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Detrital zircon U-Pb and Hf constraints on provenance and timing of deposition of the Mesoproterozoic to Cambrian sedimentary cover of the East European Craton, part II: Ukraine

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A R T I C L E I N F O

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A B S T R A C T

We present the U-Pb geochronology and Hf isotope analysis of detrital zircons from the Ediacaran/Cambrian sediments of Podillya and south Volyn in western Ukraine, supplemented by the bulk rock XRD mineralogy of the host rocks. Such a combined analytical approach allows for identifying the source areas supplying detritus to sediments and for constraining an age of deposition. Our provenance analysis is based on fourteen samples collected from six exposures, mostly in the valley of the Dniester river. 84 mudstone samples were also examined by the XRD method. U-Pb dating of detrital zircons yielded two sets of maximum depositional ages: 578–546 Ma and 547–523 Ma, for the Mohyliv-Podilsky and Kanyliv Series, respectively. This suggests that the Ediacaran-Cambrian boundary in Podillya coincides with a major erosional gap, with a major change in provenance, and the disappearance of the Ediacaran fauna at the base of the Kanyliv Series, with implications for the stratigraphy and paleogeography of the entire East European Platform. Zircon U-Pb age spectra from the lower part of the Mohyliv-Podilsky Series include a large quantity of 2.2 to 1.9 Ga grains that reveal predominantly negative to nearly chondritic ε_{Hf} values, jointly suggesting detritus supply from the crystalline basement of Sarmatia. Both U-Pb and mineralogical data also indicate a major contribution of volcanic detritus from the Volyn flood basalts. The younger Nagoryany rocks yielded zircon age spectra with peaks at c. 1.80 and 1.49 Ga, implying a shift of the catchment area to Fennoscandia. Above an erosional gap, the zircon age spectra in the Kanyliv and Baltic Series are dominated by peaks at 560–535 Ma. These data and ε_{Hf} values ranging from negative to chondritic and juvenile suggest, in line with the mineralogical data, detritus supply from a continental magmatic arc and collisional orogen. Thus, we interpret the Kanyliv Series as infill of an early Cambrian foreland basin that was established in front of the Scythides and Santacrucides orogens, overriding the SW margin of Baltica.

1. Introduction

The East European Craton (EEC) was assembled in Paleoproterozoic times (c. 2.1–1.7 Ga) from three large components – Sarmatia, Volgo-Uralia and Fennoscandia (Fig. 1a) and has remained a unified paleogeographic and tectonic entity since then (Bogdanova et al., 1996, 2008). The Proterozoic sedimentary succession of the EEC has been identified by Sokolov (1952). Lithological descriptions, paleontological and petrographic observations were made and lithostratigraphic subdivisions were established (Velikanov, 1976 and references therein, Velikanov et al., 1983; Bukatchuk et al., 1988; Makhnach et al., 2001; Velikanov and Melnychuk, 2013; Ivantsov et al., 2015 and references therein). The sedimentary cover over most of the EEC is weakly affected by diagenetic alteration (Goryl et al., 2018; Liivamägi et al., 2018; Pehr et al., 2018; Derkowski et al., 2021) and preserves original sediment characteristics, indicative of the paleoenvironment at the time of

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deposition. Therefore, the "source to sink" relationships can be effectively studied in Precambrian sediments of the EEC.

Our previous paper presented a provenance study, based on detrital zircon U-Pb ages and Hf isotopes, and bulk rock quantitative XRD analysis of borehole samples from the Proterozoic sedimentary succession in Belarus (Paszkowski et al., 2019). The latter area, located in the interior of the EEC (Fig. 1b), contains a Meso- and Neoproterozoic sedimentary record starting from 1.6 Ga. The current follow-up paper uses the same set of methods and presents provenance analysis from Podillya in western Ukraine (and one locality further north in southern Volyn). It is exclusively based on samples collected from outcrops, mostly in an extended valley of the Dniester River (Fig. 1c). The

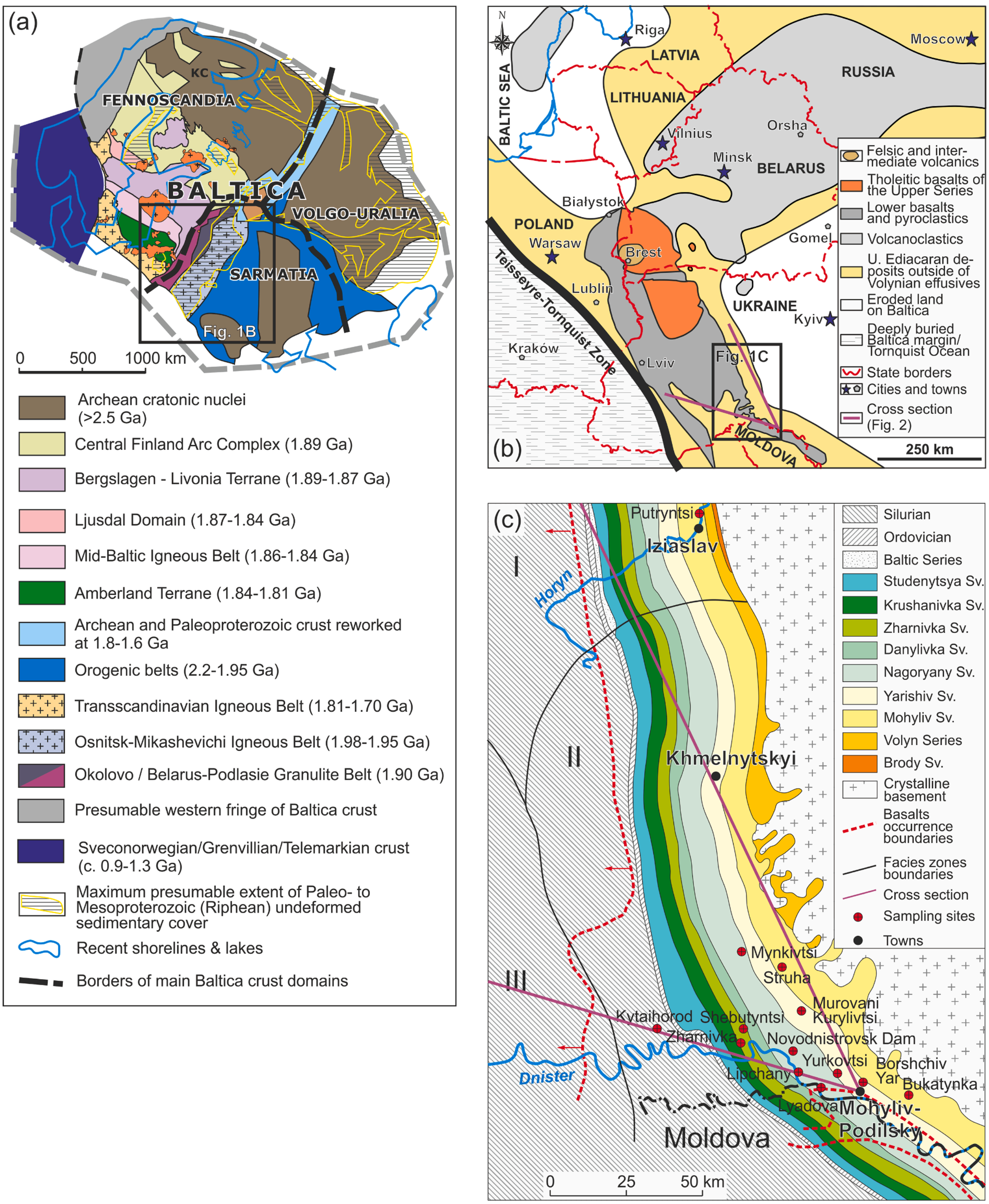

Fig. 1. Precambrian geology of the East European Craton and sample locations. (a) Potential sources of detritus within Baltica for the Ediacaran-Cambrian Podillya-Volyn sedimentary basin (after Bogdanova et al., 2015; Paszkowski et al., 2019). (b) Present day maximum extent of the upper Ediacaran sediments on the investigated part of Baltica, and the extent of underlying Volyn sediments and volcanic rocks (modified from Paszkowski et al., 2019). (c) Map of pre-Mesozoic rocks of Podillya and southern Volyn, including facial zones: I – Horyn, II – Podillya, III – western slope of the Dniester pericraton (after Velikanov and Melnychuk, 2013), with locations of sampling sites and the cross section presented in Fig. 2.

Proterozoic sediments of Podillya are entirely Ediacaran in age, thus representing a shorter time interval compared to those in Belarus. However, the geological setting of Podillya, much closer to the SW margin of the EEC, makes the Ediacaran sediments deposited there more sensitive to paleoenvironmental and tectonic signals related to the break-up of Rodinia and emergence of Baltica. The Podillyan section is considered unique in the EEC, as containing continuous transition from the Ediacaran to Cambrian (Burzin, 1996).

Our results, particularly maximum depositional ages, suggest important modifications to pre-existing lithostratigraphic schemes (Aseeva, 1976; Velikanov et al., 1983; Bukatchuk et al., 1988; Makhnach et al., 2001; Velikanov and Melnychuk, 2013, 2014; Ivantsov et al., 2015). Furthermore, they provide further evidence for the existence of the pre-Scythides orogen (Kheraskova et al., 2015) in the SW corner of Baltica at the transition from Ediacaran to Cambrian. This discovery offers an important improvement to the known history of the demise of Rodinia and the birth of Baltica (e.g., Torsvik et al., 1996; Pisarevsky et al., 2003; Li et al., 2008).

2. Geological background

The Podillya Ediacaran-Palaeozoic sedimentary epicontinental basin is part of the larger basin that covered approximately half of the platform (e.g., Sliaupa et al., 2006). The onset of the Podillya Basin dates back to the time of Rodinia fragmentation and subsequent subsidence of the newly formed passive continental margin (Poprawa et al., 2018; Poprawa, 2019). Also, the emplacement of the Volyn flood basalt province at the western margin of the East European Platform is thought to mark the inception of Rodinia break-up (Bakun-Czubarow et al., 2002; Nosova et al., 2008; Kuzmenkova et al., 2010; Shumlyanskyy et al., 2007, 2016; Shumlyanskyy, 2012).

