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Short Communication

Tephrochronology of a distal tonstein layer within the Maritsa East lignite basin, Bulgaria: Potential sources of the Miocene large explosive eruption

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Abstract: This contribution presents the age of the detrital zircons from the coal bearing Miocene succession of the Maritsa East lignite basin. We report a new finding of thin kaolinized pyroclastic beds (tonstein) in the coal bearing succession. The analysis of the detrital age component shows sedimentary input from the basement of the proximal area. The most abundant age cluster 290–315 Ma shows that the predominant sources are the Early Permian–Late Carboniferous intrusions in the area. The newly-recognized tonstein beds represent the products of large, distal pyroclastic eruptions and are an important element of the sedimentary succession. They are dated at 14.31±0.30 Ma, which corresponds to the absolute age of the organic matter deposition of the productive middle lignite seam. Their source could most likely be related to the Miocene acid paroxysm ignimbrite eruptions in the Pannonian basin.

Keywords: Maritsa East lignite basin, detrital zircon age, pyroclastic tonstein beds, distal pyroclastic deposits

Introduction

The age of the detrital component of a sedimentary basin is crucial for recognizing the potential source of the supplying provinces, as well as their oldest possible age of deposition (e.g., Fedo et al. 2003). The careful study of coal bearing successions provides the opportunity of finding unusual ("exotic") rocks that preserve evidence for large distal pyroclastic eruptions (e.g., Ponomareva et al. 2015). These rocks are known as tonsteins (Spears 2012 and references therein) and are represented as thin, yet widespread beds of clay-altered layers of volcanic ash, dominated by kaolinite with remnants of volcanogenic minerals, such as quartz, feldspars, zircon, etc. These beds are laterally well-traced and used as markers in the sedimentary succession, which can be precisely dated using different radiogenic methods (e.g., K–Ar, Ar–Ar and U–Pb) on preserved rock-forming (e.g., sanidine, biotite) and accessory (e.g., zircon) minerals or preserved volcanic glass (rare in tonstein beds).

We studied the age of the detrital zircons from the Miocene succession and the covering sediments of the Maritsa East lignite basin. We report a new finding of thin, kaolinized pyroclastic beds (tonstein) in the coal bearing succession. The aim of the study is to reveal the age of the detrital component, which provides clues for the sources and the oldest age of deposition, as well as enabling the dating of the tonsteins in order to recognize the potential sources of the large distal pyroclastic eruptions.

Geological setting

The Thrace basin covers large areas in the Balkan and Aegean region. It is filled with early Eocene to Pliocene, marine to continental sedimentary successions, reaching up to 9000 m in total thickness (Siyako & Huvaz 2007 and references therein). The Maritsa East lignite basin (Fig. 1) is located at the easternmost part of the larger Late Alpine Upper Thrace depression (SE Bulgaria). It is interpreted as an intra-orogenic extensional basin (Dabovski et al. 2002), which formed during the late Eocene–Oligocene between the southern part of the Sredna Gora and Strandzha–Sakar and Eastern Rhodopes tectonic zones. The sedimentation in the Maritza East depression commenced during the Eocene in a marine environment, with the deposition of thick coarse-grained sediments grading upwards into alternating sandstones, marls, limestones, and intermediate in composition tuffs and tuff-breccias of Eocene–Oligocene age (Boyanov et al. 1993). During the late Oligocene–early Miocene, the marine environment was replaced by limnic conditions due to a gradual eastward regression of the sea (Kojumdgieva 1983). The coal-bearing Maritsa Formation represents a succession of black, gray and grayish-green clays, varying in thickness and interbedded with three major lignite seams. The presence of pyroclastic material was schematically pointed at the regional map of the Alpine magmatism in Bulgaria (Dabovski et al. 1991) without further description. The middle lignite seam (the productive one, reaching up to 20 m) is interbedded with the newly-found thin (5–10 cm), beige-white clay bed, representing "tonstein" with pyroclastic origin. At least two tonstein beds (Fig. 2A, B; 10.4 m from the base of the medium lignite) are recognized and easily traced laterally in this coal seam. A third tonstein bed (10–15 cm) is found interbedded in black clays at 1.7 m above the top of the middle lignite seam. The pyroclastic ash is completely altered to kaolinite with some remnants of volcanogenic minerals, such as quartz with minor mica, plagioclase and K-feldspar (Yossifova et al. 2018; Dimitrova et al. 2020). Mollusk calcite shells (Fig. 2C), fish bones (apatite), framboidal pyrite, and coal matter are also present in the tonsteins. The upper part of the Maritsa Formation consists of clays with some thin and medium sand beds (Fig. 2D), as well as the uppermost lignite seam (considered uneconomic). The Maritsa Formation is overlain by up to 100 m thick Mio-Pliocene deposits (Boyanov et al. 1993). The directly-covering Miocene part of the succession (Gledachevo Formation) constitutes a succession of clays and silts with lenses of gravelites with clayey matrix, representing old river beds.

