Sapphire from Hajnáčka (Cerová Highlands, southern Slovakia)

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Abstract Tiny (≤5 mm) blue and pale violet transparent to translucent, locally of the gem-quality sapphire crystals have been found in resedimented psammitic filling of the maar near Hajnáčka village, Slovakia. The maar is associated with Pliocene-Pleistocene alkali basalt volcanism. Homogeneous to slightly zonally sapphire is close to corundum end-member: 99-100 wt.% Al₂O₃, 0.0-0.9 wt.% Fe₂O₃+FeO, 0.0-0.7 wt.% TiO₂, 0.0-0.2 wt.% SiO₂ and 0.0-0.2 wt.% Cr₂O₃; a = 4.758, c = 12.988 (10⁻¹⁰ m), α = 1.766, ε = 1.758. SEM study of sapphire surface indicates rather magmatic corrosion than alluvial transport. Zircon, monazite-(Ce), spinel, Fe-S phase (pyrrhotite?) and Y-U-Th-Nb-Ta-bearing phase are included in sapphire crystals. Olivine, zircon, garnet, titanite, magnetite, spinel, amphibole (kaersutite), plagioclase and quartz associated with sapphire. Corundum probably crystallized from felsic syenite-like melt, which fractionated from basic-ultrabasic mantle precursor and the crystals were later transported in xenoliths by younger portions of alkali basalt magma up to surface. Finally, sapphire was accumulated in resedimented volcanic and non-volcanic material filling the maar structure.

Key words: corundum, sapphire, alkali basalts, Western Carpathians, Slovakia.

Introduction

The Gemer - Malohont Museum in Rimavská Sobota, Slovakia, in cooperation with the Department of Geology and Paleontology, the Comenius University, Bratislava, has organized a research project in the Hajnáčka maar at Kostná Valley near town of Fiľakovo, approximately 200 km E of Bratislava, southern Slovakia, well-known locality of Pliocene vertebrates. Beside fossils, fine fragments of minerals and rocks have been obtained by washing of fossiliferous beds during systematic paleontological research. Tiny (≤5 mm), notably blue mineral fragments has attracted attention from the obtained material. The mineral has been identified as sapphire, the gem-quality species of corundum. Since size and amount of the mineral is unique in whole the West-Carpathian area, we have subjected the sapphire to detail research. Our article summarizes the first results of the mineralogical research of the locality.

Corundum and sapphire in Neogene volcanic rocks in Slovakia


History of Hajnáčka corundum

The Hajnáčka sapphire occurrence is not a discovery of a new locality but its rediscovery exactly one hundred years after the first description (Százeczky 1899). Dr. Gyula Százeczky, a Hungarian geologist, described for the first time a sample of basalt with corundum from "ajnácsköi Csontos-árok", i.e. from Kostolný Jarok near Hajnáčka village, the important paleontological locality known since 19th century. He described the sample found
by Dr. Alexei Pápay (Pápay Elek), which belong to the Koloszvár University collection, Transylvania, recently Cluj in Romania. The grey-blue corundum forms “flat tabular crystal 7 mm in length, outstanding 1.5 - 2 mm out of surrounding yellow-brown weathered crust of basalt, the mineral itself has thin black coating” (Százdeczky 1899). The author mentioned that the described basalt contained also other minerals, probably augite, amphibole, feldspar, pyrite, magnetite and maybe rutile, a blue obsidian and quartz were also present. Százdeczky (1899) emphasized that Hajnáčka corundum was the largest known sample of this mineral in Hungary to date. The whole data were cited later by Rozložník & Emszt (1911) in an article concerning to basaltic Cerová Highlands (Medvehegyes) and by another authors as well (Melcz 1907, Hintze 1915, Vadász 1940, Mauritz & Vendl 1942, in Kodára et al. 1986). The first, however, not precise chemical analysis of the Hajnáčka corundum showed 89.56 wt.% Al₂O₃, 6.10 wt.% Fe₂O₃ and 5.42 wt.% SiO₂ + TiO₂ (Zimányi 1915, in Kodára et al., 1986).

