

iangreyite:

a new secondary phosphate mineral closely related to perhamite

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ABSTRACT

Iangreyite, ideally $\text{Ca}_2\text{Al}_7(\text{PO}_4)_2(\text{PO}_3\text{OH})_2(\text{OH},\text{F})_{15}\cdot 8\text{H}_2\text{O}$, is a new mineral (IMA2009–087) from the Silver Coin mine, Nevada, USA and the Krásno ore district, Horní Slavkov, Czech Republic. At Silver Coin, iangreyite occurs as thin, colourless to white or cream, hexagonal tablets up to 0.4 mm in diameter and 0.02 mm thick associated with meurigite-Na, plumbogummite, kidwellite, lipscombite, strengite, chalcociderite, wardite, leucophosphite, wavellite, goethite, barite, quartz and F-rich perhamite. At Krásno, white, yellowish or light pink iangreyite coatings consist of 0.3 mm wide clusters of minute and very thin intergrown tabular crystals with a maximum diameter of 0.2 mm. Individual iangreyite crystals are transparent with a vitreous lustre, while iangreyite clusters tend to be pearly and translucent. The estimated hardness is 3 on the Mohs scale, the fracture is irregular and the mineral is non-fluorescent under SW and LW ultraviolet light. Individual crystals are somewhat flexible and there is perfect cleavage on {001}. The density (Silver Coin), measured by the sink-float method in an aqueous solution of sodium polytungstate, is $2.46(3) \text{ g/cm}^3$, while the calculated density is 2.451 g/cm^3 . Crystals from Silver Coin are uniaxial (+), with the indices of refraction: $\omega = 1.544(2)$ and $\epsilon = 1.554(2)$, measured in white light, and are non-pleochroic. The empirical formula for iangreyite from Silver Coin (calculated on the basis of 39 anions per formula unit) is: $\text{Ca}_{1.42}\text{K}_{0.22}\text{Na}_{0.09}\text{Ba}_{0.03}\text{Sr}_{0.01}\text{Al}_{6.51}\text{Mg}_{0.09}\text{Fe}_{0.02}\text{Cu}_{0.01}\text{Zn}_{0.01}\text{P}_{3.81}\text{F}_{5.24}\text{H}_{30.21}\text{O}_{33.76}$, while the empirical formula from Krásno is: $\text{Ca}_{2.15}\text{K}_{0.10}\text{Na}_{0.01}\text{Ba}_{0.02}\text{Sr}_{0.12}\text{Al}_{6.28}\text{Mg}_{0.01}\text{Fe}_{0.12}\text{Cu}_{0.08}\text{Zn}_{0.01}\text{P}_{3.64}\text{Si}_{0.43}\text{F}_{4.65}\text{H}_{29.62}\text{O}_{34.35}$. Iangreyite is trigonal, space group $P321$ and $Z = 1$, with the unit-cell parameters (Silver Coin): $a = 6.988(1)$, $c = 16.707(3) \text{ Å}$ and $V = 706.5(2) \text{ Å}^3$ and (Krásno): $a = 6.989(1)$, $c = 16.782(4) \text{ Å}$ and $V = 709.8(2) \text{ Å}^3$. The structure of iangreyite, modelled from powder data, consists of blocks of the crandallite-type structure that are interconnected along c via corner-sharing of crandallite-block PO_4 tetrahedra with $\text{AlO}_2(\text{OH})_3$ bipyramids. This linkage generates large channels along [110] bounded by 10-member rings of octahedra, tetrahedra and trigonal bipyramids, that are occupied by Ca and water molecules.

KEYWORDS: iangreyite, perhamite, crystal structure, alunite supergroup, new mineral, Silver Coin mine, USA, Krásno ore district, Czech Republic.

Introduction

THE new mineral described here was recognized independently by two different research groups at two very different deposits, but in quite similar

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mineral assemblages. The F-rich phosphate occurrences at the Silver Coin mine, Humboldt County, Nevada, USA and the Krásno ore district, Horní Slavkov, Slavkovský les area, Czech Republic, have each yielded a variety of well formed secondary phosphate species.

In their description of the new mineral *meurigite*-Na from the Silver Coin mine, Kampf *et al.* (2009) reported it to be associated with F-rich *crandallite*, possibly representing the F-analogue of the species. Sejkora *et al.* (2006a) reported on eleven probable new species from Krásno, one of which, “UNK4”, they noted to be an F-rich mineral related to *crandallite*. In this paper, both groups have combined their efforts to describe this phase as the new mineral *iangreyite*.

