

Staněkite, $\text{Fe}^{3+}(\text{Mn}, \text{Fe}^{2+}, \text{Mg})(\text{PO}_4)\text{O}$: a new phosphate mineral in pegmatites at Karibib (Namibia) and French Pyrénées (France)

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This work is dedicated to the memory of Prof. Dr. Frantisek Čech (University of Prague) who has been a delegate of the Commission on New Minerals and Mineral Names (I.M.A.) for many years and spent most of his academic life studying the phosphates in pegmatites from the Czech Republic.

Abstract: Staněkite is a new mineral with the ideal formula $\text{Fe}^{3+}(\text{Mn}, \text{Fe}^{2+}, \text{Mg})(\text{PO}_4)\text{O}$ and structurally similar to triploidite-wolfeite. It was first found in the Clementine II pegmatite, Okatjimukuju farm, Karibib (Namibia), and was later also detected in pegmatites from Albères, Eastern Pyrénées.

Staněkite exhibits a black lustre and occurs generally as unihedral grains. Simple forms with rough (120) faces were occasionally seen. The new mineral is paragenetically associated with ferrisicklerite, heterosite, kryzhanovskite, arrojadite, eosphorite, and alluaudite *s.l.* It is monoclinic, space group $P2_1/a$, a 11.844(3), b 12.662(3), c 9.989(3) Å, β 105.93(2)°, $Z = 16$, $D_x = 4.09$ g/cm³. Strongest lines of X-ray powder pattern $d(\text{hkl})$ are as follows: 2.971(100)14-1, 2.809(85)40-2, 2.857(58)023, 3.259(50) 202, 3.412 (38)122, 5.54(37)120, 3.621(35)221, 2.548(30)24-2, 1.779(28) 522/54-3/44-4. There are strong substructure reflections found on levels with k even and have indices for which $hkl: h + 1/2k + l = 2n$ and $h0l: h = 2n$. The resulting space group of the subcell is $I2/a$, with $a_{\text{sub}} = a$, $b_{\text{sub}} = 1/2b$, and $c_{\text{sub}} = c$. Microprobe analysis revealed the following chemical composition (in wt%): Na₂O 0.13, MgO 0.50, CaO 0.13, MnO 23.12, FeO 1.56, ZnO 0.22, Fe₂O₃ 41.52, and P₂O₅ 31.16. The empirical formula based on 5 O atoms is: $(\text{Fe}^{3+}_{1.16}\text{Mn}^{2+}_{0.73}\text{Fe}^{2+}_{0.05}\text{Mg}_{0.03}\text{Na}_{0.01})_{\Sigma 1.98}(\text{P}_{0.98}\text{O}_4)\text{O}$.

The name of the new mineral honours Prof. Dr. Josef Staněk, University Masarykovy of Brno, Czech Republic.

Key-words: staněkite, $\text{Fe}^{3+}(\text{Mn}, \text{Fe}^{2+}, \text{Mg})(\text{PO}_4)\text{O}$, new phosphate mineral, granitic pegmatite, Karibib (Namibia), Pyrénées (France).

Introduction

During preliminary investigations on the phosphate mineral associations of the pegmatites

at Okatjimukuju farm, Karibib (Namibia), a new mineral was detected by Keller & Von Knorring (1989). It was tentatively named "OKAA" and it was reported that "[it] could easily be misinter-

preted as either ferrisicklerite, sicklerite or kryzhanovskite". A recent study of the pegmatites in the Albères intrusion (French Pyrénées) by two of the authors of this paper (F.F. and J.C.M.D.) revealed the occurrence of a phosphate mineral identical to that identified in Namibia.

This new mineral has been named staněkite in honour of Prof. Josef Staněk from the Masarykov University in Brno (Czech Republic), who is a renown specialist of phosphate mineralogy and has intensively studied the Moravian pegmatites.

The new species and its name have been approved by the Commission on New Minerals and Mineral Names (I.M.A.), on December 30, 1994. The holotype mineral from Okatjimukuju is preserved at the University of Stuttgart and at the Musée de l'Ecole des Mines de Paris (n°T 45634).

