Mineral assemblage and provenance of the pliocene Viviparus beds from the area of Vukomeričke Gorice, Central Croatia

Kurečić, Tomislav¹,*, Kovačić Marijan² and Grizelj Anita¹

¹ Croatian Geological Survey – HGI-CGS, Sachsova 2, HR-10 000 Zagreb, Croatia; (*corresponding author: tkurecic@hgi-cgs.hr)
² University of Zagreb, Faculty of Science, Department of Geology, Horvatovac 102b, HR-10 000 Zagreb, Croatia


Abstract

Viviparus beds are sediments deposited in lacustrine and fluvial freshwater environments (Lake Slavonia) during the Pliocene and the earliest Pleistocene. A detailed field study and mineralogical, petrographic and chemical analyses were carried out to determine their composition and origin in the area of Vukomeričke Gorice, Central Croatia. Viviparus beds are characterized by the vertical and lateral exchange of mineralogically and chemically mature pellets and sands. Pelitic sediments consist mainly of detrital quartz, calcite, dolomite and feldspar grains, with smectite as the most common clay mineral. Quartz and the most resistant lithic fragments dominate the sandy detritus. The composition of the sediments indicates their origin from the recycled orogen, while their textural immaturity suggests a short transport distance. Most of the material was re-deposited from the underlying Upper Miocene sediments, originally of Alpine provenance. A lesser proportion originated from Palaeogene sediments, Triassic carbonate rocks, basic or acidic magmatic rocks and metamorphites. The Medvednica and Zmijar mountains were the most important source areas, while a smaller proportion of the material could have come from the Moslavačka gora Mt. and Banovina region. The uniform composition of the Viviparus beds over the entire vertical distribution of the sediments clearly indicates that the source areas did not change during their deposition. A significant change from the texturally and compositionally mature Upper Miocenelastic detritus of alpine origin, to the texturally immature material of the Viviparus beds of local origin is a consequence of compression and inversion of the previously extensional basin resulting in the uplifting and erosion of the mountains within the SW part of the Pannonian Basin System.

Keywords: Viviparus beds, Pliocene, mineral assemblage, provenance

1. INTRODUCTION

In most parts of the Pannonian Basin System (PBS), a large sedimentary area between the mountain ranges of the Alps, Carpathians and Dinarides, the Pliocene epoch is characterized by the deposition of predominantly fluvial sediments and sediments deposited in wetlands and small freshwater lakes (MAGYAR et al., 1999; 2013). Only along the southern edge of the PBS was a large freshwater lake formed, namely the Paludina Lake (NEUMAYR & PAUL, 1875) (Fig. 1). Today it is known as Lake Slavonia (HARZHAUSER & MANDIĆ, 2008; MANDIĆ et al., 2015; NEUBAUER et al., 2015). The lake is named after Paludina, a freshwater snail, the evolutionary lineage of which was used to divide the Pliocene deposits of the southern part of the PBS into the lower, middle and upper Paludina beds (NEUMAYR & PAUL, 1875; JENKO, 1944; ŽEMBERAK Mts. were the most important source areas, while a smaller proportion of the material could have come from the Moslavačka gora Mt. and Banovina region. The uniform composition of the Viviparus beds over the entire vertical distribution of the sediments clearly indicates that the source areas did not change during their deposition. A significant change from the texturally and compositionally mature Upper Miocene elastic detritus of alpine origin, to the texturally immature material of the Viviparus beds of local origin is a consequence of compression and inversion of the previously extensional basin resulting in the uplifting and erosion of the mountains within the SW part of the Pannonian Basin System.

Studies of the composition and origin of this material have shown that in the earlier stages of basin development, the composition of detritus varies locally. Sources of material were either located further south in the Dinarides or were locally derived elevated blocks within the basin (ŠCAVNIČAR, 1979; PAVELIĆ et al., 2003; KOVAČIĆ et al., 2011; PAVELIĆ et al., 2016; GRIZELJ et al., 2017, 2020). In contrast, the composition of the Upper Miocene detritus is very uniform and its sources were mainly the Alps and the Western Carpathian Mountains (ŠIMUNIĆ & ŠIMUNIĆ, 1987; KOVAČIĆ & GRIZELJ, 2006; GRIZELJ et al., 2007, 2008, 2018). There were no detailed investigations on the composition and provenance of the detritus comprising the Pliocene deposits. However, it was expected that the change of tectonic regime from...
extension to compression, characteristic for the Pliocene epoch in the SW part of the PBS (PAVELJEW, 2001; TOMLJEVIĆ & CSONTOS, 2001; VAN GELDER et al., 2015), formed new local sources of clastic detritus. Furthermore, Pliocene climate variations described in adjacent areas, especially changes in dry and wet periods (FEDOROV et al., 2013; WILLEIT et al., 2013), must have been reflected in the amount and type of derived clastic detritus and its mineralogical maturity.

The aim of this study was to determine the mineral and chemical composition and maturity of the VB and, based on this, to determine their source rock composition and provenance. These results will shed light on whether the provenance of the clastic detritus changed from regional to local during deposition of the VB. Such a change would be indicative of basin inversion, i.e., the onset of a new compressional phase in the evolution of the PBS. The study was conducted mainly on Vukomeričke
Gorice, an area where the VB are best exposed at the surface. For comparison with other areas, additional sites on Psunj Mt. & Dilj Mt. in Slavonia and in the Banovina region, respectively, were studied (Fig. 2).

