The influence of stereochemically active lone-pair electrons on crystal symmetry and twist angles in lead apatite-2H type structures

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Supporting Information

Table S1. Refinement parameters for vanadinite $Pb_{10}(VO_4)_6Cl_2$

Crystal size	0.07 × 0.12 × 0.15 mm	
Crystal system	Hexagonal	
Space group	$P6_3/m$ (C^2_{6h}, No. 176)	
Temperature	293K	100K
Unit cell dimensions		
a (Å)	10.3143(7)	10.2984(6)
c (Å)	7.3396(5)	7.2907(4)
V (Å^3)	676.21	669.64
Z	2	2
Density (g cm^{-3})	7.1053	7.0215
μ (cm^{-1})	64.35	64.86
Radiation Mo $K\alpha$ (Å)	0.71069	0.71069
Collection limits (θ, deg)	2.28 – 32.58	2.28 – 27.57
Data measured	12353	10104
Unique reflections	876	569
Reflections with I≥3σ(I)	741	549
R	0.0349	0.0237
R_W	0.0887	0.0748
GOF	2.76	2.47
D residual (eÅ^{-3})		
+	3.50	2.38
-	4.64	1.24

Table S2. Refined atomic positions and anisotropic displacement parameter for vanadinte single crystal X-ray diffraction data collected at RT.

s.g	$P6_3/m$	a = 10.3143(7) Å	c = 7.3396(5) Å	
Site	***x***	***y***	***z***	U_{Iso}
Pb^F	1/3	2/3	0.00797(8)	0.01281(17)
Pb^T	0.25500(5)	0.01232(5)	¼	0.0146(2)
V	0.4095(2)	0.3840(2)	¼	0.0052(8)
O(1)	0.3322(12)	0.4979(12)	¼	0.018(4)
O(2)	0.6028(11)	0.4863(11)	¼	0.020(4)
O(3)	0.3597(9)	0.2694(9)	0.0664(10)	0.023(3)
Cl	0	0	0	0.0152(13)

s.g	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pb^F	0.0145(2)	0.0145(2)	0.0095(3)	0.00723(11)	0	0
Pb^T	0.0078(2)	0.0126(3)	0.0232(3)	0.00503(19)	0	0
V	0.0054(90	0.0041(9)	0.0065(8)	0.0026(7)	0	0
O(1)	0.030(6)	0.023(5)	0.015(4)	0.025(5)	0	0
O(2)	0.007(4)	0.010(4)	0.034(6)	-0.002(4)	0	0
O(3)	0.032(4)	0.027(4)	0.021(4)	0.022(4)	-0.015(3)	-0.015(3)
Cl	0.0150(15)	0.0150(15)	0.016(2)	0.0075(8)	0	0

Table S3. Refined atomic positions and anisotropic displacement parameter for vanadinte single crystal X-ray diffraction data collected at 100K.

s.g	$P6_3/m$	a = 10.2984(6) Å	c = 7.2907(4) Å	
Site	***x***	***y***	***z***	U_{Iso}
Pb^F	1/3	2/3	0.00797(7)	0.0039(2)
Pb^T	0.25584(5)	0.01571(5)	¼	0.0048(2)
V	0.4104(2)	0.3838(2)	¼	0.0011(7)
O(1)	0.3346(11)	0.4987(10)	¼	0.008(3)
O(2)	0.6041(10)	0.4860(10)	¼	0.010(3)
O(3)	0.3593(7)	0.2694(7)	0.0636(8)	0.010(3)
Cl	0	0	0	0.0055(12)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pb^F	0.0035(3)	0.0035(3)	0.0047(3)	0.00173(14)	0	0
Pb^T	0.0005(3)	0.0023(3)	0.0116(3)	0.00066(19)	0	0
V	0.0002(9)	0.0000(9)	0.0037	0.0005(7)	0	0
O(1)	0.012(4)	0.012(4)	0.007(4)	0.012(4)	0	0
O(2)	0.006(4)	0.005(4)	0.013(4)	-0.002(4)	0	0
O(3)	0.009(3)	0.011(3)	0.012(3)	0.007(3)	0	0
Cl	0.0046(15)	0.0046(15)	0.007(2)	0.0023(7)	0	0

Table S4. Selected bond distances and angles for the refined structure of vanadinite at RT and 100K.

Bond (Å)	**293K**	**100K**
Pb^F-O(1)	2.483(13)	2.475(7)
Pb^F-O(2)	2.748(10)	2.727(9)
Pb^F-O(3)	2.945(10)	2.939(8)
Pb^T-O(1)	3.193(13)	3.297(2)
Pb^T-O(2)	2.326(10)	2.319(9)
Pb^T-O(3)	2.675(8);	2.650(7);

	2.586(9)	2.566(7)
Pb^{T}-Cl	3.1570(5)	3.1406(4)
V-O(1)	1.719(16)	1.712(13)
V-O(2)	1.727(9)	1.729(9)
V-O(3)	1.694(8)	1.701(6)

Angle (°)	**293K**	**100K**
O(1)-V-O(3)	113.2(4)	112.9(3)
O(1)-V-O(2)	111.8(5)	111.4(5)
O(3)-V-O(3)	105.4(4)	106.1(3)
O(3)-V-O(2)	106.3(4)	106.5(3)
φ	17.0_8	16.0_4

Table S5. Coordinates of the cavities in vanadinite that are ≥ 0.74 Å

Fractional coordinate			**Cavity radius (Å)**
0.0288	0.5192	0.0270	0.75
0.0288	0.5192	0.4730	0.75
0.0288	0.8365	0.2432	0.76
0.0288	0.8365	0.2568	0.76
0.0385	0.8269	0.2432	0.74
0.0385	0.8269	0.2568	0.74
0.0385	0.8365	0.2297	0.74
0.0385	0.8365	0.2432	0.77
0.0385	0.8365	0.2568	0.77
0.0385	0.8365	0.2703	0.74
0.0481	0.8269	0.2432	0.74
0.0481	0.8269	0.2568	0.74
0.1635	0.1923	0.2432	0.76
0.1635	0.1923	0.2568	0.76
0.1635	0.2019	0.2297	0.74
0.1635	0.2019	0.2432	0.77
0.1635	0.2019	0.2568	0.77
0.1635	0.2019	0.2703	0.74
0.1731	0.2115	0.2432	0.74
0.1731	0.2115	0.2568	0.74
0.1731	0.2212	0.2432	0.74
0.1731	0.2212	0.2568	0.74