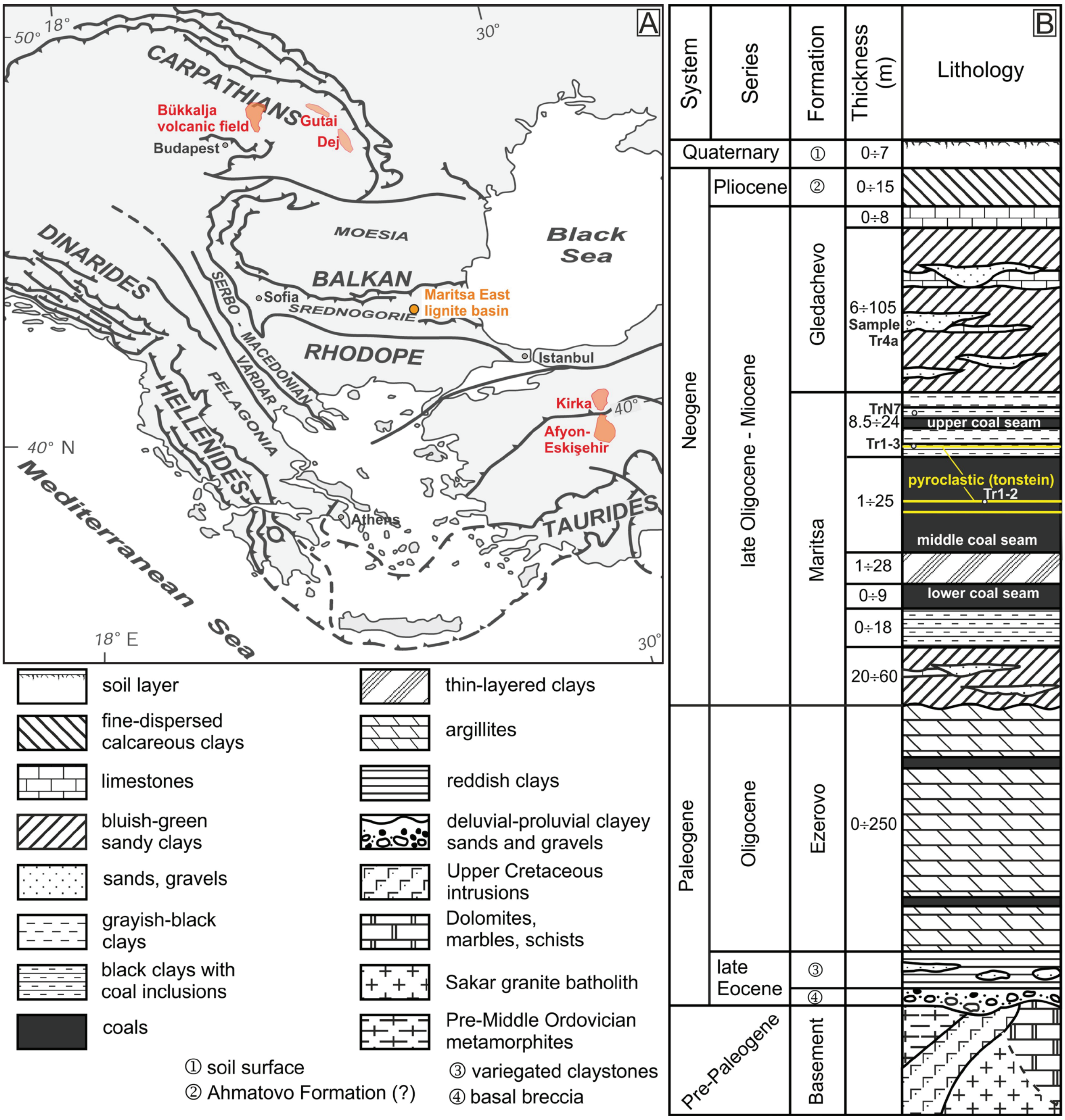

Fig. 1. Geological position: **A** – Geological tectonic scheme; **B** – Generalized stratigraphical column of the Maritsa East lignite basin modified after Yossifova et al. (2018) and references therein. The orange areas represent the potential sources of the large explosive eruption.

