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Baddeleyite: A Promising Geochronometer for Alkaline and Basic Magmatism

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Abstract—The paper is devoted to the history of the discovery, petrological and mineralogical characterization, and U–Pb dating of baddeleyite ZrO_2, which was separated from various Archean, Proterozoic, and Paleozoic rocks from Fennoscandia. The morphology of this mineral and its U–Pb age values were examined in the Archean carbonatites (2613 ± 18 Ma) of Siilinjarvi, Finland, and gabbronorite dikes (2738 ± 6 Ma) at the Kirovogorskoe deposit. U–Pb isochrons are reported for the baddeleyite–zircon pair obtained from the gabbronorites and anorthosites of the Proterozoic pyroxenite–gabbronorite–anorthosite association. The U–Pb baddeleyite dates for the early gabbronorite phase (2.5 Ga) and for a gabbronorite dike (late phase, 2.4 Ga) suggest that the basic magmatism evolved over a long time period (100 m.y.) in the Proterozoic. U–Pb dates are also reported for baddeleyite from the Paleozoic carbonatites of Kovdor, Sebljarv, and Vuorijarvi.

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INTRODUCTION

Baddeleyite ZrO_2 was discovered in 1892 by Joseph Baddeley, a tea tycoon, in Ceylon (now Sri Lanka), but it was not until 30 years ago that this mineral was first utilized in U–Pb studies. Baddeleyite crystals are usually 30–50 μm, the mineral belongs to the monoclinic system, and has a hardness of 6.5 and a density from 5.4 to 6.0 g/cm^3. Baddeleyite was found not only in terrestrial but also in lunar rocks, as well as in some achondritic meteorites. Terrestrial baddeleyite was identified in carbonatites, kimberlites, alkaline syenites, some rocks of layered mafic intrusions, diabase dikes, gabbroid sills, anorthosites, etc. The first indications that baddeleyite contains much U and is thus suitable for U–Pb dating were obtained when lunar basalts (Lovering and Wark, 1971) and kimberlites (Kresten, 1974) were studied in the 1970s, but it was no sooner than ten years afterward that baddeleyite was used as a geochronometer. The reason for its application as such was the more and more frequent finds of this mineral in various rocks, mostly of basic (intrusions, dikes, and sills) and alkaline (carbonatites) composition. According to the detailed review (Heaman and LeCheminant, 1993), baddeleyite was first dated as a “by-product” of the U–Pb studying of mantle zircon megacrysts, a research that was initiated by T. Krogh and A. Erlank in the early 1970s at the Carnegie Institute of Washington, Washington, DC.

Reference books issued in the 1950s mention that a synonym of baddeleyite is brazilite, and a variety of the former mineral is favas, which is cryptocrystalline, reniform, and fibrous–stringy or concentrically shelly aggregates of zircon. Zircon-favas is thought to be another mode of ZrO_2 occurrence that is genetically related to nepheline syenites and is likely produced by the decomposition of zircon and other Zr silicates (Lazarenko, 1951). In reference books published in the 1980s, another synonym of baddeleyite (along with brazilite) is named reitingerite, which is reportedly a rare mineral of varying color: yellow, red, greenish blue, brown, dark brown, gray, and black, or even colorless. Baddeleyite occurs as platy, tabular, short- and long-prismatic crystals, often with polysynthetic twins along (100) and (110), and as aggregates of other types (Strübel and Zimmer, 1982). Important characteristics of baddeleyite are its high melting temperature (~3000°C; Lazarenko, 1951), high inertness at high temperatures, and significant refractoriness (2100–2200°C; Toropov and Bulak, 1972).

METHODS OF U–Pb DATING OF BADDELEYITE

In the Kola territory in the eastern Baltic Shield, baddeleyite was found in rocks of various ages (from Archean to Paleozoic) and compositions: alkaline (carbonatites) and basic (dikes, layered intrusions, etc). The mineral was separated from various rocks following the conventional scheme that is also applied for zircon and involves rock crushing and the separation of minerals in heavy liquids. These techniques are adopted at the Geological Institute, Kola Science Center, Russian Academy of Sciences, for the separation of accessory and rock-forming minerals and were described in (Bayanova, 2004). It can only be added that the world literature devoted to baddeleyite separation from various rocks includes only a single publication in which it was proposed to make use of the difference between the velocities of grains of different sizes on a shaking table (Soderlund and Jahansson, 2002). Following the method (Krogh, 1973), the samples were hydrothermally decomposed in strong (48%) HF at temperatures of 205–210°C for 1–10 days. To dissolve fluorides, 3.1 N HCl was added at a temperature of 130°C during 8–10 h. To determine the Pb isotopic composition and the concentrations of Pb and U, the sample was divided into two aliquots in 3.1 N HCl, and a mixed ^{208}Pb + ^{235}U tracer was applied. Pb and U were separated on an AG 1 × 8, 200–400 mesh anion exchanger in Teflon columns. The laboratory blank for the whole analysis was less than 0.1–0.08 ng for Pb and 0.01–0.04 ng for U. All isotopic determinations for zircon and baddeleyite were conducted on Finnigan MAT-262 and MI 1201-T mass spectrometers, and the Pb isotopic composition was analyzed on secondary-ion multiplier in the mode of high-voltage measurements at a high resistance and on Finnigan MAT-262 in ion counting mode. The ion emitter was silica gel. The measurements of the Pb isotopic composition were conducted accurate to 0.025% (Finnigan MAT-262) and 0.15% (MI 1201-T) against the NBS SRM-981 and SRM-982 standards, respectively. The U and Pb concentrations were measured in single-filament mode with the addition of H_3PO_4 and silica gel, according to the method (Schärer and Gower, 1988; Schärer *et al.*, 1996). We were the first to measure the Pb and U concentrations within the temperature ranges of 1350–1450 and 1450–1550°C, respectively. All of the isotopic ratios were corrected for mass discrimination during the static processing of replicate analyses of the SRM-981 and SRM-982 standards (0.12 ± 0.04% for Finnigan MAT-262 and 0.17 ± 0.05% per a.m.u.). The errors in the U–Pb ratios were calculated during the statistical treatment of replicate analyses of the IGFM-87 standard and were assumed equal to 0.5% for Finnigan MAT-262 and 0.7% for MI 1201-T. If the actual analytical errors were higher, they are reported in the table of isotopic data. The coordinates of the points and the parameters of the isochrons were calculated by the programs (Ludwig, 1991, 1999). The age values were calculated with the conventional decay constants for U (Steiger and Jäger, 1977), all errors are reported for a 2σ level. Corrections for common Pb were introduced in compliance with (Stacey and Kramers, 1975). Corrections were also made for the composition of Pb separated from syngenetic plagioclase or microcline if the admixture of common Pb was >10% of the overall Pb concentration and the ^{206}Pb/^{204}Pb ratios were <1000.

BADDELEYITE IN ARCHEAN ROCKS OF FENNOSCANDIA

In 1992, the author identified rare baddeleyite crystals (5–7 crystals), together with zircon, in a 100-kg sample of anorthosite from a borehole at the Tsaginskii Massif in the Keivy zone, eastern Baltic Shield. The U–Pb dates of zircons from the anorthosites correspond to the Archean: 2668 ± 10 Ma. This led us to suggest that the baddeleyite should also have an Archean age (Bayanova, 2004).