2. GEOLOGICAL SETTING

North Croatian Basin (SW marginal part of PBS)
The North Croatian Basin (NCB) is located in the southwestern part of the PBS. Pannonian Basin System is a large extension structure located in Central and South-eastern Europe and surrounded by the mountain ranges of the Alps, Carpathians and Dinarides (Fig. 1). The development of the PBS commenced in the Early Miocene as a consequence of a continental collision and subduction of the Eurasian plate beneath the Apulian plate (and other continental fragments) from the south. This process caused thermal perturbations of the upper mantle, resulting in the weakening and extension of the crust and formation of a back-arc type sedimentary basin (ROYDEN, 1998; HORVÁTH, 1993, 1995; KOVÁČ et al., 1998; MATENCO & RADIVOJEVIĆ, 2013). Palaeogeographically, the PBS covered most of Central Paratethys, the realm formed between the Eocene and Oligocene by the separation of Western Paratethys into the Paratethys and the Mediterranean Sea (RÓGL, 1999). Sedimentation in the NCB began about 18 Ma ago in the syn-rift phase of basin development and is characterized by a large transgressive-regressive cycle (MAN­DIC et al., 2012; PAVELIĆ & KOVAČIĆ, 2018). In the transgressive part of the cycle, mainly clastic sediments were deposited first in alluvial and saline lake environments, and then in freshwater lacustrine environments, followed by mainly marine carbonate sediments (PAVELIĆ & KOVAČIĆ, 1999; KOVAČIĆ et al., 2011; PAVELIĆ et al., 2016). This period is also characterized by strong volcanic activity (MAN­DIC et al., 2012; PAVELIĆ & KOVAČIĆ, 2018; BRLEK et al., 2020; MARKOVIĆ et al., 2021). Deposition of marine sediments is a consequence of the ingress of the Paratethys Sea into the NCB area in the early Middle Miocene (ČORIĆ et al., 2009; MAN­DIC et al., 2012; PAVELIĆ

Figure 3. Geological map of the area of: a) Vukomeričke Gorice and Banovina; b) and c) Slavonia with indicated sampling sites. The map was produced using the Geological Map of the Republic of Croatia at the scale of 1:300.000 (HGI-CGS, 2009) and was partly modified according to the field data. The sampling sites are marked with white dots and numbers. Spatial reference: HTRS96/CroatiaTM.
Vukomeričke Gorice

The Vukomeričke Gorice area represents a series of hills in the central part of the Republic of Croatia. They are located about 20 km south of Zagreb, are about 30 km long and trend in a NW-SE direction (Fig. 2). Geologically, they represent the remains of several horsts of smaller dimensions, the formation of which is the result of vertical movements along faults of the predominantly Dinaric direction (FILJAK, 1951; VELIĆ, 1983) and subsequent horizontal displacements of the blocks along the more recent strike-slip faults (PIKIJA, 1987a, b). The oldest sediments that occur on the surface and at the same time cover most of the Vukomeričke Gorice area are Pliocene sediments deposited in Lake Slavonia (PIKIJA, 1987a, b; MANDIC et al., 2015). The northern part of the Vukomeričke Gorice area is covered with Plio-Quaternary deposits (ŠIKIC et al., 1978; 1979), and the north-eastern margin with Pleistocene sediments (PIKIJA, 1987a, 1987b) (Fig. 3a).

Pliocene sediments in the area of Vukomeričke Gorice are differentiated as an informal unit; the *Viviparus beds* (PIKIJA, 1987a, 1987b; HGI, 2009), or as sediments of the Lonja Formation (CVETKOVIC, 2013). The same deposits belong to the Vrbova fm., as recently described on a new geological map of Požeška Mt. (HALAMIĆ et al., 2019). PIKIJA (1987a) assumes an unconformity between the Upper Miocene sediments and the Pliocene sediments of the VB due to lithological differences. In contrast, CVETKOVIC (2013) pointed to the continuity of deposition at the Miocene/Pliocene boundary on the profiles covering the north-eastern margin of Vukomeričke Gorice. Within the sediments themselves, no division into lower, middle or upper VB was made. On the basis of the fossil assemblage (molluscs) however, it was found that the sediments of the lower and upper VB were deposited in the area of the Vukomeričke Gorice, while no fossil evidence was found for the middle VB (PIKIJA, 1987a; MANDIC et al., 2015).

The lower parts of the VB are dominated by various clays interspersed with sand and gravel. They also contain rare sandstone and lignite layers (ŠEBEČIĆ, 2010). The upper VB were only found in the north-eastern part of Vukomeričke Gorice, where they lie directly on the lower VB. They consist of gray and yellow-brown sands, yellow, blue and gray clays, fine-grained gravel and occasionally contain lignite lenses (PIKIJA, 1987a).

The sand is predominantly very poorly sorted and contains up to 40 % of pelite- or up to 35 % of gravel-sized detritus, so that it is defined as silty sand, silty-gravelly sand or clayey sand (KUREČIĆ, 2017). Well sorted sand rarely occurs. According to their median value they belong to the group of fine, medium or coarse-grained sands. Among the pelitic sediments, very poorly sorted silt predominates. Depending on the sand and clay content, the silt is defined as clayey silt, sandy-clayey silt or clayey-sandy silt. Rare occurrences of gravel are characterized by clast supported and poorly sorted fabric, occasionally with a fining upwards trend.

Sediments with similar lithological characteristics are found in the VB near Novska on the southwestern slopes of Psunj Mt. (Fig. 3b) (CRNKO, 1990; CRNKO & VRAGOVIĆ, 1990) and on the southern slopes of Dilj Mt. (Fig. 3c) (ŠPARICA et al., 1980). So, the VB have similar lithological characteristics across the whole investigated area of the western part of Lake Slavonia.

3. METHODS

3.1. Field methods

A total of 51 samples were collected during the field research. In the area of Vukomeričke Gorice, detailed investigations of the VB were carried out at the Lipnica, Petravec, Čakanec, Strezovejo, Kravarsko, Ključić Brdo, Vukomerić and Donji Hruševec sites (Fig. 3a). In addition, the underlying Miocene sediments were sampled at Bašica Brdo and overlying Quaternary sediments at the Žažina and Orleković sites (Fig. 3a) to draw some conclusions regarding the compositional variability through the stratigraphic sequence. Outside the area of Vukomeričke Gorice, the VB were sampled in the Banovina region near the town of Petrinja and the village of Komarevo located south of Vukomeričke Gorice (Fig. 3a). East of Vukomeričke Gorice, the VB were sampled on the southwestern slopes of Psunj Mt. near the village of Subocka (Fig. 3b) and near Sibinj on the southern slopes of Dilj Mt. (Fig. 3c).