The mineral is named in honour of Dr Ian Edward Grey (b. 1944), formerly Chief Research Scientist at CSIRO Minerals, Melbourne, Australia, for his contributions to mineralogy, crystallography and the minerals-processing industry. Recently, Dr Grey's expertise was key to solving a number of unique crystal-chemical problems related to alunite-supergroup members such as *kolitschite* (Grey *et al.*, 2008; Mills *et al.*, 2008), *kintoreite* (Grey *et al.*, 2009) and *jarosite* (Scarlett *et al.*, 2010), as well the structure of *perhamite* (Mills *et al.*, 2006). The mineral and name have been approved by the IMA-CNMNC (IMA2009–087). Because no single specimen provided all of the data for the description, there is no specimen that qualifies as the holotype. However, two cotype specimens from the Silver Coin mine are housed in the collections of Mineral Sciences Department, Natural History Museum of Los Angeles County, catalogue numbers 57661 and 62519, and one from Krásno in the collections of the Department of Mineralogy and Petrology, National Museum Prague, catalogue number PIP 20/2009.

Occurrence and paragenesis

Silver Coin mine

Iangreyite occurs at the Silver Coin mine (SW¼ sec. 1 and SE¼ sec. 2, T35N, R41E), Valmy, Iron Point district, Humboldt County, Nevada, USA. The Silver Coin mine was worked between 1918 and 1924 producing 693.5 dry tons of ore containing 30,854 ounces of silver, or an average of 44.49 ounces per ton. The ore also contained a little lead and about 0.02 ounces of gold per ton (Vanderburg, 1988). The workings consist of a number of shallow shafts, open cuts,

and surface trenches, totalling ~370 m. The principal working is the Silver Coin shaft, inclined at ~30° and 50 m deep.

The host rocks for the Pb-Zn-Ag-containing veins exploited by the Silver Coin mine are thin-bedded *quartzite*, *argillite*, and phosphatic *argillite* of late Palaeozoic age (Vanderburg, 1988). Veins consisting of *quartz*, *barite*, *pyrite*, *argentiferous galena* and *sphalerite* filled a fault zone and associated fractures. Upon exposure to oxygenated vadose water, the *pyrite* and other sulphide minerals oxidized to acidic fluids. These solutions leached P and Al from the *argillite* wall rocks leading to the formation of the prolific secondary phosphate assemblage that precipitated in fractures and bedding planes.

At the Silver Coin mine, *iangreyite* is associated with several other phosphates as part of this phosphate assemblage (Thomssen and Wise, 2004) including: *meurigite*-Na (Kampf *et al.*, 2009), *plumbogummite*, *kidwellite*, *lipscombite*, *strengite*, *chalcosiderite*, *wardite*, *leucosphite*, *wavellite*, *goethite*, *barite*, *quartz* and F-rich *perhamite*. The Silver Coin mine is also the type locality for *zinclipscombite* (Chukanov *et al.*, 2006).

Iangreyite appears to be a low-temperature alteration product of F-rich *perhamite*, where Al and Si have been leached selectively from the structure. The presence of F-rich *perhamite* at both localities suggests that this leaching process has not been pervasive over all of the phosphatic secondary zones. Other possible mechanisms which may produce *iangreyite* include the dissolution of primary phosphates such as *fluorapatite*. It is also possible that further leaching of *iangreyite* could produce *crandallite* ($\pm$ F). *Iangreyite* forms in complex phosphate assemblages rich in Ca, Fe, Al, Na and F.

Krásno

Iangreyite occurs at the Krásno ore district near Horní Slavkov, Slavkovský les area, Czech Republic (cotype locality). The Krásno ore district belongs to one of the most important areas of tin and tungsten mining in the Czech Republic (Beran and Sejkora, 2006). The district is represented by greisen mineralization in several granite cupolas of the large Krušné hory (Erzgebirge) granite batholith underlying metamorphic rock (mainly gneisses).

The largest Sn-deposit of this district is the Huber stock. In the past, it was mined *via* the

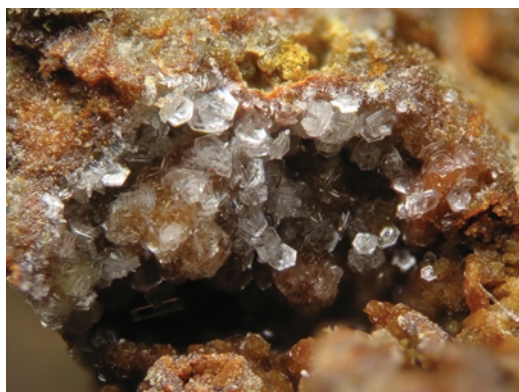


FIG. 1. Hexagonal tablets of iangreyite with brown plumbogummite from Silver Coin. Field of view = 3 mm across. Photograph and specimen, Jean-Marc Johannot.