0.1923	0.0288	0.7432	0.76
0.1923	0.0288	0.7568	0.76
0.2019	0.0385	0.7297	0.74
0.2019	0.0385	0.7432	0.77
0.2019	0.0385	0.7568	0.77
0.2019	0.0385	0.7703	0.74
0.2115	0.0385	0.7432	0.74
0.2115	0.0385	0.7568	0.74
0.2212	0.0481	0.7432	0.74
0.2212	0.0481	0.7568	0.74
0.4808	0.5096	0.0270	0.75
0.4808	0.5096	0.4730	0.75
0.4904	0.9712	0.0270	0.75
0.4904	0.9712	0.4730	0.75
0.5096	0.0288	0.5270	0.75
0.5096	0.0288	0.9730	0.75
0.5192	0.4904	0.5270	0.75
0.5192	0.4904	0.9730	0.75
0.7788	0.9519	0.2432	0.74
0.7788	0.9519	0.2568	0.74
0.7885	0.9615	0.2432	0.74
0.7885	0.9615	0.2568	0.74
0.7981	0.9615	0.2297	0.74
0.7981	0.9615	0.2432	0.77
0.7981	0.9615	0.2568	0.77
0.7981	0.9615	0.2703	0.74
0.8077	0.9712	0.2432	0.76
0.8077	0.9712	0.2568	0.76
0.8269	0.7788	0.7432	0.74
0.8269	0.7788	0.7568	0.74
0.8269	0.7885	0.7432	0.74
0.8269	0.7885	0.7568	0.74
0.8365	0.7981	0.7297	0.74
0.8365	0.7981	0.7432	0.77
0.8365	0.7981	0.7568	0.77
0.8365	0.7981	0.7703	0.74
0.8365	0.8077	0.7432	0.76
0.8365	0.8077	0.7568	0.76
0.9519	0.1731	0.7432	0.74
0.9519	0.1731	0.7568	0.74
0.9615	0.1635	0.7297	0.74
0.9615	0.1635	0.7432	0.77
0.9615	0.1635	0.7568	0.77

0.9615	0.1635	0.7703	0.74
0.9615	0.1731	0.7432	0.74
0.9615	0.1731	0.7568	0.74
0.9712	0.1635	0.7432	0.76
0.9712	0.1635	0.7568	0.76
0.9712	0.4808	0.5270	0.75
0.9712	0.4808	0.9730	0.75

Table S6. Refinement parameters for pyromorphite $Pb_{10}(PO_4)_6Cl_2$

Crystal size	0.10 × 0.17 × 0.17 mm	
Crystal system	Hexagonal	
Space group	$P6_3/m$ (C^2_{6h}, No. 176)	
Temperature	293K	100K
Unit cell dimensions		
a (Å)	9.9793(6)	9.9481(4)
c (Å)	7.3285(5)	7.3334(3)
V (Å^3)	632.04	628.52
Z	2	2
Density (g cm^{-3})	7.1245	7.1644
μ (cm^{-1})	67.02	67.40
Radiation Mo $K\alpha$ (Å)	0.71069	0.71069
Collection limits (θ, deg)	2.36 – 32.53	2.36 – 36.37
Data measured	11539	13071
Unique reflections	820	1091
Reflections with I≥3σ(I)	650	897
R	0.0263	0.0307
R_W	0.0733	0.0798
GOF	1.77	1.87
D residual (eÅ^{-3})		
+	2.50	3.59
-	1.79	3.76

Table S7. Refined atomic positions and anisotropic displacement parameter for pyromorphite single crystal X-ray diffraction data collected at RT.

s.g	$P6_3/m$	a = 9.9793(6) Å	c = 7.3285 (5) Å	
Site	***x***	***y***	***z***	U_{Iso}
Pb^F	1/3	2/3	0.00492(6)	0.01434(15)
Pb^T	0.25504(5)	0.00636(4)	¼	0.01407(18)

P	0.4107(3)	0.3791(3)	¼	0.0065(9)
O(1)	0.3420(10)	0.4887(10)	¼	0.017(3)
O(2)	0.5908(9)	0.4741(9)	¼	0.015(3)
O(3)	0.3610(7)	0.2738(7)	0.0807(7)	0.018(2)
Cl	0	0	0	0.0134(10)

s.g	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pb^F	0.0198(2)	0.0198(2)	0.0035(2)	0.00989(10)	0	0
Pb^T	0.0115(2)	0.0141(2)	0.0160(2)	0.00593(17)	0	0
P	0.0101(11)	0.0078(11)	0.0029(10)	0.0055(9)	0	0
O(1)	0.027(5)	0.021(4)	0.015(4)	0.021(4)	0	0
O(2)	0.007(3)	0.014(4)	0.020(4)	0.002(3)	0	0
O(3)	0.027(3)	0.026(3)	0.009(2)	0.018(3)	-0.013(2)	-0.014(2)
Cl	0.0141(12)	0.0141(12)	0.0119(19)	0.0071(6)	0	0

Table S8. Refined atomic positions and anisotropic displacement parameter for pyromorphite single crystal X-ray diffraction data collected at 100K.

s.g	$P6_3/m$	a = 9.9481(4) Å	c = 7.3334(3) Å	
Site	***x***	***y***	***z***	U_{Iso}
Pb^F	1/3	2/3	0.00516(5)	0.00443(12)
Pb^T	0.25446(4)	0.00677(4)	¼	0.00776(14)
P	0.4113(3)	0.3797(3)	¼	0.0012(7)
O(1)	0.3437(8)	0.4895(9)	¼	0.006(3)
O(2)	0.5909(8)	0.4750(8)	¼	0.006(2)
O(3)	0.3609(7)	0.2734(7)	0.0816(7)	0.012(2)
Cl	0	0	0	0.0046(8)

s.g	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pb^F	0.00825(15)	0.00825(15)	-0.00320(18)	0.00412(7)	0	0
Pb^T	0.00385(17)	0.00466(17)	0.0147(2)	0.00210(13)	0	0
P	0.0034(9)	0.0027(9)	-0.0025(9)	0.0016(8)	0	0
O(1)	0.012(3)	0.011(3)	0.002(3)	0.010(3)	0	0
O(2)	0.004(3)	0.007(3)	0.005(3)	0.002(3)	0	0
O(3)	0.015(3)	0.021(3)	0.006(2)	0.013(2)	-0.010(2)	-0.013(2)
Cl	0.0056(9)	0.0056(9)	0.0026(16)	0.0028(5)	0	0

Table S9. Selected bond distances and angles for the refined structure of pyromorphite at RT and 100K.

