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Fluorocronite, the natural analogue of β-PbF_2, from the Sakha Republic, Russian Federation

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Abstract: Fluorocronite (фторокронит), ideally PbF_2, is a new mineral (IMA2010–023), from the Kupol'noe deposit, Sarychev range, Sakha Republic, Russian Federation. It occurs intimately mixed with cassiterite and a potentially new Sn oxy-hydroxide with the composition $Sn_4O(OH,F)_6$, and is found in direct association with quartz, anglesite, cerussite, galena, hocartite, bindheimite and chlorargyrite. Fluorocronite forms flattened, leaf-like microcrystals up to about 20 μm across. The main form observed is {100}, while {111} may also be present. The crystals are translucent and white with a pearly lustre. The streak is also white and Mohs hardness is between 3 and 4 (estimated). No parting or twinning was observed. Fluorocronite has prefect cleavage on {111} by analogy with other minerals with the fluorite structure type. Crystals are optically isotropic; however, the refractive index could not be measured due to the small size of the crystals. The empirical formula (based on 3 *apfu*) is $Pb_{0.98}F_{2.02}$. The simplified formula is PbF_2. Fluorocronite is cubic, space group $Fm\bar{3}m$, with $a = 5.9306(5)$ Å, $V = 208.59(5)$ Å^3 and $Z = 4$. Fluorocronite is isostructural with fluorite. The five strongest lines in the powder X-ray diffraction pattern are [d_{obs} in Å (I) (hkl)]: 3.437 (100) (111); 2.976 (46) (002); 2.103 (44) (022); 1.794 (42) (311); 1.717 (21) (222). The name is in relation to the composition; *fluoro* (for fluorine) and *cron* (κρόνος, the alchemical name for lead).

Key-words: fluorocronite, Kupol'noe, Sakha Republic, β-PbF_2, new mineral, fluorite group.

1. Introduction

Lead(II) fluoride (also known as lead difluoride and plumbous fluoride) is an air-stable, partially water-soluble fluoride, which has a number of uses in material sciences. PbF_2 is used as a component in the manufacture of low-melting glasses (*e.g.* Shibata *et al.,* 1980), phosphors in television picture tubes (Schulman *et al.,* 1953) and as a catalyst for the manufacture of picoline (Minato & Yasuda, 1976). Structurally PbF_2 has both α and β forms; the former known both synthetically and in the mineral laurelite ($Pb_7F_{12}Cl_2$), which has the α-PbF_2 structure but differs from α-PbF_2 only in having some Cl substituting for F (Merlino *et al.*, 1996). Here, we report the outcome of investigations of natural β-PbF_2.

The type specimen and associated material was collected in the 1990s by one of the authors (GNG) at the Kupol'noe Ag–Sn deposit. The mineral is named in relation to the composition; *fluoro* (for fluorine) and *cron* (κρόνος, the alchemical name for lead). The Russian Cyrillic spelling for the mineral is фторокронит. The mineral and name have been approved by the IMA–CNMNC (IMA 2010–023). One co-type specimen is housed in the collections of the Fersman Mineralogical Museum, catalogue number 3987/1 and another is in the collections of Mineral Sciences Department, Natural History Museum of Los Angeles County, catalogue number 63316.

2. Geological setting, occurrence and paragenesis

The Kupol'noe Ag–Sn deposit is located on the eastern slope of the northern part of Sarychev range, within the Eimyu stream basin (a tributary of the Nera river), 130 km

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SE of the Ust'-Nera settlement, Sakha Republic, Russian Federation (Fig. 1). The deposit is situated in the centre of the large (170 × 140 km) Upper Indigirka ring structure, part of the Yana–Indigirka synclinal zone of the Verkhoyano–Kolyma fault region. The Upper Indigirka ring structure has formed at the intersection of four systems of fault dislocations. These formed in the late Jurassic as result of deformations that occurred during the collision of the Kolyma–Omolon super-terrain with the Verkhoyansk passive continental margin (Gamyanin *et al*., 2001).

