Minerals of spinel group from pyrope-bearing gravels of the České středohoří Mountains, Czech Republic

Nerosty skupiny spinelu z pyroponosných štěrků v Českém středohoří, Česká republika (Czech summary)

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Spinel, ferroan spinel (pleonaste), chromian spinel (picotite), hercynite, magnetite and titanomagnetite were identified in a heavy mineral concentrate after industrial extraction of pyrope from pyrope-bearing gravels near Podsedice in the České středohoří Mts. Very rare spinel occurs as dark grey grains exhibiting relatively enhanced content of FeO and Fe₂O₃. Ferroan spinel is the most abundant mineral of the spinel group, and amounts together with picotite to 17.5 wt. %. The average composition is Mg 72, Fe²⁺ 28 (at. %) and atomic ratio Al/Fe³⁺ = 11.9. Chromian variety of pleonaste with 10.3 wt. % Cr₂O₃ (11.2 at. %) is very rare. Pleonaste has a = 8.146(2) 10^{-1} nm and D_{calc.}= 3.848. Picotite composes about 30 wt. % of pleonaste grains. Picotite grains are smaller (≤ 4 mm): Mg (72 at. %) predominates over Fe²⁺ (30 at. %) in its tetrahedral sites, and Al (58.5 at. %) predominates over Cr (36.5 at. %) and Fe³⁺ (5.0 at. %) in octahedral sites. The content of Cr₂O₃ in picotite varies between 26.89 and 37.35 wt. %. Hercynite is very rare. Magnetite plus titanomagnetite constitute 5.6 wt. % of the concentrate. Magnetite contains ≤ 5.4 wt. % TiO₂ and ≤ 4.8 wt. % MnO. Relatively higher concentration of MnO and the absence of MgO separate this mineral from titanomagnetite which has 10.90–12.07 wt. % TiO₂. It is more abundant in the concentrate than magnetite. Its cell parameter a = 8.436 10^{-1} nm and D_{calc.}= 4.845. Various types of basalt and its tuffs, basaltic pipe breccias and particularly xenoliths of various ultramafic rocks brought to the surface through the pipe vents are thought to be the primary source of spinel-group minerals in pyrope-bearing gravels. The mode of occurrence, abundance and chemical composition of the spinel-group minerals in pyrope-bearing gravels indicate that they are genetically similar to placers at the Jizerská louka in the Jizerské hory Mts and at Seifengründel in Saxony at the northern border with Czech Republic.

Key words: minerals of spinel group, mineralogy, chemical composition, Quaternary pyrope-bearing gravels, Podsedice, České středohoří Mts.

Introduction

Pyrope-bearing gravels in the České středohoří Mts are the main source of pyrope – the "Czech garnet" for custome jewellery. Their geology, distribution and origin were studied by numerous authors, c. g., Zahálka (1884b, c, 1885), Oehmichen (1900), Hibsch (1917, 1920), recently Sýkora (1952), Kopecký et al. (1962, 1967), Turnovec et al. (1977) and Götz et al. (1979).

Mineralogical studies of pyrope and other minerals constituting the heavy fraction of the pyrope-bearing gravels were published in the past (see references above). However, members of the spinel group have been so far neglected. The purpose of this paper is to rectify this situation; major attention is paid to ferroan spinel and chromian spinel, as the extant literature does not provide any data on their chemistry.

The studied minerals were separated from a gravity concentrate which represents waste material after extraction of pyrope. Pyrope-bearing gravels are subjected to gravity separation in a local concentrator at Podsedice to obtain a rough concentrate, which is then shipped to another concentrator at Cínovec and upgraded on sieves and using gravity separation and finally hand picking of pyrope. A sample of 416 g of this concentrate from Podsedice for this study free of pyrope and with a grain size of 2–8 mm was collected by Dr. Milan Fengl.

The mineral composition of the concentrate is given in Table 1. The concentrate contained the following minerals of the spinel group: spinel, ferroan spinel (pleonaste), chromian spinel (picotite), hercynite, magnetite and titanomagnetite. In addition, some other accessory minerals not exceeding 0.2 wt. % were indentified: amphiboles, anatase, apatite, barite, galena, hematite, hercynite, quartz, kyanite, maghemite, muscovite, siderite, sillimanite, titanite, rock fragments and various artifacts. Very rare are also diamond, moissanite, topaz, cassiterite and minerals of the crandallite series (Kopecký et al. 1967, Novák et al. 1998, Turnovec et al. 1977).