The study area is located at the SW slope of the Precambrian Ukrainian Shield, in the parts of Ukraine that are known as Podillya and Volyn. The Ediacaran/Cambrian siliciclastic sediments crop out on both banks of the Dniester river and in numerous valleys and ravines of its tributaries (Fig. 1c). Outcrops of the oldest part of the section are known also from the Horyn river valley in southern Volyn. The Ediacaran sequence covers the Paleoproterozoic crystalline basement, dated at c. 2.1 Ga (Shumlyanskyy et al., 2018a). Locally, in southern Volyn (Fig. 1c), it covers the glacial Brody Svita, regarded as equivalent of the

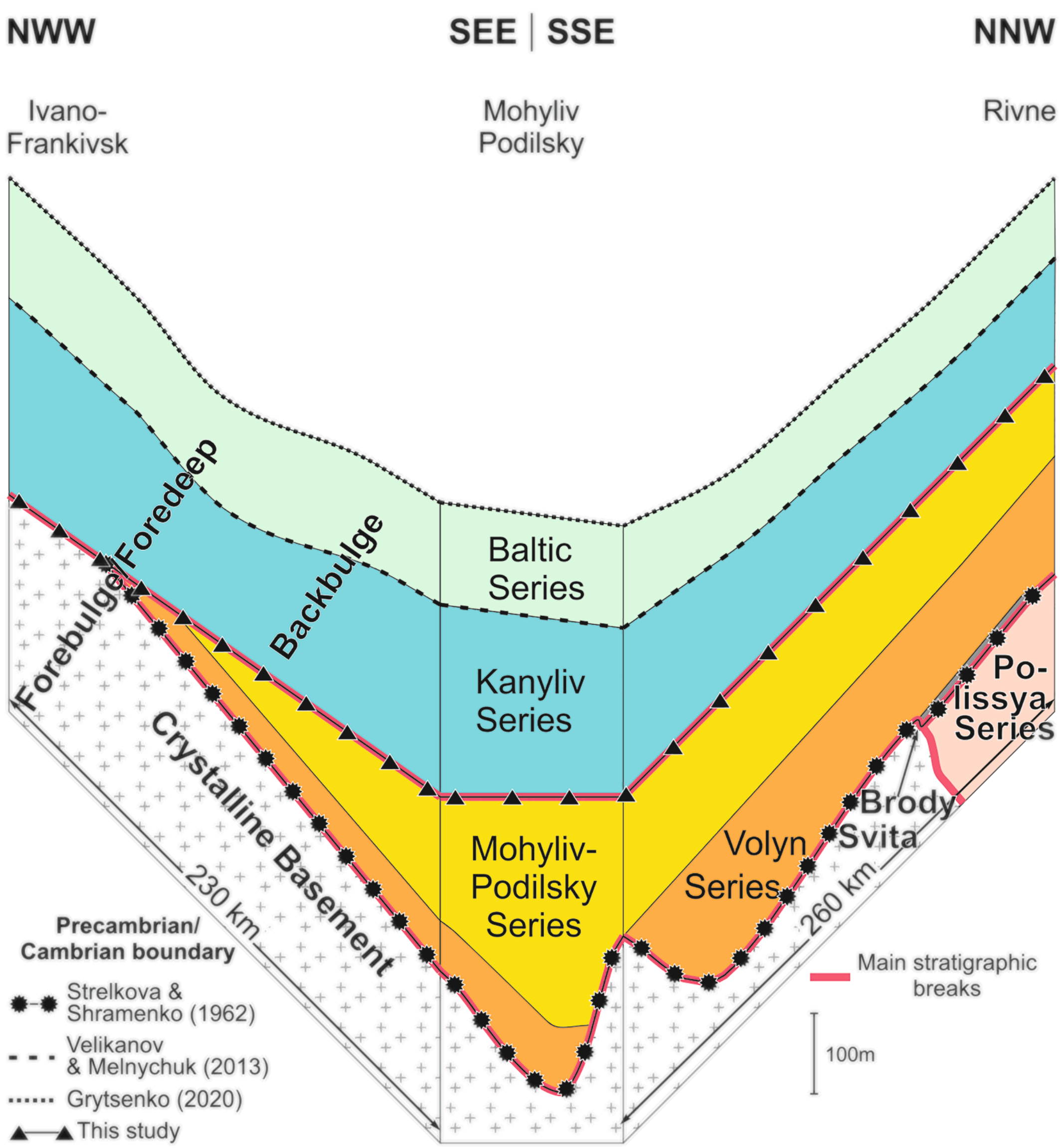

Fig. 2. Positions of the Ediacaran-Cambrian boundary in Podillya and Volyn according to different authors, presented on a conceptual cross-section, constructed from the data by Vashchenko et al. (2007), Velikanov and Melnychuk (2013) and Strelkova and Shramenko (1962) along the line marked in Fig. 1b,c.

Vilchitsy Series in Belarus. The surface of the peneplained (Fig. 2) basement is nearly flat (except for the ravines on the south-western slope of the Ukrainian Shield (Fig. 1c) and the Ediacaran sediments overlay it with a distinctive unconformity (Figs. 2, 3). The sedimentary cover forms a monocline that dips at 1° towards the south west.

The Ediacaran/Cambrian rocks in the Podillya-Volyn region are grouped into regional (horizon) and local paralithostratigraphic units called series, svita and bed, which have no formal counterpart in standard Hedberg Code-based stratigraphic units. Roughly, the local units are comparable to the group, formation, and member, respectively. The rock sequence identified currently as Ediacaran (Vendian in older Russian and Ukrainian literature) is divided into three large units: the Volyn, Mohyliv-Podilsky, and Kanyliv Series that are separated by regional unconformities (Fig. 2). The Volyn Series represents a rifting stage of Rodinia break-up, whereas younger parts of the sequence correspond to rift-drift transition and were deposited on a passive continental margin (Poprawa et al., 2018; Poprawa, 2019).

The Volyn Series rocks in Podillya, represented by the Hrushka Svita, directly overlie the crystalline basement and consist of red-coloured continental coarse-grained arkose sediments succeeded by marine, grey, fine-grained sediments (Velikanov and Melnychuk, 2013; Figs. 2, 3). Northwards, towards the Volyn province, the continental sediments are gradually substituted by volcanoclastic rocks (Fig. 3). In the SE part of the area, marine sediments contain tuffs and 1–2 basalt flows up to 50 m in thickness, which are usually correlated with the Volyn Large Igneous Province (LIP) basalts (Kopeliovich, 1965; Melnychuk, 2009), however, with no direct geochemical counterpart there (Shumlyanskyy et al., 2009). The upper part of the Hrushka Svita is regarded a time-equivalent of the Slutsk Svita in the S Volyn zone (Velikanov and Melnychuk, 2013; Polishchuk, 2014; Fig. 3). The volcanic activity of the Volyn LIP was U-Pb dated on zircons from Belarus at 579 ± 4 Ma to 545 ± 4 Ma (Paszkowski et al., 2019). A similar estimate of 588.0 ± 8 Ma to 553.0 ± 15 Ma was published by Poprawa et al. (2020), based on samples from Poland. However, the latter results must be taken with caution (cf., Francovschi et al., 2021), due to relatively low precision and high discordance of individual dates.

The Mohyliv-Podilsky Series consists of three svitas: Mohyliv, Yaryshiv and Nagoryany, each of them subdivided into beds (Fig. 3). The Mohyliv Svita (Fig. 3), records a transgression onto either the Volyn Series rocks or older crystalline basement. The oldest part represents weathering of crust in the areas where the basaltic cover has been found. The Mohyliv Svita is interpreted as deposited within a fluvial system (Velikanov and Melnychuk, 2013, 2014) with a transition to marine-influenced river channels (Gnilovskaya et al., 1988), and finally to deltaic and coastal marine conditions (Lyadova Beds). The Mohyliv Svita is the oldest succession that contains rich complexes of Ediacaran fauna

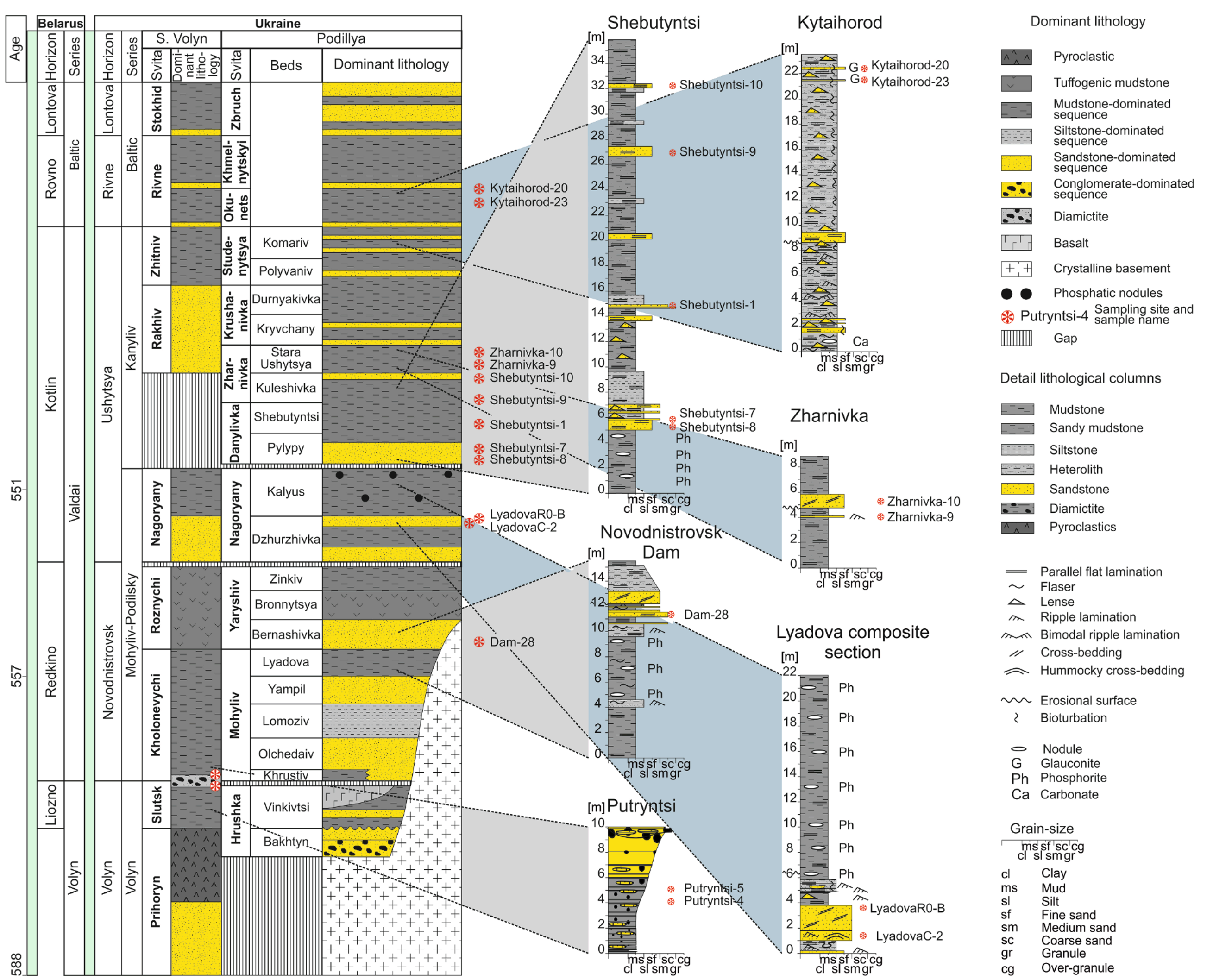

Fig. 3. Location of dated samples on the lithological columns of studied outcrops and composite stratigraphic charts for Podillya and southern Volyn, shown with a chart for Belarus. The charts compiled from Velikanov and Melnychuk (2013) for the area of Ukraine, and from Makhnach et al. (2001) for Belarus. Sources of U-Pb ages quoted in the text.

(Velikanov et al., 1983; Gnilovskaya et al., 1988; Gureev, 1988; Menasova, 2003), including a primitive organism described as *Nemiana simplex* Palij, which often forms large colonies reaching several hundred square metres in size (Velikanov and Melnychuk, 2013; Ivantsov et al., 2015). Zircons from the Lyadova Beds bentonites were dated at 556.78 ± 0.18 Ma (Soldatenko et al., 2019). The Mohyliv Svita corresponds to the Kholonevychi Svita in S Volyn zone (Velikanov and Melnychuk, 2013).

