СПИСАНИЕ НА БЪЛГАРСКОТО ГЕОЛОГИЧЕСКО ДРУЖЕСТВО, год. 81, кн. 3, 2020, с. 87–89
REVIEW OF THE BULGARIAN GEOLOGICAL SOCIETY, vol. 81, part 3, 2020, p. 87–89

Национална конференция с международно участие „ГЕОНАУКИ 2020“
National Conference with international participation “GEOSCIENCES 2020”

$^{40}Ar/^{39}Ar$ and U-Pb ages for 33.3 Ma supereruptions from Bulgaria: evidence from Eastern Rhodopes and Varna Mn mineralizations (Bulgaria) and Lemnos Island (Greece)

$^{40}Ar/^{39}Ar$ и U-Pb възрасти за 33.3 млн. г. суперерупции: доказателства от Източните Родопи, Варненските Mn минерализации (България) и остров Лемнос (Гърция)

Peter Marchev[1], Brian Jicha[2], Raya Raicheva[1], Rositsa Ivanova[1], Irena Peytcheva[1], Valentin Grozdev[1]
Петър Марчев[1], Браян Жича[2], Рая Райчева[1], Росица Иванова[1], Ирена Пейчева[1], Валентин Гроздев[1]

[1] Geological Institute, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria; E-mail: pmarchev@geology.bas.bg
[2] University of Wisconsin–Madison, Dept. of Geoscience, Madison, Wisconsin 53706, USA

Keywords: super-eruption, Borovitsa supervolcano, $^{40}Ar/^{39}Ar$ and U-Pb zircon ages, Rhodope Massif.

Introduction

During the late Eocene–early Oligocene, the Rhodope Massif was the site of intensive late-to post-collisional volcanism. A series of voluminous silicic eruptions produced ash fall and pyroclastic flow deposits that cover vast areas in the Central and Eastern Rhodopes. For 60 years now, these deposits have been used as prominent stratigraphic markers in the Eastern Rhodopes (Ivanov, 1960). Traditionally, three main phases of explosive volcanic activity are distinguished, designated as First, Second and Third acid volcanism, respectively (FAV, SAV, TAV) (e.g.,Yanev et al., 1998), with FAV and SAV originating from the Eastern Rhodopes and TAV originating from the Central Rhodopes. Previous K-Ar dating suggested that this volcanism occurred at 34, 33–32 and 31–30 Ma, respectively (Yanev et al., 1998). Later more precise $^{40}Ar/^{39}Ar$ data on sanidine and biotite and zircon U-Pb data constrained the ages of FAV, SAV and TAV at 33.23–33.75 Ma, 32.5–32.9 Ma, and 31.8 Ma, respectively (Marchev et al., 2019).

The SAV, which originates from the Eastern Rhodope Borovitsa volcano, is considered the largest volcanic eruption in the Rhodopes. The eruption produced 1000 km^3 volcanic material and resulted in the formation of a large 34x15 km caldera (Ivanov, 1972). Recently Yanev (2017) characterized the Borovitsa volcano as a supervolcano, whereas Marchev et al. (2019) described new remote deposits of the eruption and categorized it as a supereruption.

Eruptive products of the FAV in the Eastern Rhodopes are also well recognized. The stratotype of the eruption, named Dazhdovnitsa Formation (Yanev, 2007), is located close to the rim of the Borovitsa caldera, It is represented by 120 m outcrop of alternating ash and pumice tuffs and weak- to medium-welded ignimbrites. The thickness of the Eastern Rhodope deposits diminishes gradually away from Borovitsa, but in most locations it remains several tens of meters. The deposits of this volcanism outside the Rhodopes, however, are totally unknown. Here we present for the first time precise age data for the pyroclastic material outside of the Rhodopes taken from Varna Mn region and island of Lemnos in Greece, along with ignimbrites from the Eastern Rhodopes. We combine these data with published age and stratigraphic data for tuffs from other localities in order to understand the regional dispersal of the volcanic ash and to evaluate the scale of eruption.

