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The Oxygen Isotopic Composition as an Indicator of the Genesis of "Basaltic" Corundum

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Abstract—This paper reports an oxygen isotopic study of corundums and associated minerals from the Yogo lamprophyres (Montana, US), plagioclase–corundum inclusions in alkali basalt (Tunkin depression, Russia), and from modern alluvium of Podgelbanochnyi alkaline basaltic volcano (Primorye, Russia). It is shown that all sapphires genetically related to mafic magmatic rocks have a similar oxygen isotopic composition (the variations of $\delta^{18}O$ are within 2.5‰) with most values plotting between +4.5 and +7.0‰ SMOW. The oxygen isotopic ratios in the associated minerals (olivines, pyroxenes, mica, and others) and host rocks are plotted in the same interval. This indicates that the sapphire crystallized during evolution of the parental mafic magma. However, there are xenogenic corundums, which were only transported by basaltic magma to the Earth's surface. They have a sharply distinct oxygen isotopic composition, which suggests their disequilibrium with the host lavas, and, correspondingly, a different genetic nature.

Key words: oxygen isotopes, corundum, sapphire, Yogo-Gulch, Tunkin depression, Podgelbanochnyi volcano, Russia, United States.

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INTRODUCTION

Jewelry corundums have different origins. Their bedrock deposits are related to pegmatites, lamprophyres, plagioclasites, marbles, or silicate endoskarns [5]. However, one of the most important economic types of its deposits are placer, residual, and bedrock deposits spatially related to Cenozoic alkali basalts [10, 13]. These deposits are extended as a belt along the entire coast of the eastern Pacific [3].

The "basaltic" sapphires are interpreted either as xenocryst (foreign material) or megacryst (cognate with basalts). In the former case, they were formed in the deep-seated (nonbasaltic) rocks and captured as xenocrysts by basaltic magma ascending to the surface [9, 14, 17]. According to the second interpretation, sapphires crystallized from the melt during evolution of basaltic magma [5, 6, 16].

One of the arguments in support of the xenogenic nature of "basaltic" noble corundums is their fringing by spinel rims (coats), indicating mineral–melt reaction relations. However, this may also indicate only a change in the physicochemical crystallization conditions, which disturbed the previously existing equilibrium in the mineral–melt system.

Hence, additional independent methods need to be involved to solve the genesis of basaltic sapphires. One of these methods can be the determination of the oxygen isotopic composition in the minerals. As was shown previously [7, 8], sapphires of different genesis have a particular oxygen isotope ratio, which remains unchaned through external influence, if only their structure and composition are not transformed.

METHODS

The author studied sapphires from the Yogo lamprophyres (Montana, US), plagioclase–corundum inclusions in alkaline basalt (Tunkin depression, Irkutsk area, Russia), and modern alluvium of the Podgelbanochnyi alkali basaltic volcano (Primorye, Russia). All these sapphires were found in association with alkali basic rocks and were coated by spinel, i.e., interacted with melt.

The oxygen isotopic composition was analyzed at the Far East Geological institute of the Far East Branch of the Russian Academy of Sciences using a high-vacuum system with a modified laser decomposition method using BrF_5 [15]. A sapphire sample 2–3 mg in weight was loaded into the multicharge vacuum stage and heated by an infrared CO_2 laser (MIR-30) in a BrF_5 atmosphere. The released oxygen was purified from reagent residue and collected on a sorbent in an ampoule (5 Å monomolecular sieves). The oxygen isotopic composition was determined using a dual inlet Finnigan MAT-252 mass spectrometer. The extraction of oxygen from each sample was repeated 2–3 times. The obtained reproducibility was better than ±0.2‰. The standard gas was calibrated to SMOW and NBS-28.

Table 1. Composition of minerals from the Yogo lamprophyre

	Diopside					Phlogopite		Corundum	
	core	rim	core	zone 1	zone 2	core	rim	core	rim
SiO_2	53.50	47.14	52.23	53.96	49.31	32.99	35.24	–	–
TiO_2	0.26	1.73	0.32	0.33	1.47	6.63	3.74	–	–
Al_2O_3	2.91	9.20	3.93	2.93	6.14	17.08	16.9	99.13	99.54
Cr_2O_3	1.71	–	–	0.55	–	–	–	–	–
FeO	3.37	7.00	8.00	3.56	5.80	8.13	8.22	0.40	0.67
MnO	–	–	0.39	–	–	–	–	–	–
MgO	17.10	11.84	14.00	17.22	13.60	17.51	19.17	–	–
CaO	20.04	23.29	20.28	20.70	23.64	0.95	–	–	–
Na_2O	0.99	–	0.80	0.80	–	0.54	0.46	–	–
K_2O	–	–	–	–	–	7.9	9.33	–	–
Total	99.89	100.20	99.94	100.05	99.96	92.73	93.06	99.53	100.21
f	9.9	24.9	24.3	10.4	19.3	20.6	19.4		

