$^{207}\text{Pb}/^{206}\text{Pb}$ ages and Hf isotope composition of zircons from sedimentary rocks of the Ukrainian shield: crustal growth of the south-western part of East European craton from Archaean to Neoproterozoic

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The results of simultaneous LA-ICP-MS measurements of $^{207}\text{Pb}/^{206}\text{Pb}$ and Hf isotope ratios are reported for zircons separated from five Ukrainian shield sedimentary rocks: (1) c. 3.0 Ga quartzite of the Bug Series; (2) c. 2.0 Ga quartzite of the Topilnya Series; (3) c. 1.75 Ga quartzite of the Ovruch Series; (4) c. 1.2-1.0 Ga sandstone of the Polissya Series; and (5) c. 0.6 Ga conglomerate of the Volyn Series. The age-Hf isotope (ϵHf_T) data indicate four main crustal growth events at 3.75, 3.20-3.15, 2.2-2.0, and 1.5 Ga in the south-western part of the East European craton (EEC). An additional rather minor event could have place at 2.5-2.4 Ga. The oldest event is represented by enderbites of the Bug domain in the south-western part of the Ukrainian shield. The second crust-forming event occurred at c. 3.20-3.15 Ga and it is documented by detrital zircons separated from the Bug Series quartzite and metasediments of the Soroki greenstone belt, Azov domain. A small number of zircons with positive ϵHf_T values reveal some input of the juvenile material into the crust at 2.5-2.4 Ga, whereas the 2.2-2.0 Ga event is dominated by zircons with positive ϵHf_T values. The youngest event is represented by numerous zircons that crystallized at c. 1.5 Ga. The possible sources of these zircons are the rock complexes of the south-western part of the Fennoscandian shield.

1. Introduction

Combined Hf isotope and U-Pb dating of detrital zircons from clastic sedimentary rocks is a powerful tool for investigation of the sources of clastic rocks, i.e. their age and provenance, and for deciphering the evolution of the continental crust ([Stevenson and](#)

Patchett, 1990; Griffin et al., 2004, 2006; Condie et al., 2005; Pietranik et al., 2008). The time of formation of the continental crust, and the rate and regularity of juvenile input into the continental crust, and the evolution of the mantle composition remain the subjects of continuing debate (Armstrong, 1981; Allègre and Rousseau, 1984; Taylor and McLennan, 1985; Pietranik et al., 2008; Condie and Aster, 2010; Belousova et al., 2010; Dhuime et al., 2012; Hawkesworth et al., 2013; Andersen, 2014). Combined Hf isotope and U-Pb dating of zircons provide information not only about timing of the geological processes, but also about nature of these processes – the extent to which they involve “re-working” of the older continental crust or the input of a new mantle-derived material.

The EEC is one of the largest portions of the preserved continental crust formed in the Precambrian. It crops out in the Fennoscandian (or Baltic) and the Ukrainian shields, being buried under thick Phanerozoic cover in other areas. The EEC consists of three large crustal segments – Sarmatia in the south, Fennoscandia in the north, and Volgo-Uralia in the east (Fig. 1): these developed independently until their amalgamation in the Palaeoproterozoic (Bogdanova, 1993; Bogdanova et al., 2008). Sarmatia comprises the Ukrainian shield and the Voronezh crystalline massif separated by the Late Palaeozoic Dnieper-Donets Palaeorift. Sarmatia is a collage of terrains that was formed over 2 billion years from c. 3.8 to c. 1.7 Ga, and some of these terrains can be traced across the Dnieper-Donets Palaeorift (Shchipansky and Bogdanova, 1996). In the Neoproterozoic, the EEC (or Baltica) was part of the Rodinia supercontinent where it was bordered by Amazonia and Laurentia (cf. Li et al., 2008; Bogdanova et al., 2008; Johansson, 2009).

The Ukrainian Shield is commonly considered to consist of several domains separated by suture zones. The Archaean high-grade domains, Azov in the east of the shield and the Podolian to the south-west, were strongly reworked in the Palaeoproterozoic (Fig. 1). In contrast, the Meso-Neoarchaeoan granite-greenstone Middle Dnieper Domain, in the central part of the shield between the Podolian and Azov domains, was little affected by Palaeoproterozoic orogenic processes. Palaeoproterozoic rocks comprise most of the Ingul domain in the central part of the shield, and also dominate the Ros-Tikich and Volyn domains in its northwestern part. The Orekhiv-Pavlograd, Krivyy Rih and Golovanivsk suture zones separate the main domains of the shield.

Zircons from metasedimentary rocks of the Ukrainian shield are poorly studied. Some results on Precambrian zircons separated from modern and recent placers were reported by Condie et al. (2005). Bibikova et al. (2012) reported results of U-Pb dating of zircons from metasedimentary rocks sampled in greenstone belts located in the Azov and Middle Dnieper domains of the Ukrainian shield. Claesson et al. (2014) expanded these with results of Hf isotope measurements, and Stepanyuk et al. (2010a, b)

reported U-Pb ages of zircons isolated from the Archaean quartzites of the Bug Series, Podolian domain.

In this paper we report results of simultaneous $^{207}\text{Pb}/^{206}\text{Pb}$ and Hf isotope investigation of zircons separated from a number of clastic (quartzites, sandstones and conglomerate) metasediments varying in age from the Archaean to the Neoproterozoic. All the samples are from the western half of the Ukrainian shield and its western margin. The ages of all of the samples analysed were uncertain and little was known about possible sources of the detrital material. In some cases knowledge about the age and source regions is of economic importance since some of the sedimentary sequences contain diamonds (Gejko et al., 2006). In addition to resolving aspects of the regional geology we also intended to contribute to understanding of the crustal evolution of the East-European craton (EEC) as a whole.

2. Analytical methods

Zircons were extracted using conventional water table, heavy liquid and magnetic techniques. Separated and handpicked under binocular microscope crystals were mounted into a 25 mm epoxy block and polished approximately half way through. Before isotope analysis, all zircon crystals were CL-imaged to clarify internal structures and to identify portions suitable for analysis.

Contemporaneous $^{207}\text{Pb}/^{206}\text{Pb}$ and Hf isotope analyses were performed at Bristol University, UK. The data were acquired with a Thermo-Scientific Neptune multi-collector ICP-MS coupled to a New Wave 193 nm ArF laser ablation sampling system operating at 4 Hz and using a 50 μm spot size over a 60 s ablation period. The Yb isotope compositions of Segal et al. (2003) were adopted for interference corrections following the procedures developed by Kemp et al. (2009). Hf isotope data were obtained during two separate one-day analytical sessions; data for unknowns were collected along with the following standards: Plešovice [measured values: $^{176}\text{Hf}/^{177}\text{Hf} = 0.282472 \pm 2$; $^{207}\text{Pb}/^{206}\text{Pb}$ age = 346.1 ± 7.1 Ma; $n = 38$; standard values: $^{176}\text{Hf}/^{177}\text{Hf} = 0.282482 \pm 13$; U-Pb age = 337.13 ± 0.37 Ma (Sláma et al., 2008)] and Temora [measured values: $^{176}\text{Hf}/^{177}\text{Hf} = 0.282669 \pm 5$; $^{207}\text{Pb}/^{206}\text{Pb}$ age = 425.8 ± 3.5 Ma, $n = 28$; standard values: $^{176}\text{Hf}/^{177}\text{Hf} = 0.282686 \pm 8$; U-Pb age = 416.8 ± 1.1 Ma (Black et al., 2003, 2004)]. $^{176}\text{Hf}/^{177}\text{Hf}$ initial values were calculated using the ^{176}Lu decay constant of Söderlund et al. (2004). Depleted mantle (Chauvel and Blichert-Toft, 2001), and chondritic (Bouvier et al., 2008) parameters were used for model age calculations.

Concurrent measurement of $^{207}\text{Pb}/^{206}\text{Pb}$ and Hf isotope ratios offers a fast way to collect both geochronological and geochemical information from the same volume of the geological material (Kemp et al., 2009). The main shortcoming of this method is the difficulty in estimating the reliability of the geochronological data since the degree of discordance and the amount of common lead remain unknown. If zircons are discordant due to Pb-loss this may lead to some underestimation of the age of

crystallization. An addition of a moderate amount of common lead will either increase (in the case of addition of ancient Pb) or decrease (if younger Pb is added) the resulting $^{207}\text{Pb}/^{206}\text{Pb}$ age. Uncertainties in the age measurement will influence age-dependent isotope parameters such as ϵHf , whereas $^{176}\text{Hf}/^{177}\text{Hf}$ does not change drastically due to the very low Lu/Hf ratio in most zircons. Accordingly, in the ϵHf vs. age space our results will move along the trajectories that correspond to $^{176}\text{Lu}/^{177}\text{Hf} \sim 0$, resulting in some scatter of points. A similar scatter of points is typical for zircons that have experienced significant Pb-loss due to high-grade metamorphism. This circumstance complicates the interpretation of the obtained data, but still allows the main crustal-forming episodes (additions of the juvenile material to the crust) to be discriminated from crustal reworking episodes. To overcome as much as possible the difficulties with uncertain $^{207}\text{Pb}/^{206}\text{Pb}$ ages, a careful examination of optical and CL images of zircons was undertaken in order to avoid any inclusions, damaged and metamict areas.

All of our samples, except one from the Bug Series, did not experience any severe metamorphic events that might have caused Pb-loss, whereas the nature of the sedimentary process itself assists in the selection of the least damaged (i.e. more concordant) zircons. Although, $^{207}\text{Pb}/^{206}\text{Pb}$ ages must be treated with caution as a more severe problem for metamorphosed samples, in particular those that have experienced repeated granulite facies metamorphism, is to interpret whether the measured ages are representing detrital grains of igneous and metamorphic origin, or if they reflect in situ-grown metamorphic grains

3. Stratigraphic position of studied sedimentary rocks and sample description

3.1. Achaean rocks (Bug Series)

The Bug Series includes pure quartzite, feldspar-bearing and iron-bearing quartzite; garnet-biotite, sillimanite-garnet-biotite, graphite- and pyroxene-plagioclase gneisses as well as calc-silicates (calciphires). The overall thickness of the series is about 2000-3000 m and it is subdivided into two lithostratigraphical units referred to as “Suites” in the literature. The lower Kosharo-Oleksandrivka Suite is up to 800 m thick and includes quartzite, high-Al rocks and mafic gneisses. The upper Khaschuvate-Zavallya Suite is up to 2000 m thick and is composed of calciphires, graphite-, biotite- and pyroxene-plagioclase gneisses and ferrous quartzites associated with mafic gneisses (Scherbak et al., 1985).

The age of the Bug Series is poorly constrained (Fig. 2). Stepanyuk et al., (2010a, b) reported U-Pb ages of zircons separated from quartzites that crop out on the left bank of the Pivdenny Bug river nearby Kosharo-Oleksandrivka village. The U-Pb ages obtained from over 120 analyzed individual grains fall into the 2670 – 3560 Ma age interval with most of them grouped between 2915 and 3115 Ma. If all these zircons are considered as detrital, the age of sedimentation of the Kosharo-Oleksandrivka Suite

does not exceed c. 2.70 Ga, and the minimum age of these rocks is established by metamorphic monazite (2062.4 ± 4.4 Ma).

Our quartzite sample (06-BG35) was taken from the right bank of the Pivdenny Bug river opposite Zavallya village from the outcrop known as “Bila Skelya”. This quartzite, representing the Kosharo-Oleksandrivka Suite, has a medium-grained granoblastic texture and consists of moderately to strongly deformed grains of quartz (95 %), and about 5 % of muscovite and sericite that occur as small (0.2-0.5 mm) segregations within quartz. No evidences of primary relationships between detrital grains are preserved in this rock due to a high degree of metamorphism and strong recrystallization.