In 1995, A. Silvinoinen found baddeleyite in Fennoscandia also in the Archean carbonatites of the Siilinjarvi, Finland (the sample was made available for us by courtesy of A. Silvinoinen). At the laboratory of mineral separation of the Geological Institute, Kola Science Center, Russian Academy of Sciences, 10 mg of zircon–baddeleyite concentrate were separated for U–Pb dating from a 60-kg sample. A baddeleyite crystal 20 × 50 μm was detected in a zircon crystal 60 × 120 μm (Figs. 1a, 1b). Silica-undersaturated magmas of basic (in intrusions) and alkaline (in carbonatites) composition are known to contain baddeleyite as an early phase included in zircon crystals. Zircon is the first to crystallize only in kimberlites, and later, when the diatremes are formed, outer rims (or coronas) of baddeleyite grow on zircon crystals during desilication (Heaman and LeCheminant, 1993). Dark brown, almost black baddeleyite crystals up to 80 μm long were separated and hand-picked, together with zircon crystals of three types, from the Siilinjarvi carbonatites for U–Pb dating, which was carried out at the Laboratory of Geochronology and Isotopic Geochemistry of the Geological Institute, Kola Science Center, Russian Academy of Sciences. In an U–Pb concordia diagram (Fig. 2a), four points define a discordia corresponding to an age of 2613 ± 18 Ma, MSWD = 0.59, whose lower intercept with the concordia corresponds to an age of 478 ± 9 Ma. This age value reflects Pb losses during the Paleozoic tectonic reactivation. A similar U–Pb age on zircon alone (2609 ± 6 Ma) was obtained at the Geological Survey of Finland (Karhu *et al.*, 2001). It should be mentioned that the coordinates of the baddeleyite point in the U–Pb diagram is less discordant than the points of zircon. The U and Pb concentrations in accessory minerals are very low, as is typical of carbonatites.

In Fennoscandia, the oldest U–Pb age of baddeleyite was obtained for a gabbronorite dike at the Kirovogorskoe deposit of the Olenegorsk iron ore association. The baddeleyite crystals separated from a nearly 60-kg sample of the dike rock were very strongly altered. The U–Pb zircon and baddeleyite age of the gabbronorite dike was equal to 2738 ± 6 Ma, MSWD = 1.7, and the lower intercept of the discordia and concordia corresponds to Pb losses in Paleozoic time (Table 1, Fig. 2b). The baddeleyite point plots very close to the lower intercept of the discordia and concordia. Regretfully, the tiny, visually indiscernible (a few micrometers thick) rims of altered zircon around 50-μm baddeleyite crystals (we obtained only about 70 such crystals; Figs. 1c, 1d) notably disturbed the U–Pb system in baddeleyite (Bayanova *et al.*, 1998).

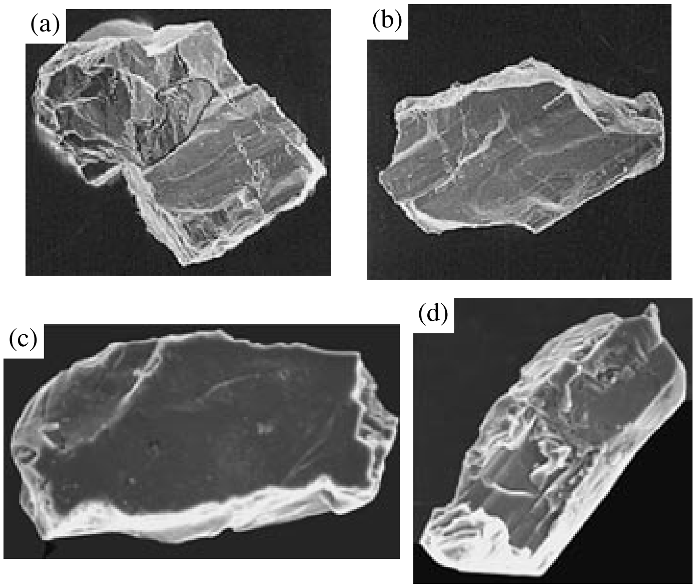


Fig. 1. Morphology of (a) baddeleyite grains (20–50 μm) in zircon (60 × 120 μm), (b) baddeleyite crystals (80 μm) from Siilinjarvi carbonatites, and (c, d) baddeleyite crystals (50 μm) from a gabbronorite dike at the Kirovogorskoe deposit of the Olenegorsk iron formation. SE images.

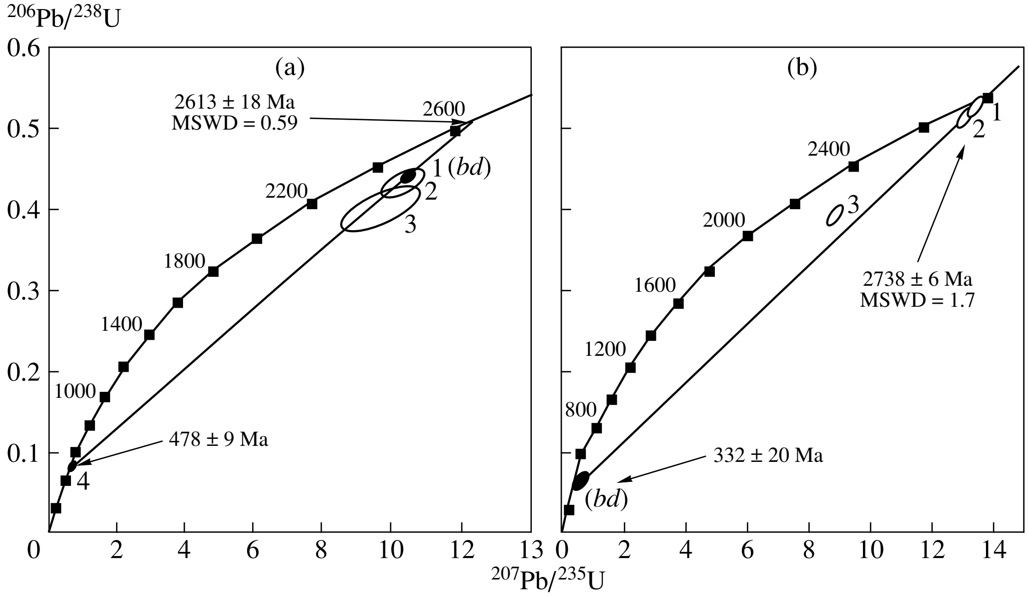


Fig. 2. U–Pb concordia diagrams for baddeleyite (*bd*) and zircon from (a) the Siilinjarvi carbonatites and (b) a gabbronorite dike at the Kirovogorskoe deposit of the Olenegorsk iron formation.

It should be mentioned that the Archean U–Pb age of 2705 ± 4 Ma was also obtained for the baddeleyite–zircon pair from gabbronorites of the Stillwater Massif in the United States (Premo *et al.*, 1990).

