Apatite, $Ca_5(PO_4)_3(OH,F,Cl)$: Structural Variations, Natural Solid Solutions, Intergrowths, and Zoning

Table S1. Chemical compositions for 33 apatite samples with general formula close to $Ca_{10}(PO_4)_6X_2$.

		1	2	3	4a	4b	5	6L	6D	7	8
P_2O_5	wt. %	41.59	42.40	42.06	41.75	40.68	42.57	41.54	41.57	41.66	41.52
SiO_2		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
SO_3		0.05	0.00	0.02	0.05	0.00	0.08	0.00	0.00	0.13	0.00
FeO		0.71	0.02	0.03	0.00	0.00	0.03	0.05	0.05	0.00	0.04
MnO		3.20	1.99	1.83	1.14	0.43	0.20	0.55	0.27	0.16	0.89
MgO		0.00	0.00	0.02	0.01	0.01	0.02	0.02	0.00	0.00	0.00
CaO		51.20	53.95	53.49	54.74	55.80	55.92	55.24	55.87	55.73	54.80
SrO		0.00	0.56	0.79	0.00	0.00	0.00	0.25	0.00	0.00	0.48
PbO		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
La_2O_3		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Nd_2O_3		0.00	0.03	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Pr_2O_3		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sm_2O_3		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ce_2O_3		0.00	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Y_2O_3		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Fe_2O_3		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Na_2O		0.07	0.02	0.01	0.01	0.02	0.00	0.00	0.02	0.11	0.05
F		3.68	3.15	3.10	3.77	3.80	3.73	3.76	3.81	3.76	3.75
Cl		0.02	0.00	0.01	0.00	0.02	0.03	0.06	0.00	0.07	0.06
OH		0.00	0.30	0.31	0.00	0.00	0.03	0.00	0.00	0.00	0.00
∑		100.52	102.44	101.68	101.47	100.76	102.61	101.46	101.59	101.62	101.59
O = F, Cl		−1.55	−1.33	−1.31	−1.59	−1.60	−1.58	−1.59	−1.60	−1.60	−1.59
Total		98.96	101.12	100.37	99.89	99.16	101.03	99.87	99.98	100.02	100.00
P	*apfu*	6.040	5.994	5.995	5.926	5.719	5.993	5.874	5.849	5.872	5.870
Si		0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
S		0.006	0.000	0.003	0.006	0.000	0.010	0.000	0.000	0.016	0.000
∑P		6.046	5.994	5.997	5.931	5.719	6.003	5.874	5.849	5.888	5.870
Fe		0.102	0.003	0.004	0.000	0.000	0.004	0.007	0.007	0.000	0.006
Mn		0.465	0.281	0.261	0.162	0.061	0.028	0.078	0.038	0.023	0.126
Mg		0.000	0.000	0.005	0.002	0.003	0.005	0.005	0.000	0.000	0.000
Ca		9.410	9.652	9.649	9.833	9.929	9.963	9.886	9.949	9.942	9.806
Sr		0.000	0.054	0.077	0.000	0.000	0.000	0.024	0.000	0.000	0.046
Pb		0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
La		0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Nd		0.000	0.002	0.001	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Pr		0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Sm		0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Ce		0.000	0.001	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Y		0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Na		0.023	0.006	0.003	0.003	0.007	0.000	0.000	0.006	0.036	0.016
∑M		10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00
F		1.995	1.663	1.651	2.000	1.993	1.961	1.984	2.000	1.980	1.983
Cl		0.005	0.000	0.003	0.000	0.007	0.008	0.016	0.000	0.020	0.017
OH		0.000	0.336	0.347	0.000	0.000	0.030	0.000	0.000	0.000	0.000
∑X		2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000

The *apfu* are based on 10 M cations. OH was calculated by assuming OH = 2 - (F+Cl). ThO_2 was below detection limit.

Table S1. Continued.

	9	10	11	12	13	14	15	16	17	18
P_2O_5 wt. %	41.96	41.37	42.33	41.57	42.12	41.05	41.70	40.76	40.18	41.03
SiO_2	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.30	0.00
SO_3	0.03	0.13	0.08	0.32	0.00	0.37	0.00	0.42	1.07	0.86
FeO	0.01	0.01	0.04	0.04	0.00	0.02	0.00	0.05	0.00	0.03
MnO	1.95	0.01	0.08	0.03	0.00	0.02	0.00	0.02	0.00	0.00
MgO	0.00	0.00	0.00	0.01	0.01	0.00	0.00	0.00	0.00	0.01
CaO	54.41	56.26	54.99	55.41	55.44	54.45	54.82	54.09	55.49	55.00
SrO	0.08	0.00	0.11	0.17	0.00	0.00	0.08	0.03	0.00	0.00
PbO	0.00	0.00	0.00	0.00	0.00	0.00	0.08	0.00	0.00	0.02
La_2O_3	0.00	0.00	0.17	0.00	0.01	0.00	0.00	0.00	0.00	0.00
Nd_2O_3	0.00	0.00	0.21	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Pr_2O_3	0.00	0.00	0.03	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sm_2O_3	0.00	0.00	0.03	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ce_2O_3	0.00	0.00	0.49	0.00	0.04	0.00	0.00	0.00	0.00	0.00
Y_2O_3	0.00	0.00	0.12	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Fe_2O_3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Na_2O	0.01	0.01	0.19	0.09	0.00	0.00	0.00	0.00	0.19	0.00
F	3.66	3.72	3.78	3.78	3.67	3.48	3.68	3.66	3.60	3.51
Cl	0.01	0.00	0.01	0.00	0.02	0.40	0.00	0.02	0.06	0.41
OH	0.06	0.04	0.00	0.00	0.04	0.00	0.02	0.00	0.07	0.00
∑	102.18	101.55	102.67	101.42	101.35	99.79	100.38	99.05	100.96	100.87
O = F, Cl	−1.54	−1.57	−1.59	−1.59	−1.55	−1.55	−1.55	−1.55	−1.53	−1.57
Total	100.64	99.98	101.08	99.83	99.80	98.23	98.83	97.50	99.43	99.30
P *apfu*	5.917	5.807	5.987	5.893	6.000	5.953	6.003	5.946	5.686	5.890
Si	0.000	0.000	0.002	0.000	0.000	0.000	0.000	0.000	0.050	0.000
S	0.003	0.016	0.010	0.040	0.000	0.048	0.000	0.054	0.134	0.109
∑P	5.921	5.823	5.999	5.934	6.000	6.001	6.003	6.001	5.870	5.999
Fe	0.001	0.001	0.006	0.006	0.000	0.003	0.000	0.007	0.000	0.004
Mn	0.275	0.001	0.011	0.004	0.000	0.003	0.000	0.003	0.000	0.000
Mg	0.000	0.000	0.000	0.002	0.003	0.000	0.000	0.000	0.000	0.003
Ca	9.711	9.994	9.844	9.942	9.994	9.994	9.988	9.987	9.938	9.992
Sr	0.008	0.000	0.011	0.017	0.000	0.000	0.008	0.003	0.000	0.000
Pb	0.000	0.000	0.000	0.000	0.000	0.000	0.004	0.000	0.000	0.001
La	0.000	0.000	0.010	0.000	0.001	0.000	0.000	0.000	0.000	0.000
Nd	0.000	0.000	0.013	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Pr	0.000	0.000	0.002	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Sm	0.000	0.000	0.002	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Ce	0.000	0.000	0.030	0.000	0.002	0.000	0.000	0.000	0.000	0.000
Y	0.000	0.000	0.011	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Na	0.004	0.005	0.062	0.029	0.000	0.000	0.000	0.000	0.062	0.000
∑M	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00
F	1.927	1.953	1.997	2.000	1.953	1.884	1.979	1.995	1.903	1.882
Cl	0.004	0.000	0.003	0.000	0.006	0.116	0.000	0.006	0.017	0.118
OH	0.070	0.047	0.000	0.000	0.042	0.000	0.020	0.000	0.080	0.000
∑X	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000

Table S1. Continued.

	19	20	21	22	23	24	25	26	27	28
P_2O_5 wt. %	41.92	40.38	41.60	40.91	40.81	39.85	41.05	41.60	41.01	41.29
SiO_2	0.08	0.26	0.00	0.72	0.38	0.62	0.00	0.05	0.00	0.00
SO_3	0.34	0.94	0.10	0.90	0.29	0.86	0.37	0.00	0.37	0.11
FeO	0.04	0.04	0.05	0.00	0.00	0.00	0.02	0.04	0.02	0.04
MnO	0.00	0.01	0.00	0.00	0.01	0.02	0.02	0.01	0.03	0.03
MgO	0.03	0.04	0.00	0.01	0.00	0.01	0.00	0.01	0.03	0.00
CaO	55.25	54.21	54.85	55.88	55.54	55.75	54.45	54.67	55.45	55.10
SrO	0.31	0.00	0.00	0.04	0.07	0.02	0.00	0.06	0.00	0.41
PbO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
La_2O_3	0.00	0.00	0.00	0.00	0.18	0.00	0.00	0.38	0.00	0.00
Nd_2O_3	0.09	0.00	0.00	0.00	0.06	0.07	0.00	0.14	0.00	0.00
Pr_2O_3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sm_2O_3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ce_2O_3	0.05	0.00	0.00	0.03	0.34	0.08	0.00	0.46	0.00	0.00
Y_2O_3	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.07	0.00	0.00
Fe_2O_3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Na_2O	0.10	0.45	0.00	0.08	0.07	0.01	0.00	0.15	0.13	0.04
F	2.82	3.46	3.51	3.00	2.73	2.54	3.48	2.32	3.45	3.48
Cl	0.17	0.52	0.40	0.06	0.43	0.09	0.40	0.62	0.61	0.52
OH	0.41	0.00	0.00	0.36	0.39	0.57	0.00	0.52	0.00	0.00
∑	101.61	100.30	100.50	101.99	101.31	100.46	99.79	101.12	101.10	101.02
O = F, Cl	−1.23	−1.57	−1.57	−1.28	−1.25	−1.09	−1.55	−1.12	−1.59	−1.58
Total	100.38	98.73	98.94	100.72	100.06	99.37	98.23	100.00	99.51	99.44
P *apfu*	5.945	5.788	5.988	5.765	5.766	5.639	5.953	5.933	5.811	5.884
Si	0.013	0.044	0.000	0.120	0.063	0.103	0.000	0.008	0.000	0.000
S	0.043	0.119	0.013	0.112	0.037	0.107	0.048	0.000	0.046	0.014
∑P	6.001	5.952	6.001	5.997	5.866	5.849	6.001	5.941	5.857	5.898
Fe	0.006	0.006	0.007	0.000	0.000	0.000	0.003	0.006	0.003	0.006
Mn	0.000	0.001	0.000	0.000	0.001	0.002	0.003	0.002	0.004	0.004
Mg	0.007	0.010	0.000	0.002	0.001	0.002	0.000	0.003	0.007	0.000
Ca	9.916	9.835	9.993	9.966	9.933	9.984	9.994	9.868	9.943	9.937
Sr	0.030	0.000	0.000	0.004	0.007	0.001	0.000	0.006	0.000	0.040
Pb	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
La	0.000	0.000	0.000	0.000	0.011	0.000	0.000	0.023	0.000	0.000
Nd	0.005	0.000	0.000	0.000	0.004	0.004	0.000	0.008	0.000	0.000
Pr	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Sm	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Ce	0.003	0.000	0.000	0.002	0.021	0.005	0.000	0.028	0.000	0.000
Y	0.000	0.000	0.000	0.000	0.001	0.000	0.000	0.006	0.000	0.000
Na	0.032	0.148	0.000	0.026	0.022	0.002	0.000	0.049	0.042	0.013
∑M	10.00	10.00	10.00	10.00	10.000	10.00	10.00	10.00	10.00	10.00
F	1.494	1.852	1.885	1.579	1.443	1.342	1.884	1.238	1.827	1.852
Cl	0.048	0.148	0.115	0.017	0.123	0.025	0.116	0.178	0.173	0.148
OH	0.458	0.000	0.000	0.404	0.434	0.633	0.000	0.585	0.000	0.000
∑X	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000

