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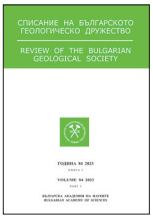

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$^{40}Ar/^{39}Ar$ and U-Pb age correlations of the large Rupelian Rhodope Massif eruptions with airfall tuffs in SE, S and Central Europe

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Корелация на $^{40}Ar/^{39}Ar$ и U-Pb възрасти на големите Рупелски ерупции от Родопския Масив с пеплопадни туфи от Югоизточна, Южна и Централна Европа

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Abstract. Numerous Eocene and Oligocene volcanic tuff layers within the Eastern, Central and Southern Europe sedimentary basins attest to extensive volcanic activity. Tephra dispersal of these tuffs covers areas of more than 1 000 000 km^2, and the volume of erupted material to 1000^s of cubic kilometers. The sources of the eruptions, however, remain unknown. Using precise $^{40}Ar/^{39}Ar$ and U-Pb radiometric dating, we correlate some of these tuff layers to three silicic Rhodope Massif Rupelian (early Oligocene) supereruptions dated at 33.2 Ma, 32.8 Ma and 31.6 Ma and named Dazhdovnitsa, Borovitsa and Perelik. Hence, these tuff layers can now be used as regional stratigraphic isochronous marker horizons for correlating, dating and synchronizing deposits and events in geologic and paleoenvironmental studies.

Keywords: $^{40}Ar/^{39}Ar$ and U-Pb age, Rhodope supereruptions.

Introduction

Large explosive volcanic eruptions, producing >1000 km^3 of tephra, cover continental scale areas with ash-flow and fallout deposits. The ash fall beds from such eruptions are widely used as chronological markers as they often can be correlated within and between sedimentary basins, providing geoscientists with important information on the eruptive volumes, magnitude and ages of individual eruptions. Among the mineralogical, geochemical and stratigraphic methods, precise age dating remains the most powerful tool that can help in linking the proximal ignimbrites with the distal deposits.

Over the last century, many volcanic tuff layers have been reported either in outcrops or drill holes in numerous upper Eocene–lower Oligocene south Tethyan basins in Italy (Coccioni et al., 2008 and references therein) in the Central and Eastern Paratethys in Hungary (Báldi, 1984; Danišík et

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al., 2015) and Thrace basin in Turkey (Okay et al., 2019; 2023), Limnos island in Greece (Innocenti et al., 2009) and Russia (van der Boon et al., 2019). The sources of these deposits remain largely unknown. Our review on the literature showed that the only extensive volcanism in the region at that period was the one in the Rhodope Massif, South Bulgaria. Rupelian pyroclastic and ignimbrite eruptions were described in the Rhodopes since the beginning of 60s (e.g. Ivanov, 1960; Goranov, 1960; Yanev, 2007, 2017; Ivanova et al., 2012, etc.). Three of them, named here Dazhdovnitsa, Borovitsa and Perelik (the last one is formerly known as 3 separate units Bratsigovo-Dospat, Smolyan and Vitina), are of size that can be categorized as supereruptions and their products should have been widely dispersed outside Bulgarian territory.

In this study we provide new precise $^{40}Ar/^{39}Ar$ sanidine and biotite ages, as well as U/Pb zircon ages and literature data in an attempt to correlate the three Rupelian Rhodope ignimbrites with their coeval tephra deposits from surrounding sedimentary basins.

Analytical methods

Sanidine, biotite and zircon were separated from collected samples from the three volcanic units. Sanidine and biotite were dated using $^{40}Ar/^{39}Ar$ single crystal laser fusion or incremental heating at the Ar Geochronology Laboratory of the University of Wisconsin, using the MAP 215–50 mass spectrometer and the Nu Instruments Noblesse 5-collector spectrometer, and the multicollector Thermo Scientific Argus VI mass spectrometer at the University of Geneva. U-Pb zircon dating was performed at the LA-ICP-MS laboratories of the Geological Institute of BAS and at ETH Zürich.

