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GEOLOGY

Anomalous Light Oxygen Isotope Composition in Minerals of Corundum-Bearing Rocks in Northern Karelia

S. V. Vysotskii, A. V. Ignat'ev, V. V. Yakovenko, and A. A. Karabtsov

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The oxygen isotope composition of genetically related minerals is known to form a compact common field of values, the area of which depends only on variations in physicochemical parameters of the mineral-forming medium. After a mineral has formed, the oxygen isotope composition does not change only if the mineral has not been transformed completely as a result of melting, chemical replacement, or other such reactions changing the primary structure. Therefore, the oxygen isotope composition has long served as an indicator of specific conditions for the formation both of minerals and rocks in general.

We have studied samples of corundum-bearing garnet–amphibole–phlogopite plagiogneiss of the Proterozoic age from the Chupa Sequence of the Belomorian Complex of the Khitostrov deposit (Fig. 1).

The oxygen isotope analysis was carried out in the Far East Geological Institute, Far East Division, Russian Academy of Sciences. Oxygen was extracted when a sample was heated with the help of an infrared laser (10.6 μm) in the presence of BrF_3 (~210 torr). After fluoridation, the extracted oxygen was purified in two cryogenic traps with liquid nitrogen and in an absorber with KBr. Then it was analyzed in a mass-spectrometer with dual exhaust system MAT-252. The procedure has been tested by international (NBS = 28) and domestic standards. The measurement accuracy made up not less than ±0.2‰ for $\delta^{18}O$.

A series of corundum occurrences is known within the Chupa Sequence of the Belomorian Complex [1–3]. Some of the occurrences (Khitostrov, Varatskoe, Height 128, etc.) are confined to kyanite–garnet–biotite plagiogneiss, while others (Dyadina Gora, Kulezhma, etc.) are related to amphibolites and amphibole schists. It is believed [1, 4] that all corundum occurrences are structurally related to overthrusts and their composition depends on the site of corundum-bearing occurrences in thrust nappes. Two viewpoints are available on the genesis of corundum-bearing rocks of northern Karelia. According to the first viewpoint, corundum mineralization is thought to be the product of regional metamorphism [3, 5]. According to the second viewpoint, which dominates at present, corundum-bearing rocks formed as the result of metasomatosis under the effect of fluid infiltration, though the process could proceed both during the main stage of regional metamorphism [1] and after it as a separate, superimposed stage [2].

We have analyzed garnet–amphibole–phlogopite plagiogneiss with well-cut crystals of crimson–pink corundum (as long as 1.5 cm, Fig. 2). It should be noted that despite the intense color of corundum, the chromium content in it is below the analysis sensitivity

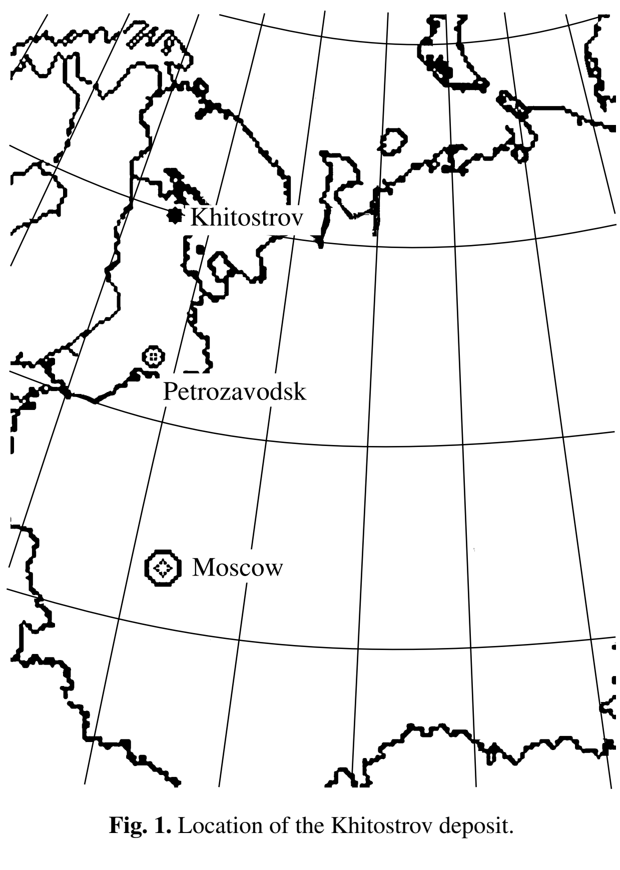

Fig. 1. Location of the Khitostrov deposit.

