Supporting Online Material

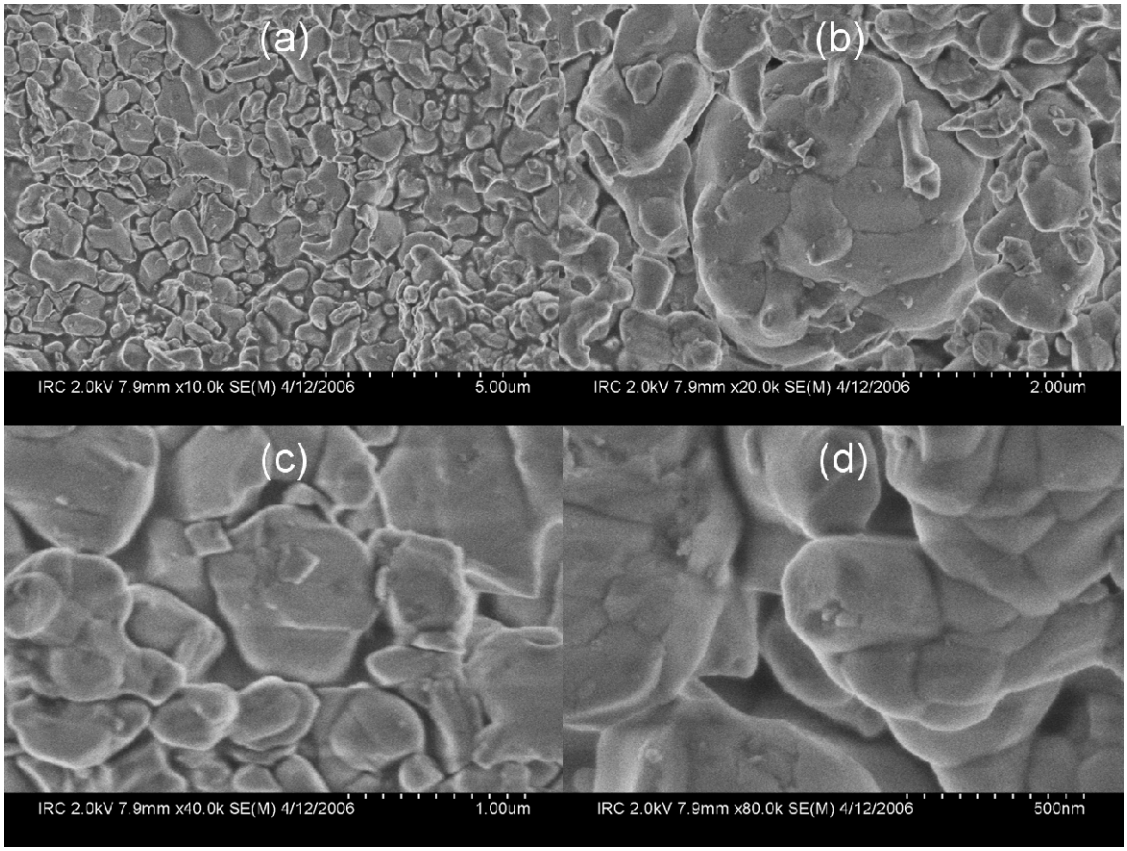


Figure S1a. SEI of $Ca_{10}(AsO_4)_6F_2$. (a) 10 (b) 20 (c) 40 (d) 80 magnification (×1000).