Bond (Å)	293K	100K
Pb^F-O(1)	2.558(6)	2.554(7)
Pb^F-O(2)	2.665(8)	2.668(7)
Pb^F-O(3)	2.871(7)	2.863(7)
Pb^T-O(1)	3.082(10)	3.091(8)
Pb^T-O(2)	2.354(8)	2.345(7)
Pb^T-O(3)	2.638(6); 2.637(7)	2.647(6); 2.622(6)
Pb^T-Cl	3.1108(4)	3.0989(4)
P-O(1)	1.554(13)	1.543(11)
P-O(2)	1.558(8)	1.548(7)
P-O(3)	1.539(6)	1.538(6)

Angle (°)	293K	100K
O(1)-P-O(3)	112.1(4)	112.3(3)
O(1)-P-O(2)	110.6(5)	110.1(4)
O(3)-P-O(3)	107.5(4)	106.9(3)
O(3)-P-O(2)	107.2(3)	107.5(3)
φ	17.8_3	17.2_6

Table S10. Refinement parameters for mimetite $Pb_{10}(AsO_4)_6Cl_2$ at RT and 100K in the space group $P6_3/m$.

Crystal size	0.10 × 0.12 × 0.16 mm	
Crystal system	Hexagonal	
Space group	$P6_3/m$ (C^2_{6h}, No. 176)	
Temperature	293K	100K
Unit cell dimensions		
a (Å)	10.2257(6)	10.1885(6)
c (Å)	7.4349(5)	7.4061(4)
V (Å^3)	673.27(6)	665.80(5)
Z	2	2
Density (g cm^{-3})	7.3383	7.4207
μ (cm^{-1})	69.876	70.661
Radiation Mo $K\alpha$ (Å)	0.71073	0.71073
Collection limits (θ, deg)	2.30 – 32.76	2.31 – 32.78
Data measured	9755	8676
Unique reflections	865	821
Reflections with I≥3σ(I)	703	711
R	0.0505	0.0956
R_W	0.1136	0.1761

GOF	2.33	3.67
D residual ($eÅ^{-3}$)		
+	7.15	22.38
-	5.69	21.59

Table S11. Refined atomic positions and anisotropic displacement parameter for mimetite single crystal X-ray diffraction data collected at RT in the hexagonal space group $P6_3/m$.

s.g	$P6_3/m$	a = 10.2257(6) Å	c = 7.4349(5) Å	
Site	***x***	***y***	***z***	U_{Iso}
Pb^F	1/3	2/3	0.00687(9)	0.0111(2)
Pb^T	0.25101(7)	0.00458(7)	¼	0.0138(3)
As	0.40933(18)	0.38444(17)	¼	0.0021(5)
O(1)	0.3300(15)	0.4931(15)	¼	0.011(5)
O(2)	0.5983(15)	0.4892(15)	¼	0.028(6)
O(3)	0.3629(16)	0.2730(16)	0.0710(16)	0.047(7)
Cl	0	0	0	0.0144(18)

s.g	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pb^F	0.0113(3)	0.0113(3)	0.0106(3)	0.00564(16)	0	0
Pb^T	0.0010(3)	0.0038(4)	0.0368(4)	0.0014(3)	0	0
As	-0.0011(7)	-0.0026(7)	0.0104(6)	-0.0007(6)	0	0
O(1)	0.016(7)	0.014(7)	0.016(5)	0.018(6)	0	0
O(2)	0.001(6)	0.009(7)	0.074(10)	0.004(6)	0	0
O(3)	0.063(9)	0.061(9)	0.053(6)	0.058(8)	-0.049(7)	-0.049(7)
Cl	0.011(2)	0.011(2)	0.021(3)	0.0056(11)	0	0

Table S12. Refined atomic positions and anisotropic displacement parameter for mimetite single crystal X-ray diffraction data collected at 100K in the hexagonal space group $P6_3/m$.

s.g	$P6_3/m$	a = 10.1885(6) Å	c = 7.4061(4) Å	
Site	***x***	***y***	***z***	U_{Iso}
Pb^F	1/3	2/3	0.00692(15)	0.0028(4)
Pb^T	0.24942(11)	0.00250(11)	¼	0.0043(4)
As	0.4089(3)	0.3856(3)	¼	-0.0044(9)
O(1)	0.330(2)	0.496(2)	¼	-0.001(8)
O(2)	0.598(3)	0.491(2)	¼	0.028(11)
O(3)	0.363(3)	0.276(3)	0.073(3)	0.051(14)

Cl	0	0	0	0.005(3)

s.g	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pb^F	0.0027(5)	0.0027(5)	0.0031(6)	0.0013(3)	0	0
Pb^T	-0.0074(5)	-0.0064(5)	0.0277(7)	-0.0028(4)	0	0
As	-0.0077(11)	-0.0089(11)	0.0042(10)	-0.0034(10)	0	0
O(1)	-0.003(9)	0.007(10)	0.005(8)	0.010(9)	0	0
O(2)	-0.002(11)	-0.007(10)	0.10(2)	0.003(9)	0	0
O(3)	0.078(18)	0.073(17)	0.054(12)	0.077(16)	-0.066(13)	-0.067(13)
Cl	0.003(3)	0.003(3)	0.009(5)	0.0017(17)	0	0

Table S13. Selected bond distances and angles for the refined structure of mimetite at RT and 100K in the space group $P6_3/m$.

Bond (Å)	**293K**	**100K**
Pb^F-O(1)	2.521(12)	2.489(18)
Pb^F-O(2)	2.791(13)	2.79(2)
Pb^F-O(3)	2.907(17)	2.90(3)
Pb^T-O(1)	3.072(16)	3.05(2)
Pb^T-O(2)	2.315(14)	2.31(2)
Pb^T-O(3)	2.626(15); 2.734(15)	2.62(3); 2.75(3)
Pb^T-Cl	3.1504(7)	3.1340(11)
As-O(1)	1.672(18)	1.68(3)
As-O(2)	1.677(13)	1.67(2)
As-O(3)	1.659(13)	1.63(2)

Angle (°)	**293K**	**100K**
O(1)-As-O(3)	112.9(7)	113.0(13)
O(1)-As-O(2)	111.2(7)	110.9(11)
O(3)-As-O(3)	106.6(7)	106.8(13)
O(3)-As-O(2)	106.4(6)	106.3(11)
φ	18.2_7	18.1_9

Table S14. Refinement parameters for the mimetite supercell derived from synchrotron X-ray diffraction data.

