Geochronology of granites of the western Korosten AMCG complex (Ukrainian Shield): implications for the emplacement history and origin of miarolitic pegmatites

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Abstract. The origin of large miarolitic (also known as “chamber”) pegmatites is not fully understood although they may have great economic value. The formation of cavities in magmatic bodies is related to melt degassing and gas or fluid flow through partially solidified magma. In this paper, the origin of the Volyn pegmatite field, located in the Palaeoproterozoic Korosten anorthosite–mangerite–charnockite–granite (AMCG) complex, North-Western region of the Ukrainian Shield, is discussed. Pegmatites of the field host deposits of piezoelectric quartz that is accompanied by gem-quality beryl and topaz. The Volyn pegmatite field is confined to granites located in the south-western part of the Korosten complex and extends for 22 km along the contact with the anorthosite massif within the Korosten plutonic complex. Geological data indicate hybridization of basic melts and partly crystallized granites, as well as direct impact of fluids derived from basic melts on the chamber pegmatites.

The new U–Pb zircon ages obtained for granites and pegmatites of the Korosten complex confirm that the rock assemblage in the northern part of the complex crystallized between 1800 and 1780 Ma, whereas rocks in the southern part intruded mainly between 1768 and 1755 Ma. U–Pb zircon ages for granites from the south-western part of the Korosten complex indicate that granites were emplaced at 1770–1765 Ma, a few million years prior to the intrusion of the gabbro–anorthosite massif (1762–1758 Ma), while chamber pegmatites in these granites crystallized at 1760 ± 3 Ma, coevally with the basic rocks. Ultimately, the formation of the chamber pegmatites was related to the reheating of the semi-crystallized granitic intrusion and to fluids migrating from the underlying gabbro–anorthosite massif.
1 Introduction

Miarolitic (also known as “chamber”) pegmatites differ from other types of pegmatites by the presence of empty cavities that enable the free growth of well-formed giant crystals of various minerals (e.g. Lazarenko et al., 1973; Zito and Hanson, 2014; Phelps et al., 2020) that may have great economic value. The sizes of miarolitic cavities are quite variable, but commonly they do not exceed centimetres or decimetres. Their occurrence indicates the process of melt degassing and gas/fluid flow through partially solidified magma (e.g. Candel and Blevin, 1995; Thomas et al., 2009; Peretyazhko, 2010; Vigneresse, 2015; Pistone et al., 2020). Large cavities, reaching sizes ranging from tens to hundreds of cubic metres, are extremely rare in nature, and their formation requires special conditions, such as the gas/fluid filling the cavity must be able to overcome the lithostatic pressure.

In this communication, the results of U–Pb dating of zircon from granites that were sampled in the western part of the Korosten anorthosite–mangerite–charnockite–granite (AMCG) plutonic complex and from a miarolitic (chamber) pegmatite representing the Voyln pegmatite field are reported. In addition, we report the results of Hf isotope studies in zircon from the same samples, as well as four specimens representing hybrid and granite rocks of the Korosten complex. All these data are discussed in the context of the magmatic evolution of the Korosten plutonic complex (KPC) and the formation of the Voyln pegmatite field.

2 Geological setting

2.1 Korosten plutonic complex

The Korosten plutonic complex occurs in the North-Western region of the Ukrainian Shield, in proximity to the junction zone between Sarmatia and Fennoscandia. It is relatively well exposed, being only partly covered by recent sediments. The KPC is one of the largest (about 10 400 km$^2$) AMCG complexes in the world (Fig. 1). Granites occupy about 75% of the complex, while the rest is dominated by basic rocks. The host rocks are Palaeoproterozoic gneisses, granites, and migmatites (Stepanyuk et al., 2000; Shcherbak et al., 2008; Shumlyanskyy et al., 2018b). Remnants of the platformational extension by quartzites and slates occur as large xenoliths among the rocks of the KPC and represent its ancient roof. Their presence indicates a relatively high level of intrusion and limited subsequent erosion not exceeding 1000 m. The same rocks can be found to the north-west of the KPC, in the Bilokorovychi graben syncline filled with platformational sediments, deposited before the KPC formation (Shumlyanskyy and Mazur, 2010). In its northern part, volcanic rocks coeval with the KPC and slightly younger tephrogenous rocks filled the Ovruch basin and partly cover the KPC (Shumlyanskyy and Bogdanova, 2009; Shumlyanskyy et al., 2015b).

