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Review

Oxygen isotopic composition as an indicator of ruby and sapphire origin: A review of Russian occurrences

S.V. Vysotskiy [a,b], V.P. Nechaev [a,b,*], A.Yu. Kissin [c], V.V. Yakovenko [a], A.V. Ignat'ev [a], T.A. Velivetskaya [a], F.L. Sutherland [d], A.I. Agoshkov [b]

[a] Far East Geological Institute, Far Eastern Branch, Russian Academy of Sciences, 159, Pr 100-let Vladivostoku, Vladivostok 690022, Russia
[b] Engineering School, Far Eastern Federal University, 8, Sukhanova Str., Vladivostok 690950, Russia
[c] Institute of Geology and Geochemistry, Ural Branch, Russian Academy of Sciences, 7, Per. Pochtovy, Ekaterinburg 620151, Russia
[d] Geoscience, Australian Museum, 6 College St, Sydney, NSW 2010, Australia

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ABSTRACT

This study combines our own new and literature data on oxygen isotopic compositions of corundum from the Russian territory including deposits in Karelia, Ural, Baikal and Far East regions. Corundum and associated minerals from placer and lode deposits are discussed in this review. The oxygen isotopic compositions of the colored corundum commonly result from mixing of meteoric (including glacial), crustal (metamorphic–metasomatic), and mantle magmatic waters. The individual values closely match the oxygen isotopic values in the host rocks. This allows identification of the sources for placer corundum using the $\delta^{18}O$ value as an important component for accurate diagnostics of the gemstones. Some corundum, especially from northwestern Karelia, has extreme isotopic characteristics ($\delta^{18}O$ down to −26.3‰), which almost invariably indicate its source location.

Contents

1. Introduction

The $^{18}O/^{16}O$ ratio between stable isotopes of oxygen ($\delta^{18}O$‰) is often used in order to determine the geological origin of colored corundum (ruby and sapphire varieties). Yui et al. (2003, 2006), Giuliani et al. (2005, 2014), Sutherland et al. (2007, 2009), Vysotskii et al. (2008), Vysotsky et al. (2009), Uher et al. (2012), and Zaw et al. (2014) provided a reliable framework for the likely identification of corundum of uncertain origin, especially those from placer deposits. Commonly, geochemistry assists in distinguishing between the magmatic and metamorphic gem corundum (Giuliani et al., 2005, 2007; Sutherland et al., 2007, 2009; Uher et al., 2012). However some isotopic compositions of oxygen in corundum are quite unique that it enables to almost exclusively locate its source (Krylov, 2008; Vysotskii et al., 2008; Vysotsky et al., 2009; Vysotskiy et al., 2014; Bindeman et al., 2010; Bindeman and Serebryakov, 2011). Source identification is especially important for some gem corundum deposits where it significantly influences their market costs.

There are about 80 corundum occurrences in Russia, three of which have been explored for jewelry raw material (Lyashenko, 2011). These

* Corresponding author at: Far East Geological Institute, Far Eastern Branch, Russian Academy of Sciences, 159, Pr 100-let Vladivostoku, Vladivostok 690022, Russia.
E-mail addresses: vysotsky@fegi.ru (S.V. Vysotskiy), nechaev@fegi.ru (V.P. Nechaev), kissin@igg.uran.ru (A.Y. Kissin), yakovenko@fegi.ru (V.V. Yakovenko), ignatiev@fegi.ru (A.V. Ignat'ev), velivetskaya@fegi.ru (T.A. Velivetskaya), Lin.Sutherland@austmus.gov.au (F.L. Sutherland), bgdtsdvfu@mail.ru (A.I. Agoshkov).

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three deposits are located in the Middle Ural, where the total ruby and sapphire reserves are evaluated as highly as 8,880 and 22,985 carats respectively. Four more localities in Karelia, Baikal region, Polar and South Ural are well known sources of minerals for collectors. Most of the occurrences and deposits are poorly studied geochemically (Fig. 1).

This paper presents new and literature data on isotopic composition of oxygen for corundum and associated minerals from Russian occurrences. The geology of these localities is summarized below in order to define the mineralization origin. There is little need for detailed geological discussion, because our data are generally in a good agreement with reviews by Giuliani et al. (2005, 2014) and Sutherland et al. (2007, 2009).

