


Article

Naryn-Gol Creek Sapphire Placer Deposit, Buryatia, Russia

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Abstract: A new gem corundum occurrence has been discovered in the Naryn-Gol Creek placer of the Dzhida volcanic field (Russia). In this placer deposit, sapphire associates with large crystals of garnet, spinel, augite, olivine, enstatite, ilmenite, Ti-magnetite, and alkali feldspar. Such a combination of minerals is typical for the placer deposits associated with alkali basalts widely distributed in Southeastern Asia and Australia. We have also found sapphire crystals in phonotephrites of the nearby Cenozoic alkali-basalt paleovolcano Barun Khobol Pravyyi, and in basalt sample and trachy-basalt from the valley flood basalts. The chemical composition of sapphire is generally typical for ‘basalt’ corundum: it is rich in Fe, and depleted in Ti and Cr. The $\delta^{18}\text{O}_{\text{SMOW}}$ values of corundum and related megacrysts range from 4.6 to 6.8 ‰, thus corresponding to the isotopic signature of igneous rocks. Etched and corroded surfaces of sapphire and other megacrysts indicate that they are in non-equilibrium with their host alkali basalts. Volatile components, CO_2 in particular, played a significant role during sapphire formation as gas inclusions reveal.

Keywords: sapphire; placer; basalts; microelement composition; oxygen isotopes

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1. Introduction

This paper is an expanded version of the conference paper [1]. The publication was supplemented with details about the history of the geological exploration of the site; its geological structure; the finding of trapiche sapphire, i.e., sectoral color distribution; the features of the external morphology of sapphire grains and other megacrysts; the composition and formation of pseudomorphs after pyrite; the mineral composition of heavy concentrate and its sources; and the composition of volcanic rocks as a source of placer megacrysts.

Sapphire is a precious variety of corundum mostly used and valued by jewelers along with ruby and emerald. Chemically, it is a trigonal modification of crystalline alumina— $\alpha\text{-Al}_2\text{O}_3$. Sapphire is characterized by admixtures of chromophore elements Fe^{2+} , Fe^{3+} , Ti^{4+} , Cr^{3+} , and V^{3+} . The blue color of natural sapphires is defined by an $\text{Fe}^{2+}/\text{Fe}^{3+}$ ion ratio and number of $\text{Fe}^{3+}+\text{Fe}^{3+}$ and $\text{Fe}^{2+}+\text{Fe}^{2+}$ ion pairs [2,3], and is divided into alternating polychrome or monotone zones of different color intensity. Less frequently, trapiche can be observed. Certain light blue and grayish-blue sapphires show the alexandrite effect, acquiring a reddish or purple–red hue in the evening artificial light [4].

Sapphire is a highly demanded and scarce mineral in Russia, since there are a few small deposits (Verbanny Log, Kornilov Log, and Polozhikha) and exploration lots (Alabashka and Nizhnyaya Alabashka) in the Middle Urals as well as two deposits (Nezametnoye, Sutara) and several local occurrences (Podgelbanochnyi, Levyi Zolotoi, and Kitscha) in the Russian Far East. None of them are currently being developed. Therefore, the discovery of the Naryn-Gol sapphire placer in Buryatia is important for expanding the mineral resource base of Russia.

The first reports of corundum findings in the studied area were made by the “Baikalkvartssamotsvety” enterprise that explored the region in 1986–1988. These works revealed increased concentrations of pyrope and chrysolite in alluvial–deluvial, alluvial–proluvial, and alluvial deposits on the slopes of the Boldosok volcano. Different-colored corundums were discovered together with pyrope and chrysolite in the stream sediment samples taken from deluvial deposits at the foot of Pravyi Barun Khobol volcano and placer samples taken from the Naryn-Gol Creek. Findings of transparent rounded grains and their light blue debris $4.5\text{ mm} \times 3.0\text{ mm} \times 1.5\text{ mm}$ in size were reported.

The “Baikalkvartssamotsvety” enterprise carried out additional research in the Naryn-Gol area in 1989–1992. Three borehole profiles 800 m long and spaced 20 m were drilled across the Naryn-Gol Creek valley. In total, thirty-eight 1–2 m deep boreholes were made. The obtained material was sampled in the form of heavy mineral concentrates and revealed small 0.3–0.5 mm single corundum grains. Increased concentrations, 30–50 grains to be precise, were detected in a borehole drilled near the Naryn-Gol Creek mouth. Findings of grey or grey–green–blue, less frequently pink or raspberry corundum grains with an uneven color distribution (we assume that garnet could have been mixed up with the pink or raspberry corundum) were reported. A 6.8 m^3 bulk sample was taken from gravel near this borehole. During the processing of the sample, twelve 4.5 mm flattened corundum grains were found in the +2 mm fraction. No corundum was found in the –2 mm fraction.

In 2011–2012, V.I. Generalov and O.I. Marchuk resumed work on the assignment of the Department for Subsoil Use in the Republic of Buryatia. Search routes were set up using 131.1 km of heavy mineral concentrate sampling, 174 m^3 of clearing, 83 m of test pits, and 64.7 m^3 of ditches. A total of 96 channel samples, 46 small laboratory samples, and 455 heavy mineral concentrate samples were selected. According to the results of mineralogical analyses, corundum is very rarely found in the form of single grains and in commercially significant concentrations, the maximum concentration being 0.007 g/m^3 . At the same time, the studied area is classified as very favorable for identifying gem minerals.

Sapphire originates from different settings, for example, to be related to deep basaltic magmas, alkaline syenite pegmatites, high-alumina metamorphic rocks, skarns, and secondary quartzites [5]. Cenozoic sapphire-bearing alkali basalts and lamprophyres with transparent corundum megacrysts associate with magmatic deposits. Sapphires are extracted from placers associated with intraplate alkali basalts in Australia, Indochinese Peninsula, West Africa, Mongolia, Russia, and other countries [6–9]. Sapphire origin in basalts is widely debated [9]. It was previously assumed that sapphire is the early crystallization phase carried up to the ground surface in an unstable form. However, basalts are not corundum-normative rocks [9–11]. The impossibility of corundum direct crystallization from basaltic melt was proven experimentally [12]. Thus, sapphire is, possibly, an upper mantle mineral transported by basalts under corrosion and dissolution. At the same time, sapphire and other minerals of megacryst association are found in lava and pyroclastic of Cenozoic alkali basalts [13,14].

