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Petříčekite, $CuSe_2$, a New Member of the Marcasite Group from the Předbořice Deposit, Central Bohemia Region, Czech Republic

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Abstract: Petříčekite, ideally $CuSe_2$, is a new mineral from the Předbořice deposit, Central Bohemia Region, Czech Republic. It occurs as rare inclusions, up to 150 μm across, in large eucairite grains closely associated with athabascaite/klockmannite and unknown selenide phases. Petříčekite is opaque with a metallic luster and shows a black streak. It is brittle; the Vickers hardness (VHN_{15}) is 33 kg/mm^2 (range: 28–40 kg/mm^2) (Mohs hardness of ~2–2½). In reflected light, petříčekite is pale blue grey to pale pinkish, weakly pleochroic and weakly bireflectant from slightly blue-grey to slightly pinkish-grey. Under crossed polars, it is anisotropic with light grey-blue to light pink rotation tints. Internal reflections are absent. Reflectance percentages for the four COM (Commission on Ore Mineralogy) wavelengths (R_{min} and R_{max}) are 42.35, 41.8 (470 nm), 42.0, 42.2 (546 nm), 41.9, 42.35 (589 nm) and 42.05, 42.85 (650 nm), respectively. Petříčekite is orthorhombic, space group *Pnnm*, with a = 4.918(2) Å; b = 6.001(2) Å; c = 3.670(1) Å; V = 108.31(1) Å^3; Z = 2. The crystal structure ($R1$ = 0.0336 for 159 reflections with $I > 2\sigma(I)$) belongs to the marcasite-type structure. It consists of edge-sharing chains of $CuSe_6$ octahedra parallel to [001] linked by sharing Se_2 dimers. The Se–Se bonds are all parallel to (001). The five strongest powder-diffraction lines (d in Å (I/I_0) (*hkl*)) are: 2.938 (70) (101); 2.639 (100) (111); 2.563 (85) (120); 1.935 (70) (211); 1.834 (30) (002). The mean of nine electron-microprobe analyses on the crystal used for the structural study gave Ag 0.22(13), Cu 15.39(15), Hg 0.01(3), Pb 0.03(2), Fe 12.18(10), Pd 0.11(4), S 0.09(1), Se 71.61(29) and total 99.64(41) wt %, corresponding on the basis of a total of three atoms, to $(Cu_{0.53}Fe_{0.48})_{\Sigma 1.01}(Se_{1.98}S_{0.01})_{\Sigma 1.99}$. Additional crystals exhibiting higher Cu contents (up to 0.74 a.p.f.u.) were also investigated. The new mineral has been approved by the IMA-NMNC Commission (2015-111) and named after Václav Petříček, renowned crystallographer of the Institute of Physics of the Czech Academy of Sciences, Prague. Optical, compositional and structural properties confirm that nearly pure petříčekite also formed as late-stage mineral in the Se mineralization at El Dragón, Bolivia. It has end-member composition, $Cu_{0.99}Se_{2.00}$ (n = 5), and is typically associated with krut'aite of ideal composition, native selenium and goethite. Finally, optical and chemical data indicate that pure petříčekite is likely present also at Sierra de Cacheuta, Argentina.

Keywords: petříčekite; marcasite-type structure; copper; selenium; Předbořice deposit; Czech Republic; El Dragón; Bolivia; Sierra de Cacheuta; Argentina

1. Introduction

The small Předbořice uranium deposit, Central Bohemia Region, Czech Republic (at ~49°32'57.590" N (latitude), 14°15'12.449" E (longitude)) is a famous mineral locality especially for its richness in rare selenides. It is the type-locality for four minerals, *i.e.*, fischesserite Ag_3AuSe_2, hakite ($Cu_6[Cu_4Hg_2]Sb_4Se_{13}$), milotaite PdSbSe, and permingeatite $(Cu,Fe)_4As(Se,S)_4$. From 1961 to 1978 a total of 250 tons of uranium was mined out of over 100 low temperature hydrothermal veins between the small villages of Předbořice and Lašovice cutting through the krásnohorsko-sedlčanský metamorphic islet, close to its contact with granitoids of central bohemian pluton. Mineralized fissures are complicated veins up to 25−100 m long, 25−50 m high and up to 30 cm (max. 1 m) thick. The main ore mineral is uraninite, and the main gangue minerals are quartz, hematite-bearing calcite, and barite. Předbořice mineralization furthermore includes among others: aguilarite Ag_4SeS, athabascaite Cu_5Se_4, berzelianite, bukovite $Tl_2(Cu,Fe)_4Se_4$, chaméanite $(Cu,Fe)_4As(Se,S)_4$, chrisstanleyite $Ag_2Pd_3Se_4$, clausthalite, eskebornite $CuFeSe_2$, eucairite AgCuSe, ferroselite $FeSe_2$, giraudite $Cu_6[Cu_4(Fe,Zn)_2]As_4Se_{13}$, jolliffeite NiAsSe, krut'aite-trogtalite series, klockmannite, merenskyite $(Pd)(Te,Se)_2$, naumannite, telargpalite $(Pd,Ag)_3(Te,Bi)$, tiemannite, tyrrellite, umangite, and native gold (chemical compositions above are given as ideal formulae). Further details of the low-temperature selenide association from the Předbořice deposit are provided by Johan (1989) [1].

