

# Sapphires related to alkali basalts from the Cerová Highlands, Western Carpathians (southern Slovakia): composition and origin

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**Abstract:** Blue, grey-pink and pink sapphires from the Cerová Highlands, Western Carpathians (southern Slovakia) have been studied using CL, LA-ICP-MS, EMPA, and oxygen isotope methods. The sapphire occurs as (1) clastic heavy mineral in the secondary sandy filling of a Pliocene alkali basaltic maar at Hajnáčka, and (2) crystals in a pyroxene-bearing syenite/anorthoclase xenolith of Pleistocene alkali basalt near Gortva. Critical evaluation of compositional diagrams (Fe, Ti, Cr, Ga, Mg contents, Fe/Ti, Cr/Ga, Ga/Mg ratios) suggests a magmatic origin for clastic blue sapphires with lower Cr and Mg, but higher Fe and Ti concentrations in comparison to the grey-pink and pink varieties, as well as similar compositional trends with blue sapphire from the Gortva magmatic xenolith. Moreover, blue sapphires show similar  $\delta^{18}\text{O}$  values: 5.1 ‰ in the Gortva xenolith, 3.8 and 5.85 ‰ in the Hajnáčka placer, closely comparable to mantle to lower crustal magmatic rocks. On the contrary, pink and grey-pink sapphires show higher Cr and Mg, but lower Fe and Ti contents and their composition points to a metamorphic (metasomatic) origin.

**Key words:** Western Carpathians, Slovakia, Hajnáčka, Gortva, CL, LA-ICP-MS, EMPA, oxygen isotopes, placer, alkali basalts, anorthoclase xenolith, corundum, sapphire.

## Introduction

Sapphire, usually a blue transparent variety of corundum is one of the most important coloured gemstones, together with diamond, ruby and emerald. It is found in three main geological environments (e.g. Simonet et al. 2004; Giuliani et al. 2007; Graham et al. 2008; Sutherland et al. 2009): (1) magmatic, mainly as xenocrysts and in xenoliths of alkali basalts, syenites, monzonites, and lamprophyres; (2) metamorphic, mainly in marbles, skarns, granulites, cordierites, gneisses to migmatite rocks, mafic-ultramafic metamorphites and as xenocrysts in basalts; and (3) secondary alluvial sedimentary deposits. In Europe, there are occurrences of sapphires in the monchiquite dike from Loch Roag, Scotland (Jackson 1984), syenite and anorthoclase xenoliths connected with basaltic volcanism (Scotland, northern Britain, Ireland — Upton et al. 1983, 2009), anorthoclase xenoliths in trachytes at Menet, French Massif Central (Brousse & Varet 1966), syenitic pegmatites in the Southern Urals and Khibiny, Russia (Kievlenko 2003), pegmatitic albite dikes in Urdach and Espechère, western Pyrenees, France (Monchoux et al. 2006), or in granitic pegmatite xenolith from Karpacz, Karkonosze Mts, Poland (Kozłowski & Sachabiński 2007). Alluvial sapphire occurrences related to alkali basalts were described in several European regions, for example in the Massif Central, France

(Giuliani et al. 2009, 2010) and Jizerská Louka, Czech Republic (Malíková 1999).

Sapphire from Hajnáčka in the alkali basalt area of the Cerová Highlands, southern Slovakia has been known for over one hundred years (Szádeczky 1899). However, additional sapphire specimens from Hajnáčka and near Gortva occurrences were obtained and briefly described only recently (Uher et al. 1999, 2006). The aim of our study is a detailed description of this sapphire and associated minerals based on current new analytical data (cathodoluminescence image, electron-microprobe and LA-ICP-MS analyses, oxygen isotopes), and discussion on their likely origin.

## Corundum within the Cenozoic volcanic fields of the Western Carpathians

Blue corundum (sapphire) occurs as an accessory mineral from several Neogene volcanic areas in the Western Carpathians, namely: in andesites and its pyroclastic rocks near Sklené Teplice and Dolné Hámre, Štiavnica Mountains (Hvožďara & Činčák 1972), in cordierite hornfels with sillimanite and spinel in andesites near Dobrá Niva, Štiavnica Mountains (Fiala 1954), in hornfels with sillimanite, andalusite and cordierite from the KR-3 borehole near Kremnica,

Kremnica Mountains (Böhmer & Šimová 1976), in sekaniite ( $Fe > Mg$  cordierite) xenoliths of andesites from Večec, Slanské Mountains (Ďuďa et al. 1981), as well as in the Börzsöny and Visegrád Mountains (Szakáll et al. 2002). Corundum also occurs in Al-Si metasomatites connected with Neogene andesitic volcanism in Kapka, Vihorlat Mountains (Derco et al. 1977) and Viglašská Huta, Javorie Mountains (Marková & Štohl 1978). Moreover, alluvial corundum occurs in the placers near the Neogene andesites of the Slanské, Börzsöny and Visegrád Mountains (Ďuďa et al. 1981; Szakáll et al. 2002). All these corundum and/or sapphire occurrences occur in Miocene to Pliocene (15 to 10 Ma), subduction-related andesitic activity in the West Carpathian area and they have no direct genetic relationships with the sapphires related to the alkali basalts in Hajnáčka and Gortva described in the present study.

### Geological setting of Hajnáčka and Gortva sapphires

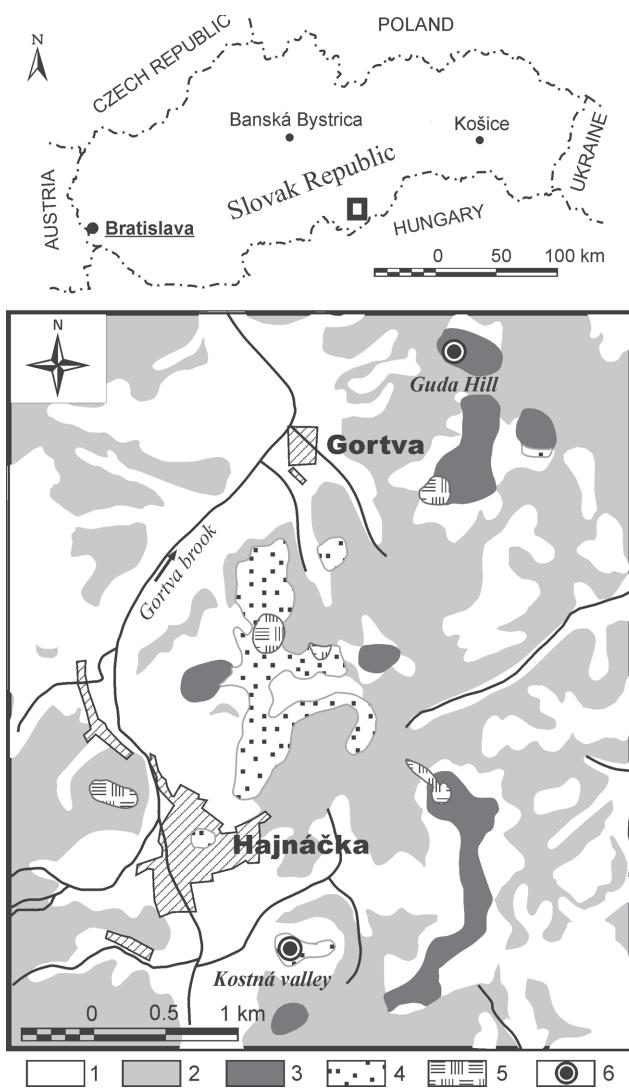
The Hajnáčka and Gortva sapphires are connected with Pliocene to Pleistocene within-plate volcanic activity in the Cerová Highlands area, southern Slovakia (Fig. 1). The studied area belongs to the Cerová Basalt Formation, formed by products of intraplate alkali basalt volcanism of Pliocene to Pleistocene age (ca. 5 to 1 Ma; Vass et al. 2000). Besides lava flows, cinder cones, diatremes, necks and dikes, several phreatomagmatic eruptions (maars) are present (Konečný & Lexa in Vass et al. 1992a,b; Vass et al. 2000).

