	0.10	0.91
Józwin IIB	JX-01	5.1	12.4	22.3	60	258	47	69	148	47	0.09	0.76
Józwin IIB	JX-02	4.6	7.6	18.4	69	298	84	147	553	74	0.07	0.88
Józwin IIB	JX-03	9.9	9.1	14.5	67	93	104	45	948	56	0.06	0.94
Józwin IIB	JX-04	7.7	12.0	15.1	65	263	209	159	640	121	0.11	0.84
Józwin IIB	JX-05	5.3	7.7	10.8	76	85	367	133	513	86	0.09	0.86
Józwin IIB	JX-06	4.2	11.3	17.9	67	234	245	120	281	81	0.14	0.78
Józwin IIB	JX-07	6.9	13.8	16.7	63	76	127	85	596	53	0.11	0.92
Tomisławice	TX-01	5.0	10.4	9.3	75	232	104	69	169	58	0.22	0.74
Tomisławice	TX-02	5.3	13.5	15.2	66	221	191	42	331	49	0.13	0.87
Tomisławice	TX-03	4.9	7.9	21.1	66	289	176	56	622	82	0.16	0.88
Tomisławice	TX-04	7.6	8.5	13.5	70	99	262	75	765	95	0.15	0.89
Tomisławice	TX-05	9.0	6.6	10.8	74	166	74	95	481	90	0.13	0.84
Tomisławice	TX-06	6.2	10.9	16.6	66	218	230	63	623	106	0.16	0.85
Tomisławice	TX-07	7.3	9.2	19.2	64	176	111	56	462	49	0.12	0.90
Tomisławice	TX-08	9.2	10.7	22.3	58	82	113	84	227	36	0.13	0.86
Tomisławice	TX-09	8.4	7.6	20.7	63	77	106	74	338	42	0.14	0.89
Tomisławice	TX-10	6.9	8.9	17.6	67	22	117	37	297	22	0.09	0.93

^a Hydrocarbons, ^b Angiosperm-derived triterpenoids, ^c Ratios of diterpenoids to the sum of di- plus triterpenoids

Table 3: Carbon isotopic composition of plant lipids and hopanoids

Deposit	Sample	<i>n</i> -C ₂₇	<i>n</i> -C ₂₉	<i>n</i> -C ₃₁	Nor-abietane	Pimarane	α -Phyllo-cladane	$\alpha\beta$ -C ₃₁ Hopane (22R)	$\beta\beta$ -C ₃₁ Hopane	Hop-17(21)-ene
$\delta^{13}\text{C}$ (‰, VPDB)										
Adamów	AX-01	-29.8	-30.6	-30.9	-24.9	n.d.	n.d.	-26.6	n.d.	n.d.
Adamów	AX-02	-30.0	-30.3	-30.5	n.d.	n.d.	-25.2	-27.2	n.d.	n.d.
Adamów	AX-03	-29.1	-29.6	n.d.	n.d.	-26.2	-24.8	-27.9	n.d.	n.d.
Adamów	AX-04	-29.9	-30.2	-30.0	n.d.	n.d.	-25.4	-26.8	n.d.	n.d.
Adamów	AX-05	-30.6	-30.9	-30.5	n.d.	n.d.	-25.7	-25.6	n.d.	n.d.
Adamów	AX-06	-29.6	-29.9	n.d.	-24.8	n.d.	-25.4	-26.5	n.d.	n.d.
Adamów	AX-07	-30.5	-31.3	-30.8	-24.8	-26.3	-25.5	-27.4	n.d.	n.d.
Adamów	AX-08	-30.0	-30.6	-29.8	n.d.	-26.3	-25.1	-25.8	n.d.	-34.2
Adamów	AX-09	-30.6	-31.0	-30.9	-25.1	-26.5	-25.6	-26.5	n.d.	-30.7
Adamów	AX-10	-29.8	-30.9	-30.7	n.d.	n.d.	-25.3	-26.4	n.d.	n.d.
Józwin IIB	JX-01	-30.5	-30.8	-30.8	-24.5	-25.8	-25.1	-25.6	-27.9	-32.3
Józwin IIB	JX-02	-30.9	-31.4	-31.1	n.d.	-26.3	-25.7	-26.2	-28.6	-34.2
Józwin IIB	JX-03	n.d. ^a	n.d.	n.d.	-24.9	-25.9	-25.2	-25.7	n.d.	n.d.
Józwin IIB	JX-04	-30.7	-31.1	-30.8	-25.0	-26.1	-25.4	-26.1	-27.5	-31.5
Józwin IIB	JX-05	n.d.	n.d.	n.d.	-24.8	n.d.	n.d.	-25.8	-26.9	-29.5
Józwin IIB	JX-06	-29.7	-30.4	-30.9	-24.7	-26.2	-25.3	-26.2	-28.3	-30.7
Józwin IIB	JX-07	n.d.	n.d.	n.d.	-24.6	-25.8	n.d.	-25.7	n.d.	-33.9
Tomisławice	TX-01	-29.6	-30.1	-30.5	n.d.	-25.9	-25.2	-26.1	n.d.	n.d.
Tomisławice	TX-02	-30.7	-31.2	-30.8	-25.1	-26.4	-25.4	-25.6	-26.9	-34.4
Tomisławice	TX-03	-30.1	-30.2	-30.4	-24.7	-26.0	-25.1	-26.3	-27.3	-33.6
Tomisławice	TX-04	-29.8	-30.1	n.d.	-24.6	n.d.	-25.2	-25.7	-27.4	n.d.
Tomisławice	TX-05	-30.9	-31.5	-31.2	-24.7	-25.9	-25.3	-26.4	n.d.	-29.3
Tomisławice	TX-06	-30.2	-30.0	-30.5	-24.4	-25.7	-25.0	-25.8	-26.6	-33.1
Tomisławice	TX-07	-30.5	-30.6	-30.5	-24.7	-26.0	-25.4	-26.0	-27.1	-31.7
Tomisławice	TX-08	-29.7	-30.5	-30.4	-24.5	n.d.	-25.1	-25.6	-26.9	-32.8
Tomisławice	TX-09	-30.6	-31.4	-30.7	-24.7	-26.1	-25.5	-26.1	-27.2	-30.3
Tomisławice	TX-10	n.d.	n.d.	n.d.	-24.2	-25.9	-25.3	-26.6	-27.4	-32.7

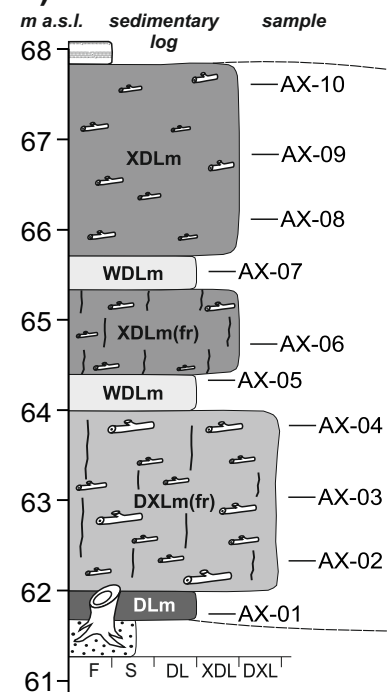
^a not detectable due to low peak intensities