Therefore, study of mineralogy, geochemistry, and isotopic composition of sapphires and related minerals in the Naryn-Gol placer will allow us to shed light on the mysterious sapphire origin. The authors of the paper participated in the exploration and assessment of the Naryn-gol conducted by the “Yuterg” company. The work results served as a basis for this article.

2. Methods

Mineralogy of the placer megacrysts was studied at the Analytical Center of the Far East Geological Institute, Russian Academy of Sciences (FEGI FEB RAS), using a JXA–8100 electron-probe microanalyser (Jeol, Tokyo, Japan) with three wave spectrometers equipped with an INCAx-sight energy dispersive spectrometer (Oxford Instruments, Abingdon, UK).

Measurement of oxygen isotope ratios was carried out at the Far East Geological Institute, Russian Academy of Sciences. Oxygen was extracted while heating the sample by an infrared laser ($10.6\text{ }\mu\text{m}$) in the steam of BrF_5 (~210 Torr). It was then analyzed using a

MAT-252 dual inlet mass spectrometer (Thermo Fisher Scientific, Karlsruhe, Germany). The method has been tested on international (NBS-28) and internal standards. The measurement accuracy for $\delta^{18}\text{O}$ is $\pm 0.2\%$.

The compositions of inclusions were tested at the Analytical Center of the Far East Geological Institute, Russian Academy of Sciences (FEGI FEB RAS), by LabRamHR 800 RAMAN spectrometer (Horiba Scientific, Palaiseau, France) with an He–Ne integrated laser (Pmax-20 mW, 632.8 nm, red). Additional Ar+ laser was used for (Pmax-200 mW, wavelength 514 nm) fluid inclusions study.

Spot concentrations of the trace elements were determined by the method of secondary ion mass spectrometry with a Cameca IMS-4F ion microprobe at the Yaroslavl Branch of the Institute of Physics and Technology, Russian Academy of Sciences.

The silicate analysis was performed on a UNICO 1201 spectrophotometer at GIN SB RAS (Ulan-Ude). Atomic absorption, spectrophotometric, flame photometric, gravimetric, and titrimetric methods were used. The atomic emission spectral analysis of Au concentration in three samples of quartz–carbonate veins from Ordovician schists was conducted at GIN SB RAS (Ulan-Ude).

The pseudomorphs after pyrite and heavy concentrate minerals were studied using a LEO 1430VP electronic scanning microscope (Carl Zeiss, Oberkochen, Germany) and an INCAEnergy 350 energy dispersive spectrometer (Oxford Instruments Analytical Ltd., Abingdon, UK) for the quantitative analysis at GIN SB RAS (Ulan-Ude).

3. Results

3.1. Geology of the Area

The Naryn-Gol placer is located near the Naryn-Gol Creek at the left tributary of the Darhintuy River in the southern part of the Dzhida volcanic field. The field is thought to be confined to the Baikal rift zone (Figure 1).

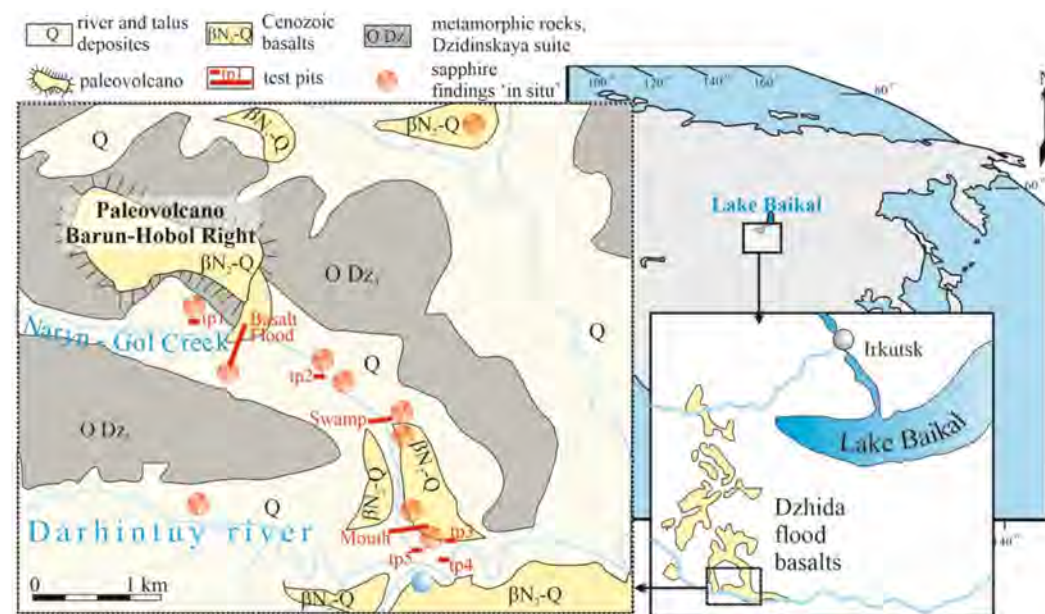


Figure 1. Geological setting of the Naryn-Gol Creek placer.

Cenozoic volcanic rocks penetrate and overlap Ordovician volcanogenic–sedimentary deposits in the studied territory. The Upper Ordovician Dzhida Formation is composed of metamorphosed sandstones, siltstones, limestones, and dolomites interbedded with breccia, conglomerate, and shale [1]. Neogene–Quaternary volcanogenic formations are represented by “top” alkali basalts of the Barun-Khobol Pravyyi (Right) stratovolcano, small lava-slag cones, pyroclastic strata, and “valley” flood basalt lava flows (Figures 1 and 2). Both phonotephrite tuffs and trachybasalt flows contain megacrysts and xenoliths of lherzolites

(Figure 2D). All these strata, in turn, covered by upper Pleistocene alluvial deposits of the I and II terrace above the floodplain and Holocene alluvial, eluvial–diluvial, diluvial, and eluvial structures (Figure 1), are where most of the sapphires were found (Figure 2B).



Figure 2. Trenches and test pits in the Naryn-Gol Creek placer. (A)—exposed permafrost layer; (B)—gem-bearing bed; (C)—residual weathered layer and pyroclastic rocks covered by basaltic flows; (D)—poorly rounded basaltic corestone containing lherzolite xenoliths and megacrysts of olivine and sanidine; and (E)—basalt flow overlying the residual weathered layer exposed at the base of the Cenozoic volcano. β —basalts; Lerz: lherzolite; Fsp: feldspar; Ol: olivine.