The Hajnáčka sapphire occurs as isolated crystals or their fragments in secondary psammitic sediments deposited in a maar structure situated at Kostná valley or Kostný Jarok, ca. 600 m north of the Matrač Hill (410 m a.s.l.), 1 km SE of Hajnáčka village, and ca. 12 km SE of Fiľakovo town (Fig. 1). The partly eroded maar is an elliptical structure, ca. 500 to 370 m in diameter with primary and secondary sedimentary filling, which intruded older Eggenburgian sandstones of the Fiľakovo Formation. The Kostná valley or Kostný Jarok (Bone Gorge) or locality was named after numerous findings of Pliocene mammal bones in the secondary maar filling; it is one of the type localities of the European Mammal time scale Zone MN16 (Vass et al. 2000). Relicts of the primary volcanic ring are preserved on the NW rim of the maar structure, formed by alkali basaltic lapilli tuff layers with fragments and blocks of sandstone. The central depression of the maar structure is filled by a primary and secondary lacustrine maar filling which consists of tuffitic siltstones to sandstones and resedimented sand (Vass et al. 2000). The sapphires were discovered together with other heavy minerals and remnants of mammal skeleton fragments in the secondary sandy filling. Correlation of magnetostratigraphic and paleontological data indicate an age of phreatomagmatic volcanic activity and maar formation at 3.3 to 3.55 Ma, whereas paleontological data constrain the age of the secondary maar filling to Villafranchian (the latest Pliocene), within the MN16a Zone, between 2.8–3.3 Ma (Vass et al. 2000).

The first corundum found in Hajnáčka, Kostná valley is a grey-blue flat tabular crystal, 7 mm across, cemented by a

yellow-brown weathered crust of basalt (Szádeczky 1899). New specimens of sapphire crystals were described in the psammitic sedimentary filling of the Hajnáčka maar (Uher et al. 1999). The sapphire associates with other heavy minerals identified in sandy filling of the Hajnáčka maar structure such as spinel, magnetite, magnesiochromite, ilmenite, titanite, forsterite, zircon, almandine, allanite-(Ce), augite, diopside, enstatite, pargasite, and kaersutite (Uher et al. 1999; Gregáňová 2002).

The sapphire from Gortva forms euhedral crystals enclosed in syenitic/anorthoclasitic rock xenolith in alkali basalt (Szakáll et al. 2002; Uher et al. 2006). The locality is situated on Guda (Buda) Hill (413 m a.s.l.), 1800 m N of Gortva settlement and ca. 6 km N of the Hajnáčka, Kostná



**Fig. 1.** Simplified geological map of studied area with location of sapphire occurrences (Vass et al. 1992a, adapted). Explanations: 1 — Quaternary sediments (sands, loess, gravels, clays, loams), 2 — Miocene sandstones; Pliocene-Pleistocene; 3 — basalt lava flows, 4 — agglomerates, tuffs and lapilli tuffs, diatreme fill (shales, sandstones and tuffs with non-volcanic material), 5 — lava necks and dikes, 6 — sample location: Hajnáčka, Kostná valley (placer) and Gortva, Guda Hill (xenolith).

valley sapphire locality. The adjacent alkali basalts form a lava flow, locally with small xenoliths (usually 1 to 5 cm across) of felsic magmatic rocks. The K-Ar whole-rock dating of alkali basalt from the Gortva, Guda Hill gave Pleistocene age of  $1.73 \pm 0.1$  Ma (Vass et al. 2000).

An additional finding of corundum has been reported in a syenitic xenolith in alkali basalt from the Pliocene maar at Pinciná near Lučenec town in the northern part of the Cerová Highlands (Hurai et al. 1998).

## Experimental methods

Sapphire crystals were isolated from the heavy mineral assemblage of ca. 1000 kg sand portion from secondary maar filling of the Hajnáčka, Kostná valley. In addition, a sapphire-bearing xenolith in alkali basalt from Gortva, ca. 6 km N of Hajnáčka, deposited in the Herman Ottó Museum, Miskolc, Hungary (inv. No. 14035), and mentioned by Szakáll et al. (2002) was investigated here.

The internal texture of the sapphire crystals was studied using cathodoluminescence at the Dionýz Štúr State Geological Institute, Bratislava, using an acceleration voltage of 18 kV and a sample current of 80 nA.

Electron-microprobe analyses (EMPA) were carried on the CAMECA SX100 probe at the Dionýz Štúr State Geological Institute, Bratislava. The following operating conditions were used: acceleration voltage of 15 kV, beam current of 20 nA (10 nA for analcime), beam diameter between 3 to 10  $\mu\text{m}$ , and a collection times of 20 to 40 s in wavelength dispersive mode. Standards and lines included wollastonite ( $\text{Si K}\alpha$ ,  $\text{Ca K}\alpha$ ),  $\text{TiO}_2$  ( $\text{Ti K}\alpha$ ),  $\text{Al}_2\text{O}_3$  ( $\text{Al K}\alpha$ ), chromite ( $\text{Cr K}\alpha$ ), fayalite ( $\text{Fe K}\alpha$ ), rhodonite ( $\text{Mn K}\alpha$ ),  $\text{MgO}$  ( $\text{Mg K}\alpha$ ),  $\text{SrTiO}_3$  ( $\text{Sr L}\alpha$ ), barite ( $\text{Ba L}\alpha$ ), albite ( $\text{Na K}\alpha$ ), orthoclase ( $\text{K K}\alpha$ ),  $\text{Rb}_2\text{ZnSi}_5\text{O}_{12}$  glass ( $\text{Rb L}\alpha$ ) and  $\text{LiF}$  ( $\text{F K}\alpha$ ) for the other minerals. The detection limits of measured elements range from 0.02 to 0.1 wt. %, and statistical errors from 0.02 to 0.1 wt. % ( $1\sigma$ ), depending on the elemental concentration. The PAP routine (Pouchou & Pichoir 1985) was applied for data correction.

Selected trace elements of sapphire were investigated by LA-ICP-MS at the Department of Chemistry, Faculty of Science, Masaryk University, Brno, using a laser ablation system UP 213 (New Wave, USA) and an ICP-MS spectrometer Agilent 7500 CE (Agilent, Japan). A commercial Q-switched Nd: YAG laser ablation device works at a wavelength of 213 nm. A sample was placed in the SuperCell (New Wave, USA). The ablated material was carried with helium (carrier gas), which transported the laser-induced aerosol to the inductively coupled plasma (1 l/min). A sample gas flow of argon was admixed to the helium carrier gas flow after the laser ablation cell. Therefore, the total gas flow was 1.6 l/min. Optimization of LA-ICP-MS conditions (gas flow rates, sampling depth, electrostatic lenses voltages of the MS) was performed with the glass reference material NIST SRM 610 in respect to maximum S/N ratio and minimum oxide formation ( $\text{ThO}^+/\text{Th}^+$  counts ratio 0.2 %,  $\text{U}^+/\text{Th}^+$  counts ratio 1.1 %). The LA-ICP-MS measurements used a single hole drilling mode for the duration of 60 seconds for

each spot. Laser ablation was performed with laser spot diameter of 100  $\mu\text{m}$ , laser fluency of  $12 \text{ J}\cdot\text{cm}^{-2}$  and repetition rate of 10 Hz. All element measurements were normalized on  $^{27}\text{Al}$  (526,609 ppm  $\text{Al} = 99.5$  wt. %  $\text{Al}_2\text{O}_3$ ; this value approximates to the real composition of the studied sapphire).

