

HARRISONITE, A RARE SILICATE-PHOSPHATE FROM GRANITIC PEGMATITES OF THE BOHEMIAN MASSIF

HARRISONIT, VZÁCNÝ SILIKÁT-FOSFÁT Z GRANITICKÝCH PEGMATITŮ ČESKÉHO MASIVU

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Abstract

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Harrisonite, a rare silicate-phosphate from granitic pegmatites of the Bohemian Massif

Harrisonite, $\text{CaFe}^{2+}_6(\text{SiO}_4)_2(\text{PO}_4)_2$, is a rare silicate-phosphate described as a rock-forming mineral from highly metamorphosed garnetites (originally BIF) from Canada. Disregarding several questionable anthropogenic occurrences of harrisonite, the mineral has also been scarcely found in the phosphate-bearing granitic pegmatites Cyrilov (Czech Republic), João (Brazil) and Příbyslavice (Czech Republic). The original harrisonite from garnetites is Mg-rich and Mn-poor, while that from pegmatites is enriched in Mn and poor in Mg. The average empirical formulae of harrisonite from Cyrilov and Příbyslavice based on 16 O are very similar, and are as follows: $\text{Ca}_{0.98}(\text{Fe}_{5.37}\text{Mn}_{0.33}\text{Mg}_{0.05}\text{Zn}_{0.01})_{\Sigma 5.76}\text{Si}_{1.87}\text{P}_{2.20}\text{O}_{16}$, and $\text{Ca}_{0.98}(\text{Fe}_{5.37}\text{Mn}_{0.33}\text{Mg}_{0.06})_{\Sigma 5.76}\text{Si}_{1.89}\text{P}_{2.19}\text{O}_{16}$, respectively. Tetrahedrally coordinated Si in harrisonite from Příbyslavice and Cyrilov is often deficient and compensated by surplus of P. This surplus of P negatively correlates with the divalent cation contents, particularly Fe^{2+} , which might indicate a participation of the MO_6 polyhedron vacancies as a charge-balancing mechanism. The presence of harrisonite in phosphate-bearing granitic pegmatites is pointing out that the mineral is stable even at lower P-T conditions than reported from the type occurrence.

Key words: harrisonite, electron microprobe, substitution, pegmatite, silicate-phosphate, phosphates, Moldanubicum, Czech Republic.

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INTRODUCTION

Harrisonite, $\text{CaFe}^{2+}_6(\text{SiO}_4)_2(\text{PO}_4)_2$, is a rare mineral occurring in several geological environments. It was first described from Arcedekne Island, Nunavut, Canada, where it occurs as one of the rock-forming minerals (ROBERTS *et al.* 1993). The structure of harrisonite was determined by GRICE and ROBERTS (1993) using a cotype material from Arcedekne. Harrisonite has a layer-like structure consisting of $(\text{SiO}_4)^4$ tetrahedron layer, $(\text{FeO}_6)^{10-}$ polyhedron layer and combined $(\text{PO}_4)^{3-}$ tetrahedron and $(\text{CaO}_6)^{10-}$ polyhedron layer.

At the type locality, harrisonite is associated with almandine, fayalite, quartz and fluorapatite. Accessory minerals include ferrosilite, ilmenite, and biotite. The harrisonite-bearing rock from Arcedekne Island is classified as banded garnetite-granofel formed under granulite-facies conditions from Banded Iron Formation (BIF; ROBERTS *et al.* 1993, FRISCH

and HERD 2010). Similar occurrence of harrisonite is reported by VERPAELST *et al.* (2001) from Kangiqsualujjuaq, Québec, Canada. Garnetites at Kangiqsualujjuaq are, similarly to Arcedeckne, metamorphosed BIF which reached high-grade amphibolite-facies (FRISCH and HERD 2010). The first found of harrisonite in the granitic environment is reported by ŠKODA *et al.* (2007) from granitic pegmatite near Cyrilov, Czech Republic. Harrisonite is represented by a single 250 µm grain enclosed in Fe-Mn phosphate nodule composed of graptolite-group minerals, wolfeite, and heterosite. Later, the mineral was discovered in granitic pegmatite João, Minas Gerais, Brasil, where it associates with spessartine, fluorapatite, heterosite and beusite (BAIJOT *et al.* 2014). Moreover, ŠKODA *et al.* (2015) briefly mentioned ~10 µm thick rim of harrisonite along the phosphate nodule from Příbyslavice, Czech Republic.

Another three questionable anthropogenic occurrences of harrisonite from various environments were recorded. ABRAHAM *et al.* (2013) identified harrisonite in PXRD spectra of the fly ash. The ash was collected in a boiler and pipes connected to the furnace burning biowaste at Akay Flavours and Aromatics Ltd., Kerala, India. The company produces oleoresins – common ingredients in perfumes and spices (ABRAHAM *et al.* 2013). Harrisonite-like, but also Al-bearing, phase was identified by WARCHULSKI and SZOPA (2014) in polymetallic slags using EDS. WARCHULSKI *et al.* (2014) discuss affinity of the phase to harrisonite, or perhamite. Harrisonite, in paragenesis with stanfieldite, $\text{Ca}_4\text{Mg}_5(\text{PO}_4)_6$, was identified as inclusions in glass coatings on various rock. Rocks with coatings were found in a small crated-shaped structure on the top of the moraine (NEUMAIR *et al.* 2016a, b). The structure itself might have been formed as a result of a meteorite impact, a lightning strike, or represents a lime kiln (NEUMAIR *et al.* 2016a).