Table 4: Hydrogen isotopic composition of plant lipids and hopanoids

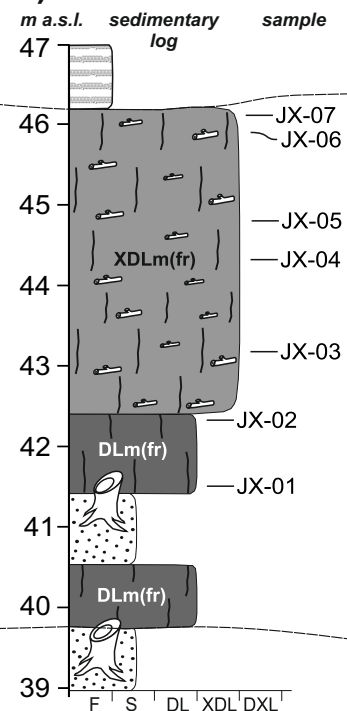
Deposit	Sample	<i>n</i> -C ₂₇	<i>n</i> -C ₂₉	<i>n</i> -C ₃₁	Nor-abietane	Pimarane	α -Phyllo-cladane	$\alpha\beta$ -C ₃₁ Hopane (22R)	Hop-17(21)-ene
$\delta^2\text{H}$ (‰, VSMOW)									
Adamów	AX-01	-170	-172	-174	-241	n.d.	n.d.	-153	n.d.
Adamów	AX-02	-168	-171	n.d.	n.d.	n.d.	-236	-156	n.d.
Adamów	AX-03	-172	-167	n.d.	n.d.	-275	-231	-157	n.d.
Adamów	AX-04	-166	-170	n.d.	n.d.	n.d.	-244	-154	n.d.
Adamów	AX-05	-171	-169	-173	n.d.	n.d.	n.d.	-147	n.d.
Adamów	AX-06	-169	-170	n.d.	-244	n.d.	-233	-159	n.d.
Adamów	AX-07	-173	-174	n.d.	-249	-289	-241	-154	n.d.
Adamów	AX-08	-169	-171	n.d.	n.d.	-282	n.d.	-160	-212
Adamów	AX-09	-168	-173	-169	-256	-290	-238	-145	-206
Adamów	AX-10	-168	-172	n.d.	n.d.	n.d.	-240	-161	n.d.
Józwin IIB	JX-01	-165	-169	-172	-259	-279	n.d.	-160	-230
Józwin IIB	JX-02	-169	-173	-173	n.d.	-289	-252	-146	-224
Józwin IIB	JX-03	n.d. ^a	n.d.	n.d.	-251	-279	-242	-159	n.d.
Józwin IIB	JX-04	-168	-171	n.d.	n.d.	-282	-248	-170	-209
Józwin IIB	JX-05	n.d.	n.d.	n.d.	-255	n.d.	n.d.	-160	-232
Józwin IIB	JX-06	-167	-168	-172	-246	-283	-236	-157	-198
Józwin IIB	JX-07	n.d.	n.d.	n.d.	n.d.	-275	n.d.	-174	-202
Tomisławice	TX-01	-162	-167	n.d.	n.d.	-276	-246	-151	n.d.
Tomisławice	TX-02	-168	-172	-174	-251	-290	-251	-175	-224
Tomisławice	TX-03	-167	-168	-172	n.d.	-275	-244	-167	-203
Tomisławice	TX-04	-167	-168	-173	-264	n.d.	-247	-162	n.d.
Tomisławice	TX-05	-170	-172	n.d.	n.d.	-294	-252	-181	-227
Tomisławice	TX-06	-166	-167	n.d.	n.d.	-286	n.d.	-159	-206
Tomisławice	TX-07	-168	-171	n.d.	-257	-289	-245	-167	-199
Tomisławice	TX-08	-168	-169	n.d.	-253	n.d.	-237	-159	-222
Tomisławice	TX-09	-166	-170	-172	-248	-279	-238	-143	-211
Tomisławice	TX-10	n.d.	n.d.	n.d.	-253	-282	n.d.	-157	-229

^a not detectable due to low peak intensities

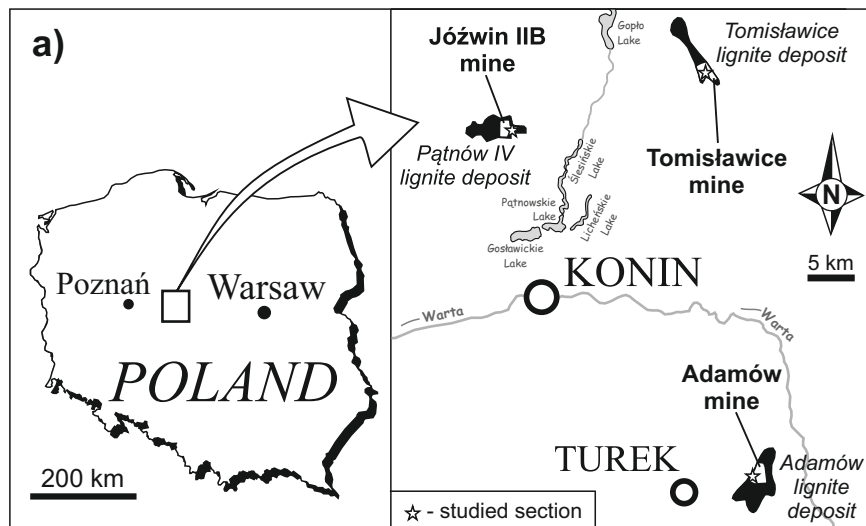
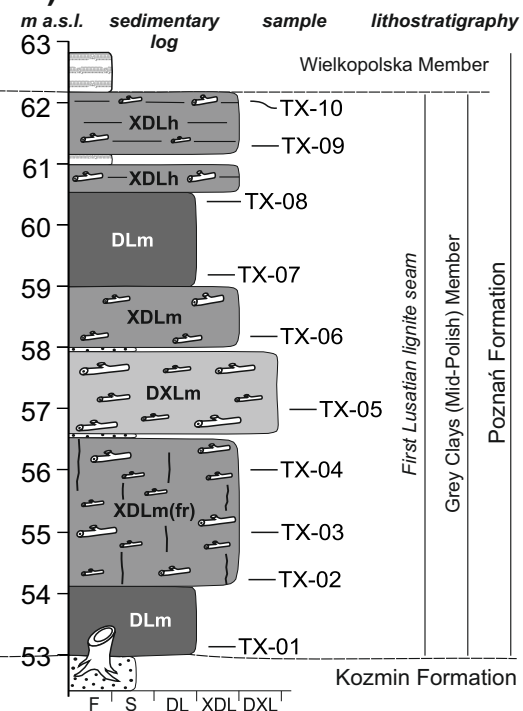
b) Adamów mine



c) Józwin IIB mine



d) Tomisławice mine



- xylites (fossilised wood) } - fractures (cleats)
— horizontal stratification
F - fines (silt and clay), S - sand — TX-03 - sample position
Texture of lignite lithotypes: DL - detritic, XDL - xylodetritic, DXL - detroxylitic,
WDL - weathered
Structure of lignite lithotypes: m - massive, h - horizontal stratification,
fr - fractured