Petříčekite, $CuSe_2$, has been identified in two specimens bought at a mineral fair. It generally occurs either as fractured inclusions in large eucairite grains closely associated with athabascaite/klockmannite and unknown selenide phases which are currently under investigation, or as fractured inclusions in tiemannite closely associated with eskebornite. Petříčekite was approved as a new mineral by the Commission of New Minerals, Nomenclature and Classification of IMA (2015-111). The mineral name honors Václav Petříček (b. 1948), Czech crystallographer (Institute of Physics of the Czech Academy of Sciences, Prague, Czech Republic), for his outstanding contributions to crystallography in general and mineralogical crystallography in particular. His pioneering studies of incommensurately modulated and composite structures and the development of the computer system *JANA*, have represented a milestone for all the members of the community working with the structural complexity of mineral structures. The holotype material from Předbořice is deposited in the reference collection of the Harvard Mineralogical and Geological Museum, reference number MGMH#2016.01.

In this study we report the description of the new mineral petříčekite, together with data on its crystal structure. In addition to the description of the new species from Předbořice, we provide the optical properties and compositional as well as structural data for petříčekite from a second occurrence, the El Dragón mine in Bolivia, and we infer the presence of petříčekite from a third occurrence, Sierra de Cacheuta in Argentina, on the basis of optical and chemical data.

2. Physical and Optical Properties

Petříčekite from Předbořice occurs as euhedral to subhedral grains (up to 150 μm in diameter) either solitary in the eucairite matrix or as angular fragments cemented prevalently by eucairite (Figures 1 and 2).

Petříčekite is black in color and shows a black streak. The mineral is opaque in transmitted light and exhibits a metallic luster. No cleavage is observed and the fracture is uneven. The calculated density (for $Z = 2$) for the empirical formula (see below) is 6.673 g/cm^3. Unfortunately, the density could not be measured because of the small grain size. Micro-indentation measurements carried out with a VHN (Vickers Hardness Number) load of 15 g give a mean value of 33 kg/mm^2 (range: 28–40) corresponding to a Mohs hardness of about 2–2½.

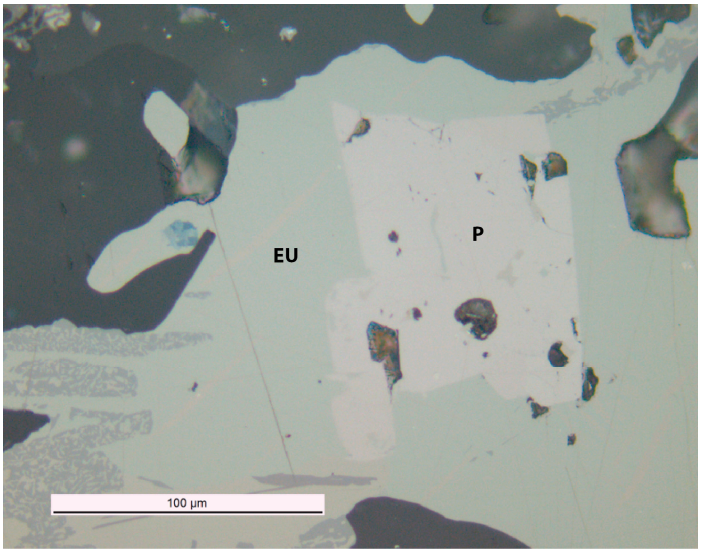

Figure 1. Reflected light photograph of the holotype grain of petříčekite (P, included in EU = eucairite) that was used for structure determination. The chemical composition of this grain is $(Cu_{0.53}Fe_{0.48})_{\Sigma 1.01}(Se_{1.98}S_{0.01})_{\Sigma 1.99}$.

