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Significance of Baddeleyite for Paleoproterozoic PGE Deposits with Pt-Pd and Cu-Ni Reefs (North-Eastern Fennoscandian Shield): New Results of U-Pb and LA-ICP-MS Studies

By Bayanova T.B., Drogobuzhskaya S.V., Subbotin V.V., Serov P.A., Steshenko E.N., Kunakkuzin E.L. & Borisenko E.S.

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Kunakkuzin **E**.L. [§] & Borisenko **E**.S. [χ]

Abstract- Baddeleyite is a significant mineral successfully applied in the U-Pb geochronology for the precise dating of mafic rocks from layered intrusions with the platinum group element (PGE) and Cu-Ni mineralization. The Fennoscandian Shield hosts several layered Pt-Pd, Co-Cr-Ni, and Ti-V occurrences in the Northern (Karelian) and Southern (Karelian-Finnish) belts. The aim of this study is to estimate the content and distribution of rare earth elements (REE) in baddeleyite and to calculate temperatures (**T,˚C**) of the U-Pb system closure and baddeleyite crystallization compared to zircon from Cu-Ni and Pt-Pd deposits in the north-eastern Fennoscandian Shield. For the first time, baddeleyite crystals from Cu-Ni (Monchepluton) and Pt-Pd (Monchetundra) reefs of the Monchegorsk ore area have been studied *in situ* by the laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) to measure the U-Pb age of formation and the REE content.

Keywords: *baddeleyite; layered intrusions; U-Pb analysis; laser ablation inductively coupled plasma mass spectrometry; fennoscandian shield.*

I. INTRODUCTION

Baddeleyite is a valued mineral for the U-Pb dating of PGE deposits (Bayanova, 2006; Mungall et al., 2016). Compared to zircon, it is more reliable for precise U-Pb dating of deposits in the north-eastern Fennoscandian (Baltic) Shield, since it is genetically magmatic. In contrast, zircon can be metamorphic, hydrothermal or occur as xenocrysts. The study of the trace element composition of zircon is a common practice, while geochemical characteristics of baddeleyite are poorly studied and contradictory. Thus, the value of Ce-anomaly varies, and the Eu-anomaly is absent in some analyses (Reischman et al., 1995; Zircon, 2003; Schaltegger et al., 2017). Also, recent studies limelight the crucial role of baddeleyite in the reconstruction of the supercontinents breakup in the history of the Earth's evolution (Bayanova et al., 2009; Bayanova et al., 2017; Bayanova et al., 2019 a; Bayanova et al., 2019 b; Mitrofanov et al., 2019).

In Paleoproterozoic PGE layered intrusions, baddeleyite is found in Pt-Pd and Cu-Ni deposits of the Monchegorsk ore area (Fig. 1).

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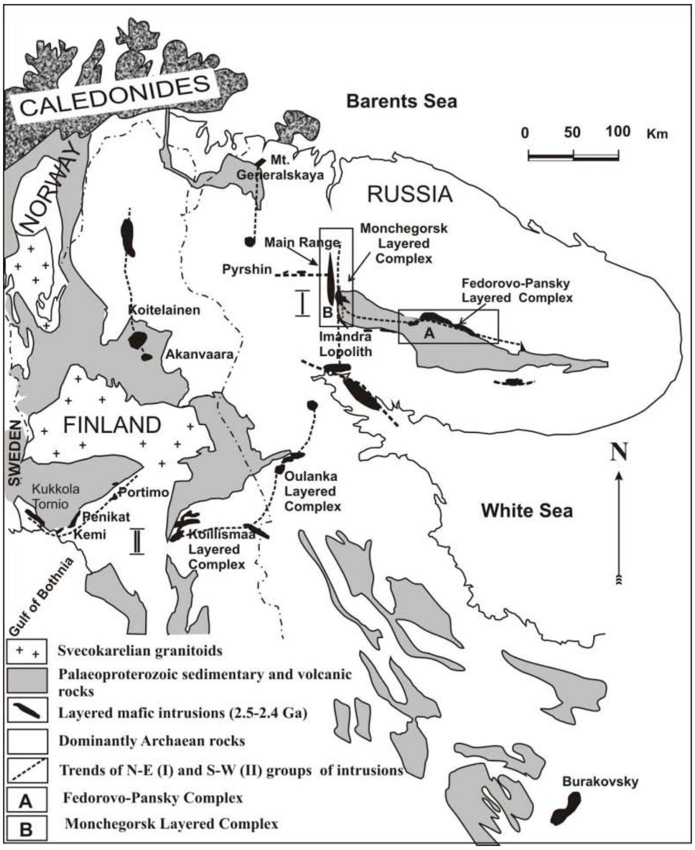

Fig. 1: Generalized geological map of the north-eastern Fennoscandian Shield and location of Paleoproterozoic layered mafic intrusions (Mitrofanov et al., 2005).

