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Polychronous zircons of volcanics of the Navysh complex of the Lower Riphean Ai Formation (Southern Urals)

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Abstract. The volcanics of the Navysh complex of the Lower Riphean Ai Formation in the Southern Urals are well studied petrochemically and dated by several methods. In 2013 zircons from a trachybasalt porphyrite (sample 2152) gave a concordant SHRIMP date 1752±11 Ma, which was used as a fundamental for the lower boundary of the Riphean with no special arguments against it. The later attempts to repeat this date for the Navysh volcanics were not successful: the collected zircons were either more ancient (>2500 Ma), or more young (<500 Ma). From the beginning, the zircons with such ages were regarded as xenogenic or secondary metasomatic, or belonging to paleozoic dykes intruding the Riphean volcanics. However, the clearly expressed mineralogical properties of the Paleozoic zircons and their frequent presence in volcanics, not dykes, led to a conclusion that the zircons and Navysh volcanics, containing them, and exposed within the area of development of the Ai Formation, are polychronous. To support this conclusion, the authors studied in more detail the zircons of the Navysh trachybasalts, developed in the Ai Formation.

The main conclusion, obtained from this new data, was that the volcanics attributed to the Navysh complex, form a polychronous system, including both the Lower Riphean (1750 Ma) and Paleozoic (450 Ma) rocks. The zircons of these age groups differ in their mineralogical and geochemical properties supporting the idea that they belong to different primary sources which may be due to repeating plume processes, which partly reanimated – heated and melted-rocks of the previous cycle and/or created new sources of melts.

Keywords: Riphean, Paleozoic, zircons, volcanics, Ai Formation, Sothern Urals

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Introduction

Volcanics of the Navysh complex of the Ai formation of the Burzyan group of the Lower Riphean in the Southern Urals are mainly represented by trachybasalts. They are well studied materially and dated by various methods (Kozlov et al., 1989; Stratigraphic schemes..., 1993). The U-Pb zircon and Rb-Sr dating obtained for them allowed the initial estimate of the age of the Navysh complex at 1615±45 Ma (Krasnobaev et al., 1992), and it was used to substantiate the radiological boundary of the Lower Riphean. Unfortunately, it is impossible to exclude the influence of crystals with altered (open) isotopic systems in the group (by weights) dating of zircons using the classical U-Pb method, since it often leads to a certain "rejuvenation" of the results. The same applies to the above-mentioned dating of zircons. A kind of alternative to the age of the Navysh complex turned out to be K-Ar dating of volcanics in the range of 400–600 Ma (Lennykh, Petrov, 1974), which were accompanied by original conclusions about the polychronism of the Ai Formation, a probable decrease in its age to the Vendian level, and even about the need to remove the Ai Formation from the Lower Riphean. These conclusions did not lead to any constructive transformations, but they were not forgotten either, being inevitably present during the discussion of any questions on the stratigraphy of the Lower Riphean of the Urals.

The need for a correct solution to the problem of the age of the Ai Formation has continuously increased and, finally, has reached a critical state that requires practical action. In 2013, using the modern SHRIMP technique for zircons from Navysh volcanics (Figure 1, sample 2152, trachybasaltic porphyrite), a concordant dating of 1752±11 Ma was obtained (Krasnobaev et al., 2013). Without any special objections, it also transformed into the geochronological boundary of the Lower Riphean, which is actively used today.

In repeated attempts to establish the age of the Navysh volcanics, we practically did not pay attention to the periodically repeated dating of zircons belonging

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either to older formations (>2500 Ma) or to younger ones (<500 Ma, Paleozoic), considering them either as xenogenic component, or as a secondary metasomatic one. However, clearly pronounced mineralogical properties of Paleozoic (PZ) zircons and their frequent presence in volcanics forced us to pay more attention to them, since they began to be perceived as a regular component of rocks. We decided to look for the answer in comparing the Riphean (R) zircons of sample K2152 and PZ-zircons of trachybasaltic amygdaloidal porphyrite of sample K2124 (southwestern slope of Maly Miass, Figure 1), for which the dating was obtained at 449.3±4.7 Ma (Krasnobaev et al., 2018), also using the SHRIMP technique (Williams, 1998). To eliminate doubts about the reliability of the analyzes, age data were obtained simultaneously for zircons from a new sample (Figure 1) of metabasalts (K2125) and sample K2124 using the TIMS method. Comparability of analyzes of both methods (SHRIMP 449.3±4.7 Ma, and TIMS 454–478 Ma) confidently confirmed the Paleozoic age of the studied zircons. In addition, it was also noted that both the mineralogical and geochemical features of the Riphean and Paleozoic zircons are qualitatively different, which already allows us to make a more confident conclusion that they are not genetically related and represent different sources. Moreover, the formation of the latter at the expense of the former is excluded, and we can confidently talk about the polychronism of both zircons and volcanics of the Navysh complex. Given the importance of this conclusion, we considered it necessary to confirm it using more representative material. For this, zircons of three additional samples of volcanic rocks were studied (K2125 – trachybasaltic porphyrite, K2123 – trachybasaltic porphyrite, K2186 – trachybasalt), taken, as before, from typical Navysh volcanic rocks in the zone of development of deposits of the Ai Formation (Figure 1). The compositions of petrogenic and trace elements of volcanics are given in Table 1 and Figure 2 (McDonough, Sun, 1995; Bogatikov et al., 1987). Determination of trace elements in volcanic rocks and in zircons from volcanic rocks of the Navysh complex was carried out on an Elan-6100 "Perkin Elmer" mass spectrometer and on an Optima-4300 DV "Perkin-Elmer" spectrometer by atomic emission methods in the laboratories of All-Russian Scientific-Research Institute of Mineral Resources (Moscow) and Institute

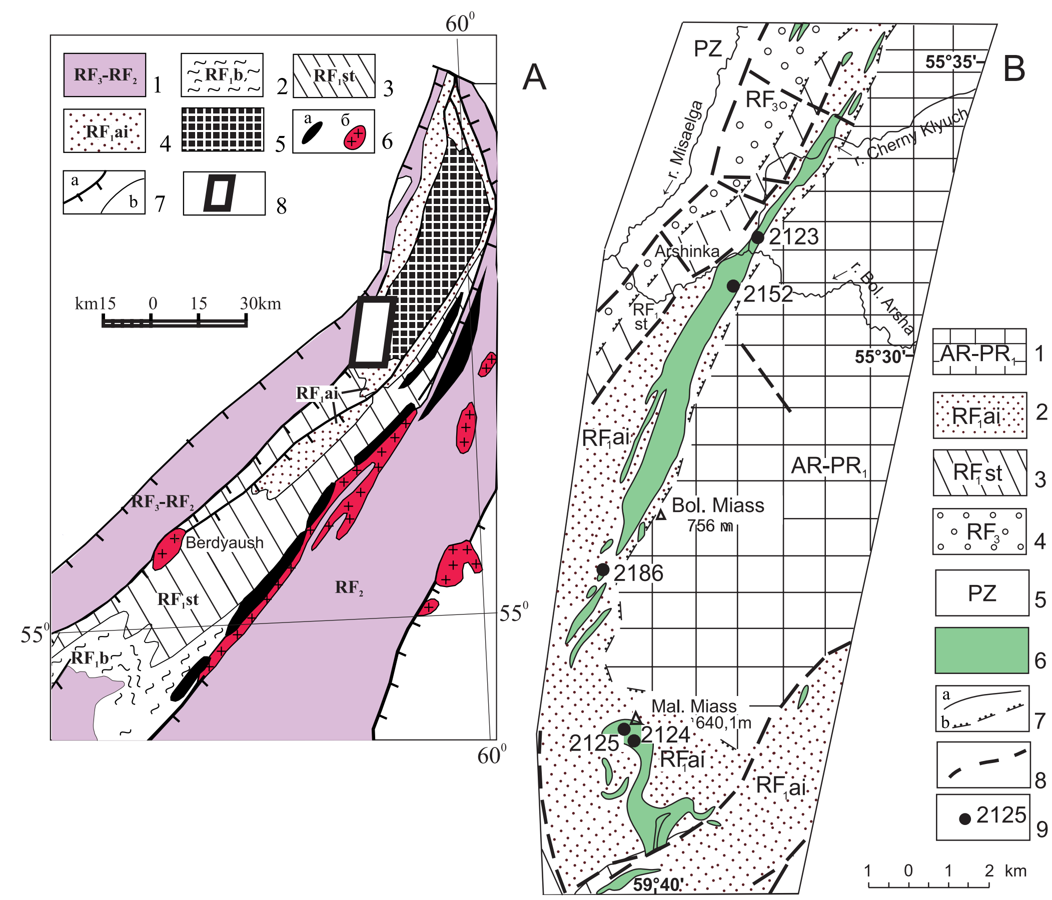


Fig. 1. A schematic geological map of the Taratash anticlinorium of the Southern Urals (A) and a fragment of a geological map of the Bolshoy and Maly Miass mountains region (B). Map (A): 1–4 – Riphean deposits: 1 – the Middle and Upper undivided; 2–4 – the Lower Riphean: 2 – Bakal, 3 – Satka and 4 – Ai Formations; 5 – Taratash metamorphic complex (AR-PR1), 6 – igneous rocks: gabbro (a) and granites (b); 7 – boundaries: tectonic (a), stratigraphic (b); 8 – position of a fragment of a geological map (B). Map (B): 1 – Taratash metamorphic complex (AR-PR1); 2–5 – deposits: 2 – Ai and 3-Satka Formations of the Lower Riphean, 4 – the Upper Riphean, 5 – Paleozoic; 6 – volcanic rocks; 7–8 – boundaries: 7 – stratigraphic (a) and unconformable (b), 8 – tectonic; 9 – places of sampling of zircons and their numbers