3.2. Proterozoic rocks

3.2.1. Topilnya Series

Volcanogenic and sedimentary rocks of the Topilnya Series fill the Bilokorovychi depression that according to [Bespalko \(1986\)](#) and [Bukovych \(1986\)](#) is 2 to 6 km wide and can be traced for 22 km in sub-meridional direction.

The Topilnya Series unconformably overlies the 2100-1980 Ma ([Scherbak et al., 2008](#)) crystalline basement composed of gneisses of the Teteriv Series, and granites of the Zhytomyr and Osnitsk Complexes. The thickness of the Topilnya Series is up to 1100 m; it is subdivided into the lower Bilokorovychi and the upper Ozeryany Suites ([Bukovych, 1986](#)). The Bilokorovychi Suite includes quartzites, siltstones, mudstones, conglomerates and gritstones. Coarse-grained terrigenous sediments are predominant in the bottom part of this Suite, which also includes two thin (up to 6.5 m) local metabasaltic flows in its lower part ([Scherbak et al., 1985](#)). The upper part of the Suite crops out in a number of quarries and consists mainly of sandstones with well developed horizontal and cross bedding. Clastic material is represented by angular to well-rounded quartz grains, and minor phases include feldspar, muscovite, biotite, zircon, ilmenite, tourmaline, fragments of metarhyolite, mudstone, silica rocks and quartzite.

Sandstones of the Bilokorovychi Suite gradually are gradually replaced upwards by the mudstones, siltstones and feldspar-quartz sandstones of the Ozeryany Suite. [Bespalko \(1986\)](#) describes siltstones and mudstones of the Ozeryany Suite as sericite-chlorite, quartz-chlorite-sericite, quartz-sericite or pure sericite and muscovite schists. The sediments are cut by series of dykes, veins and sheet-like igneous bodies of mafic and felsic compositions. At contacts with the intrusions the sedimentary rocks are thermally metamorphosed and transformed into hornfelses and schists.

There has been a number of attempts to date rocks of the Bilokorovychi depression. According to K-Ar dating ([Bespalko, 1986](#)) chlorite-sericite schists were formed at 1300-1480 Ma, while dykes and metabasalt flows crystallized at 1000-1640 Ma. [Gorokhov et al. \(1981\)](#) employed Rb-Sr isochron method which suggested that

schists of the Ozeryany Suite were altered at 1574 ± 31 Ma, and U-Pb zircon dating (Shumlyanskyy and Mazur, 2010) indicates that dolerite dykes intruded deposits of the Bilokorovychi depression at 1799 ± 10 Ma (Fig. 1, 2). For this study we have sampled sandstones that crop out in the Bilokorovychi quarry. These are light-grey, fine-grained, rough-banded rocks. Clastic material is represented mainly by quartz with fragments of jasper and biotite is even-grained and well-sorted. Interstitial cement is made of sericite and composes up to 20 vol. % of the rock.

3.2.2. Ovruch Series

The Ovruch depression occurs as a 6 to 20 km wide graben-syncline extending for over 80 km (Drannik and Bogatskaya, 1967; Bogatskaya and Drannik, 1970). It is filled with the Ovruch Series that is subdivided into two Suites. The lower Zbranki Suite is up to 320 m thick and composed of sedimentary and volcanogenic deposits. The thickness of the volcanogenic rocks varies from a few cm to 290 m, while terrigenous sediments are 0.7 to 30 m thick. The basal horizon of the Zbranki Suite was recovered by drilling in the south-western part of the depression where it is represented by quartz and silty micaceous sandstones and conglomerates. According to Drannik and Bogatskaya (1967), rocks of the Ovruch Series rest upon the weathered surface of the Korosten anorthosite-mangerite-charnockite granite (AMCG) complex, and the basal horizon is overlain by a 5 to 59 m thick metabasalt flow that locally rests directly on rapakivi-like granites of the Korosten complex. This in turn is covered by clay-sericite schists and a metarhyolite flow.

The upper, Tovkachi Suite, is over 930 m thick consisting of quartzites and sandstones which reveal clear cross-bedding and alternation of interlayers with different grain sizes. Lenses of pyrophyllite, pyrophyllite-haematite and sericite-haematite schists are common, especially in the lower part of the Tovkachi Suite.

A Rb-Sr isochron for the Ovruch Series sediments (Gorokhov et al., 1981) yielded an age of 1389 ± 71 Ma consistent with a long time span between formation of the Korosten complex and sedimentation of the Ovruch Series. Recent U-Pb ages from zircons from the metarhyolite of the Zbranki Suite (Shumlyanskyy and Bogdanova, 2009; 1761 ± 13 Ma) indicate that metarhyolite outpoured simultaneously with emplacement of the majority of the Korosten plutonic rocks (Amelin et al., 1994); and geochemically the metarhyolites are indistinguishable from the rapakivi granites of the complex (Shumlyanskyy and Bogdanova, 2009).

A sample of the Tovkachi Suite sandstone for this study was taken in the abandoned quarry some 4 km to the north from the city of Ovruch (Fig. 1). This sandstone is a red solid fine-grained massive rock, even- and fine-grained with interstitial cement. The mineral composition is approximately (vol. %): quartz – 85, sericite cement – 15, with single grains of feldspars and jasper. Quartz occurs as fine (up to 0.1 mm), isometric, angular, deformed fragments.

3.2.3. *Polissya Series*

The Polissya Series fills the south-western part of the Neoproterozoic Volyn-Orsha aulacogen (Fig. 1). It is an up to 835 m thick continental silt-sandy red bed formation that overlies the eroded Paleoproterozoic crystalline basement. The Polissya Series is subdivided into three Suites (Vlasov et al., 1972): Middle-Late Riphean (Stenian-Tonian) Romeyki Suite, and Late Riphean (Tonian) Polytsy and Zhobryn Suites. The Romeyki Suite is 380 m thick and while its lowermost part contains abundant coarse-grained conglomerates and sandstone, most of the section consists of sandstones, siltstones and argillites. Clastic fragments of quartz and potassic feldspar are well rounded and sorted. The Polytsy Suite is 110 m thick and overlies the eroded surface of the Romeyki rocks. It is composed of rather monotonous fine-grained sandstones and siltstones that form the second sedimentary rhythm. The Zhobryn Suite is 360 m thick and subdivided into three sub-suites each of which corresponds to a single sedimentary rhythm. Consistency of the siltstone beds over large distances and the presence of phosphatic cement in the sandstones indicate deposition in an epicontinental sea (Gojzhevsky et al., 1984).

There has been a number of attempts to date sediments of the Polissya Series. Makhnach et al. (1976) and Chebanenko et al. (1990) reported mica and feldspar K-Ar ages of 700-815 Ma and whole-rock ages of 880-980 Ma. Nechaev (1974) reported a K-Ar age of 1055 Ma that was considered as a time of the commencement of sedimentation of the Polissya Series (Fig. 2).

The Polissya Series was encountered in drill hole #56, near the village of Tykhodvizh at a depth of 68.8 m immediately beneath the Cretaceous sediments (Fig. 1). Our sample of quartz-feldspar (arkosic) sandstone was taken from the interval 90.0-95.0 m and represents the middle part of the Polissya sequence. The rock is fine-medium-grained light-red massive or banded sandstone composed (vol. %) of clastic grains of quartz – 30, feldspar – 30, fragments of argillaceous and siliceous rocks – 35; illite cement – 5.

3.2.4. *Volyn Series*

The Ediacaran Volyn Series overlies the Riphean – Early Vendian (Tonian and Cryogenian according to the International stratigraphic chart) sediments in a tectonic depression that developed along a NW-SE direction, parallel with the Trans-European Suture Zone in a passive continental margin setting (Poprawa and Paczeńska, 2002). The Volyn Series overlies the Polissya Series and in places rests directly on the crystalline basement (Fig. 1). It is subdivided into the lowermost part (40-50 m), called the Gorbashy Suite, which is composed mainly of arkose and sandstones, while the main part of the Volyn Series consists of basic effusive and pyroclastic rocks, forming a flood basalt province. The lower part of the Gorbashy Suite consists of siltstones and

mudstones with admixture of psammitic and gravelitic material that irregularly alternate in the vertical section. The upper part of the Gorbashy Suite is made of variably-grained arkosic sands and sandstones with interlayers of siltstones and mudstones and fine pebbles of crystalline rocks. In places the Suite contains picrite lava flows.

The coarse-grained deposits of the Gorbashy Suite emerge abruptly in the sedimentary cover of this part of the EEC. During several hundred million years before the deposition of the Gorbashy Suite, the EEC developed as a stable craton characterized by slow vertical movements, slow erosion and accumulation of a thick mainly fine-grained terrigenous sequence (Polissya Series). The abrupt appearance of the coarse-grained, poorly sorted deposits indicates a sharp change in the tectonic regime that resulted in a relatively rapid elevation of the area and more active erosion. This uplift may be linked with the formation of a crustal dome, which was initiated by a mantle plume that also caused outpouring of effusive rocks of the Volyn flood basalt province and the break-up of Rodinia.

The Gorbashy Suite is represented by a sample of a pebble (fragments' size does not exceed c. 1 cm) conglomerate, which was taken from drill-hole 8265 at the interval 320.5-327 m ([Fig. 1](#)). Conglomerates and sandstones at the sample site are underlain by Polissya Series sediments and covered by basalts of the Volyn Series. The sampled conglomerate is loosely cemented. Large well rounded fragments (pebbles) were separated and removed and zircons were isolated from the fine-grained (matrix) fraction of the sample.

4. Zircons description and U-Pb ages

4.1. Archaean samples (*Bug Series*)

The $^{207}\text{Pb}/^{206}\text{Pb}$ ages of cores of the zircon grains separated from the Bila Skelya quartzite vary from 3245 ± 250 to 2031 ± 9 Ma ([Table 1](#), [Fig. 3](#)). Under CL light zircons with ages older than 2500 Ma reveal mainly rounded (sometimes angular) bright cores rimmed by thick and dark mantles ([Fig. 4](#)). Due to the development of rims zircons often acquire angular external shapes. Grains younger than c. 2540 Ma do not contain bright cores; these are usually unzoned and dark on CL images; we consider such grains to be metamorphic. It should be noted, that most of the zircons reported by [Stepanyuk et al. \(2010a, b\)](#) from a similar quartzite of the Bug Series yielded less than 5 % discordant results. If the assumption is made that zircons from the Bila Skelya quartzite hold the same degree of discordance, then most of our $^{207}\text{Pb}/^{206}\text{Pb}$ ages closely correspond to the ages of zircon crystallization.

4.2. Proterozoic samples

4.2.1. *Topilnya Series*

Zircons from the Bilokorovychi sandstone tend to have similar external appearance. They are large, up to 0.2-0.3 mm, isometric to elongated-prismatic, and

well to very well rounded; a few grains have relicts of crystal faces. Crystals are predominantly colourless and transparent, although a few of them are brown-coloured. CL images (Fig. 4) reveal complex internal structures for most of the grains that include zonation and the presence of cores completely invisible under optical microscope. In general, zircons reveal weak luminescence, but some 10 to 15 % of them are bright to very bright on CL images. Such bright grains are rounded and isometric while elongated prismatic ones are dark on the images.

The $^{207}\text{Pb}/^{206}\text{Pb}$ ages of the Bilokorovychi Suite zircons vary from 3530 ± 17 Ma to 2031 ± 7 Ma. The most abundant population yields ages between 2000 and 2100 Ma (20 of 55 analyzed grains); grains aged between 2100 and 2200 Ma are half as abundant (11 grains). Zircons with ages between 2200 and 2900 Ma, with small peak at 2400-2500 Ma, are also common, and older grains are rare (3 grains, Table 1, Fig. 5).

