

## High-REE Gabbroids and Hornblendites of the Ilmeny Mountains (Urals)

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**Abstract**—Chaotically localized isolated small bodies of metaultrabasic rocks have been found in the quartzite-schist strata of the Ilmeny metamorphic complex in the South Urals. These are metamorphosed rootless blocks and lumps of serpentinite melange within the so-called Urazbaevo olistostrome. Sometimes they contain lumpy inclusions of massive anorthite gabbroids with gabbro, ophitic, and cumulative textures, free of crystallization schistosity, and of different mineral compositions. The rocks have abnormally high contents of  $\text{Al}_2\text{O}_3$ , CaO, MgO, and REE and low contents of  $\text{SiO}_2$  and are characterized by weak secondary alteration. Seldom, inclusions of hornblendites, along with anorthite, spinel, apatite, enstatite, diopside, and rutile, are present. Some gabbroid and hornblendite bodies have abnormally high contents of REE, with a strong predominance of LREE (81–93% of the total REE). The maximum contents of REE have been established in zoisite amphibolites (170–850 ppm) and apatite–garnet hornblendites (up to 450 ppm). The conclusion has been drawn that the rocks formed in the basement of the Earth's crust and got with protrusions of serpentinite melange to the surface.

*Keywords:* zoisite gabbro, anorthite–amphibole gabbroids, hornblendites, metaultrabasic rocks, REE, Ilmeny complex, Urals

### INTRODUCTION

In recent time, chaotically localized small rootless mafic and ultramafic bodies have been found in quartzite–schist strata on the periphery of the Ilmeny metamorphic complex in the South Urals (Korinevsky and Korinevsky, 2006). Together with the host rocks, they were ascribed to the ancient (Late Paleozoic) Urazbaevo olistostrome (Korinevsky, 2013).


In the earlier publications (Korinevsky and Korinevsky, 2004, 2006) we first described the geologic position of gabbroid and hornblendite bodies, reported their mineral and petrographic compositions, and showed that they and the host rocks are of different origin. It was established (Korinevsky and Bazhenova, 2004) that most gabbroids from olistoliths have high contents of REE ( $\geq 50$  ppm) in contrast to much lower REE contents in other mafic and ultramafic rocks in the Urals (Sobolev, 1965; Fershtater and Bea, 1996; Lesnov, 2007; Belikova and Salikhov, 2007; Fershtater, 2013). Some gabbroid varieties are extremely rich in REE (up to 850 ppm). We have not found publications about finding of such rocks in the Urals. It is known (Neumann et al., 2000), however, that some xenoliths of pyroxene–amphibole gabbroids and hornblendites in the Canary (La Palma Island) alkali basalts are also rich in REE: The total REE content varies from 25 to 935 ppm in the gabbroids (Neu-

mann et al., 2000, Table 4) and is within 189–192 ppm in the hornblendites. Note that pyroxenes, amphiboles, and biotites in all these rocks are initially magmatic minerals.

In this paper we significantly expanded the list of gabbroid varieties analyzed for trace elements, including REE, by ICP MS. Several varieties of hornblendites are described for the first time and are compared with similar rocks in other regions of the Urals (Sobolev, 1965; Fershtater and Bea, 1996; Gottman and Pushkarev, 2009; Gottman, 2014). The first information about the distribution of trace elements in the rock-forming minerals of gabbroids has been obtained. After our publications, similar studies in the Ilmeny Mountains were performed by other researchers (Rusin et al., 2006, 2010, 2012). These data help to clarify the genesis of the above specific mafic and ultramafic rocks of the Ilmeny complex and the associations to which they belong. They also indicate the finding of a new type of primary sources of REE, which might be of practical interest in the future.

### METHODS

We elucidated the geologic position of mafic and ultramafic bodies by a detailed geological mapping, using a theodolite survey. In places, trenching and pitting were performed. Minerals were sampled manually from the finest fractions of crushed samples of the least altered rocks under a binocular magnifying glass; the purity of the samples was checked using immersion liquids.

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The chemical composition of rocks was determined by the wet chemistry method with the use of AAS and flame photometry in the laboratory of the Institute of Mineralogy, Miass. The first analyses for REE were carried out by L.F. Bazhenova using paper chromatography (Korinevsky and Bazhenova, 2004, 2008). The validity of the analytical results was proved by ICP MS analyses of several samples made by Yu.L. Ronkin at the Institute of Geology and Geochemistry, Yekaterinburg, and then by the same analyses performed by K.A. Filippova and M.S. Svirenko at the Institute of Mineralogy, Miass. Both analyses showed high (or even extremely high) contents of REE in some gabbroid varieties. Below we present mainly results of ICP MS analyses carried out at the Institute of Mineralogy, Miass, and partly data obtained by Yu.L. Ronkin and Rusin et al. (2012).

The composition of minerals was determined by V.A. Kotlyarov on a REMMA-202M scanning electron microscope equipped with an LZ-5 Link Systems energy dispersive spectrometer with a Si–Li detector (accelerating voltage 20–30 kV, spot diameter 1–2  $\mu\text{m}$ ). Correction of data was made with the Magallanes and ZAF programs. The ASTM JMEX Scientific Limited MJNM 25-53 and Mineral Mount series No 01-044 reference samples and minerals of known composition were used as standards.

Acid ( $\text{HF} + \text{HCl} + \text{HNO}_3$ ) digestion of rock and mineral samples was performed in fluoroplastic autoclaves in a SpeedWave (Berghoff, Germany) microwave decomposition system with two-stage heating to 180 °C for 40 min. For metrological control of the analysis quality, the BCR-2 international standard was used. The instrument was calibrated using Agilent standard multielement solutions for the entire range of the masses of the elements to be analyzed. The prepared solutions were analyzed by ICP MS on an Agilent 7700x (Japan) mass spectrometer.

Minerals in the photographs and tables are abbreviated after Whitney and Evans (2010).

## GEOLOGIC ENVIRONMENT

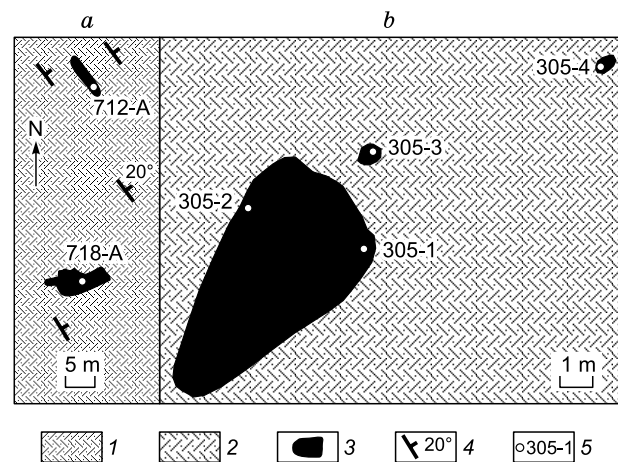
Separate rootless small mafic and ultramafic bodies are most abundant in the Kyshtym metasedimentary unit of the Saitovo Group on the eastern quartzite–schist periphery of the Ilmeny igneous and metamorphic complex localized mostly in the Ilmeny reserve (Korinevsky, 2013). The unit is composed of graphitic and micaceous quartzites, locally with interbeds and members of amphibolites, schists, and fine-grained biotite plagiogneisses.

The ultramafic (metaultrabasic) rocks are separate lumpy (often, rocky) outcrops of olivine–enstatite, olivine–enstatite–anthophyllite, anthophyllite–tremolite, and anthophyllite–talc–chlorite rocks, sometimes, with vermiculite rims and anthophyllite–asbestos clusters. Most of the outcrops of ultramafic rocks are isometric and angular. The rock bodies wedge out at a depth close to their diameter in plan, i.e., a few to tens of meters (Romanovich, 1976).

Metaultrabasic bodies are chaotically localized in the area of quartzite–schist strata. They often form swarms of spatially unassociated bodies. As seen from their stripped contacts with the host strata, layered quartzites conformably envelope the ultramafic bodies. No traces of contact impact on the quartzites and evidence for tectonic boundaries are observed. There is no reason to regard these bodies as lenticular conformable interbeds in the host metasediments. The same follows from the U/Pb dates (543–662 Ma) for zircons from garnet–anorthite gabbroid blocks (Rusin et al., 2012) localized among quartzite–schist rocks in the roof of a granite massif near the eastern shore of Lake Bol’shoe Miassovo. These aposedimentary rocks are of Late Paleozoic–Early Mesozoic age ( $252 \pm 8$  Ma) (Korinevsky and Korinevsky, 2014). It is obvious that the small gabbroid bodies differ in age from the host metasediments.

The outcrops of metaultrabasic rocks are spatially associated with gabbroid and hornblendite bodies. Most of the latter are surrounded by metaultrabasic rocks, and only few are localized among quartzites but also in zones with abundant ultramafic rocks. In some metaultrabasic blocks, gabbroid bodies have different sizes and orientations. They often stretch parallel to the strike of the cleavage planes in metaultrabasic rocks, but there are also nearby gabbroid bodies transverse to these planes (Fig. 1a). Note that the gabbroid clastolites can differ significantly in mineral composition within a metaultrabasic block (Fig. 1b). All gabbroids have sharp contacts with the host metaultrabasic strata.

Thus, most of the studied gabbroid outcrops are block inclusions in metaultrabasic rocks. Some gabbroid and ultra-



**Fig. 1.** Localization of gabbroid clastolites in metaultrabasic blocks at the Urazbaevo site. 1, large-spherulitic anthophyllitic metaultrabasic rocks, 2, small-spherulitic anthophyllitic metaultrabasic rocks, 3, gabbroid bodies, 4, dips and strikes of cleavage planes in metaultrabasic rocks, 5, sampling localities and their numbers. Samples 712-A and 718-A, coarse-grained spinel–zoisite–anorthite gabbro with ilmenite, titanite, calcite, and scarce garnet grains; samples 305-1 and 305-2, amphibole gabbroids with scarce zoisite, apatite, spinel, and ilmenite grains; sample 305-3, garnet ilmenite–spinel–zoisite–anorthite gabbro; sample 305-4, pyroxene–zoisite–anorthite gabbro with fine titanite and zircon dissemination. a, b, See text for explanation.