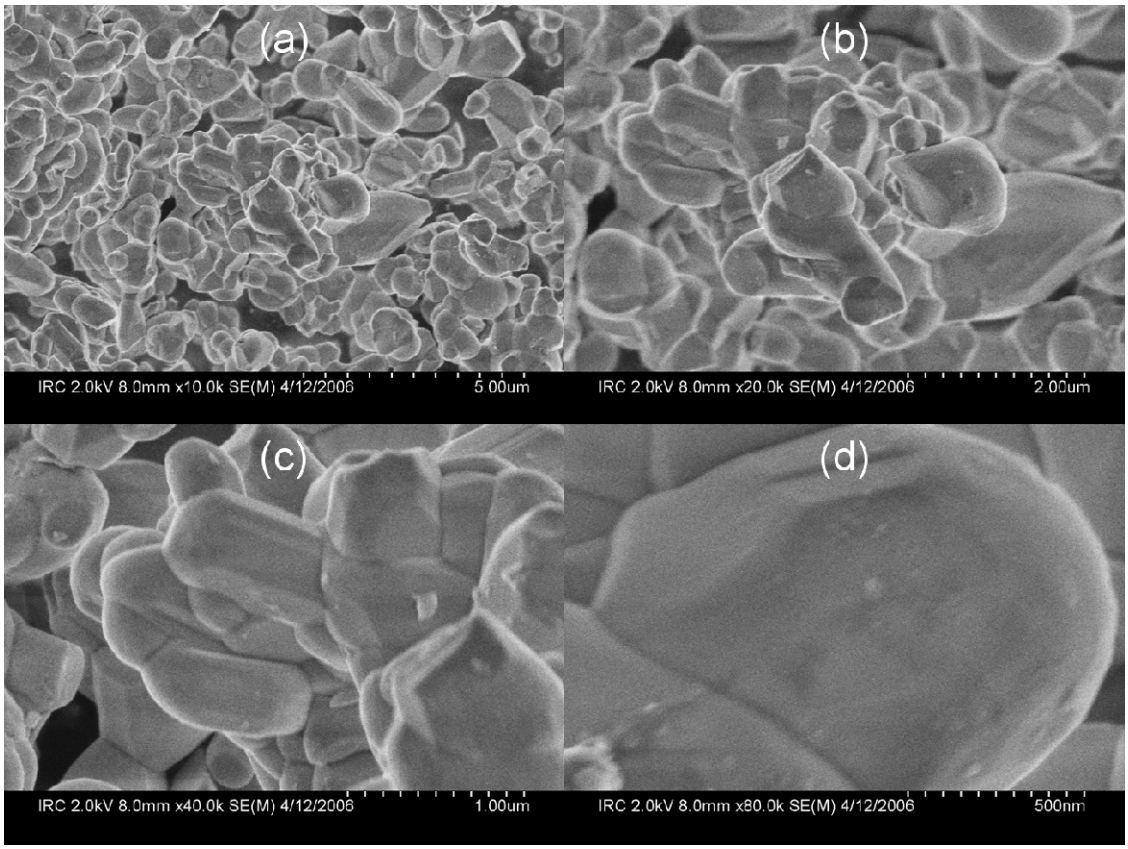
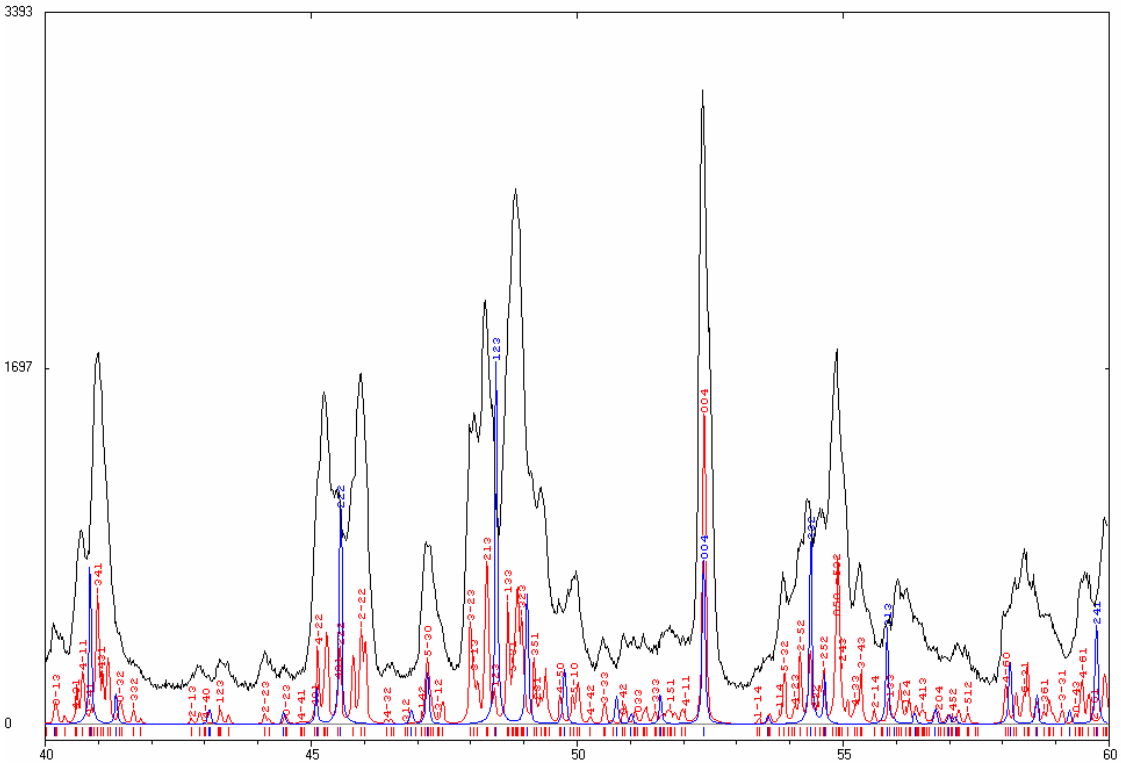


Figure S1b. SEI of $Ca_{10}(VO_4)_6F_2$. (a) 10 (b) 20 (c) 40 (d) 80 magnification (×1000).