Huber open pit and the Huber (Stannum) shaft down to 200 m under the surface (5th level at 425 m a.s.l.). The stock is bell-shaped in section or similar to a blunt cone. At the 3rd level (100 m beneath the surface), the stock is 200 m × 100 m in cross-section, while at the 4th level (150 m beneath the surface) the stock extends NE–SW and is ~400 m × 250 m in cross-section. The Huber stock consists mostly of autometamorphosed Li-mica-topaz granite with variable degrees of greisenization (Beran and Sejkora, 2006).

Iangreyite samples were found at the 5th level of the Huber shaft (50°07'27.93''N, 12°48'14.35''E), at the well documented phosphate accumulation (Sejkora *et al.*, 2006b). This accumulation consists of dominant fluorapatite and triplite aggregates from 10 cm to 1 m in size, located in white quartz in the Huber stock. Aggregates of dark Fe-Mn phosphates with

predominant frondelite occur along contacts of this phosphate accumulation with white quartz and cavernous corroded portions carrying younger phosphates (iangreyite, strengite and minerals of the chalcosiderite–turquoise series). Iangreyite from Krásno was originally described as unnamed mineral phase UNK4 by Sejkora *et al.* (2006a).

At Krásno, the associated minerals include abundant younger, white-to-pink fluorapatite and, locally, green aggregates of minerals of the chalcosiderite–turquoise series (Sejkora *et al.*, 2006a). F-rich perhamite also occurs at Krásno, but was not observed in close association with iangreyite; F-rich perhamite-containing samples originated from the supergene, strongly altered phosphate accumulations from the abandoned open pit at Huber stock.

Physical and optical properties

Silver Coin

At Silver Coin, iangreyite occurs as thin, colourless to white or cream, hexagonal tablets up to 0.4 mm in diameter and 0.02 mm thick (Fig. 1). The forms observed are {001} and {100}. Tablets are often warped and intergrown in subparallel stacks similar to those observed for perhamite, where the growth direction occurs along a vector slightly off from a direction perpendicular to the *c* axis (Fig. 2). Individual crystals are transparent with a vitreous lustre, while iangreyite clusters tend to be pearly and translucent. The estimated hardness of iangreyite is 3 on the Mohs scale, the fracture is irregular and the mineral is non-fluorescent under SW and LW ultraviolet light. Individual crystals are somewhat flexible and there is perfect cleavage on {001}. The calculated density, measured by the sink-float method in an aqueous solution of sodium polytungstate, is 2.46(3) g/cm³, while the calculated density is

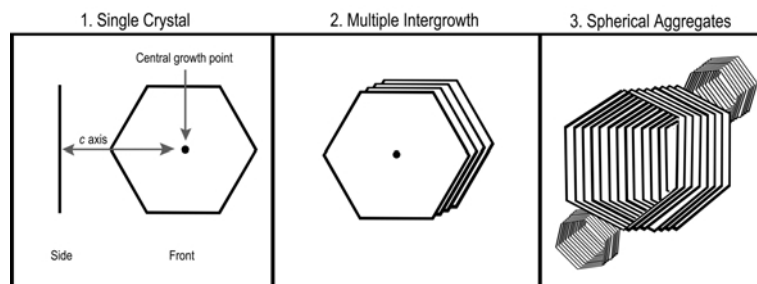


FIG. 2. Schematic diagram of the formation of intergrowth and aggregates of iangreyite and perhamite crystals.

2.451 g/cm³, using the empirical formula and single-crystal unit-cell data. Chemically, iangreyite does not react with or dissolve in 1 M hydrochloric, nitric or 0.5 M sulphuric acid.

Iangreyite crystals from Silver Coin are uniaxial (+), with the indices of refraction: $\omega = 1.544(2)$ and $\epsilon = 1.554(2)$, measured in white light. Iangreyite crystals are non-pleochroic. The Gladstone-Dale compatibility index (Mandarino, 1981) is 0.010, classed as superior.

Krásno

At Krásno, iangreyite occurs as crystalline coatings 2.5 mm $\times$ 3 cm in size in an irregular cavity of brownish fluorapatite (Sejkora *et al.*, 2006a). The surface of iangreyite coatings is formed by 0.3 mm long clusters of minute and very thin intergrown tabular crystals with a maximum diameter of 0.2 mm (Fig. 3). The iangreyite aggregates are soft and very brittle with white, yellowish or light pink colour and pearly lustre; individual transparent to translucent crystals have a vitreous lustre.