**Table 1.** Oxides (wt.%) and trace elements (ppm) in high-REE gabbroids of the Ilmeny complex

Component	84-A*	84-1*	84-2*	295-2*	712-A*	718-A*	4-98**	14-98**	173-5*	305-3*	173-1*	269-3*	173-13-1*	271-6*	Sd-13
SiO <sub>2</sub>	39.68	39.19	39.56	38.1	33.31	35.11	31.24	32.5	39.12	34.96	34.50	36.74	37.47	41.64	46.75
TiO <sub>2</sub>	1.38	2.06	1.93	3.72	2.54	1.2	1.98	0.78	1.12	1.38	2.24	1.14	1.34	1.9	0.25
Al <sub>2</sub> O <sub>3</sub>	28.68	27.73	26.28	19.31	27.24	28.15	23.40	24.28	24.09	24.52	23.23	27.44	26.91	19.03	16.88
Fe <sub>2</sub> O <sub>3</sub>	2.70	1.81	6.45	2.68	4.5	3.83	5.73	4.8	3.45	6.1	6.63	3.01	5.77	5.1	3.14
FeO	4.82	5.37	4.31	7.87	5.82	6.82	15.08	8.5	5.26	6.75	8.08	5.67	3.16	3.41	3.4
MnO	0.51	0.37	0.31	0.3	0.29	0.18	0.53	0.29	0.24	0.33	0.38	0.14	0.21	0.19	0.11
MgO	5.35	6.43	5.23	8.99	4.31	5.75	9.89	10.26	5.25	7.63	10	9.30	4.02	4.85	11.7
CaO	14.33	13.39	13.13	14.56	17.84	13.99	7.8	10.7	18.53	14.65	11.9	12.6	19.46	21.1	15.3
Na <sub>2</sub> O	1.04	1.3	1.61	1.25	0.4	1.45	0.9	1.04	0.78	0.62	1.04	1.2	0.16	0.44	0.88
K <sub>2</sub> O	0.14	0.3	0.21	0.68	0.1	0.5	0.28	0.22	0.82	0.3	0.74	0.32	0.07	0.26	0.13
LOI	0.7	1.32	1.26	0.92	2.37	1.89	1.84	2.4	1.13	1.91	0.34	1.11	0.35	1.69	0.78
P <sub>2</sub> O <sub>5</sub>	0.06	0.1	0.25	0.91	0.56	0.38	0.68	0.22	0.3	0.1	0.18	0.34	0.42	0.32	0.05
Total	99.39	99.37	100.53	99.29	99.28	99.25	99.35	95.99	100.09	99.25	99.26	99.31	99.34	99.93	99.37
<i>f</i>	0.51	0.46	0.6	0.47	0.64	0.57	0.61	0.49	0.55	0.55	0.52	0.41	0.62	0.56	0.29
Sc	41.0	43.6	41.9	27.6	22.9	33.6	75.2	39.5	35.2	28.6	38.9	28.7	40.9	40.9	43.2
Y	196	257.5	238	44.6	34.6	52.8	93.6	32.8	55.1	46.1	88.3	74.5	69.6	24.6	5.8
V	105	96.2	114	263	288	253	662.7	377.6	267.5	375	231.6	234.4	423.7	235	160
Cr	25.9	16.3	20.1	146	8.5	20.8	406.8	341.5	187.5	103	84.5	82.1	101.2	307.8	111
Co	8.9	10.1	8.4	36	32.5	34	60.5	50.1	44.6	33.3	48.6	35.2	29.6	34.3	38.5
Ni	24.4	44	30	11	11.4	16.2	417.1	208.9	95.6	53.2	56.5	62.1	67.6	118.5	118
Sr	1681	2051.5	2180	451	2219	1608	180.5	841.4	1181.1	1657.0	1050.7	1300.6	1909.7	586.9	123
Zr	141	104.3	92.2	26.4	57.6	92.7	146.2	172.7	109.4	94.4	144.5	87.7	74.8	46.3	99.7
Nb	22.9	32.3	20.5	199	65.8	15.9	11.2	3.3	16.8	14.1	15.5	23.2	12	46	<0.006
Ba	21.4	111.7	26.5	145	21	1329	412.6	710.6	176.7	50.8	85.2	87.3	28.7	55.8	19.8
Th	29.0	38.8	34.4	23.2	8	7.3	2.1	4.1	4.9	12.4	6.3	12.6	7.7	9.2	0.45
U	7.92	10.0	11.9	5.9	2.3	3.3	2.6	1.5	1.6	1.9	0.9	1.5	1.9	3.9	<0.006
∑REE	601	767.2	854.6	489.7	306.7	203.8	457.7	167	187.4	201.89	243.6	337.6	195.5	187.9	7.64
Ni/Co	2.74	4.46	3.57	3.25	0.35	0.48	6.89	4.17	2.14	1.6	1.16	1.76	2.28	3.45	3.06

Note. Site north of the Urazbaevo Village: 84-A\* and 84-1\*, fine- to medium-grained pargasite–tschermakite–garnet–zoisite–anorthite gabbro with pleonaste and corundum grains and chlorite plates, 55°11'07.48" N, 60°19'21.73" E; 84-2\*, tschermakite–zoisite–anorthite gabbro with apatite, pleonaste, ilmenite, and chlorite, 55°11'07.50" N, 60°19'21.80" E; 295-2\*, pargasite–zoisite–apatite–garnet–diopside–anorthite gabbro, 55°11'40.24" N, 60°19'24.92" E; 718-A\*, coarse-grained tschermakite–ilmenite–garnet–zoisite–anorthite gabbro with corundum, chlorite, calcite, and spinel, 55°11'10.32" N, 60°19'30.36" E; 712-A, coarse-grained sadanagaite–garnet–zoisite–anorthite gabbro with corundum and spinel, 34 m north of the sample 718-A; 305-3\*, tschermakite–garnet–diopside–zoisite–anorthite gabbro, 55°11'42.07" N, 60°19'12.61" E; 4-98\*\*, tschermakite–garnet–zoisite–anorthite gabbro from the Urazbaevo site of the same exposure as the sample 718-A\*; 14-98\*\*, tschermakite–garnet–zoisite–anorthite gabbro from the Urazbaevo site of the Savel'kul' site; 173-5\*, garnet-free K-pargasite–clinozoisite–anorthite gabbro, 55°07'40.26" N, 60°17'44.16" E; 173-1, pargasite–garnet–diopside–anorthite gabbro with corundum, spinel, and ilmenite, 55°07'42.63" N, 60°17'43.70" E; 269-3, pargasite–anorthite gabbro with apatite, spinel, and ilmenite, 55°07'37.5" N, 60°17'44.16" E; 173-13-1, pargasite–garnet–diopside–clinozoisite–anorthite gabbro with spinel and ilmenite, 55°07'36.12" N, 60°17'42.43" E; 271-6, hastingsite–epidote–hedenbergite–anorthite gabbro, 55°08'06.6" N, 60°18'48.7" E; Sd-13, diopside–amphibole–anorthite gabbro, western shore of Lake Sadok, 55°32'37.9" N, 60°23'02.7" E; wet chemistry analyses were carried out by M.N. Malyarenok, T.V. Semenova, M.S. Svireenko, and Yu.F. Mel'nova, and ICP MS analyses for trace elements, by K.A. Filippova and M.S. Svireenko (Institute of Mineralogy, Miass); analyses of the samples 84-1\* and 173-5\* were performed by Yu.L. Ronkin (Institute of Geology and Geochemistry, Yekaterinburg). *f*, Fe/(Fe + Mg), at.%.

\*Samples were taken by V.G. Korinevsky from clastolites in metaultrabasic bodies at the Urazbaevo and Savel'kul' sites of the Ilmeny Mountains.

\*\*Analytical results for samples were borrowed from Rusin et al. (2012).

basic bodies are hosted in members of graphitic quartzites or in biotite gneisses and also have sharp contacts with the host metasediments. The internal structure of the gabbroid bodies is rather homogeneous.

The lump gabbroids show a great diversity of mineral and chemical compositions. We recognized corundum, zoisite, diopside, scapolite, spinel, garnet, and other varieties of gabbroids with a wide spectrum of high-alumina calcic amphi-

boles (Korinevsky and Korinevsky, 2004). The gabbroids have abnormally high contents of Al<sub>2</sub>O<sub>3</sub>, CaO, MgO, and REE and low contents of SiO<sub>2</sub> (Table 1). Many of them contain fine granulomorphous nodular homogeneous zircon grains.

The highest contents of REE were found in zoisite varieties of mafic rocks (Korinevsky and Bazhenova, 2004).

Hornblendites are strongly inferior in amount to amphibolites. The consanguinity of the gabbroids and hornblendites

is confirmed by their interbedding (outcrops near Cape Osinovyi on Lake Bol'shoi Ishkul'). All hornblendite outcrops are clearly associated with separate metaultrabasic bodies occurring in the quartzite–schist strata. The data of ICP MS analyses of several hornblendite samples also show their anomalous REE enrichment.

As we assumed earlier (Korinevsky and Korinevsky, 2004, 2006, 2014), the mafic rocks under study are inclusions of igneous rocks (gabbro and hornblendites) in serpentinite melange composing protrusive bodies squeezed out along the fault planes in the Early Paleozoic schist strata of the Ilmeny complex. In the Late Paleozoic, thrust dislocations, probably related to orogeny, shifted blocks of melange rocks into the basins where sand–shale strata were accumulating. These blocks formed local chaotic clusters of fragments of older rocks within the host sediments (Urazbaevo olistrostrome (Korinevsky, 2013)). Together with the surrounding rocks, they were later metamorphosed to the epidote–amphibolite facies. In this paper we discuss the least altered rock varieties.

## PETROGRAPHY AND MINERAL COMPOSITION OF GABBROIDS

The mafic rocks are composed mostly of amphiboles (>50%). Plagioclase, diopside, garnet, zoisite, clinozoisite, chlorite, spinel, ilmenite, titanite, corundum, apatite, biotite, zircon, scapolite, and other minerals are subordinate. The preserved primary igneous textures (gabbro and ophitic), crystallization banding, signs of synchronous crystallization of most minerals, the presence of crystalline and gas–liquid inclusions in plagioclase, zoisite, and garnet, and minor secondary alteration and replacement of some minerals by others indicate that most of mafic inclusions from clastolites are variably metamorphosed pyroxene–amphibole and amphibole–anorthite gabbro. Since these rocks have variable (sometimes, significantly) contents of different primary min-

erals (Korinevsky and Korinevsky, 2004), we will generally call them gabbroids. The set of minerals in these rocks is similar to apogabbro amphibolites from the framing of the Kempirsai ultramafic massif in the South Urals (Efimov, 1984) and from the western gabbro–amphibolite zone of the Voikar–Syn'ya massif in the Polar Urals (Dobretsov et al., 1977; Efimov and Ryabkova, 1979). The latter zone is characterized by abundance of zoisite–anorthite gabbro.

Gabbroid lumps in different areas with lenses of serpentinite melange in quartzite–schist strata have significantly different petrographic compositions. This is well seen on comparison of the rocks in the melange plate on the eastern shore of Lake Bol'shoi Ishkul', on the northern slope of Mount Savel'kul', in the vicinity of Village Urazbaevo (Korinevsky and Korinevsky, 2004, 2006), and on the western shore of Lake Sadok. The latter area is characterized by a strong predominance of diopside–amphibole–anorthite gabbro, frequent presence of garnet clinopyroxenites, and rare occurrence of olivine orthopyroxenites and sapphirine–spinel hornblendites, but no REE varieties have been revealed among them (Korinevsky and Korinevsky, 2014). This is evidence for the heterogeneous composition of the deep-seated Urals crustal rocks involved in the formation of serpentinite protrusions. Apparently, the heterogeneity is the cause of the great diversity of amphibole varieties in the gabbroids of the Ilmeny complex (Table 2).