Crystal size	10 × 10 × 2 μm
Crystal system	Monoclinic
Space group	$P12_1/a1$ (No. 14)

Temperature	293K
Unit cell dimensions	
a (Å)	20.44(1)
b (Å)	7.437(1)
c (Å)	20.44(1)
β (°)	120
V (Å^3)	2690.85
Z	4
Density (g cm^{-3})	7.3444
μ (cm^{-1})	69.934
Radiation Synchrotron (Å)	0.711955
Collection limits (θ, deg)	1.15 – 31.46
Data measured	49774
Unique reflections	7674
Reflections with I≥3σ(I)	5984
R	0.0322
R_W	0.0438
GOF	1.69
D residual (eÅ^{-3})	
+	3.71
-	3.92

Table S15. Atomic positions and anisotropic displacement parameters of the supercell of mimetite derived from synchrotron X-ray diffraction data.

$P12_1/a1$	a = 20.44(1) Å	b = 7.437(1) Å	c = 20.44(1) Å	β = 120°
Site	***x***	***y***	***z***	$\boldsymbol{U_{Iso}}$
Pb^F(1)	0.910659(18)	0.99489(4)	0.333997(18)	0.00679(12)
Pb^F(2)	0.579280(18)	0.49464(4)	0.160559(19)	0.00733(12)
Pb^F(3)	0.589404(18)	0.00825(4)	0.172693(19)	0.00699(12)
Pb^F(4)	0.923387(18)	0.50957(4)	0.332895(18)	0.00697(12)
Pb^T(1)	0.877325(19)	0.73398(4)	0.123913(19)	0.00654(12)
Pb^T(2)	0.871853(18)	0.78111(4)	0.622914(18)	0.00635(12)
Pb^T(3)	0.749734(19)	0.74181(4)	0.37572(2)	0.00873(13)
Pb^T(4)	0.626897(18)	0.72903(4)	0.000077(19)	0.00669(13)
Pb^T(5)	0.873434(18)	0.25547(4)	0.49733(2)	0.00721(13)
Pb^T(6)	0.751320(18)	0.23213(4)	0.124379(19)	0.00668(12)
As(1)	0.73927(5)	0.75436(10)	0.19297(5)	0.0045(3)
As(2)	0.45571(5)	0.74967(10)	0.01328(5)	0.0046(3)
As(3)	0.05941(5)	0.74902(10)	0.29688(5)	0.0048(3)
As(4)	0.76287(5)	0.24907(10)	0.30660(5)	0.0047(3)
As(5)	0.94560(5)	0.25835(10)	0.20596(5)	0.0048(3)

As(6)	0.95238(5)	0.74230(10)	0.50991(5)	0.0042(3)
O(1a)	0.8335(4)	0.7470(7)	0.2456(4)	0.007(2)
O(1b)	0.7094(3)	0.9597(8)	0.1526(4)	0.012(2)
O(1c)	0.7061(4)	0.5984(9)	0.1233(3)	0.012(2)
O(1d)	0.6966(4)	0.7156(8)	0.2447(4)	0.010(2)
O(2a)	0.4141(4)	0.7552(7)	0.9189(4)	0.008(2)
O(2b)	0.4407(4)	0.5517(8)	0.0438(4)	0.013(2)
O(2c)	0.4222(4)	0.9105(8)	0.0468(4)	0.009(2)
O(2d)	0.4407(4)	0.5517(8)	0.0559(4)	0.009(2)
O(3a)	0.0070(4)	0.7480(7)	0.3396(4)	0.010(3)
O(3b)	0.0067(3)	0.7958(9)	0.2034(4)	0.011(2)
O(3c)	0.1264(4)	0.9105(9)	0.3353(4)	0.013(3)
O(3d)	0.1070(4)	0.5560(9)	0.3077(4)	0.015(3)
O(4a)	0.7624(4)	0.4099(8)	0.3741(4)	0.011(2)
O(4b)	0.6682(4)	0.2541(7)	0.2523(4)	0.008(2)
O(4c)	0.7957(3)	0.0500(8)	0.3509(4)	0.009(2)
O(4d)	0.8062(4)	0.2846(9)	0.2560(4)	0.011(3)
O(5a)	0.9994(4)	0.2485(7)	0.2523(4)	0.008(2)
O(5b)	0.8753(4)	0.1068(8)	0.1672(4)	0.013(3)
O(5c)	0.9076(4)	0.4651(8)	0.1971(4)	0.013(3)
O(5d)	0.9956(4)	0.2174(9)	0.3007(4)	0.013(3)
O(6a)	0.9435(4)	0.5387(8)	0.5403(3)	0.011(2)
O(6b)	0.9131(4)	0.7490(7)	0.4159(4)	0.008(2)
O(6c)	0.0457(3)	0.7939(8)	0.5526(4)	0.009(2)
O(6d)	0.9118(4)	0.8952(8)	0.5390(4)	0.011(2)
Cl(1)	0.73991(12)	0.0042(2)	0.49092(12)	0.0090(7)
Cl(2)	0.25188(11)	0.0124(2)	0.00009(10)	0.0076(7)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pb^{F}(1)	0.00703(14)	0.00519(13)	0.00801(16)	-0.00025(10)	0.00366(13)	-0.00010(10)
Pb^{F}(2)	0.00740(15)	0.00526(13)	0.00845(16)	0.00019(10)	0.00329(13)	-0.00012(10)
Pb^{F}(3)	0.00726(14)	0.00510(13)	0.00796(15)	-0.00008(10)	0.00332(13)	0.00005(10)
Pb^{F}(4)	0.00725(15)	0.00498(13)	0.00821(16)	-0.00025(10)	0.00351(13)	-0.00003(10)
Pb^{T}(1)	0.00653(15)	0.00671(13)	0.00587(17)	0.00151(10)	0.00273(13)	0.00060(10)
Pb^{T}(2)	0.00636(14)	0.00629(13)	0.00600(16)	-0.00072(10)	0.00279(13)	-0.00046(10)
Pb^{T}(3)	0.00840(16)	0.01164(15)	0.00641(17)	-0.00292(10)	0.00391(14)	-0.00136(10)
Pb^{T}(4)	0.00614(15)	0.00687(13)	0.00702(17)	-0.00055(10)	0.00325(14)	0.00051(10)
Pb^{T}(5)	0.00639(15)	0.00819(14)	0.00746(18)	-0.00005(10)	0.00377(14)	0.00083(10)
Pb^{T}(6)	0.00709(15)	0.00697(13)	0.00633(16)	0.00047(10)	0.00362(13)	0.00083(10)
As(1)	0.0041(4)	0.0049(3)	0.0042(4)	0.0001(3)	0.0018(4)	0.0000(2)
As(2)	0.0054(4)	0.0043(3)	0.0041(4)	-0.0003(2)	0.0024(3)	-0.0003(2)
As(3)	0.0042(4)	0.0050(3)	0.0052(4)	-0.0002(3)	0.0022(3)	-0.0004(2)
As(4)	0.0046(4)	0.0047(3)	0.0039(4)	-0.0003(3)	0.0015(4)	0.0000(2)
As(5)	0.0036(4)	0.0054(3)	0.0053(4)	0.0006(3)	0.0021(3)	0.0002(3)