Geological setting and character of pyrope-bearing gravels

Pyrope-bearing gravels are found in proluvial-deluvial placers of Pleistocene age which are widespread in the SW part of the České středohoří Mts. They represent relics of the bottom part of piedmont dejection cones (fans) on a gently inclined Cretaceous plateau. The gravels were transported in streams of the Quaternary drainage incised into the underlying Cretaceous sediments. The major concentrations of pyrope and other heavy minerals occurred in axial parts of these streams, forming discontinuous bands. All streams flow from NW to SE. Individual bands represent a continuous line of tiny basins of variable thickness, arranged along their axis. Four main bands of pyrope-bearing gravel can be recognized: from the E to the W, Podsedice, Chrášťany, Linhorka and Třebívlice. They are quite variable in thickness, attain-

ing a maximum of around 6 m. The gravels consist of unsorted material in which the detrital fraction varies from pea-size gravels to blocks of a wide variety of rocks. Most abundant are fragments of basalts, Cretaceous sediments, Oligocene conglomerates and various rocks of the crystalline basement (e. g., gneisses, granulites, granites, aplites, quartz porphyries and serpentinized peridotite with pyrope and other types of ultramafic rocks). The sandy-clayey fraction also is important and varies in color from grey-white to rusty. The rusty sandy sediments are richer in pyrope and other heavy minerals. This fraction also contains, locally, some fossils and fragments derived from weathering of Cretaceous rocks. All pyrope-bearing bands contain similar assemblages of heavy minerals. The material forming the pyrope-bearing gravels is thought to have originated by intense weathering of the filling of basaltic pipes and explosive volcanoes of Maar type which can explain larger extent of pyrope-gravels in places where breccias are missing. The total areal extent of pyrope-bearing gravels was estimated to be around 59 km² (Sýkora 1952).

Heavy minerals identified in pyrope-bearing gravels have already been quoted in the introduction (Table 1). The most characteristic are pyrope, zircon, minerals of the spinel group and ilmenite. The exotic character of some minerals indicates that the source rocks, besides alkaline basalts, included all kinds of xenoliths which

Table 1 Mineral composition of concentrate from Podsedice.

	weight (g)	wt. %
Pyroxenes monoclinic (diopside, augite)	207.2	49.8
Fe- and Cr-rich spinels (pleonaste, picotite)	72.8	17.5
Zircon	29.9	7.2
Mn-oxidic minerals (small nodules)	24.5	5.9
Magnetite and titanomagnetite	23.3	5.6
Garnet – residual pyrope	10.2	2.4
Garnet – almandine	8.4	2.0
Goethite and limonite	6.0	1.4
Ilmenite (common type		
and Fe3+- plus Mn-enriched varieties)	2.4	0.6
Olivine	1.8	0.4
Pyrite (partly altered)	1.5	0.4
Pyroxenes orthorhombic (bronzite, enstatite)	1.5	0.4
Carbonates (aragonite, calcite)	0.8	0.2
Corundum (including sapphire)	0.8	0.2
Chromium-bearing diopside (deep green)	0.5	0.1
Others (miscellaneous)	24.8	5.9
Total	416.4	100.0

were brought from the basement to the surface through volcanic pipes. These xenoliths are thought to be enclosed in pipe filling.

Methods of study

The heavy-mineral concentrate used in this study was subjected to magnetic and electromagnetic separation using a permanent magnet and electromagnet Davies, respectively. A Clerici's solution (D ca 4.1) was used to separate pleonaste from picotite.

X-ray diffraction powder data were obtained on the instrument Mikrometa II by using X-ray diffractograph GON 03 under standard conditions (CuK_{α} radiation, Ni filter, voltage 30 kV, intensity 18 mA, quartz as internal standard). Analyses were done by Dr. J. Ševců in the X-ray laboratory of Ústav nerostných surovin a. s. (Institute of Mineral Raw Materials) Kutná Hora.

The qualitative and quantitative chemical composition of minerals examined was determined by the scanning electron microprobe CamScan 4 with energy-dispersion analyser EDX system LINK eXL. Natural phases were used as standards with voltage and sample current 20 kV and 40 nA, counting time 80 s and correction procedure ZAF. The electron-microprobe analyses were executed by Dr. I. Vavřín in laboratories of the Czech Geological Survey, Prague.

Minerals of the spinel group in pyrope-bearing gravels from the Podsedice region

Spinel

Gemmy varieties of spinel of various colors from pyropebearing gravels were already known to F. X. Zippe (1827, in Kratochvíl et al. 1957–1966) and later described by Zahálka (1884a), Hibsch (1917, 1926, 1934) and other authors. Oehmichen (1900) reported that specimens of these spinels were deposited in a local museum at Třebenice. These varieties in form of grains and crystals of

Table 2 Results of electron-microprobe analyses of ferroan spinel from Podsedice.