Table S1. Continued.

	29	30	31	32	33a	33b	33c
P_2O_5 wt. %	42.14	41.02	41.32	41.24	41.30	41.26	41.28
SiO_2	0.05	0.00	0.00	0.01	0.00	0.00	0.00
SO_3	0.04	0.10	0.00	0.11	0.00	0.00	0.05
FeO	0.09	0.11	0.00	0.05	0.83	0.41	0.24
MnO	0.00	0.01	0.02	0.00	5.15	3.17	1.14
MgO	0.01	0.24	0.03	0.16	0.02	0.01	0.01
CaO	54.04	52.51	54.83	52.00	50.54	52.60	54.86
SrO	0.02	0.00	0.26	0.00	0.07	0.02	0.04
PbO	0.00	0.00	0.00	0.00	0.00	0.00	0.00
La_2O_3	0.34	0.09	0.00	0.00	0.00	0.00	0.00
Nd_2O_3	0.27	0.28	0.00	0.00	0.00	0.00	0.00
Pr_2O_3	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sm_2O_3	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ce_2O_3	0.50	0.31	0.00	0.00	0.00	0.00	0.00
Y_2O_3	0.10	0.39	0.00	0.00	0.00	0.00	0.00
Fe_2O_3	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Na_2O	0.15	0.43	0.12	0.46	0.02	0.02	0.01
F	2.19	0.45	3.74	2.01	3.70	3.74	3.79
Cl	0.65	5.91	0.00	2.95	0.09	0.03	0.01
OH	0.56	0.02	0.00	0.00	0.00	0.00	0.00
∑	101.13	101.87	100.32	99.00	101.72	101.27	101.43
O = F, Cl	−1.07	−1.52	−1.58	−1.51	−1.58	−1.58	−1.60
Total	100.06	100.35	98.75	97.48	100.15	99.69	99.84
P *apfu*	6.074	5.987	5.910	6.137	5.895	5.875	5.823
Si	0.008	0.000	0.000	0.002	0.001	0.000	0.000
S	0.004	0.013	0.000	0.015	0.000	0.000	0.006
∑P	6.086	6.000	5.910	6.154	5.896	5.875	5.830
Fe	0.012	0.016	0.000	0.007	0.117	0.058	0.033
Mn	0.001	0.001	0.003	0.000	0.736	0.452	0.161
Mg	0.002	0.062	0.008	0.042	0.004	0.004	0.003
Ca	9.857	9.699	9.925	9.794	9.131	9.480	9.795
Sr	0.002	0.000	0.025	0.000	0.007	0.002	0.004
Pb	0.000	0.000	0.000	0.000	0.000	0.000	0.000
La	0.022	0.006	0.000	0.000	0.000	0.000	0.000
Nd	0.016	0.017	0.000	0.000	0.000	0.000	0.000
Pr	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Sm	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Ce	0.031	0.020	0.000	0.000	0.000	0.000	0.000
Y	0.009	0.036	0.000	0.000	0.000	0.000	0.000
Na	0.049	0.144	0.039	0.157	0.006	0.005	0.004
∑M	10.00	10.00	10.00	10.00	10.00	10.00	10.00
F	1.180	0.245	2.000	1.120	1.975	1.991	1.998
Cl	0.188	1.727	0.000	0.880	0.025	0.009	0.002
OH	0.631	0.028	0.000	0.000	0.000	0.000	0.000
∑X	2.000	2.000	2.000	2.000	2.000	2.000	2.000

Table S2. Atom coordinates and equivalent isotropic displacement parameters ($U_{eq.} \times 10^2$ Å^2) for 33 apatite samples.

Ion		1	2	3	4a (F)	4b (OH)	5	6	7	8a
Ca1	*x*	⅔	⅔	⅔	⅔	⅔	⅔	⅔	⅔	⅔
	y	⅓	⅓	⅓	⅓	⅓	⅓	⅓	⅓	⅓
4*f*	*z*	0.0017(1)	0.0011(1)	0.0015(1)	0.0012(2)	0.0013(3)	0.0010(1)	0.0010(1)	0.0010(1)	0.0011(2)
	$U_{eq.}$	0.81	0.71	0.78	0.93(1)	0.93(1)	0.78	0.70	0.76	0.77(4)
	sof	0.987(1)	0.963(1)	0.955(1)	0.981(4)	0.972(5)	0.956(1)	0.949(1)	0.958(1)	0.963(4)
Ca2	*x*	-0.0071(1)	-0.0070(1)	-0.0066(1)	-0.0076(2)	-0.0065(3)	-0.0072(1)	-0.0071(1)	-0.0071(1)	-0.0070(3)
	y	0.2414(1)	0.2413(1)	0.2416(1)	0.2410(1)	0.2425(2)	0.2414(1)	0.2415(1)	0.2414(1)	0.2412(2)
6*h*	*z*	¼	¼	¼	¼	¼	¼	¼	¼	¼
	U_{eq}	0.83	0.59	0.59	0.74(1)	0.74(1)	0.67	0.67	0.70	0.79(3)
	sof	0.973(1)	0.948(1)	0.947(1)	0.975(3)	0.984(5)	0.961(1)	0.961(1)	0.963(1)	0.996(5)
P	*x*	0.3696(1)	0.3689(1)	0.3689(1)	0.3684(2)	0.3698(2)	0.3688(1)	0.3688(1)	0.3689(1)	0.3698(2)
	y	0.3986(1)	0.3982(1)	0.3979(1)	0.3973(2)	0.3998(3)	0.3982(1)	0.3982(1)	0.3983(1)	0.3986(2)
6*h*	*z*	¼	¼	¼	¼	¼	¼	¼	¼	¼
	U_{eq}	0.49	0.29	0.23	0.43(1)	0.43(1)	0.34	0.34	0.37	0.76(4)
	sof	0.938(2)	0.921(2)	0.911(2)	0.947(4)	0.943(6)	0.926(1)	0.928(2)	0.928(1)	1
X	*x*	0	0	0	0	0	0	0	0	0
	y	0	0	0	0	0	0	0	0	0
2*a*/4*e*	*z*	¼	¼	¼	¼	0.2272(12)	¼	¼	¼	¼
	U_{eq}	2.55	1.55	2.02	1.41(7)	1.41(7)	2.10	1.94	1.94	1.73(19)
	sof	0.993(3)	0.949(3)	0.932(3)	0.954(8)	0.598(7)	0.987(1)	0.974(2)	0.981(2)	0.976(14)
O1	*x*	0.4865(1)	0.4846(1)	0.4846(1)	0.4850(4)	0.4845(5)	0.4846(1)	0.4844(1)	0.4846(1)	0.4861(6)
	y	0.3283(1)	0.3266(1)	0.3265(1)	0.3268(4)	0.3270(6)	0.3266(1)	0.3265(1)	0.3268(1)	0.3276(6)
6*h*	*z*	¼	¼	¼	¼	¼	¼	¼	¼	¼
	U_{eq}	1.42	1.26	1.41	1.07(4)	1.07(4)	1.20	1.22	1.27	0.93(10)
O2	*x*	0.4659(1)	0.4674(1)	0.4669(1)	0.4659(4)	0.4680(6)	0.4666(1)	0.4666(1)	0.4660(1)	0.4702(6)
	y	0.5886(1)	0.5885(1)	0.5889(1)	0.5881(2)	0.5897(3)	0.5877(1)	0.5882(1)	0.5875(1)	0.5877(3)
6*h*	*z*	¼	¼	¼	¼	¼	¼	¼	¼	¼
	U_{eq}	1.89	1.12	1.25	1.41(4)	1.41(4)	1.38	1.29	1.36	1.09(11)
O3	*x*	0.2565(1)	0.2563(1)	0.2571(1)	0.2570(2)	0.2568(3)	0.2565(1)	0.2564(1)	0.2566(1)	0.2600(3)
	y	0.3401(1)	0.3415(1)	0.3411(1)	0.3402(3)	0.3408(4)	0.3408(1)	0.3408(1)	0.3409(1)	0.3478(4)
12*i*	*z*	0.0710(1)	0.0719(1)	0.0715(1)	0.0709(2)	0.0716(3)	0.0710(1)	0.0706(1)	0.0710(1)	0.0689(3)
	U_{eq}	2.26	1.71	1.96	1.58(3)	1.58(3)	1.60	1.71	1.67	1.31(7)

The *sofs* for O1, O2 and O3 were fixed at 1.0; all other *sofs* were refined. For sample 4, *U* for similar atoms were constrained to be equal. If an error is given for *U*, then it was refined as isotropic.

Table S2. Continued.

