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Refinement of the hydroxyapatite structure.*

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The $P6_3/m$ space group and the structure given by both Náray-Szabó (1930) and Mehmel (1930) for the hexagonal crystal fluorapatite, $Ca_{10}(PO_4)_6F_2$, have long been accepted as essentially correct. In view of the importance of the apatite structure in many fields, it was felt that a refinement of this structure would be of value.

The study reported here was made with crystals of synthetic hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$, prepared by hydrolyzing $CaHPO_4$ in a platinum-lined, hydrothermal bomb. The details of the synthesis are published elsewhere (Perloff & Posner, 1956). The atomic parameters given below are for hydroxyapatite. As this compound and fluorapatite are isomorphous, with nearly the same unit-cell size, the refined parameters should apply to both. Powder diffraction results gave the unit cell dimensions of hydroxyapatite as

$$a = 9{\cdot}43_2,\ c = 6{\cdot}88_1\ \text{Å}.$$

Three-dimensional, single-crystal, X-ray diffraction data were obtained, using the multiple-film technique with a Nonius integrating Weissenberg camera. Nickel-filtered, Cu $K\alpha$ radiation and Kodak NO-SCREEN film were employed. The intensities of the integrated spots were measured with a Baird Associates Inc. Densitometer-Comparator, corrected with the appropriate Lorentz and polarization factors, and converted to a set of observed structure factors. These were scaled to the calculated structure factors, based on the Náray-Szabó parameters, by matching the sums of the observed and calculated structure factors. No corrections for absorption or extinction were made. The former correction was trivial because of the small size of the crystals used. The crystals were 0·14 mm. long and 0·06 mm. wide for the *c*-axis rotation photographs, and 0·07 mm. long and 0·05 mm. wide for the *a*-axis rotation photographs.

There are about 470 possible, independent reflections for hydroxyapatite using Cu $K\alpha$ radiation. About 450 of these were within the range of the data recorded, and only 330 reflections were detectable while the remainder were considered as having an observed intensity of zero. The independent, non-zero reflections, after conversion to structure factors, were used in a least-squares refinement of the 19 variable parameters (12 atomic position parameters and seven isotropic temperature factors for the seven atoms). The parameters of the early apatite studies were used as a starting point for the least-squares refinement. The process was performed on the IBM 704 electronic computer using the program written by Dr David Sayre (the IBM 704 Program N.Y., XRI).

The new parameters obtained are listed in Table 1, where they are compared to the Náray-Szabó parameters. The reliability factor (R) obtained when comparing the observed and calculated data was 11·2%. More important than the R factor in judging the refinement is the improvement in the interatomic distances effected by the new parameters. Table 2 gives the new and the old interatomic distances.

Table 1. *Listing of new atomic parameters for hydroxyapatite as compared to old parameters for fluorapatite*

Atom	Number of atoms per unit cell	New x	New y	New z	New B(Å²)	Old* x	Old* y	Old* z
Ca_I	4	0·333	0·667	0·001	0·666	0·333	0·667	0·000
Ca_{II}	6	0·246	0·993	0·250	0·328	0·250	0·000	0·250
P	6	0·400	0·369	0·250	0·192	0·390*	0·360	0·250
O_I	6	0·329	0·484	0·250	0·295	0·333	0·500	0·250
O_{II}	6	0·589	0·466	0·250	0·496	0·600	0·467	0·250
O_{III}	12	0·348	0·259	0·073	0·632	0·333	0·250	0·063
OH	2	0·000	0·000	0·250	0·875	0·000	0·000	0·250

* All the *old* parameters are taken from Náray-Szabó (1930) with the exception of the x parameter for phosphorus, which was suggested by Beevers (private communication).

Table 2. *Comparison of new and old bond lengths in apatite*

Lengths are based on parameters given in Table 1

Bond	Old	New
P–O_I	1·656 Å	1·533 Å
P–O_{II}	1·715	1·544
P–O_{III}	1·570	1·514*
Ca_I–O_I	2·329	2·416*
Ca_I–O_{II}	2·395	2·449*
Ca_I–O_{III}	2·865	2·802*
Ca_{II}–OH	2·356†	2·354
Ca_{II}–O_I	2·832	2·712
Ca_{II}–O_{II}	2·313	2·356
Ca_{II}–O_{III}	2·292	2·367*
Ca_{II}–O_{III}	2·376	2·511*

* Bond lengths repeated by symmetry not given.
† Actually Ca_{II}–F.