	1		2		3
	range of		range of		
	3 compositions,	$\overline{\mathbf{x}}$	8 compositions,	$\overline{\mathbf{X}}$	
	in wt. %		in wt. %		
MgO	19.54-20.28	19.91	17.60-18.80	18.24	16.15
MnO	0.00- 0.16	0.08	0.00- 0.22	0.08	-
NiO	0.31- 0.44	0.38	0.00- 0.55	0.28	0.37
FeO	10.10-11.10	10.60	11.63-13.15	12.70	14.56
Fe ₂ O ₃ 1)	3.49- 6.70	5.10	7.30- 8.25	7.76	9.22
Al ₂ O ₃	60.85-64.15	62.50	55.43-59.93	58.45	48.56
Cr,O,	0.14- 0.23	0.37	0.47- 4.88	1.31	10.30
TiÔ,	0.00- 0.61	0.31	0.43- 0.64	0.52	0.80
Total		99.25		99.34	99.96
FeO 2)	13.24–17.13	15.19	18.83-20.50	19.68	

Empirical formula of average composition based on 32 oxygens per formula unit:

- $\begin{array}{l} 1-\text{spinel with enhanced proportion of ferroan component} \\ (Mg_{6.18}Fe^{2+}_{1.72}\ Ni_{0.07}Mn_{0.03})_{\Sigma 8.00}(Al_{15.44}Fe^{3+}_{0.54}Ti_{0.04}Cr_{0.02})_{\Sigma 16.04}O_{32} \\ \end{array}$
- $\begin{array}{l} 2-ferroan\ spinel-pleonaste\ variety\\ (Mg_{5,71}Fe^{2+}_{2,22}Ni_{0.05}Mn_{0.02})_{\Sigma 8.00}(Al_{14.46}Fe^{3+}_{1.22}\ Cr_{0.22}Ti_{0.08})_{\Sigma 15.98}O_{32} \end{array}$
- $\begin{array}{l} 3-\text{ferroan spinel (pleonaste) with enhanced } Cr_2O_3 \text{ content} \\ (Mg_{5,27}Fe^{2+}_{2.66}Ni_{0.07})_{\Sigma 8.00}(Al_{12.52}Cr_{1.78}Fe^{3+}_{1.52}Ti_{0.13})_{\Sigma 15.95}O_{32} \end{array}$
- $^{1)}$ Content of Fe $_2$ O $_3$ derived from empirical formula based on a total of R^{2+} equal to 8.
- 2) Total content of Fe recalculated to FeO.

various colors were very rare. Their color varied in shades of red, brown, blue, green and grey. The grains were reported to be transparent to translucent and exhibited conchoidal fracture, high hardness and specific gravity between 3.4 and 3.8 (Zahálka 1884a).

Rost (1962) did not find coloured spinels of the above character, and he doubted their occurrence in the area. Our investigations also failed to identify such spinels which were reported as tiny grains and therefore they should be expected to occur in fractions < 2 mm. Götz et al. (1979) described spinel in fine fraction of a concentrate from the Podsedice band. However, no details were given.

Two dark grey grains corresponding, by their chemical composition, to spinel with some Fe were identified among analyzed grains of ferroan spinels (comp. 1, Table 2). They differ markedly from similar pleonaste by higher contents of MgO and Al₂O₃ and lower concentrations of FeO and Fe₂O₃. Low admixture of MnO, NiO and TiO₂ is similar to that found in pleonaste but the proportion of Cr₂O₃ is relatively smaller.

The mineral in Tröger's (1971) classification diagram plots in the field of spinel close to the border with ceylanite (a black green variety of pleonaste). This spinel is likely to correspond to grey spinel reported already by Zippe.

Ferroan spinel – pleonaste

Pleonaste (or ceylanite) has been known in pyrope-bearing gravels of the České středohoří Mts already since the first half of the 18th century (Zippe quoted in Kratochvíl 1957–1966). Its detailed description was reported by Zahálka (1984a), Oehmichen (1900) and Hibsch (1917, 1926, 1934).

Pleonaste represents the most abundant mineral of the spinel group in the gravity concentrate (Table 1). Its proportion together with picotite amounts to 17.5 vol. %, the proportion of picotite component is about one quarter of this value.

Pleonaste forms as rounded grains or, to lesser extent, octahedral crystals with dull edges, or fragments. The grain size varies mostly between 2 and 8 mm. The largest grain found so far was 15 x 15 x 5 mm in size. The mineral is of velvet black to grey-black color, of dull to glassy or even semi-metallic luster on fresh fracture, and mostly with conchoidal fracture. Pleonaste exhibits pale to grey streak, and is translucent and isotropic in tiny chips. The mineral is difficult to distinguish from other similar spinels by naked eye.

Table 3 Specific gravity and cubic cell parameters of Fe-rich spinel (pleonaste) from various placers.

Locality	D meas	D calc.	a (10 ⁻¹ nm)	Reference
Podsedice	3.700a)	3.848	8.146(2)	this paper, ^{a)} after Zahálka (1884 a)
Jizerská louka	3.852	3.853	8.120(1)	Novák et al. (1975)
Seifengründel in Saxony	3.875	-	8.130	Tröger – Seifert (1963)

Physical parameters of ferroan spinel (pleonaste) from various placers are summarized in Table 3. Note that parameters of the compared pleonaste samples are very close to each other, which argues for their similar chemical composition.