Fig. 1

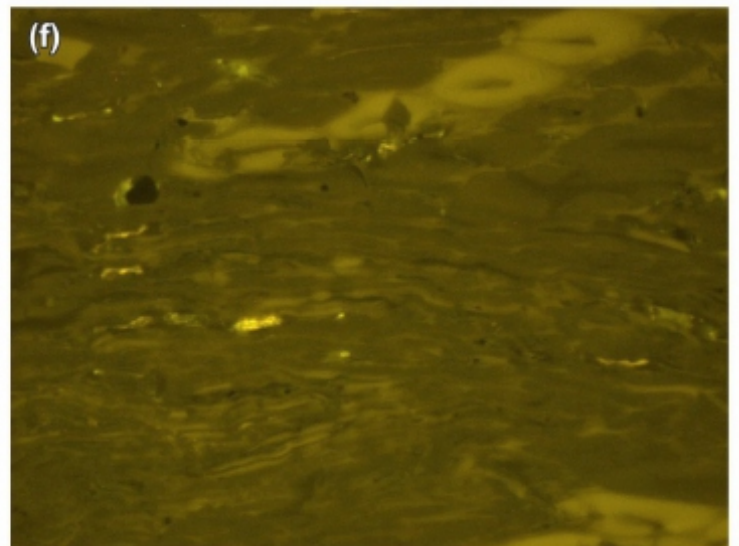
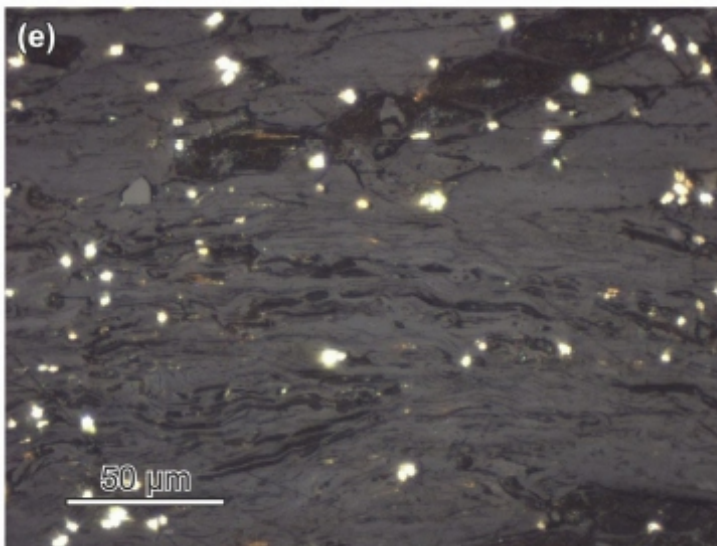
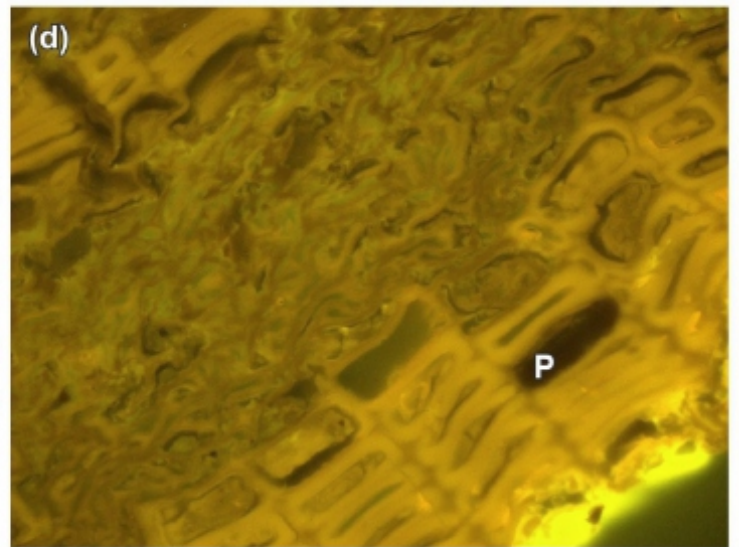
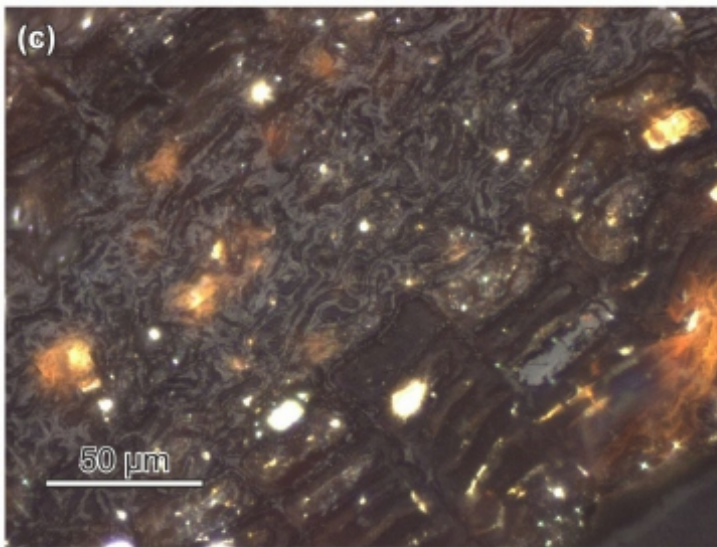
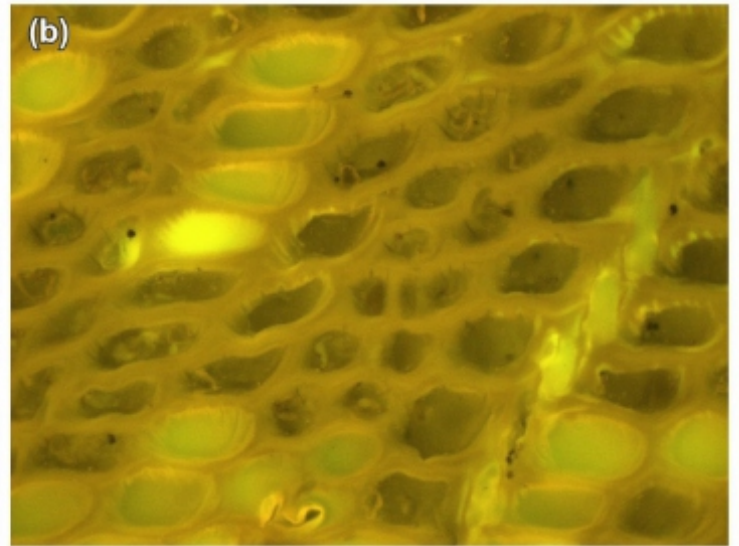
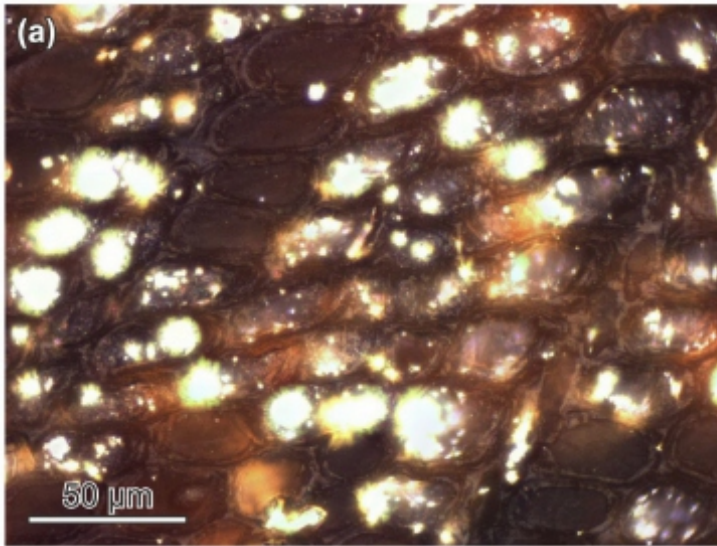
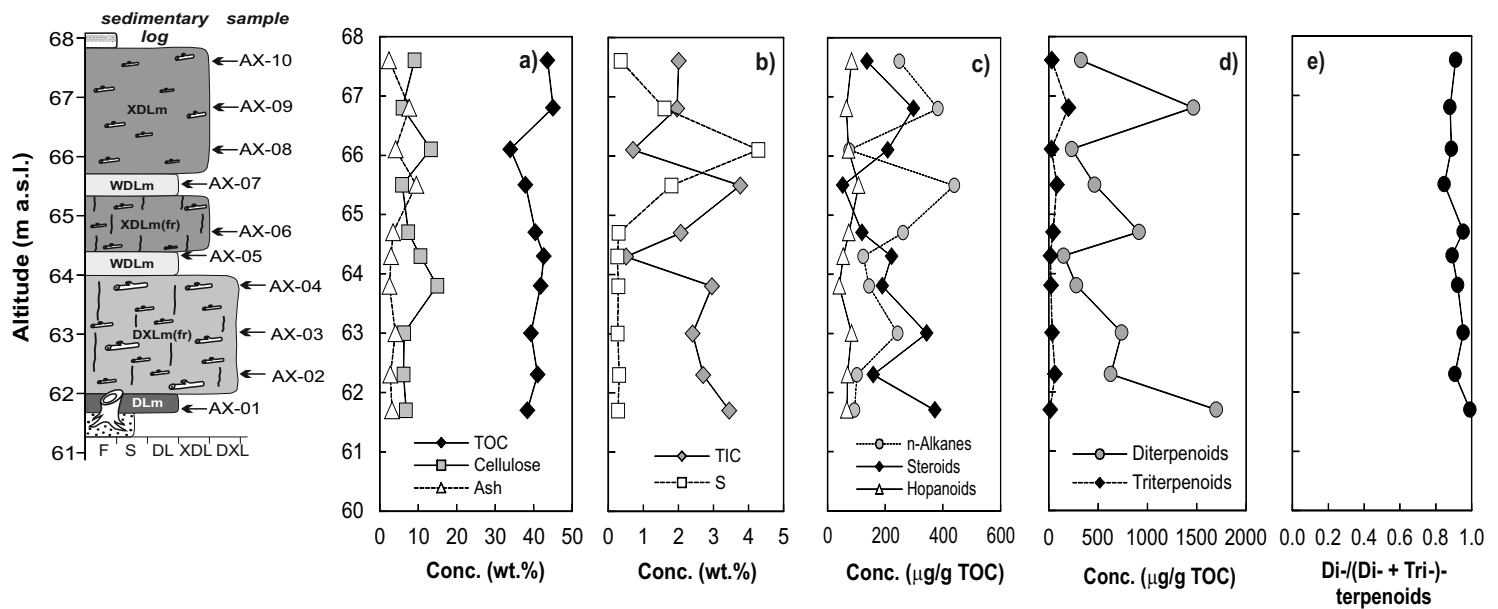
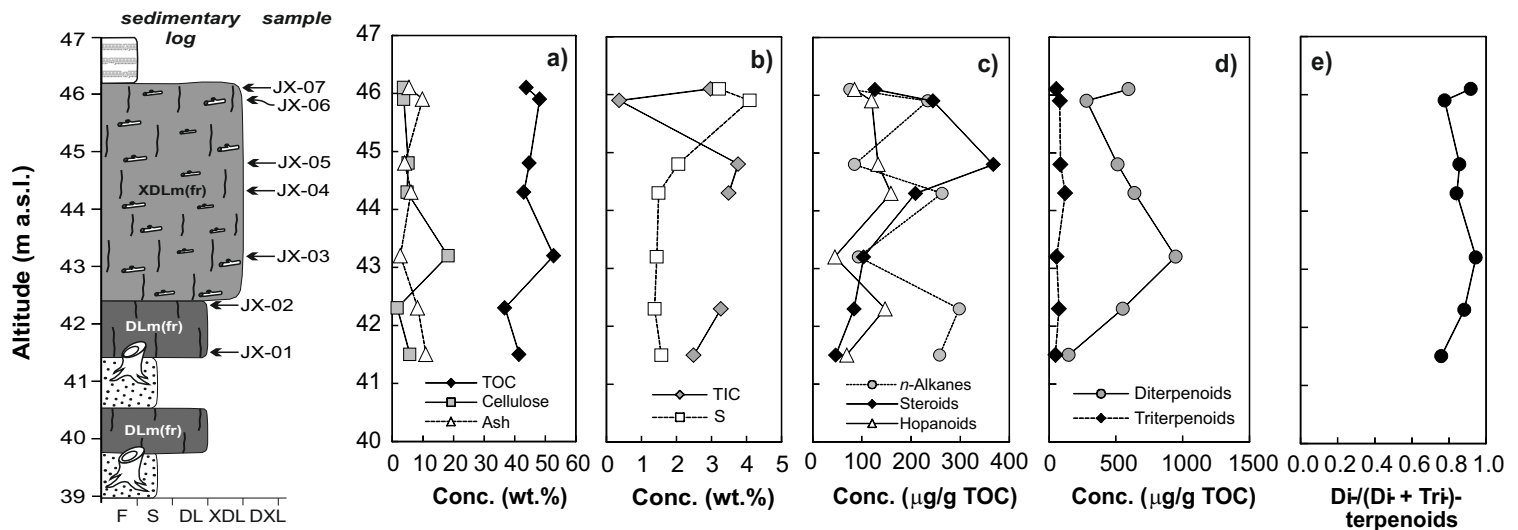