4.2.2. Ovruch Series

The size of the zircons from the Ovruch sandstones usually exceeds 0.2 mm. Crystals are transparent, colourless or sometimes weakly stained by iron oxides. Grains are very well rounded with only a few of them being angular, and the aspect ratio is 1.5-2.5; isometric grains are virtually absent, and most zircons look quite homogeneous under a binocular microscope. CL imaging demonstrates simple internal structures of the zircons with weak zonation. The central parts of grains are slightly brighter than rims (Fig. 4), and up to 10-15 % of the studied grains contain rounded cores that are much brighter than correspondent rims.

$^{207}\text{Pb}/^{206}\text{Pb}$ ages of the Ovruch Series zircons fall in the interval 2160 ± 13 to 1918 ± 22 Ma. About half of the grains crystallized at 1975-2000 Ma and c. 25 % at 1950-1975 Ma (Table 1, Fig. 5).

4.2.3. Polissya Series

Zircons from the Polissya sandstones are typically < 0.10-0.15 mm in size. They are mainly colourless and transparent. Grains are isometric or prismatic with aspect ratios of about 2, and they are predominantly well to very well rounded with only 5 % having angular outlines. One grain had perfect euhedral crystal form. Grains often contain fine mineral inclusions, and most of the grains represent whole crystals with only few of them being fragments of larger grains. Up to 70 % of the zircons display weak luminescence and look grey on CL images with complex to simple zonation patterns. Among this group, a small portion of mainly the prismatic angular grains display very weak luminescence and look dark on CL images (Fig. 4). The internal structure of such grains is homogeneous without any signs of zonation. A minor fraction of the “grey” grains reveal homogeneous internal structure without any signs of zonation. The remaining 30 % of zircons have very bright luminescence and display complex oscillatory zonation.

The $^{207}\text{Pb}/^{206}\text{Pb}$ ages of zircons separated from the Polissya sandstone vary from 3257 ± 10 to 1018 ± 21 Ma (Table 1). The youngest age defines the maximum age of sedimentation of the central part of the Polissya Series and as such it fits well with the results of the K-Ar dating.

Two of the 56 analyzed crystals yielded Archaean $^{207}\text{Pb}/^{206}\text{Pb}$ ages at 3257 ± 10 and 2532 ± 3 Ma. The rest of the grains are Proterozoic with two clear groups at 2200-1800 and 1600-1200 Ma (Fig. 5).

4.2.4. Volyn Series

Zircons recovered from the matrix of the Gorbashy conglomerates are large, up to 0.2 mm and somewhat larger. They are homogeneous with respect to their external appearance and internal structure, and display a prismatic shape with aspect ratios of c. 2-2.5. Crystals are well-developed and virtually non-rounded, predominantly euhedral with rather few grains having inductive facets due to growth in an interstitial space. Grains are transparent, colourless to slightly pinkish, and often containing inclusions. CL imaging displays a rhythmical internal structure of the zircons that supports a magmatic origin (Fig. 4).

Of the 20 complete U-Pb isotopic analyses of the Gorbashy Suite zircons (Table 2), all except one are concordant or nearly concordant (Fig. 6). The weighted average $^{207}\text{Pb}/^{206}\text{Pb}$ age is 1422 ± 19 Ma, and as a single age population is indicated it is possible that zircons were derived from a single source. Uranium and Th concentrations in the zircons are quite variable: U = 13-195 ppm, Th = 18-317 ppm, and there is a clear co-variation of these elements. The average Th/U ratio of 1.45 indicates a magmatic origin of the zircons, and an increase in Th and U abundances is accompanied by a gradual increase in the degree of discordancy.

5. Hf isotopes

5.1. Archaean sample (Bug Series)

Zircons from the strongly metamorphosed Bila Skelya quartzite display a narrow range of $^{176}\text{Hf}/^{177}\text{Hf}$ from 0.280765 to 0.281052, but this translates into a wide range of ϵHf_T values varying from 4.5 ± 1.6 in the oldest grain to -17.7 ± 0.7 in the youngest ones (Fig. 7). The oldest zircons found in this sample ($^{207}\text{Pb}/^{206}\text{Pb}$ age of around 3.24 Ga) have positive ϵHf_T values that approach depleted mantle (DM) Hf isotope compositions. Most of the studied grains are located along a straight array that intersects the DM curve at 3.32 Ga, and the slope of this array corresponds to $^{176}\text{Lu}/^{177}\text{Hf} = 0$. We conclude that zircons located along this line initially crystallized at c. 3100-3300 Ma, and that the range of U-Pb ages reflect subsequent Pb loss. The Hf isotope compositions were not affected by metamorphism, i.e. zircons were effectively “closed” with respect to Lu-Hf system, but they were “open” with respect to U-Pb. It should be noted that some of the zircons located on the $^{176}\text{Lu}/^{177}\text{Hf} = 0$ array do not contain optically or CL-visible

inherited cores. The youngest of them are probably of metamorphic origin, but the older (>3.0 Ga) ages can be considered as reliable primary crystallisation ages for the detrital zircons.

Some 30 % of the zircons deviate significantly from the $^{176}\text{Lu}/^{177}\text{Hf} = 0$ array. This cannot be explained by erroneous $^{207}\text{Pb}/^{206}\text{Pb}$ ages, since such an effect will cause analytical points to be displaced along the $^{176}\text{Lu}/^{177}\text{Hf} = 0$ array. Probably, the deviation from the array in Figure 7 is best explained by either assuming that analysed zircons contain Hf from other sources with different initial $^{176}\text{Hf}/^{177}\text{Hf}$, or that their Hf isotope ratios were moderately modified during metamorphism due to introduction of hafnium of differing composition.

5.2. Proterozoic samples

5.2.1. Topilnya Series

Most of the zircons that crystallized between 2000 and 2500 Ma have positive ϵHf_T values (Fig. 8, Table 1) that vary between CHUR and DM model compositions. Some 10 % of the zircons reveal overdepleted Hf isotope composition (i.e. data point are located above the DM curve), even taking into account analytical errors. However, this “overdepletion” may be the result of incorrect age estimates resulting from data being uncorrected for common lead. About 15 % of the Topilnya Series zircons have negative ϵHf_T values; these spread over the whole age interval embraced by zircons in this sample. In general, Archaean zircons display ϵHf_T values close to the CHUR value. With time the range of ϵHf_T variations gradually increases to extreme positive and negative values observed in the Paleoproterozoic grains.

5.2.2. Ovruch Series

Among the 22 Ovruch Series zircons analyzed for Hf isotopes only one grain has negative ϵHf_T while the other range between CHUR and DM values (Fig. 8). Fifteen grains fall into a narrow ϵHf_T (2 ± 1) and age (1990 ± 10 Ma) interval. Older grains tend to have higher ϵHf_T values.

5.2.3. Polissya Series

Polissya Series zircons can be divided into three groups on the basis of their ages and Hf isotope compositions. The first group includes 21 grains that vary in age from 1210 to 1475 Ma and ϵHf_T from 3.7 to 10.6 (Fig. 9). There is a strong correlation between age and Hf isotope composition in this group, with older grains having higher ϵHf_T values. The second group embraces 12 grains varying in age from 1430 to 1590 and ϵHf_T from -2.2 to 4.3. Finally, the third group also includes 12 grains varying in age from 1810 to 2095 Ma and with ϵHf_T from -1.2 to 3.1. Ages and Hf isotope compositions within these groups are also positively correlated. Four from the seven remainder grains can be considered as outliers from these three groups; however, their affinity to the

groups remains unclear. The three remaining grains are all old (2110-3250 Ma) and have moderately negative ϵHf_T values.

5.2.4. Volyn Series

In view of the homogeneity of the Gorbashy Suite zircons, measurements of the Hf isotopic composition were carried out on 5 individual grains ([Table 1](#)). The Hf isotopic composition is variable; $\epsilon\text{Hf}_{1422} = -4.9 \div -8.2$ with a weighted average of -6.7 ± 1.1 ([Fig. 9](#)).

6. Discussion

6.1. Deposition ages

6.1.1. Bug Series

An estimation of the maximum deposition ages defined by the youngest detrital zircon can be difficult in heavily metamorphosed terrigenous metasediments since the nature of particular zircon grains is not always clear. Indirect evidence about the nature of zircons (i.e. their morphology and internal structure, chemical composition) are not useful because detrital zircons derived from metamorphic rocks and those ones that have crystallized in the sediment during metamorphism will have similar features. It has been shown by [Claesson et al. \(2014\)](#) that rock assemblages of the Bug area experienced medium- to high-grade metamorphism at 2.6-2.8 and 2.04 Ga. Hence, metamorphic zircons of these ages in the Bug Series quartzite can either have grown in situ or have been derived from metamorphosed source rocks.

Zircon ages of the Bila Skelya quartzite vary from 3245 to 2031 Ma ([Fig. 3](#)). The age of deposition of this rock cannot be unequivocally defined, although on the basis of CL imaging and core-rim relationships it is suggested to be over 2540 Ma. However, the studied zircons plot close to a $^{176}\text{Lu}/^{177}\text{Hf} = 0$ array, that may indicate probable Pb loss during c. 2.8 Ga metamorphic event, whereas zircons could have been originally crystallized at c. 3.1-3.2 Ga ([Fig. 7](#)). In this case the age of sedimentation may exceed 3000 Ma, and this would be in agreement with the c. 3.0 Ga osmium isotope model age of the ultramafic intrusions ([Gornostayev et al., 2004](#)) that intruded into the sediments of the Bug Series.

Zircons from the Kosharo-Oleksandrivka quartzite [Stepanyuk et al. \(2010a, b\)](#) have a sharp age peak at c. 3000 Ma and several smaller peaks between 3480 and 2680 Ma ([Fig. 3](#)). Ages younger than c. 2600 Ma were not found in this rock. The prominent peak at c. 3000 Ma might either indicate abundant source rocks of this age or simply reflect metamorphic in-growth of zircons in this rock. In the latter case sedimentation would have occurred before 3000 Ma. However, such a 3.0 Ga metamorphic event is poorly supported by other samples in this area. On the basis of the variability of the internal structures of zircons that crystallized at 2.7-2.8 Ga, [Stepanyuk et al. \(2010a, b\)](#) concluded that these zircons originated from variable

sources, and that the age of deposition of this rock does not exceed 2.7 Ga. The question about whether the deposition of the Kosharo-Oleksandrivka and Bila Skelya quartzites were contemporaneous remains open.

6.1.2. Topilnya Series

Radiometric data indicate that metasedimentary rocks of the Topilnya Series were formed before c. 1800 Ma ([Shumlyanskyy and Mazur, 2010](#)). The youngest group of detrital zircons found in this rock has uniform ages, and a calculated $^{207}\text{Pb}/^{206}\text{Pb}$ age at 2062 ± 10 Ma may approximate the maximum age of sedimentation. Interestingly, these rocks do not contain younger zircons in spite of a wide distribution of c. 2000–1970 Ma rocks of the Osnitsk-Mikashevychi igneous belt (OMIB) in this area. This suggests that the real time of sedimentation may have been close to 2000 Ma.

6.1.3. Ovruch series

According to the 1.76 Ga age of metarhyolites at the base of the Ovruch Series ([Shumlyanskyy and Bogdanova, 2009](#)), sedimentation started at about that time. The weighted average $^{207}\text{Pb}/^{206}\text{Pb}$ age of the youngest zircon group found in Ovruch quartzite is 1978 ± 4 Ma. In contrast to the Topilnya Series, zircons separated from the Ovruch quartzites are dominantly younger than 2000 Ma.

6.1.4. Polissya Series

The depositional age of the Polissya Series remains poorly constrained. It overlies Paleoproterozoic basement and is covered by Neoproterozoic formations, which only constrains sedimentation to have occurred between c. 1700 and 600 Ma. The weighted average $^{207}\text{Pb}/^{206}\text{Pb}$ age of the youngest group of detrital zircon found in Polissya sandstone defines a maximum age of sedimentation at 1228 ± 15 Ma, whereas the youngest zircon found in this rock is 1018 ± 21 Ma old.