The KPC encompasses rapakivi granitoids and a suite of basic rocks that includes predominantly anorthosite and leucogabbro-norite, as well as subordinate gabbronorite rocks. Monzonites and syenites are volumetrically minor rock types. Anorthosites and related rocks form sheet-like bodies, the largest of which is the Voyln massif that occupies 1250 km$^2$ and varies in thickness from hundreds to thousands of metres. The gabbronorite series includes various rocks from leucogabbro to melanogabbro and ultramafics that form layered intrusions and sheet-like bodies in association with the anorthosite massifs. Ferromonzonidotite and quartz–ferromonzonidotite dykes are widespread in the KPC, where they cut both the basic and felsic rocks, as well as intrude on the host rocks of the complex (Duchesne et al., 2017; Shumlyanskyy et al., 2018a).

Medium-grained granites with sparse mantled ovoids are the dominant rocks at the current level of erosion, whereas coarse-grained wiborgite rapakivi is a rare rock
type. Biotite–amphibole granites with fayalite and Fe-
hedenbergite prevail near the contacts with the basic rocks.
Towards the central parts of the granitic massifs, these rocks
turn into biotite–amphibole granite. The contacts of the gab-
broic massifs with rapakivi granites are complicated and in-
dicate the emplacement of basic melts into a partly crystal-
lized granite chamber, resulting in mingling and hybridiza-
tion (Mitrokhin and Bilan, 2014). The lines of evidence for
these processes include the following: sinuous branching
veins of fayalite-hedenbergite syenite observed in gabbro;
discontinuous chilled margins occurring in gabbro but absent
in granites; mafic inclusions in granites having pillow-like
morphology and chilled margins; and alkali feldspar ovoid
phenocrysts occurring in gabbro (Fig. 2). The structure of
the hybrid rocks varies from massive to taxitic, banded, or
network-like.

From the very first geological studies of the KPC, the
question of the temporal relationships between basic and
felsic rocks has remained as one of the most controversial.
Tarasenko (1895) argued for a younger age of basic rocks
with respect to granites, whereas Sobolev (1947) presented
a model in which the emplacement and crystallization of the
basic melt were accompanied by melting of the crustal rocks,
giving rise to granite formation. Both basic and felsic rocks
are virtually coeval and may have been emplaced in sev-
eral pulses. Although this model is generally accepted (e.g.
Mitrokhin et al., 2008; Shumlyansky et al., 2017), there is
still a widespread opinion that rapakivi granites cropping out
at the modern surface are slightly younger than basic rocks
(e.g. Lichak, 1983).

2.2 Geological structure of the Volyn pegmatite field

The Volyn pegmatite field is confined to granites located in
the south-western part of the KPC, extending for 22 km along
the contact with the anorthosite massif, while the width of the
field varies between 300 and 1500 m (Fig. 3; Lazarenko
et al., 1973, Lichak, 1983). Pegmatite-bearing granites are
variable in composition, texture, and structure. They contain
small ovoids of feldspars surrounded by an aplitic to gra-
phophyric matrix. Alkali feldspars (perthitic orthoclase and
microcline) noticeably prevail over quartz and oligoclase.
Mafic minerals are extremely ferrous, and hastingsite horn-
blende and annite are the most abundant mafic minerals.
Fayalite, Fe-hedenbergite, Fe-actinolite, grunerite, and id-
dingsite are present in minor amounts. Accessories are il-
menite, zircon, apatite, fluorite, and allanite.

Several zones can be distinguished across the pegmatite
field, starting from the contact with basic rocks towards
the inner parts of the granite massif: zones with (1) peg-
mattite veinlets, (2) fully differentiated chamber pegmatites,
(3) disseminated small pegmatite bodies, and (4) quartz vein-
lets surrounded by leaching zones (Lichak and Tsarovskiy,
1957). The pegmatite bodies are unevenly distributed and
form chains, rings, or equant groups. They are not intercon-
nected, have no obvious feeders, and occur as isolated bodies.
According to Marakushev et al. (1989), pegmatite bodies in
the Volyn field either occur at the places of their segregation
or have moved upward for a short distance. They are variable
in shape and size, but all have a similar internal construc-
tion. Each pegmatite body has the outermost zone of graphic
pegmatite that turns inwards into the pegmatoid zone. The
central parts of the largest bodies contain a cavity that can
reach tens to hundreds of cubic metres in size, above which
quartz and block feldspar zones are located. Below the cav-
ity, a leaching zone composed of albitized potassium feldspar
usually occurs.

The pegmatites were mined for quartz (as raw material for
piezoelectric quartz), which occurs in metre-sized crystals
weighing tons (Lyckberg et al., 2009, and references therein).
The locality is known for gem-quality beryl crystals of the
colour variety heliodor and large amounts of topaz that have
also been mined. Another peculiarity is the occurrence of or-
ganic matter known as “kerite” (Franz et al., 2017, and ref-
ences therein) for which the age of pegmatite formation
represents the upper age limit.