Elements	K2152	K2123	K2124	K2125	K2186
SiO_2	43.20	44.05	46.20	44.60	46.50
TiO_2	2.59	2.78	2.54	3.05	2.77
Al_2O_3	13.83	12.57	14.60	12.30	15.53
Fe_2O_3	11.35	12.46	9.40	12.48	9.10
FeO	6.11	6.80	7.18	7.20	6.17
MnO	0.13	0.19	0.12	0.16	0.21
CaO	3.29	3.16	2.27	1.48	1.54
MgO	8.81	8.21	8.40	8.94	6.15
Na_2O	0.85	3.72	3.20	2.25	0.79
K_2O	4.38	1.74	1.25	2.58	4.66
P_2O_5	0.87	0.78	0.75	0.73	0.81
Li	25.23	15.12	17.44	17.38	38.75
Ho	1.32	1.04	1.11	0.96	1.34
Y	29.68	20.59	22.12	18.74	31.13
Ti	14883.67	10810.85	10776.49	9637.21	18162.27
Cu	39.15	30.61	34.92	32.57	48.60
Sc	25.08	17.73	15.94	17.04	24.33
V	213.24	180.23	212.42	209.31	238.09
Co	41.24	31.59	30.19	36.17	41.53
Cr	47.57	33.68	37.75	38.62	49.66
Ni	54.27	39.25	43.18	48.46	44.62
La	52.43	29.81	33.86	28.72	45.49
Ce	96.94	67.45	76.29	68.04	100.06
Pr	14.86	8.86	10.03	8.57	12.72
Nd	61.79	39.35	44.48	37.83	53.55
Sm	11.68	7.55	8.34	7.65	10.20
Eu	3.62	2.40	2.52	2.46	4.06
Gd	9.16	6.88	7.13	6.32	9.91
Tb	1.25	0.94	0.97	0.87	1.67
Dy	7.04	5.21	5.71	5.05	6.83
Ho	1.32	1.04	1.11	0.95	1.34
Er	3.69	2.84	3.10	2.69	3.61
Tm	0.49	0.37	0.43	0.34	0.46
Yb	3.11	2.22	2.65	2.16	3.19
Lu	0.44	0.32	0.39	0.29	0.44

Table 1. The content of petrogenic (wt%) and rare (ppm) elements in the volcanics of the Navysh complex. K2152, K2123, K2125 – trachybasaltic porphyrites, K2124 – trachybasalt amygdaloid porphyrite, K2186 – trachybasalt

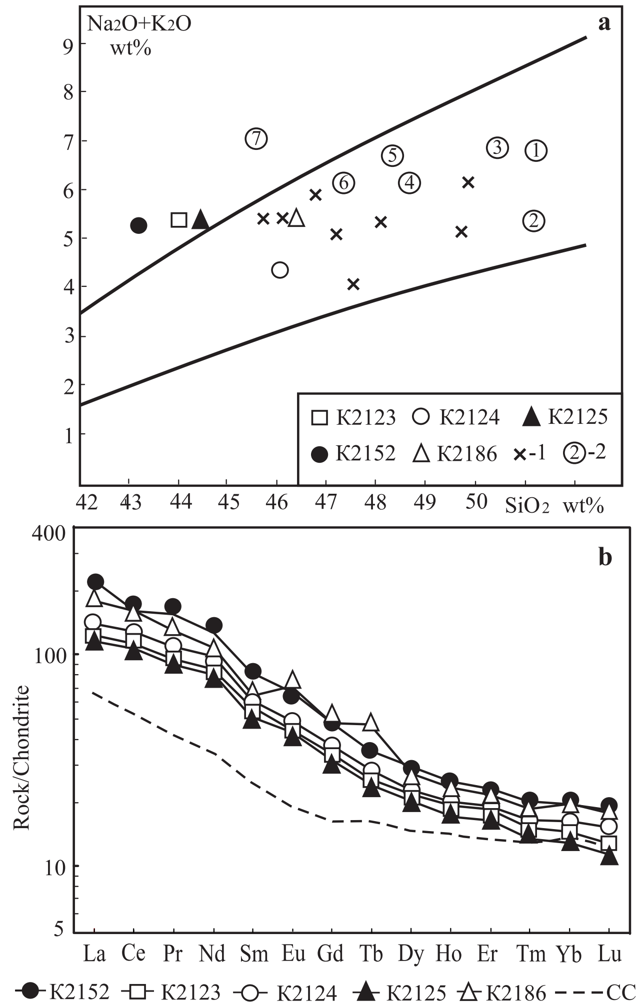


Fig. 2. Distribution of petrogenic (a) and rare earth (b) elements in the volcanics of the Navysh complex. Chondrite-normalized (McDonough, Sun, 1995). CC – continental crust after (Bogatikov et al., 1987). Lines on (2a) limit the area of distribution of subalkaline rocks. 1 – from (Lennykh, Petrov, 1974), 2 – from (Ernst et al., 2006).

of Geology and Geochemistry of the Urals Branch of the Russian Academy of Sciences (Yekaterinburg). Compared with those previously described (Lennykh, Petrov, 1974), the studied volcanics (Figure 2a) have a more basic composition and lower alkali content (Bogatikov et al., 1987; Ernst et al., 2006), and their rare-earth specialization practically coincides with the published (Ernst et al., 2006).

In terms of the REE composition, the volcanic rocks of sample K2152 and the other four have practically the same type of REE spectrum and only slightly vary in their content. As a geochemical criterion dividing them into separate genetic types, rare earths turned out to be ineffective, although their contents in sample K2152 were slightly elevated.

Mineralogical features of zircons

The main objective in the study of zircons (Figure 3) of the Navysh volcanic rocks is to identify specific features in them, which make it possible to identify genetic varieties among them. First of all, this refers to Riphean zircons coexisting in common samples with other varieties. In this case, we are talking not only about their monogenesis – polygenesis, but, to a greater extent, about the heterogeneity of the volcanics themselves, which, in fact, is a real basis for periodically arising discussions. First, let us turn to the analysis of the mineralogical features of zircons coexisting in volcanics. On the basis of the set of mineralogical features and composition, among the studied zircons, three (I, II, III) varieties were distinguished, the properties of which will be considered on specific examples in the course of presenting the material of the article.

Sample K2152 (55°31’41.7” N, 59°40’48.5” E). It represents typical Riphean zircons (Figure 3) from typical (“reference”) Ai volcanics with an age of 1752±11 Ma. Crystals are transparent, colorless, with an elongation from 1 to 3. Their characteristic feature is a combination of traces of primary idiomorphism and secondary roundness associated with crushing and surface dissolution. However, the main feature of these zircons is represented by a combination of distinct zoning and sectoriality, which together reflect their magmatic nature. Crystals with "longitudinal" zoning are encountered as single ones (crystal 5). The observed structural details reflect a high preservation of crystals, although the influence of secondary processes sometimes can be observed in them (for example, the appearance of late outgrowths – crystals 2, 2.2, or the presence of healed cracks – crystals A).

Crystal A (K2152) reflects the influence of tectonics (crushing) with the subsequent healing of the resulting cracks (chains of secondary inclusions).

We recall that the additionally selected samples of volcanics, as in the case with sample K2124, were also considered analogs of the reference K2152. The realities turned out to be "critical" for the volcanics.