The Yaryshiv Svita (Fig. 3) is characterised by the occurrence of pyroclastic material as bentonite beds, attaining up to 30 cm thickness, and tuffaceous sediments with a thickness up to 25 m (Kopeliovich, 1965; Velikanov and Melnychuk, 2013). The uppermost part of the svita contains pebble-like phosphoritic (up to 10% P_2O_5) concretions, in some parts as layered accumulations. The Yaryshiv Svita is locally rich in faunal remnants (Gureev, 1988; Menasova, 2003) and includes sediments accumulated within a shallow water basin with increasing subsidence (Bukatchuk, 1973). In the latest phase of deposition, base level fluctuations (Gnilovskaya et al., 1988) and regression resulted in partial removal of the deposits by erosion-flooding processes (Bukatchuk, 1973).

Based on the occurrence of the basal coarse-grained sandstone bed, a long hiatus in sedimentation between the Yaryshiv and Nagoryany Svitas is assumed (Bukatchuk et al., 1988). The Kalyus Beds in the upper part of the Nagoryany Svita (Fig. 3) are composed of organic-matter-rich dark grey to black mudstones that contain lenses and thin layers of carbonates with cone-in-cone texture, and numerous phosphoritic concretions and thin bentonite layers (Kopeliovich, 1965; Velikanov, 1975; Francovschi et al., 2020). Due to this very distinct composition, the Kalyus Beds can be traced over a large area of Volyn, Podillya, and Moldova and used for regional correlations. A maximum depositional age of the Kalyus Beds was estimated at 551.2 ± 4.2 Ma (Francovschi et al., 2021). An initial marine transgression led to accumulation of sediments in a nearshore – shallow marine environment (Bukatchuk, 1973; Gnilovskaya et al., 1988). The subsequent increase of the sedimentary basin depth and dimension (Bukatchuk, 1973) led to the deposition of fine-grained sediments in calm, suboxic-anoxic, starved-type sedimentary conditions (Maslov et al., 2019; Francovschi et al., 2020). The entire Nagoryany Svita was identified, based on paleontological evidence, as part of the uppermost Ediacaran and correlated with the Kotlin Regional Stage of the central basin of the EEC, while lower svitas of the Mohyliv-Podilsky Series were assigned to the Redkino Horizon of the central basin (Bukatchuk et al., 1988; Burzin, 1996). Novodnistrovsk and Ushytsya Horizons are the Podillya equivalents of Redkino and Kotlin, respectively (Fig. 3). A 1–1.5 m thick weathering zone (Kopeliovich, 1965; Velikanov, 1976; Ivantsov et al., 2015) occurs widely at the top of the Kalyus Beds.

The sediments of the Kanyliv Series (Fig. 3), the youngest regional stratigraphic unit, are separated from the underlying deposits by a regional unconformity and cover various levels of the pre-Kanyliv sequence showing onlap towards the west. In the area of Ivano-Frankivsk and Halych, the Kanyliv Series sediments rest directly on the crystalline basement (Velikanov, 1976). Besides a much wider distribution, the Kanyliv Series differs sharply from the older sedimentary rocks in the provenance of their detrital material (Kopeliovich, 1965), with the Małopolska massif in Poland being one of the main sources (Velikanov and Melnychuk, 2013). The initial stages of the Kanyliv sedimentation are characterised by almost complete disappearance of the Ediacaran fauna and flourishing of the Vendotaenidae flora (Velikanov and Melnychuk, 2013). The degree of bioturbation of the Kanyliv sediments is much higher than in the underlying rocks (Ivantsov et al., 2015) and bioglyphs are common (Gureev, 1985, 1988; Fedonkin, 1992).

The Kanyliv Series is composed of four sedimentary cycles named Danylivka, Zharnivka, Krushanivka and Studenytsya Svitas (Fig. 3). Each of them is an upward-fining sequence starting with basal sandstones grading into siltstones and mudstones. A basal conglomerate layer with pebbles of the Kalyus mudstones occurs only at the base of the Kanyliv Series, with a transition to medium- and fine-grained sandstones. The Krushanivka Svita contains limestones and phosphate-rich mudstones with variegated colouration that makes them a marker for the regional correlation.

The Baltic Series, overlying the Kanyliv Series, is subdivided into the Okunets, Khmelnitsky, and Zbruch Svitas (Fig. 3). The occurrence of the *Phycodes pedum* ichnospecies about 6.5 m above the contact between the Kanyliv and Baltic Series (Ivantsov et al., 2015) allows for undoubted designation of the overlying strata to the Cambrian. However, the Ediacaran-Cambrian boundary in the Podillya Basin is indistinct in terms of lithology and sedimentary structures. Therefore, some authors assign the Baltic Series to the Precambrian (Vendian: e.g., Burzin, 1996; Grytsenko, 2018, 2020), while others include the entire Baltic Series (e.g., Velikanov and Melnychuk, 2013; Ivantsov et al., 2015) into the Cambrian (Fig. 2). There is also an interpretation which locates the Ediacaran-Cambrian boundary within the Baltic Series, between the Khmelnytskyi and Zbruch Svitas (Grazhdankin et al., 2011). Older stratigraphic schemes can be found in Kopeliovich (1965): originally the entire Podillya sedimentary column was regarded as Ordovician (Văscăutanu, 1931), until Timofeev (1952) identified the Kalyus and older beds as Precambrian.

3. Sample selection and analytical methods

Quantitative XRD analysis of bulk rock samples was used as an independent source of information on provenance, as in our earlier study of the Belarus Proterozoic rocks (Paszkowski et al., 2019). The analyses were performed on 84 mudstone samples collected from several outcrops in Podillya and Putryntsi in southern Volyn (Fig. 1). The XRD patterns of random samples, wet-ground with ZnO internal standard to assure high reproducibility of intensities (Środoń et al., 2001), were recorded in 5–65 °2Θ range with 0.02 °2Θ step on an Xtra diffractometer, equipped with a Cu tube and solid-state detector. After mineral identification, quantitative mineral analysis was made using in-house QMin software (M. Szczerba, unpublished).

Fourteen samples of mudstone and sandstone from five exposures in Podillya and one in Volyn were selected for zircon geochronology (Fig. 3; Table 1). The Pb/U and Pb isotopic ratios in zircons were measured using a Thermo Scientific Element 2 sector field ICP-MS coupled to a 193 nm ArF excimer laser (Teledyne Cetac Analyte Excite laser) at the Institute of Geology of the Czech Academy of Sciences, Prague, Czech Republic. Analytical details can be found in Paszkowski et al. (2019). The analytical strategy involved selecting ca. 140 grains representing random detrital population for U-Pb analysis. The isotopic data were filtered by rejecting analyses with discordance higher than ± 5% or ± 10% for zircon dates of < 1 Ga and > 1 Ga, respectively, which are likely to be affected by Pb loss or high initial common Pb. The zircon grains that yielded age clusters younger than the assumed Ediacaran true depositional age were re-analysed in an additional analytical session, including an additional mount with separated zircon grains from sample Shebutyntsi-1. Maximum depositional ages were calculated following YC2σ(3+) approach of Dickinson and Gehrels (2009) that uses the youngest cluster of at least 3 dates overlapping in 2σ error. These are presented as Concordia ages calculated from up to 30 youngest zircons with < 2.0% discordance.

Hf isotope analyses were carried out at the British Geological Survey, Keyworth, Nottingham, UK, targeting most of the sample spots used for U-Pb dating. Analyses were carried out using a Thermo Scientific Neptune Plus MC-ICP-MS coupled to a New Wave Research UP193UC Excimer laser ablation system. Helium was used as the carrier gas through the ablation cell with Ar make-up gas being connected via a T-piece and sourced from a Cetac Aridus II desolvating nebulizer. 0.01 L/min of nitrogen were introduced via the nebulizer in addition to Ar in order to minimise oxide formation. Lutetium (^{175}Lu), ytterbium (^{172}Yb, ^{173}Yb), and hafnium (^{176}Hf, ^{178}Hf, ^{179}Hf and ^{180}Hf) isotopes were

Table 1
Samples used for the isotopic measurements of zircon.

Sample label	Lithology	Locality	GPS coordinates	
			Lat.	Long.
Kytaihorod-20	glauconite-bearing sandstone	Kytaihorod	48°38′18.1″N	26°46′56.2″E
Kytaihorod-23	glauconite-bearing sandstone			
Zharnivka-10	sandstone	Zharnivka	48°36′28.1″N	27°11′56.2″E
Zharnivka-9	cross-bedded sandstone			
Shebutyntsi-10	sandstone	Shebutyntsi	48°40′29.2″N	27°12′37.2″E
Shebutyntsi-1	sandstone			
Shebutyntsi-9	sandstone			
Shebutyntsi-7	sandstone			
Shebutyntsi-8	sandstone			
LyadovaR0-B	glauconite-bearing sandstone	Lyadova	48°29′41.2″N	27°36′37.9″E
LyadovaC-2	sandstone		48°29′04.1″N	27°36′21.7″E
Dam-28	dark turbiditic sandstone	Novodnistrovsk Dam	48°35′23.7″N	27°27′57.5″E
Putryntsi-5	diamictite	Putryntsi	50°09′18.1″N	26°48′53.9″E
Putryntsi-4	diamictite			

measured simultaneously during static 30 s ablation analyses. The spot size used was 25 μm; fluence = 8 J/cm^2.

Hf reference solution JMC475 was analysed during the analytical session and sample $^{176}Hf/^{177}Hf$ ratios are reported relative to a value of 0.282160 for this standard. Reported ratios are relative to $^{179}Hf/^{177}Hf$ = 0.7325. Correction for ^{176}Yb on the ^{176}Hf peak was made using reverse-mass-bias correction of the $^{176}Yb/^{173}Yb$ ratio empirically derived using Hf mass bias corrected Yb-doped JMC475 solutions (Nowell and Parrish, 2001). ^{176}Lu interference on the ^{176}Hf peak was corrected by using the measured ^{175}Lu and assuming $^{176}Lu/^{175}Lu$ = 0.02653.

Hf-isotope data was processed using the Iolite data reduction package (Paton et al. 2011).

Three zircon reference materials (91500, Mud Tank, GJ-1) were analysed throughout the analytical session at regular intervals (typically after every 20–25 unknowns). The 91,500 zircon reference material was used as the primary standard in Iolite, and was used to normalise the $^{176}Lu/^{177}Hf$ ratio assuming a value of 0.000311 (Woodhead and Hergt, 2005).

Analytical uncertainties for unknowns were propagated by quadratic addition to include the standard error of the mean of the analysis and the reproducibility of the 91,500 reference material. εHf values were calculated using a ^{176}Lu decay constant of 1.867×10^{-11} y^{-1} (Söderlund et al., 2004), the present-day chondritic $^{176}Lu/^{177}Hf$ value of 0.0336 and $^{176}Hf/^{177}Hf$ ratio of 0.282785 (Bouvier et al., 2008).