Variation in chemical composition and calculated chemical formulae of pleonaste are given in Table 2, No. 2. In Tröger's (1972) classification diagram, all compositions plot in the field of ceylanite = pleonaste. Chemical compositions indicate that the mineral is a ferrous spinel, i. e. pleonaste with an average content of Fe^{2+} component 28 at. %. The variation in major elements is small, but Cr_2O_3 shows a considerable range between 0.14–4.88 wt. %. One analyzed grain showed enhanced content of Cr_2O_3 (comp. 3, Table 2), thus corresponding to Cr-rich pleonaste with 11.2 at. % of Cr component. In contrast to other pleonaste grains analyzed, this variety is also richer in FeO (33 at. %), Fe_2O_3 (9.5 at. %) and TiO_2 . However, the content of Cr_2O_3 is the only criterion how to distinguish Cr-poor pleonaste from Cr-rich picotite.

Chemical composition of pleonaste from Podsedice is very close to that from similar placers in the Malá Jizerská louka (Novák et al. 1979) and Seifengründel near Hinterhermsdorf in Saxony (Tröger – Seifert 1963) which indicates their similar origin.

Chromian spinel - picotite

The occurrence of picotite in pyrope-bearing gravels of the České středohoří Mts. was first noticed by Rost (1962) and later by Píšová (1964 in Kopecký et al. 1967). However, its chemical composition was so far not established. Picotite in this area is, together with bronzite and chromium-diopside, a constituent of olivine nodules which, according to Hibsch (1934), occur in some basalts and their tuffs. These olivine clusters also compose xenoliths in pipe breccias at Linhorka and in particular in a neighbouring basanite diatreme at Kuzov (Kopecký – Kodymová 1986). Here, picotite forms tiny octahedral crystals but mostly occurs as black or dark brown, almost opaque, irregular grains.

Picotite composes about 30 % of dark spinel grains from tailings of the Podsedice concentrator. Picotite forms mostly black, 2–3 mm large, opaque, perfectly rounded, grains which cannot be distiguished by naked eye from pleonaste. Picotite is slightly magnetic which allows to separate it using a DAVIES electromagnetic separator at an interval between 0.4 and 0.6 A. However, it is impossible to separate picotite from pleonaste because of close magnetic properties of both minerals. These minerals can be separated using a Clerici's solution (pleonaste D 3.7–4.0, picotite > 4.0).

Variation in chemical composition of picotite and its average chemical formula are given in Table 4. In Tröger's (1972) classification diagram, the analyzed mineral plots in the field of picotite. Its formula is characterized by Mg 70 at. % > Fe²⁺ 30 at. % and Al 58.5 at. % > Cr 36.5 at. %. The chemical composition of the Pod-

Table 4 Results of electron-microprobe analyses of Cr-spinel (picotite) from Podsedice.

	range of 5 compositions in wt. %	$\overline{\mathbf{x}}$
MgO	13.44-18.29	16.20
MnO	0.00- 0.23	0.11
NiO	0.22- 0.47	0.31
FeO	10.40-15.82	12.58
Fe ₂ O ₃ 1)	4.09- 5.46	4.61
Al,O,	28.51-38.07	34.51
Cr,O,	26.89-37.35	32.12
TiO,	0.00- 0.34	0.11
SiO,	0.00- 0.21	_
Total	_	100.55
FeO 2)	14.21-19.50	16.73

Empirical formula of average composition based on 32 oxygens per formula unit:

$$(Mg_{5.52}Fe^{2+}_{2.40}\ Ni_{0.06}Mn_{0.02})_{\Sigma 8.00}(Al_{9.30}Cr_{5.80}Fe^{3+}_{0.79}Ti_{0.02})_{\Sigma 15.91}O_{32}$$

sedice picotite is close to that of this mineral from similar placers at the Malá Jizerská louka (24.8–32.2 wt. % Cr_2O_3 ; Novák et al. 1979).

Hercynite

The mineral was found as a single 2 mm large crystal-line aggregate enclosed in a small rock fragment with brown garnet and black amphibole. Hercynite is magnetic, black, with metallic luster and dark green when pulverized. EDS measurements gave Fe and Al as major elements and Mg as a minor component. The accompanying garnet contains major Al, Fe, Mg and Si with minor Ca which corresponds to almandine-pyrope composition. The amphibole showed major Al, Fe and Si with minor Ca and Mg and traces of Mn and K.

Magnetite

This mineral was reported already by F. A. Reuss in 1790 (in Kratochvíl 1957–1966), but is not abundant (Rost 1962). Magnetite is accompanied by maghemite and ilmenite in magnetic fraction of heavy mineral concentrates. About 5.6 wt. % of magnetite and titanomagnetite were extracted using permanent magnet from the studied concentrate (Table 1).