Note: The mineral analyses were performed using a JXA-8100 microprobe at the Far East Geological Institute of the Far East Branch of the Russian Academy of Sciences. Hereinafter, a dash means below the detection limit; $f = Fe_{tot}/(Fe_{tot} + Mg_{tot})$, at %

RESULTS

The Yogo lamprophyre dike in Montana, US is the only magmatic rock that has been mined for jewelry sapphires for a long time. According to Meyer and Mitchell [12], the average phenocryst composition of the lamprophyres is phlogopite (38%), diopside (12%), Ti-bearing magnetite (4%), and apatite (less than 1%). Clinopyroxene microcrystals form polycrystalline aggregates in the groundmass. The groundmass (about 45%) is made up of chlorite, serpentine, calcite, and very scarce K-feldspar. In addition, there are carbonate inclusions that are considered to be fragments of limestones of the Carboniferous Madison Formation.

The study of a sample from the Yogo lamprophyre showed that its minerals have an extremely heterogeneous composition, marking multistage formation. The first stage involved formation of diopside with an Fe mole fraction of about 10 at %, which composes the core of most phenocrysts. The clinopyroxenes of this stage are enriched in Cr, Mg, and Na at relatively lowered contents of Ti and Ca (Table 1). This indicates the onset of crystallization at relatively high temperatures and pressures. However, the magmatic crystallization was presumably overprinted by skarn formation related to assimilation of host calcareous rocks. This process produced large clinopyroxene phenocrysts with distinctly expressed zoning (Fig. 1). Three zones (besides the core) are distinguished, with one Al-rich zone (Table 1). The aluminum content in this zone is two times higher than that in the core, reaching 6 wt % Al_2O_3. In the finer unzoned or weakly zoned grains, the concentration of Al_2O_3 reaches 9–10 wt %. Simultaneously, aluminous pyroxenes become lower in Si and higher in Fe and Ca; i.e., the melt was depleted in Si and enriched in Al. This is presumably the time of the abundant crystallization of corundum and phlogopite. The former entrained excess Al from the melt, while the latter took alkali, magnesium, and iron.

At the final stage of the evolution of the Yogo lamprophyre, minerals interacted with the melt to form rims around the sapphires (spinel), clinopyroxene (acmite), and phlogopite (chlorite).

Though Meyer and Mitchell [12] believe that the sapphires in the Yogo dike are alien to basalts and were only transported by lamprophyre magma from an unknown basement, they do not exclude the simultaneous formation of corundum and phlogopite. Of par-

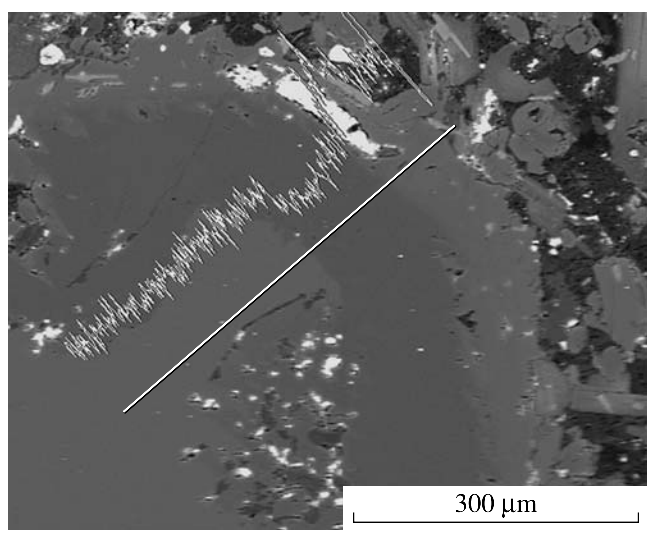

Fig. 1. Variations of the Al_2O_3 contents in the zoned diopside from the Yogo lamprophyre. The maximal Al content was identified in the second (from the core) zone.