Sample K2125 (55°25'35.5" N, 59°38'30.4" E). The main variety of zircons of this sample is represented by zonal crystals, sometimes with weak sectoriality and traces of various-scale transformations. Characterized by transparency, idiomorphism, elongation 1.5–3.5, development of {111} and {311} faces, which can replace each other during crystal growth. The edge boundaries are visible, that is, the surface dissolution of crystals (crystal 2) was insignificant. In crystal 5, an early generation relic is easily confused with a xenogenic core.

Combinations of light-dark zones (CL) in crystals 2, 4, 6, classified as type I, reflect their magmatic nature, formation in an environment of variable composition. The specific structure of crystal 1 is the reason for classifying it as type II, also magmatic.

Sample K2124 (55°25'39.1" N, 59°38'27.7" E). The prominent representatives of type I zircons are crystals 2–5, crystal 1 belongs to type II. Under conditions of stable crystallization, crystal 6 appeared, referred to as type III. All varieties of zircons reflect their magmatic nature.

Sample K2123 (55°33'20.2" N, 59°41'33" E). The first type of zircons is confidently distinguished by crystals 2, 3, 7, crystal A belongs to type II. The structure of crystals 1, 4, and B allows us to classify them as type III, although crystal 4 is closer to type I in age. Crystal B illustrates the true example of shell formation with replacement (!) of early generation material.

Sample K2186 (55°27'22.9" N, 59°37'41.2" E). Zonal crystals 1, 6 and a distinct sectorial crystal 7 correspond to type I. Crystals 3 and 5 of a different structure, although with an age corresponding to crystals of type I, as well as crystals 4 and 8 of the same age with partial dissolution of the early generation, can be classified as type III. Crystal A confirms the presence of type II grains in the sample.

From a comparison of the morphological features of the main variety of crystals in samples 2124, 2125, 2123 and 2186 with crystals of sample K2152, their qualitative differences become obvious with a stable appearance and structure of the former.

U-Th in zircons

The content (ppm) of U and Th in zircons from volcanics is given in Table 2, and Figure 4 shows their distribution in zircons.

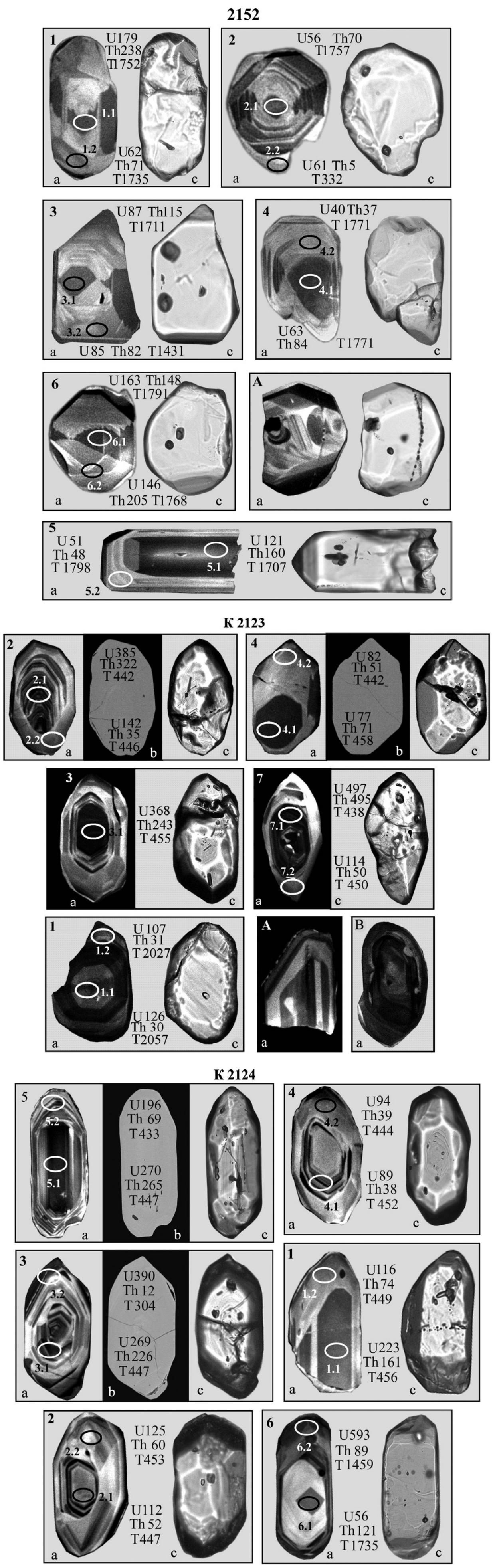
Most of the zircons of the main (I, II) types are represented by depleting trends in Tp, and analyzes of type III crystals that go beyond the trend boundaries are points with changed coordinates U and Th. For sample K2152, this is crystal 2.2, in which Th is 5 ppm, for crystal 8.2 of sample K2186 U is 3 ppm, for crystal 3.2 of sample K2124 Th is 12 ppm. All these "biased" analyzes do not affect the general distribution of U and Th in zircons of the main varieties, while maintaining the possibility of their comparison. Their main feature is the progressive decrease in U and Th in later generations. Another important conclusion, reflecting the compositional variations, is determined by the elevated contents of U and Th in the K2152 zircons compared to the rest. Their trend is "to the left" and "above" the point of intersection of analyzes 100 U – 100 Th (ppm), and the trends of the remaining samples are "below" and "to the right". Thus, the mineralogical differences between the zircons of the compared samples are also confirmed by geochemical data, although the evolutionary development of all zircons is undoubtedly similar.

REE in zircons

The REE spectra in zircons were obtained at points – craters with SHRIMP dating. The REE content in zircons is shown in Table 3, and the peculiarities of their distribution are reflected in the diagrams (Fig. 5), built with the REE content normalization to chondrite (Mc Donough, Sun, 1995).

Most of the REE spectra of zircons with varying Ce* and Eu* anomalies and at heavy REE (HREE, Er-Lu) > light REE (LREE, La-Nd) reflect their magmatic nature. This applies to both early and late generations, the REE spectra of which may not only be close or coincide (K2152, crystals 3, 5; K2125, crystal 1), but also indicate a significant decrease in REE in late generations (K2125 – crystal 6; K2124, crystal 5; K2123 – crystal 2).

An unusual situation with crystals 1 (K2123) and 6 (K2124). In the former, the spectrum of early generation along the middle REE dip corresponds largely to the metasomatic type, although both subsequent ones are of the magmatic type. The opposite tendency is manifested in crystal 6 with a clearly pronounced belonging of the early generation to the magmatic type. An increase in U (from 56 to 593 ppm) for generation 6.2 (Table 2) is



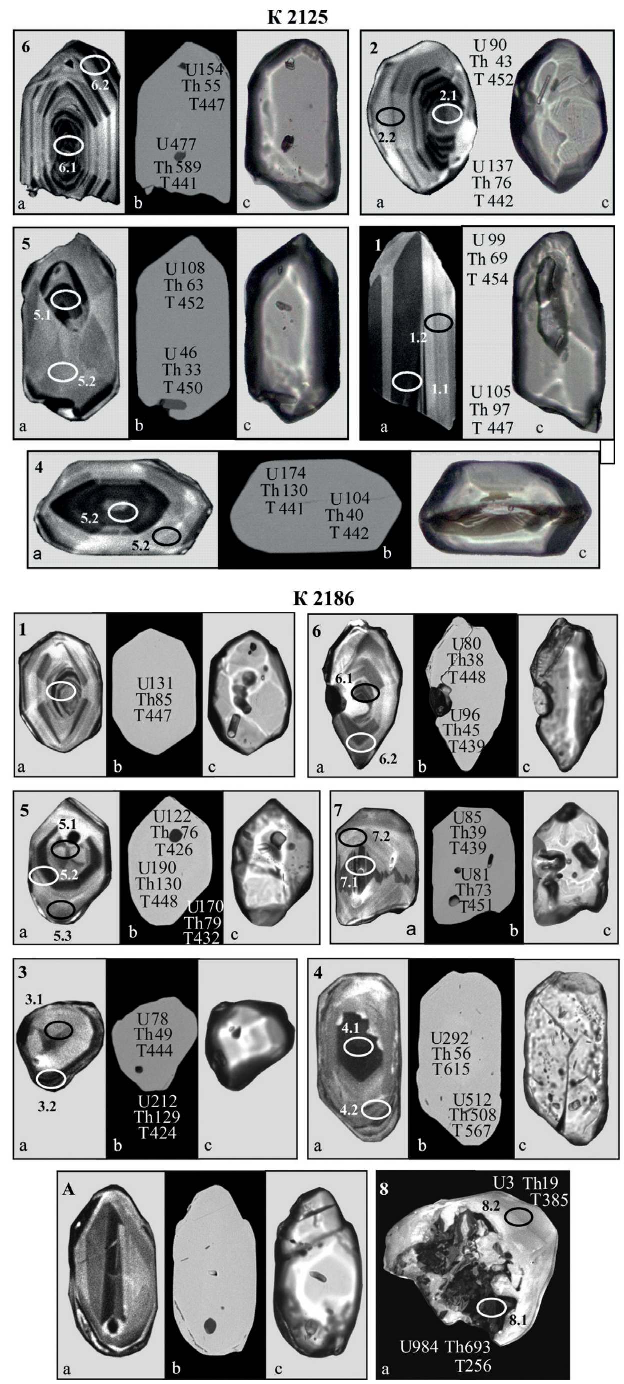


Fig. 3. Mineral and geochemical features of zircons. Contents of U and Th – ppm, T – age, million years ($^{206}Pb/^{238}U$), a – CL, b – BSE, c – optics, transmitted light. Numbers – crystals and craters numbers (Table 2)