BADDELEYITE IN THE ROCKS OF PROTEROZOIC LAYERED INTRUSIONS IN THE BALTIC SHIELD

The first find of baddeleyite in mafic rocks from the Baltic Shield was reported by Olavi Kuovo (Geological Survey of Finland) at the Fifth European Symposium on Geochronology in 1977. He described the U–Pb dating of zircon from mafic pegmatoid rocks and mentioned that zircon coexists with baddeleyite in the coarser grained parts of the mafic dikes (Kuovo, 1977). This observation can be regarded as the beginning of baddeleyite studying in mafic rocks. It was, however, not until almost a decade later that baddeleyite from mafic rocks was widely applied to the U–Pb dating. Since the density of baddeleyite is slightly higher than that of zircon, the former commonly enriches the heavy

Table 1. U–Pb isotopic data on baddeleyite (*bd*) and zircon from the Siilinjarvi carbonatites, Finland, and Olenegorsk iron formation of the Kirivogorskoe deposit

Sample	Weight, mg	Concentration, ppm		Pb isotopic composition[1]			Isotopic ratios[2]		Age, Ma	Rho
		Pb_{tot}	U	$^{206}Pb/^{204}Pb$	$^{206}Pb/^{207}Pb$	$^{206}Pb/^{208}Pb$	$^{207}Pb/^{235}U$	$^{206}Pb/^{238}U$	$^{207}Pb/^{206}Pb$	
Siilinjarvi carbonatites										
1 (*bd*)	1.20	5.8	11.6	1720	5.670	7.319	10.432	0.4386	2550 ± 18	0.73
2	0.50	4.4	8.6	1420	5.483	5.364	10.314	0.4305	2594 ± 60	0.71
3*	0.25	4.3	7.0	220	4.308	2.529	9.688	0.3993	2615 ± 60	0.73
4*	0.45	1.2	33.6	690	5.124	4.167	1.016	0.0922	2629 ± 30	0.71
Gabbronorite dike at the Kirovogorskoe deposit										
1	0.3	58.7	101.4	2080	5.121	9.961	13.595	0.5193	2741	
2	0.4	48.3	85.0	1600	5.122	10.302	13.300	0.5111	2726	
3**	0.3	74.6	142.3	400	4.971	3.161	9.159	0.3888	2566	
4 (*bd*)**	0.3	2.2	33.5	124	6.023	3.002	0.392	0.0530	353	

[1] The ratios are corrected for blanks of 0.1 ng for Pb and 0.04 ng for U and for mass discrimination of 0.17 ± 0.05%.

[2] Correction for common Pb was determined for the age according to (Stacey and Kramers, 1975).

* Correction was made for the composition of syngenetic microcline from carbonatite: $^{206}Pb/^{204}Pb = 16.49 \pm 0.02$, $^{207}Pb/^{204}Pb = 15.17 \pm 0.03$, and $^{208}Pb/^{204}Pb = 35.17 \pm 0.01$.

** Correction was made for the composition of plagioclase from the dike: $^{206}Pb/^{204}Pb = 14.32 \pm 0.03$, $^{207}Pb/^{204}Pb = 14.82 \pm 0.03$, and $^{208}Pb/^{204}Pb = 33.43 \pm 0.02$.

fraction, and its crystals can be separated for U–Pb dating only by hand-picking. Single baddeleyite crystals are often confused with those of titanite and rutile, but baddeleyite differs from titanite in being more elongated but not tabular and from rutile in having a darker brownish black color without reddish brown tints typical of rutile. Baddeleyite was very rarely identified in thin sections because its crystals are usually no larger than 50 μm.

In the rocks of layered PGE-bearing intrusions that are classed with the pyroxenite–gabbronorite–anorthosite (PGA) association, baddeleyite was first found by the author in the lherzolites of the Lukkulaisvaara Massif in Karelia (Olangskaya group) (Balashov *et al.*, 1993). Baddeleyite was included in a cumulus orthopyroxene grain. American geologists have found a baddeleyite crystal 50 μm long in a cumulus plagioclase grain from the Laramie anorthosites in the Wyoming Province, North America (Scoates and Chamberlain, 1995). These exclusively rare observations of relations between the rock-forming and accessory minerals suggest that baddeleyite was formed in the cumulus mineral grains from basic rocks early during the crystallization of the melt. It is reasonable to hypothesize that the interstitial baddeleyite and zircon crystallized later, during the fractionation of the primary melt. Thus, baddeleyite can be both an early and a late mineral of the rocks of layered intrusions, but it always has a primary magmatic genesis. The character of the paragenetic relations of accessory baddeleyite and zircon with rock-forming minerals was observed in the rocks of the Imandra lopolith, in which baddeleyite was first identified in thin sections. In the ferrogabbro and anorthosites of the Imandra lopolith, baddeleyite grains of uniform dark brown color and up to 100 μm long occur as single flattened crystals and aggregates with ilmenite in the interstices of plagioclase, pyroxene, and younger quartz and biotite (Fig. 3). In all of these instances, baddeleyite and ilmenite were older minerals than quartz and micropegmatite, i.e., they were formed early in the course of crystallization of the intercumulus melt, at a low silica activity. In addition to individual crystals 100–120 μm, zircon occurs as thin rims (no thicker than 10 μm) around baddeleyite grains, which are, similarly to titanite that replaces ilmenite, products of subsolidus transformations (Fig. 3). Thinly zonal short-prismatic pale (in transmitted light) zircon crystals often occur as aggregates in a micropegmatite–quartz matrix. This is the first, and still the only one, find of baddeleyite in a thin section of a rock from a Proterozoic layered intrusion in the eastern part of the Baltic shield (Galimzyanova *et al.*, 1988). The chemical compositions of baddeleyite and zircon from rocks of the Imandra lopolith are presented in Table 2. The baddeleyite is characterized by Hf concentrations more than twice higher than in the zircon, and this mineral always contains Ti. The U–Pb isotopic age of baddeleyite (Fig. 4a) separated from anorthosites of the Imandra lopolith is 2437 ± 11 Ma (Table 3, Fig. 5a). The lower intercept of the discordia and concordia corresponds to the time of the Paleozoic tectono-magmatic reactivation at the Baltic Shield and reflects the disturbance of the U–Pb system. While the discordance of the U–Pb ratios of zircons is caused by Pb loss, this discordance in baddeleyite stems from the growth of very thin (micrometer- and submicrometer-sized) rims of altered zircon around baddeleyite crystals (Fig. 4b). These rims around baddeleyite crystals are almost indiscernible under a binocular microscope, but an increase in their thickness results in a significant increase in the discordance of the U–Pb ratios of the baddeleyite.

Individual baddeleyite crystals were also found and dated in the anorthosites of the Fedorovo–Pana Massif (second phase of the PGA association). Those baddeleyite crystals were dark brown and as large as 50–70 μm (Fig. 6a). The U–Pb isotopic age of two baddeleyite samples and three zircon types was estimated at 2447 ± 12 Ma, MSWD = 2.7. The lower intercept of the discordia and concordia is equal to zero and corresponds to the modern loss of Pb (Table 3, Fig. 5b). It is pertinent to mention that the two baddeleyite points plot almost exactly on the concordia (within the measurement errors) in the U–Pb concordia diagram, whereas the three zircon points plot away from the concordia.

Baddeleyite was also found in the most ancient rocks of the Monchegorsk pluton: in veins of gabbronorite pegmatites (main phase of the PGA association), which are accompanied by ore sulfide veins from the Basal Zone at Mount Travyanaya and the Critical Unit at Mount Nyud (Terrasa Cu–Ni deposit) (Bayanova and Mitrofanov, 2005). Platy baddeleyite crystals of pale brown color, up to 80 μm in size were separated from an almost 100-kg rock sample (Fig. 6b). These crystals are well preserved, and the U–Pb age of two types of baddeleyites and three types of zircons is equal to 2500 ± 5 Ma, MSWD = 1.7. The lower intercept of the discordia and concordia yeilds an age of 349 ± 81 Ma and corresponds to the Paleozoic reactivation and the disturbance of the U–Pb system (Table 4, Fig. 7a). In the gabbroids of Mount General'skaya (main phase of the PGA association), whose U–Pb zircon age is 2496 ± 10 Ma, baddeleyite was found in the form of crystals up to 20 μm long included in altered zircon (Fig. 6c) (Bayanova *et al.*, 1996, 1999).

