

Hydrocarbon source rock potential of Miocene diatomaceous sequences in Szurdokpüspöki (Hungary) and Parisdorf/Limberg (Austria)

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KEYWORDS

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Abstract

Diatomaceous sediments are often prolific hydrocarbon source rocks. In the Paratethys area, diatomaceous rocks are widespread in the Oligo-Miocene strata. Diatomites from three locations, Szurdokpüspöki (Hungary) and Limberg and Parisdorf (Austria), were selected for this study, together with core materials from rocks underlying diatomites in the Limberg area. Bulk geochemical parameters (total organic carbon [TOC], carbonate and sulphur contents and hydrogen index [HI]) were determined for a total of 44 samples in order to study their petroleum potential. Additionally, 24 samples were prepared to investigate diatom assemblages.

The middle Miocene diatomite from Szurdokpüspöki (Pannonian Basin) formed in a restricted basin near a volcanic silica source. The diatom-rich succession is separated by a rhyolitic tuff into a lower non-marine and an upper marine layer. An approximately 12-m thick interval in the lower part has been investigated. It contains carbonate-rich diatomaceous rocks with a fair to good oil potential (average TOC: 1.28% wt.; HI: 178 to 723 mg HC/g TOC) in its lower part and carbonate-free sediments without oil potential in its upper part (average TOC: 0.14% wt.). The composition of the well-preserved diatom flora supports a near-shore brackish environment. The studied succession is thermally immature. If mature, the carbonate-rich part of the succession may generate about 0.25 tons of hydrocarbons per square meter. The diatomaceous Limberg Member of the lower Miocene Zellerndorf Formation reflects upwelling along the northern margin of the Alpine-Carpathian Foreland. TOC contents are very low (average TOC: 0.13% wt.) and demonstrate that the Limberg Member is a very poor source rock. The same is true for the underlying and overlying rocks of the Zellerndorf Formation (average TOC: 0.78% wt.). Diatom preservation was found to differ considerably between the study sites. The Szurdokpüspöki section is characterised by excellent diatom preservation, while the diatom valves from Parisdorf/Limberg are highly broken. One reason for this contrast could be the different depositional environments. Volcanic input is also likely to have contributed to the excellent diatom preservation in Szurdokpüspöki. In contrast, high-energy upwelling currents and wave action may have contributed to the poor diatom preservation in Parisdorf. The hydrocarbon potential of diatomaceous rocks of Oligocene (Chert Member; Western Carpathians) and Miocene ages (Groisenbach Member, Aflenz Basin; Kozakhurian sediments, Kaliakra canyon of the western Black Sea) has been studied previously. The comparison shows that diatomaceous rocks deposited in similar depositional settings may hold largely varying petroleum potential and that the petroleum potential is mainly controlled by local factors. For example, both the Kozakhurian sediments and the Limberg Member accumulated in upwelling environments but differ greatly in source rock potential. Moreover, the petroleum potential of the Szurdokpüspöki diatomite, the Chert Member and the Groisenbach Member differs greatly, although all units are deposited in silled basins.

1. Introduction

Diatomaceous sediments may form important hydrocarbon source rocks (e.g. Shukla and Mohan, 2012). Well-known examples include the Miocene Monterey Formation in California (Isaacs and Rullkötter, 2001);

the Oligocene to lower Miocene Menilite Formation in the Carpathians (Kotarba and Koltun, 2006), which includes chert layers interpreted as diagenetically altered diatomite; and the middle Miocene Diatom Suite in

Azerbaijan (Alizadeh et al., 2017 cum lit.; Sachsenhofer et al., 2018b). Moreover, diatom-rich lower Miocene sediments, which accumulated in a canyon offshore in Bulgaria, are important potential source rocks in the western Black Sea (Mayer et al., 2018; Sachsenhofer et al., 2018a).

A number of Miocene diatomaceous deposits are documented in Central Europe (Fig. 1). Middle Miocene deposits within the Pannonian Basin are typically related to volcanic activity (Dill et al., 2008), whereas the accumulation of lower Miocene diatomaceous rocks in the Alpine-Carpathian Foreland Basin has been linked to upwelling (Grunert et al., 2010).

The main aim of the present paper was to study the source rock potential of diatomaceous rocks, both within the Pannonian Basin and in the Alpine-Carpathian Foreland Basin. For this purpose, abandoned diatomite quarries have been selected for sampling, Szurdokpüspöki (Hungary) and Parisdorf/Limberg (Austria), together with a borehole drilled near Limberg, which are located within a sub-basin of the Pannonian Basin

and the Alpine-Carpathian Foreland Basin, respectively (see Fig. 1 for locations). Although the diatom assemblages of Szurdokpüspöki (Hajós, 1959; 1968; 1986) and Parisdorf/Limberg (Řeháková, 1994; Roetzel et al., 2006) have been described in detail by previous workers, some additional observations are added briefly in this contribution.

2. Geological setting

2.1 Szurdokpüspöki (Hungary)

The Szurdokpüspöki quarry is located about 50 km northeast of Budapest and 3.2 km southeast (SE) from the Szurdokpüspöki locality at the southwestern slope of the Mátra Mountains (Fig. 2). The diatomaceous rocks of Szurdokpüspöki accumulated in the Gyöngyöspata Basin, a small sub-basin of the Pannonian Basin. The basement of the Gyöngyöspata Basin is composed of pyroxene-andesite, andesite, rhyolite, dacite and tuff from Karpatian to Badenian (early to middle Miocene) (Hajós, 1968, Varga et al., 1975). The

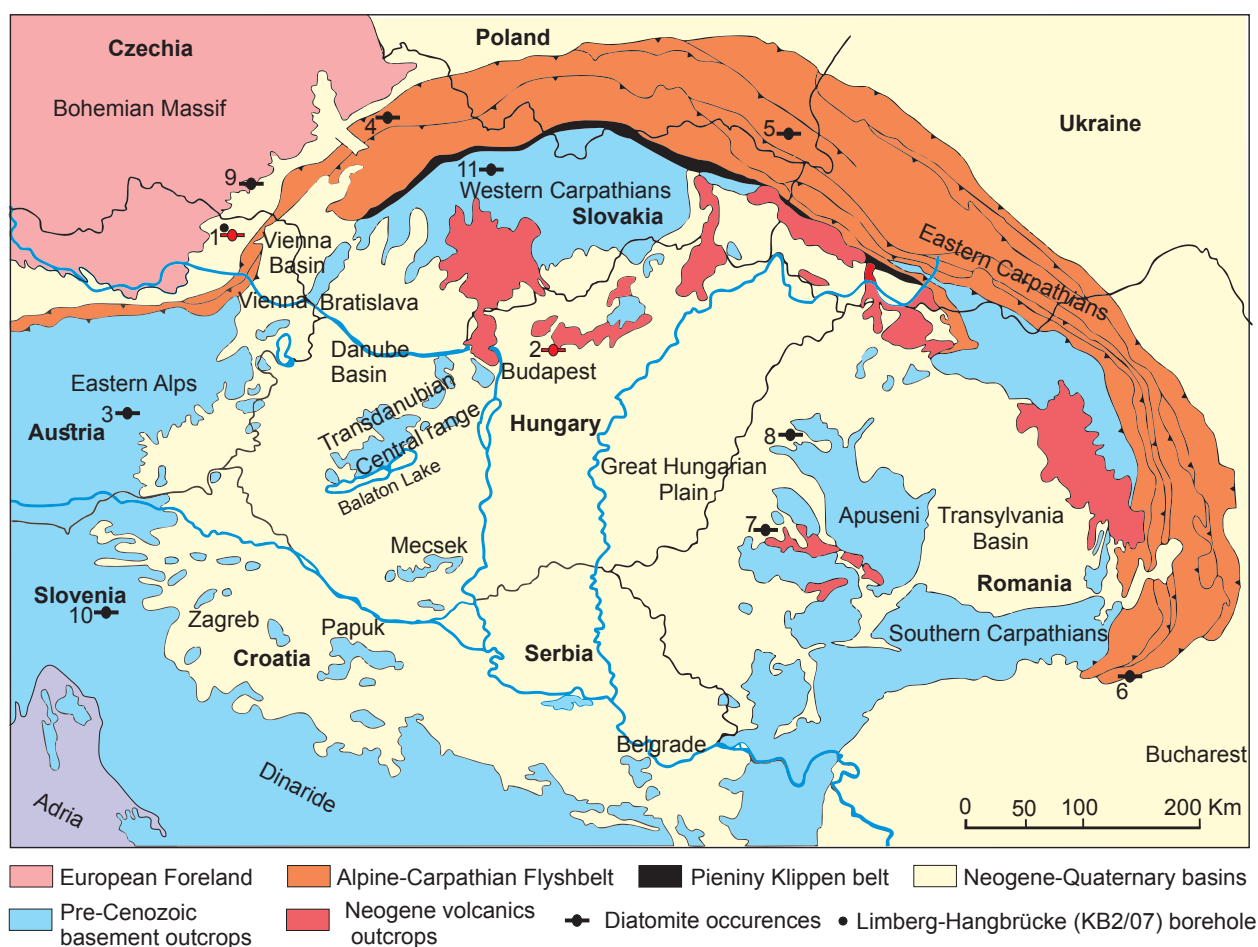


Figure 1: Occurrences of significant Oligocene and Miocene diatomaceous rocks in the Central Paratethys (redrawn after Tari and Horváth, 2006). 1 – Parisdorf quarry; 2 – Szurdokpüspöki quarry; 3 – Aflenz Basin (Sachsenhofer et al., 2003); 4 – Loučka section (Jirman et al., 2019); 5 – Jawornik deposit (Figarska-Warchoł et al., 2015); 6 – Sibiciu de Sus quarry (Funzescu and Brănoiu, 2004; Tulan et al., 2019); 7 – Zaránd Basin; 8 – Vad-Borod Basin (Codrea et al., 2018); 9 – Brno-Královo Pole (Basistova, 2007); 10 – Krško Basin (Horvat, 2004) and 11 – Turiec Basin (Ognjanova-Rumenova and Radovan, 2015).

irregular volcanic surface is covered by middle Miocene rocks, up to 300 m thick. The middle Miocene sediments in the Szurdokpüspöki quarry were described in detail by Hajós (1986) and include from base to top (a) an approximately 50-m-thick sequence with freshwater to oligohaline diatomite; (b) light greyish to white rhyolite tuff with pumice and mollusc shell remains, about 20 m thick; (c) brackish-marine calcareous and marly diatomite, approximately 90 m thick and 60 m of brackish-freshwater diatomite, which are overlain by

(d) ("Leitha-") limestone, 24 m thick. The Pliocene and Quaternary covers are represented by andesitic tuffs (30 m) and tuffaceous clays (20 m).

The lower freshwater to oligohaline diatomite is calcareous in its lower part and carbonate free in its upper part. Chert layers ("limnoopalite") are characteristic features within the lower diatomites. Apart from fish remains and ostracodes, a remarkably well-preserved toad fossil is found in this lower freshwater interval (Szentesi, 2008).