A specific feature of these gabbroids (Table 2) is the presence of high-alumina calcareous minerals: highly basic plagioclase (mostly anorthite, 0–50%), zoisite, clinozoisite, and high-alumina high-magnesium calcic amphiboles (20–90%), including pargasite (Table 2, sample 84-A), tschermakite (Table 2, samples 84-1 and 718-A), K-pargasite (Table 2, sample 173-5), and, seldom, ferropargasite (Table 2, sample 293-5), sadanagaite (Table 2, sample 712-A), and hastingsite. Note that each outcropped gabbro has only one of these amphibole varieties. The amphibole varieties were identified according to the classification by Hawthorne et al. (2012), using a computer program proposed by Locock

**Table 2.** Probe microanalyses (wt.%) of minerals from the Ilmeny REE gabbroids and hornblendites (Urals)

Component	Gabbroids						Hornblendites				Gabbroids	
	Hbl										Cpx	
	84-A	84-1	712-A	718-A	293-5	295-A	173-5	Sd-13	211-6	261-6	293-5	295-A
SiO <sub>2</sub>	41.22	42.25	39.40	39.28	41.91	43.88	39.11	46.65	45.59	43.01	52.30	52.84
TiO <sub>2</sub>	0.52	0.47	0.58	0.45	0.44	0.50	1.00	0.22	0.82	1.01	–	0.02
Al <sub>2</sub> O <sub>3</sub>	18.66	18.50	20.30	20.56	13.28	12.56	16.10	12.27	14.08	16.62	1.02	1.03
FeO*	10.48	10.13	12.70	14.51	19.54	15.99	16.00	8.55	3.65	3.64	9.21	7.83
MnO	0.21	0.28	–	0.08	0.11	0.21	0.29	0.04	–	0.07	0.23	0.37
MgO	11.73	12.35	9.32	8.77	8.05	10.38	9.19	16.21	18.53	17.88	12.38	13.39
CaO	12.83	11.73	12.72	12.25	12.48	12.66	12.37	12.17	12.10	13.01	24.41	24.02
Na <sub>2</sub> O	1.93	1.68	1.66	1.40	1.42	1.44	1.29	1.50	2.20	2.41	0.03	0.12
K <sub>2</sub> O	0.43	0.36	0.61	0.70	0.79	0.63	2.25	0.24	0.30	0.57	–	–
Total	98.01	97.75	97.29	98.00	98.02	98.25	97.60	97.75	96.97	98.22	99.58	99.62
Fe/(Fe + Mg)	0.53	0.51	0.64	0.68	0.76	0.67	0.69	0.40	0.20	0.17	0.48	0.43

(continued on next page)

Table 2 (continued)

Component	Grt											
	84-A		84-1		718-A		293-5		712-A		173-13-1	
	c	r	c	r	c	r	c	r	c	r	c	r
SiO <sub>2</sub>	37.23	38.00	38.53	38.63	37.16	37.01	37.78	38.03	37.46	36.91	39.38	39.16
TiO <sub>2</sub>	0.18	0.20	–	0.14	н.д.	н.д.	0.04	0.05	0.11	0.16	–	0.07
Al <sub>2</sub> O <sub>3</sub>	21.01	20.78	22.23	21.50	20.92	21.04	20.98	20.91	21.14	20.58	21.95	22.01
FeO*	19.84	19.56	22.39	23.13	28.38	28.54	20.30	19.51	21.86	23.27	13.53	13.92
MnO	9.89	9.70	4.65	5.32	2.09	1.93	2.23	2.02	2.90	3.98	1.68	2.11
MgO	3.07	3.26	6.07	6.51	3.38	3.56	1.59	2.35	3.03	3.03	3.41	3.83
CaO	8.70	8.14	6.08	4.73	7.81	7.89	16.98	16.72	13.35	11.97	19.95	18.85
Total	99.92	99.64	99.95	99.96	99.74	99.97	99.90	99.59	99.85	99.90	99.90	98.02
Fe/(Fe + Mg)	0.89	2.12	0.84	0.82	0.92	0.91	0.94	0.95	0.90	0.90	0.89	0.88

Component	Zo			Czo								
	84-A	712-A	293-5	84-A	84-1	712-A	718-A	293-5	295-A	173-5	173-13-1	
	SiO <sub>2</sub>	40.52	39.68	39.90	40.87	39.50	38.94	38.91	40.15	39.46	38.90	39.31
TiO <sub>2</sub>	–	0.03	–	–	0.05	0.05	0.05	0.07	–	0.09	0.07	
Al <sub>2</sub> O <sub>3</sub>	31.96	32.27	32.29	28.52	29.60	29.46	28.85	27.20	28.23	28.02	29.31	
Fe <sub>2</sub> O <sub>3</sub> *	1.36	1.77	1.17	5.16	4.47	5.65	6.85	7.07	7.21	7.17	5.33	
MnO	0.01	–	–	0.22	0.10	–	–	–	0.08	0.02	0.02	
MgO	0.26	0.15	0.33	0.43	0.38	0.22	0.32	0.26	0.19	0.43	0.22	
CaO	23.95	24.00	24.18	22.06	22.43	23.96	23.80	23.89	23.74	24.11	24.55	
Total	98.06	97.90	97.87	97.26	96.53	98.28	98.78	98.64	98.91	98.74	98.81	
Fe/(Fe + Mg)	0.61	0.93	0.78	0.93	0.98	0.97	0.98	0.82	0.98	0.95	0.97	

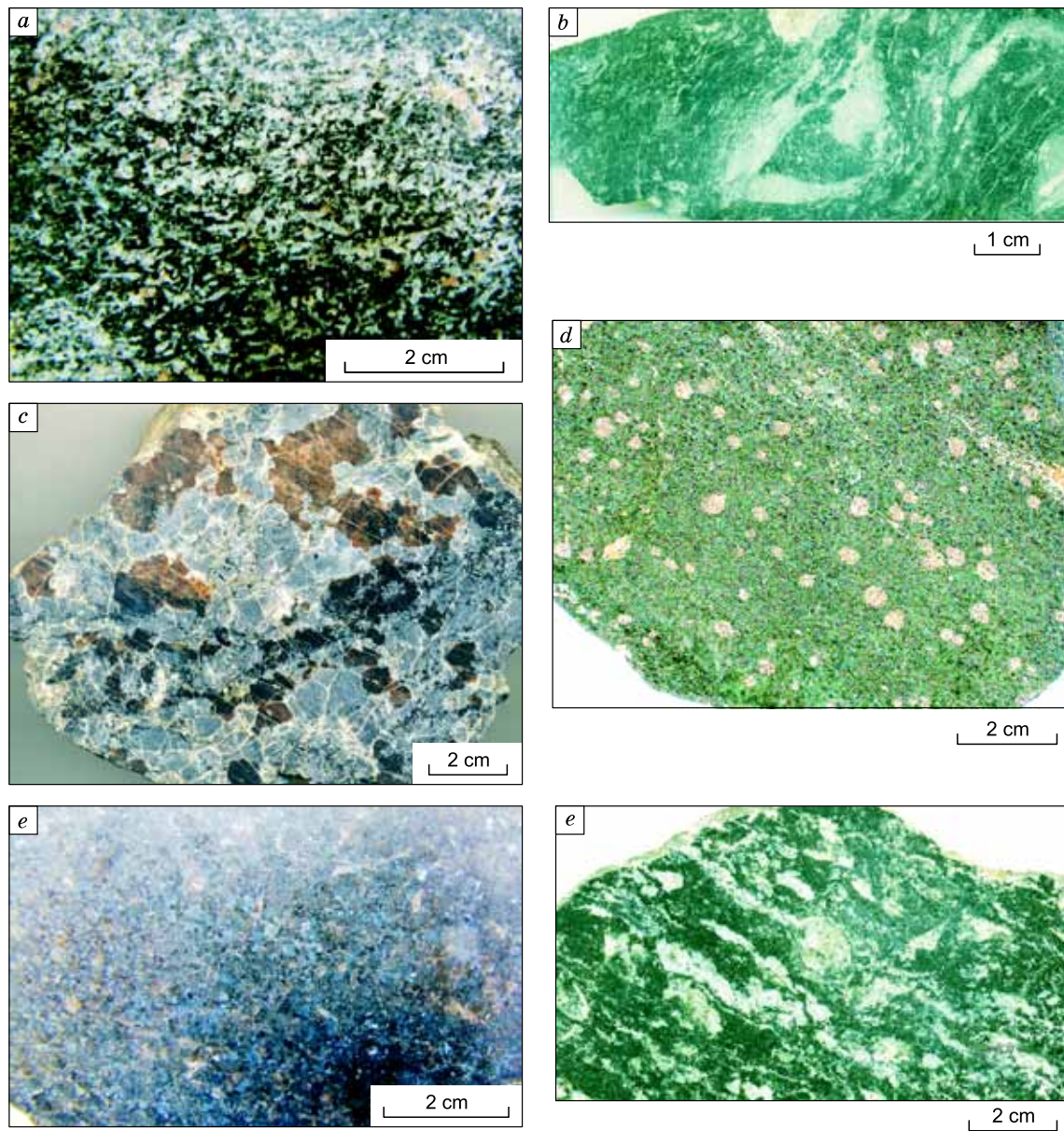
  

Component	An			Ttn				Ilm	Spl	
	84-A	712-A	Sd-13	84-A	293-5	295-A	173-5	712-A	712-A	718-A
	SiO <sub>2</sub>	42.31	42.33	43.26	30.28	30.01	30.88	29.63	–	–
TiO <sub>2</sub>	–	–	–	40.03	39.12	37.83	39.81	53.92	–	–
Al <sub>2</sub> O <sub>3</sub>	36.99	37.06	37.25	1.60	2.02	1.94	1.67	–	56.77	60.54
FeO*	0.01	0.38	–	0.04	0.46	N.d.	0.25	41.87	34.47	31.27
MnO	–	–	–	–	–	–	–	4.22	0.33	0.24
MgO	–	–	–	–	–	–	–	–	7.47	7.86
CaO	19.86	19.74	19.27	27.44	28.30	29.25	28.22	–	–	–
Na <sub>2</sub> O	0.20	–	–	–	–	–	–	–	–	–
SrO	1.21	N.d.	N.d.	N.d.	N.d.	N.d.	N.d.	N.d.	N.d.	N.d.
Total	100.58	99.51	99.78	99.39	99.91	99.90	99.58	100.01	99.04	99.91
Fe/(Fe + Mg)	1.0	1.0	1.0	1.0	–	1.0	–	0.93	0.99	0.99

Note. Analyses were carried out by V.A. Kotlyarov (Institute of Mineralogy, Miass) on a REMMA-202M scanning electron microscope equipped with an LZ-5 Link Systems energy dispersive spectrometer. All samples lack Cr and V. Dash, not found; n.d., no data; c, core; r, rim. Minerals: Hbl, amphibole; Cpx, clinopyroxene; Grt, garnet; Zo, zoisite; Czo, clinozoisite; An, anorthite; Ttn, titanite; Ilm, ilmenite; Spl, spinel. For sample description, see Tables 1 and 5. \*Total iron content.

