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Geochemistry of Stable Oxygen and Hydrogen Isotopes in Minerals and Corundum-Bearing Rocks in Northern Karelia as an Indicator of Their Unusual Genesis

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Abstract—The paper presents newly obtained data on the oxygen and hydrogen isotopic composition of minerals in corundum occurrences and their host rocks in northern Karelia. Minerals in the Khitoostrov and Varaka corundum-bearing zones have extremely low $\delta^{18}O$ (lower than –26‰) and δ D (lower than –215‰), which suggest that the mineral-forming process involved glacial waters and that the minerals preserve the isotopic ratios of their protolith. Aluminous corundum plagioclasites were produced by high-pressure Svecofennian (1.9–1.8 Ga) metamorphism of Paleoproterozoic rocks that had been metasomatized with the involvement of meteoric waters during the Guronian glaciation epoch.

Keywords: stable isotopes, oxygen, hydrogen, isotopic dating, corundum, Khitoostrov, Varatskoye, Karelia

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INTRODUCTION

Terrestrial rocks and minerals are usually enriched in the ^{18}O isotope relative to seawater, i.e., have positive $\delta^{18}O$ values, which lie within the range of +4 to +15‰ relative to SMOW for most silicate rocks [1]. However, several sites are currently known worldwide where this regularity is disturbed and the $\delta^{18}O$ SMOW of the rocks and minerals are anomalously lower than the typical magmatic values (≪5‰). For example, propylitized Cenozoic basalts, hyaloclastic rocks, and rhyolites in Iceland locally have anomalously low values of $\delta^{18}O$ (as low as –13‰ in the epidote) and δD (as low as –125‰ in the epidote) in fault zones in combination with a mild decrease (by as little as a few permille) in these parameters of large lava volumes (dozens of cubic kilometers) relative to their mantle values [2–4]. The local anomalies are reportedly explained by direct influence of meteoric waters, which are involved in the hydrothermal circulation to depth of no less than 2 km [2–4], whereas the anomalies within vast rock volumes are accounted for by the assimilation of large rock volumes that had been previously modified by hydrothermal solutions (for example, hyaloclastic rocks) by the magmas [3]. Note that the negative $\delta^{18}O$ anomalies were detected only in purely hydrothermal minerals and metasomatic rocks, whereas the magmatic minerals (olivine and plagioclase) show a merely insignificant decrease in the $\delta^{18}O$ values.

Anomalously low $\delta^{18}O$ values were also found in older rocks, such as metamorphosed Cretaceous volcanic rocks in Antarctica and New Zealand [5], Triassic high- and ultrahigh-pressure metamorphic complexes in the Dabieshan–Sulu orogenic belt in central China [6, 7, and others], Cambrian–Ordovician high- and ultrahigh-pressure metamorphic complexes of the Kokchetav Massif in Kazakhstan [8], and Neoproterozoic high-pressure metamorphic complexes in the Belomorian orogen in northwestern Russia [9, 10, and others]. The anomalies are commonly local, and their areas do not exceed a few dozen square kilometers; outside the anomalies, rocks of the same type as within these anomalies have a normal oxygen isotopic composition. The isotopic anomalies are everywhere explained by the effect of meteoric waters.

Occurrences of corundum in northern Karelia are somewhat different from the aforementioned anomalies in having the lowest $\delta^{18}O$ (up to –26‰ for the garnet) and δD (up to –216‰ for the amphibole) values and showing fairly large variations in these values from one anomaly to another [11–16]. The anomalous zone is restricted to the contact between the Chupa Unit and gabbroid bodies (drusites, "garnet gabbro") and continues as discrete fragments for a few hundred kilometers.

The metamorphic complexes were affected by polymetamorphic processes in a number of episodes, and their rocks are usually metamorphosed to the amphibolite or, more rarely, granulite facies of elevated pressure. The protolith age is estimated at almost 3.0 Ga, whereas the corundum rocks are dated at 1.9–1.8 Ga [15, 17, 18].

Detailed data were lately published on three relatively closely spaced corundum occurrences: Khitoostrov, Varatskoye, and Dyadina Gora [9–16, 19–20]. All of their researchers admit that the extremely low $\delta^{18}O$ values of minerals in the corundum rocks testify that they crystallized in the presence of meteoric waters that had underwent multiple liquid–vapor transitions in a cold climate. The following two constructive models were advanced to account for the genesis of the corundum-bearing rocks:

(1) The protoliths of the corundum rocks were ancient weathering crusts that contained meteoric fluid enriched in the oxygen isotope as a result of high-grade metamorphism at 2750–2720 Ma [13, 20].

(2) The protoliths of the corundum rocks were metasomatized (hydrothermally altered, propylitized) volcanic and sedimentary Paleoproterozoic rocks that underwent high-pressure Svecofennian (1.9–1.8 Ga) metamorphism [11, 12, 15, 16].

It was important to elucidate the proportions of the light isotopes at other occurrences of corundum-bearing rocks in northern Karelia (Perusel'ka, Nigrozero, Notozero, etc.) to outline the anomalous zone. Also, it was expedient to compare the oxygen and hydrogen isotopic ratios in the same minerals (for instance, disthene) from rocks of similar composition within and outside the corundum-bearing occurrences of the Chupa Unit in order to map more accurately the boundaries of the anomalous zone and gain insight into its genesis. The results of these studies are reported below.

METHODS

Oxygen and hydrogen isotopic ratios were measured at the Far East Geological Institute, Far East Division, Russian Academy of Sciences. Oxygen was extracted by heating the sample by an IR laser (10.6 μm) in the presence of BrF_5 (~210 Torr). Oxygen was then purified at two cryogenic traps with liquid nitrogen and on absorber with KBr and was analyzed on a MAT-252 mass spectrometer with a dual inlet system. The method was tested using internationally certified (NBS-28) and in-house standards. The $\delta^{18}O$ values were measured accurate to ±0.2‰.

Hydrogen was also extracted from OH-bearing minerals using a laser, which made it possible to reach a reproducibility level of ±2‰ for material amounts ranging from 1 to 5 mg. The concentrations of hydrogen isotopes were analyzed in a continuous He flow on a MAT-253 mass spectrometer. The original method [21] is an alternative to the classic technique of hydrogen extraction in vacuum.