Description of the deposits and sampling

Samples for the FAV from the Eastern Rhodopes were taken from ignimbrite outcrops close to the

villages Kovil and Bryagovo (Plovdiv district). The Kovil ignimbrite consists of two medium welded pyroclastic flows separated by a layer enriched in metamorphic lithics at the base of the upper flow. The two flow units have similar composition, comprising large (up to 6 cm) pumice clasts, shards and crystal clasts of plagioclase, sanidine quartz, amphibole, clinopyroxene, biotite and magnetite. The ignimbrite of Bryagovo is nonwelded, composed of pumices, ash and rare large perlite (up to 50 cm) and rhyolite clasts and crystal clasts of plagioclase, sanidine, quartz, biotite, magnetite and rare amphibole.

Material for dating from Varna manganese region was taken from two localities. The first locality is near the village of Pripek. It represents several thin tuffite layers in the Mn ore. The dated tuffite is composed of terrigenous (plagioclase, K feldspar, quartz, muscovite, epidote) and volcanogenic (plagioclase, sanidine, biotite, amphibole, clinopyroxene) crystal clasts. The second sample comes from the collection of L. Vasilev, Geological Institute, Bulgarian Academy of Science (GI, BAS). It represents a manganese ore from Obrochishte mine consisting of brown Mn carbonate pisolites hosted in a grey clay mesostasis which contain large volume of volcanogenic (amphibole, biotite, clinopyroxene, plagioclase, sanidine, quartz and glass) and terrigenous (plagioclase, K feldspar, quartz, muscovite) crystals.

The locality in the Greek Island of Lemnos occurs at St. Sozon Cape in the SE part of the island. It represents two 6–7 m tuff beds separated by 6–7 m of sediments from the Priabonian–Rupelian Fissini-Sardes unit. The dated sample is taken from the lower and upper part of the lower tuff layer. It is composed of large (up to 2 mm) crystals and fragments of plagioclase, amphibole, biotite, magnetite, quartz and rare sanidine, comprising about 60–70% of the rock set in the predominantly clay matrix.

Samples, analytical methods and results

The samples from Kovil, Bryagovo, Pripek and Obrochishte were dated by $^{40}Ar/^{39}Ar$ dating of K feldspar separated and analyzed using the Noblesse multicollector mass spectrometer in the University of Wisconsin-Madison, USA. Zircon from the Lemnos Island sample was dated by U-Pb method using the LA-ICP-MS equipment at the Geological Institute, BAS, Sofia.

Separated K feldspar grains from Kovil (sample BG25b), and Briagovo (sample BG1a) was pure sanidine (125–180 mμ), which yielded ages of 33.376±0.034 Ma, and 33.303±0.044 Ma, respectively. Eight sanidine crystals from Pripek (sample Bg27d) gave an age of 33.309±0.057 Ma, closer to the age of Briagovo sample. K feldspar crystals separated from sample Bg50 were predominantly terrigenous microcline and orthoclase with only one sanidine crystal which gave an age of 33.380±0.078 Ma. U-Pb zircon age of the sample S17 and S14 from island Lemnos yielded concordia age of 33.38±0.37 Ma and 33.31±0.61 respectively, indistinguishable within the error from those obtained from the $^{40}Ar/^{39}Ar$ sanidine ages.

Discussion and conclusions

Previous age data (33.23–33.75 Ma) demonstrated that the FAV is close to the Priabonian–Rupelian boundary. Although the stratigraphic studies in Varna Mn deposits (300 km NE) and Lemnos Island (200 km south) from the stratotype locality showed that their eruptive materials are also close to the Priabonian–Rupelian boundary (Aleksiev, 1959; Innocenti et al., 2009), the lack of age data did not allow their direct correlation with the FAV eruption. The newly obtained precise $^{40}Ar/^{39}Ar$ and zircon U-Pb age data clearly show that the eruption covers a vast area in Bulgaria and Southern Thracian Basin. Additional evidence for the space distribution of the eruption comes from the age and stratigraphic data from other remote localities. For example, Balog and Pecskay (2001) yielded an age of 33.7±1.0 Ma from a biotite in a tuff layer from Buda Basin, in Hungary. Okay et al. (2019) reported a U-Pb zircon age of 33.9±0.4 Ma from a tuff layer near Kıyıköy in the Turkish Thrace basin. Apart from Varna Mn region, alteration products of volcanic ash have been described in all other stratigraphically similar Parathetis Mn deposits in Ukraine, Georgia, Turkey, Slovakia, and Kazakhstan (review in Varentsov, 2002). Even the rough calculation for the space dispersal of this eruption shows that it covered more than 1 000 000 km^2. Thus, our data demonstrate that the FAV is comparable or even larger than SAV and it can be categorized as another supereruption. The FAV and SAV supereruptions highlight the regional geologic importance of these eruptions and the possibility to use their volcanic products to better constrain the regional chronostratigraphy in Southeastern and Central Europe. Finally, the large amount of the volcanic material from FAV in the manganese deposit can throw a light on the long standing debate about the source of metals in the largest Phanerozoic Mn deposits in the Parathetis region.