Chemical composition

Samples of iangreyite from both occurrences were analysed using a Cameca SX-100 electron microprobe (joint laboratory of electron microscopy and microanalysis of Masaryk University and the Czech Geological Survey, Brno) operating in the wavelength-dispersion mode with an accelerating voltage of 15 kV, a specimen current of 4 nA, and a beam diameter of 3 μ m. The following lines and standards were used: $K\alpha$: albite (Na), sanidine

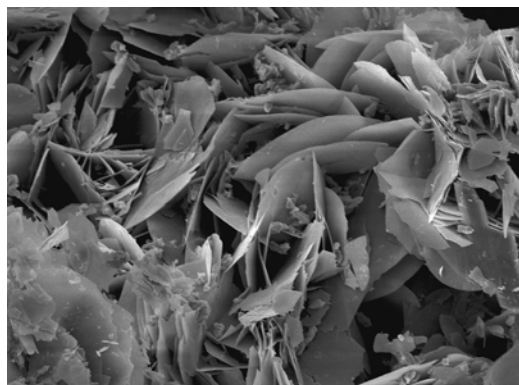


FIG. 3. Intergrown crystals of iangreyite from Krásno. Field of view = 0.3 mm across.

(K), Mg₂SiO₄ (Mg), grossular (Al), almadin (Si), fluorapatite (Ca and P), hematite (Fe), spessartine (Mn), gahnite (Zn), Cu (Cu), SrSO₄ (Sr), NaCl (Cl), topaz (F); $L\alpha$: lammerite (As), SrSO₄ (Sr); $L\beta$: benitoite (Ba). Peak counting times (CT) were 20 s for the main elements and 60 s for the minor elements; CT for each background was half of peak time. The raw intensities were converted to the concentrations automatically using the 'PAP' (Pouchou and Pichoir, 1985) matrix-correction software. There was insufficient material available for direct determination of H. The presence of H₂O and OH, and the absence of CO₃ was confirmed by infrared (IR) and Raman spectroscopy (Fig. 4). Analytical data are given in Table 1.

The empirical formula for iangreyite from Silver Coin (calculated on the basis of 39 anions per formula unit) is: Ca_{1.42}K_{0.22}Na_{0.09}Ba_{0.03}Sr_{0.01}Al_{6.51}Mg_{0.09}Fe_{0.02}Cu_{0.01}Zn_{0.01}P_{3.81}F_{5.24}H_{30.21}O_{33.76}. The ideal formula, which takes into consideration the crystal-structure model is: Ca₂Al₇(PO₄)₂(PO₃OH)₂(OH,F)₁₅·8H₂O, with grouping of the phosphate and hydrogen phosphate ions in line with the structural results reported below. The formula (also confirmed by single-crystal structure analysis) Ca₂Al₇(PO₄)₂(PO₃OH)₂(OH)₁₀F₅·8H₂O requires CaO 10.58, Al₂O₃ 33.66, P₂O₅ 26.78, F 8.96, H₂O 23.80, F = O −3.77, total 100.00 wt.%.

The empirical formula (calculated on the basis of 39 anions) for iangreyite from Krásno is: Ca_{2.15}K_{0.10}Na_{0.01}Ba_{0.02}Sr_{0.12}Al_{6.28}Mg_{0.01}Fe_{0.12}Cu_{0.08}Zn_{0.01}P_{3.64}Si_{0.43}F_{4.65}H_{29.62}O_{34.35}. We note that the cation content for the Krásno iangreyite is slightly larger than that for Silver Coin. This larger cation incorporation is accompanied by Si-for-P exchange to maintain charge neutrality. This excess cation content also contributes to expansion of the *c* axis seen in the Krásno sample (see below).

Crystallography

It was not possible to complete a full single-crystal structure investigation due to the quality of the crystals; several twinned individuals were always present. A unit cell was obtained on Silver Coin iangreyite using a Rigaku R-Axis Rapid II large area curved imaging plate microdiffractometer with monochromatized Mo- $K\alpha$ radiation on a multiply twinned crystal of dimensions 170 μ m $\times$ 120 μ m $\times$ 15 μ m. This cell was used as the basis for refinement of the powder data