2. Samples and methods

The studied corundum and associated mineral species were sampled in the Russian territory, where host deposits cover almost all the corundum genetic types (Kievlenko, 2003), and include both lode and placer deposits.

The isotopic composition of oxygen was determined at the Far East Geological Institute facilities with the help of the vacuum camera and laser isotope separation (Ignat'ev and Velivetskaya, 2004a,b). The infrared CO_2-laser (MIR-30) was used for sample heating. Its isotopic composition was then determined using the Finnigan MAT-253 mass-spectrometer. The standard gas was calibrated at the SMOW scale applying NBS-28 ($\delta^{18}O = 9.6‰$). The outer truncation error of the method was less than $\pm 0.2‰$.

3. Geological settings

The studied corundum varieties were divided into four groups according to their geological setting:

1. *Sapphire from basaltic sourced placers* was sampled from river and slope sediments in southern Far East region, where it was first discovered in gold placers in 1980s (Esin and Peretyat'ko, 1992). Later, further sapphire sites were found in the tuff of Cenozoic alkaline basalt and in modern sediments of streams draining paleovolcanic edifices (Vysotskii et al., 2002). The basalt ages range between 14.5 and 7.5 Ma (Nechaev et al., 2009). This corundum is commonly blue and green, sometimes yellow and pink in color. Its large (>1 cm) crystals are chiefly flattened, while smaller crystals are prismatic, barrel-shaped and sharp bipyramidal. They commonly have traces of magmatic dissolution on the surface (Table 1).
2. *Sapphire and ruby from syenitic pegmatite, mica- and plagioclase-dominated metasomatic rocks in middle- and high-grade metamorphic suites* are well known in Russia. They were studied at the Ilmen Mountains of South Ural, the Komarovskoye and Izumrudnye Kopi occurrences of Middle Ural, the Makar-Ruz' occurrence of Polar Ural, Tazheran Massif in the western Baikal coast, and from a xenolith site in the Tunkin-basin basalts of the southwestern Baikal region. At all these localities, magmatic rocks, namely syenite and nepheline syenite, host metamorphosed rocks of the epidote-amphibolite and amphibolite facies, and associated pegmatite and other metasomatic rocks have similar ages: Cambrian–Ordovician in the Baikal region and Permian in Urals. In addition, the magmatic rocks are completely or partly metamorphosed, especially along their margins. Consequently, distinguishing between magmatic or metamorphic origin of corundum from these rocks is very difficult.
In the Ilmen Mountains, corundum (sapphire and ruby) was found in syenite and nepheline syenite pegmatite veins with bulges or branching lenses and, less commonly, in garnet-bearing crystalline schists, amphibolites, plagioclase-dominated rocks, and metamorphosed ultramafic rocks (Nikandrov et al., 2000; Popov and Popova, 2006). The studied sapphire-bearing pegmatite forms veins 10–15 m long and 0.5–1.5 m thick among gneisses. Corundum crystals are usually enclosed within microcline-perthite aggregates and occur as clusters. The feldspathic pegmatite usually contains prismatic, barrel-shaped and sharp bipyramidal corundum crystals 2–8 cm long, rarely up to 20–39 cm long. They are bluish gray, bronze

Fig. 1. Distribution of corundum occurrences in Russia.

Table 1
Oxygen isotopic composition (δ^{18}Osmow) of corundum and associated minerals from the Russian occurrences.