Magnetite occurs mostly as rounded grains or to lesser extent as angular grains with worn edges, 3–6 mm in size. Slightly rounded octahedral crystals are rare. The mineral is grey to grey-black, with dull to slightly metallic luster on rounded planes, black with strong metallic luster on conchoidal fracture surfaces. Tiny pebbles with finely granular surface are sporadic.

Irregular finely granular aggregates of magnetite, up to 8 mm across, are rare. They are intergrown with quartz, augite, yellow to brown-yellow olivine or as dark grey fine-grained rock in which they form impregnations. Grey-black to black lamellae formed by very fine-grained aggregate of magnetite with bubble-shaped pockets resembling slag structure, and small balls of the same color shades max. 3 mm in diameter, hollow inside and partly filled with yellowish brown limonite, were also observed. The latter forms of magnetite are of supergene origin, derived most likely from sediments.

Secondary alteration of magnetite or titanomagnetite leads to formation of maghemite which accompanies these minerals in pyrope-bearing gravels (Rost 1962). Maghemite occurs as brown-red grains of dull luster having brown-red streak and low hardness. Similar pattern was observed in placers near Seifengründel in Saxony, where magnetite is the dominant heavy mineral in which the major part is constituted by Ti-component as solid solution (Rentzsch 1958).

Electron-microprobe analyses of magnetite (comp. 1, Table 5) showed that the mineral contains TiO_2 (≤ 5.4 wt. %) and MnO (≤ 4.8 wt. %). Enhanced content of MnO and absence of MgO in magnetite distinguishes this mineral from titanomagnetite (comp. 5, Table 5).

Ti-rich variety of magnetite - titanomagnetite

Titanomagnetite has been reported from pyrope-bearing gravels of the České středohoří Mts. already by A. E. Reuss in 1867 (in Kratochvíl 1957–1966). Titanomagnetite was also identified as inclusions in pyrope-bearing grav-

Table 5 Results of electron-microprobe analyses of magnetite from Podsedice.

	range of 3 compositions, in wt. %	$\bar{\mathbf{x}}$	2 range of 8 compositions, in wt. %	$\overline{\mathbf{x}}$
MgO	_	-	2.10- 3.07	2.69
MnO	3.09- 4.77	3.93	0.37- 0.56	0.45
NiO	0.29- 0.41	0.35	0.00- 0.40	0.13
FeO	26.75-28.20	27.48	27.90-28.50	28.18
Fe ₂ O ₃ 1)	61.17-61.67	61.42	50.50-52.88	51.92
Al ₂ O ₃	1.06- 1.32	1.19	3.79- 5.61	4.44
TiŌ,	5.21- 5.40	5.31	10.90-12.07	11.48
SiO ₂	0.20- 0.24	0.22	0.20- 0.30	0.25
Total		99.90		99.54
FeO 2)	81.81-83.71	82.76	73.60–76.10	74.92

Empirical formula calculated from average composition and adjusted to 32 oxygens per formula unit:

1 - magnetite

$$(Fe^{2+}_{6.91}Mn_{1.00} Ni_{0.09})_{\Sigma 8.00} (Fe^{3+}_{13.89}Ti_{1.20} Al_{0.42}Si_{0.07}\square_{0.42})_{\Sigma 16.00}O_{32}$$

 $2\,-\,titanomagnetite$

$$(Fe^{2+}_{6.71}Mg_{1.14}Mn_{0.10}Ni_{0.05})_{\Sigma 8.00}(Fe^{3+}_{11.13}Ti_{2.46}\ Al_{1.49}\ Si_{0.07}\square_{0.85})_{\Sigma 16.00}O_{32}$$

Contents of CaO, Cr_2O_3 , K_2O and Na_2O are below detection limits in all samples.

 $^{^{1)}}$ Content of Fe $_2{\rm O}_3$ derived from empirical formula based on a total of R $^{2+}$ equal to 8.

²⁾ Total content of Fe recalculated to FeO.

 $^{^{(1)}}$ Content of Fe_2O_3 derived from empirical formula based on a total of \mathbb{R}^{2+} equal to 8.

²⁾ Total content of Fe recalculated to FeO.

els from the Třebenice region (Ulrych – Langrová 1997). Hibsch (1923) described its primary occurrence in a basalt at Ovčín near Třebenice. Titanomagnetite segregations of metallic luster as much as 2 cm large were observed at the Košťál Hill near Třebenice in a hybrid olivine sodalite trachyandesite (in Bernard et al. 1981).

Titanomagnetite cannot be distinguished from magnetite unless the content of TiO₂ is established.

The content of ${\rm TiO_2}$ in magnetite reduces the values of specific gravity from 5.175 to 4.78 in titanomagnetite with ~25 wt. % of ${\rm TiO_2}$ (Table 6). Titanomagnetite with medium content of ${\rm TiO_2}$ ranging between 12 and 14 wt. % has specific gravity around 4.84.

$$(Fe^{2+}_{-6.42}Mg_{1.47}Mn_{0.09}Ca_{0.03})_{\Sigma 8.01}(Fe^{3+}_{-10.53}Ti_{2.49}Al_{2.04}V^{3+}_{-0.09}Si_{0.02}Cr^{3+}_{-0.01}\square_{0.82})_{\Sigma 16.00}O_{32}$$

Titanomagnetite from Podsedice and its inclusion in ilmenite from the Třebenice region exhibit very similar compositions. Similarly deficient octahedral occupancies are shown by Ti-rich magnetite composition from foreign localities (cf. Deer et al. 1962).