The deposit is bounded on the west by the Eiemyun brachianticlinal fold, on the southwest by the Nera (Ayan–Uryakh) anticline and in the east by the Taryn–Yuryakh graben–syncline. The deposit is comprised of Early- and Middle Jurassic marine terrigenous sediments and aleurolites, as well as sandstones and slates of Middle to Upper Triassic age. Magmatic formations (167–86 Ma) are developed extensively within Upper Indigirka ring structure. Ore bodies of the deposit are connected with outcrops of the granitoid intrusives Trud and Kapriznyi, belonging to a granodiorite complex of Aptian age (122 Ma), and located within massive magmatic rocks and their exocontacts (Gamyanin *et al*., 2001).

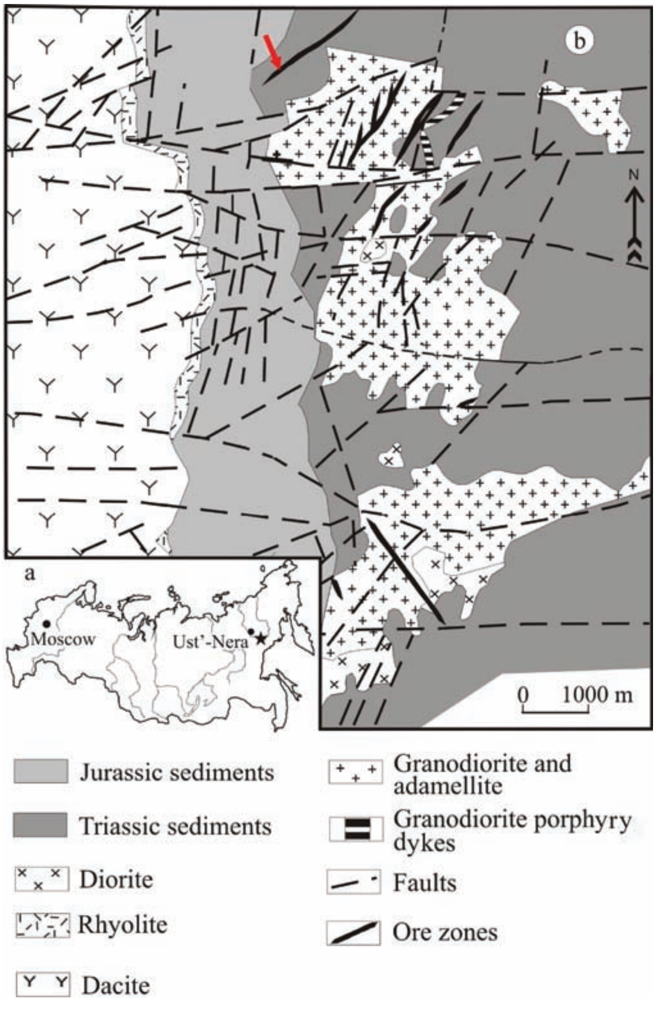

Fig. 1. Schematic of the Kupol'noe deposit, with arrow indicating the area where the type material was collected.

The two largest parts of the deposit (Kupol'noe and Kapriznoe) have about 20 separate ore bodies, represented by mineralised crushing zones, lens-like veins, zones of linear stockwork and impregnated ores. The largest known ore body is 1500 m in length and 10 m in thickness. All ore bodies are accompanied by metasomatic alteration of the host rock (Gamyanin *et al*., 2001).

In the ore bodies of Kupol'noe, about 40 hypogenic minerals are known, of which quartz (>40 vol%) and different carbonates (>30 vol%) are the most abundant. The main ore minerals (5–10 vol%) are galena, pyrite and sphalerite. In some parts of the ore bodies, accumulations of sulphosalts (<2 vol%) are observed (Gamyanin *et al.*, 2001). Several mineralisation events can be observed within the ore body. The earliest mineralisation event is comprised of cassiterite–wolframite–arsenopyrite–quartz, located in sublatitudinal dislocations within tourmaline hornfels and is separated spatially from other Sn–Ag polymetallic ore bodies. The later mineralisation events consisted of rhythmically zoned siderite → cassiterite–arsenopyrite–quartz → rhythmically banded chalcopyrite–sphalerite–galena–quartz → freibergite–pyrargyrite–Fe-rich dolomite → hocartite–franckeite–canfieldite and finally marcasite–ankerite–calcite.