Occurrence: host rocks	Corundum sample	Color	δ^{18}O corund.	δ^{18}O ass.min.	Reference
1. Basaltic sourced placers					
Podgelbanochny Creek, Primorye:	P-2	Green	6.4	4.2Zr	Vysotsky et al. (2009)
	P-3	Blue	5.5		"
Levy Zolotoy Creek, Primorye	Lz-2	"	6.3	6.0Zr	Nechaev et al. (2009)
	Lz-3	"	6.5		"
Kedrovka River, Primorye	P-1	"	5.5	4.6Zr	Nechaev et al. (2009)
			6.4		"
	Kedr-1	Green	6.8	5.4Sp	This work
Khicha River, Khabarovsk region	VN07/9a	Blue	4.3	4.8Zr	"
2. Pegmatite, mica- and plagioclase-dominated metasomatic rocks					
Ilmen Mnts.: syenite pegmatite	Ur-1	Blue	5.4	7.8Fsp	Yakovenko et al. (2014)
	Ur-2	Gray	6.5	8.2Fsp	"
	Ur-3	"	5.9	8.4Fsp	"
	Ur-4	"	5.0	7.0Fsp	"
	214	"	5.4		"
	Ur-6	"	4.6		"
Komarovskoye: plagioclase-dominated rock	Ur-5	Violet	9.2		This work
Izumrudnye Kopi: margarite veinlet	No number	Blue	2.0		Ustinov et al. (2008)
Makar Ruz': plagioclase- and mica-dominated rocks	No number	Red	3.1		Ustinov et al. (2008)
	216	"	4.9		Yakovenko et al. (2014)
	Kr-11/16	Gray	5.4	9.0Fsp	This work
Tazheran massif: syenite pegmatite	Tzh-1	Gray	10.6	10.6Mc 11.9Fsp	Yakovenko et al. (2014)
Tunkin basin: xenolith in basalt	159-72	"	9.1		Vysotsky et al. (2009)
3. Marble					
Alabashka: marble	A-2	Red	19.4		This work
	Nal-1	"	19.8		"
	Nal-2	"	19.9		"
	Nal-3	"	19.7		"
Alabashka: breccia in marble and granite	P-1	"	16.7		"
	P-2	"	16.5		"
	P-3	"	16.6		"
	P-4	"	17.6		"
	No #	"	9.1		Ustinov et al. (2008)
Lipovka: mica schist marble	L-1	Pink	18.9		This work
	L-2	"	20.3		"
Kuchino: marble	K-1	Red	23.3		"
	K-2	"	22.9		"
	K-3	"	23.2		"
Chuksa: marble	Ch-1	"	22.4		"
4. High- and mid-grade metamorphic complexes of northwestern Karelia					
Unnamed: gneiss (granulite)	Karelia 1	Pink	3.0		Garnier et al. (2005)
	Karelia 2	"	2.9		"
Khitostrov: plagiogneiss	KR-2	"	−22.5	−21.4Fsp	Vysotskii et al. (2008)
	No number	"	−26.3 to −17.7 (n = 25)	−23.4 to −14.7Fsp (n = 21)	Bindeman et al. (2010, 2014), Bindeman and Serebryakov (2011)
	No number	"	−11.3	−21.0Fsp	Ustinov et al. (2008)
Varatskoye: plagiogneiss	K-227\3	"	−18.8	−18.7Fsp	Vysotskiy et al. (2014)
	K-231\6	"	−17.2	−18.0Fsp	"
	V45	"	−19.2		Bindeman and Serebryakov (2011)
	V81a	"	−17.27		
Notozero: plagiogneiss	K-159/15	"	−5.2	−1.8Am	Vysotskiy et al. (2014)
	K-159/15a	"	−1.7	−1.1Am	"
	K-159/15b	"	−1.5	−1.1Am	"
Perusel'ka: amphibolite	K-113/8	"	0.6	3.2Am	"
	No number	"	1.5		"
	P-11	"	0.26		Bindeman and Serebryakov (2011)
	P-3	"	3.45	3.67Am	
Dyadina Gora: amphibolite	Kr11-17	"	0.4 (core)	3.1Am	Vysotskiy et al. (2014)
		"	0.8 (rim)		"
	K-237/11	"	2.5	2.1Am	"
	DG-117i	"	0.49	2.12Am	Bindeman and Serebryakov (2011)
	DG64A	"	0.10	1.67Am	"
Kiy Ostrov: plagioclase-bearing amphibolite	Ki-2	"	2.8		This work
	K11-9	"	7.0		Bindeman and Serebryakov (2011)
	Kii-1	"	5.04	4.24–5.57Am	Bindeman and Serebryakov (2011)
Mironova Guba: amphibolite	Not-15	"	−2.34	−1.99Am	"
Khetolambina: amphibolite	DK484	"	4.82		"

Am — amphibole, Fsp — feldspar, Mc — mica, Sp — spinel from inclusion in corundum, Zr — zircon; n — number of analyses.

gray and dark gray. The coloration is allochromatic, related to mineral inclusions and idiochromatic with Fe and Ti chromophores with blue, light blue and yellow colors. There are syntactic intergrowths of corundum with biotite, muscovite and feldspar. Some corundum crystals are fractured, with muscovite and biotite filling in the fractures.