4. Results

4.1. Mineral composition

Table 2 and Fig. 4 present selected mineral data, averaged separately for the Mohyliv-Podilsky Series, excluding the Kalyus Beds (i.e., for the Novodnistrovsk Horizon), and for the Kanyliv Series, including the Kalyus Beds (Ushytsya Horizon; Fig. 3), because starting from the Kalyus Beds a striking change in the mineral composition takes place. In the Ushytsya Horizon rocks, an essential increase of quartz and $2M_1$ dioctahedral mica is observed, while contents of 2:1 dioctahedral clays (illite + illite–smectite) decrease considerably, from a high level, characterising the Novodnistrovsk Horizon. Also, orthoclase is decreasing significantly. Such a pattern is consistent with a major provenance change – from a major contribution of volcanic detritus in the Novodnistrovsk Horizon (low quartz and high dioctahedral clays) to the dominant detritus from a metamorphic terrane (high quartz and $2M_1$ mica) in the younger rocks. These characteristics are similar to the data from Belarus, where analogous level of quartz and $2M_1$ mica increase is observed only in the Cambrian (Paszkowski et al., 2019). Also similar are the increase of authigenic minerals and of quartz/sum of primary minerals ratio in the younger beds. The Podillyan data differ from the Belarussian by their much lower level of K-feldspars and biotite – apparently the source supplying these minerals to the Belarussian basins was not very active in Podillya – and by the increased kaolinite/dioctahedral 2:1 clay index in the younger beds.

4.2. LA-ICP-MS U-Pb zircon geochronology

The majority of zircon crystals in each sample display oscillatory zoning, with less common homogeneous and patchy zoned internal textures (Fig. 5). The Th/U ratio is well above 0.1 (mostly between c. 0.3–1.8) in the majority of zircon grains, which indicates their magmatic origin (Hoskin and Black, 2000; Kelly and Harley, 2005; Rubatto, 2017).

4.2.1. The Mohyliv-Podilsky Series

In the lowest part of the Mohyliv-Podilsky Series (Fig. 3), the zircon populations in two samples (Putryntsi-4 and Putryntsi-5) from the boundary of Slutsk and Kholonevychi Svitas demonstrate a similar predominant Paleoproterozoic age peak at c. 2.02–2.08 Ga, and minor peaks at c. 1.48–1.50 Ga and c. 570 Ma (Fig. 6; Supplementary Data Table S1). The Putryntsi-4 sample also contains the oldest zircon of c. 2.97 Ga. The zircon population in Putryntsi-5 contains several minor clusters at c. 2.62–2.71 Ga, c. 2.17–2.21 Ga, c. 1.06–1.07 Ga, and c. 665–740 Ma. The youngest zircon grains from Putryntsi-4 and Putryntsi-5 yielded similar maximum depositional ages of 575 ± 7 Ma (n = 11, MSWD = 0.16) and 578 ± 14 Ma (n = 3, MSWD = 0.03), respectively (Fig. 6, Supplementary Data).

The zircon age population from sample Dam-28 from the Yaryshiv Svita shows a major peak at c. 2.09 Ga, similar to zircons from the boundary of the Slutsk and Kholonevychi Svitas. The remaining data include minor age peaks at c. 2.16 Ga, c. 2.03 Ga and c. 1.49 Ga as well as minor age clusters at c. 768–796 Ma and c. 542–598 Ma (Fig. 6). Three youngest zircons within 2σ error range yielded a maximum depositional age of 551 ± 13 Ma (MSWD = 0.40).

Two samples representing the Nagoryany Svita show a distinct change in age distribution. U-Pb data from the LyadovaC-2 sample show a major peak at c. 2.09 Ga, and minor peaks at c. 2.2, 1.8, 1.51 Ga and 550 Ma, similar to the samples in the lower part of a profile (Fig. 6). Two Archean zircon grains yielded ages of c. 2.84, and 2.93 Ga. U-Pb data obtained for the LyadovaR0-B sample demonstrate a significant shift in the age population with two major peaks at c. 1.49 and 1.80 and a minor peak at 2.09 Ga. A maximum depositional age obtained for the LyadovaC-2 sample is 546 ± 10 Ma (n = 6, MSWD = 0.96), whereas the LyadovaR0-B sample lacks young zircons except for one grain at c. 554 Ma.

4.2.2. The Kanyliv Series

The Kanyliv Series is represented by four samples of the Danylivka Svita and three samples of the Zharnivka Svita (Fig. 6). Zircon populations in the Danylivka Svita are dominated by major peaks at c.

Table 2
Quantitative mineral composition data averaged for the Novodnistrovsk (Redkino) and Ushytsya (Kotlin and Cambrian) Horizons. Kaolinite/illite plus illite–smectite and quartz/sum of primary minerals are two weathering and provenance mineral indices.

Averaged sections of Podillya + S. Volyn profile	Quartz	Orthoclase	Microcline	Albite/ oligoclase	2M1 mica	Tri-mica	Hematite	Pyrite	Apatite	Calcite	Berthierine	Kaolinite	Illite + IS	Chlorite	Anatase	Gypsum	Jarosite	Sum	Sum authigenic	Kaolinite / (Illite + IS)	Q / SUM primary
Ushytsya Horizon	30.7	1.0	2.8	4.5	6.2	0.7	1.1	0.0	0.8	3.8	3.7	8.6	32.5	3.0	0.4	0.0	0.1	100.0	8.5	0.3	0.7
Novodnistrovsk Horizon	17.8	3.5	3.2	5.4	0.3	0.8	1.8	0.7	2.0	0.0	2.9	6.7	51.7	2.2	0.4	0.1	0.6	100.0	6.2	0.1	0.6

535–560 Ma with minor clusters at c. 2.1 Ga, 1.7–1.8 Ga, 1.5 Ga, 1.3–1.4 Ga, 610–620 Ma and 660–670 Ma (Shebutyntsi-8, Shebutyntsi-7, Shebutyntsi-9, Shebutyntsi-1). The Archean zircon grains include those dated at c. 2.95 Ga (Shebutyntsi-7), c. 2.6 Ga (Shebutyntsi-9) and c. 2.9 Ga (Shebutyntsi-1).

The presence of zircons with ages younger than the Ediacaran stratigraphic age assigned to the Kanyliv Series (Velikanov and Melnychuk, 2013) was unexpected, therefore the youngest zircon grains were re-analysed in an additional analytical session. An extra mount with a new set of zircon grains from the Shebutyntsi-1 sample (dominated by c. 530 Ma peak) was analysed in the second analytical session. The data from the first and second session are similar within an error range of individual data, but in some cases, they do not correspond and are either younger or older. The youngest single dates with $<$ 2% discordance include c. 517 Ma, 524 Ma, 518 and 508 Ma in the Shebutyntsi-8, Shebutyntsi-7, Shebutyntsi-9 and Shebutyntsi-1 samples, respectively. The maximum depositional ages constrained for these samples are 529 $\pm$ 10 Ma (n = 8, MSWD = 0.64; Shebutyntsi-8), 532 $\pm$ 6 Ma (n = 14, MSWD = 0.92; Shebutyntsi-7), 531 $\pm$ 8 Ma (n = 14, MSWD = 0.41; Shebutyntsi-9), and 523 $\pm$ 5 Ma (n = 30; MSWD = 2.14; Shebutyntsi-1, first session) and 542 $\pm$ 5 Ma (n = 19, MSWD = 0.03; Shebutyntsi-1, second session). Because the investigated zircon grains show no textural features characteristic of secondary alteration and the maximum depositional ages were calculated using cluster of at least 3 youngest dates with $<$ 2.0% discordance, overlapping in 2σ error (YC2σ (3+) approach of Dickinson and Gehrels, 2009), it is unlikely that the data are affected by (ancient) Pb loss. The zircon ages most probably reflect true depositional age, and the previous stratigraphy requires revision.

The zircon population demonstrates a significant shift in the age distribution in the Zharnivka Svita. Zircon from the Shebutyntsi-10 sample yielded dates from c. 465 Ma to 3.02 Ga with a major peak at c. 530–550 Ma, minor peak at 2.09 Ga, and smaller clusters at c. 2.9–2.95 Ga, 2.7 Ga, and 708–722 Ma (Fig. 6). In contrast, the Zharnivka-9 and Zharnivka-10 samples contain zircon with major age peaks at 2.01–2.08 Ga, c. 2.6–2.7 Ga and 540–600 Ma. Individual zircon dates range from c. 477 Ma to 2.9 Ga and from c. 508 Ma to 2.95 Ga in the Zharnivka-9 and Zharnivka-10 samples, respectively. The maximum depositional age constrained in both samples is within error, i.e., 547 $\pm$ 9 Ma (n = 5, MSWD = 0.16) and 535 $\pm$ 7 Ma (n = 12, MSWD = 0.54), respectively. Slightly younger maximum depositional age 531 $\pm$ 4 Ma (n = 25, MSWD = 2.63) was obtained in the Shebutyntsi-10 sample.

4.2.3. *The Baltic Series rocks*

The Baltic Series rocks are represented by two samples, Kytaihorod-23 from the upper part of the Okunets Svita and Kytaihorod-20 from the boundary of the Okunets and Khmielnitsky Svita (Fig. 6). Zircon in both samples presents a similar age distribution with individual dates ranging from c. 528 Ma to 2.84 Ga, and from c. 551 Ma to 2.73 Ga, respectively. The age distribution is dominated by a c. 1.5 Ga major peak, with minor peaks at c. 560–620 Ma. The youngest zircons from Kytaihorod-23 and Kytaihorod-20 samples yielded similar maximum depositional ages of 562 $\pm$ 20 Ma (n = 5, MSWD = 0.19) and 561 $\pm$ 19 Ma (n = 4, MSWD = 0.24).

4.3. *Hf isotopes*

The zircon grains from the Putryntsi-4 sample that were selected for Hf isotopic measurements represent three age groups. The oldest (c. 2.0–2.1 Ga, n = 16) and intermediate (c. 1.46–1.49 Ga, n = 5) groups have negative ε_{Hf} values from –11.7 to –0.7, and –4.1 to –1.6, respectively (Fig. 7, Supplementary Data Table S2), which are characteristic of a continental collision setting (e.g., Gardiner et al., 2016). The youngest group of zircons (c. 556–597 Ma, n = 8) has ε_{Hf} values varying from negative (from –14.0 to –12.8) and nearly chondritic (from –0.7 to +2.2) to one juvenile grain (+11.2). A single c. 2.97 Ga zircon has ε_{Hf} of +5.0.

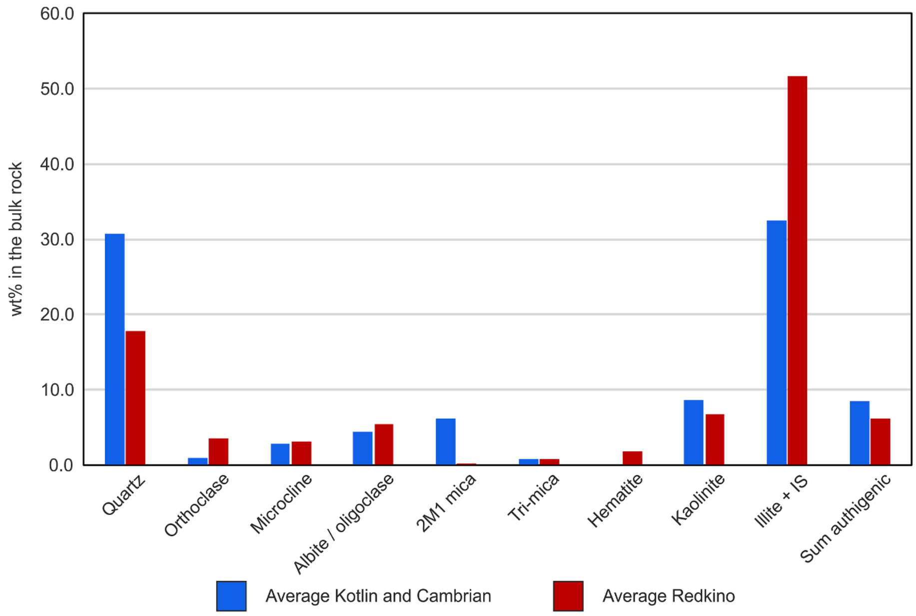

Fig. 4. Selected data from Table 2, illustrating the change in quantitative mineral composition between the Novodnistrovsk (Redkino) and Ushytsya (Kotlin and Cambrian) Horizons.