The chemical composition of harrisonite was published for specimens from Arcedeckne and Kangiqsualujjuaq, Canada, from Cyrilov, Czech Republic and from João, Brasil. Iron in harrisonite is often substituted by Mg, Mn and rarely by trace amounts of Zn, revealing simple homovalent substitution. Amount of Mg in harrisonite from Canadian localities is quite high (≤ 0.89 apfu), Mn content is very low (≤ 0.02 apfu; ROBERTS *et al.* 1993, FRISCH and HERD 2010, SHARMA *et al.* unpublished). In contrary, harrisonite from pegmatites is Mg-poor (≤ 0.07 apfu) and Mn-rich (≤ 0.36 apfu at Cyrilov, 1.06 apfu at João). Harrisonites from both pegmatites also contain small amounts of Zn (0.00–0.02 apfu; ŠKODA *et al.* 2007, BAIJOT *et al.* 2014). Harrisonite from metamorphosed BIFs shows equal amount of Si and P, whereas one from the pegmatitic occurrences prefers higher amount of P compared to Si, up to $(\text{P}_{2.24}\text{Si}_{1.78})_{\Sigma 4.02}$. No substitutions involving Ca were recorded (ROBERTS *et al.* 1993, ŠKODA *et al.* 2007, FRISCH and HERD 2010, BAIJOT *et al.* 2014, SHARMA *et al.* unpublished).

In this paper, we show new electron microprobe analyses of harrisonite from Cyrilov and Příbyslavice, describe the mineral association and discuss the chemical variability with respect to the degree of geochemical fractionation of the host rock.

GEOLOGICAL SETTING

The phosphate-bearing granitic pegmatite at Cyrilov forms a dike about 100 m long, 2–5 m wide. The pegmatite body penetrates the granulite of the Bory Massif, near its contact with migmatites of the Strážek Unit (E Bohemian Massif). The dike crops out about 200 m west from Cyrilov, Bory, Czech Republic, at the place called “Požárová mez” (WGS84: N 49.4160, E 16.0445). It has been mined in the end of 19th century by a small quarry for feldspar and quartz. Nowadays, the quarry is recognizable only by the position of small dumps. Dike is believed to be simply zoned with typical granitic, graphic, blocky feldspar and albite unit and quartz core (ŠKODA *et al.* 2007). The pegmatite is known for occurrence of Fe-Mn phosphates and belongs to the primitive type, phosphate subtype group after NOVÁK (2005). Phosphate mineralization from Cyrilov has been studied for over 120 years (JOHN 1900, KOVÁŘ and SLAVÍK 1900, 1901, STANĚK 1955, 1968, ŠKODA *et al.* 2007) and a new phosphate mineral, cyrilovite, was described from there (NOVOTNÝ and STANĚK

1953). PERTOLDOVÁ *et al.* (2009) reported a polyphase evolution of surrounding migmatites: a) in amphibolite to granulite facies, T up to ~850–900 °C, P up to ~12–18 kbar and b) fast decompression stage at T ~700 °C and P ~4–6 kbar. Pegmatite bodies in the Strážek Unit originated at T <~500–600 °C and P <~3–4 kbar (GADAS *et al.* 2012). The andalusite-diaspore nodule from central part of adjacent pegmatite dike No. 3 at Dolní Bory - Hatě, belonging to the same pegmatite population, solidified at T <400 °C and P=2 kbar (NOVÁK *et al.* 2008).

The Příbyslavice complex (BREITER *et al.* 2010) is ~3 × 2 km body located in the northern part of Moldanubian Zone, 5 km SSE from Čáslav, Czech Republic. It represents well evolved orthogneiss-granite-pegmatite system rich in P, Li, and Sn, with common occurrences of almandine, tourmalines and primary and secondary phosphates. The Příbyslavice complex is enclosed in the two-mica and biotite paragneiss. The volumetrically dominant rock of the complex is represented by medium- to coarse-grained muscovite-tourmaline orthogneiss, whereas fine- to medium-grained and locally foliated muscovite metagranite is subordinate. Lenticular or schlieren-like pegmatoid bodies locally occur in the host muscovite-tourmaline orthogneiss (POVONDRA *et al.* 1987). Several small pegmatite dikes penetrate the complex as well. The rocks of the Příbyslavice complex are exposed in several small quarries (e.g. BREITER *et al.* 2010). Mineralogy of the locality (including phosphates) was studied e.g. by ČECH and PADĚRA (1958) and POVONDRA *et al.* (1987). Příbyslavice is a type locality of oxy-schorl (BAČÍK *et al.* 2013). Amphibolite xenoliths enclosed in the Příbyslavice orthogneiss enabled calculation of metamorphic conditions peaking at T ~650–700 °C and P ~7–9 kbar, which corresponds to the amphibolite-facies conditions (ŠKODA *et al.* 2017). The phosphate nodules occur in pegmatoid schlieren in metagranite. The nodules are composed of primary graftonite, sarcopside, and triphylite, and are often altered along the rim to various secondary phosphates (POVONDRA *et al.* 1987, ŠKODA *et al.* 2017).