In the rocks of the dike series of the PGA association (third phase), baddeleyite was first found in olivine gabbronorites of the Imandra lopolith (Fig. 6d). Very thin rims of altered zircon around the baddeleyite crystals of almost black color, up to 80 μm slightly distort its U–Pb system, and the baddeleyite point plots below the zircon point in the U–Pb concordia diagram (Fig. 7b). The U–Pb isotopic age of baddeleyite and zircon from an olivine gabbronorite dike in the Imandra lopolith is 2395 ± 5 Ma and corresponds to the timing of the emplacement of the third PGA phase.

Hence, the association of PGE-bearing intrusions was emplaced within an age range of 2.5–2.4 Ga (100 m.y.). The main phase of this association (gabbronorite) has an age of 2.5 Ga, according to the U–Pb dating of baddeleyite and zircon from these rocks; the second phase (anorthosites) was dated at 2.45 Ga, and the third phase (dike series) has an age of 2.4 Ga (Mitrofanov and Bayanova, 1999; Mitrofanov *et al.*, 2002).

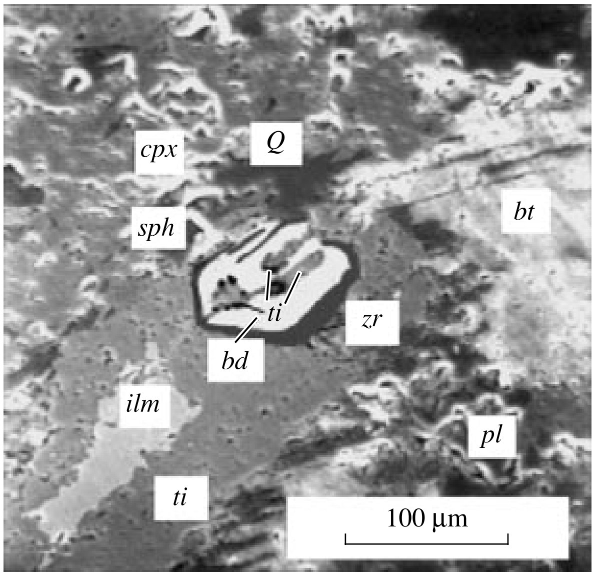


Fig. 3. SE image of a baddeleyite crystal (80 μm) from ferogabbro of the Imandra lopolith. Mineral symbols: *bd*—baddeleyite, *zr*—zircon, *bt*—biotite, *ilm*—ilmenite, *Q*—quartz, *sph*—sphene, *cpx*—clinopyroxene, *pl*—plagioclase, *ti*—titanite.

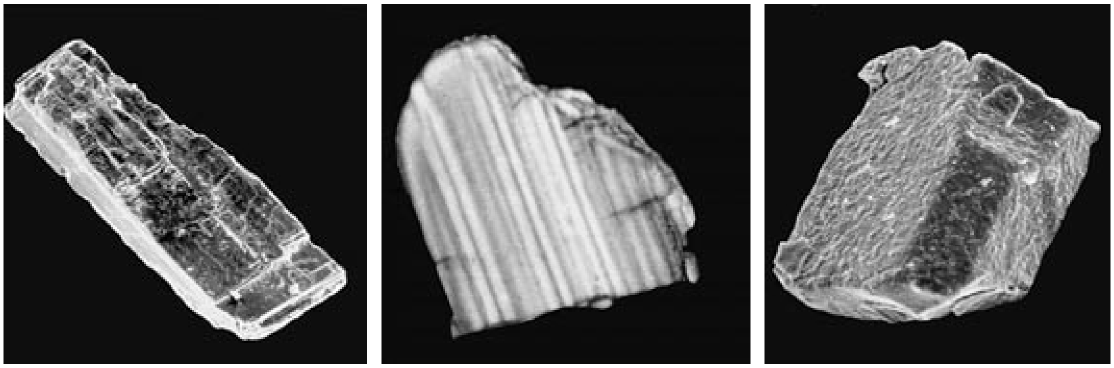
BADDELEYITE IN PALEOZOIC ROCKS OF THE BALTIC SHIELD

Detailed information on finds of baddeleyite and its mineral assemblages in alkaline rocks around the world is still very scarce. The first reports of baddeleyite

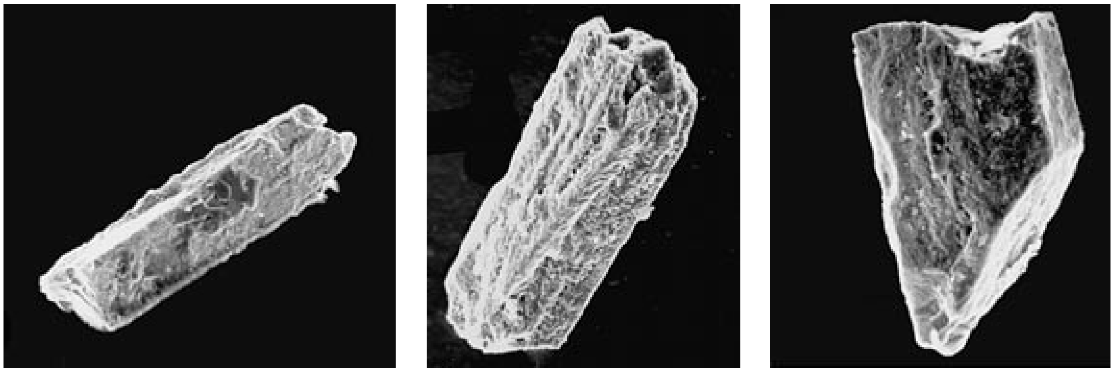
Table 2. Chemical composition (wt %) of (1, 2) baddeleyite and (3, 4) zircon from anorthosites of the Imandra lopolith

Oxide	Baddeleyite		Zircon	
	1	2	3	4
ZrO_2	97.55	97.55	65.32	63.42
HfO_2	2.55	1.29	1.00	1.06
Fe_2O_3	0.00	0.03	0.02	0.69
CaO	0.00	0.00	0.01	0.42
Al_2O_3	0.00	0.00	0.00	0.07
V_2O_3	0.11	0.00	0.33	0.35
TiO_2	0.27	0.49	0.00	0.00
UO_2	0.00	0.00	0.36	0.36
SiO_2	0.00	0.00	32.61	32.62
	100.48	99.36	99.65	98.99

Note: Analyses were conducted on a Cameca MS-46 microprobe, analyst E.E. Savchenko.