Ion		8b	9	10	11	12	13	14	15	16
Ca1	*x*	⅔	⅔	⅔	⅔	⅔	⅔	⅔	⅔	⅔
	y	⅓	⅓	⅓	⅓	⅓	⅓	⅓	⅓	⅓
4*f*	*z*	0.0014(2)	0.0010(1)	0.0011(1)	0.0010(1)	0.0010(1)	0.0010(1)	0.0010(1)	0.0010(1)	0.0010(1)
	$U_{eq.}$	1.01(4)	0.73	0.73	0.89	0.85	0.83	0.84	0.89	1.02
	sof	1.064(4)	0.958(1)	0.953(1)	0.943(1)	0.944(1)	0.952(1)	0.952(1)	0.957(2)	0.971(2)
Ca2	*x*	−0.0078(2)	−0.0069(1)	−0.0070(1)	−0.0077(1)	−0.0075(1)	−0.0070(1)	−0.0073(1)	−0.0073(1)	−0.0076(1)
	y	0.2417(2)	0.2421(1)	0.2416(1)	0.2407(1)	0.2412(1)	0.2417(1)	0.2417(1)	0.2412(1)	0.2407(1)
6*h*	*z*	¼	¼	¼	¼	¼	¼	¼	¼	¼
	U_{eq}	0.59(3)	0.67	0.68	0.81	0.80	0.77	0.74	0.89	0.96
	sof	1.034(4)	0.964(1)	0.965(1)	0.982(1)	0.972(1)	0.975(1)	0.971(1)	0.993(1)	1.010(1)
P	*x*	0.3685(2)	0.3687(1)	0.3688(1)	0.3692(1)	0.3688(1)	0.3688(1)	0.3687(1)	0.3692(1)	0.3692(1)
	y	0.3981(2)	0.3981(1)	0.3981(1)	0.3984(1)	0.3983(1)	0.3981(1)	0.3983(1)	0.3984(1)	0.3983(1)
6*h*	*z*	¼	¼	¼	¼	¼	¼	¼	¼	¼
	U_{eq}	0.44(3)	0.30	0.34	0.42	0.41	0.40	0.34	0.47	0.56
	sof	1	0.931(1)	0.932(2)	0.911(2)	0.914(1)	0.932(2)	0.915(1)	0.925(2)	0.920(2)
X	*x*	0	0	0	0	0	0	0	0	0
	y	0	0	0	0	0	0	0	0	0
2*a*/4*e*	*z*	¼	¼	¼	¼	¼	¼	¼	¼	¼
	U_{eq}	2.08(18)	2.28	2.05	2.51	2.39	2.22	2.50	2.89	3.05
	sof	1.05(1)	0.973(2)	0.982(3)	0.977(3)	0.973(2)	0.981(3)	0.981(2)	1.005(3)	0.982(3)
O1	*x*	0.4844(5)	0.4841(1)	0.4845(1)	0.4842(1)	0.4843(1)	0.4848(1)	0.4844(1)	0.4838(1)	0.4839(1)
	y	0.3267(6)	0.3263(1)	0.3265(1)	0.3267(1)	0.3271(1)	0.3266(1)	0.3267(1)	0.3262(1)	0.3263(1)
6*h*	*z*	¼	¼	¼	¼	¼	¼	¼	¼	¼
	U_{eq}	0.71(9)	1.19	1.08	1.39	1.27	1.24	1.26	1.29	1.41
O2	*x*	0.4617(5)	0.4665(1)	0.4662(1)	0.4662(1)	0.4660(1)	0.4662(1)	0.4666(1)	0.4657(1)	0.4665(1)
	y	0.5874(2)	0.5877(1)	0.5881(1)	0.5871(1)	0.5876(1)	0.5881(1)	0.5881(1)	0.5874(1)	0.5875(1)
6*h*	*z*	¼	¼	¼	¼	¼	¼	¼	¼	¼
	U_{eq}	0.85(9)	1.24	1.18	1.49	1.37	1.27	1.24	1.57	1.6
O3	*x*	0.2540(3)	0.2568(1)	0.2566(1)	0.2559(1)	0.2567(1)	0.2567(1)	0.2563(1)	0.2567(1)	0.2570(1)
	y	0.3342(3)	0.3412(1)	0.3409(1)	0.3406(1)	0.3412(1)	0.3412(1)	0.3408(1)	0.3406(1)	0.3414(1)
12*i*	*z*	0.0730(2)	0.0711(1)	0.0710(1)	0.0714(1)	0.0709(1)	0.0708(1)	0.0709(1)	0.0707(1)	0.0709(1)
	U_{eq}	0.93(6)	1.54	1.57	1.96	1.89	1.72	1.81	1.84	2.04

Table S2. Continued.

Ion		17	18	19	20	21	22	23	24	25
Ca1	*x*	⅔	⅔	⅔	⅔	⅔	⅔	⅔	⅔	⅔
	y	⅓	⅓	⅓	⅓	⅓	⅓	⅓	⅓	⅓
4*f*	*z*	0.0019(1)	0.0007(1)	0.0011(1)	0.0005(1)	0.0011(1)	0.0010(1)	0.0012(1)	0.0011(1)	0.0012(1)
	$U_{eq.}$	0.87	0.84	0.91	1.23	0.90	0.89	0.81	0.97	0.94
	sof	0.969(1)	0.939(1)	0.964(2)	0.956(2)	0.952(2)	0.947(2)	0.949(2)	0.960(1)	0.982(1)
Ca2	*x*	−0.0068(1)	−0.0071(1)	−0.0071(1)	−0.0068(1)	−0.0068(1)	−0.0072(1)	−0.0071(1)	−0.0075(1)	−0.0066(1)
	y	0.2426(1)	0.2422(1)	0.2430(1)	0.2428(1)	0.2436(1)	0.2428(1)	0.2440(1)	0.2427(1)	0.2442(1)
6*h*	*z*	¼	¼	¼	¼	¼	¼	¼	¼	¼
	U_{eq}	0.86	0.83	0.85	1.28	1.02	0.83	0.89	1.01	0.93
	sof	0.985(1)	0.971(1)	0.971(1)	0.984(2)	0.966(2)	0.947(1)	0.972(2)	0.973(1)	1.009(1)
P	*x*	0.3692(1)	0.3690(1)	0.3688(1)	0.3692(1)	0.3692(1)	0.3689(1)	0.3688(1)	0.3692(1)	0.3691(1)
	y	0.3986(1)	0.3988(1)	0.3983(1)	0.3986(1)	0.3989(1)	0.3985(1)	0.3987(1)	0.3989(1)	0.3988(1)
6*h*	*z*	¼	¼	¼	¼	¼	¼	¼	¼	¼
	U_{eq}	0.43	0.37	0.37	0.78	0.51	0.40	0.42	0.51	0.44
	sof	0.949(2)	0.917(1)	0.934(2)	0.941(3)	0.928(2)	0.907(2)	0.930(2)	0.935(2)	0.958(2)
X	*x*	0	0	0	0	0	0	0	0	0
	y	0	0	0	0	0	0	0	0	0
2*a*/4*e*	*z*	¼	¼	¼	¼	¼	¼	¼	¼	¼
	U_{eq}	2.86	3.02	3.53	3.66	5.04	4.90	5.70	5.14	5.17
	sof	1.013(3)	0.972(2)	0.987(3)	1.009(5)	1.019(4)	0.963(3)	1.017(4)	0.997(3)	1.004(3)
O1	*x*	0.4842(1)	0.4847(1)	0.4840(1)	0.4837(2)	0.4850(2)	0.4858(1)	0.4855(1)	0.4841(1)	0.4843(1)
	y	0.3269(1)	0.3275(1)	0.3267(1)	0.3270(2)	0.3282(2)	0.3282(1)	0.3281(1)	0.3270(1)	0.3275(1)
6*h*	*z*	¼	¼	¼	¼	¼	¼	¼	¼	¼
	U_{eq}	1.01	1.38	1.23	1.45	1.43	1.60	1.18	1.30	1.13
O2	*x*	0.4657(1)	0.4669(1)	0.4662(1)	0.4665(2)	0.4652(2)	0.4664(1)	0.4665(2)	0.4665(1)	0.4659(1)
	y	0.5880(1)	0.5876(1)	0.5876(1)	0.5874(2)	0.5870(2)	0.5863(1)	0.5878(1)	0.5872(1)	0.5874(1)
6*h*	*z*	¼	¼	¼	¼	¼	¼	¼	¼	¼
	U_{eq}	1.50	1.33	1.46	1.44	1.52	1.61	1.37	1.56	1.48
O3	*x*	0.2566(1)	0.2563(1)	0.2571(1)	0.2561(2)	0.2565(1)	0.2566(1)	0.2570(1)	0.2562(1)	0.2572(1)
	y	0.3411(1)	0.3413(1)	0.3412(1)	0.3411(2)	0.3411(1)	0.3418(1)	0.3418(1)	0.3416(1)	0.3422(1)
12*i*	*z*	0.0718(1)	0.0715(1)	0.0714(1)	0.0714(2)	0.0709(1)	0.0717(1)	0.0712(1)	0.0713(1)	0.0705(1)
	U_{eq}	1.72	1.99	1.89	1.95	2.07	2.17	2.03	2.32	1.79

Table S2. Continued.