The aim of this study is (i) to estimate the REE content and distribution in baddeleyite, (ii) to calculate temperatures (T,˚C) of the U-Pb system closure and baddeleyite crystallization compared to zircon from Cu-Ni and Pt-Pd deposits in the Monchegorsk ore area, hosting the recently discovered Pt-Pd Vurechuayvench deposit (north-eastern Fennoscandian Shield, Russia).

II. Resources and Techniques

Baddeleyite was extracted from gabbro-anorthosites with the Pt-Pd mineralization in the middle of the Monchetundra massif (Fig. 1). The age of baddeleyite was estimated (Nerovich et al., 2014) by the U-Pb method at 2476±5 Ma and 2471±3 Ma (Fig. 2, Table 1).

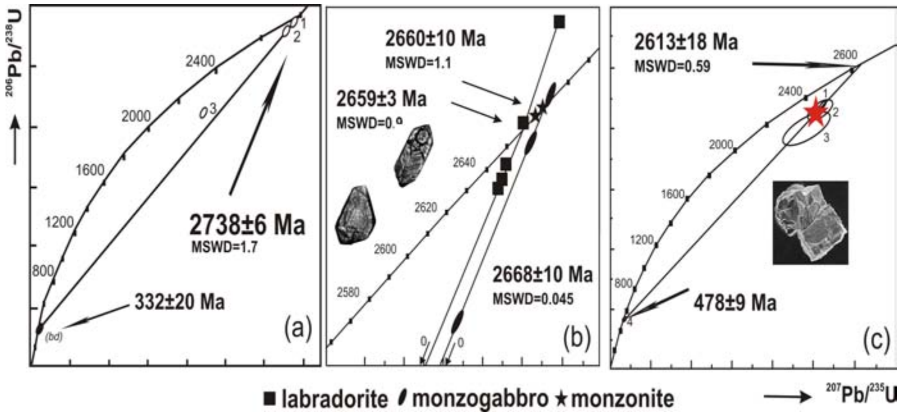

Fig. 2: Isotope U-Pb plots with Concordia for baddeleyite (*bd*) at the western slope of the Monchetundra: *a* – medium- to coarse-grained gabbronorite-anorthosite, partly amphibolite, *b* – medium- to coarse-grained leucogabbronorite.

Table 1: Isotope U-Pb data on baddeleyite from the Monchetundra massif.

Sample, No.	Weighted sample, mg	Contents, ppm		Isotope composition of Pb*			Isotope ratio and 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	
for baddeleyite and gabbronorite-anorthosite (medium- to coarse-grained, partly amphibolized)										
1	0.25	94.48	114.75	86	3.3003	2.2134	9.92226	0.450763	2500	0.70
2	0.20	57.60	123.14	570	5.5602	11.459	9.08165	0.417879	2430	0.93
3	0.25	30.09	67.86	557	5.6496	8.0718	8.19067	0.385383	2392	0.88
for baddeleyite from medium- to coarse-grained gabbronorite-anorthosite										
1	0.50	110.70	244.90	1478	5.9187	23.690	9.504470	0.429716	2460	0.94
2	0.35	152.60	359.10	3510	6.1640	35.011	9.119096	0.413367	2441	0.95
3	0.50	60.479	136.81	830	5.5615	13.663	8.820570	0.400447	2453	0.91
4	0.20	98.025	246.35	1539	6.3461	24.580	8.368770	0.382377	2437	0.83

* *The ratios are corrected for blanks of 0.8 ng for Pb and 0.04 ng for U and mass discrimination 0.12 ± 0.04%.*

** *Correction for common Pb is estimated for the age, according to Stacey and Kramers (1975).*

The REE content and distribution in baddeleyite were estimated by the following technique. The method of the electron (LEO-1415) and optic (LEICA OM 2500 P, camera DFC 290) spectroscopy was used to study the morphology of samples. Points for local analyses on baddeleyite crystals were selected based on the study of their back-scattered electron (BSE) and cathodoluminescence (CL) images.