(a) grains 80–120 μm



(b) grains up to 150 μm

Fig. 4. SE image of (a) well-preserved and (b) altered baddeleyite crystals from the rocks of the Imandra lopolith.

found in carbonatites were published in the 1950s (Hiemstra, 1955). In the Baltic Shield, baddeleyite in association with alkaline feldspar and nepheline was first detected in larvikites in Norway (Widenfalk and Gorbatschev, 1971). As follows from binary phase diagrams for the ZrO_2–SiO_2 system (Butterman and Foster, 1967), baddeleyite should be spread in alkaline rocks more widely than it was thought previously. Indeed, both zircon and baddeleyite were lately found in alkaline rocks in many areas around the world (Hea-

Table 3. U–Pb isotopic data on baddeleyite (*bd*) and zircon from the Imandra lopolith and the Fedorovo–Pana intrusion

Sample	Weight, mg	Concentration, ppm		Pb isotopic composition[1]			Isotopic ratios[2]		Age, Ma[2]
		Pb	U	$^{206}Pb/^{204}Pb$	$^{206}Pb/^{207}Pb$	$^{206}Pb/^{208}Pb$	$^{207}Pb/^{235}U$	$^{206}Pb/^{238}U$	$^{207}Pb/^{206}Pb$
Anorthosites of the Imandra lopolith									
1034-1 (*bd*)	1.0	174.6	410.7	6280	6.316	87.0	9.108	0.4219	2419
1034-2 (*bd*)	0.8	330.6	790.5	14210	6.351	93.5	9.000	0.4162	2422
1034-3 (*bd*)	0.9	457.9	1032.6	28560	6.334	117.5	9.609	0.4419	2431
Anorthosites of the Fedorovo–Pana intrusion									
P6-1	0.75	218	322	5740	6.230	3.263	11.682	0.5352	2438
P6-2	0.10	743	1331	3960	6.191	3.151	9.588	0.4393	2438
P6-3	0.20	286	577	2980	6.021	3.192	8.643	0.3874	2474
P5 (*bd*)	1.00	176	396	14780	6.290	63.610	9.548	0.4380	2435
P6 (*bd*)	0.26	259	560	3360	6.132	54.950	9.956	0.4533	2443

[1] All ratios are corrected for blanks of 0.1 ng for Pb and 0.04 ng for U and for mass discrimination of 0.17 ± 0.05%.
[2] Correction for common Pb was determined for the age according to (Stacey and Kramers, 1975).

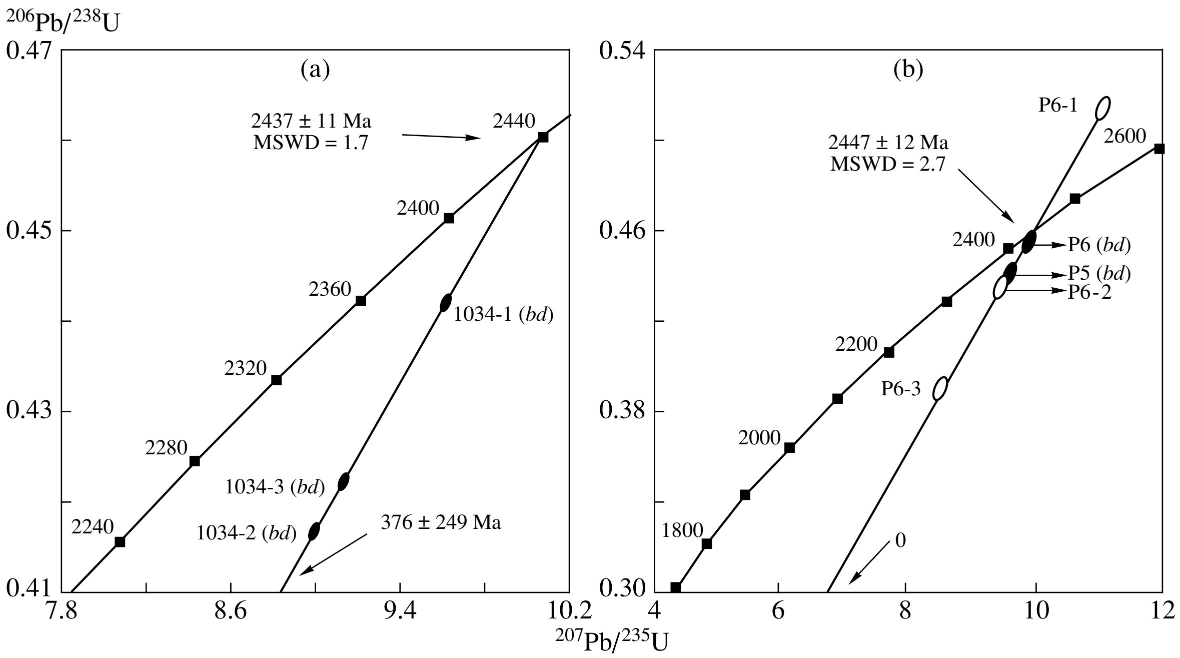


Fig. 5. U–Pb concordia diagrams for baddeleyite (*bd*) from (a) the Imandra lopolith and (b) baddeleyite and zircon from anorthosites of the Fedorovo–Pana Massif.

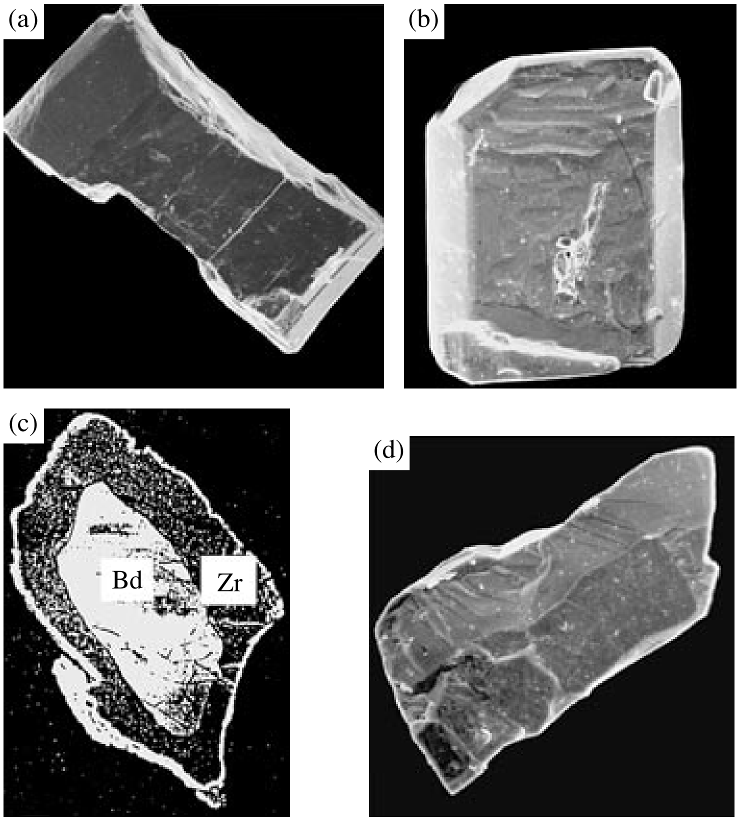


Fig. 6. Morphology of (a) baddeleyite crystals (50–70 μm) from anorthosites of the Fedorovo–Pana Massif, (b) baddeleyite crystals (80–120 μm) from gabbronorite-pegmatite of the Critical Unit, Mount Nyud, of the Moncha pluton, (c) baddeleyite (20 μm) in zircon (80 μm) from gabbronorite of Mount General'skaya, and (d) baddeleyite (100 μm) from a gabbronorite dike in the Imandra lopolith.

