GFF

ISSN: 1103-5897 (Print) 2000-0863 (Online) Journal homepage: <http://www.tandfonline.com/loi/sgff20>

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To cite this article: Leonid Shumlyanskyy, Anna Nosova, Kjell Billström, Ulf Söderlund, Per-Gunnar Andréasson & Oksana Kuzmenkova (2016) The U–Pb zircon and baddeleyite ages of the Neoproterozoic Volyn Large Igneous Province: implication for the age of the magmatism and the nature of a crustal contaminant, GFF, 138:1, 17-30, DOI: [10.1080/11035897.2015.1123289](https://doi.org/10.1080/11035897.2015.1123289)

To link to this article: <http://dx.doi.org/10.1080/11035897.2015.1123289>

Published online: 08 Jan 2016.

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The U–Pb zircon and baddeleyite ages of the Neoproterozoic Volyn Large Igneous Province: implication for the age of the magmatism and the nature of a crustal contaminant

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Shumlyanskyy, L., Nosova, A., Billström K., Söderlund U., Andréasson, P.-G. & Kuzmenkova, O., 2016: The U–Pb zircon and baddeleyite ages of the Neoproterozoic Volyn Large Igneous Province: implication for the age of the magmatism and the nature of a crustal contaminant. *GFF*, Vol. 138, No. 1, pp. 17–30. © Geologiska Föreningen. doi: <http://dx.doi.org/10.1080/11035897.2015.1123289>.

Abstract: The Volyn continental flood basalt province is situated on the western margin of the East European platform and constitutes a significant portion of the passive continental margin sequence formed along the Trans-European Suture Zone in response to Rodinia break-up in the Neoproterozoic. In Ukraine, the volcanogenic sequence is subdivided into suites called Zabolottya, Babyne and Ratne, which together with the lowermost terrigenous Gorbashy suite comprise the Volyn series. Magmatic zircons from one high-Ti basalt sample yielded an age of 573 ± 14 Ma, whereas grains isolated from a rhyolitic dacite yielded an age of 571 ± 13 Ma. Baddeleyite from the olivine dolerite sample gave an older $^{206}\text{Pb}/^{238}\text{U}$ age of 626 ± 17 Ma, whereas the $^{207}\text{Pb}/^{206}\text{Pb}$ weighted average age of 567 ± 61 Ma is close to the zircon ages. Zircons separated from the other basaltic samples are much older and crystallized at c. 1290, 1470, 1820–1860, 1930–2050 and 2660 Ma. Ages in the 1820–1860 and 1930–2050 Ma time spans correspond to the ages of the Precambrian basement that underlies the Volyn province. However, the sources for the 1290, 1470 and 2660 Ma zircons are unknown, and these zircons must have been derived from more distal areas.

Keywords: Volyn; basalts; Vendian; zircon; baddeleyite; geochronology

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Manuscript received 02 February 2015; accepted 17 November 2015.

1. Introduction

Continental flood basalts are often related to the break-up of supercontinents such as Gondwana and Pangaea in Phanerozoic times or Rodinia in Late Neoproterozoic time and commonly associated with volcanic rifted margins (Ernst et al. 2005; Ernst 2014 and references therein) that often appear on opposite sides of the ocean basins that have formed during continental break-up. However, in older continents, former volcanic rifted margins may now constitute the inner portions of large continental plates. One such palaeomargin is confined to the Trans-European Suture Zone (TESZ; Fig. 1). Being mainly amagmatic, the TESZ nevertheless

contains a few important magmatic provinces one of which is the Volyn continental flood basalt province, or Volyn Large Igneous Province, that is located in western Ukraine, eastern Poland and southern Belarus occupying an area over 200,000 km². This province, although situated in the inner part of the European continent and rather small in size, occurs as a typical continental flood basalt province related to the Neoproterozoic break-up of Rodinia supercontinent and separation of Baltica and Amazonia.

U–Pb dating of U-bearing minerals separated from mafic rocks (gabbro, dolerites and basalts) has proved efficient to

Fig. 1. Schematic map of distribution of the Volyn flood basalts. Asterisk indicates location of the Compston et al. (1995) sample. Numbers in circles: 1 – Devonian Prypyat aulacogen; 2 – Brest depression. Ar – Archaean Dniester-Bug domain of the Ukrainian shield; Pr – Palaeoproterozoic domain. Area located to the west of the Ukrainian shield is known as Volyno-Podolian monocline. Inset map: VOA indicates Volyn-Orsha depression; E stands for Egersund dyke swarm and TZ – for Tornquist zone.

produce reliable geochronological information (see for instance Kamo et al. 1989; Bingen et al. 1998; Wingate et al. 1998). Two dateable minerals that may occur in mafic rocks are baddeleyite and zircon. Baddeleyite is considered as a syn-magmatic mineral and is common in slowly cooled mafic rocks such as gabbro and coarse dolerite, while such rocks usually are too silica-poor to crystallize zircons. However, syngenetic zircon can be found in pods of diorite or even granite material in mafic intrusions and thick dykes (Svenningsen 2001; Shumlyanskyy et al. 2008; Shumlyanskyy & Zagnitko 2010). Zircon may also be found as a syn-genetic mineral in a variety of continental flood basalt related effusive rocks including basalt, rhyodacite and quartz latite (Pinto et al. 2011). It must be recalled that mafic magmatic rocks may contain xenocrystic zircon captured en route to the place of ultimate crystallization or picked up at the source region. For instance, Zheng et al. (2011) used zircons separated from mafic rocks in the Cathaysia Block, South China, to demonstrate the presence of unexposed Archaean rocks. Similarly, Hodych et al. (2004) used U–Pb ages of zircons separated from basaltic and trachytic flows of the Skinner Cove Formation, western Newfoundland, to prove not only their Late Neoproterozoic age, but also to demonstrate its relation to the Laurentia continent.

The age of the Volyn flood basalt province remains poorly constrained (see below) which is complicating the correlation of this province with other manifestations of igneous activity that were related to the break-up of the Rodinia supercontinent and the understanding of the process of break-up. The knowledge about the age of the Volyn province is also essential in order to gain further insights into the evolution of the western part of the East European craton in the Neoproterozoic. In this article, we consider new *in situ* ion microprobe U–Pb ages on zircons from basalts, dolerites and felsic volcanic rocks of the Volyn flood basalt province, and baddeleyite multigrain thermal ionization mass-spectrometry

(TIMS) U–Pb data in order to constrain the time of their eruption and of the continental break-up. However, analyses have also revealed the presence of much older, Proterozoic–Archaean, zircons in both mafic and felsic rocks of the Volyn province. We use these results to understand the origin and nature of an inferred old crustal component in the basaltic and felsic melts.

2. Tectonic setting

The Volyn flood basalt province is located on the western margin of the East European platform, where it straddles the boundary between two main segments of Baltica, namely Sarmatia and Fennoscandia (Fig. 1). In the Sarmatian part of the province (Fig. 2), the basement is represented by two orogenic belts – Zhytomyr (ca. 2.10–2.04 Ga) and Osnitsk-Mikashkevychi (ca. 2.00–1.97 Ga) that developed on the margin of the Archaean Bug terrain (Scherbak et al. 2008). This part was later influenced by the collision with Fennoscandia as reflected in the formation of the extensive 1.81–1.74 Ga old Korosten anorthosite–mangerite–charnokite–granite plutonic complex (Amelin et al. 1994; Bogdanova et al. 2004). The Fennoscandian part of the basement that underlies the Volyn province consists of 2.00–1.90 Ga rocks of the Central Belarus belt and, to a lesser extent, 1.85–1.79 Ga rocks of the Baltic-Belarus granulite belt (Claesson et al. 2001). These rocks have experienced some influence of a magmatic event at 1.54–1.45 Ga which resulted in the formation of the Mazury anorthosite–mangerite–charnokite–granite complex (Skridlaite et al. 2006).