The cation content of the Podsedice and Třebenice samples is distributed here over octahedral and tetrahedral sites in accordance with the structure refinement of titanomagnetite from the Mc Kinney lava flow in Idaho (Stout – Bayliss 1975):

Table 6 Comparison of specific gravity and cubic cell parameter versus TiO, and MgO contents in titanomagnetite from selected localities.

Locality	D	a (10 ⁻¹ nm)	TiO ₂ wt. %	MgO wt. %	References
Magnet Cove, Arkansas, USA		8.3960	6.98	7.12	Basta (1957)
New South Wales, Australia		8.4100	9.57	0.60	Wilkinson (1965)
Ilmenskiy zapovednik, Chelyabinsk, Russia	5.090		9.92	-	Semenov, 1945 (in Chukhrov et al., 1967)
Podsedice region, Czech Republic	(4.845)	8.4360	12.07	3.07	this work
Jizerská louka, Czech Republic	4.837	(8.4400)	13.00	4.60	Blumrich (1915), Chevallier et al. (1955)
region between rivers Ircha and Trostyanica, Ukraine	4.850		15.22	0.28	Diadchenko, Khatunseva, 1985 (in Chukhrov et al., 1967)
New South Wales, Australia		8.4200	16.34	0.57	Wilkinson (1965)
Kusinskoye deposit, Chelyabinsk region, Russia	4.998		16.55	0.89	Malyshev et al., 1934 (in Chukhrov et al., 1967)
Seifengrűndel, Saxony, Germany	4.886	8.4200	18.35	1.66	Trőger – Seifert (1963)
Skaergaard intrusion, Greenland		(8.4500)	19.42	2.29	Vincent et. al. (1957)
Snake River Plain, Idaho, USA		8.3976	21.10	0.90	Stout – Bayliss (1957)
Ireland		8.4697	24.86	2.07	Basta (1960)
River Uborot, Yurovo, Ukraine	4.777	(8.4010)	25.21	0.07	Diatchenko - Khatunseva, 1985 (in Chukhrov et al., 1967)
New South Wales, Australia		8.4930	25.65	2.04	Wilkinson (1957)
New South Wales, Australia		8.4800	26.76	1.93	Wilkinson (1957)
Blabolkot, India		8.4490	27.77	2.54	Basta (1960)

Note: Calculated values are given in parentheses.

Cell parameter of titanomagnetite from Podsedice is equal to $8.436\ 10^{-1}nm$. The content of TiO_2 in magnetite enlarges its a from 8.391 to $8.49\ 10^{-1}nm$ at 26 wt. % of TiO_2 , whereas at intermediate values of TiO_2 the cell edge varies between 8.42 and $8.44\ 10^{-1}nm$ (Table 6).

The term titanomagnetite is usually applied to magnetite with 7–28 wt. % ${\rm TiO_2}$ dissolved as ulvöspinel component in structure this mineral. Electron-microprobe analyses of titanomagnetite from Podsedice (comp. 2, Table 5) revealed that the mineral also exhibits relatively high concentrations of MgO and ${\rm Al_2O_3}$ but is depleted in MnO. The formula shows deficient octahedral occupancy which may be influenced by distribution of determined Fe between calculated FeO and ${\rm Fe_2O_3}$ in a spinel-type formula. A similar octahedral deficiency is shown by the formula of titanomagnetite inclusion in ilmenite from pyrope-bearing gravels, calculated in the same manner from the composition given by Ulrych – Langrová (1997):

$$\begin{array}{l} (Fe^{2+}_{7,820}Mn_{0.114}Si^{4+}_{0.067})_{\Sigma 8.001} (Fe^{3+}_{5.245}Ti_{4.726}Fe^{2+}_{4.420}Al_{0.706} \\ Mg_{0.400}Cr^{3+}_{0.310}V^{3+}_{0.155}Ca_{0.040})_{\Sigma 16.002}O_{32} \end{array}$$

However, titanomagnetite from mineralogically similar placers at Jizerská louka (Novák 1986a) and Seifengründel in Saxony (Tröger – Seifert 1963) exhibits the following formulae in which the excess of Fe²⁺ satisfactorily compensates the octahedral deficiency:

$$\begin{array}{l} \text{Jizersk\'a louka} - (F{e^{2+}}_{6.00}Mg_{2.00})_{\Sigma 8.00} (F{e^{3+}}_{9.52}F{e^{2+}}_{3.12}T{i^{4+}}_{2.80}\\ \text{Al}_{0.56})_{\Sigma 16.00}O_{32}; \end{array}$$

$$\begin{array}{l} Seifengründel - (Fe^{2+}_{6.80}Mg_{1.04}Mn_{0.16})_{\Sigma 8.00}(Fe^{3+}_{9.52}Ti^{4+}_{4.08}\\ Fe^{2+}_{1.52}Al_{1.04}V^{4+}_{0.08})_{\Sigma 16.24}O_{32} \end{array}$$