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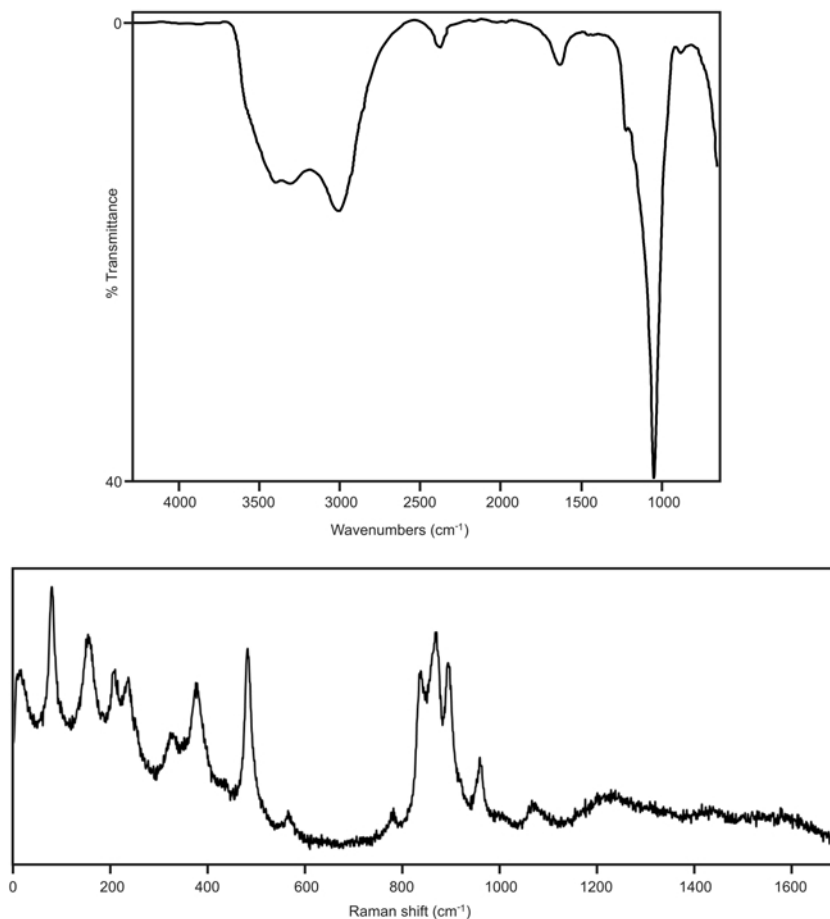


FIG. 4. IR (upper) and Raman (lower) spectra of iangreyite from Silver Coin.

(collected on the same instrument, shown below). Iangreyite is trigonal, space group $P321$, with the unit-cell parameters: $a = 6.988(1)$, $c = 16.707(3)$ Å, $V = 706.5(2)$ Å³ and $Z = 1$. The X-ray powder diffraction data for iangreyite from Silver Coin and Krásno (Bruker D8 Advance diffractometer with the LynxEye 1D detector) are presented in Table 2. The refined cell parameters for Krásno iangreyite are: $a = 6.989(1)$, $c = 16.782(4)$ Å, $V = 709.8(2)$ Å³ and $Z = 1$.

The crystal structure was solved using crystal-chemical reasoning, based on the close geometrical relationship of the unit cell to that for perhamite. It was noticed that the powder diffraction pattern showed a close resemblance to that of perhamite [$P321$, with $a = 7.021$, $c = 20.218$ Å] (Mills *et al.*, 2006), but with a shift to higher angles of the (00 l) reflections, corre-

sponding to a decrease in c from 20.218 Å in perhamite to 16.713 Å in iangreyite (Table 2). Its structure consists of blocks of crandallite-type structure (Blount, 1974) alternating with aluminosilicate blocks containing corner-connected AlO_4 and SiO_4 tetrahedra. Removal of the SiO_4 tetrahedra from the aluminosilicate blocks and replacement of pairs of AlO_4 tetrahedra centred at (0,0,0.4) by $AlO_2(OH)_3$ trigonal bipyramids centred at (0,0,½) gave the observed c -axis periodicity for iangreyite and a good match to the powder XRD pattern. Coordinates for the crandallite-block atoms were obtained by scaling the perhamite coordinates by the ratio of the c cell parameters (Table 3). Difference-Fourier maps were used to locate Ca atoms and water molecules in the large cavities in the structure. Complete atom coordinates for iangreyite are given in

TABLE 1. Analytical data for iangreyite.

	Krásno*	Standard dev.	Silver Coin*	Standard dev.	Probe standard
Na ₂ O	0.04	0.04	0.27	0.05	Albite
K ₂ O	0.45	0.17	1.01	0.20	Sanidine
CaO	11.28	1.29	7.62	0.42	Fluorapatite
FeO	0.82	1.92	0.16	0.04	Hematite
BaO	0.26	0.23	0.45	0.23	Benitoite
SrO	1.13	0.36	0.10	0.11	SrSO ₄
MgO	0.04	0.02	0.34	0.14	Mg ₂ SiO ₄
PbO	0.04	0.05	0.00	0.00	Anglesite
CuO	0.06	0.08	0.06	0.06	Cu metal
MnO	0.00	0.03	0.00	0.00	Spessartine
ZnO	0.05	0.05	0.10	0.09	Gahnite
Al ₂ O ₃	29.55	2.80	31.80	1.26	Grossular
SiO ₂	2.42	2.30	0.19	0.08	Almandine
As ₂ O ₅	0.04	0.06	0.00	0.00	Lammerite
P ₂ O ₅	24.05	2.14	25.90	0.61	Fluorapatite
SO ₃	0.05	0.05	0.40	0.10	SrSO ₄
F	8.23	1.35	9.53	0.53	Topaz
Total	78.52		77.94		
–F=O	–3.46		–2.81		
	75.06		75.13		
H ₂ O _{diff}	24.96		24.87		

* Krásno average of 12 analyses, Silver Coin average of seven.