GEOLOGICAL SETTING AND AGE

Most of the examined occurrences of corundum-bearing rocks are hosted in the Chupa nappe (Fig. 1), which is the basement of the Belomorian allochthon [22]. The latter is interpreted as resulting from collision between the Karelian and Kola geoblocks of the Baltic Shield. The Chupa nappe is believed to be dominated by supracrustal rocks: various paragneisses, which are metamorphosed graywackes [23]. As a consequence of collision, the rocks of the Belomorian allochthon were affected by high-gradient metamorphism at 1.9–1.8 Ga and then brought to shallower depths at 1.75 Ga [17].

The occurrences of corundum-bearing rocks are thought [24–26] to be structurally related to overthrusts, and the composition of these rocks is believed to depend on their setting in the nappes. Their corundum mineralization is usually related to the contact zones between silicic (either metamorphic or magmatic) and other rocks and is thought to have been produced by metasomatism, with the gradual transition from metasomatic to magmatic replacement; the predominant rocks were enriched in basic components: basificates [27] and plagioclasites. The latter often show cutting relations with the metamorphic and metasomatic associations and can thus be ascribed to magmatic rocks.

According to an alternative viewpoint, the corundum-bearing rocks are restricted to shear deformation zones and occur as lenses and tabular bodies within these zones [18, 28]. Their genesis is thus considered in close relation to high-temperature high-pressure alkaline metasomatism.

The corundum-bearing rocks usually occur as single veins, arrays of subparallel or branching veins, segregations, and pockets, and their thicknesses vary from 40–50 cm to 5–10 m.

Because of the complicated inner structures and genesis of the corundum bodies, their dating is problematic. It is usually thought that the sedimentary material of the protolith of the Chupa plagiogneisses (metagraywackes) of the Belomorian Complex was accumulated at 2.82–2.86 Ga, i.e., this process lasted for no more than 40 Ma, and the rocks were then metamorphosed at 2855 ± 5 to 2814 ± 20 Ma [29]. The Chupa rocks were migmatized at 2615 ± 15 [17] to 2691 ± 15 [30] Ma. The predominant rootless metagabbroids (drusites, "garnet gabbro" according to V.S. Stepanov) in the supracrustal Chupa nappe in the Belomorian Mobile Belt were dated at 2.43–2.46 Ga, although both older (2.69) and younger (2.4–1.9 Ga) age values were obtained for the garnet gabbro [31]. The Svecofennian episode of the tectono-metamorphic recycling of the Belomorian Mobile Belt, which was reportedly related to continent–continent collision, is dated at 1.95–1.85 Ga [29].

The K/Ar dating of the corundum-bearing rocks using their equilibrium minerals yielded consistent age values within the range of 1811 ± 45 to 1824 ± 45 Ma for the Varatskoye and 1814 ± 63 to 1895 ± 47 Ma for the

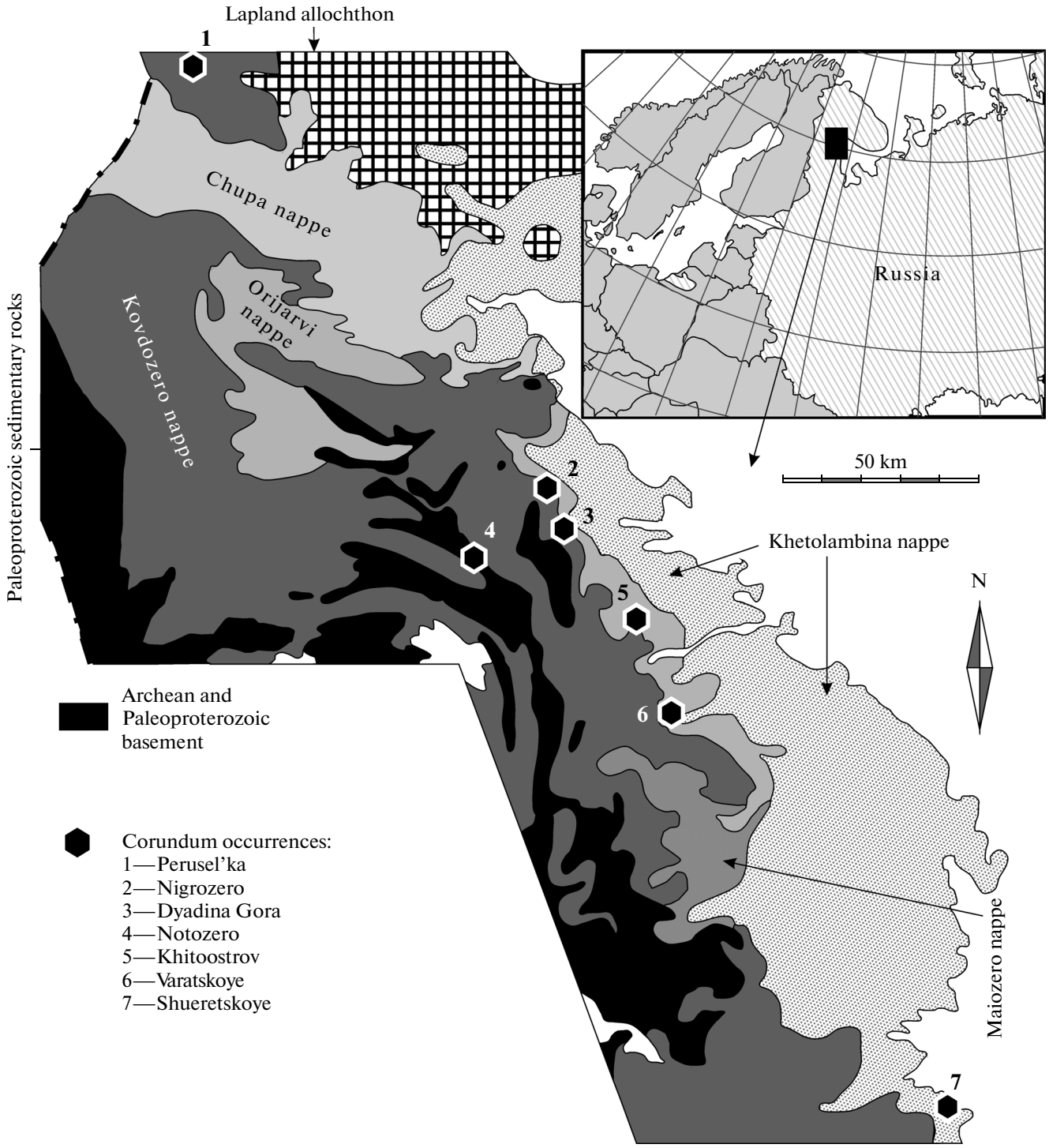

Fig. 1. Geological–tectonic map of the Belomorian Mobile Belt showing the location of corundum occurrences (simplified from [22]).