3.2 Laboratory methods

Laboratory analyses included chemical and mineralogical-petrographic analyses of the sediments. The chemical analyses were carried out at the ACME Analytical Laboratories LTD in Vancouver, Canada, and all other analyses were performed at the laboratory of the Croatian Geological Survey (HGI) in Zagreb.

The mineral and petrographic composition of the sandy-gravelly sediments was determined using an optical microscope. The mineral composition of sands was determined for 37 samples in total by analysis of heavy (HMF) and light mineral fractions (LMF) ranging from 0.063 – 0.16 mm grain-size fraction. Before separation, the carbonate component was dissolved (when present) with 4% HCl. The separation was performed with Bromoform (2.9 g/cm³). The qualitative and quantitative composition of both the LMF and HMF was determined by the ribbon counting method on at least 300 grains (>150 translucent grains), (MANGE & MAURER, 1992). Mineral grains from the LMF were grouped according to the method used by DICKINSON (1985). Petrographic thin sections were prepared on 9 samples of coarse sand and fine gravel from the fractions 0.90 – 1.25 mm and 1.25 – 2.80 mm respectively.

The mineral composition of 8 pelitic sediment samples was determined by X-ray powder diffraction (XRPD) using a PANalytical X’Pert PRO MPD diffractometer with a PW 3018/00 PIXcel detector. Experimental conditions were: CuKα radiation, 45 kV, 40 mA, primary beam divergence 1/4°, continuous scanning (step 0.02°/20/s). The analyses were recorded from random mounts of bulk samples and oriented mounts of the <2 µm fraction of the insoluble rock residue.

Preparation for the XRPD analyses included: grinding samples for bulk sample analysis, dissolution of the carbonate component where present (only for clay mineral analysis), and separation of the <2 µm grain fraction using centrifuge methods described by KRUMM (1994). To remove the carbonates the samples were treated with a 1 M NH₄Ac solution buffered with HOAc at pH 5 (JACKSON, 1956).
The determination of clay minerals on a fraction of <2 µm oriented mounts, was carried out according to the method of STARKEY et al (1984), which comprises: a) air drying, b) ethylene glycol solution, d) heating to 400°C and 550°C. The interpretation of XRPD was performed using the calculation from HIGH SCORE PLUS (2008) and the databases PDF-4 / MINERALS 4.5 (2016). The quantitative analysis was performed with the RockJock software and the method described by EBERL (2003). Preparation for quantitative analysis described by EBERL (2003) included addition of internal standard zincite (0.111 g ZnO to 1 g sample) and grinding the mixture in a McCrone mill for 5 minutes with 4 ml methanol. Ground samples were dried, sieved, well mixed, packed into a holder and then recorded from 5 to 65° 2θ using Cu Kα radiation, with step 0.02°2θ/s.

Chemical analyses of samples were performed in the AcmeLabs, a Bureau Veritas Group Company (www.acmelab.com) in Vancouver (Canada). Chemical analyses were obtained on 24 sand samples and 10 pelitic sediment samples having had their carbonates previously dissolved. The major elements content was determined by inductively coupled plasma emission spectroscopy (ICP-ES), while trace elements were measured with an inductively coupled plasma mass spectrometer (ICP-MS). Major and trace elements were analysed after heating of the samples with lithium metaborate (LiBO₂), while precious and non-precious metals were analysed from a solution prepared by dissolving the samples in aqua regia (HNO₃+3 HCl). The accuracy and precision of the chemical data calculated based on internal standards (SO-18, DS10, GS-311-1, GS910-4 and ORESAS45EA) and repetition of the chemical data calculated based on internal standards (SO-18, DS10, GS-311-1, GS910-4 and ORESAS45EA) and repetition of analyses on three samples (Str-II 7/1, Pet-1 1/1, Cak-I 7/1) was satisfactory for all elements used in the provenance analyses (KUREČIĆ, 2017).

4. RESULTS

4.1. Modal composition of sand

4.1.1. Composition of lithic particles from coarse sand

Thin section analyses of the sand fraction > 0.9 mm in samples from different localities in the area of Vukomeričke Gorice showed that all sands consist of particles from older sedimentary rocks including quartzite, acidic to basic igneous rocks and metasediments, but differ in the quantitative amount of the individual particle groups (Fig. 4a). In the sands of the Strezojevo locality, grains of radiolitites (Fig. 4a, b, c) and quartzite (Fig. 4a, d) predominate. Radiolite particles comprise up to 40% and quartzite about 20% of all particles. About 25% of the lithic fragments are igneous rocks, among them basalt-diabase (Fig. 4a, e) and basalts are the most abundant, while andesite-basalts and andesites occur only sporadically. In the sample Str-I 1/1, neutral igneous rocks are completely absent. Among other particles, metasediments (metapsammite and rarely quartz-sericite schists), sandstone and individual quartz grains are relatively common. The Str-I 5/1 sample also included a particle with microperthite veins characteristic of granite rocks (Fig. 4f). In the same sample, the planktonic foraminifera Globigerina sp. was also observed (Fig. 4g). Coarse-grained sandy and fine-grained gravelly detritus from the Lipnica and Ključić Brdo locality contains less chert particles than the Strezojevo locality (Fig 4a). At the Lipnica locality, the number of metasediments, mostly metapsammites (Fig. 4h), is about 5% (Fig 4a), while clasts of neutral-acid igneous rocks are almost absent. Furthermore, only chert-like particles were detected at the Lipnica site (Fig. 4i), with radiolitite absent. In addition, the detritus of the Ključić Brdo site is characterized by the highest proportion (up to 25%) of neutral-mafic igneous rocks (Fig. 4a, 4j, 4k). The sand detritus of the Petravec site is similar to the samples from the previously described sites, although with reduced quantities of individual groups. It is characterized by the almost complete absence of radiolite particles (chert is present) and particles of neutral-mafic igneous rocks. An important feature that distinguishes the Petravec site from all other sites is the occurrence of carbonate grains, comprise 50% of the detritus (Fig 4a). These are dolomite grains and recrystallized (Fig. 4l) and partially recrystallized micrite limestones (Fig. 4m). A carbonate particle composed of the fossil remains of red algae was also recorded.