As(6)	0.0039(4)	0.0043(3)	0.0045(4)	0.0000(2)	0.0021(3)	0.0001(2)
O(1a)	0.005(3)	0.007(3)	0.011(3)	-0.0011(19)	0.006(3)	0.001(2)
O(1b)	0.007(3)	0.007(3)	0.017(3)	0.002(2)	0.003(3)	0.009(2)
O(1c)	0.012(3)	0.016(3)	0.007(3)	-0.006(2)	0.004(3)	-0.009(2)
O(1d)	0.007(3)	0.014(3)	0.006(3)	-0.003(2)	0.002(3)	0.003(2)
O(2a)	0.006(3)	0.011(3)	0.006(3)	0.001(2)	0.002(3)	0.004(2)
O(2b)	0.019(3)	0.008(3)	0.011(3)	-0.004(2)	0.008(3)	0.000(2)
O(2c)	0.016(3)	0.007(2)	0.009(3)	0.001(2)	0.010(3)	-0.003(2)
O(2d)	0.008(3)	0.014(3)	0.005(3)	-0.001(2)	0.001(3)	-0.002(2)
O(3a)	0.008(3)	0.010(3)	0.011(4)	0.000(2)	0.004(3)	0.000(2)
O(3b)	0.003(3)	0.022(3)	0.005(3)	-0.002(2)	-0.001(2)	0.001(2)
O(3c)	0.005(3)	0.017(3)	0.017(3)	-0.009(2)	0.005(3)	-0.011(3)
O(3d)	0.020(3)	0.015(3)	0.016(3)	0.009(3)	0.012(3)	0.008(3)
O(4a)	0.010(3)	0.013(3)	0.009(3)	0.001(2)	0.004(3)	-0.002(2)
O(4b)	0.005(3)	0.011(3)	0.010(3)	0.000(2)	0.006(3)	0.000(2)
O(4c)	0.008(3)	0.007(2)	0.014(3)	0.002(2)	0.005(3)	0.006(2)
O(4d)	0.011(3)	0.015(3)	0.011(3)	-0.007(2)	0.009(3)	-0.001(2)
O(5a)	0.009(3)	0.011(3)	0.004(3)	-0.002(2)	0.003(3)	-0.004(2)
O(5b)	0.006(3)	0.014(3)	0.019(4)	-0.007(2)	0.007(3)	-0.008(3)
O(5c)	0.024(4)	0.007(3)	0.020(4)	0.012(3)	0.019(3)	0.008(2)
O(5d)	0.008(3)	0.018(3)	0.010(3)	0.000(2)	0.002(3)	0.009(3)
O(6a)	0.015(3)	0.009(3)	0.005(3)	0.001(2)	0.003(3)	0.003(2)
O(6b)	0.010(3)	0.003(2)	0.007(3)	0.0013(19)	0.002(3)	0.0017(19)
O(6c)	0.005(3)	0.014(3)	0.005(3)	-0.004(2)	0.000(2)	-0.002(2)
O(6d)	0.012(3)	0.012(3)	0.012(3)	0.004(2)	0.009(3)	0.000(2)
Cl(1)	0.0113(9)	0.0071(8)	0.0095(9)	0.0008(7)	0.0059(8)	0.0007(7)
Cl(2)	0.0068(9)	0.0086(8)	0.0065(10)	-0.0007(7)	0.0026(8)	-0.0001(7)

Table S16. Selected bond distances (Å) for the $Pb_{10}(AsO_4)_6Cl_2$ supercell model derived from synchrotron single-crystal XRD data.

Bond	Dist. (Å)	Bond	Dist. (Å)	Bond	Dist. (Å)	Bond	Dist. (Å)
$Pb^F(1)$–O(6b)	2.463(7)	$Pb^F(2)$–O(5a)	2.475(7)	$Pb^F(3)$–O(4b)	2.442(5)	$Pb^F(4)$–O(3a)	2.419(7)
$Pb^F(1)$–O(1a)	2.510(5)	$Pb^F(2)$–O(2a)	2.515(7)	$Pb^F(3)$–O(5a)	2.534(7)	$Pb^F(4)$–O(1a)	2.530(5)
$Pb^F(1)$–O(6c)	2.563(7)	$Pb^F(2)$–O(4b)	2.571(6)	$Pb^F(3)$–O(2a)	2.544(7)	$Pb^F(4)$–O(6b)	2.539(7)
$Pb^F(1)$–O(4c)	2.573(8)	$Pb^F(2)$–O(3b)	2.587(8)	$Pb^F(3)$–O(1d)	2.642(9)	$Pb^F(4)$–O(5c)	2.651(8)
$Pb^F(1)$–O(3a)	2.653(7)	$Pb^F(2)$–O(2b)	2.672(6)	$Pb^F(3)$–O(1b)	2.706(8)	$Pb^F(4)$–O(6a)	2.683(5)
$Pb^F(1)$–O(5d)	2.720(9)	$Pb^F(2)$–O(1d)	2.699(6)	$Pb^F(3)$–O(2d)	2.743(7)	$Pb^F(4)$–O(4d)	2.691(6)
$Pb^F(1)$–O(4d)	2.888(6)	$Pb^F(2)$–O(2d)	2.817(7)	$Pb^F(3)$–O(1d)	2.911(6)	$Pb^F(4)$–O(5d)	2.882(8)
$Pb^F(1)$–O(5b)	3.221(8)	$Pb^F(2)$–O(1c)	3.141(9)	$Pb^F(3)$–O(3b)	3.070(8)	$Pb^F(4)$–O(6c)	3.081(7)
$Pb^F(1)$–O(6d)	3.340(6)	$Pb^F(2)$–O(3c)	3.277(8)	$Pb^F(3)$–O(2c)	3.167(6)	$Pb^F(4)$–O(4a)	3.268(9)
$Pb^T(1)$–O(3b)	2.356(6)	$Pb^T(2)$–O(5d)	2.356(6)	$Pb^T(3)$–O(1d)	2.340(7)	$Pb^T(4)$–O(2d)	2.364(9)
$Pb^T(1)$–O(5c)	2.386(6)	$Pb^T(2)$–O(6d)	2.394(9)	$Pb^T(3)$–O(3c)	2.497(7)	$Pb^T(4)$–O(1c)	2.414(6)
$Pb^T(1)$–O(2c)	2.434(8)	$Pb^T(2)$–O(3c)	2.442(7)	$Pb^T(3)$–O(4c)	2.621(7)	$Pb^T(4)$–O(2b)	2.416(6)

