**TRANS-SAHARAN BELT PROVENANCE: A POTENTIAL
SOURCE FOR THE ORDOVICIAN SUCCESSION
OF THE BALKAN TERRANE (SVOGE UNIT) – CLUES
FROM LA-ICP-MS DETRITAL ZIRCON DATING ANALYSIS**

Stoyan Georgiev*, Valeri Sachanski*,,#, Polina Andreeva*,
Hristo Kiselinov*, Eleonora Balkanska***, Iskra Lakova*,
Stoyan Tanatsiev****

Received on June 29, 2021

Presented by I. Zagorchev, Member of BAS, on September 29, 2021

Abstract

Two sandstone samples from the upper and lower part of the Ordovician succession of Svoge Unit were analyzed in order to determine their detrital zircon U–Pb age spectra using laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS). One sample was collected from the Hirnantian siliciclastic glaciomarine deposits of the Sirman Formation. The other sample is a middle Darriwilian sandstone from the lower half of the Grohoten Formation. Additionally, micropetrographic studies were performed. They are composed predominantly of detrital monocrystalline quartz grains with uniform or rarely undulose extinction and only sporadically presented feldspar grains, muscovite flakes and single rock fragments. The heavy mineral assemblages are also characterized mostly by detrital zircon. As suggested from previous studies of the Hirnantian glaciomarine deposits of Sirman Formation, the provenance of siliciclastic material was most probably associated with sedimentary recycling of mature sands deposited across the North Gondwana Platform. Multi-dimensional

This work has been carried out in the framework of the National Science Programme “Environmental Protection and Reduction of Risks of Adverse Events and Natural Disasters”, approved by the Resolution of the Council of Ministers No 577/17.08.2018 and supported by the Ministry of Education and Science of Bulgaria (Agreement No D01-363/17.12.2020).

DOI:10.7546/CRABS.2022.02.09

scaling statistical technique allowed a reliable objective identification of the potential source areas in Northern Africa and palaeogeographic reconstructions were made. Both samples are close to the Trans-Saharan Belt provenance, which is the most probable source for the detrital component. Our data support the idea proposed by previous researchers that the present-day position of some of these terranes implies significant dextral strike-slip displacement, probably due to the movement on the Pangea megashear during the Carboniferous and Permian.

Key words: detrital zircon, Ordovician, Trans-Saharan Belt provenance, Balkan Terrane, Svoge Unit, Bulgaria

Introduction. Early-middle Palaeozoic sediments in Bulgaria are considered within two terranes with significant differences in their rock sequences – the Balkan and the Moesian terranes [1]. The territory south of the Balkan Terrane, where no non-metamorphosed sedimentary Palaeozoic rocks occur, was considered independent Thracian Terrane during the Palaeozoic (Fig. 1A) [1]. These terranes originate from different parts of Gondwana and peri-Gondwana. Regional data indicate an en echelon movement of the Moesian and the Balkan (incl. Thracian?) Terranes from the southern humid zone (in the Ordovician), across the southern arid zone (Moesian Terrane during the Devonian) and the equatorial zone (during the Carboniferous), to the northern arid zone (in the Permian) [1]. Devonian convergence brought the Moesian Terrane and the Dobrudgea periphery of Palaeo-Europe into a collisional contact. The collision between the Moesian and the Balkan (incl. Thracian) Terranes took place during the Late Carboniferous and Permian and was related to the formation of the Variscan Orogen [1].

The geological development and palaeogeography of the Moesian and the Balkan Terranes have been regarded in the scope of the palaeogeodynamical evolution of Baltica-Gondwana interface as Ordovician to Carboniferous. The Balkan Terrane was a part of the Armorican Terrane Assemblage during its whole Palaeozoic evolution [5]. The origin and palaeogeographic affinities of the Moesian Terrane during the Early Palaeozoic remain unclearly defined – Baltica, Avalonia or Armorican Terrane Assemblages [5].

Detrital zircon U–Pb geochronology has revealed a great potential for deciphering the early histories of terranes that underwent intense Variscan and Alpine reworking [6]. In the present work, we have analyzed two sandstone samples from the Ordovician succession of Svoge Unit in order to determine their detrital zircon U–Pb age spectra using laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS). Additionally, micropetrographic studies of both sandstone samples were performed.