accompanied by a transition to the metasomatic type, and a decrease in age also occurs (from 1735 to 1459 Ma, Figure 3, K2124, curve 6). Such changes indicate that crystals 1 (K2123) and 6 (K2124) are not associated with sources corresponding to the main type of zircons.

The appurtenance of the volcanic rocks of the Navysh complex to polygenic formations according to these REE variations only increases, continuing the trends noted during mineralogical and geochemical studies.

Based on the ratio of individual parts of the REE spectra of zircons (Hoskin, 2005), it is possible to clarify some features of their origin (Figure 6).

The magmatic nature (M) is confirmed for almost all crystals of K2152 and most crystals of sample K2125. Only the early generation 6.1 of crystal 6 of sample 2125, probably due to increased concentrations of U and Th, contains signs of structural imperfection (metamictization), which shifted its analysis towards hydrothermal (H) type zircons. However, the final growth of the crystal (the appearance of generation 6.2) brings it closer to the M type, restoring its initial status. In crystal 1 (sample K2123), the early generation 1.1 confidently belongs to the H type. The obvious reason for this is in its considerable age (>2000 Ma), in a high dose of absorbed α-irradiation, and, accordingly, in the development of radiation metamictization. Generations 1.2 and 1.1 of this crystal demonstrate an increase in structural perfection and, accordingly, an approach to the M type. Such changes are associated primarily with the complex evolution of the LREE spectrum (Figure 5). The transformations of the REE spectrum of variety 6.2 of crystal 6 (sample K2124), its closeness to the H type are caused by the influence of not only age, but also a significant (593 ppm, Table 2) content of U.

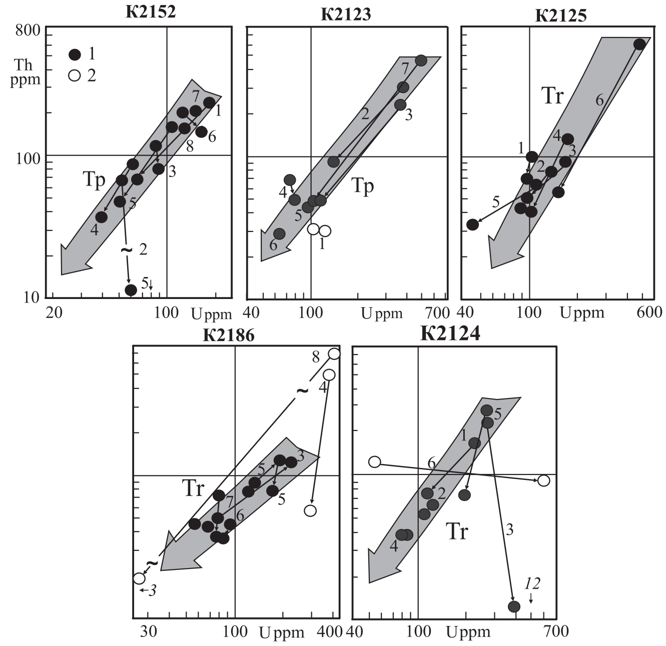


Fig. 4. U and Th in zircons of the Navysh volcanics. 1 – zircons (types I and II) of the main and 2 – additional (III) varieties. Early – late generations of zircons are connected by arrows. Analysis offsets are indicated by additional information (K2152, 2.2, Th – 5; K2186, 8.2, U – 3; K2124, 3.2, Th – 12)

Crystal Crater	$^{206}Pb_c$, %	Content, ppm U	Th	$^{206}Pb^*$	$\frac{^{232}Th}{^{238}U}$	$\frac{^{206}Pb}{^{238}U}$ age, Ma	D, %	Isotopic correlation $^{207}Pb^*/^{206}Pb^*$	±%	$^{207}Pb^*/^{235}U$	±%	$^{206}Pb^*/^{238}U$	±%	Rho
							K2152							
1.1	0.10	179	238	48	1.38	1752±20	-1	0.1066	1.3	4.588	1.8	0.3123	1.3	0.698
1.2	0.41	62	71	16.6	1.17	1735±24	-2	0.1039	2.9	4.42	3.3	0.3088	1.5	0.476
2.1	0.26	56	70	15.2	1.28	1757±29	2	0.1094	2.4	4.72	3.1	0.3133	1.9	0.606
2.2	1.55	61	5	2.8	0.08	332.1±7.0	162	0.068	12	0.496	12	0.0529	2.2	0.177
3.1	0.12	87	115	22.7	1.37	1711±19	1	0.1054	1.7	4.418	2.1	0.3039	1.3	0.608
3.2	0.00	85	82	18.3	0.99	1431±17	24	0.1083	1.7	3.713	2.1	0.2486	1.3	0.620
4.1	0.24	63	84	17.2	1.37	1771±30	-3	0.1057	2.4	4.61	3.1	0.3161	1.9	617
4.2	0.00	40	37	10.9	0.96	1771±25	1	0.1093	2	4.76	2.6	0.3161	1.6	0.641
5.1	-	121	160	31.5	1.36	1707±18	3	0.1077	1.8	4.504	2.1	0.3033	1.2	0.554
5.2	0.20	51	48	14	0.98	1798±23	-2	0.1078	2.2	4.78	2.6	0.3217	1.5	0.568
6.1	0.07	163	148	44.8	0.94	1791±19	-2	0.1078	1.5	4.759	1.9	0.3202	1.2	0.618
6.2	0.00	146	205	39.6	1.45	1768 ± 16	-1	0.1067	1.2	4.643	1.6	0.3155	1.1	0.672
7	0.00	150	206	37.2	1.42	1638±15	8	0.1077	1.2	4.298	1.6	0.2893	1.1	0.661
8	0.31	122	161	31.4	1.37	1690±17	-1	0.1031	1.9	4.263	2.2	0.2998	1.1	0.518
							K2123							
1.1	0.08	126	30	40.6	0.25	2057±19	-1	0.1255	1	6.505	1.5	0.3758	1.1	0.730
1.2	0.22	107	31	34.2	0.29	2027±21	2	0.1274	1.3	6.49	1.8	0.3694	1.2	0.671
2.1	0.46	385	322	23.6	0.87	442.6±4.5	-18	0.0539	3.7	0.528	3.8	0.07107	1.1	0.276
2.2	0.30	142	95	8.76	0.69	446.2 ±5.4	-10	0.0548	4.2	0.541	4.4	0.07168	1.3	0.288
3.1	0.06	368	243	23.1	0.68	455.2±5.6	-6	0.0554	2.3	0.558	2.6	0.07317	1.3	0.486
3.2	0.00	106	47	6.42	0.46	439.3±5.9	17	0.0576	3.4	0.56	3.7	0.07052	1.4	0.376
4.1	0.00	77	71	4.85	0.96	458.4±6.9	19	0.0584	3.9	0.593	4.2	0.0737	1.6	0.371
4.2	0.52	82	51	5.04	0.64	442.2±6.6	10	0.0569	6.3	0.557	6.4	0.071	1.5	0.239
5.1	0.48	100	45	5.99	0.46	432.1±6.1	-20	0.0534	6.1	0.511	6.3	0.0693	1.5	0.233
6.1	0.00	66	29	4.13	0.44	450.8±7.1	10	0.0571	4.2	0.571	4.5	0.0724	1.6	0.360
7.1	0.21	497	495	30.1	1.03	438.4±4	-10	0.0546	2.3	0.53	2.5	0.07037	0.94	0.381
7.2	0.00	114	95	7.08	0.45	450.4±5.8	-8	0.0551	3.3	0.549	3.6	0.07236	1.3	0.377