3. Regional stratigraphy

The Palaeoproterozoic basement of the western East European platform is overlain by a platform sedimentary cover that includes

Fig. 2. Schematic map showing the relationship between Volyn flood basalts and the basement structure. Zhytomyr Belt (ZhB, c. 2.1 Ga), Osnytsk-Mikashkevychi Igneous Belt (OMIB, c. 2.0 Ga), Central Belarus Belt (CBB, c. 2.0–1.9 Ga), Vitebsk Granulite Belt (VGB, c. 1.9–1.8 Ga), Belarus-Baltic Granulite Belt (BBGB, c. 1.85–1.79 Ga) and East-Lithuanian Belt (ELB, c. 1.85–1.79 Ga) are shown on the map. Korosten (1.82–1.74 Ga, K), Mazury (1.54–1.45 Ga, M), and Riga (1.58 Ga, R) anorthosite-mangerite-charnokite-granite complexes are also shown. TESZ – Trans-European Suture Zone. Basement map is simplified after Claesson et al. (2001) and Krzeminska et al. (2005). VP stands for the Volyn continental flood basalt province.

Riphean, Vendian, Early Palaeozoic, Devonian, Carboniferous and Jurassic deposits, which are almost everywhere covered by Cretaceous sediments (Kruglov & Tsytko 1988; Poprawa & Paczeńska 2002). The thickness of the sedimentary cover is variable: it does not exceed a few tens of metres in the Belarusian massif or even a few metres in parts of the Ukrainian shield, but increases westwards to reach more than 8000 m at the margin of the East European platform. The slope of these sediments is generally very gentle (0.5–1.0°). In Ukraine, this monocline, known as Volyno-Podolian, is tilted from the Ukrainian shield towards the TESZ (Fig. 1).

In the south-western part of the platform, the sedimentary cover can be subdivided into two parts that fill different depressions (Fig. 3). The lower part comprises the Polissya Series and glacial Early Vendian deposits and fills out the middle-late Riphean Volyn-Orsha depression which is oriented at an oblique angle to TESZ (Fig. 1). The Polissya Series includes red sandstones and siltstones with minor amounts of clays. It is characterized by horizontal bedding, fine banding and rhythmical sedimentation and reaches 835 m thickness at the axis of the depression (Vlasov et al. 1972). The youngest detrital zircon found in the Polissya Series sandstone is 1018 ± 20 Ma ($^{207}\text{Pb}/^{206}\text{Pb}$ age, Shumlyanskyy et al. 2015). Glacial Early Vendian deposits (Brody suite) are reddish-brown clay-silt-sandy unstratified rocks with a massive structure varying in thickness from 15 to 44 m (Nitke et al. 1976). The second (upper) part of the sedimentary cover starts with the Volyn Series that overlies the Riphean–Early Vendian sediments and fills out a tectonic depression that developed along a NW–SE direction, parallel with the TESZ in a passive continental margin setting (Poprawa & Paczeńska 2002). Rocks of the Volyn

Fig. 3. Simplified stratigraphic column of the Late Proterozoic–Early Palaeozoic formations of the Volyno-Podolian monocline. Not to scale. Location of the zircon samples studied in this work is shown. Zircon samples 955/17, 955/14, 954-3, 60/1 and baddeleyite sample 68/147-154 were taken from the dolerite intrusions (not shown on the column) that cut sediments of the Polissya Series.

sequence rest upon the Polissya Series and Brody suite and in places directly overlies the crystalline basement (Figs. 1 and 3). The Volyn Series can be traced over a distance of 770 km from Bialystok in Poland to Chernivtsy in Ukraine. Its width exceeds 300 km in the central part while the maximum thickness (up to 400–600 m) is confined to the axial part of the Volyn-Orsha depression. The Volyn Series can be further subdivided into a lowermost part (40–50 m), termed the Gorbashy suite, which is composed mainly of conglomerates and sandstones, while the main part of the Volyn Series consists of basic effusive and pyroclastic rocks, forming a flood basalt province. Thin picrite flows can be occasionally found among clastic sediments of the Gorbashy suite.

The volcanogenic sequence of the Volyn Series which constitutes the Volyn Large Igneous Province is subdivided into three parts in Ukraine (from bottom to top) called the Zabolottya, Babyne and Ratne suites (Birulyov 1968). These rocks are poorly exposed and mainly available from numerous drillings only few of which have penetrated the whole volcanogenic sequence. Tuffs and basalts of the uppermost Ratne suite crop out in several quarries and were extensively investigated. Effusive rocks of the lowermost Zabolottya suite are less abundant and found almost entirely within the Volyn-Orsha depression. They consist of one to eight basaltic flows with a subordinate (<25% of the total suite thickness) amount of pyroclastic material. The maximal thickness of the suite reaches 166 m but is usually a few tens of metres. The Babyne suite is the most widely distributed and composed mainly of volcanoclastic sediments. In the flanks of the province, tuffs of the Babyne suite rest directly on the Polissya sediments and crystalline basement. The suite comprises layered, mainly fine- to medium-grained vitroclastic basaltic tuffs with abundant interlayers of fine-grained vitro-crystalloclastic and coarse lithoclastic tuffs. Tuffs are brown, reddish-brown and greenish-grey. Fine-grained tuffs usually appear as thin parallel-bedded rocks, whereas coarse-grained tuffs possess a faint cross-bedding. One to two basaltic flows occur in the central part of the Babyne suite, the thickness of which reaches 180 m. In distal areas, pyroclastic rocks of the suite often contain a significant portion of terrigenous material represented by interlayers of sandstones and tuffites. The Ratne suite is the uppermost one and is the best studied (Białowolska et al. 2002; Nosova et al. 2008; Shumlyanskyy 2008). Tuffs are rare while basaltic flows vary in thickness from 5–10 to 50–60 m and are separated from each other by volcanic breccias. Basaltic fragments are cemented either by fine ash or by aphanitic lava. There are up to ten basaltic flows and the total thickness of the suite can exceed 220 m. Intermediate and felsic (andesite-dacite) rocks appear locally in the north-western part of the Volyn province known as the Brest depression in Belarus (Makhnatch 1968). The maximum thickness of the felsic rocks is 112 m, but due to a small areal occurrence, they only constitute a few per cent of the total volume of the Volyn province.

Reddish sandstones, argillites and siltstones of the Chartory suite overlie locally outcropping volcanogenic rocks of the Volyn Series and contain a small amount of volcanoclastic material. The Chartory suite completes the “Volyn” cycle of the depression development. After its formation, a short break in sedimentation occurred during which both volcanic rocks of the Volyn Series and Palaeoproterozoic crystalline rocks of the Ukrainian shield experienced some weathering and erosion. In general, the Volyn Series is overlain by Early Palaeozoic continental sedi-

ments that include deltaic river bed deposits that pass upwards into coastal and shallow marine sediments, in turn overlain by transgressive deep sea terrigenous formations (Znamenskaya & Chebanenko 1985).