To identify the structural features of the sapphire-bearing placer, three trenches and several test pits were excavated in different locations revealing a considerable variety in the placer structure (Figures 1 and 3). Enrichment with sapphire and garnet was observed at the junction of the Naryn-Gol Creek and the Darhintuy River (Mouth Trench, Figure 3) and further upstream in the Naryn-Gol Creek (Swamp Trench, Figure 3). The layers are mainly composed of basalt fragments irrespective of size and distribution of the material in the placer (Figure 3). Alluvial–diluvial deposits at the foot of the Barun-Hobol Pravyyi volcano (exposed in the Root Trench, Figure 3) are characterized by permafrost in the subsoil layer and a thick heavy residual layer made mostly of spinel, ilmenite, garnet, and goethite after pyrite. Corundum is rare, but a few crystals were found in situ in basalts and in weathered tuffs (Figure 4).

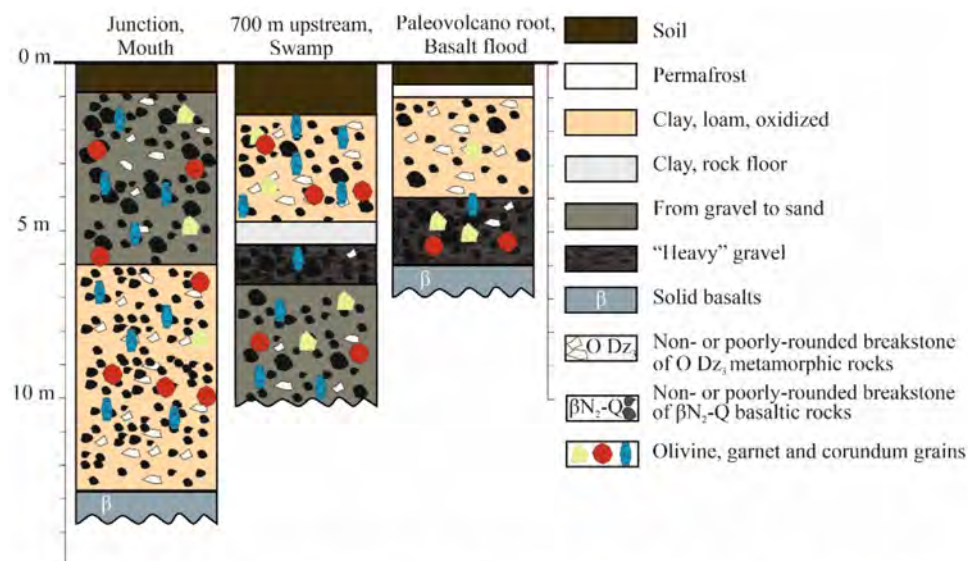


Figure 3. Composition charts of 3 trenches (7 to 15 m deep): root, swamp, and mouth.

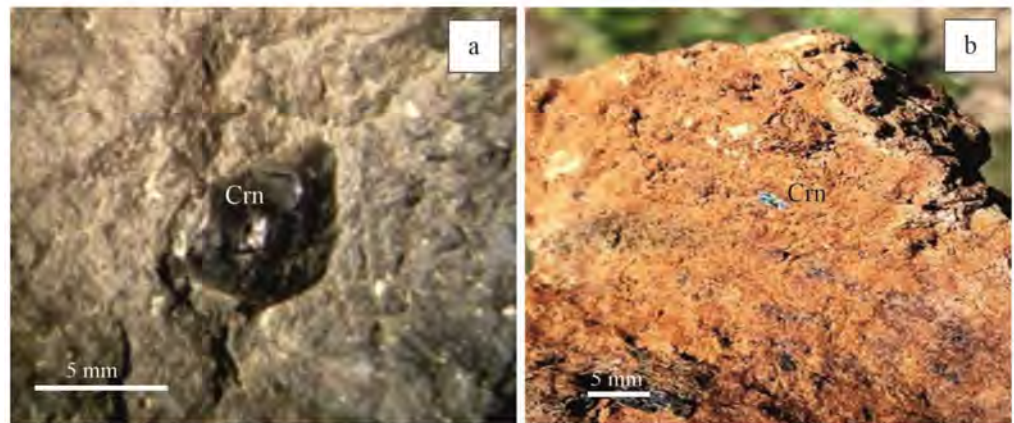


Figure 4. Sapphire grains. (a) Sapphire grain in basalt, Darkhintuy River vicinity. A.V. Tatarinov's photo. (b) Blue sapphire crystal in weathered tuff Naryn-Gol River, near Root Trench. O.Yu. Korshunov's photo. Crn: corundum.

3.2. Corundum

The Naryn-Gol corundum is blue, light blue, green, yellow, gray, brown, and even dirty pink, though rare (Figure 5). The stones are mostly blue and light blue, often with zonal and spotty coloration.



Figure 5. The 22 stone collection of the Naryn-Gol placer sapphires.

In addition, sectoral (trapiche) corundums were found (Figure 6). The trapiche-patterned stone has a dark blue color and is translucent. Hexagonal growth is also observed. The core of the sample is colorless. The trapiche has six white symmetrical radial patterns contrasted with the blue body color. The size of biggest sapphire is 1.7 cm × 1.2 cm × 0.7 cm. Earlier trapiche sapphires of metamorphic origin were found

in the Sutara placer, Russian Far East [15]. The Naryn-Gol is in fact the first discovered occurrence of basaltic trapiche sapphire in Russia.

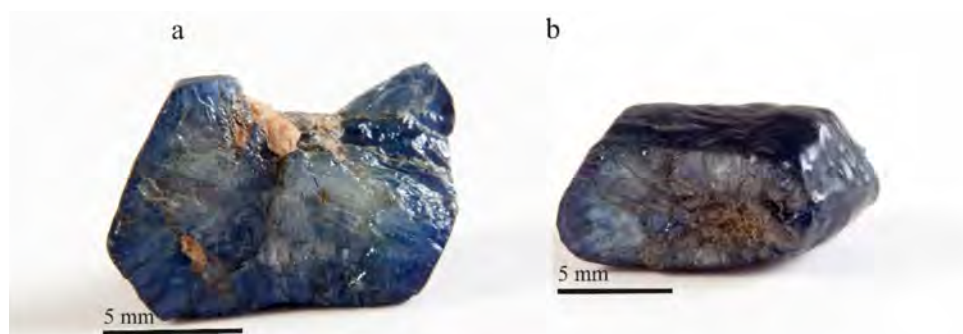


Figure 6. Trapiche sapphires. (a) Cleavage plate of a large prismatic crystal with chipped and induction surfaces of co-growth with other crystals, the grains are melted and corroded, contains inclusions of altered feldspar; (b) a flattened prismatic crystal, the grains are melted and corroded.