Grey-blue corundum from Hajnáčka (still not denoted as sapphire) was later almost forgotten. There were only few records about it, in mineralogical monographs of Slovakia by Kouřimský (1958) and Herčko (1984), and, of course, in Topographic Mineralogy of Slovakia (Kodára et al., 1986). There were no more records about the corundum from the Hajnáčka, Kostná Valley. The exact localization of the occurrence was forgotten, in later papers it was referred only as Hajnáčka locality, what could be misunderstood with well-known site on the Hajnáčka castle hill. Only recent extended paleontological research of the Kostná Valley, with several deep pits and washing of large amount of sand has rediscovered not only paleontological material but also sapphire and other minerals from the locality.

**Geological settings**

The Hajnáčka, Kostná Valley locality is situated 600 m N of the Matrač Hill (410 m a.s.l.), 1 km SE of Hajnáčka village, and around 12 km SE of Fiľakovo town in southern Slovakia (Fig. 1). According to the geomorphological and regional geological division of the subprovince of the Inner Carpathians Mts., the studied locality belongs to the unit of Cerová Highlands. The site is an important European paleontological locality of Upper Pliocene age located in an erosional valley, 400 m in length, 30 m in width and up to 20 m deep, with E-W orientation. In 1994, the site with surrounding area were pronounced for the Kostná Valley Natural Reservation with area of 4.92 hectares.

The site is part of the Cerová Basalt Formation (Vass & Kraus 1983), which contains mainly alkali basalts and volcanic clasts. K-Ar radiometric dating of the basalts revealed Pliocene - Pleistocene ages between 1 - 5 Ma (Orlický et al. 1996, Vass et al. in press).

The Hajnáčka, Kostná Valley occurrence is located in a volcanic maar structure (Konečný & Lexa in Vass et al. 1992, Vass et al. in press). The maar has elliptic shape about 400-500 m in diameter, partly covered by Pleistocene alluvial sediments. Erosion relics of volcanic ring on the maar margin are formed by basaltic lapilli tuff deposited during freotamagmatic eruptions. Central part of the maar is built by redepsoited sedimentary filling, which is composed of the Tachyty sands to sandstones of the Fiľakovo Formation (Egenburgian) in the basalt part. In overlaying beds, there are layers of lapilli tuffs and tuffites with fragments of basalts and burnt sandstones enveloped by limonite crusts, less frequently occur redepsoited palagonite tuffs and breccias. Locally, there are relics of laminated bituminous beds, remains of original lacustrine maar filling, which is partly covered by Quaternary loamy and argillaceous deposits (Fig. 2).

Results of remanent magnetism analysis from the ring tuff of maar corresponds to an event with normal Earth magnetic polarity (3n) in a lower part of the C2An chron, what indicates the age of maar formation between 3.3 to 3.55 Ma ago (Vass et al. in press). An accumulation of fragments of mammalian skeletons is younger, it was created during redepsoition of original and input of new clastic sediments, when the original sedimentary maar filling has been almost entirely eroded away. Fossil findings were found in more or less preserved beds with completely preserved stratigraphic beds without hiatus. The mammalian bone remnants from the Hajnáčka, Kostná Valley was dated to biozone MN 16a, late Villafranch (topmost Pliocene), on the basis of index fossils, such as Mimosys (Cseria) stehlini, Mimomys (Mimomys) hajnackensis, Tapiurus arvernensis, Dicerosinus jevanviri and Anancus arvernensis, what belongs to the middle part of the C2An chron and time interval between 2.8 to 3.3 Ma ago (Lindsay et al. 1997, Vass et al. in press).

![Fig. 1. Location of the sapphire occurrence, the Hajnáčka maar, Kostná Valley.](image-url)
**Experimental methods**

Sapphire and other accessory minerals were obtained by washing of ca. 1,000 kg of resedimented psammitic sediments from fossils-bearing layers of the Hajnáčka, Kostná Valley.

The crystal morphology, internal zonality and inclusions in sapphire were studied by a JEOL JSM-840 scanning electron microscope, at Geological Survey of Slovak Republic, Bratislava. Secondary (SEI) and back-scattered (BSE) electron modes were used. The accelerating voltage was 25 kV, beam current was 1 nA (SEI) and 30 nA (BSE).

Electron-microprobe analysis was done on a JEOL-733 Superprobe instrument equipped with KEVEX energy dispersive system (EDS), at Geological Survey of Slovak Republic, Bratislava. Operating conditions were 15 kV accelerating voltage, 1.2 nA beam current and 130 s count time. Synthetic standards: SiO₂ (Si Kα), TiO₂ (Ti Kα), Al₂O₃ (Al Kα), Fe₂O₃ (Fe Kα), and chromite (Cr Kα), were used. The detected concentrations of elements were recalculated by the XPP correction.