Occurrences

Staněkite has been found in the pegmatite Clementine II at Okatjimukuju farm, Karibib (Namibia). The pegmatite is a steeply SE dipping, 30 m thick dike exposed over a distance of about 100 m, striking approximately SW-NE. The pegmatite body is well zoned and is in sharp contact with the wall-rocks. It is moderately discordant with respect to the foliation of the calc-silicate rocks at the foot wall and to the dolomitic marbles at the hanging wall. The pegmatite is moderately fractionated, with a dominant K-stage and moderate Na- and Li-stages. A most remarkable feature is the development of a zone, intercalated between the outer and the inner intermediate zones, on both sides of the nearly symmetrical pegmatite body. The large inner intermediate zone consists mainly of reddish orthoclase or microcline perthite in huge phenocrysts. The „intercalated zone“ consists of a quartz-muscovite-albite rock with beryl, columbite-tantalite, and amblygonite/montebasite. As a result, this zone was economically interesting and has been extensively mined. In contrast to many other phosphate-bearing pegmatites, there are no large, blocky masses of Fe-Mn phosphates exposed along the core margin, but nodules with staněkite associations are dispersed over the intercalated and the inner intermediate zone (Keller & Von Knorring, 1989, Fig. 2 and 3).

The intrusion of Albères is located at the eastern end of the French Pyrénées. Four types of pegmatites intruding metamorphic terrain (cordierite micaschists) have been identified and named I, II, III, and IV, respectively, (Malló *et al.*, 1995). Staněkite has been found in type-III pegmatite, which is characterized by an aplitic border zone, an intermediate zone, and a core with well-developed quartz crystals. The degree of albitization increases from the aplite toward the intermediate zone. Sugary albite veins and later quartz-muscovite veins crosscut the pegmatitic bodies. Li-Fe-Mn phosphates, beryl, and Nb-Ta species represent the most common ore minerals. The pegmatite bodies range in length from 10 meters to 300 meters and are 3 to 5 meters in width.

Besides the two occurrences described above, staněkite has also been found in other Namibian pegmatites, *e.g.* Cameroon (Usakos, Namibia), Helikon (Karibib, Namibia), and in pegmatites at Cap de Creus (Spain).

Appearance and physical properties

In the Clementine II pegmatite staněkite occurs in small (0.2 to 5 mm) unihedral grains. They are usually elongated along the c-axis, up to 2 cm in length, and are generally subparallel intergrown to form aggregates (Fig. 1). A few subhedral crystals with rough {120} faces have been iden-

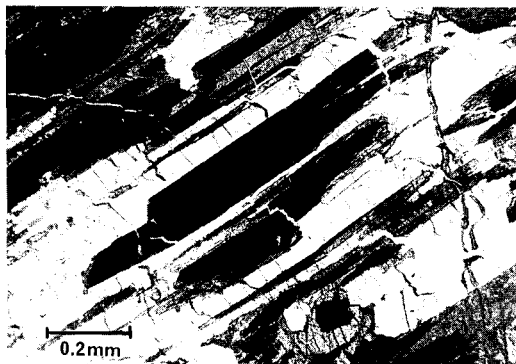


Fig. 1. Photomicrograph of staněkite (black), elongated along the c-axis, intergrown with quartz (white) and kryzhanovskite (grey). Plane polarized light.

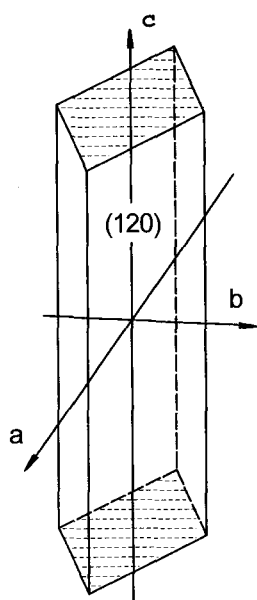


Fig. 2. Clinographic projection of staněkite. The indices are given for the supercell. The dashed faces are not indexed, because all known single crystals are terminated only by parting.

tified (Fig. 2 and 3). At Albères, staněkite is intergrown with ferrisicklerite and heterosite to form small aggregates up to 1 mm in diameter.