3393
1697
0
40
45
50
55
60

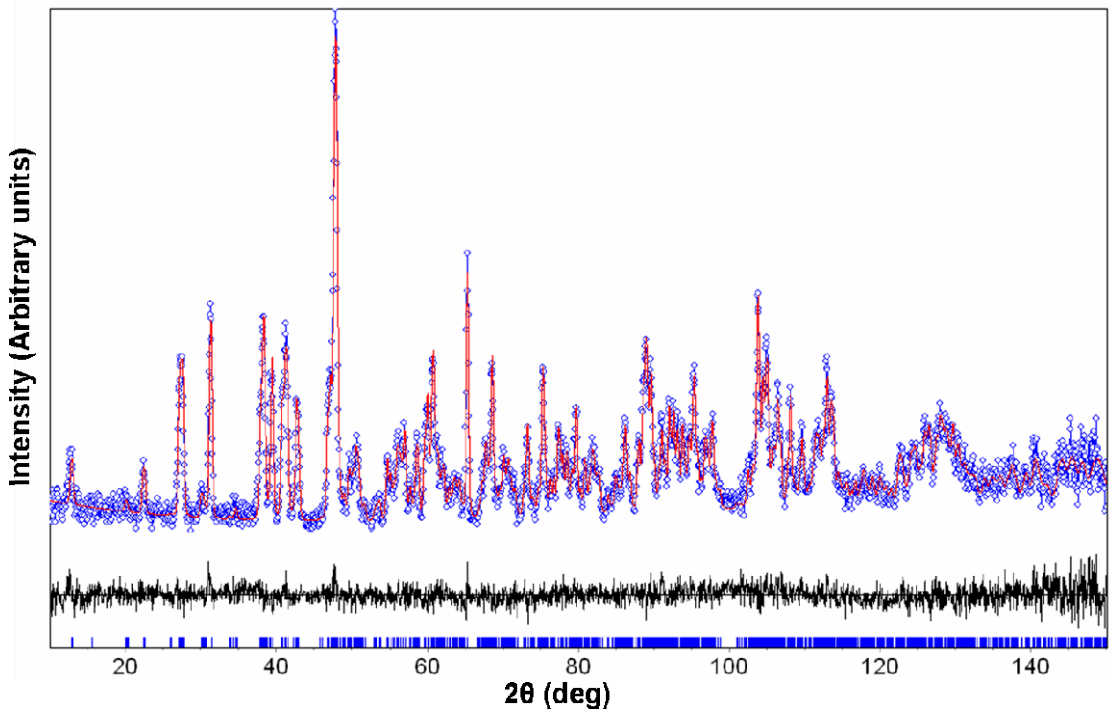
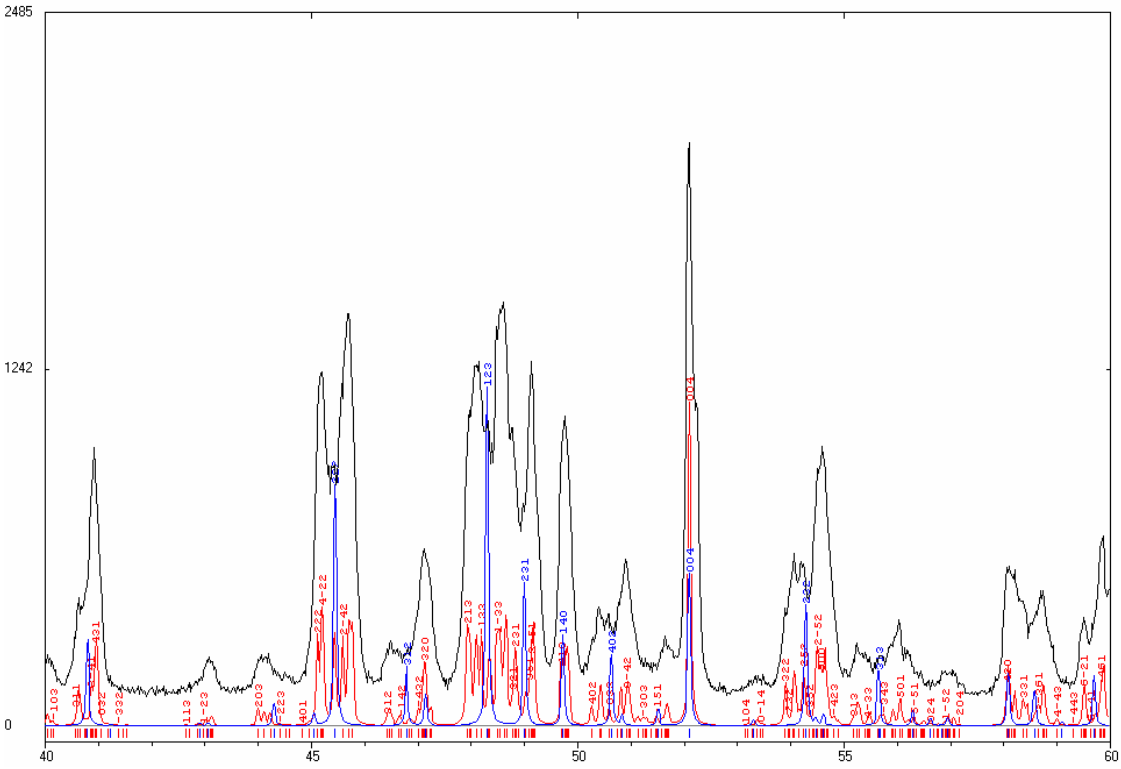

Intensity (Arbitrary units)
20
40
60
80
100
120
140
2θ (deg)

Figure S2a. (top) PXRD pattern of $Ca_{10}(AsO_4)_6F_2$ (black) compared with calculated reflection positions for hexagonal $P6_3/m$ (blue) and P-1(red) symmetries. (bottom) Neutron diffraction refinement profile for $Ca_{10}(AsO_4)_6F_2$, showing the observed (blue), calculated (red) and difference profiles (black).



