Mineralogy and sedimentology of diatomaceous sediments of Slovenia

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Abstract: The aim of this paper is to describe the diatomaceous sediments discovered in Slovenia and to classify and clarify the differences between them on basis of the mineralogical and geochemical characteristics. In the entire Central Paratethys diatomaceous sediments occur in temporally limited sequences, usually in sedimentary rocks that do not contain carbonates. In Slovenia diatomaceous sediments have only been discovered in four fragmentary Middle Miocene sections. The diatomaceous sediments of Slovenia can be placed into three groups, with respect to their contents of opal-A, clay minerals and carbonate. In first group are the samples containing the highest quartz and opal-A and no carbonates. They can be termed diatomaceous siltstones. The second group may associate the samples with a high carbonate content, low quartz and opal-A content, and relatively low clay mineral content. They can be termed diatomaceous siltstones. The third group of samples has a wider dispersion than the first two. Typical in this group are the high contents of quartz and opal-A, and relatively low contents of carbonates, and, in some samples, high percent of a tuff component. The samples of this group could also be attributed to diatomaceous carbonate siltstone, with the exception of sample Bc1-1. As the proportion of tuffaceous component exceeds 20 %, it may be termed tuffaceous diatomite.

Key words: diatomaceous sediments, diatoms, mineralogy, sedimentology, opal-A, biogenic silica, Miocene, Central Paratethys.

Introduction

Diatomaceous sedimentary rocks are sediments rich in diatom skleletons. Usually they indicate relatively high rates of paleobioproduction, which are correlated with the upwelling zones. For the formation of such sediments in the Central Paratethys the most favourable paleooceanographic conditions were in the Middle Miocene. Middle Miocene diatomaceous sedimentary rocks have been recorded from the entire Central Paratethys. Badenian diatoms from localities in Austria, Slovakia and Bohemia were described by Řeháková (1977, 1978), those from the Pannonian basin of Hungary by Hajós (1968, 1986), and those from the Badenian beds of Bulgaria by Temniskova-Topalova (1981). Sarmatian diatoms from localities in Slovakia, Bohemia and Hungary

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were described by HAJÓS & ŘEHÁKOVÁ (1974), from Hungary by HAJÓS (1978, 1986), from Romania by KRESTEL (1962), and from Bulgaria by TEMNISKOVA-TOPALOVA (1979, 1982).

In spite of their wide geographical range, diatomaceous sediments in the entire Central Paratethys occur in temporally limited sequences, usually in sedimentary rocks that do not contain carbonates. Therefore, they are rarely found in connected sections that could be lithologically and regionally comparable, and they are not easily inserted into the defined formations. This is also the case in Slovenia where diatomaceous sediments have only been discovered in four fragmentary Middle Miocene sections.

In Slovenia diatoms appear in various sedimentary rocks that have not been classified yet. Therefore, the aim of the paper was to describe the diatomaceous sediments and clarify the differences between them on the basis of the mineralogical characteristics.

GEOLOGICAL SETTING

In Slovenia the diatomaceous sediments have been found only in the Middle Miocene in the Krško basin and in the Tuhinj syncline (Fig. 1). All localities are situated south of the Sava and Donat faults. The base for the Miocene sediments in the westernmost parts of the Pannonian basin (*sensu lato*) is built-up by sediments of the Internal and External Dinarides.

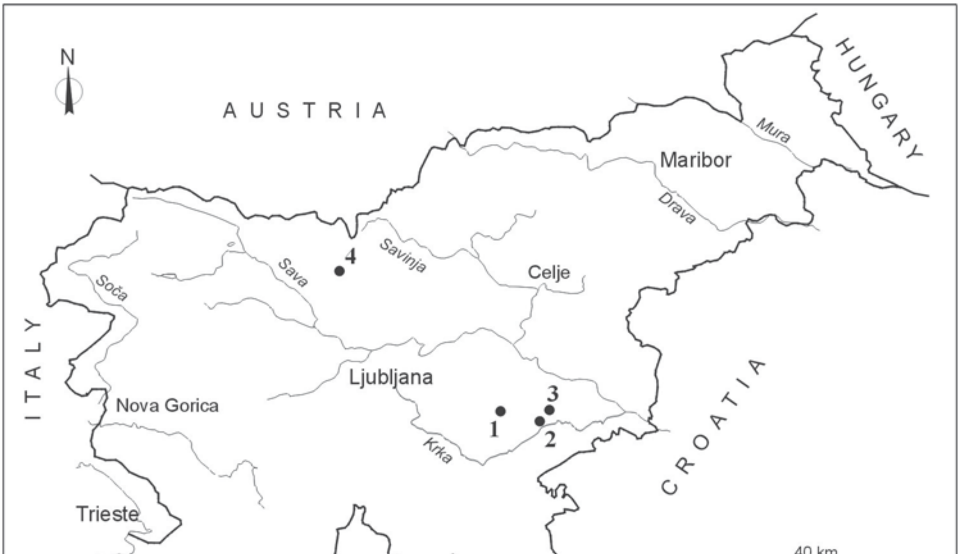

Figure 1. Location map of diatomaceous deposits localities in Slovenia.
1 - section Šmarjeta; 2- section Bela Cerkev 1; 3 - section Bela cerkev 2; 4 - section Tunjice

The Šmarjeta section was recorded in the roadcut of the Šmarjeta - Zbure road. The section consists of dark grey to green grey carbonate siltstone beds (Fig. 2). The beds under- and over-lying the profile were not visible in the field. In the rocks frequent fragments of turritellids and rare remains of scaphopods, ostreans and very rare perreiraeas occur. Siliceous microfossils in all samples are rare. In general, only the remains of sponge spicules and rare endoskeletal dinoflagellates can be found. Modest and poorly preserved diatom and silicoflagellate flora were found only in the sample Šm-5. The age of the diatomaceous sediments in the Šmarjeta section is Upper Badenian (Horvat, 2004).