Staněkite is black in hand specimens with a dark brown streak. The mineral is brittle, does

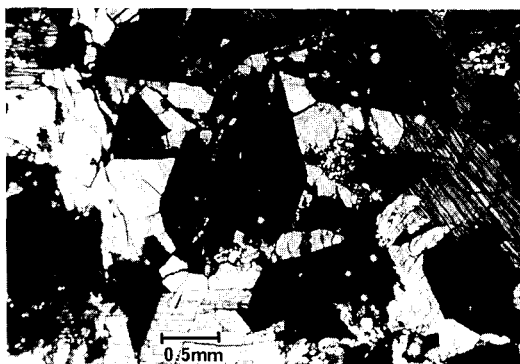


Fig. 3. Photomicrograph of staněkite (black) cut approximately perpendicular to {120}. The matrix consists of kryzhanovskite parallel and perpendicular to the cleavage {010}, (light grey and medium grey, respectively). Plane polarized light.

not show any cleavage, but splintered fractures. Parting perpendicular to the *c*-axis is occasionally developed. Staněkite is characterized by a weak submetallic lustre, absence of fluorescence, and Mohs hardness of 4 to 5. Density was obtained by measurement in heavy liquid: $D_{(\text{meas.})} = 3.80$, $D_{(\text{calc.})} = 4.09 \text{ g/cm}^3$. The large difference between $D_{(\text{meas.})}$ and $D_{(\text{calc.})}$ is due to impurities of mainly kryzhanovskite.

X-ray crystallography

The unit-cell dimensions and the space group of staněkite were derived from structure determination procedures. A small fragment of a crystal was mounted on a Siemens P2₁ automated four-circle diffractometer with graphite-monochromated MoK α radiation (Institut für Anorganische Chemie & Institut für Mineralogie und Kristallchemie, University of Stuttgart). Twenty-five reflections over the range $20^\circ \leq 2\theta \leq 35^\circ$ were used to refine the cell dimensions by least-squares techniques. Intensity data up to $2\theta = 60^\circ$ were collected.

It became evident from the structure determination that staněkite belongs to the triploidite group (Keller & Schwarz, 1995, and in prep.). The monoclinic structures of the triploidite group - triploidite, $\text{Mn}_2(\text{PO}_4)(\text{OH})$, wolfeite, $\text{Fe}_2(\text{PO}_4)(\text{OH})$, wagnerite, $\text{Mg}_2(\text{PO}_4)\text{F}$, and sarkinite, $\text{Mn}_2(\text{AsO}_4)(\text{OH})$ - are characterized by strong substructure reflections (Waldrop, 1970; Keller & Schwarz, 1995, and in prep.). They are found on levels with *k* even and have indices for which $hkl: h + 1/2k + l = 2n$ and $h0l: h = 2n$. The resulting space group is, in the setting of triploidite by Waldrop (1970), $I2/a$, whereas the superstructure has $P2_1/a$ (Table 1). For the type staněkite, the weak reflections of the complementary-structure were not seen on usual rotation, Weissenberg and precession photographs, but only after long exposure time. With the four-circle diffractometer a number of the weak reflections are detectable.

The powder diffraction data were indexed for space group $P2_1/a$, although only the subcell reflections are detectable (Table 2). Indexing was carried out using only the indices of reflections with high intensity on four-circle measurement. The powder diffraction data were corrected for both, zero 2θ and sample displacement error and refined with the LCLSQ8R program (Burnham,

Table 1. Miscellaneous crystal data.

	Clementine II		Albères
	supercell	subcell	
Space group	P 2 ₁ /a	I 2/a	
a [Å]	11.844 (3)	11.844 (3)	11.795 (4)
b [Å]	12.662 (3)	6.331 (3)	2x6.292 (5)
c [Å]	9.989 (3)	9.989 (3)	9.987 (5)
β [°]	105.93 (2)	105.93 (2)	106.289 (4)
Z	16	8	16
D _(meas.) [g/cm ³]			
D _(calc.) [g/cm ³]	4.09	4.09	4.09
2θ _{max.} [°]	60	60	
Reflections	4209	1053	
Refl. F ₀ >4σ(F ₀)	1236	983	

Clementine II: Space group and unit cell dimensions of single-crystal X-ray study. Albères: Unit cell dimensions derived from X-ray powder pattern, indexed for the subcell.