Table 2. U-Pb age of zircons from volcanic rocks of the Navysh complex of the Ai Formation (K2152, K2123, K2124, K2125, K2186)

Crystal Crater	$^{206}Pb_c$, %	Content, ppm U	Th	$^{206}Pb^*$	$^{232}Th/^{238}U$	$^{206}Pb/^{238}U$ age, Ma	D, %	Isotopic correlation $^{207}Pb^*/^{206}Pb^*$	±%	$^{207}Pb^*/^{235}U$	±%	$^{206}Pb^*/^{238}U$	±%	Rho
K2124														
3.2	0.00	390	12	16.2	0.03	304±4	19	0.0540	2.1	0.359	2.5	0.04821	1.3	0.51
5.2	0.00	196	69	11.7	0.36	433±7	24	0.0590	5.5	0.565	5.7	0.06949	1.6	0.29
4.2	0.00	94	39	5.77	0.43	444±8	22	0.0588	3.7	0.578	4.1	0.07128	1.8	0.43
3.1	-	269	226	16.6	0.87	447±6	11	0.0572	2.7	0.566	3.0	0.07177	1.3	0.44
2.1	0.00	112	52	6.93	0.48	447±8	-12	0.0547	3.6	0.541	4.0	0.07181	1.7	0.43
5.1	0.00	270	265	16.7	1.01	447±6	-41	0.0528	2.4	0.524	2.8	0.07187	1.4	0.52
1.2	-	116	74	7.2	0.65	449±7	9	0.0570	5.5	0.567	5.7	0.07218	1.5	0.27
4.1	-	89	38	5.57	0.44	452±7	11	0.0574	6.8	0.574	7.0	0.07259	1.7	0.24
2.2	-	125	60	7.84	0.49	453±7	6	0.0567	6.2	0.569	6.5	0.07278	1.7	0.26
1.1	0.17	223	161	14	0.75	456±6	0	0.0561	3.7	0.567	3.9	0.07334	1.3	0.34
6.2	0.03	593	89	129	0.15	1459±20	15	0.1038	0.8	3.634	1.7	0.25393	1.5	0.89
6.1	-	56	121	14.9	2.22	1735±32	0	0.1063	2.3	4.529	3.1	0.30889	2.1	0.68
K2125														
3.2	0.68	169	90	9.61	0.55	413±7	25	0.058	7.4	0.533	7.6	0.06615	1.7	0.22
4.1	0.00	174	130	10.5	0.77	441±7	-1	0.0556	2.9	0.542	3.3	0.07073	1.6	0.48
6.1	0.00	477	589	29	1.28	441±6	-4	0.0553	3.6	0.540	3.8	0.07076	1.3	0.35
4.2	0.00	104	40	6.34	0.40	442±7	29	0.0603	3.6	0.590	4.0	0.07093	1.8	0.44
2.1	0.00	137	76	8.36	0.57	442±7	25	0.0594	3.1	0.581	3.5	0.07097	1.6	0.47
3.1	0.00	98	50	6	0.52	444±8	18	0.0582	7.0	0.572	7.3	0.07132	1.8	0.25
1.1	0.00	105	97	6.47	0.96	447±8	19	0.0585	3.7	0.580	4.1	0.07185	1.8	0.43
6.2	0.00	151	55	9.34	0.38	447±7	8	0.0568	3.1	0.563	3.5	0.07185	1.6	0.46
5.2	0.00	46	33	2.84	0.75	450±10	5	0.0565	5.6	0.564	6.0	0.07238	2.3	0.38
5.1	0.00	108	63	6.72	0.60	452±8	12	0.0575	3.5	0.576	4.0	0.07258	1.8	0.45
2.2	0.00	90	43	5.63	0.49	452±8	-11	0.0549	4.2	0.549	4.6	0.07258	1.9	0.40
1.2	0.00	99	69	6.21	0.72	454±8	-2	0.0558	4.6	0.561	4.9	0.07288	1.8	0.36

Crystal Crater	$^{206}Pb_c$, %	Content, ppm U	Th	$^{206}Pb^*$	$^{232}Th/^{238}U$	$^{206}Pb/^{238}U$ age, Ma	D, %	Isotopic composition $^{207}Pb^*/^{206}Pb^*$	±%	$^{207}Pb^*/^{235}U$	±%	$^{206}Pb^*/^{238}U$	±%	Rho
K2186														
1.1	1.48	131	85	8.18	0.67	447±10	-12	0.0666	3.2	0.54	9.6	0.0718	2.4	0.249
2.1	3.42	58	46	3.66	0.82	442±13	11	0.0846	6.8	0.56	23	0.071	3	0.127
2.2	1.83	69	44	4.24	0.65	434±11	-3	0.0701	4.1	0.53	15	0.0696	2.6	0.176
3.1	2.10	78	49	4.86	0.65	444±11	-20	0.0708	5.8	0.527	17	0.0713	2.6	0.154
3.2	1.62	212	123	12.6	0.60	424±10	28	0.0714	5.6	0.546	13	0.679	2.4	0.193
4.1	0.26	512	508	40.6	1.03	567±11	-6	0.06028	1.5	0.738	2.7	0.092	2	0.746
4.2	0.51	292	56	25.2	0.20	615±13	-9	0.063	2.3	0.812	4.8	0.1001	2.2	0.452
5.1	2.03	122	76	7.32	0.64	426±10	-12	0.0706	3.9	0.51	14	0.0684	2.5	0.177
5.2	1.49	190	130	11.9	0.71	448.1±10	-33	0.0645	2.8	0.52	9.3	0.072	2.3	0.247
5.3	0.70	170	79	10.2	0.48	432.9±9.2	6	0.0619	2.9	0.538	6.4	0.0695	2.2	0.342
6.1	1.95	80	38	5.06	0.49	448±11	-31	0.0684	3.6	0.521	14	0.0719	2.5	0.181
6.2	1.32	96	45	5.88	0.48	439±11	-36	0.0627	6.44	0.504	18	0.0704	2.6	0.143
7.1	2.17	81	73	5.14	0.94	451±11	-26	0.0708	7.5	0.531	17	0.0725	2.5	0.150
7.2	2.01	85	39	5.29	0.47	439±11	-55	0.0664	4.2	0.487	16	0.0705	2.6	0.162
8.1	2.51	984	693	35.2	0.73	256.1±5.2	9	0.07197	1.3	0.29	6.1	0.04053	2.1	0.335
8.2	0.00	3	19	0.169	5.97	385±21	732	0.252	7.8	2.14	9.6	0.0615	5.6	0.582

Continuation of table 2. Note: Accuracy ± 1σ, Pb_c and Pb – total and radiogenic lead. Calibration error of the K2152 standard – 0.37%; K2186 – 0.60%; K2123 – 0.42%; K2124 and K2125 – 0.47%. Correction – by ^{204}Pb. D – discordance. Rho is the correlation coefficient. The isotopic composition and age of zircons were determined using the SHRIMP II ion microprobe at the Center for Research and Development of the All-Russian Geological Institute (St. Petersburg) using the standard technique (Williams, 1998)*

Age of zircons

Figure 7 shows the dates of the main types of zircons for all volcanic samples. The age of type III zircons can be judged from Figure 3, Table 2, as mentioned in the text.

The main varieties of zircons from the amygdaloidal trachybasaltic porphyrite K2124 are characterized by concordant dating T=449.3±4.7 Ma. Ancient varieties (6.1–6.2) have an age of T_0=1738±48 Ma, comparable to the age of K2152 zircons. However, it is not possible to identify them with the Riphean ones due to the differences in both mineralogical and geochemical features. In particular, the Th/U ratio for K2124 (6.1) zircons corresponds to 2.22, and for K2152 zircons does not exceed 1.45, starting from 0.08 (Table 2). We have to conclude that crystal 6 of the sample K2124 is a xenogenic addition in it, i.e., it is not associated with the substrate of the established Riphean volcanics.