Age data and distribution of the ignimbrites and fallout

Dazhdovnitsa eruption. In the earliest studies of the Rhodope volcanism this eruption was known as the First acid volcanism (Ivanov, 1960; Goranov, 1960). Detailed description of its volcanic products in the Eastern Rhodope is made by Yanev (2007), who denoted it as a new lithostratigraphic unit, named Dazhdovnitsa Formation. The type locality of the formation is 120 m thick deposits of ignimbrites and air fall tuffs located at the SE rim of the large 34/15 km Borovitsa caldera (Yanev, 2017 and references therein). Yanev proposed that it is the result of four volcanic phases that generated pyroclastic flows (both ash and pumice), accompanied by pyroclastic fallouts. However, since the entire section is separated only by a thin volcano-sedimentary layer, we interpret the eruption as the result of two consecutive eruptions, divided by short time break.

Ages of Dazhdovnitsa ignimbrites. First $^{40}Ar/^{39}Ar$ ages for the eruption are published by Marchev and Singer (2002). The age of (32.53±0.20 Ma), recalculated using astronomically calibrated Fish Canyon sanidine standard (FCs) age of 28.201±0.022 Ma (Kuiper et al., 2008), gave an age of 33.23±0.18 Ma. The newest 3 precise $^{40}Ar/^{39}Ar$ from the type locality, yielded ages of 33.167±0.040 Ma and 33.176±0.041 Ma from the lower eruption and 33.050±0.039 Ma from the upper eruption. A slightly older age has been obtained from Bryagovets ignimbrite (33.376±0.034 Ma), which suggests multiple explosive episodes.

Mid-distance deposits. To these deposits we refer ash material in the Varna Mn deposit, and Turkish and Greek Thrace basin, located 200–300 km from Borovitsa. Ash from the Mn deposit yielded a sanidine $^{40}Ar/^{39}Ar$ age of 33.380±0.078 Ma. The deposits in Turkish Thrace basin and Greek island of Lemnos are represented by two tuff beds separated by 5–10 m turbidites, which confirms the two-stage character of the Dazhdovnitsa eruption. The upper tuff bed in the Turkish Thracian basin yielded a $^{40}Ar/^{39}Ar$ age of 33.185±0.047 Ma, whereas the lower bed in Limnos gave U-Pb zircon ages of 33.38±0.37 Ma and 33.31±0.61 Ma (Marchev et al., 2021), identical within the error to the age obtained for the ignimbrites.

Distal deposits. These deposits lie at a distance more than 800–1300 km. Such deposits have been identified in Italy, Hungary and northern Caucasus, Russia. A biotite from a thin tuff layer from the Monte Cagnero section in the Umbria-Marche basin in Italy has been astronomically dated at 33.3 Ma. Biotite from airfall tuffs sampled from a borehole core in the Pannonian basin yielded 33.7±1.0 Ma using K-Ar method (Balogh, Pécskay, 2001). The most remote precisely dated outcrop of ash, ~1300 km NE of Borovitsa, is from the Belaya River, northern Caucasus, Russia, which yielding an biotite $^{40}Ar/^{39}Ar$ age of 33.2±0.34 Ma (van der Boon et al., 2019).

***Borovitsa eruption*.** Borovitsa eruption, known as Plazishte formation (Ivanova et al., 2012), is the second large eruption in the Eastern Rhodopes. A voluminous part of the erupted ignimbrites fill the Borovitsa caldera. Best extracaldera outcrops can be seen at the edge of the caldera, however, the most detailed description of the erupted ignimbrites and ash-fall deposits have been made in the outcrops close to the village of Plazishte (Ivanova et al., 2012). The thickness of the section here is 60 m. The preliminary calculation of the volume of the erupted material is ~1000 km^3.

Age of the Borovitsa eruption. The first precise data of proximal deposits of the eruption are published by Singer and Marchev (2000) and Moskovski et al. (2004). Recalculations of these ages, using the astronomically calibrated FCs age of 28.201±0.022 Ma, are 32.85±0.16; 32.69±0.12 and 32.97±0.14 Ma. Here we provide new high-precision ages of 32.662±0.041; 32.71±0.16; 32.68±0.16 Ma of samples from different localities in the Eastern Rhodopes, along with an intracaldera ignimbrite age from Belintash of 32.77±0.13 Ma.