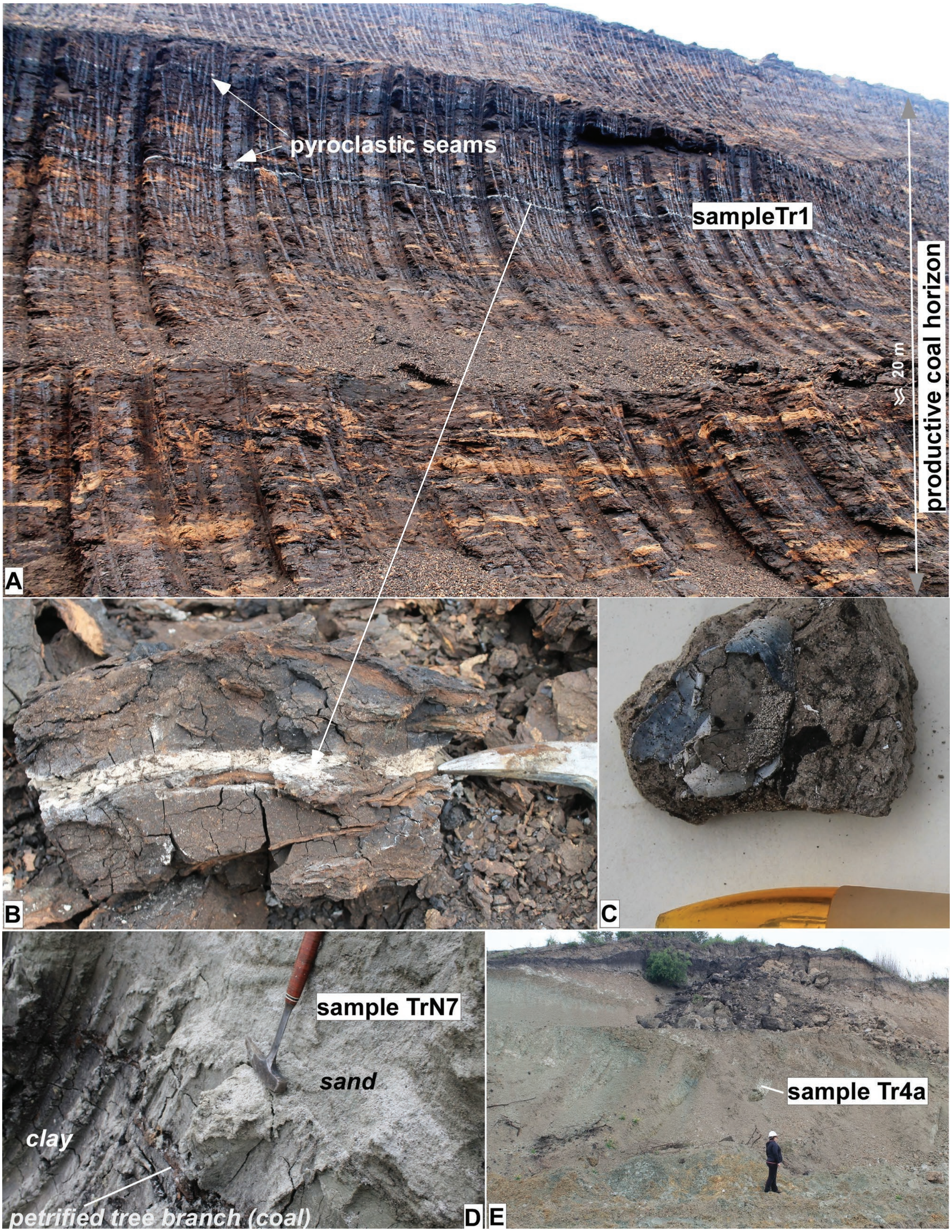

Fig. 2. Characteristics of the Maritsa East lignite basin succession: **A** — Productive lignite layer with pyroclastic seams (tonsteins); **B** — Closer view of the tonstein; **C** — A mollusk fragments; **D** — Sand in the upper parts of Maritsa Formation; **E** – Overview of Gledachevo Formation.

Sampling and methods

Two samples from tonsteins were collected – one from the bed intercalated in the middle lignite seam (Tr1-2, Fig. 2A, B) and the other (Tr1-3) from the tonstein bed, located 1.7 m above the top of the seam. For the detrital zircon study, two samples were collected: TrN7 – from the sands in the upper part of the Maritsa Formation (Fig. 2D) and Tr4a – from the gravels with clayey matrix from the Gledachevo Formation (Fig. 2E).

Zircon grains were separated from a 5 kg rock sample by standard gravimetric and isodynamic magnetic techniques. After that, the separated zircons were embedded in epoxy resin and polished to expose sections through their centers. Cathodoluminiscence (CL) images were collected prior to zircon analyses to identify inherited cores, cracks and inclusions. U–Pb isotope analyses of particular zircon zones were carried out using a New Wave Research (NWR) Excimer 193 nm laser-ablation system attached to a Perkin-Elmer ELAN DRC-e inductively-coupled plasma mass spectrometer (LA–ICP–MS) at the Geological institute, Bulgarian Academy of Science. The spatial resolution was 35 μm with frequency of 7 Hz. The measurement procedure involved calibration against an external zircon standard GJ1 (≈604±3 Ma, Jackson et al. 2004) measured at the beginning, middle, and at the end of the analytical block. Plešovice (≈337±0.37 Ma; Sláma et al. 