Geological setting. In terms of regional tectonic zonation, the study area (Fig. 1A, B) is a part of a first-rank Late Alpine tectonic unit, the Srednogorie Zone, represented by the Svoge Unit [3]. The Svoge Unit is the northernmost fragment of the Srednogorie Zone, and is thrust to the north over the West Balkan

Fig. 1. A – Geological sketch showing the Palaeozoic terranes [2] and Alpine tectonic subdivision of Bulgaria [3] with designated location of the study area; B – Simplified geological map [4] showing the location of the samples A7 and J4; C – Lithologic log of the Ordovician in the Svoqe Unit with stratigraphic position of the samples A7 and J4. Abbreviations: Hir. – Hirnantian; Kos. – Kosovian; Kralodv. – Kralodvorian; Dobrot. – Dobrotivian; U – Upper; M – Middle; L – Lower

Unit of the Balkan Zone. The pre-Mesozoic basement of the unit is a tectonically overprinted Palaeozoic, mainly shale succession that is topped by Upper Devonian to lowermost Carboniferous flysch. This sequence is part of the Palaeozoic Balkan Terrane [1,2,5]. The latter is overlain with angular unconformity by Upper Carboniferous and/or Permian clastics. The pre-Mesozoic basement of the Svoje Unit was greatly influenced by Variscan and Alpine deformations [1,2,5].

The Ordovician succession, that is cropping out in the Svoje Unit, consists of five lithostratigraphic units [7]: siltstone-argillite metaformation, Grohoten Formation, Tseretsel Formation, Sirman Formation, and the lowermost part of Saltar Formation (Fig. 1C).

The Grohoten Formation is composed of grey, dark grey and black shales, and grey and light grey quartzites. In general, the lowermost and middle levels are built up of packages of quartzites. The thickness of these packages varies from a few meters to several tens of meters. They can be traced over distances of several hundred to several thousand meters. The lower boundary of the unit is a lithologic gradation from the light grey, green to beige metashales of the siltstone-argillite metaformation, or is a sharp lithologic contact with the latter at the base of the lowermost continuous quartzite packages in the section. The upper boundary is a short lithologic gradation into the green shales of the Tseretsel Formation. The thickness of the formation is estimated within wide limits: 750–800 m to 3300 m.

The oldest fossils are found at the basal part of this unit and consist of upper Arenigian acritarchs [8]. Middle Ordovician fossils can be grouped into three successive stratigraphical assemblages included within the Grohoten Formation. The first and the oldest palaeontological assemblage derives from lower Oretanian shales with nodules bearing pendent and extensiform didymograptids, some biserials, a single benthic atheloptic trilobite and probably also a rare pelagic form. All of them lie below the thick quartzite body recognized in the lower half of the Grohoten Formation. The second and the middle palaeontological assemblage is dominated by pelagic trilobites, with some sparse benthic elements. Its co-occurrence with the graptolite *Didymograptus murchisoni* (Beck) and a rare indeterminable biserial form, characterize an upper Oretanian age for the assemblage. This assemblage occurs within siltstones and silty shales that directly overlie the heterogeneous quartzitic member. The third and the youngest Middle Ordovician palaeontological horizon is characterized by the occurrence of the cyclopygid trilobite, indicative of a lower Dobrotivian age and belonging to the basal upper half of the Grohoten Formation. Upper Ordovician trilobites and brachiopod have only been recovered in the upper part of the Grohoten Formation. This assemblage most probably corresponds to a middle or late Berounian age [8].

The Tseretsel Formation comprises predominantly light grey to grey-green, indistinctly bedded shales, locally containing in some places siderite concretions. Dark grey centimeter-scale mottles with irregular outlines are also common feature of this unit. The upper boundary of the unit with the sandstones of the

Sirman Formation is a sharp lithologic contact. The total thickness of the formation varies between 100 m and 350 m. Despite the absence of fossils, the age of the sediments is assumed to be Ashgill or Kralodvorian on the basis of their stratigraphic position.

The Sirman Formation consists of dark grey to black, thin- to medium-bedded, very fine- to fine-grained sandstones alternating with thin beds of dark grey shales. Diamictites are encountered mainly in the lower levels of the section. The upper boundary with the black lydites of the Saltar Formation is a sharp lithologic contact. The total thickness is about 5–10 m. A detailed sedimentological study of the Hirnantian siliciclastic deposits of the Sirman Formation has been performed by CHATALOV [9], who interpreted a part of them as glaciomarine sediments deposited in an ice-intermediate to ice-distal, low-energy shelf environment of the intracratonic North Gondwana Platform. Based on the received sedimentological results, the same author concluded that these Hirnantian siliciclastic rocks could be correlated with other similar glaciomarine deposits known from the peri-Gondwana terranes in Europe showing a clear “Armorican affinity” [9].