Ion		26	27	28	29a	29b	30a (Cl)	30b (OH)	31a (F)	31b(OH)
Ca1	*x*	⅔	⅔	⅔	⅔	⅔	⅔	⅔	⅔	⅔
	y	⅓	⅓	⅓	⅓	⅓	⅓	⅓	⅓	⅓
4*f*	*z*	0.0011(1)	0.0012(1)	0.0019(1)	0.0008(2)	0.0022(2)	0.0030(1)	0.0007(7)	0.0010(1)	0.0052(13)
	$U_{eq.}$	0.86	0.92	0.62	0.75	0.92	0.92	0.41(10)	0.96	1.39(11)
	sof	0.953(1)	0.940(2)	0.940(2)	0.951(3)	0.958(4)	0.947(1)	1	1.020(2)	1
Ca2	*x*	–0.0068(1)	–0.0066(1)	–0.0062(1)	–0.0068(1)	–0.0065(1)	0.0020(1)	–0.0050(4)	–0.0077(1)	–0.0085(5)
	y	0.2445(1)	0.2444(1)	0.2461(1)	0.2442(1)	0.2457(1)	0.2581(1)	0.2512(3)	0.2433(1)	0.2457(4)
6*h*	*z*	¼	¼	¼	¼	¼	¼	¼	¼	¼
	U_{eq}	0.99	1.11	0.81	0.85	1.16	1.25	0.36(7)	0.97	1.39(9)
	sof	0.994(1)	0.954(1)	0.974(2)	1.006(3)	0.987(3)	0.976(1)	1	1.020(1)	1
P	*x*	0.3691(1)	0.3687(1)	0.3674(1)	0.3689(1)	0.3691(1)	0.3737(1)	0.3672(4)	0.3694(1)	0.3733(6)
	y	0.3990(1)	0.3990(1)	0.3993(1)	0.3987(1)	0.3992(1)	0.4063(1)	0.4012(5)	0.3991(1)	0.4019(6)
6*h*	*z*	¼	¼	¼	¼	¼	¼	¼	¼	¼
	U_{eq}	0.46	0.48	0.25	0.35	0.42	0.68	0.50(10)	1.26	2.71(15)
	sof	0.938(2)	0.909(2)	0.932(3)	0.953(4)	0.920(5)	0.939(2)	1	1	1
X	*x*	0	0	0	0	0	0	0	0	0
	y	0	0	0	0	0	0	0	0	0
2*a*/4*e*	*z*	¼	¼	¼	¼	¼	0.4347(2)	0.1937(31)	¼	¼
	U_{eq}	6.62	6.52	7.55	8.61	5.60	3.01	3.35(80)	5.38	5.6(6)
	sof	1.038(3)	1.038(4)	0.972(4)	1.066(6) F	1.056(8) F	0.452(1) Cl	0.5 OH	1.053(4) F	1 F
O1	*x*	0.4847(1)	0.4859(1)	0.4873(2)	0.4849(2)	0.4849(3)	0.4928(1)	0.4807(8)	0.4856(2)	0.4842(9)
	y	0.3286(1)	0.3289(1)	0.3288(2)	0.3286(2)	0.3292(3)	0.3426(1)	0.3301(8)	0.3296(2)	0.3260(9)
6*h*	*z*	¼	¼	¼	¼	¼	¼	¼	¼	¼
	U_{eq}	1.27	1.44	0.88	1.12	1.15	1.91	1.15(14)	0.60	0.04(26)
O2	*x*	0.4655(1)	0.4655(2)	0.4638(2)	0.4655(2)	0.4661(3)	0.4630(1)	0.4660(9)	0.4660(2)	0.4646(11)
	y	0.5878(1)	0.5867(1)	0.5850(2)	0.5878(2)	0.5877(3)	0.5902(1)	0.5872(5)	0.5865(2)	0.5897(6)
6*h*	*z*	¼	¼	¼	¼	¼	¼	¼	¼	¼
	U_{eq}	1.33	1.74	1.47	1.10	1.48	1.69	1.15(14)	0.49	0.48(28)
O3	*x*	0.2570(1)	0.2571(1)	0.2580(1)	0.2567(2)	0.2574(2)	0.2646(1)	0.2503(5)	0.2569(1)	0.2610(9)
	y	0.3416(1)	0.3421(1)	0.3426(1)	0.3426(2)	0.3411(2)	0.3528(1)	0.3343(6)	0.3413(2)	0.3458(9)
12*i*	*z*	0.0706(1)	0.0714(1)	0.0691(1)	0.0709(2)	0.0709(3)	0.0678(1)	0.0764(6)	0.0689(2)	0.0718(9)
	U_{eq}	1.91	2.13	1.50	1.85	2.28	2.51	1.15(14)	2.10	2.60(27)

Table S2. Continued.

Ion		32	33a (F)	33b (F)	33c (F)
Ca1	*x*	⅔	⅔	⅔	⅔
	y	⅓	⅓	⅓	⅓
4*f*	*z*	0.0026(1)	0.0011(1)	0.0015(3)	0.0017(3)
	$U_{eq.}$	0.91	0.85(1)	0.85(1)	0.85(1)
	sof	0.964(1)	1.011(2)	1.038(5)	1.081(4)
Ca2	*x*	0.0019(1)	–0.0070(1)	–0.0074(3)	–0.0064(2)
	y	0.2579(1)	0.2421(1)	0.2413(2)	0.2419(2)
6*h*	*z*	¼	¼	¼	¼
	U_{eq}	1.16	0.545(9)	0.545(9)	0.545(9)
	sof	0.988(1)	0.989(2)	1.009(5) F	1.014(3)
P	*x*	0.3742(1)	0.3692(1)	0.3694(3)	0.3706(2)
	y	0.4063(1)	0.3981(1)	0.3987(3)	0.3982(2)
6*h*	*z*	¼	¼	¼	¼
	U_{eq}	0.60	0.43(1)	0.43(1)	0.43(1)
	sof	0.946(2)	1	1	1
X	*x*	0	0	0	0
	y	0	0	0	0
2*a*/4*e*	*z*	0.43174(17)	¼	¼	¼
	U_{eq}	3.44	1.98(6)	1.98(6)	1.98(6)
	sof	0.455(1)	0.956(5) F	1.152(15) F	1.135(11) F
O1	*x*	0.4906(1)	0.4855(2)	0.4847(6)	0.4851(5)
	y	0.3424(1)	0.3269(2)	0.3266(7)	0.3253(5)
6*h*	*z*	¼	¼	¼	¼
	U_{eq}	1.63	0.67(3)	0.67(3)	0.67(3)
O2	*x*	0.4651(1)	0.4664(3)	0.4669(7)	0.4651(5)
	y	0.5913(1)	0.5883(2)	0.5877(3)	0.5874(3)
6*h*	*z*	¼	¼	¼	¼
	U_{eq}	1.52	0.84(3)	0.84(3)	0.84(3)
O3	*x*	0.2650(1)	0.2552(2)	0.2561(4)	0.2565(3)
	y	0.3518(1)	0.3398(2)	0.3420(5)	0.3405(4)
12*i*	*z*	0.0680(1)	0.0713(2)	0.0721(4)	0.0717(3)
	U_{eq}	2.49	0.95(2)	0.95(2)	0.95(2)

Table S3. Apatite samples: anisotropic displacement parameters (U_{ij} x 10^2 Å^2) and U_{eq} x 10^2 Å^2, and the ratio (U_{33}/U_{11}).

Ion	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	U_{eq}	(U_{33}/U_{11})
Sample 1								
Ca1	0.97(1)	0.97(1)	0.46(2)	0.49(1)	0	0	0.81	
Ca2	0.77(2)	0.90(2)	0.74(1)	0.40(2)	0	0	0.83	
P	0.46(3)	0.52(2)	0.49(2)	0.28(2)	0	0	0.49	
F	1.50(6)	1.50(6)	4.60(9)	0.75(3)	0	0	2.55	3.07
O1	1.30(7)	1.99(7)	1.52(7)	1.46(6)	0	0	1.42	
O2	1.24(7)	0.90(7)	3.58(9)	0.51(6)	0	0	1.89	
O3	1.74(5)	3.90(6)	0.90(4)	1.83(5)	−0.57(4)	−0.88(4)	2.26	
Sample 2								
Ca1	0.85(1)	0.85(1)	0.40(2)	0.43(1)	0	0	0.71	
Ca2	0.69(1)	0.58(2)	0.58(1)	0.36(1)	0	0	0.59	
P	0.38(2)	0.31(2)	0.31(2)	0.26(2)	0	0	0.29	
F	0.81(4)	0.81(4)	3.01(9)	0.41(2)	0	0	1.55	3.72
O1	0.92(6)	1.32(5)	1.75(6)	0.84(5)	0	0	1.26	
O2	0.91(5)	0.20(5)	2.22(6)	0.07(4)	0	0	1.12	
O3	1.29(4)	3.03(5)	0.63(3)	1.42(4)	−0.59(3)	−0.88(3)	1.71	
Sample 3								
Ca1	0.93(1)	0.93(1)	0.45(2)	0.47(1)	0	0	0.78	
Ca2	0.72(2)	0.59(2)	0.52(1)	0.34(1)	0	0	0.59	
P	0.28(2)	0.31(2)	0.16(2)	0.20(2)	0	0	0.23	
F	1.54(5)	1.54(5)	2.93(9)	0.77(3)	0	0	2.02	1.90
O1	1.71(7)	2.04(6)	1.06(6)	1.51(6)	0	0	1.41	
O2	0.86(5)	0.46(5)	2.39(7)	0.21(4)	0	0	1.25	
O3	1.45(4)	3.53(5)	0.51(4)	1.51(4)	−0.35(3)	−0.59(3)	1.96	
Sample 5								
Ca1	0.96(1)	0.96(1)	0.41(1)	0.48(1)	0	0	0.78	
Ca2	0.66(1)	0.70(1)	0.59(1)	0.33(1)	0	0	0.67	
P	0.35(1)	0.40(1)	0.29(1)	0.22(1)	0	0	0.34	
F	1.14(3)	1.14(3)	3.99(6)	0.57(1)	0	0	2.10	3.49
O1	1.16(3)	1.51(3)	1.38(3)	1.11(3)	0	0	1.20	
O2	0.98(3)	0.58(3)	2.48(4)	0.23(3)	0	0	1.38	
O3	1.30(2)	2.50(3)	0.84(2)	1.16(2)	−0.50(2)	−0.67(2)	1.60	
Sample 6								
Ca1	0.87(1)	0.87(1)	0.35(2)	0.44(1)	0	0	0.70	
Ca2	0.69(1)	0.71(2)	0.61(1)	0.36(1)	0	0	0.67	
P	0.33(2)	0.39(2)	0.32(2)	0.23(2)	0	0	0.34	
F	1.03(5)	1.03(5)	3.75(9)	0.51(2)	0	0	1.94	3.64
O1	1.25(6)	1.60(6)	1.30(6)	1.21(5)	0	0	1.22	
O2	1.09(5)	0.63(5)	2.12(7)	0.31(4)	0	0	1.29	
O3	1.30(4)	2.66(5)	0.81(3)	1.08(4)	−0.42(3)	−0.64(3)	1.71	
Sample 7								
Ca1	0.93(1)	0.93(1)	0.40(1)	0.47(1)	0	0	0.76	
Ca2	0.72(1)	0.72(1)	0.66(1)	0.37(1)	0	0	0.70	
P	0.32(2)	0.39(2)	0.38(2)	0.20(2)	0	0	0.37	
F	1.15(4)	1.15(4)	3.49(9)	0.57(2)	0	0	1.94	3.04
O1	1.21(6)	1.50(5)	1.53(6)	1.10(5)	0	0	1.27	
O2	0.94(5)	0.77(5)	2.33(6)	0.37(4)	0	0	1.36	
O3	1.32(4)	2.69(4)	0.75(3)	1.20(3)	−0.39(3)	−0.65(3)	1.67	
Sample 9								
Ca1	0.91(1)	0.91(1)	0.36(1)	0.46(1)	0	0	0.73	