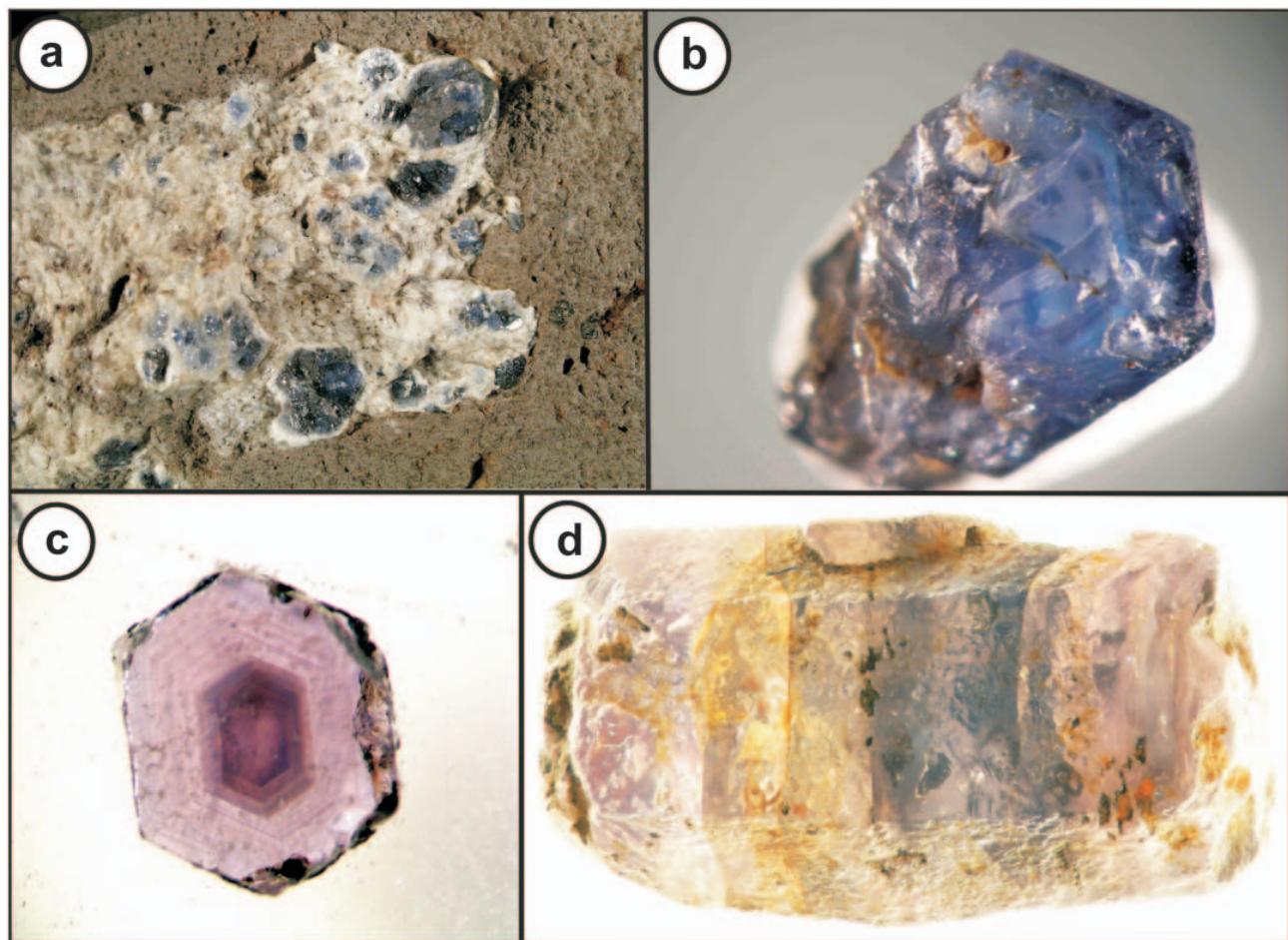
Oxygen isotope values of sapphire were determined at the SUERC, Glasgow, United Kingdom, using the laser fluorination technique described by Sharp (1990). The method involves complete reaction of  $\sim 1$  mg of powdered sapphire, heated by a  $\text{CO}_2$  laser, with  $\text{ClF}_3$  as the fluorine reagent. The released oxygen is passed through an in-line Hg-diffusion pump before conversion to  $\text{CO}_2$  on platinized graphite. The yield is measured by a capacitance manometer and the gas-handling vacuum line is connected to the inlet system of a dedicated VG PRISM3 dual inlet isotope ratio mass spectrometer. Precision and accuracy on quartz standards are  $\pm 0.1\text{‰}$  ( $1\sigma$ ) and duplicate analyses of sapphire sample confirm this error range. Data are reported in the conventional delta notation ( $\delta^{18}\text{O}$ , expressed as  $^{18}\text{O}/^{16}\text{O}$ , ‰) relative to the Vienna Standard Mean Ocean Water (V-SMOW).

## Results

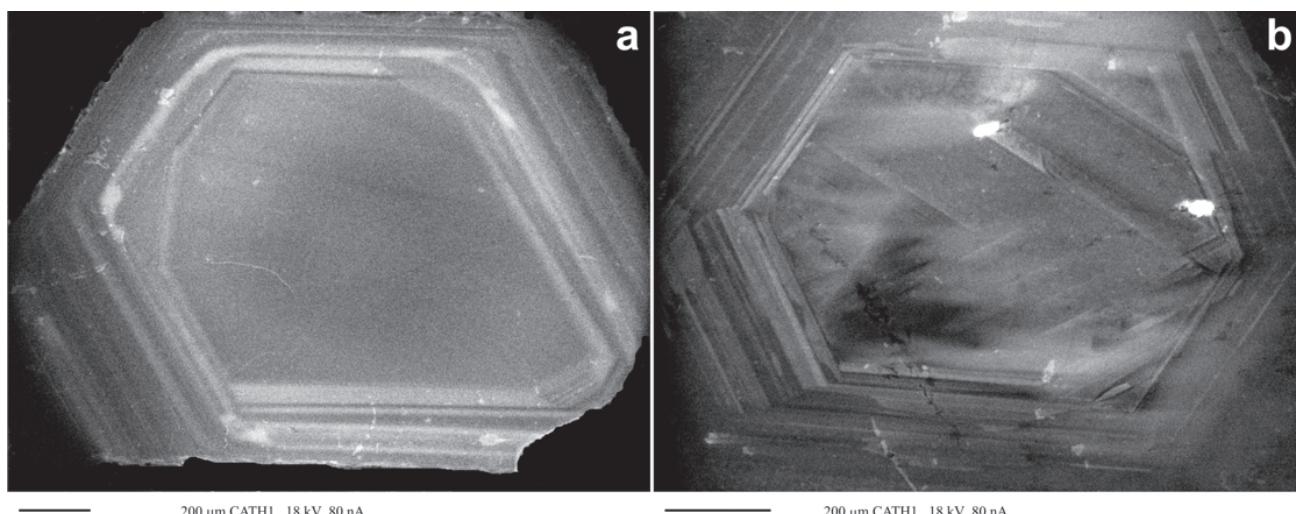
### Physical properties, internal zoning and mineral association of sapphires

Sapphire crystals or their fragments in psammitic sedimentary filling of the Hajnáčka maar show common hexagonal prismatic {1010} and pinacoidal {0001} faces, locally also with {1011} dipyramids. Locally, basal cleavage along the (0001) plane is visible (Fig. 2d). Optical photomicrographs and especially CL images show apparent fine oscillatory zoning along the (1010) plane of the sapphire (Figs. 2 and 3). Sapphire crystals are transparent with glassy to diamond lustre. The Hajnáčka sapphires have three basic colours: the most common are light to dark blue, scarcer are grey-pink and pale pink crystals (Fig. 2). Some pink crystals show concentric colour zoning with a darker bluish or violet central zone and pale pink external zone (Fig. 2c) and visible pleochroic (dichroic) colour change from darker to lighter pink. Locally, sapphire contains tiny inclusions of zircon, rarely ilmenite, and hercynite to spinel overgrowths. One blue sapphire crystal also contains inclusions of monazite-(Ce), iron sulphide (pyrrhotite?), and Y-U-Th-Nb-Ta oxide mineral, probably euxenite-(Y)? (Uher et al. 1999).