Ore zone #21, where fluorocronite was discovered, is a single outcropping zone. This ore zone is so well exposed by outcrops, including 30 m high cliffs, that it was the only ore zone that was not discovered by exploration methods – trenches, adits and mines. The entire ore zone is about 3 km long and about 100 m wide and up to 30 m in depth at its southern flank. The ore zone is represented by two-metre-thick zoned veins (zonation from outer contacts to centre): cassiterite–sphalerite–quartz → cassiterite–galena–sphalerite–quartz → quartz–chalcopyrite–stannite–sphalerite–galena → galena–freibergite–miargyrite– pyrargyrite and, finally, Fe-rich dolomite–franckeite–canfieldite. The hand specimen with fluorocronite was collected from colluvium on the northern flank of the ore zone. The ore colluvium (~6 × 2 m) consists of anglesite ore debris. Fluorocronite is intimately mixed with secondary cream-coloured cassiterite and a potentially new Sn oxy-hydroxide with the composition $Sn_4O(OH,F)_6$, which is currently under investigation. Quartz, anglesite, cerussite, galena, hocartite, bindheimite and chlorargyrite are also associated with fluorocronite.

Fluorocronite is a product of supergene alteration and has formed under ambient surface conditions from the weathering of galena and other Pb-bearing sulphosalts. Minor Sn found in some fluorocronite crystals is probably derived from the breakdown of hocartite (Ag_2FeSnS_4), franckeite ($Fe(Pb,Sn^{2+})_6Sn^{4+}Sb_2S_{14}$) and canfieldite ($Ag_8SnS_6$). Fluorocronite is extremely rare at the deposit because of its overall depletion in fluorine. Fluorite, fluorapatite or F-bearing micas have not been observed in any of the ore bodies. Thus, the source of the fluorine is an enigma. Anomalous enrichment of fluorocronite, within a small area of ore zone #21, may represent very local and extremely rare fluorite impregnation.

3. Morphology, physical and optical properties

Fluorocronite forms flattened, leaf-like microcrystals (similar to those observed for gold) up to about 20 µm across, but generally less than 10 × 10 µm, with a thickness of less than 1 µm (Fig. 2). The main form developed appears to be {100} due to the rectangular outline observed in the leaf-like crystals, although crystals may also be flattened on {111}. Macroscopically, white fluorocronite masses coat larger encrustations of cream-coloured cassiterite. Fluorocronite crystals are translucent with a pearly lustre. The streak is white and Mohs hardness is estimated at between 3 and 4. Fluorocronite has perfect cleavage on {111} by analogy with other minerals of the fluorite