The Bela Cerkev 1 section is situated at the roadcut of the road bridge for Bela Cerkev that passes above the Ljubljana - Zagreb highway. The section can be divided into a lower carbonate part and an upper non-carbonate part (Fig. 2). The transition from carbonate to noncarbonate parts is covered. At the base of the section lies a 60 cm thick bed of laminated carbonate silt. Then follows 35 cm of bedded carbonate siltstone, and above a 15 cm thick layer of massive, intensely lithified carbonate silt containing rare cardiids and numerous fragments of mollusc shells. Above that lies 30 cm of finely layered carbonate silty clay without any visible fossil remains. The lower part of the profile is terminated by a 10 cm thick layer of lithified massive carbon-

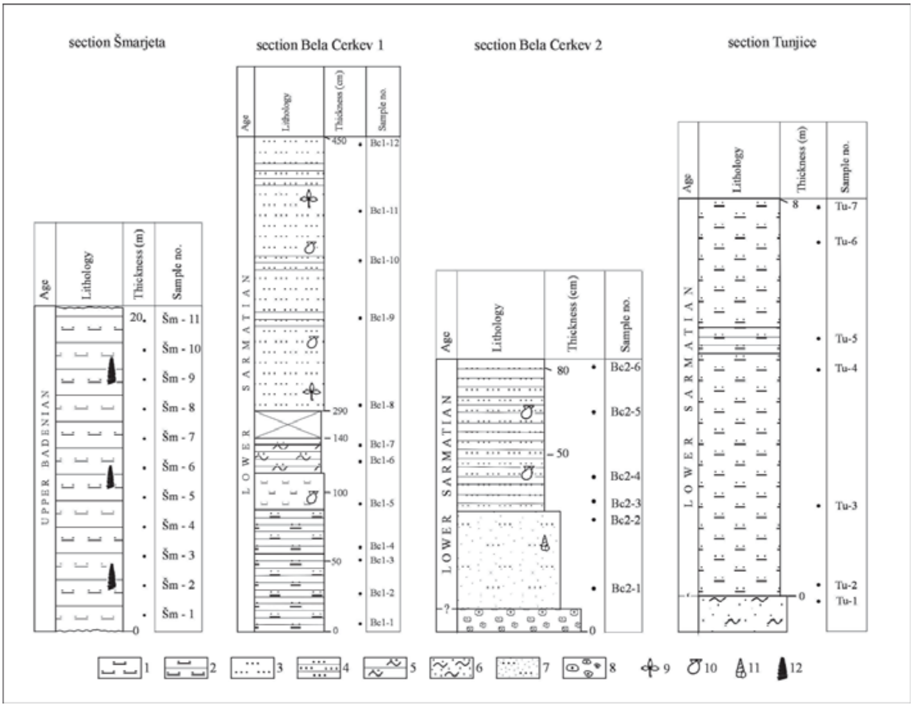

Figure 2. Geological columns of investigated diatomaceous sediments.
1 – carbonate siltstone; 2 – laminated carbonate siltstone; 3 – massive siltstone, 4 – laminated silstone; 5 – carbonate silty clay; 6 – sandy mud; 7 – sandy silt; 8 – oncolite; 9 – plant remains; 10 – bivalve moulds; 11 – molluscs (*Cerithium, Ervilia, Rissoa*); 12 – turritellid gastropods

ate silty clay. In the lower part of the section, diatoms are most abundant and best preserved in the samples Bc1-1 and Bc1-2. The samples Bc1-3, Bc1-4, Bc1-5, and Bc1-6 are quite similar to each other given the state of preservation and abundance of diatoms, but lag behind the samples Bc1-1 and Bc1-2 in terms of preservation and abundance. The sample Bc1-7 does not contain any siliceous microflora. In the lower part of the section diatoms prevail, while silicoflagellates and ebridians are rare. The upper part of the section is characterised by monotonous sedimentation of fine-bedded grey siltstone and laminated siltstone. When dried, the rock is light grey, very light, and it splits into thin sheets. It is often limonitised along laminas. In certain horizons there are frequent imprints of cardiid bivalves, whose shells are, as a rule, dissolved. The base and cover of the profile are not visible in the field. All samples from the section's upper part contained relatively well-preserved and abundant diatom flora characteristic for Lower Sarmatian (HORVAT, 2004).

The Bela Cerkev 2 section was recorded in an excavation for a house in the Bela Cerkev village. At the base of the section a several-centimetre thick layer of oncolite that is overlain conformingly by a 30 cm thick bed of sandy siltstone with numerous gastropod and bivalve remains. The section is terminated by a 40 cm thick slaty siltstone with imprints of cardiid shells (Fig. 2). The bivalve shells are always dissolved. At first sight, the bed resembles the upper part of the Bela Cerkev 1 section. This resemblance also extends to mineralogy. Beds overlying the section are not exposed. Well-preserved and abundant siliceous microflora are only contained in samples from the upper siltstone bed. Siliceous microflora are typical for Lower Sarmatian (HORVAT, 2004).

The Tunjice section of Lower Sarmatian diatomaceous sediments is situated in a ravine of a creek about 500 m west of the Tunjice village. It starts in sandy mudstone that does not contain any siliceous microfossils. Following upwards is grey massive carbonate siltstone. Six metres above the siltstone/mud contact occurs a 40 cm thick bed of laminated carbonate silstone. To the top of the section massive carbonate silstone occure (Fig. 2). The top part of section, however, is not accessible. In all samples the siliceous microflora is moderately well-preserved. For details see HORVAT (2004).

METHODS

The bulk mineral composition and coarse clay fraction of samples were scanned by X-ray diffraction technique (XRD) using a Philips difractometer (PW 3710), goniometer 1820, with automatic divergence slit and curved monochromator, operating at 40 kV, 30 mA with CuK_{α} radiation and Ni filter available at the Department of Geology, University of Ljubljana. The coarse clay fraction (2 μm) of oriented samples onto glass slides was scanned as well. This examination did not give the expected results due to clay fraction coagulation, which is probably a consequence of the presence of opal in the water solution. In spite of that, it was possible to roughly determine the clay fraction mineral composition from the oriented samples, which was taken into account during the interpretation of the mineral composition of the whole sample. Qualitative and quantitative mineral composition was established using methods cited in MIŠIČ (1998). Opal content was calculated after BOSTRÖM ET AL. (1972) and BREWSTER (1983; cf. BUSTILLLO & LOPEZ GARCÍA, 1997).