Data scattering in the Putryntsi-4 sample, similarly to other samples investigated for Hf isotopes, prevents distinguishing principal crust formation event(s) with confidence.

The zircon population from the Putryntsi-5 sample includes several age groups. Zircon grains of the major group (c. 2.00–1.13 Ga, n = 17) have negative ε_{Hf} values, characteristic of continental collision, to nearly chondritic values (from –10.7 to +0.9), and one mantle derived grain with ε_{Hf} of +9.3 value (Fig. 7, Supplementary Data Table S2). Four minor groups are dominated by negative ε_{Hf} values; these include c. 2.62–2.71 Ga (n = 3) with ε_{Hf} values from –5.5 to –3.7; c. 1.49–1.51 (n = 3) with ε_{Hf} values from –3.5 to –3.1; c. 1.06–1.07 Ga (n = 3) including zircons with ε_{Hf} –6.0, –5.6 and +2.1; and c. 555–689 Ma (n = 6) with strong to intermediate negative ε_{Hf} values from –22.2 to –5.6. One group of c. 2.17–2.22 Ga (n = 3) zircon grains has positive ε_{Hf} values from +2.3 to +4.6, and one zircon grain of c. 1.21 Ga with an ε_{Hf} value of +3.6.

The zircon population from sample Dam-28 is dominated by a major group of c. 2.03–2.22 Ga (n = 18) with ε_{Hf} values ranging from –5.1 to +2.8 (Fig. 7, Supplementary Data Table S2). Zircons with ages of c. 1.48–1.61 Ga (n = 3) have negative, nearly chondritic ε_{Hf} values of –3.5 to –0.5; one c. 768 Ma zircon has ε_{Hf} of –5.7, whereas a group of zircons of c. 542–598 Ma (n = 6) revealed one negative ε_{Hf} value of –13.6 and juvenile values from +4.5 to +7.6.

Sample LyadovaR-0B demonstrates two age groups (c. 2.11–2.07 Ga, n = 6; c. 1.77–1.81, n = 9) of zircon that have ε_{Hf} nearly chondritic values from –6.1 to +0.7 and from –2.1 to +4.1, respectively (Fig. 7, Supplementary Data Table S2). A large group of c. 1.44–1.52 Ga zircons (n = 15) has negative ε_{Hf} values from –5.5 to –2.2.

A majority of zircon of the Shebutyntsi-7 sample, analysed for Hf isotopes, form a group at c. 530–746 Ma (n = 21) with ε_{Hf} values ranging from negative related to continental collision granites to chondritic and juvenile, i.e., from –17.0 to +9.1 (Fig. 7, Supplementary Data Table S2). The second group of zircons (c. 2.05–2.12 Ga) show juvenile characteristics (ε_{Hf} from +1.2 to +5.0). Remaining individual zircons with dates ranging from 1.20 to 1.84 Ga and one c. 2.94 Ga grain have ε_{Hf} values –0.1 to +0.7 and +2.0, respectively.

The Shebutyntsi-9 sample contains zircon forming age groups c. 2.05–2.11 Ga (n = 6) and c. 524–744 Ma (n = 21) with ε_{Hf} values ranging from +2.9 to +5.3 and from –15.0 to +7.1, respectively (Fig. 7, Supplementary Data Table S2). The individual grains have negative (c. 2.73 Ga, –2.7; c. 2.59 Ga, –7.3; c. 2.00 Ga, –4.9), nearly chondritic (c. 1.84 Ga, +0.1; c. 1.72 Ga, –0.5) to positive (c. 1.44 Ga, +7.7) ε_{Hf} values.

In the Zharnivka-9 sample, zircons belong to several age groups. The oldest one c. 2.66–2.90 Ga (n = 7) has zircons with nearly chondritic ε_{Hf} values from –1.9 to +0.7, which vary in younger groups from –4.4 to +3.4 (c. 2.55–2.61 Ga; n = 4), and from –3.6 to +5.9 (2.01–2.14 Ga, n = 11) (Fig. 7, Supplementary Data Table S2). Individual zircon grains with dates ranging from c. 1.01 to 1.75 Ga (n = 6) have ε_{Hf} values from +0.2 to +6.9, except for one grain of –1.3 (c. 1.17 Ga). The youngest groups show nearly chondritic ε_{Hf} values of –2.0 to +0.8 (c. 622–734 Ma, n = 5) and strongly negative ε_{Hf} values from –27.4 to –5.2 (c. 549–601 Ma), except for one c. 580 Ma grain with positive ε_{Hf} of +4.0.

Zircons from the Kytaihorod-23 sample belong to 8 age populations. The oldest minor populations include grains dated at c. 2.84–2.58 (n = 4; ε_{Hf} from –6.3 to +2.1), c. 1.97–2.10 (n = 3; ε_{Hf} –6.6, +1.9 and +2.4), c. 1.77–1.83 (n = 3; ε_{Hf} –1.3, +0.6, +0.7), and c. 1.60–1.63 (n = 4; ε_{Hf} from –3.6 to +4.3) (Fig. 7, Supplementary Data Table S2). The intermediate group c. 1.43–1.54 Ga (n = 9) has zircons characterized by negative ε_{Hf} values from –4.6 to –1.1. Zircons from the youngest groups have ε_{Hf} values from –8.7 to +6.8 (c. 961 Ma – 1.25 Ga, n = 3), –12.6 and –2.6 (c. 732–736 Ma) and from –2.6 to +8.3 (c. 528–611 Ma, n = 6).

5. Discussion

5.1. *Maximum depositional ages versus stratigraphy*

In this section, we compare our present geochronological results with the pre-existing Ediacaran stratigraphy of Podillya and southern Volyn based on Velikanov and Melnychuk (2013). We use maximum depositional ages calculated from single grain zircon data to constrain a possible age of lithostratigraphic subdivisions.

Two oldest samples, Putryntsi-4 and –5, come from the diamictite (Paszkowski et al., 2018) at the contact of the Mohyliv-Podilsky Series with the underlying Volyn Series. According to the published bentonite U-Pb ages from Podillya (Soldatenko et al., 2019) these rocks must be older than 556.78 ± 0.18 Ma, but younger than the onset of Volyn LIP volcanism (Fig. 3). The maximum depositional ages calculated for these samples are 575 ± 7 Ma and 578 ± 14 Ma, respectively (Fig. 6). Consequently, the maximum sedimentation ages are consistent with the expected stratigraphic age.

Three samples collected from the middle part Mohyliv-Podilsky

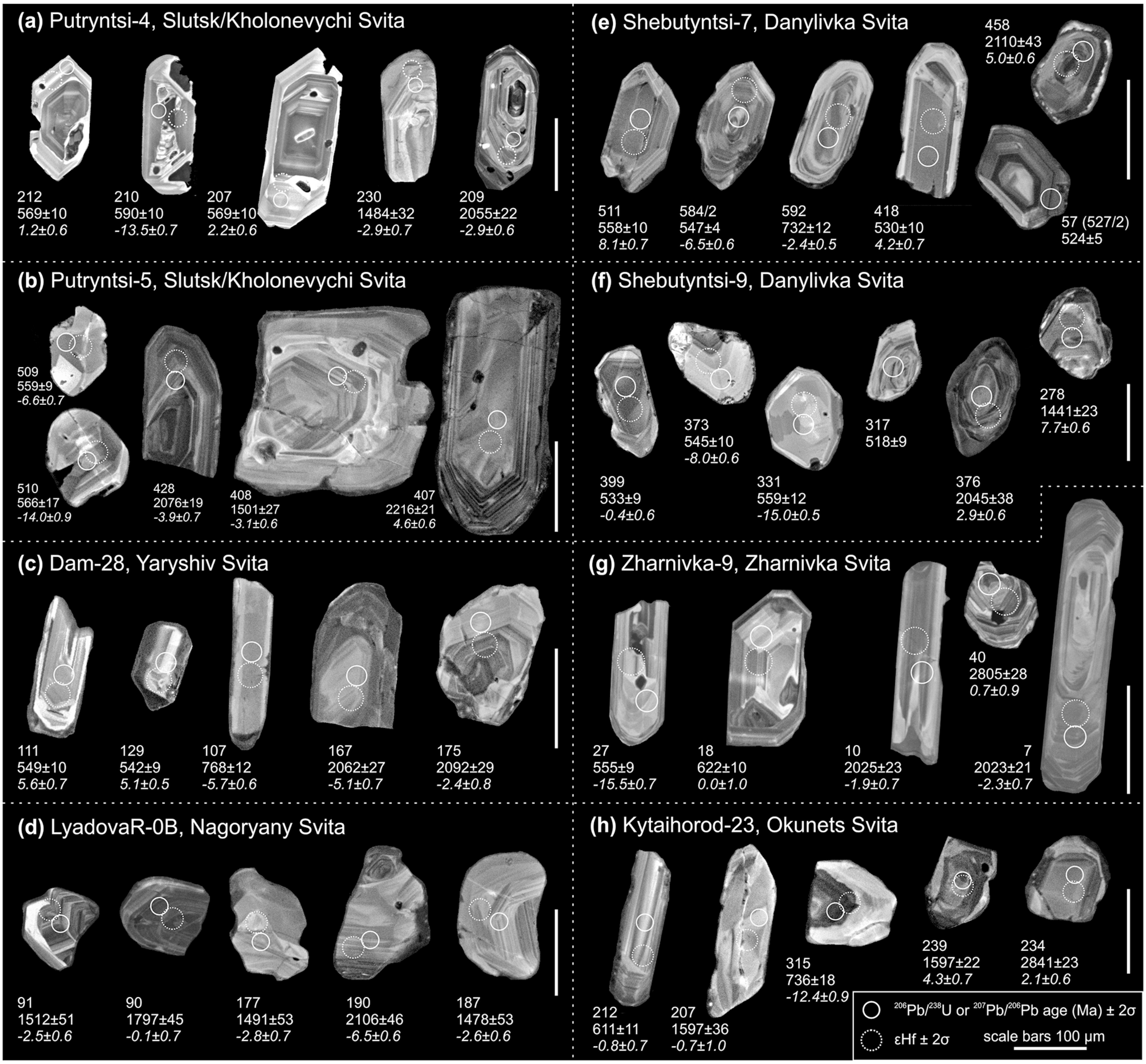

Fig. 5. Representative cathodoluminescence (CL) images of the analysed zircon grains. Presented data include spot number, ^{206}Pb/^{238}U date for data < 1000 Ma and ^{207}Pb/^{206}Pb date for data > 1000 Ma with $\pm$ 2σ error (Ma) and ε_{Hf} with $\pm$ 2σ error (in italic).

