

Krásnoite, the fluorophosphate analogue of perhamite, from the Huber open pit, Czech Republic and the Silver Coin mine, Nevada, USA

S. J. MILLS^{1,*}, J. SEJKORA², A. R. KAMPF³, I. E. GREY⁴, T. J. BASTOW⁵, N. A. BALL⁶, P. M. ADAMS⁷, M. RAUDSEPP⁸ AND M. A. COOPER⁶

¹ Geosciences, Museum Victoria, GPO Box 666, Melbourne 3001, Australia

² Department of Mineralogy and Petrology, National Museum Prague, Vaclavské nám. 68, CZ-115 79 Praha 1, Czech Republic

³ Mineral Sciences Department, Natural History Museum of Los Angeles County, 900 Exposition Boulevard, Los Angeles, California 90007, USA

⁴ CSIRO Process Science and Engineering, Box 312, Clayton South, Victoria 3169, Australia

⁵ CSIRO Materials Science and Engineering, Private Bag 33, Rosebank MDC, Clayton, Victoria 3169, Australia

⁶ Department of Geological Sciences, University of Manitoba, Winnipeg, Manitoba R3T 2N2, Canada

⁷ 126 South Helbera Avenue, #2, Redondo Beach, California 90277, USA

⁸ Department of Earth and Ocean Sciences, University of British Columbia, Vancouver, British Columbia V6T 1Z4, Canada

[Received 11 January 2012; Accepted 22 March 2012; Associate Editor: Giancarlo Della Ventura]

ABSTRACT

Krásnoite is a new mineral (IMA2011-040) from the Huber open pit, Krásno ore district, Czech Republic and the Silver Coin mine, Nevada, USA. Krásnoite is the fluorophosphate analogue of perhamite. Krásnoite occurs as compact to finely crystalline aggregates, balls and rosette-like clusters up to 1 mm across. Individual crystals are platy, show a hexagonal outline and can reach 0.1 mm on edge at Krásno and 0.4 mm at Silver Coin. At both localities, krásnoite occurs very late in phosphate-rich paragenetic sequences. Krásnoite crystals are partly transparent with a typically pearly lustre, but can also appear greasy (Krásno) or dull (Silver Coin). The streak is white and the hardness is 5 on the Mohs scale. Crystals are brittle, have an irregular fracture, one imperfect cleavage on {001} and are not fluorescent under SW and LW ultraviolet light. Penetration twinning \perp {001} is common. The density for both Krásno and Silver Coin material is 2.48(4) g cm⁻³, measured by the sink–float method in an aqueous solution of sodium polytungstate. The calculated density is 2.476 g cm⁻³ (Krásno). Krásnoite crystals are uniaxial (+), with $\omega = 1.548(2)$ and $\epsilon = 1.549(2)$ (Krásno) and $\omega = 1.541(1)$ and $\epsilon = 1.543(1)$ (Silver Coin). The simplified formula of krásnoite is: Ca₃Al_{7.7}Si₃P₄O_{23.5}(OH)_{12.1}F₂·8H₂O. Krásnoite is trigonal, space group *P* $\bar{3}$ *m*1, with $a = 6.9956(4)$, $c = 20.200(2)$ Å, $V = 856.09(9)$ Å³ and $Z = 3$. Raman and infrared spectroscopy, coupled with magic-angle spinning nuclear magnetic resonance (MAS–NMR) spectrometry, confirmed the presence of PO₃F, PO₄, SiO₄, H₂O and OH in the crystal structure of krásnoite.

KEYWORDS: krásnoite, perhamite, new mineral, Krásno ore district, Czech Republic, Silver Coin mine, USA, NMR, fluorophosphate.

Introduction

DURING investigations of supergene F-rich phosphate assemblages by two different research groups, one working on the occurrence at the

* E-mail: smills@museum.vic.gov.au
DOI: 10.1180/minmag.2012.076.3.13

abandoned Huber open pit, Krásno ore district, Czech Republic, and the other on that at the Silver Coin mine, Nevada, USA, a number of rare and unusual minerals have been discovered. Collaboration between the groups has already yielded the new mineral iangreyite, $\text{Ca}_2\text{Al}_7(\text{PO}_4)_2(\text{PO}_3\text{OH})_2(\text{OH},\text{F})_{15}\cdot 8\text{H}_2\text{O}$ (IMA2009-087; Mills *et al.*, 2011). Both groups had also previously noted the new mineral reported herein. Sejkora *et al.* (2006a) first reported 13 EMPA analyses, with powder X-ray diffraction data, on unnamed mineral UNK1 from Krásno, which they described as a possible F-analogue of perhamite. The same phase was also noted at the Silver Coin mine, during the investigations which led to the description of meurigite-Na (Kampf *et al.*, 2009).

The mineral is named in honour of the district where it was first discovered, the Krásno ore district, and because it was found to be more abundant at this occurrence than at the Silver Coin mine. In addition, we were able to obtain more and higher quality data from the material from Krásno. Both, however, are considered type localities. The mineral and name have been approved by the IMA-CNMNC (IMA2011-040). The cotype material is housed in the collections of the Department of Mineralogy and Petrology, National Museum Prague, catalogue number PIP 2/2011 (Krásno) and in the collections of Mineral Sciences Department, Natural History Museum of Los Angeles County catalogue numbers 62372 and 62373 (Silver Coin).

