ISSN 1028-334X, Doklady Earth Sciences, 2011, Vol. 439, Part 1, pp. 964–966. © Pleiades Publishing, Ltd., 2011.
Original Russian Text © S.V. Vysotskii, A.V. Ignat'ev, V.I. Levitskii, S.Yu. Budnitskii, T.A. Velivetskaya, 2011, published in Doklady Akademii Nauk, 2011, Vol. 439, No. 1, pp. 95–98.

GEOCHEMISTRY

New Data on Stable Isotopes in Minerals from Corundum-Bearing Formations of Northern Karelia (Russia)

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Presented by Academician A.I. Khanchuk December 20, 2010

Received January 12, 2011

DOI: 10.1134/S1028334X11070117

Rocks and minerals of the Earth are usually enriched in ^{18}O isotope in comparison with its concentration in modern seawater; i.e., they have positive $\delta^{18}O$ values. Most silicate rocks are characterized by $\delta^{18}O$ values from +4 to +15‰. Until recently, noble corundum and associating minerals did not often fall outside the limits of this range [1, 2]. The appearance of data on corundum of Northern Karelia strongly depleted in heavy oxygen isotope in comparison with SMOW [3–5] caused significant interest, since this suggests quite specific conditions of their formation.

Corundum occurrences in Northern Karelia at a small number of minerals are characterized by a wide diversity of textural and structural peculiarities. Variations of quantitative relationships, abundance of generations of mineral phases (garnet, amphibole, and plagioclase), and the presence of early corroded mineral relics in late newly formed assemblages are controlled by the zoned structure of the bodies and evolution of parageneses formed in a wide range of temperatures and pressures [6]. This paper contains the results of study of corundum-bearing rocks in their own and host plagiogneiss and amphibolite of the Khitostrovskoe and Varatskoe deposits in the Chupinskaya Series of the Belomorian Complex.

Methods of investigation. The isotope composition of oxygen and hydrogen was analyzed at the Far East Geological Institute, Far East Branch, Russian Academy of Sciences. Oxygen was extracted by sample heating using an IR laser (10.6 μm) in the presence of BrF_5 (~210 Torr). After fluorination extracted oxygen was purified on two cryogenic traps with liquid nitrogen and on an absorber with KBr. Then it was analyzed on a mass-spectrometer with the double leak-in system MAT-252. The methodology was tested on the international (NBS-28) and internal standards. The accuracy of $\delta^{18}O$ measurement was not less than ±0.2‰.

Hydrogen was extracted from OH-bearing minerals using a laser as well, which allowed us to reach reproducibility of ±2‰ for samples with a weight from 1 to 5 mg. The hydrogen isotope composition was determined in constant helium flow on a mass-spectrometer MAT-253. The developed method [7] is an alternative to the classic method of hydrogen extraction under vacuum conditions.

The K/Ar dating of the samples was performed by an original methodology worked out by the researchers of the Laboratory of Stable Isotopes, Far East Geological Institute, Far East Branch, Russian Academy of Sciences [8]. Extraction, collection, purification, and measurement of the argon isotope composition were performed in a continuous flow of ultrapure helium. A CO_2 laser (10.6 μm) was applied for argon extraction from samples. The argon isotope composition was measured on a MAT-253 mass spectrometer (Thermo Scientific). The concentration of potassium was analyzed by the method of atomic–emission spectrometry with inductively coupled plasma on an ICAP 6500Duo spectrometer (Thermo Scientific).

Geology. The Khitostrovskoe and Varatskoe occurrences are located ~15 km from each other, close to the Chupa settlement in the Loukhskii region of Karelia, and have similar geological structures. They are located in garnet–biotite plagiogneiss of the Chupinskaya Series in the permeable shift zones. Corundum-bearing rocks are observed as individual bodies, a system of subparallel or branching veins, segregations, and nests. Their thickness varies from 40–50 cm to 5–10 m, and the thickness of corundum-bearing rocks ranges from 1 to 50 cm (rarely up to 1.5 m).