Far East Geological Institute, Far East Division, Russian Academy of Sciences (DVGI FED RAS), pr. Stoletiya Vladivostoka 159, Vladivostok, 660022 Russia

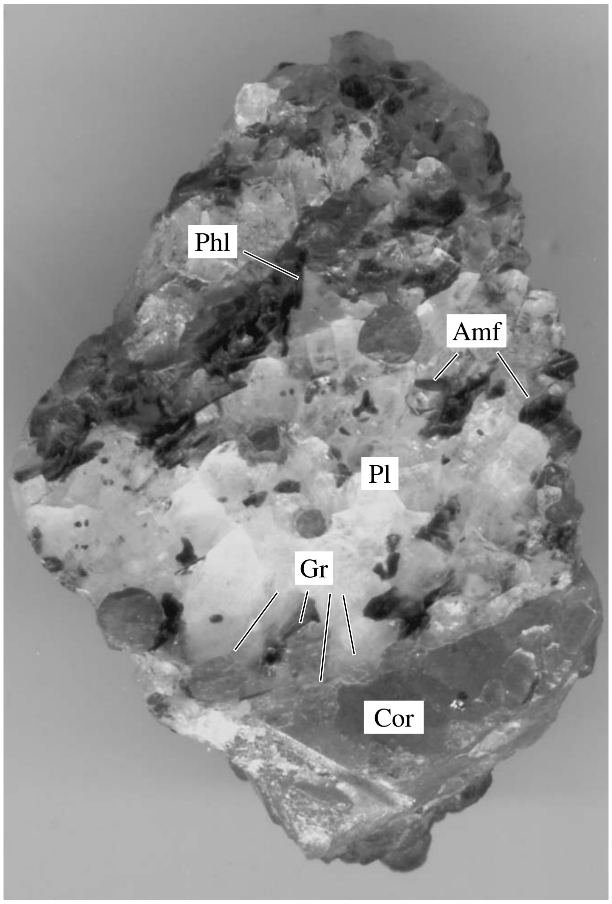

Fig. 2. Corundum-bearing garnet–amphibole–phlogopite plagiogneiss. Sample size 25 × 15 mm. Corundum size 15 × 6 mm. (Cor) corundum, (Gar) garnet, (Pl) plagioclase, (Amf) amphibole, (Phl) phlogopite. Repr. 4/5.

(0.02 wt %). We have revealed amidst trace elements only insignificant contents of iron and traces of titanium (Table 1). The main rock mass is composed of crystals of acid ($An_{24–25}$) plagioclase, hornblende (f = 39–41), and phlogopite (f = 27–28) (see Table 1). Rounded crystals of almandine (f = 62–65) are irregularly disseminated in rock and sometimes concentrated near corundum, and comprise inclusions of acid ($An_{28–32}$) plagioclase, apatite, and phlogopite (Fig. 3a). Found amidst accessory minerals were ilmenite, apatite, orthite, and zircon. Secondary alterations are represented by hydromica and chlorite, which replace amphibole (Fig. 3b).

P–T conditions for crystallization of the studied rocks can be assessed with a great approximation. Based on garnet–amphibole geothermometers [6], the formation temperature varies within 670–740°C, which is slightly higher than the interval of temperatures (650–700°C) established by Serebryakov and Aristov [2] for analogous rocks. Preliminary computations of formation conditions for corundum-bearing rocks on the basis of the method of thermodynamic potential minimization with the help of the software complex "Selector-C" [7] showed that the temperature should be not less than 720°C and the pressure not lower than 10 kbar. It is only under such conditions that the set and compositions of calculated minerals correspond to natural ones.