Occurrence and paragenesis

Krásno

Samples of krásnoite were found at the abandoned Huber open pit (50°07'21.28" N, 12°47'59.15" E), Krásno ore district near Horní Slavkov, Slavkovský les mountains, western Bohemia, Czech Republic (Sejkora *et al.*, 2006a). Krásnoite occurs in strongly altered areas (Sejkora *et al.*, 2006b), which range in size from 1 cm to 10 cm across. Accumulations of krásnoite up to 3.5 cm across are present; however, the mineral is always intergrown with white to pale yellow supergene fluorapatite. Fluorine-rich crandallite, whitish crystals of kolbeckite, and whitish earthy aggregates of younger generation of isokite are also found with some specimens of krásnoite. Two different mineral assemblages commonly host krásnoite: (1) plimerite (Sejkora *et al.*, 2011), kolbeckite, pharmacosiderite and minerals of the chalcosiderite–turquoise series; and (2) fluellite and milky-

coloured fluorapatite in cavities in a quartz gangue (Sejkora *et al.*, 2006a).

Krásnoite belongs to the last stage of supergene mineralisation at the Huber open pit, where it forms from the breakdown of fluorapatite, triplite and isokite in the presence of acidic groundwaters. The krásnoite–fluorapatite intergrowths are similar to the perhamite–fluorapatite intergrowths found in South Australian phosphate deposits (e.g. Mills, 2003; Dunn and Appleman, 1977), and this suggests that both krásnoite and perhamite may form under the same conditions.

Silver Coin

Krásnoite occurs at the Silver Coin mine (SW¼ sec. 1 and SE¼ sec. 2, T35N, R41E), Valmy, Nevada, USA, as part of a rich secondary phosphate assemblage (e.g. Thomssen and Wise, 2004), which formed on phosphatic argillite wall rocks of the abandoned Pb–Zn–Ag mine. Krásnoite occurs very late in a paragenetic sequence that includes (in approximate order from early to late) quartz, baryte, fluorapatite, goethite, rockbridgeite, cacoxenite, alunite, wardite, turquoise/chalcosiderite, leucophosphite, lipscombite/zinclipcombite, kidwellite, strengite/variscite, iangreyite, krásnoite, meurigite-Na and jarosite (minerals separated by slashes exhibit variations in chemistry between the two species). At the Silver Coin mine, krásnoite is likely to have formed under acidic conditions mainly from the breakdown of primary fluorapatite found within the phosphatic argillite.

Physical and optical properties

Krásno

Krásnoite occurs as compact to finely crystalline aggregates, generally about 0.1 mm across, which are further intergrown, forming millimetre-size clusters (Fig. 1). The crystals are platy, have a hexagonal outline and can reach 0.1 mm on edge (Fig. 2); isolated crystals have not been found. The form {001} is prominent and crystals are bounded by faces of the {100} form. Krásnoite varies in colour from snow white (most common) to pale yellowish white and white with a greenish tint. Crystals are partly transparent with a pearly to greasy lustre, have a white streak and an estimated hardness of 5 on the Mohs scale. Crystals are brittle, have an irregular fracture, one imperfect cleavage on {001}, and are not fluorescent under SW and LW ultraviolet light.

KRÁSNOITE



FIG. 1. Pearly aggregates of krásnoite from Krásno, Czech Republic. The field of view is 4.5 mm.

Penetration twinning \perp {001} is common. The density, measured by the sink–float method in an aqueous solution of sodium polytungstate, is $2.48(4) \text{ g cm}^{-3}$. The calculated density is 2.476 g cm^{-3} , based on the empirical formula and refined unit cell, and is in excellent agreement with the measured density.

Krásnoite crystals are uniaxial (+), with $\omega = 1.548(2)$ and $\varepsilon = 1.549(2)$, measured at 589 nm. Krásnoite crystals are not pleochroic. The Gladstone–Dale compatibility index calculated

for all the data from Krásno is 0.005, which is classed as superior.

Silver Coin

At Silver Coin, krásnoite forms as off-white coloured balls and rosette-like clusters up to about 1 mm across. Within these clusters, hexagonal plates may reach 0.4 mm in diameter, but are exceedingly thin ($\leq 1 \mu\text{m}$ thick) and always intergrown. The crystals have a dull to pearly lustre. The density, measured as described above, is $2.48(4) \text{ g cm}^{-3}$. The indices of refraction, measured in white light, $\omega = 1.541(1)$ and $\varepsilon = 1.543(1)$, are slightly lower than those obtained for the Krásno sample.

Chemical composition

Chemical analyses (60) on krásnoite from Krásno were carried out using an electron microprobe in wavelength-dispersive spectrometry (WDS) mode (Table 1) at 15 kV, 4 nA with a $10 \mu\text{m}$ beam diameter. The elements Sb, V, Co, Ni, U and Bi were sought, but not detected. Peak counting times were 20 s for the major elements and 30 to 60 s for the minor and trace elements. The presence of H_2O and OH was confirmed by Raman and infrared spectroscopy (see below). The empirical formula, based on $(\text{Al} + \text{Fe}) + (\text{Si} + \text{P} + \text{Ti}) + (\text{P} + \text{As}) = 14.70$,