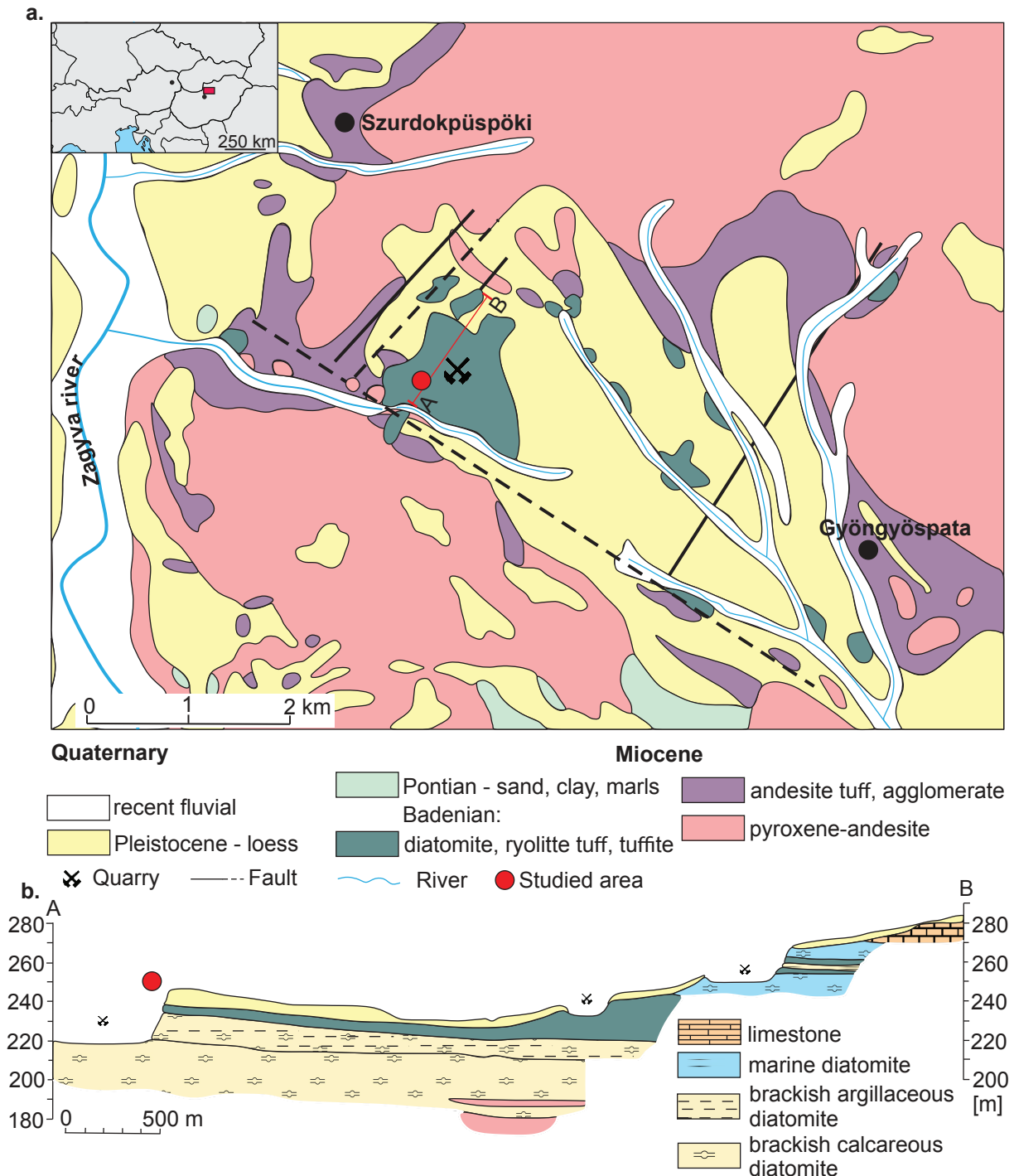


Figure 2: Geological map (a) and geological cross-section (b) of the Szurdokpüspöki quarry indicating the study area (after Hajós, 1986).

The upper interval with brackish-marine diatomite includes marine diatoms, siliceous sponges, foraminifera, shark teeth, fish scales and several tuff layers.

2.2 Parisdorf/Limberg (Austria)

Diatomaceous rocks of early Oligocene (mid-Burdigalian) age in the Alpine-Carpathian Foredeep accumulated along the south-eastern margin of the Bohemian Massif and are attributed to the Limberg Member of the Zellerndorf Formation (Roetzel et al., 2006; Grunert et al., 2010). Based on sedimentological and paleontological evidence, as well as foraminiferal stable isotope data and dinocyst assemblages, Grunert et al. (2010) suggested that the clay-diatomite succession of the Limberg Member accumulated along the steep escarpment of the Bohemian Massif due to upwelling.

In the study area, Palaeozoic crystalline rocks of the Bohemian Massif are overlain by lower Miocene nearshore sands and gravels (upper Eggenburgian Burgschleinitz Formation) and sandy shallow marine limestones (lower Oligocene Zogelsdorf Formation), which laterally and vertically pass into deep-water pelitic sediments (Zellerndorf Formation), 25 to 100 m thick. The laminated diatomaceous sediments of the Limberg Member within the Zellerndorf Formation reach a maximum thickness of 5 to 7.5 m but pinch out laterally. The top of the Zellerndorf Formation is disconformably overlain by lower-middle Miocene marine and freshwater sediments covered by Pleistocene loess (Grunert et al., 2010).

Diatomaceous sediments of the Limberg Member have been mined in small quarries, currently abandoned. The Parisdorf diatomite mine is located about 400 m SE of Parisdorf (Fig. 3). Here, the diatomites are exposed at the base, followed by pelites of the Zellerndorf Formation. The Neogene sediments are covered by Pleistocene deposits. The Limberg quarry is located 800 m northeast of Limberg (Fig. 3). Similar to the Parisdorf mine, the finely stratified diatomites of the Limberg Member are exposed at the base, followed by the pelites of the Zellerndorf Formation.

3. Methods

Two sample sets are used in this paper. The first set consisting of 44 samples have been collected from abandoned diatomite quarries in 2017 by E. Tulan, G. Tari, R. F. Sachsenhofer and J. Mayer and include 24 samples from Szurdokpüspöki, 13 samples from Parisdorf and 7 samples from Limberg. The samples from the quarries are referred to in the text as quarry samples. The second set consisting of 12 samples have been collected by P. Grunert and R. Roetzel from the Limberg-Hangbrücke (KB2/07) borehole drilled north of Limberg in 2007, and the samples are here referred as borehole samples.

Total carbon (TC), total sulphur (S) and total organic carbon (TOC) contents were analysed for all samples using a LECO CS-300 carbonate-sulphur analyser (borehole samples) or an ELTRA Elemental Analyzer (quarry samples). Samples for TOC measurements were decarbonised

with HCl and concentrated phosphoric acid, respectively. Results are given in weight percent (wt.%). Total inorganic carbon (TIC) was determined ($TIC = TC - TOC$) and used to calculate calcite equivalent percentages ($TIC \times 8.333$).

Pyrolysis measurements were performed for 24 samples (quarry samples) using a "Rock-Eval 6" instrument. The S1 and S2 peaks (mg HC/g rock) were used to calculate the petroleum potential ($S1 + S2$ [mg HC/g rock]), the production index ($PI = S1/(S1 + S2)$; Lafargue et al., 1998) and the hydrogen index (HI ; $HI = S2/TOC \times 100$ [mg HC/g TOC]). The Rock-Eval parameter T_{max} was used as a thermal maturity indicator in the present study. The amount of hydrocarbons, which can be generated below 1 m² of surface area, was calculated using the Source Potential Index (SPI; $SPI = thickness \times (S1 + S2) \times bulk\ density/1000$) (Demaison and Huizinga, 1994).

The mineral composition of the 44 samples (quarry samples) was determined using a Bruker AXS D8 Advance X-ray diffraction spectrometer (copper radiation generated at 40 kV and 40 mA). The powdered samples have been placed carefully in sample holders to create a flat upper surface to achieve a random distribution of lattice orientation. To identify the different mineral phases, the software Diffrac.Eva and the method described by Schultz (1964), which is based on peak heights, were used. X-ray powder diffraction was the main technique used to determine the type of silica phase.

Thin sections were prepared from 8 samples (quarry samples). The low number is due to high friability of the diatomites. The thin sections were studied using a Leica DM 2500P microscope, and pictures were taken using a Leica DFC490 camera.

Flame atomic absorption spectroscopy was performed on 29 (quarry) samples to determine biogenic silica contents using the methods described by Zolitschka (1988). Approximately 100 mg of the sample material and 50 ml of 0.5 mol/l potassium hydroxide solution were boiled for an hour to dissolve the opaline diatom shells. Afterwards, 5 ml of the solution was diluted with distilled water (1:1). A Perkin Elmer 3030 Atomic Absorption Spectrometer (AAS) was used for analysis and operated with a CH₄-N₂O flame to create free Si atoms in a gaseous state. A Si-hollow cathode lamp was used as a spectral line source. The AAS was calibrated using a Merck CertiPUR* silicon-standard solution (No. 1.1231.0500).

For siliceous microfossil examination, 1 g of dry sediment from each of the 24 quarry samples was treated for two days with 30 ml of 33% hydrochloric acid (HCl) and 30 ml of 33% hydrogen peroxide (H₂O₂) (Schrader, 1973). After the reaction settled, the solution was heated at 90°C to finish the rest of the reaction. The samples were cooled and washed three times with 30 ml of distilled water. The solution was then sieved through a 50 µm sieve to concentrate the fine fraction. For microscope slides, 5 ml of solution was strewn on a glass slide. For the determination of the relative abundance of diatom genera, the first 300 valves were counted following

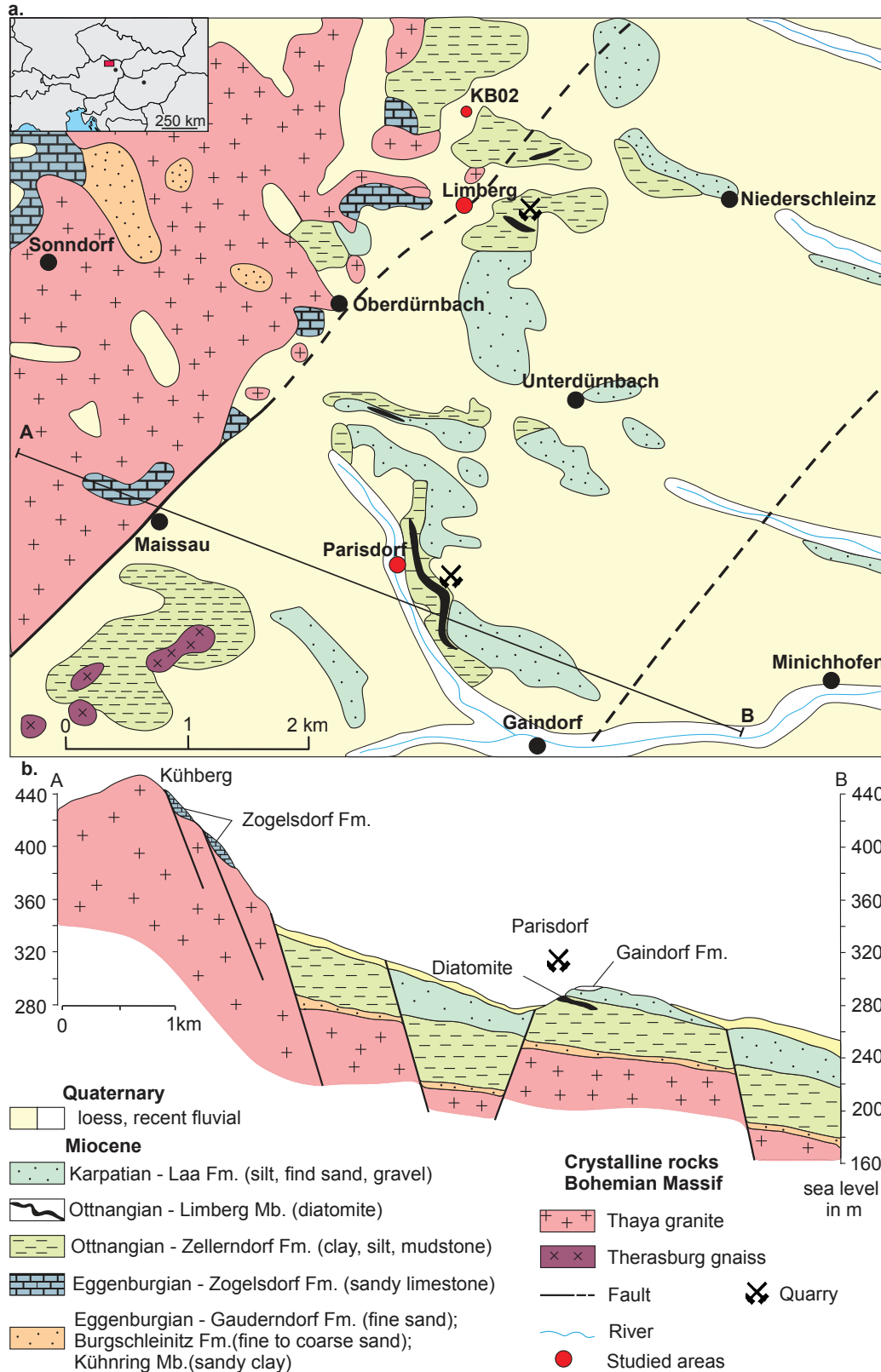


Figure 3: Geological map (a) and cross-section (b) of the Limberg and Parisdorf study sites together with the position of the studied borehole (after Roetzel, 1999; 2004).

the method by Schrader and Gersonde (1978). Siliceous microfossil slides were studied using a Leica DM 2500P microscope, and pictures were taken using a Leica DFC490 camera.