Table 4. U–Pb isotopic data on baddeleyite (*bd*) and zircon from rocks of the Monchegorsk cluster of deposits and the Imandra lopolith

Sample	Weight, mg	Concentration, ppm		Pb isotopic composition[1]			Isotopic ratios[2]		Age, Ma	Rho
		Pb	U	^{206}Pb/^{204}Pb	^{206}Pb/^{207}Pb	^{206}Pb/^{208}Pb	^{207}Pb/^{235}U	^{206}Pb/^{238}U	^{207}Pb/^{206}Pb	
Pegmatite-gabbronorites of Mount Nyud										
1 (*bd*)	0.70	93.1	198.8	9432	6.0586	103.8300	10.4643	0.4636	2495	0.90
2 (*bd*)	0.40	170.8	364.4	3589	5.9833	50.7070	10.3199	0.4574	2494	0.89
3	0.40	117.4	183.1	4590	6.0153	1.8703	9.8274	0.4359	2492	0.90
4	0.80	187.9	308.4	13664	6.1169	1.9750	9.4740	0.4227	2483	0.99
5	0.50	152.2	252.5	5302	6.0842	1.8994	9.2129	0.4125	2477	0.99
Olivine gabbronorites of Mount Bol'shaya Varaka										
1	0.82	127	241	1630	6.173	4.5011	9.2951	0.4372	2393	
2 (*bd*)	0.60	104	212	1490	5.547	8.2507	9.0262	0.4237	2397	
3	0.63	332	607	1280	6.072	2.9501	8.9004	0.4171	2399	
4	0.68	286	626	1590	6.144	3.1284	7.5613	0.3543	2399	

[1] The ratios are corrected for blanks of 0.08 ng for Pb and 0.04 ng for U and for mass discrimination of 0.12 ± 0.04% (for the Mount Nyud pegmatite-gabbronorites) and 0.17 ± 0.05% (for the Mount Bol'shaya Varaka gabbronorites).

[2] Correction for common Pb was determined for the age according to (Stacey and Kramers, 1975).

man and Machado, 1992), but their relations remain uncertain.

In Paleozoic rocks of the Kola Peninsula, baddeleyite is widespread in carbonatites (Rimskaya-Korsakova and Dinaburg, 1964; Kukharenko *et al.*, 1965). Several publications were devoted to the petrological and mineralogical studies of baddeleyite from the Kovdor Massif (Ternovoi, 1977; *Apatite Potential*..., 1991), to which the world's second largest reserves of baddeleyite are related [the first one is the Phalaborwa deposit, which is related to African carbonatites (Reischmann, 1995)]. The Kovdor Massif of ultramafic and alkaline rocks and with carbonatites is located in the southwestern Kola Peninsula and is one of the largest massifs of this genetic type (Kirnarskii, 1979).

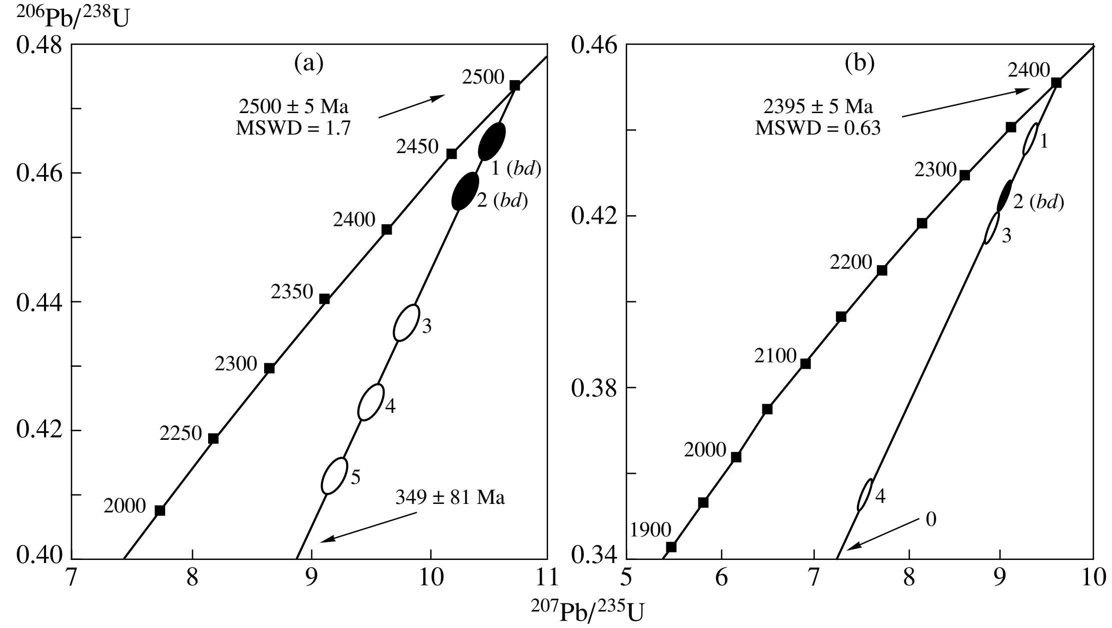
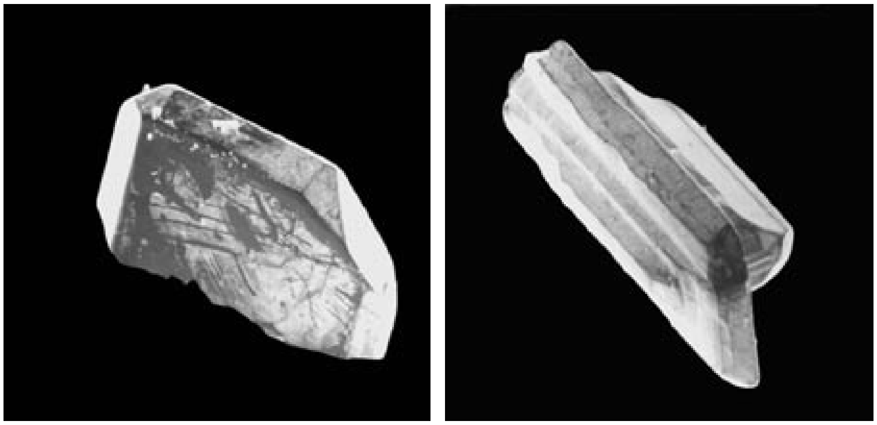
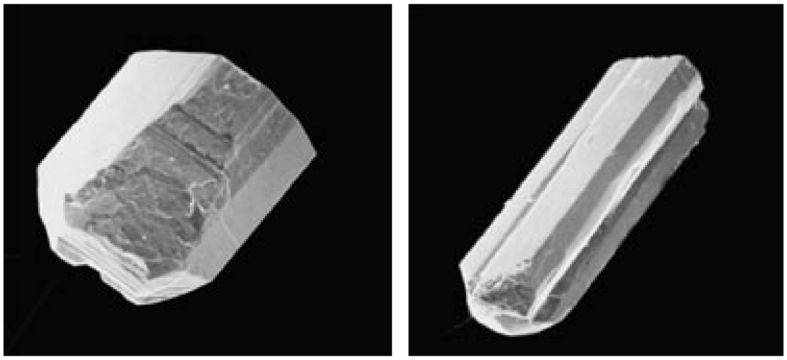


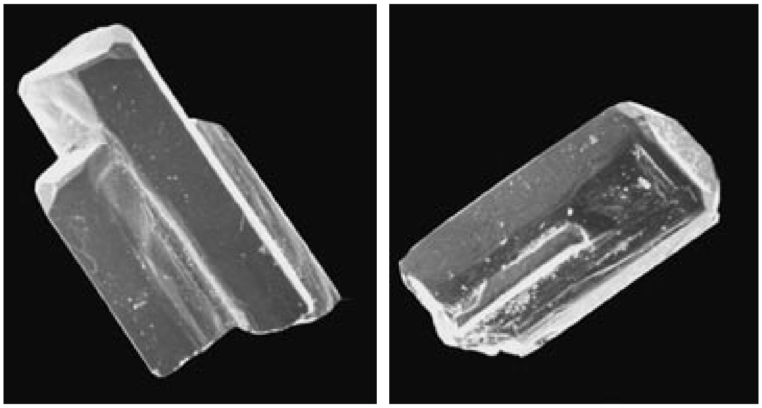
Fig. 7. U–Pb concordia diagrams for (a): (1, 2) baddeleyite (*bd*) and (3–5) zircon from gabbronorite-pegmatite of the Critical Unit, Mount Nyud, of the Moncha pluton and (b): (2) baddeleyite and (1, 3, 4) zircon from a gabbronorite dike in the Imandra lopolith.