(2014). The specific mineral composition of the studied gabbroids is given in the captions to Table 1. The often found garnet varieties are characterized by a predominance of pyrope-containing grossular–almandine or, sometimes, almandine–grossular (1–30%). The isolated outcrops of such rocks show the presence of coarse-grained pegmatoid varieties (Korinevsky, 2012). Such high-Ca garnet gabbroids were earlier found in the Urals only in eclogite associations (Bel-

kovskii, 1989). Note that the metaultrabasic bodies also host gabbroids containing corundum, ferrosphenel (pleonaste), diopside, zoisite, ilmenite, titanite, rutile, apatite, zircon, and biotite (from 0 to 10% each). These gabbroids are virtually free of quartz and magnetite and have weak directive textures and traces of replacement of some minerals by others. Based on the induction surfaces of contacting grains, Popov (2011) established that most of the rock-forming minerals in



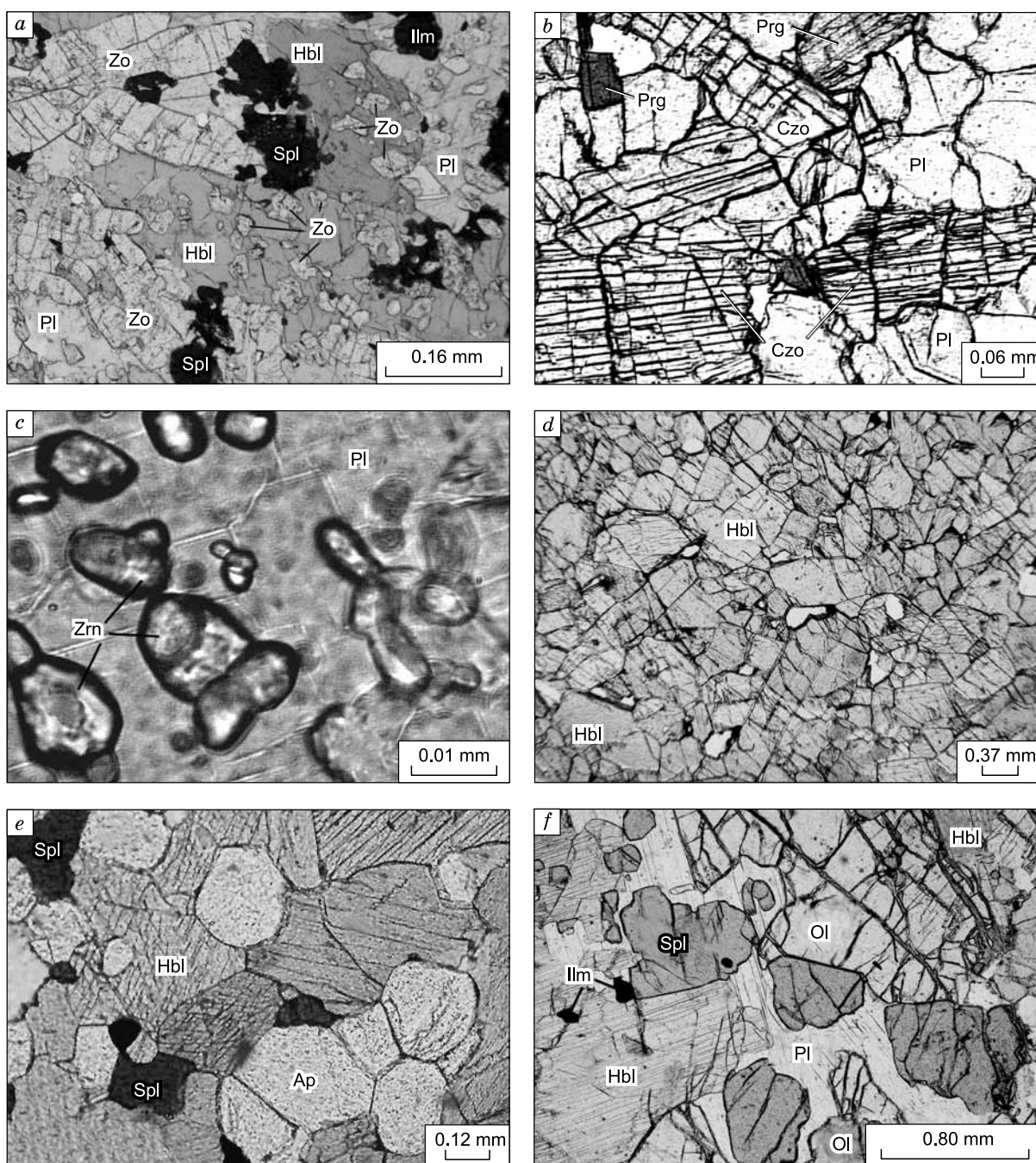
**Fig. 2.** Ilmeny gabbroids and hornblendites with high REE contents. Photographs of the polished surfaces of samples: *a*, garnet–zoisite–anorthite gabbro (sample 84-1); *b*, clinzoisite–anorthite gabbro (sample 173-5); *c*, garnet–clinozoisite–anorthite pegmatoid gabbro (sample 173-13-1); *d*, garnet hornblende (sample 211-1); *e*, garnet–spinel hornblende (sample 211-6); *f*, apatite–spinel hornblende (sample 211-10).

gabbroids grew synchronously. This refutes the hypothesis of the metasomatic nature of minerals. We should emphasize that clinzoisite and zoisite occur in the described gabbroids as individual grains that grew synchronously with the surrounding plagioclase crystals but not replace the latter, as was commonly believed. The gabbroids have predominantly inequigranular and polygonal textures and, often, spotted, banded, and streaky structures because of the uneven distribution of amphibole, clinopyroxene, garnet, and zoisite grain clusters. Garnet, anorthite, and, less often, amphibole crystals contain inclusions of ilmenite, zircon, and rutile. Anorthite from the gabbroids is enriched in SrO (0.1–0.3 wt.%),

which is typical of the deep-seated rocks of the Urals dunite–clinopyroxenite association (Efimov et al., 1989).

The rocks containing zoisite and clinzoisite are of our greatest interest (Fig. 2*a, b*). These minerals are found together in varying proportions. Macroscopically, they differ slightly; on a probe microanalysis, zoisite is distinguished by a significantly lower content of Fe. For simplicity, we will call such rocks zoisite rocks.

Zoisite gabbro are widespread as isolated blocks in the Urazbaevo and Savel'kul' areas. These rocks often have banded and taxitic structures. Medium-grained aggregate of amphibole and plagioclase crystals has distinct lighter fine-



**Fig. 3.** Microtextures of the Ilmeny REE gabbroids and hornblendites. Photographs of thin sections without an analyzer. *a, b*, Chaotically located large zoisite (Zo) and clinozoisite (Czo) prisms form a prismatic granular texture of gabbroids. Interstices contain anorthite (Pl), amphibole (Hbl, Prg), ilmenite (Ilm), and spinel (Spl) segregations; *c*, inclusions of rounded zircon grains (Zrn) in amphibole and anorthite crystals. *a*, Sample 712-A; *b, c*, sample 173-5; *d*, cumulative structure of medium-grained hornblende (sample 194-4); *e*, isometric granular structure of spinel-apatite hornblende. There are surfaces of simultaneous growth between all minerals (sample 211-1); *f*, medium-grained spinel-olivine hornblende containing synchronously grown clinoclone, apatite, ilmenite, and anorthite crystals. Orthopyroxenites have an intercalate (sample 211-6).

grained bands or numerous oval or irregular-shaped segregations composed by predominant zoisite and subordinate amphibole, plagioclase, garnet, and apatite (Fig. 2*a, b*). There are also coarser-grained massive varieties of zoisite gabbro without linear textures. Zoisite often amounts to >20 vol.%. Its long (up to 1–7 mm) prisms together with

isometric anorthite grains form sites of prismatic texture in gabbro (Fig. 3*a, b*). Garnet is present in zoisite gabbro as separate grains up to 1.5–3.0 mm across, amounting to 7 vol.%, but it is often absent. It has a high content of the grossular component (40–51%) and close low contents of the pyrope and spessartine end-members (8–9 and 7–11%,

respectively). These garnets demonstrate a typical (in gabbroids) tendency of MgO content to increase from grain core to rim but show an unusual phenomenon: a significant increase in MnO content and a synchronous decrease in CaO content toward the grain rim. Zoisite varieties of other anorthite gabbroids show a large number of fine (10–50  $\mu\text{m}$ ) rounded colorless or light yellow nonzoned zircon grains. Zircon is present in anorthite, zoisite, and amphibole crystals as a “captive” mineral (Fig. 3c). It amounts to hundredths of a percent in the rock. Twinned anorthite crystals often contain primary inclusions of zoisite, spinel, and zircon and form uneven rounded surfaces of synchronous growth with zoisite and amphibole crystals (Fig. 3f). Secondary minerals are seldom developed after anorthite. These are spotted calcite or zeolite segregations of intricate shape (in the weathering crust). Clusters of fine titanite grains are localized at the boundaries of crystals of other minerals, often forming thin strips.

#### PETROGRAPHIC TYPES OF HORNBLENDITES FROM CLASTOLITES IN METAULTRABASIC BODIES

Hornblendites in clastolites are seldom found among metaultrabasic bodies. They have many petrographic varieties (Korinevsky and Korinevsky, 2006). Some of them have abnormal contents of REE.

Hornblendites are divided into garnet-free and garnet-containing. Garnet hornblendites are rare in the Urals (Fig. 2d). They expose in the walls of an old trench on the northern slope of Mount Savel'kul', near its peak. Alternating bands of exposed hornblendites and melanocratic gabbroids are traceable for 2 m. The bands are no thicker than 10–20 cm, with clear (but not sharp) and steeply dipping boundaries between them. This fragment of the banded complex is hosted by medium-grained orthopyroxenites. All hornblendite samples of this banded complex has varying contents of high-Ca garnet (almandine-grossular) and chlorapatite (Figs. 2d and 3e, samples 211-1, 5, and 12). These minerals are present in the rock both as dissemination and as nests and bands. In places, the content of garnet reaches 15 vol.%, and that of apatite, 10 vol.% (Fig. 2f). The rock is composed mostly (~65%) of dark brown short-prismatic K-pargasite grains. Isometric dark green pleonaste segregations (10–15%) are unevenly distributed in this aggregate; there are also sporadic anorthite, ilmenite, and calcite nests and veins. The composition of minerals in these hornblendites indicates their formation at high pressures and temperatures (Krylova et al., 1991).

Most of the garnet-free hornblendites contain spinel. The fine octahedral spinel crystals are most often ferromagnesian (pleonaste), with minor contents of ZnO (Fig. 2e). It is seen in the preserved fragments of rock lumps that these hornblendites form beds alternating with other hornblendite varieties or gabbro or, sometimes, pyroxenites, and the rock texture is similar to the near-cumulative one in layered intrusions (Fig. 3d).

A rare clinocllore–spinel–olivine variety of hornblendites was found on the northwestern slope of Mt. Savel'kul' (Fig. 3f, sample 211-6). The outcrop shows a block of alternating hornblendites and orthopyroxenites, with one of the bands formed by the above rock. This band is 15 cm thick. The rock occurs at the boundary of apatite–spinel hornblendites and chloritrolites developed after orthopyroxenites. Brownish-yellow transparent nonserpentinous olivine crystals (~35 vol.%) are well discernible on the background of dark amphibole (50 vol.%) and spinel (10–15 vol.%) crystalline mass. Synchronously formed clinocllore crystals form intergrowths with these minerals. There are also minor anorthite, ilmenite, and apatite grains. The rock has an equigranular texture and medium grains (1–4 mm across). The structural relationship of the minerals, no zoning in them, and the homogeneous structure of the rock testify to its deep-level magmatic origin.

Massive fine- to medium-grained hornblendites with uniformly dispersed fresh fine olivine crystals form clastolites in serpentinite melange near Cape Osinoyi on Lake Bol'shoi Ishkul'. Hornblendite blocks in the melange are often rounded.