Table 2. Oxygen isotopic composition of the studied corundums and associated minerals

Country	Deposit	Sample	Mineral	$\delta^{18}O$ (SMOW), ‰	$\delta^{13}C$ (PDB), ‰
United States	Yogo-Gulch (Montana)	AM-1	sapphire	5.6 ± 0.2	
			phlogopite	6.0 ± 0.2	
			brown carbonate	17.5 ± 0.2	1.06
			white carbonate	14.5 ± 0.2	–2.86
Russia	Podgelbanochnyi volcano, Primorskii krai	P-2	green sapphire	6.4 ± 0.2	
		P-3	blue sapphire	5.5 ± 0.2	
		P-4	olivine	5.0 ± 0.2	
		P-5	spinel	4.8 ± 0.2	
Russia	Khabok River, Tunkin depression, Irkutsk district	159-72	basalt	6.1 ± 0.2	
			corundum	9.1 ± 0.2	

ticular interest in this respect are the oxygen isotope data on these minerals (Table 2). It is seen that they have a similar oxygen isotopic composition (5.6–6.0 ‰). Since the formation temperature of phlogopite in the Yogo lamprophyres is no less than 900°C [12] and the crystallization temperature of corundum is also no less than this value (based on its melting temperature), the oxygen isotope fractionation is insignificant. Therefore, the obtained data indicate an isotopic equilibrium and genetic affinity of corundum and phlogopite.

The studied sample contains two types of carbonates. The first type is represented by a white calcite–dolomite mixture, which fills thin fissures in the rock. The second type is represented by a brown calcite–dolomite–aragonite–quartz aggregate that composes geodes and small fragments of irregular shape. They differ not only in mineral composition but also in oxygen and carbon isotopic composition (Table 2), which suggests that they are genetically unrelated with each other and the minerals of the host lamprophyre magma.

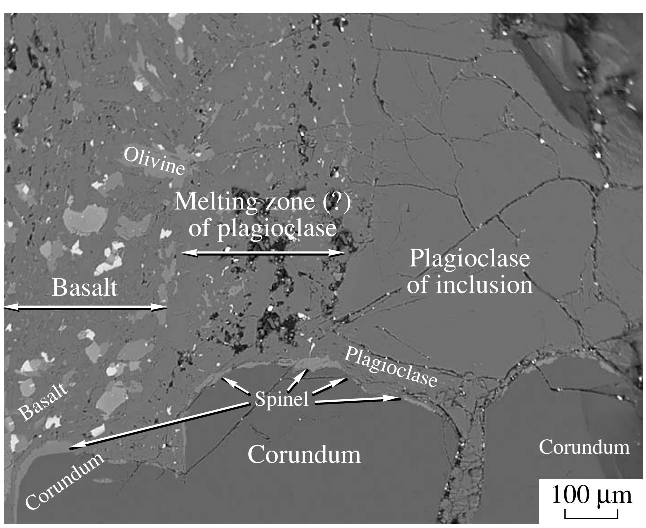

Fig. 2. Contact between a plagioclase–corundum inclusion and alkali basalt from the Tunkin depression.

The plagioclase–corundum inclusion in the basalt of the Tunkin depression (fragment of the Baikal rift zone) was found and described by N.Ya. Volyanyuk with coauthors in the early 1970s [1]. This inclusion has a coarse-grained texture and consists of plagioclase, corundum, and accessory zircon and ore minerals. Grains of grayish blue corundum reach 1.5–2 cm in size. Authors believed that this inclusion is xenogenic and represents a fragment of a "…crustal intrusive body of ultrabasic composition."

We studied a small fragment of this inclusion and demonstrated its complex structure. It contains plagioclase of different compositions. Large plagioclase grains comparable in size with corundum have an An_{36} composition. At the contact with basalt, the plagioclase has a thin 200–300 μm rim of weakly crystallized glass, while corundum is fringed by pleonaste (Table 3, Fig. 2). Grains of corundum contain fractures healed by more calcic plagioclase (An_{40-50}) with an insignificant amount of iron. At the contact with this plagioclase, corundum has a thin spinel rim, which propagates beyond the fractures, thus isolating the corundum from basalt. This more calcic plagioclase presumably has a secondary origin and was formed owing to penetration of basaltic melt in the inclusion through thin fractures. Judging from the established relations, the plagioclase–corundum intergrowth was partially melted when it was entrained in the alkali basaltic melt, which supports the assumption of the xenocrystic nature of this inclusion. *An* additional argument in favor of this interpretation is the 3‰ difference in the oxygen isotopic compositions between the corundum and basalt (Table 2).

