Table S1. Powder X-ray data (*d* in Å) for hydroxylpyromorphite.

I_{obs}	d_{obs}	d_{calc}	I_{calc}	*hkl*
8	4.900	4.8936	7	1 1 0
16	4.251	4.2380	16	2 0 0
18	**4.079**	4.0660	16	1 1 1
6	3.669	3.6660	1	2 0 1
		3.6535	4	0 0 2
29	**3.359**	3.3551	24	1 0 2
21	**3.207**	3.2036	25	1 2 0
100	**2.934**	2.9340	55	1 2 1
		2.9276	45	1 1 2
13	2.822	2.8253	19	3 0 0
		2.7672	1	2 0 2
		2.4468	1	2 2 0
		2.4087	1	2 1 2
3	2.323	2.3202	2	2 2 1
9	2.239	2.2378	1	1 3 1
		2.2350	7	3 0 2
8	2.183	2.1805	7	1 1 3
4	2.114	2.1190	3	4 0 0
21	**2.0355**	2.0330	20	2 2 2
9	1.9795	1.9769	8	1 3 2
23	**1.9417**	1.9445	4	3 2 0
		1.9389	18	2 1 3
9	1.8821	1.8791	9	3 2 1
15	1.8501	1.8496	17	1 4 0
25	**1.8340**	1.8330	17	4 0 2
		1.8268	7	0 0 4
		1.7262	1	2 2 3
3	1.7141	1.7165	1	2 3 2
		1.7114	1	1 1 4
4	1.6786	1.6775	2	2 0 4
2	1.6385	1.6502	1	4 1 2
17	**1.5919**	1.6018	3	4 2 0
		1.5920	5	3 3 1
		1.5869	8	2 1 4
13	1.5376	1.5377	8	5 0 2
		1.5340	5	3 0 4
5	1.5229	1.5223	1	1 5 0
		1.5196	3	2 3 3
10	1.4900	1.4903	2	1 5 1
		1.4895	7	3 3 2
3	1.4084	1.4003	1	1 1 5
3	1.3856	1.3934	1	3 4 0
		1.3836	1	4 0 4
5	1.3583	1.3688	1	3 4 1
		1.3572	1	5 2 0
		1.3553	2	3 3 3
10	1.3329	1.3344	3	2 5 1
		1.3314	2	3 2 4
		1.3296	4	1 2 5
4	1.3192	1.3176	3	6 0 2
14	1.2995	1.3020	1	4 3 2
		1.2997	10	1 4 4
		1.2926	2	6 1 0
		1.2909	1	1 5 3
10	1.2726	1.2728	3	6 1 1
		1.2723	7	5 2 2

Table S2. Data collection and structure refinement details for hydroxylpyromorphite.

Diffractometer	Bruker Apex II Quazar
X-ray radiation/power	Mo$K\alpha$ (λ = 0.71075 Å)/50 kV, 60 mA
Temperature	100(2) K
Structural Formula	$Pb_5P_3O_{12.72}F_{0.30}Cl_{0.06}H_{0.72}$
Space group	$P6_3/m$
Unit cell dimensions	a = 9.7872(14) Å
	c = 7.3070(10) Å
V	606.16(19) Å^3
Z	2
Density (for above formula)	7.347 g/cm^3
Absorption coefficient	69.685 mm^{-1}
F(000)	1122
Crystal size	15 × 15 × 63 μm
θ range	2.403 to 25.242°
Index ranges	$-12 \le h \le 12$, $-7 \le k \le 12$, $-6 \le l \le 8$
Reflections collected/unique	2452/546; R_{int} = 0.0484
Reflections with $F > 2\sigma F$	494
Completeness to θ = 25.242°	99.3%
Refinement method	Full-matrix least-squares on F^2
Restraints/parameters	0/46
GoF (ref/all)	0.945/0.945
Final R indices [$F > 4\sigma(F)$]	R_1 = 0.0181, wR_2 = 0.0290
R indices (all data)	R_1 = 0.0214, wR_2 = 0.0284
Largest diff. peak/hole	+1.622/–2.010 e·A^{-3}

Table S3. Atomic coordinates and displacement parameters (Å^2) for hydroxylpyromorphite.

Atom	*Occ.*	*x/a*	*y/b*	*z/c*	U_{eq}/U_{iso}	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Pb1	1	0.3333	0.6667	0.00277(5)	0.01382(12)	0.01488(12)	0.01488(12)	0.0117(3)	0	0	0.00744(6)
Pb2	1	0.23638(3)	0.23223(3)	0.25	0.01952(12)	0.01184(14)	0.01329(14)	0.0351(3)	0	0	0.00754(11)
P1	1	0.40473(19)	0.02325(19)	0.25	0.0095(4)	0.0085(7)	0.0076(8)	0.0125(13)	0	0	0.0041(6)
O1	1	0.5863(5)	0.1013(5)	0.25	0.0167(12)	0.008(2)	0.020(2)	0.025(4)	0	0	0.009(2)
O2	1	0.1578(5)	0.4843(5)	0.25	0.0127(11)	0.010(2)	0.015(2)	0.007(3)	0	0	0.0013(19)
O3	1	0.3546(4)	0.0817(3)	0.0803(5)	0.0154(8)	0.0213(17)	0.0140(16)	0.011(2)	-0.0027(15)	-0.0081(17)	0.0089(13)
O4	0.72(12)	0	0	0	0.031(5)	0.01488(12)	0.01488(12)	0.0117(3)	0	0	0.00744(6)
Cl4	0.06	0	0	0	0.03(2)	0.01184(14)	0.01329(14)	0.0351(3)	0	0	0.00754(11)
H1	0.359	0	0	0.14(5)	0.037	0.0085(7)	0.0076(8)	0.0125(13)	0	0	0.0041(6)
F1	0.15(6)	0	0	0.086(19)	0.04(2)	0.008(2)	0.020(2)	0.025(4)	0	0	0.009(2)

