=== **GEOCHEMISTRY** ===

The First Finding of Corundum in Exsolution Structures of Oxides in Gabbroic Rocks from the Polar Urals

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In the present-day geological structure of the Schuch'ya area in the Polar Urals, the ultramafic and dunite–wehrlite–clinopyroxenite complex (DWC) rocks of the Syumkeu massif (the northernmost ophiolitic massif of the Urals) give way eastward to amphibolites and gabbroic rocks of the Malyko–Kharampe Complex (Fig. 1). These rocks belong to the tholeiitic series crystallized from the high-alumina melt. The melt was formed in the backarc-basin setting under the influence of both hydrous fluids released from the subducted plate and the influx of aluminous sediments [1]. The high-alumina gabbroic rocks of the Malyko–Kharampe Complex contain aggregates of Fe–Ti–Al oxides as intergrowths of magnetite, ilmenite, hercynite, and corundum. The amounts of these aggregates occasionally reach economic concentrations. In general, corundum is infrequent in exsolution structures of oxides, and the mode of corundum occurrence described below has been found for the first time in gabbroic rocks from the Polar Urals. The phases that make up the intergrowths were identified with a microprobe, and their compositions are presented in the table.

As follows from experiments on crystallization of basic rocks, the mutual intergrowths are a result of exsolution of the initially homogeneous Ti–Al–Fe oxide solid solution of protospinel composition [4, 6]. The exsolution gives rise to several specific features of oxide aggregates revealed in the studied samples [2].

The magnetite includes ilmenite ingrowths of a number of varieties. The first variety is characterized by parallel and crosscutting thin (6–25 μm) lamellas oriented along planes (111) of the primary protospinel (Fig. 2a). Plates of ilmenite ranging from 25–50 to 80–100 μm in thickness occur as layers, commonly 2–3 plates within a grain (Fig. 2b). In turn, the tiny segregations of hercynite and, to a lesser extent, corundum are observable within ilmenite. Both minerals are confined most frequently to the boundaries between the ilmenite lamellas or grains and host magnetite. Their dimensions are 2–4 μm in isometric sections and 10–15 μm in elongated sections (Fig. 2).

Another structural variety of ilmenite phase is represented by relatively large euhedral and subhedral grains incorporated into the magnetite matrix (Figs. 2e, 2f). Ilmenite of this type also contain either oblong or nearly isometric (in plan view) hercynite Sp_1 and corundum ingrowths. The fine (up to 6–10 μm) segregations of "ferropseudobrookite" have been found within ilmenite in some samples (Fig. 2e).

The magnetite matrix contains a network of fine, mutually perpendicular needles of hercynite Sp_2, 0.1–10 μm in size, oriented parallel to crystallographic planes (100) of the primary protospinel. These needles are commonly discordant relative to the direction of ilmenite lamellas (Figs. 2c, 2d).

The previously unknown corundum segregations within ilmenite (occasionally in appreciable amounts) are the most interesting from the mineralogical point of view. The aforementioned structural features allowed us to trace the formation of oxide phases in the course of subsolidus cooling and to estimate the thermal history of rocks in qualitative terms.

In our view, the first stage is characterized by the formation of ilmenite lamellas along planes (111) within spinel matrix. Such exsolution is a result of oxidation in solid state [3]. The lamellas and larger grains of ilmenite as products of oxi-exsolution of the Ti–Al–Fe protospinel is very typical of oxides from the Malyko–Kharampe Complex (Fig. 2).

The second stage likely consists of the formation of hercynite Sp_1 and corundum along the margins of ilmenite lamellas and grains and occasionally within them. One may suggest that hercynite Sp_1 and corundum were formed simultaneously with ilmenite. Never-

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Fig. 1. Geological scheme of the Syumkeu –Shchuch'ya area. Based on original data and materials reported by V.N. Okhotnikov, M.N. Kostyukhin, D.N. Remizov, A.K. Afanas'ev, V.N. Voronov, and S.N. Pchelintsev. Western Megazone: (*1*) Late Precambrian metamorphic sequences of the Nyarope–Kharbei zone; Eastern Megazone: (*2–6*) Syumkeu subzone: (*2, 3*) Syumkeu ultramafics–pyroxenite complex, (*4*) Malyko–Kharampe gabbroic and metagabbroic rock complex, (*5*) Yanganape volcanosedimentary sequence, (*6*) Yun'yakha gabbro–granodiorite–granite complex; Shchuch'ya subzone: (*7*) Maslo gabbroic complex, (*8–10*) volcanosedimentary and carbonate sequences, (*11*) Yurmenek biotite gabbro complex, (*12*) granodiorite and granite; (*13*) Mesozoic and Cenozoic sedimentary cover; (*14, 15*) faults.

theless, we recognize a separate late stage of their formation in order to work up the general sequence. "Ferropseudobrookite" (conditionally named after its composition) associated with the aforementioned hercynite and corundum within ilmenite (Fig. 2e) has also been referred to this stage.