Khitoostrov occurrences [12]. With regard for the extremely high mobility of Ar, the above dates should be considered as the upper constraint for the age of the corundum-bearing rocks at these two occurrences.

The rocks from Khitoostrov were previously dated by the Th–U–Pb SHRIMP zircon method: the cores of the zircons yielded a concordant value of 2857 ± 30 Ma, the age of the intermediate zones is 2692 ± 68 Ma (for the upper intercept), and the outermost rims were dated at 1894 ± 17 Ma [18]. Later Bindeman et al. [15, 16] dated zircons from corundum-bearing rocks from the Khitoostrov occurrence and correlated these

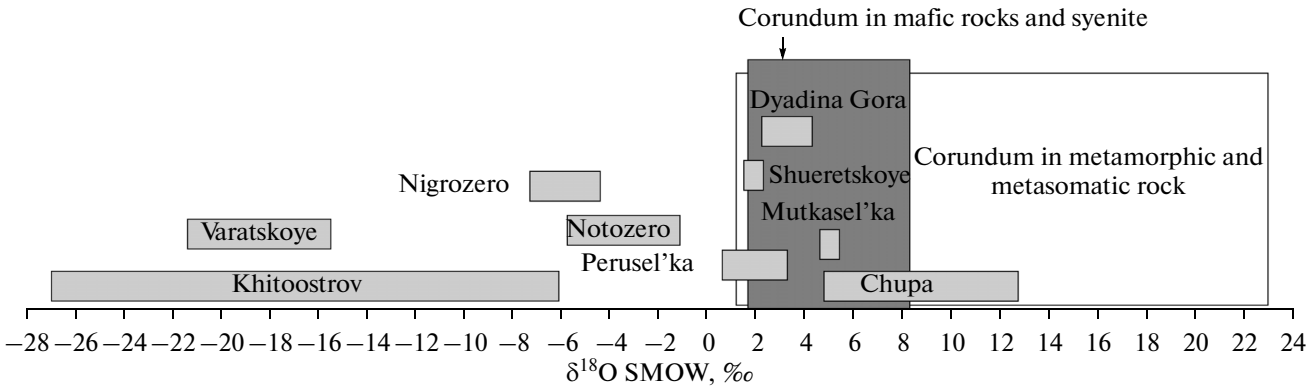

Fig. 2. $\delta^{18}O$ SMOW of minerals in corundum-bearing rocks from northern Karelia. The fields of corundum from mafic, metamorphic, and metasomatic rocks are given according to [37, 38].

values with the oxygen isotopic ratios: the ancient (2.75–2.45 Ga) zircons have $\delta^{18}O$ from +4 to +8‰, whereas the $\delta^{18}O$ of the younger zircons (1.9–1.8 Ga) ranges from –23 to –27‰. However, Krylov et al. [20] argue that the most intense fluid recycling took place at 2747 ± 6 Ma, and events at 1.9–1.8 Ga did not play a significant role.

These data provide insight into the complicated polycyclic mechanism that produced the zircons, and the age of their outer rims corroborates the currently predominant opinion that the corundum occurrences have a Svecofennian age. This also implies that the anomalies were produced within the time span between 2.45 and 1.8 Ga.

ISOTOPIC DATA

We have studied samples from seven corundum occurrences and a few samples of the host gneisses of the Chupa Unit and metamagmatic rocks (eclogite, amphibolite, and garnet amphibolite). Whenever possible, we have analyzed more than one equilibrium mineral in a single sample. The data thus obtained allowed us to distinguish the following localities variably depleted in the heavy oxygen isotope:

(1) Corundum occurrences anomalously strongly depleted in the oxygen and hydrogen isotopes (Varatskoye and Khitoostrov), where $\delta^{18}O$ reaches –26.4‰ and δD is as low as –216‰ relative to SMOW (Table 1).

(2) Corundum occurrences relatively depleted in the heavy oxygen and hydrogen isotopes (Nigrosero and Notozero), where $\delta^{18}O$ is no lower than –7.3‰ and must be deleted mostly lies within the range of –1 to –2‰ (Table 2).

(3) Corundum occurrences (Dyadina Gora and Perusel'ka) with low but never negative $\delta^{18}O$ values (Table 3).

The latter are similar to the garnet amphibolites replacing gabbro at the Shueretskoye garnet deposit and eclogite-like garnet–pyroxene rocks replacing basalt in the Lapland Granulite Belt at the Tuadash Tundra–Mount Mutkasel'ka, whose $\delta^{18}O$ are also low but always positive.

As can be clearly seen in Fig. 2, the Dyadina Gora and Perusel'ka occurrences are closely similar to corundum occurrences produced in ultramafic rocks and syenites, with the $\delta^{18}O$ of minerals in this group varying from +0.4 to +5‰ and overlap the minimum values for the Chupa Unit (Table 3). Such $\delta^{18}O$ values were also found in corundum from the peridotite complexes Beni-Bousera in Morocco, Ronda in Spain, Val Malenco in Italy, and a number of deposits at Chantaburi-Trat in Thailand [32–35], which are thought to have been produced at temperatures of 800–1150°C and pressures of 10–25 kbar in the upper mantle [36].

Data of sampling conducted over the territory of the Khitoostrov occurrence indicate that the depletion of the minerals in the heavy oxygen isotope is correlated with the composition of the rocks and their settings within the occurrence as a whole and in the zonal bodies. The minimum $\delta^{18}O$ values were obtained from leucocratic corundum-bearing rocks: corundum–garnet plagioclasites (samples KP-1 and KP-2) with low contents of amphibole and biotite, which occur approximately in the central part of the Khitoostrov corundum occurrence. An increase in the content of mafic minerals in the zonal bodies is correlated with an increase in their $\delta^{18}O$ values. In minerals of the garnet amphibolites (sample K-81/1) in the marginal part of the occurrence, $\delta^{18}O$ is 14–17‰ higher than in the corresponding minerals of the leucocratic plagioclasites. These tendencies reflect either the uneven enrichment of the protolith in the light oxygen isotope or the effect of metasomatic zoning and the corresponding variable reworking of the rocks by isotopically light solutions.

