

Supplementary 1

RESEARCH METHODS

The chemical composition of the rocks was determined at the Center for Collective Use of the Institute of Geology, Mineralogy, and Geochemistry of the Russian Academy of Sciences by research fellow A.I. Yakushev.

The concentration of rock-forming and individual impurity elements in the samples was determined by X-ray fluorescence analysis (XRF) using a sequential vacuum spectrometer (with wavelength dispersion), model Axios The mAX spectrometer is manufactured by PANalytical (Netherlands, 2012, www.panalytical.com). The spectrometer is equipped with a 4 kW X-ray tube with a Rh-anode. The maximum tube voltage is 60 kV, and the maximum anode current is 160 mA. Industry and national standard samples of rock chemical composition were used for calibration.

The analysis was performed using Method 439-RS NSAM VIMS, which yields results of Category III quantitative analysis accuracy according to OST RF 41-08-205-04. This accuracy category is used for mass analysis of mineral samples, control analysis, and mineral resource estimation.

Samples dried at 110°C were prepared for measurements in the spectrometer as follows.

High-speed melting of the sample material in an induction furnace with lithium borates at 1200°C resulted in melt homogenization. The resulting melt formed glassy disks, which were analyzed in a spectrometer. To prevent the sulfide sulfur from burning off, ammonium nitrate was added to the batch before melting.

Loss on ignition was determined gravimetrically at 1000°C. If sulfur was present in the samples in sulfide form, it partially burned out, increasing the LOI value.

The total iron content in the samples was determined as Fe₂O₃ total, regardless of the actual valence state, which is a feature of the analysis method used.

The analysis of microelements in silicate samples was carried out at the Center for Collective Use of the Institute of Geology, Mineralogy, and Geochemistry of the Russian Academy of Sciences by Doctor of Geological and Mineralogical Sciences D.V. Kovalenko.

The samples were opened using the acid digestion method in a MULTIWAVE microwave oven [Anton Paar [GmbH, Graz, Austria, 1998]. A 50–100 mg sample was decomposed in a Teflon capsule in a mixture of hydrofluoric and nitric acids at a temperature of 260°C and a pressure of no more than 72 bar for 50 minutes. Metal fluorides were destroyed by evaporating the dry sample residue in 5–7 ml of 6.2 N hydrochloric acid at a temperature of 90°C for 1 hour. Then, the internal standard (In) and 3 ml of 3 N nitric acid were added to the sample. Within 15–20 minutes at a temperature of about 200°C, chlorides were completely converted to nitrates. The final nitric acid

concentration was 0.5 N, and the sample dilution factor was approximately 1000. The method ensured complete decomposition of most igneous, metamorphic, and sedimentary rocks, including the difficult-to-discover minerals they contain (zircon, monazite, etc.). Exceptions could be made for rocks with a high organic content and spinels. A corresponding version of the method has been developed for rocks with a high organic content, while reliable analysis of spinels using the acid decomposition method is apparently impossible (therefore, the method does not allow for the accurate and reliable determination of chromium in the presence of chromite in the rocks). All acids used were double-distilled in a quartz (Teflon – for hydrofluoric acid) apparatus from starting reagents of chemically pure or extra-pure grade.

Mass spectrometric analysis on the Elan 6100 DRC [ELAN 6100 DRC, Software Kit, May 2000, PerkinElver SCIEX instrument] was carried out in standard mode with the following parameters:

Argon atomizing flow	91–93 l/min
Auxiliary argon flow	1.17 l/min
Plasma-forming argon flows	15 l/min
Plasma generator power	1270–1300 W
The voltage on the detector in counting mode is	1000 V

The instrument's sensitivity was calibrated across the entire mass scale using standard solutions containing all the elements analyzed in the samples. Indium was used as an internal standard. The performance of the device was also assessed by periodic measurements of element concentrations in standard ICP-MS-68A (Al, As, Ba, Be, Bi, B, Cd, Ca, Ce, Cs, Cr, Co, Cu, Dy, Er, Eu, Gd, Ga, Ho, In, Fe, La, Pb, Li, Lu, Mg, Mn, Nd, Ni, P, K, Pr, Re, Rb, Sm, Sc, Se, Na, Sr, Tb, Tl, Th, Tm, U, V, Yt, Y, Zn) – 10 mg/l and ICP-MS-68B (Sb, Ge, Hf, Mo, Nb, Si, Ag, Ta, Te, Sn, Ti, W, Zr) – 10 mg/l. Corrections were introduced where necessary. To control the quality of measurements and take into account the drift of the instrument's sensitivity, sample analyses were alternated with analyses of a standard sample with a frequency of 1:5–1:10. An in-house certified rock sample, decomposed according to the same method as the real samples, was used as a standard sample. The quality of sample preparation was assessed using rock standards: andesite (AGV-2), basalt (BIR-1a, BHVO-2), granodiorite (GSP-2). The detection limits (DL) of elements ranged from 1–5 mg/t for heavy and medium-weight elements (uranium, thorium, REE, etc.) with an increase to 20–50 mg/t for light elements (beryllium, scandium, etc.). The accuracy of the analysis was 3–10 rel. % for element concentrations greater than 20–50 DL. The content of Nb, Zr, Th obtained by the ICP-MS method was controlled based on the results of X-ray fluorescence analysis.