1993). Powder and single-crystal data agree well with each other.

Although staněkite belongs to the triploidite structure type, its structure is distinct from triploidite-wolfeite because of different coordina-

tion of the cations and of the oxygen; the latter does not belong to the PO₄-tetrahedron, but corresponds with the OH in triploidite-wolfeite (Keller & Schwarz, 1995, and in prep.). Staněkite is structurally different from synthetic (Fe³⁺)₂

Table 2. X-ray powder diffraction patterns for staněkite.

Clementine II, Okatjimukuju, Namibia						Albères, France		Clementine II, Okatjimukuju, Namibia						Albères, France	
d(OBS)	d(CALC)	h	k	l	I/I ₀	d(OBS)	I/I ₀	d(OBS)	d(CALC)	h	k	l	I/I ₀	d(OBS)	I/I ₀
5.70	5.697	2	0	0	10			1.903	{1.903	2	6	1	13		
5.54	5.534	1	2	0	37	5.52	30		{1.899	6	0	0			
4.20	4.202	2	2	-1	23	4.25	10	1.877	1.879	6	2	-1	10		
3.621	3.614	2	2	1	35	3.602	20	1.840	1.839	0	2	5	10		
3.412	3.411	1	2	2	38	3.381	30	1.796	{1.796	6	2	-3	15		
3.259	3.260	2	0	2	50	3.222	100		{1.794	5	2	2			
2.971	2.970	1	4	-1	100	3.968	100	1.779	{1.781	5	4	-3	28	1.765	20
2.857	2.858	0	2	3	58				{1.777	4	4	-4			
2.810	2.809	4	0	-2	85	2.806	90b	1.748	1.748	3	2	4	13		
2.769	2.767	2	4	0	27			1.719	1.718	4	6	-1	10	1.727	10
2.644	2.643	0	4	2	20			1.630	1.630	2	2	5	15		
2.548	2.548	2	4	-2	30	2.553	10		{1.621	6	0	2			
2.467	{2.467	2	0	-4	23	2.449	10	1.617	{1.616	2	6	3	17	1.610	20
	{2.462	3	4	-1										1.563	5
2.363	2.364	4	2	1	15	2.377	5b	1.525	{1.525	2	8	0	15	1.526	5
2.321	2.318	1	2	-4	15				{1.524	6	4	-4			
2.264	2.271	2	4	2				1.508	{1.510	5	4	-5	13		
2.264	2.265	3	4	1	12	2.259	5		{1.503	0	8	2			
2.177	2.177	5	2	-2	18	2.179	20	1.483	{1.485	7	4	-1	15		
	{2.104	1	2	4					{1.485	2	8	-2		1.480	5
2.100	{2.101	4	4	-2	18			1.482	1.480	8	0	-2	13		
	{2.075	1	6	0		2.077	5		{1.432	6	0	-6			
2.064	{2.061	0	6	1	22			1.431	{1.430	8	2	-1	17	1.421	5
2.023	2.024	2	0	4	15	1.995	5		{1.429	6	2	3			

Clementine II: Siemens D500/5000 powder diffractometer, CuKα, 35kV, 30mA. Indexed for P 2₁/a with a 11.844(5), b 12.662(6), c 9.985(6) Å, and β 105.82(4)°, corrected for zero 2θ and sample-displacement error.

Albères: 114.6 mm Debye-Scherrer camera, FeKα, Mn-filtered. Indexed with a 11.795, b 2x6.292(5), c 9.987(5) Å, and β 105.82(4)°.

(PO₄)O (Modaressi *et al.*, 1981), which may be a polymorph.

Optical properties

Staněkite is nearly opaque in thin sections. Consequently, it had to be investigated in reflected light. The polishing hardness is very low and the polishing quality varies depending on the degree of alteration and grain size. In polished sections the mineral is pale grey, displaying very weak birefractance and a low reflection pleochroism. In immersion oil the mineral is darker than in air, with a blue-grey hue. Anisotropy in air is moderate, but it is distinct in immersion oil, where pale brownish-grey colours are visible. The internal reflections vary from reddish yellow to brownish red and are always distinct, particularly next to microfissures and to the grain rims.