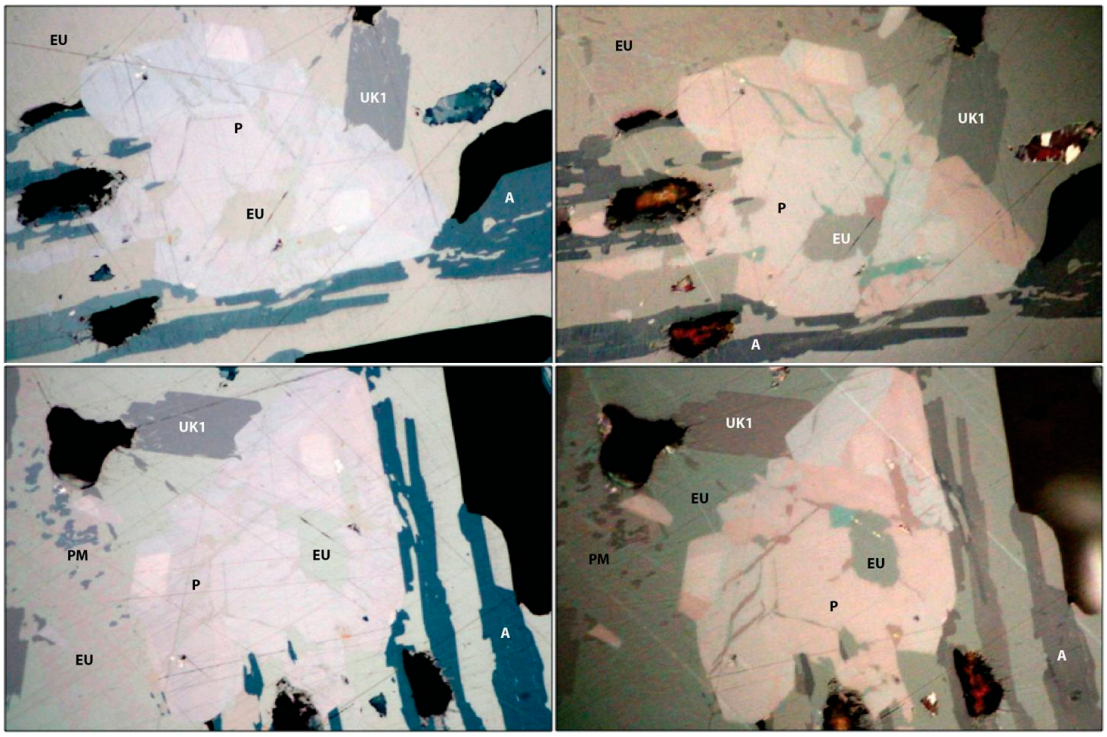

Figure 2. Reflected light images of petříčekite from Předbořice, all images have 200 µm width. **Right** hand side with partly crossed polarizers, **left** hand side without. **Top** and **bottom** row correspond to different extinction rotations. P = petříčekite, EU = eucairite, PM = permingeatite, A = athabascaite, UK1 corresponds to an unknown selenide currently under investigation. In plane-polarized incident light, petříčekite is pale blue grey to pale pinkish in color, weakly bireflectant and weakly pleochroic from slightly blue-grey to slightly pinkish-grey. With crossed polars, petříčekite is weakly anisotropic with light grey-blue to light pink rotation tints.

In plane-polarized incident light, petříčekite from the type locality is pale blue grey to pale pinkish, weakly pleochroic and weakly bireflectant from slightly blue-grey to slightly pinkish-grey. Between

crossed polars, it is anisotropic with light grey-blue to light pink rotation tints. Internal reflections are absent and there is no optical evidence of oriented growth zonation. Notably, pleochroism and anisotropy increase significantly in near end-member petříčekite from El Dragón. Reflectance measurements for petříčekite from both occurrences were obtained in air relative to a WTiC standard by means of a J & M TIDAS diode array spectrometer (J & M Analytik AG, Essingen, Germany) using ONYX software on a Zeiss Axioplan ore microscope (Carl Zeiss AG, Oberkochen, Germany) (Table 1).

Table 1. Reflectance data for petříčekite from Předbořice (1) and from El Dragón (2).

λ (nm)	1		2	
	R_1	R_2	R_1	R_2
400	42.80	41.90	26.90	50.70
420	42.60	41.50	25.70	44.00
440	42.50	41.50	24.90	40.20
460	42.40	41.70	24.20	37.50
480	42.30	41.90	23.70	35.10
500	42.20	42.10	23.10	32.80
520	42.10	42.10	22.30	30.60
540	42.00	42.20	21.50	28.60
560	41.90	42.20	21.10	27.10
580	41.90	42.30	21.40	25.70
600	41.90	42.40	22.50	24.40
620	41.90	42.50	24.60	23.30
640	42.00	42.70	27.90	22.80
660	42.10	43.00	31.70	23.00
680	42.40	43.65	35.80	24.30
700	42.80	44.60	39.40	27.10

Reflectance percentages for the four COM wavelengths (R_1 and R_2) for petřičekite from Předbořice and from El Dragón are: 42.35, 41.8 (470 nm), 42.0, 42.2 (546 nm), 41.9, 42.35 (589 nm), 42.05, 42.85 (650 nm) and 24.0, 36.3 (470 nm), 21.4, 28.2 (546 nm), 21.9, 25.1 (589 nm), 29.8, 22.9 (650 nm) respectively.