In addition, some of the diatom valves were examined and photographed using the scanning electron microscope (SEM) Leo 1450EP. In all, 2 ml of the fine fraction was placed on an aluminium stub covered with conductive

carbon tab and set for the water to evaporate in a fume hood. After the water evaporated, the stubs were gold sputtered for a maximum 20 s.

4. Results

4.1. Szurdokpüspöki

4.1.1. Lithology

A 12-m-thick section representing diatomaceous rocks has been studied in the abandoned Szurdokpüspöki quarry (Figs. 2 and 4). Unexposed parts are marked in Figure 4 with question marks. The diatomite is laminated (paper like) and very fragile with dark grey to yellow-whitish colour when freshly broken. Few dark-grey chert layers have been observed to be intercalated with the diatomaceous rock. In thin-section observation, the rock contains diatom valve masses in an argillaceous matrix with very rare detrital grains (Fig. 5). The detritus is represented by angular quartz, plagioclase, volcanic clasts and volcanic glass. Few samples are heavily altered, but in sample III-Sp, the siliceous diatom valves are replaced by calcite or clay minerals.

In X-ray diffractograms, opal-A is present in the majority of the samples from Szurdokpüspöki. Opal-CT is present only in sample 6-Sp. The diffractograms show that clay minerals, biogenic silica and varying amounts of calcite are the major constituents of the studied rocks (Fig. 6).

A change in mineralogy with height is observed on XRD diffractograms. The base of the section (samples I-Sp to 9-Sp) is calcite dominated, whereas the upper part of the section (samples 10-Sp to 21-Sp) is dominated by clay minerals.

The same trend has been observed in the carbonate contents, where the lower 6-m-thick interval is characterised by high carbonate contents (samples I-Sp to 9-Sp, 10%–70% wt.; Table 1), whereas the rest of the section is largely carbonate free (samples 10-Sp to 21-Sp). The percentage of biogenic silica ranges from 15% to 30% and is typically higher in the carbonate-poor upper part than in the carbonate-rich lower part (Figure 4).

Chert layers are found both in the carbonate-rich lower part (between samples 6-Sp and 7-Sp; Fig. 4) and in the carbonate-free upper part (between samples 15-Sp and 16-Sp).

Based on the very low carbonate contents in the upper part and the presence of chert layers, this section can be correlated to the lower freshwater to oligohaline interval with diatomite described by Hajós (1986). The overlying andesite tuffs (Fig. 4) are exposed in the south-eastern sector of the quarry.

4.1.2. Bulk geochemical parameters

Bulk parameters for the Szurdokpüspöki sections are listed in Table 1 and plotted versus height in Figure 4. TOC contents are high (0.2%–3.0% wt.; average 1.28% wt.) in the lower part of the Szurdokpüspöki section (samples I-Sp to 13-Sp) and very low (average 0.14% wt.) in the carbonate-free upper part of the section (samples 14-Sp to 21-Sp). Within the organic matter-rich section, the interval around the lower chert layers is poor in TOC, but TOC contents increase upwards and are in the order of 1.5% wt. in the middle part (samples 10-Sp to 13-Sp).

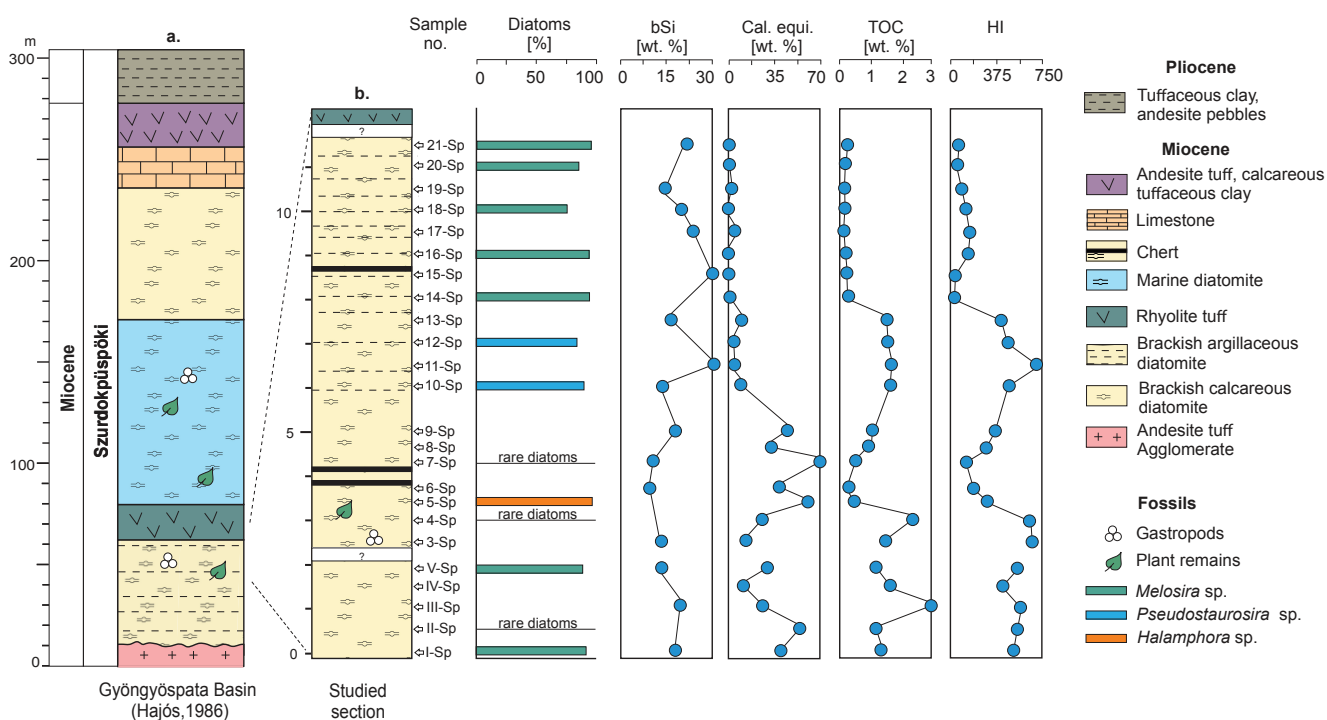


Figure 4: Szurdokpüspöki quarry, Hungary. (a) Lithology of the Gyöngyöspata Basin established on the Szurdokpüspöki quarry and the wells drilled in the area (after Hajós, 1986) and (b) lithology of the studied section with the geochemical parameters and the predominant diatom genera. bSi – biogenic silica, cal. equiv. – calcite equivalent, TOC – total organic carbon, HI – hydrogen index.

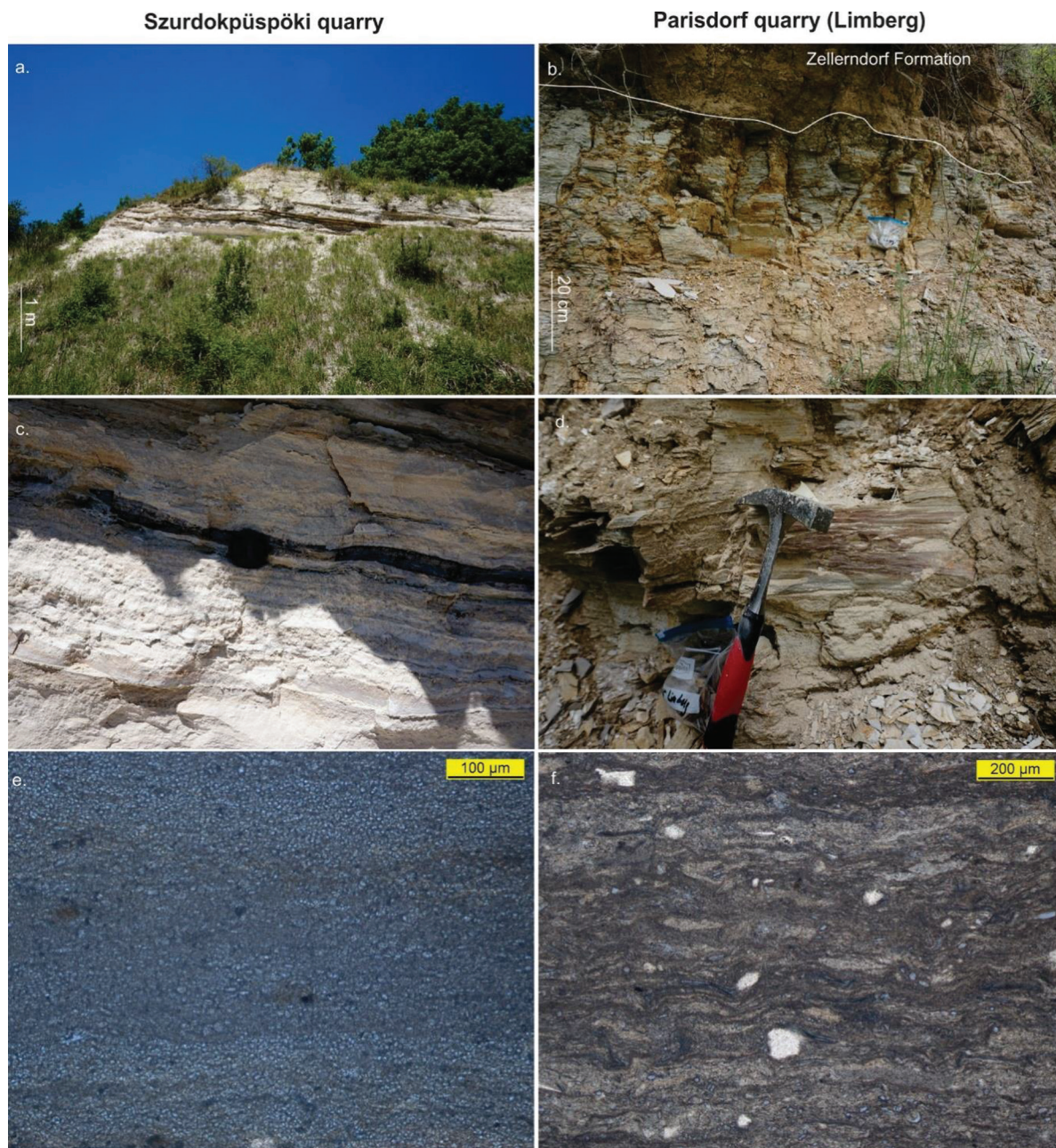


Figure 5: Photographs of diatomite in Szurdokpüspöki and Parisdorf quarries. (a) and (b) – overview of studied sections, (c) – calcareous diatomite with chert intercalate (sample 7-Sp), (d) – argillaceous diatomite (sample 15-Li), and (e) and (f) – thin-section microphotographs: (e) – abundant diatom valves with argillaceous matrix (21-Sp) and (f) – argillaceous diatomite with common diatom valves and relatively large angular quartz grains (4-Pa).

Sulphur (S) contents ranging up to 1.16% wt. TOC/S ratios are meaningful only for the organic matter-rich lower portion of the section. For samples with TOC contents exceeding 0.3% wt., TOC/S ratios range from 1 to 8 (Table 1) and show an upward decreasing trend.

S₂ values reach a maximum of 14.4 mg HC/g rock and strongly relates to TOC contents. HI values in the lower organic matter-rich section range from 178 to 723 mg HC/g TOC. A plot of S₂ versus TOC suggests that the true HI is in the order of 640 mg HC/g TOC, which suggests the prevalence of type I to II kerogen. T_{max} is on average 406°C, indicating that the organic matter is immature.