Series (Yaryshiv Svita; Fig. 3) should represent a time interval of 556–551 Ma (Soldatenko et al., 2019; Francovschi et al., 2021), the younger date representing a maximum depositional age. This is generally consistent with the two maximum depositional ages of 551 $\pm$ 13 and 546 $\pm$ 10 Ma obtained for the samples Dam-28 and LyadovaC-2, respectively (Fig. 6). The maximum depositional age of the latter overlaps within error the younger date of 551.2 $\pm$ 4.2 Ma (Francovschi et al., 2021), obtained for a sample located closely in the profile (Fig. 3).

All seven samples acquired from the Kanyliv Series reveal early Cambrian maximum depositional ages (Fig. 6). This also applies to sample Zharnivka-9 with a maximum depositional age of 547 $\pm$ 9 Ma that substantially overlaps the early Cambrian within error (Fig. 6). This result is inconsistent with the expected Ediacaran age (Fig. 3) and calls for the reinterpretation of the Podillyan stratigraphy. We interpret our dates as true ages, as they were rigorously selected to eliminate the measurements suspected of the Pb loss. Our data imply that the Podillya Ediacaran ends at the top of the Kalyus Beds, where a major hiatus, marked by a thick weathering zone (paleosol), a major change in the detrital material composition, and an angular disconformity have been noted earlier (Velikanov, 1976; Velikanov and Melnychuk, 2013). If our interpretation is correct, it implies that a few million years of uplift, erosion, and weathering must have passed until sedimentation returned to this area in the Cambrian. The hiatus known from Podillya expands towards Volyn and Belarus (Makhnach et al., 2001; Velikanov and Melnychuk, 2013). This hiatus may correspond to the global hiatus at the Ediacaran-Cambrian boundary known as The Great Unconformity (Shahkarami et al., 2020).

Two youngest samples, Kytaihorod-23 and −20, were collected from the Baltic Series that according to new paleontological data (Ivantsov et al., 2015) belongs to the lower Cambrian (Fig. 3). Both samples yielded Ediacaran maximum depositional ages, 562 $\pm$ 20 and 561 $\pm$ 19 Ma, due to a large spread of single grain ages (Fig. 6; Supplementary Data Table S1). They are to a certain degree similar to lower Cambrian sample Kob-57 from Belarus (Paszkowski et al., 2019) that contains a nearly continuous spectrum of ages ranging from 3.41 Ga to c. 542 Ma with dominant peaks at c. 550 and 620 Ma and a maximum depositional age of 543 $\pm$ 4 Ma. Furthermore, a dominant age peak of c. 1.5 Ga in the zircon populations from samples Kytaihorod-23 and −20 echoes the age

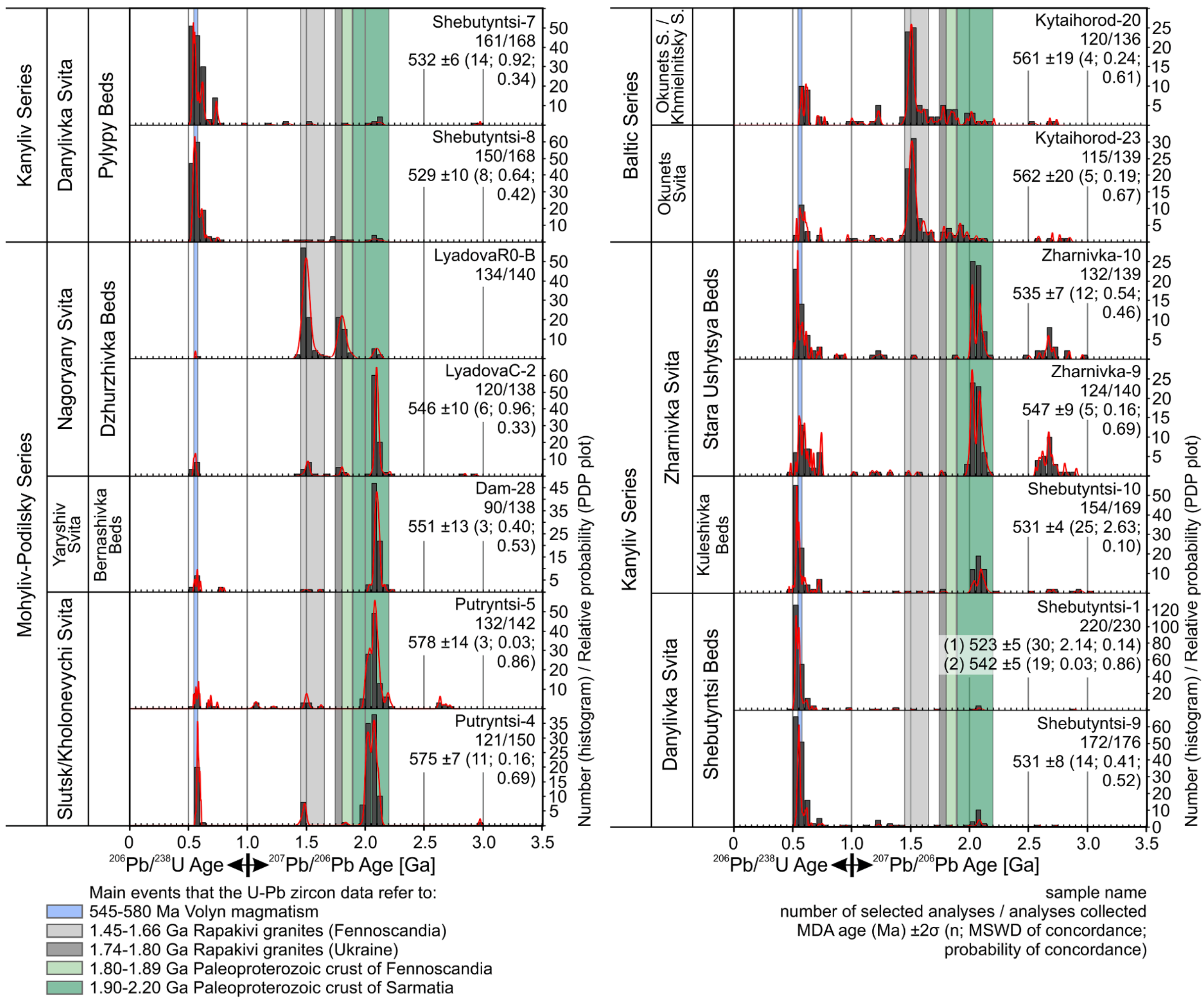

Fig. 6. Histogram plots presenting U-Pb age data yielded by the investigated zircon grains.

record from lower Cambrian sample Kob-54 of Paszkowski et al. (2019) that reveals a homogeneous zircon population with a single peak at c. 1.49 Ga.

5.2. New U-Pb data vs. current definition of the Ediacaran-Cambrian boundary in Podillya and the EEC

Globally, the Ediacaran-Cambrian boundary has been defined by the first appearance of a trace fossil (preserved burrow of an animal) in the stratotype profile of Newfoundland, primarily named *Phycodes pedum* (Seilacher, 1955), renamed later as *Treptichnus pedum* (Jensen and Grant, 1998), *Trichophycus pedum* (Geyer and Uchman, 1995), *Manykodes pedum* (Dzik, 2005). The boundary, located in the stratotype profile c. 1000 m below the lowest trylobites (Narbonne et al., 1987), has been U-Pb dated on zircons from a bentonite layer in Oman at 541 Ma (Bowring et al., 2007). This age, accepted in the International Stratigraphic Chart (Cohen et al., 2013, updated), will probably be revised to 539.5 Ma, the age obtained by Linnemann et al. (2019) from pyroclastics of the Swartpunt-Swartkloofberg profile in Namibia. In the EEC, bentonite layers at the Ediacaran-Cambrian transition are lacking, thus this boundary has been defined using paleontological criteria.

In Podillya, the Ediacaran-Cambrian boundary has been contrastingly interpreted (cf. Geological background). Using fossils, the Ediacaran/Cambrian boundary was defined by the disappearance of *Vendotaenia antiqua* (Aseeva, 1988), and the disappearance of *Harlaniella podolica* and appearance of *Planolites* (Gureev, 1988). Afterward, Ivantsov et al. (2015) reported the occurrence of *Phycodes (Treptichnus) pedum* ichnospecies about 6.5 m above the contact between the Kanyliv and Baltic Series (in the Khmelnytskyi Beds). This last finding allows for certain designation of the overlying Baltic Series strata to the Cambrian. However, the age assignment of the Kanyliv Series relies on the temporal ranges of *Vendotaenia, Harlaniella, and Planolites*.

Vendotaenia antiqua is an alga(?), known from Podillya and Finnmark (North Norway) (Högström et al., 2013) and from the Cambrian of southern China (Steiner et al., 2001). In Podillya, it first appears at the bottom of the Kalyus Beds (Fig. 3) and it is known from the entire Kanyliv series. Ivantsov et al. (2015) reported it also from the Baltic Series, thus it does not differentiate Ediacaran from the Cambrian.

Harlaniella is a trace fossil known from the Ediacaran and lower Cambrian of the EEC, North America and Australia. In the EEC, *Harlaniella ingriana* is known from the Redkino and Kotlin Horizons of the Arkhangelsk area (Winter Coast) and the Kotlin Horizon of the Baltic region, while *Harlaniella podolica* only from the Kanyliv Series of Podolia (Ivantsov, 2013). Another species of *Harlaniella* is known from the stratotype profile of Newfoundland, below *Phycodes pedum* but co-occurring with *Planolites,* in the rocks tentatively assigned to the Ediacaran (Crimes and Anderson, 1985). Also, in other parts of the world, *Planolites* is known both from the late Ediacaran and early Cambrian (O'Neil et al., 2020 and literature therein). As both *Harlaniella* and *Planolites* have wide temporal ranges, encompassing late Ediacaran and early Cambrian, they do not seem to be reliable tools for discriminating the two.

A new argument in this discussion is the temporal range of a small carbonaceous fossil *Cochleatina,* known in the EEC, both from the