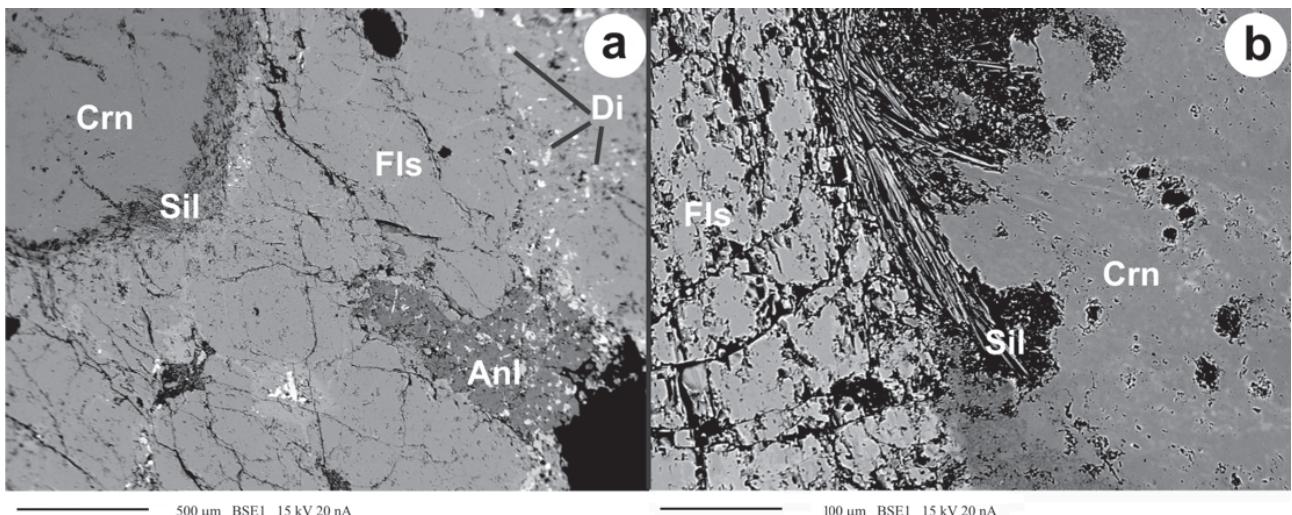
Sapphire in the Gortva syenite/anorthoclase xenolith forms 0.5 to 3.5 mm euhedral hexagonal deep blue crystals ( $\sim 5\text{--}10$  vol. %) in white several cm-sized syenite to anorthoclase xenolith in alkali basalt (Fig. 2a). Under CL image, the sapphire shows fine oscillatory zoning along the (1010) plane. The composition of the alkali feldspar is  $\text{Ab}_{63\text{--}67}\text{An}_{24}\text{Or}_{10\text{--}13}$  (Table 1). Fibres of the  $\text{Al}_2\text{SiO}_5$ -phase, probably sillimanite form a corona 0.1 to 0.4 mm thick between the sapphire and the feldspar (Fig. 4a,b). It probably formed during post-magmatic contact re-equilibration between corundum and alkali feldspar, possibly during heating of the xenolith by the hot alkali basalt lava. Leucite occurs as



**Fig. 2.** Photographs of sapphire: **a** — Blue sapphire crystals (0.5 to 3.5 mm across) with white corona of sillimanite (?) in syenite/anorthoclase xenolith in alkali basalt, Gortva; **b** — Blue sapphire crystal (3 mm across) with colour oscillatory zoning, Hajnáčka placer; **c** — Pink sapphire crystal (2 mm across) with fine colour oscillatory zoning, Hajnáčka placer; **d** — Pink sapphire with bluish-violet central part (4 mm in size) and apparent basal cleavage along the (0001) plane, Hajnáčka placer.



**Fig. 3.** CL images of sapphire crystals with apparent fine oscillatory zoning: **a** — Blue sapphire, Hajnáčka placer; **b** — Pink sapphire with tiny white zircon inclusions, Hajnáčka placer.



**Fig. 4.** BSE images of the sapphire-bearing syenite/anorthoclase xenolith from Gortva: **a** — Corundum (sapphire) crystal (Crn) rimmed by sillimanite (?) corona (Sil) associated with anorthoclase (Fls), diopside (Di) and analcime (Anl); **b** — Detail of sillimanite (?) fibres (Sil) formed at the contact between anorthoclase (Fls) and the sapphire (Crn).

**Table 1:** Representative electron-microprobe compositions of minerals in syenite/anorthoclase xenolith in alkali basalt from Gortva (wt. %).

	Sillimanite?	Plagioclase	Anorthoclase	Diopside	Diopside	Diopside	Leucite	Analcime
<b>SiO<sub>2</sub></b>	36.87	61.89	64.09	52.69	51.46	50.41	55.60	56.47
<b>TiO<sub>2</sub></b>	0.00			0.82	1.28	1.62		0.14
<b>Al<sub>2</sub>O<sub>3</sub></b>	62.06	23.52	19.77	1.66	2.42	1.82	22.58	23.02
<b>Cr<sub>2</sub>O<sub>3</sub></b>	0.05			0.04	0.02	0.00		
<b>Fe<sub>2</sub>O<sub>3</sub></b>	0.24	0.00	0.29		5.75	6.19	10.95	
<b>FeO</b>					0.20	0.18	0.33	
<b>MnO</b>	0.03							
<b>MgO</b>	0.00	0.00	0.00	15.15	14.46	11.57	0.00	
<b>CaO</b>	0.00	5.05	1.30	23.81	23.34	22.27	0.02	0.22
<b>SrO</b>			0.27					
<b>BaO</b>			1.25					
<b>Na<sub>2</sub>O</b>	0.00	7.26	6.57	0.48	0.47	0.61	0.08	11.04
<b>K<sub>2</sub>O</b>	0.03	2.28	5.75	0.06	0.03	0.21	21.12	1.33
<b>Rb<sub>2</sub>O</b>			0.04					
<b>Total</b>	99.28	100.00	99.33	100.66	99.85	99.79	99.74	92.49
<b>Anions pfu</b>	5	8	8	6	6	6	6	6
<b>Si</b>	1.002	2.762	2.921	1.937	1.912	1.917	2.022	2.042
<b>Ti</b>	0.000			0.023	0.036	0.046		0.004
<b>Al</b>	1.987	1.237	1.062	0.072	0.106	0.082	0.968	0.981
<b>Cr</b>	0.001			0.001	0.001	0.000		
<b>Fe<sup>3+</sup></b>	0.005	0.000	0.010		0.177	0.192	0.348	
<b>Fe<sup>2+</sup></b>					0.001	0.001	0.009	0.007
<b>Mn</b>	0.001				0.006	0.006	0.011	
<b>Mg</b>	0.000	0.000	0.000	0.830	0.801	0.656	0.000	
<b>Ca</b>	0.000	0.241	0.063	0.938	0.929	0.908	0.001	0.009
<b>Sr</b>			0.007					
<b>Ba</b>			0.022					
<b>Na</b>	0.000	0.628	0.580	0.034	0.034	0.045	0.006	0.774
<b>K</b>	0.001	0.130	0.334	0.003	0.001	0.010	0.980	0.061
<b>Rb</b>			0.001					
<b>Cation sum</b>	2.997	4.998	5.000	4.021	4.018	4.023	3.986	3.878

subhedral crystals (0.1 to 0.5 mm in size) in association with K-feldspar, pyroxene and Ti-rich magnetite. Feldspar composition in leucite- and pyroxene-rich areas changes to Na,K-rich, anorthoclase or sanidine-like members ( $Ab_{51-59}An_{02-07}Or_{34-46}$ ), enriched in Ba (0.5 to 1.3 wt. % BaO — Table 1). Pyroxene forms 20 to 150  $\mu$ m long columnar crystals of diopside (wollastonite<sub>47-51</sub>, clinoenstatite<sub>34-43</sub>,

clinoferrosilite<sub>09-19</sub>; Table 1). Locally, analcime forms fillings in feldspar + pyroxene groundmass (Fig. 4a). The prevailing Na,K-feldspar, the lack of quartz and the presence of pyroxene indicate a syenitic or anorthoclasic character for the sapphire-bearing xenolith. Unfortunately, the small size of the studied xenolith precludes making a more detailed petrographic and whole-rock geochemistry investigation.