METHODS AND SAMPLES

Chemical analysis

The chemical composition of phosphate minerals was determined using Cameca SX100 electron microprobe at the Joint Laboratory of Electron Microscopy and Microanalysis, Department of Geological Sciences, Masaryk University and Czech Geological Survey in Brno. The microprobe was operated in the wavelength-dispersive mode with acceleration voltage of 15 kV, a beam current of 8 nA (10 nA for the Příbyslavice specimen, respectively) and a spot size of 8 µm (2 µm for harrisonite from Příbyslavice, respectively). Following well defined standards and X-ray lines were used: Na Kα – albite, Al Kα – andalusite, Mg Kα – pyrope, Si Kα – wollastonite, Ca Kα – fluorapatite, Sr Lα – SrSO₄, P Kα – fluorapatite, Ti Kα – anatase, K Kα – sanidine, Fe Kα – almandine, Mn Kα – spessartine, F Kα – topaz, Zn Kα – gahnite, Cu Kα and As Lα – lammerite, Ba Lα – baryte and Pb Mα – vanadinite. All data were processed using routine PAP matrix correction (POUCHOU and PICHOU 1985). Prior the analysis, the sample was thoroughly sought by back-scattered electron (BSE) image. Following elements were below detection limits (bd.): Na, K, F, Sr, Ba, Al, Cu, As, Ti, and Pb. Atomic proportions in empirical formulae are expressed in atoms per formula unit (*apfu*).

Symbols of mineral names are taken from the official IMA symbol list (WARR 2021).

All harrisonite analyses, including published data, were normalized to 16 O in order to make data consistent. Graftonite analyses were normalized to 8 O, all Mn and Fe was considered divalent. Individual cations were assigned to their sites following rules for the graftonite group nomenclature (HAWTHORNE and PIECZKA 2018).

Samples

Studied fragments of phosphate nodules from Cyrilov pegmatite were collected at small quarry dumps by Josef Staněk during the 1960's. Therefore, no precise information

on geological position of phosphate nodules within the pegmatite is known. Based on massive quartz intergrowths with phosphates, and by analogy with other Fe-Mn phosphate-bearing pegmatites, the nodules were probably enclosed or attached to the blocky quartz unit in the central part of the pegmatite body.

Sample from Příbyslavice consists of massive graftonite-triophyllite nodule in association with quartz, muscovite, and K-feldspar. The primary phosphates are altered to the secondary ones along the contact with host silicates. Harrisonite has been found only in one sample from ~30 phosphate samples investigated.

HARRISONITE PARAGENESIS IN CYRILOV, CZECH REPUBLIC

Harrisonite from the Cyrilov phosphate pegmatite is represented by a single irregular 250 µm grain (fig. 1a). It was found in central, less altered part of the graftonite nodule (in sense of ŠKODA *et al.* 2007). The part of the nodule is about 3 cm in size, lustrous and of a reddish-brown color. The whole sample is severely fractured. Harrisonite in the sample intimately intergrows with other primary and secondary Fe-Mn phosphates, such as

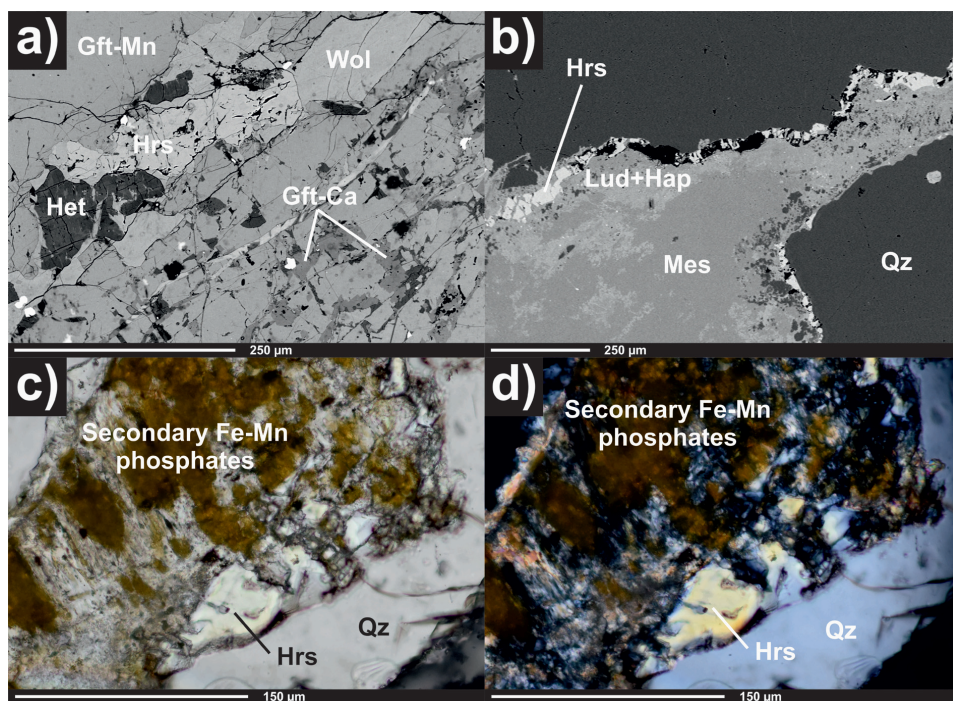


Fig. 1. a) Harrisonite (Hrs) from Cyrilov intergrown with graftonite-(Mn) (Gft-Mn), graftonite-(Ca) (Gft-Ca), wolfeite (Wol) and heterosite (Het), BSE image, b) harrisonite (Hrs) from Příbyslavice forming a rim between messelite (Mes), ludlamite (Lud), hydroxylapatite (Hap) and quartz (Qz), BSE image, c) harrisonite (Hrs) with secondary Fe-Mn phosphates and quartz (Qz) from Příbyslavice, plane-polarized light and d) the same view in crossed polarizers.