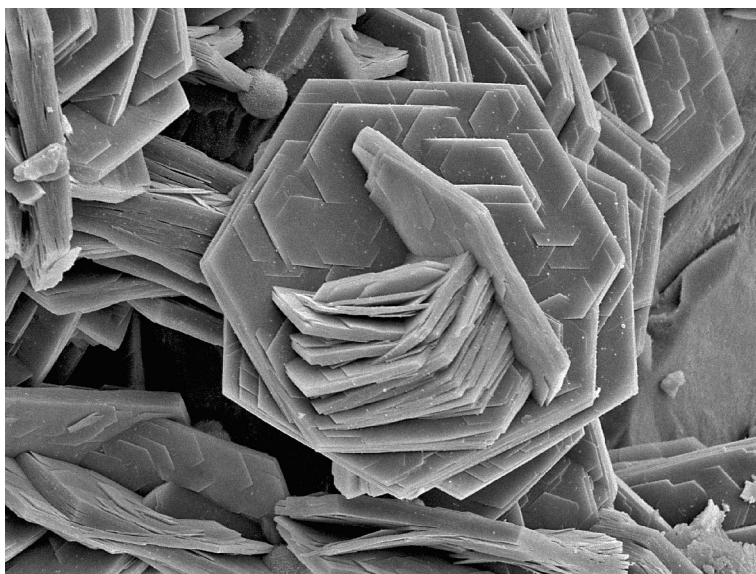


FIG. 2. Photomicrograph of intergrown crystals of krásnoite from Krásno, Czech Republic. The field of view is $80 \mu\text{m}$.

TABLE 1. Chemical composition of krasnoite from Krásno.

Constituent	Mean (wt.%)	Range	SD	Probe standard
Na ₂ O	0.08	0.00–0.16	0.04	albite
K ₂ O	0.21	0.07–0.39	0.07	sanidine
CaO	10.13	7.24–11.88	1.03	andradite
MgO	0.02	0.00–0.07	0.02	olivine
MnO	0.03	0.00–0.11	0.03	spessartine
BaO	0.15	0.00–0.60	0.16	benitoite
SrO	3.19	0.53–8.06	1.77	SrSO ₄
ZnO	0.31	0.04–0.69	0.15	ZnO
PbO	0.04	0.00–0.25	0.06	vanadinite
CuO	0.05	0.00–0.40	0.09	Cu metal
TiO ₂	0.24	0.00–0.55	0.13	titanite
SiO ₂	11.87	9.51–14.49	1.37	sanidine
SO ₃	0.03	0.00–0.14	0.04	baryte
Al ₂ O ₃	29.05	26.46–32.71	1.24	sanidine
Fe ₂ O ₃	0.48	0.01–1.94	0.32	almandine
As ₂ O ₅	0.05	0.00–0.48	0.07	InAs
P ₂ O ₅	22.99	20.51–26.76	1.10	fluorapatite
Cl	0.01	0.02–0.04	0.02	vanadinite
F	2.38	1.84–3.34	0.40	topaz
H ₂ O _{diff}	19.69			
O=Cl	0.0			
O=F	–1.00			
Total	100.00			

These data are an average of 60 analyses, water is calculated by difference, SD is standard deviation.

in line with the formula of perhamite (Mills *et al.*, 2006), Ca₃Al_{7.7}Si₃P₄O_{23.5}(OH)_{14.1}·8H₂O, and with rounding errors, is (Ca_{2.41}Sr_{0.41}K_{0.06}Zn_{0.05}Na_{0.03}Mg_{0.01}Ba_{0.01}Mn_{0.01}Cu_{0.01})_{Σ3.00}(Al_{7.61}Fe_{0.08})_{Σ7.69}(Si_{2.64}P_{0.32}Ti_{0.04})_{Σ3.00}(P_{4.00}As_{0.01})_{Σ4.01}O_{23.57}(OH)_{13.20}F_{1.67}·8H₂O. The simplified formula is Ca₃Al_{7.7}Si₃P₄O_{23.5}(OH)_{12.1}F₂·8H₂O.

The minor element composition of krasnoite is variable. The most variable elements are Sr, and to a lesser extent Ba, with substitution up to ~1 a.p.f.u. Sr (~33:67 Sr:Ca) making most analysed samples Sr-rich krasnoite (Fig. 3). There were no analyses, however, in which Sr exceeded Ca. This type of chemical substitution is not unexpected. The structure of perhamite (Mills *et al.*, 2006) and krasnoite contains a crandallite-like layer with the composition [Ca₂Al₆P₄(OH,F)₁₃O₁₃O_{2/2}]⁺. Within this layer large cations can easily substitute, in a similar way to the crandallite–goyazite solid-solution series (e.g. Cortesogno *et al.*, 1987; Goldberg and Nathan, 1975; Triplehorn and Bohor, 1983; Jambor, 1999). This shows that Sr analogues of both

perhamite and krasnoite could occur, given the right conditions. Semi-quantitative analyses of the Silver Coin krasnoite confirm an almost identical chemistry, including variable Ba and Sr contents.

It is important to note that the F contents in krasnoite are fairly constant at about 1.75±0.25 a.p.f.u. In the 60 analyses of krasnoite undertaken, the limit of F incorporation in krasnoite appears to be 2 a.p.f.u. The structural significance of this is discussed below.