The structural identification of sapphire was done by the powder Debye - Scherrer X-ray diffraction method using a Philips PW 1710 diffractometer, at Geological Institute, Slovak Academy of Sciences, Bratislava. Pulverized sample was mixed up with α-SiO₂ internal standard. Cu-anticathode (λ₀=1.54060 x 10⁻⁴’m), 20 mA current, 35 kV voltage, interval of 2 Θ equals to 10-80° and step speed of 0.3° 2Θ/min was used for measurement. Presence of plagioclase and titanite was also determined by the powder X-ray diffraction analysis.

Index of refraction (n, ε) was done on a two-circle Freiberger Präzisionsmekhanik goniometer, at Czech Geological Institute, Prague. The method of minimal deviation in sodium light was used. The sapphire crystal was embedded into epoxy, and a prism with angle 48°27’ was shaped from it, such a way, that the c crystallographic axis lays in a plane dividing the prism’s angle into two halves.
Results

Physical properties

Sapphire occurs as well shaped prismatic crystals with \{1010\} and \{1011\} faces, locally also with \{1011\} dipyramidal faces. In most cases, sapphire crystals occur as fragments (1-5 mm in size), locally partly rounded. The largest crystal has weight about 0.1 g (0.5-0.6 metric carats). Sapphire shows mostly light to deep blue color, in some cases grey blue to pale violet, the mineral is perfectly transparent to translucent with vitreous to dull luster (Fig. 3A-C). Some crystals have gentle dichroism. Locally, the sapphire reveals visible growth zones (Fig. 3C).

The refractive index of Hajnáčka sapphire is ω = 1.7664(5), ε = 1.7581(5), birefringence B = 0.0083, the values are well corresponding with corundum data (ω = 1.765-1.779; ε = 1.757-1.770; B = 0.008-0.009; Bernard & Rost 1992; Duďa & Rejl 1998).

Crystal morphology

Details of sapphire crystal morphology show various roundness degree of originally flat and smooth crystal faces (Fig. 4A-D). Figures 4A-B show alteration of primary sapphire surface along lines parallel to the \{0001\} face as a plane of corundum jointing together with
rounding of surface elevations. Fig. 4C shows another sapphire with system of straight ribbed projections and neighboring holes with slight trend orientation. Finally, Fig. 4D shows surface of finely sculptured sapphire with straight thin scratches and holes of prismatic shape. Details of sapphire crystal morphology reminds mainly signs of magmatic corrosion, however, scratches on the crystal surface indicates also mechanical transport and the elongated holes are probably negatives after inclusions of unknown minerals (cf. Coenraads et al. 1990, 1995, Maliková 1996).

Structural parameters

X-ray diffraction pattern, as well as calculated structural parameters based on four sapphire crystals from Hajněčka, proved sapphire’s identity with a tabulated corundum, calculated structural parameters of sapphire: 

$$a = 4.758(4) \text{ and } c = 12.988(7) \times 10^{-10} \text{ are almost identical with JCPDS values (α-Al}_{2}\text{O}_{3}, \text{ JCPDS #10-173). This result indicates a high purity of the Hajněčka sapphire which approaches theoretical Al}_{2}\text{O}_{3}, what has been proved also by electron microprobe analyses.}

Internal zonation and chemical composition

The study of polished sections of the Hajněčka sapphire by backscattered electrons image (BEI) didn’t show any chemical zonality of the mineral, crystals with distinct optical zonation (Fig. 3B) are also chemically homogeneous.

Electron microprobe analysis, done on 20 points of 7 crystals, shows a high purity of the mineral (99-100 wt.% Al}_{2}\text{O}_{3}, Table 1). Isomorphemic admixtures comprise 0.0-0.9 wt.% Fe}_{2}\text{O}_{3} (however it is probably a mixture of both Fe}^{3+} \text{ and Fe}^{2+}), 0.0-0.7 wt.% Ti}_{2}\text{O}_{3} and 0.0-0.2 wt.% Si}_{2}\text{O}_{3}.