4. Geochemistry of Volyn flood basalts: a brief description

A detailed geochemical description of the Volyn flood basalt sequence is beyond the scope of this article and will be reported elsewhere. Aspects of the geochemistry of the Volyn flood basalt and related rocks were reported by Bakun-Czubarow et al. (2002), Białowolska et al. (2002), Nosova et al. (2008), Shumlyanskyy (2008, 2012), Shumlyanskyy et al. (2011). In general, the Volyn province embraces the following rock types, from bottom to top: (1) locally distributed picrites among terrigenous rocks of the Gorbashy suite; (2) olivine basalts of the Zabolottya suite; (3) low-Ti, high-Al basalts (one to two flows or possibly sheet intrusions) in the middle part of the Babyne suite; these are underlain and covered by thick tuff horizons; (4) low-Ti and low-Nb tholeiite basalts of the lower part of the Ratne suite; (5) felsic volcanics, locally distributed in the northern Belarus; (6) high-Ti tholeiite basalts of the upper part of the Ratne suite that rest either on low-Ti tholeiite basalts or on felsic volcanics. High-Ti dolerite sills geochemically close to the high-Ti tholeiite basalts are rather common immediately beneath the Volyn flood basalt sequence where they cut terrigenous sediments of the Polissya Series.

Chemical compositions of minerals and rocks vary regularly in the vertical section of the Volyn Series. In particular, calcic plagioclases (up to An_{86}), magnesian orthopyroxene ($En_{82}Fs_{13}Wo_5$) and clinopyroxene ($En_{59}Fs_9Wo_{32}$) are characteristics for picrites. These rocks contain olivine phenocrysts while the opaques are represented by chromite. Upwards in the section, plagioclase becomes more sodic and pyroxenes more ferrous. Olivine is still present in the Babyne suite basalts but disappears in basalts of the Ratne suite. Plagioclase phenocrysts found in the Ratne suite basalts are very close in composition to plagioclases present in groundmass of picrites or Zabolottya suite basalts. Intrusive dolerites are very close in mineral chemistry to the Ratne suite basalts but contain olivine instead of orthopyroxene.

The whole-rock #Mg, ranging between 69 and 73 in picrite, gradually decreases upwards and reaches 35–60 in high-Ti basalts of the Ratne suite and intrusive dolerites. REE abundances and degree of their fractionation gradually increase upwards in the section. A negative Eu anomaly is characteristic for picrites and for some of the Babyne suite basalts, while a weak positive Eu anomaly was found in low-Ti basalts of the Ratne suite and in dolerites. ϵNd in rocks gradually increases upwards from –12 in picrites to between –1 and –6 in high-Ti Ratne basalts and reaches values of –1 to –3 in dolerites.

5. Previous geochronological data on Volyn flood basalts

The radiometric age of the Volyn flood basalts is poorly constrained, although on the basis of the described above stratigraphical evidence, this is attributed to the Early Vendian (Kruglov &

Tsytko 1988). The basalts of the Ratne suite were extensively investigated using the K–Ar method (Semenenko 1975; Starytskyy 1981), but results are not conclusive. Ages generally fall within the interval 650–540 Ma, with some as young as 180 Ma, indicating recent Ar loss. Postnikova (1977) reported K–Ar ages of the Volyn flood basalt province between 690 and 560 Ma. Recently, Elming et al. (2007) carried out $^{40}\text{Ar}/^{39}\text{Ar}$ whole-rock age determinations on a set of the Ratne basalt samples. In general, their results fall into two groups. The first group includes four samples with ages in the range of 590–560 Ma and is indicating some excess Ar. The second group embraces samples with plateau ages varying from 393 to 369 Ma that broadly correspond to the time of formation of the Devonian Prypyat aulacogen (Fig. 1).

Compston et al. (1995) investigated zircons from the uppermost tuff bed sampled from a drill core in eastern Poland (Fig. 1), believed to represent the last eruptive event related to the Volyn volcanism. Their preferred U–Pb age (SHRIMP method) was 551 ± 4 Ma, with a few inherited grains (558 ± 8 Ma and 635 ± 10 Ma).

Shumlyanskyy & Derevska (2001) used the Rb–Sr isochron method on three samples of basalt and one sample of footwall lava breccia taken from the same flow in the basal part of the Ratne suite. A regression line drawn through all four samples yielded 552 ± 59 Ma which was interpreted as the age of hydrothermal alteration. In fact, this regression line is essentially controlled by one point, a lava breccia that is heavily altered.

It must be noted that the whole Volyn continental flood basalt sequence, including dolerite intrusions, was subjected to a pervasive hydrothermal alteration that includes both massive percolation of fluids into rocks and more channelled veins filled with secondary minerals that include among others analcite, zeolites, silica minerals, chlorite, calcite and native copper. The timing of this alteration is not well established. The general idea is that it developed immediately after eruption due to penetration of volcanic-derived fluids into still hot rocks. However, a developed horizontal zonation of secondary mineral assemblages indicates alteration during the basinal stage of evolution, at which the flood basalt sequence was buried under thick sedimentary cover and subjected to influence of the heated basin waters. In this case, alteration may have occurred several tens of millions of years after eruption. Finally, this area was affected by severe heating during the Devonian development of the Prypyat branch of the Prypyat–Dnieper–Donets palaeorift. Some mineral assemblages may have developed in response to this process.

6. Analytical methods and sampling

Our primary intention was to refine the time of eruption of mafic and felsic rocks of the Volyn province using U–Pb SIMS technique on zircons and TIMS multigrain dating on baddeleyite. Our samples belong to the basalts that represent the Ratne suite (Fig. 1). In total, zircons were separated from 8 basalt samples (Table 1) of which one represents a high-Ti (upper part of the suite), while the rest of samples represent low-Ti (lower part of the suite) varieties of the Ratne basalts. In addition, we analysed zircons separated from three samples and baddeleyites isolated from one sample that represent dolerite (sill-like) bodies found among Polissya sandstones beneath the Volyn Series (Tables 2 and 3). In all cases, zircon yield was very low, generally only a

few grains were recovered from samples varying in weight from few to over 100 kg. Most of them were dated in this study.

A rhyolitic dacite flow, recovered from a drill hole in Belarus (1c at 1108–1157 m depth), that represents a rare suite of felsic rocks locally present in the Brest depression and stratigraphically occurring between the low- and high-Ti Ratne basalts was also studied (Table 4). This drill core specimen yielded much more zircons – over 100 grains, some of which were analysed in course of this study.

Individual zircon grains separated from basaltic and dolerite samples were analysed at the Swedish Museum of Natural History. Such crystals were mounted in epoxy along with the 91500 standard zircon (Wiedenbeck et al. 1995) and then sectioned and polished to approximately half of their thickness. Polished grains were investigated with a Hitachi SEM equipped with a CL detector. Obtained images were used for choosing areas suitable for U–Pb dating. U–Th–Pb geochronological data were obtained using the Cameca 1270 ion microprobe at the NORDSIM facility. The determinations of the Pb/U ratio, element concentration and calibration of the Th/U ratio were performed relative to the Geostandard zircon 91500. The analytical method follows that described by Whitehouse & Kamber (2005). The common lead correction, when needed, was made using the measured ^{204}Pb signal and modern Pb isotope composition (Stacey & Kramers 1975). Data reduction employed Excel macros developed by M.J. Whitehouse.