The improved atomic positions provide a more regular phosphate tetrahedron with rather short P–O distances. Each of the Ca_I atoms lying along the threefold axes is bonded, at essentially equal distances, to six oxygens, which form a twisted triangular prism. There is also bonding between these Ca_I atoms and three O_{III} atoms at a longer interatomic distance. Thus the Ca_I atoms are coordinated by nine oxygen atoms situated in six different phosphate tetrahedra. The Ca_{II} atoms, situated around the hexagonal screw axes, each have an irregular sevenfold coordination with six oxygens of five phosphate groups in addition to the hydroxyl ion.

Table 3 lists the observed and calculated structure factors, as well as the differences of their absolute values for each reflection used.

References

Náray-Szabó, S. (1930). *Z. Kristallogr.* **75**, 387.
Mehmel, M. (1930). *Z. Kristallogr.* **75**, 323.
Perloff, A. & Posner, A. S. (1956). *Science*, **124**, 583.

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Table 3

hkl	F_c	F_o	$\lvert\Delta F\rvert$
100	-20.84	22.40	1.56
200	-27.46	25.20	2.26
300	116.98	105.59	11.39
400	19.86	22.40	2.54
500	13.87	12.00	1.87
600	14.01	18.40	4.39
800	44.67	43.60	1.07
900	21.46	22.40	0.94
10·0·0	-19.28	16.80	2.48
110	-12.67	11.20	1.47
210	-52.69	46.79	5.89
310	-38.18	37.60	0.57
410	53.41	57.60	4.19
510	-36.72	38.79	2.08
610	-38.72	39.60	0.88
710	14.21	20.00	5.79
810	11.95	10.80	1.15
910	-16.59	16.80	0.21
120	-14.70	15.20	0.50
220	6.46	8.80	2.33
420	-15.21	15.20	0.01
520	50.84	54.79	3.96
720	-27.36	30.00	2.63
820	23.60	30.80	7.19
920	-10.34	6.80	3.54
130	67.07	73.60	6.52
230	-44.76	47.60	2.84
330	21.46	24.80	3.34
430	-19.74	21.20	1.46
530	12.78	18.80	6.01
730	-29.71	32.40	2.69
140	58.22	60.40	2.18
240	-61.30	60.79	0.50
440	54.36	56.08	1.72
540	6.32	9.60	3.28
740	21.03	24.80	3.77

hkl	F_c	F_o	$\lvert\Delta F\rvert$
250	22.92	26.80	3.87
350	29.24	29.20	0.04
450	-9.09	12.00	2.91
550	29.45	31.60	2.15
650	-11.00	8.40	2.60
750	-20.77	21.20	0.43
160	-33.36	34.40	1.04
260	-21.31	20.80	0.51
360	-13.41	13.20	0.21
460	-23.60	26.80	3.20
560	-30.21	30.00	0.21
660	7.15	10.40	3.25
170	55.66	59.60	3.94
270	-23.27	25.60	2.33
370	-7.42	6.40	1.02
470	35.24	40.00	4.75
280	10.80	14.40	3.60
380	15.94	16.40	0.46
190	-20.51	23.60	3.09
290	-23.79	27.20	3.40
101	12.29	12.73	0.44
201	12.77	14.79	2.02
301	21.68	23.78	2.10
401	10.10	9.17	0.93
501	22.25	26.88	4.63
901	17.27	19.90	2.63
10·0·1	-12.77	10.54	2.23
111	15.94	21.68	5.73
211	-89.12	79.32	9.80
311	-14.14	16.66	2.51
411	11.46	11.64	0.18
511	-57.74	56.04	1.70
611	-15.33	14.37	0.96
711	-7.78	10.13	2.35
811	-9.17	13.55	4.38
911	-18.05	16.66	1.39

hkl	F_c	F_o	$\lvert\Delta F\rvert$
121	-59.68	55.77	3.91
221	-18.90	17.57	1.33
321	49.29	46.09	3.20
421	-15.74	17.93	2.19
521	-30.85	31.49	0.64
721	22.78	21.77	1.01
821	13.71	14.79	1.08
921	-7.09	6.94	0.16
131	30.70	28.11	2.59
231	49.98	46.09	3.89
331	38.43	37.97	0.46
431	47.73	46.46	1.27
531	-9.49	10.95	1.46
631	41.86	45.04	3.18
731	20.85	22.73	1.88
831	-13.76	15.47	1.71
141	8.63	10.59	1.96
241	-35.04	33.22	1.82
341	-10.16	10.95	0.79
441	-26.32	28.48	2.16
541	-23.04	24.74	1.70
741	-16.50	18.21	1.71
151	-20.18	22.73	2.55
251	-20.17	19.71	0.46
451	25.25	22.59	2.66
551	-21.64	22.00	0.36
651	-24.09	23.50	0.59
161	-15.40	17.84	2.44
261	-7.64	7.80	0.16
361	24.30	22.96	1.34
461	21.37	23.27	1.90
561	-27.88	30.76	2.88
371	15.59	16.34	0.75
181	-7.18	7.44	0.26
281	16.17	19.21	3.04
381	-3.99	5.43	1.44
291	-35.83	32.68	3.15