Magic-angle spinning nuclear magnetic resonance spectroscopy

Magic-angle spinning nuclear magnetic resonance (MAS–NMR) spectra of krasnoite from Krásno were recorded on a Bruker Avance 400 spectrometer using a nominal field of 9.395 T, at frequencies of around 161.98 (³¹P), 376.50 (¹⁹F) and 104.26 MHz (²⁷Al), in a probe with a 2.5 mm rotor spinning at 30 kHz (Fig. 4). At this rotation frequency, the innermost spinning side bands were well separated from any spectroscopic

KRÁSNOITE

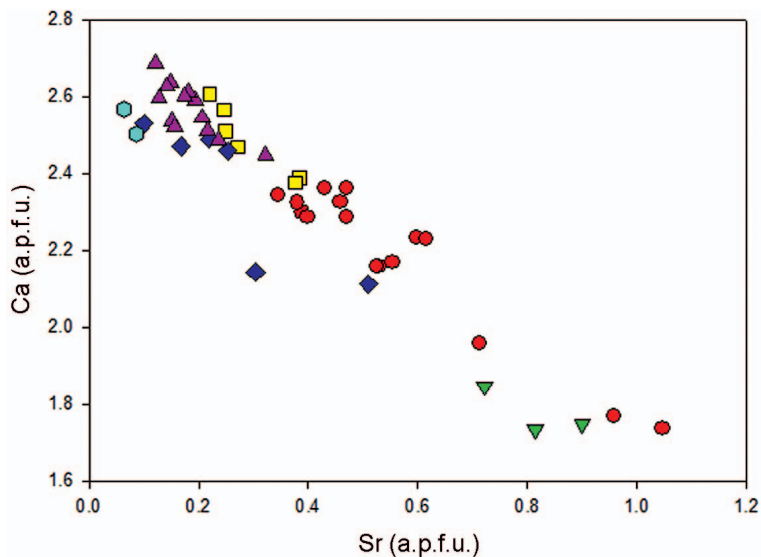


FIG. 3. Strontium concentrations in different samples of krásnoite from Krásno, Czech Republic.

features. The pulse length and pulse sequence repetition time in file acquisition for the three isotopes were 1 μ s and 2 s for ^{31}P , 1 μ s and 5s for ^{19}F and 1 μ s and 0.2 s for ^{27}Al . Care was taken with the repetition times to avoid signal saturation. The reference shift zeros were set using solid $\text{NH}_4\text{H}_2\text{PO}_4$ at 0.9 ppm (with respect to 85% H_3PO_4 at 0 ppm), solid CaF_2 at 0 ppm, and $\text{AlCl}_3(\text{aq})$ at 0 ppm. The sharp spectra for the reference compounds showed no spurious background peaks. The mass of the krásnoite sample was 11.9 mg. Approximately 1000 scans were collected for ^{31}P and ^{19}F and 200 scans for ^{27}Al .

A minor amount of fluorapatite (observed in duplicate runs) was observed in the spectrum; nevertheless, full characterisation was possible. The relatively large mass required for the experiment and the nature of the intergrowths, meant that we were unable to obtain a pure sample. The ^{31}P NMR spectrum shows two independent phosphate atoms (lines 2 and 3) with line 1 due to fluorapatite. The ^{27}Al NMR shows two main lines centred near 50 and 0 ppm. The former is due to AlO_4 tetrahedra and the latter is due to AlO_6 octahedra. Both observations are consistent with the crystal structure of perhamite (Mills *et al.*, 2006). The ^{19}F NMR spectrum indicates that predominantly one site (presumably an OH) is favoured for F substitution (line 1). Lines 3 and 4 appear to be due to minor F substitution in other sites, whereas line 2 is due to the fluorapatite.

Raman and infrared spectroscopy

Raman spectroscopy

Krásnoite from Krásno was investigated using a dispersive Raman spectrometer with confocal optics. The Raman signal was excited by a 532 or 780 nm laser and detected using a multichannel air-cooled CCD camera. The laser power at the sample was limited to 12 mW to avoid possible thermal degradation of the samples. Spectra were recorded between 100 and 1500 cm^{-1} , with a resolution of $\pm 4 \text{ cm}^{-1}$ and a minimum lateral resolution of $\sim 1 \mu\text{m}$ on the sample (Fig. 5). The main bands observed at the following wavelengths, 532 nm (785 nm) are as follows: 1425 (1422), (1289), 1190 (1196), 1091 (1091), 1032 (1032), 1009 (1007), 960 (962), 920 (920), 705 (706), 634 (638), 620 (621), 512 (508), 477 (460), 424 (430), 364 (363), 271, 190 and 143 cm^{-1} . The bands at 1190 and 1090 cm^{-1} are probably due to SiO_4 symmetric stretching vibrations, the band at 1425 cm^{-1} may be due to SiO_4 asymmetric stretching vibrations. Bands at 1009 and 960 cm^{-1} can be assigned to PO_4 symmetric stretching mode ν_1 and the bands at 1091 and 1032 cm^{-1} to the PO_4 asymmetric stretching mode ν_3 (Farmer, 1974). The band at 920 cm^{-1} may be attributed to the PO_3F symmetric stretching mode analogous to that observed in bobdownsite at 923 cm^{-1} (Tait *et al.*, 2011). Bands in the region 500–600 cm^{-1} are likely to be due to a combination of the ν_4 asymmetric