Corundum occurrences have a complex geological structure and genesis; because of this, there are problems with the study of their age and origin. The datings of three generations of zircons were obtained by the Th–U–Pb SHRIMP method for the Khitostrovskoe occurrence: grain cores provided a concordant value of 2857 ± 30 Ma; intermediate rim, 2692 ± 68 Ma, by

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Table 1. Age datings of minerals from rocks of the Varatskoe and Khitostrovskoe corundum occurrences

Sample	Mineral	Potassium, %	Ar_{air}, %	Ar_{rad}, ppb	Age, Ma
Varatskoe deposit					
K-231/6	Biotite	6.22	0.7	1330	1824 ± 45
K-231/6	Amphibole	0.45	1.2	95.49	1811 ± 45
Khitostrovskoe deposit					
K-90/23	Biotite	5.13	1.0	1166	1895 ± 47
K-90/23	Amphibole	0.16	3.0	34.35	1814 ± 63

Note: $\lambda_k = 0.581 \times 10^{-10}$ and $\lambda_\beta = 4.962 \times 10^{-10}$ year^{-1} are applied for calculation.

the upper crossing of discordia; outer rims, 1894 ± 17 Ma [9]. Later I. Bindeman and coworkers [10] also conducted dating of zircons from corundum-bearing rocks of the Khitostrovskoe occurrence and the oxygen isotopes related to them: zircons with ancient ages (2.75–2.45 Ga) contained heavy oxygen ($\delta^{18}O$ in the range from +4 to +8‰), whereas younger zircons (1.9–1.8 Ga) contained light oxygen ($\delta^{18}O$ in the range from –23 to –27‰). These data provide evidence for the complex polycyclic mechanism of zircon formation, and the age obtained for its outer rims is consistent to the currently dominating ideas about the Svecofennian period of genesis of corundum occurrences.

We performed the K/Ar dating of coexisting minerals in two samples from the Khitostrovskoe and Varatskoe occurrences (Table 1). As is evident, our data are quite consistent with the Th–U–Pb datings.

Most corundum-bearing rocks are composed of mesocratic plagioclasite. These are corundum–biotite–garnet–amphibole varieties in the Khitostrovskoe occurrence (Samples KP-1 and K90/14) and garnet–corundum–kyanite–amphibole varieties in the Varatskoe occurrence (Sample K227/3). Inclusions in plagioclasite comprise melanocratic garnet amphibolite (Sample K152/1), garnet–pyroxene–plagioclase schist, kyanite–quartz, kyanite–corundum, quartz, monomineral garnet, and quartz–garnet rocks altered by low-temperature secondary processes to various degrees.

Garnet–biotite fine-granular banded plagiogneiss (Sample K-154/1) and garnet–pyroxene–plagioclase fine-granular schist (Sample K158) are the host rocks for this complex.

The results of measurements of the oxygen and hydrogen isotope ratios are given in Table 2. Most of the analyzed minerals are characterized by extremely low (from –15.5 to –23.7‰) $\delta^{18}O$ values.

Until recently, such $\delta^{18}O$ values were not known in rocks of the Earth. At the same time, these are not extraordinary for ice and snow–glacier water of Greenland and Antarctica; even lower (≤60‰) $\delta^{18}O$ values were registered in these regions [11]. It is necessary to mention that low, but not negative $\delta^{18}O$ values were previously registered for corundum-bearing rocks and minerals of Belomor'e; this was explained by the influence of waters of meteoric origin.

The considered facts provide evidence for the conclusion that corundum-bearing rocks of the Khitostrovskoe and Varatskoe occurrences were formed with participation of glacial waters. As this takes place, such waters do not need to be cool, as is suggested in [5]. Hydrotherms with a temperature of >100°C and $\delta^{18}O$ of ≤22‰ were recently discovered in Siberia, in the zone of the Baikal rift. The isotope composition of water corresponds to the position of the point on the global line of meteoric waters. Thus, having an extremely light oxygen isotope composition, corun-

Table 2. Isotope compositions of oxygen and hydrogen in minerals from corundum-bearing plagioclasite and host rocks of the corundum occurrences of Karelia