METAMORPHISM

The P–T parameters at which the mineral assemblages were formed can be evaluated only approximately. The temperatures yielded by the garnet–

Table 1. Oxygen and hydrogen isotopic compositions in minerals from the Khitoostrov and Varatskoye corundum occurrences

Sample no., rock	Mineral	$\delta^{18}O$, ‰ (SMOW)	δD, ‰
Khitoostrov			
KP-1 corundum–biotite–garnet–amphibole plagioclasite	Garnet	–26.0	n.d.
		–26.4	n.d.
		–25.7	n.d.
	Plagioclase	–19.9	n.d.
	Biotite	–15.5	–77
KP-2 corundum–biotite–garnet–amphibole plagioclasite	Garnet	–25.7	n.d.
	Corundum	–22.5	n.d.
	Plagioclase	–21.4	n.d.
K-90\14 biotite–garnet–amphibole plagioclasite	Amphibole	–20.0	–215
	Plagioclase	–23.1	n.d.
	Biotite	–8.0	n.d.
K-90\23 amphibolite (metahyperbasite)	Amphibole	–21.4	–117
	Plagioclase	–20.1	n.d.
	Biotite	–18.7	n.d.
K-152/1 garnet amphibolite	Chlorite	7.0	–43
	Garnet	–23.7	n.d.
K-90/1 quartz–amphibole–garnet plagioclasite	Amphibole	–20.5	n.d.
	Garnet	–22.1	n.d.
K-90-19 corundum–garnet–kyanite–plagioclase–biotite rock	Garnet	–19.3	n.d.
	Kyanite	–20.0	n.d.
	Sericitized plagioclase	–15.9	n.d.
	Fresh plagioclase	–16.6	n.d.
K-91/1 garnet amphibolite	Garnet	–8.9	n.d.
	Garnet	–7.4	n.d.
	Amphibole	–6.2	n.d.
Varatskoye			
K-227/3 garnet–corundum–kyanite–amphibole plagioclasite	Amphibole	–19.9	–214
	Plagioclase	–18.7	n.d.
	Corundum	–18.8	n.d.
	Staurolite	–18.9	n.d.
K-231/6 corundum–staurolite–amphibole plagioclasite	Amphibole	–19.6	–216
	Plagioclase	–18.0	n.d.
	Biotite	–16.8	n.d.
	Corundum	–17.2	n.d.
	Staurolite	–18.5	n.d.
K-226/4 garnet amphibolite	Amphibole	–17.2	n.d.
	Garnet	–18.6	n.d.
K-227/7 zoisite amphibolite	Zoisite	–17.3	n.d.
	Amphibole	–17.6	n.d.
K-226/2 corundum–staurolite–kyanite plagioclasite	Amphibole	–16.9	n.d.
	Kyanite	–18.9	n.d.
K-229/3 garnet–kyanite–biotite plagiogneiss	Garnet	–17.3	n.d.
K-225/3 garnet granosyenite	Garnet	–20.2	n.d.
K-231/5 zoisite rock with garnet and amphibole relics	Garnet	–19.4	n.d.
	Amphibole	–15.8	n.d.
	Zoisite	–17.7	n.d.

Table 2. Oxygen isotopic compositions in minerals from the Nigrozero and Notozero corundum occurrences

Sample no., rock	Mineral	$\delta^{18}O$ ‰ (SMOW)
Nigrozero		
K-149/4 plagioclase–garnet amphibolite	Garnet	–7.3
	Amphibole	–4.5
K-80/3 gabbro	Garnet	5.4
Notozero		
K-159/15 gedrite–garnet rocks with corundum and staurolite	Amphibole	–1.8
	Amphibole	–1.1
	Corundum (bulk)	–5.2
	Corundum (core)	–1.7
	Corundum (margin)	–1.5
K-159/18 corundum–staurolite amphibolite	Amphibole	–1.6
	Staurolite	–1.8

Sample K-149/4 is from a corundum occurrence, and sample K-80/3 is form the host rocks of the Chupa Unit.

amphibole thermometer [39] varies from 670 to 740°C, i.e., is slightly higher than the temperatures (650–700°C) determined in [40] for analogous rocks. The calculation of these parameters via minimizing the thermodynamic potential using the SELECTOR-S [41] software indicates that the temperature and pressure should have been no lower than 720°C and 10 kbar, with the assemblages and compositions of the calculated minerals corresponding to their natural counterparts only at these parameters.

At the same time, the crystallization temperatures of these minerals calculated from isotopic data [13, 14, 20] range from 350 to 470°C, i.e., are much lower than the temperatures yielded by mineral geothermometers and by the method based on minimization of the thermodynamic potential. The low temperatures may likely be explained by the effect of secondary low-temperature alterations, which are reflected in saussuritization of the plagioclase and replacement of the amphibole and biotite by hydromica and chlorite. The difference between the oxygen isotopic compositions of various minerals in a single rock ranges between 3 and 10‰.

The absence of reaction relations between the primary minerals testifies that they were in thermodynamic equilibrium and were possibly affected by secondary low-temperature alterations.

Both garnet and corundum are minerals highly resistant to such alterations and thus have lower negative $\delta^{18}O$ values. Plagioclase, amphiboles, and micas are more susceptible to such alterations, and their initial isotopic ratios are often disturbed. For example, the δD values of unaltered and partly chloritized amphibole in sample K-90/14 differ by 80‰ (Table 1). The manifestations of this process are the most contrasting in sample K-152/1, in which unaltered garnet has negative $\delta^{18}O$ values (–23.7‰), and chlorite replacing the mica has positive $\delta^{18}O$ values (+7‰). The garnet is practically unaltered and preserves its initial oxygen isotopic ratios. At the same time, the mafic mineral is completely chloritized, and the oxygen isotopic composition of the chlorite corresponds to the oxygen isotopic composition of the host rocks of the Chupa Unit. In terms of oxygen and hydrogen isotopic ratios, the hydroxyl group of micas and amphiboles from the host rocks (samples K-158 and K-154/1) plots within the field of magmatic waters, and this suggests a magmatic (volcanic) nature of a certain part of the protolith.

