NATIONAL BUREAU OF STANDARDS REPORT

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Progress Report

on

REFINEMENT OF THE HYDROXYAPATITE STRUCTURE

by

Aaron S. Posner
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U. S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

THE NATIONAL BUREAU OF STANDARDS

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U. S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

REFINEMENT OF THE HYDROXYAPATITE STRUCTURE *

Abstract

Pure hydroxyapatite [$Ca_{10}(PO_4)_6(OH)_2$] crystals were synthesized and studied with integrating Weissenberg techniques using Ni-filtered Cu K-α radiation. A least-squares refinement of the atomic position coordinates and the individual, isotropic, atomic temperature factors was performed on the IBM 704 electronic computor, using approximately 400 independent observed structure factors. A reliability value of 0.11 was found when the observed and calculated structure factors were compared. The improved atomic positions provided a more regular phosphate tetrahedron than provided by the earlier work on this substance.

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1. INTRODUCTION

The $P6_3/m$ space group and the structure given by both Naray-Szabo [1] and Mehmel [2] 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.

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2. EXPERIMENTAL PROCEDURE

The study reported here was done 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 [3]. 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 $a = 9.43_2$ A, $c = 6.88_1$ A.

Three-dimensional, single-crystal, X-ray diffraction data were obtained using the multiple-film technique with a Nonius integrating Weissenberg camera. Nickel-filtered, copper 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 Naray-Szabo 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 due to the small size of the crystals used.

3. RESULTS AND DISCUSSION

There are about 470 possible, independent reflections for hydroxyapatite using copper 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 [1] 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 Sayre [4].

The new parameters obtained are listed in Table Number 1, where they are compared to the Naray-Szabo 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 Number 2 gives the new and the old interatomic distances.

The improved atomic positions provide a more regular phosphate tetrahedron with rather short phosphorus to oxygen distances. Each of the Ca(I) atoms lying along the three-fold 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 oxygen (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 seven-fold coordination with six oxygens of five phosphate groups in addition to the hydroxyl ion.

A table listing the observed and calculated structure factors as well as the differences of their absolute values for each reflection used in the least-squares analysis will be printed in a future issue of Acta Crystallographica.

4. REFERENCES

1. Naray-Szabo, S., Z. Krist. 75, 387 (1930).
2. Mehmel, M., Z. Krist. 75, 323 (1930).
3. Perloff, A. and Posner, A. S. Science 124, 583 (1956).
4. The IBM 704 Program NY XR1.
5. Beevers, C. A. Private Communication.

Table No. 1

Listing of new atomic parameters for hydroxyapatite as compared to old parameters for fluorapatite

Atom	No. atoms per unit cell	New				Old*		
		x	y	z	B(in A^2)	x	y	z
Ca_I	4	0.333	0.667	0.001	0.666	0.333	0.667	0.000
Ca_{II}	6	.246	.993	.250	.328	.250	.000	.250
P	6	.400	.369	.250	.192	.390*	.360	.250
O_I	6	.329	.484	.250	.295	.333	.500	.250
O_{II}	6	.589	.466	.250	.496	.600	.467	.250
O_{III}	12	.348	.259	.073	.632	.333	.250	.063
OH	2	.000	.000	.250	.875	.000	.000	.250

* All the old parameters taken from Naray-Szabo [1] with the exception of the x parameter for phosphorus which was suggested by Beevers [5].

Table No. 2

Comparison of new and old bond lengths in apatite based on parameters given in Table 1

Bond	Old	New
$P\text{-}O_I$	1.656 A	1.533 A
$P\text{-}O_{II}$	1.715	1.544
$P\text{-}O_{III}$	1.570	1.514 1/
$Ca_I\text{-}O_I$	2.329	2.416 1/
$Ca_I\text{-}O_{II}$	2.395	2.449 1/
$Ca_I\text{-}O_{III}$	2.865	2.802 1/
$Ca_{II}\text{-}OH$	2.356 2/	2.354
$Ca_{II}\text{-}O_I$	2.832	2.712
$Ca_{II}\text{-}O_{II}$	2.313	2.356
$Ca_{II}\text{-}O_{III}$	2.292	2.367 1/
$Ca_{II}\text{-}O_{IV}$	2.376	2.511 1/

1/ Bond lengths repeated by symmetry not given.

2/ Actually $Ca_{II}\text{-}F$.

U. S. DEPARTMENT OF COMMERCE
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THE NATIONAL BUREAU OF STANDARDS

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• Office of Basic Instrumentation.

• Office of Weights and Measures.

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Radio Propagation Engineering. Data Reduction Instrumentation. Modulation Systems. Navigation Systems. Radio Noise. Tropospheric Measurements. Tropospheric Analysis. Radio Systems Application Engineering. Radio Meteorology.

Radio Standards. High Frequency Electrical Standards. Radio Broadcast Service. High Frequency Impedance Standards. Calibration Center. Microwave Physics. Microwave Circuit Standards.


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