6.2. Possible sources of detrital material

6.2.1. Bug Series

It is generally considered (for instance, [Stepanyuk et al., 2010a, b](#)) that sediments of the Bug Series were deposited in small synformal depressions on the Eoarchaeon basement. Hence, it is natural to presume that clastic material for the Bug Series quartzites was derived from the Eoarchaeon rocks, similar to those exposed in quarries and natural outcrops nearby which contain zircons up to 3790 Ma old ([Claesson et al., 2006, 2014](#); [Lobach-Zhuchenko et al., 2011](#)). However, zircons older than 3245 Ma were not found in the Bila Skelya quartzite and are rather rare in the Kosharo-Oleksandrivka quartzite. Comparison of the Hf isotope compositions in zircons from the Bila Skelya quartzite with contemporaneous zircons from the Odesa quarry enderbite ([Fig. 7](#)) reveals significant differences between them. The Hf isotope ratios of

zircons from enderbites are some 10-15 ϵ units lower than those in contemporaneous Bila Skelya zircons. That is, fields of zircons from enderbites and quartzites do not overlap in ϵHf – age space. The rarity of old zircons in quartzites, and differences in the Hf isotope compositions, indicate that Eoarchaeon enderbites were not the main source for the clastic material in the Bug Series quartzites in spite of their present close proximity.

It is noteworthy that the largest population of zircons separated from both Bila Skelya and Kosharo-Oleksandrivka quartzites were formed between c. 2900 and 3200 Ma. The Hf isotope data demonstrate that these zircons are predominantly derived from juvenile source rocks, i.e. they have positive ϵHf_T values approaching compositions characteristic of the depleted mantle at this time (Fig. 7). Local sources of these zircons are still not identified. The ϵHf -age pattern of the Bila Skelya zircons closely resembles that of the ‘young’ zircons found in the Soroki greenstone belt metasediments from the Azov area of the Ukrainian shield (Fig. 7).

6.2.2. Topilnya Series

In contrast to the Bila Skelya quartzite, Proterozoic samples did not experience any strong regional metamorphism, so we assume that Pb loss is not the main reason for variation of ages of zircons found in these sediments. This is supported by the absence of the well-defined $^{176}\text{Lu}/^{177}\text{Hf} = 0$ arrays in the ϵHf -age space. Our further discussion is based on the assumption that ages of zircons in Proterozoic samples closely correspond to ages of their primary crystallization.

Our results indicate that the main source for the sedimentary rocks of the Bilokorovychi depression were most probably granites of the Zhytomyr complex and metamorphic rocks of the Teteriv Series which are widely distributed in the North-Western region of the Ukrainian shield. ϵHf in zircons separated from these rocks varies from c. -2.5 to 5 at 2040 to 2090 Ma (Fig. 8). However, the Bilokorovychi quartzite also contains zircons that are much older and have much higher ϵHf_T values than the Zhytomyr and Teteriv zircons. Some of the Bilokorovychi zircons have very high (overdepleted) ϵHf_T values that clearly indicate a depleted mantle origin of their parental melts.

Rocks older than c. 2.2 Ga are unknown in the North-Western region of the Ukrainian shield. Besides this, zircons of Archaean age are very rare in the c. 2.2 Ga old metasediments of the Teteriv Series and in the c. 2.0-2.1 Ga granites of the Zhytomyr complex (Shumlyanskyy, 2012). Hence, it is inferred that the old zircon population found in the Topilnya Series sediments originated from the neighbouring Archaean terrains. This indicates a large source region for the clastic material that hampers the search of the bedrock source of the diamonds that have been found in the bottom conglomerates of the Bilokorovychi depression.

The absence of 2.0-1.97 Ga zircons originating from the Osnitsk-Mikashevychi igneous belt (OMIB) rocks, which are widely distributed in the region, is difficult to explain. Either the Osnitsk rocks were not exposed at the time of sedimentation of the Topilnya Series, or the local relief at that time precluded delivery of clastic material from the OMIB which was located slightly to the north. This belt represents a Paleoproterozoic active continental margin that probably appeared at 2.0-1.9 Ga as a mountainous area with local intermountain troughs, one of which may be represented by the Bilokorovychi depression.

6.2.3. Ovruch series

The main source for the sandstones of the Ovruch depression appears to be the local rocks of the 2.0-1.95 Ga OMIB belt. This is evident from striking coincidence of ages and Hf isotope compositions in zircons separated from the Ovruch Series quartzites and OMIB rocks (Fig. 8). The scarcity of older zircons in the Ovruch quartzite is very notable. Another important feature of the Ovruch Series is the absence of zircons formed at 1800-1760 Ma, i.e. during formation of the Korosten anorthosite-mangerite-charnokite-granite complex which immediately underlies the Ovruch depression. This probably indicates that rocks of the Korosten complex did not crop out at the surface at the time of sedimentation of the Ovruch Series.

6.2.4. Polissya Series

The common 2200-1800 Ma old zircons in the Polissya Series correspond to the time of formation of the North-Western region of the Ukrainian shield, which immediately surrounds and underlies the western part of the Volyn-Orsha depression. Orogenic belts in the western part of the EEC encompass the same age interval (Bogdanova et al., 2006). However, in detail the age distribution of the 1800-2200 Ma Polissya zircons differs significantly from the distribution of rock ages in the North-Western region of the Ukrainian shield. Zircons formed between 1800 and 1740 Ma are absent from the Polissya sandstones while this interval corresponds to the formation of the Korosten AMCG plutonic complex that constitutes a huge source of zircons. Crystals formed at c. 2100 Ma are rare in the Polissya sandstones while Teteriv Series metasediments and metavolcanics formed at this time are quite abundant in the area. Zircons that crystallized at c. 2000 Ma are present in reasonable amounts in the Polissya sediments, and this age closely corresponds with the formation of the OMIB. However, the largest population of the Palaeoproterozoic zircons has $^{207}\text{Pb}/^{206}\text{Pb}$ ages of 1920-1800 Ma, a period characterized by cessation of endogenous activity in the North-Western region of the Ukrainian shield. These zircons may have been derived from the southern part of the Fennoscandian segment of the EEC.

There are no sources of young (1600-1000 Ma) Polissya zircons among the local rocks since the endogenous activity in the Ukrainian shield has to our knowledge

completely terminated after c. 1720 Ma. However, possible sources for these Meso-Neoproterozoic zircons can be found in the south-western and western parts of the Fennoscandia. For instance, the large Mazury AMCG complex in north-eastern Poland formed at 1548-1499 Ma ([Wiszniewska et al., 2007](#); [Skridlaite et al., 2008](#)). The Baltic countries and the south-eastern part of the Baltic shield (southern Finland, southwestern Karelia) also host a number of AMCG complexes that were formed at 1640-1630 Ma (Viborg pluton, [Larin et al., 1996](#); [Neymark et al. 1994](#); [Belyaev et al., 1998](#)), 1580 Ma (Riga pluton, [Rämö et al., 1996](#)), and at 1547-1529 Ma (Salmi pluton, [Amelin et al., 1996](#); [Larin et al., 1996](#); [Neymark et al., 1994](#)). At least some of the Polissya zircons of this age interval may have been derived from these AMCG complexes.

The western part of the EEC (southern and western Norway and Sweden) was an area of active geological activity between 1700-900 Ma ([Bingen and Solli, 2009](#), and references therein). Mesoproterozoic magmatism occurred at 1659-1517 Ma in the Idefjorden terrain, at 1572-1460 Ma in the Bamble and Kongsberg terrains, and at 1555-1459 Ma in the Telemark terrain. The Sveconorwegian belt contains rocks that were formed during the time intervals 1473-1130 Ma and 1060-914 Ma.

In order to clarify possible sources of the zircons we have compared ages and Hf isotope ratios of zircons separated from the Polissya sandstone with some of the granites of the south-western part of the Baltic shield (e.g. [Andersen et al. 2002, 2009](#)) and with the rapakivi granites and associated mafic rocks of southern Finland reported by [Heinonen et al. \(2010\)](#). Zircon data, plotted on age vs. ϵHf diagram ([Fig. 9](#)), demonstrate that granites and associated rocks of the SW part of the Baltic shield could be a source of some of the youngest (1500-1000 Ma) zircons found in the Polissya sandstone. Zircons extracted from Finnish rapakivi and associated rocks may also have been a source of some of the Polissya zircons, although the fit in this case is not excellent.

Other possible sources of the clastic material for the Polissya Series sandstones are the rocks of the continent that was next to the EEC across the Trans-European suture zone in the structure of Rodinia. The most probable candidate for this is Amazonia ([Li et al., 2008](#); [Johansson, 2009](#)), in which case it is not necessary to infer distal sources for the clastic material of the Polissya Series.

6.2.5. Volyn Series

All of the studied Gorbashy Suite zircons are homogeneous with respect to their external appearance, internal structure, geochemical characteristics (Th/U ratio and Hf isotopic composition) and age. Hence, all of them evidently originated from similar sources. The angular external habit of the zircons, the homogeneity of their population, and immature nature of the sediment indicate a local source. However, there is no other evidence of magmatic (or any other endogenous) activity at ~1400 Ma in the Ukrainian

shield. Given that the Gorbashy Suite conglomerates are likely to have been derived from a local source, these data provide new evidence of still unknown crustal-derived igneous rocks formed at ~1400 Ma. It is symptomatic that the Hf depleted mantle model ages are c. 2150 Ma ([Table 1](#)), corresponding to the time of crustal formation in this area. It is noteworthy that, the Polissya Series sandstone also contains zircons that crystallized at c. 1420-1430 Ma. However, the latter are fine, well-rounded crystals with ϵ_{Hf} varying from -1 to +9, and were probably derived from a distal source as discussed above.

6.3. Crustal evolution of the south-western part of the East-European craton

The new data on the U-Pb ages and the Hf isotope ratios of zircons separated from Archaean to Neoproterozoic metasediments from the western part of the Ukrainian shield allow us to track the crustal evolution of the south-western part of the East European Craton in the Precambrian.

The oldest zircons analyzed in the Ukrainian shield were separated from enderbites of the Bug area (Podolian domain), south-western part of the shield, and from metasediments (biotite gneisses and schists) of the Soroki greenstone belt located some 500 km away, in the Azov domain in the south-eastern part of the shield. Both enderbites and metasediments contain zircons with widely varying U-Pb ages (mainly due to Pb-loss and re-crystallization during several stages of metamorphism), but the oldest zircons in both cases are c. 3.75 Ga old and crystallized from melts with chondritic to mildly depleted Hf isotope characteristics. [Claesson et al. \(2014\)](#) argued that the Podolian and Azov Domains, which constitute essential parts of the Ukrainian Shield, evolved independently of each other before their ultimate amalgamation in the Palaeoproterozoic. In line with this, the 3.75 Ga detrital zircons in the Azov Domain may have other sources than the Bug area enderbites. However, such old zircons are virtually unknown in the Late Archaean and younger metasediments.

The next important crust-forming event identified in this study occurred at c. 3.15-3.20 Ga. Zircons of this age are predominant in the Bila Skelya quartzite and are also present in the metasediments of the Soroki greenstone belt, Azov domain ([Claesson et al., 2014](#)). The highest ϵ_{Hf} values (up to +3.4) in zircons from the Bila Skelya quartzite approach the depleted mantle value. This event is supported also by some of the zircons found in the Topilnya Series quartzite.