The relationships and composition of rock-forming and ore minerals were studied using a JSM-5610LV scanning electron microscope with an Ultim-Max-100 SDD detector and AZtec 5.1 Oxford software package. The following parameters were used: W-cathode voltage of 20 kV, spectrum acquisition in a standard experiment up to 1 million pulses. Energy calibration was performed using metallic cobalt. Reference was made to the following metals and synthetic standards: Al₂O₃ (Al, K-series), wollastonite CaSiO₃ (Ca, K-series), CePO₄ (Ce, L-series), KCl (Cl, K-series), DyPO₄ (Dy, L-series), ErPO₄ (Er, L-series), BaF₂ (F, K-series), FeS₂ (Fe, K-series), Hf (Hf, L-series), GdPO₄ (Gd, L-series), KBr (K, K-series), LaPO₄ (La, L-series), MgO (Mg, K-series), Mn (Mn, K-series), Nakafit Na₂CaPO₄F (Na, K-series; P, K-series), Nb (Nb, L-series), NdPO₄ (Nd, L-series), PbTe (Pb, L-series), Rb (v) (Rb, L-series), SiO₂ (Si, K-series), SmPO₄ (Sm, L-series), SrF₂ (Sr, L-series), Ta (Ta, L-series), ThO₂ (Th, M-series), Ti (Ti, K-series), U (U, M-series), W (W, L-series), Y₃Al₅O₁₂ (Y, L-series), YbPO₄ (Yb, L-series), Zn (Zn, K-series), Zr (Zr, L-series). The standard deviation of the content determination of most elements did not exceed 0.3 wt %.

REFERENCES

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Table 1. Standard deviations (rel.%) of the results X-ray fluorescence analysis performed using category III methods

Interval contents	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	K ₂ O	CaO	TiO ₂	MnO	Fe ₂ O ₃ tot	P ₂ O ₅	LOI*
60–100			1.1	0.7					0.7		
50–60		1.4	1.2	0.8		1.2	0.8	0.8	0.8		
40–50		1.7	1.6	1.0		1.4	1.0	0.9	0.9		0.9
30–40		1.8	2.1	1.3		1.8	1.2	1.1	1.1	1.1	1.1
20–30		2.5	2.8	1.9		2.1	1.5	1.4	1.4	1.6	1.4
10–20	3.5	3.4	3.5	3.2	3.5	3.2	2.1	2.1	2.1	2.7	2.1
5–10	5.4	4.6	5.4	5.0	5.4	5.0	3.5	4.3	4.3	3.2	3.5
2–5	8.0	6.5	8.0	6.8	8.0	6.8	5.4	7.0	7.0	5.0	5.4
1–2	10.0	9.0	11.0	9.3	10.0	9.3	7.0	10.0	10.0	4.3	7.0
0.5–1	12.0	13.0	15.0	12.0	12.0	12.0	9.0	13.0	13.0	6.0	9.0
0.2–0.5	16.0	16.0	20.0	17.0	16.0	17.0	11.0	17.0	17.0	8.2	11.0
0.1–0.2	20.0	21.0	25.0	21.0	20.0	21.0	14.0	21.0	21.0	9.3	
0.05–0.1	24.0	27.0	28.0	27.0	24.0	27.0	18.0	25.0	25.0	12.0	
0.02–0.05	28.0	30.0	30.0	30.0	28.0	30.0	21.0	28.0	28.0	16.0	
0.01–0.02	30.0	30.0	30.0	30.0	30.0	30.0	27.0	30.0	30.0	21.0	
0.005–0.01						30.0	29.0	30.0	30.0	24.0	
0.002–0.005							30.0	30.0		25.0	
0.001–0.002								30.0			