Marakushev et al. (1989) also described zones of mafic
mineral enrichment in the host granites that accompany each
pegmatite body. The size of such zones correlates with the
size of the pegmatite body. The amount of mafic minerals
varies from 15 vol % to 50 vol % or more. In contrast to the
ovoid texture of the host granite, melanocratic zones contain
euhedral zoned plagioclase. The core parts of plagioclase are
composed of andesine (An$_{34-30}$), whereas the outer parts are
composed of oligoclase (An$_{26-20}$), both being more calcic
than plagioclase in the host granite. The main mafic mineral
is biotite, while amphibole may occur at some distance from
the pegmatites. Olivine and pyroxene are also present in mi-
nor amounts. Such zones of mafic mineral enrichment oc-
cur immediately below the pegmatite bodies and, rarely, may
also surround them. Enrichment in ilmenite and zircon in the
host rocks has also been reported by Ivantyshyn et al. (1957).

Host granites contain areas of micropegmatite or graphic
textures that were described as incipient pegmatite. In addi-
tion, granites contain accessory minerals typical of pegmatite
bodies, such as black quartz (morion), fluorite, topaz, and fer-
riferous micas, among others. Lichak (1983) emphasized that
pegmatite bodies are cognate to their host granites and often
reveal gradual contacts.

Based on the results of studies of primary fluid inclusions
in the outer zones of beryl crystals, Vozniak et al. (2012) de-
defined $P$–$T$ (pressure and temperature) parameters for the in-
termediate to late stages of pegmatite crystallization at 190–
200 °C and 10–13 MPa (corresponding to depths of 1000–
1300 m). Vozniak (2007) also used the “chemical dating
method” (based on the measurements of U, Th, and Pb
concentrations) applied to zircon and uraninite inclusions
in topaz to demonstrate that pegmatites crystallized at ca.
1750 Ma.
3 Samples and analytical methods

In this study, the results of laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) Hf isotope studies from eight zircon samples representing rocks of the KPC are reported (Table 1, Fig. 1). All eight samples were dated using secondary ion mass spectrometry (SIMS): four as part of this study, while the other four were dated previously by Shumlyansky et al. (2017). The samples from the earlier study are monzodiorite (sample 71-1M) and syenite (sample 71-9), which occur at the eastern contact of the Volyn gabbro–anorthosite massif with rapakivi granites of the Malyn massif. The other two samples represent rapakivi granites (samples 95005 and 53-7) of the Malyn massif.

Our four new samples represent granites of the western part of the KPC (sample 18K-1: granite from the open pit in Novi Bilokorovychi village; sample 18K-3: granite from the open pit in Sukhovolya village), one pegmatite sample (18K-2, from the dump of the underground mine near the city of Khoroshev), and one sample (18K-2-1) represents the granite host of the pegmatite from the same locality.

For the SIMS analysis, obtained using the CAMECA 1280-HR SIMS instrument at the GFZ Potsdam, the analytical set-up largely follows that of Ashwal et al. (2017) and Glynn et al. (2017). The U–Pb calibration for the analytical session was based on the primary zircon reference material 91500 (206Pb / 238U age: 1062.4 ± 0.4 Ma; 207Pb / 206Pb age: 1065.4 ± 0.3 Ma; Wiedenbeck et al., 1995), while Temora 2 (206Pb / 238U age: 416.78 ± 0.33 Ma; Black et al., 2004) reference material has been used to evaluate the accuracy and stability of the calibration.

Data reduction employed the Excel-based programme “NordAge” (Martin J. Whitehouse, NORDSIM facility, Stockholm), for which 18 measurements made on 91500 were used to establish the U–Pb inter-element fractionation against which the unknowns were calibrated using a Pb / UO vs. UO² / UO relationship employing a power-law fit. This resulted in a mean 206Pb / 238U age of 1062 ± 6 Ma (mean squared weighted deviation, MSWD, = 0.39) for 91500 standard. Temora 2, when treated as an unknown, produced a 206Pb / 238U age of 420 ± 3 Ma (MSWD = 0.69, N = 10). Thus, the reference materials are within the reasonable agreement of their published 206Pb / 238U ages of 1062.4 and 416.78 Ma respectively, indicating that no gross bias is present in the U–Pb determinations.

The Excel programme “Isoplot” (Ludwig, 2012) was used to plot the data using the decay constants recommended by the International Union of Geological Sciences (IUGS) subcommission on geochronology (Steiger and Jäger, 1977), whereas corrections for common lead were based on the observed 204Pb / 206Pb ratio in conjunction with the common lead composition from the model of Stacey and Kramers (1975).