Equigranular medium-grained massive spinel hornblendites containing up to 15–20% pleonaste make contact with orthopyroxenites in another outcrop on the slope of Mt. Savel'kul'. Dark brown aluminopargasite crystals here reach 10–15 mm in length and are chaotically localized. The rock contains numerous fine chlorapatite crystals, rutile prisms, and ilmenite and titanite grains. Sometimes fine zircon and orthite crystals occur. Amphibole contains small ( $\leq 100 \mu\text{m}$ ) chlorite inclusions. Plagioclase is absent.

Hornblendites in the northern shore cliffs of Lake Bol'shoi Miassovo expose as massive black rocks in the basement of ultramafic rocks. These hornblendites occur as a large block inclusion in olivine–enstatite–tremolite–anthophyllite rocks, being separated from them by a 10–15 cm thick chloritrolite rim with thin prismatic tschermakite meta-crysts. The rock groundmass is composed of chaotically localized pargasite crystals up to 15–25 mm in length. Coarse (1–5 to 10–20 mm) zoned pyrope-almandine crystals and scarce anorthite, apatite, spinel, and ilmenite grains amount to <10%. They are unevenly distributed in the rock, concentrating at some sites. Spinel is also present as small octahedral inclusions in anorthite and pargasite. The rock also contains 1–5 mm long colorless (with blue sites) corundum grains of irregular shape and clusters of clinocllore and biotite plates. Garnet grains show not only a typical chemical zoning but also a sector structure.

#### MAJOR PETROCHEMICAL FEATURES OF GABBROIDS AND HORNBLENDITES

Besides low contents of  $\text{SiO}_2$ , the considered exotic Ilmeny rocks have abnormally high contents of  $\text{Al}_2\text{O}_3$  and CaO and high contents of MgO (Table 1). Therefore, the



**Table 3.** Contents of REE (ppm) in gabbroids from clastolites from the Urazbaevo olistostrome of the Ilmeny complex

Element	84-A*	84-1*	84-2*	295-2*	712-A*	718-A*	305-3*	4-98**	14-98**	173-5*	173-1*	269-3*	173-13-1*	271-6*
La	97.7	136.1	140	119	67.9	35	30.2	329.3	49.6	26.3	36.2	51	33.8	46.9
Ce	232	275.6	322	216	128	73.9	80.6	65.4	55.1	65.3	81.9	166.4	73.1	74.6
Pr	26.1	32.6	35.8	22.8	15.5	9.3	8.9	7.8	6.5	8.5	10.8	12.7	8.5	8.4
Nd	104	142.9	163	79.9	56.9	38.8	38	37.3	27.5	38.3	49.3	50.5	35.6	32.5
Sm	22.8	31.2	35.2	13.7	10	8.3	8.6	11.5	6.3	10.2	12.6	10.4	7.7	5.8
Eu	7.4	6.6	9.5	4.2	3.3	2.4	2.9	10.9	1.9	2.3	2.3	5.1	2.7	1.7
Gd	23.9	33.4	37.4	13	9	8.8	8.8	13.9	5.9	9.8	13	11.8	8.5	5.2
Tb	4	5.9	6.5	1.5	1.2	1.4	1.4	2.4	0.9	1.7	2.3	1.8	1.4	0.8
Dy	26.9	37.8	38.5	8.3	6.7	8.6	8.8	14.2	5.2	9.9	14.3	10.6	9.2	4.6
Ho	6.4	8.6	8.2	1.5	1.3	1.8	1.8	3.1	1.1	2.1	2.9	2.3	2.1	1
Er	20.8	25.1	26.6	4.6	3.3	8.3	5.3	8.6	3.1	6	8.1	6.6	5.6	2.9
Tm	3.4	3.6	3.8	0.6	0.4	0.8	0.8	1.3	0.4	0.8	1.2	1	0.9	0.4
Yb	22.4	24.1	24.7	4.1	2.8	5.5	5.3	9.6	3	5.4	7.6	6.4	5.6	2.7
Lu	3.2	3.7	3.4	0.5	0.4	0.9	0.7	1.4	0.5	0.8	1.1	1	0.8	0.4
∑ REE	601	767.2	854.6	489.7	306.7	203.8	201.89	457.7	167	187.4	243.6	337.6	195.5	187.9
∑ LREE	490	625.0	705.5	455.6	281.6	167.7	169.13	403.2	146.9	150.9	193.1	296.1	161.4	169.9
∑ HREE	111	142.2	149.1	34.1	25.1	36.1	32.76	54.5	20.1	36.5	50.5	41.5	34.1	18
% LREE	81.5	81.5	82.6	93	91.8	82.3	83.86	88.1	88	80.5	79.3	87.7	82.6	90.4
% HREE	18.5	18.5	17.4	7	8.2	17.7	16.14	11.9	12	19.5	20.7	12.3	17.4	9.6
Eu/Eu*	0.97	0.62	0.8	0.96	1.06	0.86	1.02	2.63	0.95	0.7	0.55	1.4	1.02	0.94
(Gd/Yb) <sub>CN</sub>	0.86	1.12	1.23	2.57	2.6	1.29	1.34	1.17	1.59	1.47	1.38	1.49	1.23	1.56
(La/Sm) <sub>CN</sub>	2.68	2.72	2.48	5.43	4.24	2.63	2.19	17.88	4.92	1.61	1.79	3.06	2.74	5.05

Note. For description of the samples, see Table 1. Here and in Table 4, LREE—La, Ce, Pr, Nd, Sm, and Eu; HREE—Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu.  
 \* The ICP MS analyses of samples from clastoliths from metaultrabasic bodies were carried out at the Mineralogical Institute, Miass (analysts K.A. Filip-pova and M.S. Svireenko).

\*\* The analyses of samples were borrowed from Rusin et al. (2012).

known TAS diagrams for classification of igneous rocks (Gon'shakova, 1983) cannot be applied to them. Being formally ultramafic ( $\text{SiO}_2 < 45\%$ ), the Ilmeny rocks have no analogs in  $\text{Al}_2\text{O}_3$ , CaO, and  $\text{Na}_2\text{O}$  contents among igneous rocks of this class.

The described gabbroids (Tables 3 and 4) have abnormally high contents of REE (170–850 ppm), with LREE strongly dominating over HREE (81–93% of the total REE content). The rocks are also enriched in Sr (451–2219 ppm), Ni (24–417 ppm), and Cr (8–701 ppm) and have extremely high contents of Ca and Al, which distinguishes them from ultramafic rocks. The above petrographic description shows that the metaultrabasic rocks in clastolites are dominated by specific high- $\text{Al}_2\text{O}_3$  high-Ca apogabbro rocks. They have a nearly complete analog in the framing of the Voikar–Syn'ya massif in the Polar Urals (Efimov and Ryabkova, 1979).

The studied mafic and ultramafic rocks have high total REE contents, usually more than 74 ppm (Tables 3). Maximum contents were determined in zoisite gabbro (170–850 ppm) and apatite–garnet hornblendites (up to 450 ppm). Garnet-free hornblendites and gabbroids are poorer in REE. Light REE significantly dominate over heavy REE in all types of mafic and ultramafic rocks (>60–80% of the total

REE content). The portion of LREE significantly increases (often, >80% of the total REE content) in mafic rocks (gabbroids).

The similar relative contents and patterns of REE of the studied Ilmeny gabbroids and hornblendites are explained by their localization within a narrow zone (Fig. 4). All this suggests their consanguinity.

The REE contents in mafic and ultramafic rocks of the Urals harzburgite and Pt-bearing dunite–pyroxenite–gabbro associations are estimated at 10–70 ppm (Sobolev, 1965; Fershtater and Bea, 1996; Fershtater et al., 2004; Lesnov, 2007; Fershtater, 2013). The lowest REE contents (<10 ppm) were found in monomineral rocks (dunites, hornblendites, anorthosites, etc.). The only exception is the hornblendites of the Svetlyi Bor massif (sample Pe-926, Table 5), which have nearly the same content of REE as the Ilmeny hornblendites. Hornblendites of other Urals massifs have low total contents of REE, 31–75 ppm (Gottman, 2014). The REE contents in the Ilmeny mafic and ultramafic rocks are much higher than those in similar rocks of the Urals harzburgite and Pt-bearing associations (Table 3).

Rare-earth elements in the mafic and ultramafic rocks are strongly dominated by LREE, like the Ilmeny metamor-

**Table 4.** Contents of REE (ppm) and trace elements in rock-forming minerals from zoisite gabbro and hornblendites from clastolites in metaultrabasic bodies of the Ilmeny complex

Component	84-A		84-1		718-A				211-6				211-10		261-6		Sd-13	
	Zo	Grt	Hbl	Grt	Grt	An	Ap	Cm	Hbl	Spl	Ol	Clc	Ap	Hbl	Hbl	Pl (An)		
La	97.7	16.5	41.9	31.2	4.94	7.78	20.7	2.34	20	0.46	7.83	2.42	36.4	23.3	1.29	0.74		
Ce	232	48.6	102	88.2	10.9	16.6	51.1	5.86	99.8	1.14	15.2	4.74	64.1	99.6	2.89	1.17		
Pr	26.1	4.53	11.1	8.08	1.36	1.95	6.73	0.68	18.1	0.13	1.46	0.59	11.4	19.9	0.4	0.14		
Nd	104	19.2	47.7	32.1	6.34	9.35	33.1	3.17	89.4	0.51	4.83	2.15	55.1	133	2.09	0.64		
Sm	22.8	4.01	1.9	7.1	1.51	1.84	9.34	0.65	20.2	0.1	0.64	0.45	15.2	45	0.82	0.12		
Eu	7.37	1.25	3.18	1.57	0.33	1.9	12.6	0.65	4.18	0.02	0.11	0.11	4.49	9.59	0.4	0.11		
Gd	23.9	4.91	12.3	7.06	1.87	1.61	9.23	0.6	15.3	0.12	0.41	0.39	17.6	52.30	1.26	0.13		
Tb	4.01	1.42	2.34	1.76	0.39	0.21	1.24	0.09	2.07	0.01	0.04	0.04	2.69	9.53	0.24	0.02		
Dy	26.9	20.2	18.7	23	3.06	0.95	6.75	0.46	11.6	0.13	0.27	0.33	15.1	57.8	1.68	0.12		
Ho	6.38	8.46	4.74	9.28	0.77	0.19	1.34	0.08	2.19	0.03	0.05	0.06	3.13	12.2	0.35	0.03		
Er	120.8	49.3	16.7	51.4	2.75	0.54	4.09	0.25	6.06	0.11	0.2	0.23	8.56	65.2	1.11	0.09		
Tm	3.35	10.9	2.71	11.8	0.51	0.09	0.60	0.04	0.93	0.02	0.03	0.04	1.15	4.52	0.15	0.01		
Yb	22.4	106	17.5	116	4.2	0.62	3.87	0.23	6.05	0.13	0.19	0.3	6.89	26	1.29	0.11		
Lu	3.16	18.4	2.25	19.6	0.76	0.11	0.66	0.03	20	0.02	0.03	0.05	0.97	3.67	2.89	0.02		
Sc	41	24.5	37.6	24.9	16.7	2.34	1.18	1.01	99.80	0.64	1.7	3.72	0.60	82.6	66.5	0.99		
Y	196	250	101	279	21.1	5.2	40.3	1.92	18.1	0.7	1.6	2.03	90	298	8.65	0.75		
V	105	19.3	182	21.9	107	15.2	7.11	16.7	89.4	338	2.84	205	4.65	354	276	2.31		
Cr	25.9	7.56	93.9	7.94	8.33	2.86	1.07	147	20.2	144	1.22	65.4	0.87	25.2	270	3.13		
Co	8.9	7.04	8.81	8.01	15.3	1.2	0.95	0.69	4.18	142	97.9	37.9	0.82	27.8	60.6	0.89		
Ni	24.4	3.56	21.6	2.04	1.10	2.29	1.73	1.56	15.3	337	541	319	4.3	273	197	2.38		
Sr	1681	109	549	166	132	3042	1239	30.1	2.07	21.1	79.6	81.3	1859	379	93.7	337		
Zr	141	40.3	41.2	129	45	94.5	23.8	12.5	11.6	58.1	104	220	31.7	225	69.3	90.8		
Nb	22.9	9.05	12.7	8.09	0.67	8.1	0.31	0.66	2.19	2.55	4.9	5.6	2.04	12.9	5.85	0.31		
Ba	21.4	1422	35	34.3	50.7	1584	226	40.6	6.06	126	38.1	41.8	15.9	7432	52.8	18.2		
Th	29	4.52	10.4	8.26	1.52	2	1.29	1.15	6.73	2.62	2.11	2.09	2.45	3.28	0.3	0.09		
U	7.92	1.13	4.51	2.25	0.89	1.57	7.52	0.52	10.5	10.8	3.82	3.39	18.5	2.01	0.41	0.21		
∑ REE	700.87	313.68	285.02	408.15	39.69	43.74	161.35	15.13	296.84	2.93	31.29	11.9	242.78	561.61	16.86	3.45		
∑ LREE	489.97	94.09	216.78	168.25	25.38	39.42	133.57	13.35	251.68	2.36	30.07	10.46	186.69	330.39	7.89	2.92		
∑ HREE	210.9	219.59	77.24	239.9	14.31	4.32	27.78	1.78	45.16	0.57	1.22	1.44	56.09	231.22	8.97	0.53		
% LREE	69.9	30	73.73	41.2	63.9	90.1	82.8	88.2	84.8	80.5	96.1	87.9	76.9	58.83	46.79	84.64		
% HREE	30.1	70	26.27	58.8	36.1	9.9	17.2	11.8	15.2	19.5	3.9	12.1	23.1	41.17	53.20	15.36		