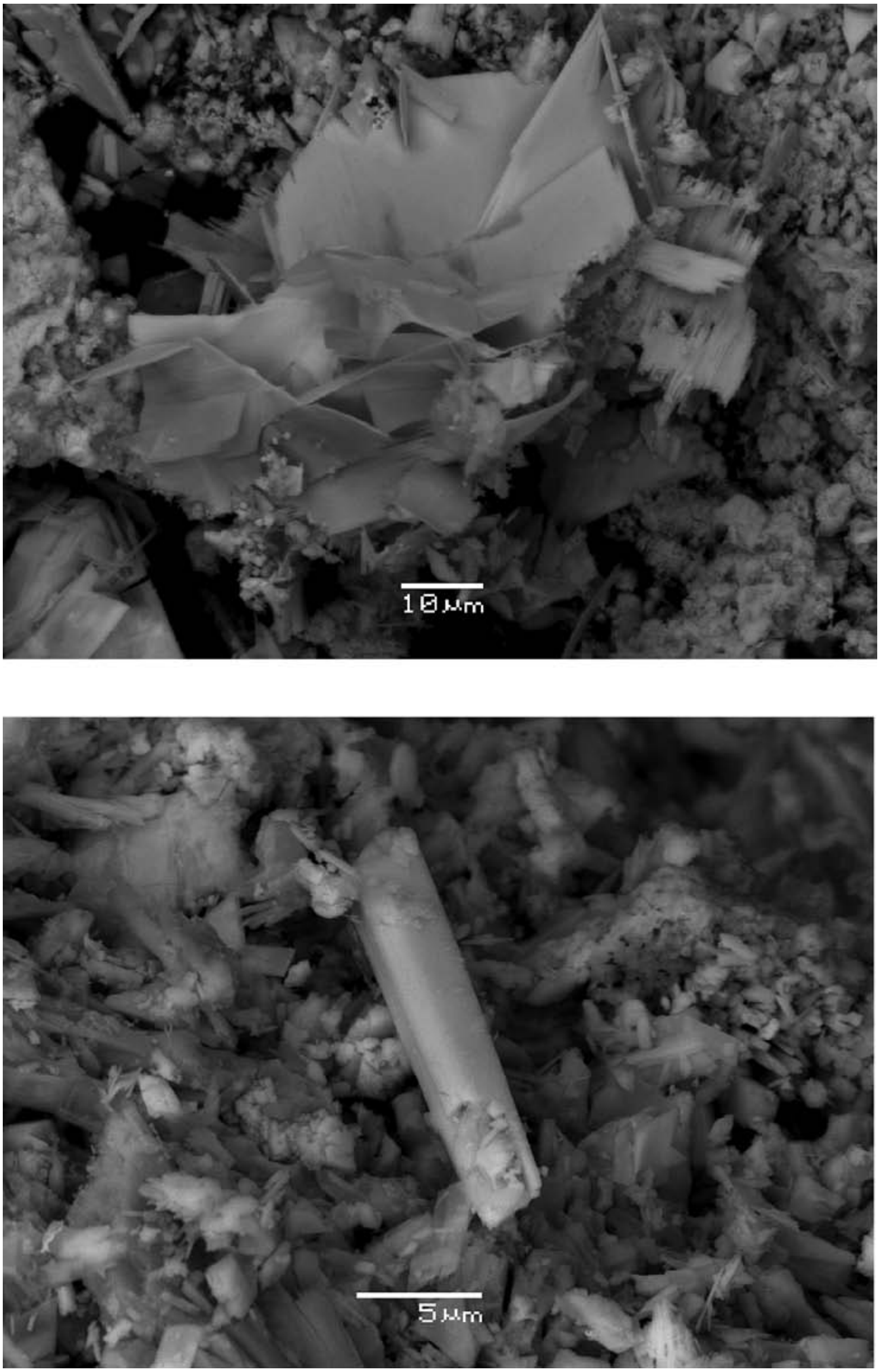

Fig. 2. SEM-BSE photomicrographs of intergrown crystals of fluorocronite (top) and Sn-bearing fluorocronite (bottom).

structure type. No parting or twinning was observed. The density could not be measured because of the small grain size. The calculated density from the empirical formula and powder unit-cell is 7.619 g/cm^3; however, the density of Sn-bearing fluorocronite varies dramatically with the amount of Sn substituting for Pb. The calculated density for $(Pb_{0.89}Sn^{2+}_{0.11})F_2$ is 7.462 g/cm^3 and 7.210 g/cm^3 for $(Pb_{0.80}Sn^{2+}_{0.20})F_2$. Fluorocronite is non-fluorescent under unfiltered ultraviolet light.

Sn-bearing fluorocronite has a different morphology and appearance; however PXRD confirms its identity. Sn-bearing fluorocronite forms as single, elongated prismatic crystals (with elongation about 5:1) up to 15 μm long (Fig. 2). These single crystals are always found on aggregates of the Sn oxy-hydroxide. Frequently, Sn-bearing fluorocronite single prisms grow over tabular aggregates of fluorocronite, indicating two generations of fluorocronite formation.