4.1.3. Diatom assemblages and depositional environment

Samples from the Szurdokpüspöki quarry contain diverse and abundant diatom assemblages, including numerous extant brackish and marine forms alongside fossil taxa that were likely brackish or freshwater. Fossil brackish and freshwater diatoms are generally poorly known, and therefore, we focus on genus-level rather than species-level identifications in the paleo-environmental interpretation given in the following. For the present, we generally follow the identifications by Hajós (1986) but make the necessary amendments where newer taxonomic concepts are involved. We also stress that further work is needed in order to obtain a

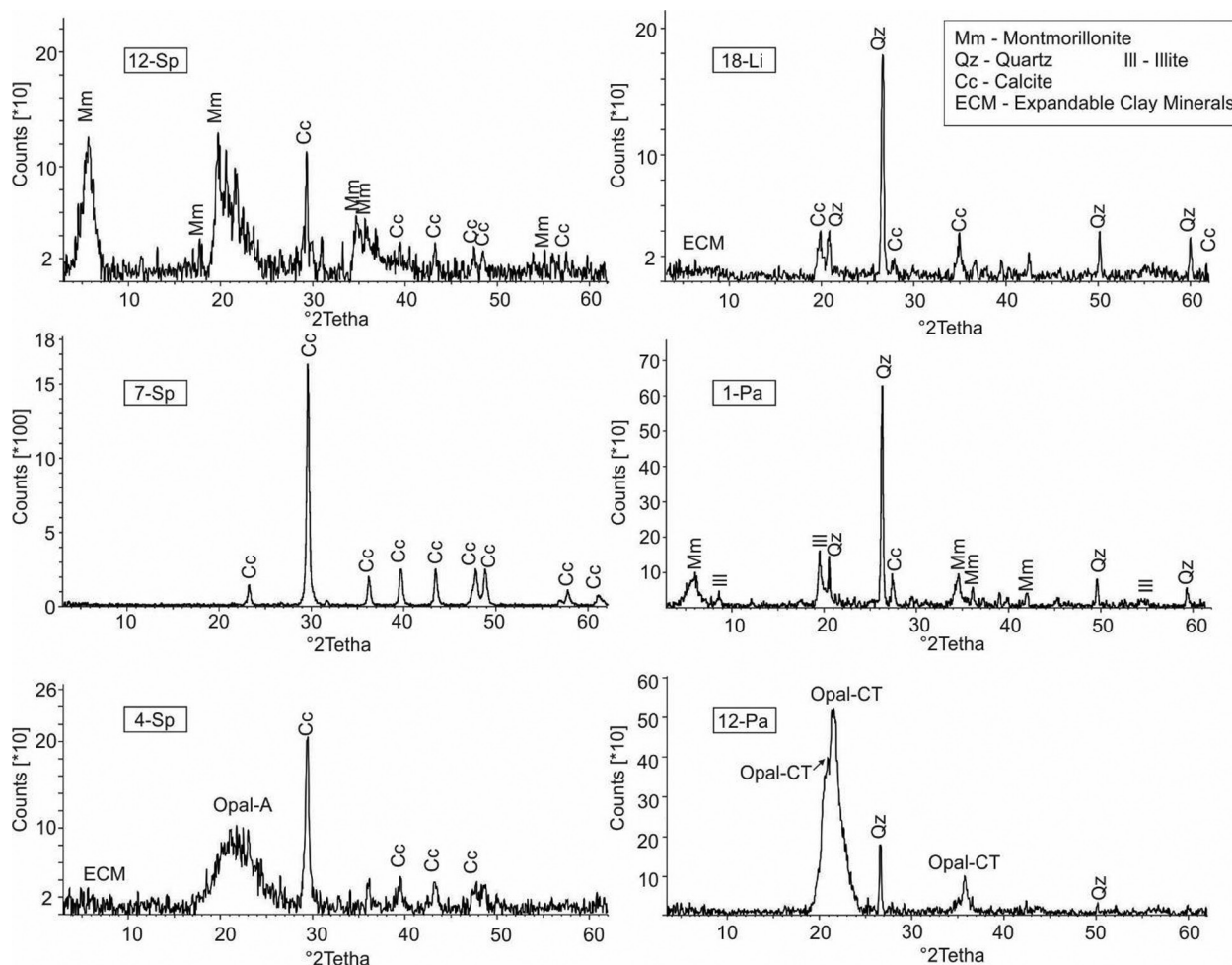


Figure 6: X-ray diffractograms of diatomaceous sediments in Szurdokpüspöki (4-Sp, 7-Sp, 12-Sp), Parisdorf (12-Pa, 1-Pa) and Limberg (18-Li).

proper understanding of Central Paratethys' diatom assemblages.

We identify the dominant diatom as *Melosira bituminosa* Pantocsek following Hajós (1986). This species is morphologically dissimilar from *Melosira sensu stricto*, however, certainly belongs to another genus. In SEM, we note that the valve structure of *M. bituminosa* generally resembles that of *Ehrenbergia granulosa* (Grunow) (Witkowski, Lange-Bertalot and Metzeltin 2000), especially in the placement of the marginal processes and the presence of carinoportulae. However, a formal taxonomic transference is beyond the scope of the present study.

Hajós (1959) identified *Amphora* sp. Ehrenberg ex Kützing in the brackish section. Nevertheless, the genus *Amphora* was divided into several subgenera, one of them being *Halamphora* Cleve. In 2009, Levkov raised the subgenus *Halamphora* to the genus level and transferred many *Amphora* spp., which presented all morphological features of the new genus to *Halamphora*. In our identification, the diatom from Szurdokpüspöki previously identified as *Amphora* presents the features of the new genus *Halamphora*. A similar case is represented by *Fragilaria*

Lyngbye, from which Williams and Round (1988) separated the genus *Pseudostaurosira*.

Diatom assemblages from the Szurdokpüspöki quarry are often dominated by single genera. Seven samples (I-Sp, V-Sp, 14-Sp, 16-Sp, 18-Sp, 20-Sp, 21-Sp) are dominated (average 92%) by "*Melosira*" (refer to the Discussion section) and in two samples (10-Sp, 12-Sp). *Pseudostaurosira* (previously part of *Fragilaria*) is the most abundant (81%). *Halamphora* (previously a subgenus within *Amphora*) dominates only in sample 5-Sp (98%). Less-frequent genera include *Brachysira* Kützing (including the extant *Brachysira aponina* Kützing), *Cocconeis* Ehrenberg, *Cymbella* C. Agardh, *Diploneis* Ehrenberg ex Cleve, *Epithemia* Kützing, *Navicula* Bory, *Nitzschia* Hassall (including the extant *Nitzschia inconspicua*), *Planothidium* Round and Bukhtiyarova, *Podosira* Ehrenberg, *Seminavis* Mann and *Surirella* Turpin (Figs. 7 and 8), including the extant *Surirella striatula*. Only few samples (II-Sp, 4-Sp, 7-Sp) contained sparse diatoms (Fig. 4).

Based on the valve structure similarity discussed earlier, we hypothesise that *M. bituminosa* must have occupied a similar ecological niche to *E. granulosa*, i.e. in littoral and often in tidal flats (Witkowski et al., 2000).

Table 1: Bulk parameters of Szurdokpüspöki quarry

Sample Location	Sample number	Height (m)	Calc. equiv. (%)	TOC	Sulphur	S1 (mg HC/g)	S2 (mg HC/g)	T_{max} (°C)	PI (-)	HI (mg HC/g TOC)	TOC/S (-)
Szurdokpüspöki quarry	21-Sp	11.4	0.00	0.31	0.05	0.09	0.27	379	0.24	88	5.8
	20-Sp	11.0	0.24	0.20	0.1	0.07	0.15	384*	0.30	74	2.0
	19-Sp	10.5	0.71	0.14	0.13	0.03	0.15	403	0.17	102	1.1
	18-Sp	10.0	0.32	0.13	0.06	0.03	0.19	403	0.14	143	2.0
	17-Sp	9.5	1.42	0.10	0.03	0.01	0.15	407	0.06	158	3.2
	16-Sp	9.0	0.36	0.13	0.11	0.05	0.19	387	0.21	146	1.1
	15-Sp	8.6	0.05	0.14	0.48	0.02	0.08	399*	0.20	59	0.3
	14-Sp	8.9	0.30	0.19	0.63	0.04	0.12	413	0.26	61	0.3
	13-Sp	7.5	4.62	1.42	1.12	0.28	5.68	415	0.05	399	1.3
	12-Sp	7.0	3.40	1.39	1.16	0.33	6.18	415	0.05	445	1.2
	11-Sp	6.5	3.40	1.53	0.83	0.48	11.05	418	0.04	723	1.8
	10-sp	6.0	5.13	1.47	0.8	0.2	6.61	416	0.03	450	1.8
	9-Sp	5.0	37.05	1.03	0.91	0.2	3.45	402	0.05	336	1.1
	8-Sp	4.5	28.55	0.91	0.74	0.17	2.39	387	0.06	261	1.2
	7-Sp	4.2	70.89	0.44	0.33	0.05	0.78	412	0.05	178	1.3
	6-Sp	3.8	33.62	0.22	0.44	0.02	0.43	422	0.04	193	0.5
	5-Sp	3.5	59.94	0.37	0.14	0.06	1.11	407	0.05	298	2.6
	4-Sp	3.0	18.88	2.31	0.52	0.96	14.4	405	0.06	623	4.5
	3-Sp	2.5	10.36	1.41	0.44	0.46	9.71	404	0.05	689	3.2
	V-Sp	2.0	25.79	1.11	0.14	0.23	6.05	402	0.04	544	7.7
	IV-Sp	1.5	10.59	1.47	1	0.27	6.18	406	0.04	421	1.5
III-Sp	1.0	22.16	2.95	0.73	1.67	16.25	418	0.09	551	4.1	
II-Sp	0.5	47.44	1.20	0.63	0.35	6.49	412	0.05	540	1.9	
I-Sp	0.0	34.50	1.22	0.75	0.32	6.35	407	0.05	519	1.6	

TOC – total organic carbon, HI – hydrogen index, PI – production index, calc. equi. – calcite equivalent. * T_{max} is unreliable, because of low S2 peak.

Halamphora is a relatively large, widely distributed genus, with most of the species being found in marine or brackish water habitats, some in coastal environment and only a few in freshwater. Most of the genera found in Szurdokpüspöki are periphytic and benthic, and some are haptobenthic (*Cocconeis*), i.e. living in near-shore littoral brackish water. A few planktonic genera are found, represented by *Nitzschia* and *Navicula*. This is generally consistent with previous interpretations (Hajós, 1986) of the paleoenvironment, which is mainly near-shore littoral brackish water. In addition, we observe favourable conditions for single genera blooms (5-Sp: *Halamphora* sp.; 10- and 12-Sp: *Pseudostaurosira* sp.), which were most likely a result of the volcanic activity in the area.

Thus, the diatom assemblage composition strongly indicates a brackish marine environment. Modern taxa such as *S. striatula*, *N. inconspicua* and *B. aponina* generally occur in salinities lower than 10 psu (e.g. Hajós, 1973; Gaiser et al., 2005; Rovira et al., 2015), for instance in modern-day Mediterranean lagoons, which perhaps could be

viewed as an analogue for the depositional setting of the Szurdokpüspöki site.

4.2. Parisdorf and Limberg

4.2.1. Lithology

The Zellerndorf Formation below the diatomaceous Limberg Member has been studied in borehole KB 02. In the borehole, the Zellerndorf Formation is 19.3 m thick and contains a layer with well-rounded quartz gravels at its base. The main part of the formation is dominated by laminated silty clay, often with sea urchin spines and phytoclasts. Carbonate contents are low (1%–8% wt.).