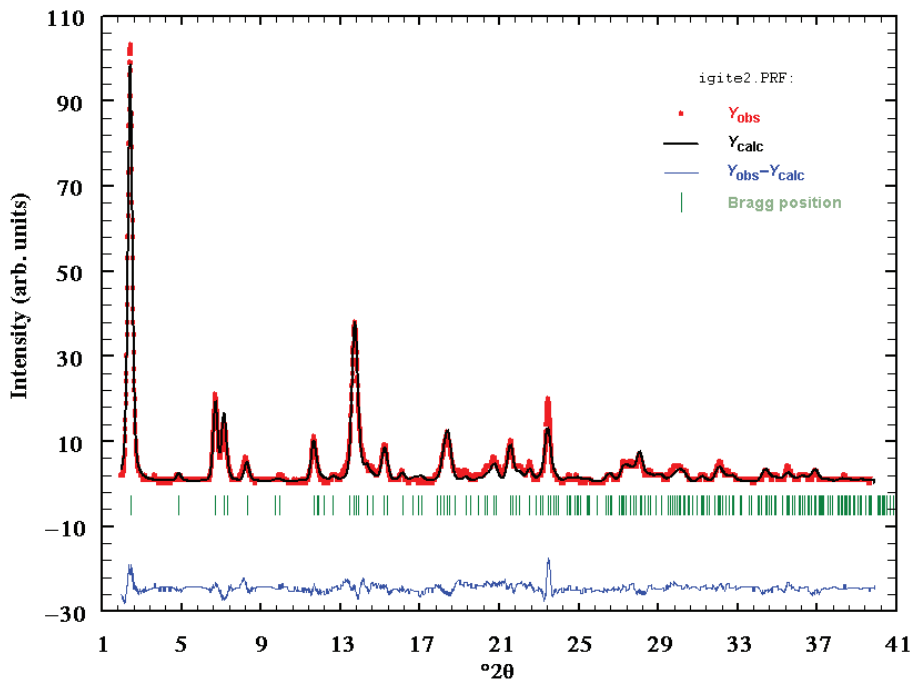


FIG. 5. Rietveld plot of iangreyite.

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TABLE 2. Powder XRD data for iangreyite from Silver Coin and Krásno.

Silver Coin					Krásno							
<i>hkl</i>	<i>d</i> _{obs}	<i>d</i> _{calc}	<i>I</i> _{obs}	<i>I</i> _{calc}	<i>hkl</i>	<i>d</i> _{obs}	<i>d</i> _{calc}	<i>I</i> _{obs}	<i>hkl</i>	<i>d</i> _{obs}	<i>d</i> _{calc}	<i>I</i> _{obs}
001	16.739	16.711	100	100	001	16.760	16.780	100	034	1.818	1.818	3
002	8.373	8.355	1	2	002	8.380	8.390	4	118	1.796	1.799	1
010	6.054	6.048	18	18	010	6.050	6.050	29	126	1.770	1.771	2
011	5.687	5.687	13	16	011	5.690	5.690	38	220	1.747	1.747	17
012	4.933	4.899	6	5	003	5.610	5.590	2	035	1.727	1.729	1
110	3.488	3.492	9	6	012	4.901	4.909	2	028	1.722	1.724	2
021	2.976	2.976			013	4.110	4.108	2	00.10	1.678	1.678	1
113	2.967	2.959	45	44	110	3.493	3.494	19	223	1.670	1.668	1
					014	3.443	3.448	6	127	1.652	1.655	1
114	2.677	2.679	8	8	111	3.418	3.421	2	036	1.637	1.636	1
025		2.242			005	3.342	3.356	1	01.10	1.617	1.617	<1
017	2.219	2.221	19	20	021	2.978	2.978	27	133	1.608	1.608	1
122		2.205			015	2.940	2.935	10	029	1.587	1.588	<1
018	1.971	1.974	5	4	022	2.846	2.847	4	225	1.547	1.550	
033	1.896	1.896	13	11	006	2.799	2.797	14	128	1.547	1.546	1
034	1.816	1.816	4	4	114	2.686	2.685	9	00.11	1.522	1.526	<1
220	1.744	1.746	17	15	023	2.662	2.662	3	040	1.515	1.513	1
041	1.504	1.506			016	2.542	2.539	2	041	1.507	1.507	1
135		1.499	4	4	024	2.454	2.454	1	135	1.502	1.501	1
					115	2.421	2.421	1	042	1.489	1.489	1
042	1.484	1.488	3	3	007	2.398	2.397	1	226	1.483	1.482	2
02.10	1.463	1.463	8	10	120	2.289	2.288	1	01.11	1.479	1.479	1
137	1.370	1.372			025	2.249	2.247	9	02.10	1.468	1.468	4
211		1.357	5	4	017	2.231	2.229	8	038	1.452	1.454	1
					122	2.207	2.207	6	129	1.446	1.445	1
140	1.318	1.320	2	2	116	2.181	2.184	1	136	1.440	1.439	2
310	1.284	1.287			123	2.118	2.117	2	044	1.424	1.423	1
143		1.284	5	5	026	2.049	2.054	1	227	1.413	1.412	1
					030	2.017	2.017	1	00.12	1.400	1.399	<1
					124	2.009	2.008	1	230	1.388	1.389	<1
					031	2.002	2.003	2	231	1.384	1.384	1
					032	1.961	1.962	2	045	1.380	1.379	1
					033	1.895	1.898	11	137	1.376	1.375	1
					027	1.882	1.879	2	232	1.370	1.370	1
					009	1.867	1.865	2	01.12	1.365	1.363	2