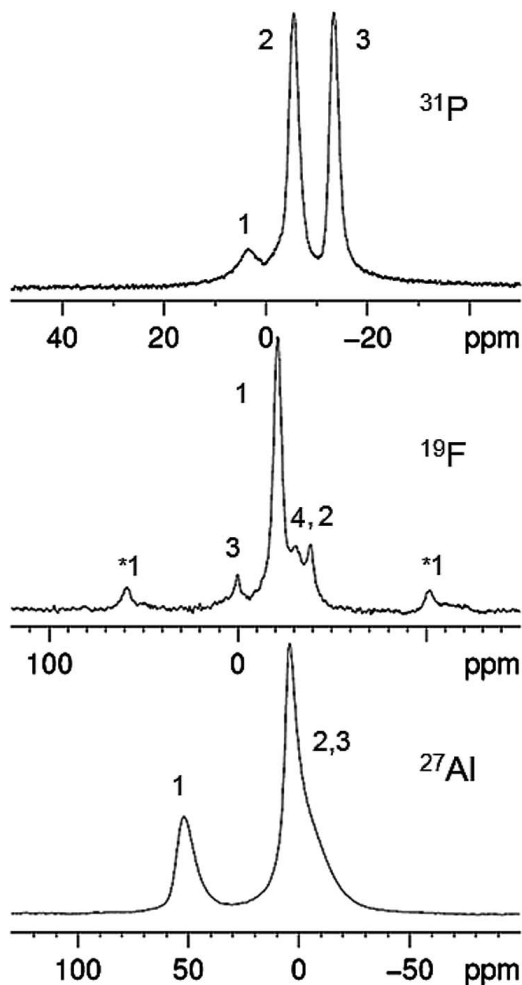


FIG. 4. Solid state NMR spectra of krásnoite from Krásno, Czech Republic.

bending modes for SiO_4 , PO_4 and PO_3F , whereas those in the $400\text{--}500\text{ cm}^{-1}$ region are due to the ν_2 symmetric bending modes (Farmer, 1974; Tait *et al.*, 2011).

Infrared spectroscopy

The infrared spectrum of krásnoite from Krásno was recorded by the micro-diffuse reflectance method (DRIFTS) on a Nicolet Magna 760 FTIR spectrometer (range $4000\text{--}400\text{ cm}^{-1}$, resolution 4 cm^{-1} , 128 scans and Happ–Genzel apodisation). The sample was dispersed in a mixture of KBr without using any pressure. The

Kubelka–Munk units used formally correspond to absorbance values obtained by the conventional KBr disk technique (Fig. 5). The main bands observed are as follows: 3463, 3017, 1741, 1645, 1465, 1453, 1429, 1223, 1175, 1098, 1048, 963, 865, 820, 647, 608, 580, 542 and 467 cm^{-1} . The infrared spectrum confirms the presence of water and hydroxyl ions in the structure (3463, 3017, 1741 and 1645 cm^{-1} ; Farmer, 1974), as well as the PO_3F symmetric stretching mode at 820 cm^{-1} .

Crystallography

The nature of the crystal aggregates and intergrowths with fluorapatite hampered any single crystal investigation of krásnoite. Neither occurrence produced crystals suitable for single-crystal investigations. Instead, only powder X-ray diffraction could be used on one Krásno sample. The pattern was measured using $\text{CuK}\alpha$ radiation on a Philips X'Pert diffractometer. The data were processed using ZDS X-ray analysis software (Ondruš, 1993) and the X-ray powder pattern (Table 2) was indexed on the basis of crystal structure data for perhamite (Mills *et al.*, 2006). Unit-cell parameters were refined by the least-squares program of Burnham (1962). Krásnoite is trigonal, space group $P\bar{3}m1$ with $a = 6.9956(4)$, $c = 20.200(2)\text{ \AA}$, $V = 856.09(9)\text{ \AA}^3$ and $Z = 3$. These cell parameters are slightly smaller than those reported for perhamite ($a = 7.021(1)$ and $c = 20.218(1)\text{ \AA}$; Mills *et al.*, 2006).

As noted above, krásnoite is considered to be isostructural with perhamite. The structure of perhamite consists of ordered blocks of crandalite-type structure, $[\text{Ca}_2\text{Al}_6\text{P}_4(\text{OH},\text{F})_{13}\text{O}_{13}\text{O}_{2/2}]^+$, centred at $z = 0$, intergrown parallel to $\{001\}$ with disordered aluminosilicate structure blocks, $[\text{CaAl}_{1.7}\text{Si}_3\text{O}_{8.5}(\text{OH})_{1.1}\text{O}_{2/2}\cdot 8\text{H}_2\text{O}]^-$, centred at $z = 1/2$, to form a microporous structure containing large channels along $[100]$ (Fig. 6). These channels are bounded by 8-membered rings of 6 tetrahedra (2SiO_4 , 2AlO_4 and 2PO_4) and 2AlO_6 octahedra. Calcium atoms and water molecules are distributed in the $[100]$ channels (Mills *et al.*, 2006).