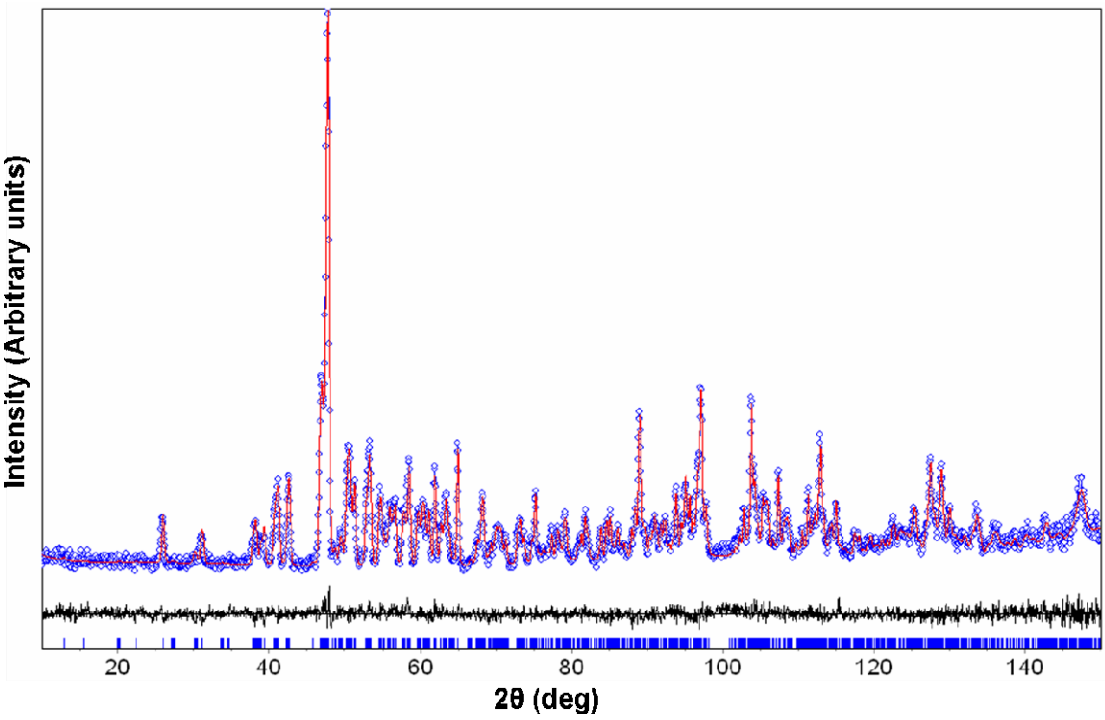


Figure S2b. (top) PXRD pattern of $Ca_{10}(VO_4)_6F_2$ (black) compared with calculated reflection positions for hexagonal *P*6$_3$/*m* (blue) and *P*-1(red) symmetries. (bottom) Neutron diffraction refinement profile for $Ca_{10}(VO_4)_6F_2$, showing the observed (blue), calculated (red) and difference profiles (black).