The Ordovician succession ends in the basal meter of lydites and silicified shales that characterize the beginning of the Saltar Formation. This unit includes over 30 m of graptolitic strata ranging in age from lowermost Rhuddanian to early Telychian, except for its first basal meter, which bears the last Ordovician graptolites.

Materials and methods. Micropetrographic study was carried out on two sandstone samples (A7 and J4) that were examined under standard petrographic microscope. Sample A7 originates from the upper part of the Sirman Formation, exposed in Saltarski dol near Batuliya village (coordinates WGS84 N 42°53'22.3", E 23°26'12.0"). Sample J4 is from the lower half of Grohoten Formation, cropping out at Grohoten Peak, north of Svoje town (coordinates WGS84 N 42°58'43.82", E 23°20'31.60").

The samples were taken from fresh rocks weighing about 10 kg each. Zircon grains were separated by standard gravimetric and isodynamic magnetic techniques. After that, the separated zircons were embedded in epoxy resin and polished to expose sections through their centres. Cathodoluminescence (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 Sciences. The spatial resolution was 35 µm and the frequency – 7 Hz. Measurement procedure involved calibration against an external zircon standard GJ-1 ($\approx 604 \pm 3$ Ma; [10]) at the beginning, middle part and at the end of the analytical block and crosscheck with secondary zircon standard – Plezovitche ($\approx 337.13 \pm 0.37$ Ma; [11]). This technique allows a suitable correction for instrumental drift along with the minimization of

elemental fractionation effects. Raw data were processed using Iolite software [12]. Thus, $^{207}\text{Pb}/^{206}\text{Pb}$, $^{208}\text{Pb}/^{232}\text{Th}$, $^{206}\text{Pb}/^{238}\text{U}$, and $^{207}\text{Pb}/^{235}\text{U}$ 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 [13] and MDS diagrams using IsoplotR [14].

Results. Micropetrographic study (Fig. 2, 3) and U–Pb zircon dating analyses were performed (Fig. 4):

Sample A7 (Sirman Formation). Under the microscope (Fig. 2a–g), the sandstone consists of poorly sorted subangular to well-rounded monocrystalline or rarely polycrystalline clastic quartz, sporadic detrital feldspar grains and sparse muscovite flakes. Elongate, concave-convex (Fig. 2b) and microstylolitic (Fig. 2g) grain contacts are often presented. Some well-rounded quartz grains represent reworked sedimentary quartz and are characterized by abraded quartz overgrowths (Fig. 2b). Others display wavy extinction (Fig. 2c). Feldspar crystals (mostly plagioclase) are also locally observed and are partly replaced by clay minerals (Fig. 2d, e). Some clastic grains are replaced by calcite (Fig. 2f) or opaque minerals (Fig. 2g). Rock fragments are very scarce. Various in size zircon grains (Fig. 2f) are also sporadically noted.

One hundred spot analyses, predominantly from the rims of the zircon crystals, were performed. The zircons are represented by whole crystals or fragments often with oval shapes due to sedimentary transport, typically 100–250 μm in size. They are clear, long to short prismatic. Some of them show well-expressed zonation, while others have unclear oscillatory zonation. The ages form several clusters between: 515–800 Ma (most pronounced), 1026–1030 Ma, 1423–2323 Ma, and 2941–3178 Ma (Fig. 4A).

Sample J4 (Grohoten Formation). This sandstone is composed predominantly of monocrystalline quartz grains (Fig. 3a–g). Elongate, concave-convex and microstylolitic grain contacts are very common, indicating pressure-solution processes. Fine-grained rock matrix is not presented. A part of the quartz grains displays wavy (undulose) extinction (Fig. 3e) due to plastic deformation. A single quartz grain is characterized by abraded quartz overgrowths (Fig. 3f) and represents reworked sedimentary quartz. Feldspar crystals (Fig. 3b) are only sporadically noted. Muscovite flakes (Fig. 3g) are also locally presented. Lithic fragments occur very scarcely. Sericite (Fig. 3d) locally replaces a part of the clastic grains. The sandstone is characterized by moderate sorting. The heavy minerals are mostly presented by single zircon grains (Fig. 3c).