Granulometric analysis was performed in the Geological Survey of Slovenia's laboratories using a laser grain size measurer Fritsch, Analysette 22 device.

Chemical analyses were carried out at the ACME Laboratory in Canada. For whole rock analysis by ICP 0.2 g of sample was melted with 1.2 g $LiBO_2$ and dissolved in 100 ml 5 % HNO_3. LOI was calculated as a sample mass loss after one hour of ignition at 1000 °C temperature.

Results

Grain-size analyses of diatomaceous sediments showed that in all samples prevailed silt fraction (54.5–90.1 %). Amount of clay did not exceed 33 % except in sample Bc1-6. Amount of sand fraction did not exceed 1 % (Fig. 3).

The Bela Cerkev 1 Section

In mineralogical terms, the Bela Cerkev 1 section can be divided into two parts (Table 1). In the lower part, the samples contain a relatively high proportion of carbonates (19–77 %), and relatively low quartz amounts (1–23 %). Samples in the upper part of the section do not contain carbonates, and the amount of quartz is relatively higher, attaining 33–38 % (Fig. 4).

The total amount of carbonates (calcite + aragonite) is high in the entire lower part of the section (except for sample Bc1-1), varying between 77 and 86 %. The contents of calcite and aragonite are inversely proportional: higher calcite abundance results in a proportionally lower abundance of aragonite (Fig. 5). The high amounts of carbonates can be explained by the fragments of mollusc skeletons that are common in this part. In

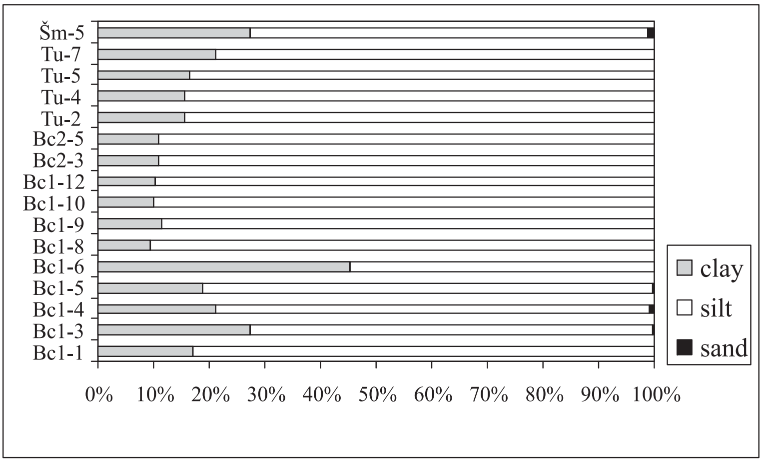

Figure 3. Grain-size distribution of the Middle Miocene diatomaceous sediments in Slovenia. Bc1 - section Bela Cerkev 1; Bc2 - section Bela cerkev 2; Tu - section Tunjice; Šm - section Šmarjeta

Table 1. Mineralogical composition of powdered samples of the Middle Miocene diatomaceous sediments. All values in wt. %.
Bc1 - section Bela Cerkev 1; Bc2 - section Bela cerkev 2; Tu - section Tunjice; Šm - section Šmarjeta
Ms/Ill = muscovite/illite, Chl = chlorite, Ca-Mnt = Ca montmorillonite; Qtz = quartz; Pl = plagioclase, Cal = calcite; MgCal = Mg calcite with x%mol $MgCO_3$ in $CaCO_3$; Dol = dolomite; Arg = aragonite, Py = pyrite.

Sample	Ms/Ill	Chl	Ca-Mnt	Qtz	Pl	Cal	MgCal	Dol	Arg	Py
Bc1-1	23	0	24	23	0	19	0	0	11	0
Bc1-3	19	0	0	2	0	51	0	0	28	0
Bc1-4	6	0	0	7	0	77	0	0	10	0
Bc1-5	10	0	0	6	0	75	0	0	9	0
Bc1-6	0	14	0	8	0	37	0	0	41	0
Bc1-8	36	12	15	32	4	0	0	0	0	1
Bc1-9	47	11	0	35	4	0	0	0	0	3
Bc1-10	31	18	16	32	3	0	0	0	0	0
Bc1-12	36	10	16	34	4	0	0	0	0	0
Bc2-3	39	13	8	40	0	0	0	0	0	0
Bc2-5	41	15	8	30	6	0	0	0	0	0
Tu-7	28	10	12	17	6	22	0	4	0	1
Tu-5	25	11	8	20	3	14	11, 7.8%	3	5	0
Tu-4	28	10	10	15	4	14	12 ,4.8%	5	0	2
Tu-2	21	10	0	11	4	26	19, 7.8%	7	2	0
Šm-5	9	4	7	14	2	48	0	4	12	0