The diatomaceous sediments of the Limberg Member are exposed in Parisdorf (c. 6 m height) and Limberg (<4 m height) (Fig. 9). The exposed rocks are finely laminated diatomite with few clay intercalations. At Parisdorf, the exposed section starts at the bottom with a chert layer. The carbonate content is very low. Both outcrops are overlain by pelitic rocks of the upper part of the Zellerndorf

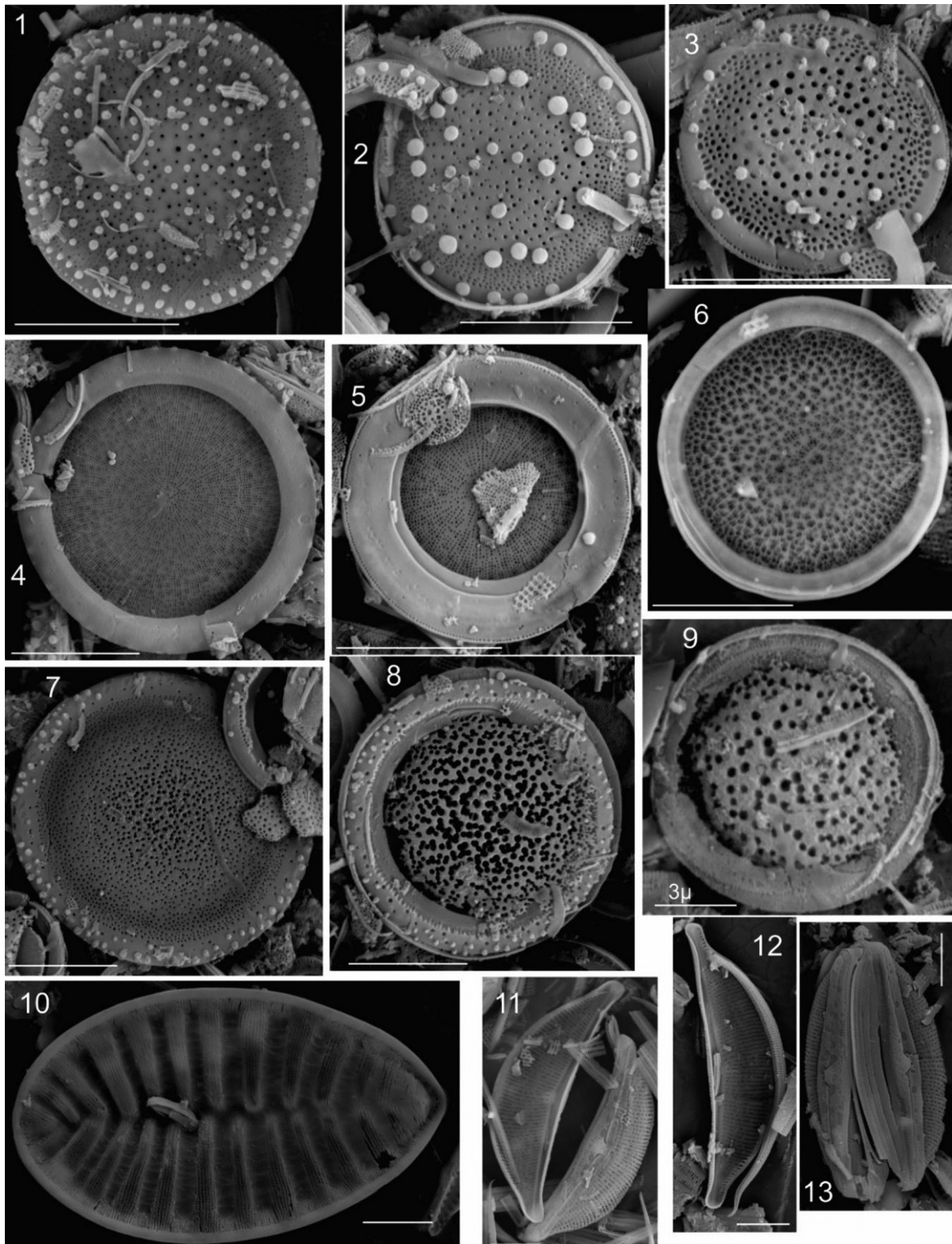


Figure 7: SEM photographs of diatoms from Szurdokpüspöki quarry; scale bar is 10 μm unless specified otherwise. Explanations of figures: 1–3 and 7–9 tentative identification: *Melosira bituminosa* Pantocsek, 4–6 tentative identification: *Melosira nuda*? Hajós, 10 *Surirella striatula* Turpin and 11–13 *Halamphora* sp. (Kützing) Levkov. SEM – scanning electron microscope.

Formation. The Parisdorf outcrop is partly covered with vegetation, and the missing section is marked in Figure 9 with question mark.

Clay minerals form the main component of most samples. Detrital quartz grains are rare. The average biogenic silica content has 9% wt. with higher contents in

samples 12-Pa (23.7%), 8-Pa (15.4%), 16-Li (22.7%) and 17-Li (14.5%). In thin sections, the lithology is represented by an argillaceous mass with frequent diatom valves and rare detritus (Fig 5).

X-ray diffractograms support that clay minerals, biogenic silica and calcite are the major constituents of

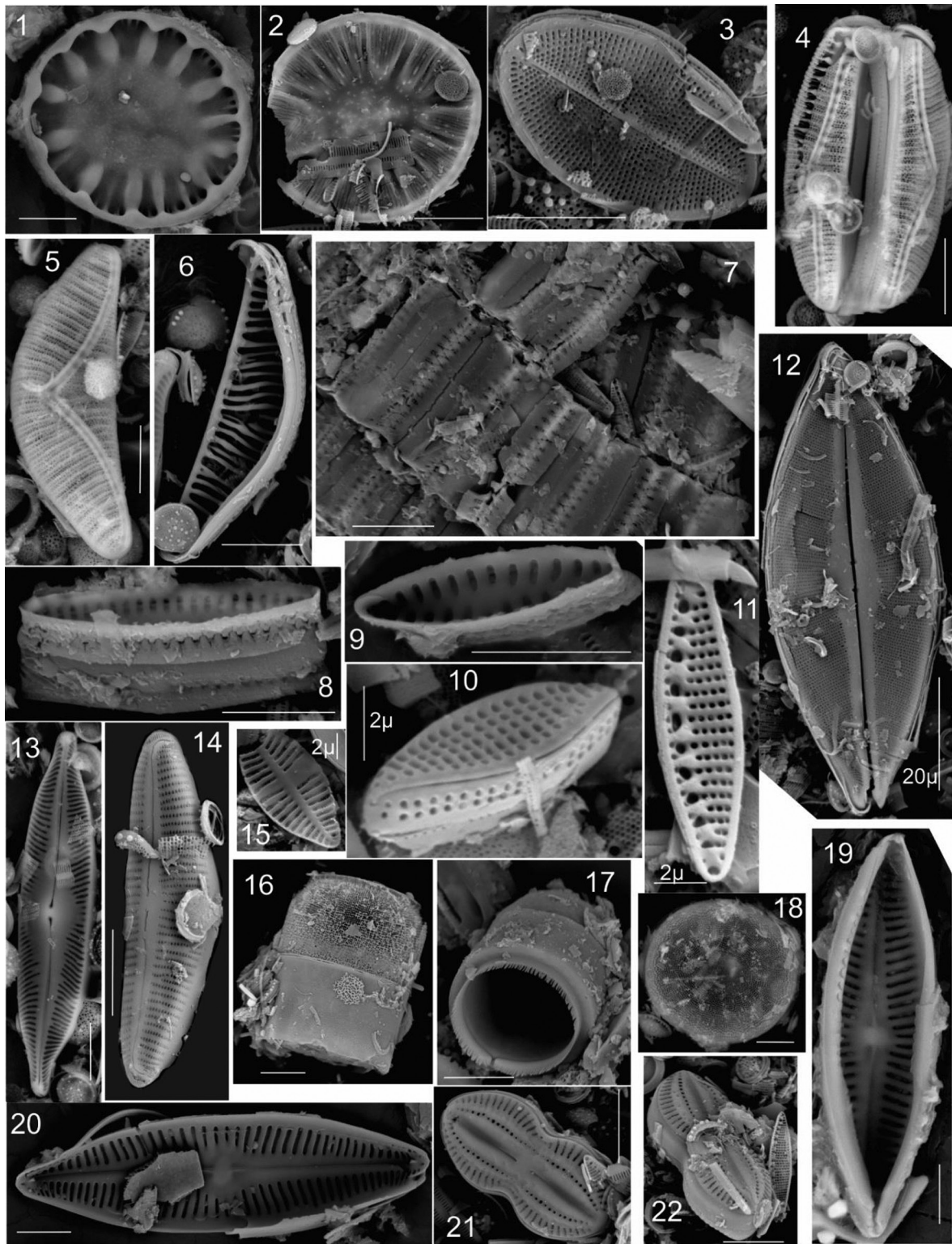


Figure 8: SEM photographs of diatoms from Szurdokpüspöki quarry; scale bar is 10 µm unless specified otherwise. Explanations of figures: 1–2 *Surirella* sp. Turpin, 3 *Cocconeis californica*? Grun, 4–6 *Epithemia turgida*? (Ehrenberg) Kützing, 7–9 *Pseudostaurosira* sp. Williams and Round, 10–11 *Nitzschia frustulum* (Kützing) Grunow, 12 *Brachysira* Kützing, 13 *Cymbella* sp. Agardh, 14 *Seminavis* sp. Mann, 15 *Planothidium* sp. Round and Bukhtiyarova, 16–18 *Podosira robusta* Pantocsek, 19 *Seminavis* sp. Mann, 20 *Navicula* sp. and 21–22 *Diploneis* sp. Ehrenberg ex Cleve. SEM – scanning electron microscope.

diatomaceous rocks. In contrast to Szurdokpüspöki samples, diffractograms from the Limberg Member do not indicate opal-A in any of the samples; only two samples from Parisdorf show opal-CT (e.g. chert sample 12-Pa; Fig. 6).

4.2.2. Bulk geochemical parameters

TOC contents in the Zellerndorf Formation borehole samples range from 0.58% to 0.91% wt. (Table 2). Sulphur contents are relatively high (0.48%–1.38% wt.) resulting in low TOC/S ratios (0.57–1.73).

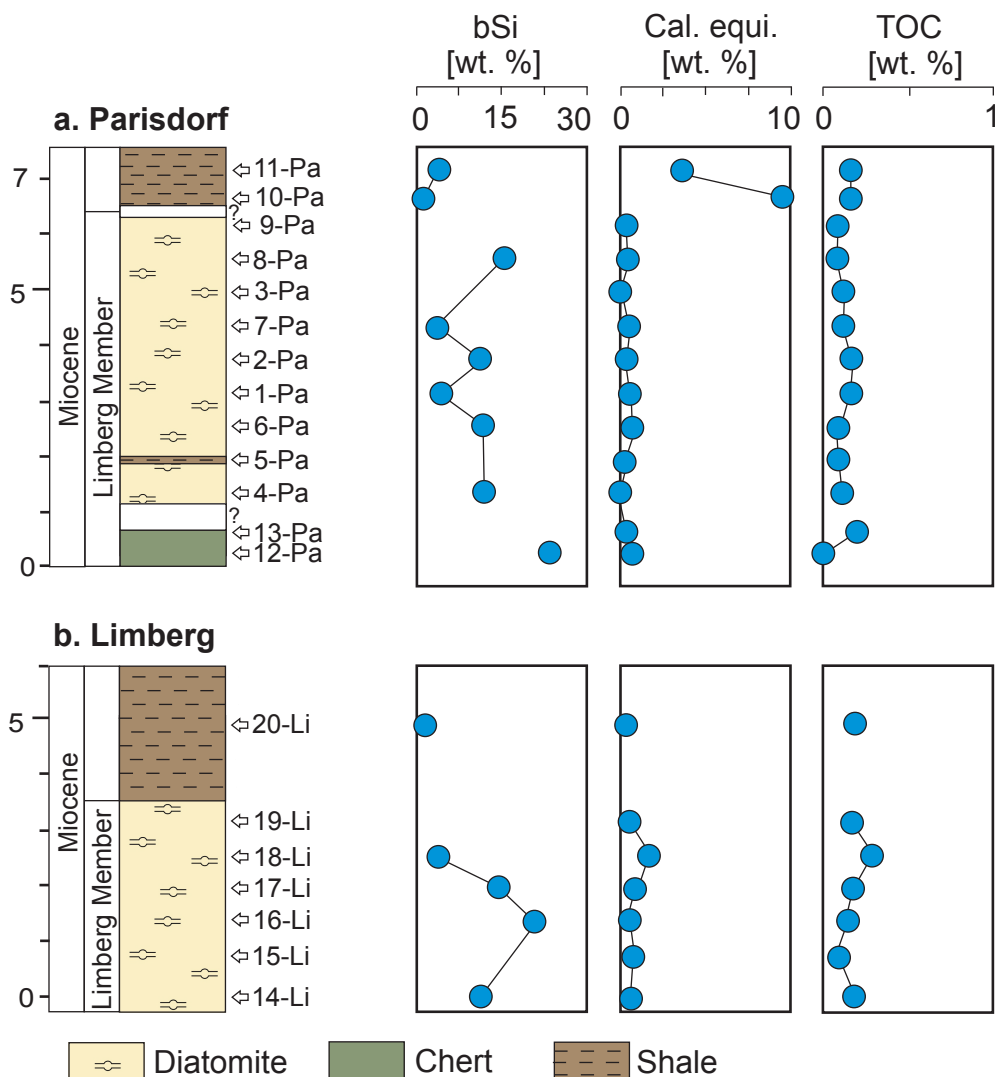


Figure 9: Outcrops of Limberg Member, Austria. (a) Lithology of the Limberg Member in Parisdorf quarry and (b) lithology of the Limberg Member in Limberg. bSi – biogenic silica, cal. equiv. – calcite equivalent, TOC – total organic carbon.

Bulk parameters for the diatomaceous rocks in the Parisdorf and Limberg quarries are listed in Table 2 and plotted versus height in Figure 9. TOC contents are very low (average 0.13% wt.), and the S content does not exceed 0.08% wt. S2 values reach a maximum of 0.36 mg HC/g TOC but are typically less than 0.2 mg HC/g TOC. HI and TOC/S values are unreliable due to low TOC contents. T_{max} has to be considered with caution, because of low S2 values, but is typically in the order of 400 to 420°C.