Obr. 1. a) Harrisonit (Hrs) z Cyrilova srůstající s graftonitem-(Mn) (Gft-Mn), graftonitem-(Ca) (Gft-Ca), wolfeitem (Wol) a heterositem (Het), obraz v BSE, b) harrisonit (Hrs) z Příbyslavic vytvářející lem mezi messelitem (Mes), ludlamitem (Lud), hydroxylapatitem (Hap) a křemenem (Qz), obraz v BSE, c) harrisonit (Hrs) se sekundárními Fe-Mn fosfáty a křemenem (Qz) z Příbyslavic, jeden polarizátor a d) stejný pohled ve zkřížených polarizátorech.

grafonite *s. l.*, heterosite and wolfeite. Other minerals in the less altered part of the sample include sarcopside, monazite-(Ce), xenotime-(Y), and minor Mn-oxides. The outer, strongly altered part of the sample consists of mitridatite, lipscombite or barbosolite, cyrilovite and Mn-oxides.

Harrisonite is chemically homogenous and closer to the end-member composition than the type material (ROBERTS *et al.* 1993). The Fe^{2+} is partly substituted by Mn^{2+} (0.33–0.35 *apfu*) and minor Mg (0.06–0.07 *apfu*; fig. 2). Slight Si deficiency (1.84–1.96 *apfu*) in tetrahedral position is compensated by elevated P content (2.05–2.22 *apfu*; fig. 3).

The graffonite group minerals in the studied sample are represented by graffonite-(Mn) and graffonite-(Ca). Graffonite-(Mn) is the main phase present in the less altered part of the sample, whereas graffonite-(Ca) forms isolated domains up to 100 μm in size, darker in BSE (fig. 1a). Graffonite-(Ca) grains are often elongated, following apparently the fracture systems. Harrisonite intimately intergrows with graffonite-(Mn). Graffonite-(Ca) is abundant within the less altered part of the sample, but not present in the close vicinity of harrisonite at all. An elevated Ca content was observed in the graffonite-(Mn) (0.40–0.43 *apfu*). Graffonite-(Ca) is chemically homogenous, with relatively low Mn + Mg

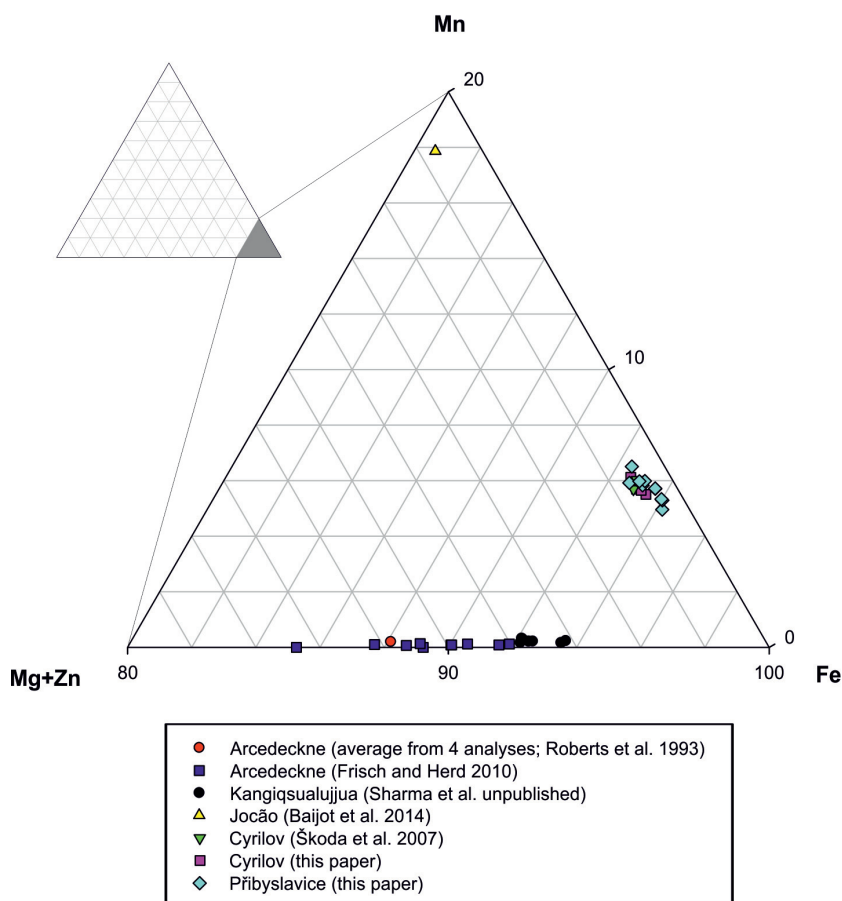


Fig. 2. Chemical variability of harrisonite from garnetites and pegmatites.

Obr. 2. Chemická variabilita harrisonitu z granátovců a pegmatitů.

contents in the $M(1)$ site (0.09–0.23 *apfu*; fig. 4; see HAWTHORNE and PIECZKA (2018) for details on assignment of individual elements into the structural sites). The manganese contents at $M(2)$ and $M(3)$ sites reveal the content of the beusite component. In graftonite-(Ca) it is $\text{Gft}_{60}\text{Beu}_{40}$, while graftonite-(Mn) yields $\text{Gft}_{82}\text{Beu}_{18}$ composition.