At El Dragón, petříčekite occurs in euhedral to subhedral crystals and partly oriented crystal aggregates forming skeletal and/or myrmekitic aggregates of up to 200 μm (Figure 3). Petříčekite aggregates cement (usually together with krut'aite and needle-like crystals of a yet undescribed anisotropic mineral resembling the ideal composition Cu_3Se_4) shrinkage cracks and any kind of pores and vugs or fill interstices in brecciated krut'aite-penroseite. It is locally also present as euhedral to subhedral crystals up to 25 μm in width, occurring either isolated, rarely twinned, or intergrown with krut'aite and Cu_3Se_4, formed as late-stage replacement product of clausthalite and/or krut'aite-penroseite (Figure 4). Homogeneous grains are exceptional; typically, they are replacement remnants constituting intimate intergrowths with krut'aite and other primary and secondary species down to the nm-scale, including native selenium and goethite (Figure 5). The El Dragón petříčekite itself is usually partly or completely replaced by krut'aite. Minerals that are occasionally in grain-boundary contact are klockmannite, watkinsonite and native selenium. Other minerals adjacent to petříčekite encompass quartz, calcite, barite, covellite, goethite, lepidocrocite, chalcomenite, molybdomenite, olsacherite, schmiederite, ahlfeldite, favreauite, felsőbányaite and allophane. Petříčekite from El Dragón is non-fluorescent, black and opaque with a metallic luster and black streak. It is brittle with an irregular fracture and no obvious parting or cleavage.

Optical properties of end-member petříčekite from El Dragón are displayed in Figure 3. In plane-polarized incident light, it is violet in color, slightly bireflectant and strongly pleochroic from violet to blue. The mineral does not show any internal reflections. Between partly crossed polars, petříčekite is strongly anisotropic, with copper-red to light grey rotations tints.

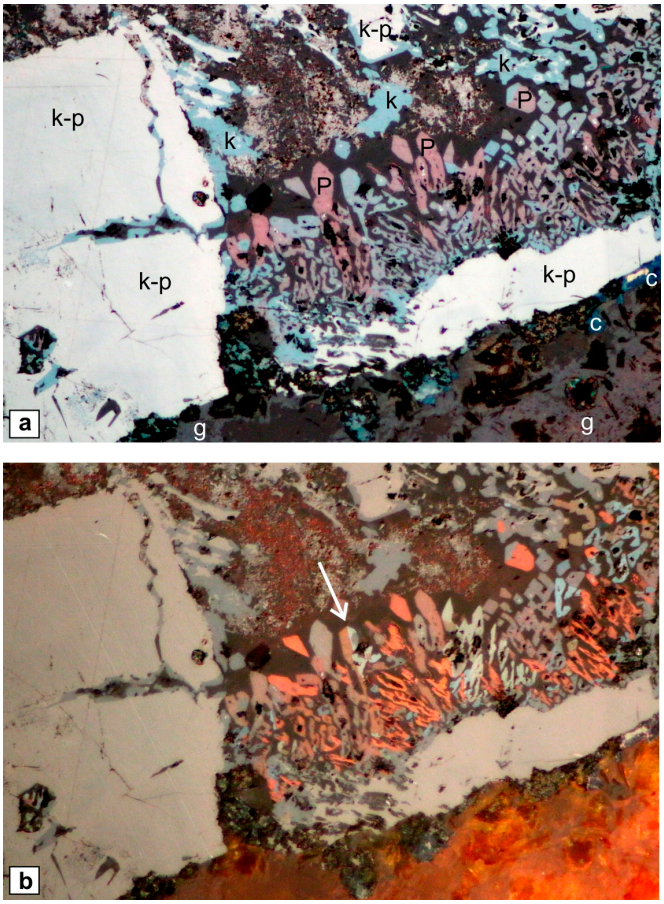

Figure 3. Fragments of krut'aite-penroseite (k-p) cemented by skeletal palisades of subhedral petříčekite crystals (P), end-member krut'aite (k), goethite (g), and covellite (c). The arrow marks a twinned petříčekite grain. (**a**) Without polarizers; (**b**) with partly crossed polarizers. Image width = 200 μm. Sample from El Dragón.

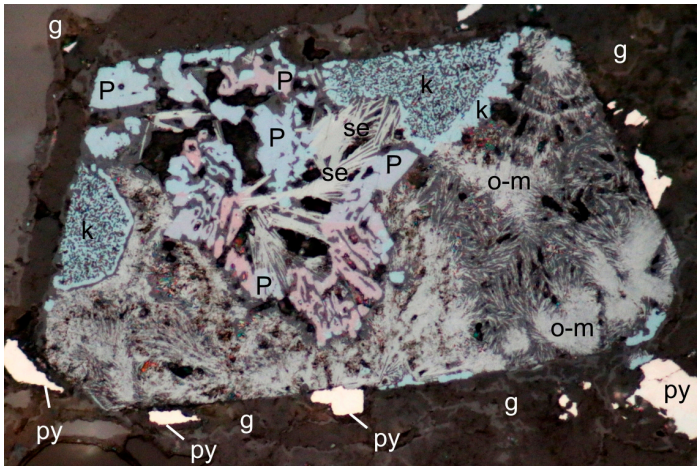

Figure 4. Petříčekite (P), end-member krut'aite (k), native selenium (se), and olsacherite-molybdomenite (o-m) pseudomorph after clausthalite, surrounded by pyrite (py) and goethite (g). Width = 200 μm, without polarizers. Sample from El Dragón.