Quantitative reflectance measurements were performed at 20 nm intervals from 400 to 700 nm (visible spectrum) in polarized light on several grains. The apparatus used was a Leitz microscope photometer MPV on an Ortholux-Pol polarizing microscope, running interference-filter type Veril S-200 with continuous line (calibrated by the manufacturer). A Zeiss SiC (No. 131) reflectance standard was employed. The objec-

tives were x16 air and x25 oil for all measurements and an immersion oil in accordance with the requirements of the COM (I.M.A.), was used ($n^{23} = 1.515$, $v = 49$, DIN 58.884). All statistical and systematic errors in reflectivity measurements have been taken into account and minimized (Piller, 1977).

Table 3 gives the air and oil reflectivity values, showing approximately constant dispersion in both air and oil, and a very slight birefractance. The maximum reflectivity values are observed when the elongation of the crystals (c-axis) is parallel to the polarizing plane of the microscope. Values of the refractive indices (n), and absorption coefficients (k), calculated with the Fresnel formula, are also listed in Table 3. They are used to calculate the quantitative colour values by the weight-ordinate method (Atkin & Harvey, 1979), using an illuminant C-source with $x = 0.3103$ and $y = 0.3162$.

The total birefractance in air varies more than 1.5 % in all visible spectra, because of a very flat reflectance curve. At 540 nm, the calculated index of refraction is about 2.00, and the absorption coefficient near 0.30. The colour values plotted on a chromatic diagram give evidence for the pale blue grey hue complementary of the dark reddish yellow colour, observed in transmitted light. In air and oil, the dominant wavelength is next to about 400 nm causing a bluish colour.

Table 3. Optical data of staněkite from Clementine II (Okatjimukuju, Namibia).

λ (nm)	Reflectance values				Other optical values			
	Air		Oil		n_{\max}	n_{\min}	k_{\max}	k_{\min}
R_{\max}	R_{\min}	R_{\max}	R_{\min}					
400	15.20	12.86	3.50	2.49	2.43	2.18	0.54	0.31
420	14.00	11.90	2.80	2.00	2.34	2.11	0.52	0.30
434	13.40	11.38	2.50	1.62	2.28	2.10	0.48	0.36
440	13.05	11.15	2.30	1.60	2.26	2.07	0.48	0.31
460	12.75	10.90	2.20	1.45	2.22	2.05	0.44	0.33
480	12.46	10.75	2.15	1.41	2.18	2.04	0.39	0.31
500	12.33	10.57	2.12	1.41	2.16	2.01	0.36	0.27
520	12.33	10.41	2.13	1.33	2.16	2.00	0.36	0.27
500	12.26	10.48	2.15	1.36	2.14	2.01	0.32	0.27
544	12.25	10.46	2.18	1.43	2.13	1.99	0.30	0.22
560	12.25	10.52	2.23	1.45	2.12	2.00	0.27	0.23
580	12.29	10.68	2.30	1.50	2.11	2.01	0.23	0.24
587	12.28	10.70	2.31	1.50	2.11	2.01	0.22	0.24
600	12.31	10.69	2.42	1.54	2.09	2.00	0.13	0.22
618	12.30	10.74	2.45	1.54	2.08	2.01	0.07	0.23
620	12.30	10.75	2.37	1.55	2.10	2.01	0.18	0.23
640	12.35	10.77	2.52	1.67	2.08	1.99	0.11	0.14
660	12.42	10.80	2.49	1.70	2.09	1.99	0.10	0.13
680	12.33	10.72	2.50	1.75	2.08	1.97	0.09	0.09
700	12.15	10.54	2.60	1.80	2.03	1.93	0.26	0.20

Table 4. Chemical composition of staněkite from Clementine II, (Okatjimukuju, Namibia).