Pb^T(1)–O(5b)	2.917(7)	Pb^T(2)–O(3d)	2.806(7)	Pb^T(3)–O(4a)	2.624(6)	Pb^T(4)–O(2c)	2.855(6)
Pb^T(1)–O(2b)	3.004(9)	Pb^T(2)–O(4b)	3.049(10)	Pb^T(3)–O(3d)	2.940(7)	Pb^T(4)–O(5a)	3.072(6)
Pb^T(1)–O(1a)	3.038(9)	Pb^T(2)–O(6a)	3.273(8)	Pb^T(3)–O(6b)	3.014(8)	Pb^T(4)–O(1b)	3.202(6)
Pb^T(1)–Cl(2)	3.1380(16)	Pb^T(2)–Cl(1)	3.0918(18)	Pb^T(3)–Cl(1)	3.141(2)	Pb^T(4)–Cl(2)	3.122(2)
Pb^T(1)–Cl(2)	3.2037(17)	Pb^T(2)–Cl(1)	3.1667(17)	Pb^T(3)–Cl(1)	3.166(2)	Pb^T(4)–Cl(2)	3.138(2)
Pb^T(5)–O(6c)	2.365(9)	Pb^T(6)–O(4d)	2.374(7)				
Pb^T(5)–O(6a)	2.449(6)	Pb^T(6)–O(1b)	2.381(7)				
Pb^T(5)–O(4a)	2.496(6)	Pb^T(6)–O(5b)	2.416(7)				
Pb^T(5)–O(6d)	2.802(6)	Pb^T(6)–O(1c)	2.873(7)				
Pb^T(5)–O(3a)	2.989(6)	Pb^T(6)–O(2a)	3.038(8)				
Pb^T(5)–O(4c)	3.011(6)	Pb^T(6)–O(5c)	3.267(7)				
Pb^T(5)–Cl(1)	3.066(2)	Pb^T(6)–Cl(2)	3.101(2)				
Pb^T(5)–Cl(1)	3.256(2)	Pb^T(6)–Cl(2)	3.177(2)				

Bond	**Dist. (Å)**				
As(1)–O(1a)	1.673(6)	As(2)–O(2a)	1.676(7)	As(3)–O(3a)	1.687(10)
As(1)–O(1b)	1.697(6)	As(2)–O(2b)	1.685(7)	As(3)–O(3b)	1.695(6)
As(1)–O(1c)	1.694(7)	As(2)–O(2c)	1.685(8)	As(3)–O(3c)	1.691(6)
As(1)–O(1d)	1.700(9)	As(2)–O(2d)	1.696(7)	As(3)–O(3d)	1.686(7)
As(4)–O(4a)	1.693(7)	As(5)–O(5a)	1.669(10)	As(6)–O(6a)	1.681(7)
As(4)–O(4b)	1.683(6)	As(5)–O(5b)	1.681(6)	As(6)–O(6b)	1.673(7)
As(4)–O(4c)	1.689(6)	As(5)–O(5c)	1.691(7)	As(6)–O(6c)	1.698(6)
As(4)–O(4d)	1.684(9)	As(5)–O(5d)	1.705(7)	As(6)–O(6d)	1.681(8)

Table S17. Coordinates of the cavities in the mimetite supercell that are greater than 0.72 Å

Fractional coordinate			**Cavity radius (Å)**
0.0146	0.8800	0.4390	0.72
0.0732	0.1200	0.7610	0.72
0.0780	0.1200	0.7610	0.72
0.0780	0.1333	0.7659	0.73
0.1171	0.6800	0.9024	0.73
0.1268	0.6800	0.9073	0.72
0.1561	0.2133	0.0244	0.72
0.1610	0.2000	0.0244	0.73
0.1610	0.2133	0.0195	0.74
0.1951	0.1467	0.1707	0.72
0.2195	0.1867	0.8780	0.74
0.2195	0.2000	0.8780	0.73
0.2244	0.3067	0.3805	0.72
0.2780	0.6933	0.1171	0.73

0.2780	0.6933	0.1220	0.73
0.2780	0.8000	0.6244	0.73
0.2829	0.6800	0.1220	0.72
0.2829	0.6933	0.1268	0.74
0.3366	0.7200	0.9805	0.73
0.3415	0.7067	0.9756	0.73
0.3707	0.1867	0.0927	0.73
0.3805	0.1867	0.0976	0.73
0.4195	0.6400	0.2293	0.72
0.4244	0.6267	0.2341	0.73
0.4244	0.6400	0.2341	0.72
0.4829	0.3733	0.5610	0.74
0.5171	0.6267	0.4390	0.74
0.5756	0.3600	0.7659	0.72
0.5756	0.3733	0.7659	0.73
0.5805	0.3600	0.7707	0.72
0.6195	0.8133	0.9024	0.73
0.6293	0.8133	0.9073	0.73
0.6585	0.2933	0.0244	0.73
0.6634	0.2800	0.0195	0.73
0.7171	0.3067	0.8732	0.74
0.7171	0.3200	0.8780	0.72
0.7220	0.2000	0.3756	0.73
0.7220	0.3067	0.8780	0.73
0.7220	0.3067	0.8829	0.73
0.7756	0.6933	0.6195	0.72
0.7805	0.8000	0.1220	0.73
0.7805	0.8133	0.1220	0.74
0.8049	0.8533	0.8293	0.72
0.8390	0.7867	0.9805	0.74
0.8390	0.8000	0.9756	0.73
0.8439	0.7867	0.9756	0.72
0.8732	0.3200	0.0927	0.72
0.8829	0.3200	0.0976	0.73
0.9220	0.8667	0.2341	0.73
0.9220	0.8800	0.2390	0.72
0.9268	0.8800	0.2390	0.72
0.9854	0.1200	0.5610	0.72

Table 18. Data collections parameters and refinement indices for single crystal XRD data of finnemanite collected at both RT and 100K.