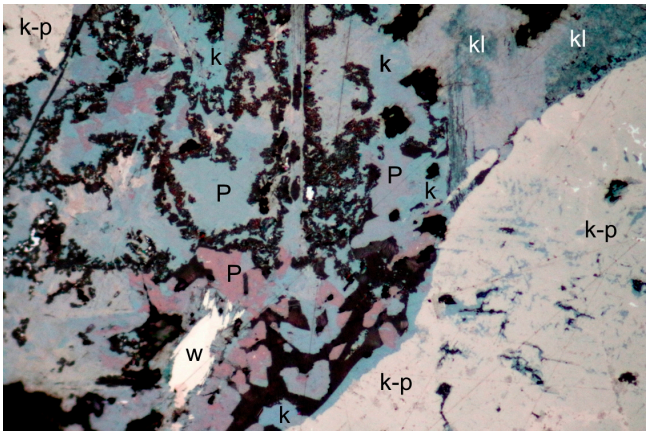

Figure 5. Petříčekite (P), krut'aite (k), watkinsonite (w), and klockmannite (kl) filling a small crack in krut'aite-penroseite (k-p). Note the fine-scale intergrowth of P and k and the partial replacement of k-p, P and w by krut'aite. Width = 200 μm, without polarizers. Sample from El Dragón.

Finally, petříčekite of end-member composition ($CuSe_2$) is likely present also at the selenium mineralization near Cerro de Cacheuta (= Sierra de Cacheuta), Luján de Cuyo Department, Mendoza, Argentina (Figure 6).

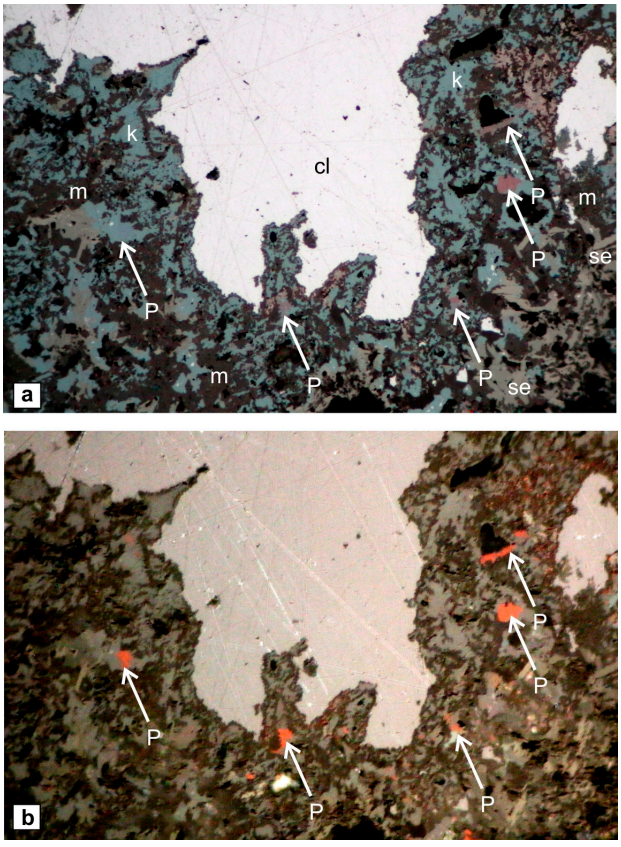

Figure 6. Sample from Sierra de Cacheuta, Argentina: Clausthalite (cl) partly replaced by krut'aite of ideal composition (blue, k), end-member petříčekite (blue-light violet, P), molybdomenite (dark grey, m) and native selenium (light grey, se). (**a**) Without polarizers; (**b**) with partly crossed polarizers. Image width = 200 μm.

The Sierra de Cacheuta deposit (at ~33°01'18" S (latitude), 69°07'40.50" W (longitude)) is at an altitude of about 1580 m above sea level and is the type locality for achávalite (Fe,Cu)Se and molybdomenite $PbSeO_3$. In the 1860s, the selenium mineralization was discovered in calcitic veinlets in porphyry forming a fine-grained mixture of clausthalite, naumannite, klockmannite, umangite, berzelianite, eucairite, tyrrellite and eskebonite. The petříčekite-bearing specimen from Cacheuta described herein was purchased in the late 1970s from an American mineral dealer at the Munich Mineral Fair.

Despite detailed investigations during the last years, petříčekite, of nearly end-member composition from El Dragón and Sierra de Cacheuta obviously remained undetected probably to have been classified as umangite because of very similar optical properties.

3. Chemical Data

Quantitative chemical analyses were performed using a JEOL Hyperprobe JXA-8500F electron-microprobe (Akishima, Tokyo, Japan), operating in WDS (Wavelength Dispersive Spectrometry) mode. The experimental conditions were: accelerating voltage 20 kV, beam current 20 nA, beam size 1 μm. No elements other than those indicated below with atomic number greater than 5 were detected. Standards are (element, emission line): naumannite (Ag, Se *Lα*), Cu metal (Cu *Kα*), cinnabar (Hg *Lα*), clausthalite (Pb *Mα*), pyrite (Fe *Kα*), Pd metal (Pd *Lα*), and sphalerite (Zn *Kα*). The crystal fragment is homogeneous within analytical errors. Table 2 gives analytical data (average of nine spot analyses) for the grains from which the structural data were obtained.