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Table 1 Compositions of sapphire from Hajněčka (wt %)

Content of Cr}_{2}\text{O}_{3} is usually under detection limit of the microprobe (<0.2 wt.% Cr}_{2}\text{O}_{3). The concentrations of the admixtures are almost identical in the centre and the rim of sapphire crystals, small variations are not systematic.

Mineral inclusions in sapphire

Zircon occurs as idiomorphic to xenomorphic inclusions, 50-200 μm in size.

Monazite-(Ce) forms 100-200 μm large euhedral inclusions. Locally, it occurs in the same crystals as inclusions of zircon. Microprobe analyses reveal compositional zonality of monazite-(Ce) with edges slightly enriched in Th (2.6 wt.% Th}_{2}\text{O}_{3}.

Spinel was found only in one case, as ~500 μm irregular inclusion near the rim of the sapphire crystal. The mineral reveals compositional zonality in Cr and Fe (2.8-8.8 wt.% Cr}_{2}\text{O}_{3} and 14-16 wt.% FeO+Fe}_{2}\text{O}_{3}.

Fe-S-bearing phase, most probably pyrrhotite(?) forms inclusions of 200-300 μm large tabular crystals together with zircon and monazite-(Ce) inclusions.

Y-U-Th-Nb-Ta-bearing phase, probably euxenite-(Y)? or mineral of pyrochlore group (?), was observed only in one case, as ~250 μm irregular inclusion near the edge of sapphire.

Associated minerals

Zircon occurs as red transparent short-prismatic-dipyramidal crystals (variety hyacinth). Olivine, probably forsterite, forms light blue fragments and prismatic tabular crystals. Garnet (pyrop or almandine) forms dark blue, partly altered crystals, locally containing inclusions of ilmenite and allanite. Titanite occurs as transparent to translucent honey-like colored fragments, locally as intergrown with magnetite. Plagioclase forms relatively large fragments (~8 mm) of prismatic and tabular crystals of white color and typical striated crystal face. Greyish-black spinel of typical dipyramidal shape and black amphibole, probably kaersuite are less frequent Relatively abundant colorless quartz forms irregular fragments or dipyramidal transparent crystals. The size of above mentioned minerals in the maar filling vary from 1 to 8 mm, 3-4 mm in average.

Discussion

World alluvial and eluvial occurrences of gem-quality sapphire are associated mainly with alkaline basalt rocks, namely with explosive continental alkaline volcanism with predominance of basanite, often with abundant ultramafic mantle xenoliths, e.g. East Australia, Thailand, Cambodia, Vietnam, south China, Colombia, Nigeria and Czech Republic (Coenraads et al. 1990, 1995, Sutherland et al. 1998, Kotrlý et al. 1997). Alluvial and eluvial sapphire-bearing deposits connected with the alkali-basalt volcanism contain a characteristic heavy-mineral assemblage, including zircon, spinel, ilmenite, occasionally olivine, clinopyroxene, garnet, magnetite and locally also diamond (Australia, Coenraads 1990). Sapphire crystals from alluvial and eluvial deposits have, beside signs of mechanical transport, also features of magmatic corrosion (Coenraads et al. 1990, 1995, Maliková 1996, Kotrlý et al. 1997). Inclusions of zircon, magnetite, spinel
Fig. 4A-D. Morphology of sapphire from Hajnáčka, southern Slovakia (SEI, K. Horák photo).
(also Co-rich), hercynite (often Zn-rich), ferrocolombite, niobian rutile, thorite, U-Ti-rich pyrochlore, apatite, REE-phosphate, pyrhotite, almandine, pyrope, alkali-feldspar and plagioclase are present in sapphire (Sutherland et al. 1998, Guo et al. 1994). Surprisingly, these incorporated minerals contain elements incompatible in basic magma such as Zr, Nb, Ta, U, Th, REE’s and elements of alkali metals. Sapphire often contain fluid inclusions, often CO₂-rich (Coenraads et al. 1990, 1995, Guo et al. 1994, Maliková 1996, Sutherland et al. 1998). A detailed study of the fluid inclusions, Fe-Ti-oxides and feldspars indicates the temperature of corundum formation in the range of 685 to 900 °C (Sutherland et al. 1998). Zircon inclusions in sapphire from Australia and Thailand, dated by U-Pb method, yield ages similar to alkali-basalt eruptions (Coenraads et al. 1990, 1995).