4.2.3. Diatom assemblages and depositional environment

Samples from Parisdorf and Limberg contain a high amount of broken diatom valves (Fig. 10). Very rare, small diatoms valves and cryophyte scales have been preserved. Two samples were barren (2-Pa from Limberg Member and 20-Li from Zellerndorf Formation). Therefore, diatom genera identification and quantification were impossible. Previous work in the area yielded better results. Řeháková (1994) and Roetzel et al. (2006) described 46 diatom genera from Parisdorf sediments, the most common genera being *Thalassionema*, *Chaetoceros*,

Coscinodiscus, *Rhizosolenia*, *Stephanopyxis* and *Thalassiosira*, and noticed a lack of shallow-water benthic taxa. Hence, Řeháková (1994) postulated a sublittoral deeper marine depositional environment with neritic and pelagic marine plankton.

5. Discussion

5.1 Maturity and hydrocarbon potential of diatomite in Szurdokpüspöki and Parisdorf/Limberg

None of the studied successions experienced deep burial. Therefore, as expected, very low T_{max} values (Tables 1 and 2) show that all studied rocks are immature. For Szurdokpüspöki samples, this is also proven by the presence of opal-A.

With TOC contents up to 3.0% wt. and partially high HI values, the lower part of the diatomaceous succession at Szurdokpüspöki contains a good hydrocarbon potential (Fig. 11). In contrast, the hydrocarbon potential of the upper part of the studied section is very low. The average hydrocarbon potential (S1+S2) of the lower

Table 2: Bulk parameter of the Limberg Member and the Zellerndorf Formation

Sample locations	Sample number	Height (m)	Calc. equ. (%)	TOC (%)	S (%)	S1 (mg HC/g)	S2 (mg HC/g)	T _{max} (°C)	PI (-)	HI (mg HC/g TOC)	TOC/S (-)
Parisdorf quarry	Zellerndorf Formation (above Limberg Member)										
	11-Pa	7.0	3.82	0.16	0.01	0.02	0.04	*	0.33	25	20.6
	10-Pa	6.5	9.67	0.16	0.01	0.01	0.03	*	0.25	19	11.4
	Limberg Member										
	9-Pa	6.2	0.21	0.11	0.00	0.02	0.12	401*	0.14	106	26.2
	8-Pa	5.5	0.32	0.11	0.01	0.03	0.17	408	0.15	151	20.7
	3-Pa	5.0	0.09	0.13	0.01	0.02	0.08	396*	0.17	58	20.7
	7-Pa	4.2	0.31	0.13	0.01	0.02	0.09	403*	0.19	68	20.8
	2-Pa	3.5	0.13	0.15	0.08	0.03	0.10	386*	0.20	67	1.9
	1-Pa	3.0	0.28	0.15	0.11	0.02	0.08	395*	0.20	54	1.3
	6-Pa	2.5	0.33	0.11	0.01	0.03	0.09	402*	0.25	85	20.1
	5-Pa	2.0	0.17	0.10	0.01	0.01	0.03	*	0.29	25	11.7
	4-Pa	1.2	0.00	0.13	0.01	0.02	0.08	*	0.20	61	15.7
	13-Pa	0.5	0.16	0.21	0.01	0.04	0.12	*	0.23	56	24.6
12-Pa	0.0	0.43	0.07	0.01	0.02	0.16	420	0.11	236	8.1	
Zellerndorf Formation (above Limberg Member)											
Limberg	20-Li	4.9	0.19	0.16	0.01	0.02	0.06	423*	0.25	0	11.1
	Limberg Member										
	19-Li	3.1	0.29	0.17	0.32	0.02	0.13		0.25	34	0.5
	18-Li	2.4	1.44	0.30	0.02	0.03	0.25	379*	0.13	43	12.7
	17-Li	1.9	0.45	0.18	0.07	0.03	0.29	414	0.11	135	2.6
	16-Li	1.2	0.32	0.16	0.01	2.06	0.31	436	0.10	174	14.4
	15-Li	0.5	0.56	0.13	0.01	1.03	0.36	421	0.87	233	13.4
	14-Li	0.0	0.29	0.18	0.18	0.04	0.11		0.74	205	1.0
Zellerndorf Formation (below Limberg Member)											
Limberg KB02 (Hangbrücke)	KB 02/1	-16.05 to -16.15	7.08	0.85	0.57						1.5
	KB 02/2	-16.55 to -16.60	4.58	0.82	0.69						1.2
	KB 02/3	-17.00 to -17.10	6.06	0.83	0.48						1.7
	KB 02/4	-17.50 to -17.55	5.13	0.84	1.48						0.6
	KB 02/5	-18.10 to -18.15	5.54	0.80	0.86						0.9
	KB 02/6	-18.55 to -18.60	4.65	0.73	0.92						0.8
	KB 02/7	-19.00 to -19.10	5.48	0.75	0.86						0.9
	KB 02/8	-19.55 to -19.60	7.04	0.58	0.87						0.7
	KB 02/9	-20.10 to -20.15	6.31	0.64	0.72						0.9
	KB 02/10	-20.55 to -20.60	4.81	0.74	0.74						1.0
	KB 02/11	-21.10 to -21.15	2.66	0.91	0.73						1.2
	KB 02/12	-21.45 to -21.55	1.75	0.86	0.76						1.1

TOC – total organic carbon, S – sulphur, HI – hydrogen index, PI – production index, calc. equi. – calcite equivalent. *T_{max} is unreliable, because of low S2 peak.

part is 6.8 mg HC/g rock. The thickness of the exposed organic matter-rich succession is 7.5 m, but because the base of the succession is not exposed, it is likely that its thickness is significantly higher (see also Figure 4 based on Hajós, 1986) and may be as high as 20 m. The density of diatomite is typically low. Assuming a density of 1.8 g/cm³ and applying the approach of Demaison and Huizinga (1994), it is suggested that the succession may generate about 0.25 tons of hydrocarbons per square meter, if mature.

The diatomites of the Limberg Member in Parisdorf and Limberg do not hold any hydrocarbon potential. This is valid also for the under- and overlying pelitic rocks of the Zellerndorf Formation.

5.2. Comparison of hydrocarbon potential of different diatomaceous rocks within Paratethys

In this section, we briefly review the depositional environment and geodynamic setting of some Oligocene to middle Miocene diatomaceous rocks in the Paratethys

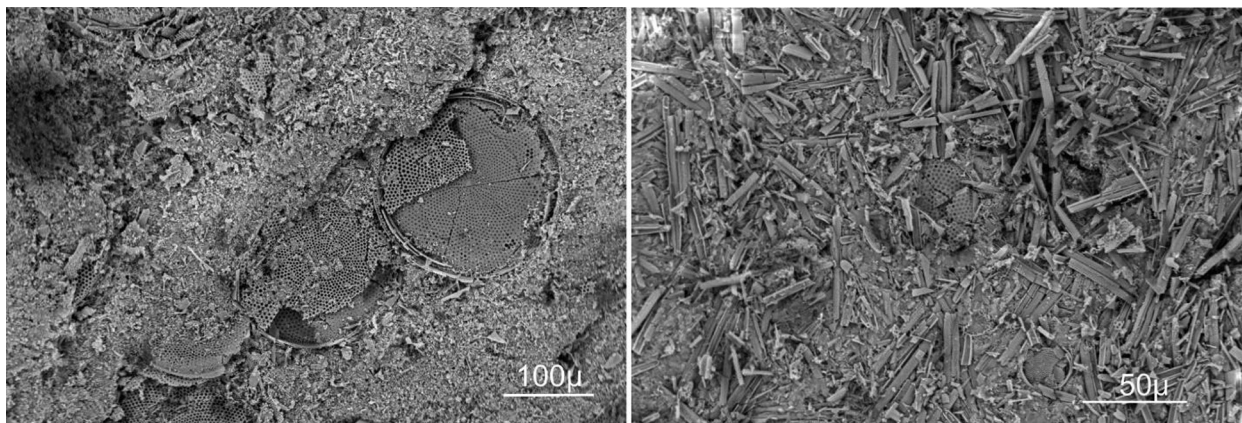


Figure 10: SEM photographs of broken diatoms observed on the rock surface of Parisdorf diatomite. SEM – scanning electron microscope.

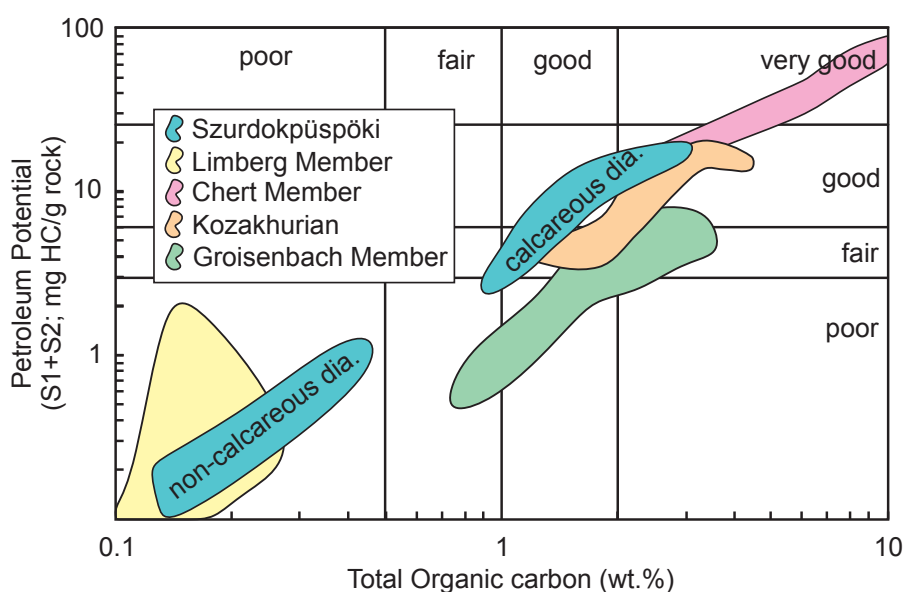


Figure 11: Petroleum potential of Szurdokpüspöki and Limberg Member in comparison with that of different Oligocene to middle Miocene siliceous sediments. Data are from Jirman et al. (2019), Chert Member of the Oligocene Menilite Formation (Western Carpathians); Mayer et al. (2018), lower Miocene (Kozakhurian) from the Kaliakra Canyon (West Black Sea Basin) and Sachsenhofer et al. (2003), middle Miocene Groisenbach Member (Aflenz Basin). dia. – diatomite.

area and compare their hydrocarbon potential with that of the studied sections. Their stratigraphic position is shown in Figure 12.

Similar to the middle Miocene Limberg Member, the Oligocene Menilite Formation represents a foreland basin setting. In the Western Carpathians (the Czech Republic), the Menilite Formation comprises from base to top the following: Subchert Member, Chert Member, Dynów Marlstone and Šitbořice Member. The lower Oligocene Chert Member is represented by laminated cherts and non-calcareous siliceous shales, which were deposited in an anoxic bathyal environment with a limited influx of detritus (Krhovský, 1981). High silica contents are due to diatom blooms. Picha and Stráník (1999) postulated that cherty rocks were deposited due to high siliceous bio-productivity caused by upwelling. In contrast, based on fish and trace fossil assemblages, Kotlarczyk and Uchman (2012) argued that lower Oligocene cherts accumulated in a silled, anoxic basin with a stratified water column.

Jirman et al. (2019) investigated the Menilite Formation exposed in the Loučka section of the Silesian Unit (Western Carpathians, Czech Republic) and found that the best source rocks occur within the Chert Member (TOC 1.51%–16.5% wt.; average 5.9% wt.; type II-I kerogen; HI up to 725 mg HC/g TOC). The very good petroleum potential (see Figure 11) is mainly due to excellent organic matter preservation caused by strictly anoxic conditions in a silled basin.