The sapphires are translucent to semi-translucent, 3–7 mm, sometimes 15 mm or more in size. Barrel-shaped crystals and their fragments are most common, while bipyramids are rare. Corundum does not have crystal cleavage but separates along parting planes into hexagonal plates (Figure 6). The surface of the sapphire crystals bears traces of melting and/or dissolution (Figures 5 and 6).

The sapphires of the Naryn-Gol occurrence contain only one major impurity—iron. Its concentrations vary from 0.5 to 2 wt. % (Table 1). Concentrations of Ti, Cr, V, Ni, Mg, Mn, and Ga are much lower. The isotopic values for the Naryn-Gol Creek corundums are presented in Table 1 and lie within a narrow range of 4.5‰–6.5‰ [1].

Table 1. Chemical composition and isotopy of the Naryn-Gol Creek corundums.

Method	Isotopy ‰	Microprobe *					Ion Probe **				
		Weight %					Ppm				
Sample	$\delta^{18}\text{O}$ SMOW	Al ₂ O ₃	FeO	Mg	Mn	Cr	Fe	Ti	V	Ni	Ga
J8	6.2	98.35	1.23	27.4	5.34	0.07	6538	55.59	7.87	5.57	210
J1	4.6	96.76	0.61	19.7	3.51	5.37	2499	91.50	12.78	9.60	267
J3	6.4	98.12	1.93	16.4	3.11	0.25	3701	120.90	8.67	14.36	197

* analyst G.B. Molchanova; ** analyst S.G. Simakin. Reprinted with permission from [1].

The Naryn-Gol sapphire colors depend on the ratio of ferric and ferrous iron ions. Due to isomorphism, Fe ions replace Al³⁺ ones in the corundum crystal structure. Blue shades in the green sapphire are caused by Fe³⁺ and Fe³⁺–Fe³⁺ optical centers. There are also exchange-coupled pairs of Fe²⁺–Fe³⁺ [16].

The clarity of the sapphire samples from the Naryn-Gol Creek occurrence varies from VS (very slightly included) to I₃ (heavily included) according to the GIA Gem Clarity Grading Codes. Inclusions in some samples are visible to the naked eye (Figure 7). Most examined samples contain inclusions, both monophase (Figure 7a) and multiphase (Figure 7b). Mineral, fluid, and melt inclusions are in abundance. According to preliminary RAMAN investigations, most gas inclusions contained a certain share of carbon dioxide. Mineral inclusions in the corundum are mainly fluorapatite (Figures 7a and 8), sometimes zircon (Figure 8c), and less frequently feldspar (sanidine) and Fe-bearing spinel (pleonaste). Primary melt inclusions are rare in the Naryn-Gol sapphires, while the secondary ones, in contrast, prevail and consist mainly of iron oxides and hydroxides (Figure 8b,c) [1].

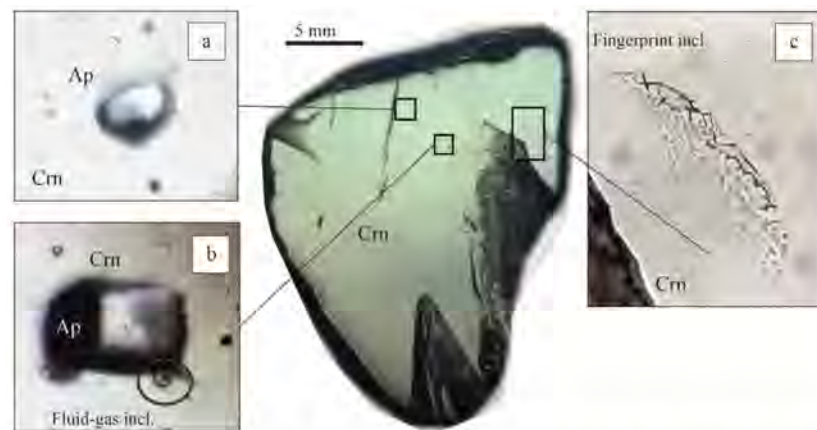


Figure 7. Mineral and fluid inclusions in the Naryn-Gol Creek sapphires. (a)—monophase apatite inclusion; (b)—multiphase inclusion; (c)—fingerprint inclusions. Ap: apatite; Crn: corundum; incl.: inclusion.

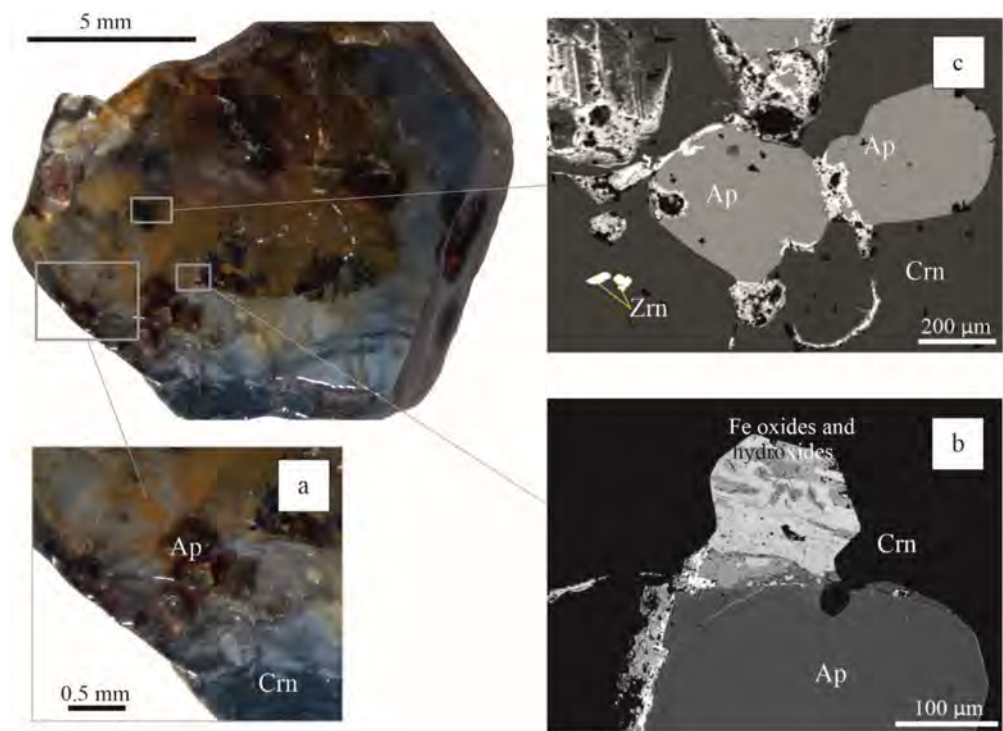


Figure 8. Mineral and melt inclusions in the Naryn-Gol Creek sapphires. (a)—apatite inclusions; (b)—apatite and primary melt inclusions; (c)—apatite, zircon and primary melt inclusions.