Table S4. Selected bond distances (Å) for hydroxylpyromorphite.

Pb1–O1$^{\#9}$	2.720(3)	Pb2–O1$^{\#3}$	2.397(4)	P1–O1	1.544(5)
Pb1–O1$^{\#8}$	2.720(3)	Pb2–O3	2.598(4)	P1–O2$^{\#3}$	1.539(5)
Pb1–O1$^{\#7}$	2.720(3)	Pb2–O3$^{\#10}$	2.598(4)	P1–O3$^{\#10}$	1.545(4)
Pb1–O2$^{\#3}$	2.517(3)	Pb2–O3$^{\#6}$	2.638(4)	P1–O3	1.545(4)
Pb1–O2	2.517(3)	Pb2–O3$^{\#9}$	2.638(4)	<P1–O>	1.543
Pb1–O2$^{\#2}$	2.517(3)	Pb2–O2	2.928(6)		
Pb1–O3	2.870(4)	Pb2–O4	2.932(1)	O4—O4$^{\#4}$	3.654(1)
Pb1–O3	2.871(3)	Pb2–O4$^{\#4}$	2.932(1)	O4···F1	3.02(13)
Pb1–O3$^{\#10}$	2.871(3)	<Pb2–O>	2.708	Pb2–F1	2.58(6)
<Pb1–O>	2.703				

Symmetry transformations used to generate equivalent atoms: #2 –y, x-y, z; #3 –x+y, -x, z; #4 –x, -y, z+1/2; #7 –x, -y, -z; #8 y, -x+y, -z; #9 x-y, x, -z; #10 x, y, -z-1/2; #11 –y, x-y, -z-1/2.

Table S5. Bond-valence analysis for hydroxylpyromorphite. Values are expressed in valence units.

Atom	**Pb1**	**Pb2**	**P1**	**Σ_{an}**
O1	0.21 ×3↓ × 2→	0.44	1.23	2.09
O2	0.33 ×3↓ × 2→	0.13	1.23	2.02
O3	0.15×3↓ × 2→	0.28 ×2↓ 0.25 ×2↓	1.22 ×2↓	2.05
O4*		0.13 ×2↓ × 6→		0.75
F1*		0.23×2↓ × 3→		
Σ_{cat}	2.07	1.96	4.89	

Bond-valence parameters for Pb–F were taken from Brese and O'Keeffe (1991), all other bond-valence parameters are from Gagné and Hawthorne (2015). *The refined site occupancies of O (0.72) and F (0.15) were considered during calculations.

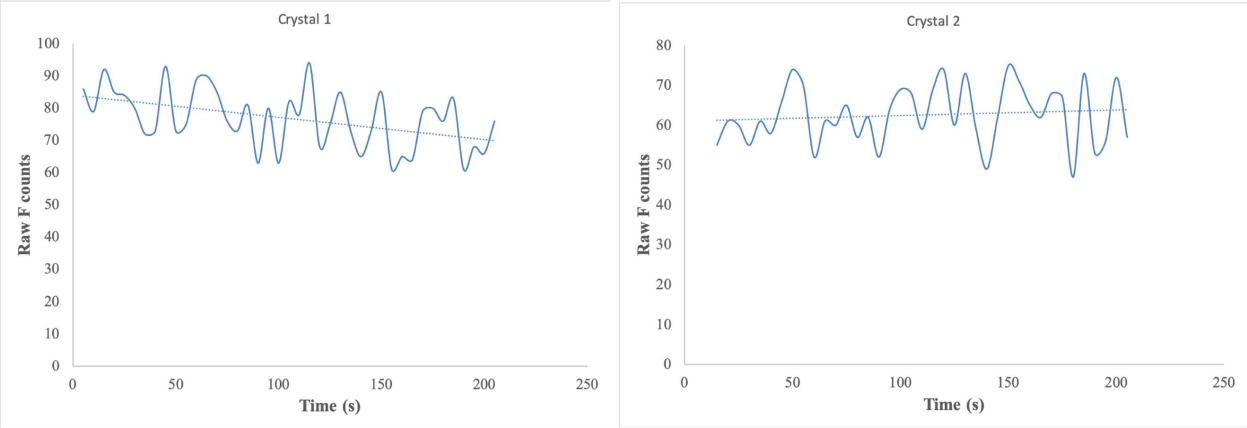

Figure S1. Change in FKα X-ray counts over time in the electron microprobe of hydroxylpyromorphite type material; suggesting no significant electron beam induced migration of F occurred during the chemical analyses.