In some other samples (KP-1, K-90/23, and K-90/14), chlorite has only partly replaced the primary minerals, and the disturbance in the isotopic ratios is thus not as significant. These ratios were likely disturbed with the participation of meteoric water whose isotopic composition was similar to that of modern groundwaters in Karelia and Scandinavia. Because of this, the data points of the altered micas and amphiboles plot near the global line for meteoric waters (Fig. 3).

DISCUSSION

The $\delta^{18}O$ values of the aqueous phase of the mineral-forming fluid calculated according to [44, 45] for the amphibole at 600–700°C vary from –18 to –19‰ and the δ D values are from –193 to –199‰. Taking into account the fact that the $\delta^{18}O$ values of the garnet and corundum are lower than in the amphiboles, the degree of enrichment in the light oxygen isotope of the aqueous constituent of the fluid should have been even greater, with $\delta^{18}O$ from approximately –27 to –30‰, and the volume of this water should have been at least twice to thrice greater than the volume of the altered rock whose initial oxygen isotopic composition was as in rocks of the Chupa Unit ($\delta^{18}O$ from +5 to +12‰). Because of this, the hypothesis of fragments of ancient weathering crusts that contained meteoric fluid enriched in isotopically light oxygen seems not to be realistic. Conversely, the hypothesis of hydrothermal poropilites that were metamorphosed at a high grade seems to be plausible.

In this context, an illustrative example is provided by the oxygen isotopic composition of secondary minerals and altered Holocene basalts in Iceland recovered by a deep borehole. According to Hattori and Muehlenbachs (1982), the hydrothermally altered basalts in Iceland have $\delta^{18}O$ lower than –10‰ relative to SMOW, and secondary epidote from these rocks has $\delta^{18}O$ from –11.8 to –12.7‰The hydrothermal fluid reportedly [2] contained meteoric water, whose $\delta^{18}O$ in Iceland is from –8 to –11‰.

Table 3. Oxygen and hydrogen isotopic compositions in minerals from the Dyadina Gora and Perusel'ka corundum occurrences, Shueretskoye garnet deposit, host rocks of the Chupa Unit, and granulites from Mount Mutkasel'ka

Sample no., rock	Mineral	$\delta^{18}O$, ‰ (SMOW)	δD, ‰
Dyadina Gora			
Kr11-17 corundum amphibolite	Corundum (core)	0.4	n.d.
	Corundum (margin)	0.8	n.d.
	Amphibole	3.1	n.d.
K-237/11 plagioclase–garnet–kyanite–corundum amphibolite	Amphibole	2.1	–78
	Corundum	2.5	n.d.
Shueretskoye			
K-107/14 quartz–gedrite–garnet rock	Garnet	1.7	n.d.
	Amphibole	2.2	n.d.
Perusel'ka			
K-111/14 corundum–plagioclase amphibolite	Amphibole	3.0	n.d.
K-112/4 corundum–kyanite amphibolite	Amphibole	2.8	n.d.
K-113/8 corundum–kyanite amphibolite	Corundum	0.6	n.d.
	Amphibole	3.2	n.d.
Corundum amphibolite	Corundum	1.5	n.d.
Chupa Unit			
K-156/3 leucocratic granite	Plagioclase	9.3	n.d.
	Quartz	11.6	n.d.
K-154/1 garnet–biotite plagiogneiss	Biotite	6.5	–75
	Garnet	6.4	n.d.
K-158 garnet amphibolite ("gabbro")	Biotite	4.9	–86
	Garnet	5.6	n.d.
K-84/6 kyanite–biotite–garnet plagiomigmatite	Quartz	12.4	n.d.
	Kyanite	8.7	n.d.
Mount Mutkasel'ka			
K-115/19 garnet–pyroxene granulit	Pyroxene	5.0	n.d.

It should also be taken into account that the lower the temperature of water–rock exchange, the greater the negative $\delta^{18}O$ and δD values of this water. As is demonstrated in [46], Quaternary carbonate sediments that were deposited from cold glacial water in Antarctica have $\delta^{18}O$ from –14.1 to –17.3‰ relative to SMOW. The calculated $\delta^{18}O$ of the ice melt water should have been between –47.2 to –50.3‰.

In view of this, modern hydrothermal waters in Earth's middle and high latitudes are too low in the ^{16}O isotope. For instance, hydrothermal waters in the Sikhote Alin have $\delta^{18}O$ from –10.8 to –18.8‰ [47]. Hot thermal waters in Chukotka, for which mixing of surface and glacial (derived via melting ancient ice) waters was postulated, are also insufficiently enriched in the light oxygen and hydrogen isotopes and reach only values of $\delta^{18}O = -17.6$‰ and $\delta D = -134.2$‰ at a temperature slightly lower than 100°C [48].

This fluid, which was derived only from ice and snow melt waters, could have had a required oxygen and hydrogen isotopic composition. Water of such an isotopic composition can be nowadays generated only in polar areas. Very low (lower than –60‰) $\delta^{18}O$ values were documented in snow and ice melt waters in Greenland and Antarctica [49]. However, these conditions could occur much closer to the equator during global glacial periods. For example, the $\delta^{18}O$ values of fossil Holocene ice in eastern Siberia reach –29.2‰ [50, 51].

As was mentioned above, the anomaly was generated at 2.45–1.8 Ga. According to paleomagnetic data, the