The Lu–Hf isotope composition was measured on a Nu Plasma II multi-collector inductively coupled plasma mass spectrometer at the John de Laeter Centre, Curtin University, Perth, Australia. All isotopes (180Hf, 179Hf, 178Hf,
prismatic–bipyramidal crystals, hosting numerous mineral euhedral and rather large (up to 200–300 µm in all samples) inclusions. In many cases, zircons do not reveal zoning and appear mostly homogeneous in backscattered electron (BSE) and cathodoluminescence (CL) images. Oscillatory or simple concentric zoning is relatively rare but prevails in zircons from pegmatite sample 18K-2. In all four samples, narrow dark alteration rims can be seen in BSE images in some of the crystals. In general, though, all zircons have a typical igneous appearance, being only slightly altered by hydrothermal fluids.

4.2 U–Pb geochronology

Sample 18K-1 (granite from the open pit in Novi Bilokorovychi village) yielded variably discordant results (Table 2, Fig. 5), with an upper intercept age of 1782 ± 19 Ma and a lower intercept age of 550 ± 46 Ma. This age is based on 17 individual measurements. Zircons in this sample are characterized by high concentrations of U and Th, which have resulted in partial metamictisation of zircons, a high degree of discordance, and a relatively low accuracy of the age determination. Sample 18K-3 (granite from the open pit in Sukhovolya village) yielded a concordia age of 1771 ± 9 Ma, with all 10 measurements carried out in this sample being concordant. Zircons from this sample have low to moderate U and Th concentrations (Table 2). Zircons from granite sample 18K-2-1, which hosts the pegmatite) sampled at the city of Khoroshiv produced predominantly (10 out of 12 analyses) concordant results yielding a concordia age of 1766 ± 3 Ma. The upper intercept age based on all 12 results is 1760 ± 7 Ma (Fig. 5). Most of the zircons, except two, analysed in this sample have low to moderate U and Th concentrations. The remaining two crystals revealed high
concentrations of U (over 2400 ppm) and yielded heavily discordant ages. Finally, the pegmatite (sample 18K-2) yielded a concordia age of 1760 ± 3 Ma (based on 8 out of 12 measurements). In general, zircons from pegmatite have the lowest U and Pb concentrations among all four studied samples.

A few of the results obtained for granites and pegmatite were heavily discordant with Mesozoic lower intercept ages. No differences between core and rim ages have been detected in any of the samples. Irregular dark areas seen in some zircon grains (see above) all yielded strongly discordant results.

### 4.3 Hf isotopes

Hafnium isotopes were measured in zircons from eight samples, four of which were dated as part of this study, and the other four represent previously dated granites and hybrid rocks. Zircons from these rocks reveal rather wide variations in the initial 176Hf/177Hf values (Table 3), similar to, or slightly exceeding, those which were previously reported for the rocks of the KPC (Shumlyanskyy et al., 2017). In general, weighted average εHf values for all eight samples vary between 0.1 and −1.2. The highest weighted average εHf value of 0.1 ± 0.7 was found in monzogabbro sample 71-1M that represents the marginal facies of the Volyn massif. Hybrid syenite from the same location revealed an εHf value of −0.5 ± 0.7. Rapakivi granites have the following weighted average εHf values: sample 95005 = −0.4 ± 1.3; sample 18K-3 = −0.8 ± 0.5; sample 53-7 = −0.8 ± 1.1; sample 18K-2-1 = −0.5 ± 0.4; and sample 18K-1 = −1.2 ± 0.5. Finally, zircons from granite pegmatite have a weighted average εHf value of −1.1 ± 0.4.

### 5 Discussion

#### 5.1 General magmatic evolution of the Korosten AMCG complex

The evolution of the KPC, based on the results of the U–Pb dating of various rocks, has been discussed by Shumlyanskyy et al. (2017). Here we provide new data regarding granites, which remain relatively poorly studied in comparison with basic rocks. According to the data, the first pulse of magmatic activity in the KPC took place between 1800 and 1780 Ma when the whole range of magmatic rocks, including anorthosite, gabbro, syenite, jotunite, and granite, crystallized in the northern part of the KPC (Figs. 1, 6). This first pulse started with the emplacement of the early anorthosite series represented by anorthosite and leuconorite-bearing megacrysts of lower-crustal high-alumina orthopyroxene (Mitrokhin et al., 2008). These rocks crystallized in the lower crust and occur either as xenoliths in younger rocks or relatively large bodies brought to the surface by tectonic movements. Granites in the northern part of the KPC were formed coevally with the early anorthosite series, as can be seen from relationships with the Davydky gabbro–syenite intrusion, which intruded into granite at 1790 ± 2 Ma (Shumlyansky et al., 2015a). U–Pb zircon ages were determined for three granite samples belonging to this magmatic pulse: 1780 ± 6 Ma (Bondary open pit; Shumlyansky et al., 2017), 1781 ± 3 Ma (Usove village; Amelin et al., 1994), and 1782 ± 19 Ma (Bilokorovychi granite; this study). In contrast to the northern part, most of the rocks exposed in the southern half of the KPC crystallized between ca. 1768 and 1755 Ma. Large anorthosite bodies of the Volyn massif intruded between ca. 1761 and 1758 Ma, while residual melts, represented by pegmatic pods, crystallized at ca. 1758 Ma, indicating that these anorthosite bodies, which are up to 2 km thick and occupy up to 1000 km², solidified within a few million years (Shumlyansky and Zahniitko, 2011). Numerous gabbroic intrusions in the internal and marginal parts of the anorthosite massifs intruded between 1763 and 1757 Ma; their ages are indistinguishable within error from that of the host anorthosite.