Table 2. Chemical data (in weight percent (wt %) of elements) and estimated standard deviations (e.s.d.) of the structurally studied petříčekite.

Element	wt (%) (*n* = 9)	Range	e.s.d.
Ag	0.22	0.09–0.46	0.13
Cu	15.39	15.10–15.56	0.15
Hg	0.01	0.00–0.07	0.03
Pb	0.03	0.00–0.07	0.02
Fe	12.18	12.02–12.34	0.10
Pd	0.11	0.02–0.17	0.04
S	0.09	0.08–0.10	0.01
Se	71.61	71.10–71.90	0.29
Total	99.64	99.06–100.13	0.41

The empirical formula of holotype petříčekite from Předbořice (based on three atoms *pfu*, Me + 2(Se + S)) is $(Cu_{0.53}Fe_{0.48})_{\Sigma 1.01}(Se_{1.98}S_{0.01})_{\Sigma 1.99}$. The simplified formula is $CuSe_2$, which requires Cu 28.69 wt % and Se 71.31 wt %, total 100.00 wt %.

The formula of the Cu-richest grain additionally studied from a structural point of view corresponds to $(Cu_{0.70}Fe_{0.30})_{\Sigma 1.00}Se_{2.00}$ (using the same instrument and the same experimental conditions as above). The domain closest to end-member composition measured in petříčekite from the type sample has the composition $(Cu_{0.74}Fe_{0.27}Ag_{0.01})_{\Sigma 1.02}Se_{1.98}$.

Petříčekite from Předbořice displays a wider range in composition than indicated in Table 2. Compositional data (n = 66) are summarized in Table 3. The mean formula is $(Cu_{0.58}Fe_{0.38}Pd_{0.03}Ag_{0.01}Ni_{0.01})_{\Sigma 1.01}(Se_{1.99}Se_{0.01})_{\Sigma 2.00}$. Concentrations of "minor" elements (in wt %) maximize to: Ag = 1.5, Hg = 3.6, Ni = 1.8, Pd = 9.6. The composition of the most Pd-rich grain is $(Cu_{0.49}Fe_{0.22}Pd_{0.21}Ni_{0.05}Ag_{0.03})_{\Sigma 1.00}Se_{2.00}$.

Petříčekite from El Dragón and from Sierra de Cacheuta has practically end-member composition $(Cu_{0.99}Se_{2.00})$. Elements other than Cu and Se detected by microprobes (Ag, Co, Ni, S) occur at concentrations <0.1 wt % (*cf.* Table 3). Associated krut'aite is also devoid of non-stoichiometric elements $(Cu_{1.00}Se_{2.00})$; a composition not yet reported from any other occurrence.

Table 3. Composition of petříčekite from Předbořice and El Dragón.

wt %	Předbořice			El Dragón		
	Mean	**Min**	**Max**	**Mean**	**Min**	**Max**
Cu	16.81 (2.62)	13.81	21.45	28.42 (0.14)	28.21	28.58
Ag	0.37 (0.31)	0.00	1.46	0.04 (0.01)	0.04	0.05
Hg	0.33 (0.69)	0.00	3.61	–	–	–
Pb	0.01 (0.02)	0.00	0.07	–	–	–
Fe	9.47 (2.60)	5.34	12.64	–	–	–
Co	–	–	–	0.03 (0.01)	0.02	0.03
Ni	0.25 (0.50)	0.00	1.75	0.08 (0.01)	0.07	0.09
Pd	1.26 (2.74)	0.00	9.64	–	–	–
As	0 (0.01)	0.00	0.05	–	–	–
Sb	0.01 (0.03)	0.00	0.10	–	–	–
S	0.08 (0.05)	0.00	0.19	0.03 (0.01)	0.02	0.03
Se	71.19 (0.77)	68.83	71.97	71.53 (0.13)	71.39	71.72
Total	99.78 (0.45)	98.46	101.02	100.12 (0.17)	99.88	100.29

4. X-Ray Crystallography

For the X-ray single-crystal diffraction study, the intensity data were collected using an Oxford Diffraction Xcalibur 3 diffractometer (Oxford Diffraction, Oxford, UK), equipped with a Sapphire 2 CCD area detector, with Mo $K\alpha$ radiation. The detector to crystal working distance was 6 cm. Intensity integration and standard Lorentz-polarization corrections were performed with the *CrysAlis* RED [2] software package. The program ABSPACK in *CrysAlis* RED [2] was used for the absorption correction. Tests on the distribution of $|E|$ values agree with the occurrence of an inversion centre ($|E^2 - 1| = 0.967$). This information, together with the observed systematic absences, suggested the space group *Pnnm*. The refined unit-cell parameters are a = 4.918(2) Å, b = 6.001(2) Å, c = 3.670(1) Å, V = 108.31(1) Å^3.

The crystal structure was refined with *Shelxl*-97 [3] starting from the atomic coordinates of synthetic $CuSe_2$ [4]. The site occupancy factors (s.o.f.) were refined using the scattering curves for neutral atoms given in the *International Tables for Crystallography* [5]. Crystal data and details of the intensity data collection and refinement are reported in Table 4.