The U–Pb analysis of zircons separated from the rhyolitic dacite was conducted using the ion microprobe SHRIMP-II in the Center for Isotopic Studies (VSEGEI, St. Petersburg, Russia) following routines described in Rodionov et al. (2012). The Pb/U values were normalized to the ratio of 0.0665 for $^{206}\text{Pb}/^{238}\text{U}$ in the zircon standard TEMORA, which corresponds to an age of 416.7 ± 1.30 Ma (2σ) (Black et al. 2003).

The baddeleyite-bearing sample 68/147–154 was processed at the Department of Geology at Lund University, following the standard procedures of Söderlund & Johansson (2002). Extracted baddeleyite grains are up to 50 μm in length and moderately brown. Approximately 40 grains in total were recovered from ca 150 g of sample. A total of 5–10 grains were combined in each fraction and the grains were transferred into a Teflon dissolution capsule using a handmade micropipette. The grains were washed in several steps, including a wash in 3 N HNO_3 on hotplate for ca. 30 min. Each fraction was spiked with a ^{205}Pb – ^{233}U – ^{236}U isotopic tracer solution. The grains were dissolved in a 10:1 HF:HNO₃ at 190 °C for 3 days and then evaporated on a hot plate at 100 °C.

The fractions were dissolved in 10 drops of 6 N HCl and 1 drop of 0.25 N H_3PO_4 acid and then dried down on a hot plate at 90 °C. The sample was re-dissolved in 1.8 μl of silica gel and loaded on outgassed Re single filaments. Uranium and Pb isotopic ratios were measured on a TIMS Finnigan Triton mass spectrometer at the Museum of Natural History in Stockholm, Sweden. The U and Pb isotopic composition were analysed using a Secondary Electron Multiplier (SEM) equipped with RPQ in the peak-switching mode. The procedural total blank was estimated to be 0.5 pg for Pb and 0.05 pg for U. The decay constants are those from Jaffrey et al. (1971), and the initial common lead composition was based on the terrestrial model of Stacey & Kramers (1975) at the age of the sample. All age errors are given at the 95% confidence level. U–Pb concordia plots and age calculations were made using ISOPLOT version 3.75 of Ludwig (2012).

Table 1. Results of SIMS U-Pb dating of zircons from basaltic samples.

Ana-lysis	Isotopic ratios					Concentration, ppm					Age, Ma $\pm \sigma$				
	$^{207}\text{Pb}/^{206}\text{Pb}$ $\pm\sigma, (\%)$	$^{207}\text{Pb}/^{235}\text{U}$ $\pm\sigma, (\%)$	$^{206}\text{Pb}/^{238}\text{U}$ $\pm\sigma, (\%)$	r	$^{206}\text{Pb}/^{204}\text{Pb}$ f206(%)	U	Th	Pb	$^{207}\text{Pb}/^{206}\text{Pb}$	$^{207}\text{Pb}/^{235}\text{U}$	$^{206}\text{Pb}/^{238}\text{U}$	Disc., %			
1	0.0587	1.3	2.6	0.0936	2.3	0.87	12158	0.15	363	481	49.6	554 $\pm$ 27	572 $\pm$ 12	577 $\pm$ 13	4.2
2	0.0552	2.1	3.1	0.0900	2.3	0.73	6544	0.29	192	168	22.7	418 $\pm$ 46	530 $\pm$ 13	556 $\pm$ 12	34.3
3	0.0579	1.3	2.6	0.0926	2.3	0.87	11024	0.17	242	243	30.4	526 $\pm$ 28	562 $\pm$ 11	572 $\pm$ 13	8.8
4	0.0591	1.3	2.6	0.0929	2.3	0.87	148356	0.01	330	386	43.4	570 $\pm$ 28	572 $\pm$ 12	573 $\pm$ 13	0.6
5	0.0592	2.5	3.3	0.0824	2.2	0.66	4874	0.38	101	122	12.0	575 $\pm$ 54	523 $\pm$ 14	511 $\pm$ 11	-11.6
6	0.0604	3.1	3.8	0.0806	2.2	0.58	5134	0.36	89.2	154	11.7	618 $\pm$ 65	522 $\pm$ 16	500 $\pm$ 11	-19.9
7	0.0573	3.3	3.9	0.0824	2.2	0.55	5266	0.36	133	193	16.4	502 $\pm$ 71	509 $\pm$ 16	510 $\pm$ 11	1.7
8	0.0576	2.1	3.0	0.0831	2.2	0.71	>10 ⁶	0.00	138	195	17.3	516 $\pm$ 46	515 $\pm$ 12	515 $\pm$ 11	-0.3
9	0.0915	1.7	2.8	0.2548	2.2	0.78	3496	0.53	103	159	40.2	1456 $\pm$ 33	1460 $\pm$ 22	1463 $\pm$ 29	0.5
10	0.0940	1.7	2.7	0.2313	2.1	0.78	4581	0.41	51.6	40.6	15.9	1509 $\pm$ 32	1407 $\pm$ 21	1341 $\pm$ 26	-12.3
11	0.1246	0.9	3.6	0.3385	3.5	0.97	32392	0.06	172	65.1	71.9	2023 $\pm$ 15	1949 $\pm$ 32	1879 $\pm$ 58	-8.2
12	0.1206	0.9	2.3	0.2845	2.1	0.91	154644	0.01	183	64.0	64.2	1966 $\pm$ 17	1773 $\pm$ 20	1614 $\pm$ 30	-20.2
13	0.1096	0.8	3.6	0.2998	3.5	0.97	17554	0.11	218	20.8	74.0	1793 $\pm$ 15	1737 $\pm$ 31	1690 $\pm$ 53	-6.5
14	0.1112	0.9	2.3	0.2503	2.1	0.92	7651	0.24	200	15.1	57.0	1820 $\pm$ 16	1601 $\pm$ 19	1440 $\pm$ 28	-23.3
15	0.1064	0.5	3.6	0.1877	3.5	0.99	2641	0.71	3010	630	661	1739 $\pm$ 9	1343 $\pm$ 27	1109 $\pm$ 36	-39.4
16	0.1209	0.4	2.2	0.3543	2.1	0.99	10986	0.17	1624	1074	763	1969 $\pm$ 6	1962 $\pm$ 19	1955 $\pm$ 36	-0.8
17	0.0918	1.2	2.4	0.2632	2.1	0.88	8805	0.21	129	149	48.8	1462 $\pm$ 22	1488 $\pm$ 19	1506 $\pm$ 29	3.3
18	0.0914	1.9	2.8	0.2631	2.1	0.75	6719	0.28	44.1	48.8	16.6	1456 $\pm$ 35	1485 $\pm$ 22	1506 $\pm$ 29	3.9
19	0.0952	1.4	2.6	0.2216	2.1	0.83	30283	0.06	87.3	80.6	27.1	1532 $\pm$ 27	1384 $\pm$ 20	1290 $\pm$ 25	-17.4
20	0.1127	0.9	2.3	0.2998	2.1	0.93	36214	0.05	271	98.9	98.8	1844 $\pm$ 15	1760 $\pm$ 19	1690 $\pm$ 32	-7.2
21	0.1112	0.5	2.2	0.3028	2.1	0.97	41328	0.05	683	227	249	1820 $\pm$ 9	1757 $\pm$ 19	1705 $\pm$ 32	-9.4
22	0.0934	2.1	3.0	0.2280	2.1	0.71	7950	0.24	71.6	80.6	23.0	1495 $\pm$ 39	1391 $\pm$ 23	1324 $\pm$ 26	-12.7
23	0.1122	1.7	2.7	0.2847	2.1	0.78	5818	0.32	92.0	140	40.7	1836 $\pm$ 30	1713 $\pm$ 23	1615 $\pm$ 30	-13.6

Initial common Pb corrected with isotopic compositions from the model of Stacey & Kramers (1975) at the age of the sample.