Violet and pink sapphire from high-aluminum gneiss was studied from the Komarovskoye occurrence located west of Murzinka Town, Middle Ural (Popov, 2003) and 5–7 km to the southwest of the Alabashka marble-hosted occurrence described below. The corundum-bearing leucocratic metasomatite forms thin (5–30 cm) veins conformable to host gneisses and schists of the late Paleozoic metamorphic complex intruded by granite and ultramafic rocks. The corundum is associated with plagioclase (albite-oligoclase, 65–70%), biotite (14–20%), and garnet (up to 7–8%) there. Staurolite, sillimanite, tourmaline, ilmenite, and rutile are also present in accessory amounts. Corundum occurs as both bipyramidal and barrel-shaped crystals up to 1.5 cm in size, sometimes surrounded by plagioclase aggregates and as small rounded shapes.

The Izumrudnye Kopi occurrence, which is a famous source of emerald and alexandrite from pegmatite and micaceous metasomatite in Russia, is poorly studied. The studied blue sapphire, however, is hosted by tourmaline–phlogopite–margarite veins cutting the metamorphosed ultramafic massif at the eastern margin of the Aduysky granite-gneiss complex (Ustinov et al., 2008; Olysych et al., 2005).

Ruby and gray sapphire were studied from plagioclase-corundum and mica-corundum rocks forming small, steeply dipping bodies at the Makar-Rus' occurrence, southwestern Ray-Iz dunite-harzburgite massif, Polar Ural. The largest body has a symmetric zonation (plagioclase-dominated core surrounded by phlogopite and pargasite zones) and is about 30 m long and 20–22 m thick (Shcherbakova and Suturin, 1990; Ustinov et al., 2008). The samples include well shaped corundum crystals and corundum–corundum intergrowths in association with chromite in a plagioclase–phlogopite and phlogopite matrix. The corundum is covered by a fringe of milky-white plagioclase or is enclosed in the micaceous aggregate. It is dark red, containing up to 3.2 mass % of Cr_2O_3. The ruby crystals commonly have numerous inclusions of chrome-bearing spinel, plagioclase, mica, and fluids.

West and southwest of Baikal Lake, corundum occurs in pegmatites in the Tazheran alkaline massif (the western Baikal coast) and smaller syenite intrusions of Cape Budun in the Olchon Island. Numerous ruby and sapphire occurrences were also found in marble layers of Cape Khoboy at the same island, all hosted by Lower Paleozoic gneisses and crystalline schists of the Olchon Series (Konev and Samoylov, 1974; Tatarinov et al., 1992; Grudinin and Chuvashova, 2011), as well as in the similar metamorphic complex (Syudynka Series) that extends for 150–200 km to the northwest of the southwestern Baikal, including the area of Tunkin basin (Levitsky and Pavlova, 1998).

In the Tazheran alkaline massif, sapphire was sampled from pegmatite veins, which cut the lens- and sill-like bodies of syenite and nepheline syenite intruding metamorphic rocks of the Olchon Series. The sapphire forms gray, dark brown, black and blue crystals up to 8 cm in length, associated with albite-oligoclase and biotite.

Gray to blue corundum from a small ($4 \times 5.5 \times 3.5$ cm) plagioclase-corundum xenoliths in Late Cenozoic basalt was sampled and primarily described by Volyanyuk et al. (1974). The basalt is located in the Tunkin basin that belongs to the Baikal rift zone. The studied inclusion is coarse-grained and consists of plagioclase (An = 36–37%), corundum (FeO_{total} = 1.4–1.5%) with spinel (ceylonite, Mg# = 44–53%) rims, and accessory zircon, ilmenite, and magnetite. The corundum grains are up to 1.5–2 cm in size. Volyanyuk et al. (1974) suggested that this inclusion is derived from pegmatite complex similar to that in the Tazheran massif and the Ural locations described above.

3. *Ruby and sapphire from marble* was sampled at the Alabashka and Lipovka occurrences of Middle Ural and the Kuchino and Chuksa occurrences in the South Ural. The Alabashka and Lipovka occurrences lie 100 and 70 km to NNE of Ekaterinburg respectively, and Kuchino and Chuksa occurrences are 100 km to the south of Chelyabinsk.