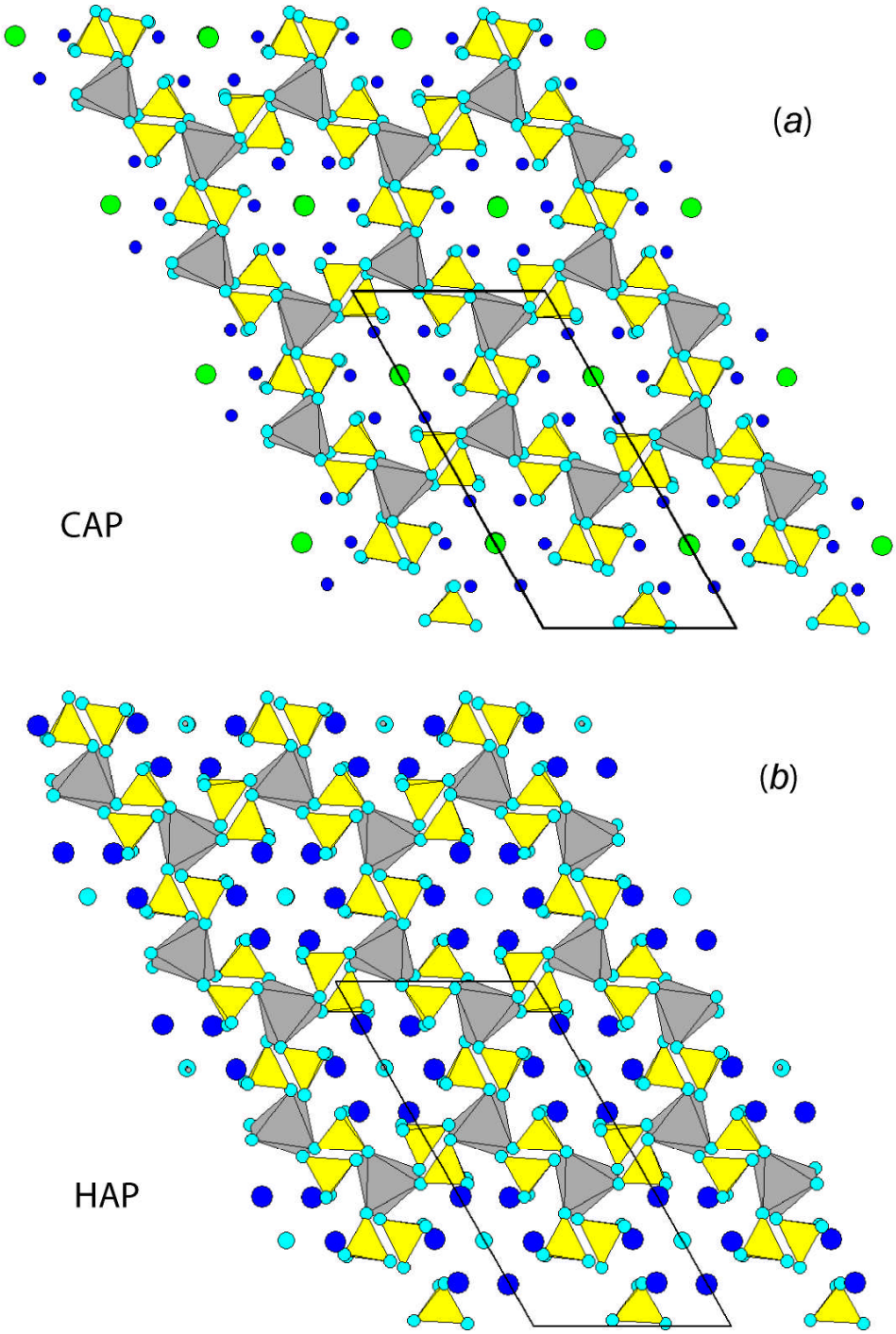


Figure S3. Polyhedral representation of monoclinic (a) $Ca_{10}(PO_4)_6Cl_2$ and (b) $Ca_{10}(PO_4)_6(OH)_2$. The $Ca^{I}_4(PO_4)_6$ framework creates channels containing $Ca^{II}_6Cl_2$ or $Ca^{II}_6(OH)_2$. Note the slight rotation of the

PO_4 tetrahedra to satisfy bond valence requirements and the doubling of the *b*-axis through destruction of the mirror plane and the creation of a *b*-glide.

Table S1a. Neutron diffraction Rietveld refinement of $Ca_{10}(AsO_4)_6F_2$.

Space Group		*P*-1		
a = 9.6841(5) Å		b = 9.6906(5) Å		c = 6.9815(3) Å
α = 90.623(3)°		β = 88.869(3)°		γ = 120.371(3)°
R_{Bragg} = 1.7 %		R_{wp} = 6.8 %		
a/b = 0.9993		c/b = 0.7204		
Atom	***x***	***y***	***z***	***B***
Ca1	0.234(2)	0.990(2)	0.249(3)	0.8(3)
Ca2	0.005(2)	0.251(2)	0.262(3)	0.7(2)
Ca3	0.770(2)	0.767(2)	0.245(2)	0.7(3)
Ca4	0.345(2)	0.653(2)	0.003(2)	0.9(4)
Ca5	0.343(2)	0.681(2)	0.499(2)	1.0(3)
As1	0.398(1)	0.374(1)	0.261(2)	0.4(2)
As2	0.628(1)	0.024(1)	0.239(2)	0.5(2)
As3	0.975(2)	0.606(1)	0.243(2)	0.7(2)
O1	0.311(2)	0.480(2)	0.275(2)	0.6(2)
O2	0.510(2)	0.827(2)	0.243(2)	0.8(2)
O3	0.173(2)	0.681(2)	0.226(2)	1.0(3)
O4	0.604(2)	0.475(2)	0.277(2)	0.8(2)
O5	0.530(2)	0.124(2)	0.220(2)	1.1(2)
O6	0.878(2)	0.407(2)	0.274(2)	1.2(2)
O7	0.351(2)	0.263(2)	0.063(2)	1.4(3)
O8	0.774(2)	0.079(2)	0.072(2)	1.4(3)
O9	0.905(2)	0.639(2)	0.040(2)	1.1(2)
O10	0.669(2)	0.766(2)	0.552(2)	0.9(2)
O11	0.274(2)	0.907(2)	0.555(2)	1.1(2)
O12	0.068(2)	0.301(2)	0.584(2)	1.3(2)
F1	0.007(2)	0.007(2)	0.245(2)	0.8(2)
All sites are fully occupied Wyckoff positions of the type 2i				

Table S1b. Combined neutron/X-ray Rietveld refinement of $Ca_{10}(VO_4)_6F_2$.