Fig. 2

Adamów mine



Józwin IIB mine



Tomisławice mine

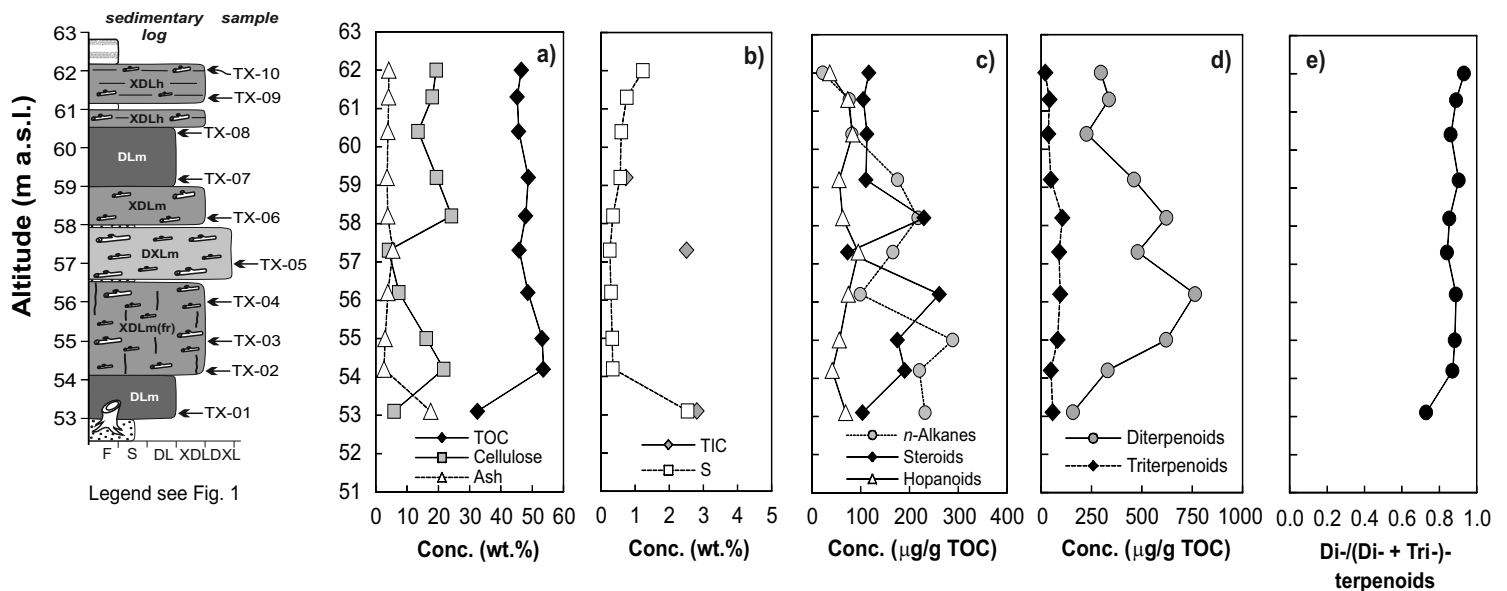


Fig. 3

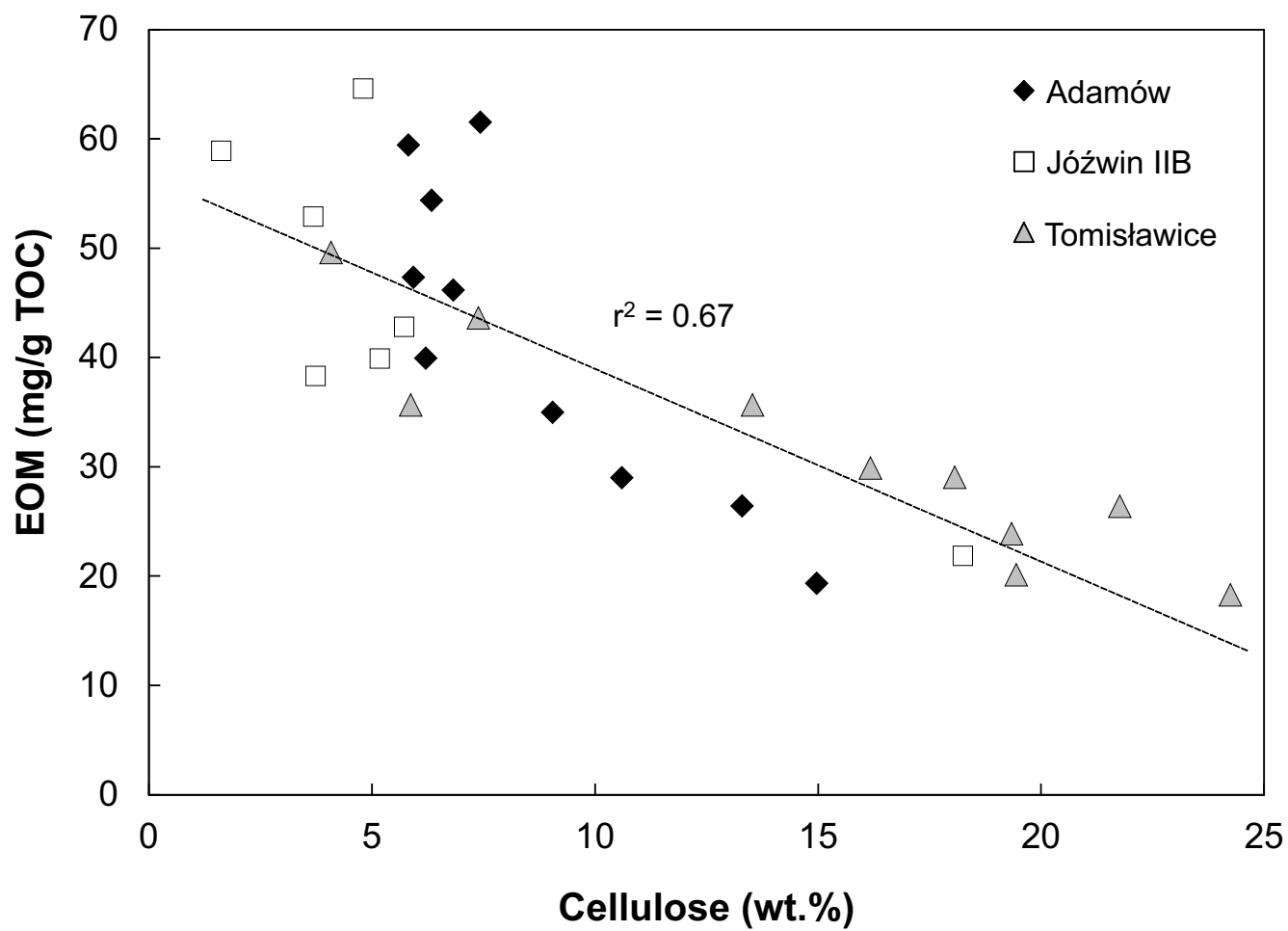


Fig. 4