3.3. Mineral Assemblage

In both placers and volcanic rocks, corundum co-exists with large crystals of garnet, feldspar, pyroxene, olivine, spinel, ilmenite. Iron hydroxide pseudomorphs after pyrite (co-called devil's dice) are common in Naryn-Gol placer [1] (Figure 9).



Figure 9. Minerals of the Naryn-Gol placer. (a)—garnet, (b)—feldspar, (c)—olivine, (d)—spinel, (e)—orthopyroxene, (f)—clinopyroxene, (g)—ilmenite, and (h)—pseudomorphs after pyrite.

Garnet is represented by pyrope–almandine Prp 0.545, Alm 0.312, Grs 0.118 (Figure 9a); feldspar by sanidine (Figure 9b); olivine by forsterite with Mg # 90.27 (Figure 9c); spinel by pleonaste low in chromium (0.57 wt. %) and in titanium (0.81 wt. %) (Figure 9d); orthopyroxene by enstatite (Figure 9e); and clinopyroxene by Ti-bearing augite (Figure 9f). Large silver-black ilmenite, on the whole, resembles spinel but is distinguished by a flinty fracture (Figure 9g) [1].

Grains of the megacryst assemblage minerals in placer were formed by washing and weathering of fresh fractures, their surfaces bear traces of melting and dissolution. The oxygen isotopic composition of the megacrysts demonstrates $\delta^{18}\text{O}$ SMOW values ranging between 4.8 and 5.7‰.

3.4. Pseudomorphs after Pyrite

A large amount of brown pseudomorphs after pyrite were found in the Naryn-Gol placer (Figure 9h). The pseudomorphs are represented by unrounded and weakly rounded hexahedra with distinguishable combinational striation of a pentahondodecahedron. The pseudomorphs drew our attention because of their ability to be attracted to a magnet. Pyrite crystals of a similar appearance, some of which are fragmentary or completely replaced, were found during fieldwork in light-colored metamorphosed sandstones of the Dzhida formation.

Laboratory study showed that the pyrite is replaced with goethite. The goethite develops along the periphery of large crystals and then completely replaces the crystals, which are less than 1 mm in size. In the placer, the pseudomorphs on the surface and cracks are partially replaced by hydrogoethite. Xenomorphic grains of quartz and barite, idiomorphic zircon grains (up to 50 μm in size), and irregular-shaped apatite grains (up to 30 μm) are found as inclusions in the pyrite. Muscovite and rhabdophane were found in cracks.

3.5. Mineral Composition of Heavy Concentrate

During a geological survey, a productive corundum-bearing layer of sand 30–50 cm thick was found at a depth of 1.5 m in the left side of the Naryn-Gol river. The seat rocks are black basalts, the overlaying rocks are pebble-boulder deposits consisting mainly of fragments of black basalts. The concentrate was mechanically panned from the productive layer during the extraction of gemstone raw materials, and further, it underwent magnetic separation.

Native gold is observed in the form of rounded grains, 300–500 μm in size. The external part of the grains consists of high-graded gold almost without impurities. Silver impurity in two samples were determined (10.62 wt. % and 1.95 wt. % of Ag).

Zircon forms elongated prismatic crystals with sharp bipyramids about 100 μm in size. It is colorless, transparent and contains no admixtures. Zircon demonstrates zonation and poly-cycles (core–rim structure).

Ti-bearing magnetite is one of the most common minerals in heavy concentrate. Grains of various morphology are observed there: from rounded fragments to cubic crystals. The size of the grains varies from 50 to 200 μm .

Ilmenite is observed in the form of rounded grains with corroded facets 100 to 200 μm in size.

Scheelite is represented by detrital grains up to 200 μm in size.

Uraninite was found as a single detrital grain with rounded facets about 80 μm in size.

Monazite is in the form of rounded fragments of crystals, some grains contain inclusions of ilmenite.

Chromite is represented by well-rounded grains up to 100 μm in size. Chromite composition: FeO-50.68 wt. %, Cr_2O_3 -45.7 wt. %, TiO_2 -2.82 wt. %, Al_2O_3 -3.14 wt. %, MnO-1.3 wt. %, and MgO-1.66 wt. %.

3.6. Volcanic Rocks

Volcanic rocks of the Dzhida field have attracted scientific attention for a long time. In 1970–1975, V.I. Antoshenko-Olenov studied the Cenozoic stratigraphy, history of the relief, and described quaternary deposits. He described the Bartoy group of volcanoes [17].

S.V. Rasskazov and co-authors [18] determined the lava age of the Dzhida River basin using the ^{40}Ar - ^{39}Ar method. The results indicate that volcanism of this territory began in the Temnikovsky fault zone in the early Miocene 22–19 million years ago. K-Ar dating does not exclude the possibility of earlier (Late Oligocene) eruptions. The “valley” flows of the Khamney River are estimated to be 3.0 ± 0.4 million years old. Half a kilometer above the mouth of the Khamney River, eroded by the Dzhida River valley, volcanics from the middle part of the lava flow were dated by K-Ar method at 2.89 ± 0.03 Ma. In the center of the Bartoy area, the eruptions began with a 15 km flow of hawaiites about 1.08 million

years ago. The final volcanic activity resulted in the formation of cinder cones. One of such cones—Bolshoy, is 0.79 ± 0.02 million years old. The age of porphyry lavas of the Tsakir volcano is about 0.6 Ma (the ages obtained by ^{40}Ar - ^{39}Ar and K-Ar methods) [18].

V.V. Yarmolyuk and co-authors [19] established that the formation of Bartoy volcanoes occurred in two stages: the first 1.17 Ma stage and the second 0.8 Ma one. Thus, eruptions of Khobol volcanoes are consistent in time with early outflows in the Bortoy River valley [19].