2008) was measured as a secondary zircon standard. This technique allows a suitable correction for instrumental drift along with the minimization of elemental fractionation effects. Raw data were processed using Iolite software (Paton et al. 2011). ^{207}Pb/^{206}Pb, ^{208}Pb/^{232}Th, ^{206}Pb/^{238}U and ^{207}Pb/^{235}U ratios were calculated, and the time-resolved ratios for each analysis were then carefully examined. Optimal signal intervals for the background and ablation data were selected for each sample and automatically matched with the standard zircon analyses. U–Pb Concordia ages were calculated and plotted using ISOPLOT 3.75 (Ludwig 2012).

Results

Detrital zircon dating

Eighty-two analyses were made preferentially at the rims of the zircons from the sands from the upper parts of the Maritsa Formation (sample TrN7). The zircons are various in size and morphology, some of them showing complex structure with the presence of inherited cores. Most of the crystals are with rounded peripheries due to sediment reworking. Several detrital age clusters were distinguished (Fig. 3A): 255–274 Ma; 296–315 Ma (the most abundant); ≈400 Ma; 430–440 Ma, ≈550 Ma; 603–612 Ma; 756–768 Ma and 1780 Ma (1 grain).

Eighty-eight analyses were made preferentially at the rims of the zircons from the gravels of the Gledachevo Formation (sample Tr4a). The zircons are with variable morphology, some of them showing oscillatory zoning and some of them containing inherited cores. Most of them show signs of sediment reworking and have rounded rims. Several detrital age clusters were distinguished (Fig. 3B): 35 Ma (1 grain); 49 Ma (1 grain); 240–277 Ma; 290–313 Ma (most abundant); 402 Ma (1 grain); 430–443 Ma; 610 Ma (1 grain).