Despite the commonly held opinion about the younger age of large granite massifs associated with anorthosite bodies, available geochronological data indicate that this is not the case for the KPC. All rapakivi granites and syenites in the southern half of the KPC have ages within a narrow interval of 1765–1762 Ma. Granites from the city of Khoroshiv (1766 ± 3 Ma) and Sukhovolya village (1771 ± 9 Ma) also, within error, fall into this same narrow interval. Small bodies of biotite granite porphyry intruded at ca. 1758 Ma, while the youngest rocks of the KPC are subalkaline granites of the Lezniki massif and veins of Li–F microcline–albite granites.

Figure 4. Representative images of zircons extracted from the samples dated as part of this study. Backscattered electron (BSE) images at the top and cathodoluminescence (CL) images at the bottom. (a) Sample 18K-1; (b) sample 18K-2; (c) sample 18K-2-1; (d) sample 18K-3.
(1752 ± 8 and 1742 ± 9 Ma, respectively; Shumlyansky et al., 2017).

Hence, during the first phase of magmatic activity basic and felsic rocks crystallized coevally. During this phase, anorthosites crystallized mainly in the lower crust, whereas felsic melts intruded into the upper crust. Upper-crustal mafic rocks of this phase are gabbro–syenites of the Davydsky inlier and several jotunite dykes. The second phase of magmatic activity started with emplacement of the large rapakivi granite massifs, followed soon by several large gabbro–anorthosite intrusions into the upper crust.

Hafnium isotope compositions in zircons from different granite massifs do not reveal systematic variations with age (Fig. 7). All rocks, irrespective of their composition (except sample 06-BG47: the late jotunite silt from the Bondary open pit), have near-chondritic Hf isotope values between +3 and −3. On average, zircons from gabbros and anorthosites reveal slightly higher εHf values than felsic rocks, but considering
significant within-sample variations (Table 3), isotope compositions of different lithologies overlap. Hence, our new Hf isotope data agree with the previous conclusions proposed by Shumlyanskyy et al. (2006, 2017) regarding a predominantly crustal source for the parental magma, with some input of juvenile material from coeval mantle-derived tholeiite melts.

### 5.2 Origin and evolution of chamber pegmatites

According to Voznyak and Pavlyshyn (2008), chamber pegmatites of the Volyn pegmatite field crystallized at a relatively shallow depth of less than 3.5 km. As the level of erosion throughout the KPC does not exceed the first few kilometres, chamber pegmatites can potentially be found everywhere in the complex, and indeed, miorolitic cavities up to a dozen centimetres in size are common in granites of the KPC and are found in multiple different places (Lazarenko et al., 1973). However, large chamber pegmatites, reaching hundreds of cubic metres in volume (e.g., Lyckberg et al., 2019), occur only in the Volyn pegmatite field.

Pegmatite chambers are formed when the host granite remains in a semi-crystallized, plastic state, thus allowing the fluid to overcome the lithostatic pressure and inflate the chamber. At a later stage, the semi-crystallized granite forms an interlocking crystal network thereby losing its ability to form cavities. As a result, the time interval during which pegmatite chambers can be formed is relatively short. So, there must be some additional factor acting specifically in the Volyn pegmatite field which is extending the common miorole-forming process allowing for the formation of large chamber pegmatites.
Volatile gases dissolved in rising crystallizing magmatic melts can exsolve when they reach the solubility limit due to cooling, decompression, or magma crystallization. As melts rise in the crust, they gradually become saturated with respect to exsolving volatiles as a fluid phase (e.g. Baker and Alletti, 2012; Masotta et al., 2010; Blundy et al., 2015; Afanasyev et al., 2018). For the Volynt pegmatite field the magma must have been rich in CO₂ because the pegmatites are characterized by a large amount of topaz, which would decrease the lowest melt temperature significantly. However, for a detailed evaluation of the type of evolving fluids, the necessary geochemical data (e.g. concentration of F, Cl, S) for the magmas are missing. Exsolution of gases and hydrous fluids is a very common process during the late stages of crystallization and an input of sufficient amounts of CO₂, which probably corresponds to the emplacement of basic melts.