Provenance of the spinelides

Hibsch (1917) considered red spinel to have been derived from olivine-pyroxene source rocks of pyrope which occurred in pyrope-bearing basalt breccia near Měrunice. Similarly, Kopecký et al. (1967) ascribed minerals of the spinel group to xenoliths of peridotite brought to the surface together with vent breccias. Red and blue varieties of spinel were also found together with similar heavy minerals in placers in the Jizerská louka, where their origin is also enigmatic (Novák 1986a).

Pleonaste is a common mineral in mafic volcanics and in differentiated gabbros but it is occasionally also abundant in metamorphic and contact-metamorphic rocks, specifically in marbles. No pleonaste was found in primary rocks of the České středohoří Mts. Pleonaste in pyrope-bearing gravels belongs to characteristic and abundant heavy minerals, and it is mostly highly abraded. Basalts (Hibsch 1917, 1926) and pyroxene peridotites (Hibsch 1934) and more recently peridotite xenoliths (Kopecký et al. 1967, Götz et al. 1979) are believed to be the source rocks of pleonaste. Similar origin (from basalt breccia) is ascribed to pleonaste from Seifengründel in Saxony. However, spinelides of other composition (picotite) are thought to have been derived from xenoliths of peridotite and gabbro (Wiedemann 1962). Pleonaste often accompanies sapphire in placer deposits in areas of alkaline basalts in eastern Australia, Cambodia, Thailand and Laos (Kievlenko et al. 1982, anon. 1982, Novák 1986).

Picotite is mostly related to mafic and ultramafic rocks and their contacts with Al-rich sediments, to serpentinites and to olivine nodules in some basalts. Picotite in the České středohoří Mts. is known from olivine nodules in some basalt bodies and basalt tuffs (Hibsch 1934, Rost 1962), and from material originated through weathering of basalt diatremes in which it occurs together with chromium-bearing diopside, ilmenite, corundum, pleonaste and zircon (Kopecký 1960, Rost 1962). The source of picotite in local pyrope-bearing gravels are olivine nodules, and peridotite xenoliths enclosed in pipe breccias of basaltic volcanoes (Kopecký et al. 1967, Götz et al. 1979). The present author identified tiny inclusions of picotite in chromian diopside, which argues for its origin from peridotites. Another notable occurrence of picotite was described in completely kaolinized neovolcanic polzenite dike penetrating Cretaceous sediments in the uranium deposit Hamr near Česká Lípa (Novák – Jansa 1977).

Ultramafic rocks of the peridotite suite (amphibole eclogite or garnetiferous hornblendite?) brought from the crystalline basement to the surface by volcanic eruptions seem to be the source of hercynite.

Rost (1962) reported that magnetite was derived from basalts, basalt tuffs and pipe breccias. The mineral was found to occur in the Podsedice and Třebivlice bands and also in basalt deluvial sediments of the central and eastern parts of the České středohoří Mts and in diatremes of Linhorka and Šibenice (Götz et al. 1979). Tiny inclusions of magnetite in zircon from pyrope-bearing gravels were described by Bauer (1966).

Some basalts, their tuffs and tephroites in the České středohoří Mts. seem to be the source rocks for coarse ti-

tanomagnetite cotaining 12–16 wt. % TiO₂ (Hibsch 1934). Götz et al. (1979) reported this mineral to also occur in a pipe breccia at Lihorka. Kopecký et al. (1967) ascribe the origin of titanomagnetite to alkaline metasomatic rocks and pyroxenites. Titanomagnetite from similar placers at Malá Jizerská louka (Novák 1986a) and Seifengründel in Saxony (Tröger – Seifert 1963) shows similar provenances, from alkaline basalts and their breccias.

Conclusion

In heavy mineral concentrates from Podsedice, the most abundant spinelide is ferroan spinel (pleonaste) predominant over titanomagnetite, magnetite and chromian spinel (picotite). Iron-enriched spinel and hercynite are rare.

Dominant occurrence of pleonaste grains, mostly perfectly rounded, is characteristic of heavy mineral assemblages in placers derived from basalts. Pleonaste is often accompanied by corundum and sapphire (Malá Jizerská louka, Seifengründel and sapphire placers in SE Asia and SE Australia). Pleonaste occasionally exhibits enhanced concentrations of Cr_2O_3 , which indicates its provenance from ultramafic rocks brought to the surface as xenoliths (together with corundum and sapphire) from deeper parts of the basement. The occurrence of picotite suggests that a part of mineral assemblage comes from olivine nodules in basalts or from xenoliths of peridotite enclosed in pipe breccias. This concept is supported by inclusions of picotite in chromian diopside which, together with pyrope, is undoubtedly related to peridotites.