Crystal size	0.11 × 0.16 × 0.21 mm	
Crystal system	Hexagonal	
Space group	$P6_3/m$ (C^2_{6h}, No. 176)	
Temperature	293K	100K
Unit cell dimensions		
a (Å)	10.3097(5)	10.2800(14)
c (Å)	7.0700(4)	7.0413(10)
V (Å^3)	650.79	644.42
Z	2	2
Density (g cm^{-3})	7.3469	7.4196
μ (cm^{-1})	72.26	72.97
Radiation Mo$K\alpha$ (Å)	0.71069	0.71069
Collection limits (θ, deg)	2.28 – 27.67	2.29 – 27.45
Data measured	7686	7039
Unique reflections	551	536
Reflections with I≥3σ(I)	517	495
R	0.0401	0.0625
R_W	0.0971	0.1369
GOF	2.84	3.55
D residual (eÅ^{-3})		
+	7.14	9.38
-	5.11	8.28

Table 19. Refined atomic coordinates and anisotropic displacement parameters for finnemanite at 293K in the space group $P6_3/m$.

s.g	$P6_3/m$	a = 10.3097(5) Å	c = 7.0700(4) Å	
	x	***y***	***z***	U_{Iso}
Pb^F	1/3	2/3	0.98971(11)	0.0179(3)
Pb^T	0.26487(7)	0.03696(7)	1/4	0.0100(3)
As	0.41419(19)	0.40075(19)	1/4	0.0101(7)
O(1)	0.6140(13)	0.4645(13)	1/4	0.010(5)
O(2)	0.3711(12)	0.2786(10)	0.0605(14)	0.020(4)
Cl	0	0	0	0.0085(18)

s.g	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pb^F	0.0239(4)	0.0239(4)	0.0059(4)	0.0120(2)	0	0
Pb^T	0.0040(4)	0.0075(4)	0.0183(4)	0.0026(3)	0	0
As	0.0048(9)	0.0052(9)	0.0211(9)	0.0032(7)	0	0
O(1)	0.010(6)	0.013(6)	0.006(5)	0.004(5)	0	0
O(2)	0.026(6)	0.012(5)	0.018(4)	0.007(4)	-0.011(4)	-0.002(4)
Cl	0.009(2)	0.009(2)	0.008(3)	0.0044(11)	0	0

Table S20. Refined atomic coordinates and anisotropic displacement parameters of finnemanite collected at 100K.

s.g	$P6_3/m$	a = 10.2800(14) Å	c = 7.0413(10) Å	
	x	***y***	***z***	U_{Iso}
Pb^F	1/3	2/3	0.99026(16)	0.0077(4)
Pb^T	0.26487(10)	0.03772(10)	1/4	0.0023(5)
As	0.4145(3)	0.4013(3)	1/4	0.0025(10)
O(1)	0.6167(19)	0.4666(18)	1/4	0.001(7)
O(2)	0.3704(16)	0.2793(14)	0.060(2)	0.009(6)
Cl	0	0	0	0.001(2)

s.g	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pb^F	0.0101(6)	0.0101(6)	0.0028(6)	0.0050(3)	0	0
Pb^T	-0.0030(6)	-0.0011(6)	0.0109(6)	-0.0012	0	0
As	-0.0031(12)	-0.0021(13)	0.0132(13)	-0.0009(10)	0	0
O(1)	0.000(9)	0.001(8)	-0.005(7)	-0.006(7)	0	0
O(2)	0.020(8)	0.001(6)	0.007(6)	0.006(6)	0	0
Cl	-0.002(3)	-0.002(3)	0.007(5)	-0.0009(15)	0	0

Table S21. Selected bond distances and angles for finnemanite at RT and 100K.

Bond(Å) / Angle (°)	**293K**	**100K**
Pb^F environment		
Pb^F-O(1)	2.394(10)	2.388(14)
Pb^F-O(2)	2.830(12)	2.832(17)
Pb^T environment		
Pb^T-O(1)	2.427(12)	2.402(17)
Pb^T-O(2)	2.544(10)	2.539(13)
Pb^T-O(2)	2.610(12)	2.594(17)
Pb(2)-Cl	3.1122(6)	3.0996(9)
As environment		
As-O(1)	1.823(13)	1.838(19)
As-O(2)	1.737(10)	1.733(14)
O(1)-As-O(2)	95.4(5)	95.9
O(2)-As-O(2)	100.9(5)	101.2(7)

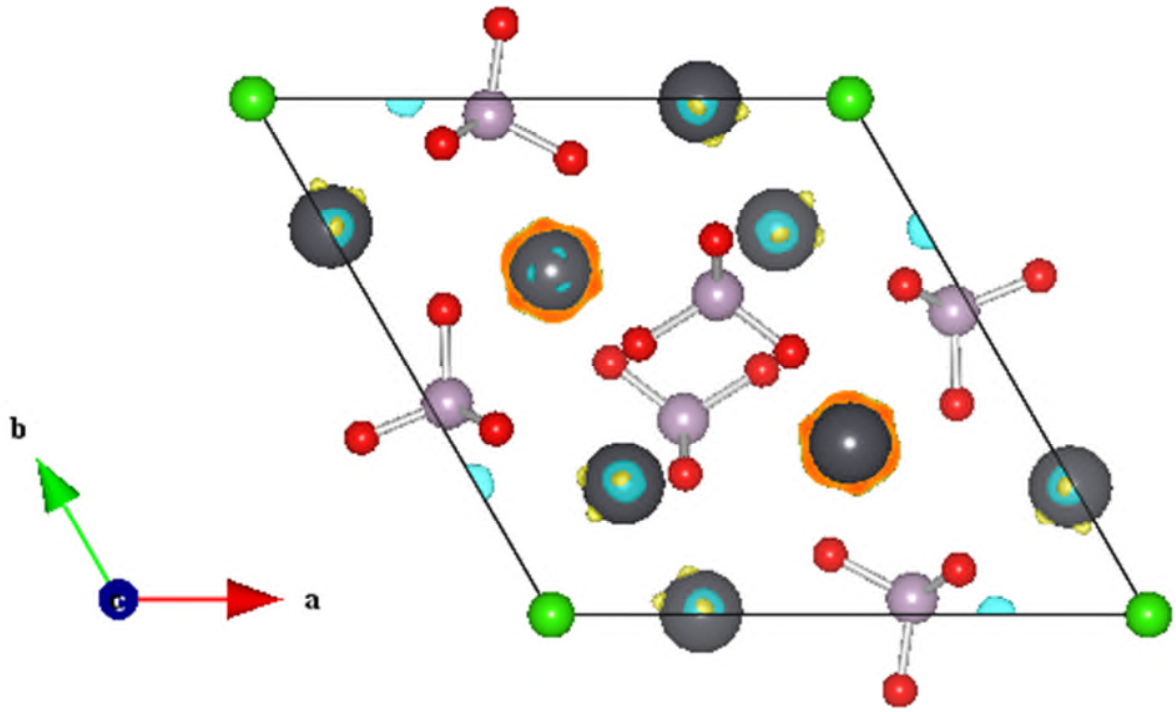

Figure S1. Three dimensional difference Fourier map of pyromorphite that was derived from single crystal XRD data at 100K. Indicated are the regions of electron density greater than 2.5 electrons which mainly surround the Pb sites.