Our model for the formation of chamber pegmatites in the Volynt pegmatite field includes several stages. The first stage corresponds to the formation of rather small “incipient” chambers (i.e. the mafic mineral enrichment is that they contain more calcic plagioclase than the surrounding granite). An even more pronounced impact of the basic melts on granites which was noticed in zones of mafic mineral enrichment is that they contain more calcic plagioclase than the surrounding granite (Marakushev et al., 1989). Considering all these lines of evidence, we assume that the emplacement of basic melts and their subsequent interaction with the partly solidified granites played a crucial role in the formation of the chamber pegmatites: the degassing of basic magmas at shallow levels resulted in the infiltration of additional fluids and gases into the overlying partly crystallized granite massif, ultimately resulting in the formation of the chamber pegmatites. Vozniak and Pavlyshyn (2008) and Vozniak et al. (2012) were the first to demonstrate the role of gases and fluids derived from the basic melts on the formation of the chamber pegmatites in the Volynt pegmatite field. Studying fluid inclusions in quartz, topaz, and beryl, they have recorded a temperature increase during the late stages of crystallization and an input of sufficient amounts of CO₂, which probably corresponds to the emplacement of basic melts.

The formation of huge pegmatite chambers requires special conditions, which can occur (a) when the process of granitic melt crystallization is extended, i.e. when the mafic mineral enrichment is that they contain more calcic plagioclase than the surrounding granite. However, the formation of huge pegmatite chambers requires special conditions, which can occur (a) when the process of granitic melt crystallization is extended, i.e. when the mafic mineral enrichment is that they contain more calcic plagioclase than the surrounding granite.
Table 3. Hafnium isotope compositions in zircons from the studied rocks of the Korosten plutonic complex.

| No. | 176 Lu / 177 Hf | 176 Yb / 177 Hf | 176 Hf / 177 Hf ±1σ | 176 Hf / 177 HfT εHfT ±2σ |
|-----|----------------|----------------|---------------------|--------------------------|
| 1   | 0.000574       | 0.015900       | 0.281645 0.000034   | 0.281626 −1.2 2.4       |
| 2   | 0.000767       | 0.021500       | 0.281650 0.000033   | 0.281624 −1.3 2.3       |
| 3   | 0.000720       | 0.019510       | 0.281636 0.000034   | 0.281612 −1.7 2.4       |
| 4   | 0.000673       | 0.018200       | 0.281621 0.000039   | 0.281598 −2.2 2.7       |
| 5   | 0.000950       | 0.025500       | 0.281738 0.000036   | 0.281706 1.6 2.6        |
| 6   | 0.000656       | 0.017690       | 0.281623 0.000037   | 0.281601 −2.1 2.6       |
| 7   | 0.000975       | 0.026100       | 0.281751 0.000035   | 0.281718 2.0 2.5        |
| 8   | 0.000539       | 0.014310       | 0.281638 0.000035   | 0.281620 −1.4 2.5       |
| 9   | 0.000500       | 0.013250       | 0.281623 0.000034   | 0.281606 −1.9 2.4       |
| 10  | 0.000798       | 0.021960       | 0.281691 0.000036   | 0.281664 0.1 2.6        |

Sample 53-7, wiborgite, Myrne village, 1763 ± 6 Ma

| No. | 176 Lu / 177 Hf | 176 Yb / 177 Hf | 176 Hf / 177 Hf ±1σ | 176 Hf / 177 HfT εHfT ±2σ |
|-----|----------------|----------------|---------------------|--------------------------|
| 1   | 0.003140       | 0.090100       | 0.281804 0.000044   | 0.281699 1.4 3.1         |
| 2   | 0.000755       | 0.020500       | 0.281669 0.000034   | 0.281644 −0.6 2.4       |
| 3   | 0.001390       | 0.039500       | 0.281655 0.000035   | 0.281608 −1.8 2.5       |
| 4   | 0.001283       | 0.036010       | 0.281716 0.000032   | 0.281673 0.5 2.2        |
| 5   | 0.000967       | 0.026500       | 0.281708 0.000029   | 0.281676 0.6 2.0        |
| 6   | 0.001187       | 0.033850       | 0.281674 0.000040   | 0.281634 −0.9 2.8       |
| 7   | 0.002410       | 0.069500       | 0.281773 0.000047   | 0.281692 1.2 3.4         |
| 2   | 0.001900       | 0.055000       | 0.281735 0.000038   | 0.281671 0.4 2.7        |
| 3   | 0.002190       | 0.062500       | 0.281759 0.000033   | 0.281686 0.9 2.3        |
| 4   | 0.002540       | 0.071200       | 0.281728 0.000037   | 0.281643 −0.6 2.6       |
| 5   | 0.001230       | 0.034900       | 0.281655 0.000033   | 0.281614 −1.6 2.4       |
| 6   | 0.002779       | 0.077800       | 0.281817 0.000037   | 0.281724 2.3 2.6        |
| 7   | 0.001310       | 0.037100       | 0.281600 0.000035   | 0.281556 −3.7 2.5       |
| 8   | 0.001507       | 0.041800       | 0.281706 0.000041   | 0.281655 −0.1 2.9       |
| 9   | 0.002180       | 0.066200       | 0.281675 0.000028   | 0.281602 −2.0 2.0       |
| 10  | 0.002737       | 0.078600       | 0.281798 0.000039   | 0.281706 1.7 2.8        |