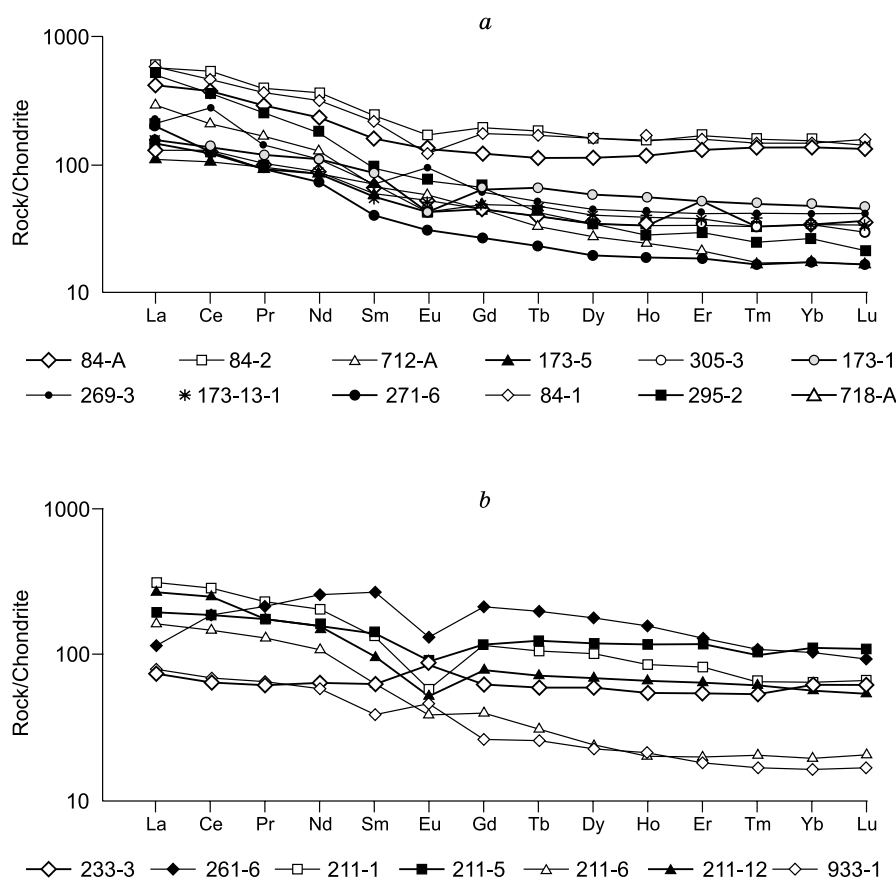
Note. The ICP MS analyses were carried out at the Mineralogical Institute, Miass (analysts K.A. Filippova and M.S. Svirenko). Minerals: Ap, apatite; Cm, corundum; Ol, olivine; Clc, clinocllore; other designations follow Table 2. For description of the samples, see Table 1.

phosed mafic rocks (Korinevsky and Bazhenova, 2004), which indicates that REE have been preserved during metamorphism. A specific geochemical feature of ultramafic rocks in folded areas is their depletion in REE, particularly LREE (Lesnov, 2007). This distinguishes them from the Ilmeny ultramafic rocks, which were earlier assigned to ophiolite association (Varlakov et al., 1998).

### REE-CONCENTRATING MINERALS

Rock-forming minerals, such as amphibole, garnet, plagioclase, and pyroxene, are major concentrators of REE in

mafic and ultramafic rocks (Sobolev, 1965; Lesnov, 2007). Zoisite, apatite, and amphibole make the main contribution to the amount of REE and the domination of LREE over HREE in gabbroids (Table 4, Fig. 5a). The rather high contents of Ce and Nd in the Ilmeny mafic and ultramafic rocks are evident of a predominance of amphiboles concentrating these elements (Lesnov, 2007). Garnet is characterized by a predominance of heavy elements and a negative Eu anomaly. There are also intense positive anomalies of Eu in apatite and of Er in zoisite and a negative anomaly of Sm in amphibole, which are usually not observed in these minerals from ophiolite associations (Lesnov, 2007) and metamorphosed mafic rocks (Skublov, 2005).

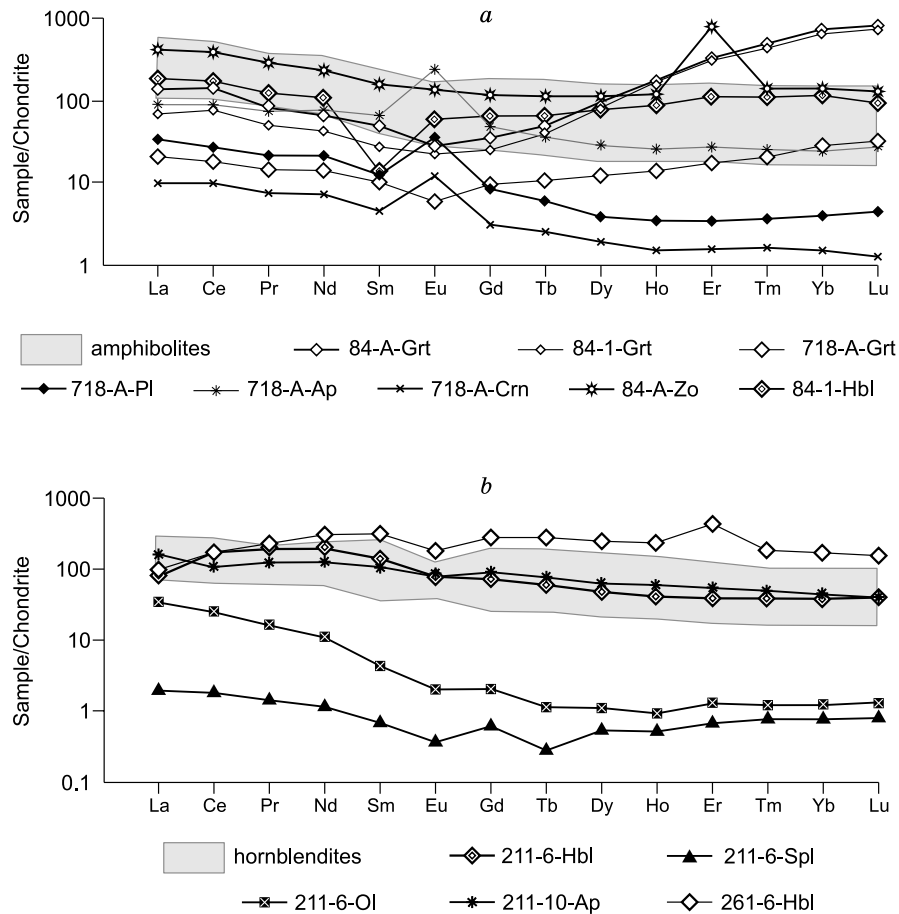


**Fig. 4.** Chondrite-normalized (McDonough and Sun, 1995) REE patterns of the Ilmeny and Urals REE gabbroids (a) (from the data in Table 3) and hornblendites (b) (from the data in Table 6). Sample numbers follow Tables 1 and 5.

Our data for the Urals rocks (Table 4, Fig. 5a) for the first time show the leading role of zoisite in the concentration of REE as compared with amphibole, garnet, and apatite. Note that zoisite and apatite of the studied rocks have abnormally high contents of Eu, even higher than that in plagioclase. Zoisite (clinozoisite) in these rocks is the main concentrator of all REE, Dy, Er, Nb, and Th. In contents of Sr it is inferior to anorthite and apatite only, and in contents of Y, to garnet only. Amphiboles from gabbroids and hornblendites also have much higher contents of REE (~294 ppm) than those reported in literature (Frei et al., 2004; Skublov, 2005; Lesnov, 2007). In contents of La, Ce, and Nd they are inferior to zoisite only, and in contents of Dy, to zoisite and garnet. The contents of Sc in amphiboles are close to those in zoisite. The contents of Eu in REE-containing amphiboles from both gabbroids and hornblendites are always 2–5 times higher than those in anorthite. Amphibole from these rocks is also 2–5 times richer in Sr than amphibole from compositionally similar low-REE diopside–anorthite gabbro in the melange blocks (Table 4, sample Sd-13). Garnet is the main concentrator of Y (250–279 ppm) and Yb (106–116 ppm), and its Ba content is only slightly lower than that in anorthite. The contents of Y in the rocks show a direct correla-

tion with their total REE contents. As seen from Table 4, the contents of REE and trace elements in the studied minerals are much higher than those in similar minerals of other rock complexes and associations (Skublov, 2005; Lesnov, 2007). Note that LREE are strongly predominant in all these minerals. Zoisite and anorthite (and, often, amphibole and garnet) from all rocks contain fine rounded zircon inclusions (Fig. 3c) contributing to the total content of REE. We also found fine uraninite and scheelite inclusions in ilmenite and rutile grains. Sometimes, small REE-zoned orthite grains are observed. Amphiboles and garnets show abnormally high REE contents (up to 408 and 346 ppm, respectively).