Acknowledgments: This study was funded by the Bulgarian Science Fund, grant N24/3 and partially supported by National Research Programme "Environmental Protection and Reduction of Risks of Adverse Events and Natural Disasters" approved by DCM # 577/17.08.2018.

References

Alexiev B. 1959. Pyroclastic sedimentary rocks of Oligocene age from the district of Varna. – *Bull. Inst. géol.*, *7,* 101–117 (in Bulgarian, with English summary).

Balogh, K., Z. Pécskay. 2001. K/Ar and Ar/Ar geochronological studies in the Pannonian-Carpathians-Dinarides (PANCARDI) region. – *Acta Geol. Hung*., *44*, 2–3, 281–299.

Innocenti F., P. Manetti P, R. Mazzuoli, P. Pertusati, M. Fytikas et al. 2009. Geological map (scale 1:50,000) of Limnos Island (Greece): Explanatory notes. – *Acta Vulcanol.*, *21 (1-2),* 123–134.

Ivanov, R. 1960. Der Magmatismus in der Paläogenen Senkung der Ostrodopen. 1 Teil – Geologie. *Travaux sur la géologie de Bulgarie, Série de géochimie et des gîtes métallifères et non-métallifères*, *1*, 311–387 (in Bulgarian with German abstract).

Ivanov, R. 1972. Volcano-tectonic structures in the Borovitsa Depression. – *Bull. Geol. Inst., Ser. Geochem. Mineral. and Petrogr*., *21*, 193–210 (in Bulgarian with English summary).

Marchev, P., R. Spikings, B. Singer, B. Jicha, R. Raicheva. 2019. $^{40}Ar/^{39}Ar$ and U-Pb ages of the biggest Oligocene explosions in the Eastern Rhodopes, Bulgaria and their impact on the Eocene–Oligocene global climatic changes: Preliminary data. – *IESCA Abstracts*, Izmir, p. 58.

Okay, A. I., E. Özcan, A. Hakymez, M. Siyako, G. Sunal. 2019. The Thrace Basin and the Black Sea: the Eocene–Oligocene marine connection. – *Geol. Mag*., *156*, 1, 39–61.

Varentsov, I. M. 2002. Genesis of the Eastern Paratethys manganese ore giants: impact of events at the Eocene/Oligocene boundary. – *Ore Geol. Rev*., *20*, 65–82.

Yanev, Y. 2007. Lower Oligocene Dazhdovnitsa Formation (new Formation) in the Eastern Rhodopes: description and volcanological interpretation. – *Rev. Bulg. Geol. Soc*., *68*, 1–3, 131–142 (in Bulgarian, with English abstract).

Yanev, Y. 2017. On the geology and volcanology of the Paleogene Borovitsa caldera and its frame (Eastern Rhodopes, Bulgaria). – *Rev. Bulg. Geol. Soc*., *78*, 1–3, 97–128 (in Bulgarian with English abstract).

Yanev, Y., F. Innocenti, P. Manetti, G. Serri. 1998. Upper Eocene–Oligocene collision-related volcanism in Eastern Rhodopes (Bulgaria)-Western Thrace (Greece): Petrogenetic affinity and geodynamic significance. – *Acta Vulcanol.*, *10*, 2, 279–292.