Table 2. Results of SIMS U–Pb dating of zircons separated from dolerite samples.

Analysis	Isotopic ratios								Concentration, ppm				Age, Ma			
	$^{207}\text{Pb}/^{206}\text{Pb}$	$\pm s, (\%)$	$^{207}\text{Pb}/^{235}\text{U}$	$\pm s, (\%)$	$^{206}\text{Pb}/^{238}\text{U}$	$\pm s, (\%)$	r	$^{206}\text{Pb}/^{204}\text{Pb}$	$t_{206}(\%)$	U	Th	Pb	$^{207}\text{Pb}/^{206}\text{Pb}$	$^{207}\text{Pb}/^{235}\text{U}$	$^{206}\text{Pb}/^{238}\text{U}$	Disc., %
Sample 955/17																
1	0.0834	0.7	2.015	2.4	0.1752	2.3	0.96	6875	0.27	224	130	49.5	1279 $\pm$ 13	1121 $\pm$ 17	1041 $\pm$ 22	−20.1
Sample 955/14																
2	0.0839	1.2	2.547	2.6	0.2200	2.3	0.88	2767	0.68	104	77.2	29.4	1291 $\pm$ 24	1285 $\pm$ 19	1282 $\pm$ 27	−0.8
Sample 954–3																
3	0.1004	0.4	4.409	2.3	0.3186	2.3	0.98	54729	0.03	274	453	143	1631 $\pm$ 8	1714 $\pm$ 19	1783 $\pm$ 36	10.7
4	0.0811	0.7	2.249	2.4	0.2013	2.3	0.96	100653	0.02	171	67.9	41.7	1223 $\pm$ 13	1197 $\pm$ 17	1182 $\pm$ 25	−3.6
5	0.1624	0.7	5.111	2.4	0.2283	2.3	0.95	586	3.19	877	504	261	2480 $\pm$ 12	1838 $\pm$ 21	1326 $\pm$ 27	−51.3
6	0.0957	0.8	3.495	2.4	0.2650	2.3	0.95	104390	0.02	187	49.6	58.6	1541 $\pm$ 14	1526 $\pm$ 19	1515 $\pm$ 31	−1.9
Sample 60/1																
7	0.1079	0.6	4.602	1.6	0.3092	1.4	0.91	35478	0.05	61.6	49.9	25.3	1765 $\pm$ 12	1750 $\pm$ 13	1737 $\pm$ 22	−1.8
8	0.1204	1.9	3.640	7.7	0.2192	7.5	0.96	970	1.93	358	106	99.0	1963 $\pm$ 34	1558 $\pm$ 64	1278 $\pm$ 88	−38.4

Initial common Pb corrected with isotopic compositions from the model of Stacey & Kramers (1975) at the age of the sample.

Table 3. Results of U–Pb dating of baddeleyite from olivine dolerite, sample 68/147–154.

Analysis no. (# of grains)	U/Th	Pbc/Pbtot ^a	Isotope ratios				Age, Ma							
			$^{206}\text{Pb}/^{204}\text{Pb}$	$^{207}\text{Pb}/^{235}\text{U}$	$\pm 2 \sigma, \%$	$^{206}\text{Pb}/^{238}\text{U}$	$\pm 2 \sigma, \%$	$^{207}\text{Pb}/^{235}\text{U}$	$\pm 2 \sigma$	$^{206}\text{Pb}/^{238}\text{U}$	$\pm 2 \sigma$			
			raw ^b	corr ^c										
1 (5 grains)	8.4	0.857	88.3	0.8220	12.92	0.10452	18.38	609.1	59.2	640.8	112.1	492.9	281.6	1.300
2 (7 grains)	3.6	0.841	40.9	0.8434	5.96	0.10221	4.24	621.0	27.7	627.4	25.4	596.2	96.9	1.052
3 (10 grains)	5.0	0.537	102	0.7839	6.34	0.10165	4.17	587.7	28.3	624.1	24.8	449.5	107.4	1.388

Initial common Pb corrected with isotopic compositions from the model of Stacey & Kramers (1975) at the age of the sample.

^aPbc = common Pb, Pbtot = total Pb (radiogenic + blank + initial).^bmeasured ratio, corrected for fractionation and spike.^cisotopic ratios corrected for fractionation (0.1 % per amu for Pb), spike contribution, blank (0.5 pg Pb and 0.05 pg U) and initial common Pb.

Table 4. Results of SIMS U–Pb dating of zircons separated from a rhyolitic dacite, sample 1c (Skveriki drill hole).

Analysis	Isotopic ratios							Concentrations, ppm			Age, Ma	
	²⁰⁷ Pb/ ²⁰⁶ Pb	±s, (%)	²⁰⁷ Pb/ ²³⁵ U	±s, (%)	²⁰⁶ Pb/ ²³⁸ U	±s, (%)	r	U	Th	Pb	²⁰⁷ Pb/ ²⁰⁶ Pb	²⁰⁶ Pb/ ²³⁸ U
1C.3.1*	0.0582	1.4	0.700	2.1	0.0873	1.6	0.75	665	314	49.9	539 ± 8	540 ± 8
1C.3.1	0.0559	5.4	0.699	5.7	0.0906	1.9	0.33	88	102	6.9	448 ± 24	559 ± 10
1C.10.1	0.0568	9.4	0.722	9.7	0.0923	2.1	0.22	45	47	3.6	484 ± 45	569 ± 12
1C.7.1	0.0542	13.0	0.693	13.0	0.0927	2.4	0.19	44	46	3.6	380 ± 49	571 ± 13
1C.8.1	0.0572	9.3	0.734	9.5	0.0929	2.0	0.21	66	59	5.3	500 ± 47	573 ± 11
1C.5.1	0.1597	1.6	5.960	2.3	0.2705	1.5	0.68	949	1118	221	2453 ± 28	1543 ± 21
1C.11.1	0.1058	2.3	4.390	3.0	0.3006	1.9	0.65	56	6	14.5	1729 ± 42	1694 ± 29
1C.1.1	0.1186	1.1	5.007	2.0	0.3063	1.6	0.82	170	99	44.7	1934 ± 20	1723 ± 25
1C.2.1	0.1125	0.8	4.859	1.8	0.3133	1.6	0.90	611	467	164	1840 ± 14	1757 ± 25
1C.5.1*	0.1772	0.5	7.680	1.6	0.3141	1.5	0.95	531	605	144	2627± 9	1761 ± 24
1C.4.1	0.1145	0.9	5.241	1.9	0.3320	1.6	0.88	350	268	100	1872± 16	1848 ± 26
1C.6.1	0.1809	0.9	12.000	1.8	0.4812	1.5	0.87	467	197	193	2661 ± 14	2532 ± 32

Fig. 4. Results of U–Pb ion probe analyses of zircons separated from the rocks of the Volyn flood basalt province. **A.** Concordia diagram giving an overview of the obtained results. Black filled symbols signify zircons from basalts, grey symbols are zircons from dolerites, and black unfilled symbols are zircons from a rhyolitic dacite. **B.** Tera–Wasserburg diagram showing data for zircons from the high-Ti basalt sample 5881/61, 5-63 (black symbols), and for zircons from the rhyolitic dacite sample 1c (grey symbols). **C.** Detailed concordia diagram for zircons formed at c. 1.5, 1.8 and 2.0 Ga (symbols as in A).