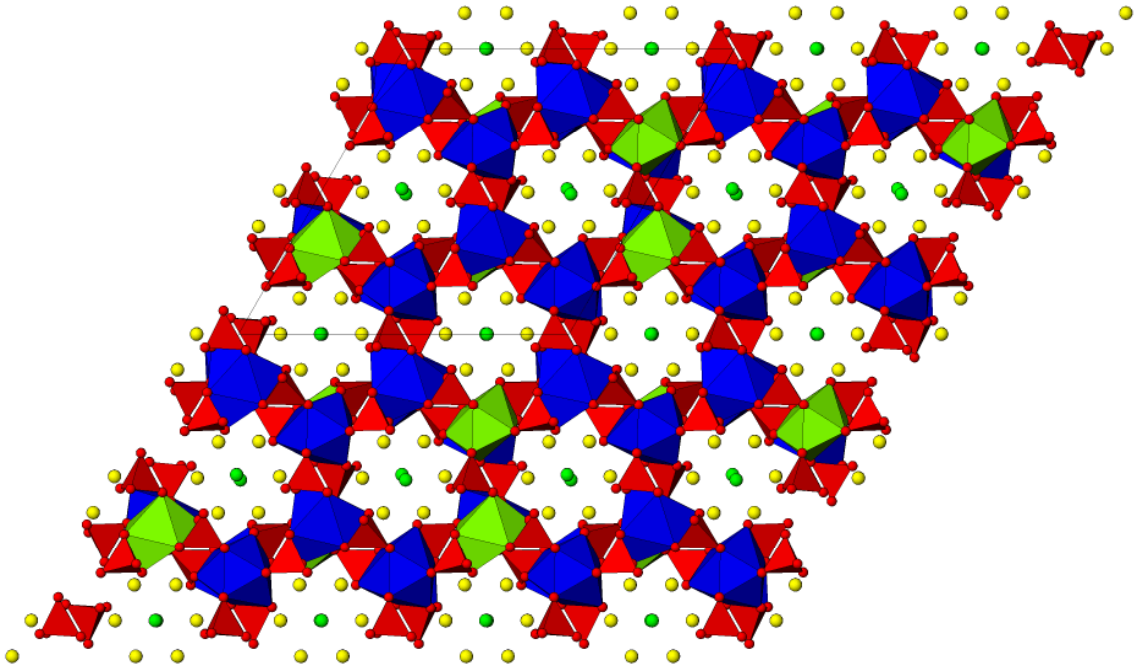

Figure S2. A polyhedral representation of the mimetite supercell. The $Pb^{F}(1)$ polyhedra are shown in green with the remaining Pb^{F} shown in blue. The Cl ions in the channel containing two adjacent $Pb^{F}(1)$ polyhedra are displaced whereas the remaining channel with a more regular Pb polyhedra show the Cl ions in a more linear arrangement.

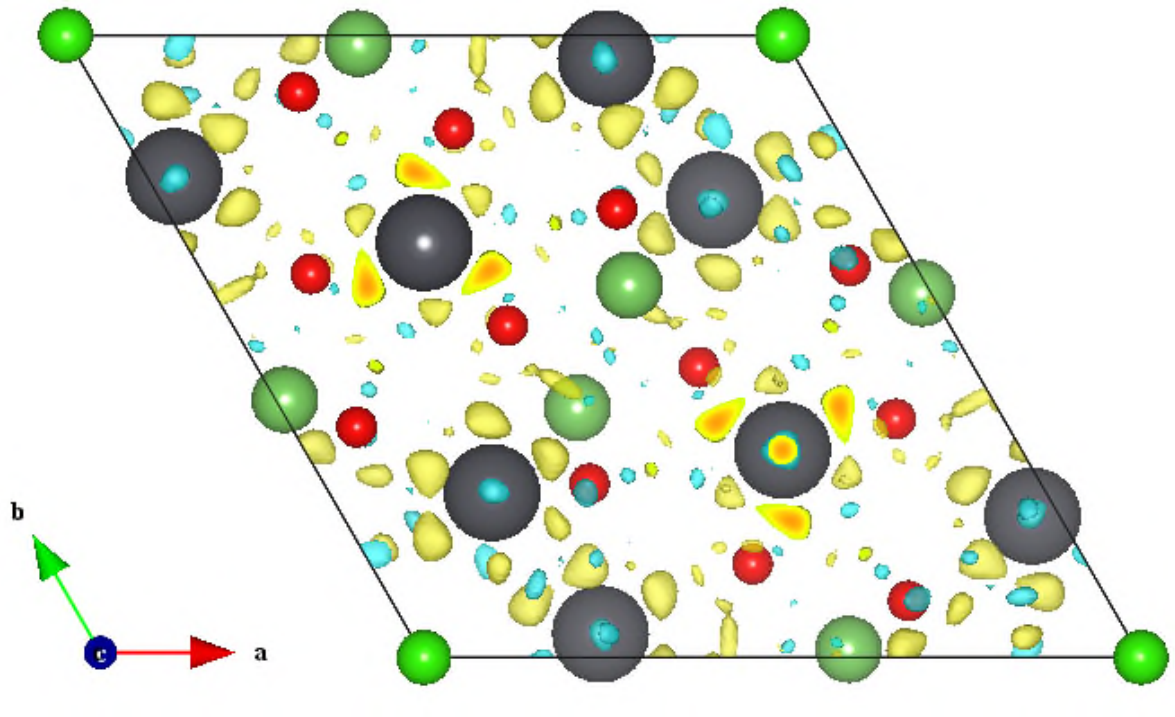

Figure S3. Three dimensional difference Fourier map from the X-ray diffraction data for finnemanite collected at 100K. The regions of electron density > 4electrons (max. 9.5 electrons) are shown in yellow/orange.