Upwelling locally enhanced by the geometry of a shelf-break canyon (e.g. Kaempfer, 2007) has been postulated for the lower Miocene (Kozakhurian) diatomaceous sediments in the Kaliakra Canyon in the West Black Sea Basin (Mayer et al., 2018; Sachsenhofer et al., 2018a). Here, Kozakhurian rocks contain high biogenic opal (up to 87% wt.) and TOC contents (1.2%–4.3% wt.). HI values (180–530 mg HC/g TOC) show the presence of type II kerogen (Mayer et al., 2018). Their petroleum potential is good but not as high as in the Chert Member (Figure 11). In case of

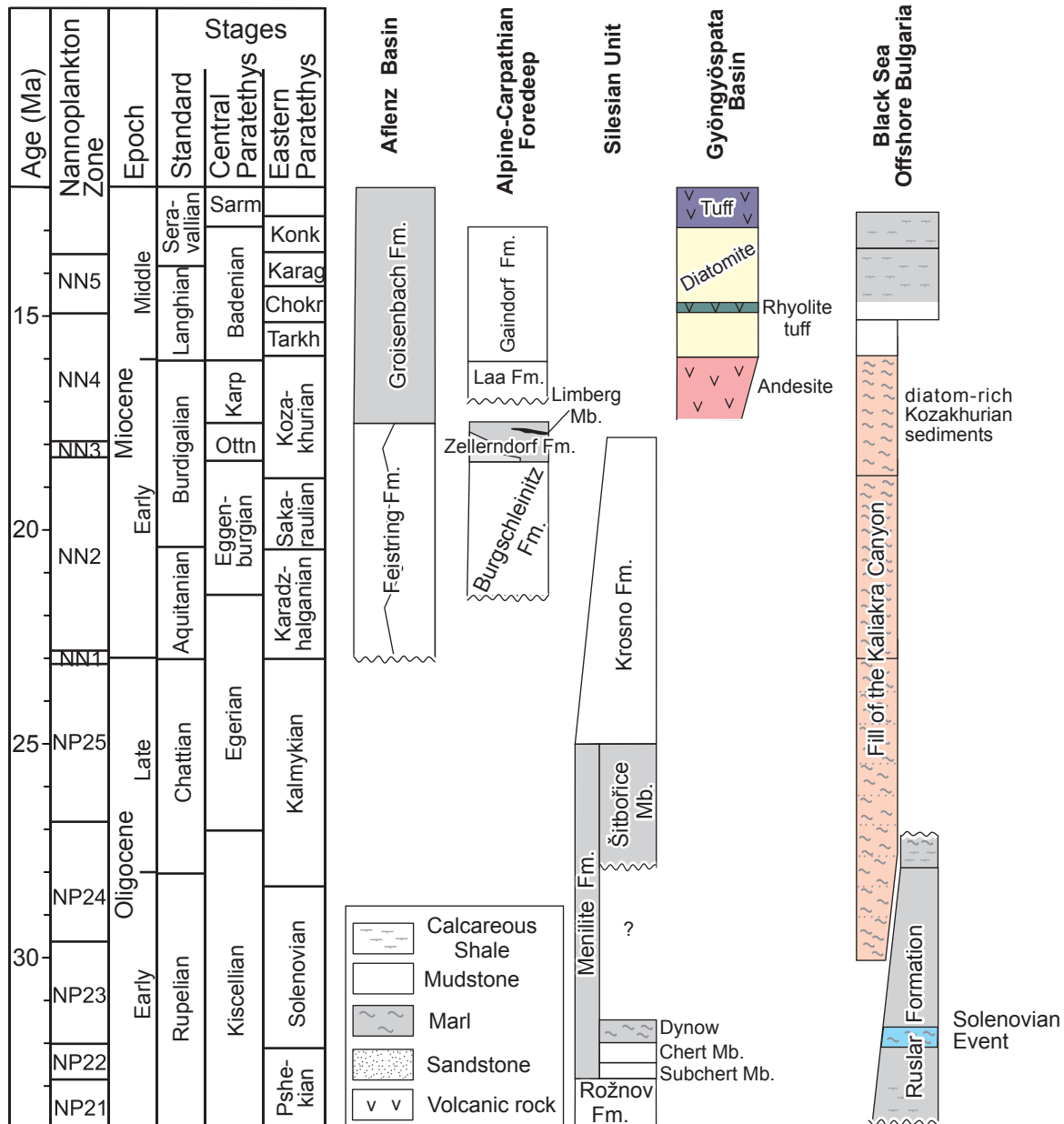


Figure 12: Stratigraphy of Oligocene to Miocene sediments within the Paratethys (compiled from Jirman et al., 2019; Hajós, 1986; Roetzel, 1999; Sachsenhofer et al., 2003 and Sachsenhofer et al., 2018).

the Kozakhurian rocks, high TOC contents and moderately high HI values reflect high bioproductivity typical for upwelling settings and deposition in an oxygen-depleted environment (Mayer et al., 2018), which facilitated the preservation of the organic matter.

This is in major contrast to the roughly coeval (Ottngian) Limberg Member, where poor organic matter preservation caused very low TOC contents. According to Roetzel et al. (2006), the Limberg Member accumulated in a pelagic, deep-neritic zone. Maybe depositional depth was still not deep enough to reach the Oxygen Minimum Zone (0.2–1.5 km).

In addition to the marine diatomaceous sediments, the lacustrine middle Miocene Groisenbach Member in the Aflenz pull-apart basin (Sachsenhofer et al., 2003) is worth mentioning. The pelitic Groisenbach Member forms the

lower part of the Göriach Formation. It was deposited in shallow fresh to oligosaline waters (Hajós, 1972) within an anoxic water column (Sachsenhofer et al., 2003) and contains high biogenic silica contents (~30%). Sachsenhofer et al. (2003) assumed that volcanic ashfalls provided both nutrients and the high dissolved-silica content in the lake water stimulating diatom productivity. The rocks contain an average TOC of 1.78% wt. and mixed type III and type II kerogen (80–330 mg HC/g TOC; Sachsenhofer et al., 2003). Their petroleum potential is similar to that of Szurdokpüspöki, although relatively low HI values may reflect a high contribution of land plants transported into the relatively small basin from its margins.

Overall, the compilation in Figure 11 shows that diatomaceous rocks may contain largely varying petroleum potential. Nevertheless, anoxic events play one of the

biggest roles in preservation of the organic matter as seen in the Chert Member, Groisenbach Member and Kozakhurian sediments. In the Limberg Member, even though bioproductivity was probably high due to upwelling, TOC contents are very low due to poor preservation of organic matter in a high energy environment (see section 5.3). In the Szurdokpüspöki sediments, the organic matter preservation at the first glance seems to be controlled by the calcite content, although there is no clear causal relation. The presence of periphytic and benthic diatoms suggests that anoxic conditions were not present. Probably, excellent organic matter preservation in the lower part of the Szurdokpüspöki quarry was caused by other factors such as high rates of deposition.

5.3 Comparison of diatom preservation in Szurdokpüspöki and Parisdorf/Limberg

The Szurdokpüspöki diatomite yields abundant and unusually well-preserved diatom frustules (Figs. 7 and 8). The fact that even the most fragile raphid diatoms are well preserved makes Szurdokpüspöki one of the best sites for studying fossil diatoms. This was realised early on in the history of diatom study, as a cleaned sample from this locality has been distributed among early 20th-century European diatom researchers under the name “Castel” (e.g. Ross, 1995). The excellent preservation testifies to an unusual mode of biogenic silica preservation. Nowadays, a direct relationship of the volcanic activity and diatom blooms is accepted (i.e. volcanic ash weathering provides silica supplies and nutrients; Cressman, 1962). Nevertheless, a discussion on the relationship between volcanic activity and diatom preservation has emerged. Harper et al. (2015) demonstrated an excellent relationship between the volcanic tephra and the diatom preservation in Quaternary sediments, as well as the change in the environment caused by volcanism. In Szurdokpüspöki, the tuff layers are present in between the diatomaceous layers (Fig 4), which, besides providing silica supplies, act as a barrier in the preservation of diatom valves.

In contrast to Szurdokpüspöki, frustules in Parisdorf/Limberg are heavily broken (Fig. 10). The siliceous exoskeleton of the diatom valves is usually tough, and they can resist decaying (Weckström et al., 2017). Dissolution and physical fragmentation are the two main damages on diatom valves. The dissolution of the diatom valves appears when there is a shortage in biogenic silica (Olli et al., 2008); however, this is not the case in Parisdorf/Limberg. The physical fragmentation can be caused by high-energy environments (i.e. friction with sand grains) or racking by zooplankton (Flower 1993; Flower and Ryves, 2009). As observed on the rock surface, the diatoms were not broken before settling down to the substratum since their shape is still recognisable (Figure 10). The breakage to the diatom valves in Parisdorf and Limberg was probably caused by a high-energy environment in the coastal upwelling condition (Roetzel et al., 2006). Wave action may have also contributed to poor diatom

preservation. Furthermore, fragmentation due to sediment compaction cannot be excluded.

6. Conclusions

Diatomaceous sediments in the abandoned Szurdokpüspöki, Parisdorf and Limberg quarries have been studied for their hydrocarbon potential. The results indicate a fair–good potential for the lower part of the middle Miocene Szurdokpüspöki succession. In contrast, the upper part of the Szurdokpüspöki succession and the lower Miocene Limberg Member contain very poor potential. At both locations, the sediments are thermally immature. If mature, the Szurdokpüspöki succession may generate about 0.25 tons of hydrocarbons per square meter.

The detected diatom assemblage in the Szurdokpüspöki succession, deposited in a restricted basin, supports a near-shore, littoral, brackish depositional environment.

The preservation of diatom valves in Szurdokpüspöki is excellent, probably due to the presence of tuff layers providing silica. In contrast, diatom frustules in Parisdorf, deposited in a sublittoral deeper marine setting, are severely broken, probably because of a high-energy environment related to upwelling currents.

The comparison of Oligocene to middle Miocene diatomaceous rocks in different environmental and geodynamic settings reveals major differences in petroleum potential varying from excellent source rocks (e.g. Chert Member of the Maikop Formation) to very poor source rocks (Limberg Member).

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References

- Alizadeh, A.A., Guliyev, I.S., Kadirov, F.A., Eppelbaum, L.V., 2016. Geosciences of Azerbaijan. Stuttgart, Springer, 340 pp.
- Basistová, P., 2007. Diatomaceae in the sediments of the Carpathian Foredeep (locality Brno-Královo Pole), Brno, Bachelor thesis. Masaryk University, Faculty of Science, 37 pp. <https://is.muni.cz/th/rnscx>
- Codrea, V., Barbu, O., Bedelea, H., 2018. Middle Miocene diatomite-bearing formations from western Romania. Bulletin of the Geological Society of Greece, 40/1, 21. <http://doi.org/10.12681/bgsg.16329>