7. Isotope age data and zircon characteristics

7.1. U–Pb dating of zircons isolated from basaltic samples

The zircons separated from Ratne basalts can be divided into four principle groups according to their $^{207}\text{Pb}/^{206}\text{Pb}$ dates, suggesting crystallization at about 550–570, 1470, 1820 and 2050 Ma (Fig. 4(A)).

7.1.1. High-Ti basalt. All the zircons yielding a Vendian age (Fig. 4(B)) were from the high-Ti basalt sampled in drill hole 5881. These zircons vary in size from 70×120 – 150 to $150 \times 350 \mu\text{m}$ and occur as pink (sometimes almost colourless), euhedral, prismatic grains with very well-developed prism facets and reduced pyramidal ones. The latter can be entirely lacking. All of the studied crystals contain small rounded inclusions and display oscillatory rhythmical zoning (Fig. 5). Small cores are present in some grains. Sector zoning is a very characteristic feature for some of the crystals. Eight U–Pb analyses were performed on seven grains (Table 1, Figs. 4(B) and 5), and six of these analyses yielded concordant or nearly concordant results. Unfortunately, obtained results do not allow unequivocal interpretation of the age of crystallization of this rock as a regression comprising four of the analyses yields an upper intercept age of 577 ± 22 Ma, whereas a regression constructed for the rest four analyses indicates an age of 513 ± 15 Ma. We interpret these younger ages as those that have suffered from the recent Pb-loss (Fig. 4(B)). The weighted average $^{206}\text{Pb}/^{238}\text{U}$ age for the three older crystals is 573 ± 14 Ma (MSWD = 0.06). We accept this age as the most probable time of crystallization of the high-Ti basalt.

7.1.2. Low-Ti basalts. Zircons separated from seven low-Ti basalt samples yielded ages much older than c. 570 Ma (Table 1), which clearly must represent the presence of zircon xenocrysts in these samples. Several analyses group at c. 1470 Ma (Fig. 4(C)). These zircons possess an elongated prismatic habit and rather poorly developed pyramid facets. Crystal apices are often rounded, probably indicating some resorption. Mineral inclusions are common. Zoning is prism-parallel or concentric with distinctive cores (cores were not analysed). All analysed crystals are characterized by rather low and variable concentrations of U (44–129 ppm) and Th (49–159 ppm). The analysed points may be approximated by a regression line that intersects the concordia at 1467 ± 23 Ma with a lower intercept at -812 ± 890 Ma. There are no known magmatic or metamorphic rocks of this age directly underlying the Volyn continental flood basalt province. However, rocks of such age are common in north-eastern Poland and Lithuania where they belong to the Mazury anorthosite–mangerite–charnokite–granite complex (Skridlaite et al. 2006; Wiszniewska et al. 2007).

Another group of morphologically distinct zircons was formed at about 1820 Ma. These appear as elongated prismatic grains with well-developed prismatic facets and poor pyramids.

Fig. 5. A selection of CL images of zircons separated from the high-Ti basalt sample 5881/61, 5–63. Numbers correspond to analyse # in Table 1 and $^{206}\text{Pb}/^{238}\text{U}$ age in Ma.

Distinct cores and complex prismatic zoning can often be seen. Crystals are grey or very light pinkish. In the concordia diagram, the age of rims of this group can be approximated by a discordia indicating an upper intercept age at 1819 ± 51 Ma, with a lower intercept at ca. 0 Ma (Fig. 4(C)).

Two zircon grains separated from the low-Ti basalts (samples 5905/20.5–29.7 and 5878/117.2) of the Volyn province yielded even older ages (Fig. 4(A)). One of them is translucent, white-pinkish, clearly zoned and yielded a $^{207}\text{Pb}/^{206}\text{Pb}$ age of 2023 ± 15 Ma for the core portion, while the mantle formed at 1793 ± 15 Ma. The second crystal is grey, euhedral, slightly zoned with a large homogeneous core and a thin mantle. In contrast to the external habit, the core is rounded. In spite of very high concentrations of U (1624 ppm), Th (1074 ppm) and Pb (763 ppm), the core yielded a concordant ($^{207}\text{Pb}/^{206}\text{Pb}$) age at 1969 ± 6 Ma.

7.2. U–Pb dating of zircons isolated from dolerite samples

Zircons were separated from four dolerite samples (60/1, 954–3, 955/14 and 955/17) that represent numerous sheet-like intrusive bodies located immediately beneath the Volyn flood basalt sequence. Zircons from dolerites are usually fine (0.1–0.15 mm and less) and variable in terms of their external appearance and internal texture. Eight grains were analysed (Table 2); six of them yielded concordant to nearly concordant results and their approximate $^{207}\text{Pb}/^{206}\text{Pb}$ ages are as follows: 1.76, 1.63, 1.54, 1.29 and 1.22 Ga. The two discordant analyses indicate even older ages, one of them possibly Archaean.

Fig. 6. Concordia diagram for baddeleyite from the olivine dolerite sample 68/147-154.

7.3. U–Pb dating of baddeleyite isolated from dolerite sample

The three multigrain fractions of baddeleyite from sample 68/147-154 all yielded nearly concordant results (Table 3). Unfortunately, due to the small amount of material (low radiogenic/common lead ratios) and low signal intensities, the precision of measurements is poor. The $^{207}\text{Pb}/^{206}\text{Pb}$ weighted average is 567 ± 61 Ma (MSWD = 0.51), whereas the $^{206}\text{Pb}/^{238}\text{U}$ weighted average is 626 ± 17 Ma (MSWD = 0.05, Fig. 6).

7.4. U–Pb dating of zircons isolated from a rhyolitic dacite

A rather small sample (<3 kg, sample 1c) yielded about 100 zircon grains which are variable with respect to appearance and age. According to their characteristics, grains were subdivided into four groups.

The first group comprises about 70% of all zircon grains that appear as prismatic colourless crystals with well-developed facets. These can be either homogeneous or contain poorly distinguishable cores. Some of them contain inclusions. Two morphological sub-groups of zircons of this type were recognized, and both groups display well-developed magmatic zoning (Fig. 7) and high Th/U ratios (0.9–1.2), suggesting a magmatic origin: (a) fine (0.1–0.2 mm) short to moderately elongated prismatic grains with an aspect ratio of about 1.5. Pyramidal facets are well developed, edges are somewhat smoothed. Some of the grains are slightly resorbed; (b) larger (0.2–0.4 mm) elongated prismatic crystals with an aspect ratio up to 4. These are well-formed, with sharp edges and smooth facets, transparent, colourless, with rare inclusions. The weighted average $^{206}\text{Pb}/^{238}\text{U}$ age for four of five analysed zircon grains from this group is 567 ± 11 Ma; the fifth grain is somewhat younger with $^{206}\text{Pb}/^{238}\text{U} = 540 \pm 8$ Ma (Table 4).