The Archaean evolution of the southern part of the EEC was concluded by a certain input of juvenile material at c. 2.5-2.4 Ga. A relatively small number of zircons with positive ϵ_{Hf} values, that formed at this time interval are present in the Topilnya Series quartzite and in the recent sediments studied by [Condie et al. \(2005\)](#). The source of these zircons remains unknown as igneous or metamorphic rocks of this age are not common in the Ukrainian shield. Considering the oldest zircons of this age, with ϵ_{Hf} values of around +5, origin due to reworking of older crust appears improbable. The

same crust-forming event was recognized by [Condie et al. \(2005\)](#). On the other hand, there are also several 2.5-2.4 Ga zircons having negative ϵ_{Hf} values in the Topilnya Series quartzite. Altogether, it is indicated that this time interval was typified by a juvenile input of the mantle material into the crust coupled with reworking of older crust.

Interestingly, some of the 2.4–2.2 Ga old zircons reveal very high ϵ_{Hf} values (+10 to +12) and plot over the depleted mantle reference curve, inevitably indicating a crustal-growth event that involved the input of the mantle material into the crust. On a global scale ([Condie et al., 2005](#)), crust-forming events in the 2.4-2.2 Ga interval are relatively rare, and as our zircon dating technique does not allow a correction for common Pb, the indicated Ukrainian 2.4-2.2 Ga ages must be treated with caution.

The 2.2-2.0 Ga time interval in the Ukrainian Shield was characterized by widespread metamorphism at amphibolite and granulite facies, emplacement of abundant granitic intrusions throughout the shield, and finally by the formation of the Osnitsk-Mikashevychi igneous belt on the northwestern margin of the Sarmatia. Interestingly, metamorphic and igneous rocks that formed in this time interval reveal mainly juvenile Sr and Nd isotope characteristics. The juvenile nature of these rocks is confirmed by Hf isotope ratios in 2.2-2.0 Ga zircons separated from metamorphic and igneous rocks ([Fig. 8](#)). The majority of zircons separated from the Topilnya Series quartzite, and virtually all zircons from the Ovruch quartzite fall within this time interval and have positive ϵ_{Hf} values, some of them very close to the depleted mantle evolution curve. In fact, zircons from the sedimentary rocks reveal even more depleted Hf isotope compositions than their counterparts in the sampled metamorphic and igneous rocks. Altogether, this indicates a significant input of mantle derived material to the crust during this time interval.

It is worth noting that igneous processes that took place at 1.80-1.75 Ga and resulted in the formation of the voluminous Korosten and Korsun-Novomyrghorod AMCG complexes are not revealed in our detrital zircon data. Only a few zircons from the Polissya Series sandstone may have originated from the Korosten rocks. Zircons separated from the Topilnya and Ovruch Series quartzites, which are closely associated in space with the Korosten AMCG complex, do not display ages younger than c. 1950 Ma.

Variations in the Hf isotope ratios in zircons from the Polissya Series sandstone allows the recognition of one additional crust-forming event in Mesoproterozoic, at c. 1.5 Ga, that is identical to one of the events revealed by [Condie et al. \(2005\)](#). A significant input of mantle material at c. 1.5 Ga is well established by numerous zircons that plot close to the depleted mantle curve, whereas data for the younger zircons (1.4-1.0 Ga) are consistent with a subsequent evolution of this mantle-derived source. As mentioned above, rocks of these ages are unknown in the Ukrainian shield, and those zircons may have been derived from the Fennoscandian shield or from a neighbouring terrain (Amazonia?) that was rifted away during the break-up of Rodinia. Taking into

account the immature nature of the Polissya sandstone, these zircons could also been derived from local, but yet undiscovered sources, which perhaps are now buried under the thick sedimentary cover (reaching up to 8 km in the Lviv depression).

In summary, the U-Pb ages and Hf isotope ratios of zircons separated from sedimentary rocks in the Ukrainian shield, allows the recognition of four major crustal growth events in the geological history of the south-western part of the EEC – at c. 3.75, 3.15, 2.2-2.0, and 1.5 Ga ([Fig. 10](#)). An additional rather minor event could have taken place at 2.5-2.4 Ga, but since no firm age constraints can be placed there are as yet no conclusive evidence for the significance of this event. The spread in age data which mirror the formation of the continental crust of the EEC at a local scale, suggests a discontinuous, episodic process. Our data indicate that only a small amount of the modern continental crust was formed in the Early Archaean, although the amount of the continental crust that was destroyed since the Early Archaean remains unconstrained. Late Archaean and Proterozoic zircons with juvenile isotope characteristics predominate in the detrital record. Zircons also display gradual increase of degree of depletion of the source of Hf with time, in accordance with the DM model proposed by [Chauvel and Blichert-Toft \(2001\)](#). This also contradicts models in which the bulk of the preserved continental crust was formed in the Early Archaean ([Armstrong, 1981](#)).

[Griffin et al. \(2014\)](#) have compiled a global record based on over 6500 zircon analyses with ages over 2.0 Ga that allowed them to define a series of major pulses of juvenile magmatic activity at c. 4.2, 3.8, 3.3-3.4, 2.75, and 2.5 Ga. One more pulse at c. 2.20-2.05 Ga is evident from their cumulate probability curve (Fig. 2 in [Griffin et al., 2014](#)). Interestingly, as most of the crustal growth events in the Ukrainian shield correspond to these pulses of juvenile magmatic activity their global significance is reinforced. At the same time, Archaean and Palaeoproterozoic crustal growth events recognized in the Ukrainian shield are quite different from those that are known from the Fennoscandian shield ([Andersen, 2014](#)). This adds support to the model where the Sarmatian and Fennoscandian segments of the EEC evolved independently before their ultimate amalgamation in the Palaeoproterozoic ([Bogdanova et al. 2006](#)). However, the very prominent crustal growth event between c. 2.0 and 1.5 Ga that is evident from the Fennoscandian shield is almost completely absent from the Ukrainian zircon record.

7. Conclusions

The combination of U-Pb ages and Hf isotope compositions of detrital zircons separated from metasedimentary clastic rocks can provide important information about ages of deposition of these rocks, the possible sources of the detrital material, and the evolution of the crust in the region as a whole. We have studied zircons separated from 5 sedimentary rocks varying in age from c. 3.0 Ga to c. 600 Ma. These rocks represent various stages of the evolution of the EEC in the Precambrian.

The age of deposition of the Bug Series, represented in our collection by quartzites of the Kosharo-Oleksandrivka Suite, is poorly constrained due to a granulite stage metamorphism that has affected these rocks. The deposition age may vary from 2.5 to 3.0 Ga, although our preferred estimate is c. 2.9-3.0 Ga based on the geological setting of the Series, the distribution of zircon ages and Hf isotope compositions. The main source of zircons in the Bug Series quartzites were c. 2.9-3.2 Ga mantle-derived rocks that have still to be identified, whereas the Early Archaean enderbites of the Dniester-Bug Series were at the most minor suppliers of clastic material. The ϵ_{Hf} -age pattern of the Bug Series zircons closely resembles that of the 'young' zircon generation found in metasediments from the Soroki greenstone belt, Azov area.

The assessment of the time of deposition of the other younger samples is more straightforward since these did not experience strong metamorphism and therefore do not contain zircons that have grown in-situ in the sediments in response to metamorphism. In some cases depositional ages can be defined on the grounds of the geological setting, and we suggest that the time of deposition of the Topilnya Series is c. 2.0 Ga, that of the Ovruch Series is c. 1.75 Ga, and of the Polissya Series is c. 1.2-1.0 Ga.

The main source of material for the sedimentary rocks of the Topilnya Series deposited in the Bilokorovychi depression was the local granites of the Zhytomyr complex and metamorphic rocks of the Teteriv Series. A much less important source was the neighbouring Archaean terrains. This implies a wide source region for the clastic material in the Bilokorovychi depression. Probably the single source of the Ovruch Series sandstones was the local rocks of the 2.0-1.95 Ga Osnitsk-Mikashevychi igneous belt. Polissya Series sandstones were derived from several sources widely varying in age and, probably, location. Most of the zircons may have been derived from the western and south-western parts of the Fennoscandian segment of the EEC, or from a continent that was rifted away during the Rodinia break-up. However, zircon data for the Polissya sandstone is in apparent conflict with the immature nature of this rock. The same can be said about the source of conglomerates of the Late Neoproterozoic Gorbashy Suite. The nature of this rock precludes long transportation distances whereas zircon data indicates a single 1422 ± 19 Ma source of material that is unknown in that area. An alternative interpretation is to invoke the presence of still undiscovered Meso- and Neoproterozoic rock complexes now hidden beneath the thick sedimentary cover on the western slope of the Ukrainian shield.

An inspection of available data plotted in age-Hf isotope composition (ϵ_{Hf}) diagrams allows the recognition of the main events of crustal growth that led to formation of the south-western part of the EEC. The oldest (c. 3.75 Ga) event is represented by enderbites of the Bug domain in the south-western part of the Ukrainian shield (Claesson et al., 2014). The next important event occurred at c. 3.15 Ga and is documented by detrital zircons separated from the Bug Series quartzite and from

metasediments of the Soroki greenstone belt, Azov domain. The highest ϵHf_T values (+3.4) in zircons from the Bug Series quartzite approach that of the contemporaneous depleted mantle.

A few zircons with high positive ϵHf_T values indicate some input of the juvenile material into the crust at 2.5 Ga, whereas a 2.2-2.0 Ga crust-forming event is documented by numerous zircons with positive ϵHf_T values. Zircons of the same age and similar Hf isotope composition are known from felsic igneous and metamorphic juvenile rocks that compose the north-west region of the Ukrainian shield and probably are wide-spread in many other locations within the shield. We consider the 2.2-2.0 Ga event as one of the most important crustal growth events in the studied area.

The youngest event of crustal growth in the south-western part of the EEC is represented by data from a group of zircons separated from the Polissya Series sandstone and from recent sediments ([Condie et al., 2005](#)) that have crystallized at c. 1.5 Ga and have ϵHf_T in the range $\sim +11$ to $\sim +4$. Recalling that rocks younger than c. 1700 Ma are unknown in the Ukrainian shield, the 1.5 Ga zircons may be derived either from the Fennoscandian shield or from a neighbouring terrain (Amazonia?) that was rifted away during the break-up of Rodinia. Other possible sources of the young zircons are rocks that may be buried under the thick sedimentary cover at the western slope of the Ukrainian shield.

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Figure captions:

Figure 1. Schematic map of the south-western part of the East European craton. Ar indicates Archaean Dniester-Bug domain of the Ukrainian shield; Pr – Palaeoproterozoic domain. Inset map: VOA stands for Volyn-Orsha depression. Samples location: 1 – Bug Series (sample 06-BG35); 2 – Topilnya Series (sample Bilok); 3 – Ovruch Series (sample Ovruch); 4 – Polissya Series (sample 56/90-95); 5 – Volyn Series (sample 8265/320.5-327).

Figure 2. Schematic stratigraphic position of the studied sedimentary sequences.

Figure 3. Distribution of $^{207}\text{Pb}/^{206}\text{Pb}$ ages in zircons from two quartzite samples of the Bug Series. Peaks at c. 2750 and 2050 Ma correspond to two amphibolite- to granulite facies metamorphic event. The data on the Kosharo-Oleksandrivka quartzite are from [Stepanyuk et al. \(2010b\)](#).

Figure 4. Selected CL images of zircons. Numbers beneath the images correspond to the analyses reported in the Table 2. Numbers next to images indicate $^{207}\text{Pb}/^{206}\text{Pb}$ ages and calculated $\varepsilon_{\text{Hf}_T}$ values.

Figure 5. Distribution of $^{207}\text{Pb}/^{206}\text{Pb}$ ages in zircons separated from the Proterozoic sandstones of the Topilnya, Ovruch and Polissya Series.

Figure 6. U-Pb concordia diagram for zircons separated from matrix of the Gorbashi Suite conglomerate.