The sand at the Orlekovica locality is similar in composition to the sand of the Strezojevo, Lipnica and Ključić Brdo localities, but contains a much smaller amount of radiolite/chert particles followed by increased amounts of sandstone (mostly quartz arenite) particles (Fig 4a).

4.1.2. Heavy and light mineral composition of sand and sandy silt

Analyses of the finer sand fractions (0.063-0.16 mm) at all the investigated sites in the area of Vukomeričke Gorice, Slavonia and Banovina showed that there are no significant differences in the composition of the LMF of sand detritus of the VB depending on the sampling area (Tab. 1). Monocrystalline quartz grains with an average content of 76% predominate in all the samples. The grains are moderately rounded, with uniform undulose extinction. Among the rock particles, (average content of 18%), the most common types are chert, quartzite (Qzp in Table 1) and volcanlastic (tuff) particles. Fragments of schists with a low degree of metamorphism have also been observed. Feldspar is represented in the form of weathered potassium feldspar and averages about 6% in composition. Mica (muscovite) occurs only sporadically in concentrations of less than 1% in the form of transparent thin plates with rounded edges.

In the HMF, the quantity of which ranges between 0.6% and 9%, opaque minerals and translucent heavy minerals dominate, while the quantity of biotite and chlorite is generally below 1% (Tab. 2). The average amount of opaque minerals is 63% (Tab. 2). Completely opaque black grains and reddish grains along the edges are observed.

Among the translucent heavy minerals, garnets are commonly found in most samples. Their average content in the samples is about 34%. They are most abundant in the locality of Petravec, where their share reaches up to 60%. In the localities of Žažina and Orlekovici, garnets only sporadically occur, while they were not found at all in the locality of Bašića Brdo (Tab. 2). Regarding weathering stages, garnet grains range from unweathered to slightly corroded. Besides garnets, epidote and staurolite are also significantly represented. Their share among the translucent heavy minerals is about 12% on average, in the Ptt-1 sample it reaches 31% (Tab. 2). Staurolite was found in all samples except the Kom-1 sample, and ranges from unweathered to slightly corroded grains, similar to epidote. The highest percentage (23%) occurs in the Str-I 2/1 sample (Tab. 2). The most resistant translucent heavy minerals such as zircon, rutile and tourmaline were found in all samples with an average content of between 6% and 9% (Tab. 2). Tourmaline occurs in the form of subrounded to angular, usually prismatic grains, with brown pleochroism. Rutile occurs in slightly rounded forms, often with a prismatic habit or occasionally as broken fragments. Its colour is usually reddish-brown or dark red. Zircons are usually short-prismatic, and in most cases subrounded. Crystal fragments or...
Euhedral zircon crystals are relatively rare. The largest amount of zircon occurs in the Quaternary sediment from the Žažina site, where their concentration reaches up to 27% (Tab. 2). Other translucent heavy minerals are found only in very small percentages (Tab. 2). Kyanite, for example, is present in most of the analysed samples, but its content does not exceed 5%, except at the Sibinj site. Amphiboles were found in all samples, but their average content was only about 6%. They are available in greenish-blue to green varieties, or colourless, angular to subrounded, slight corroded grains. Pyroxenes occur only in some samples with the amount of less than 3%, except at the Sibinj site where they contribute up to 8% of the composition of the translucent

Figure 4. Petrographic composition of coarse-grained sand of the Viviparus beds from the area of Vukomeričke Gorice: a) Pie charts showing the composition of the grain fraction with particle diameters between 0.25 mm and 0.9 mm. Photomicrographs of lithic particles: b) radiolarite from the sample Str-I 5/1, (A-); c) radiolarite from the sample Str-I 5/1, (A+); d) quartzite from sample Str-I 5/1, (A+); e) diabase from sample Str-I 5/1, (A-); f) microperthite growth from sample Str-I 5/1, (A+); g) Globigerina sp. from sample Str-I 5/1, (A-); h) metapsammite from sample Lip-I 21/1, (A-); i) chert from sample Lip-I 21/1, (A+); j) andesite-basalt from sample KBr-I, (A-); k) basalt- diabase from sample KBr-I, (A-); l) recrystallized limestone from sample Pet-I 10/2, (A-); m) partially recrystallized micrite limestone from sample Pet-I 10/2, (A-). Legend: (A-) – photographed without included analyzer; (A+) – photographed with the included analyzer.
minerals of the HMF (Tab. 2). They occur in green and colourless varieties with vivid interference colours and correspond to the hypersthene in their optical properties. Regarding weathering of unresistant heavy minerals, pyroxene shows a higher degree of weathering than amphiboles. Therefore, the degree of pyroxene alteration could be roughly estimated on C1, E2, and D2 classes (according to ANDÒ et al., 2012). Minerals such as zoisite/clinozoisite, titanite, Cr-spinel and brookite/anatase have only rarely been recorded (Tab. 2).