The second main group of magmatic zircons embraces two morphological varieties which together represent up to 20% of the sample. The first variety includes large (up to 0.4 mm) resorbed colourless, transparent crystals. CL imaging demonstrates

Fig. 7. A selection of CL images of the young igneous population of zircons separated from a rhyolitic dacite sample. Numbers correspond to analyse # in Table 4 and $^{206}\text{Pb}/^{238}\text{U}$ age in Ma.

the presence of inherited cores with rough sector zoning rimmed by mantles with fine oscillatory zoning. One analysis obtained for the core portion of grain 1C.1.1 is discordant (12%); its $^{207}\text{Pb}/^{206}\text{Pb}$ age is 1934 ± 20 Ma. Concentrations of U and Th in the core are moderate, while the Th/U ratio is rather high (0.58). The second variety contains fine (0.15–0.20 mm) moderately elongated (aspect ratio ca. 2.0–2.5) semitransparent, yellowish-grey grains with smoothed edges and resorbed surfaces. These crystals possess a rough rhythmical zoning, high Th and U concentrations and a high (0.77) Th/U ratio. Two analyses (1C.2.1 and 1C.4.1) are slightly discordant and yield an upper intercept age of 1853 ± 20 Ma.

Zircons of a probable metamorphic origin constitute the third group and are represented by fine (0.1–0.2 mm) short-prismatic (isometric) grains with smoothed edges and perfect facets, transparent, pinky and visually homogeneous. CL imaging demonstrates a pattern which is typical for granulitic zircons: a contrast rough zoning with a wide, light-grey low-U mantle around a dark core. Both core and mantle are characterized by a low Th concentration and low Th/U ratio (0.10). The $^{207}\text{Pb}/^{206}\text{Pb}$ age of the single measured grain (1C.11.1) is 1729 ± 42 Ma (Fig. 4).

A few zircons of the fourth group occur as semi-transparent, brownish short-prismatic grains with well-defined edges and smooth facets. One of the analysed crystals (1C.6.1) yielded a near-concordant result with a $^{207}\text{Pb}/^{206}\text{Pb}$ age of 2661 ± 14 Ma. Regression line constructed through this crystal and two other grains (1C.5.1* and 1C.5.1) intersects the concordia at 2664 ± 32 Ma.

8. Discussion

8.1. Age of eruption

The samples analysed in this study represent magmatic lithologies (basalts and dolerites) of the Volyn series in Ukraine as well as a rhyolitic dacite from Belarus occupying a nearly equal stratigraphical position, which is roughly constrained to the Late

Fig. 8. Distribution of $^{207}\text{Pb}/^{206}\text{Pb}$ ages of zircons from rocks of the Volyn flood basalt province and from the Polissya sandstone. The raw data for the Polissya sandstone can be found in Shumlyanskyy et al. 2015.

Precambrian. However, a significant number of xenocrystic zircons with a wide range of Precambrian to Archaean ages were also found. Except for data from the high-Ti basalt, it appears that whenever several analyses are available from a single rock, such data reflect a number of different age populations. Obviously, inheritance is an important process to consider and it remains to be proven if any of the obtained younger ages corresponds to the time of rock eruption as there is no reliable way to distinguish xenocrystic from syn-genetic zircons. Hence, even youngest ages obtained for zircons in this study may belong to the xenocrysts.

Both the stratigraphic and tectonic position of the Volyn flood basalts clearly suggest an Ediacaran age of this magmatic province. Although less conclusive, available results from K–Ar, Ar–Ar and Rb–Sr dating are consistent with such an interpretation. The U–Pb zircon results obtained by Compston et al. (1995) for the uppermost tuffs (551 ± 4 Ma) in eastern Poland can be regarded as the most well-founded published ages. However, it is unclear to which degree this age is applicable to effusive rocks of other parts of the province. The studied rocks are unmetamorphosed, and although we have tried to sample as fresh rocks as possible, the lithologies have suffered post-crystallization hydrothermal alteration, and therefore, some disturbances of the U–Pb system in zircon cannot be ruled out.

Our new U–Pb data for young populations of zircons separated from the high-Ti basalt are somewhat confusing and

apparently indicate different processes separated in time by some 60 Myrs. Such a long period of time is unlikely to reflect the duration of the outpouring of the sampled basaltic flow, and also greatly exceeds the duration of the typical igneous pulse (~1–5 Myrs) that normally leads to the formation of the main portion of large igneous provinces (Bryan & Ernst 2008). Of the two indicated ages, the c. 570 Ma zircons in basalt and rhyolitic dacite could be inherited, and in this case, the real age of eruption is represented by c. 510 Ma zircons. However, a 510 Ma age appears to be too young and contradicts the stratigraphic and tectonic evidence which clearly argue for a Late Precambrian age. Although it cannot be completely ruled out that zircons yielding the 570 Ma age also are inherited, we believe that the fact that these originate from the least contaminated variety of the Volynian basalt (the high-Ti basalt) would argue for that assimilation of older crustal components is minimal or non-existing. Moreover, zircons, seemingly of a magmatic origin in the rhyolitic dacite, support that magmatism occurred in the 560–570 Ma interval. Thus, our preferred interpretation is that a ~ 570 Ma age represents the time of eruption of both high-Ti basalts and rhyolitic dacite. Following this, 510 Ma old zircons in the basalt probably represent a post-effusive stage of hydrothermal alteration, although no obvious support for this assumption is given by CL or morphological evidence.

Baddeleyite, unlike zircon, cannot be of xenocrystic or metamorphic origins (unless extreme conditions) why baddeleyite is often preferred over zircon for dating the crystallization of silica-undersaturated rocks. Unfortunately, the three analysed baddeleyite fractions do not allow for a definite interpretation of the age of sample 68/147-154. The $^{207}\text{Pb}/^{206}\text{Pb}$ weighted average age of 567 ± 61 Ma is close to the zircon ages dating the time of eruption of basalts and felsic volcanites. However, the $^{206}\text{Pb}/^{238}\text{U}$ weighted average of 626 ± 17 Ma is a more precise estimate. Both estimates provide acceptable MSWD values (below 1) and are marginally overlapping. We conclude that this sample must have crystallized roughly at 600 Ma and that additional analyses, or datings of samples with a higher amount of baddeleyite from structurally coeval units, are required to better constrain the crystallization age. Further efforts to date other basaltic and dolerite samples and alteration mineral parageneses are required for a more thorough understanding of age relationships and of evolution of this province as a whole.

8.2. Possible sources of old xenocrystic zircons

As has been noted above, zircons from rocks of the Volyn flood basalt province can be divided into several groups according to their $^{207}\text{Pb}/^{206}\text{Pb}$ ages (Fig. 8). The zircon population yielding ca. 570 Ma is likely to represent the age of the eruption. Thus, the fact that much older zircons are present in the Volyn province suggests that alien crystals were inherited from the source region during magma-forming process or assimilated from the wall rocks during magma ascent.

Although data are relatively few and have yielded scattered ages, it is nevertheless possible to discuss potential sources for xenocrystic zircons. The thick sedimentary sequence of the Polissya Series that represents a huge reservoir of zircons must be considered as a possible source of detrital zircons that can be captured by the mafic magma during its ascent to the surface. However, we consider such a scenario as less likely. Polissya sediments are rather loose rocks that were probably penetrated by

ascending magmas quite quickly. Tentatively, on the other hand, their loose nature would favour a tendency for being captured and assimilated by the melts. However, Polissya sands contain up to 80–85% of SiO₂ but silica enrichment has never been noted in the studied basalts which would argue against such a hypothesis. Moreover, the distribution of ages of zircons separated from the Polissya sandstones (Shumlyanskyy et al. 2015) is somewhat different from that typical for the Volyn continental flood basalts. For instance, Polissya rocks contain predominantly zircons of two age intervals – 1200–1600 and 1800–2000 Ma. Although there are distinct ²⁰⁷Pb/²⁰⁶Pb peaks at 1470 and 1820 Ma in our analytical data, the c. 1620 Ma peak is not characteristic for the sandstones (Fig. 8). Moreover, zircons aged between 1450 and 1200 Ma are rare in the Volyn basalts but are very abundant in the Polissya sediments.