The above mentioned results indicate a magmatic origin of sapphire and associated minerals from a felsic melt enriched in incompatible elements. Some authors - supposed phonolite (or nepheline syenite) composition of this melt originated by fractionation of mantle-derived - basalt rich in kaersutite, clinopyroxene, olivine, Fe-Ti spinel, etc. (Irving & Price 1981, Irving 1986). The latest petrological model assumes low-degree partial melting of amphibole-bearing mantle pyroxenite and its subsequent fractionation which produced a fluid-enriched felsic magma (Sutherland et al. 1998). Sapphire and other phases solidified from the felsic melt in lower crust and later they have been transported to the surface as xenocrysts or xenoliths in alkali-basalt magma (e.g. Coenraads et al. 1995).

According to another model, the origin of sapphire and diamond in Victoria, Australia is associated with - Paleozoic subduction and the minerals remained in upper mantle until their uplift by Tertiary alkali-basalt magma (Birch 1998). Some authors prefer processes of magma mixing in lower crust with contemporaneous crystallization of sapphire and other minerals (Guo et al. 1994). Others relate the origin of some alluvial sapphires with metamorphic processes in the crust (e.g. Garland 1998).

Mineral inclusions containing elements incompatible in basalts (monazite-(Ce), zircon and Y-Th-U-Nb-Ta-bearing phase) and character of sapphire morphology with signs of magmatic corrosion indicate that the Hajnáčka sapphire was originated in felsic melt and uplifted to the surface as xenocrysts which were not in equilibrium with surrounding alkali basalt magma. This assumption supports also nepheline-olivine normative, not corundum normative compositions of the alkali basalts from Hajnáčka area (Konečný & Lexa in Vass et al. 1992) showing that the alkali basalts are not in equilibrium with corundum and therefore they don’t represent the parental magma for sapphire.

As a possible parental rock of the Hajnáčka sapphire, we suggest felsic syenite-like xenoliths. Although these xenoliths are unknown from the Hajnáčka maar to date, syenite and anorhostite xenoliths are present at the Pincíná maar belonging to older, Pliocene the Podrečany Basalt Formation, situated 23 km NW of Hajnáčka. Moreover, the Pincíná syenite xenoliths contain corundum and other accessory minerals similar to Hajnáčka, such as zircon, spinel, amphibole, apatite, titanite, monazite, xenotime, Y-U-Th-Nb-bearing oxides, Y-silicates and REE-minerals (Huraiová et al. 1996, Hurai et al. 1998). Consequently, the analogous syenites represent - probably the host rocks of the Hajnáčka sapphire and some other associated minerals.

Presented geological and mineralogical data indicate that the sapphire from Hajnáčka, Kostná Valley is spatially related to the Cerová alkali basalt Formation of Pliocene to Pleistocene age. We assume that corundum from redeposited sedimentary filling of the Hajnáčka maar is most probably related by the syenite-like magma. This felsic syenitic melt could be generated by fractionation of basic magma originated by partial melting of upper mantle rocks. Subsequently, syenitic magma solidified probably in the lower crust level and later it was uplifted to the surface as xenoliths. Finally, sapphire and other minerals accumulated in redeposited sediments that filled the maar structure. It is not clear so far, whether sapphire come from nearby basalt lava flows or from the maar itself.

Conclusions

Blue and pale violet sapphire, locally of gem-quality, was obtained from Upper Pliocene resedimented psammite maar filling at Hajnáčka, Kostná Valley in southern Slovakia, well-known paleontological occurrence for findings of mammalian fossils. Sapphire was firstly described by Szádeczy (1899) one hundred years ago and it was in fact rediscovered at present only. Physical and structural parameters of the sapphire are in good agreement with published data. Sapphire is relatively very pure with low contents of Fe, Ti and Si.

Crystal surface, mineral inclusions and spatial relationship with alkali basalts indicate sapphire crystallization probably from a fractionated felsic syenite-like melt. The melt was generated by fractionation of basic magma on the mantle/crust boundary or in the lower crust. In later stage sapphire was transported up to the surface as xenocrysts or in syenitic xenoliths by a new portion of alkali basaltic melt. Accessory minerals including sapphire separated from host rocks and sediments in the maar filling. It remains questionable, whether sapphire was transported in some of nearby alkali basalt lava flows or in volcanoclastics building up the Hajnáčka maar structure.

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References