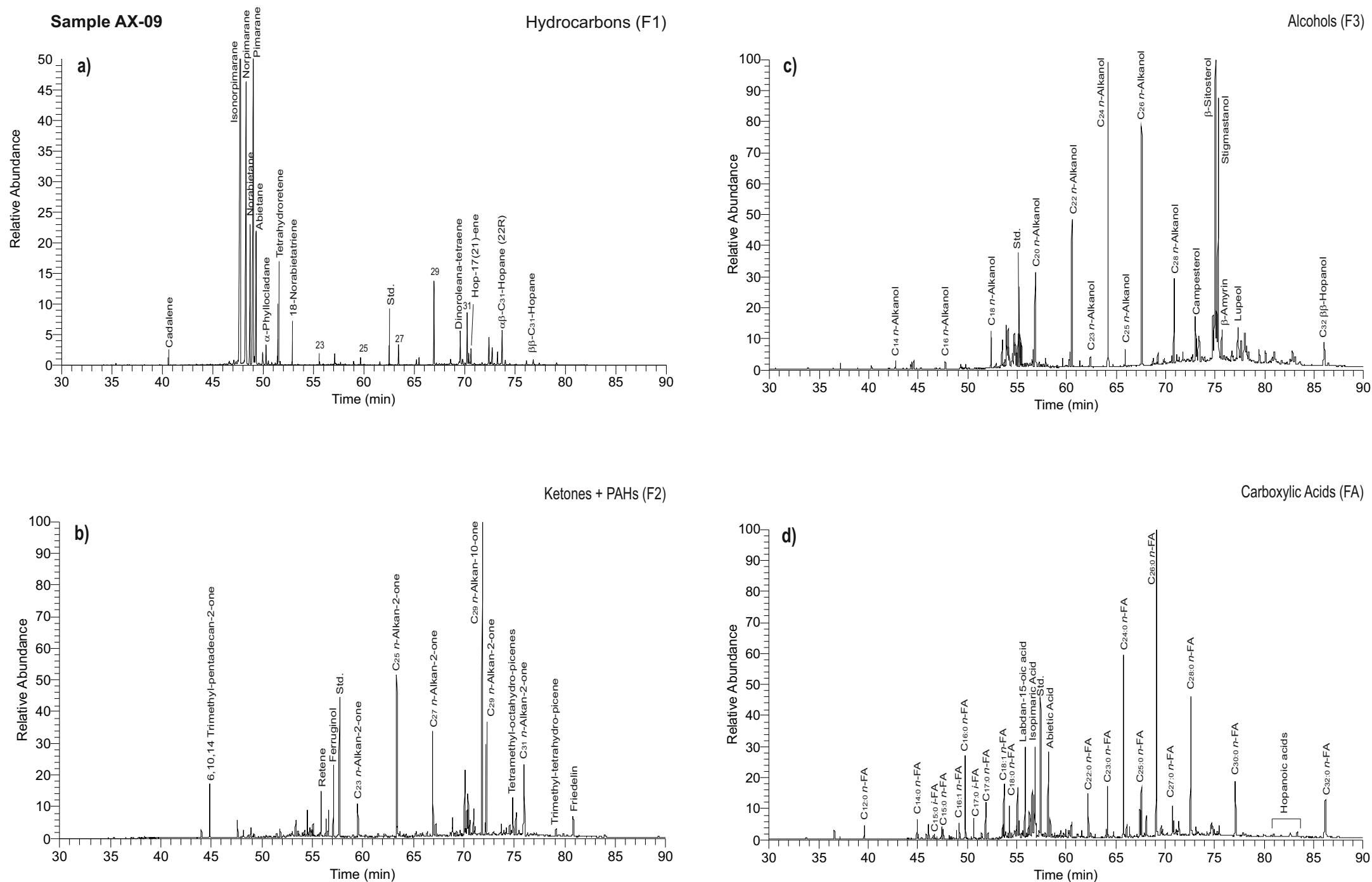


Fig. 5

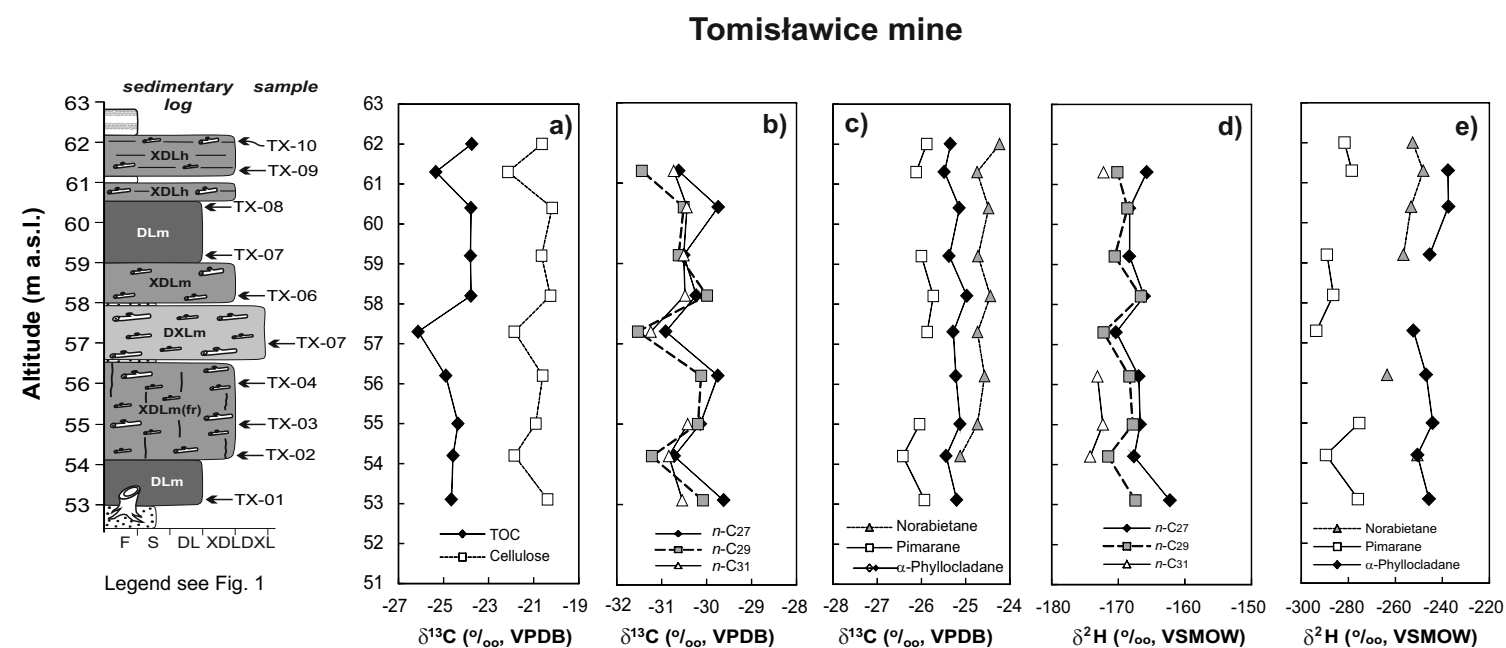
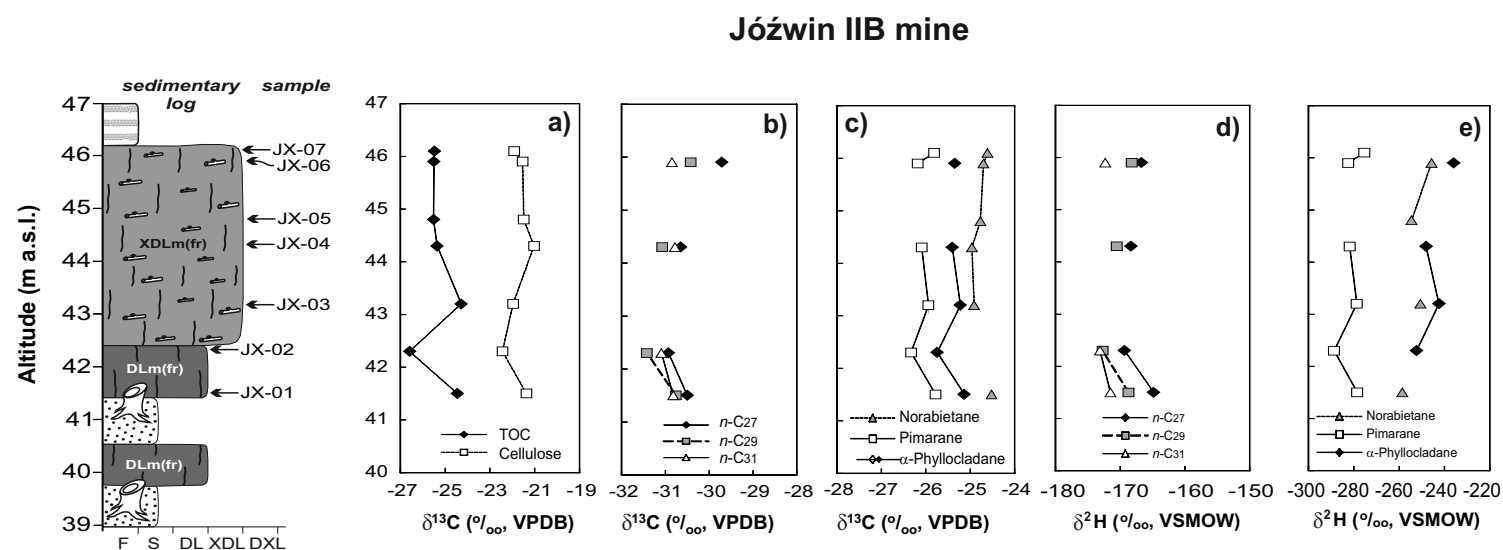
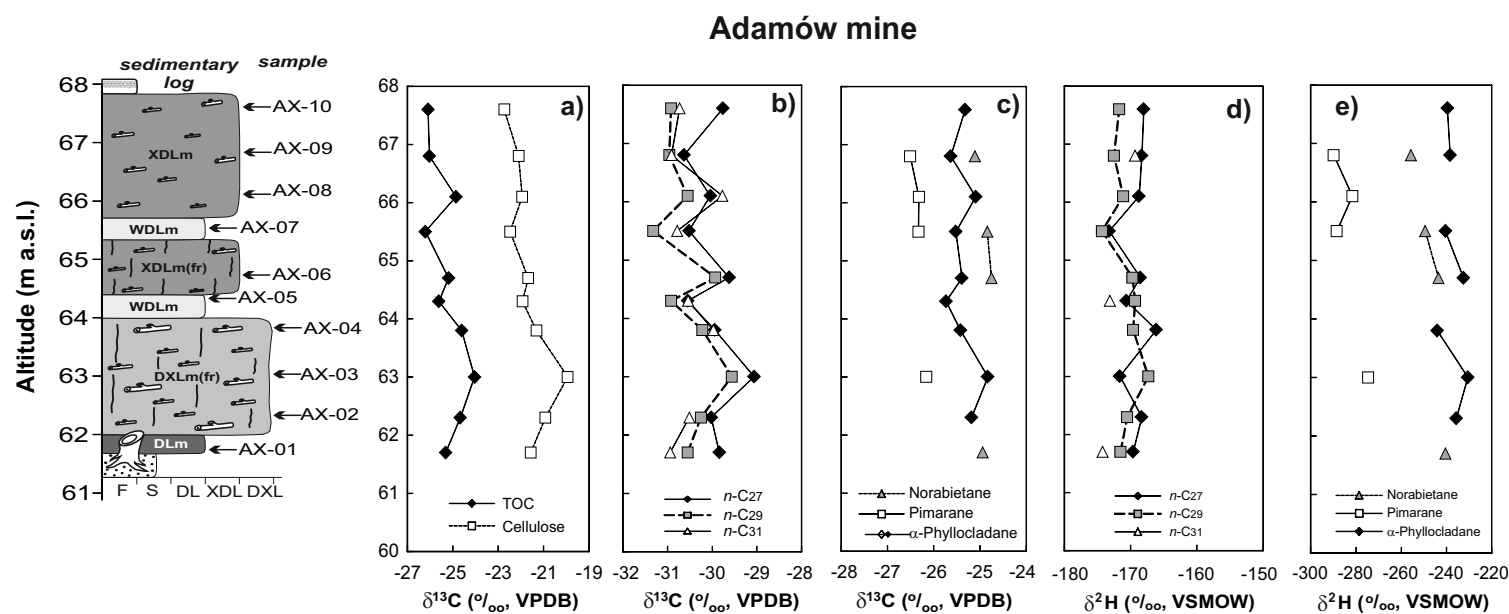