   At Alabashka, the marbles form lenses and interlayers among the Upper Paleozoic gneisses and rarer amphibolites. Corundum irregularly impregnates Mg-calcite marbles and creates sublongitudinal (conformable to cleavage), steeply dipping mineralization zones. Crystals are red and pink, tabular and barrel-shaped, often with numerous cavities on the surface, and are commonly 1–3 mm and up to 3 cm in size. They are associated with Cr-bearing phlogopite, muscovite, margarite, pink spinel, sphene, pargasite, diopside, as well as apatite, adularia, graphite, pyrite, pyrrhotite, and other minerals. Pyrite inclusions are common. The Alabashka occurrence includes a ruby-bearing breccia that is 4 m thick. This dips at 80° east, extends in northerly direction from marble to granite, and consists of clasts of leucocratic granite, pegmatite, amphibolite, and quartz. The micaceous breccia matrix contains Cr-bearing phlogopite, muscovite, chlorite, and, less commonly, adularia, sphene, rutile, and pyrite. Ruby is irregularly disseminated (up to 5% by volume) throughout the breccia including both granite- and marble-hosted parts. It forms steeply dipping tubular clusters, four of which were recorded in breccia along a 20-m part studied in detail. The ruby's color, crystalline shapes and defects are similar to those described for corundum in the Alabashka marble.

   At Lipovka, corundum-bearing marble is similar to that in Alabashka. It intercalates with crystalline schists and amphibolites intersected by serpentinite along reverse faults. Dykes of granite and pegmatite (locally with lepidolite, rubellite, pollucite, and molybdenite) are widespread. Corundum is confined in zones controlled by steeply dipping cleavage fractures, where it is associated with phlogopite, fuchsite, margarite, chlorite, rutile, pyrite, pyrrhotite, and less commonly Cr-bearing diopside, Cr-bearing pargasite, sphene, forsterite, kämmererite, adularia, and graphite. Generally, corundum forms small (up to 3 mm, exclusively up to 2 carats in the polished form), poorly shaped crystals, which are purple, red, pink, violet, blue and colorless. Mica predominates over carbonate in some zones, where ruby becomes dark red and cloudy.

   Kuchino and Chuksa occurrences are situated about 100 km south of Chelyabinsk and 18 km from each other, ruby and multicolored sapphire was found in marble intercalated with crystalline schists and amphibolites. These rocks are at the margins of granite-gneiss domes that are intruded by numerous granitic and pegmatite dykes, some of which host rare-metal mineralization with beryl, topaz, and tourmaline. There are three types of corundum: (1) small (1–3 mm, up to 3 cm), tabular, red and dark red ruby crystals with 1–3 wt.% of Cr_2O_3 disseminated in the very coarse Mg-calcite marble, where they are associated with apatite, anhydrite and pyrite, and replaced by pink spinel in the calcite-dolomite marble; (2) isometric rounded pink sapphires associated with pyrite, rutile, colorless phlogopite, pink spinel, and norbergite form disseminations in the calcite-dolomite marble; and (3) grains of irregular shape, different sizes (commonly up to 15 mm, rarely 50 mm) and colors (red, blue, white, yellow). These are associated with phlogopite, fuchsite, margarite, pyrite, rutile, sphene, adularia, Cr-bearing pargasite, tourmaline, and fluorite, and positioned in the cleavage fractures of a very coarse Mg-calcite marble.

4. *Ruby and pink sapphire from high- and medium-grade* metamorphic complexes of northwestern Karelia were sampled at several separate occurrences that extends over several hundred kilometers (Terekhov and Levitskii, 1991; Serebryakov and Aristov, 2004). They are located in the Chupinsky nappe that consists of supracrustal paragneiss derived from graywakes (Myskova et al.,