Although we were unable to undertake a single-crystal study, we can use the information obtained from the chemical composition and spectroscopic methods, along with the known structure of perhamite, to deduce the role of F in the krásnoite structure. Considering a maximum of 2 F a.p.f.u. in the structure, and assuming that F predominantly occupies a single site, as confirmed by the MAS-NMR, 'O sites' (in the perhamite structure

KRÁSNOITE

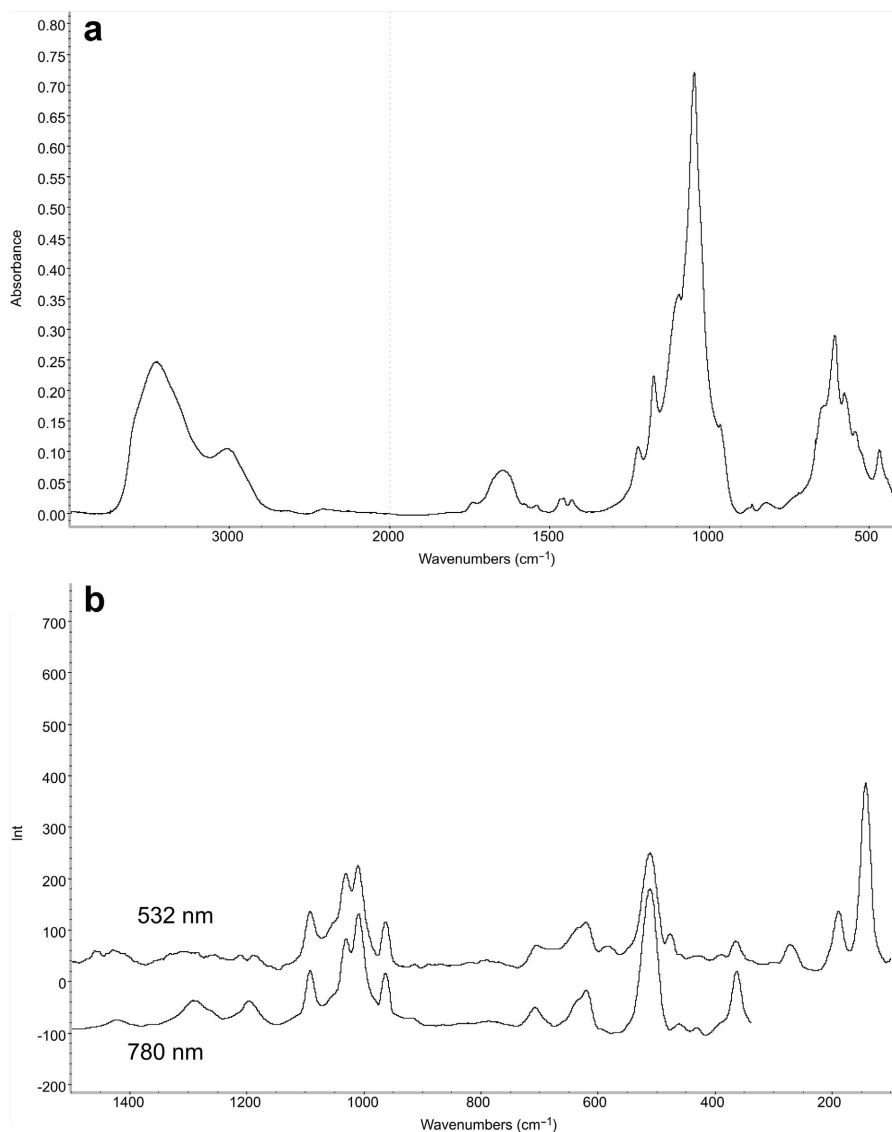


FIG. 5. Infrared (top) and Raman spectra (bottom) for krásnoite from Krásno, Czech Republic.

type) with a multiplicity of 2 are possible candidates. The sites with the correct multiplicity are O2, O6, O10 and Ow1. The Ow1 site can be discounted as it does not bond to any cations; O6 and O10 can also be discounted as they have formal valences of 2⁻, so they must be O²⁻ rather than OH or F. The O2 site is thus the only likely site and it bonds to P. In krásnoite, this creates a PO₃F tetrahedron and confirms the band assignments made by Raman and infrared spectroscopy.

Following the rules for formal group nomenclature for minerals as provided by Mills *et al.* (2009), the perhamite group is hereby established and includes perhamite and krásnoite as its only members.

Identifying krásnoite and other occurrences

Krásnoite is an extremely difficult mineral to identify visually. At both Krásno and the Silver

TABLE 2. Powder X-ray diffraction data for krásnoite from Krásno.