Ca2	0.66(1)	0.70(1)	0.60(1)	0.34(1)	0	0	0.67	
P	0.32(2)	0.36(2)	0.26(2)	0.21(1)	0	0	0.30	
F	1.18(4)	1.18(4)	4.47(9)	0.59(2)	0	0	2.28	3.79
O1	1.22(5)	1.59(5)	1.23(5)	1.17(4)	0	0	1.19	
O2	0.95(5)	0.60(5)	2.15(6)	0.29(4)	0	0	1.24	
O3	1.30(3)	2.45(4)	0.72(3)	1.16(3)	−0.37(3)	−0.60(3)	1.54	
Sample 10								
Ca1	0.92(1)	0.92(1)	0.34(2)	0.46(1)	0	0	0.73	
Ca2	0.69(2)	0.73(2)	0.59(1)	0.36(1)	0	0	0.68	
P	0.31(2)	0.41(2)	0.27(2)	0.19(2)	0	0	0.34	
F	1.09(5)	1.09(5)	3.96(10)	0.55(3)	0	0	2.05	3.63
O1	1.09(6)	1.41(6)	1.09(6)	1.01(5)	0	0	1.08	
O2	1.06(6)	0.59(6)	1.97(7)	0.37(5)	0	0	1.18	
O3	1.28(4)	2.46(5)	0.71(4)	1.06(4)	−0.40(3)	−0.66(3)	1.57	
Sample 11								
Ca1	1.11(1)	1.11(1)	0.43(2)	0.55(1)	0	0	0.89	
Ca2	0.83(2)	0.86(2)	0.73(1)	0.45(1)	0	0	0.81	
P	0.37(2)	0.49(2)	0.41(2)	0.26(2)	0	0	0.42	
F	1.56(6)	1.56(6)	4.39(11)	0.78(3)	0	0	2.51	2.81
O1	1.24(6)	1.83(6)	1.51(6)	1.27(6)	0	0	1.39	
O2	0.95(6)	0.93(6)	2.41(7)	0.34(5)	0	0	1.49	
O3	1.52(4)	3.03(6)	1.00(4)	1.31(4)	−0.53(3)	−0.76(4)	1.96	
Sample 12								
Ca1	1.07(1)	1.07(1)	0.40(1)	0.54(1)	0	0	0.85	
Ca2	0.81(1)	0.86(1)	0.73(1)	0.43(1)	0	0	0.80	
P	0.37(2)	0.46(2)	0.39(2)	0.23(2)	0	0	0.41	
F	1.30(5)	1.30(5)	4.54(10)	0.65(2)	0	0	2.39	3.49
O1	1.25(6)	1.54(5)	1.41(5)	1.11(5)	0	0	1.27	
O2	1.03(5)	0.73(5)	2.22(6)	0.28(4)	0	0	1.37	
O3	1.45(4)	3.02(5)	0.93(3)	1.35(4)	−0.40(3)	−0.66(3)	1.89	
Sample 13								
Ca1	1.03(1)	1.03(1)	0.43(2)	0.51(1)	0	0	0.83	
Ca2	0.79(2)	0.88(2)	0.61(1)	0.42(2)	0	0	0.77	
P	0.40(2)	0.46(2)	0.34(2)	0.23(2)	0	0	0.40	
F	1.40(6)	1.40(6)	3.83(11)	0.70(3)	0	0	2.22	2.74
O1	1.28(7)	1.53(6)	1.26(6)	1.07(6)	0	0	1.24	
O2	1.09(6)	0.89(6)	1.83(7)	0.45(5)	0	0	1.27	
O3	1.61(5)	2.74(5)	0.72(4)	1.33(4)	−0.50(3)	−0.77(3)	1.72	
Sample 14								
Ca1	1.05(1)	1.05(1)	0.41(1)	0.52(1)	0	0	0.84	
Ca2	0.72(1)	0.86(1)	0.58(1)	0.41(1)	0	0	0.74	
P	0.33(2)	0.41(2)	0.34(2)	0.25(1)	0	0	0.34	
F	1.25(4)	1.25(4)	4.97(9)	0.63(2)	0	0	2.50	3.98
O1	1.11(5)	1.65(5)	1.37(5)	1.11(4)	0	0	1.26	
O2	0.94(5)	0.49(4)	2.20(5)	0.19(4)	0	0	1.24	
O3	1.42(3)	2.91(4)	0.85(3)	1.31(3)	−0.40(3)	−0.72(3)	1.81	
Sample 15								
Ca1	1.08(2)	1.08(2)	0.49(2)	0.54(1)	0	0	0.89	
Ca2	0.81(2)	0.95(2)	0.80(2)	0.41(2)	0	0	0.89	
P	0.38(3)	0.48(3)	0.51(2)	0.19(2)	0	0	0.47	
F	1.35(6)	1.35(6)	5.93(14)	0.68(3)	0	0	2.89	4.39
O1	1.15(8)	1.43(7)	1.70(8)	1.06(6)	0	0	1.29	
O2	1.10(7)	0.89(7)	2.89(9)	0.60(6)	0	0	1.57	

O3	1.58(5)	2.85(6)	0.91(4)	1.32(5)	−0.56(4)	−0.82(4)	1.84	
Sample 16								
Ca1	1.25(1)	1.25(1)	0.53(2)	0.63(1)	0	0	1.02	
Ca2	0.95(2)	1.10(2)	0.82(1)	0.55(2)	0	0	0.96	
P	0.50(3)	0.59(2)	0.62(2)	0.31(2)	0	0	0.56	
F	1.35(6)	1.35(6)	6.42(14)	0.68(3)	0	0	3.05	4.76
O1	1.31(7)	1.71(7)	1.63(7)	1.21(6)	0	0	1.41	
O2	1.00(6)	0.65(7)	3.02(9)	0.22(5)	0	0	1.60	
O3	1.86(5)	3.31(6)	0.93(4)	1.70(5)	−0.48(4)	−0.73(4)	2.04	
Sample17								
Ca1	1.11(1)	1.11(1)	0.38(2)	0.56(1)	0	0	0.87	
Ca2	0.80(2)	0.96(2)	0.71(1)	0.40(2)	0	0	0.86	
P	0.40(2)	0.56(2)	0.40(2)	0.35(2)	0	0	0.43	
F	1.28(6)	1.28(6)	5.97(13)	0.64(3)	0	0	2.86	4.66
O1	1.03(7)	1.25(6)	0.99(6)	0.83(6)	0	0	1.01	
O2	0.85(6)	0.68(7)	2.78(8)	0.20(5)	0	0	1.50	
O3	1.21(4)	3.21(6)	0.38(4)	1.38(4)	−0.30(3)	−0.65(4)	1.72	
Sample 18								
Ca1	1.03(1)	1.03(1)	0.43(1)	0.52(1)	0	0	0.84	
Ca2	0.75(1)	1.02(1)	0.55(1)	0.39(1)	0	0	0.83	
P	0.31(1)	0.48(1)	0.30(1)	0.23(1)	0	0	0.37	
F	1.12(4)	1.12(4)	6.79(11)	0.56(2)	0	0	3.02	6.06
O1	1.39(5)	1.71(5)	1.56(4)	1.28(4)	0	0	1.38	
O2	0.70(4)	0.46(4)	2.43(5)	-0.07(3)	0	0	1.33	
O3	1.70(3)	3.55(4)	0.63(3)	1.76(3)	−0.54(2)	−0.84(3)	1.99	
Sample 19								
Ca1	1.09(1)	1.09(1)	0.52(2)	0.54(1)	0	0	0.91	
Ca2	0.75(2)	0.97(2)	0.69(2)	0.40(2)	0	0	0.85	
P	0.39(3)	0.39(2)	0.40(2)	0.25(2)	0	0	0.37	
F	1.66(7)	1.66(7)	7.22(16)	0.83(3)	0	0	3.53	4.35
O1	1.20(8)	1.56(7)	1.26(7)	1.07(6)	0	0	1.23	
O2	1.30(7)	0.74(7)	2.53(8)	0.52(6)	0	0	1.46	
O3	1.54(5)	3.01(6)	0.93(4)	1.40(5)	−0.58(4)	−0.79(4)	1.89	
Sample 20								
Ca1	0.77(2)	0.77(2)	0.53(3)	-0.87(1)	0	0	1.23	
Ca2	0.73(3)	1.19(3)	0.80(2)	-0.24(3)	0	0	1.28	
P	0.44(4)	0.54(4)	0.48(3)	-0.41(3)	0	0	0.78	
F	0.82(9)	0.82(9)	7.70(25)	-0.84(5)	0	0	3.66	9.39
O1	1.42(12)	1.65(11)	2.03(12)	1.44(10)	0	0	1.45	
O2	1.05(11)	0.81(11)	2.38(13)	0.35(9)	0	0	1.44	
O3	1.41(7)	3.26(10)	0.92(7)	1.49(7)	−0.29(6)	−0.81(6)	1.95	
Sample 21								
Ca1	1.10(2)	1.10(2)	0.46(3)	0.55(1)	0	0	0.90	
Ca2	0.72(2)	1.15(3)	0.85(2)	0.33(2)	0	0	1.02	
P	0.42(3)	0.57(3)	0.46(3)	0.24(3)	0	0	0.51	
F	1.72(8)	1.72(8)	11.64(25)	0.86(4)	0	0	5.04	6.77
O1	1.40(10)	1.91(9)	1.43(9)	1.33(8)	0	0	1.43	
O2	1.21(9)	0.93(9)	2.56(11)	0.59(7)	0	0	1.52	
O3	1.54(6)	3.41(8)	1.13(6)	1.66(6)	−0.56(5)	−0.99(5)	2.07	
Sample 22								
Ca1	1.10(1)	1.10(1)	0.45(2)	0.55(1)	0	0	0.89	
Ca2	0.83(2)	0.85(2)	0.78(1)	0.42(2)	0	0	0.83	
P	0.31(2)	0.63(2)	0.32(2)	0.36(2)	0	0	0.40	