A.V. Aseeva and co-authors [20] studied garnet megacrysts from Bartoy volcanoes of the Dzhida volcanic field. It is shown that these megacrysts are not in equilibrium relative to alkali basalts. They formed in mantle spots in lower parts of the Earth's crust, and subsequently they were captured and brought to the surface by alkali basaltic magma [20].

In this area, geologists traditionally distinguish “valley” and “top” volcanic rocks.

The “valley” volcanic rocks resulted from areal effusions, they are commonly found in the valleys of the Naryn-Gol Creek and Darkhintuy River in the form of alluvial and deluvial deposit boulder and pebble material exposed on the Darkhintuy River banks (Figure 10). The rocks are represented by dark-grey massive basalts with inclusions of megacrysts, sapphire, olivine, sanidine, pyroxene, spinel, and ilmenite. The rocks of the “valley” type are characterized by porphyritic texture with phenocrysts of olivine, plagioclase, and pyroxene. The texture of the main bulk is intersertal, composed of microliths of plagioclase and pyroxene and a small amount of volcanic glass. In thin sections, a large amount of Ti-bearing magnetite is observed. Plagioclase is represented in phenocrysts by elongated idiomorphic grains with characteristic polysynthetic twinning. No alterations have been found. Olivine appears as idiomorphic grains of various shapes, from elongated dipyramidal crystals to isometric. There are both fresh and altered grains. Elongated crystals of pyroxene, represented by Ti-bearing augite, are extremely rare.



Figure 10. “Valley” volcanic rocks: (a) alluvial and deluvial deposits of the Naryn-Gol Creek and (b) rocks exposed in the Darkhintuy River bank.

In terms of geomorphology, the “top” volcanic rocks can be easily recognized due to the cone form of their volcanic structures with visible craters in the upper part. They influenced the formation of the Naryn-Gol placer, and the walls at the foot of the Barun-Khobol Pravyyi volcano, outcropped by the Naryn-Gol Creek (Figure 2). In the walls, there is an alternation of layers of red and gray tuffs with layering of pyroclastic material (Figure 2E). Megacrysts of sapphire, sanidine, and lherzolite xenoliths are observed in the volcanic rocks of the “top” type.

In grey tuffs, a vitroclastic structure characterized by a large amount of non-crystallized volcanic glass and mineral and rock fragments is observed. Phenocrysts are sanidine and plagioclase. Sanidine is distributed evenly in the thin section and has isometric to angular shape. It has gray interference colors and is colorless with parallel nicols. Plagioclase is present as elongated crystals with typical polysynthetic twinning. It has gray interference colors and is colorless with parallel nicols.

Gray porous tuffs are overlapped by red baked tuffs exposed to intensive weathering. They have a vitroclastic structure due to a large amount of non-crystallized volcanic glass.

Phenocrysts are mainly represented by Ti-bearing augite. It forms elongated crystals identified by a typical extinction in the form of an “hourglass”. The volcanic glass is intensively subjected to ferruginization, which is well observed under a microscope with parallel nicols.

The “top” volcanic rocks are represented by high alkaline phonotephrites, and the “valley” ones by basalts and trachybasalts (Figure 11).

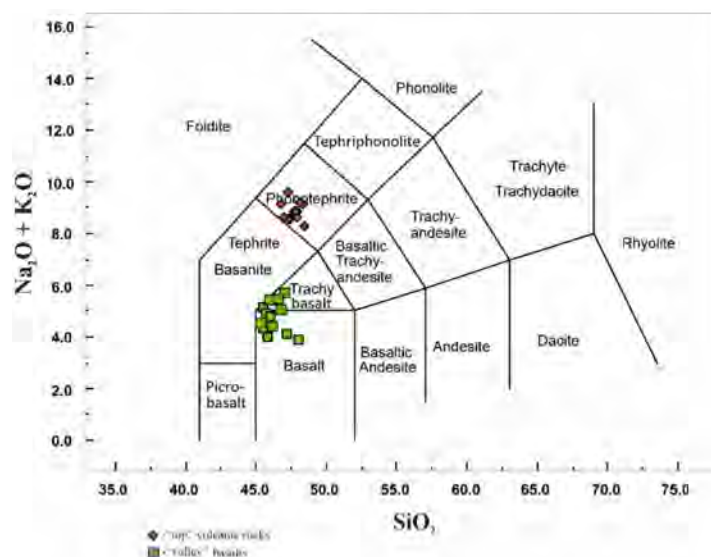


Figure 11. Chemical composition of volcanic rocks, fields according to [21].

Petrochemical data show that the Naryn-Gol placer volcanic rocks are calc-alkaline and rich in K (Figure 12), which is typical of continental rift volcanic rocks. The “top” volcanic rocks have a higher K_2O concentration varying from 2.5 to 4 wt. %, while the “valley” rocks contain only 1 to 2 wt. %. Based on the obtained results, we constructed an AFM-diagram showing that volcanic rocks of the Naryn-Gol region belong to the calc-alkaline series (Figure 12).

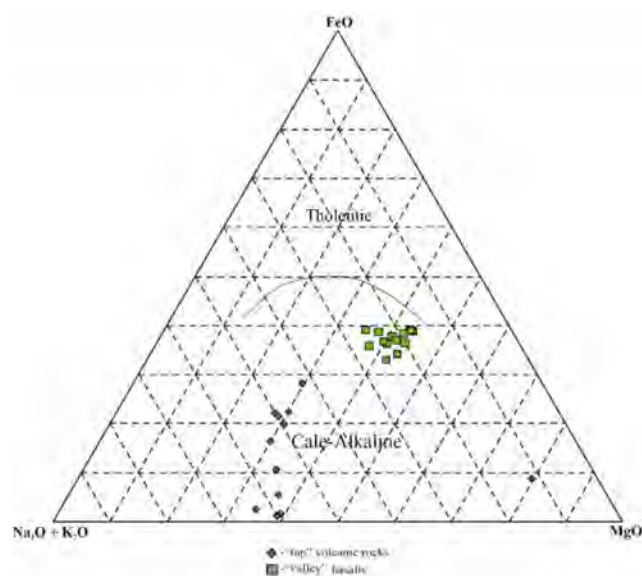


Figure 12. AFM diagram for volcanic rocks, fields according to [22].