Fig. 6

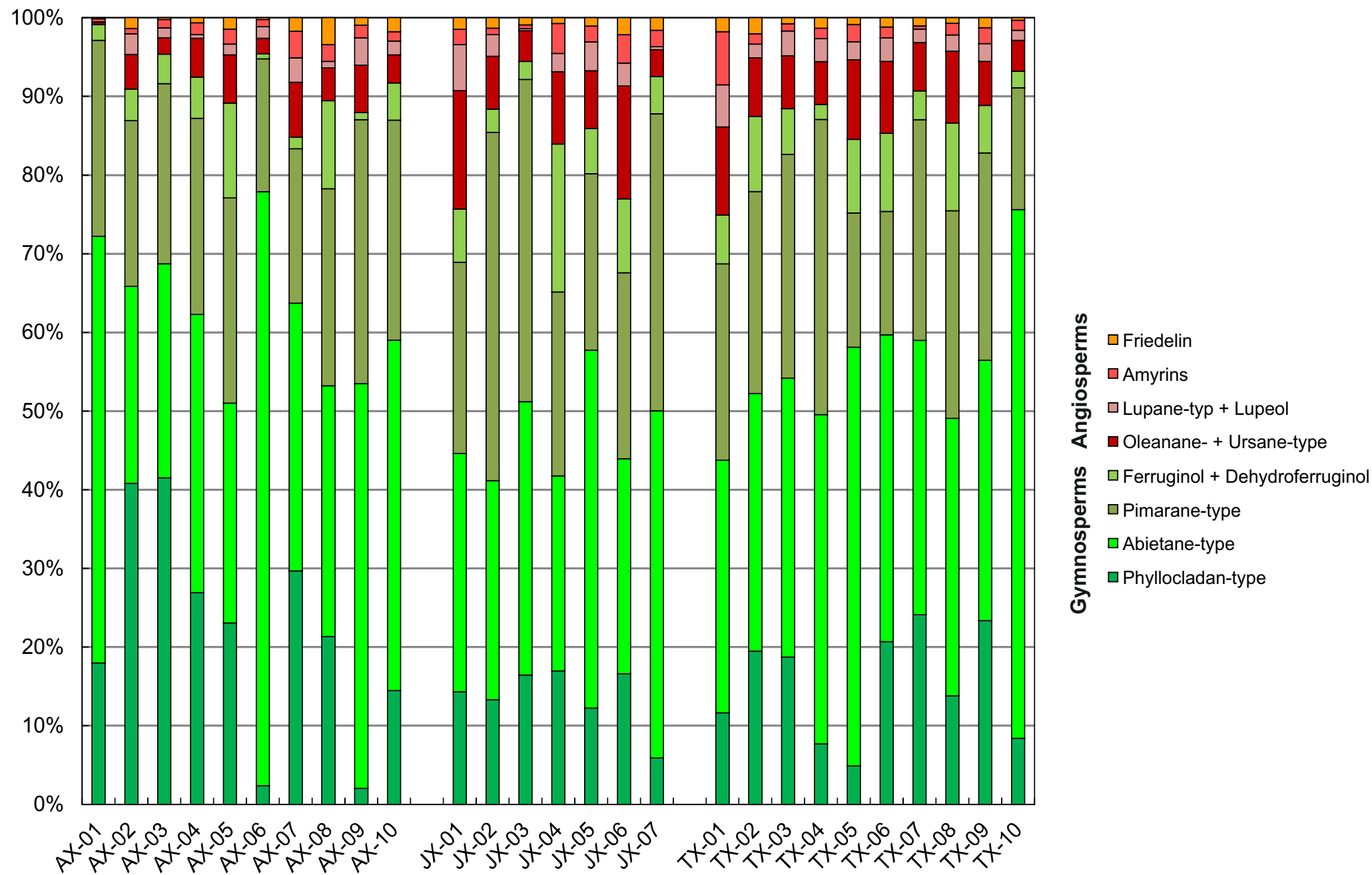


Fig. 07

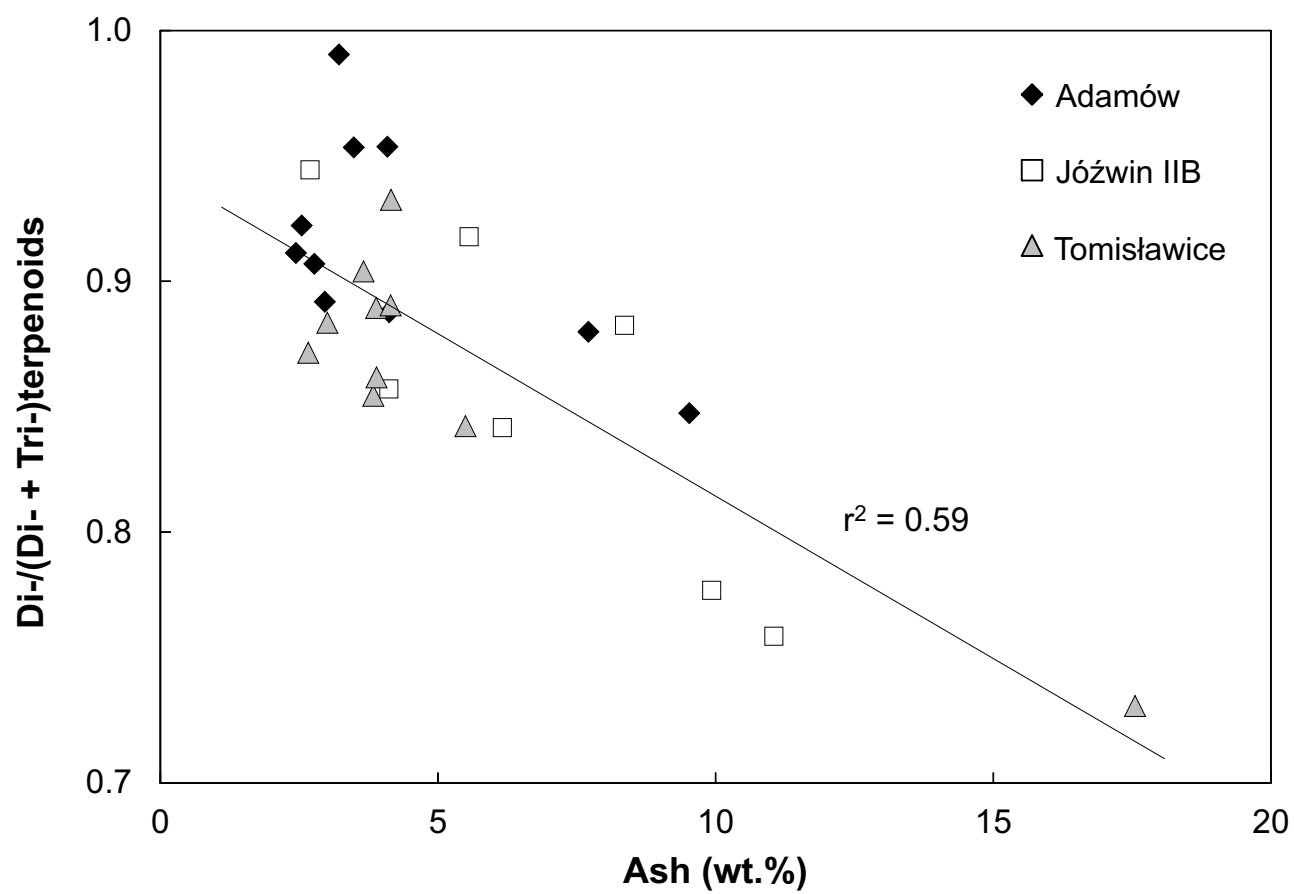


Fig. 8