Table 3. The coordinates for all atoms except OH2 conform to the higher-symmetry space group $P\bar{3}m1$. A lowering of symmetry to $P321$ was required to obtain ordering of the trigonal bipyramids. In $P\bar{3}m1$, the equatorial OH2 atoms are split into two sets, rotated by 60°. A comparison of observed and calculated powder patterns obtained from the Rietveld refinement is shown in Fig. 5. The Rietveld program *FULLPROF* (Rodríguez-Carvajal, 1990) was used to refine the PXRD data. The low resolution of the powder data restricted the refinement to profile parameters only, giving $R_B = 9.6\%$. The coordinates given in Table 3, although unrefined,

give sensible bond distances for all atoms, with octahedral Al1–O distances in the range 1.81 to 1.97 Å (average 1.89 Å), trigonal bipyramidal Al2–O distances of 1.77 ($\times 3$) Å and 1.85 ($\times 2$) Å and tetrahedral P–O distances in the range 1.50 to 1.57 Å (averages of 1.52 Å for P1 and 1.53 Å for P2). Ca1 is 12-coordinated with Ca–O distances of 2.67 Å ($\times 6$) and 2.74 ($\times 6$) Å, while Ca2 has nine O neighbours at distances in the range 2.55 to 2.70 Å.

As shown in Fig. 6, the structure of iangreyite contains pairs of crandallite-like composite layers of corner-connected Al1-centred octahedra and P-centred tetrahedra, with Ca2 atoms located

TABLE 3. Atom coordinates for iangreyite in space group $P321$.

Atom	Wyckoff position	x	y	z
Ca1	1a	0	0	0
Ca2*	2d	$\frac{2}{3}$	$\frac{1}{3}$	0.316
Al1	6g	0.166	$\frac{1}{3}$	0.835
Al2	1b	0	0	$\frac{1}{2}$
P1	2d	$\frac{2}{3}$	$\frac{1}{3}$	0.020
P2	2c	0	0	0.295
O1	6g	0.429	0.214	0.052
O2	6g	0.240	0.120	0.268
O3	2c	0	0	0.389
OH1	2d	$\frac{1}{3}$	$\frac{2}{3}$	0.070
OH2	3f	0.253	0	$\frac{1}{2}$
OH3	6g	0.126	0.252	0.131
OH4	6g	0.914	0.457	0.192
Ow1	2d	$\frac{1}{3}$	$\frac{2}{3}$	0.250
Ow2	6g	0.030	0.515	0.402

* Refined occupancy of Ca2 is 0.50(1). P1 is bonded to O1 ($\times 3$) (1.534 Å) and OH1 ($\times 1$) (1.504 Å); P2 is bonded to O2 ($\times 3$) (1.521 Å) and O3 ($\times 1$) (1.571 Å).