4.1.3. Modal composition of the pelitic sediments

The main mineral constituents of the pelitic sediments of all the analysed samples are clay minerals and quartz, while the content of other mineral species (calcite, dolomite and minerals from the feldspar group) varies from sample to sample (Tab. 3; Fig. 5a). Among the clay minerals determined from oriented samples of the <2 µm grain fraction, the most common are smectite and illite/muscovite. Chlorite occurs only in samples Kra-I 5/1 and Vuk-I 7/1.
Table 2. Modal composition of the heavy mineral fraction (0.09-0.16 mm) of the *Viviparus* beds from the Vukomeričke Gorice, Banovina and Slavonia together with the surrounding underlying and overlying deposits. Opq – opaque minerals, Bt – Biotite, Chl – chlorite, THM – translucent heavy minerals, Tur – tourmaline, Zrn – zircon, Rt – rutile, Px – pyroxene, Amp – amphibole, Ep – epidote; Zo-Czo – zoisite, clinozoisite, Grt – garnet, Ky – kyanite, St – Staurolite, Ttn – titanite, Spn – Cr-spinel, Brk/Ant – brookite/anatase, Oth. – mineral grains which were not possible to determine.

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<th>Area</th>
<th>Locality</th>
<th>Sample</th>
<th>Opq (%)</th>
<th>Bt (%)</th>
<th>Chl (%)</th>
<th>THM (%)</th>
<th>Tur (%)</th>
<th>Zrn (%)</th>
<th>Rt (%)</th>
<th>Px (%)</th>
<th>Amp (%)</th>
<th>Ep (%)</th>
<th>Zo-Czo (%)</th>
<th>Grt (%)</th>
<th>Ky (%)</th>
<th>St (%)</th>
<th>Ttn (%)</th>
<th>Spn (%)</th>
<th>Brk/Ant (%)</th>
<th>Oth. (%)</th>
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<td>48</td>
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<td>4</td>
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**Notes:**
- Opq – opaque minerals
- Bt – Biotite
- THM – translucent heavy minerals
- Tur – tourmaline
- Zrn – zircon
- Rt – rutile
- Px – pyroxene
- Amp – amphibole
- Ep – epidote
- Zo-Czo – zoisite, clinozoisite
- Grt – garnet
- Ky – kyanite
- St – Staurolite
- Ttn – titanite
- Spn – Cr-spinel
- Brk/Ant – brookite/anatase
- Oth. – mineral grains which were not possible to determine.
while in sample Sub-I 8/1 its occurrence is uncertain. (Fig. 5b). Namely, chlorite has a diffraction maximum at a similar position (7 Å) to kaolinite, and the problem with determination occurs when it is present in small quantities.

### Table 3. Quantitative mineral composition of bulk sample and semi-quantitative mineral composition of the <2 µm fraction of pelitic Viviparous beds samples from Vukomeričke Gorice and Slavonia, obtained by XRPD and Rock Jock software (EBERL, 2003). The quantitative composition is given in weight %, **** - dominant (60-100%), *** - abundant (30-60%), ** - considerable (10-30%), * - minor (1-10%), + - traces (< 1%).

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#### Semi-quantitative mineral composition of the <2 µm fraction

| Sillimanite    | ***          | ***          | ***       | ***       | ***       | ***       | ***     | ***     |
| Illite/Muscovite | ***        | ***          | ***       | ***       | ***       | ***       | ***     | ***     |
| Kaolinite      | ***          | ***          | ***       | ***       | ***       | ***       | ***     | ***     |
| Chlorite       | ***          | ***          |           |           |           |           | *       | +?      |

4.2. Chemical composition of sediments

The results of the chemical analysis of the major and trace elements are shown in Tables 4 and 5. Chemical analysis showed that the VB consist mostly of SiO₂ (53.83–90.95 %), Al₂O₃ (3.81–
Table 4. Major elements (% by weight) composition of bulk sediments (sands and pelitic sediments) and insoluble rock residue (*) from Vukomeričke Gorice. CIA - chemical index of alteration, (NESBIT & YOUNG, 1982) and ICV - Index of Compositional Variability (COX et al., 1995). LOI - loss on ignition. Pelitic sediments are marked by italics.

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<td>8.27</td>
<td>2.22</td>
<td>0.35</td>
<td>0.20</td>
<td>0.80</td>
<td>1.34</td>
<td>0.08</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>1.42</td>
<td>1.09</td>
<td>1.22</td>
</tr>
</tbody>
</table>

**Note:** CIA and ICV calculations are based on the LOI-corrected data.
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20.78%) and minor contents of Fe₂O₃ (1.28–6.47%), K₂O (0.84–3.87%), MgO (0.25–2.38%), CaO (0.04–2.68%), TiO₂ (0.18–0.98%), Na₂O (0.17–0.97%), MnO (0.01–1.05%) and P₂O₅ (0.04–0.14%). In addition, Table 4 shows the data on the calculated values of the chemical index of alteration (CIA = [Al₂O₃/(Al₂O₃+CaO*+Na₂O+K₂O)]x100, CaO* is the amount of CaO only in silicate minerals) (NESBIT & YOUNG, 1982) & Index of Compositional Variability (ICV=(Fe₂O₃+K₂O+Na₂O+CaO+MgO+MnO+TiO₂)/Al₂O₃) (COX et al., 1995). The CIA for sandy samples varies from 58.73–85.69, and 67.22–83.97 for pelitic sediments. The ICV for sandy samples varies from 0.62–1.37, while for pelitic sediments it is 0.68–1.16.