2000), which is considered as a fragment of the Belomorian allochton in a collision zone between the Karelia and Kola blocks of the Baltic Shield (Miller, 1997). Some of the occurrences (Hitostrovskoe, Varatskoe, Vysota 128, and others) are hosted by garnet-biotite (± kyanite) plagiogneisses, whereas others (Dyadina Gora, Kiy Ostrov, and others) are hosted in amphibolites and amphibole schists. The host rocks commonly form separate, parallel or branching veins from 0.4–0.5 m to 5–10 m in thickness and smaller (1–50 cm, rarely up to 1.5 m) bodies of irregular shape. Some authors believe that all the corundum occurrences in the region are structurally related to the nappes, being situated near the contact of felsic and mafic rocks (Terekhov and Levitskii, 1991; Levitskii, 2005; Terekhov, 2007). Others, however, suggest an association of the corundum-bearing rocks with zones of strike–slip displacement, where they form lens- and bed shape bodies resulted from high-pressure alkaline metasomatism (Serebryakov and Aristov, 2004; Serebryakov et al., 2007). In any case, the corundum-bearing metamorphic units consist of high-pressure amphibolite and less commonly granulite, with a protolith with ages of between 3 and 2.5 Ga. The ruby and sapphire mineralization appeared between 1.9 and 1.8 Ga, during the collision-related metamorphism. An intermediate event of mafic magmatism is reflected by zircon ages between 2.4 and 2.2 Ga, a time that corresponds to the Siderian–Rhyacian glaciation (Bibikova et al., 2004; Serebryakov et al., 2007; Vysotskii et al., 2011; Bindeman et al., 2014).

4. Results

The oxygen isotope systematics allows the distinction between six different types of corundum:

1. Multi-colored corundum from syenite pegmatite of the Ilmen Mountains and placers in the Cenozoic alkaline basalt fields of the southern Russian Far East (14 analyses), all show δ^{18}Osmow between 4.3‰ (4.2‰ for associated zircon) and 6.8‰ (8.4‰ for associated microcline). This range is within that attributed to magmatic rocks (lamprophyre, basalt, syenite) by Giuliani et al. (2005, 2014) (Fig. 2).
2. A wider, but within the same range of δ^{18}O values (3.1–10.6‰ for corundum and up to 11.9‰ for associated plagioclase) is shown by red, gray and blue corundums (7 analyses) from pegmatite and related mica- and plagioclase-dominated metasomatic rocks included in the granite-gneiss complexes of Middle Ural (Komarovskoe, Izumrudnye Kopi), Ray Iz metamorphosed ultramafic massif (Makar-Ruz', Polar Ural), the Tazheran alkaline massif and basalt of the Tunkin basin the southwestern Baikal region. This range is very close to that attributed to metamorphic rocks (granulite, cordieritite, gneiss, mafic and ultramafic rocks, and migmatite) by Giuliani et al. (2005, 2014) although shifted to lighter O-isotopic values relative to the metamorphic–metasomatic range (Fig. 2).
3. Blood-red and pink corundum (9 analyses) from the marbles of the Alabashka, Lipovka, Kuchino, and Chuksa occurrences in Middle and South Ural has δ^{18}O between 19.4‰ and 23.2‰ that is a little heavier than the values indicated by Giuliani et al. (2005, 2014) for marbles. However, the values range into those reported from the marble and skarn rocks of the Mogok area, Myanmar (Zaw et al., 2014; Sutherland et al., 2015).
4. Marble and adjacent granite at Alabashka are cut by breccia with pegmatite clasts, where corundum is visually similar to the marble-hosted one, but characterized by lower δ^{18}Osmow: 9.1–17.6‰ (5 analyses). The Lipovka marble hosts a vein of mica schist bearing pink corundum with δ^{18}Osmow as high as 18.9‰. A range of these values partly overlaps with the metamorphic–metasomatic and marble values reported by Giuliani et al. (2005, 2014) (Fig. 2).
5. Pink corundum from the Proterozoic gneiss of the northwestern Karelia shows anomalous δ^{18}Osmow between −26.3‰ and +3.0‰ (36 analyses; Garnier et al., 2005; Ustinov et al., 2008; Bindeman et al., 2010, 2014; Bindeman and Serebryakov, 2011; Vysotskiy et al., 2014).
6. The associated same-color corundum from amphibolites contains a heavier oxygen, with δ^{18}Osmow values between −2.3‰ and +7.0‰ obtained from 14 analyses (Bindeman and Serebryakov, 2011; Vysotskiy et al., 2014). This range is close to that indicated by Giuliani et al. (2005, 2014) for various metamorphic rocks and partly overlaps those indicated by Giuliani et al. (2005, 2014) for magmatic rocks and metamorphic–metasomatic rocks. The associated plagioclase and amphibole have similar O-isotopic characteristics.