The “valley” volcanic rocks contain a higher amount of TiO_2 (from 2.6 to 2.8 wt. %) than the “top” volcanic rocks (from 2.3 to 2.5 wt. %). The same trend is observed for the values of CaO : for the “valley” volcanic rocks, the values range from 8.5 to 9.75 wt. %; for

the “top”—from 6 to 7.25 wt. %. Values of Al_2O_3 for the “top” volcanic rocks vary from 15.5 to 16.5 wt. %, and for the “valley”, the same values range from 13.5 to 14.7 wt. %. The “top” volcanic rocks are richer in FeO (from 6.3 to 9.3 wt. %) than the “valley” rocks (from 0.16 to 3.2 wt. %). As to Fe_2O_3 , the trend is opposite: the “valley” volcanic rocks contain 4.3 to 11.2 wt. % and the “top” ones 2 to 6 wt. %. The volcanic rocks of the region show composition evolution: TiO_2 and CaO concentrations decrease and Al_2O_3 concentrations and total alkalinity increase with the growth of SiO_2 content.

4. Discussion

The territory under consideration, despite the simplicity of its relief, has an extraordinarily complex history. It is located in the cup-shaped swampy valley of the Naryn-Gol Creek (Figure 2A). When the volcanic activity began, the river network had already been formed, and erupting basalts and pyroclastic strata overlapped the ancient river terraces. Each subsequent eruption added lava and pyroclastic layers. As a result, the valleys became nested into one another. The buried residual weathered layer on the upper part of the basalt section (Figure 2B,E) points to the existence of a subtropical climate, which over several million years was changed by glaciation. Still, permafrost is found today as a subsoil layer in some sections of the placer (Figures 2A and 3, section “Root”).

Alluvial placers associated with weathered alkali basalts are the most commercially important type of sapphire-bearing deposits. It is well-known that such deposits are widely exploited throughout the western margin of the Pacific Ocean, from Australia to Russia [7,23]. The sapphires of these placers belong to the so-called Blue–Green–Yellow (BGY)-type according [10,11] involving predominantly blue, green, and yellow gems which are characterized by spotty coloration, zoning, and abundance of inclusions [1]. Recently, one BGY-type deposit (placer of the Kedrovka River) and several local occurrences (Podgelbanochnyi, Levyi Zolotoi, and Kitscha) were discovered in the Far East of Russia [6,14,24]. The studied Naryn-Gol Creek occurrence also belongs to this type [1].

Iron, the only significant impurity of the Naryn-Gol sapphires, vary from 0.5 to 2 wt. % (Table 1) which is typical for “magmatic” BGY-sapphires (Figure 13) [1]. Minor Ti, Cr, V, Ni, Mg, Mn, and Ga concentrations are also typical for BGY-sapphires (Figure 13). Overall, trace-element distribution (Table 1) is typical of “magmatic” sapphires [9,25,26].

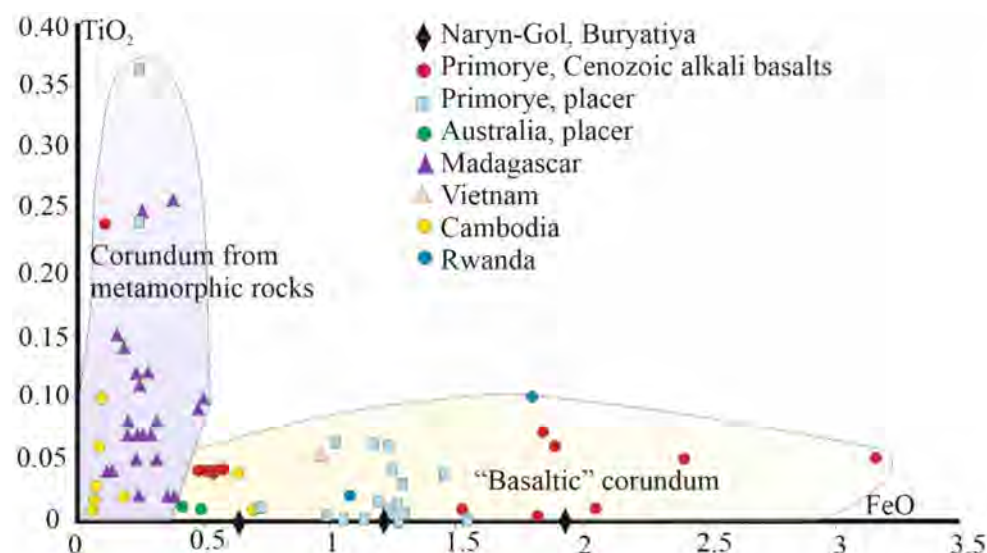


Figure 13. The difference between sapphires of various genesis in respect of the content of titanium and iron (wt. % oxides). Adapted with permission from [6]; Primorye, Cenozoic alkali basalts [6]; Primorye, placer [6]; Australia, placer [27–30]; Madagascar [31–33]; Vietnam [34]; Cambodia [27,35,36]; and Rwanda [37]. Naryn-Gol—this study.

Formation of blue sapphires at the Naryn-Gol occurred under a stronger reduction, and under oxidation. Fe ions are oxidized to the trivalent state, which led to the formation of an intensive green shade in sapphires [16].

Genetic identity of corundum can be determined by its oxygen isotopes [10,28]. ^{18}O isotope fractionates differently dependent on the mineral growth conditions. Thus, $\delta^{18}\text{O}$ values for metamorphic minerals are depleted relative to V-SMOW, while the $\delta^{18}\text{O}$ values for corundum of magmatic origin are enriched, varying from +4 to +8. The isotopic values of the Naryn-Gol Creek corundum (Table 1) lie within a narrow range of 4.5‰–6.5‰, falling into the field of igneous rocks (Figure 14).

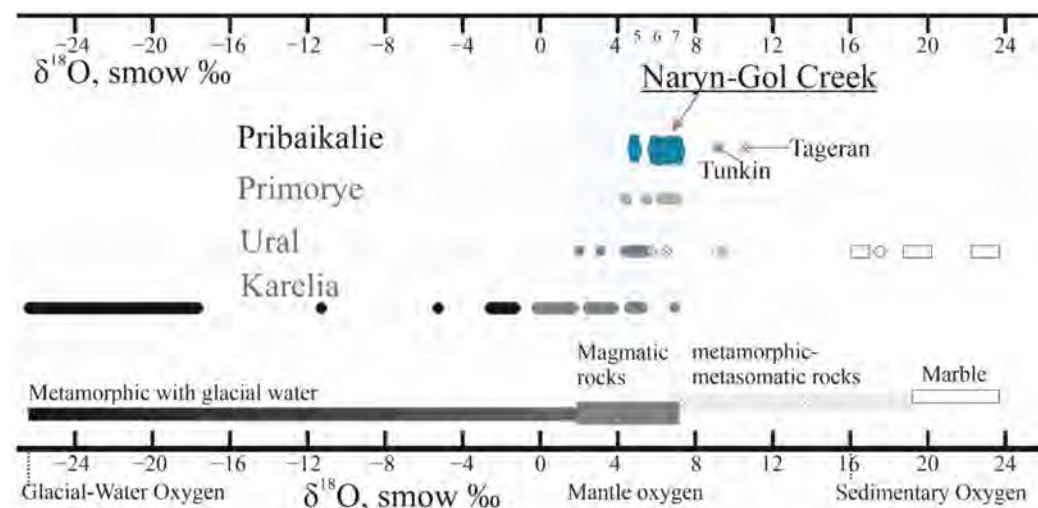


Figure 14. Isotopic composition of corundum of various genesis. Adapted with permission from [38] using [5,10,11,24–26,31,35,39,40]. Naryn-Gol—this study.