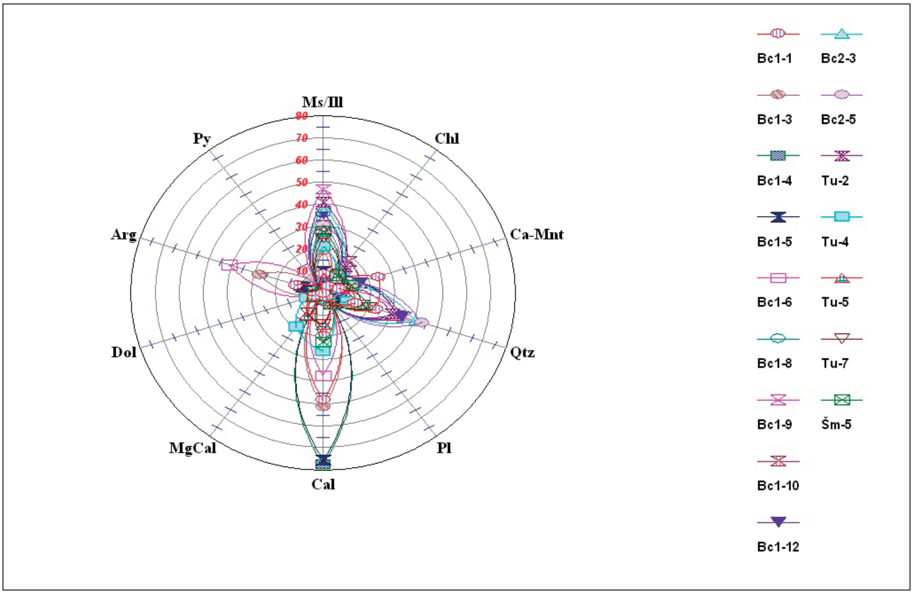

Figure 4. Bulk samples mineralogical composition of investigated samples of diatomaceous sedments in wt. %. Minerals legend as in Tab. 1.
Bc1 - section Bela Cerkev 1; Bc2 - section Bela cerkev 2; Tu - section Tunjice; Šm - section Šmarjeta

addition, the amount of phyllosilicates and clay minerals in the lower part of the section is lower, between 6 and 19 % (Tab. 1). The only clay mineral in the lower part of the section is muscovite/illite, except for sample Bc1-6 in which chlorite occurs (Fig. 6).

At variance with the samples of the lower part of the section is the sample Bc1-1. In comparison with other samples from this part of this section it contains relatively less carbonates (34 %) and more quartz (19 %). Also higher in Bc1-1 are the amounts of phyllosilicates (Table 1, Fig. 6) and clay minerals (47 %). Next to muscovite/illite, Ca montmorillonite is also present (Fig. 6). Associated with Ca montmorillonite in all samples are mixed-layered clay minerals with random ordering, R = 0. The minerals are of the illite/montmorillonite type with an I/M ratio between 15/85 and 10/90.

All samples in this part of the section contain diatoms in spite of the low quartz contents. In sample Bc1-1 the quartz content is high, but the abundance and state of preservation of diatoms is about the same as in all samples of this part of the section. Samples from the upper part of the section contain above 30 % quartz and no carbonates. The absence of carbonate minerals can be explained by diagenesis since in the samples carbonate fragments of mollusc shells are no longer found, only the imprints of valves remain which, however, were dissolved. In the same line no carbonate-skeleton microfauna are left in the samples. The samples of the upper part of the section also contain a considerably higher amount of clay minerals. The most frequent is muscovite/illite and, in comparable amounts, also chlorite and Ca montmorillonite (Table 1, Fig. 6). Samples of this upper part of the section also contain,

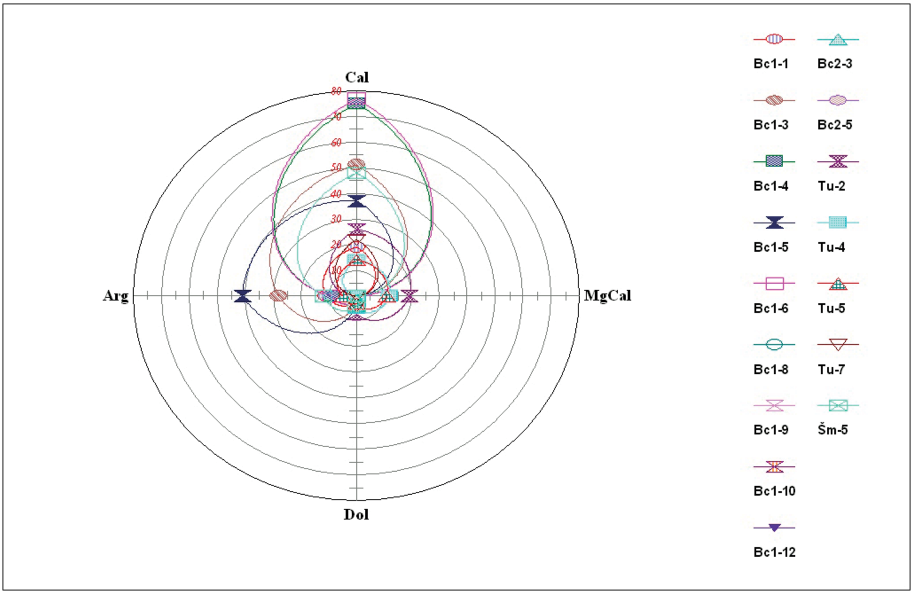

Figure 5. Mineralogical compositoin of carbonate componente of diatomaeceous sediments in Slovenia in wt. %. Minerals legend as in Tab. 1.
Bc1 - section Bela Cerkev 1; Bc2 - section Bela cerkev 2; Tu - section Tunjice; Šm - section Šmarjeta

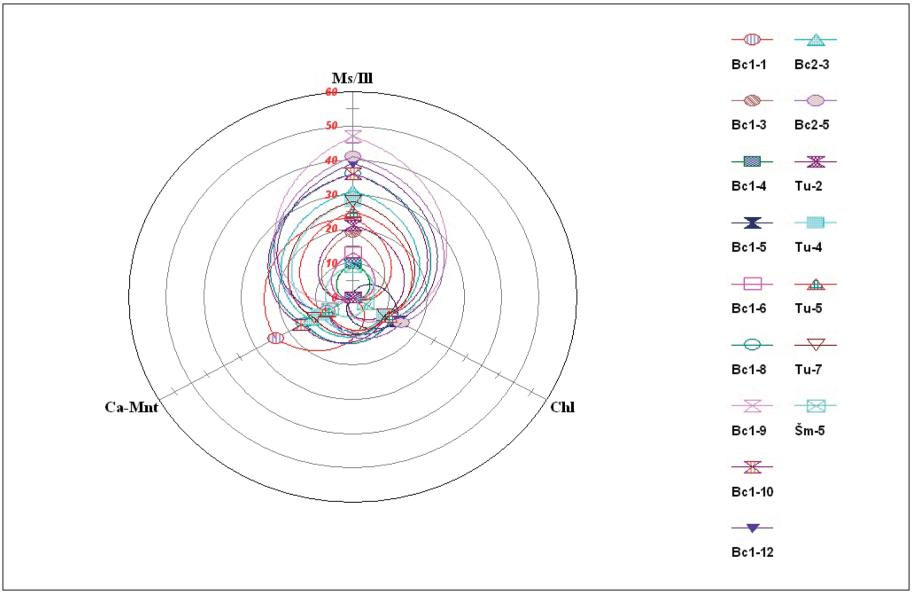

Figure 6. Mineralogical composition of phyllosilicates and clay minerals of diatomaeceous sediments in Slovenia in wt. %. Minerals legend as in Tab. 1.
Bc1 - section Bela Cerkev 1; Bc2 - section Bela cerkev 2; Tu - section Tunjice; Šm - section Šmarjeta

in contrast to those from the lower part of the section, plagioclases (Table 1).