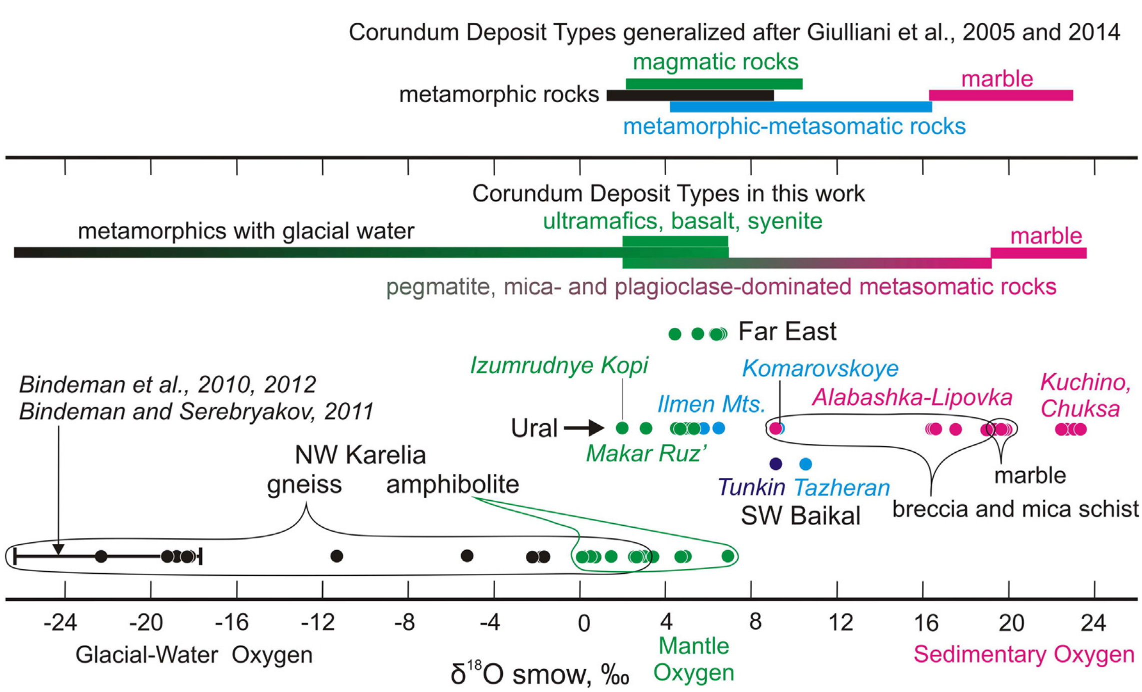

Fig. 2. Oxygen isotopic composition of corundum from the Russian occurrences compared with those from other parts of the world (Giuliani et al., 2005, 2014).

5. Discussion

The range of oxygen isotopic composition is extremely wide in colored corundum. However minerals of similar geological origin commonly have relatively small variations of this parameter. Nowadays, almost all the significant ruby and sapphire deposits have been characterized by $\delta^{18}O$ systematics, showing that it reflects the environment of corundum formation (Giuliani et al., 2005, 2007; Sutherland et al., 2009; Vysotsky et al., 2009; Zaw et al., 2014). The range of values help researchers to distinguish between ultramafic, felsic, or carbonate associations of this mineral, although temperature of crystallization can shift the $\delta^{18}O$ value of the corundum-equilibrated fluid by more than 2‰ (Giuliani et al., 2007).

For example, $\delta^{18}O$ varies between +2‰ and +7.5‰ in corundum of magmatic origin crystallized in mantle-derived ultramafic, syenitic, and alkaline basaltic melts. This isotopic range corresponds well to that of the associated rock-forming minerals, although feldspar commonly has higher $\delta^{18}O$ values, which may be attributed to crystallization differentiation. Similar values have been determined in colored corundum from the Cenozoic basalt of Primorye, as well as Southeast Asia and eastern Australia (Sutherland et al., 2009).

The high-grade metamorphic processes during marble formation have resulted in crystallization of ruby and sapphire having $\delta^{18}O$ as high as +19‰ to +24‰ corresponding to that of sediments (Giuliani et al., 2007; Sutherland et al., 2009; Zaw et al., 2014).