F	1.93(7)	1.93(7)	10.80(20)	0.96(4)	0	0	4.90	5.60
O1	1.05(7)	1.92(7)	2.05(7)	1.16(6)	0	0	1.60	
O2	0.56(6)	0.82(7)	2.58(8)	-0.24(5)	0	0	1.61	
O3	1.67(5)	3.96(6)	0.66(4)	1.87(5)	−0.68(4)	−1.18(4)	2.17	
Sample 23								
Ca1	0.89(2)	0.89(2)	0.63(2)	0.44(1)	0	0	0.81	
Ca2	0.74(2)	0.99(2)	0.78(2)	0.38(2)	0	0	0.89	
P	0.29(3)	0.50(3)	0.44(3)	0.24(2)	0	0	0.42	
F	1.63(8)	1.63(8)	13.79(25)	0.82(4)	0	0	5.70	8.46
O1	1.14(9)	1.34(8)	1.63(8)	1.13(7)	0	0	1.18	
O2	0.86(8)	0.44(8)	2.75(10)	0.17(6)	0	0	1.37	
O3	1.25(6)	3.16(7)	1.21(5)	1.27(5)	−0.60(4)	−0.66(5)	2.03	
Sample 24								
Ca1	1.18(1)	1.18(1)	0.53(2)	0.59(1)	0	0	0.97	
Ca2	0.92(2)	1.14(2)	0.83(1)	0.48(2)	0	0	1.01	
P	0.45(2)	0.63(2)	0.44(2)	0.31(2)	0	0	0.51	
F	1.98(7)	1.98(7)	11.41(19)	0.99(3)	0	0	5.14	5.76
O1	1.00(7)	1.75(7)	1.53(7)	1.20(6)	0	0	1.30	
O2	1.07(6)	0.66(7)	2.92(8)	0.31(5)	0	0	1.56	
O3	2.01(5)	3.88(6)	1.18(4)	2.08(5)	−0.79(4)	−0.93(4)	2.32	
Sample 25								
Ca1	1.13(1)	1.13(1)	0.53(2)	0.57(1)	0	0	0.94	
Ca2	0.83(2)	1.11(2)	0.63(1)	0.42(2)	0	0	0.93	
P	0.47(2)	0.49(2)	0.43(2)	0.29(2)	0	0	0.44	
F	1.41(6)	1.41(6)	12.65(20)	0.71(3)	0	0	5.17	8.97
O1	1.38(7)	1.51(7)	1.17(6)	1.31(6)	0	0	1.13	
O2	0.74(6)	0.73(7)	2.80(8)	0.26(5)	0	0	1.48	
O3	1.51(5)	2.96(6)	0.75(4)	1.41(4)	−0.61(4)	−0.81(4)	1.79	
Sample 26								
Ca1	1.07(2)	1.07(2)	0.43(2)	0.53(1)	0	0	0.86	
Ca2	0.77(2)	1.26(2)	0.59(1)	0.39(2)	0	0	0.99	
P	0.38(3)	0.56(3)	0.40(2)	0.26(2)	0	0	0.46	
F	1.35(7)	1.35(7)	17.15(23)	0.674(34)	0	0	6.62	12.70
O1	1.31(8)	1.82(8)	1.19(7)	1.33(7)	0	0	1.27	
O2	1.10(7)	0.70(7)	2.32(8)	0.45(6)	0	0	1.33	
O3	1.59(5)	3.06(6)	0.96(4)	1.48(5)	−0.59(4)	−0.96(4)	1.91	
Sample 27								
Ca1	1.06(2)	1.06(2)	0.62(2)	0.53(1)	0	0	0.92	
Ca2	0.91(2)	1.26(2)	0.78(2)	0.37(2)	0	0	1.11	
P	0.35(3)	0.63(3)	0.45(3)	0.31(2)	0	0	0.48	
F	1.51(8)	1.51(8)	16.50(26)	0.76(4)	0	0	6.52	10.93
O1	1.25(8)	1.43(8)	2.02(8)	1.04(7)	0	0	1.44	
O2	0.85(8)	0.89(8)	3.56(10)	0.52(6)	0	0	1.74	
O3	2.00(6)	3.50(7)	0.59(5)	1.57(5)	−0.39(4)	−0.48(4)	2.13	
Sample 28								
Ca1	0.60(3)	0.60(3)	0.65(3)	0.30(1)	0	0	0.62	
Ca2	0.58(3)	0.77(3)	0.96(2)	0.31(3)	0	0	0.81	
P	0.31(5)	0.32(4)	0.36(4)	0.35(4)	0	0	0.25	
F	1.04(12)	1.04(12)	20.6(4)	0.52(6)	0	0	7.55	19.81
O1	0.26(12)	1.55(12)	1.61(11)	1.40(11)	0	0	0.88	
O2	1.43(12)	0.46(12)	3.00(13)	0.61(10)	0	0	1.47	
O3	0.91(8)	2.53(9)	1.07(7)	1.32(7)	−0.56(6)	−0.35(6)	1.50	
Sample 29a								

Ca1	1.00(3)	1.00(3)	0.23(5)	0.50(1)	0	0	0.75	
Ca2	0.77(3)	1.25(4)	0.23(4)	0.40(3)	0	0	0.85	
P	0.39(5)	0.60(4)	0.07(5)	0.33(3)	0	0	0.35	
F	0.97(11)	0.97(11)	23.9(6)	0.49(6)	0	0	8.61	24.64
O1	1.25(13)	1.64(12)	1.17(18)	1.40(11)	0	0	1.12	
O2	1.10(11)	0.77(12)	1.53(19)	0.48(9)	0	0	1.10	
O3	1.71(9)	3.39(11)	0.10(9)	1.47(8)	−0.82(7)	−1.04(8)	1.85	
Sample 29b								
Ca1	1.01(4)	1.01(4)	0.73(6)	0.50(2)	0	0	0.92	
Ca2	0.70(4)	1.30(5)	1.08(5)	0.37(4)	0	0	1.16	
P	0.32(6)	0.40(6)	0.57(8)	0.23(5)	0	0	0.42	
F	1.96(16)	1.96(16)	12.8(5)	0.98(8)	0	0	5.60	6.53
O1	1.11(17)	1.71(17)	0.94(21)	1.12(15)	0	0	1.15	
O2	1.83(17)	0.38(16)	2.79(26)	0.63(13)	0	0	1.48	
O3	1.10(11)	3.40(14)	2.01(14)	1.51(11)	−0.54(10)	−0.84(11)	2.28	
Sample 30a								
Ca1	1.06(1)	1.06(1)	0.62(2)	0.53(1)	0	0	0.92	
Ca2	1.19(2)	1.48(2)	0.94(1)	0.66(2)	0	0	1.25	
P	0.74(3)	0.67(2)	0.69(2)	0.40(2)	0	0	0.68	
Cl	1.55(4)	1.55(4)	5.91(10)	0.78(2)	0	0	3.01	3.81
O1	1.99(7)	2.95(8)	1.79(7)	2.29(7)	0	0	1.91	
O2	1.03(6)	0.92(6)	2.85(7)	0.26(5)	0	0	1.69	
O3	2.98(6)	3.87(6)	1.44(4)	2.57(5)	−1.21(4)	−1.28(4)	2.51	
Sample 31a								
Ca1	1.24(2)	1.24(2)	0.40(3)	0.62(1)	0	0	0.96	
Ca2	0.89(3)	0.98(3)	0.98(2)	0.46(3)	0	0	0.97	
P	1.26(5)	1.44(4)	1.11(4)	0.75(4)	0	0	1.26	
F	1.52(10)	1.52(10)	13.06(28)	0.76(5)	0	0	5.38	8.59
O1	0.00(10)	1.74(11)	0.67(10)	1.37(9)	0	0	0.60	
O2	0.05(9)	-0.44(10)	1.79(12)	-0.29(8)	0	0	0.49	
O3	1.50(7)	4.57(10)	0.26(6)	2.38(7)	−0.75(6)	−1.35(6)	2.10	
Sample 32								
Ca1	1.09(1)	1.09(1)	0.54(2)	0.55(1)	0	0	0.91	
Ca2	1.22(2)	1.34(2)	0.75(2)	0.56(2)	0	0	1.16	
P	0.66(3)	0.74(2)	0.41(2)	0.38(2)	0	0	0.60	
Cl	1.92(4)	1.92(4)	6.45(11)	0.96(2)	0	0	3.44	3.36
O1	2.22(8)	2.13(7)	1.51(7)	1.85(7)	0	0	1.63	
O2	1.38(7)	0.65(7)	2.30(7)	0.15(6)	0	0	1.52	
O3	1.92(5)	3.91(6)	1.44(4)	1.87(5)	−1.19(4)	−1.69(4)	2.49	

Table S4. Bond distances (Å), angles (°), and averages for 33 apatite samples.