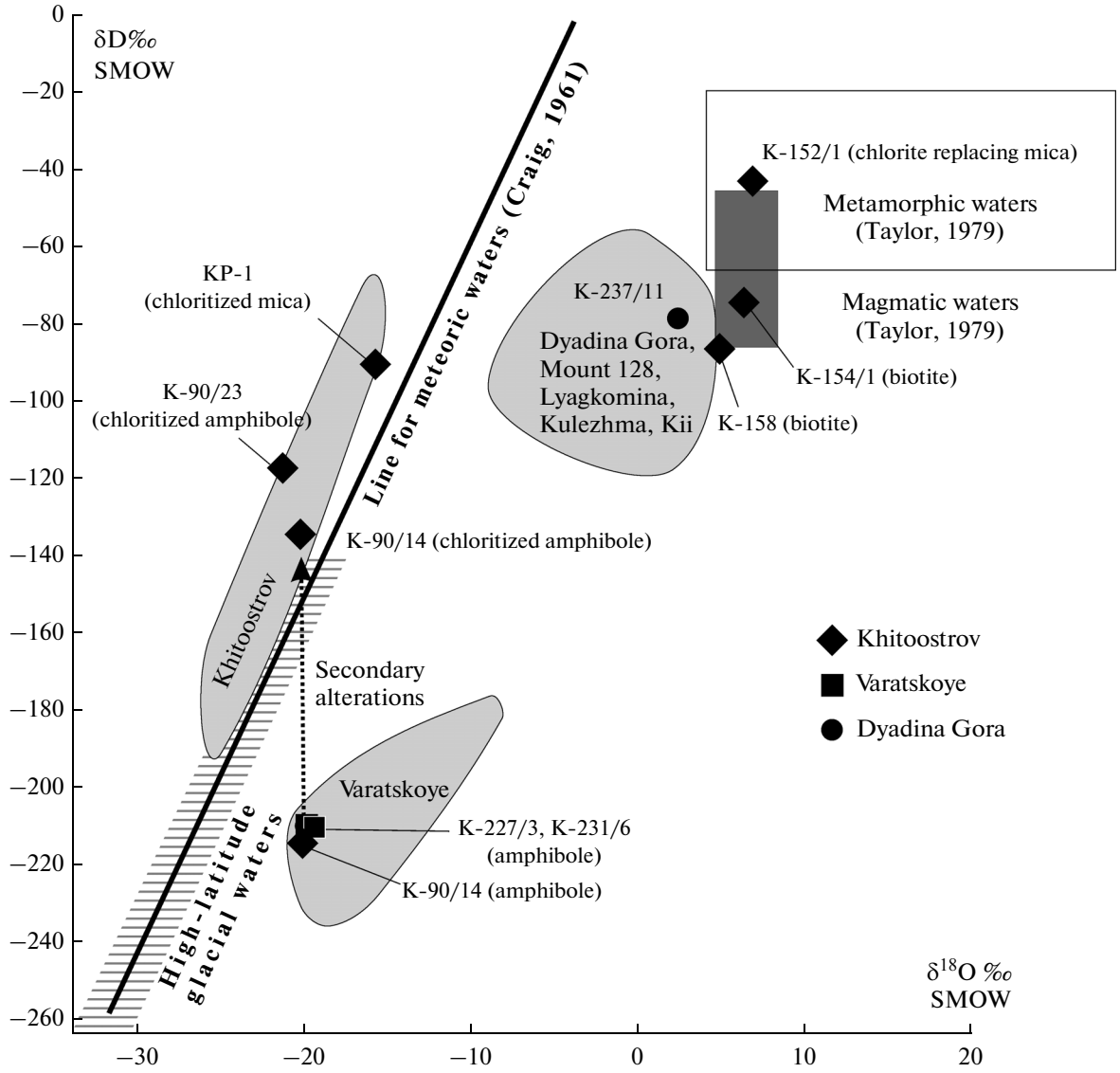

Fig. 3. Oxygen and hydrogen isotopic composition of water-bearing minerals from corundum occurrences in northern Karelia. Fields of corundum occurrences are according to [15, 16].

territories of the Kola and Karelian geoblocks were then located at middle altitudes [52], far away from polar areas. However, the beginning of this period was marked by global Paleoproterozoic glaciation, whose peak occurred at 2.3 Ga [53].

We are prone to believe that the extremely low $\delta^{18}O$ and δD values of the corundum and accompanying minerals were not direct consequences of the corundum-forming metamorphic process itself. This follows from the broad variations in these parameters in the rocks through the region. The anomalous values were most likely inherited from glacial waters that had been involved in local hydrothermal transformations of the volcano-sedimentary protolith during volcanic activity before the metamorphic episode. The precursors of the Svecofennian corundum-bearing plagioclasites were likely metasomatized Paleoproterozoic rocks that had been formed in a shallow-depth zone of the subglacial fumarole field. Fields of this type are widespread in modern volcanic areas (for example, in Kamchatka and Iceland). The enrichment of all minerals of the corundum-bearing rocks in the light oxygen and hydrogen isotopes testifies that the Meso- to Neoarchean rocks were completely transformed into aluminous metasomatites in the Paleoproterozoic. This required a significant volume of melt water, and the hydrothermal cell should have operated for a long enough time at the same site. This metasomatism was likely synchronous with the most ancient Huronian glaciation, which reached a peak at 2.3 Ga. The metasomatic rocks were later affected by high-pressure Svecofennian metamorphism (at 1.9–1.8 Ga), which resulted in mineral assemblages with corundum.

CONCLUSIONS

The data reported above show that the protolith of the Khitoostrov, Varatskoye, Nigrozero, and Notozero corundum deposits was produced by metasomatism within a shallow-depth zone of a fumarole field, with the involvement of glacial waters, which predetermined the anomalously light oxygen and hydrogen isotopic composition of the minerals. At the same time, the oxygen isotopic composition of rocks at other corundum occurrences (Dyadina Gora and Perusel'ka) is analogous to that in corundum occurrences produced in ultramafic rocks and syenite. No evidence of the involvement of glacial water was discerned in these rocks. The corundum-bearing rocks were produced in their final form under the effect of high-grade Svecofennian (1.9–1.8 Ga) metamorphism.