Space Group	*P*-1	
a = 9.6987(4) Å	b = 9.6933(4) Å	c = 7.0171(2) Å

α = 90.637(3)°		β = 89.172(2)°		γ = 120.136(3)°
R_{Bragg} = 1.7 %		R_{wp} = 5.7 %		
a/b = 1.0006		c/b = 0.7239		
Site	***x***	***y***	***z***	***Beq.***
Ca1	0.244(2)	0.004(2)	0.250(2)	0.7(2)
Ca2	0.001(2)	0.245(2)	0.261(2)	0.7(2)
Ca3	0.762(2)	0.769(1)	0.244(2)	0.4(2)
Ca4	0.339(2)	0.654(2)	0.000(2)	1.0(3)
Ca5	0.336(2)	0.677(2)	0.497(2)	1.5(3)
V1	0.396*	0.373*	0.257*	1.0*
V2	0.633*	0.026*	0.248*	1.0*
V3	0.970*	0.602*	0.240*	1.0*
O1	0.310(1)	0.486(1)	0.267(2)	0.9(2)
O2	0.510(1)	0.827(1)	0.249(2)	1.2(2)
O3	0.176(2)	0.689(2)	0.230(2)	2.0(3)
O4	0.604(2)	0.474(1)	0.270(2)	1.4(2)
O5	0.527(1)	0.129(1)	0.224(1)	0.7(2)
O6	0.870(2)	0.404(2)	0.271(2)	2.0(3)
O7	0.342(1)	0.256(2)	0.064(2)	1.2(2)
O8	0.765(2)	0.074(1)	0.071(2)	1.5(2)
O9	0.901(2)	0.647(1)	0.049(2)	1.7(2)
O10	0.662(2)	0.758(2)	0.555(2)	1.3(2)
O11	0.266(2)	0.903(2)	0.550(2)	1.4(2)
O12	0.069(1)	0.308(1)	0.575(2)	0.7(2)
F	0.006(2)	0.005(2)	0.252(2)	2.1(2)

All sites are fully occupied Wyckoff positions of the type 2i.
*Atom coordinates for V sites were evaluated by Rietveld refinement of XRD powder data; the same value of isotropic thermal displacement parameter *Beq* was assumed for all three V sites.

Table S2. Selected bond distances (Å) for $Ca_{10}(AsO_4)_6F_2$.

Ca1-O3	2.744(3)	Ca2-O1	2.658(2)	Ca3-O2	2.853(2)
Ca1-O5	2.486(2)	Ca2-O6	2.376(2)	Ca3-O4	2.455(2)
Ca1-O7	2.636(3)	Ca2-O8	2.410(2)	Ca3-O7	2.414(2)
Ca1-O8	2.328(2)	Ca2-O9	2.319(2)	Ca3-O9	2.611(2)
Ca1-O10	2.482(2)	Ca2-O11	2.645(2)	Ca3-O10	2.329(2)
Ca1-O11	2.400(3)	Ca2-O12	2.322(2)	Ca3-O12	2.339(2)
Ca1-F1	2.290(2)	Ca2-F1	2.371(3)	Ca3-F1	2.301(1)
Ca4-O1	2.455(2)	Ca5-O1	2.376(2)		
Ca4-O2	2.352(2)	Ca5-O2	2.326(2)		

Ca4-O3	2.371(3)	Ca5-O3	2.540(3)		
Ca4-O4	2.476(2)	Ca5-O4	2.420(3)		
Ca4-O5	2.434(2)	Ca5-O5	2.573(2)		
Ca4-O6	2.756(2)	Ca5-O6	2.430(2)		
Ca4-O7	2.656(3)	Ca5-O10	2.860(3)		
Ca4-O9	2.650(2)	Ca5-O11	2.617(3)		
As1-O1	1.628(2)	As2-O2	1.664(2)	As3-O3	1.676(2)
As1-O4	1.726(2)	As2-O5	1.667(3)	As3-O6	1.679(2)
As1-O7	1.668(2)	As2-O8	1.681(2)	As3-O9	1.688(2)
As1-O10	1.756(2)	As2-O11	1.669(2)	As3-O12	1.674(2)
<As1-O>	1.695	<As2-O>	1.670	<As3-O>	1.679

Table S3. Comparison of the number of refined parameters and agreement factors R_{wp} and R_{Bragg} for different structural models of $Ca_{10}(AsO_4)_6F_2$ and $Ca_{10}(VO_4)_6F_2$.

Space Group	$P6_3/m$		$P2_1/m$		P-1	
Formula	As-AP	V-AP	As-AP	V-AP	As-AP	V-AP
Number of refined parameters	30	30	67	67	101	101
Number of unique reflections	236	236	699	700	1278	1291
R_{wp}	15.7	17.0	15.5	16.7	6.8	5.7
R_{Bragg}	4.9	6.7	7.0	8.7	1.7	1.7

Note: Unless otherwise stated all atom sites given in Tables 3-9 are Wyckoff positions of the type 2i of the P-1 space group.

Table S4. Energy minimised *ab initio* structure of $Ca_{10}(AsO_4)_6F_2$.

