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THE MINERALOGY AND GENESIS OF HYDROXYLAPATITE

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ABSTRACT

The mineral species hydroxylapatite has been re-examined. Two new occurrences have been found, Cherokee County, Georgia, and von der Rossa, Val Devero, Italy. The Swiss so-called "hydroxyiapatite" is actually a fluor-hydroxylapatite. Physical, chemical, and mineralogical constants have been determined and in part interpreted. When sufficient hydroxyl is present in an apatite, it is reflected in the increase in refractive indices and birefringence. *Hydroxylapatite has only been found associated with talc and chlorite schists, which indicates that it is formed by metamorphism in the presence of much water and with the simultaneous formation of other minerals rich in the hydroxyl group.*

INTRODUCTION

Apatite is a very common mineral, being regarded by Clarke and Washington as one of the ten most abundant minerals in the earth's crust. Although much advance has been made in our knowledge of the mineralogy of the apatite group of minerals during the last decade, some important members of the group have not been adequately studied. It is the purpose here to deal with the mineralogy and interesting mineral association of the hydroxyl-bearing variety, hydroxylapatite.

LITERATURE AND NOMENCLATURE

In 1856, A. A. Damour[1] analyzed an apatite from the vicinity of St. Girons in the Pyrenees, which he found to contain 3.36% F and 5.30% H_2O, and to which he gave the name hydro-apatite, in allusion to its hydrous character. Schaller[2] examined this analysis and concluded that it corresponded to the less hydrous mineral francolite. Schaller as a result of his study of the work of Lacroix[3] suggested a theoretical end-member of the apatite group, rich in hydroxyl, which he called hydroxyapatite. This compound had been synthesized by Warrington,[4] in 1873, who referred to it as hydrated oxygen apatite. The synthesis was repeated by Bassett[5] in 1917, who used the term hydroxyapatite.

The first natural occurrence of material approaching hydroxylapatite in composition was reported by Burri, Jakob, Parker, and Strunz.[6] They used the name "hydroxylapatit" for the naturally occurring mineral and thus established this species. "Hydroxylapatit" is universally used in the recent rather extensive German literature[7] on the chemistry of this compound. In the English chemical literature, since the time of Bassett, the name hydroxyapatite has been used.

CRYSTALLOGRAPHY

Hydroxylapatite from the old Verde Antique serpentine quarry near Holly Springs, Cherokee County, Georgia, exhibits only a small number of forms. The best crystal observed measured 6 by 6 by 11 mm. It was elongated parallel to the *c* axis, and the developed forms were the prism terminated by the basal pinacoid. Natural etch figures on the prism faces and etch grooves on the basal pinacoid are sketched in Fig. 1. The etch pits on the prism faces are alike in shape and orientation and confirm the hexagonal character of the *c* axis. Moreover, they are divisible by one plane of symmetry parallel to the equatorial plane, and they show that a center of symmetry is present. The etch data agree with the requirements of the hexagonal dipyramidal class. The etch grooves on the base form an hexagonal pattern, the principal system of grooves being parallel to the sides of the prism while the secondary system is perpendicular to these. Honess[8] has described similar etching produced on apatite crystals in the laboratory.

The best developed crystal of the Swiss material was 4.5 mm. long and 4.0 mm. in diameter. It consisted of a prism terminated by a bipyramid. of the same order as the prism, as well as by the basal pinacoid. This crystal was so corroded by wavy grooves as to have no value for symmetry determination.

X-ray powder diffraction photographs were made on samples of hydroxylapatites from Switzerland and Georgia. The diffraction patterns, portions of which are reproduced in Fig. 2, are similar to those obtained

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[1] Damour, A. A., Sur l'hydro-apatite, espèce minéral; *Annales des mines*, **10**, 65–68 (1856).

[2] Schaller, W. T., Mineralogical Notes—Series 2, *U. S. Geol. Surv., Bull.* **509**, 89–100 (1912).

[3] Lacroix, A. L., Sur la constitution mineralogique des phosphorites francaises: *Compt. rend.*, **150**, 1213 (1910); Mineralogie de la France. **4**, part 2, 555 (1910).

[4] Warrington, R., On the decomposition of tricalcic phosphate by water: *Jour. Chem. Soc.* (*London*), **26**, 983–989 (1873).

[5] Bassett, H., The phosphates of calcium. IV. The basic phosphates: *Jour. Chem. Soc.* (*London*), **111**, 620–642 (1917).

[6] Burri, C., Jakob, J., Parker, R. L., and Strunz, H., Über hydroxylapatit von der Kemmelton, bei Hospenthal, (Kt. Uri): *Schweiz Min. Petr. Mitt.*, **15**, #2, 327–399 (1935).