Fluorocronite is optically isotropic; however, the refractive index could not be measured due to the small size of the crystals. Synthetic β-PbF_2 has $n = 1.766$ at 587 nm (Bass *et al.*, 2010).

4. Chemical composition

Quantitative chemical analyses (10) were carried out at IGEM, Russia using a JSM-5610LV analytical scanning electron microscope equipped with the INCA-450 EDS system. Due to the size of single plates of fluorocronite (<1 μm thickness), its delicate structure and porosity, preparation of polished microprobe epoxy mounts was impossible. Therefore, microprobe preparates were made following the method described by Kartashov *et al.* (2010) using an accelerating voltage of 15 kV, beam current of 0.5 nA and a 1 μm spot size. Ag, As, Sb, Bi, In, Cd, Fe and Cl were sought, but were below detection limits. Analytical data are given in Table 1. Two other spot analyses showed substantial Sn substitution, providing the formulae $(Pb_{0.80}Sn^{2+}_{0.20})F_2$ and $(Pb_{0.89}Sn^{2+}_{0.11})F_2$.

The empirical formula (based on 3 *apfu*) is $Pb_{0.98}F_{2.02}$. The simplified formula is PbF_2, which requires Pb 84.50, F 15.50, total 100.00 wt%.

5. Powder X-ray diffraction and group nomenclature

Single-crystal X-ray studies could not be carried out due to the nature and size of the fluorocronite crystals. X-ray powder-diffraction data (Table 2) were collected on a small aggregate of crystals on a Rigaku R-Axis Rapid II curved imaging plate microdiffractometer utilising monochromatised Mo$K\alpha$ radiation at the Natural History Museum of Los Angeles County. Observed d spacings and intensities were derived by profile fitting using JADE 9.1 software. The unit-cell parameter refined from the powder data using whole-pattern fitting is $a = 5.9306(5)$ Å. The space group is $Fm\bar{3}m$ and Z = 4. Fluorocronite has the fluorite structure type, with Pb located at the origin and F located at (¼, ¼, ¼). Fluorocronite is the natural

Table 1. Analytical data for fluorocronite.

Constituent	Fluorocronite wt%*	Range	SD	Sn-bearing fluorocronite wt%		Probe standard
Pb	84.02	83.36–84.35	0.32	72.75	78.14	PbTe
Sn	–	–	–	10.42	16.37	SnO_2
F	15.9	15.54–16.40	0.23	16.94	16.37	Nacaphite
Total	99.92	99.56–100.27	0.25	100.11	100.04	

Note: *average of 10 analyses.

Table 2. X-ray powder diffraction data for fluorocronite and synthetic β-PbF_2.

	Fluorocronite (Ag $K\alpha$)*			Fluorocronite (Mo $K\alpha$)**		β-PbF_2***	
hkl	d_{obs}	d_{calc}	I_{obs}	d_{obs}	I_{obs}	d_{calc}	I_{calc}
111	**3.437**	**3.434**	**100**	3.424	100	3.429	100
002	**2.976**	**2.974**	**46**	2.965	36	2.970	31
022	**2.103**	**2.103**	**44**	2.097	54	2.100	48
311	**1.794**	**1.793**	**42**	1.788	54	1.791	38
222	**1.717**	**1.717**	**21**	1.712	11	1.715	7
004	–	–	–	1.483	11	1.485	6
331	1.366	1.364	20	1.361	21	1.363	12
042	1.329	1.330	20	1.326	15	1.328	8
422	1.214	1.214	19			1.212	10
511,333	1.144	1.145	15			1.143	8
531	1.005	1.005	12			1.005	3

Note: *$a = 5.947(3)$ Å; **$a = 5.9306(5)$ Å; ***Achary & Tyadi (2005), $a = 5.9397(2)$ Å.

analogue of β-PbF_2 (Koto *et al.,* 1980). The β-PbF_2 structural motif is found as layers in the minerals matlockite (Pasero & Perchiazzi, 1996), grandreefite (Kampf, 1991), pseudograndreefite (Kampf *et al.,* 1989) and aravaipaite (Kampf *et al.*, 1989, 2011).