Trachybasaltic porphyrite K2123 is represented by two types of zircons. The concordant age of T=444.3±3.5 Ma was established for the main varieties (Figure 7). For both generations of crystal 1, the concordant dating corresponds to T_0=2044±20 Ma. The age preservation of this crystal (discordance is not worse

Crystal	K2152					
Crater	3		4		5	
	3.1	3.2	4.1	4.2	5.1	5.2
La	0.13	0.11	0.14	0.06	0.25	0.15
Ce	12.19	16.37	7.29	7.43	13.22	10.79
Pr	0.24	0.29	0.38	0.09	0.82	0.33
Nd	4.35	4.23	5.44	1.37	13.01	5.60
Sm	6.45	6.68	8.54	2.38	11.17	5.34
Eu	0.60	0.39	0.82	0.19	0.63	0.40
Gd	19.95	18.46	21.31	8.03	34.84	15.69
Tb	6.90	5.78	6.92	2.56	10.42	5.99
Dy	86.31	79.73	79.51	31.27	110.50	70.60
Ho	27.44	25.77	26.91	10.10	36.58	23.94
Er	109.59	116.56	104.61	43.21	132.65	99.79
Tm	21.58	22.00	20.17	9.43	26.43	22.87
Yb	218.84	192.56	181.15	88.25	223.87	229.23
Lu	35.89	31.63	29.40	15.36	34.43	37.13
Total	494.54	467.02	438.59	197.64	575.39	527.87
$(Sm/La)_N$	79.45	97.25	97.68	63.52	71.54	57.00
$(Yb/La)_N$	2478.02	2576.89	1904.73	2165.14	1318.19	2249.59
Ce/Ce*	16.69	22.17	7.65	24.46	7.06	11.73
Eu/Eu*	0.16	0.11	0.19	0.13	0.09	0.13

Crystal	K2124				
Crater	1	5		6	
	1.1	5.1	5.2	6.1	6.2
La	0.09	0.70	0.27	0.20	1.04
Ce	24.30	39.00	29.50	31.90	34.80
Pr	0.23	1.09	0.14	0.83	4.85
Nd	3.26	14.41	1.21	11.90	9.09
Sm	5.95	18.96	1.85	11.75	1.53
Eu	1.46	2.83	0.72	2.23	0.38
Gd	25.37	82.37	10.07	37.56	4.03
Tb	-	-	-	-	-
Dy	86.40	238.60	40.90	100.30	20.20
Ho	-	-	-	-	-
Er	207.80	452.00	106.50	163.20	52.60
Tm	-	-	-	-	-
Yb	473.10	802.30	292.20	258.00	140.00
Lu	87.00	136.30	59.50	42.50	27.70
Total	914.92	1788.50	542.95	600.40	305.56
$(Sm/La)_N$	97.55	43.03	10.95	92.72	2.31
$(Yb/La)_N$	7135.07	1674.29	1591.73	1871.87	19.79
Ce/Ce*	39.29	10.72	36.23	18.74	1.18
Eu/Eu*	0.36	0.21	0.511	0.32	0.46

Crystal	K2123						
Crater	1			2		4	
	1.1	1.3	1.2	2.1	2.2	4.1	4.2
La	493.11	0.09	0.66	0.97	0.23	0.08	0.05
Ce	692.30	22.20	19.20	135.20	45.30	23.80	21.90
Pr	162.7	0.25	0.49	0.87	0.14	0.16	0.06
Nd	655.90	4.10	3.30	6.60	1.20	2.80	0.90
Sm	95.60	6.50	2.90	8.60	2.40	6.30	2.00
Eu	4.22	0.46	0.49	2.17	0.48	1.62	0.48
Gd	48.10	28.50	8.20	42.80	13.80	30.60	10.50
Tb	-	-	-	-	-	-	-
Dy	176.00	108.00	33.00	163.00	55.00	93.00	41.00
Ho	-	-	-	-	-	-	-
Er	280.00	219.00	89.00	416.00	143.00	194.00	96.00
Tm	-	-	-	-	-	-	-
Yb	455.00	395.00	194.00	969.00	334.00	373.00	206.00
Lu	73.00	66.00	35.00	177.00	61.00	64.00	37.00
Total	3146.42	849.97	386.20	1922.67	656.12	789.66	416.48
$(Sm/La)_N$	0.31	114.81	7.08	14.26	17.28	119.61	59.88
$(Yb/La)_N$	1.36	6424.94	431.86	1473.70	2173.90	6478.27	5594.62
Ce/Ce*	0.59	35.66	8.14	35.69	62.51	49.67	90.08
Eu/Eu*	0.19	0.10	0.30	0.34	0.25	0.35	0.32

Crystal	K2125							
Crater	1		2		6		5	
	1.1	1.2	2.1	2.2	6.1	6.2	5.1	5.2
La	0.08	0.12	0.12	0.14	1.81	0.21	0.12	0.05
Ce	24.10	17.50	20.00	9.50	39.80	19.30	20.70	8.90
Pr	0.16	0.08	0.08	0.07	0.77	0.18	0.09	0.03
Nd	2.80	1.00	1.00	0.70	5.50	1.60	1.30	0.40
Sm	6.10	1.80	2.00	0.90	4.30	2.10	2.40	0.70
Eu	1.70	0.65	0.74	0.39	1.22	0.69	1.01	0.30
Gd	27.20	10.10	11.00	5.60	17.20	8.40	14.6	4.30
Tb	-	-	-	-	-	-	-	-
Dy	80.00	39.00	46.00	23.00	66.00	38.00	64.00	19.00
Ho	-	-	-	-	-	-	-	-
Er	159.00	89.00	137.00	69.00	181.00	118.00	184.00	54.00
Tm	-	-	-	-	-	-	-	-
Yb	297.00	203.00	370.00	209.00	476.00	351.00	480.00	152.00
Lu	51.00	38.00	75.00	44.00	99.00	75.00	100.00	33.00
Total	648.81	400.91	662.87	362.95	892.55	614.42	868.59	271.59
$(Sm/La)_N$	116.19	24.58	27.16	10.97	3.81	16.35	32.75	21.42
$(Yb/La)_N$	5227.99	2509.31	4628.32	2272.90	387.79	2502.93	5959.87	4089.03
Ce/Ce*	50.70	42.91	49.36	24.02	8.16	24.36	49.63	53.27
Eu/Eu*	0.40	0.46	0.48	0.53	0.43	0.50	0.52	0.51

Table 3. The content of REE (ppm) in zircons of the Navysh complex. Note: $(Sm/La)_N$, $(Yb/La)_N$, Ce/Ce, Eu/Eu* – normalized to chondrite (Mc Donough, 1995) before fission. $Ce/Ce^* = Ce/(La \times Pr)^{1/2}$; $Eu/Eu^* = Eu/(Sm \times Gd)^{1/2}$. The analyzes were carried out at the Center for Research and Development of the All-Russian Geological Institute (St. Petersburg) (the numbers of the crystal-craters correspond to those used in determining the age, Table 2)*