Eighty-two spot analyses, predominantly from the rims of the zircon crystals, were performed. The zircons are represented by fragments and whole crystals, often with oval shapes due to sedimentary transport, typically 80–150 μm in size. They are clear, long to short prismatic. Most of them show unclear oscillatory

Fig. 2. Photographs of sample A7 (Sirman Fm.): a) Dark grey sandstone crosscut by quartz (Qz) veins. Pyrite mineralisation (Py) is also locally observed; b) Quartz grain with abraded quartz overgrowths (yellow arrows). Concave-convex grain contacts are also observed (red arrow); c) Quartz grains with wavy (undulose) extinction (yellow arrows); d) Feldspar grain partly replaced by clay minerals (black arrow); e) Plagioclase detrital grain (black arrow); f) Detrital zircon grain (black arrow). Carbonate minerals locally replace some clastic grains (yellow arrow); g) Opaque minerals (pyrite?) (black arrows) and microstylolitic grain contact (red arrow).

Note: All photomicrographs in cross-polarized light

Fig. 3. Photographs of sample J4 (Grohoten Fm.): a) Dark grey quartzite; b) Plagioclase clastic grain (red arrow); c) Detrital zircon grain (yellow arrow); d) Sericite (red arrows) locally replaces a part of the clastic grains; e) Quartz grain with wavy (undulose) extinction (black arrow); f) Quartz grain with abraded quartz overgrowths (red arrow); g) Muscovite flakes (black arrows). Note: All microphotographs in cross-polarized light

zonation but well-expressed one can also be observed. Some grains show signs of recrystallization and new overgrowth. The ages form several clusters. The most pronounced one is between 479–645 Ma, but also several peaks between

Fig. 4. A – Relative probability plots built up with data from samples A7 and J4; B – Multi-dimensional scaling plot (MDS) of the analyzed samples compared to potential source areas in Northern Africa (grey). Summarized data of the African detrital provenances from Žák et al. [6]. Abbreviations: Pz – Palaeozoic; Ed. – Ediacaran; Cr. – Cryogenian; Calym. – Calymmian; Stather. – Statherian

745–845 Ma, 979–1076 Ma, 1248–2588 Ma, and a single peak of 3350 Ma were observed (Fig. 4A).

The statistical comparison is made through multi-dimensional scaling (MDS) to examine the degree of inter-sample similarity and the potential detrital source provenance areas (Fig. 4B).

Conclusions. Both sandstone samples (A7 and J4) are composed predominantly of detrital monocrystalline quartz grains with uniform or rarely undulose extinction and only sporadically presented feldspar grains, muscovite flakes and single rock fragments. The heavy mineral assemblages are also characterized mostly by detrital zircon. The same mineralogically mature sandstone composition was described previously in Hirnantian glaciomarine deposits of the Sirman Formation [9]. Based on the combined analysis of micropetrographical and geochemical data obtained from this siliciclastic sequence, Chatalov [9] assumed that the provenance of the siliciclastic material was associated with sedimentary recycling of mature sands deposited across the North Gondwana Platform in Cambrian and pre-glacial Ordovician times.

Recently, ŽÁK et al. [6] have made an attempt to reveal the detrital provenance of some of the Lower Palaeozoic sedimentary rocks from the Balkan region. They showed a “westerly” terrane assemblage, characterized by Mesoproterozoic ages and sourced from the West African Craton and the Trans-Saharan Belt, and an “easterly” assemblage formed next to the Saharan Metacraton and the Arabian–Nubian Shield. Multi-dimensional scaling statistical technique allowed a reliable identification of the potential source areas in northern Africa and palaeogeographic reconstructions (Fig. 4B). It is visible that both samples from the studied Ordovician sandstones are close to the Trans-Saharan Belt provenance. That allows us to consider that this is the most probable source for the detrital component. Our data support the idea [6] that the present-day position of some of these terranes implies significant dextral strike-slip displacement, probably due to the movement on the Pangea megashear during the Carboniferous and Permian.