Contents of REE and other elements were estimated *in situ* by ICP-MS on an ELAN 9000 DRC-e (Perkin Elmer) quadrupole mass spectrometer equipped with a 266 nm UP-266 MACRO laser (New Wave Research). LA-ICP-MS was performed using argon with a repetition rate of 10 Hz, pulse duration of 4 ns, the energy density of 14-15 J/cm^2 at a spot with a diameter of 35-100 μm or using scanning "in a line" (length 35-70 μm), monitoring and measuring produced craters. NIST 612 glass with the known concentrations of REE, U, Ti, and Th of 40 ppm was used for external calibration as a multi-point calibration forced through the origin after blank correction (Pearce et al., 1997, Certificate of Analysis, 2012). NIST SRM 610 sample (450 ppm concentration) was used to check the accuracy of estimations (Yuan et al., 2004; Jochum et al., 2011). The laser beam diameter was changed, while the rest parameters were stable: from 35 to 240 μm (point sampling) and from 20 to 155 μm ($r = 0.999$) (scanning "in a line"). As for calibration standards, measurements of the elements were in the range of 15% relative deviations. Determination limits were within 0.01 ppm, a diameter of the laser beam of 155 μm. It complies with the available data (Yuan et al., 2004). This technique was tested, using analyses of internationally approved standard zircon samples 91500, TEMORA 1, Mud Tank, and inter-laboratory cross-checks (Boynton, 1984).

III. Results

Table 2 and Figure 3 provide new data on the contents of REE and other elements in baddeleyite from Pt-Pd occurrences of the Monchetundra massif.

Baddeleyite from vein pegmatites with the gabbronorite composition from the Monchepluton with Cu-Ni reefs (Mt. Nyud, Terrace deposit) was studied. Its U-Pb age was estimated at 2505±5 Ma (Bayanova, 2006). Figures 4 and 5 display new LA-ICP-MS data on baddeleyite, which was measured along and across its section.

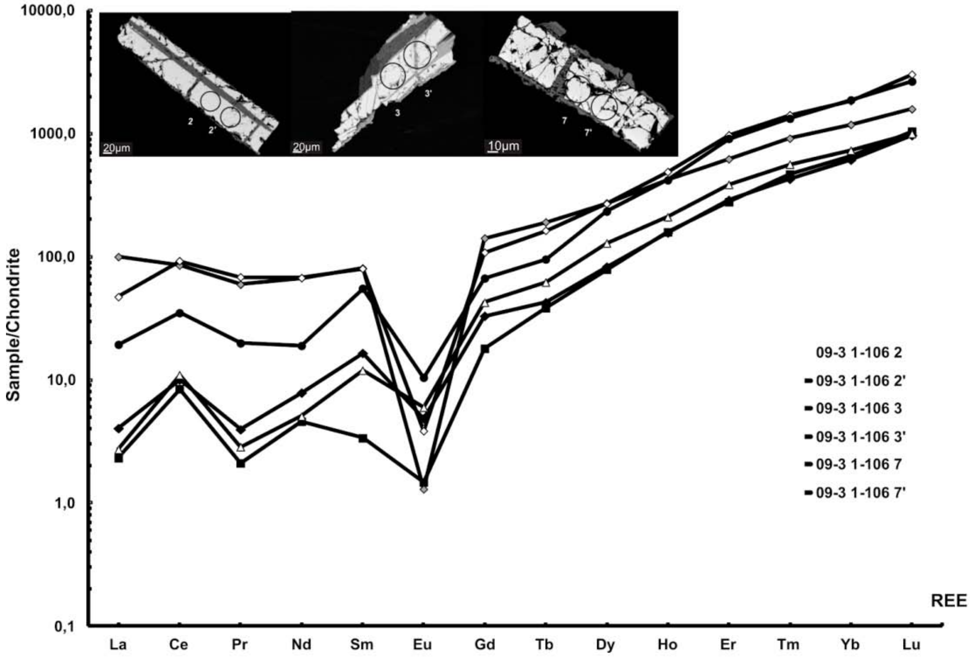

Fig. 3: Chondrite-normalized plots of REE distribution in baddeleyite from medium- to coarse-grained leucogabbronorite of Pt-Pd occurrences, Monchetundra massif (Boynton et al., 1984).