This direct connection of $\delta^{18}O$ between corundum and host rocks may be explained as follows. Oxygen isotopic composition of the Al-bearing fluid is buffered by that of host rocks during corundum crystallization, when water–rock or water–magma interaction takes place (Giuliani et al., 2007; Sutherland et al., 2009). This suggests that the volume of the Al-bearing fluid is negligible and quickly comes to equilibrium with host rocks in most cases.

A special case is represented by the Karelian occurrences, where corundum with the lowest $\delta^{18}O$ has been found. As shown by numerous previous studies, this mineral resulted from high-grade metamorphism at 1.9–1.8 Ga (Serebryakov et al., 2007; Vysotskii et al., 2011; Vysotskiy et al., 2014; Bindeman and Serebryakov, 2011). The protolith consists of Archean and Paleoproterozoic volcano-sedimentary rocks that were totally altered to the low-temperature aluminous metasomatite under the influence of glacial water at 2.2–2.4 Ga, during the Siderian–Rhyacian (Paleoproterozoic) glaciation (Vysotskiy et al., 2014; Bindeman et al., 2014). For this, a very high volume of water with light oxygen circulating for a long time was necessary. This process, however, preceded the corundum formation.

Meanwhile, the range of $\delta^{18}O$ values determined in corundums of different origin indicates that their oxygen is commonly hybrid. This is obvious for numerous metasomatic deposits like pegmatite, skarn, mica- and plagioclase-dominated rocks, although most of the corundum-bearing gneisses and crystalline schists seem to be metasomatized as well. Among the studied cases, the mixed origin nicely establishes the origin of the oxygen from rubies and sapphires of Alabashka and Karelia showing very wide $\delta^{18}O$ variations. Thus, all of these corundums oxygen may be conceived as a mixture between oxygen of common sedimentary rocks (derived from continental crust, marine and meteoric waters), magmatic (mantle-derived) rocks, and that of glacial origin (Fig. 2). Only the proportion of these three sources changes from place to place. Finally, this leads to the conclusion that the $\delta^{18}O$ systematics for determining the geological origin of such corundum is restricted to two extreme cases, one hosted by marble, in which the oxygen is almost totally derived from common sedimentary and crustal-metamorphic waters, and the other, where oxygen is significantly contributed by glacial waters. Other corundum oxygen may be a mixture between the last two. The mantle-derived oxygen certainly is a major constituent of multi-colored corundum from ultramafics, alkali basalt, and syenite, as well as a significant contributor for some ruby and sapphire of metamorphic–metasomatic origin. Its confident identification, however, requires additional petrological study.

6. Conclusions

The data presented above on the Russian corundum samples are essentially similar to those described and classified in the well known world-wide occurrences and deposits (Giuliani et al., 2005, 2014). However, the characterization of corundum from many Russian occurrences is not well described in the English literature. In addition, this work presents data on the unique Karelia occurrences, where δ^{18}Osmow changes show wider ranges than those in the rest of the world: from −26.3‰ to +7‰ in corundum (original data; Ustinov et al., 2008; Bindeman et al., 2010, 2014; Bindeman and Serebryakov, 2011).

Oxygen isotopic composition of colored corundum is controlled by the host rocks. It is one of the quantitative parameters allowing recognition of the mineral genesis. In most cases, $\delta^{18}O$ in corundum of mantle-magmatic origin varies between $+2‰ < \delta^{18}O < +7.5‰$. This range is characteristic for corundum from ultramafic rocks, syenite, alkaline basalt and associated volcaniclastics. Corundum formed during metamorphism of carbonate sedimentary rocks has the highest heavy oxygen isotopes, with $\delta^{18}O$ ranging from +19‰ to +24‰. Corundum from northwestern Karelia formed during high-temperature and high-pressure metamorphism of hydrothermally altered Paleoproterozoic and Archean rocks. They inherited the extreme isotopic characteristics of the protolith, whose alteration occurred under influence of glacial water during the Siderian-Rhyacian time. This corundum has δ^{18}Osmow varying from −26‰ to +7‰, preserving such abnormal characteristics for almost 2 Ga. All other corundum deposits, which are hosted by pegmatite, skarn, mica- and plagioclase-dominated rocks, result from metamorphic–metasomatic processes that mix oxygen of crustal and mantle origin. This oxygen has $\delta^{18}O$ ranging from +7.5‰ to +19‰.

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