(a) Kovdor, grains 120–200 μm



(b) Sebljavr, grains 100 μm



(c) Vuorijarvi, grains 150 μm

Fig. 8. SE images of baddeleyite from Paleozoic carbonatites: (a) Kovdor, (b) Sebljavr, and (c) Vuorijarvi.

We separated brown baddeleyite crystals from the phoscorite ores of this massif to conduct their U–Pb dating. The grains selected for this purpose were mostly individual untwined crystals of simple morphology (Fig. 8a) up to 200 μm long. Larger crystals and twins were found out to have rims and hardly discernible films (1–2 μm thick) of altered zircon and other minerals. The U–Pb isotopic age of six baddeleyite samples was measured at 382 ± 3 Ma, with all of the data points plotting near the concordia in the U–Pb diagram (Table 5, Fig. 9a). Thus, baddeleyite from the phoscorite ores can reliably date the origin of the rocks of this world's largest deposit (Bayanova *et al.*, 1997).

The Sebljavr Massif on the Tuloma River in the northwestern Baltic Shield contains rare-metal ore mineralization and carbonatites, in which baddeleyite was found. According to (Subbotin *et al.*, 1999), the massif comprises there phases: hyperbasite, alkaline, and carbonatite. The detailed examination of the carbonatite phase indicates that it was produced in five

Table 5. U–Pb isotopic data on baddeleyite (*bd*) and zircon (*zr*) from rocks of the Kovdor, Sebljavr, and Vuorijarvi massifs

Sample	Weight, mg	Concentration, ppm		Pb isotopic composition[1]			Isotopic ratios and age, Ma[2]			Rho
		Pb	U	$^{206}Pb/^{204}Pb$	$^{206}Pb/^{207}Pb$	$^{206}Pb/^{208}Pb$	$^{207}Pb/^{235}U$	$^{206}Pb/^{238}U$	$^{207}Pb/^{206}Pb$	
Phoscorite ores, Kovdor										
1, *bd*	16.80	18.3	318.8	7660	17.88	23.61	0.4541	0.06086	376	
2, *bd*	18.90	9.8	170.3	4790	17.53	44.67	0.4612	0.06194	371	
3, *bd*	29.40	9.2	161.9	4520	17.71	44.11	0.4483	0.06111	338	
4, *bd*	25.00	7.9	139.7	4020	17.66	44.47	0.4457	0.06099	329	
5, *bd*	29.90	9.6	160.9	2920	17.54	50.78	0.4391	0.06123	286	
6, *bd*	30.40	7.6	133.9	3170	17.69	50.75	0.4364	0.06127	281	
7, *bd*	19.90	4.4	73.9	1680	15.89	18.33	0.4584	0.06131	381	
Late carbonatites, Sebljavr										
11/1, *bd*	15.70	12.2	211.1	8900	17.98	18.44	0.44913	0.06036	370	0.46
11/2, *bd*	16.90	16.1	281.2	8850	17.90	18.72	0.44893	0.06007	379	0.40
11/3, *bd**	21.60	15.4	266.0	9500	17.84	17.67	0.45406	0.06041	392	0.70
Carbonatites and pyroxenites, Vuorijarvi										
2, *bd*	14.50	4.3	71.9	1220	15.120	12.027	0.442	0.0593	376	0.35
3, *bd*	11.00	6.5	113.3	2840	16.866	19.240	0.447	0.0599	377	0.37
1, zr**	8.62	6.7	10.7	670	8.717	0.118	0.951	0.0735	1513	0.48

[1] All ratios are corrected for blanks of 0.1 ng for Pb and 0.04 ng for U and for mass discrimination of 0.17 ± 0.05%.
[2] Correction for common Pb was determined for the age according to (Stacey and Kramers, 1975).
* Abraded baddeleyite crystals.
** Correction was made for the isotopic composition of galena: $^{206}Pb/^{204}Pb = 18.36$, $^{207}Pb/^{204}Pb = 15.44$, and $^{208}Pb/^{204}Pb = 37.77$.

stages (Sorokhtina, 2000; Subbotin *et al.*, 1999). The early stages (from 1 through 4) were responsible mostly for the origin of phoscorites and carbonatites of magmatic and metamorphic genesis, and the last stage gave rise to hydrothermal–metamorphic carbonatites. We dated the early and late carbonatites by U–Pb and Rb–Sr isotopic systematics.

The minerals separated from the late carbonatites were mostly individual baddeleyite crystals and their fragments (flattened crystals up to 100 μm, Fig. 8b). The three baddeleyite points in the U–Pb diagram plot concordantly and correspond to an age of 378 ± 4 Ma, which reflects the origin of the late carbonatites of hydrothermal genesis (Fig. 9b, Table 5).

The rocks of the early clinopyroxenites and carbonatites were dated by the Rb–Sr method on rock-forming minerals. Based on the initial ratios $(^{87}Sr/^{86}Sr)_0$ = 0.7031 ± 2, the ages of these rocks were estimated at 410 ± 7 and 408 ± 7 Ma, respectively (Bayanova, 2004). The difference between the U–Pb and Rb–Sr ages (410–378 Ma) allowed us to determine that the rare-metal mineralization of the Sebljavr Massif was produced over a time interval of >30 m.y.

The Neskevara rare-metal deposit at the Vuorijarvi Massif is of principal economic importance for the Kola territory (Subbotin *et al.*, 1999). Pyroxenites and carbonatites obtained from the core of a borehole drilled at this massif were used to separate rock-forming and accessory minerals for U–Pb, Rb–Sr, and K–Ar dating. The baddeleyite grains from the carbonatites are well preserved. The brown crystals and twins are as large as 150 μm (Fig. 8c). The U–Pb age of two baddeleyite samples is 377 ± 4 Ma, and the U–Pb isotopic age of the zircon from the pyroxenites is equal to 1.5 Ga and is explained by the xenogenic nature of this mineral (Fig. 9c). This old zircon was likely inherited from rocks of the Archean basement during the emplacement of the pyroxenite magma. The Rb–Sr isotopic age of rock-forming minerals from the pyroxenites is equal to 383 ± 7 Ma, $(^{87}Sr/^{86}Sr)_0 = 0.7032 \pm 1$, and the K–Ar age of biotite from the pyroxenite is 376 ± 9 Ma. The Rb–Sr age of the carbonatites (determined using their rock-forming minerals) equals 375 ± 7 Ma, and their K–Ar phlogopite age ranges from 364 to 375 Ma (Bayanova *et al.*, 2001).

Hence, the U–Pb dating of the carbonatites with the use of baddeleyite of magmatic or postmagmatic genesis proved to be more reliable than the U–Pb dating on zircon, which can be of xenogenic nature.