5. DISCUSSION
5.1. Modal composition and origin of the detritus
5.1.1. Composition of sand
Analyses of the modal composition of the sandy detritus of the VB from the area of Vukomeričke Gorice showed that it was formed by the erosion of various magmatic, metamorphic and sedimentary rocks (Fig. 4; Tab. 1, Tab. 2). Among the magmatic rocks, basic ones were the most common in source rock composition and, to a lesser extent, neutral and acidic rocks. These rocks have been identified as a component of the Palaeogene conglomerates and sandstones from Banovina (ŠEBEČIĆ, 1971; MAJER, 1983; PIKIJA, 1987a), which crop out on the surface southeast of Vukomeričke Gorice in the area of Banovina (HGI, 2009) (Fig. 2). Fragments of basic igneous rocks could have originated from Upper Cretaceous-Palaeogene basic effusions, which occur on the surface very close to the Vukomeričke Gorice area on the southern bank of the Kupa River (HGI, 2009), or from an ophiolite melange, as occurs today on the surface of Medvednica Mt. (HALAMIĆ et al., 1999; GORIČAN et al., 2005; LUŽAR-OBERITER et al., 2009; SLOVENEC & ŠEGVIĆ, 2019) (Fig. 2). Alternatively, fragments of the acid igneous rocks, apart from the Palaeogene clasts of Banovina, could have originated directly from the granite complex of Mošlavacka Gora (CRNKO, 1990; CRNKO & VRAGOVIĆ, 1990, HGI, 2009; STARIJAŠ et al., 2010). Particles of metasedimentary rocks could have originated from Palaeozoic metamorphic rocks that crop out north of the study area of Vukomeričke Gorice on Medvednica Mt. (BELAK et al., 1995; HGI, 2009; MIŠUR, 2017). They also might have been derived from the Upper Palaeozoic metasedimentary rocks of Petrova Gora and Trgovska Gora in Banovina (ŠIKIĆ et al., 1978; ŠIKIĆ et al., 1990a; ŠIKIĆ et al., 1990b; BELAK et al., 1995; HGI, 2009; MIŠUR, 2017). Carbonate
detritus possibly originated from the older Triassic carbonate rocks. Thus, the lithic fragments of recrystallized micrite limestones resemble the Early Triassic limestones found in the surrounding areas of Žumberak Mt., Banovina and Medvednica Mt., while the dolomite particles originate from the dolomites of the Middle and Upper Triassic, which occur in the same areas (ŠIKIĆ et al., 1978; ŠIKIĆ et al., 1990; HGI, 2009). The radiolarite fragments that appear together with the lithic carbonate fragments do not have the microphysiographic characteristics of the radiolites of Žumberak Mt., so they are assumed to be transported from the Banovina and/or Medvednica Mt. areas (GORIČAN et al., 2005; HALAMić et al., 1999). The rounded lithic chert fragments could probably have undergone several phases of redeposition.

The composition of the HMF, in which garnets predominate among the translucent heavy minerals, with abundant minerals from the epidote group, and also with regularly present amphiboles (Tab. 2), indicates that a significant part of the detritus was redeposited from the Early Miocene sediments. Such a mineral composition is characteristic for the Upper Miocene sediments, which form a large part of the infilling of the NCB. On the surface, they occur on the edges of mountains in the north-western part of Croatia and in the Banovina region (ŠIMUNIĆ & ŠIMUNIć, 1987; KOVAČIć et al., 2004; KOVAČIć & GRIZELJ, 2006; HGI, 2009). The absence of garnets in heavy mineral associations from the Upper Miocene was recorded at the Basića Brdo site in the area of Vukomeričke Gorice (Fig. 2). This is characteristic of the youngest Upper Miocene sediments and was previously recorded in the north-western part of NCB in the area of Hrvatsko Zagorje (KOVAČIć & GRIZELJ, 2006). The significant occurrence of Cr-spinel in the sands of the same locality has not yet been recorded in the Upper Miocene sands of the NCB. This important fact could possibly be related to the Upper Cretaceous-Palaeogene source rocks from the area of Banovina and the Medvednica or Žumberak Mts. (Fig. 3). In these deposits, LUŽAR OBERITER et al. (2019) identified the occurrence of Cr-spinel. The dominance of the chemically most resistant particles, such as quartz, quartzite and chert (occasionally well-rounded spinel. The dominance of the chemically most resistant particles, such as quartz, quartzite and chert (occasionally well-rounded spinel. The dominance of the chemically most resistant particles, such as quartz, quartzite and chert (occasionally well-rounded

5.1.2. Composition of pelitic sediments

The pelites from the investigated VB consist mainly of quartz and clay minerals, in some cases they also contain carbonate minerals and feldspar (Tab. 3). Quartz, feldspar and carbonate minerals are of detrital origin and are present in the coarser fractions too. Pliocene pelitic sediments have a similar clay mineral composition as the Upper Miocene marly sediments (GRIZELJ et al., 2017). The appearance of smectite is usually associated with increased volcanic activity in the sedimentary area (CHAMLEY, 1989), however there is no other evidence of such an event in the studied sediments, nor has such activity been observed in the Pliocene deposits of the NCB. Therefore, the origin of smectite, the most abundant clay mineral in the analysed samples (Tab. 3; Fig. 5b), is probably related to the reworking of older sediments or volcanic material from older formations. The origin of illite/muscovite, the second most common clay mineral, is most likely related to the weathering of schist and metapsammitic rocks which was determined by the analysis of lithic fragments and the LMF. Namely, illite/muscovite and chlorite represent the typical terrigenous mineral species, which were formed directly from eroded intrusive and metamorphic rocks (CHAMLEY, 1989). The presence of chlorite in only a few samples as part of the clay mineral composition of pelitic sediments and the HMF of the silty-sandy fraction, could be an indicator of more intensive chemical weathering of the sediments to which this mineral is poorly resistant (CHAMLY, 1989; WEAVER, 1989). Kaolinite is present in all samples in small quantities. It forms fromfeldspars and micas in areas when precipitation is relatively high and where there was good drainage to ensure the leaching of cations (MITCHELL & SOGA, 2005). The studied sediments indicate a relatively warm and humid climate, as was the case during the Cernikian (MANDIC et al., 2015). Nevertheless, the composition of clay minerals in lake environments is mainly a reflection of the composition of the source area (WEAVER, 1989).