Table 4. Crystal and experimental details for petříčekite from Předbořice.

Crystal Data	
Crystal size (mm^3)	0.035 × 0.045 × 0.050
Cell setting, space group	Orthorhombic, *Pnnm*
a, b, c (Å)	4.918(2), 6.001(2), 3.670(1)
V (Å^3)	108.31(1)
Z	2
Data Collection and Refinement	
Radiation, wavelength (Å)	Mo $K\alpha$, λ = 0.71073
Temperature (K)	293
$2\theta_{max}$ (°)	64.00
Measured reflections	1496
Unique reflections	212
Reflections with $F_o > 4\sigma(F_o)$	159
R_{int}	0.0329
$R\sigma$	0.0425
Range of h, k, l	$7 \leqslant h \leqslant 7$, $8 \leqslant k \leqslant 8$, $5 \leqslant l \leqslant 5$
R ($F_o > 4\sigma(F_o)$)	0.0336
R (all data)	0.0343
wR (on F^2)	0.0615
GooF	1.339
Number of least-square parameters	13
Maximun and minimum residuals (e/Å^3)	1.67−1.13

After several cycles of isotropic refinement, the R_1 converged to 0.13, thus confirming the correctness of the structural model. The refinement of the mean electron number at the Cu site (against structural vacancy) produced an occupancy of Cu = 95.1%, thus indicating a population that can be written as $Cu_{0.53}Fe_{0.47}$. With the introduction of an anisotropic model for all the atoms, the R_1 dropped to 0.034. Atom coordinates and isotropic displacement parameters are given in Table 5.

Table 5. Atoms, site occupancy factors (s.o.f.), atom coordinates and equivalent isotropic displacement parameters (Å^2) for petříčekite from Předbořice.

Atom	s.o.f.	*x*/*a*	*y*/*b*	*z*/*c*	U_{iso}
Cu	$Cu_{0.53}Fe_{0.47}$	0.0000	0.0000	0.0000	0.0125(7)
Se	$Se_{1.00}$	0.1964(4)	0.3783(3)	0.0000	0.0222(7)

The refined crystal chemical formula $(Cu_{0.53}Fe_{0.47})Se_2$ is in perfect agreement with that derived from the electron microprobe data, *i.e.*, $(Cu_{0.53}Fe_{0.48})_{\Sigma 1.01}(Se_{1.98}S_{0.01})_{\Sigma 1.99}$.

Powder X-ray data (Cu $K\alpha$ radiation) were collected with an automated CCD-equipped Oxford Diffraction Xcalibur PX single-crystal diffractometer using a Cu $K\alpha$ radiation (Gandolfi-type data collection). The measured and calculated (using the software *PowderCell* 2.3 [6]) powder diffraction patterns are given in Table 6. Unit-cell parameters refined from the collected data are as follows: a = 4.9072(3) Å, b = 6.0116(4) Å, c = 3.6671(5) Å, V = 108.180(7) Å^3.

Table 6. Measured and calculated X-ray powder diffraction data for petříčekite from Předbořice. Only reflections with $I_{calc} > 5$ are listed. The seven strongest reflections are given in bold.

hkl	d_{meas}	I_{obs}	d_{calc}	I_{calc}
110	–	–	3.8038	9
011	3.135	20	3.1309	19
020	2.991	15	3.0005	17
101	**2.938**	**70**	**2.9413**	**86**
111	**2.639**	**100**	**2.6411**	**100**
120	**2.563**	**85**	**2.5614**	**95**
200	–	–	2.4590	7
210	–	–	2.2754	14
121	2.098	20	2.1004	20
211	**1.935**	**70**	**1.9339**	**82**
220	–	–	1.9019	6
130	–	–	1.8529	15
002	**1.834**	**30**	**1.8350**	**36**
031	**1.760**	**25**	**1.7564**	**36**
221	1.685	15	1.6886	22
131	1.656	20	1.6541	26
310	1.579	15	1.5814	22
122	**1.492**	**25**	**1.4917**	**32**
212	–	–	1.4284	6
132	–	–	1.3038	8
240	–	–	1.2807	14
312	1.195	10	1.1979	16
113	–	–	1.1646	6
051	–	–	1.1407	9
421	–	–	1.0867	11
213	–	–	1.0775	10
341	1.060	15	1.0596	16
242	–	–	1.0502	14
033	–	–	1.0436	6
133	–	–	1.0209	5

Powder X-ray data (Cu $K\alpha$ radiation) were also collected with the same instrument on an end-member petříčekite grain intermixed with krut'aite of ideal stoichiometry and goethite from El Dragón. The fragment consisted of roughly 60% petříčekite, 25% krut'aite, and 15% goethite. The number of diffraction lines surely attributable to petříčekite was 8, which gave the following unit-cell values: with a = 5.014(1) Å, b = 6.203(1) Å, c = 3.740(1) Å, V = 116.31(5) Å^3. These values are in excellent agreement with those observed for pure synthetic $CuSe_2$ (a = 5.0226(7) Å, b = 6.1957(7) Å, c = 3.7468(6) Å, V = 116.59(2) Å^3, [4]). Unfortunately, the crystal structure was not refined.