**Table 2a:** LA-ICP-MS analyses of sapphire (ppm). Clastic sapphire from sedimentary filling of the Hajnáčka maar.

Crystal	Colour	Spot	Mg	Ti	V	Cr	Mn	Fe	Ga	Zr	Fe/Ti	Cr/Ga	Ga/Mg	Fe/Mg
1	blue	1	9	618	5	<2	<2	1455	42	<0.2	2.4		4.8	164
1	blue	2	11	770	5	<2	<2	1512	42	0.5	2.0		3.8	136
1	blue	3	15	907	5	<2	4	1789	45	<0.2	2.0		3.0	119
1	blue	4	17	735	6	<2	<2	2301	53	0.4	3.1		3.1	135
1	blue	5	21	600	10	<2	<2	1522	50	1.0	2.5		2.4	74
4	blue	1	7	309	9	8	<2	1283	43	<0.2	4.2	0.18	5.9	177
4	blue	2	9	51	10	16	<2	1410	44	<0.2	27.4	0.36	5.1	164
4	blue	3	13	24	12	31	<2	1598	49	<0.2	67.3	0.62	3.7	121
4	blue	4	13	23	10	32	<2	1445	47	<0.2	64.0	0.68	3.6	112
4	blue	5	13	21	11	39	<2	1517	48	<0.2	71.3	0.81	3.7	118
4	blue	6	6	201	8	17	<2	1250	42	<0.2	6.2	0.41	6.7	199
5	blue	1	4	798	5	<2	28	1670	36	0.2	2.1		9.8	456
5	blue	2	4	839	5	<2	20	1717	32	0.2	2.0		8.8	469
5	blue	3	4	934	5	<2	67	1868	29	<0.2	2.0		6.9	437
5	blue	4	5	1107	7	<2	62	2181	38	<0.2	2.0		7.6	432
3	blue	1	29	475	23	<2	<2	1318	40	<0.2	2.8		1.4	46
3	blue	2	31	525	25	<2	<2	1417	41	<0.2	2.7		1.3	46
3	blue	3	43	677	25	<2	6	1462	41	<0.2	2.2		1.0	34
3	blue	4	35	599	23	<2	<2	1277	37	<0.2	2.1		1.1	37
3	blue	5	29	451	22	<2	<2	1318	39	<0.2	2.9		1.3	45
3	blue	6	22	335	21	<2	<2	1359	43	<0.2	4.1		1.9	62
3	blue	7	18	196	19	<2	<2	1335	42	<0.2	6.8		2.4	75
6	grey-pink	1	31	208	26	82	8	1722	40	<0.2	8.3	2.03	1.3	56
6	grey-pink	2	61	584	39	119	24	1975	49	0.2	3.4	2.44	0.8	32
6	grey-pink	3	67	529	34	33	12	2079	47	<0.2	3.9	0.70	0.7	31
6	grey-pink	4	38	362	29	139	<2	1925	44	<0.2	5.3	3.14	1.2	50
2	pink	1	10	45	24	162	<2	828	42	<0.2	18.2	3.83	4.3	84
2	pink	2	11	73	26	173	<2	959	39	<0.2	13.1	4.42	3.7	89
2	pink	3	13	113	29	187	<2	981	42	<0.2	8.7	4.43	3.3	77
2	pink	4	36	742	39	164	<2	1099	48	<0.2	1.5	3.44	1.3	31
2	pink	5	44	306	56	308	<2	1131	49	<0.2	3.7	6.23	1.1	26
2	pink	6	41	318	52	256	<2	1096	45	<0.2	3.4	5.64	1.1	27
2	pink	7	53	547	48	153	<2	1124	50	<0.2	2.1	3.08	0.9	21
2	pink	8	28	401	33	161	<2	991	45	<0.2	2.5	3.56	1.6	35
2	pink	9	11	83	26	155	<2	847	37	<0.2	10.2	4.17	3.3	75
detection limit			2	9	1	2	2	6	1	0.2				
blue sapphire (average)			16	509	12	<39	<67	1546	42	<1.0	12.9	0.1	4.1	96
grey-pink sapphire (average)			49	421	32	93	<24	1926	45	<0.2	5.2	2.1	1.0	39
pink sapphire (average)			27	292	37	191	<2	1006	44	<0.2	7.0	4.3	2.3	37

### Chemical composition and oxygen isotopic characteristics of sapphires

The concentrations of Mg, Ti, V, Cr, Mn, Fe, Ga, and Zr in the coloured sapphires from the Hajnáčka placer and the sapphire-bearing syenite/anorthoclase xenolith from Gortva are given as LA-ICP-MS spot analyses (Table 2a).

Iron shows the highest concentrations in coloured sapphires from the Hajnáčka placer: ca. 830 to 2300 ppm; and averages 1550, 1930, and 1000 ppm Fe for blue, grey-pink and pink varieties, respectively (Table 2a). The blue sapphires contain higher Ti (mean ~510 ppm) in comparison to the grey-pink and especially the pink varieties (~420 and ~290 ppm in average). The pink sapphires show the highest average concentrations of Cr and V, 191 and 37 ppm, in comparison to 93 and 32 ppm in the grey-pink, and <39 (usually <2 ppm) and 12 ppm in the blue sapphires, respectively (Table 2a). Average Mg concentrations attain 16, 49, and 27 ppm in blue, grey-pink and pink varieties, respectively. Contents of Ga are similar in the all colour varieties (42 to 45 ppm in average). The concentrations of Be, Mn, Zr and other measured elements (Li, B, Sc, Co, Y, and Hf) were usually below the detection limit of LA-ICP-MS.

Blue sapphires from the Gortva syenite/anorthoclase xenolith have iron contents between ca. 2100 and 3400 ppm (mean ~2700 ppm), Ti concentrations vary between ~130 and averages ~2400 ppm, ~1200 ppm (Table 2b). The contents of Cr are <2 ppm and those of Ga are constant in the range 71–97 ppm (mean 82 ppm). Vanadium contents are between 40 and 94 ppm (58 ppm on average) and Mg between 16 and 148 ppm (mean 61 ppm).

The  $\delta^{18}\text{O}$ -values (V-SMOW) of two blue sapphires from the placer of Hajnáčka are 3.80 and  $5.85 \pm 0.1 \text{ ‰}$  respectively. The  $\delta^{18}\text{O}$ -value of the blue sapphire from the syenite/anorthoclase xenolith of Gortva is  $5.1 \pm 0.1 \text{ ‰}$  ( $n=3$ ).

### Discussion

#### Composition of sapphires: magmatic versus metamorphic origin

The Fe, Ti, Cr, Ga, Mg contents and chemical ratios such as Ga/Mg, Fe/Ti, Fe/Mg and Cr/Ga of the corundum xenocrysts or corundum-bearing xenoliths carried by continental alkali

**Table 2b:** LA-ICP-MS analyses of sapphire (ppm). Sapphire from syenite/anorthoclase xenolith in alkali basalt from Gortva.