Although Sobolev (1965) reported the negligible role of accessory minerals as REE carriers, they can be of crucial importance in the Ilmeny ultramafic rocks. For example, rutile–spinel hornblendite (Table 5, sample 261-6) contains fine monazite and orthite segregations, one of which has 5.43 wt.%  $\text{La}_2\text{O}_3$  and 14.81 wt.%  $\text{Ce}_2\text{O}_3$ . This fact and the abnormally high content of REE in amphibole (561.6 ppm) might be the cause of the high total content of REE and Y (675 ppm) in the above hornblendite sample (Table 6). Nevertheless, amphibole and apatite are the main concentrators of REE in the hornblendites (Table 4).



**Fig. 5.** Chondrite-normalized (McDonough and Sun, 1995) REE patterns of minerals from the Ilmeny REE gabbroids (a) and hornblendites (b) (from the data in Table 4). Sample numbers follow Tables 1 and 5.

## FORMATION CONDITIONS AND PROBABLE GENESIS

Petrographic examination shows that the studied zoisite gabbro and hornblendites meet the microtexture and petrologic criteria for a mineral equilibrium defined by Skublov (2005). Taking into account their microtextures (ophitic, gabbro, and cumulative), the absence of metamorphic schistosity and relics (shadows) of assumed protolith minerals, and the ubiquitous surfaces of synchronous growth of minerals, we consider these rocks igneous. Gottman and Pushkarev (2009) presented convincing arguments for the magmatic (intrusive) nature of the Urals hornblendites. They assume that the rocks resulted from crystallization of residual fluid-saturated melts generated during the differentiation of primary highly calcareous clinopyroxenitic or ankaramitic magmas. The predominance of hydrous minerals (primary amphiboles, zoisite, and clinocllore) in the rocks and the permanent presence of chlorapatite, titanite, zircon, orthite, scheelite, and uraninite confirm this hypothesis. The high Ni/Co ratios (usually,  $>2$ , Tables 1 and 5) in the rocks also argue for their igneous nature (Kogarko, 1973). Since anor-

thite in these rocks is extremely rich in Sr (up to 3042 ppm in the sample 718-A, Table 4) as compared with amphiboles (332–549 ppm, samples 211-6, 261-6, and 84-1, Table 4), we assume, like Gottman (2014), that the rocks crystallized in cotectic conditions.

The above specific chemical and mineral compositions of rocks, the high contents of REE, and the predominance of LREE among them give grounds to compare these rocks with a rock complex of layered mafic–ultramafic intrusions in the basement of rigid crustal blocks. We have already noted (Korinevsky and Korinevsky, 2008) that the gabbroid and hornblendite bodies are older than the host metasediments, in which they form isolated rather than sheet bodies. For this reason, they cannot belong to ophiolite association. Their significant difference from the mafic and ultramafic rocks of ophiolite associations is also evidenced from their bulk chemical composition (Tables 1 and 5) and the REE contents and patterns (Tables 3 and 6) in both types of rocks and in the same minerals in them. In mineral composition, the presence of relics of cumulative textures, and primary layering (an example is outcropped hornblendites at Mt. Savel'kul' alternating with orthopyroxenites) the studied

**Table 5.** Oxides (wt.%) and trace elements (ppm) in high-REE hornblendites of the Ilmeny complex and in hornblendites of the Urals intrusive massifs

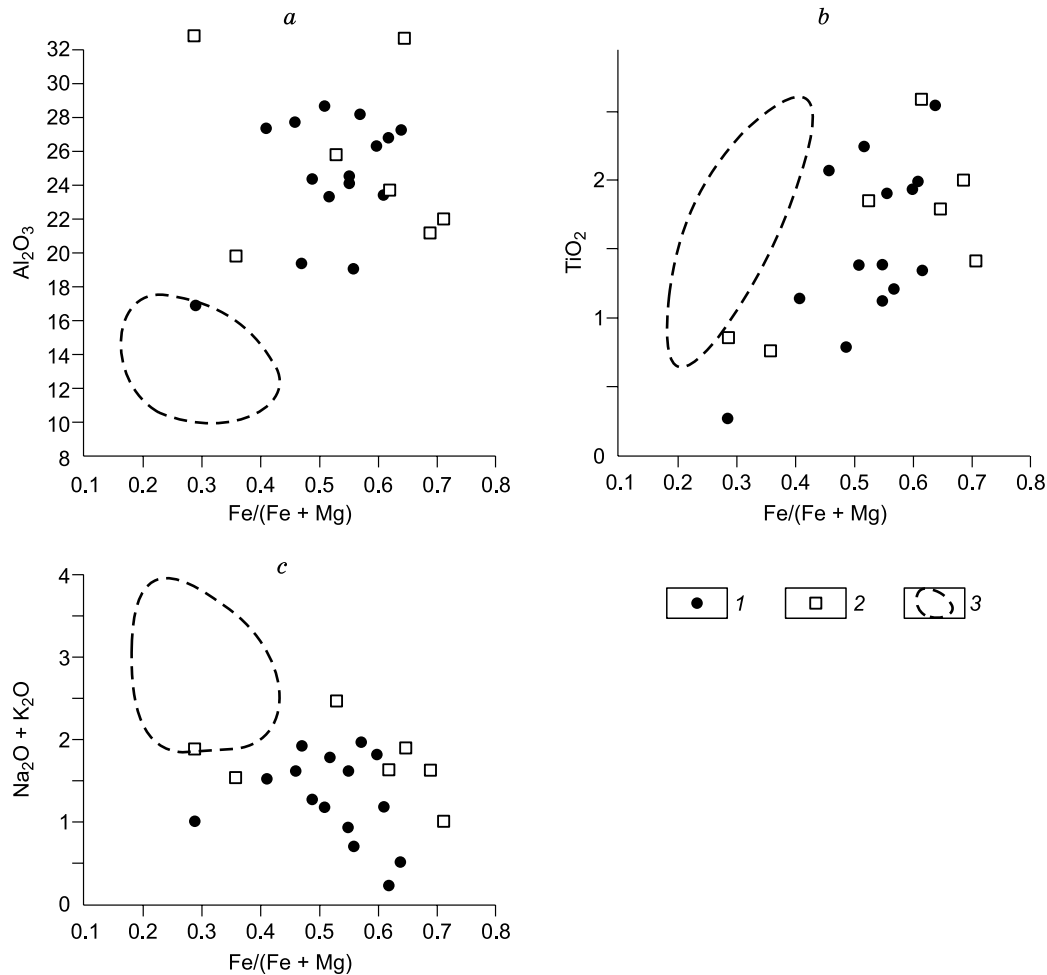
Component	Ilmeny complex							Urals intrusive massifs		
	233-3	261-6	933-1	211-1	211-5	211-6	211-12	Pe-926*	Pe-305*	Khb-1575*
SiO <sub>2</sub>	27.13	29.71	29.52	31.84	28.90	33.68	29.64	35.66	44.19	38.99
TiO <sub>2</sub>	1.79	0.86	1.42	2.58	1.84	0.75	2.00	1.67	1.37	1.45
Al <sub>2</sub> O <sub>3</sub>	32.56	32.85	22.00	23.72	25.69	19.80	21.21	8.96	9.11	9.10
Fe <sub>2</sub> O <sub>3</sub>	8.76	3.85	7.45	8.01	8.26	6.40	4.89	–	–	–
FeO	7.90	1.94	13.03	7.20	4.50	4.32	8.10	23.89	14.72	17.92
MnO	0.28	0.07	0.33	0.41	0.15	0.11	0.65	0.24	0.18	0.26
MgO	10.99	17.20	10.61	11.19	13.50	22.75	7.30	9.91	12.91	15.31
CaO	7.30	9.35	9.00	11.30	11.60	7.61	15.80	15.60	12.70	10.49
Na <sub>2</sub> O	1.40	1.66	0.81	0.76	1.84	1.32	0.93	1.46	2.25	1.46
K <sub>2</sub> O	0.50	0.22	0.21	0.87	0.61	0.21	0.67	0.89	0.29	0.91
LOI	0.55	1.19	4.94	0.72	0.55	2.74	5.00	1.66	1.78	4.09
P <sub>2</sub> O <sub>5</sub>	0.12	0.61	0.18	1.36	2.54	0.59	3.74	1.92	0.04	0.49
Total	99.28	100.12	99.50	99.96	100.04	100.28	99.93	101.86	99.54	100.47
f	0.65	0.29	0.71	0.62	0.53	0.36	0.69	0.76	0.59	0.81
Sc	67.8	66	60.9	58.6	52.7	17	34.5	30.6	57.9	69.2
Y	83.3	221.0	29.5	29.5	140.7	182.2	30.8	121.7	19.8	19.5
V	398	294.3	487.3	595.2	699.6	247.6	564.1	591.5	451.3	427.6
Cr	86.4	333.3	82	197.6	218.6	89.3	131.6	145.7	719.1	411.9
Co	30.8	55.5	60.9	53.6	77.8	65.2	48.5	63.2	62.5	58.1
Ni	49.9	317.2	45.4	222.9	212.1	237.5	203.6	39.2	197.6	87.3
Sr	237	270.7	260	1879.8	695.2	207.3	1878.3	576.2	191.3	214.2
Zr	139	291.4	15.6	286.1	46.1	89.6	77.8	45.6	19.9	43.9
Nb	29.8	173.7	5.4	46.7	19.3	13.9	43.5	1.3	0.7	3
Ba	318	42.2	9.9	192.8	83.7	390.2	156.6	108.5	24.7	128.7
Th	3.2	3.3	3.1	18.1	10.2	9.2	11.1	0.2	0.1	0.4
U	0.7	1.3	0.4	4.9	3.0	15.2	4.8	0.1	0.04	0.2
∑ REE	157.2	454.3	117.4	117.4	453.8	373.7	224.5	144.6	31.1	74.8
Ni/Co	1.62	5.71	0.75	4.16	2.73	3.64	4.2	0.62	3.16	1.5

Note. Samples were taken by V.G. Korinevsky from clastolites in metaultrabasic bodies at the Miass and Savel'kul' sites of the Ilmeny Mountains. 233-3, northern shore of Lake Bol'shoe Miassovo, 55°10'31.2" N, 60°16'41.8" E. Northern piedmont of Mt. Savel'kul': 261-6, rutile–spinel–pargasite hornblendite with apatite and orthite grains, 55°07'45.8" N, 60°17'33.5" E; 933-1, garnet–clinocllore–pargasite hornblendite with spinel, ilmenite, apatite, and anorthite grains, north of Village Urazbaevo, 55°11'09.53" N, 60°19'53.90" E; 211-1, apatite–garnet–spinel–pargasite hornblendite with anorthite, ilmenite, and calcite grains; 211-5, spinel–apatite–pargasite hornblendite; 211-6, spinel–olivine–clinocllore–pargasite hornblendite with anorthite, apatite, and ilmenite grains; 211-12, apatite–garnet–pargasite hornblendite with anorthite grains. All samples 211 were taken from trenches near the point 55°07'37.96" N, 60°17'55.25" E. Wet chemistry analyses were carried out by M.N. Malyarenok, T.V. Semenova, M.S. Svirengo, and Yu.F. Mel'nova, and ICP MS analyses for trace elements, by K.A. Filippova and M.S. Svirengo (Institute of Mineralogy, Miass).