The third stage is characterized by development of a network of acicular hercynite Sp_2 in the magnetite matrix (Figs. 2c, 2d) as a result of exsolution of the Al–Fe solid solution depleted in titanium by that moment.

The separation of ilmenite phase from the primary Ti–Al–Fe oxide solid solution is a consequence of

increasing oxygen fugacity at the stage of subsolidus cooling [3]. The coexistence of ilmenite, hercynite Sp_1, corundum, and ferropseudobrookite testifies to the simultaneous formation of the minerals listed above. The phase relations in this system might be described as follows. The mixture of iron and aluminum oxides is not a simple binary system. Therefore, their relationships are more complex. Spinel and corundum show a restricted mutual solubility in solid state due to differences in crystal structures. Hence, the phase diagram has asymmetric solvus. Moreover, the experimental results have shown that solubility of Al_2O_3 in $MgAl_2O_4$

Chemical compositions of oxides from gabbroic rocks of the Malyko–Kharampe Complex, wt %

Compo-nent	Mt			Il			Sp₁		Sp	Fpbr		Cor	
SiO₂	0.38	0.31	0.46	0.47	0.36	0.02	0.25	0.00	0.11	0.20	0.27	0.31	0.17
TiO₂	0.58	2.04	1.84	51.09	51.59	51.21	0.44	1.05	1.75	75.04	69.67	0.08	0.07
Al₂O₃	1.12	0.99	1.20	0.05	0.00	0.00	59.60	59.45	56.94	0.90	0.25	93.14	95.89
Cr₂O₃	0.37	0.00	0.17	0.32	0.17	0.03	0.98	1.08	2.39	0.03	0.00	1.20	0.40
FeO*	89.07	89.12	88.68	45.09	44.55	44.01	26.36	27.93	24.73	20.25	26.57	2.03	1.84
MnO	0.18	0.27	0.07	1.82	3.19	3.58	0.35	0.16	0.49	0.27	0.00	0.13	0.00
MgO	0.00	0.00	0.00	0.16	0.09	0.09	9.62	9.13	10.05	0.23	0.07	0.01	0.17
V₂O₃	1.10	0.84	0.68	0.00	0.04	0.04	0.13	0.16	0.09	0.10	0.43	0.13	0.22
ZnO	0.00	0.00	0.00	0.00	0.00	0.00	1.37	2.75	1.81	0.06	0.00	0.13	0.00
Total	92.80	93.57	93.10	99.00	99.99	98.98	99.10	101.71	98.36	97.08	97.26	97.16	98.76
Formula coefficients													
Si	0.015	0.012	0.018	0.012	0.009	0.001	0.007	0.000	0.003	0.008	0.011	0.005	0.003
Ti	0.017	0.059	0.053	0.983	0.982	0.981	0.009	0.021	0.037	2.121	2.037	0.001	0.001
Al	0.051	0.045	0.054	0.001	0.000	0.000	1.930	1.902	1.865	0.040	0.012	1.940	1.957
Cr	0.011	0.000	0.005	0.006	0.003	0.001	0.021	0.023	0.053	0.001	0.000	0.017	0.005
Fe³⁺	1.773	1.737	1.736	0.026	0.033	0.038	0.030	0.050	0.041	0.000	0.000	0.030	0.027
Fe²⁺	1.093	1.109	1.110	0.937	0.909	0.899	0.575	0.584	0.534	0.637	0.864	0.000	0.000
Mn	0.006	0.009	0.002	0.039	0.068	0.077	0.008	0.004	0.012	0.009	0.000	0.002	0.000
Mg	0.000	0.000	0.000	0.006	0.003	0.003	0.394	0.369	0.416	0.013	0.004	0.000	0.004
V³⁺	0.034	0.026	0.021	0.000	0.001	0.001	0.002	0.003	0.002	0.003	0.013	0.002	0.003
Zn	0.000	0.000	0.000	0.000	0.000	0.000	0.028	0.055	0.037	0.002	0.000	0.002	0.000

Note: Measurements were carried out on a CamScan MV2300 SEM equipped with a Link INCA energy-dispersive X-ray microprobe at the Institute of Experimental Mineralogy; accelerating voltage is 15 kV; pure elements, synthetic oxides, and silicates were used as standards; (FeO*) total iron; (Mt) magnetite (areas with fine dissemination of exsolved spinel were measured); (Il) ilmenite (large lamellas within magnetite); (Sp₁) hercynite (segregations within ilmenite); (Fpbr) ferropseudobrookite FeTi₂O₅ (segregations within ilmenite); (Cor) corundum (small grains within ilmenite).

drastically decreases with pressure [10]. This is crucial for our case, because separation of corundum serves as indirect evidence for a rather high pressure during the formation of gabbroic rocks of the Malyko–Kharampe Complex. In light of experimental data on the equilibrium of magnetite with hematite and corundum [7], the gap in solubility between Fe_2O_3 and Al_2O_3 appears below 1318°C.