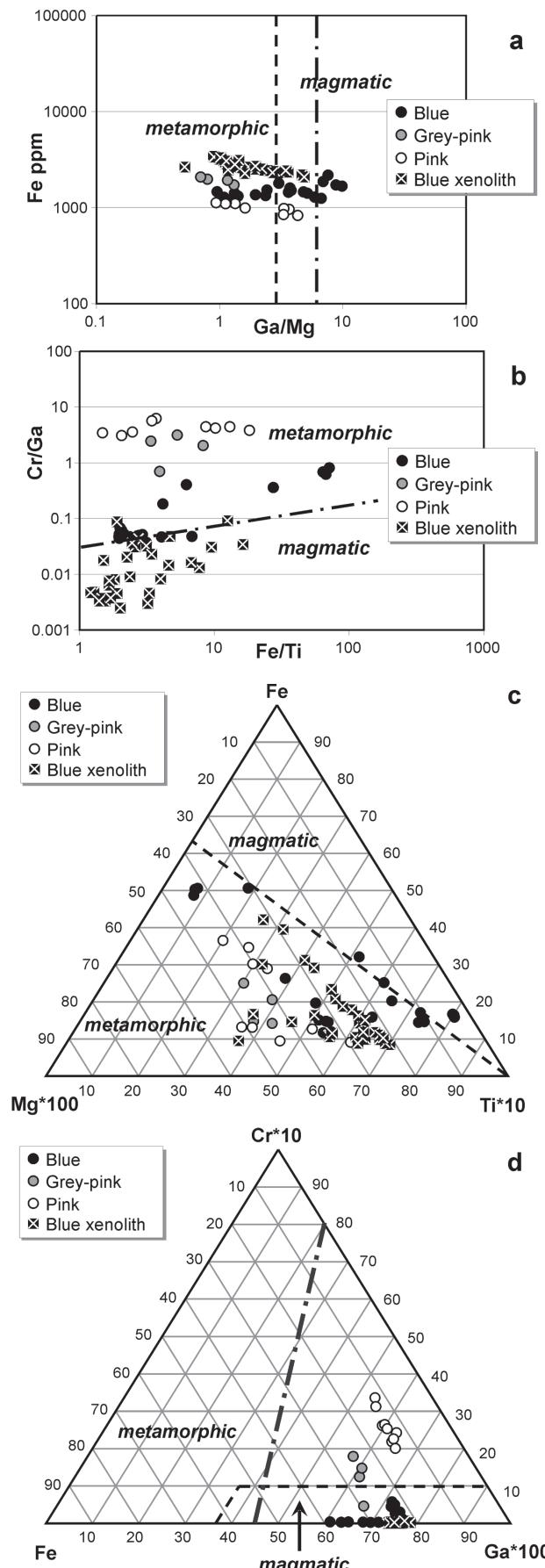
Crystal	Colour	Spot	Mg	Ti	V	Cr	Mn	Fe	Ga	Zr	Fe/Ti	Cr/Ga	Ga/Mg	Fe/Mg
1	blue	1	96	1603	94	<0.2	9.4	3181	96	1.59	2.0	0.002	1.0	33
1	blue	2	98	1651	91	0.2	10.9	3304	97	0.76	2.0	0.002	1.0	34
1	blue	3	107	1800	86	0.4	5.7	3415	95	0.64	1.9	0.005	0.9	32
1	blue	4	86	1475	80	<0.2	1.7	3118	92	0.44	2.1	0.003	1.1	36
1	blue	5	78	1936	63	0.3	6.8	2992	85	0.32	1.5	0.003	1.1	38
1	blue	6	75	1808	65	0.5	4.2	2984	85	0.17	1.7	0.006	1.1	40
1	blue	7	72	2240	59	0.4	0.7	2857	83	0.12	1.3	0.005	1.2	40
1	blue	8	71	2356	57	0.4	1.5	2841	81	0.18	1.2	0.005	1.1	40
1	blue	9	66	2053	54	<0.2	1.8	2634	78	0.13	1.3	0.005	1.2	40
1	blue	10	62	1826	53	0.3	1.3	2666	83	0.09	1.5	0.004	1.3	43
1	blue	11	45	1092	44	0.7	0.3	2577	76	0.08	2.4	0.009	1.7	57
1	blue	12	50	1423	49	0.6	0.5	2582	78	0.10	1.8	0.008	1.6	52
1	blue	13	52	1559	52	0.6	0.5	2595	77	0.08	1.7	0.008	1.5	50
1	blue	14	46	1177	57	1.6	<0.2	2643	80	0.04	2.2	0.020	1.7	57
1	blue	15	34	778	56	2.5	<0.2	2436	76	0.03	3.1	0.032	2.3	72
1	blue	16	16	174	46	6.8	<0.2	2185	74	<0.01	12.5	0.092	4.6	137
1	blue	17	16	127	41	2.6	<0.2	2073	76	0.01	16.3	0.034	4.8	132
1	blue	18	75	1669	66	0.3	2.4	2838	84	0.25	1.7	0.004	1.1	38
1	blue	19	106	2385	83	0.3	2.7	3339	95	1.16	1.4	0.003	0.9	31
1	blue	20	92	1611	74	<0.2	<0.2	3297	94	0.33	2.0	0.003	1.0	36
1	blue	21	82	947	60	0.3	<0.2	3034	92	0.06	3.2	0.003	1.1	37
1	blue	22	64	944	66	0.4	<0.2	3106	91	0.04	3.3	0.005	1.4	49
2	blue	1	31	606	46	0.6	0.5	2417	78	0.05	4.0	0.008	2.5	77
2	blue	2	69	535	44	1.2	0.3	2451	80	0.02	4.6	0.015	1.2	36
2	blue	3	21	300	40	1.0	<0.2	2320	76	<0.01	7.7	0.013	3.6	110
2	blue	4	23	357	42	1.3	0.3	2404	78	<0.01	6.7	0.016	3.4	106
2	blue	5	35	734	45	1.8	0.3	2515	78	0.04	3.4	0.023	2.2	71
3	blue	1	37	910	53	3.1	0.4	2495	71	0.04	2.7	0.044	1.9	67
3	blue	2	148	1019	54	2.4	0.3	2626	77	0.04	2.6	0.031	0.5	18
3	blue	3	60	1847	57	1.4	<0.2	2781	79	0.06	1.5	0.018	1.3	47
3	blue	4	27	506	47	3.6	<0.2	2369	75	0.01	4.7	0.048	2.8	88
3	blue	5	29	241	45	2.4	<0.2	2292	78	0.00	9.5	0.031	2.7	79
3	blue	6	48	1187	56	6.7	3.8	2245	77	0.33	1.9	0.088	1.6	47
3	blue	7	41	1092	57	3.0	<0.2	2680	81	0.03	2.5	0.037	1.9	65
detection limit			0.1	0.6	0.1	0.2	0.2	0.4	0.04	0.01				
average			61	1234	58	1.6	2.6	2714	82	0.23	3.5	0.021	1.8	57

basalts are used to discuss their magmatic versus metamorphic origin (e.g. Sutherland et al. 2002, 2009; Garnier et al. 2005; Zaw et al. 2006; Peucat et al. 2007). Generally, Fe and Ga reveal higher concentrations in magmatic sapphires (~1800 to 13,000 ppm Fe and ~70 to 570 ppm Ga), than in metamorphic ones which have Fe and Ga contents less than 3000 and 75 ppm, respectively. In contrast, low Cr and Mg contents are typical for magmatic sapphires (both usually <40 ppm), whereas gem corundum of metamorphic origin is enriched in these elements (both generally >60 ppm). Therefore, the Ga/Mg ratio is commonly >6 in magmatic sapphires and <3 in metamorphic ones. Conversely, the Cr/Ga ratio is <0.1 for magmatic sapphires and >1 for metamorphic sapphires. The Fe/Ti ratio is generally higher in magmatic than metamorphic sapphires. The Fe/Mg ratio is significantly higher for magmatic sapphires (Fe/Mg >> 100) and lower for metamorphic and metasomatic ones (Fe/Mg < 100; Peucat et al. 2007).

The sapphires from the Hajnáčka placer and the Gortva syenite/anorthoclase show relatively low to medium Fe and Ga contents, indicating a rather metamorphic affinity despite the petrological evidence of a magmatic origin for the syenite/anorthoclase xenolith. The low Mg concentrations of Hajnáčka (4 to 67 ppm) are more characteristic of magmatic

suites while those of Gortva (16 to 148 ppm) suggest metamorphic ones (Table 2a-b). The Cr contents are comparable both to magmatic and metamorphic groups (commonly <2 ppm for blue, 33–140 ppm for grey-pink, and 153–308 ppm for pink varieties).

The range and mean Fe/Ti, Cr/Ga, Ga/Mg, and Fe/Mg values also indicate bimodal origins, with stronger affinity of blue sapphires (both Hajnáčka and Gortva) to magmatic domain, and of grey-pink and pink sapphires more related to the metamorphic one. The Ga/Mg vs. Fe diagram (Peucat et al. 2007; Sutherland et al. 2009) shows both magmatic and metamorphic origins for the Hajnáčka and Gortva sapphires (Fig. 5a). The Fe/Ti vs. Cr/Ga diagram (Sutherland et al. 2009) is the equivalent of the  $\text{Fe}_2\text{O}_3/\text{TiO}_2$  vs.  $\text{Cr}_2\text{O}_3/\text{Ga}_2\text{O}_3$  diagram proposed by Sutherland et al. (1998) for classification of corundum in the alkali basalts domain. The diagram separates efficiently the metamorphic from the magmatic corundum (Sutherland et al. 2003), it indicates that the Gortva sapphires differs from the Hajnáčka ones, and they plot obviously in the field of the magmatic sapphires in agreement with their petrological nature (Fig. 5b). The Gortva sapphires have a Ga content in the range of the magmatic sapphires (>70 ppm) but their Mg content is too high (up to 148 ppm)



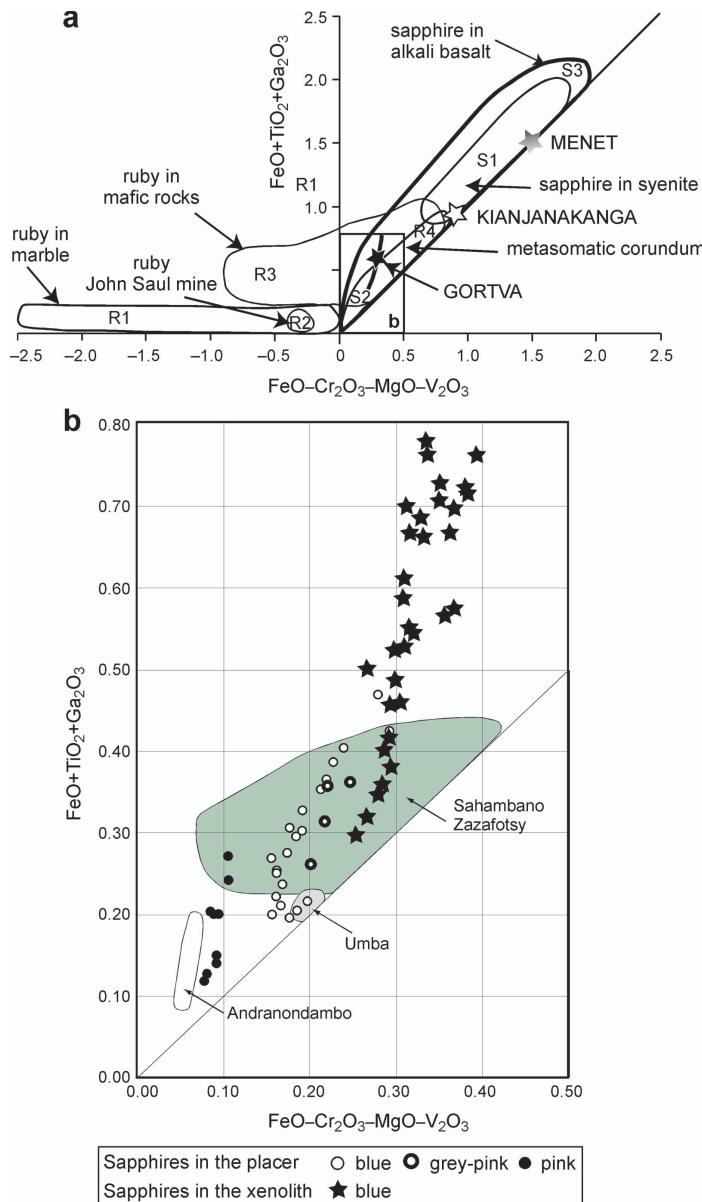
to assure a Ga/Mg ratio typical of a magmatic origin. The blue sapphires from Bo Phloi in Thailand have shown a similar trend, namely both metamorphic and magmatic domains (Peucat et al. 2007) despite their magmatic origin.