hkl	F_c	F_o	$\lvert\Delta F\rvert$
102	-33.14	26.94	6.20
202	-57.58	56.15	1.44
302	11.38	18.80	7.42
402	-61.99	61.14	0.85
502	-66.18	67.28	1.10
602	27.73	27.78	0.05
702	-31.04	32.41	1.37
802	-58.80	61.03	2.23
902	16.62	20.52	3.90
112	78.10	76.01	2.08
212	-26.12	26.29	0.17
312	-36.56	36.47	0.10
412	16.72	20.04	3.33
512	27.45	26.77	0.68
712	31.19	35.99	4.80
812	-6.97	7.91	0.94
122	13.06	17.84	4.79
222	85.34	88.75	3.41
322	-50.34	48.18	2.16
422	19.62	21.12	1.50
522	20.20	22.54	2.34
622	-29.37	32.18	2.81
822	10.17	7.02	3.15
922	-11.23	4.16	7.07
132	-45.50	44.73	0.77
232	-7.24	8.39	1.15
332	26.70	27.18	0.48
432	-7.27	9.40	2.13
532	-45.41	46.10	0.69
632	38.29	41.46	3.17
832	-21.33	19.81	1.52
142	-1.57	6.66	5.09
242	19.25	20.70	1.45
342	-41.91	45.03	3.12
442	-20.47	17.01	3.46
542	-14.76	13.92	0.85
642	-6.01	9.99	3.99
742	4.18	6.07	1.89

hkl	F_c	F_o	$\lvert\Delta F\rvert$
152	-24.06	24.03	0.04
252	60.18	64.78	4.60
352	-51.87	55.14	3.27
452	-14.50	13.92	0.58
552	24.33	26.17	1.84
652	-3.98	8.15	4.17
162	22.33	22.42	0.09
262	9.30	8.56	0.73
362	41.36	46.63	5.27
462	-1.74	7.74	6.00
562	7.23	8.09	0.86
172	-21.04	18.50	2.54
372	-6.09	7.49	1.40
472	-6.91	5.95	0.96
182	-28.52	30.93	2.40
282	33.30	37.95	4.65
382	-13.74	18.80	5.06
292	14.10	12.61	1.49
103	8.97	9.90	0.93
203	32.69	34.08	1.40
303	-21.09	21.04	0.05
503	10.89	11.74	0.85
603	-7.57	10.21	2.64
703	-18.89	20.96	2.07
903	-20.80	24.80	4.00
113	37.61	34.85	2.76
213	88.27	88.51	0.24
313	-32.10	32.55	0.45
413	-16.89	18.50	1.61
513	55.76	61.88	6.11
813	8.22	12.75	4.53
913	23.15	25.95	2.80
123	58.52	61.11	2.59
323	-53.76	58.50	4.74
423	15.56	17.12	1.56
523	32.67	37.70	5.02
623	12.52	13.28	0.76
723	-17.11	18.35	1.24
823	-18.98	19.35	0.76

hkl	F_c	F_o	$\lvert\Delta F\rvert$
133	-29.42	31.40	1.97
233	-19.13	17.89	1.24
333	-14.02	16.04	2.02
433	-56.28	63.87	7.59
533	13.39	14.82	1.43
633	-29.05	35.23	6.19
733	-33.28	37.31	4.03
143	-21.60	23.18	1.58
243	50.46	56.35	5.89
543	19.51	23.72	4.21
743	14.28	17.58	3.30
153	9.51	12.44	2.93
253	19.38	23.57	4.18
453	-18.45	22.26	3.81
553	20.74	21.34	0.60
653	28.45	29.10	0.65
163	17.66	15.73	1.93
263	7.92	10.52	2.60
363	-5.85	9.90	4.05
463	-15.50	20.96	5.45
563	15.74	20.73	4.99
173	-15.54	17.65	2.11
273	-12.09	9.67	2.42
373	-9.33	8.29	1.03
473	-7.22	6.07	1.16
183	-4.48	8.60	4.12
283	-17.27	21.27	4.00
193	15.22	12.13	3.09
104	-16.97	23.23	6.26
204	-2.85	9.43	6.58
304	71.79	74.66	2.87
404	19.58	13.01	6.57
504	27.57	22.96	4.61
604	20.17	21.92	1.75
804	37.60	37.20	0.40
904	17.18	14.50	2.68