Wolfeite forms two $\sim 150\ \mu\text{m}$ grains placed next to harrisonite in the studied sample (fig. 1a). The mineral contains triploidite (Mn^{2+}), hydroxylwagnerite (Mg) and $\text{Zn}_2(\text{PO}_4)(\text{OH})$ molecule “ZnM” components in the proportional ratio $\text{Wol}_{75}\text{Tpd}_{20}\text{Hwag}_4\text{ZnM}_1$.

Heterosite is the last phase in the immediate association with harrisonite. It forms frequent grains of up to $200\ \mu\text{m}$ in the less altered part of the sample. Heterosite is Fe^{3+} dominant (0.83–0.86 *apfu*) with elevated Mn^{3+} contents (0.18–0.23 *apfu*) and traces of Mg and Ca. ŠKODA *et al.* (2007) consider heterosite to be an alteration product of triphylite.

Mitridatite was identified only on the specimen containing harrisonite. The mineral forms irregular masses up to $500\ \mu\text{m}$ in size in more altered parts of the sample. It is Fe^{3+} dominant, with a Mn content of 0.15–0.17 *apfu*. Lipscombite/barbosallite has been locally recorded in the more altered part of the sample but it is more widespread in other phosphate assemblages in the Cyrilov pegmatite (see ŠKODA *et al.* 2007). It forms severely fractu-

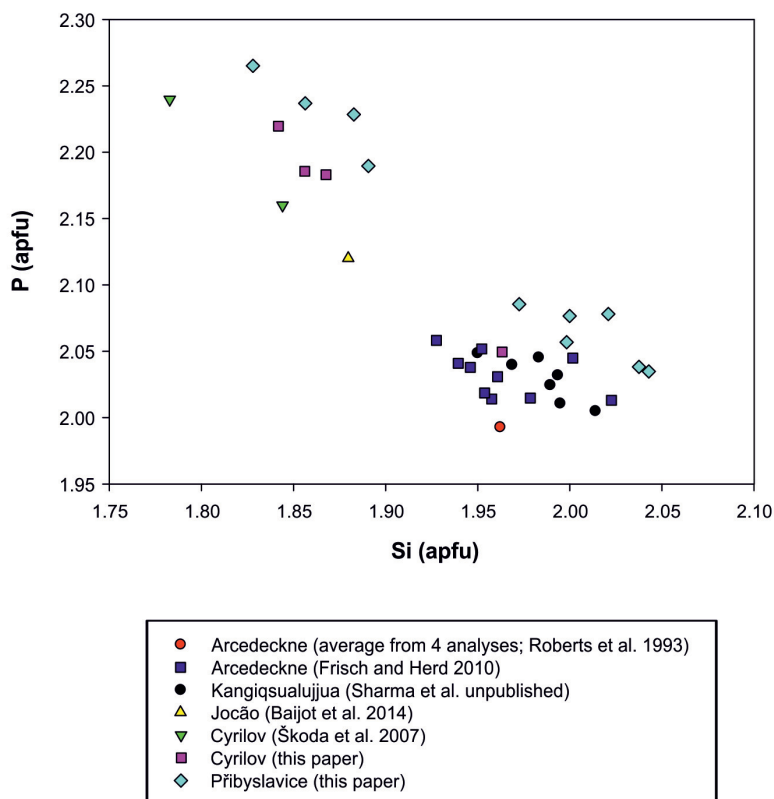


Fig. 3. Tetrahedral-site occupancy in harrisonite is almost perfectly stoichiometric at Arcedekne and Kangiqsualujua, while Si-deficiency is compensated by P at Cyrilov, João and Příbyslavice.

Obr. 3. Obsazení tetraedrické pozice v harrisonitu z lokalit Arcedekne a Kangiqsualujua je téměř ideálně stechiometrické, zatímco harrisonit z Cyrilova, João a Příbyslavice vykazuje zvýšený obsah P kompenzovaný deficitem Si.

red 100–300 μm grains enclosed in mitridatite, cyrilovite and Mn-oxides. Mn^{2+} contents in lipscombite/barbosolite vary from 0.09 to 0.15 *apfu*, traces of Ca are also present.

Cyrilovite is the most abundant phase in the more altered part of the sample. It forms large irregular masses and small ($\sim 40 \mu\text{m}$) crystals attached to each other, or neighboring phosphates. Cyrilovite is chemically homogenous, only trace amounts of Ca, Mn^{3+} and Al were recorded.

HARRISONITE PARAGENESIS IN PŘIBYSLAVICE, CZECH REPUBLIC

Harrisonite from the Příbyslavice complex forms irregular discontinuous rim (fig. 1b-d) around the fist-sized graftonite-sarcopside-triophyllite nodule associated with quartz, muscovite and K-feldspar. Individual parts of the rim vary in size, usually from 5 to 30 μm , sometimes larger domains up to 100 μm are formed. Harrisonite is located along the contact of magmatic phosphates and silicates and locally protrudes into the phosphate nodule. Coexisting minerals include graftonite-(Mn), hydroxylapatite, ludlamite, sarcopside and messelite.