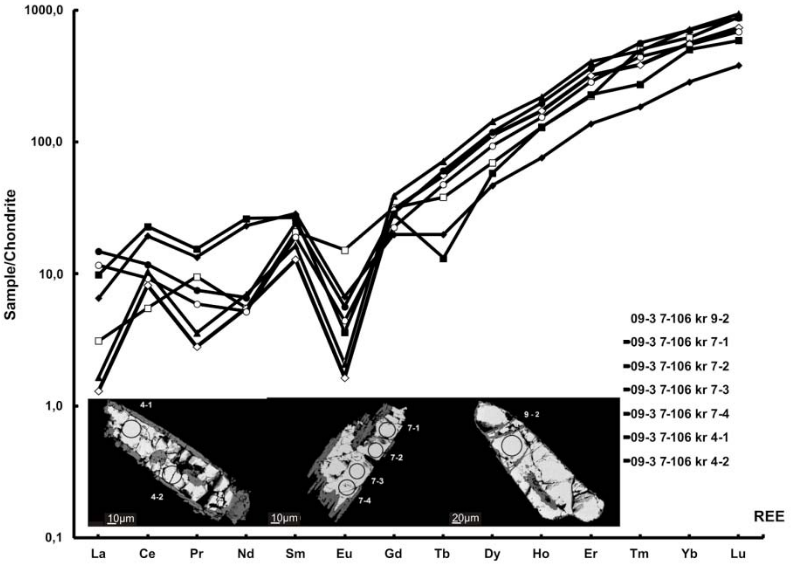

Fig. 4: Chondrite-normalized plots of REE distribution in baddeleyite from gabbronorite-anorthosite of Pt-Pd occurrences, Monchetundra massif (Boynton et al., 1984).

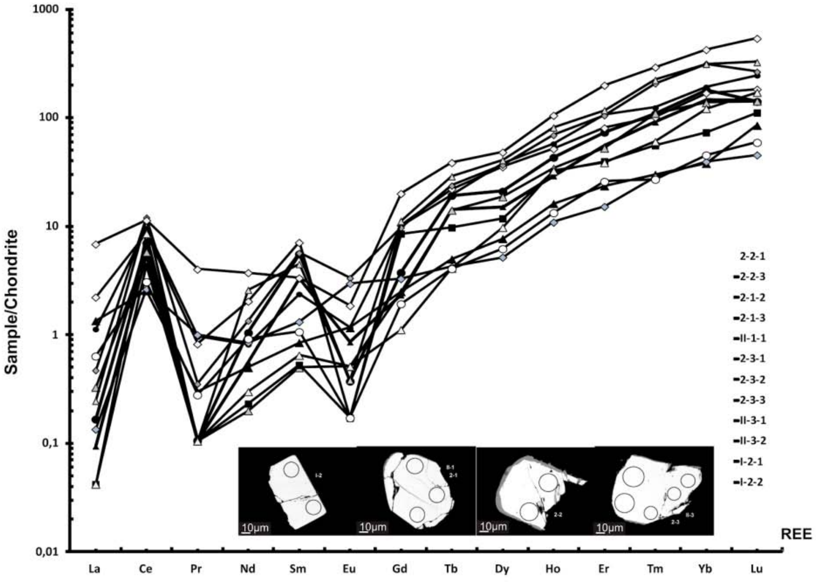

Fig. 5: Chondrite-normalized plots of REE distribution in baddeleyite from vein pegmatites of the gabbronorite composition, Cu-Ni Terrace deposit, Mt. Nyud, Monchetundra massif (Boynton et al., 1984).

Notably, spectra of REE distribution in baddeleyite grains from PGE rocks of the Monchegorsk ore area indicate low concentrations of light elements, high concentrations of heavy ones, steep positive slope with a negative Eu-anomaly and a positive Ce-anomaly. The spectra also reflect the magmatic origin of baddeleyite (Zircon, 2003; Watson et al., 2006).

IV. Conclusion

For the first time, the provided research revealed a direct relation between the REE content in baddeleyite and the formation of Pt-Pd and Cu-Ni reefs. The higher concentrations of HREE in baddeleyite, the higher temperatures of the U-Pb systematics closure and formation are. Pt-Pd reefs are likely to occur under such conditions. Cu-Ni reefs form at lower temperatures of the U-Pb systematics closure and crystallization of accessory minerals. These occurrences display low HREE and a wide range of LREE concentrations (Table 2).

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Table 2: LA-ICP-MS data on contents of REE and other elements in grains of baddeleyite and zircon from Pt-Pd and Cu-Ni reefs of the Monchegorsk ore area.