Tonstein geochronology

The zircon separation from the tonsteins was not an easy task. Zircons were found only in the sample from the bed (sample Tr1-2) and intercalated in the middle lignite seam. Thirty-four zircons (preferentially rims) were analyzed. The zircons are small (Fig. 4A), predominantly long to medium prismatic, showing well-expressed oscillatory zoning typical for crystallization from intermediate to acid magmas. Their size and morphology are suitable for distal air transport during a large pyroclastic eruption. Most of the analyses (19 spots) give clear Concordia magmatic age of 14.28±0.42 Ma (Fig. 4B; middle Miocene–Langhian) and ^{206}Pb/^{238}U weighted mean (29 spots) age of 14.31±0.30 Ma. The Th/U ratio is in the range of

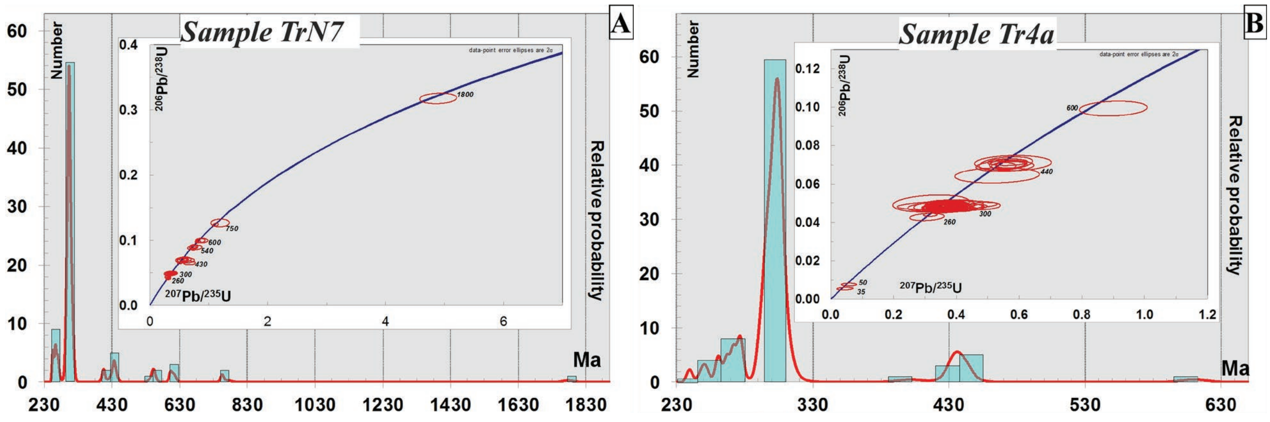

Fig. 3. Detrital zircon geochronology – probability density plots and Concordia diagrams of: **A** — Sands from upper parts of Maritsa East Formation; **B** — Gravels from Gledachevo Formation.