Variable count (VCT) X-ray powder diffraction data (Madsen & Hill, 1994) were also collected on several aggregates of fluorocronite–cassiterite–Sn oxy-hydroxide in a 0.3 mm glass capillary using a Bruker D8 Advance diffractometer with a focusing primary mirror and a high-energy optimised LynxEye detector utilising Ag*K*α radiation at Bruker AXS GmbH, Germany (Table 2; Fig. 3). The high absorption of the samples made data collection in a capillary impossible with more conventional laboratory wavelengths. The Rietveld analyses ($R_{wp} = 1.31$, $R_p = 4.57$ and GooF = 3.49) were undertaken using TOPAS V4.2 (Bruker AXS, 2008) and gave the refined unit-cell parameter $a = 5.947(3)$ Å for fluorocronite ($R_B = 1.4$). The capillary absorption corrections used in the analysis of powder diffraction data (*e.g.* Sabine *et al.,* 1998) become unreliable when the values of μR (μ = mass absorption coefficient, R = capillary radius) exceed 5, which dictates the use of a small capillary and high energy X-rays. The very large scattering contrast between lead and fluorine meant that an overall B_{iso} had to be used instead of individual values for the atoms. Reflections belonging to the Sn oxy-hydroxide were fitted using single reflections to avoid misfits biasing the least-squares process. 2θ, d_{obs} and I_{obs} for the potentially new Sn oxy-hydroxide are presented in Table 3. Further work is needed to confirm any potential relationship between this mineral and Sn_4OF_6 (Abrahams *et al.*, 1994).

Fluorocronite is the Pb-analogue of fluorite, frankdicksonite and strontiofluorite (IMA2009–014; Yakovenchuk *et al.*, 2010). Group nomenclature has not previously been established for minerals with the fluorite structure; therefore, it is appropriate to do so following the rules of Mills *et al.* (2009). Since fluorite is the oldest known mineral in the group, the group takes this name.

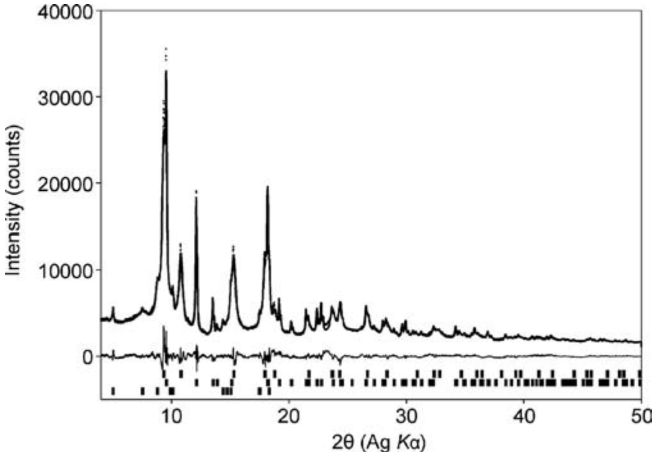

Fig. 3. Difference plot from the Rietveld refinement of the fluorocronite–cassiterite–Sn oxy-hydroxide mix. Uppermost lines = observed data overlain by calculated pattern; line below = residual pattern; vertical lines = positions of Bragg reflections for each phase (top = fluorocronite, centre = cassiterite, bottom = Sn oxy-hydroxide).

Table 3. X-ray powder diffraction data for the potentially new Sn oxy-hydroxide.

2θ (Ag*K*α 0.56 Å)	d_{obs} (Å)	I_{obs}
5.025	6.3862	11
7.540	4.2585	3
8.813	3.6440	100
9.902	3.2442	24
10.130	3.1715	28
14.409	2.2326	14
14.743	2.1823	9
15.069	2.1354	44
17.529	1.8375	16
18.315	1.7593	13

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