Microprobe data		Idealized formula	Atomic proportions*	
Na ₂ O	0.13	-	Na	0.009
K ₂ O	0.05	-	K	0.002
MgO	0.50	0.55	Mg	0.028
CaO	0.13	-	Ca	0.005
MnO	23.12	24.72	Mn	0.725
FeO [#]	1.56	6.50	Fe ²⁺	0.048
ZnO	0.22	-	Zn	0.006
Al ₂ O ₃	0.01	-	Al	0.0
Fe ₂ O ₃ [#]	41.56	36.12	Fe ³⁺	1.158
TiO ₂	0.02	-	Ti ⁴⁺	0.0
P ₂ O ₅	31.16	32.11	P ⁵⁺	0.977
Total	98.42	100.00		

#: for the microprobe data given according to the results of Mössbauer spectroscopy, for the idealized formula calculated from stoichiometry.

*: The atomic proportions are based on 5 oxygens.

The low luminance ($Y\% = 12$ to 2) and the weak excitation purity ($Pe\% < 5$), in both air and oil, is argument for the absence of hue characteristics. In summary, the calculated refractive index, the reflectivity, and the very low absorption coefficients account for the opaque appearance when staněkite is observed in reflected light.

The air and oil reflectance data may be compared with other measurements collected for the staněkite from Albères (Pyrénées). Although the composition of the minerals from the two occurrences is different, the optical properties show strong similarities, especially in the central part of the visible spectrum. The most striking optical difference is the higher excitation purity (6 to 13%) for the staněkite from Albères, in accordance with its brighter appearance.

Chemistry

Microprobe analyses

Chemical analyses of staněkite were performed with a Cameca Camebax SX50 electron microprobe (University Paul Sabatier, Toulouse, France) using an operating voltage of 15 kV and a beam current of 20 nA for all elements. The following standards were used for calibration: albite (Na), orthoclase (K), corundum (Al), wollastonite (Ca), MgO (Mg), sphalerite (Zn),

titanite (Ti), hematite (Fe), and graffonite (Mn, P). No other elements than those mentioned above have been detected. The oxidation state of Fe was analysed by Mössbauer spectroscopy and the water content by DTG (see below).

Numerous analyses of samples from Clementine II and Albères revealed a very homogeneous composition of staněkite. Results for Clementine II are summarized in Table 4. The empirical formula of staněkite from Clementine II based on 5 oxygen is $(\text{Fe}^{3+}_{1.16}\text{Mn}^{2+}_{0.73}\text{Fe}^{2+}_{0.05}\text{Mg}_{0.03}\text{Na}_{0.01})_{\Sigma 1.98}(\text{P}_{0.98}\text{O}_4)\text{O}$. The idealized formula $\text{Fe}^{3+}(\text{Mn}, \text{Fe}^{2+}, \text{Mg})(\text{PO}_4)\text{O}$ with $\text{Mn}:\text{Fe}:\text{Mg} = 0.77:0.20:0.03$ requires MgO 0.55 , MnO 24.71 , FeO 6.65 , Fe₂O₃ 36.12 , and P₂O₅ 32.11 , and total 100.00 wt.%.

Mössbauer spectrum

A ⁵⁷Fe Mössbauer absorption spectrum over the range ± 4 mm/s in 512 channels was recorded in the Laboratoire de Chimie de Coordination, Toulouse (France). The Mössbauer spectrometer is composed of a compact detector γ -system for high counting rates and a conventional constant acceleration Mössbauer device (Wisel). A ⁵⁷Co (in Rh) source with nominal activity of 50 mCi was used. The spectrum was obtained at room temperature and recorded on a multichannel analyzer Cambera, coupled to a computer. The isomer shift was recorded with respect to α -Fe metal. The absorber sample contains less than 10 mg Fe/cm² to avoid effects of absorber thickness. Lorentzian line shapes were assumed for deconvolutions, based on least squares fitting procedures. The χ^2 and misfit values were used to measure the goodness of the computer fit.

The Mössbauer spectrum of staněkite for room temperature consists of a large quadrupole doublet ascribed to Fe³⁺ and a small quadrupole doublet ascribed to Fe²⁺. The area of these two doublets permits the evaluation of the $\text{Fe}^{2+}/(\text{Fe}^{2+} + \text{Fe}^{3+})$ ratio, here close to 4% . That corresponds to 1.21% Fe²⁺ of the total iron content of 30.28% (Table 5).