Sample 95005, granite, Huta-Potiivka village, 1765 ± 3 Ma

| No. | 176 Lu / 177 Hf | 176 Yb / 177 Hf | 176 Hf / 177 Hf ±1σ | 176 Hf / 177 HfT εHfT ±2σ |
|-----|----------------|----------------|---------------------|--------------------------|
| 1   | 0.006582       | 0.015140       | 0.281647 0.000032   | 0.281628 −1.2 2.3       |
| 2   | 0.001283       | 0.021500       | 0.281650 0.000037   | 0.281650 −0.4 2.6       |
| 3   | 0.002566       | 0.013570       | 0.281653 0.000033   | 0.281635 −0.9 2.3       |
| 5   | 0.000506       | 0.013570       | 0.281653 0.000033   | 0.281636 −0.9 2.3       |
| 6   | 0.002566       | 0.072700       | 0.281819 0.000042   | 0.281733 2.5 3.0        |
| 7   | 0.000804       | 0.022070       | 0.281718 0.000033   | 0.281691 1.0 2.3        |
| 8   | 0.000984       | 0.027090       | 0.281726 0.000032   | 0.281693 1.1 2.2        |
| 9   | 0.000608       | 0.016400       | 0.281644 0.000030   | 0.281624 −1.4 2.1       |
| 10  | 0.000491       | 0.013060       | 0.281706 0.000032   | 0.281690 1.0 2.3        |

drothermal assemblages can be distinguished (Lazarenko et al., 1973). The magmatic assemblage includes minerals that form the outer parts of the pegmatite bodies, first of all eutectic intergrowths of quartz and feldspars (so-called “graphic granite”). Our zircons were separated from this part of the pegmatite, and their age thus corresponds to the early stages of the pegmatite formation. In contrast, internal portions of the pegmatite bodies are composed of giant crystals of various minerals, which, according to the results of fluid inclusion studies (e.g. Lazarenko et al., 1973; Vozniak and...
Table 3. Continued.

| No. | 176\(^{Lu}\)/177\(^{Hf}\) | 176\(^{Yb}\)/177\(^{Hf}\) | 176\(^{Hf}\)/177\(^{Hf}\) | ±1σ | 176\(^{Hf}\)/177\(^{Hf}\) + T | ε\(^{Hf}\) + T | ±2σ |
|-----|-----------------|-----------------|-----------------|-----|-----------------|-----------------|-----|

Sample 18K-1, granite, Novyi Bilokorovychi village, 1782 ± 18 Ma

1.000796 0.031100 0.281634 0.000017 0.281607 1.5 1.2
2.0003307 0.140300 0.281744 0.000022 0.281632 1.6 1.2
3.0000429 0.015590 0.281687 0.000039 0.281672 2.7 1.2
4.0000535 0.021100 0.281614 0.000018 0.281596 1.3 1.2
5.0001005 0.042500 0.281656 0.000029 0.281622 2.0 1.2
6.0002770 0.122200 0.281697 0.000016 0.281603 1.1 1.2
7.0004857 0.203100 0.281829 0.000032 0.281665 2.2 1.2
8.0001671 0.072000 0.281724 0.000090 0.281667 0.7 1.2
9.0000953 0.037920 0.281664 0.000021 0.281632 1.5 1.2
10.0001008 0.040460 0.281630 0.000016 0.281596 1.1 1.2

Sample 18K-2, pegmatite, city of Khoroshiv, 1760 ± 3 Ma

1.000745 0.030300 0.281555 0.000015 0.281630 1.2 1.2
2.0001354 0.055300 0.281672 0.000019 0.281627 1.3 1.2
3.0001000 0.040000 0.281679 0.000016 0.281646 1.1 1.2
4.0000506 0.023500 0.281626 0.000015 0.281609 1.1 1.2
5.0002110 0.091600 0.281694 0.000065 0.281623 1.4 1.2
6.0000925 0.037800 0.281665 0.000022 0.281634 1.6 1.2
7.0000472 0.017900 0.281688 0.000023 0.281672 1.6 1.2
8.0001713 0.080500 0.281667 0.000022 0.281610 1.5 1.2
9.0001172 0.040500 0.281875 0.000023 0.281836 1.6 1.2
10.0000486 0.018690 0.281662 0.000019 0.281646 0.6 1.2