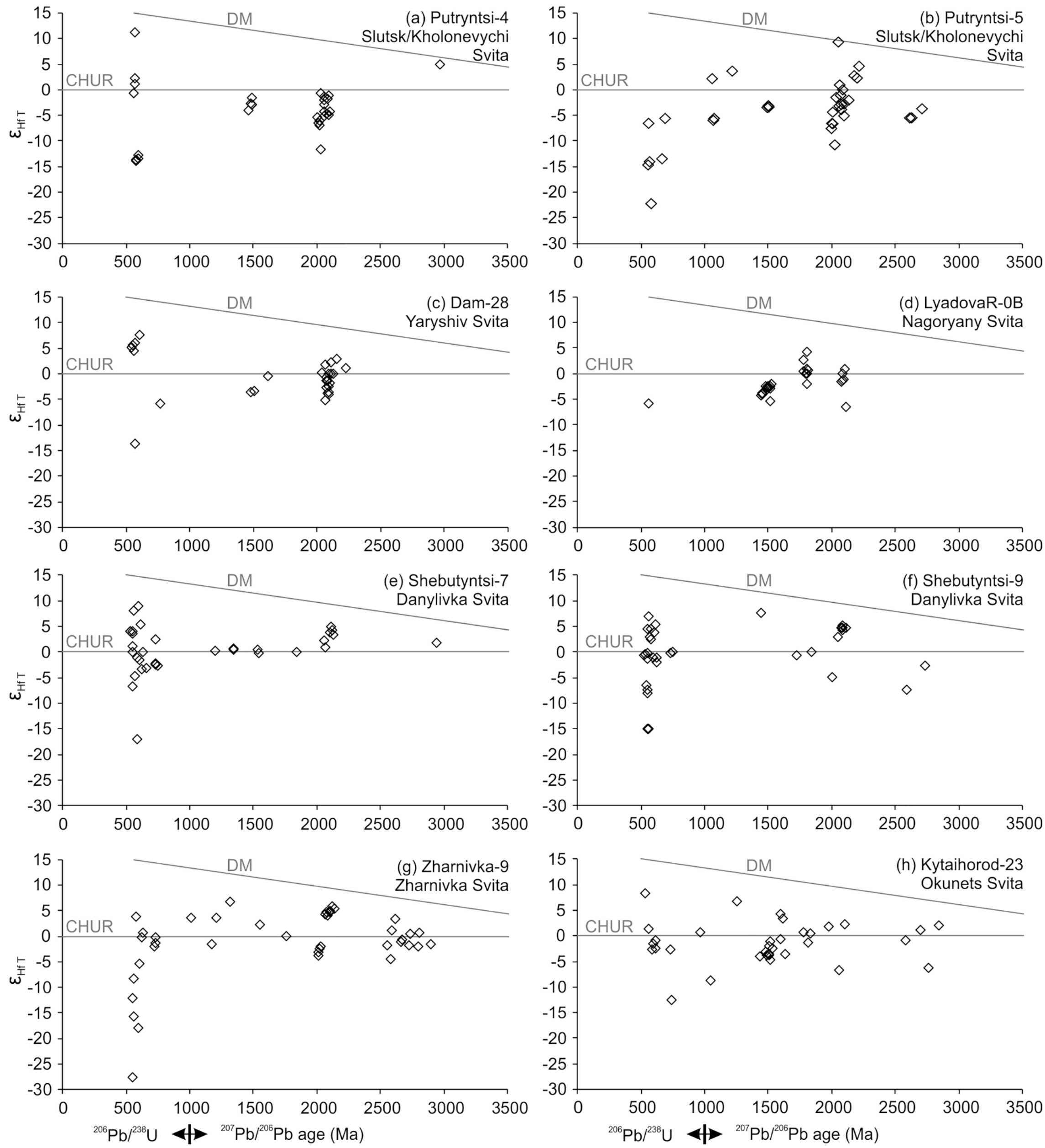

Fig. 7. ε_{Hf} vs. time plots presenting results for each investigated sample. $^{206}Pb/^{238}U$ age is given for data < 1000 Ma and $^{207}Pb/^{206}Pb$ age is given for data > 1000 Ma.

Ediacaran and Cambrian, while in the rest of the world only from Cambrian (Slater et al., 2020). This may indicate the Cambrian age of the Kanyliv Series, where this fossil was found.

Another paleontological argument deserving consideration is the finding of *Dickinsonia costata* and *Swartpuntia* in the Phylypy Beds of Tymkiv section (Nesterovsky et al., 2019). These organisms, often regarded as the Ediacaran index fossils, are also known from Phanerozoic, e.g. *Swarpuntia* in the Cambrian of California (Hagadorn et al., 2000). *Dickinsonia*, if poorly preserved, is very similar to the post-Ediacaran problematicum *Rutgersella* (Retallack, 2015). A separate problem concerning this finding is the location of Kalus-Phylypy border in this particular profile, where no sedimentation break is visible and transition is very gradual, thus perhaps the termination of the Ediacaran Kalyus Beds should be looked for higher in the section.

Micropalaeonology could help to discriminate the Ediacaran from Cambrian, if a rich Cambrian acritarch association was available, which is not the case of Podillya. In summary, the paleontological evidence does not seem to contradict the assignment of the Kanyliv Series of Podillya to Cambrian.

5.3. *The Hf isotope record from detrital zircons*

The most consistent isotope record comes from 3 samples representing the Kanyliv Series: Shebutyntsi-7, −9 and Zharnivka-9 (Fig. 7). These samples show a large vertical spread of isotopic data from strongly negative to chondritic and juvenile for detrital zircons dated at c. 550–530 Ma (Fig. 6). The variety of ε_{Hf} values for one age population of detrital zircons may suggest the location of the source area at a continental magmatic arc, mixing juvenile magmatic components with those derived from melting of pre-existing continental crust. The ε_{Hf} values for older zircon grains spread along the CHUR (Chondritic Uniform Reservoir) reference line, especially for the Shebutyntsi-7 sample. The isotopic data show no evidence for Pb loss, including no steep linear trend in ε_{Hf}-time space (Fig. 7; cf. Vervoort and Kemp, 2016). Since initial ε_{Hf}

values for zircon are highly sensitive to the assigned age (e.g., Vervoort and Kemp, 2016) zircon ages rejuvenated due to Pb loss would result in excessively negative ε_{Hf}. Consequently, the lower Cambrian maximum deposition ages that are calculated for samples of the Kanyliv Series seem to represent a reliable constraint on the timing of their sedimentation. Two oldest age clusters, particularly in sample Zharnivka-9, are characterised by slightly negative and positive ε_{Hf} values that are consistent with the derivation of detritus from the Paleoproterozoic mobile belts and cratonic Archean terranes of Sarmatia.

The nearly horizontal trend in ε_{Hf} versus age space in the Kytaihorod-23 sample suggests no Pb loss (Fig. 7; cf. Spencer et al., 2020). Therefore, the large spread of single grain ages within its zircon age spectrum (Fig. 6) might suggest mixing of zircons from exotic and local sources. The age peaks seemingly representing genuine age groups are dated at c. 2.84–2.58, 1.97–2.10 Ga and 528–611 Ma (Fig. 6). The latter is characterised by ε_{Hf} values in the range of –2.6 to +8.3 and may correspond to a continental arc source comparable to that identified in samples Shebutyntsi-7, −9 and Zharnivka-9 (Fig. 6).

Four older samples collected from the Volyn and Mohyliv-Podilsky Series display less distinct isotope record (Putryntsi-4 and −5, Dam-28, LyadovaR-0B; Figs. 6, 7). Three discrete age groups of the LyadovaR-0B sample (c. 2.11–2.07, 1.77–1.81, and 1.44–1.52 Ga) show fairly similar isotopic signature with ε_{Hf} values between −6.1 and +4.1. These nearly chondritic ε_{Hf} values associated with the lack of a noticeable age scatter are reconcilable with the derivation of detritus from three distinct crustal segments, corresponding to Paleoproterozoic rocks of the Ukrainian Shield (Shumlyanskyy et al., 2018b), Korosten AMCG complex and coeval mafic dykes (Shumlyanskyy et al., 2012, 2017) and Fennoscandian AMCG plutons (Dörr et al., 2002; Heinonen et al., 2010), respectively. Consequently, a viable explanation is a depositional mixing of zircons delivered from discrete source areas. A similar solution might be applied to the remaining three samples (Putryntsi-4 and −5, Dam-28) despite their less certain isotopic patterns (Fig. 7). Importantly, the zircon age group corresponding to Fennoscandian crust is absent from these samples, except for a minor group dated at c. 1.5 Ga. A characteristic feature of samples Putryntsi-4 and −5, Dam-28 is the group of detrital zircons in the age range of 600–540 Ma (Fig. 6). They reveal mostly juvenile ε_{Hf} values in sample Dam-28, mixed juvenile, nearly chondritic and negative ε_{Hf} values in sample Putryntsi-4 and entirely negative ε_{Hf} signature in sample Putryntsi-5 (Fig. 7). This isotopic record combined with an Ediacaran age of detrital zircons may suggest a mantle source with various degree of crustal contamination such as the Volyn flood basalts.

5.4. Paleogeographic implications

Our mineralogical data indicate a major contribution of volcanic detritus into the rocks of the Novodnistrovsk Horizon (low content of quartz and high content of dioctahedral clays: Fig. 4). The Volyn flood basalts and associated more felsic rocks (c. 579–545 Ma in Belarus, Paszkowski et al., 2019) seem the most likely source area, taking into account their age and a proximate geographic location (Paszkowski et al., 2019).

A characteristic feature of the samples from the Novodnistrovsk Horizon (Fig. 3; Putryntsi-4 and −5, Dam-28), compared to those from the Volyn and Redkino Series of Belarus (Paszkowski et al., 2019), is an almost complete lack of signal from the Fennoscandian crust (Fig. 6) and a large quantity of zircons dated between 2.2 and 1.9 Ga (Fig. 6). This indicates that the main catchment area of sediments in Podillya was located within the Paleoproterozoic belts of Sarmatia (Bogdanova et al., 2008; Shcherbak et al., 2008; Shumlyanskyy, 2014; Shumlyanskyy et al., 2018b; Terentiev et al., 2016, 2020; Terentiev and Santosh, 2020), with only a weak connection to Fennoscandian distributary systems and sedimentary basins. The only probable record of detritus supply from Fennoscandia is a minor cluster of detrital zircons that was dated at c. 1.5 Ga (Fig. 6), the age characteristic of the Fennoscandian AMCG plutons. Abundant zircons of similar age (c. 1.5 Ga) were earlier documented in sedimentary rocks of the Ukrainian Shield and interpreted as detritus supplied from the Fennoscandian Shield (Shumlyanskyy et al., 2015).

Samples LyadovaC-2 and LyadovaR0-B (Fig. 6) record a gradual shift of the source area to Fennoscandia that is characterised by Paleoproterozoic c. 1.89–1.8 Ga old crust (e.g., Bogdanova et al., 2008, 2015; Lahtinen et al., 2009) and Mesoproterozoic (1.66–1.45 Ga) AMCG plutons (Dörr et al., 2002; Skridlaite et al., 2003; Bogdanova et al., 2008; Shumlyanskyy et al., 2017). The 1.5 Ga cluster is particularly strong in the Lyadova R0-B sample, representing the Nagoryany Svita, i.e., the top of the Ediacaran according to our data. The zircon population from this sample is similar to those from the Kotlin Svita of Belarus (Paszkowski et al., 2019) and the Kalyus Beds (Francovschi et al., 2021) from the Nagoryany Svita (Fig. 3). It demonstrates a shift of a catchment area from Sarmatia to Fennoscandia and a full connection between distributary systems across both areas in the Nagoryany times.

Another major reorganization of the sediment supply routes is revealed by samples from the Kanyliv Series. The four oldest samples from the Kanyliv Series, collected from the Danylivka Svita (Fig. 3), are dominated by early Cambrian and Ediacaran zircons and depleted in older detrital grains, the population suggesting detritus supply from rocks of nearly the same age (Fig. 6). Detrital zircon populations from the lowermost Danylivka Svita (samples Shebutyntsi-7, −8) contain grains practically from a single source area, corresponding to a continental magmatic arc and, possibly, a successive collisional orogen. Upward in the Kanyliv Series profile, source areas located in Sarmatia had been gradually switched on, but a continental arc/orogenic source still remained important (Fig. 6). The two youngest samples (Zharnivka-9 and −10) additionally contain a considerable population of Archean zircons in the range of 2.9–2.6 Ga, the age interval abundant in cratonic terranes of Sarmatia that are presently exposed in the Ukrainian Shield and the Voronezh Massif (Shcherbak et al., 2005, 2008; Bogdanova et al., 2006, 2008, and references therein). This evolution of detrital zircon age spectra reveals an increasing input of detritus from the Sarmatia basement throughout the early Cambrian. However, even the youngest samples in the Kanyliv Series (Zharnivka-9 and −10) contain no zircons older than 3.0 Ga that have been retrieved from the oldest crust of the Podolian and Azov domains of the Ukrainian Shield (Bibikova et al., 2012, 2015; Claesson et al., 2015; Lobach-Zhuchenko et al., 2017; Shumlyanskyy et al., 2021).We attribute the lack of detritus derived from Eoarchaean sources to their relative scarcity, coupled with shallower erosional exhumation of the Archean basement in the early Cambrian.