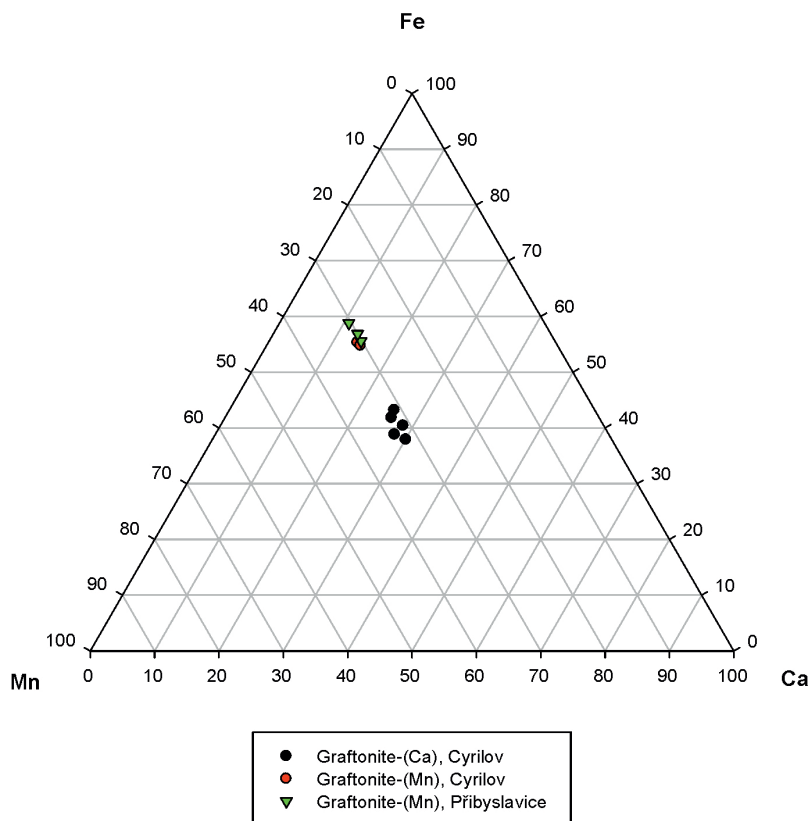


Fig. 4. Chemical composition of the graftonite-group minerals from Cyrilov and Příbyslavice.

Obr. 4. Chemické složení minerálů graftonitové skupiny z Cyrilova a Příbyslavic.

Harrisonite composition does not vary strongly (fig. 2). Iron is substituted by Mn^{2+} (0.31–0.38 *apfu*), minor Mg (0.04–0.06 *apfu*) and trace Zn (≤ 0.03 *apfu*). The usually deficient Si (1.83–2.04 *apfu*), is compensated by surplus of P (2.03–2.27 *apfu*) to keep the tetrahedral position fully occupied (fig. 3).

Harrisonite is associated with secondary phosphates formed by hydrothermal alteration of primary Fe-Mn-(Li) phosphates. Thus, it is often accompanied by massive ludlamite and other secondary Fe phosphate minerals. Divalent Fe in ludlamite is substituted by a noticeable amount of Mn^{2+} (0.27–0.55 *apfu*) and minor Mg, Ca and Zn.

Hydroxylapatite is one of the rarer phases present in the sample. It has more complicated chemical composition with many substitutions taking place. The empirical formula can be expressed as $(\text{Ca}_{4.40}\text{Fe}_{0.21}\text{Mn}_{0.19}\text{Na}_{0.15}\text{Mg}_{0.01}\text{Pb}_{0.01})_{\Sigma 4.97}(\text{P}_{2.76}\text{Si}_{0.26})_{\Sigma 3.02}\text{O}_{12}(\text{OH}_{0.45}\text{F}_{0.18})_{\Sigma 0.63}$.

Another secondary phosphate, occurring rarely in the irregular aggregates associated with harrisonite, is messelite. Ca in messelite is substituted by trace Sr (0.02 *apfu*), Fe^{2+} is substituted by low amounts of Mn^{2+} and Mg (0.08 and 0.06 *apfu*, respectively).

The primary phosphates in the non-altered part of the nodule are represented by sarcopside, graftonite and rare triphylite. Sarcopside is Fe^{2+} dominant, with significant amount of Mn^{2+} (0.51–0.54 *apfu*) and smaller amount of Mg (0.07–0.08 *apfu*). Graftonite is Mn^{2+} dominant in the *M*(1) site, yielding 0.64–0.53 *apfu* Mn^{2+} , but close to graftonite-(Ca) border (0.32–0.42 *apfu* Ca; fig. 4). The combined *M*(2) and *M*(3) site is occupied by Fe^{2+} (1.63–1.73 *apfu*), Mn^{2+} (0.25–0.35 *apfu*) and trace Mg and Zn, plotting far from the beusite field.

DISCUSSION

Chemical composition of harrisonite from the metamorphosed BIFs and pegmatitic occurrences clearly shows, that the amount of Mg or Mn entering the harrisonite structure is dependent on the chemical composition of the source. Harrisonite from Mg-rich and Mn-poor garnetites from Arcedekne and Kangiqsualujuaq is enriched in Mg and depleted in Mn (ROBERTS *et al.* 1993, SHARMA *et al.* unpublished). In contrast, harrisonites from Mn-rich and Mg-poor granitic pegmatites João (BAIJOT *et al.* 2014), Cyrilov and Příbyslavice are rich in Mn and poor in Mg, which is consistent with a degree of geochemical fractionation of the source, from which harrisonite crystallized. Additionally, the amount of Mn in harrisonite is much higher at João (1.06 *apfu*), where it coexists with abundant Mn-dominant beusite (0.57 Mn/(Mn+Fe); BAIJOT *et al.* 2014). At Cyrilov and Příbyslavice, the degree of Mn/(Mn+Fe) fractionation is not as high as in João, which is documented by the lower Mn/(Mn+Fe) ratio in primary graftonite (0.36 and 0.34–0.35, respectively) and harrisonite is thus Mn poorer (0.33 *apfu* in average for both localities; fig. 2). Significantly higher Mn in associated phosphates also indicates, that harrisonite structure prefers Fe over Mn, which is consistent with observation of BAIJOT *et al.* (2014).