- Cressman, E.R., 1962. Nondetrital siliceous sediments. In: Fleischer M. (ed.) Data of Geochemistry. Geological survey professional paper, 1-23. <http://doi.org/10.3133/pp440t>
- Demaison, G., Huizinga B.J., 1994. Genetic classification of petroleum systems using three factors: charge, migration and entrapment. *AAPG Memoirs* 60, 73–92.
- Dill, H.G., Sachsenhofer, R.F., Grecula, P., Sasvári, T., Palinkas, L.A., Borojevic-Šostaric, S., Strmic-Palinkas, S., Prochaska, W., Garuti, G., Zaccarini, F., Arbouille, D., Schulz, H.-M. 2008. Fossil fuels, ore and industrial minerals. In: McCann, T. (eds.), *The Geology of Central Europe. Volume 2: Mesozoic and Cenozoic*, Geological Society, London, 1341–1449. <https://doi.org/10.1144/cev2p.9>
- Figarska-Warchoł, B., Stańczak, G., Rembiś, M., Tobała, T., 2015. Diatomaceous rocks of the Jawornik deposit (the Polish Outer Carpathians): petrophysical and petrographical evaluation. *Geology, Geophysics and Environment*, 41/4, 311–331. <https://doi.org/10.7494/geol.2015.41.4.311>
- Flower, R.J., 1993. Diatom preservation: experiments and observations on dissolution and breakage in modern and fossil material. In: Twelfth International Diatom Symposium, pp. 473–484. Springer, Dordrecht. https://doi.org/10.1007/978-94-017-3622-0_48
- Flower, R.J., Ryves, D.B., 2009. Diatom preservation: differential preservation of sedimentary diatoms in two saline lakes. *Acta Botanica Croatica*, 68/2, 381–399.
- Frunzescu, D., Brănoiu, G., 2004. Monografia geologică a Bazinului râului Buzău. Editura Universităţii din Ploieşti, 309 pp.
- Gaiser, E., Wachnicka, A., Ruiz, P., Tobias, F. and Ross, M., 2005. Diatom indicators of ecosystem change in subtropical coastal wetlands. In: Bortone, S.A. (ed.) *Estuarine Indicators*. CRC Press Marine Science Series, Boca Raton, 599 pp.
- Grunert, P., Soliman, A., Harzhauser, M., Müllegger, S., Piller, W., Roetzel, R., Rögl, F., 2010. Upwelling conditions in the Early Miocene Central Paratethys Sea. *Geologica Carpathica*. 61/2, 129–145.
- Hajós, M.A., 1959. Szurdokpüspöki kovaföldrétegek algái (Die Algen des Kieselgurschichten von Szurdokpüspöki). *Földtani Közlöny*. 89/2, 155–169.
- Hajós, M.A., 1968. Die Diatomeen der Miozanen Ablagerungen des Matravorlandes. *Geologica Hungarica*. 37, 1–401.
- Hajós, M.A., 1973. The Mediterranean diatoms. *Initial Reports of the Deep-Sea Drilling Project*, 13 (Part 2), 944–951.
- Hajós, M.A., 1986. Magyarországi miocén diatomás képződmények rétegtana/Stratigraphy of Hungary's miocene Miocene diatomite deposits. *Institutum Geologicum Hungaricum Series Paleontologica*, 49, 1–339.
- Harper, M.A., Pledger, S.A., Smith, E.G.C., Van Eaton, A.R., Wilson, C.J.N., 2015. Eruptive and environmental processes recorded by diatoms in volcanically dispersed lake sediments from the Taupo Volcanic Zone, New Zealand. *Journal of Paleolimnology*, 54/4, 263–277. <https://doi.org/10.1007/s10933-015-9851-5>
- Horvat, A., 2004. Middle Miocene siliceous algae of Slovenia. *Narodna in univerzitetna knjiznica, Ljubljana*, 255 pp.
- Isaacs, C.M., Rullkötter, J. (eds.), 2001. *The Monterey Formation: From Rocks to Molecules*. Columbia University Press, New York 268–295. <https://doi.org/10.1017/S0016756802246506>
- Jirman, P., Geršlová, E., Bubík, M., Sachsenhofer, R. F., Bechtel, A., Więclaw, D. (2019). Depositional environment and hydrocarbon potential of the Oligocene Menilite Formation in the Western Carpathians: A case study from the Loučka section (Czech Republic). *Marine and Petroleum Geology*, 107, 334–350. <https://doi.org/10.1016/j.marpetgeo.2019.05.034>
- Kaempfer, J., 2007. On the magnitude of upwelling fluxes in shelf-break canyons. *Continental Shelf Research*, 27, 2211–2223. <https://doi.org/10.1016/j.csr.2007.05.010>
- Kotarba, M.J., Koltun, Y.V., 2006. The origin and habitat of hydrocarbons of the Polish and Ukrainian parts of the Carpathian Province. In: Golonka, J. & Picha, F.J. (eds.) *The Carpathians and Their Foreland: Geology and Hydrocarbon Resources*. AAPG Memoirs, 84, 395–442. <https://doi.org/10.1306/985614m843074>
- Kotlarczyk, J., Uchman, A., 2012. Integrated ichnology and ichthyology of the Oligocene Menilite Formation, Skole and Subsilesian nappes, Polish Carpathians: a proxy to oxygenation history. *Palaeogeography, Palaeoclimatology, Palaeoecology*, 331, 104–118. <https://doi.org/10.1016/j.palaeo.2012.03.002>
- Krhovský, J., 1981. Stratigraphy and palaeoecology of the Menilite Formation of the Ždánice unit and of the diatomites of the Pouzdřany unit (the western Carpathians, Czechoslovakia) (in Czech with English summary). *Zemny Plyn. a Nafta* 26, 45–62.
- Lafargue, E., Marquis, F., Pillot, D., 1998. Rock-Eval 6 applications in hydrocarbon exploration, production, and soil contamination studies. *Revue de l'institut français du pétrole* 53/4, 421–437. <https://doi.org/10.2516/ogst:1998036>
- Levkov, Z., 2009. *Amphora* sensu lato. In: Lange-Bertalot, H. (ed.) *Diatoms of Europe, Volume 5*. A.R.G. Gantner, 916 pp.
- Lohman, K.E., 1957. Cenozoic nonmarine diatoms from the Great Basin. Doctoral dissertation, California Institute of Technology, 208 pp.
- Mayer, J., Rupprecht, B.J., Sachsenhofer, R.F., Tari, G., Bechtel, A., Coric, S., Siedl, W., Kosi, W., 2018. Source Potential and Depositional Environment of Oligocene and Miocene rocks Offshore Bulgaria. In: Simmons, M. et al. (eds.), *Geological Society, London, Special Publications* 464, 307–328. <https://doi.org/10.1144/SP464.2>
- Ognjanova-Rumenova, N., Radovan P., 2015. Stratigraphic and taxonomic significance of siliceous microfossils collected from the Turiec Basin, Western Carpathians (Slovakia). *Acta Botanica Croatica* 74/2, 345–361. <https://doi.org/10.1515/botcro-2015-0023>
- Olli, K., Clarke, A., Danielsson, Å., Aigars, J., Conley, D.J., Tamminen, T., 2008. Diatom stratigraphy and long-term

- dissolved silica concentrations in the Baltic Sea. *Journal of Marine Systems*, 73/3-4, 284–299. <https://doi.org/10.1016/j.jmarsys.2007.04.009>
- Pantocsek, J., 1889. Beiträge zur Kenntnis der Fossilen Bacillarien Ungarns. Teil II. Brackwasser Bacillarien. Anhang: Analyse de marine Depots von Bory, Bre-mia, Nagy-Kurtos in Ungarn; Ananio und Kusnetzki in Russland. Nagy-Tapolcsány, Buchdruckerei von Julius Platzko, 123 pp.
- Pícha, F.J., Stráník, Z., 1999. Late Cretaceous to early Mio-cene deposits of the Carpathian foreland basin in south-ern Moravia. *International Journal of Earth Sciences*, 88, 475–495.
- Řeháková, Z., 1997. Bericht 1997 über mikropaläontolo-gische Untersuchungen der diatomeenführenden Sed-imente auf Blatt 22 Hollabrunn. — unveröffentlichter Bericht, Archiv der Geologischen Bundesanstalt, Inv.Nr. ALK-022REH/97, pp. 5, Wien.
- Roetzel, R., (Eds.), 1999. Arbeitstagung der Geologischen Bundesanstalt 1999, Geologische Karten ÖK 9 Retz und ÖK 22 Hollabrunn, Geogenes Naturraumpotential der Bezirke Horn und Hollabrunn, Retz, Wien.
- Roetzel, R., Ćoric, S., Galovic, I., Rögl, F., 2006. Early Mio-cene (Ottangian) coastal upwelling conditions along the southeastern scarp of the Bohemian Massif (Paris-dorf, Lower Austria, Central Paratethys). *Beiträge zur Paläontologie*, 30, 387–413.
- Ross, R., 1995. Revision of *Rutilaria* Greville (Bacillariophy-ta). *Bulletin of the Natural History Museum. Botany Se-ries*, 104 pp.
- Round, F.E., Crawford, R.M., Mann, D.G., 1990. *Diatoms: bi-ology and morphology of the genera*. Cambridge Uni-versity Press, 747 pp.
- Ross, R., 1995. Revision of *Rutilaria* Greville (Bacillariophy-ta). *Bulletin of the Natural History Museum. Botany Se-ries. Bulletin of the Natural History Museum of London Botany*, 25 1–93.
- Rovira, L., Trobajo, R., Sato, S., Ibáñez, C., Mann, D.G., 2015. Genetic and physiological diversity in the diatom *Nitzschia inconspicua*. *Journal of Eukaryotic Microbiolo-gy*, 62/6, 815–832.
- Sachsenhofer, R.F., Bechtel, A., Reischenbacher, D., Weiss, A., 2003. Evolution of lacustrine systems along the Mio-cene Mur-Mürz fault system (Eastern Alps, Austria) and implications on source rocks in pull-apart basins. *Marine and Petroleum Geology*, 20, 83–110. [https://doi.org/10.1016/s0264-8172\(03\)00018-7](https://doi.org/10.1016/s0264-8172(03)00018-7)
- Sachsenhofer, R.F., Popov, S.V., Bechtel, A., Coric, S., Fran-cu, J., Gratzner, R., Grunert, P., Kotarba, M., Mayer, J., Pupp, M., Rupprecht, B.J., 2018a. Oligocene and Lower Mio-cene source rocks in the Paratethys: Palaeogeographic and stratigraphic controls. In: Simmons M, (editor) *Petroleum Geology of the Black Sea*. Geological Society London, Special Publication, 464, 267–306. <https://doi.org/10.1144/sp464.1>
- Sachsenhofer, R.F., Popov, S.V., Coric, S., Mayer, J., Misch, D., Morton, M.T., Pupp, M., Rauball, J., Tari, G., 2018b. Paratethyan petroleum source rocks: An overview. *Journal Petroleum Geology* 41/3, 219–245. <https://doi.org/10.1111/jpg.12702>
- Schrader H.J., 1973. Proposal for a standardized method of cleaning diatoms-bearing deep-sea and land-ex-posed marine sediments. In: Simonsen, R. (eds.) *Second symposium on recent and fossil diatoms*. Nova Hedwigia, supplement 45, 409.
- Schrader, H., Gersonde R., 1978. Diatoms and silicoflagel-lates. In: Zachariasse et al. *Microplaeontological count-ing methods and techniques - an exercise on an eight metres section of the lower Pliocene of Capo Rossello*. Sicily. *Utrecht Micropaleontological Bulletin*, 17, 129–76.
- Schultz, L., 1964. Quantitative interpretation of miner-alogical composition from X-ray and chemical data for the Pierre Shale. *United States Geological Survey*, 391 pp.
- Shukla, S.K., Mohan, R., 2012. The Contribution of Di-atoms to Worldwide Crude Oil Deposits. In: Gordon R., Seckbach J. (eds.) *The Science of Algal Fuels*. Cel-lular Origin, Life in Extreme Habitats and Astrobiolo-gy, Springer, Dordrecht, 25, 355–382. https://doi.org/10.1007/978-94-007-5110-1_20
- Szentesi, Z., 2008. *Bufo* aff. *viridis* (Anura: Bufonidae) from the Middle Miocene diatomite of Szurdokpüspöki, northeastern Hungary. *Central European Geology*, 51/4, 315–324. <https://doi.org/10.1556/ceugeol.51.2008.4.2>
- Tari, G., Horváth, F., 2006. Alpine evolution and hydro-carbon geology of the Pannonian Basin: an over-view. In: Golonka J., Pícha F. (eds.), *The Carpathians and their Foreland: Geology and Hydrocarbon Re-sources*. AAPG Memoir, 84, 605–618. <https://doi.org/10.1306/985733m843141>
- Tulan, E., Sachsenhofer, R.F., Horvat, A., Tari, G., Olaru-Flo-rea, R.F., 2019. Hydrocarbon source rock potential of Oligo-Miocene diatomaceous rocks in Sibiciu de Sus, Romania, Abstracts AAPG Paratethys Petroleum Sys-tems between Central Europe and the Caspian Region, Vienna.
- Varga, G., Csillag-Teplánszky, E., Félegyházi, Z., 1975. *Geol-ogy of the Mátra Mountains (in Hungarian)*. Annual Re-port of the Hungarian Geological Institute 57/1, 575 pp.
- Weckström, K., Saunders, K.M., Gell, P.A., Skilbeck, C.G. (eds.), 2017. *Applications of Paleoenvironmental Techniques in Estuarine Studies*. *Developments in Paleoenvironmental Research*. <https://doi.org/10.1007/978-94-024-0990-1>
- Wehr, J.D., Sheath, R.G., Kociolek, J.P. (eds). 2015. *Freshwa-ter algae of North America: Ecology and Classification*. Elsevier, 918 pp.
- Williams, D.M., Round, F.E., 1987. Revision of the genus *Fragilaria*. *Diatom research*, 2/2, 267–288.
- Witkowski, A., Lange-Bertalot, H., Metzeltin, D., 2000. *Dia-tom flora of marine coasts I*. *Iconographia Diatomologi-ca* 7. ARG Gantner Verlag KG, Ruggell, 7, 950 pp.
- Zolitschka B., 1998. Paläoklimatische Bedeutung lami-nierter Sedimente. Holzmaar (Eifel, Deutschland), Lake C2 (Nordwest-Territorien, Kanada) und Lago Grande di Monticchio (Basilicata, Italien). *Bornträger*, Berlin, 176 pp.

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