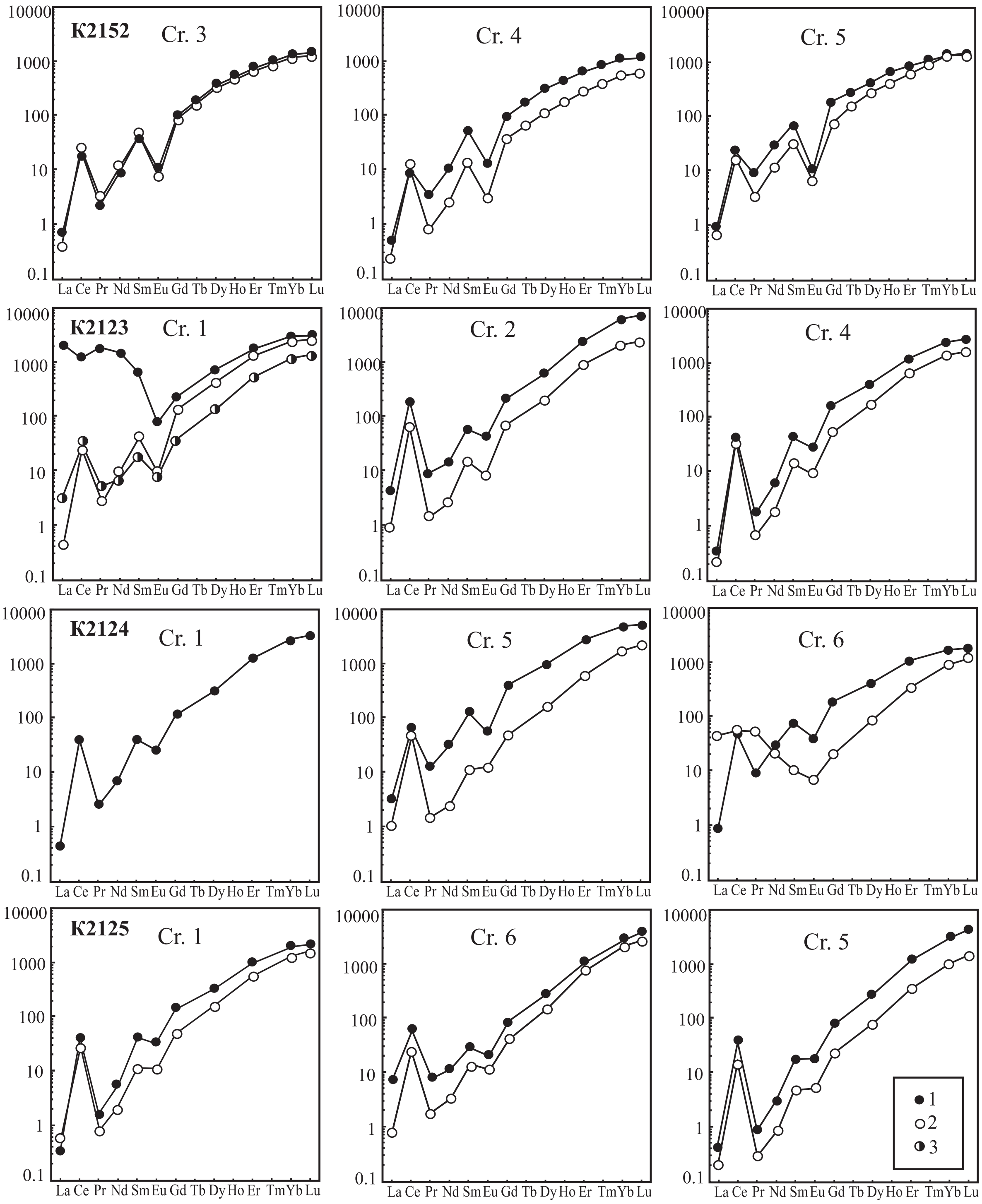


Fig. 5. REE spectra in zircons of volcanic rocks of the Navysh complex. 1 – early generations, 2 – late generations, 3 – intermediate, coexisting in a single crystal. Crystal numbers – Fig. 3. Analytical data – Tab. 3. Analyzes were performed at the points used in determining the age

than 1–2, Table 2), despite the complex internal structure and duration of its existence, seems to be unique, since all other "younger" varieties have undergone significant transformations (their discordance varies from –20 to 19), which turned out to be neutral for crystal 1 (1.1 and 1.2).

The zircons of the K2186 trachybasalts have a concordant date of T=438.9±6.1 Ma (Figure 7). The average statistical age of these crystals for $^{206}Pb/^{238}U$ is T_1=439.1±6.1 million years, and then, the most reasonable age can be considered as T=439±6 million years. The sample contains type III crystal 4 with the age of both generations T_3=590±12 Ma and crystal 8, enriched in U (984 ppm) and Th (693 ppm) with an age of 256.1±5.2 Ma, corresponding to the metasomatic variety.

The community of most crystals of the main type of trachybasalts K2125 is characterized by an age of T=446±4 Ma. Surprisingly, this sample does not contain zircons of a different age level at all (Table 2).

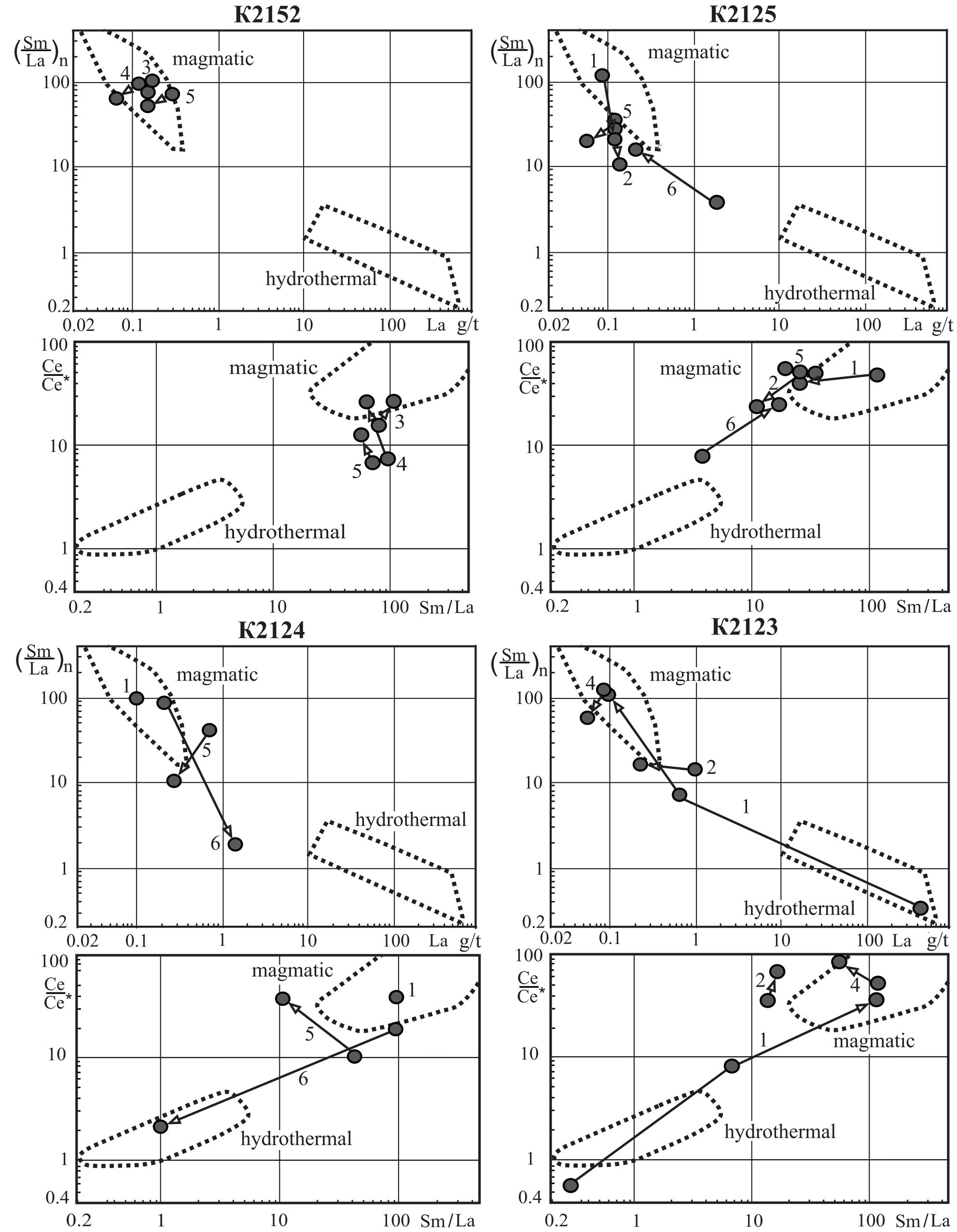


Fig. 6. Genetic classification of zircons from volcanic rocks of the Navysh complex after (Hoskin, 2005). Fields: M (magmatic) – magmatic, H (hydrothermal) – hydrothermal zircons. All elements are normalized to chondrite (McDonough, Sun, 1995). Early – late generations are connected by arrows

The set of dating of crystals of the main type reflects the stable relationship of their structure, composition, and time evolution. It can be assumed that a similar situation is possible with the formation of crystals associated not only with the same type of crystallization, but also with a similar evolution and subsequent transformations. The contribution of secondary processes to it is probably capable of disrupting some signs of their genetic commonality, or even leading to a rupture of particular material-geochemical characteristics, but is not capable of depriving them of information about the primary basic conditions of formation.

The age comparability of the main types of zircon in samples K2123, K2124, K2125, and K2186 makes it possible to estimate their total age, corresponding to the age of volcanics, with the dating T=445 Ma. Earlier, the interval of 400–600 Ma was considered as an alternative age of volcanics.