The results of oxygen isotope ratios measured are presented in Table 2. All the minerals analyzed exhibit anomalously low (–15.5…–26‰ $\delta^{18}O$ values, which is 10–15‰ less than values cited previously for corundum from this deposit [10]. The isotopic compositions of minerals in the association differ from 3 to 10‰, which is indicative of the absence of isotopic equilibrium. At the same time, minerals are in thermodynamic equilibrium as evidenced by the absence of reactive relationships between them (Fig. 3).

Similar or even lower $\delta^{18}O$ values are known only for ice and thawed glacial water of Greenland and Antarctica. It should be noted that lower but not negative $\delta^{18}O$ values were reported for corundum-bearing rocks and minerals previously as well [8, 9], and it was related to the effect of meteoric water. Hence, it is

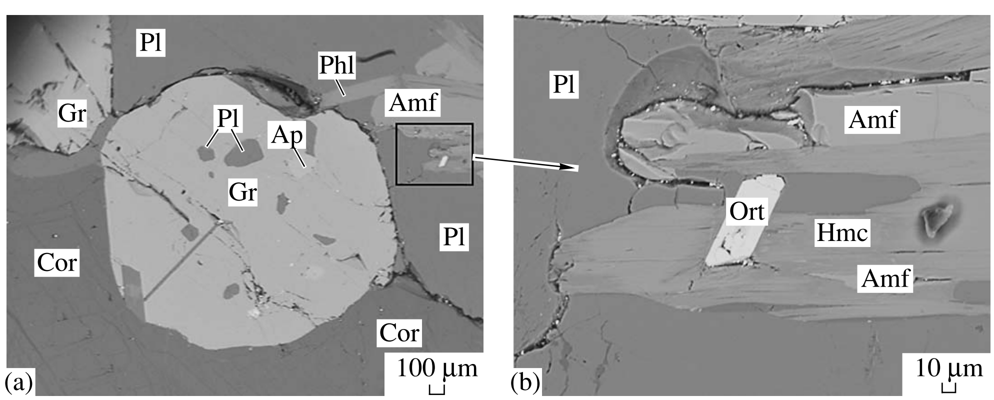

Fig. 3. Relationships between main minerals of corundum-bearing plagiogneiss. Photo in reflected electrons, microanalyzer JXA-8100. Absence of reactive relationships between coexisting minerals indicates that they were in the equilibrium position at the moment of formation. Hydromica (Hmc) partially replacing hornblende (Amf) marks a later stage of low-temperature metamorphism.

Table 1. Chemical composition of minerals of corundum-bearing garnet–amphibole–phlogopite plagiogneiss

Component	Corundum		Garnet		Plagioclase			Phlogopite		Hornblende			
			center	edge	edge	center	edge						
SiO_2	–	–	39.11	39.20	62.62	62.19	62.03	36.74	36.80	41.05	41.17	41.09	40.73
TiO_2	0.02	0.02	–	–	–	–	–	1.69	1.90	1.21	1.37	1.03	1.00
Al_2O_3	98.98	99.37	21.97	21.98	23.87	23.77	23.83	17.87	18.52	17.83	18.08	17.92	18.21
FeO	0.15	0.34	26.61	27.95	–	–	–	12.26	10.90	12.88	13.29	13.35	12.30
MgO	0.08	0.06	8.99	8.44	–	–	–	18.12	15.63	10.47	10.88	10.70	10.66
CaO	–	–	3.57	3.40	5.07	4.95	5.25	–	–	9.87	9.06	9.28	9.20
Na_2O	–	–	–	–	8.74	8.72	8.65	0.87	1.61	2.70	2.86	2.91	2.80
K_2O	–	–	–	–	–	–	–	4.66	7.37	0.19	0.18	0.21	0.28
F	–	–	–	–	–	–	–	–	–	0.71	–	–	0.82
Cl	–	–	–	–	–	–	–	–	–	0.05	0.01	0.07	0.03
Cr_2O_3	–	–	–	–	–	–	–	–	–	0.32	0.26	–	–
V	–	–	–	–	–	–	–	–	–	–	–	0.33	0.36
Sum	99.23	99.8	100.25	100.97	100.30	99.63	99.76	92.21	92.73	97.28	97.16	96.89	96.39
f, (An)			62.39	64.99	(24)	(24)	(25)	27.49	28.10	40.81	40.64	41.15	39.27