\* Results of analyses of samples were borrowed from Gottman (2014): Pe-926, hornblendite from the Svetlyi Bor massif, Pe-305, hornblendite from the Kytlym massif, and Khb-1575, hornblendite from the Khabarnyi massif. *f*, Fe/(Fe + Mg), at.%.

rocks seemed to be most similar to the rocks of the Urals Platinum Belt (Korinevsky and Korinevsky, 2006). However, our new data on the geochemistry of the studied rocks do not confirm this assumption. In particular, in variation diagrams (Fig. 6), most of their composition points lie beyond the fields of the Urals Platinum Belt hornblendites and gabbro (Gottman, 2014). The compared rocks show a great difference in radiological age: 430–400 Ma for the rocks of the Platinum Belt (Gottman, 2014) and 543–662 Ma for the gabbroids from the Ilmeny olistoliths (Rusin et al., 2006). Apparently, the blocks of serpentinite melange are com-

posed of rocks of different genesis. Part of the gabbroids might be of apoclogitic nature (Korinevsky and Korinevsky, 2004, 2006). The high contents of Ni and Cr in them testify to their consanguinity with mafic and ultramafic rocks. During the formation of protrusions of the serpentinite melange and its plastic squeezing-out along tectonic planes, these genetically different rocks might have been intermixed, forming clastolites in the melange and then getting into the olistostrome complex. The high contents of Zr, Nb, Th, and U do not rule out that the rocks might be disintegrated fragments of ultramafic alkaline intrusion from the



**Fig. 6.**  $f(\text{Fe}/(\text{Fe} + \text{Mg}))$ , at.%– $\text{Al}_2\text{O}_3$  (wt.%) (a),  $f(\text{Fe}/(\text{Fe} + \text{Mg}))$ , at.%– $\text{TiO}_2$  (wt.%) (b), and  $f(\text{Fe}/(\text{Fe} + \text{Mg}))$ , at.%– $(\text{Na}_2\text{O} + \text{K}_2\text{O})$  (wt.%) (c) variation diagrams for the Ilmeny REE gabbroids (1) and hornblendites (2) (from the data in Tables 1 and 5) and the rocks from the Urals Platinum Belt (3) (Gottman, 2014).

Urals crustal base (Rusin et al., 2006). On this basis, Rusin et al. (2010) assumed that the rocks are similar in mineral composition to gabbroids composing xenoliths in kimberlite pipes. The authors believe that gabbroids are stable in the pressure range from 22.5 to 27 kbar. This analogy is rather hypothetical, but the significant quantity (1.5 to 7%) of Eskola molecules in clinopyroxenes (Serdyuchenko, 1982; Korinevsky, 2013) indirectly confirms the high-pressure conditions of the rock formation. Our geothermobarometric data also point to the high temperature and pressure of the rock formation (Table 7). The estimated values vary considerably depending on the evaluation method, but most of them are within 8–12 kbar and 490–890 °C (or, probably, even higher than 1000 °C), thus confirming the great depths of the rock formation. At the same time, the Ilmeny REE gabbroids are much similar in petrographic criteria and mineral composition to hornblende gabbroids associated with ultramafic rocks in the Urals ophiolite associations (Fershtater et al., 2004; Belikova and Salikhov, 2007). Both rocks are highly enriched in  $\text{Al}_2\text{O}_3$  and CaO, have high contents of

Sr, and contain basic plagioclases. The main difference is extremely low REE contents (5–71 ppm, Table 1 (Belikova and Salikhov, 2007) and Table 2 (Fershtater et al., 2004)), a higher iron index ( $f = \text{Fe}/(\text{Fe} + \text{Mg})$ ), and lower Al contents in the hornblende gabbroids of ophiolite associations.

Thus, the Ilmeny REE gabbroids and hornblendites have no complete analogs among petrographically similar rocks of the Urals ophiolite associations and the Platinum Belt. They are older. The specific REE composition of these rocks is probably due to their consanguinity with the rocks of the assumed (Rusin et al., 2010) ultramafic alkaline intrusion in the Urals crustal base. Fragments of this intrusion might have got into the rock fragments during the formation of protrusive serpentinite melange.

## CONCLUSIONS

As follows from the available data (Semenov, 2001; Usova, 2001; Mikhailov, 2010), REE deposits are usually localized in pegmatites, carbonatites, and hydrothermal-metaso-

**Table 6.** Contents of REE (ppm) in hornblendites from clastolites in metaultrabasic bodies of the Ilmeny complex and in hornblendites from the Urals intrusive massifs

Element	Ilmeny complex							Urals intrusive massifs		
	233-3	261-6	933-1	211-1	211-5	211-6	211-12	Pe-926*	Pe-305*	Khb-1575*
La	17.9	26	17.4	71	44.8	38.9	62.2	18.2	1.6	6.8
Ce	38.7	110.5	41.2	169.9	113.9	89.7	153.1	50.9	5.8	24.2
Pr	5.7	19.1	5.9	20.7	15.9	12	16.3	7.5	1.2	3.8
Nd	28.5	113.5	26.4	89.3	71	49.2	68.8	36.8	7.9	16.9
Sm	9.0	38.1	5.4	19.1	20.2	9.4	14.3	8.9	2.6	4.7
Eu	4.8	7.1	2.5	3.2	5	2.2	2.9	2.7	0.9	1.4
Gd	12.1	40.5	5.1	22.4	22.7	7.9	15.4	8.6	2.8	4.8
Tb	2.1	6.9	0.9	3.7	4.4	1.1	2.6	0.9	0.5	0.8
Dy	14.4	42.9	5.3	24	28.9	5.8	16.8	4.9	3.3	4.2
Ho	2.9	8.3	1.1	4.5	6.2	1.1	3.6	0.9	0.7	1
Er	8.6	20.4	2.8	12.7	18.5	3.1	10.4	2.2	1.8	2.9
Tm	1.3	2.6	0.4	1.6	2.5	0.5	1.5	0.3	0.3	0.4
Yb	9.7	16.2	2.6	10.1	17.1	3.1	9.1	1.6	1.5	2.5
Lu	1.5	2.2	0.4	1.6	2.6	0.5	1.3	0.2	0.2	0.4
∑ REE	157.2	454.3	117.4	453.8	373.7	224.5	378.3	144.6	31.1	74.8
∑ LREE	104.6	314.3	98.8	373.2	270.8	201.4	317.6	125.0	20	57.8
∑ HREE	52.6	140	18.6	80.6	102.9	23.1	60.7	19.6	11.1	17
% LREE	66.5	69.2	84.2	82.2	72.5	89.7	84	86.4	64.3	77.3
% HREE	33.5	30.8	15.8	17.8	27.5	10.3	16	13.6	35.7	22.7
Eu/Eu*	1.4	0.55	1.43	0.47	0.71	0.78	0.6	0.94	1.02	0.9
(Gd/Yb) <sub>CN</sub>	1.01	2.02	1.62	1.79	1.07	2.06	1.37	4.35	1.51	1.55
(La/Sm) <sub>CN</sub>	1.24	0.43	1.99	2.32	1.39	2.58	2.72	1.28	0.38	0.9

Note. The ICP MS analyses of samples from clastolites in metaultrabasic bodies were carried out at the Mineralogical Institute, Miass (analysts K.A. Filipova and M.S. Svireenko). For sample description, see Table 5.

**Table 7.** Approximately estimated *P–T* conditions of formation of the Ilmeny zoisite gabbro

Sample	<i>P</i> , kbar			<i>T</i> , °C							
	a	b	c	d	e	f	g	h	i	j	k
84-A	12	12	12	480	550	545	540	665	750	890	–
84-1	12	12	12	525	490	630	550	890	–	–	–
293-5	8	8	8	550	735	600	790	665	–	–	710

Note. The compositions of coexisting minerals given in Table 2 were used. The temperatures were calculated from the average pressures. a, b, Amphibole geobarometers: a, (Hammarström and Zen, 1986); b, (Schmidt, 1991); c, average of a and b; d–h, garnet–amphibole geothermometer: d, (Perchuk, 1990); e, (Krogh Ravna, 2000); f, (Wells, 1979); g, (Powell, 1985); h, (Perchuk and Lavrent'eva, 1990); i–l, amphibole–plagioclase geothermometer: i, (Holland and Blundy, 1994); j, (Jaques et al., 1982); k, garnet–clinopyroxene geothermometer (Powell, 1985). Dash, not determined.

matic rocks. We have revealed a new type of rocks which can be enriched in REE (up to 250–1050 ppm, including Y and Sc). These are garnet–zoisite–anorthite gabbroids (slightly metamorphosed amphibole and pyroxene–amphibole–anorthite gabbro) and some hornblendites, including spinel-, apatite-, and olivine-containing ones. They have abnormally high contents of Al<sub>2</sub>O<sub>3</sub>, CaO, and MgO and extremely low contents of SiO<sub>2</sub> and underwent minor secondary alteration. In these features they differ considerably from the known mafic and ultramafic varieties of ophiolite asso-

ciations but are similar to rocks of layered intrusive massifs in the basement of ancient platforms. In the Urals, these rocks expose as isolated blocks in serpentinite melange plates in metamorphic strata and as metamorphosed blocks and lumps of the same melange in olistoliths in the aposedimentary matrix of the Late Paleozoic Urazbaevo olistostrome (Korinevsky, 2013). No other visible outcrops of such rocks are observed in the vicinity of these exposures. We think that the above exposed rocks are outliers of the ancient rocks of the Urals crustal base, which cropped out as a result

of protrusive squeezing-out of serpentinite masses. We have first established the important role of the Urals zoisite and clinozoisite as the main concentrators of REE in the discussed rocks. The well-known publications on REE geochemistry (Balashov, 1976; Sklyarov, 2001; Skublov, 2005; Lesnov, 2007) did not consider this issue. Only Hickmott et al. (1992) mentioned the leading role of zoisite in the accumulation of LREE and MREE. Note that they also observed such high REE contents in garnet amphibolites composing (like the Ilmeny amphibolites) lumps in melange. The data presented by Frei et al. (2004) for the Matabu sheet gabbroid bodies (Tanzania) indicate extremely low total contents of REE (0.47–0.49 ppm) in the hosted zoisite. Zoisites from eclogite blocks localized among the garnet mica schists of the Adula nappe in the Central Alps are poorer in the most widespread REE than the Ilmeny gabbroids ( $\Sigma(\text{Ce}, \text{Nd}, \text{Sm}) = 70\text{--}121$  ppm) (Zack et al., 2002). Only zoisites from the Weissenstein pegmatites (Germany) have REE contents close to those in the Ilmeny zoisites (767–1044 ppm) (Frei et al., 2004). This emphasizes the uniqueness of the studied Ilmeny REE gabbroids and hornblendites. Abundant zoisite-containing gabbroids in other areas of the Ural Fold Belt (Ufalei complex, framing of the Voikar–Syn'ya massif, etc.) should be studied with regard to our data for assessing their REE concentration capacity.

We thank V.A. Kotlyarov, K.A. Filippova, M.S. Svireenko, M.N. Malyarenok, T.V. Semenova, and Yu.F. Mel'nova for compositional chemical analyses of minerals and rocks.

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