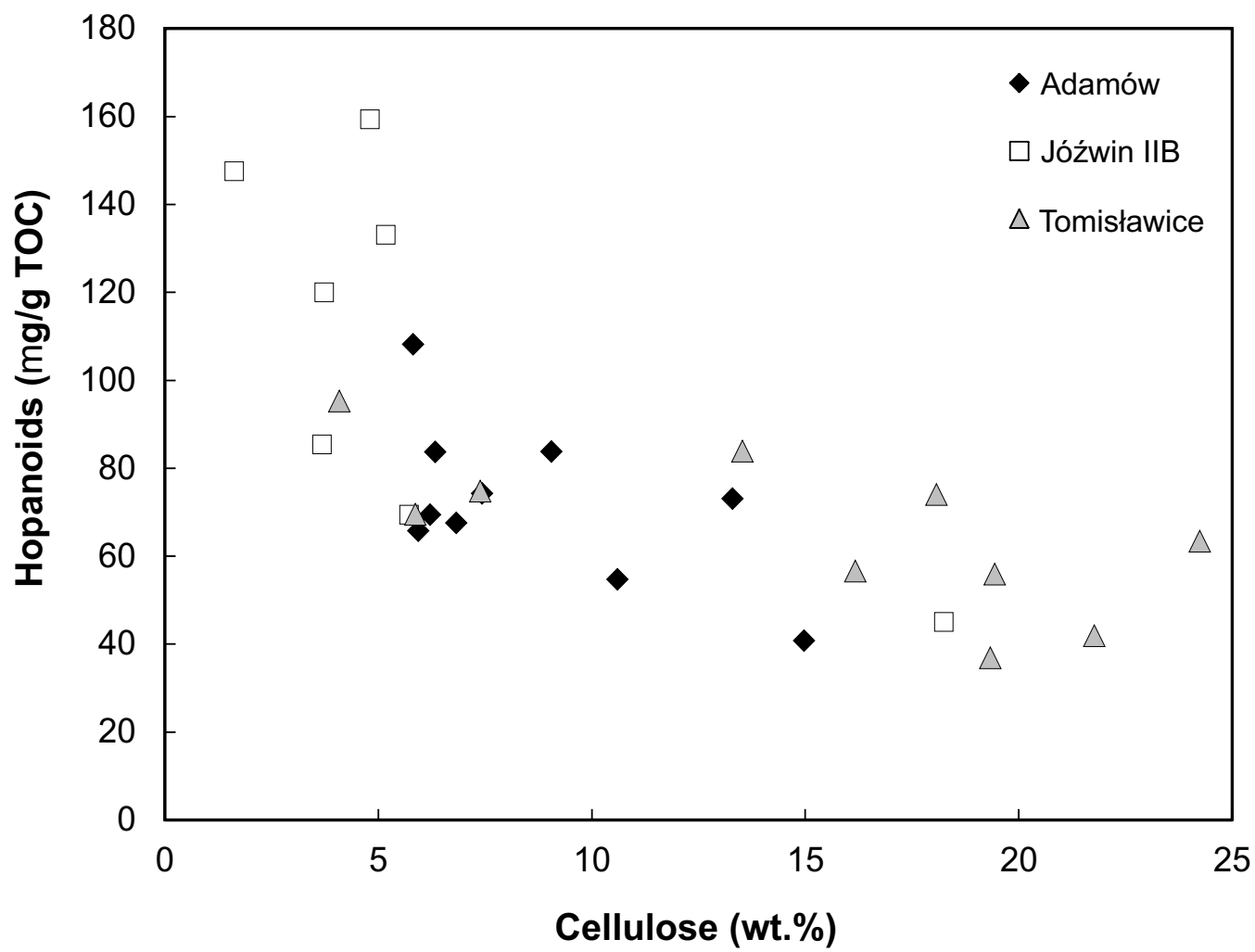


Fig. 9

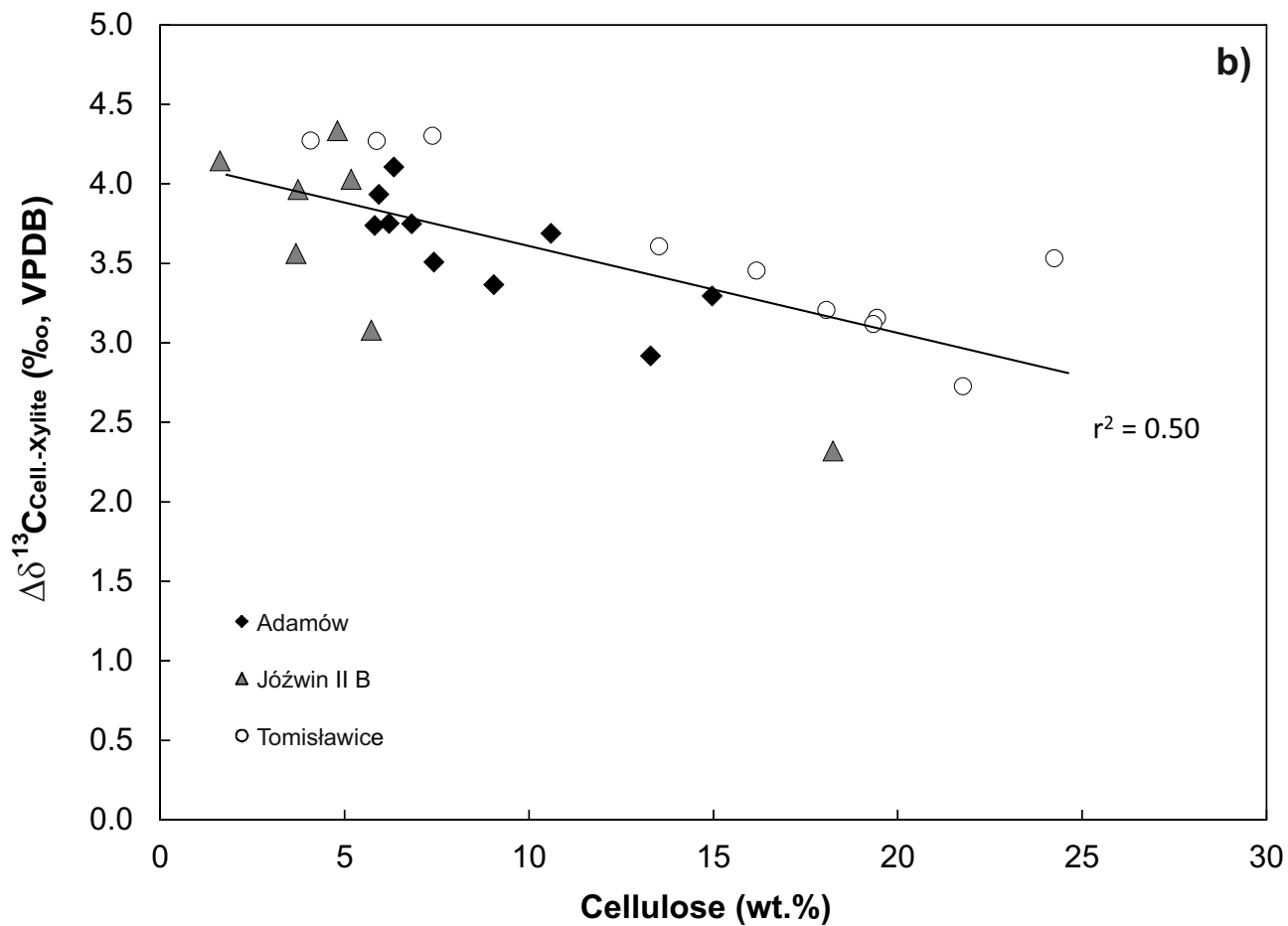
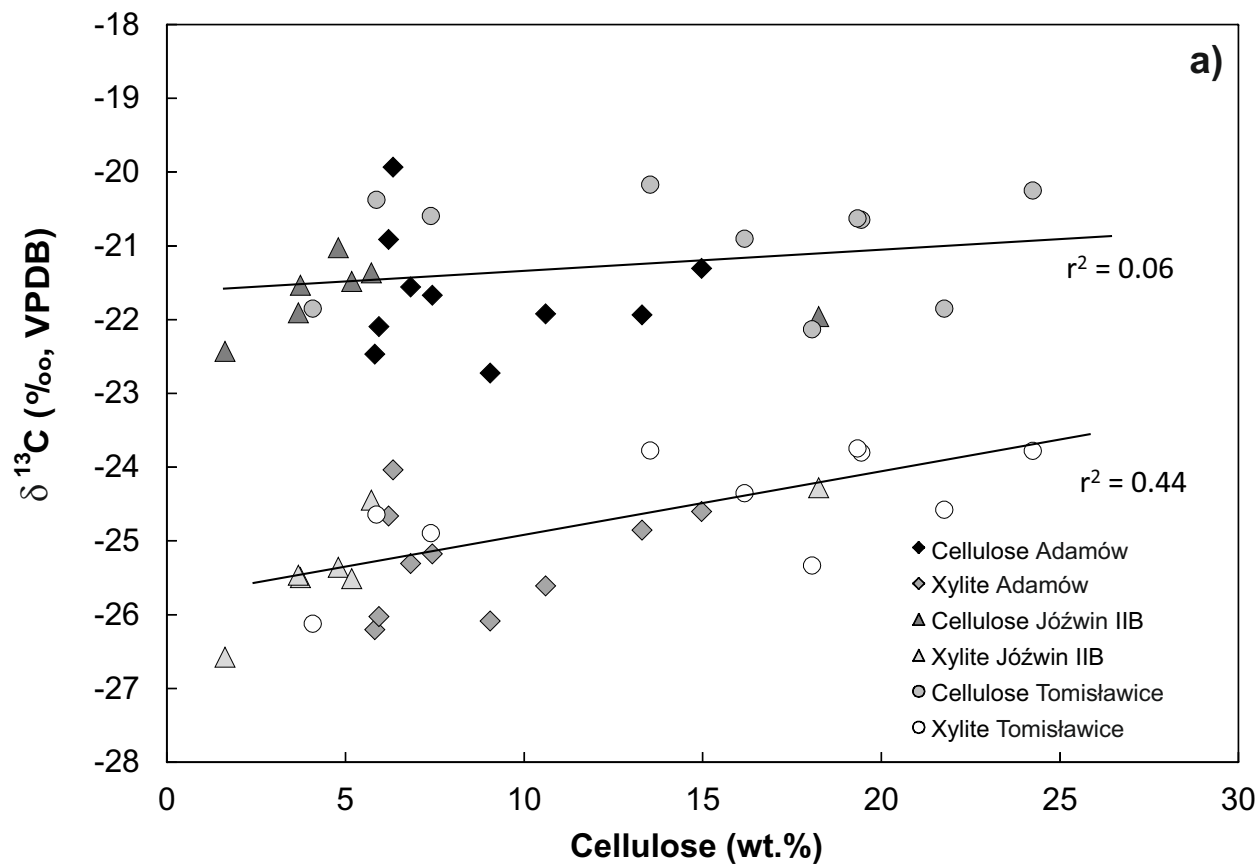