If the Polissya sediments constitute a less likely source for old zircons in the studied rocks, it follows that more deep-seated rocks supplied at least the vast majority of xenocrystic zircons. For instance, the older groups (ca. 1820 and 2050 Ma) of zircons may have been extracted from basement rocks that immediately underlie the Volyn province. Zircon ages at ca. 1820 Ma correspond roughly to the time of formation of the Baltic-Belarus granulite belt and the collision of Sarmatia and Fennoscandia (Bogdanova et al. 2001; Claesson et al. 2001; Elming et al. 2010), while a 2050 Ma age corresponds to the time when a major part of the Zhytomyr Complex granites was formed (Scherbak et al. 2008). However, a significant portion of the analysed zircons is much younger (ca. 1470 Ma). Appropriate rocks with ages ≤ 1500 Ma are absent beneath the Volyn flood basalt province; however, such rocks are widely distributed north-westwards of the study area where these are represented by anorthosite–mangerite–charnokite–granite complexes, e.g. the 1.45–1.54 Ga old Mazury complex, see Fig. 2 (Skridlaite et al. 2006; Wisniewska et al. 2007).

Yet another possibility is that xenocrystic zircons were derived from the Amazonia craton that in the Neoproterozoic time was conjuncted to Baltica across the TESZ and was rifted away during the Vendian (see below). An overview of the ages obtained for the south-western part of the Amazonia (Teixeira et al. 2015) clearly indicates that Amazonia could represent an important source of Neoproterozoic zircons, both for the Polissya Series sediments and for the Volyn flood basalts. However, as the exact position of the Amazonia relative to Baltica remains unknown this complicates an assessment about the possible role of Amazonia as a source of detrital (and xenocrystic) zircons found in the western part of the East European craton.

8.3. Volyn flood basalt province in the context of Rodinia break-up

There is a general consensus that Baltica existed as a part of the supercontinent known as Rodinia in the Late Proterozoic times. A wide range of reconstructions of the position of Baltica in relation to neighbouring continents, Laurentia and Amazonia, has been proposed. These include the work presented by Li et al. (2008) and Johansson (2009), in which the western margin of Baltica is located in front of Amazonia. A model for the break-up of these three continental masses was presented by Bingen et al. (1998) who considered a two-stage separation of (1) Baltica from Laurentia at 615–590 Ma and (2) break-up of all three continental masses at ca. 565–550 Ma.

Relevant ages to consider in this context include precise U–Pb dates of baddeleyite separated from the Egersund dykes in Norway, located along the TESZ, yielded an age of 616 ± 3 Ma (Bingen et al. 1998), while the zircon age for the Sarek Dyke Swarm, northern Swedish Caledonides is 608 ± 1 Ma (Svenningsen 2001). In general, the majority of dates obtained by different methods (U–Pb of zircon and baddeleyite; whole-rock Sm–Nd and Rb–Sr isochrones) for mafic intrusions of the Baltoscandian margin fall into the interval 615–590 Ma (Andréasson et al. 1998; Bingen et al. 1998; Svenningsen 2001).

The emplacement of the Egersund and Sarek dykes closely corresponds to the ages of the Long Range swarm of Labrador that was formed at 615 ± 2 Ma (Kamo et al. 1989). Puffer (2002) considered a large body of dates related to mafic intrusions of the eastern Laurentia and divided the occurrences of mafic magmatism in this area into two groups: (1) the Mid-Vendian flood basalt group that was formed between 615 and 564 Ma and (2) the Late-Vendian (LOIB) group formed between 554 and 550 Ma. The latter group is particularly well-defined and embraces 13 occurrences of mafic volcanism. While the Mid-Vendian group of Puffer (2002), in general, corresponds to the first stage of separation of Baltica from Laurentia defined by Bingen et al. (1998), the Late-Vendian group is synchronous with the final break-up of the three continental masses. These circumstances suggest that the eastern Laurentia Late-Vendian group of Puffer (2002) was related to the ocean opening between Laurentia and Amazonia.

It has been repeatedly shown that the break-up of the Rodinia supercontinent was a complex and prolonged process that lasted about 275 Myrs, from 825 to 550 Ma (see Li et al. 2008, and references therein). The above given examples of palaeotectonic reconstructions of the Baltica–Laurentia–Amazonia configuration allow the recognition of the three arms of the rift system that led to the continental break-up. From geochronological data, it is evident that one of the arms was active at 615–590 Ma (and probably also somewhat later) and connected with the formation of the Iapetus Ocean. The formation of the Egersund dykes (616 ± 3 Ma) during this time interval probably signifies the initiation of the separation of Baltica and Amazonia. Two other arms that separated Amazonia from both Baltica and Fennoscandia, as evident from our new data, were active at c. 620–570 Ma, i.e. simultaneously with the separation of Baltica and Amazonia.

9. Conclusions

The Volyn flood basalt province occurs on the western margin of the East European platform and is clearly confined to the TESZ. Volcanogenic rocks of the province rest upon Neoproterozoic sediments or directly on the Palaeoproterozoic basement that in this area is represented by a transition zone between two segments of the East European craton – Sarmatia and Fennoscandia. Volyn flood basalts, in turn, are overlain by Late Vendian and Early Palaeozoic sediments that accumulated in a regime of a subsided passive continental margin.

Ion microprobe dating was carried out on texturally quite complex zircons separated from basaltic, doleritic and rhyolitic dacite samples. Magmatic zircons separated from one high-Ti basalt sample yielded an age of 573 ± 14 Ma, whereas grains isolated from a rhyolitic dacite yielded 571 ± 13 Ma. Baddeleyite from the olivine dolerite sample gave an older ²⁰⁶Pb/²³⁸U age of 626 ± 17 Ma, whereas the ²⁰⁷Pb/²⁰⁶Pb weighted average age of

567 ± 61 Ma is close to the zircon ages. These ages constrain the age of the province to c. 570 Ma. Other low-Ti basaltic samples, dolerites and a rhyolitic dacite contain much older zircons that crystallized at c. 1290, 1470, 1820–1860, 1930–2050 and 2660 Ma. Ages in between 1820–1860 and 1930–2050 Ma correspond to the ages of the Precambrian basement that underlies the Volyn flood basalt province. However, the source(s) for the 1290, 1470 and 2660 Ma zircons is unknown and must be derived from more distal sites.

Acknowledgments The first author acknowledges financial support from the Swedish Institute (Svenska Institutet). We are grateful to S.M. Tsybmal, K.I. Derevska and geologists of the Rivne geological enterprise for providing samples. Martin Whitehouse, Lev Ilyinski and Kerstin Lindén are thanked for their assistance at the NORDSIM facility. The NORDSIM facility is operated under an agreement between the research funding agencies of Denmark, Norway, Iceland and Sweden, and the Geological Survey of Finland and the Swedish Museum of Natural History. This article is NORDSIM contribution number 426. This is publication number 46 of the large igneous provinces – supercontinent reconstruction – resource exploration project (www.supercontinent.org; www.camiro.org/exploration/ongoing-projects). The manuscript benefitted greatly from careful reviews by two anonymous reviewers and Associate Editor Dr. Martin Klausen.

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