The volumetric amount of harrisonite present in the Arcedekne rock is surprising, considering the fact, that the rock contains 0.78–6.46 wt.% P_2O_5 (FRISCH and HERD 2010). The levels of Si and P, entering harrisonite from garnetites, are almost perfectly stoichiometric, despite 39.0–47.3 wt.% SiO_2 in the whole rock (FRISCH and HERD 2010). Harrisonite associated with phosphate nodules from granitic pegmatites is much scarcer. Textural relations of harrisonite and associated minerals obviously show, that harrisonite is of either late magmatic, or early metasomatic origin. Harrisonite from all three pegmatitic localities shows noticeable Si deficiencies compensated by surplus of P (fig. 3). This phenomenon is well documented even in harrisonite from Příbyslavice, where it occurs along the phosphate-silicate border. The induced P_1Si_1 substitution together with the absence of larger harrisonite crystals or aggregates may indicate lower Si activity at the time

of harrisonite crystallization or may reflect different P-T conditions for harrisonite crystallization. As P^{5+} and Si^{4+} possess a different charge, the P_1Si_{11} substitution must also involve additional mechanisms to keep the electroneutrality. Our data indicate a positive correlation of the surplus of P with the vacancy in the MO_6 polyhedron site (fig. 5). A possible substitution vector can be expressed as $P_2\Box_1Si_2R^{2+}_{-1}$, where R^{2+} is represented by Fe^{2+} , Mn^{2+} , Mg^{2+} and Zn^{2+} . Calcium does not seem to be involved in the substitution, as it is almost invariantly fully occupied. Calcium octahedrons are linked in a sheet with (PO_4) tetrahedrons, whereas (FeO_6) polyhedral sheet is adjacent to the (SiO_4) tetrahedral sheet. Therefore, a substitution of P for Si likely induced charge balancing mechanism in the nearest environment to keep the charge of neighboring sheets unchanged. However, the data plotted in fig. 5 from Příbyslavice and Cyrilov do not unambiguously confirm the trend.

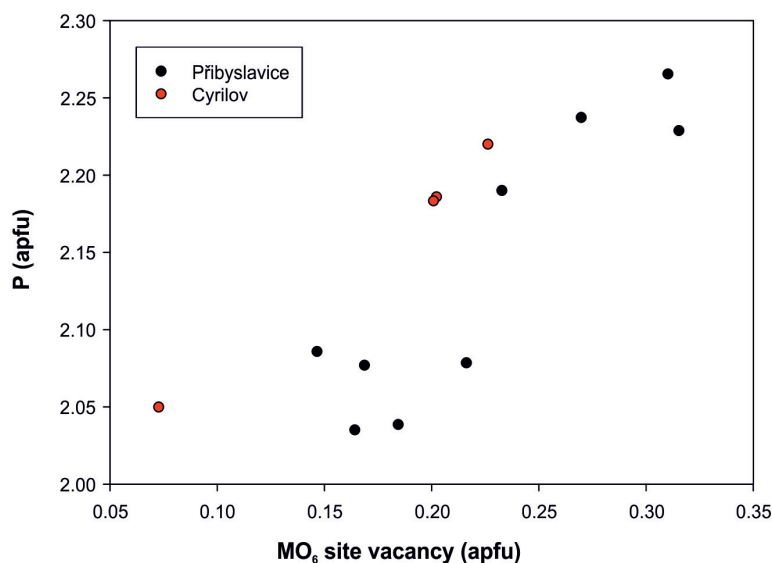


Fig. 5. A positive correlation of the MO_6 polyhedron vacancies with the P content in harrisonite from Cyrilov and Příbyslavice.

Obr. 5. Pozitivní korelace mezi vakanci na MO_6 polyedru a obsahem P v harrisonitu z Cyrilova a Příbyslavice.

There are three known harrisonite occurrences in phosphate assemblages of pegmatitic origin up to date. Harrisonite associates in all cases directly with the minerals of the graftonite group, graftonite or beusite. In contrast, harrisonite has never been found in association with minerals of the triplite-zwieselite series, $(Mn,Fe)_2PO_4F$, which are other widespread primary Fe-Mn phosphates in granitic pegmatites. It might indicate that conditions at which minerals of the graftonite group crystallize, can rarely intersect with a stability field of harrisonite and the moderate to low activity of F might play an important role during the harrisonite formation. The presence of harrisonite in granitic pegmatites further indicates that this mineral can be stable even at lower P-T conditions than reported from the type locality.

SHRNUTÍ

Článek prezentuje nová data o harrisonitu z granitických pegmatitů Českého masivu. Harrisonit z granitického prostředí je výrazně chemicky odlišný od harrisonitu z Fe-bohatých metamorfitů (včetně toho z typové lokality). V pegmatitech je harrisonit vždy obohacený Mn a s nízkými obsahy Mg (obr. 2) a tím se liší od harrisonitu z typové lokality a podobného výskytu (metamorfované BIF, obě lokality Kanada), který je vždy obohacený Mg a naopak chudý Mn (obr. 2). V článku poprvé prezentujeme chemické složení harrisonitu z Příbyslavic, které je nápadně podobné složení harrisonitu z Cyrilova.