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REFERENCES

1. G. Faure, *Principles of Isotope Geology. 2nd Edition* (John Wiley & Sons, New York, 1986).
2. K. Hattori and K. Muehlenbachs, "Oxygen isotope ratios of the Icelandic crust," J. Geophys. Res. **87** (B8), 6559–6565 (1982).
3. I. N. Bindeman, C. K. Brooks, A. R. McBirney, and H. P. Taylor, "The low-δ^{18}O late-stage ferrodiorite magmas in the Skaergaard Intrusion: result of liquid immiscibility, thermal metamorphism, or meteoric water incorporation into magma?," J. Geol. **116**, 571–586 (2008).
4. E. C. Pope, D. K. Bird, S. Arnorsson, Th. Fridriksson, W. A. Elders, and G. O. Fridleifsson, "Isotopic constraints on ice age fluids in active geothermal systems: Reykjanes, Iceland," Geochim. Cosmochim. Acta **73**, 4468–4488 (2009).
5. P. Blattner, G. W. Grindley, and C. J. Adams, "Low-δ^{18}O terranes tracking Mesozoic Polar climates in the South Pacific," Geochim. Cosmochim. Acta **61** (3), 569–576 (1997).
6. Y.-F. Zheng, B. Fu, Y. Li, Y. Xiao, and Sh. Li, "Oxygen and hydrogen isotope geochemistry of ultrahigh-pressure eclogites from the Dabie Mountains and the Sulu Terrane," Earth Planet. Sci. Lett. **155**, 113–129 (1998).
7. Y.-F. Zheng, Y.-B. Wu, F. K. Chen, B. Gong, L. Li, and Z.-F. Zhao, "Zircon U–Pb and oxygen isotope evidence for a large-scale 18O depletion event in igneous rocks during the Neoproterozoic," Geochim. Cosmochim. Acta **68**, 4145–4165 (2004).
8. H. Masago, D. Rumble, W. G. Ernst, C. D. Parkinson, and S. Maruyama, "Low δ^{18}O eclogites from the Kokchetav Massif, Northern Kazakhstan," J. Metamorph. Geol. **21**, 579–587 (2003).
9. V. V. Yakovenko, S. V. Vysotskii, and A. V. Ignat'ev, "Features of oxygen isotope composition of corundum and associated minerals of North Karelia," in *Geodynamics, Magmatism, Sedimentogenesis, and Metallogeny of Northwest Russia. Proceedings of All-Russian Conference, Russia, Petrozavodsk, 2007* (Petrozavodsk, 2007) [in Russian].
10. D. P. Krylov, "O^{18} depletion in corundum bearing rocks from North Karelija (the Baltic Shield)," in *Water-Rock Interaction 12*, Ed. by T.D. Bullen and Y. Wang (Taylor and Francis Group, London, 2007), pp. 87–89.
11. S. V. Vysotskii, A. V. Ignat'ev, V. V. Yakovenko, and A. A. Karabtsov, "Anomalous light oxygen isotope composition in minerals of corundum-bearing rocks in Northern Karelia," Dokl. Earth Sci. **423** (8), 1216–1219 (2008).
12. S. V. Vysotskii, A. V. Ignat'ev, V. I. Levitskii, S. Yu. Budnitskii, T. A. Velivetskaya, "New data on stable isotopes in minerals from corundum-bearing formations of Northern Karelia (Russia)," Dokl. Earth Sci. **439** (1), 964–966 (2011).
13. D. P. Krylov, "Anomalous $^{18}O/^{16}O$ ratios in the corundum-bearing rocks of Khitostrov, Northern Karelia," Dokl. Earth Sci. **419A** (3), 453–456 (2008).
14. V. I. Ustinov, I. A. Baksheev, and N. S. Serebryakov, "Oxygen isotopic composition of the mineral-forming fluids of corundum-bearing metasomatic rocks at the Khitoostrov and Varatskoye mineral occurrences, Northern Karelia," Geochem. Int. **46** 11, 1174–1177 (2008).
15. I. N. Bindeman, A. K. Schmitt, and D. A. D. Evans, "Limits of hydrosphere-lithosphere interaction: origin of the lowest-known δ^{18}O silicate tock on Earth in the Paleoproterozoic Karelian Rift," Geology **38** (7), 631–634 (2010).
16. I. N. Bindeman and N. S. Serebryakov, "Geology, petrology and O and H isotope geochemistry of remarkably 18O depleted Paleoproterozoic rocks of the Belomorian Belt, Karelia, Russia, attributed to global glaciation 2.4 Ga," Earth Planet. Sci. Let **306**, 163–174 (2011).
17. E. V. Bibikova, S. V. Bogdanova, V. A. Glebovitsky, S. Claesson, and T. Skiold, "Evolution of the Belomorian Belt: NORDSIM U-Pb zircon dating of the Chupa Paragneisses, magmatism, and metamorphic stages," Petrology **12** (3), 195–210 (2004).
18. N. S. Serebryakov, B. Yu. Astaf'ev, O. A. Voinov, and S. L. Presnyakov, "First Th–U–Pb single zircon dating of metasomatites from the Belomorian Mobile Belt," Dokl. Earth Sci. **413A** (3), 388–392 (2007).
19. D. P. Krylov and V. A. Glebovitsky, "Oxygen isotopic composition and nature of fluid during the formation of high-Al corundum-bearing rocks of Mt. Dyadina, Northern Karelia," Dokl. Earth Sci. **413** (2), 210–212 (2007).
20. D. P. Krylov, E. B. Sal'nikova, A. M. Fedoseenko, S. Z. Yakovleva, Yu. V. Plotkina, and I. V. Anisimova, "Age and origin of the corundum-bearing rocks of Khitostrov Island, Northern Karelia," Petrology **19** (1), 79–86 (2011).
21. A. V. Ignatiev and T. A. Velivetskaya, "A laser GC-IRMS technique for determination of hydrogen isotope ratios from microgram quantities hydrous minerals," in *Abstract Book European Society for Isotope Research X Isotope Workshop, 2009* (Zbotniki Lubanskie Univ., Wroclaw, 2009), p. 101.
22. Yu. V. Miller, "Late Archean nappe structure of the Belomorian mobile belt," Vestn. St. Petersb. Gos. Univ., Ser. 7., No. 3, 28–40 (1997).
23. E. A. Myskova, R. I. Mil'kevich, A. B. L'vov, and Yu. V. Miller, "Origin of the Belomorian Chupa