Bond/angle		1	2	3	4a (F)	4b (OH)	5	6	7	8a
Ca1-O1/Å	× 3	2.3798(7)	2.3956(7)	2.3930(7)	2.3928(17)	2.3973(24)	2.3967(4)	2.3979(6)	2.3972(6)	2.3932(25)
Ca1-O2/Å	× 3	2.4407(8)	2.4524(7)	2.4503(7)	2.4461(27)	2.452(4)	2.4529(4)	2.4496(7)	2.4508(6)	2.475(4)
<Ca1-O>[6]/Å		2.4103	2.4240	2.4217	2.4195	2.4247	2.4248	2.4238	2.4240	2.4327
Ca1-O3/Å	× 3	2.8127(7)	2.8031(7)	2.8083(7)	2.8155(24)	2.8105(35)	2.8091(4)	2.8081(6)	2.8084(6)	2.7532(31)
<Ca1-O>[9]/Å		2.5444	2.5504	2.5505	2.5515	2.5533	2.5529	2.5519	2.5521	2.5395
Ca2-X/Å	× 1	2.2932(3)	2.2936(3)	2.2949(3)	2.2946(10)	2.3083(16)	2.2964(2)	2.2963(3)	2.2958(2)	2.2938(16)
Ca2-O1/Å	× 1	2.7019(11)	2.6906(10)	2.6933(10)	2.688(4)	2.695(5)	2.6892(5)	2.6883(9)	2.6909(9)	2.702(6)
Ca2-O2/Å	× 1	2.3777(10)	2.3699(9)	2.3708(9)	2.3829(32)	2.355(5)	2.3756(5)	2.3745(9)	2.3804(8)	2.350(4)
Ca2-O3/Å	× 2	2.4835(8)	2.4801(7)	2.4858(7)	2.4946(26)	2.484(4)	2.4878(4)	2.4879(7)	2.4883(6)	2.5122(34)
Ca2-O3/Å	× 2	2.3399(7)	2.3588(6)	2.3546(6)	2.3455(15)	2.3546(22)	2.3510(3)	2.3487(6)	2.3516(5)	2.3561(20)
<Ca2-O>[6]/Å		2.4544	2.4564	2.4575	2.4585	2.4545	2.4571	2.4560	2.4585	2.4648
<Ca2-O,X>[7]/Å		2.4314	2.4331	2.4343	2.4351	2.4336	2.4341	2.4332	2.4353	2.4403
P-O1/Å	× 1	1.5336(10)	1.5331(9)	1.5329(9)	1.5327(3)	1.5336(3)	1.5348(5)	1.5334(9)	1.5336(8)	1.5347(9)
P-O2/Å	× 1	1.5395(10)	1.5450(9)	1.5494(9)	1.5485(3)	1.5416(3)	1.5379(5)	1.5420(8)	1.5355(8)	1.5359(9)
P-O3/Å	× 2	1.5316(7)	1.5281(6)	1.5267(7)	1.5278(2)	1.5328(2)	1.5324(4)	1.5352(6)	1.5324(6)	1.5326(7)
<P-O>[4]/Å		1.5341	1.5336	1.5339	1.5342	1.5352	1.5344	1.5365	1.5335	1.5340
O1-P-O2/°	× 1	111.37(6)	111.13(5)	111.32(6)	111.18(22)	111.54(32)	111.17(3)	111.35(5)	111.33(5)	109.99(32)
O1-P-O3/°	× 2	111.08(4)	111.34(3)	111.06(4)	110.99(13)	110.56(19)	110.99(2)	110.94(3)	110.98(3)	112.19(18)
O2-P-O3/°	× 2	108.31(4)	108.13(4)	108.05(4)	108.05(13)	108.79(19)	108.26(2)	108.18(3)	108.16(3)	106.68(18)
O3-P-O3/°	× 1	106.51(6)	106.58(5)	107.14(6)	107.42(19)	106.45(26)	107.02(3)	107.10(5)	107.07(5)	108.82(21)
<O-P-O>[6]/°		109.44	109.44	109.45	109.45	109.45	109.45	109.45	109.45	109.43

Table S4. Continued.

		8b	9	10	11	12	13	14	15	16
Ca1-O1/Å	× 3	2.3971(22)	2.4001(6)	2.3973(7)	2.4011(7)	2.4013(6)	2.3971(7)	2.4005(6)	2.4032(8)	2.4034(8)
Ca1-O2/Å	× 3	2.4274(32)	2.4523(6)	2.4494(7)	2.4543(8)	2.4511(7)	2.4492(8)	2.4523(6)	2.4508(9)	2.4560(8)
<Ca1-O>[6]/Å		2.4123	2.4262	2.4234	2.4277	2.4262	2.4232	2.4264	2.4270	2.4297
Ca1-O3/Å	× 3	2.8652(28)	2.8076(6)	2.8085(7)	2.8098(7)	2.8060(6)	2.8072(7)	2.8101(6)	2.8134(8)	2.8075(8)
<Ca1-O>[9]/Å		2.5632	2.5533	2.5517	2.5551	2.5528	2.5512	2.5543	2.5558	2.5556
Ca2-X/Å	× 1	2.3031(14)	2.3027(2)	2.2980(3)	2.2930(3)	2.2964(2)	2.2993(3)	2.3016(2)	2.2969(3)	2.2945(3)
Ca2-O1/Å	× 1	2.683(5)	2.6880(8)	2.6894(10)	2.6857(10)	2.6901(9)	2.6928(11)	2.6898(8)	2.6868(11)	2.685(1)
Ca2-O2/Å	× 1	2.411(4)	2.3713(8)	2.3767(9)	2.3842(10)	2.3824(8)	2.3778(10)	2.3746(8)	2.3869(11)	2.384(1)
Ca2-O3/Å	× 2	2.4765(31)	2.4883(6)	2.4882(7)	2.4862(7)	2.4918(6)	2.4896(8)	2.4893(6)	2.4932(8)	2.4970(8)
Ca2-O3/Å	× 2	2.3449(18)	2.3521(5)	2.3516(6)	2.3547(7)	2.3528(6)	2.3517(6)	2.3516(5)	2.3503(7)	2.3549(7)
<Ca2-O>[6]/Å		2.4561	2.4567	2.4576	2.4586	2.4603	2.4589	2.4577	2.4601	2.4621
<Ca2-O,X>[7]/Å		2.4343	2.4347	2.4348	2.4350	2.4369	2.4361	2.4354	2.4368	2.4382
P-O1/Å	x 1	1.5345(9)	1.5332(8)	1.5343(9)	1.5284(10)	1.5301(8)	1.5364(10)	1.5349(8)	1.531(1)	1.530(1)
P-O2/Å	× 1	1.5361(9)	1.5394(7)	1.5421(9)	1.5317(10)	1.5368(8)	1.5431(10)	1.5423(7)	1.5352(11)	1.537(1)
P-O3/Å	× 2	1.5337(7)	1.5303(6)	1.5325(7)	1.5364(7)	1.5334(6)	1.5336(7)	1.5351(5)	1.5368(8)	1.5346(8)
<P-O>[4]/Å		1.5345	1.5333	1.5354	1.5332	1.5334	1.5367	1.5369	1.5349	1.5342
O1-P-O2/°	× 1	112.7(3)	111.32(5)	111.39(6)	111.46(6)	111.30(5)	111.36(6)	111.24(5)	111.81(7)	111.53(7)
O1-P-O3/°	× 2	109.8(2)	110.96(3)	111.00(3)	111.09(4)	111.04(3)	111.10(4)	111.01(3)	110.74(4)	110.93(4)
O2-P-O3/°	× 2	109.5(2)	108.15(3)	108.09(4)	108.29(4)	108.07(3)	107.98(4)	108.23(3)	108.18(4)	108.04(4)
O3-P-O3/°	× 1	105.2(2)	107.14(5)	107.10(6)	106.43(6)	107.16(5)	107.15(6)	106.96(5)	107.02(7)	107.19(6)
<O-P-O>[6]/°		109.43	109.45	109.45	109.44	109.45	109.45	109.45	109.45	109.44

Table S4. Continued.

		17	18	19	20	21	22	23	24	25
Ca1-O1/Å	× 3	2.3985(7)	2.4033(6)	2.4035(8)	2.4090(12)	2.4026(10)	2.3991(8)	2.3995(9)	2.4068(7)	2.4055(8)
Ca1-O2/Å	× 3	2.4529(8)	2.4566(6)	2.4550(9)	2.4547(13)	2.4526(11)	2.4639(9)	2.4570(10)	2.4607(8)	2.4560(8)
<Ca1-O>[6]/Å		2.4257	2.4300	2.4293	2.4319	2.4276	2.4315	2.4283	2.4338	2.4308
Ca1-O3/Å	× 3	2.8132(7)	2.8110(6)	2.8140(8)	2.8133(12)	2.8151(10)	2.8095(8)	2.8132(9)	2.8109(8)	2.8090(8)
<Ca1-O>[9]/Å		2.5549	2.5570	2.5575	2.5590	2.5568	2.5575	2.5566	2.5595	2.5568
Ca2-X/Å	× 1	2.3099(3)	2.3093(2)	2.3158(3)	2.3140(5)	2.3228(4)	2.3170(3)	2.3296(4)	2.3182(3)	2.3295(3)
Ca2-O1/Å	× 1	2.6946(10)	2.7002(8)	2.6916(12)	2.6976(18)	2.7075(15)	2.7067(12)	2.7076(13)	2.6944(11)	2.7041(11)
Ca2-O2/Å	× 1	2.3763(10)	2.3720(7)	2.3704(11)	2.3721(17)	2.3766(14)	2.3738(11)	2.3645(12)	2.3742(10)	2.3675(10)
Ca2-O3/Å	× 2	2.4879(7)	2.4891(6)	2.4958(9)	2.4869(13)	2.4937(10)	2.4939(8)	2.4994(10)	2.4944(8)	2.4999(8)
Ca2-O3/Å	× 2	2.3572(6)	2.3547(5)	2.3530(7)	2.3532(11)	2.3491(9)	2.3583(7)	2.3503(8)	2.3552(7)	2.3483(7)
<Ca2-O>[6]/Å		2.4602	2.4600	2.4599	2.4583	2.4616	2.4642	2.4619	2.4613	2.4613
<Ca2-O,X>[7]/Å		2.4387	2.4384	2.4393	2.4377	2.4418	2.4431	2.4430	2.4409	2.4425
P-O1/Å	× 1	1.5319(10)	1.5355(7)	1.5334(11)	1.5282(17)	1.5338(14)	1.5397(11)	1.5412(12)	1.5344(10)	1.5335(10)
P-O2/Å	× 1	1.5396(9)	1.5362(7)	1.5399(11)	1.5369(16)	1.5312(13)	1.5289(11)	1.5414(12)	1.5339(10)	1.5372(10)
P-O3/Å	× 2	1.5310(7)	1.5329(5)	1.5288(8)	1.5353(12)	1.5367(10)	1.5312(8)	1.5317(9)	1.5374(7)	1.5358(7)
<P-O>[4]/Å		1.5334	1.5344	1.5327	1.5339	1.5346	1.5328	1.5365	1.5358	1.5356
O1-P-O2/°	× 1	111.75(6)	110.97(5)	111.32(7)	111.37(10)	111.36(8)	110.56(7)	110.82(8)	111.31(6)	111.36(6)
O1-P-O3/°	× 2	111.02(4)	111.14(3)	110.91(4)	111.16(6)	111.09(5)	111.47(4)	111.24(5)	111.18(4)	111.14(4)
O2-P-O3/°	× 2	108.13(4)	108.45(3)	108.22(4)	108.30(7)	108.22(5)	108.23(4)	108.22(5)	108.27(4)	107.93(4)
O3-P-O3/°	× 1	106.58(6)	106.53(5)	107.10(7)	106.34(10)	106.68(8)	106.72(6)	106.94(8)	106.43(6)	107.16(6)
<O-P-O>[6]/°		109.44	109.45	109.45	109.44	109.44	109.45	109.45	109.44	109.44

Table S4. Continued.