On the X-ray diffractograms of all samples from the upper part of the section, a somewhat elevated background at the place of the principal quartz peak can also be observed, an indication of the presence of the amorphous phase, respectively opal that occurs in the skeletons of siliceous algae.

The Bela Cerkev 2 Section

The mineral composition of samples in the Bela Cerkev 2 section (Tab. 1) resembles that of samples from the upper part of the Bela Cerkev 1 section: an absence of carbonates, more than 30 % quartz content, the presence of plagioclases and similar clay contents (Figs. 4-6). Also similar is the amount of phyllosilicates and clay minerals (61–64 %): the highest is muscovite/illite, and in similar amounts in all samples are also chlorite and Ca montmorillonite. In addition, in all x-ray diffractograms of the Bela Cerkev 2 samples the presence of amorphous silica can also be observed.

The Tunjice Section

In the Tunjice section no essential differences in mineralogy between the samples can be seen. The amount of quartz (Table 1; Figs. 4 and 7) varies between 11 and 20 %. Quartz is lowest in the lower part of the section (11 %), and highest in the laminated parts of the section (20 %). The slightly elevated background on the x-ray diffractograms of all samples, except for Tu-7, suggests the presence of an amorphous phase of quartz associated with siliceous skeletons. The amount of calcite (Fig. 5) varies between

14 and 22 %. Its maximum value is attained at the lowest point of the section, and its minimum in the middle of the section. Samples Tu-2 and Tu-4 contain aragonite, probably associated with the skeletons of foraminifers and/or ostracods since no fragments of mollusc shells can be seen.

According to the composition of clay minerals the Tunjice section is similar to the upper part of the Bela Cerkev 1 and Bela Cerkev 2 sections, with the amount of clay minerals in the Tunjice section being lower (21–50 %). The highest are contents of muscovite/illite, and about equal are those of chlorite and Ca montmorillonite (Fig. 6). In all samples plagioclases and dolomite also occur (Table 1).

The Tunjice section samples differ in mineralogy from those of the Bela Cerkev sections. They contain fewer carbonates than the samples from the lower part of the Bela Cerkev 1 section, and more carbonates than samples from the upper part of the Bela Cerkev 1 and Bela Cerkev 2 sections (Fig. 5). Calcite and aragonite also do not show an inverse relationship as in the Bela Cerkev 1 section. The same is valid for the presence of quartz (Figs. 4 and 7) and clay minerals (Fig. 6). Quartz is more abundant in the Tunjice section than in the lower part of the Bela Cerkev 1 section, and less abundant than in the upper part of the Bela Cerkev 1 and Bela Cerkev 2 sections. The Tunjice section samples most resemble in their amounts of quartz and calcite the Bc1-1 sample from Bela Cerkev 1, but they contain considerably less aragonite. The amount of clay minerals is about equal. They differ in the presence of plagioclases and dolomite.

The Šmarjeta Section

The mineralogy of the examined Badenian sample (Šm-5) most resembles the samples of the lower part of the Bela Cerkev 1 section. According to the abundance of individual minerals, it can be ranged between sample Bc1-1 and the remaining samples in that part of the section (Bc1-2 - Bc1-7). The most abundant is calcite, followed by quartz and aragonite (Table 1; Figs. 4-7). Among clay minerals, muscovite/illite, chlorite and Ca-montmorillonite are present. Plagioclase and dolomite also appear in lower amounts.

Discussion

The presence and amounts of biogene opal cannot easily be detected in X-ray diffractograms. The X-ray examination indicated relatively low or zero organic silica in the samples (lower part of the Bela Cerkev 1 section), although all examined samples contain siliceous algae. It is possible that a large part of amorphous quartz passed into crystalline quartz. It is also difficult to determine the amount of opal in the thin sections where the anisotropic opal occurs mixed with clay minerals (Horvat, 2004, Pl. 2, Figs. 1 and 2).

The primary biogenic phase of silica is opal-A. With time and increasing temperature opal-A passes into opal-CT. Crystallographic descriptions of opal-CT vary: mixture of α-cristoballite and α-tridymite, tridymite and α-tridymite (Hein et al., 1985). Opal-A passes into opal-CT by crystal growth of the crystallites from silica added to the system by the continued dissolution of siliceous skeletons. The solubility of siliceous skeletons increases relatively from sponge spikules across radiolarians, silicoflagellates to diatoms. Since the opal-A and opal-CT differ in morphology, the diffractograms permit the detection of the opal phases occurring in the sample. Under X-ray the opal-A is almost totally amorphous and it provokes a broad reflection that results in an elevated background between 2Θ° = 18-26° (d = 4.84-2.88 Å). Maximum intensity is attained at d = 4,01 Å (2Θ° = 22°). Reflections of opal-CT are higher and sharper, but they still have a very broad base (d = 4.32-4.22 Å), and the main reflection lies at d = 4.12-4.05 Å (HEIN ET AL., 1985).

In the examined samples the main opal reflections are very broad, without an expressed peak, indicating only the presence of opal-A in all samples. This observation allows the conclusion that the sediments were not diagenetically altered since the forming of opal-CT already starts at temperatures between 35 and 50 °C. In sediments at shallow depths and low temperatures (15-30 °C) for the forming of opal-CT at least 30 million years are necessary, at moderate temperatures (35-55 °C) and relatively great depths (> 500 m) 10 million years, whereas at temperatures > 55 °C the transition from opal-A into opal-CT takes place fast, irrespective of sediment depth (HEIN ET AL., 1985).