Figure 7. ε_{Hf} -age diagram for zircons from the Bila Skelya quartzite. Data for the Eoarchaeon enderbite of the Dniester-Bug Series and metasediments of the Azov domain greenstone belts are from [Claesson et al. \(2014\)](#). Most of the zircons from the Bila Skelya quartzite plot close to $^{176}\text{Lu}/^{177}\text{Hf} = 0$ array that is caused by Pb loss during c. 2.8 Ga metamorphic event. Originally, zircons are probably derived from a single 3.1-3.2 Ga-old source. Some 30 % of the zircons deviate from this array and might have originated either from other source with a different initial $^{176}\text{Hf}/^{177}\text{Hf}$ or they have crystallized in situ during 2.8 Ga metamorphism.

Figure 8. ϵ_{Hf} -age diagram for zircons from the Palaeoproterozoic sandstones.

Figure 9. ϵ_{Hf} -age diagram for zircons from the Proterozoic sediments of the Polissya and Volyn Series. Data for the Finnish AMCG complexes are from [Heinonen et al. \(2010\)](#), and for granites of the SW part of the Baltic shield are from [Andersen et al. \(2002, 2009\)](#).

Figure 10. Summarizing ϵ_{Hf} -age diagram for zircons from the sedimentary rocks of the Ukrainian shield. Stars indicate main crust-forming events in the south-western part of East European craton, whereas arrows demonstrate evolution of Hf isotope compositions with time in zircons. Slope of the two oldest (3.75 and 3.15 Ga) arrows corresponds to $^{176}\text{Lu}/^{177}\text{Hf} = 0$, i.e. widely varying in age zircons have nearly the same Hf isotope composition, and their age variations are caused by Pb loss in zircons. Slope of the 'felsic crustal evolution' array corresponds to $^{176}\text{Lu}/^{177}\text{Hf} = 0.015$ ([Griffin et al., 2004](#)).

Bug Series

Topilnya Series

Ovruch Series

Polissya Series

Volyn Series

Relative probability

Topilnya Series

n = 48

Ovruch Series

n = 22

Polissya Series

n = 55

$^{207}\text{Pb}/^{206}\text{Pb}$ age, Ma

Table 1. Hf isotope composition and $^{207}\text{Pb}/^{206}\text{Pb}$ ages in studied zircons

#	$^{176}\text{Hf}/^{177}\text{Hf} \pm 1\sigma$	$^{176}\text{Lu}/^{177}\text{Hf}$	$^{176}\text{Yb}/^{177}\text{Hf} \pm 1\sigma$	$^{207}\text{Pb}/^{206}\text{Pb}$	$^{207}\text{Pb}/^{206}\text{Pb} \pm 2\sigma$	age, Ma	$^{176}\text{Hf}/^{177}\text{Hf}_T$	εHf_T	$\pm 2\sigma$	T(DM), Ma		
										felsic	mafic	
Bug Series (sample 06-BG35)												
1	0.281014 $\pm$ 10	0.00084	0.02793	0.1252 $\pm$ 3	2032 $\pm$ 7	0.280996	-17.4	0.7		3078	3764	4349
3	0.280893 $\pm$ 18	0.00104	0.03245	0.2450 $\pm$ 143	3153 $\pm$ 185	0.280844	3.4	1.4		3258	3330	3392
4	0.281014 $\pm$ 12	0.00058	0.01951	0.1560 $\pm$ 35	2413 $\pm$ 76	0.281001	-8.4	0.8		3058	3500	3870
5	0.280910 $\pm$ 15	0.00165	0.05634	0.1648 $\pm$ 37	2506 $\pm$ 76	0.280845	-11.7	1.1		3286	3785	4219
6	0.280887 $\pm$ 22	0.00097	0.03066	0.1813 $\pm$ 62	2665 $\pm$ 113	0.280852	-7.8	1.6		3260	3661	4001
7	0.280776 $\pm$ 9	0.00043	0.01389	0.2298 $\pm$ 5	3050 $\pm$ 7	0.280765	-1.8	0.6		3362	3585	3768
9	0.280863 $\pm$ 7	0.00081	0.02648	0.1682 $\pm$ 25	2540 $\pm$ 49	0.280838	-11.2	0.5		3278	3778	4199
10	0.280873 $\pm$ 19	0.00118	0.03712	0.1943 $\pm$ 80	2779 $\pm$ 135	0.280824	-6.1	1.4		3297	3644	3938
11	0.281045 $\pm$ 11	0.00101	0.04392	0.1663 $\pm$ 29	2521 $\pm$ 59	0.281010	-5.5	0.9		3051	3405	3707
12	0.280859 $\pm$ 12	0.00084	0.02700	0.2342 $\pm$ 1	3081 $\pm$ 2	0.280823	1.0	0.9		3287	3431	3551
13	0.281001 $\pm$ 10	0.00071	0.02405	0.1252 $\pm$ 3	2031 $\pm$ 9	0.280987	-17.7	0.7		3086	3784	4376
14	0.281061 $\pm$ 6	0.00052	0.01756	0.1476 $\pm$ 22	2318 $\pm$ 50	0.281052	-8.8	0.5		2991	3451	3836
16	0.280886 $\pm$ 15	0.00122	0.04116	0.1496 $\pm$ 61	2341 $\pm$ 139	0.280845	-15.6	1.2		3283	3896	4422
17	0.280979 $\pm$ 13	0.00132	0.04390	0.2180 $\pm$ 21	2966 $\pm$ 30	0.280917	1.6	1.1		3166	3300	3415
18	0.281027 $\pm$ 11	0.00056	0.01842	0.1918 $\pm$ 4	2757 $\pm$ 6	0.281011	0.0	0.8		3040	3237	3402
19	0.280859 $\pm$ 10	0.00111	0.03406	0.1935 $\pm$ 82	2772 $\pm$ 139	0.280813	-6.6	0.8		3311	3673	3980
20	0.280799 $\pm$ 8	0.00031	0.00968	0.2225 $\pm$ 10	2999 $\pm$ 15	0.280795	-1.9	0.6		3321	3553	3743
Topilnya Series (sample Bilok)												
1	0.281640 $\pm$ 12	0.00063	0.01958	0.1316 $\pm$ 3	2119 $\pm$ 7	0.281628	7.1	0.9		2217	2284	2340
2	0.281405 $\pm$ 14	0.00042	0.01262	0.1367 $\pm$ 3	2185 $\pm$ 7	0.281402	0.6	1.0		2521	2752	2946
3	0.281531 $\pm$ 12	0.00190	0.06584	0.1577 $\pm$ 18	2431 $\pm$ 38	0.281457	8.3	1.0		2445	2454	2462
4	0.281577 $\pm$ 20	0.00063	0.01906	0.1278 $\pm$ 2	2068 $\pm$ 5	0.281566	3.7	1.4		2303	2461	2597
5	0.281757 $\pm$ 16	0.00112	0.03190	0.1279 $\pm$ 11	2069 $\pm$ 30	0.281727	9.4	1.2		2083	2093	2101
6	0.281434 $\pm$ 12	0.00048	0.01512	0.1377 $\pm$ 4	2198 $\pm$ 11	0.281428	1.8	0.8		2487	2685	2852
7	0.281534 $\pm$ 10	0.00030	0.00896	0.1284 $\pm$ 2	2076 $\pm$ 6	0.281536	2.8	0.7		2341	2524	2678
8	0.281589 $\pm$ 13	0.00078	0.02395	0.1481 $\pm$ 62	2324 $\pm$ 143	0.281568	9.7	0.9		2296	2276	2260
9	0.281320 $\pm$ 14	0.00027	0.00788	0.1547 $\pm$ 3	2398 $\pm$ 6	0.281322	2.7	1.0		2626	2785	2918
10	0.280454 $\pm$ 12	0.00037	0.01028	0.3118 $\pm$ 34	3530 $\pm$ 34	0.280443	-1.9	0.9		3781	3965	4115
12	0.281566 $\pm$ 16	0.00071	0.02094	0.1274 $\pm$ 5	2062 $\pm$ 13	0.281552	3.1	1.2		2322	2496	2645
13	0.281676 $\pm$ 12	0.00058	0.01685	0.1296 $\pm$ 9	2092 $\pm$ 25	0.281667	7.8	0.8		2165	2215	2257
14	0.281521 $\pm$ 12	0.00066	0.02039	0.1292 $\pm$ 7	2087 $\pm$ 19	0.281509	2.1	0.9		2380	2578	2747
15	0.280969 $\pm$ 10	0.00115	0.04238	0.1893 $\pm$ 28	2736 $\pm$ 48	0.280923	-3.6	0.8		3165	3452	3696
16	0.281548 $\pm$ 9	0.00043	0.01345	0.1351 $\pm$ 2	2166 $\pm$ 4	0.281544	5.2	0.6		2330	2443	2538
17	0.281601 $\pm$ 10	0.00104	0.03175	0.1552 $\pm$ 35	2404 $\pm$ 76	0.281568	11.6	0.8		2294	2219	2156
18	0.281581 $\pm$ 11	0.00041	0.01304	0.1271 $\pm$ 6	2058 $\pm$ 17	0.281579	3.9	0.8		2283	2438	2568
19	0.281200 $\pm$ 13	0.00110	0.03570	0.1293 $\pm$ 3	2089 $\pm$ 8	0.281171	-9.9	0.9		2846	3338	3762
20	0.281760 $\pm$ 15	0.00194	0.05329	0.1287 $\pm$ 2	2080 $\pm$ 4	0.281698	8.7	1.1		2125	2152	2177
22	0.281626 $\pm$ 17	0.00059	0.01840	0.1289 $\pm$ 6	2083 $\pm$ 17	0.281616	5.8	1.2		2234	2336	2422
23	0.281384 $\pm$ 9	0.00048	0.01320	0.1383 $\pm$ 6	2206 $\pm$ 15	0.281378	0.2	0.7		2554	2792	2992
24	0.281026 $\pm$ 7	0.00061	0.02197	0.2037 $\pm$ 31	2856 $\pm$ 50	0.281007	2.2	0.5		3044	3176	3286
25	0.281526 $\pm$ 11	0.00066	0.02099	0.1304 $\pm$ 6	2103 $\pm$ 17	0.281513	2.6	0.8		2374	2556	2711
26	0.281517 $\pm$ 10	0.00039	0.01206	0.1313 $\pm$ 4	2115 $\pm$ 11	0.281515	3.0	0.7		2369	2544	2691
27	0.281721 $\pm$ 10	0.00042	0.01298	0.1262 $\pm$ 1	2046 $\pm$ 3	0.281718	8.6	0.7		2095	2129	2158
29	0.280673 $\pm$ 8	0.00071	0.02280	0.2504 $\pm$ 2	3188 $\pm$ 2	0.280643	-2.9	0.6		3525	3763	3960
30	0.281565 $\pm$ 11	0.00142	0.04777	0.1397 $\pm$ 39	2223 $\pm$ 97	0.281519	5.6	1.0		2367	2460	2541
32	0.281171 $\pm$ 11	0.00027	0.00831	0.1646 $\pm$ 10	2504 $\pm$ 21	0.281173	-0.2	0.8		2824	3050	3237
33	0.280910 $\pm$ 10	0.00048	0.01451	0.2088 $\pm$ 3	2896 $\pm$ 5	0.280897	-0.8	0.7		3189	3396	3568
34	0.281624 $\pm$ 13	0.00176	0.05887	0.1502 $\pm$ 63	2348 $\pm$ 144	0.281559	9.9	1.4		2307	2280	2257
35	0.281323 $\pm$ 11	0.00042	0.01354	0.1611 $\pm$ 2	2467 $\pm$ 3	0.281317	4.1	0.8		2632	2747	2844
37	0.281613 $\pm$ 8	0.00040	0.01205	0.1264 $\pm$ 3	2049 $\pm$ 9	0.281612	4.9	0.6		2240	2370	2481
38	0.281283 $\pm$ 6	0.00008	0.00274	0.1536 $\pm$ 3	2387 $\pm$ 7	0.281293	1.4	0.4		2663	2859	3021
39	0.281324 $\pm$ 13	0.00092	0.02824	0.1617 $\pm$ 6	2473 $\pm$ 13	0.281295	3.5	0.9		2665	2794	2904
40	0.281368 $\pm$ 9	0.00077	0.02150	0.1491 $\pm$ 25	2335 $\pm$ 57	0.281348	2.1	0.7		2595	2771	2921
41	0.280813 $\pm$ 13	0.00033	0.00909	0.2433 $\pm$ 5	3142 $\pm$ 6	0.280807	1.8	0.9		3305	3423	3520