Sample 18K-2-1, granite, city of Khoroshiv, 1766 ± 3 Ma

1.0000938 0.037600 0.281667 0.000019 0.281636 0.8 1.3
2.0001850 0.077600 0.281718 0.000026 0.281656 1.8 1.3
3.0000911 0.037200 0.281685 0.000019 0.281654 0.2 1.4
4.00001080 0.046500 0.281618 0.000018 0.281582 1.3 1.2
5.0001697 0.071200 0.281707 0.000023 0.281650 0.3 1.6
6.0000702 0.029240 0.281676 0.000019 0.281652 0.2 1.3
7.0001150 0.046400 0.281659 0.000013 0.281620 0.9 1.4
8.0001048 0.043000 0.281674 0.000022 0.281639 0.7 1.5
9.0001130 0.046700 0.281707 0.000018 0.281669 0.4 1.2
10.0000887 0.036200 0.281686 0.000020 0.281656 0.1 1.4

Sample 18K-3, granite, Sukhovolya village, 1771 ± 9 Ma

1.000894 0.036435 0.281656 0.000018 0.281626 1.3 1.3
2.0000395 0.014240 0.281717 0.000033 0.281704 2.3 1.3
3.0000612 0.024240 0.281646 0.000018 0.281625 1.1 1.3
4.0001006 0.039610 0.281656 0.000015 0.281622 1.2 1.0
5.0000945 0.038300 0.281662 0.000019 0.281630 1.3 1.3
6.0001254 0.052530 0.281701 0.000021 0.281659 0.1 1.5
7.0000834 0.033040 0.281648 0.000015 0.281620 1.3 1.1
8.0001160 0.042100 0.281765 0.000031 0.281726 2.2 2.2
9.0001190 0.047900 0.281676 0.000017 0.281636 0.7 1.2

Several pulses of CO₂-rich fluids have been registered. Secondary inclusions in beryl contain 87 vol % CO₂ and 13 vol % CH₄ (Vozniak et al., 2012). Hydrocarbons can be derived either from basic melts during their degassing or from decomposition of organic matter that was found in several pegmatite bodies in the form of “kerite” (e.g. Gorlenko et al., 2000; Zhmur, 2003; Franz et al., 2017). Muscovite that occurs intimately intergrown with NH₄-feldspar (buddingtonite) yielded a \(^{39}\)Ar/\(^{40}\)Ar age of 1486 ± 33 Ma (Franz et al., 2021). As this age probably corresponds to the thermal event that was responsible for the muscovite.
formation, Franz et al. (2021) concluded that the age of 1486 ± 33 Ma represents a minimum age of the kerite formation, whereas the age of zircon crystallization (1760 ± 3 Ma) corresponds to the maximum age. Buddingtonite has yielded a $^{39}$Ar/ $^{40}$Ar age of 561 ± 33 Ma, which can be explained by a weak re-heating of the area during the formation of the Volyn flood basalt province (Kuzmenkova et al., 2010; Shumlyanskyy et al. 2016). This figure defines the absolute minimum age of the microfossils responsible for the formation of organic matter in the Volyn chamber pegmatites (Franz et al., 2021).

6 Conclusions

New U–Pb data obtained for granites and pegmatites of the KPC confirm that the rock assemblage in its northern part belongs to the first pulse of magmatic activity between 1800 and 1780 Ma, whereas rocks in the southern part of the KPC intruded mainly between 1768 and 1755 Ma. Additionally, the first reliable U–Pb zircon ages for granites of the southwestern part of the KPC and for pegmatites of the Volyn pegmatite field indicate that granites were emplaced a few million years prior to the intrusion of the gabbro–anorthosite massif and that the chamber pegmatites crystallized coevally with the basic rocks. Field relationships indicate hybridization and mingling at the contacts between the basic rocks and granites and also that granites in a few-kilometre-wide band surrounding the younger basic intrusion experienced a significant influence from the basic melts in the form of the crystallization of ferrous olivine and clinopyroxene due to partial recrystallization and remobilization of interstitial melts. Ultimately, the formation of the chamber pegmatites was related to the secondary reheating of the semi-crystallized granitic intrusion and to the fluids migrating from the underlying gabbro–anorthosite massif.

Data availability. All the processed results are presented in the paper.

Author contributions. LS was responsible for the conceptualization of the research. LS, SG, OM, DV, and OB performed the field work and laboratory measurements. LS and GF coordinated the research. LS prepared the original draft. GF, SG, OM, and DV reviewed and edited the manuscript.

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