Along with the dating of accessory and rock-forming minerals by the U–Pb, Rb–Sr, and K–Ar methods, we also examined noble gases separated from minerals from various massifs of the Paleozoic alkaline association of the Baltic Shield. The isotopic composition of

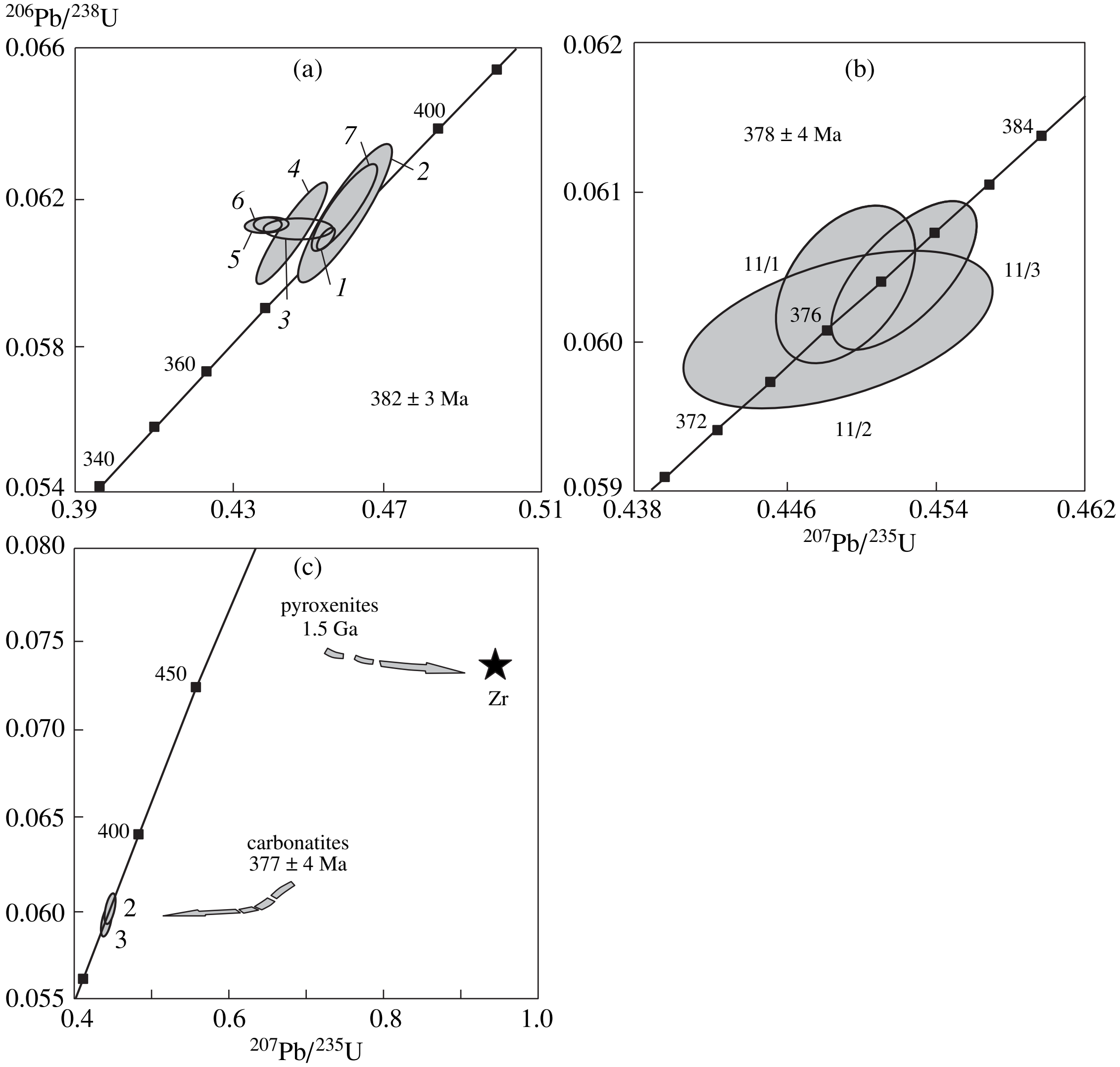


Fig. 9. U–Pb concordia diagrams for (a) baddeleyite from phoscorite ores of the Kovdor Massif, (b) late Sebljarv carbonatites, and (c) Vuorijarvi carbonatites and pyroxenites.

He and the concentrations of ^{3}He appeared to be the most informative in the context of this research. A record-breaking high value of the ^{3}He/^{4}He ratio of 3.3×10^{-5} was detected in pyroxenites from the borehole core at the Sebljavr Massif. The rocks of the Vuorijavr and Kovdor massifs had ^{3}He/^{4}He ratios of 2.1×10^{-5} and 1.5×10^{-5}, respectively (Ikorskii *et al.*, 1998). Based on extensive data on the isotopic composition and concentrations of noble gases (He, Ar, and Ne), which are indicators of mantle plumes (Tolstikhin *et al.*, 1999), we arrived at the conclusion that the material of a lower mantle plume had contributed to the Paleozoic rocks of the Kola alkaline association. Finds of magmatic baddeleyite, the low initial Sr ratios, the high concentrations of ^{3}He, and the high ^{3}He/^{4}He ratios provide further arguments in support of the plume nature of the Paleozoic alkaline rocks.

CONCLUSIONS

Baddeleyite is a promising mineral suitable for precise U–Pb dating, although it occurs even more rarely, and in smaller grains, than zircon. Baddeleyite can be separated from large rock samples (50–100 kg) together with zircon. In rocks of basic and alkaline composition, baddeleyite crystals can be separated only by hand-picking from the heavy fraction. Baddeleyite grains are commonly confused with titanite and rutile, but it differs from the former in having more elongated (but not tabular) habits of crystals and from the latter in having a darker brownish black color, without brownish red shades typical of rutile. Baddeleyite differs from zircon by more than twice higher concentrations of Hf and also contains Ti as a minor element.

Baddeleyite can only very rarely be found in thin sections, and thus, there is little published information on its relations with rock-forming minerals. Our petrographic data indicate that this mineral can be a cumulus or an intercumulus phase in basic rocks. Correspondingly, its dates can be used to constrain the age of early or late melt crystallization stages. In the carbonatites of various genesis examined in the course of our research, baddeleyite is usually an earlier mineral than zircon, and its grains occur as inclusions in zircon crystals. It should also be mentioned that the U–Pb baddeleyite isotopic age of these rocks is more concordant than their U–Pb zircon age, with the latter mineral abounding in fluid inclusions, which testify to active postmagmatic processes.

The dates obtained on the baddeleyite–zircon pair were the first to provide information on the long-lasting character of basic magma crystallization. The utilization of petrological–mineralogical data and U–Pb dating of the baddeleyite–zircon pair led us to determine that the Proterozoic pyroxenite–gabbronorite–anorthosite association (to which large Cu–Ni and PGE deposits are related) in the eastern part of the Baltic Shield was produced within the age range of 2.5–2.4 Ga, i.e., during a time span of 100 m.y. The U–Pb age of baddeleyite identified as inclusions in zircon grains from Sudbury dikes was proved to be older than the age of the zircon by 110 m.y. (Davidson and van Breemen, 1988). The study of baddeleyite from Proterozoic dikes and the precise U–Pb dating of this mineral were conducted for the purposes of paleoreconstructuions of ancient continents (Buchan, 2000, 2001; Heaman, 1997).

Baddeleyite is always related to magmatic processes, in contrast to zircon, which can be of metamorphic or other genesis.

The U–Pb ages of baddeleyite are usually less discordant than those of zircon. The degree of baddeleyite discordance depends on the presence of tiny (submicrometer-sized) rims or shells on its grains, whereas the discordance of zircons always results from Pb loss from this mineral.

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