The large quadrupole doublet unambiguously attributed to Fe³⁺ is composed, with respect to the shape-line width, of two doublets: one with Mössbauer parameters close to those of Fe³⁺ in octahedral coordination, and a second doublet due to Fe³⁺ in another, probably more strongly distorted octahedral site, where the coordination number five can not be excluded (Table 5). The

Table 5. Mössbauer data of staněkite from Clementine II (Okatjimukuju, Namibia), for room temperature.

	Isomer shift (mm/s) *	Quadrupole splitting (mm/s)	Area (%)	Fe relative to Fe _{total} = 30.28 % (wt.%)
[?] Fe ³⁺	0.249	1.041	29	8.78
[VI] Fe ³⁺	0.500	1.064	67	20.29
[VI] Fe ²⁺	1.196	2.183	4	1.21

* The isomer shift is recorded with respect to α -Fe metal.

small doublet can be unambiguously attributed to Fe²⁺ in an octahedral site.

The principle results of Mössbauer spectroscopy are:

(i) two oxidation states with strongly predominant Fe³⁺, which is 96 % of total Fe, and (ii) two different site occupancies for Fe³⁺.

Thermal analysis

Thermogravimetric analyses (DTG) of samples from Clementine II and Albères were performed in nitrogen. Staněkite from Albères does not show any weight loss. By contrast, the Clementine II material has a total weight loss between 2.6 and 5.0 wt% from 120°C to about 700°C. The weight loss up to 120°C is about 1 wt%. This water content is certainly due to different amounts of impurities of kryzhanovskite. The two phosphates are not resolvable under the binocular microscope, as proved by X-ray powder diffraction patterns.

The DTG curves in air are similar to those obtained in nitrogen. At 970°C staněkite recrystallizes to a phase isostructural with alluaudite *s.l.* and hematite, as confirmed by X-ray diffractometry.

Paragenesis

Clementine II: Six different phosphate-mineral associations have been observed in the Clementine II pegmatite with respect to both (i) the minerals involved and (ii) the Fe/(Fe+Mn) ratio of triphylite and their topotactic alteration products ferrisicklerite (*s.l.*) and heterosite (*s.l.*), respec-

tively (Keller & Von Knorring, 1989). Staněkite is present in three associations.

Association I: The most striking feature of this association is the development of dendrites consisting of ferrisicklerite or heterosite with an Fe/(Fe+Mn) ratio of 0.78. Associated minerals are eosphorite, arrojadite, kryzhanovskite, and late secondary phosphates.

Association II is characterized by ferrisicklerite or heterosite with an Fe/(Fe+Mn) ratio of 0.61 to 0.68. These phosphates are usually developed as nodular masses, but skeletal crystals have also been seen. The associated phosphate minerals are as in association I, but alluaudite is also present.

Association III: Besides triphylite and its Quensel-Mason sequence with a Fe/(Fe+Mn) ratio of 0.59, the frequent occurrence of kryzhanovskite is a typical feature. Additionally, the same alteration products as in association II are developed, together with large amounts of late secondary phosphates in dense, dark-green masses.

Staněkite derives from the alteration of ferrisicklerite and of heterosite, or from the initially crystallized triphylite. However, staněkite has never been seen intergrown with triphylite. If kryzhanovskite occurs, it is present as a rim between staněkite and heterosite.

Albères: At Albères, staněkite is closely associated with ferrisicklerite and heterosite in a triple-junction-type structure. The Fe/(Fe+Mn) ratio (0.75) is the same for the three phosphates, suggesting simultaneous crystallization. In contrast, however, the Fe/(Fe+Mn) ratio for graf-tonite, wyllieite, and rosemaryite, which are also associated with the former phosphates is different (0.63).

The very complex and complicated mineral associations and their probable origin will be

discussed, together with the occurrences in Cameroon, Helikon (Karibib, Namibia) and Cap de Creus (Pyrénées, Spain) in a future publication.

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