d_{obs} (Å)	hkl	d_{calc} (Å)	h	k	l	d_{obs} (Å)	hkl	d_{calc} (Å)	h	k	l
20.186	97	20.200	0	0	1	1.7947	9	1.7937	2	1	$\bar{7}$
10.100	23	10.100	0	0	2			1.7937	1	2	7
6.736	100	6.733	0	0	3	1.7484	64	1.7489	2	2	0
6.051	47	6.058	1	0	0	1.6808	15	1.6806	2	0	10
5.800	67	5.803	1	0	1	1.6546	49	1.6545	3	0	7
		5.803	0	1	1	1.6030	11	1.6029	2	1	$\bar{9}$
5.190	20	5.195	1	0	2			1.6029	1	2	9
5.047	37	5.050	0	0	4	1.5783	4	1.5771	0	3	8
4.043	15	4.040	0	0	5			1.5771	3	0	8
3.872	15	3.879	1	0	4	1.5520	7	1.5514	1	3	$\bar{5}$
		3.879	0	1	4			1.5514	3	1	5
3.496	60	3.498	1	1	0	1.5173	17	1.5168	1	1	12
3.441	11	3.446	1	1	1			1.5168	1	1	$\bar{1}2$
		3.446	1	1	$\bar{1}$	1.5158	8	1.5148	1	2	$\bar{1}0$
3.361	27	3.367	0	0	6			1.5148	2	1	10
3.103	57	3.104	1	1	3	1.5041	7	1.5034	3	1	6
		3.104	1	1	$\bar{3}$			1.5034	1	3	$\bar{6}$
2.9940	41	2.9957	2	0	1	1.4965	1	1.4978	0	4	2
		2.9957	0	2	1	1.4957	12	1.4956	2	2	$\bar{7}$
2.9420	56	2.9428	0	1	6			1.4956	2	2	7
		2.9428	1	0	6	1.4780	11	1.4777	0	4	3
2.8997	50	2.9015	2	0	2	1.4710	51	1.4714	0	2	12
		2.9015	0	2	2	1.4520	7	1.4521	1	3	$\bar{7}$
2.8864	31	2.8857	0	0	7			1.4521	3	1	7
2.8730	87	2.8754	1	1	4	1.4374	10	1.4377	2	2	8
		2.8754	1	1	$\bar{4}$			1.4377	2	2	$\bar{8}$
2.7633	73	2.7625	2	0	3	1.3985	6	1.3989	3	1	$\bar{8}$
2.6442	33	2.6444	1	1	5			1.3989	1	3	8
		2.6444	1	1	$\bar{5}$	1.3824	30	1.3825	0	2	13
2.6050	36	2.6052	0	1	7	1.3584	12	1.3586	0	3	11
		2.6052	1	0	7	1.3450	4	1.3451	1	3	9
2.5993	14	2.5977	2	0	4			1.3451	3	1	$\bar{9}$
2.5236	59	2.5250	0	0	8	1.3223	11	1.3220	1	4	0
2.4247	25	2.4236	2	0	5			1.3220	4	1	0
		2.4236	0	2	5	1.2976	5	1.2973	4	1	$\bar{3}$
2.3295	48	2.3306	1	0	8			1.2973	1	4	3
		2.3306	0	1	8			1.2973	4	1	3
2.2860	8	2.2898	2	1	0			1.2973	1	4	$\bar{3}$
		2.2898	1	2	0	1.2933	8	1.2930	0	3	12
2.2744	5	2.2753	2	1	1	1.2792	7	1.2789	1	4	4
		2.2753	1	2	$\bar{1}$			1.2789	1	4	$\bar{4}$
2.2504	51	2.2518	2	0	6			1.2789	4	1	$\bar{4}$
		2.2518	0	2	6			1.2789	4	1	4
2.2313	15	2.2332	1	2	2	1.2563	6	1.2565	4	1	$\bar{5}$
		2.2332	2	1	$\bar{2}$			1.2565	4	1	5
2.1676	21	2.1679	1	2	3			1.2565	1	4	5
		2.1679	2	1	$\bar{3}$			1.2565	1	4	5
2.1042	75	2.1046	1	0	9	1.2316	9	1.2315	0	3	13
2.0476	20	2.0473	1	1	8	1.2178	11	1.2176	2	3	8
		2.0473	1	1	$\bar{8}$			1.2176	3	2	$\bar{8}$
2.0179	10	2.0194	3	0	0			1.2176	3	2	8
1.9921	15	1.9921	1	2	$\bar{5}$			1.2176	2	3	$\bar{8}$
		1.9921	2	1	5	1.1888	5	1.1892	3	1	$\bar{1}2$
1.9338	56	1.9343	0	3	3			1.1892	1	3	12
1.9163	18	1.9163	1	0	10	1.1818	9	1.1817	3	2	9
1.8754	30	1.8751	0	3	4			1.1817	2	3	9
1.8349	55	1.8363	0	0	11	1.1661	11	1.1659	3	3	0
1.8060	15	1.8063	0	3	5						

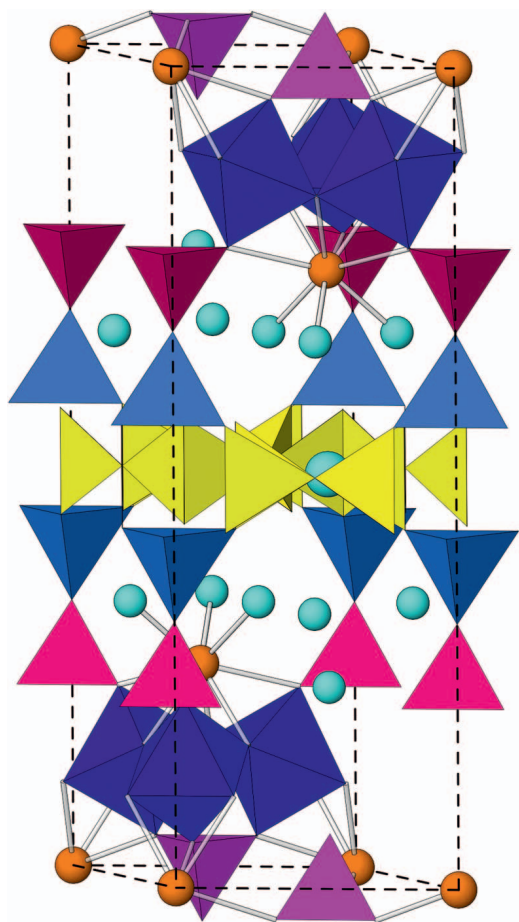


FIG. 6. The hypothetical crystal structure of krásnoite based on the structure of perhamite (Mills *et al.*, 2006). The Ca atoms are orange spheres; PO_3F tetrahedra are light pink; PO_4 tetrahedra are dark pink; AlO_6 octahedra are dark blue; AlO_4 tetrahedra are light blue; SiO_4 tetrahedra are yellow and O atoms of the water molecules are cyan spheres.