Note: Analyses of minerals were carried out at the Far East Geological Institute, Far East Division, Russian Academy of Sciences on the X-ray microanalyzer JXA-8100. A dash designates values below the threshold of detectability, $f = Fe_{tot}/(Fe_{tot} + Mg_{tot})$, at %.

beyond question that corundum-bearing rocks of the Khitostrov deposits exhibit an anomalous light oxygen isotope composition that is indicative of very specific formation conditions for them.

The analysis of the materials suggests that it is only exchange processes between the rock under transformation and the water fluid that could yield such oxygen isotope ratios in minerals. It is only thawed glacial waters that could possess enough potential for the formation of such fluid. We think that there are two scenarios conceivable for the formation of such an anomaly.

1. If corundum-bearing rocks are the result of regional metamorphism, then extremely low $\delta^{18}O$ values in minerals are indicative of the protolith oxygen isotope ratios remaining in them and a premetamorphic exchange with meteoric, thawed glacial waters. Taking into account data on oxygen isotopy in ice of Antarctica and Greenland where still lower ratios were registered, such a process is quite possible. For instance, P. Aharon [11] showed that Quaternary carbonaceous sediments of Antarctica deposited from thawed glacial water exhibit $\delta^{18}O$ values within the range of –14.1…–17.3‰ relative to SMOW. In this case, the calculated value of the oxygen isotope composition ($\delta^{18}O$) in thawed glacial water varies within the range of –47.2…–50.3‰.

Table 2. Oxygen isotope composition of minerals of corundum-bearing rocks in Karelia, the Khitostrov deposit

Sample no.	Mineral	$\delta^{18}O$ (SMOW), ‰
KP-1	Garnet	–26.0
		–26.4
		–25.7
	Plagioclase	–19.9
	Phlogopite	–15.5
KP-2	Garnet	–25.7
	Corundum	–22.5
	Plagioclase	–21.4

It seems plausible that part of alumina gneiss, the age of which was determined at 2.8–2.65 Ga [12], could be generated from sedimentary rocks deposited in one of the early glacial epochs, the epoch preceding the Huronian Glaciation, the peak of which was 2.3 Ga and lasted several hundred million years [13]. These were most likely local complexes since the anomalous light oxygen isotope composition has thus far been established in only one deposit.

2. According to the metasomatic concept of corundum-bearing rock formation, the anomaly is the result of isotopic exchange in the infiltration of fluid, which exhibited an extremely light oxygen isotope composition. In this case we should also admit the presence of a considerable amount of thawed glacial water in the fluid. This seems quite possible taking into account the fact that corundum-bearing rocks are structurally related to gently sloping tectonic zones (overthrusts), which are permeable for groundwater and serve as reservoirs for migration of mineralized water in the Earth's crust at considerable depths. Such watered horizons were penetrated by the Kola Superdeep Borehole at depths down to 9 km, and these horizons are registered

at a greater depth by geophysical data [14]. Moreover, despite high mineralization, present-day groundwater of Scandinavia exhibits a low oxygen isotope composition ($\delta^{18}O = -13‰$) even at depths exceeding 1 km [15].

As the formation temperature for corundum-bearing rocks is rather high (720–740°C), exchange processes had to proceed rather fast, which predetermined a high rate of a change in the oxygen isotope composition in the fluid. In case of the metasomatic genesis of corundum-bearing rocks, we observe a continuous change in oxygen isotope values in rocks and minerals along the metasomatic column in the direction of fluid migration. If we deal with the result of regional metamorphism and premetamorphic exchange with thawed glacial water, then here we should expect a sharp gradient of oxygen isotope values at the boundary between protoliths of different genesis.

Judging from the fragmentary data available, variations in the oxygen isotope composition in minerals of the Khitostrov deposit are marked with confidence, although it is difficult to say now what process they are marking. In any case, we are dealing with a unique case and still the only region in the world where such an isotopic anomaly has been revealed.

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