#	$^{176}\text{Hf}/^{177}\text{Hf} \pm 1\sigma$	$^{176}\text{Lu}/^{177}\text{Hf}$	$^{176}\text{Yb}/^{177}\text{Hf} \pm 1\sigma$	$^{207}\text{Pb}/^{206}\text{Pb}$	$^{207}\text{Pb}/^{206}\text{Pb} \pm 2\sigma$	$^{176}\text{Hf}/^{177}\text{Hf}_T$	ϵHf_T	$\pm 2\sigma$	T(DM), Ma		
									felsic	mafic	
42	0.281055 $\pm$ 8	0.00051	0.01735	0.1692 $\pm$ 14	2550 $\pm$ 27	0.281044	-3.7	0.6	2998	3308	3568
43	0.281552 $\pm$ 11	0.00065	0.02006	0.1376 $\pm$ 7	2197 $\pm$ 18	0.281539	5.7	0.8	2337	2433	2514
44	0.281706 $\pm$ 12	0.00065	0.02207	0.1352 $\pm$ 39	2166 $\pm$ 100	0.281693	10.5	0.9	2129	2103	2082
45	0.281627 $\pm$ 16	0.00119	0.03685	0.1387 $\pm$ 45	2212 $\pm$ 111	0.281591	7.9	1.1	2267	2304	2335
47	0.281452 $\pm$ 8	0.00035	0.01117	0.1320 $\pm$ 4	2125 $\pm$ 12	0.281452	1.0	0.6	2454	2680	2870
48	0.281599 $\pm$ 9	0.00041	0.01300	0.1417 $\pm$ 63	2249 $\pm$ 154	0.281596	8.9	0.6	2259	2267	2273
49	0.281200 $\pm$ 15	0.00066	0.01982	0.1801 $\pm$ 61	2654 $\pm$ 112	0.281181	3.6	1.1	2814	2925	3018
50	0.281122 $\pm$ 9	0.00018	0.00571	0.1582 $\pm$ 13	2436 $\pm$ 29	0.281127	-3.4	0.7	2884	3200	3461
51	0.281591 $\pm$ 11	0.00044	0.01307	0.1279 $\pm$ 3	2069 $\pm$ 9	0.281587	4.5	0.8	2272	2411	2529
52	0.281376 $\pm$ 11	0.00028	0.00861	0.1532 $\pm$ 1	2383 $\pm$ 3	0.281377	4.3	0.7	2552	2670	2769
53	0.281163 $\pm$ 11	0.00045	0.01469	0.1405 $\pm$ 7	2233 $\pm$ 18	0.281158	-7.0	0.8	2849	3270	3623
54	0.280806 $\pm$ 14	0.00083	0.02634	0.2066 $\pm$ 90	2879 $\pm$ 141	0.280775	-5.5	1.1	3356	3685	3960
Ovruch Series (sample Ovruch)											
1	0.281622 $\pm$ 11	0.00115	0.03583	0.1281 $\pm$ 9	2072 $\pm$ 24	0.281591	4.7	0.8	2272	2402	2515
2	0.281578 $\pm$ 7	0.00040	0.01221	0.1218 $\pm$ 1	1982 $\pm$ 3	0.281577	2.1	0.5	2287	2495	2670
3	0.281610 $\pm$ 10	0.00112	0.03391	0.1222 $\pm$ 6	1989 $\pm$ 17	0.281582	2.4	0.7	2286	2480	2648
4	0.281609 $\pm$ 8	0.00133	0.04154	0.1212 $\pm$ 4	1974 $\pm$ 12	0.281574	1.8	0.5	2300	2509	2692
5	0.281591 $\pm$ 13	0.00107	0.03302	0.1213 $\pm$ 4	1975 $\pm$ 12	0.281565	1.5	1.0	2309	2527	2716
6	0.281597 $\pm$ 8	0.00116	0.03548	0.1211 $\pm$ 3	1972 $\pm$ 7	0.281567	1.5	0.6	2308	2525	2714
7	0.281587 $\pm$ 10	0.00131	0.04069	0.1254 $\pm$ 10	2035 $\pm$ 29	0.281550	2.3	0.7	2331	2521	2687
8	0.281598 $\pm$ 8	0.00129	0.04039	0.1243 $\pm$ 9	2018 $\pm$ 27	0.281563	2.4	0.6	2313	2503	2669
9	0.281594 $\pm$ 19	0.00147	0.04441	0.1323 $\pm$ 18	2129 $\pm$ 48	0.281548	4.5	1.4	2330	2459	2572
10	0.281593 $\pm$ 11	0.00052	0.01605	0.1201 $\pm$ 31	1958 $\pm$ 91	0.281587	1.9	0.8	2275	2488	2670
11	0.281571 $\pm$ 15	0.00056	0.01860	0.1227 $\pm$ 3	1996 $\pm$ 10	0.281564	1.9	1.0	2306	2515	2693
12	0.281576 $\pm$ 26	0.00131	0.04333	0.1217 $\pm$ 2	1982 $\pm$ 7	0.281540	0.8	1.9	2345	2578	2783
13	0.281639 $\pm$ 10	0.00115	0.03943	0.1256 $\pm$ 13	2038 $\pm$ 35	0.281608	4.5	0.7	2248	2386	2505
15	0.281573 $\pm$ 12	0.00083	0.03013	0.1225 $\pm$ 4	1993 $\pm$ 11	0.281556	1.6	0.8	2319	2536	2721
16	0.281598 $\pm$ 11	0.00124	0.04036	0.1248 $\pm$ 14	2026 $\pm$ 40	0.281564	2.6	0.8	2310	2494	2655
17	0.281604 $\pm$ 19	0.00152	0.05125	0.1210 $\pm$ 1	1971 $\pm$ 3	0.281561	1.2	1.4	2320	2540	2735
18	0.281695 $\pm$ 17	0.00138	0.04600	0.1227 $\pm$ 12	1996 $\pm$ 35	0.281657	5.2	1.2	2184	2305	2410
20	0.281605 $\pm$ 14	0.00109	0.03595	0.1208 $\pm$ 1	1968 $\pm$ 3	0.281579	1.8	1.0	2291	2501	2684
21	0.281660 $\pm$ 13	0.00067	0.02395	0.1347 $\pm$ 10	2160 $\pm$ 26	0.281646	8.7	0.9	2192	2213	2231
22	0.281317 $\pm$ 10	0.00067	0.02339	0.1218 $\pm$ 1	1983 $\pm$ 2	0.281305	-7.5	0.7	2658	3107	3489
23	0.281647 $\pm$ 11	0.00118	0.04008	0.1213 $\pm$ 2	1976 $\pm$ 6	0.281616	3.3	0.8	2240	2411	2560
24	0.281592 $\pm$ 10	0.00106	0.03526	0.1223 $\pm$ 7	1990 $\pm$ 21	0.281566	1.9	0.7	2308	2516	2696
Polissya Series (sample 56/90-95)											
1	0.281899 $\pm$ 17	0.00078	0.02797	0.0940 $\pm$ 16	1509 $\pm$ 64	0.281891	2.3	1.2	1871	2106	2311
2	0.282056 $\pm$ 18	0.00093	0.02888	0.0879 $\pm$ 4	1380 $\pm$ 17	0.282045	4.9	1.3	1661	1841	1999
4	0.281615 $\pm$ 25	0.00106	0.03462	0.1111 $\pm$ 9	1818 $\pm$ 30	0.281592	-1.2	1.8	2276	2573	2830
5	0.282061 $\pm$ 8	0.00102	0.04051	0.0898 $\pm$ 13	1421 $\pm$ 56	0.282048	5.9	0.6	1658	1809	1942
7	0.281815 $\pm$ 18	0.00080	0.02607	0.0926 $\pm$ 9	1479 $\pm$ 38	0.281807	-1.3	1.3	1987	2315	2601
8	0.281595 $\pm$ 15	0.00119	0.04053	0.1211 $\pm$ 1	1973 $\pm$ 3	0.281565	1.4	1.0	2311	2530	2721
9	0.282154 $\pm$ 22	0.00320	0.11114	0.0835 $\pm$ 5	1280 $\pm$ 22	0.282090	4.2	1.6	1622	1806	1986
10	0.281707 $\pm$ 14	0.00159	0.05335	0.1140 $\pm$ 12	1864 $\pm$ 39	0.281664	2.5	1.0	2181	2379	2555
11	0.281703 $\pm$ 7	0.00142	0.05696	0.1025 $\pm$ 8	1670 $\pm$ 27	0.281672	-1.7	0.6	2176	2492	2772
12	0.281959 $\pm$ 30	0.00253	0.09741	0.1150 $\pm$ 21	1879 $\pm$ 66	0.281883	10.6	2.2	1873	1870	1866
13	0.281542 $\pm$ 11	0.00060	0.02254	0.1216 $\pm$ 9	1980 $\pm$ 27	0.281533	0.5	0.9	2348	2596	2807
14	0.281563 $\pm$ 11	0.00025	0.01011	0.1201 $\pm$ 5	1958 $\pm$ 14	0.281567	1.2	0.8	2299	2533	2730
15	0.282139 $\pm$ 14	0.00076	0.02108	0.0893 $\pm$ 6	1411 $\pm$ 24	0.282132	8.7	1.0	1539	1622	1695
16	0.282095 $\pm$ 12	0.00152	0.05036	0.0870 $\pm$ 10	1360 $\pm$ 44	0.282070	5.3	0.9	1631	1798	1949
17	0.281888 $\pm$ 10	0.00054	0.01844	0.0802 $\pm$ 18	1201 $\pm$ 86	0.281890	-4.7	0.7	1874	2309	2686
18	0.281633 $\pm$ 12	0.00116	0.03923	0.1176 $\pm$ 17	1920 $\pm$ 51	0.281605	1.6	0.8	2258	2476	2666
19	0.281621 $\pm$ 11	0.00049	0.01665	0.1155 $\pm$ 2	1888 $\pm$ 6	0.281617	1.4	0.8	2234	2468	2666
20	0.282140 $\pm$ 29	0.00088	0.03021	0.0836 $\pm$ 2	1283 $\pm$ 12	0.282133	5.8	2.0	1542	1708	1854
22	0.281615 $\pm$ 13	0.00046	0.01556	0.1107 $\pm$ 3	1811 $\pm$ 10	0.281613	-0.6	0.9	2242	2531	2777
23	0.281859 $\pm$ 12	0.00065	0.02201	0.0911 $\pm$ 3	1449 $\pm$ 11	0.281856	-0.3	0.9	1918	2225	2490