The Fe-Mg\*100-Ti\*10 triangular diagram defined by Peucat et al. (2007) indicates a metamorphic affinity for the whole sapphires (Fig. 5c). Conversely, the Cr\*10-Fe-Ga\*100 triangular diagram (Sutherland et al. 2009) shows a magmatic origin for the blue sapphires from both studied occurrences, and an undefined origin for the grey-pink and pink sapphires from Hajnáčka, out of the defined magmatic or metamorphic fields (Fig. 5d). Therefore, both diagrams using Ga/Mg ratio or Mg (Fig. 5a,c) reveal different results in comparison to the diagrams which apply Cr and Ga as discriminating elements (Fig. 5b,d). Consequently, the Hajnáčka and Gortva sapphires belong to the “problematic” or “debatable origin” group (Peucat et al. 2007), related to magmatic environment but with both magmatic and metamorphic or metasomatic geochemical features. Similar occurrences include mixed metamorphic/magmatic sapphire suites from eastern Australia (Sutherland et al. 2002), Rio Mayo sapphires, Colombia (Sutherland et al. 2008), as well as lamprophyre-related Yogo Gulch (Montana, USA), and basalt-related Bo Phloi (Thailand) sapphires (Peucat et al. 2007). In such cases, contents of some trace elements, especially Mg, did not effectively differentiate magmatic from metamorphic blue sapphires.

Recently Giuliani et al. (2010) proposed the use of the  $\text{FeO-Cr}_2\text{O}_3-\text{MgO-V}_2\text{O}_3$  vs.  $\text{FeO+TiO}_2+\text{Ga}_2\text{O}_3$  diagram (Fig. 6a) for the classification of primary deposits. This diagram uses Fe (FeO) as a major or a minor trace element of corundum; the FeO content enables us to discriminate between the two main types of ruby namely iron-poor rubies in marbles and iron-rich rubies in mafic-ultramafic rocks (Pham Van et al. 2004). The second device used for the discrimination of ruby and sapphire is the addition (parameter on the X-axis) or subtraction to FeO (parameter on the Y-axis) of trace elements associated preferentially with ruby ( $\text{Cr}_2\text{O}_3$ ,  $\text{V}_2\text{O}_3$ , and  $\text{MgO}$ ) or sapphire ( $\text{TiO}_2$  and  $\text{Ga}_2\text{O}_3$ ). The different types of gem corundum deposit are: *for ruby*, marble (R1); John Saul Ruby Mine (Kenya) type (R2); mafic and ultramafic rocks (R3); metasomatites (R4); *for sapphire*, syenitic rocks (S1); metasomatites (S2); xenocrysts in alkali-basalt and lamprophyre (S3). The domains of R4 and S2 which correspond to metasomatic-metamorphic corundum are overlapping.

The  $\text{FeO-Cr}_2\text{O}_3-\text{MgO-V}_2\text{O}_3$  vs.  $\text{FeO+TiO}_2+\text{Ga}_2\text{O}_3$  diagram (Fig. 6a-b) suggests a metasomatic-metamorphic origin for the Hajnáčka alluvial sapphires (field S2). The chemical composition fits into the domain of sapphires ( $\text{Fe} > \text{Cr}$ ) related to biotite developed in gneisses within

**Fig. 5.** Positions of blue, grey-pink and pink sapphires from Hajnáčka placer in comparison to blue sapphire from Gortva syenite/anorthoclase xenolith in magmatic versus metamorphic discrimination diagrams. Modified after Peucat et al. (2007) and Sutherland et al. (2009), values are in ppm: **a** —  $\text{Ga/Mg}$  vs.  $\text{Fe}$ ; **b** —  $\text{Fe/Ti}$  vs.  $\text{Cr/Ga}$ ; **c** —  $\text{Fe}-\text{Mg}^*100-\text{Ti}^*10$ ; **d** —  $\text{Cr}^*10-\text{Fe}-\text{Ga}^*100$ .



**Fig. 6.** a —  $\text{FeO}-\text{Cr}_2\text{O}_3-\text{MgO}-\text{V}_2\text{O}_3$  versus  $\text{FeO}+\text{TiO}_2+\text{Ga}_2\text{O}_3$  diagram (in wt %) used for the geological classification of the corundum deposits. The main fields defined for these different types of deposit worldwide are reported (Giuliani et al. 2010); b — Chemical distribution of the coloured sapphires from Hajnáčka and Gortva in the diagram.

shear zones such as the Sahambano and Zazafotsy deposits, Madagascar (Rakotondrazafy et al. 2008), blue sapphires from the skarn deposit of Andranondambo, Madagascar (Giuliani et al. 2007), and sapphires in plumbosilicate, that is desilicated pegmatites in ultramafic-rocks from Umba in Tanzania (Seifert & Hyršl 1999). They are clearly outside of the field of sapphires associated with syenites but they plot in the field of corundum xenocrysts associated with alkali-basalts worldwide (field S3) and towards the low Cr-Mg-V-Ti and Ga-bearing sapphires in metasomatisites.

The sapphires from the Gortva xenolith do not plot in the S1 magmatic domain defined for syenites (Fig. 6a) in con-

trast to the blue sapphires from the anorthoclases of Menet in the French Massif Central and Kianjanakanga in central Madagascar (Rakotosamimanana 2009a,b). The representative points of the Gortva sapphires indicate a trend crosscutting the domains S2 (metasomatic) and S3 (xenocrysts in alkali-basalt and lamprophyre). Consequently, the  $\text{FeO}-\text{Cr}_2\text{O}_3-\text{MgO}-\text{V}_2\text{O}_3$  vs.  $\text{FeO}+\text{TiO}_2+\text{Ga}_2\text{O}_3$  diagram ambiguously indicates metasomatic or magmatic origin of the Hajnáčka and Gortva sapphires again.

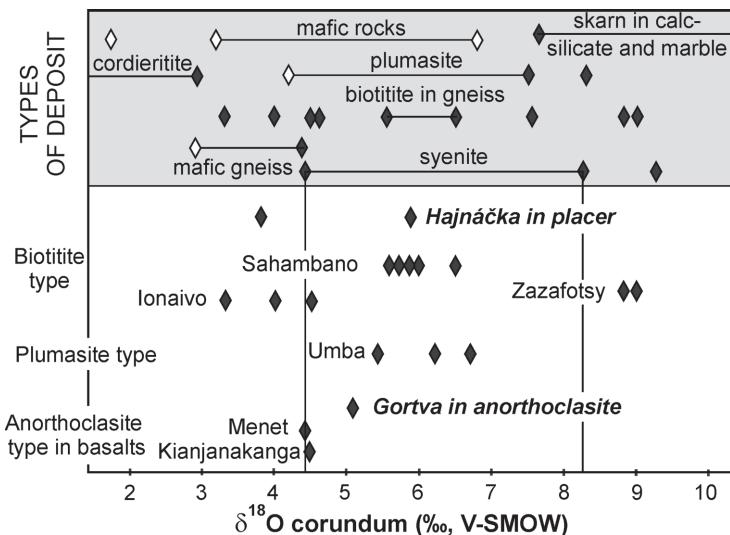
Different geochemical diagrams applied to the Hajnáčka and Gortva sapphires illustrate the complexity of the use of classification for sapphires which have special composition and representative chemical field overlapping the limits of metamorphic and magmatic domains (Figs. 5a-d, 6). The diagrams are the result of the combination of the chemical composition with the type of deposit which is sometimes not well defined.