			Contents (average in crystal), *ppm*																			
Sample			Ti	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Hf	Th	U	Σ REE	T°C
Sample *1*	*Bd*	2	645.2	230.3	0.75	5.65	0.29	2.90	1.52	0.18	5.23	1.51	20.5	8.90	46.8	11.4	107.4	25.5	4617	2.82	68.2	238.5	> 1000° C
		3	468.7	429.5	12.1	29.4	2.96	16.9	7.08	0.21	18.9	4.72	50.9	17.8	83.1	18.8	162.2	32.7	2970	9.51	212.6	457.8	
		7	1212	848.5	7.89	39.0	4.19	20.1	10.3	0.41	18.0	4.83	63.8	25.7	155.5	34.9	315.3	72.0	7453	73.8	172.4	771.9	
Sample 2	*Bd*	4	260.0	108.6	0.38	2.11	0.43	1.60	1.58	0.55	3.46	0.88	11.1	4.80	24.6	8.30	69.2	14.5	3060	12.6	58.2	143.5	
		7-1-2	432.2	264.0	1.54	5.35	0.41	2.50	2.45	0.18	5.47	1.94	26.2	9.30	50.1	10.5	94.6	18.1	1413	25.9	89.4	228.6	
		7-3-4	549.9	335.9	1.96	6.80	0.53	3.17	3.11	0.22	6.96	2.47	33.4	11.8	63.8	13.4	120.4	23.0	1797	32.9	113.7	291.0	
		9	878.5	155.7	1.95	12.9	1.37	11.5	4.23	0.30	4.94	0.62	11.3	5.85	30.3	5.85	67.1	12.4	5653	31.1	108.1	170.6	
Sample 3	*Bd*	I 2	1637	21.1	0.09	1.76	0.06	0.41	0.18	0.09	0.54	0.16	1.45	0.69	3.41	0.71	7.22	1.33	6132	2.83	196.5	18.1	
		II 3	2358	38.6	0.01	3.95	0.01	0.06	0.01	0.02	1.00	0.06	2.49	1.82	6.49	1.48	16.6	3.60	5761	3.04	213.8	37.6	
		II 2	3949	132.9	3.88	26.1	0.60	5.96	1.52	2.22	5.58	1.40	14.4	4.19	19.1	4.81	49.1	10.6	10225	27.6	1057	149.5	
		II 1	940.1	20.4	0.32	1.56	0.03	0.23	0.13	0.07	0.51	0.19	1.96	0.92	3.90	0.77	6.47	2.16	3068	3.51	135.8	19.2	
		2-1	6015	52.4	0.20	4.33	0.03	0.57	0.81	0.03	1.12	0.69	6.06	2.34	11.6	2.56	28.2	3.96	17905	13.5	306.1	62.5	
		1-1	3742	60.6	0.17	4.56	0.04	0.24	0.37	0.14	1.35	0.62	7.18	2.56	12.5	3.04	29.3	4.85	8096	14.7	185.8	66.9	
		1-3	4876	108.1	0.60	7.16	0.14	1.20	0.69	0.11	2.81	1.14	10.7	4.84	23.4	6.16	59.8	9.59	17543	10.6	303.3	128.3	
	Zr	II 1	51.1	638.3	0.18	15.6	0.31	5.51	7.77	0.80	32.6	6.63	71.7	20.9	75.5	12.5	96.6	14.2	9009	559.0	242.5	360.8	aver. 894° C
		II 2	44.6	322.1	0.13	15.7	0.95	7.47	8.17	1.07	26.7	5.58	43.2	10.4	32.4	4.96	32.4	3.99	7311	166.6	71.9	193.1	
		II 3	35.2	718.0	0.03	13.4	0.06	0.70	2.03	0.14	15.3	4.66	61.2	22.2	100.0	18.3	148.5	23.1	9133	207.9	121.9	409.6	
		II 4	37.6	392.1	0.34	11.9	0.30	3.17	4.54	0.80	16.9	4.16	42.3	11.9	44.3	7.60	60.7	8.91	8570	346.2	217.6	217.8	
		III 1	13.1	649.3	0.22	14.3	0.43	6.13	7.57	0.38	30.8	7.44	74.8	21.6	71.9	11.4	90.2	10.7	3696	325.8	122.5	347.9	
		III 2	64.1	3112	0.26	69.2	1.43	17.4	31.7	2.45	140.0	32.0	327.4	100.1	386.3	63.1	524	73.9	8374	1271	428.6	1769	
		III 3	118.4	703.4	0.13	19.9	0.85	11.2	10.0	2.03	34.7	8.69	81.8	21.9	71.8	13.0	104.6	13.5	21422	1669	664.8	394.1	

Note: 1- baddeleyite from gabbronorite -anorthosite, 2 - baddeleyite from medium- to coarse -grained leucogabbronorite, 3- sample from vein pegmatites of the gabbronorite composition. Temperature of zircon and baddeleyite crystallization is calculated according to [3].