Mid-distance deposits. A tuff, ~6 m thick, was described by Innocenti et al. (2009) at the Limnos Island in Greece, ~200 km S of the Borovitsa caldera. Recently, it was correlated with the Borovitsa eruption on the basis of two U-Pb zircon ages of 32.6±0.4 and 32.9±0.5 (Marchev et al., 2020). Here, we provide a new precise $^{40}Ar/^{39}Ar$ (32.781±0.039 Ma) and less precise U-Pb (32.67±0.41 Ma) from a tuff bed from the village of Kıyıköy (Turkey). Four U-Pb zircon ages from tuffs within Ganos turbidites in the Thrace basin fall in the range 32.4±0.7 – 32.6±0.4 Ma data (Okay et al., 2023).

Distal deposits. Ages from tuffs comparable to the Borovitsa eruptions have been previously dated with zircon U-Pb from drillholes in the Pannonian basin (32.72±0.15; Danišík et al., 2015). Three new U-Pb zircon ages (32.49±0.65; 32.02±1.2; 32.28±0.32 Ma) have been obtained from another drill core in this study, which are in good agreement with the other ages.

Perelik eruption. The three large scattered outcrops of crystal-rich rhyodacitic ignimbrites (Bratsigovo-Dospat, Perelik and Kotili-Vitina) in the Central Rhodopes, previously have been considered as different eruptions. The space covered by these ignimbrites has been estimated at 700 km^2, 220 km^2 and 350 km^2 and volumes 200 km^3, 65 km^3 and 105 km^3, respectively, an average thickness of ~300 m (Harkovska et al., 1998).

Age of the Perelik ignimbrite. Filipov et al. (2017) published the first more precise U-Pb zircon ages for the Bratsigovo-Dospat locality of 30.93±0.28 Ma and 30.55±0.25 Ma. More recent U-Pb zircon age from the same locality gave 31.63±0.40 Ma (Marchev et al., 2022). New high-precision single-crystal fusion analyses from Perelik yielded a multi-modal distribution with dates ranging from 31.539±0.028 Ma to 31.884±0.030 Ma. The measurement of the same sample in Geneva lab yielded weighted plateau of 31.56±0.16 Ma and total fusion age of 31.57±0.16 Ma. The Vitina part was dated with zircon U-Pb method which gave an age of 31.71±0.43 Ma.

Proximal and distal deposits. The ages of seven tuff samples, dated with zircon U-Pb method from different parts of the Thrace basin in Turkey, range between 31.7±0.4 and 30.4±0.8 Ma (Okay et al., 2023), and fall in the range of Perelik ignimbrite. Distal biotite-bearing layer in the Contessa quarry in Italy, yielded U-Pb zircon ages of 31.4±0.14 Ma (Oberli, Meier, 1991), identical to the $^{40}Ar/^{39}Ar$ age of 31.5±0.2 Ma from a tuff layer from Monte Cagnero (Coccioni et al., 2008). Our zircon U-Pb ages from Pannonian drillhole (31.56±0.62 and 31.31±0.38 Ma) are in agreement with the other ages.

Conclusions

Using our new $^{40}Ar/^{39}Ar$ sanidine and U-Pb zircon ages from Rhodope Massif ignimbrites and fall deposits, correlations are made with previously and newly dated tuff layers in the Central and Eastern Paratethys and South Tethyan basin in Italy. These correlations show that at least three eruptions derived from the Rhodope Massif thus resolving a long-standing question about the source of these deposits. These large silicic eruptions in the Rhodope Massif lasted about 2 Ma, bracketing a flare-up period between 33.2 and 31.6 Ma. The ejected material covered areas of more than 1 000 000 km^2 and the volume of erupted material of 1000^s cubic kilometers. Therefore, these eruptions can be categorized as supereruptions and can be used as a correlation tool for creation of a regional stratigraphic scheme for that time interval in the Central and SE Europe.

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