#### Oxygen isotopes of sapphire

The  $\delta^{18}\text{O}$  value in gem corundum represents a useful tool for deciphering its geological origin (Yui et al. 2003, 2006; Giuliani et al. 2005, 2007, 2009; Garnier et al. 2005; Zaw et al. 2006; Sutherland et al. 2009). As the mantle and crustal rocks show distinct oxygen isotope compositions, the  $\delta^{18}\text{O}$  value enables us to investigate the origin and source of corundum. Several principal genetic groups can be subdivided based on sapphire  $\delta^{18}\text{O}$  values (Giuliani et al. 2007): pink sapphires hosted in cordierite ( $\delta^{18}\text{O}=1.7$  to 2.9 ‰), coloured and blue sapphires in lamprophyre ( $\delta^{18}\text{O}=5.4$  to 6.8 ‰), in syenitic rocks (4.4 to 8.3 ‰), in desilicated pegmatites associated with amphibolites and pyroxenites (4.2 to 7.5, locally to 11.2 ‰), in biotite in gneiss (4.6 to 9.0 ‰), in calc-silicates and skarns (7.7 to 10.7 ‰), in desilicated pegmatites in marble (15.5 to 15.9 ‰), and blue-reddish sapphires with ruby in marble (16.3 to 22.3 ‰).

The  $\delta^{18}\text{O}$  measurements of blue sapphires from Hajnáčka (3.80 and 5.85 ‰) fit into the ranges of sapphires originating from mantle-related magmatic rocks such as lamprophyres and syenitic rocks, as well as desilicated pegmatites in mafic rocks or

biotite in gneiss. The  $\delta^{18}\text{O}$  values are different from those of sapphires in Ca-rich metamorphic rocks, mainly skarns and marbles ( $\delta^{18}\text{O}>9$  ‰; Giuliani et al. 2005, 2007; Zaw et al. 2006). Additional O-isotopic composition of sapphires from biotites in gneiss from Madagascar are presented in order to complete an earlier database (Giuliani et al. 2005, 2007, 2009). The sapphires from Ionaivo located in the south of the Sahambano deposit have  $\delta^{18}\text{O}$  of 4.5, 4.0 and 3.3 ‰ respectively (Fig. 7). The  $\delta^{18}\text{O}$  measurements of both Hajnáčka sapphires overlap the  $\delta^{18}\text{O}$ -range of sapphires in (i) biotite formed in gneiss such as those of the Sahambano, Zazafotsy and Ionaivo deposits in Madagascar ( $\delta^{18}\text{O}=3.3$  to 9.0 ‰),



**Fig. 7.** Oxygen isotope values ( $\delta^{18}\text{O}$ ) of sapphires from Hajnáčka placer and Gortva syenite/anorthoclase xenolith, with reference to the worldwide  $\delta^{18}\text{O}$  database (Giuliani et al. 2005, 2007, 2009, this work). The diamond symbols indicates the rubies (white), coloured sapphires and sapphires (black). V-SMOW — Vienna Standard Mean Ocean Water.

mean  $\delta^{18}\text{O} = 6.1 \pm 1.8 \text{ ‰}$ ,  $n = 11$ ) or (ii) plumasite in ultramafic rocks such as the Umba deposit in Tanzania ( $\delta^{18}\text{O} = 5.4$  to  $6.7 \text{ ‰}$ ;  $n = 3$ ; Giuliani et al. 2005).

The  $\delta^{18}\text{O}$ -value of  $5.1 \text{ ‰}$  obtained for the blue sapphire in the syenite/anorthoclase xenolith from Gortva fits into the  $\delta^{18}\text{O}$ -range of sapphires associated with syenites/anorthoclases, and it is in agreement with the  $\delta^{18}\text{O}$ -values of  $4.4$  and  $4.5 \text{ ‰}$  (Giuliani et al. 2005, 2009), respectively obtained for the blue sapphires of Menet (France) and Kianjanakanga (Madagascar) anorthoclases (Fig. 7). This  $\delta^{18}\text{O}$ -value also corresponds to the  $\delta^{18}\text{O}$  values obtained for olivine from mid-ocean ridge ( $\delta^{18}\text{O} = 5.16 \text{ ‰}$ ), ocean island basalt ( $\delta^{18}\text{O} = 5.17 \text{ ‰}$ ) and continental flood basalt ( $\delta^{18}\text{O} = 5.16 \text{ ‰}$ ; Eiler et al. 1997; Baker et al. 2000). Sapphire genesis in felsic melts by partial melting and/or metasomatism of mantle spinel lherzolite with an original  $\delta^{18}\text{O}$  isotope composition (5 to  $6 \text{ ‰}$ ), has been proposed by several authors (Oakes et al. 1996; Yui et al. 2003; Pin et al. 2006).

### Possible genetic scenario of sapphire origin: a summary

The oxygen isotopic composition of sapphire from the Gortva syenite/anorthoclase indicates that it was derived from an igneous reservoir in the sub-continental spinel lherzolitic mantle. In the lithospheric mantle, felsic melts crystallized to form anorthoclases, the most evolved peraluminous variant of the alkaline basaltic melt. This hypothesis is in agreement with the genesis proposed for the anorthoclasic sapphires of Menet, France and Kianjanakanga, Madagascar (Giuliani et al. 2009; Rakotosamizanany 2009a,b). However, the chemistry of the sapphires from Hajnáčka and Gortva is different from those of Menet and Kianjanakanga (Fig. 6a)

especially for iron: they contain 2 or 3 times less iron than the sapphires of the French and Malagasy anorthoclases. Their origin is similar but the evolution of their parent magma is probably quite different. The final product is an anorthoclase rich in Si, Al, K and Na but the quantity of iron was probably different due to the precipitation of iron-rich phase such as Ti-rich magnetite and biotite. In the French Massif Central, Brousse & Varet (1966) described different types of anorthoclase with diverse modal composition for iron-bearing phases (maghemite-, almandine-, and corundum-bearing anorthoclase). Early magmatic precipitation of Fe-rich phases can explain an origin of fractionated, iron depleted felsic melt and crystallization of relatively Fe-poor sapphire in the Hajnáčka and Gortva occurrences. The behaviour of the other elements, such as Ti, Ga, Cr, V and Mg in the sapphires, could be discussed in the same way by analysing their content in the different minerals of the host syenite/anorthoclase. The control of the final composition of the magmatic sapphires by the behaviour of the parent magma during its crystallization can generate discrepancies with the use of the chemical diagrams of corundum classification as illustrated by the Hajnáčka and Gortva sapphires.

Assuming our data, the blue sapphire from Gortva and mostly also from Hajnáčka solidified from a fractionated melt, probably in the upper mantle or lower crust before their transport to the surface as syenite/anorthoclase xenoliths (or corundum xenocrysts) by alkali basalt lava. This model is consistent with an origin of analogous felsic syenitic xenoliths from the nearby Pinciná maar, southern Slovakia, where a fluid-inclusion and petrological study indicated a pressure around 600 MPa (ca. 22 km of lithostatic load) and liquidus temperature of inclusion melts at  $\sim 1080 \text{ }^{\circ}\text{C}$  (Huraiová et al. 1996). Similar models for corundum origin from upper mantle to lower crustal, fractionated syenitic/anorthoclasic magma are also proposed for other sapphire occurrences (e.g. Coenraads et al. 1995; Sutherland et al. 1998, 2009; Upton et al. 1999, 2009; Graham et al. 2008).

The genetic scenario of pink and grey-pink sapphires from Hajnáčka is still unresolved, but their composition (mainly higher Cr and Mg content) suggest a metamorphic (metasomatic) origin comparable to compositions of sapphires from plumasites, skarns or biotites developed in gneisses (Seifert & Hyršl 1999; Giuliani et al. 2007; Rakotondrazafy et al. 2008). Xenoliths of Paleozoic gneisses and migmatites of the Veporic Superunit in andesites from the vicinity of Hajnáčka (Hovorka & Lukáčik 1972) indicate such a possibility.

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