#	$^{176}\text{Hf}/^{177}\text{Hf} \pm 1\sigma$	$^{176}\text{Lu}/^{177}\text{Hf}$	$^{176}\text{Yb}/^{177}\text{Hf} \pm 1\sigma$	$^{207}\text{Pb}/^{206}\text{Pb}$	$^{207}\text{Pb}/^{206}\text{Pb} \pm$	$^{176}\text{Hf}/^{177}\text{Hf}_T$	ϵHf_T	$\pm 2\sigma$	T(DM), Ma		
					2σ age, Ma				felsic	mafic	
24	0.280763 $\pm$ 13	0.00193	0.06409	0.2617 $\pm$ 17	3257 $\pm$ 20	0.280656	-0.8	0.9	3514	3682	3828
25	0.281523 $\pm$ 12	0.00098	0.03439	0.1299 $\pm$ 4	2096 $\pm$ 10	0.281498	1.9	0.9	2397	2595	2766
26	0.282286 $\pm$ 18	0.00432	0.14821	0.0851 $\pm$ 15	1317 $\pm$ 70	0.282193	8.7	1.4	1472	1548	1628
27	0.282150 $\pm$ 11	0.00068	0.02335	0.0924 $\pm$ 25	1475 $\pm$ 104	0.282145	10.6	0.8	1520	1549	1575
28	0.281646 $\pm$ 10	0.00062	0.02150	0.1112 $\pm$ 2	1820 $\pm$ 8	0.281638	0.5	0.7	2209	2468	2689
29	0.281871 $\pm$ 14	0.00055	0.01867	0.0969 $\pm$ 4	1565 $\pm$ 16	0.281869	2.8	1.0	1897	2118	2307
30	0.281857 $\pm$ 9	0.00062	0.02133	0.0981 $\pm$ 6	1589 $\pm$ 23	0.281852	2.8	0.7	1921	2139	2328
31	0.282034 $\pm$ 11	0.00111	0.03498	0.0890 $\pm$ 12	1404 $\pm$ 52	0.282019	4.5	0.8	1699	1885	2051
32	0.282150 $\pm$ 17	0.00093	0.03175	0.0872 $\pm$ 4	1365 $\pm$ 19	0.282140	7.9	1.2	1530	1636	1729
33	0.282100 $\pm$ 11	0.00051	0.01582	0.0857 $\pm$ 3	1331 $\pm$ 12	0.282101	5.7	0.8	1582	1748	1891
34	0.282163 $\pm$ 13	0.00050	0.01677	0.0816 $\pm$ 2	1236 $\pm$ 8	0.282165	5.8	0.9	1496	1666	1814
35	0.282104 $\pm$ 22	0.00059	0.02007	0.0843 $\pm$ 6	1300 $\pm$ 26	0.282104	5.1	1.5	1580	1763	1922
36	0.282112 $\pm$ 18	0.00050	0.01736	0.0810 $\pm$ 2	1223 $\pm$ 9	0.282114	3.7	1.3	1566	1791	1985
37	0.281885 $\pm$ 16	0.00080	0.02605	0.0984 $\pm$ 12	1593 $\pm$ 45	0.281875	3.7	1.2	1891	2085	2254
38	0.281456 $\pm$ 14	0.00060	0.01854	0.1155 $\pm$ 3	1888 $\pm$ 9	0.281448	-4.7	1.0	2465	2851	3178
39	0.281921 $\pm$ 17	0.00082	0.02800	0.0968 $\pm$ 2	1564 $\pm$ 9	0.281911	4.3	1.2	1842	2023	2181
40	0.282106 $\pm$ 23	0.00153	0.05297	0.0939 $\pm$ 2	1507 $\pm$ 8	0.282076	8.9	1.7	1617	1685	1746
41	0.281224 $\pm$ 16	0.00079	0.03046	0.1310 $\pm$ 3	2111 $\pm$ 8	0.281207	-8.1	1.1	2791	3243	3628
42	0.281806 $\pm$ 17	0.00062	0.01896	0.0910 $\pm$ 4	1447 $\pm$ 16	0.281803	-2.2	1.2	1989	2344	2650
43	0.281800 $\pm$ 19	0.00096	0.03151	0.0959 $\pm$ 1	1545 $\pm$ 6	0.281786	-0.6	1.4	2016	2319	2583
44	0.282107 $\pm$ 25	0.00175	0.05560	0.0861 $\pm$ 4	1341 $\pm$ 16	0.282077	5.1	1.8	1625	1796	1952
45	0.282193 $\pm$ 18	0.00077	0.02576	0.0880 $\pm$ 17	1382 $\pm$ 75	0.282187	9.9	1.3	1464	1517	1564
47	0.281836 $\pm$ 20	0.00038	0.01230	0.0931 $\pm$ 10	1490 $\pm$ 41	0.281840	0.1	1.4	1936	2234	2488
48	0.281121 $\pm$ 12	0.00033	0.01070	0.1674 $\pm$ 3	2532 $\pm$ 6	0.281119	-1.4	0.8	2896	3152	3364
49	0.282121 $\pm$ 26	0.00060	0.02032	0.0887 $\pm$ 11	1397 $\pm$ 48	0.282119	7.9	1.9	1558	1663	1754
50	0.281840 $\pm$ 15	0.00050	0.01547	0.0903 $\pm$ 3	1432 $\pm$ 14	0.281841	-1.2	1.1	1937	2270	2555
51	0.282094 $\pm$ 21	0.00060	0.01614	0.0923 $\pm$ 10	1474 $\pm$ 40	0.282091	8.6	1.5	1594	1674	1743
52	0.282160 $\pm$ 20	0.00099	0.02924	0.0821 $\pm$ 3	1249 $\pm$ 15	0.282151	5.6	1.4	1518	1689	1841
53	0.282102 $\pm$ 10	0.00057	0.01732	0.0842 $\pm$ 13	1298 $\pm$ 62	0.282102	5.0	0.7	1582	1767	1929
54	0.281720 $\pm$ 21	0.00088	0.02966	0.1119 $\pm$ 4	1830 $\pm$ 11	0.281704	3.1	1.5	2121	2313	2478
55	0.281862 $\pm$ 12	0.00047	0.01522	0.0924 $\pm$ 2	1476 $\pm$ 7	0.281863	0.6	0.8	1906	2191	2435
56	0.282130 $\pm$ 16	0.00106	0.03576	0.0806 $\pm$ 5	1211 $\pm$ 24	0.282120	3.7	1.1	1564	1785	1981
57	0.282150 $\pm$ 12	0.00063	0.01959	0.0732 $\pm$ 8	1018 $\pm$ 43	0.282152	0.4	0.8	1519	1839	2119
58	0.281635 $\pm$ 16	0.00162	0.04874	0.1238 $\pm$ 3	2011 $\pm$ 8	0.281587	3.1	1.1	2283	2454	2605
59	0.281567 $\pm$ 22	0.00122	0.04542	0.1207 $\pm$ 12	1967 $\pm$ 37	0.281535	0.3	1.6	2352	2600	2817
Volyn Series (sample 8265/320.5-327)											
1	0.281747 $\pm$ 13	0.00046	0.01136	see Table 2	1422 $\pm$ 40	0.281743	-4.9	0.9	2070	2497	2949
2	0.281652 $\pm$ 14	0.00034	0.00876		1422 $\pm$ 40	0.281650	-8.2	1.0	2193	2703	3241
3	0.281687 $\pm$ 15	0.00037	0.00927		1422 $\pm$ 40	0.281685	-6.9	1.1	2146	2625	3131
4	0.281680 $\pm$ 14	0.00033	0.00876		1422 $\pm$ 40	0.281679	-7.2	1.0	2153	2638	3149
5	0.281709 $\pm$ 15	0.00045	0.01164		1422 $\pm$ 40	0.281705	-6.3	1.1	2121	2582	3069

Note: depleted mantle model ages are calculated using measured $^{176}\text{Lu}/^{177}\text{Hf}$ ratio, whereas 'felsic crust' model ages are calculated using average continental crust $^{176}\text{Lu}/^{177}\text{Hf}$ = 0.015 ([Griffin et al., 2004](#)), and 'mafic crust' model ages are calculated using $^{176}\text{Lu}/^{177}\text{Hf}$ = 0.021 ([Kemp et al., 2006](#)).

Table 2. Results of U-Pb dating of zircons from the Gorbashy suite conglomerate (sample 8265/320.5-327)

#	Concentrations, ppm				Isotope ratios							Ages, Ma			%Disc
	U	Th	Pb	Th/U	²⁰⁴ Pb/ ²⁰⁶ Pb	²⁰⁷ Pb/ ²³⁵ U 1σ	²⁰⁶ Pb/ ²³⁸ U 1σ	Rho	²⁰⁷ Pb/ ²⁰⁶ Pb 1σ	²⁰⁶ Pb/ ²³⁸ U 1σ	²⁰⁷ Pb/ ²³⁵ U 1σ	²⁰⁷ Pb/ ²⁰⁶ Pb 1σ			
1	25	29	8	1.17	0.0031	3.147 0.068	0.2573	0.0025	0.4	0.0887	0.0017	1476 13	1444 17	1398 37	-5
2	61	124	24	2.05	0.0014	3.193 0.061	0.2554	0.0022	0.4	0.0907	0.0016	1467 11	1455 15	1439 33	-2
3	124	317	54	2.56	0.0001	3.160 0.059	0.2610	0.0022	0.4	0.0878	0.0015	1495 11	1447 14	1378 32	-8
4	15	17	5	1.17	0.0043	3.133 0.090	0.2496	0.0032	0.4	0.0910	0.0023	1437 16	1441 22	1447 49	1
5	125	70	35	0.56	0.0001	3.128 0.058	0.2562	0.0021	0.4	0.0885	0.0015	1470 11	1440 14	1394 32	-5
6	28	57	11	2.03	0.0005	3.144 0.065	0.2563	0.0023	0.4	0.0890	0.0016	1471 12	1444 16	1404 35	-5
7	17	27	6	1.58	0.0001	3.239 0.082	0.2532	0.0028	0.4	0.0928	0.0021	1455 15	1467 20	1483 43	2
8	71	82	22	1.16	0.0000	3.160 0.060	0.2536	0.0021	0.4	0.0904	0.0015	1457 11	1447 15	1434 33	-2
9	61	82	20	1.34	0.0003	3.180 0.061	0.2557	0.0022	0.4	0.0902	0.0015	1468 11	1452 15	1429 33	-3
10	101	193	36	1.90	0.0000	3.132 0.059	0.2510	0.0021	0.4	0.0905	0.0015	1444 11	1441 15	1436 32	-1
11	75	139	27	1.86	0.0005	3.001 0.037	0.2509	0.0012	0.4	0.0868	0.0010	1443 6	1408 9	1355 22	-6
12	57	71	18	1.25	0.0013	3.155 0.040	0.2560	0.0013	0.4	0.0894	0.0010	1469 6	1446 10	1413 22	-4
13	45	52	14	1.16	0.0000	3.172 0.042	0.2577	0.0013	0.4	0.0893	0.0011	1478 7	1450 10	1410 23	-5
14	117	192	42	1.63	0.0002	3.178 0.038	0.2603	0.0012	0.4	0.0886	0.0010	1491 6	1452 9	1395 21	-7
15	29	28	9	0.94	0.0000	3.270 0.048	0.2581	0.0015	0.4	0.0919	0.0012	1480 8	1474 11	1465 25	-1
16	17	45	7	2.61	0.0001	3.189 0.061	0.2549	0.0020	0.4	0.0908	0.0016	1464 10	1455 15	1441 33	-2
17	13	18	4	1.39	0.0064	3.099 0.057	0.2504	0.0019	0.4	0.0897	0.0015	1441 10	1432 14	1420 32	-1
18	195	129	30	0.66	0.0000	1.748 0.021	0.1375	0.0006	0.4	0.0922	0.0010	830 3	1026 8	1472 21	77
19	61	59	19	0.98	0.0003	3.084 0.039	0.2527	0.0012	0.4	0.0885	0.0010	1453 6	1429 10	1393 22	-4
20	17	18	5	1.09	0.0001	3.236 0.054	0.2477	0.0017	0.4	0.0948	0.0014	1427 9	1466 13	1523 29	7