[7] For a summary of the chemical literature, note Eisenberger, S., Lehrman, A., and Turner, W. D., The basic calcium phosphates and related systems. Some theoretical and practical aspects: *Chem. Rev.*, **26**, 257–296 (1940).

[8] Honess, A. P., The Nature, Origin and Interpretation of the Etch Figures on Crystals. John Wiley & Sons, Inc., New York, p. 171 (1927).

from fluorapatite and synthetic hydroxylapatite. These patterns do not show the separation of the (121), (112), and (300) reflections found by Thewlis, Glock, and Murray[9] which would result from changing the axial ratio from $a:c = 1.000:0.734$ to $a:c = 1.000:0.730$. These reflections might be slightly shifted since the lines are somewhat broadened. However, the lines at large angles from the various materials have similar spacings and intensities. Lattice dimensions of these samples of hydroxylapatite and fluorapatite, therefore, are identical within limits of experimental error. Close similarity of lattice dimensions of course is a result of the approximately equal ionic radii of F^- and $(OH)^-$.

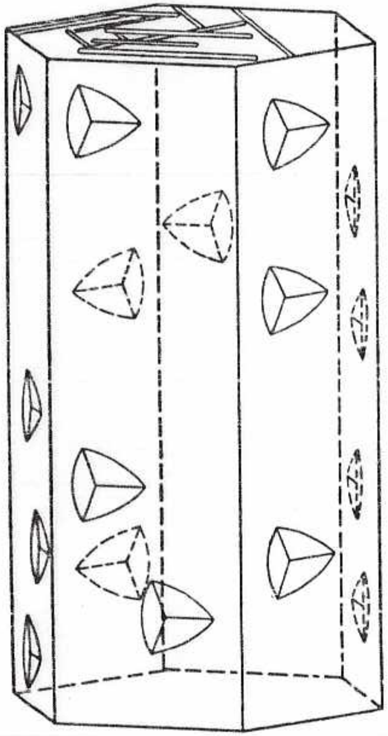

FIG. 1. Crystal forms and natural etching of the Georgia hydroxylapatite.

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[9] Thewlis, J., Glock, G. E., and Murray, M. M., Chemical and x-ray analysis of dental, mineral, and synthetic apatites: *Trans. Faraday Soc.*, **35**, 358–363 (1939).

COLOR

The color of a number of the Georgian hydroxylapatites occurring in talc schists was determined by comparison with Ridgway's tables and found to range from wax yellow (21'.0—yy) to strontian yellow (23'.yellow). The Swiss mineral in the nomenclature of Ridgway was found to be sea-foam green (27".g—y.f.), while synthetic hydroxylapatite is a white powder. The fluor-hydroxylapatite of the chlorite schists from Georgia ranges from deep chrysolite green (27".g—y) to deep sea-foam green (27".g—y.d).

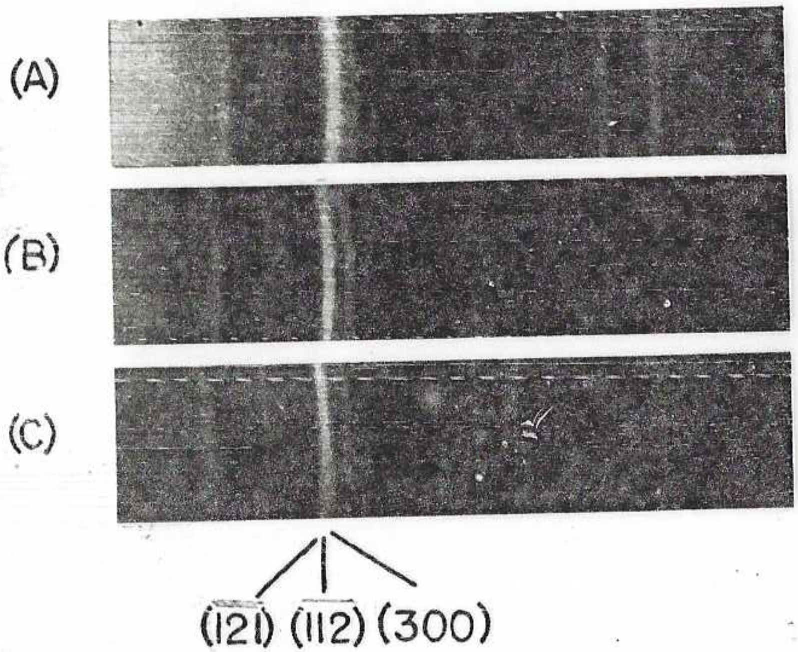

FIG. 2. X-ray powder diffraction patterns, Cu Kα radiation, of (A) synthetic hydroxylapatite (heated for one hour at 800°C.), (B) hydroxylapatite from Georgia, (C) fluorapatite.