Since the detrital zircon age spectrum of the Kanyliv Series is unique and has no equivalent in Belarus (Paszkowski et al., 2019), the source of detritus must have been located farther south and south-east. Kopeliovich (1965) and Velikanov (1976) came to the same conclusion, based on the mineral composition of pebbles. Indeed, the subsidence analysis published by Poprawa et al. (2018) shows that, while the majority of the SW Baltica margin remained relatively stable in the latest Ediacaran and early Cambrian, Baltica's southern section, adjacent to the Scythian Platform, underwent rapid subsidence at the transition from the Ediacaran to Cambrian. The analysis by Poprawa et al. (2018) reveals a subsidence evolution indicative of a flexural basin, suggesting the Baltica continental margin being overridden by a collisional orogen. This is consistent with a concept of a *peri*-Gondwanan Neoproterozoic terrane (Scythia) docked to the Baltica margin (Fig. 8) and giving rise to the pre-Scythides orogen (Kheraskova et al., 2015). A continental magmatic arc, supplying detritus to sediments of Podillya, must have been established on the Scythia terrane and became a source area only after its docking to the passive margin of Baltica. This tentative interpretation is linked to a wider problem of Pannotia, an ephemeral supercontinent that was assembled at that transition from the Ediacaran to Cambrian (e.g., Murphy et al., 2021). Although the provenance of Scythia remains largely unknown, it may have been derived from the Avalonian Arc that

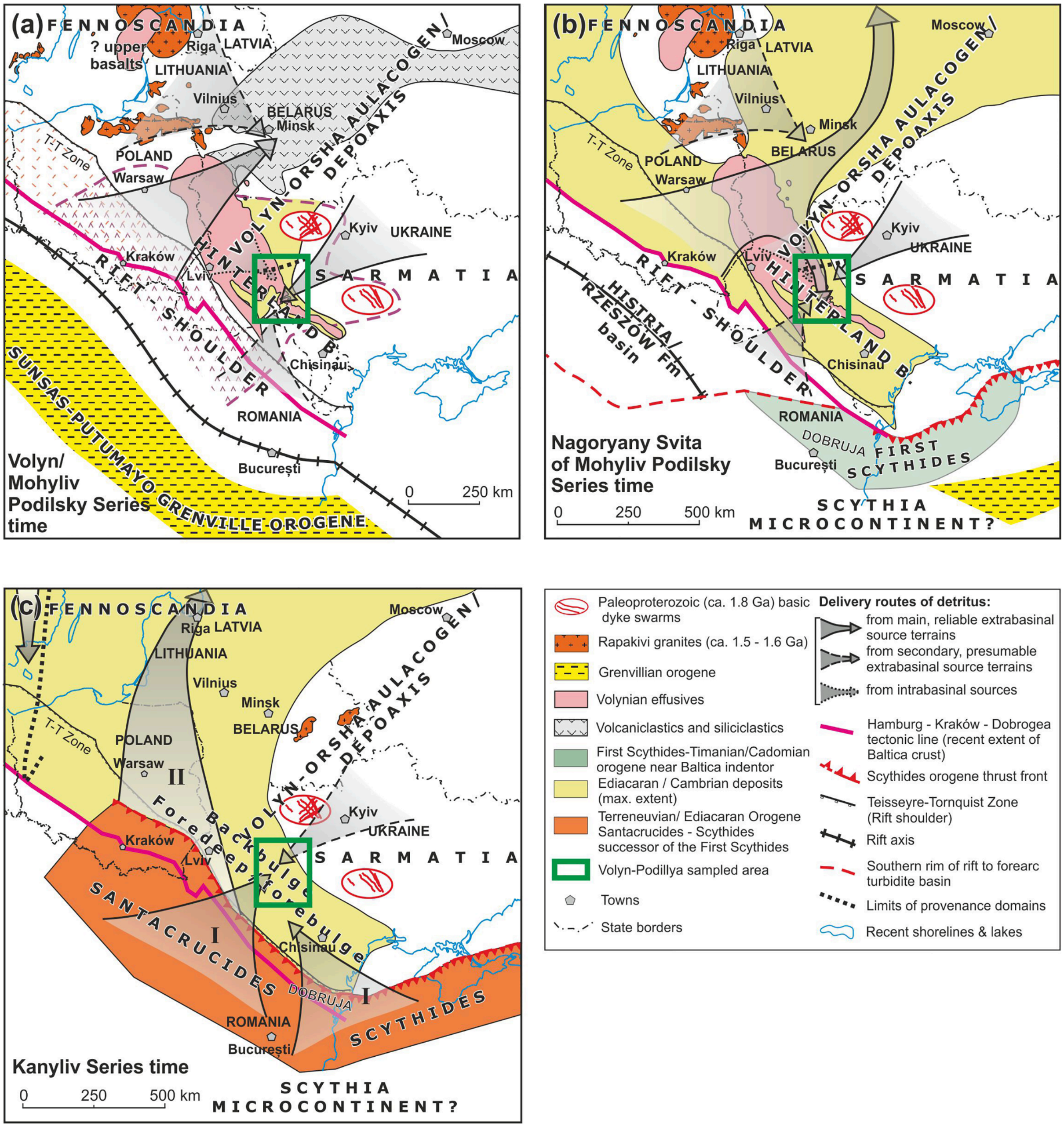

Fig. 8. Paleogeographic reconstruction of the SW part of the Baltica paleocontinent for three subsequent development stages of the Ediacaran-Cambrian basin: (a) Volyn/Mohyliv Podilsky Series time, (b) Nagoryany Svita of Mohyliv Podilsky Series time, and (c) Kanyliv Series time, arranged in chronological order. Reconstructions (partly based on Paszkowski et al., 2019) illustrate the evolution of detritus delivery routes. Details discussed in the text.

developed outboard of Gondwana (e.g., Nance et al., 2002; Murphy et al., 2021).

The Kanyliv Series represents, in our interpretation, a few hundred meters thick succession of a foreland basin associated with an orogen overriding the passive margin of Baltica in the early Cambrian. A connection with the foredeep sediments is confirmed by mineral composition of samples collected from the Kanyliv Series that are dominated by detritus from a metamorphic terrane (high contents of quartz and $2M_1$ mica, Fig. 4). Also, the lithological composition of pebbles from the base of the Kanyliv Series (Velikanov and Melnychuk, 2013) is consistent with such a provenance.

In our interpretation, the SW margin of Baltica since the time of deposition of the Volyn Series (Fig. 8a) showed the characteristics of a hinterland rift-shoulder basin (Van der Beek et al., 1994; Tari et al., 1997), but since the time of deposition of the Nagoryany Svita (Fig. 8b) it was transformed into a foreland basin of the advancing Pre-Scythian orogen. Farther NW along the Baltica margin, the time equivalent of the Pre-Scythian orogen might be found in the Małopolska Massif and the southern Holy Cross Mts. (e.g., Gągała, 2005; Żelaźniewicz et al., 2009; Buła and Habryn, 2011), the deformation belt that we call Santacrucides (Fig. 8c). This belt comprises low-grade metamorphic deep water siliciclastics that were deposited in a wide basin (Fig. 8b) of the Rzeszów Fm (Beds) in the NW (Pożaryski and Tomczyk, 1968) and the Histria Fm in the SE (Seghedi et al., 2005).

The detrital zircon age spectra from the Baltic Series should represent "proper early Cambrian" according to biostratigraphic data. Indeed, they are similar to those obtained from the lower Cambrian rocks of Belarus (Paszkowski et al., 2019; their sample Kob-57). The zircon population of the Kob-57 sample includes a broad 500–700 Ma Neoproterozoic cluster and marks a major provenance shift to polymodal distribution of detrital zircon ages. A corresponding change of detrital zircon signature within the Cambrian strata was reported from Estonia (Isozaki et al., 2014), the Russian part of the Baltic Monoclise (Kuznetsov et al., 2011; Ivleva et al., 2016) and Scandinavia (Lorentzen et al., 2017; Sláma and Pedersen, 2015; Sláma, 2016). Similarly, the middle Cambrian sediments of the Podlasie Depression (Valverde-Vaquero et al., 2000) and Lublin Basin (Porębski et al., 2019) in Poland contain a Neoproterozoic zircon cluster.

Although the source of Neoproterozoic detrital zircons in the Cambrian strata of the East European Platform has been previously linked to the Timanide belt of northern Baltica (Kuznetsov et al., 2011, 2014; Isozaki et al., 2014; Sláma and Pedersen, 2015; Ivleva et al., 2016; Sláma, 2016), we favour the pre-Scythides orogen as a possible source area. This is primarily supported by the characteristics of the Kanyliv Series in Podillya, representing an earliest Cambrian foreland basin, the extent of which points to the south-easterly location of an orogenic load. In our interpretation, the overlying Baltic Series and its time equivalents may represent the early post-orogenic sediments, containing material that was widely distributed across the East European Platform and mixed with detritus delivered from other sources.

6. Conclusions

U-Pb ages of detrital zircons from sandstones of the Podillya – southern Volyn sedimentary section so far regarded as Ediacaran yielded two sets of maximum depositional ages. The Mohyliv-Podilsky Series provided upper Ediacaran ages in the range of 578–546 Ma, corresponding to the age of bentonite interlayers (Soldatenko et al., 2019), and the age of the Volyn LIP (Paszkowski et al., 2019). The overlying Kanyliv Series rocks provided predominantly early Cambrian maximum depositional ages from 547 to 523 Ma (Fig. 6). They are interpreted as true ages, as they are concordant, and both the pattern of εHf values (Fig. 7) and zircon growth structures (Fig. 5) exclude Pb loss. Consequently, the Ediacaran-Cambrian boundary in Podillya coincides in our opinion with the major erosional gap, angular disconformity (Fig. 2), radical provenance change, and the disappearance of the Ediacaran fauna at the top of Kalyus Beds, which were noted by earlier workers. Paleontological evidence does not seem to contradict this hypothesis, which assigns the entire Kanyliv Series to Cambrian.

Zircon U-Pb age spectra reveal three development stages of the Podillya-Volyn Basin (Fig. 8). In the oldest stage, represented by the Novodnistrovsk Horizon rocks (Redkino), the detritus was transported from the north, but rather locally, from the Volyn LIP and the Sarmatia crystalline basement. During the Nagoryany time (Kotlin), the connection with the northern part of the EEC was established, and the detritus from Fennoscandia appeared, resulting in the zircon age spectra analogous to those documented in the Kotlin rocks of Belarus. The erosional gap at the top of the Kalyus Beds (Kotlin) corresponds to a major shift of the supply routes: most of the material of the Kanyliv and Baltic Series was delivered from the SE. We identify the catchment area as a continental magmatic arc and successive collisional orogen overriding Baltica (Scythides and Santacrucides). Consequently, we interpret the Kanyliv Series as deposits of an earliest Cambrian foreland basin, and the analogous provenance signal, detected in the Cambrian rocks of Belarus, as indicative of the Santacrucide material penetrating far into the interior of the EEC.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.precamres.2021.106282.

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