Biogenic silica is an important paleoproductivity factor since silicon in the water column is poorly recycled, and more than 90 % of silicon organic production remains in the sediments (BRUMSACK, 1989; WIGNALL, 1994). In recent sediments, the accumulation of opal is restricted to regions of high bioproduction (BOSTRÖM ET AL., 1973). Therefore, we attempted to quantify the amount of organic opal (Table 2; Fig. 7) in the ways proposed by BREWSTER (1983 CF. BUSTILLO & LÓPEZ GARCÍA, 1997) and BOSTRÖM ET AL. (1972) and SCHMITZ (1987). For estimating biogenic opal (opal-A) in sediments BUSTILLO & LÓPEZ GARCÍA (1997) used a combination of data resulting from chemical analysis and x-ray diffraction according to the equation:

$$\text{Opal-A} = \text{total } SiO_2 - SiO_2 \text{ bound in clay minerals} - \text{detrital quartz.}$$

The method of BOSTRÖM ET AL. (1972) gives a relatively rough estimate of opal-A contents in sediments since it starts from the assumption that all silicon that surpasses the amount of aluminium by a factor of three is biogenic. The proportion of biogenic opal in the sample is calculated according to the expression:

$$\text{Opal silica} = SiO_2 - 3 \times Al_2O_3.$$

The biogenic opal contents calculated according to the two methods vary considerably (Table 2). However, the results of the two methods show similar trends. Both methods confirm the presence of opal in samples for which the amorphous phase is indicated by X-ray diffractograms. In addition, the results show that opal also occurs in all samples containing siliceous algae, a fact that is not indicated by the x-ray diffractograms. Both methods result in the highest amounts of opal in the samples that contain the highest quartz and lowest carbonates.

Table 2. SiO_2 and opal-A content in the Middle Miocene diatomaceous sediments. All values in %.
Bc1 - section Bela Cerkev 1; Bc2 - section Bela cerkev 2; Tu - section Tunjice; Šm - section Šmarjeta
Opal[1] = total SiO_2 - SiO_2 bound in clay minerals - detritial quartz
Opal[2] = SiO_2 - 3 x Al_2O_3

Sample	SiO_2	Quartz	Opal[1]	Opal[2]
Bc1-1	52.23	23	6.4	33.21
Bc1-3	10.35	2	-0.6	4.59
Bc1-4	5.90	7	-3.9	2.18
Bc1-5	9.32	6	-1.4	3.89
Bc1-6	11.22	8	-0.4	2.22
Bc1-8	67.97	32	5.4	39.35
Bc1-9	67.64	35	7.8	33.22
Bc1-10	68.36	32	9.1	33.77
Bc1-12	63.99	34	-1.5	27.81
Bc2-3	70.06	40	0.4	35.86
Bc2-5	65.87	30	8.7	28.58
Tu-7	40.93	17	2.1	3.85
Tu-5	51.21	20	11.2	26.25
Tu-4	51.11	15	14.4	26.96
Tu-2	42.12	11	18.6	10.44
Šm-5	20.83	14	-2.8	0.64

The opal contents calculated according to the method of Boström et al. (1973) vary between 0.5 and 39.35 % (Table 2). As for opal, the sample Bc1-1 from the lower part of the Bela Cerkev 1 section, samples from the upper part of the Bela Cerkev 1 section (Bc1-8 to Bc1-12) and the Bela Cerkev 2 section (Fig. 7) are comparable.

Somewhat lower are the opal contents in samples from the Tunjice section.

Distinguished by low opal content among these is sample Tu-7 which only contains 3.85% opal, although there are no essential differences between these samples from the paleontological point of view. Likewise, low contents of opal (< 5 %) also occur in samples from the lower part of the Bela Cerkev 1 section (Table 2, Fig. 7), which again is inconsistent with paleontological analyses. The samples Bc1-7 and Šm-5 contain less than percentage of calculated opal. This is in agreement with paleontological examinations; namely, in the mentioned samples only sparse fragments of siliceous sponges and algae are preserved.

The amounts of biogenic opal calculated after Brewster are significantly lower (with a maximum of 18.6 % opal), and they also contain negative values. Negative values are obviously the consequence of combining the X-ray and chemical analyses owing to the high contents of carbonates. In sediments with prevailing carbonates, opal-A passes directly into quartz without an intermediate phase of opal-CT (Greenwood, 1973; Kastner et al., 1977). The opal contents calculated according to Brewster are also highly variable within the sections, and they do not agree with the results of mineralogic and chemical analyses. As an example, in the upper part of the Bela Cerkev 1 section the contents of opal vary between –1.5 and 8.7 %. The highest opal values calculated according to Brewster's method appear in the samples of the Tunjice section where the amounts are similar, again with the exception of sample Tu-7.

For these reasons, the amounts of opal are calculated below after the method of Boström et al. (1973), although these estimates are considered less precise.

Most of the clay minerals were brought into the sedimentary basin from the land. The mineral composition of clay minerals and mixed-layered clay minerals indicates that the differences are the result of paleotrans-