The relations of the corundum from the alluvium of Podgelbanochnyi volcano (Primorye) with the surrounding basaltoids were not established reliably. However, sapphire crystals associate in the modern alluvium with megacrysts of hyacinth, sanidine, Ti-augite, kaersutite, phlogopite, Al spinel, magnesian ilmenite, Ti-magnetite, and garnet, which occur in the vent and

Table 3. Composition of minerals from plagioclase–corundum inclusions in the alkali basalt from the Tunkin depression

	Minerals of the inclusion						Minerals of basalt		
	plagioclase		corundum		rim spinel		plagioclase	olivine	pyroxene
SiO_2	58.88	59.00	–	–	–	–	55.37	37.59	49.32
TiO_2	–	–	–	–	–	0.4	–	–	2.06
Al_2O_3	25.62	25.54	98.09	99.09	62.28	60.52	27.64	–	4.03
Cr_2O_3	–	–	–	–	–	–	–	–	0.21
FeO	–	–	1.45	1.43	22.42	26.47	0.61	26.12	8.75
MnO	–	–	–	–	0.24	0.24	–	0.33	0.14
MgO	–	–	–	–	14.18	11.53	–	35.38	13.08
CaO	7.63	7.44	–	–	–	–	10.35	0.25	21.11
Na_2O	6.62	6.69	–	–	–	–	5.14	–	0.48
K_2O	0.96	1.16	–	–	–	–	0.49	–	–
NiO	–	–	–	–	–	–	–	0.18	–
Total	99.71	99.83	99.54	100.52	99.12	99.20	99.6	37.59	49.32
% An	(37)	(36)			47.0	56.4	(51)	29.3	27.3

pyroclastic facies of the volcano [2]. It is suggested that they were formed in the vent of basaltic volcano owing to gas epitaxy and later were exhumed during an eruption [4].

DISCUSSION

As is seen from Table 2, $\delta^{18}O$ in all the studied sapphires, with the exception of the sample from the Tunkin depression, varies between +5.5 and +6.4‰ SMOW. Similar values (from +4.8‰ to +6.1‰) were obtained for associated minerals and host basalt, suggesting their genetic relation. At the same time, the oxygen isotopic composition of distinctly xenogenic carbonates from the lamprophyres of the Yogo dike is 8–10‰ heavier than that of the studied "basaltic" corundum. The heavier oxygen isotopic composition ($\delta^{18}O$ = +9.1‰) was also found in corundum from inclusions in the alkali basalt from the Tunkin depression. This suggests that their minerals are in disequilibrium with the host lavas and have distinct xenogenic nature.

As is seen in Fig. 3, the oxygen isotopic composition can serve as a reliable criterion for determining the genetic nature of corundum. All the sapphires genetically related to mafic magmatic rocks have a close isotopic composition ($\delta^{18}O$ variations within 2.5‰ with most values varying between +4.5 and +7.0‰ SMOW. The isotopic ratios of the associated minerals (olivines, pyroxenes, micas) and host rocks are plotted in the same interval. Hence, mafic lavas (basalts, lamprophyres, and others) are parental for sapphire megacrysts and other less exotic minerals (olivines, pyroxenes, micas, and others); i.e., the sapphires crystallized during evolution of the parental magma. The sapphires from the deposits of the Yogo dike and Podgelbanochnyi volcano are ascribed to this group.

At the same time, there are xenogenic corundums that were transported by basaltic magmas from their origination site to the Earth's surface. Their genesis can be different. The plagioclase–corundum inclusions in basalts from the Tunkin depression can be of metamorphic genesis. It is highly possible that these inclusions were derived from corundum-bearing syenite–pegmatites, which are known in the Tazheran alkaline massif on the western shore of Lake Baikal.

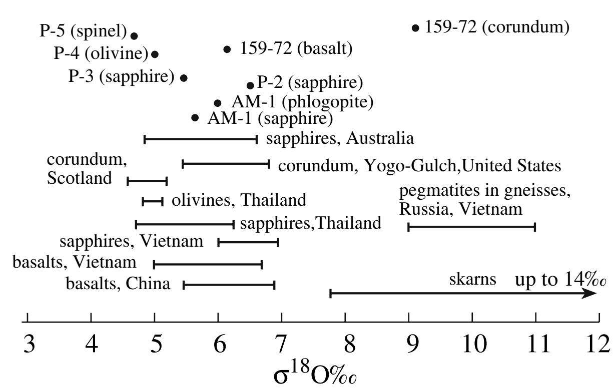

Fig. 3. Ranges of $\delta^{18}O$ in some corundums, associated basalts, and basaltic megacrysts. The ranges of oxygen isotopic ratios are after [8, 11, 17]. The points show the author's data.

CONCLUSIONS

The oxygen isotopic composition of "basaltic" corundum varies between +4.5 and +7.0‰ SMOW, which coincides with the compositional field of magmatic minerals (olivine, plagioclase, pyroxene, and others). The corundum from the Primorye placers is plotted in the same field. Since the oxygen isotopic composition depends on the formation conditions of the minerals and does not depend on their means of transportation to the Earth's surface, this indicates the genetic relation of corundum with basaltic magmas or their differentiates.

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