5. Results and Discussion

The crystal structure of petříčekite (Figure 7) belongs to the marcasite-type structure. It consists of edge-sharing chains of $CuSe_6$ octahedra parallel to [001] linked by sharing Se_2 dimers. The Se–Se bonds are all parallel to (001). The structure determination and refinement of pure synthetic $CuSe_2$ has been previously published [4,7].

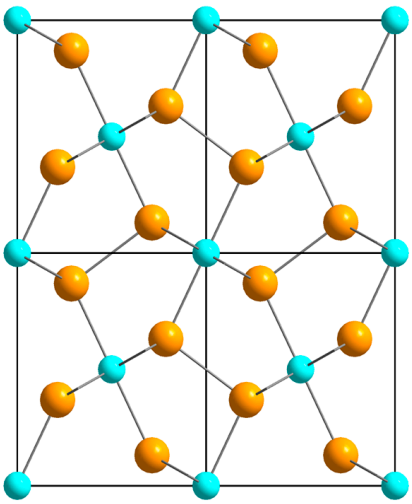

Figure 7. The crystal structure of petříčekite down the *c*-axis. Light-blue and golden circles indicate (Cu,Fe) and Se, respectively. Four unit-cells are depicted.

The chemistry obtained with electron microprobe is in perfect agreement with the results of the structure refinement. Indeed, the mean electron number at the metal site taking into account the electron microprobe data is 27.9, in good agreement with that obtained from the structure refinement, *i.e.*, 27.6. The mean bond distance observed for the (Cu,Fe)-octahedron (2.473 Å) matches very well that calculated from the weighted bond distance 0.53(Cu–Se) + 0.47(Fe–Se) = 2.474 Å from the ideal (pure) end-members [4].

A second crystal from Předbořice was studied by single-crystal X-ray diffraction, but, unfortunately, the diffraction quality did not allow a full data collection to refine the structure. However, the refined unit-cell parameters are: a = 4.96(1), b = 6.07(1), c = 3.70(1) Å. The chemistry of such a grain is $(Cu_{0.70}Fe_{0.30})Se_2$. Interestingly, if we plot the unit-cell parameters of the two studied petříčekite crystals from Předbořice together with the two synthetic end-members ($FeSe_2$ and $CuSe_2$ [4]) against the Cu contents in atoms per formula unit (Figure 8), the trend is totally obeyed.

Petříčekite from Předbořice and El Dragón are distinct with respect to their temporal position within the selenide assemblage. In Předbořice, it constitutes an early formed species, precipitated together with eucairite, but slightly predates the associated minerals athabascaite, klockmannite, permingeatite, chameanite, and others. Its association with klockmannite implies high selenium fugacities during formation, hence the above values defined by the umangite–klockmannite reaction [8]. At El Dragón, petříčekite is late-stage, postdating the bulk of selenides, such as penroseite-krut'aite, eldragónite, petrovicite, grundmannite, tiemannite, and several others [9,10]. Its association with

klockmannite, krut'aite, and native selenium suggests similar, if not higher selenium fugacities as prevailed during the precipitation of petříčekite at Předbořice, possibly representing values above the klockmannite−krut'aite univariant reaction.

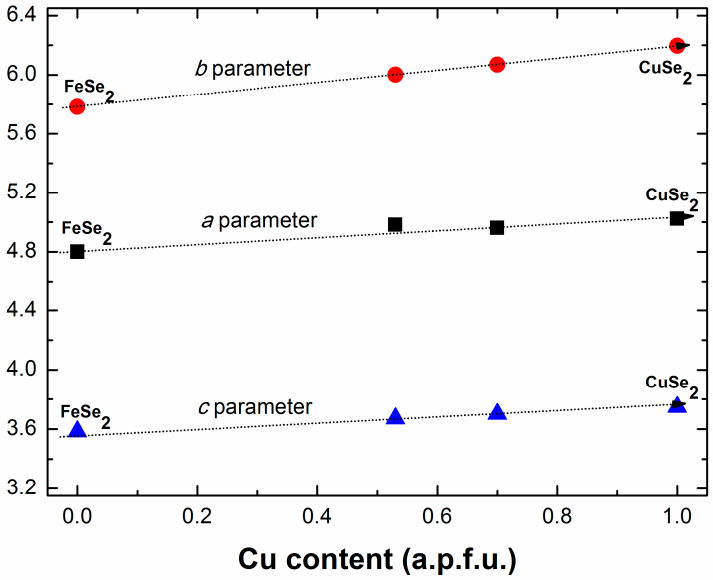

Figure 8. Unit-cell parameters (values in Å) of the two petříčekite crystals from Předbořice, plotted together with the two synthetic end-members $FeSe_2$ and $CuSe_2$ [4], as a function of the Cu content (a.p.f.u.).

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Conflicts of Interest: The authors declare no conflict of interest.

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