Space group		P-1
a = 9.61608 Å	b = 9.64372 Å	c = 6.95712 Å
α = 90.779°	β = 88.528°	γ = 120.613°
a/b = 0.9971	c/b = 0.7214	

Atom	*x*	*y*	*z*
Ca1	0.23637	0.99456	0.25593
Ca2	0.00493	0.24847	0.26412
Ca3	0.76322	0.77124	0.23253
Ca4	0.33899	0.64542	0.00121
Ca5	0.34103	0.68771	0.49738
As1	0.39836	0.37301	0.27354
As2	0.63190	0.02683	0.23482
As3	0.97770	0.61118	0.23576
O1	0.30497	0.48335	0.28035
O2	0.51222	0.82182	0.24163
O3	0.18134	0.68997	0.22524
O4	0.60559	0.48247	0.27908
O5	0.52775	0.12661	0.20795
O6	0.87568	0.40704	0.27131
O7	0.35471	0.26566	0.06263
O8	0.78115	0.08036	0.06649
O9	0.89257	0.63895	0.03605
O10	0.66596	0.76920	0.54600
O11	0.27134	0.90136	0.54994
O12	0.06161	0.28672	0.58705
F	0.00820	0.01189	0.24512

Table S5. Crystal structure model for $Ca_{10}(VO_4)_6F_2$ in the metrically hexagonal cell equivalent to that of Dong and White (2004). It is derived from Table 1 by 2% expansion of V-O bond lengths to accommodate the larger V^{5+} ion. Average valence sums are respectively 1.972, 1.948 and 5.022 v.u. at A^I, A^{II} and B showing that the triclinic distortion of apatites can relieve stresses at A^{II} and B sites through tilting/rotation of BO_4 tetrahedra, even in a metrically hexagonal cell.

Space group	*P*-1	
a = 9.7364 Å	b = 9.7364 Å	c = 7.0057 Å
α = 90.000°	β = 90.000°	γ = 120.000°
a/b = 1.0000	c/b = 0.7195	
Atom	***x***	***y***	***z***
Ca1	0.23380	0.98980	0.24940
Ca2	0.00470	0.25070	0.26170
Ca3	0.76950	0.76690	0.24520
Ca4	0.34470	0.65270	0.00260
Ca5	0.34320	0.68050	0.49860

V1	0.39800	0.37400	0.26090
V2	0.62830	0.02430	0.23930
V3	0.97500	0.60560	0.24300
O1	0.30875	0.48181	0.27569
O2	0.50712	0.82554	0.24328
O3	0.17737	0.68281	0.22586
O4	0.60802	0.47722	0.27687
O5	0.52824	0.12569	0.21972
O6	0.87626	0.40252	0.27421
O7	0.35047	0.26032	0.05894
O8	0.77712	0.08030	0.06906
O9	0.90319	0.63997	0.03614
O10	0.67024	0.76839	0.54775
O11	0.27245	0.90532	0.55129
O12	0.06886	0.29883	0.58013
F	0.00680	0.00730	0.24460

Table S6. *Ab initio* results for V-AP starting from metrically hexagonal cell in Table S4.

Space group	*P*-1		
a = 9.62264 Å	b = 9.63036 Å		c = 6.96677 Å
α = 90.507°	β = 89.253°		γ = 120.303°
a/b = 0.9992	c/b = 0.7234		
Atom	***x***	***y***	***z***
Ca1	0.23765	0.99587	0.25306
Ca2	0.00351	0.24451	0.26189
Ca3	0.76442	0.76823	0.23846
Ca4	0.33494	0.64545	0.00217
Ca5	0.34095	0.68622	0.49860
V1	0.39926	0.37066	0.26743
V2	0.63261	0.02909	0.23595
V3	0.97575	0.60757	0.23575
O1	0.30631	0.48353	0.27772
O2	0.51325	0.82190	0.24444
O3	0.17948	0.68888	0.22890
O4	0.60835	0.48095	0.27070
O5	0.52748	0.13122	0.21307
O6	0.87263	0.40052	0.26687
O7	0.34705	0.26128	0.05912
O8	0.77806	0.08245	0.06231
O9	0.89473	0.64320	0.03600
O10	0.66790	0.76959	0.55244
O11	0.26475	0.90250	0.55249

O12	0.06265	0.29382	0.58446
F	0.00709	0.00841	0.24574

Table S7. *Ab initio* results for Oxy-HAP (all atom sites are Wyckoff positions of the type 1a in space group *P*1)

Space Group	*P*1		
a = 9.35862 Å	b = 9.35096 Å		c = 6.86607 Å
α = 90.162°	β = 89.583°		γ = 120.052°
a/b = 1.0008	c/b = 0.7343		
Atom	***x***	***y***	***z***
Ca1	0.33643	-0.35332	0.00424
Ca2	-0.33568	0.34440	0.00421
Ca3	-0.33113	0.32622	-0.50586
Ca4	0.33220	-0.31872	0.49320
Ca5	0.23047	-0.00426	0.23792
Ca6	-0.26964	0.01118	-0.24624
Ca7	0.00516	0.22961	0.25978
Ca8	-0.01363	-0.28005	-0.26145
Ca9	-0.22780	-0.22341	0.24676
Ca10	0.27364	0.25878	-0.24411
P1	0.40713	0.37643	0.26260
P2	-0.38710	-0.35769	-0.25863
P3	-0.37476	0.02869	0.24547
P4	0.35540	-0.02776	-0.25620
P5	-0.02886	-0.40542	0.23929
P6	0.02918	0.38281	-0.23952
O1	0.32380	0.48343	0.26972
O2	-0.32112	-0.48035	-0.26227
O3	-0.48698	-0.16188	0.24904
O4	0.48507	0.15989	-0.25651
O5	0.16144	-0.32331	0.22752
O6	-0.15847	0.32130	-0.23514
O7	-0.40139	0.47902	0.27305
O8	0.42086	-0.45519	-0.27579
O9	-0.47357	0.12083	0.22803
O10	0.44462	-0.12738	-0.21330
O11	-0.11718	0.40324	0.25454
O12	0.12468	-0.42489	-0.26524
O13	0.36833	0.28111	0.06622
O14	-0.34306	-0.25631	-0.06784
O15	-0.25184	0.08268	0.07297
O16	0.21720	-0.06044	-0.10600