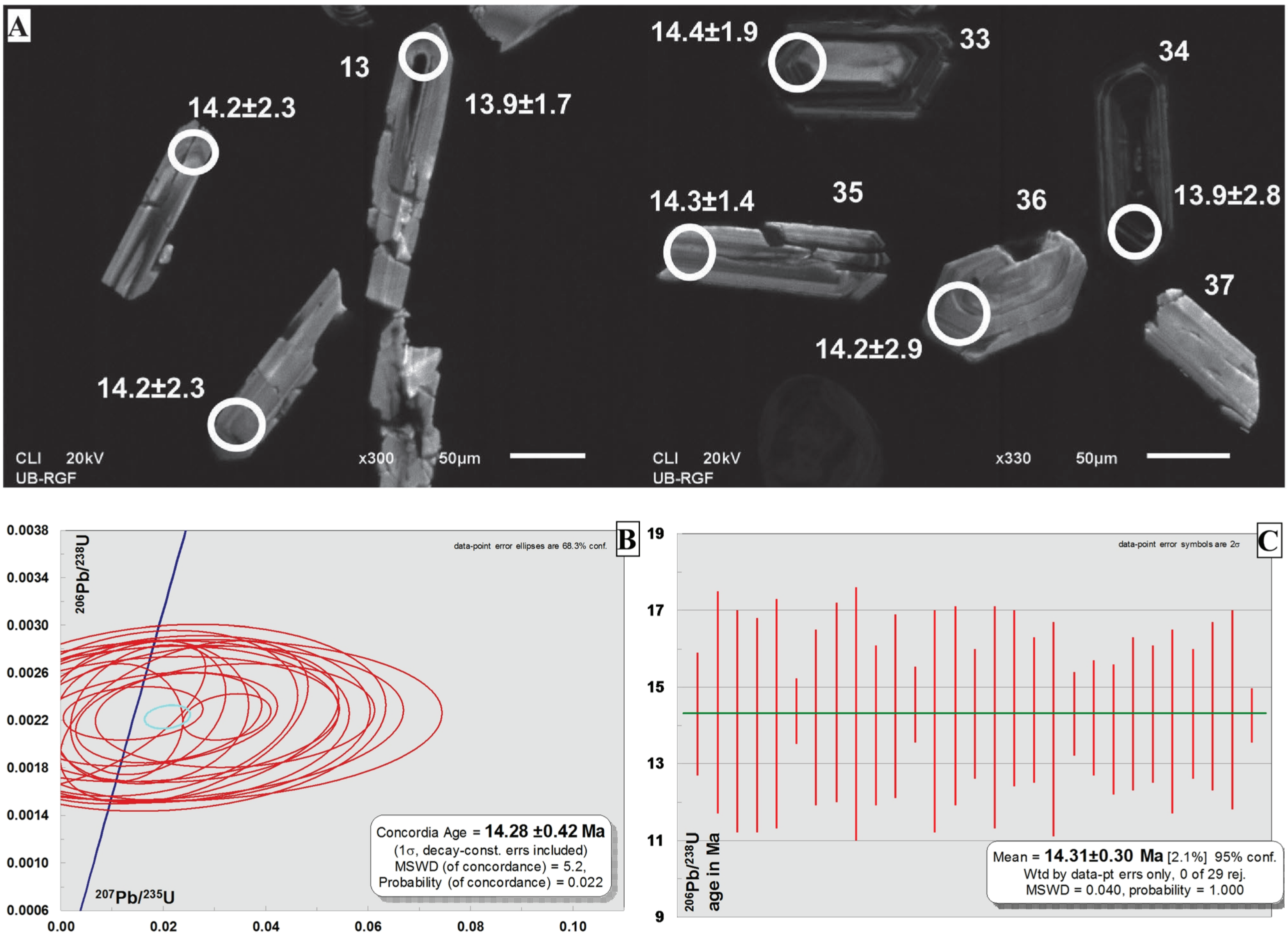

Fig. 4. Tonstein geochronology: **A** — CL images of the zircons; **B** — Concordia diagram; **C** — Weighted average diagram.

0.41–0.95. One zircon gives an age of 18 Ma and most probably represents antecryst, while two analyses show a xenocrystic component of ≈390 Ma.