		26	**27**	**28**	**29a**	**29b**	**30a (Cl)**	**30b (OH)**	**31a (F)**	**31b (OH)**
Ca1-O1/Å	× 3	2.4070(8)	2.3991(9)	2.3874(10)	2.4070(15)	2.4030(19)	2.3999(7)	2.446(4)	2.4006(12)	2.382(7)
Ca1-O2/Å	× 3	2.4511(8)	2.4571(9)	2.4606(11)	2.4493(17)	2.4615(21)	2.4404(8)	2.461(6)	2.4563(13)	2.456(9)
<Ca1-O>[6]/Å		2.4291	2.4281	2.4240	2.4282	2.4323	2.42015	2.4535	2.4285	2.419
Ca1-O3/Å	× 3	2.8160(8)	2.8129(9)	2.8103(11)	2.8062(15)	2.8264(19)	2.7915(7)	2.892(5)	2.8022(12)	2.792(8)
<Ca1-O>[9]/Å		2.5580	2.5564	2.5528	2.5542	2.5636	2.5439	2.5997	2.5530	2.5433
Ca2-X/Å	× 1	2.3350(3)	2.3338(4)	2.3486(5)	2.3324(6)	2.3477(7)	2.7718(5)	2.439(4)	2.3162(5)	2.3507(32)
Ca2-O1/Å	× 1	2.7115(11)	2.7182(13)	2.7220(16)	2.7121(20)	2.7195(25)	2.9384(11)	2.736(8)	2.7013(16)	2.671(10)
Ca2-O2/Å	× 1	2.3695(10)	2.3713(12)	2.3729(15)	2.3722(19)	2.3581(24)	2.3282(9)	2.329(7)	2.3640(15)	2.361(9)
Ca2-O3/Å	× 2	2.5016(8)	2.4976(9)	2.5125(11)	2.4974(16)	2.5055(20)	2.5366(8)	2.449(6)	2.5038(14)	2.535(10)
Ca2-O3/Å	× 2	2.3447(7)	2.3526(8)	2.3369(10)	2.3508(16)	2.3429(20)	2.3347(7)	2.359(4)	2.3352(10)	2.357(6)
<Ca2-O>[6]/Å		2.4623	2.4650	2.4656	2.4635	2.4624	2.5015	2.4468	2.4572	2.4693
<Ca2-O,X>[7]/Å		2.4441	2.4462	2.4489	2.4447	2.4460	2.5401	2.4457	2.4371	2.4524
P-O1/Å	× 1	1.5314(11)	1.5443(12)	1.5706(15)	1.5332(18)	1.5323(24)	1.5458(10)	1.5294(14)	1.5230(15)	1.5296(12)
P-O2/Å	× 1	1.5397(10)	1.5314(12)	1.5161(15)	1.5422(18)	1.5389(23)	1.5328(10)	1.5294(14)	1.5206(14)	1.5295(12)
P-O3/Å	× 2	1.5360(7)	1.5287(9)	1.5320(10)	1.5343(16)	1.5325(20)	1.5336(7)	1.5319(10)	1.5461(10)	1.5307(9)
<P-O>[4]/Å		1.5358	1.5333	1.5377	1.5360	1.5341	1.5365	1.5307	1.5340	1.5301
O1-P-O2/°	× 1	111.31(7)	110.70(7)	110.22(9)	111.18(12)	110.95(15)	111.02(6)	110.4(5)	110.7(1)	114.7(6)
O1-P-O3/°	× 2	111.09(4)	111.30(4)	110.70(6)	111.56(7)	110.87(9)	112.68(4)	109.9(4)	110.97(6)	110.6(4)
O2-P-O3/°	× 2	108.12(4)	108.22(5)	108.21(6)	107.74(8)	108.54(10)	106.40(4)	112.2(3)	108.20(7)	106.9(4)
O3-P-O3/°	× 1	106.94(6)	106.94(7)	108.72(9)	106.83(13)	106.95(17)	107.25(6)	102.0(5)	107.7(1)	106.6(8)
<O-P-O>[6]/°		109.45	109.45	109.46	109.44	109.45	109.41	109.42	109.45	109.38

In sample 30a, Cl-Cl = 0.886(2), 2.503(2), and 3.3887(1) Å. In sample 32, Cl-Cl = 0.926(2), 2.466(2), and 3.3916(1) Å. In sample 4b, OH-OH = 0.31(2) Å. In sample 30b, OH-OH = 0.77(4) Å.

Table S4. Continued.

		32	33a (F)	33b (F)	33c (F)
Ca1-O1/Å	× 3	2.4165(7)	2.3897(12)	2.3937(29)	2.3797(25)
Ca1-O2/Å	× 3	2.4473(8)	2.4475(16)	2.458(4)	2.4415(34)
<Ca1-O>[6]/Å		2.4319	2.4186	2.42585	2.4106
Ca1-O3/Å	× 3	2.8008(8)	2.8152(15)	2.800(4)	2.8110(32)
<Ca1-O>[9]/Å		2.5549	2.5508	2.5506	2.5441
Ca2-X/Å	× 1	2.7618(6)	2.3027(6)	2.2973(17)	2.2963(13)
Ca2-O1/Å	× 1	2.9304(11)	2.6929(22)	2.688(6)	2.685(5)
Ca2-O2/Å	× 1	2.3114(9)	2.3713(20)	2.375(5)	2.382(4)
Ca2-O3/Å	× 2	2.5411(8)	2.4773(16)	2.482(4)	2.476(4)
Ca2-O3/Å	× 2	2.3333(7)	2.3479(11)	2.3619(27)	2.3456(23)
<Ca2-O>[6]/Å		2.4984	2.4524	2.4585	2.4517
<Ca2-O,X>[7]/Å		2.5361	2.4310	2.4354	2.4295
P-O1/Å	x 1	1.5230(11)	1.5367(13)	1.5359(19)	1.5317(18)
P-O2/Å	× 1	1.5407(10)	1.5441(12)	1.5340(19)	1.5348(18)
P-O3/Å	× 2	1.5334(7)	1.5379(9)	1.5318(13)	1.5325(13)
<P-O>[4]/Å		1.5326	1.5392	1.5334	1.5329
O1-P-O2/°	× 1	111.01(6)	111.4(1)	111.4(4)	112.8(3)
O1-P-O3/°	× 2	112.21(4)	111.31(7)	111.5(2)	111.3(2)
O2-P-O3/°	× 2	106.94(4)	108.30(8)	108.1(2)	107.7(2)
O3-P-O3/°	× 1	107.23(7)	106.0(1)	106.2(3)	105.7(3)
<O-P-O>[6]/°		109.42	109.44	109.45	109.42

Table S5. Information for some apatite samples from the literature, which are included in some Figures below for comparison to data from this study.

Group	Locality	Composition	Reference
1	Four synthetic samples	$Ca_5[PO_4]_3(F_{0.5}Cl_{0.5})_{\Sigma 1.00}$	Hughes et al. [36]
2a	Durango, Mexico	$\{Ca_{4.90}Fe_{0.01}Sr_{0.01}Ce_{0.02}\}_{\Sigma 4.94}[P_{2.96}Si_{0.02}S_{0.03}O_{12}](F_{0.94}Cl_{0.08})_{\Sigma 1.02}$	Hughes et al. [20]
2b	Holly Springs, Georgia	$Ca_{4.98}[P_{2.99}O_{12}](F_{0.06}Cl_{0.03}OH_{0.91})_{\Sigma 1.00}$	Hughes et al. [20]
2c	Kragero, Norway	$\{Ca_{4.98}Fe_{0.01}Na_{0.08}Ce_{0.01}\}_{\Sigma 4.98}[P_{3.01}O_{12}](F_{0.09}Cl_{0.88})_{\Sigma 0.97}$	Hughes et al. [20]
3	Gunnison Formation, Jackson Peak, SW Utah	$Ca_5[PO_4]_3(F_{0.39}Cl_{0.33}OH_{0.28})_{\Sigma 1.00}$	Hughes et al. [37]
4a	Branchville, Connecticut ($Mn_{1.21}$)	$\{Ca_{4.41}Mn_{0.5}Fe_{0.05}Na_{0.04}Ce_{0.01}\}_{\Sigma 5.00}[P_3O_{12}](F_{0.74}OH_{0.26})$	Hughes et al. [38]
4b	Harding pegmatite, Taos County, NM ($Mn_{0.42}$)	$\{Ca_{4.80}Mn_{0.21}Sr_{0.01}Na_{0.01}Ce_{0.01}\}_{\Sigma 5.01}[P_{2.99}O_{12}](F_{0.93}OH_{0.07})$	Hughes et al. [38]
4c	Kola Peninsula ($Sr_{0.63}$)	$\{Ca_{4.77}Sr_{0.20}Na_{0.05}Ce_{0.03}\}_{\Sigma 5.04}[P_{2.94}Si_{0.03}O_{12}]F_{1.09}$	Hughes et al. [38]
4d	Kola Peninsula ($Sr_{0.63}$)	$\{Ca_{4.88}Sr_{0.14}Na_{0.03}Mn_{0.01}Ce_{0.01}\}_{\Sigma 5.05}[P_{2.93}Si_{0.02}O_{12}](F_{0.89}OH_{0.11})$	Hughes et al. [38]
4e	Lavozero Massif, Kola Peninsula	$\{Ca_{4.46}Sr_{0.55}\}[P_{2.93}O_6](F_{0.94}OH_{0.06})_{\Sigma 1.00}$	Rokovan & Hughes [40]
4f	Eibenstein an Der Thaya, Austria	$\{Ca_{4.28}Mn_{0.71}Fe_{0.01}\}_{\Sigma 4.99}[PO_4]_3F_{1.00}$	Hughes et al. [39]

In the legends of Figures 8, group-1 contains four samples and is indicated by 1. syn (F1,Cl1)-Ap, group-2 by 2. (F,OH,Cl)-Ap, group-3 by 3. ter-(F,OH,Cl)-Ap, and group-4 by 4. (Sr,Mn)F-Ap.