Magnetite, in contrast to other placer deposits of similar origin, is relatively rare. Titanomagnetite seems to be slightly more abundant. It occurs in various forms which indicate diverse primary derivations, and partly even secondary origin. Phenocrysts of titanomagnetite contain enhanced MnO and TiO₂. Titanomagnetite is richer in MgO and Al₂O₃ and depleted of MnO relative to magnetite. Titanomagnetite is altered to maghemite and limonite. Various types of alkali basalt and their tuffs, basalt breccias and enclosed xenoliths of mafic to ultramafic rocks are considered the source rocks for Ti-rich magnetite in pyrope-bearing gravels.

Minerals of the spinel group and their geochemical characteristics, together with some other heavy minerals in pyrope-bearing gravels, obviously prove their affinity to basalt volcanism and also to xenoliths in diatremes which were transported from deeper parts of the crystalline basement. Kopecký (1966) described, from a pipe breccia at the Košťál Hill, N of Třebenice, xenoliths of some new types of rock, such as alkaline metasomatites (fenites) and various alkaline intrusives. Magnetite and titanomagnetite commonly occur in some of these rocks.

The present author also described in pyrope-bearing gravels from Podsedice grains of Nb- and Mn-bearing ilmenite which are believed to be derived from a pegmatite facies of nepheline syenites or syenite fenites (Novák 1999). This find may also indicate that the source rocks

for minerals of the spinel group may include rocks resembling those described in the pipe breccia from the Košťál hill, as in the case of manganoan-ilmenite

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Nerosty skupiny spinelu z pyroponosných štěrků v Českém středohoří, Česká republika

V koncentrátu těžkých minerálů po těžbě pyropu z pyroponosných štěrků z oblasti Podsedic v Českém středohoří byly identifikovány tyto minerály skupiny spinelu: spinel, železem bohatý spinel (pleonast), chromem bohatý spinel (picotit), hercynit, magnetit a jeho titanem bohatá odrůda (titanomagnetit). Je uvedena jejich makroskopická charakteristika, zastoupení, chemické složení, fyzikální parametry a diskutována možnost jejich zdroje.

Spinel se vyskytuje jako tmavě šedá zrna jen velmi vzácně. Obsahuje relativně zvýšenou příměs FeO a Fe₂O₃. Přítomnost barevných odrůd spinelu nebyla potvrzena. Pleonast je nejhojnějším zástupcem nerostů skupiny spinelu, jeho obsah spolu s picotitem je 17,5 hmot. %. Jeho průměrné složení odpovídá přítomnosti 72 atom. % Mg a 28 % Fe²⁺. Atomový poměr Al/Fe³⁺ = 11,9. Velmi vzácně se vyskytuje též jeho chromitá odrůda s 10,3 hmot. % Cr₂O₃ (11,2 at. %). Jeho mřížkový parametr je a = 8.146(2) 10⁻¹nm a h_{vyp} = 3,848. Picotit představuje cca 30% zastoupení pleonastu a jeho zrna jsou menší (do 4 mm). V jeho tetraedrických pozicích převládá Mg (72 at. %) nad Fe²⁺ (30 at. %) a v oktaedrických pozicích Al (58,5 at. %) nad Cr (36,5 at. %) a Fe³⁺ (5,0 at. %). Obsah Cr₂O₃ v něm kolísá mezi 26,89–37,35 hmot. %. Hercynit je velmi vzácný a identifikován byl pomocí EDM. Magnetit spolu s titanomagnetitem tvoří 5,6 hmot. % koncentrátu. Magnetit obsahuje TiO₂ (do 5,4 hmot. %) a MnO (do 4,8 hmot. %). Relativně vyšší příměsí MnO a nepřítomností MgO se odlišuje od titanomagnetitu. Titanomagnetit s příměsí 10,90–12,07 hmot. % TiO₂ je v koncentrátu zastoupen poněkud hojněji než magnetit. Má a = 8.436 10⁻¹ nm a h_{vyp} = 4,845. Druhotně se v rozsypech přeměňuje na maghemit a limonit. Zdrojem minerálů skupiny spinelu v pyroponosných štěrcích jsou různé typy čedičů a jejich tufy (magnetit, část titanomagnetitu), čedičové komínové brekcie a zejména jimi vynesené xenolity různých ultrabazických hornin (spinel, pleonast, picotit, hercynit, část titanomagnetitu).

Spinelidy v pyroponosných štercích jsou svým způsobem výskytu, zastoupením a chemickým složením blízké těmto nerostům geneticky podobných rozsypových lokalit Jizerská louka a Seifengrűndel v Sasku (těsně při severní státní hranici s Českou republikou).