Conclusion

From the obtained zircon data, the main conclusion is that the volcanites of the Navysh complex form a polychronous system that combines both Lower Riphean formations (1750 Ma) and Paleozoic ones (450 Ma). Zircons of these age groups differ significantly in both mineralogical and geochemical (U, Th, REE) properties, confirming that they belong to different primary sources. However, it should be taken into account that Paleozoic zircons of igneous nature are distributed over a large area, and cannot be considered as transformed ancient

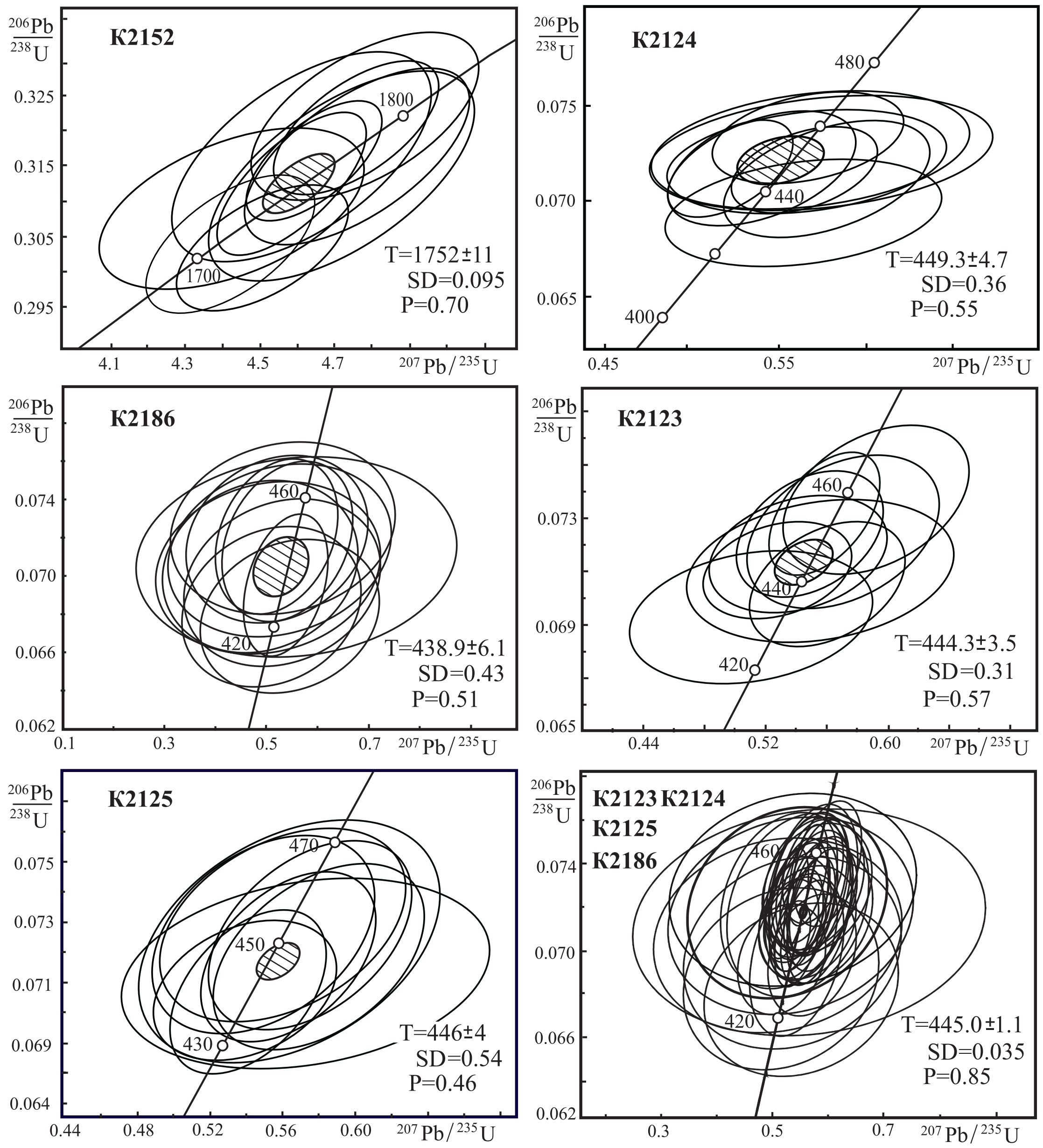


Fig. 7. U-Pb age of zircons from volcanic rocks of the Navysh complex. SD – Standard deviation

varieties, i.e. as belonging to the metamorphogenic type. At the same time, the insignificant influence of metasomatic processes on them is not excluded.

The situation with the Navysh volcanics is significantly complicated by the presence of zircons of both Paleoproterozoic (2000–2100 Ma) and Neoproterozoic (550–600 Ma) ages, as well as metasomatic varieties with an age of 250–360 Ma. And if you look at this issue more broadly, it turns out that the manifestations of the Mashak magmatism of the Middle Riphean are also superimposed on the development area of the Ai Formation, further complicating and confusing the relationship of magmatic complexes. The rather long time (from 1752 Ma to 450 Ma) and repeated manifestation of magmatism (volcanism) in the area under consideration is most likely due to repeated plume processes, which partly reanimated, warmed up, and involved in remelting magma chambers of the previous stages and created new melting points.

A specific feature of the Paleozoic Navysh volcanics is their rather wide distribution within the boundaries of the volcanogenic-sedimentary formations of the Ai Formation of the Lower Riphean and their close conjugation with both Riphean volcanics and sedimentary rocks of the Ai Formation. However, the Early Riphean (but not Paleozoic) age of the latter has been convincingly confirmed by studying detrital zircons from this formation (Romanyuk et al., 2018). We specially selected samples of the Ai Formation in the immediate vicinity of the Paleozoic volcanics on the river Ushat, and the study of zircons from them gave the same result. In order to distinguish Paleozoic volcanics in the section and laterally, it is necessary to conduct new targeted studies at the modern level, including a more thorough analysis of both zircons and volcanics, and the geological situation related to their origin, development and existence.

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References

Bogatikov P.A., Kosareva L.V., Sharkov E.V. (1987). The average chemical compositions of igneous rocks. Moscow: Nedra, 152 p. (In Russ.)

Ernst R.E., Pease V., Puchkov V.N., Kozlov V.I., Sergeeva N.D., Hamilton M. (2006). Geodynamical characterization of Precambrian magmatic suites of the south-eastern margin of the east European craton, Southern Urals, Russia. Ufa, 54 p.

Hoskin P.W. (2005). Trace-element composition of hydrothermal zircon and the alternation of hydrothermal zircon from the Jack-Hills, Australia. *Geochim. Cosmochim. Acta*, 69(3), pp. 637–648.

Kozlov V.I., Krasnobaev A.A., Larionov N.N., Maslov A.V., Sergeeva N.D., Bibikova E.V., Genina L.A., Ronkin Yu.L. (1989). Lower Riphean of the Southern Urals. Moscow: Nauka, 208 p. (In Russ.)

Krasnobaev A.A., Bibikova E.V., Ronkin Yu.L.,Kozlov V.I. (1992). Geochronology of volcanic rocks of the Ai Formation and isotopic age of the lower boundary of the Riphean. *Izv. AN RAN. Ser. geol*, 6. pp. 25–41. (In Russ.)

Krasnobaev A.A., Puchkov V.N., Kozlov V.I., Sergeeva N.D., Busharina S.V., Lepekhina E.N. (2013). Zirconology of the Navysh volcanic rocks of the Ai Formation and the problem of the age of the lower Riphean border in the Southern Urals. *Dokl. AN*. 448 (4), pp. 437–442. (In Russ.)

Krasnobaev A.A., Puchkov V.N., Sergeeva N.D. (2018). Polychronous Zirconology of Navysh Volcanics of the Ai Formation (Southern Urals). *Doklady Earth Sciences*, 478(1), pp. 56–61. DOI: 10.1134/S1028334X18010038

Lennykh V.I., Petrov V.I. (1974). About potassium alkaline basaltoids in the frame of the taratash complex. *Vulkanizm Yuzhnogo Urala*. Sverdlovsk: UNTs AN SSSR, pp. 146–164. (In Russ.)

McDonough W.F., Sun S.S. (1995). The Composition of the Earth. *Chem. Geol*., 120, pp. 223–253.

Romanyuk T. V., Kuznetsov N. B., Belousova E. A., Gorozhanin V. M., Gorozhanina E. N. (2018). Paleotectonic and paleogeographic conditions of accumulation of the Lower Riphean Ai Formation of the Bashkir Rise (Southern Urals) based on the study of detrital zircons by the method «TERRANECHRONE®». *Geodynamics &Tectonophysics*, 9(1), pp.1−37. (In Russ.)

Stratigraphic schemes of the Urals (Precambrian, Paleozoic). Interdepartmental Stratigraphic Committee of Russia. Yekaterinburg. 1993. 151 scheme. 152 p. (In Russ.)

Williams I.S. (1998). U-Th-Pb Geochronology by ion microprobe. In: Applications in microanalytical techniques to understanding mineralizing processes. *Reviews in Economic Geology*, 7, pp. 1–35.

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