hkl	F_c	F_o	$\lvert\Delta F\rvert$
114	12.94	9.17	3.77
214	-25.95	30.03	4.08
314	-10.29	15.63	5.34
414	41.80	42.44	0.63
514	-47.01	49.42	2.42
614	-28.19	32.92	4.73
714	10.77	14.15	3.38
814	-5.79	8.73	2.94
124	-38.18	38.16	0.02
324	13.09	7.86	5.23
424	-37.84	39.99	2.15
524	31.24	30.12	1.12
724	-25.30	28.99	3.68
824	21.12	22.27	1.14
234	-24.91	31.43	6.52
334	25.87	26.28	0.42
434	-17.13	23.14	6.01
534	18.98	14.23	4.75
734	-20.43	23.57	3.15
144	56.29	59.47	3.18
244	-46.18	49.25	3.06
344	12.37	8.91	3.47
444	58.76	60.86	2.09
644	-8.74	8.73	0.01
354	26.45	25.24	1.21
454	-5.79	8.04	2.25
554	13.90	15.54	1.64
164	-40.08	46.80	6.72
264	-27.18	33.01	5.83
464	-16.52	20.17	3.66
174	56.74	61.91	5.17
274	-15.07	21.92	6.84
374	-10.16	8.20	1.95
205	13.25	13.22	0.03
505	21.00	16.69	4.31
115	15.58	15.86	0.28
215	-60.27	54.73	5.53
515	-49.91	48.03	1.88

hkl	F_c	F_o	$\lvert\Delta F\rvert$
125	-39.90	36.01	3.89
225	-18.18	13.89	4.29
325	35.09	29.55	5.54
525	-25.46	20.58	4.88
725	21.71	16.74	4.97
135	24.23	20.95	3.28
235	43.10	34.58	8.52
335	34.47	28.45	6.02
435	36.88	32.68	4.20
535	-6.76	5.35	1.41
635	38.66	36.91	1.75
245	-26.96	25.50	1.46
445	-25.72	23.65	2.07
545	-20.42	24.47	4.05
155	-19.70	15.84	3.86
255	-17.51	15.05	2.46
455	23.08	23.23	0.15
365	25.29	22.12	3.17
106	-22.45	16.28	6.17
206	-17.58	14.05	3.53
406	-39.45	31.54	7.90
506	-36.92	37.93	1.01
116	67.74	63.59	4.15
416	14.35	22.33	7.98
516	9.41	10.70	1.29
716	22.92	23.36	0.44
126	-17.17	12.31	4.86
226	52.77	52.38	0.38
326	-27.38	21.92	5.46
626	-13.29	14.31	1.02
136	-55.76	45.66	10.10
336	30.38	35.38	5.00
536	-29.73	29.07	0.65
146	7.32	7.52	0.21
246	22.24	19.80	2.44
346	-26.92	23.77	3.15

hkl	F_c	F_o	$\lvert\Delta F\rvert$
156	-19.09	9.80	9.29
256	25.99	34.83	8.84
356	-41.09	39.74	1.35
217	49.95	40.30	9.65
517	41.80	38.96	2.84
127	36.14	34.27	1.87
327	-33.76	27.56	6.21
427	10.86	3.93	6.93
527	23.85	19.53	4.32
137	-21.97	21.67	0.30
237	-27.34	21.25	6.09
337	-23.04	20.76	2.28
437	-36.49	31.80	4.69
147	-8.67	2.93	5.74
247	26.96	25.16	1.81
157	15.20	15.43	0.24
257	16.22	10.26	5.96
108	-9.35	8.12	1.24
308	43.39	39.98	3.41
118	6.48	3.93	2.55
218	-16.43	20.18	3.75
318	-2.86	3.18	0.32
128	-27.57	27.79	0.22
138	-1.85	6.35	4.50
025	-13.25	6.58	6.67
055	-21.00	18.39	2.61
016	-22.45	8.15	14.30
046	-39.45	33.39	6.06
056	-36.92	34.47	2.44
066	31.09	39.42	8.34
076	-15.61	7.33	8.28
018	-9.35	8.12	1.23
038	43.39	39.42	3.97