Discussion

Tonstein age and potential sources

The LA–ICP–MS zircon U–Pb age of the tonstein dated during the present study is 14.28±0.42 Ma (middle Miocene–Langhian), which correlates with the age (Boyanov et al. 1993) of the deposition of the organic matter that led to the formation of the productive middle lignite seam in the Maritsa East basin. The abundance of fossil mollusk shells and remnants of fish bones is most probably due to the transient catastrophic influence of the volcanic event. The revealing of the potential source of the large pyroclastic eruption that formed the pyroclastic layers in the Maritsa Formation is an intriguing problem. In Bulgaria, volcanic rocks with such an age are not found. The closest by age is the trachydacite cryptodome of Kozhuh volcano, dated at ≈12 Ma (Georgiev et al. 2013 and references therein); however, along with the age difference there are also no signs for large pyroclastic eruptions related to it. Analysis of the volcanic events in Greece and Turkey showed that there were no large pyroclastic eruptions of this concrete age, and most of the volcanic activity was related to subvolcanic bodies, domes, and lava flows with minor explosive products. Nevertheless, in the area of Afyon–Eskişehir (Turkey), there are large Miocene ignimbrite deposits related to caldera formations – the Kirka–Phrigian caldera formed at around 18.9 Ma (Seghedi & Helvaci 2016), as well as the Koroğlu caldera (Aydar et al. 1998). The region between the towns of Afyon and Eskisher exposes a thick pyroclastic succession (Agro 2014) represented by Incik ignimbrite (18 Ma, Kirka source), Seydiler ignimbrite (product of Koroğlu caldera, considered to be older than 14.8 Ma, as revealed from the age of an overlying lava flow) and Sabuncu ignimbrite dated at 9.43±0.09 (supposed Kirka source area). The age of the pyroclastic activity described above cannot be precisely correlated with the tonsteins studied, however, they could still be considered a probable source area. One of the most possible sources of the pyroclastic material can be related to the Bükkalja Volcanic Field (NE Pannonian Basin, Hungary), where successive ignimbrite sheets are dated in the interval 18.2–14.4 Ma (Lukács et al. 2015, 2018). One of the last large pyroclastic eruptions is precisely dated using zircon U–Pb CA–ID–TIMS at 14.361±0.016 Ma. This represents the non-welded acid in the composition ignimbrite of "Harsány", with thickness up to 40 m, and crystaloclasts of feldspars, quartz, and biotite. Distal pyroclastics are correlated with this eruption in Romania (Dej tuff) and also as thin beds in the Miocene successions of Western Europe (Lukács et al. 2018). Another possibility for the volcanic source is the Gutai ignimbrite (Lexa et al. 2010; Rocholl et al. 2017) in Romania, which is also considered a proximal part of the Dej tuff, dated around 14.4–15 Ma (Szakács et al. 2012; de Leeuw et al. 2013, by K–Ar and Ar–Ar methods, respectively).

Analysis of the detrital zircon component in the Miocene sediments

The studied detrital zircon populations of the samples from the upper part of the Maritsa Formation and the Gledachevo Formation show a resemblance. Most of the detrital age clusters correspond to the local basement in the area of the basin. Younger single zircon ages are found only in the Gledachevo gravels and correspond to 35 Ma. The source can be related to the lower parts of the basin succession (Boyanov et al. 1993) or to the intermediate to acid in composition volcanic material from the Eastern Rhodopes volcanic area (e.g., Yanev & Bardintzeff 1997). The 49 Ma correspond to the ages of some of the granodioritic intrusions (Marchev et al. 2013) found west and southwest of the area. The age cluster of 240–270 correlates with the Permo–Triassic granodiorite to the granite intrusions in the areas of Sredna Gora and Sakar (Bonev et al. 2021). The most abundant detrital age cluster in both samples is 290–315 Ma, which could be referred to the Early Permian–Late Carboniferous granodiorite to granite intrusions that crop out in the Eastern Rhodopes, Sakar (Bonev et al. 2019, 2021) and the Central Sredna Gora (Carrigan et al. 2005). The age cluster of 430–440 Ma could be related to the high-grade metamorphic rocks found in the Sakar, Eastern Rhodopes and Central Sredna Gora zones (Bonev et al. 2021; Carrigan et al. 2006). The age clusters of 550 Ma, 603–612 Ma, 756–768 Ma and 1780 Ma most likely represent a reworked component from the Early Permian–Late Carboniferous intrusions. Rare findings of metamorphic rocks with ages around 550 Ma and 600 Ma are reported from the Central Sredna Gora Zone (Carrigan et al. 2006) which can also be a potential source.

Conclusions

The analysis of the detrital age component in the sediments of the Maritsa coal bearing basin shows sedimentary supply from the basement of the proximal area. The most abundant age cluster of 290–315 Ma shows that the predominant source is the Early Permian-Late Carboniferous intrusions in the area. The newly-recognized tonstein beds represent the products of large distal pyroclastic eruptions and are an important element of the sedimentary succession. They are dated at 14.31±0.30 Ma, which corresponds to the absolute age of the organic matter deposition of the productive middle lignite seam. Their source could most likely be related to one of the Miocene acid paroxysm ignimbrite eruptions in the Pannonian basin, i.e., Harsány, Gutai or Dej tuff.

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