O17	-0.09765	-0.36477	0.05497
O18	0.09933	0.34634	-0.05463
O19	-0.31013	-0.22715	-0.42339
O20	0.34601	0.25224	0.43402
O21	0.26490	-0.09479	-0.45161
O22	-0.27678	0.08930	0.43908
O23	0.06727	0.29448	-0.40609
O24	-0.07898	-0.34288	0.42185
O25	0.00468	0.00138	0.24145

Table S8. *Ab initio* results for $La_{10}(GeO_4)_6O_3$

Space group	*P*-1		
a = 9.87262 Å	b = 9.85491 Å		c = 7.32819 Å
α = 89.628°	β = 89.721°		γ = 120.405°
a/b = 1.0018	c/b = 0.7436		
Atom	***x***	***y***	***z***
La1	0.21498	0.99029	0.25994
La2	0.00786	0.21908	0.27932
La3	0.78668	0.79776	0.23764
La4	0.33665	0.64320	0.00013
La5	0.33555	0.68324	0.49800
Ge1	0.41127	0.38439	0.26094
Ge2	0.62586	0.03161	0.23163
Ge3	0.97573	0.60027	0.21891
O1	0.30730	0.48758	0.27832
O2	0.50400	0.82074	0.24199
O3	0.18119	0.68583	0.22673
O4	0.62138	0.49247	0.27319
O5	0.52304	0.13718	0.21747
O6	0.86682	0.39162	0.24810
O7	0.37605	0.29064	0.04411
O8	0.77228	0.07916	0.06320
O9	0.89064	0.63960	0.02450
O10	0.65118	0.76346	0.54891
O11	0.26780	0.90147	0.55119
O12	0.06681	0.31200	0.59227
O13	0.02644	0.01791	0.16306
O14	0	0	0.5

N.B Atom site O14 occupies a Wyckoff position of type 1b

Table S9. *Ab initio* results for $Cd_{10}(PO_4)_6F_2$

Space group	*P*-1		
a = 9.33872 Å	*b* = 9.32307 Å		*c* = 6.69183 Å
α = 90.509°	*β* = 88.874°		*γ* = 120.283°
a/*b* = 1.0017	*c*/*b* = 0.7178		
Atom	***x***	***y***	***z***
Cd1	0.24021	0.99050	0.25184
Cd2	0.00838	0.25379	0.26238
Cd3	0.75764	0.76730	0.23626
Cd4	0.33568	0.64884	0.00014
Cd5	0.33921	0.68196	0.49735
P1	0.39446	0.36815	0.25917
P2	0.63458	0.02682	0.23517
P3	0.97932	0.61293	0.23454
O1	0.31723	0.48183	0.27038
O2	0.51441	0.83394	0.24887
O3	0.16759	0.68212	0.22793
O4	0.58879	0.47175	0.26753
O5	0.53695	0.11940	0.19650
O6	0.88799	0.42269	0.27948
O7	0.34868	0.26925	0.06078
O8	0.77056	0.07104	0.07203
O9	0.90293	0.63580	0.04072
O10	0.67030	0.76067	0.56817
O11	0.27562	0.90698	0.56316
O12	0.05732	0.29263	0.59845
F1	0.00818	0.00906	0.24623

Table S10. *Ab initio* results for $Ca_{10}(CrO_4)_6F_2$

Space group	*P*-1		
a = 9.55250 Å	*b* = 9.57319 Å		*c* = 6.98317 Å
α = 90.659°	*β* = 89.084°		*γ* = 120.313°
a/*b* = 0.9978	*c*/*b* = 0.6992		
Atom	***x***	***y***	***z***
Ca1	0.23704	0.99507	0.25775
Ca2	0.00429	0.24656	0.26195
Ca3	0.76370	0.76922	0.23586
Ca4	0.33621	0.64444	0.00113

Ca5	0.34396	0.68787	0.50189
Cr1	0.39942	0.37179	0.26962
Cr2	0.63226	0.02777	0.23290
Cr3	0.97718	0.60928	0.23445
O1	0.30220	0.48046	0.27997
O2	0.51705	0.82070	0.24385
O3	0.18147	0.69421	0.22870
O4	0.60816	0.48128	0.27128
O5	0.52797	0.12989	0.21182
O6	0.87329	0.40250	0.26307
O7	0.34917	0.26359	0.06168
O8	0.77649	0.08050	0.06001
O9	0.89529	0.64457	0.03696
O10	0.66269	0.76693	0.55081
O11	0.26539	0.90307	0.55644
O12	0.06222	0.29378	0.58624
F1	0.00724	0.00931	0.24718