5.1.3. Origin of the detritus

Considering the physiographic or mineralogical features of the detritus, it can be concluded that the main sources of the sand detritus of the VB from Vukomeričke Gorice were the nearby areas of the Medvednica and Žumberak Mts and to a lesser extent Moslavačka gora Mt. The composition of the detritus indicates that part of the material most likely originated from the Banovina region, primarily from the Cretaceous-Palaeogene clastics. The results obtained support the hypothesis of extension of the Pliocene Lake Slavonia (NEUBAUER et al., 2015, 2016; MANDIC et al., 2015), according to which the investigated area of Vukomeričke Gorice represents the north-western edge of the lake. This means that most of the detritus from the southern sources was deposited further south and east of the studied area (Fig. 1). The Inner Dinarides of Bosnia and Banovina might represent such southern source areas. The contribution of the southern sources was recorded in the detritus of the VB in Slavonia. The occurrence of pyroxene and Cr-spinel from Bosnia, (at the Sibinj site), indicate the south-north direction of palaeotransport (KOVAČIć et al.,
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2011) (Tab. 2). The increased content of pyroxene and/or Cr-spinel was also observed at the Komarevo and Petrinja sites in the Banovina area (Tab. 2), so it additionally documents the south-north direction of palaeotransport or a nearly local origin (within Banovina area).

The obtained results on the local origin of the detritus deposited in the NCB area during the Pliocene indicate that a major change occurred regarding the source area during the transition from the Miocene to the Pliocene. Indeed, during the Late Miocene, detritus of a uniform modal composition was deposited throughout the NCB area, which was derived from the Alps and the Western Carpathians (KOVAČIĆ & GRIZELJ, 2006; ŠIMUNIĆ & ŠIMUNIĆ, 1987; GRIZELJ et al., 2017). Such a change is most likely caused by basin inversion, which started in the SW part of the PBS at the end of the Miocene and was intensified in the Pliocene and Quaternary (TOMLJENOVIĆ & CSONTOS, 2001; PAVELIĆ, 2001; VAN GELDER et al., 2015). Compression uplifted individual blocks along the basin rim or

Figure 6. Cross-plots of major oxides (wt. %) against Al₂O₃ (wt. %) showing their correlations for sandy and pelitic Viviparus beds samples from the area of Vukomeričke Gorice. Data from Table 4.
within the basin, and their erosion resulted in the locally influenced detritus composition of the sediments deposited in the surrounding depressions of the NCB.

5.2. Chemical composition and origin of the detritus

The relationship between chemical and mineral composition is shown using correlation diagrams in Fig. 6. It can be seen that SiO$_2$ has strong negative correlation with Al$_2$O$_3$ (Fig. 6a), which can be interpreted as much of the SiO$_2$ being represented by quartz and chert grains. Therefore, a further correlation was mainly made with Al$_2$O$_3$ which represents the association of certain elements within clay minerals. With the exception of Na$_2$O (Fig. 6b) the other oxides and LOI (loss on ignition) shown in the Fig. 6 have a positive correlation with Al$_2$O$_3$. Positive correlation of K$_2$O with Al$_2$O$_3$ (Fig. 6c) reflects its presence in micaceous minerals and K-feldspar, while CaO, MgO, TiO$_2$ and Fe$_2$O$_3$ (Fig. 6d-6g) are mostly associated with clay minerals. CaO and MgO have a strong positive correlation (Fig. 6h), which probably stems from their interrelationship in dolomite and in clay minerals as cations. The content of Na$_2$O and CaO in silicate minerals is usually associated with plagioclase. Consequently, the negative correlation of Na$_2$O with Al$_2$O$_3$ and the weak correlation with SiO$_2$ (Fig. 6i) probably reflects the depletion of Na$_2$O suggesting chemical weathering or recycling of plagioclase.

The discriminant functions defined by ROSER & KORSCH (1988) for distinguishing source rocks of clastic sediments on the basis of the content of certain macroelements confirmed the results of analyses of the modal composition of the detritus, according to which the latter originated predominantly from older siliciclastic sedimentary rocks and acidic and neutral magmatic rocks (Fig. 7). Geochemical analyses also showed that pelitic sediments have a more homogeneous chemical composition than the sandy sediments. They are usually grouped around the boundary of felsic igneous and quartz sedimentary rocks. Sandy material is distributed in the fields of neutral and felsitic igneous rocks and quartz sediments (Fig. 7). The highest concentration of quartz in the sands is the probable reason for the movement of this group of samples towards the field of felsitic igneous and quartz sedimentary rocks.

The SiO$_2$ / Al$_2$O$_3$ ratio is a measure of the maturity of clastic sediments, and a measure of the presence of quartz and chert versus clay minerals and feldspars (POTTER, 1978; CULLERS, 2000). In the analysed samples, this ratio ranged from 2.59 to 23.87. High values of this ratio, as in the analysed sands and pelitic sediments (Tab. 4), indicate the chemical maturity of the VB from Vukomeričke Gorice which as expected, is higher for the sandy samples. This is consistent with the results of the analysis of the modal composition of the same sediments. The K$_2$O / Al$_2$O$_3$ ratio is used as an indicator of the source composition of pelitic sediments. This ratio ranges from 0.3 to 0.9 (COX et al., 1995). Analysed pelitic samples have a K$_2$O / Al$_2$O$_3$ ratio which averages 0.18 in the analysed pelitic sediments (Tab. 4), indicating older pelitic sediments as source rocks or pelitic detritus. The CIA index, as defined by NESBIT & YOUNG (1982), indicates medium to high intensity of chemical weathering in the source area (Tab. 4), and the same is indicated in a ternary diagram based on the ratios of Al$_2$O$_3$-(CaO + Na$_2$O)-K$_2$O (Fig. 8). The samples from the area of Vukomeričke Gorice are grouped near the Al$_2$O$_3$-K$_2$O line and follow the trend of granodiorite weathering. The ICV index defined by COX et al. (1995), measures the abundance of alumina in relation to the other cations in a rock or minerals with the elimination of quartz dilution. This index varies for the analysed pelitic sediments from 0.68–1.16 indicating that most of the sediments are compositionally mature and were likely dominated by recycling processes. However, several samples have an ICV > 1 (Tab. 4), suggesting the input of material only from rocks of the first sedimentary cycle. Namely, according to COX et al. (1995), compositionally mature mudrocks have low values of ICV (<1) and are poor with nonclay silicates or rich in the kaolinite group of minerals. Such sediments are associated with tectonic quiescent areas or cratons (WEAVER, 1989) with multiple recycled sediments, but can also...
be formed as a product of the intensive chemical weathering of materials within the first sedimentary cycle (BARSAD, 1966). Compositionally immature mudrocks have high values of the ICV index (>1) and a high proportion of nonclay minerals or, are rich with smectites and illitic material. They are characteristic for the first sedimentary cycle deposits and tectonically active settings (COX et al., 1995 and references therein).