Coin mine, krásnoite, iangreyite, perhamite and crandallite are very similar in appearance. Krásnoite and perhamite can be distinguished from iangreyite and crandallite by their PXRD patterns, and, in particular, by the d spacing of the (001) reflection. Krásnoite can then be differentiated from perhamite by the presence of F.

During our investigations, we also found a third locality for krásnoite at the Utahlite claim, Lucin, Box Elder County, Utah, USA (41°20'N, 113°54'W). As with iangreyite, we suspect that

further occurrences of krásnoite will be found at phosphate deposits rich in F around the world.

Acknowledgements

Reviewers Francesco Capitelli and Andre-Mathieu Franolet provided helpful comments on the manuscript and are thanked. Part of this work was supported financially by the Ministry of Culture of the Czech Republic (DKRVO National Museum, Prague) to JS. The remainder of this study was funded by the John Jago Trelawney Endowment to the Mineral Sciences Department of the Natural History Museum of Los Angeles County.

References

- Burnham, C.W. (1962) Lattice constant refinement. *Carnegie Institute Washington Year Book*, **61**, 132–135.
- Cortesogno, L., Gaggero, L. and Lucchetti, G. (1987) Phosphate mineralizations in a Permo-Triassic sequence (Giogo di Toirano, Italy). *Neues Jahrbuch für Mineralogie, Monatshefte*, **1987**, 305–313.
- Dunn, P.J. and Appleman, D.E. (1977) Perhamite, a new calcium aluminium silico-phosphate mineral, and a re-examination of viseite. *Mineralogical Magazine*, **41**, 437–442.
- Farmer, V.C. (1974) *The Infrared Spectra of Minerals*. Mineralogical Society Monograph, **4**. Mineralogical Society of Great Britain & Ireland, London, 539 pp.
- Goldberg, P.S. and Nathan, Y. (1975) The phosphate mineralogy of ele-Tabun cave, Mount Carmel, Israel. *Mineralogical Magazine*, **40**, 253–258.
- Jambor, J.L. (1999) Nomenclature of the alunite supergroup. *The Canadian Mineralogist*, **37**, 1323–1341.
- Kampf, A.R., Adams, P.M., Kolitsch, U. and Steele, I.M. (2009) Meurigite-Na, a new species, and the relationship between phosphofibrite and meurigite. *American Mineralogist*, **94**, 720–727.
- Mills, S.J. (2003) A note on perhamite from the Moculta (Klemms) phosphate quarry, South Australia. *Australian Journal of Mineralogy*, **9**, 43–45.
- Mills, S., Grey, I., Mumme, G. and Bordet, P. (2006) The crystal structure of perhamite. *Mineralogical Magazine*, **70**, 201–209.
- Mills, S.J., Hatert, F., Nickel, E.H. and Ferraris, G. (2009) The standardisation of mineral group hierarchies: application to recent nomenclature proposals. *European Journal of Mineralogy*, **21**, 1073–1080.
- Mills, S.J., Kampf, A.R., Sejkora, J., Adams, P.M.,

- Birch, W.D. and Plášil, J. (2011) Iangreyite: a new secondary phosphate closely related to perhamite. *Mineralogical Magazine*, **75**, 327–336.
- Ondruš, P. (1993) ZDS – a computer program for analysis of X-ray powder diffraction patterns. *Materials Science Forum*, **133–136**, 297–300.
- Sejkora, J., Škoda, R. and Ondruš, P. (2006a) New naturally occurring mineral phases from the Krásno-Horní Slavkov area, western Bohemia, Czech Republic. *Journal of the Czech Geological Society*, **51**, 159–187.
- Sejkora, J., Škoda, R., Ondruš, P., Beran, P. and Süsner, C. (2006b) Mineralogy of phosphate accumulations in the Huber stock, Krásno ore district, Slavkovský les area, Czech Republic. *Journal of the Czech Geological Society*, **51**, 103–147.
- Sejkora, J., Plášil, J. and Filip, J. (2011) Plimerite from Krásno near Horní Slavkov ore district, Czech Republic. *Journal of Geosciences*, **56**, 215–229.
- Tait, K.T., Barkley, M.C., Thompson, R.M., Origlieri, M.J., Evans, S.H., Prewitt, C.T. and Yang, H. (2011) Bobdownsite, a new mineral species from the Big Fish River, Yukon, Canada, and its structural relationship with whitlockite-type compounds. *The Canadian Mineralogist*, **49**, 1065–1078.
- Thomssen, D. and Wise, W.S. (2004) Special list: Silver Coin Mine, Iron Point district, Edna Mountains, Humboldt Co., Nevada, USA. *International Micromounter's Journal*, **13**, 7–8.
- Triplehorn, D.M. and Bohor, B.F. (1983) Goyazite in kaolinitic altered tuff beds of Cretaceous age near Denver, Colorado. *Clays and Clay Minerals*, **31**, 299–304.