Na obou výskytech harrisonitu z pegmatitů v Českém masivu a také z pegmatitu v João, Brazílie, byl zaznamenán výrazný přebytek P substituujícího tetraedrický Si ve struktuře (obr. 3). Tato substituce navíc negativně koreluje s obsahem Fe, zatímco obsahy Ca, Mn a Mg zůstávají nezměněné. Získaná data naznačují, že vstup P substituujícího Si by mohl způsobovat vakance v MO_6 pozici (obr. 5). Přítomnost harrisonitu v granitických pegmatitech ukazuje, že může být stabilní i za nižších P-T podmínek, než jsou uváděny z typové lokality.

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Table 1. Chemical composition of harrisonite from Arcedeckne (FRISCH and HERD 2010), João (BAIJOT *et al.* 2014), Cyrilov and Příbyslavice.

Tabulka 1. Chemické složení harrisonitu z ostrova Arcedeckne (FRISCH a HERD 2010), pegmatitu João (BAIJOT *et al.* 2014), Cyrilova a Příbyslavic.

Locality Analysis	Arcedeckne (TL)	João	Cyrilov			Příbyslavice		
	FH 1	BA 1	CY1_5	CY1_6	CY1_8	VS9Pr6b_2	VS9Pr6b_5	VS9Pr6b_15
P ₂ O ₅ (wt. %)	19.75	20.61	21.31	19.41	21.07	20.08	21.28	22.04
SiO ₂	16.42	15.47	14.97	15.74	15.26	16.38	15.56	15.06
ZnO	bdl.	0.25	bdl.	bdl.	bdl.	bdl.	bdl.	bdl.
MnO	0.04	10.33	3.39	3.09	3.16	3.27	3.18	3.28
FeO	52.86	47.24	51.97	53.08	52.81	53.17	53.09	52.12
MgO	3.77	0.36	0.40	0.35	0.37	0.34	0.24	0.34
CaO	7.73	7.60	7.54	7.66	7.69	7.47	7.51	7.63
Total	100.57	101.86	99.57	99.33	100.36	100.71	100.85	100.47
Ca ²⁺	0.998	0.989	0.978	0.965	1.008	0.978	0.978	0.992
Zn ²⁺	0.000	0.022	0.000	0.033	0.000	0.000	0.000	0.000
Fe ²⁺	5.327	4.800	5.397	5.312	5.404	5.431	5.397	5.291
Mn ²⁺	0.004	1.063	0.327	0.339	0.328	0.338	0.327	0.337
Mg ²⁺	0.677	0.065	0.043	0.046	0.067	0.062	0.043	0.062
Σ	6.008	5.951	5.767	5.730	5.799	5.831	5.767	5.690
P ⁵⁺	2.015	2.120	2.190	2.237	2.183	2.077	2.237	2.265
Si ⁴⁺	1.979	1.880	1.891	1.856	1.868	2.000	1.856	1.828
Σ	3.993	4.000	4.081	4.093	4.051	4.077	4.093	4.093
O ²⁻	16.000	16.000	16.000	16.000	16.000	16.000	16.000	16.000

Table 2. Representative analyses of minerals of the graftonite group from Cyrilov and Příbyslavice.
Tabulka 2. Reprezentativní analýzy minerálů graftonitové skupiny z Cyrilova a Příbyslavice.

Locality Mineral Analysis	Cyrilov				Příbyslavice	
	griftonite-(Ca)	griftonite-(Ca)	griftonite-(Mn)	griftonite-(Mn)	griftonite-(Mn)	griftonite-(Mn)
	CY1 9	CY1 17	CY1 1	CY1 2	VS9Pr6b 8	VS9Pr6b 22
P ₂ O ₅ (wt. %)	42.11	42.00	42.14	40.43	41.06	41.15
SiO ₂	0.14	0.11	0.11	0.11	0.11	bdl.
ZnO	bdl.	0.41	bdl.	bdl.	0.32	bdl.
MnO	19.07	19.12	18.41	18.14	18.16	18.35
FeO	25.03	26.87	33.49	32.89	33.89	35.92
MgO	0.14	0.41	0.53	0.49	0.37	0.45
CaO	13.76	12.46	6.57	6.87	6.81	5.15
Total	100.25	101.36	101.25	98.94	100.73	101.01
Zn ²⁺	0.000	0.017	0.000	0.000	0.014	0.000
Mn ²⁺	0.155	0.198	0.555	0.527	0.534	0.644
Mg ²⁺	0.012	0.034	0.045	0.042	0.032	0.038
Ca ²⁺	0.833	0.751	0.400	0.430	0.420	0.318
Σ	1.000	1.000	1.000	1.000	1.000	1.000
Fe ²⁺	1.183	1.265	1.591	1.609	1.632	1.731
Mn ²⁺	0.758	0.714	0.331	0.372	0.351	0.251
Σ	1.940	1.978	1.922	1.981	1.984	1.982
P ⁵⁺	2.014	2.001	2.027	2.002	2.002	2.007
Si ⁴⁺	0.008	0.006	0.006	0.007	0.006	0.000
Σ	2.023	2.007	2.023	2.009	2.008	2.007
O ²⁻	8.000	8.000	8.000	8.000	8.000	8.000

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