REFERENCES

- [1] YANEV S. (2000) Palaeozoic terranes of the Balkan Peninsula in the framework of Pangea assembly, *Palaeogeogr. Palaeoclimatol. Palaeoecol.*, **161**(1–2), 151–177.
- [2] YANEV S., M. C. GÖNCÜOĞLU, I. GEDIK, I. LAKOVA, I. BONCHEVA et al. (2006) Stratigraphy, correlations and palaeogeography of Palaeozoic terranes of Bulgaria and NW Turkey: a review of recent data, *Geol. Soc. Spec. Publ.*, **260**, 51–67.
- [3] DABOVSKI H., I. ZAGORCHEV (2009) Introduction: Mesozoic evolution and Alpine structure. Alpine structure. In: *Geology of Bulgaria, Vol. II, Mesozoic Geology* (eds I. Zagorchev, H. Dabovski, T. Nikolov), Sofia, “Prof. M. Drinov” Academic Press, 30–37 (in Bulgarian, with English abstract).
- [4] ANGELOV V., M. ANTONOV, S. GERDZHIKOV, V. SIRAKOV, S. TANATSIEV et al. (2011) Map sheet Svoge. In: *Geological Map of the Republic of Bulgaria in Scale 1:50 000*, Sofia, APIS, 50 (in Bulgarian).

- [5] YANEV S., I. LAKOVA, I. BONCHEVA, V. SACHANSKI (2005) The Moesian and Balkan Terrans in Bulgaria: Palaeozoic marine basin development, palaeogeography and tectonic evolution, *Geologica Belgica*, **8**(4), 185–192.
- [6] ŽÁK J., M. SVOJTKA, I. GERDJKOV, A. KOUNOV, D. VANGELOV (2021) The Balkan terranes: a missing link between the eastern and western segments of the Avalonian–Cadomian orogenic belt?, *Int. Geol. Rev.*, <https://doi.org/10.1080/00206814.2020.1861486>.
- [7] SACHANSKI V. (2015) The Silurian in the West Balkan Mts. (Svoje Unit, Srednogorie Zone) – 110 years later, *Geologica Balcanica*, **44**(1–3), 3–15.
- [8] GUTIERREZ-MARCO J. C., S. YANEV, V. SACHANSKI, I. RABANO, I. LAKOVA et al. (2003) New biostratigraphical data from the Ordovician of Bulgaria, *INSUGEO, Serie Correlación Geológica* **17**, 79–85.
- [9] CHATALOV A. (2017) Sedimentology of Hirnantian glaciomarine deposits in the Balkan Terrane, western Bulgaria: Fixing a piece of the north peri-Gondwana jigsaw puzzle, *Sediment. Geol.*, **350**, 1–22, <http://dx.doi.org/10.1016/j.sedgeo.2017.01.004>.
- [10] JACKSON S. E., N. J. PEARSON, W. L. GRIFFIN, E. A. BELOUSOVA (2004) The application of laser ablation-inductively coupled plasma-mass spectrometry to in situ U/Pb zircon geochronology, *Chem. Geol.*, **211**, 47–69, <https://doi.org/10.1016/j.chemgeo.2004.06.017>.
- [11] SLÁMA J., J. KOŠLER, D. J. CONDON, J. L. CROWLEY, A. GERDES et al. (2008) Plešovice zircon – a new natural reference material for U–Pb and Hf isotopic microanalysis, *Chem. Geol.*, **249**, 1–35, <https://doi.org/10.1016/j.chemgeo.2007.11.005>.
- [12] HELLSTROM J. C., B. PAUL, J. WOODHEAD, J. HERGT (2011) Iolite: freeware for the visualisation and processing of mass spectrometric data, *J. Anal. At. Spectrom.*, **26**, 2508–2518, doi: 10.1039/c1ja10172b.
- [13] LUDWIG K. J. (2012) User's Manual for Isoplot 3.75. A Geochronological Toolkit for Microsoft Excell. In: Berkeley Geochronology Center Special Publication, Berkeley CA, Berkeley Geochronology Center, 75 pp.
- [14] VERMEESCH P. (2018) IsoplotR: a free and open toolbox for geochronology, *Geo-science Frontiers*, **9**(5), 1479–1493, doi: 10.1016/j.gsf.2018.04.001.

**Geological Institute*
Bulgarian Academy of Sciences
Akad. G. Bonchev St, Bl. 24
1113 Sofia, Bulgaria
 e-mails: kantega@abv.bg
 v_sachanski@geology.bas.bg
 polina_a@geology.bas.bg
 hristo_bk@geology.bas.bg
 lakova@geology.bas.bg

***University of Mining*
and Geology "St. Ivan Rilski"
Studentski Grad
Prof. Boyan Kamenov St
1700 Sofia, Bulgaria
 e-mails: valeri.sachanski@mgu.bg
 stanatsiev@gmail.com

****Sofia University "St. Kliment Ohridski"*
15 Tsar Osvoboditel Blvd
1504 Sofia, Bulgaria
 e-mail: balkanska@gea.uni-sofia.bg