Study of corundum and minerals of the megacryst association in the Naryn-Gol vicinity revealed that, firstly, corundum from the placer is identical to the corundum from the Barun Hobol Pravyyi paleovolcano and valley basalts, which was the source of the placer. Secondly, the corundum belongs to an assemblage of alkali basalt megacrysts (large crystal size, identical features of the crystal growth, and the same $\delta^{18}\text{O}$ values); garnet, augite, spinel, and olivine are also part of this association. Minerals of the megacryst assemblage, including corundum, have similar $\delta^{18}\text{O}$ values and are undoubtedly related to basalts [1].

Corundum megacrysts are in disequilibrium with host basalts (quenching coats, corrosion, and xenomorphic habitus of crystals); in other words, they are non-cogenetic. The abundance of the fluid inclusions and high content of the volatile components in some mineral phases reflect the significant role of volatiles and, in particular, CO_2 during the process of the corundum formation. Thus, the relationship between alkali basalts and corundum megacrysts is evident but, at the same time, it indicates disequilibrium of the corundum and the hosting basalt. A similar point of view was expressed earlier [41,42].

One unusual aspect of the mineral gem suite should also be emphasized: it is the apparent lack of zircon megacrysts that typically accompany such magmatic sapphire suites [43], which probably may indicate specific combination of pressure, temperature, and volatile components in the crystallization conditions.

Pseudomorphs after pyrite are also unusual for Russian placers but found in some Australian deposits. Pyrite is replaced by various oxides and hydroxides of iron, from magnetite to hydrogoethite (lepidocrocite). Most often, pseudomorphs of hydrogoethite occur in near-surface conditions. Replacement with goethite is less common [44,45]. We found that goethite after pyrite pseudomorphic alterations occurred in the Ordovician shales. Hydrogoethite did not develop due to water shortage caused by an overlap of Ordovician shales with effusives. After the pseudomorphs of goethite enter the placer, partial replacement with hydrogoethite begins along the edges and cracks. The insignifi-

cance of such replacement indicates the close transfer of pseudomorphs directly from the Ordovician shales of the placer site.

The mineral composition of the heavy mineral concentrate turned out to be extremely diverse. We assume heavy minerals to originate from a few sources. Quartz–carbonate veins in the upper Ordovician schists are a possible source of gold, although the atomic emission spectral analysis of these veins did not reveal increased Au contents (0.075–0.01 g/t). A further transfer is also possible. A number of gold-bearing placers, both developed in the past, and being currently on the reserve balance sheet, are known in the basin of the Darkhintuy River, into which the Naryn-Gol River flows.

Zircon demonstrates zonation and poly-cycles (core–rim structure) which is not characteristic of homogeneous ‘basaltic’ hyacinth. The source of zircon is most likely Ordovician schists or granites of the Dzhida complex, located in the vicinity of the placer.

Ti-bearing magnetite is typical for basalts. Ilmenite presumably originates from basalts, since ilmenite is a common mineral of sapphire-bearing placers associated with basalts of Primorye [6] and Central Vietnam [46]. Large grains of ilmenite up to 1.5 cm in size were found in the Naryn-Gol placer (see Section 3.3).

Scheelite is supposed to be transported from remote sources, since there are deposits (Kholtosonskoye, Inkurskoye, Barun-Narynskoye, and Malo-Oinogorskoye) and ore localities of wolframite and scheelite widely distributed in the Dzhida ore district. The source of uraninite may be the granites. It is assumed that the source of monazite are the granites, which can also be the source of uraninite, or Ordovician schists.

The source of chromite is probably ultramafic rocks of the large Darkhintuy ultramafite massif, located northeast of the placer. The Dzhida ultramafite belt, comprising 50 massifs, can be traced for 130 km along the left bank of the Dzhida River northeast of the Naryn-Gol placer.

5. Conclusions

The following conclusions can, therefore, be drawn. Sapphires found in the Naryn-Gol Creek alluvial deposit are identical to gems both from pyroclastic rocks erupted from the nearby Cenozoic Barun Hobol Pravyyi alkali basalt volcano, and from “valley” basalts.

The Naryn-Gol corundums are blue, light blue, green, yellow, gray, brown, and rarely pink. Blue and light blue crystals prevail, zonal and spotty coloration is common, including sectoral (trapiche) variety.

Sapphires belong to the BGY-type associated with other megacryst minerals (garnet, spinel, augite, olivine, enstatite, ilmenite, magnetite, and feldspar). The chemical, trace-element, and oxygen isotopic compositions of the corundum, olivine, garnet, and spinel megacrysts indicate their magmatic origin. The study of sapphire inclusions reveals the significant influence of volatile components, especially CO₂, during sapphire formation. Etched and corroded surfaces of sapphire and other megacrysts indicate disequilibrium with transporting alkaline basalts.

Two types of volcanic rocks are distinguished in the studied area: “valley” rocks, corresponding in composition to basalts and trachybasalts, and “top” rocks, corresponding in composition to phonotephrites. The effusives belong to the calc-alkaline series and are characterized by high K content, which is typical for volcanic rocks of continental rifts. We assume that the “top” volcanic rocks are the source of sapphire and sanidine while the “valley” rocks are sapphire, pyroxene, and garnet.

A wide range of minerals in the placer and their chemical features indicates several placer sources. Basalts associated with the placer were undoubtedly the source of magnetite and ilmenite, while the Ordovician schists are the most likely source of native gold and monazite. Long-range transport played an important role in the placer composition as evidenced by the presence of uraninite, chromite, scheelite, monazite, and, probably, gold.

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