The stability of ferropseudobrookite $FeTi_2O_5$ at a high temperature and under reducing conditions in the equilibrium with spinel, corundum, and ilmenite in the presence of melt has been confirmed by experiments. It has also been shown that addition of Al_2O_3 to the FeO–TiO_2 mixture promotes the formation of spinel and ferropseudobrookite in neighborhood with ilmenite [7]. Ferropseudobrookite as a self-dependent phase is stable within a narrow temperature range and this phase becomes instable already at 1140°C [5]. Thus, the oxides that bear ferropseudobrookite phase were quenched above this temperature.

The exsolution of hercynite Sp_2 from the Ti-depleted Al–Fe solid solution after oxi-exsolution of ilmenite from the same matrix is also a result of reactions during the cooling. Because the mixture of magnetite, ulvöspinel, and hercynite is a complex compound, a number of spinel solvuses should be kept in mind. According to the experimental data, a maximum temperature of 1450°C is noted for the ulvöspinel–hercynite pair, whereas a minimum temperature of 500°C has been established for the magnetite–ulvöspinel pair [4, 6]. A gap in solubility between magnetite and hercynite was recorded below 900°C [9]. In other words, the temperature of exsolution depends on the bulk Ti content and may be equal to or even higher than 1000°C for intermediate compositions between the homogeneous magnetite–ulvöspinel solid solution and hercynite. The separation of fine needles of hercynite Sp_2 in the studied samples most likely occurred at such a high-temperature level.

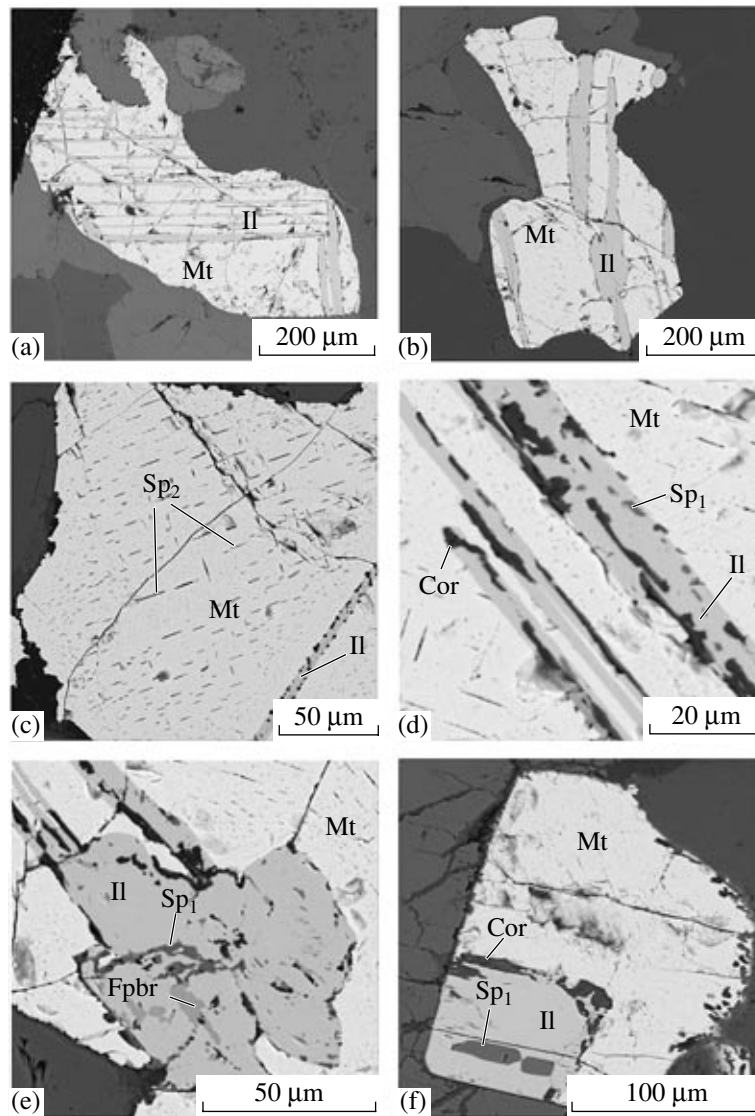The sequence of oxide solid solution breakdown and the composition of phases formed in this process bear

Fig. 2. Exsolution structures in oxides from gabbroic rocks of the Malyko–Kharampe Complex (back-scattered electron images). (Mt) magnetite, (Il) ilmenite, (Sp$_1$) hercynite, (Cor) corundum, (Fpbr) ferropseudobrookite. The network of tiny acicular segregations within the magnetite matrix is hercynite (Sp$_2$).

information on the thermal history of rocks. The critical temperatures estimated from structures and phases that arise owing to exsolution of Ti–Al–Fe protospinel allow specifying the initial temperature of crystallization of gabbroic rocks. At the same time, the temperature calculated from orthopyroxene–clinopyroxene pairs is hardly related to the crystallization of rocks, but this temperature eventually records the subsolidus cooling of pyroxenes and termination of cation exchange within and between the grains.

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