Fig. 10

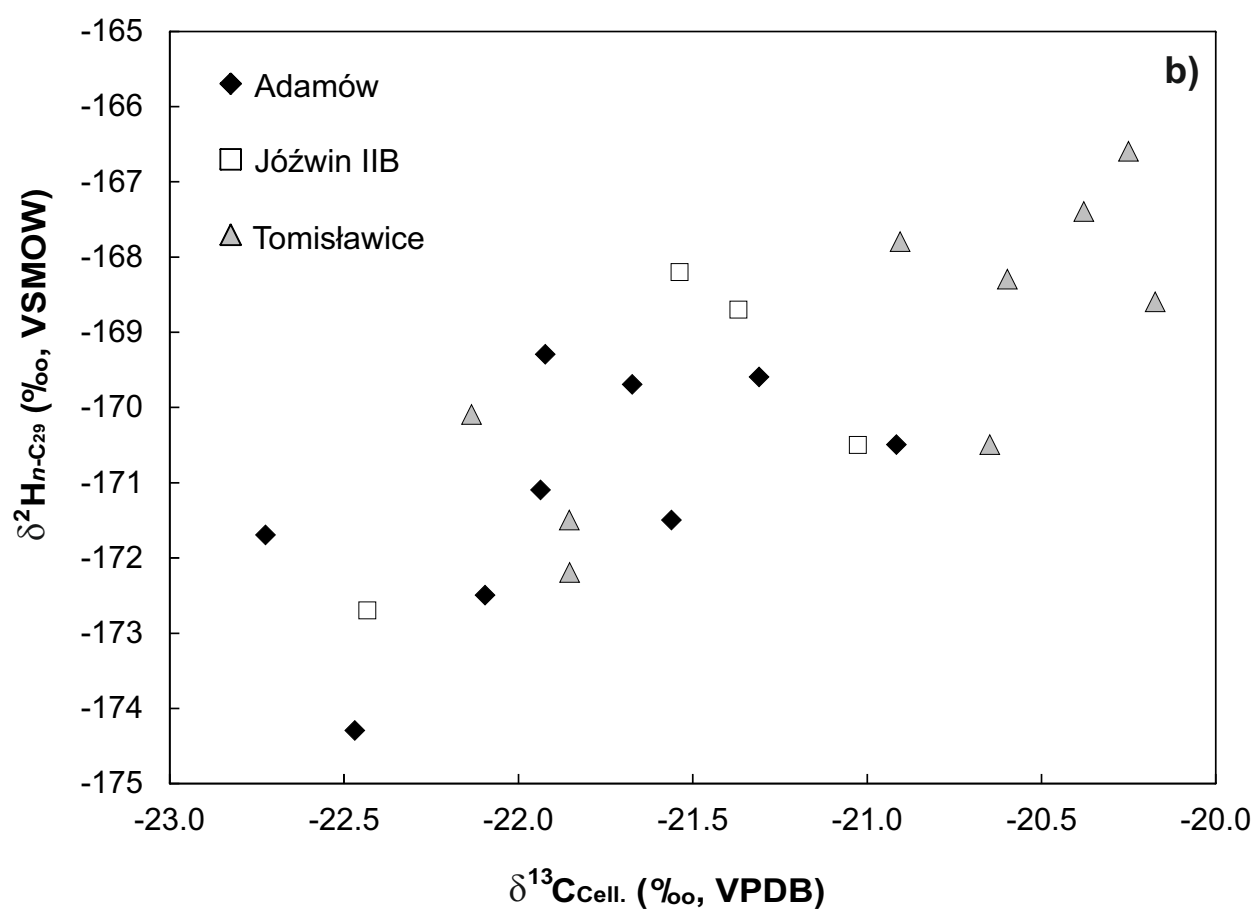
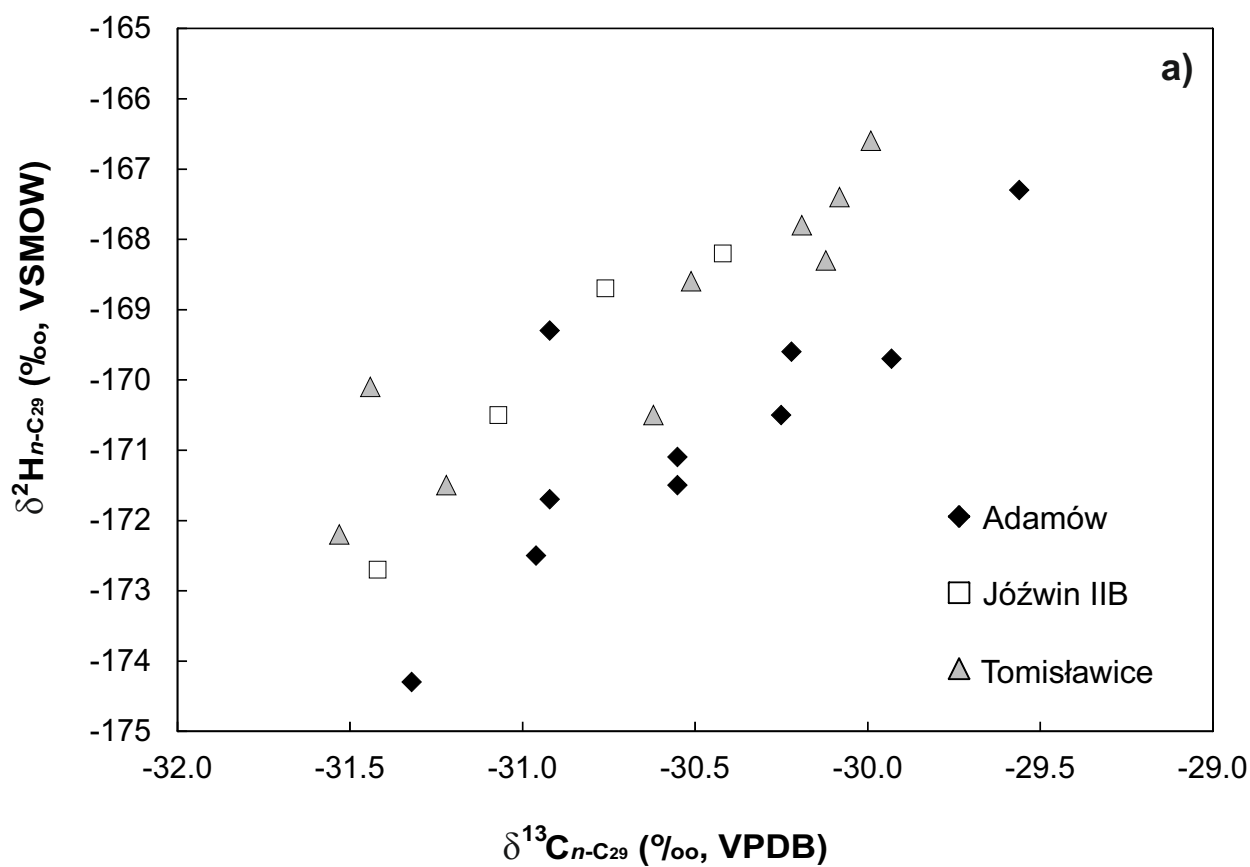


Fig. 11