between the layers, as in crandallite. The apical oxygen atoms of the PO_4 tetrahedra are corner-connected to $\text{Al}_2\text{O}_2(\text{OH})_3$ trigonal bipyramids to complete the polyhedral framework. The connection of crandallite blocks *via* the trigonal bipyramids generates large channels bounded by 10-membered rings as shown in Fig. 6. The channels are occupied by the Ca2 ions and the water molecules Ow1 and Ow2. The unit-cell compositions of the crandallite blocks and the intervening region containing the trigonal bipyramids are $\text{CaAl}_6(\text{PO}_3\text{O}^*)_2(\text{PO}_3\text{OH})_2(\text{OH},\text{F})_{12}$ and $\text{CaAlO}^*_2(\text{OH})_3 \cdot 8\text{H}_2\text{O}$, respectively, where O atoms marked with an asterisk are shared between crandallite blocks and the intervening regions (oxygen atoms shared between PO_4 tetrahedra and $\text{AlO}_2(\text{OH})_3$ trigonal bipyramids). This gives the overall unit-cell composition as $\text{Ca}_2\text{Al}_7(\text{PO}_4)_2(\text{PO}_3\text{OH})_2(\text{OH})_{15} \cdot 8\text{H}_2\text{O}$, which ignores F incorporation on the OH sites, consistent with the analytical data reported above.

Spectroscopy

Raman spectra were acquired using a Renishaw inVia Raman microprobe utilizing a laser wavelength of 785 nm on a sample from Silver Coin. Transmission Fourier-transform infrared

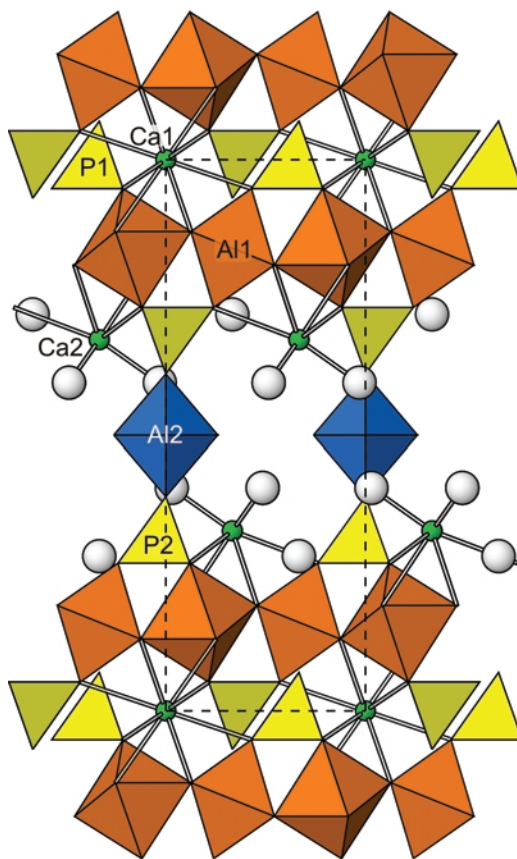


FIG. 6. The structure of iangreyite showing the connection between the $\text{CaAl}_6(\text{PO}_3\text{O}^*)_2(\text{PO}_3\text{OH})_2(\text{OH},\text{F})_{12}$ crandallite blocks and the intervening $\text{CaAlO}^*_2(\text{OH})_3 \cdot 8\text{H}_2\text{O}$ trigonal bipyramids.

(FTIR) spectra were obtained on Silver Coin iangreyite using a Nicolet 6700 spectrometer equipped with a Continuum microscope, from 32 scans with a 1 cm^{-1} resolution, over the $400\text{--}4000\text{ cm}^{-1}$ region. A small amount of sample was crushed in a Spectra Tech diamond compression cell prior to analysis.

Band assignments for the FTIR and Raman spectra were made by analogy to crandallite (Farmer, 1974). In the IR spectrum (Fig. 4) there are three broad bands at 3406, 3308 and 3016 cm^{-1} attributed to H_2O and $(\text{OH})^-$ stretching modes with another broad band at 1641 cm^{-1} assigned to the H_2O bending mode. A small but broad band in the Raman at $\sim 1635\text{ cm}^{-1}$ in the Raman spectrum confirms H_2O within the structure. The O...O distances,

calculated from the water stretching bands using the Libowitzky (1999) curve, give bond lengths of ~2.80, 2.75 and 2.65 Å, which are indicative of medium-to-weak-strength bonds and consistent with the crystal structure derived above.

The strong sharp band at 1048 cm⁻¹ in the IR spectrum and strong bands at 979, 1009, 1033 and 1095 cm⁻¹ in the Raman spectrum, are attributed to the (PO₄)⁻³ stretching mode (ν₃), while a small band at 860 cm⁻¹ in the IR spectrum is attributed to the symmetric stretching mode of ν₁. The Raman spectrum also has strong bands at 622 and 510 cm⁻¹ attributed to the (PO₄)⁻³ (ν₃) mode.

Other possible occurrences

Occurrences of F-bearing crandallite should be reinvestigated as possible iangreyite occurrences. The F-rich crandallite occurring at the Utahlite claim, Lucin, Utah (41°20'N, 113°54'W), however, has been determined to be F-bearing crandallite rather than iangreyite by PXRD.

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