Results of the trace element analysis (Tab. 5) show strong correlation with the mineral and petrographic composition of the sediment. Figure 9. shows that the major part of the analysed samples is from the rhyodacite dacite field and a smaller part from the trachyandesite field. Only a few samples are distributed over the andesite field. These results of the provenance analyses correspond to the results of the discriminant diagram according to ROSER & KORSCH (1988) (Fig. 7).

5.2. Geotectonic setting of the source area

Diagrams for determining the geotectonic position of the source areas based on the composition of the main detrital modes (Fig. 10) show that most of the sand detritus from the VB is of orogenic origin, i.e., it comes from a recycled orogen. The very high content of monocrystalline quartz and polycrystalline quartz particles together with fragments of older sedimentary rocks and low-grade metamorphic rocks (metapsamites), suggests the origin of the sand detritus from the collision orogen (according to DICKINSON & SUCZEK, 1979). This interpretation is supported by the low concentration of feldspar and particles of volcanic origin. A much smaller number of samples indicates the origin of material from the inner craton (Fig. 10). However, as the investigated area of Vukomerička Gorice is located in the wider area surrounded by high orogens such as the Dinarides and the Alps, it can be assumed that this material is also of orogenic origin, only it has been modified more. In addition, the chemical composition of the sandy and pelitic sediments from the VB indicates the orogenic origin of the material. Ternary diagrams based on the ratio of trace elements (Fig. 11) showed that the analysed sediments originated from the area of continental island arcs, to which magmatic arcs and recycled orogens are assigned as provenance types according to BHATIA & CROOK (1986). These results are consistent with the results of KOVAČIĆ (2004) and GRIZELJ et al. (2017), who investigated Upper Miocene sands and pelitic sediments in the southwestern part of the Pannonian basin system, according to which most of this detritus originates from the recycled orogen.

Summarizing all data concerning the provenance, leads to the conclusion that the clastic debris of the VB originated in a tectonically complex and lithologically heterogeneous source area. The rocks, which were originally located at different geotectonic positions, were weathered with moderate or high chemical and mechanical intensity. However, due to Cretaceous-Miocene subduction and the continental collision of the European Plate and several smaller continental fragments from the south, the rocks formed at different geotectonic positions were brought into contact with each other and lifted to the surface, creating large mountain ranges around the PBS (ROYDEN, 1988; SCHMIT 2008). During the Late Miocene, weathering of newly uplifted orogens (mainly the Alps and Western Carpathians) led to the production of huge amounts of clastic detritus that infilled the southwestern part of the PBS (KOVAČIĆ & GRIZELJ, 2006).
Later, at the end of the Miocene and during the Pliocene, some blocks within the PBS itself were uplifted due to compression (TOMLJENOVIĆ & CSONTOS, 2001). This led to the erosion and redeposition of the Upper Miocene detritus of the Alpine-Carpathian provenance, and also to the weathering of newly uplifted older rocks within the southwestern part of the PBS and to a lesser extent to the transport of material from the Inner Dinarides. All this material together forms the present detritus of the investigated VB deposits.

6. CONCLUSIONS

The results of analyses of the chemical, mineralogical and petrographic composition of the Pliocene Viviparus beds from Vukomeričke Gorice showed that:

1) The Viviparus beds are characterized by vertical and lateral interweaving of relatively compositionally mature and texturally immature pelitic and sandy sediments.

2) Pelitic sediments consist mainly of quartz and smectite, and to a lesser extent of calcite, dolomite, feldspar, illite/muscovite and kaolinite, while chlorite is present in only a few samples. This composition of pelitic sediments is mainly of detrital origin, but is also partly the product of chemical weathering in relatively warm and humid climates.

3) The composition of the sand detritus is dominated by quartz and particles of highly resistant rock, which are formed by weathering of rock from a recycled orogen.

4) The majority of the sand detritus from the Viviparus beds is of orogenic origin, i.e., bulk of the detritus was derived from recycled orogen.

5) The source rocks of the detritus of the Viviparus beds were moderately to intensively chemically weathered, mostly Upper Miocene sediments of alpine origin. To a lesser extent Palaeogene clastics, Triassic limestones and dolomites were the source of detritus, and of the material also originated from older volcanic and low-grade metamorphic rocks.

6) Clastic detritus can also be of local origin. The most important sources were located in the area of the Medvednica and Žumberak Mts. A smaller amount of detritus was derived from the area of Moslavačka Gora Mt. and Banovina.

7) A small amount of the detritus of the Viviparus beds from Slavonia and Banovina was brought from the south and originated in the Inner Dinarides.

8) Differences in the composition of the clastic detritus of the underlying Upper Miocene sediments deposited in Lake Pannon and of the detritus of the Viviparus beds deposited in Lake Slavonia are a consequence of the PBS inversion, which during the Pliocene led to uplift and erosion of the mountains in the SW part of the PBS.

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