Sample	Mineral	$\delta^{18}O$, ‰ (SMOW)	δD, ‰ (SMOW)
Khitostrovskoe deposit			
KP-1	Chloritized biotite	–15.5	–77
K-90/14	Amphibole	–20.0	–215
K-90/14	Chloritized amphibole	–	–135
K-90/14	Plagioclase	–23.1	–
K-90/23	Amphibole	–21.4	–117
K-90/23	Plagioclase	–20.1	–
K-152/1	Chlorite after biotite	7.0	–43
K-152/1	Garnet	–23.7	–
K-154/1	Biotite	6.5	–75
K-158	Biotite	4.9	–86
Varatskoe deposit			
K-227/3	Amphibole	–19.9	–214
K-227/3	Plagioclase	–18.7	–
K-231/6	Amphibole	–19.6	–216
K-231/6	Plagioclase	–18.0	–

Note: Dash means that the compositions of oxygen and hydrogen were not analyzed.

dum-bearing rocks of Northern Karelia were undoubtedly formed under quite specific conditions.

The isotope composition of minerals from corundum-bearing plagioclasite, both hydrous and anhydrous, is light, strongly different from the composition of host schist and gneiss. The analysis of available materials demonstrates that exchange processes between transformed rock and hydrous fluid are the main processes that could result in such ratios of stable isotopes in minerals. Glacial waters have the potential for the formation of such a fluid. Considering the data on oxygen isotopes in ice of Antarctica and Greenland, where much lower ratios were registered, such a process is entirely possible. For example, as was demonstrated by P. Aron [12], Quaternary carbonate sediments of Antarctica deposited from glacial waters had $\delta^{18}O$ values in the range from –14.1 to –17.3‰ in relation to SMOW. In this case the calculated oxygen isotope ratio ($\delta^{18}O$) in thawing glacier water ranges from –47.2 to –50.3‰.

Another significant example is provided by the lightened oxygen isotope composition in secondary minerals and altered Holocene basalt of Iceland revealed by the deep drill holes. According to the data of [13], hydrothermally altered basalt has a $\delta^{18}O$ value of ≤10‰ in relation to SMOW, whereas the $\delta^{18}O$ values in secondary epidote range from –11.8 to –12.7‰. It is suggested that hydrothermal fluid contained meteoric waters, which had $\delta^{18}O$ values from –8 to –11‰ in Iceland [13]. Thermal waters of Sikhote-Alin' are characterized by $\delta^{18}O$ variations in the range from –10.8 to –18.8‰, whereas these values in hot thermal waters of the Baikal rift fall below –22‰ [14]. Thus, participation of glacial waters in the process of hydrothermal rock alterations in the zone of volcanic activity could result in the formation of metasomatites with an extremely light ratio of stable isotopes.

We suggest that the extremely low values of $\delta^{18}O$ and δD in minerals may provide evidence for preservation of the isotope ratios of oxygen and hydrogen from the protolith, as well as for premetamorphic exchange with glacial waters. Most likely Svecofennian aluminiferous corundum-bearing plagioclasite were formed after metasomatized Paleoproterozoic rocks from the shallow zone of the fumarole field beneath the glacier. Such fields are widely abundant in modern volcanic areas (for example, in Kamchatka or Iceland). The lightened oxygen and hydrogen isotope composition in all minerals of corundum occurrences provides evidence for complete transformation of the ancient Meso- and Neo-Archean substrates into low-temperature aluminiferous metasomatites in the Paleoproterozoic. This requires a quite large volume of water with a light isotope composition, and the hydrothermal cell should be active for a long time. Most likely, metasomatism occurred in the period of the ancient Huronian glaciations with the peak at 2.3 b. y. ago [15]. Subsequently these rocks underwent high-pressure Svecofennian (1.9–1.8 Ga) metamorphism.

Thus, it was established that minerals of corundum-bearing zones of the Khitostrovskoe and Varatskoe deposits of Northern Karelia were characterized by the lowermost values of $\delta^{18}O$ (≤26‰) and δD (≤215‰) providing evidence for participation of glacial waters in the mineral-forming fluid and for preservation of oxygen and hydrogen isotope ratios from the protolith.

ACKNOWLEDGMENTS

This study was supported by the Russian Foundation for Basic Research (project no. 10-05-00371-a).

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