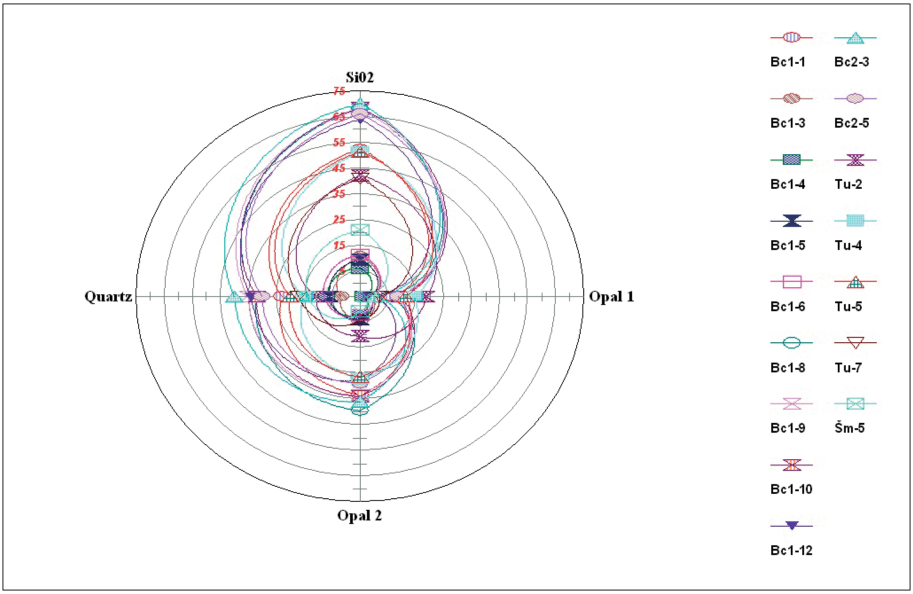

Figure 7. Quartz, opal-A and SiO_2 content of the Middle Miocene diatomaceous sediments in wt. %.
Bc1 - section Bela Cerkev 1; Bc2 - section Bela cerkev 2; Tu - section Tunjice; Šm - section Šmarjeta
opal 1 = total SiO_2 - SiO_2 bound in clay minerals - detritial quartz
opal 2 = SiO_2 - 3 x Al_2O_3

port and not of diagenesis, since the minerals were transported into the sedimentary basin from the land (ANIČIĆ ET AL., 2002). The resedimented mixed-layered clay minerals illite/montmorillonite with R=0 ordering as diagenetic indicators suggest the beginning stage of diagenetic alteration of montmorillonite to illite and at a temperature at the most of 70 °C (HOWER, 1981).

The presence of montmorillonite in certain samples indicates volcanism and possible transport by wind. In spite of the relatively important proportion of clay minerals in the examined samples, it does not necessary mean that the prevailing input was by rivers, which would lower the salinity in the sedimentary basin.

The examined sections can best be distinguished by their contents of carbonates. The absence of carbonates in the Bela Cerkev 1 and 2 sections is probably a consequence of diagenesis, as supported by finds in the beds of frequent mollusc imprints, mainly of bivalves, whose skeletal parts are entirely dissolved. In other samples, the amount of removed calcite is not easy to determine. The proportion of biogenic carbonate is not only associated with aragonite since this mineral is unstable at low temperatures and passes into calcite (DEER ET AL., 1992). The transition of aragonite into calcite does not only depend on temperature but also on trace element contents. The admixture of strontium in the aragonite of skeletons prevents its transition into calcite (YOSHIOKA ET AL., 1986).

In the examined samples the amounts of aragonite vary greatly, which is in a good correlation with the strontium contents in the sediments (HORVAT, 2004). The samples with maximum strontium contain the highest aragonite. Therefore, it is possible to conclude that carbonate in the examined samples has a mostly biogenic origin. This is also confirmed by the thin section, in which most of the carbonate clasts comprise the foraminifers and skeletal fragments of molluscs (HORVAT, 2004, Pl. 2, Fig. 2).

Plagioclase and dolomite were resedimented into the sedimentary basin.

The described lithologic difference among samples can be visualised in three-component diagrams. These are considered the minerals exhibiting the highest variability: opal (siliceous skeletons), carbonates (skeletons of molluscs + foraminifers + ostracods + micrite) and clay minerals.

The examined diatomaceous sediments have a variable composition, but not a single sample belongs to the real diatomites. In the literature numerous terms are found for naming diatomaceous sediments. In addition, these sediments are also distinguished by a highly variable mineral composition. For diatomaceous sediments of the Pannonian basin, BÁRDOSSY AND HAJÓS (1963) established a classification based on the contents of opal-A, clay minerals, carbonates and amount of clay fraction. The rocks of the Bela cerkev 1 section were determined as diatomites (HORVAT ET AL., 1996) without, however, con-

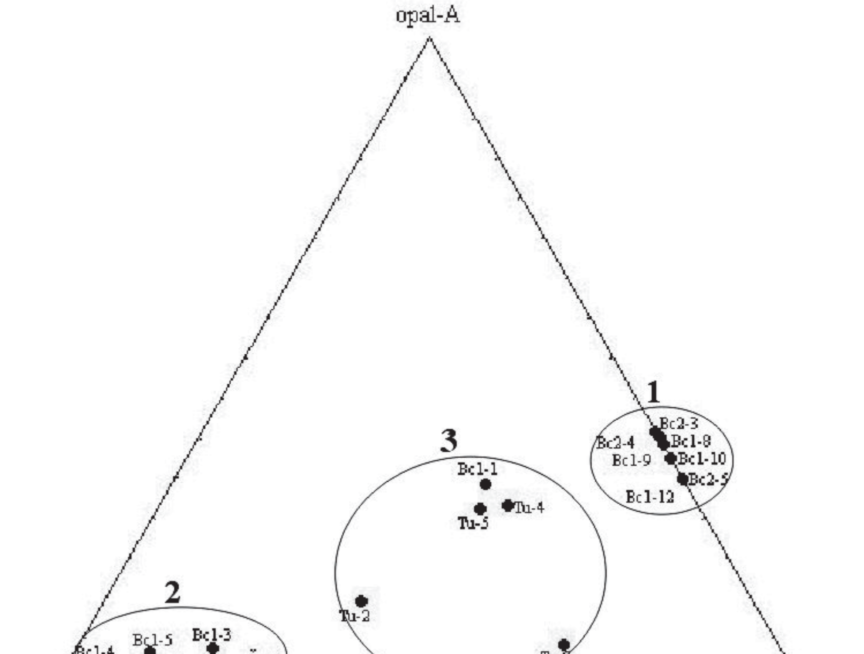

Figure 8. Lithological composition of the Middle Miocene diatomaceous sediments.
Bc1 - section Bela Cerkev 1; Bc2 - section Bela cerkev 2; Tu - section Tunjice; Šm - section Šmarjeta

sidering the contents of opal-A, which is essential for classifying diatomites as organogenic sediments. The studied samples can be subdivided with respect to their contents of opal-A, clay minerals and carbonate into three groups (Fig. 8).