Gneiss in the light of new lithogeochemical data," Lithol. Miner. Resour. **35** (6), 583–593 (2000).
24. E. N. Terekhov and V. I. Levitskii, "Geological-structural regularities in the distribution of corundum mineralization in the northwestern Belomorian area," Izv. Vyssh. Uchebn. Zaved., Geol. Razved., No. 6, 3–13 (1991).
25. V. I. Levitskii, *Petrology and Geochemistry of Metasomatism during Formation of the Continental Crust* ("Geo", Novosibirsk, 2005) [in Russian].
26. E. N. Terekhov, "REE distribution in corundum-bearing and other metasomatic rocks during the exhumation of metamorphic rocks of the Belomorian Belt, Baltic Shield," Geochem. Int. **45** (4), 364–380 (2007).
27. *Classification and Nomenclature of Metamorphic Rocks* (Nauka, Novosibirsk, 1992) [in Russian].
28. N. S. Serebryakov and V. L. Rusinov, "High-grade calcium–sodium metasomatism and corundum formation in the Precambrian Belomorian Mobile Belt, Karelia," Dokl. Earth Sci. **395A** (3), 389–393 (2004).
29. *Early Precambrian of the Baltic Shield*, Ed. by V. A. Glebovitsky (Nauka, St. Petersburg, 2005) [in Russian].
30. O. A. Levchenkov, O. I. Volodichev, T. F. Zinger, S. Z. Yakovleva, A. F. Makeev, I. K. Shuleshko, and V. I. Kevlich, "Age of metamorphism of aluminous gneisses from the Pon'goma Inlet Region of the Belomorian Mobile Belt, Baltic Shield," Dokl. Earth Sci. **377** (2), 168–171 (2001).
31. V. S. Stepanov, *Precambrian Mafic Magmatism of the Western Belomorian Region* (Nauka, Leningrad, 1981) [in Russian].
32. J. Kornprobst, M. Piboule, M. Roden, and A. Tabit, "Corundum-bearing garnet clinopyroxenites at Beni Bousera (Morocco): original plagioclase-rich gabbros recrystallized at depth within the mantle?," J. Petrol. **31**, 717–745 (1990).
33. O. Muntener and J. Hermann, "The Val Malenco lower crust–upper mantle complex and its field relations (Italian Alps)," Schweiz. Mineral. Petrogr. Mitt. **76**, 475–500 (1996).
34. T. Morishita, S. Arai, and F. Gervilla, "High-pressure aluminous mafic rocks from the Ronda Peridotite Massif, Southern Spain: significance of sapphirine- and corundum-bearing mineral assemblages," Lithos **57**, 143–161 (2001).
35. Tzen-Fu Yui, Chao-Ming Wu, Phisit Limtrakun, Weerapan Sricharn, and Apichet Boonsoong, "Oxygen isotope studies on placer sapphire and ruby in the Chanthaburi-Trat alkali basaltic gemfield, Thailand," Lithos **86** 197–211 (2005).
36. C. Sutthirat, S. Saminpanya, G. T. R. Droop, C. M. B. Henderson, and D. A. C. Manning, "Clinopyroxene–corundum assemblages from alkali basalt and alluvium, eastern Thailand: constraints on the origin of Thai rubies," Mineral. Mag. **65**, 277–295 (2001).
37. G. Giuliani, A. Fallic, V. Garnier, C. France-Lanord, D. Ohnenstetter, D. Schwarz, "Oxygen isotope composition as a tracer for the origins of rubies and sapphires," Geology **33**, 249–252 (2005).
38. F. L. Sutherland, K. Zaw, S. Meffre, G. Giuliani, A. E. Fallick, I. T. Graham, and G. B. Webb, "Gem-corundum megacrysts from East Australian basalt fields: trace elements, oxygen isotopes and origins," Aust. J. Earth Sci. **56** (7), 1003–1022 (2009).
39. C. M. Graham and R. Powell, "A garnet–hornblende geothermometer: calibration, testing and application to the Pelona Schist, Southern California," J. Metamorph. Geol. **2**, 13–31 (1984).
40. N. S. Serebryakov and Vs. V. Aristov, "Setting of collection-quality corundum occurrences in the Chupa Sequence of the Belomorian Complex, North Karelia," Izv. Vuzov., Geol. Razv., No. 4, 36–42 (2004).
41. O. V. Avchenko, S. V. Vysotskiy, and K. V. Chudnenko, "Experience of modeling the garnet + orthopyroxene + spinel + plagioclase reaction by the method of thermodynamic potential minimization," Dokl. Earth Sci. **415** (5), 773–776 (2007).
42. H. I. Craig, "Isotopic variations in meteoric waters," Science **133**, 1702–1703 (1961).
43. H. P. Taylor Jr., "Oxygen and hydrogen isotope relationships in hydrothermal mineral deposits," in *Geochemistry of Hydrothermal Ore Deposits. 2nd ed.*, Ed. by H.L. Barnes (Wileys, New York, 1979), pp. 236–277.
44. T. Suzuoki and S. Epstein, "Hydrogen isotope fractionation between OH-bearing minerals and water," Geochim. Cosmochim. Acta **40**, 1229–1240 (1976).
45. Y.-F. Zheng, "Calculation of oxygen isotope fractionation in hydroxyl-bearing silicates," Earth Planet. Sci. Lett. **120**, 247–263 (1993).
46. P. Aharon, "Oxygen, carbon and U-series isotopes of aragonites from Vestfold Hills, Antarctica: clues to geochemical processes in subglacial environments," Geochim. Cosmochim. Acta **52**, 2321–2331 (1988).
47. I. V. Bragin, G. A. Chelnokov, O. V. Chudaev, and V. A. Chudaeva, "Low-temperature geothermal waters of continental margin of Far East of Russia, in *Proceedings of the 12th International Symposium on WRI-12*," (Balkema Publishers, 2007), pp. 481–484.
48. J. Hoefs *Stable Isotope Geochemistry* (Springer, Berlin, 1997).
49. B. G. Polyak, E. O. Dubinina, V. Yu. Lavrushin, and A. L. Cheshko, "Isotopic composition of thermal waters in Chukotka," Lithol. Miner. Resour. **43** (5), 429–453 (2008).
50. Yu. K. Vasil'chuk, *Oxygen Isotopic Composition of Groundwaters* (RAN, MGU, PNIIIS, Moscow, 1992), Vol. 1 [in Russian].
51. Yu. K. Vasil'chuk and V. M. Kotlyakov, *Principles of Isotope Geochronology and Glaciology* (Izd-vo MGU, Moscow, 2000) [in Russian].
52. D. A. D. Evans and S. A. Pisarevsky, "Plate tectonics on the early Earth? Weighing the paleomagnetic evidence," in *When Did Plate Tectonics Begin?* Ed. by K. Condie and V. Pease, Geol. Soc. Am. Sp. Pap. **440**, 249–263 (2008).
53. D. H. Tarling, "The geological–geophysical framework of ice ages," in *Climatic Change*, Ed. by J. Gribbin (Cambridge Univ. Press, Cambridge, 1978), pp. 3–24.

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