In the first group are the samples containing the highest quartz (> 30 %) and opal-A (around 30 %). In addition, they also contain a high proportion of clay minerals (53–64 %). All samples of this group also contain a tuff component (Ca montmorillonite) which, however, does not exceed 20 %. This group unites the samples of the Bela Cerkev 2 and the upper part of the Bela Cerkev 1 sections. According to the classification of BÁRDOSSY AND HAJÓS (1963), they can be termed diatomaceous siltstones.

The second group may associate those samples with a high carbonate content (> 60 %) and low quartz (< 15 %) respectively opal-A (< 4 %). The clay mineral contents are below 20 %. Samples of this group do not contain a tuff component. The samples of the lower part of the Bela Cerkev 1 and Šmarjeta sections belong to this group. According to the classification of BÁRDOSSY AND HAJÓS (1963) they should be termed diatomaceous limestones. Because the rocks have a clastic texture, a more suitable term for them would be diatomaceous marlstone or diatomaceous carbonate siltstone.

The third group of samples has a wider dispersion than the first two. Typical are the high contents of quartz (15–20 %) and opal-A (around 25 %), and relatively low contents of carbonates (< 45 %). The proportion of clay minerals is less than 50 %. Except for sample Tu-2 all samples contain tuffaceous minerals. Within this group, the samples Tu-2 and Tu-7 are distinguished by their lower contents of opal-A (< 10 %). The samples of this group could also be attributed to diatomaceous marlstone respectively diatomaceous carbonate siltstone with the exception of sample Bc1-1. As the proportion of tuffaceous component in the latter sample exceeds 20 %, it may be termed tuffaceous diatomite. Belonging to this group are samples from the Tunjice section and one single sample from the Bela Cerkev 1 section (Bc1-1).

POVZETEK

Diatomejske sedimentne kamnine so kamnine bogate s skeleti diatomej, ki nastajajo v območjih povišane bioprodukcije, ki so povezane s procesi "upwellinga". Na območju Centralne Paratetide so bili ugodni paleoceanografski pogoji za nastanek tovrstnih sedimentov v srednjem miocenu. V Sloveniji so bili diatomejski sedimenti odkriti in opisani v štirih profilih v Krškem bazenu in Tuhinjski sinklinali (slika 1).

Opisano litološko razliko med vzorci lahko prikažemo s trikomponentnim diagramom (slika 8), kjer upoštevamo minerale, ki kažejo največjo spremenljivost (tabela 1–2; slika 3–7): opal (kremenični skeleti), karbonati (skeleti mehkužcev + foraminifer + ostrakodov + mikrit) in glineni minerali.

Preiskani diatomejski sedimenti kažejo spremenljivo sestavo, vendar pravim diatomitom ne pripada noben vzorec. V literaturi najdemo za poimenovanje diatomejskih sedimentov številne izraze. Prav tako imajo diatomejski sedimenti tudi zelo spremenljivo mineralno sestavo. Za diatomejske sedimente Panonskega bazena sta Bárdossy in Hajós-eva (1963) izdelala klasifikacijo na osnovi vsebnosti opala-A, glinenih mineralov, karbonata in količino gline. Kamnine iz profila Bela cerkev 1 so Horvat in sodelavci (1996) opredelili kot diatomite, vendar pri tem niso upoštevali količine opala-A, kar je za klasifikacijo diatomitov kot organogenih sedimentov bistveno. Preiskane vzorce lahko glede na količino opala-A, glinenih mineralov in karbonata ločimo v tri skupine (slika 8).

V prvo se uvrščajo vzorci, ki vsebujejo največ kremena (> 30 %) in opala-A (okoli 30 %). Razen tega vsebujejo tudi velik delež glinenih mineralov (53 - 64 %). Vsi vzorci te skupine vsebujejo tudi tufsko komponento (Ca montmorillonit), ki ne presega 20 %. Ta skupina združuje vzorce iz profila Bela Cerkev 2 in zgornjega dela profila Bela Cerkev 1. Po klasifikaciji Bárdossy in Hajós-eve (1963) bi jih lahko uvrstili v diatomejske meljevce.

V drugo skupino lahko uvrstimo vzorce z visoko vsebnostjo karbonatov (> 60 %) ter majhno količino kremena (< 15 %) oziroma opala-A (< 4 %). Količina glinenih mineralov je manjša od 20 % (tabela 1). Vzorci te skupine tudi ne vsebujejo tufske komponente. V to skupino se uvrščajo vzorci iz spodnjega dela profila Bela Cerkev 1 in profila Šmarjeta. Po klasifikaciji Bárdossy in Hajós-ove (1963) bi jih glede na to, da vsebujejo več kot 50 % karbonatov, uvrstili med diatomejski apnenec. Ker imajo kamnine klastično strukturo, bi bilo zanje ustreznejše poimenovanje diatomejski laporovec oziroma diatomejski karbonatni meljevec.

Tretja skupina vzorcev je veliko bolj razpršena kot prvi dve. Zanje je značilna dokaj visoka količina kremena (15 - 20 %) in opala-A (okoli 25 %) in sorazmerno majhna količina karbonatov (< 45 %). Količina glinenih mineralov je manjša od 50%. Razen vzorca Tu-2 vsi vsebujejo tufsko komponento. Med vzorci te skupine izstopata vzorca Tu-2 in Tu-7 z manjšo vsebnostjo opala-A (< 10 %). Vzorce te skupine bi lahko prav tako uvrstili med diatomejski laporovec oziroma diatomejski karbonatni meljevec, razen vzorca Bc1-1. Ker delež tufske komponente v vzorcu Bc1-1 preseže 20 %, ga lahko opredelimo kot tufski diatomit. V to skupino spadajo vzorci iz profila Tunjice in en vzorec profila Bela Cerkev 1 (Bc1-1).

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