OPTICS

Optical properties were determined by the immersion method using sodium light and are given in Table 1. To these values have been added the so-called "oxyapatite" of Bianchi[10] and the data for fluorapatite and chlorapatite.

TABLE 1. OPTICAL PROPERTIES OF SOME APATITES

	Georgia Hydroxyl-apatite	Georgia fluor-Hydroxyl-apatite	Swiss fluor-Hydroxyl-apatite	Italian Hydroxyl-apatite	Fluor-apatite	Chlor-apatite
Uniaxial	(−)	(−)	(−)	(−)	(−)	(−)
ω_{Na}	1.651±0.001	1.645±0.001	1.6452	1.6507	1.633±0.001	1.667
ϵ_{Na}	1.644±0.001	1.640±0.001	1.6413	1.6452	1.629±0.001	1.664
$(\omega-\epsilon)_{Na}$	0.007	0.005	0.0039	0.0055	0.004	0.003
Observer	Faust, this paper	Faust, this paper	Burri et al.[6]	A. Bianchi[10]	D. McConnell & J. W. Gruner[11] Wratten filter W-90	Larsen & Berman[12]

Schneiderhöhn[13] states that synthetic hydroxylapatite has indices of refraction near those of hilgenstockite, ($4CaO\cdot P_2O_5$), $\gamma_{Na}=1.647$, $\alpha_{Na}=1.643$. The *x*-ray diffraction patterns are also similar.

The presence of hydroxyl instead of fluorine in apatite increases the refractive indices. This increase has also been observed, for like substitution, in topaz.[14] This is to be expected from a consideration of the ionic refractivities of fluorine, hydroxyl, and chlorine ions for which Wasastjerna[15] calculated the values 2.20, 4.68, and 8.45, respectively. This relationship between the refractive indices of apatite and the ionic refractivities of the replacing atoms is shown graphically in Fig. 3, where data for the end-members are plotted.

The sample analyzed by Bianchi appears to be an hydroxylapatite. Its refractive indices and double refraction are almost identical with the data obtained on the Cherokee County, Georgia, material. It could not be a mixture of chlorapatite and fluorapatite since its double refraction is roughly twice as great as either one. Although it was called an "oxy-apatite" by Burri et al., the existence of such a compound is yet to be demonstrated.[13]

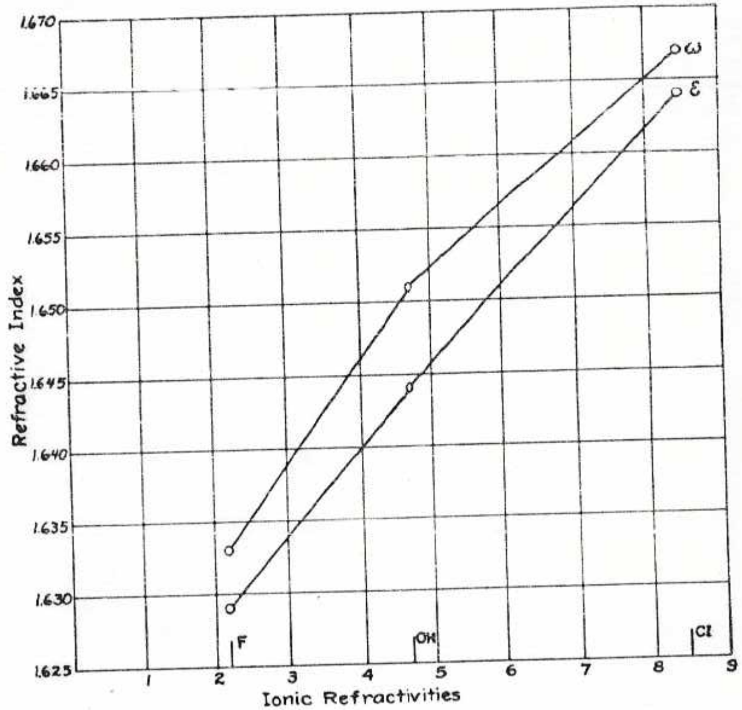

FIG. 3. Refractive indices of fluorapatite, hydroxylapatite, and chlorapatite as functions of ionic refractivities.

CLEAVAGE AND FRACTURE

The Georgia hydroxylapatite possesses a distinct conchoidal fracture whereas the Swiss mineral[6] (poorer in hydroxyl) exhibits a fairly good cleavage parallel to the prism and an interrupted cleavage parallel to the basal pinacoid. The fluor-hydroxylapatite (Georgia), on the other hand, has a cleavage parallel to the prism. Sometimes trains of tiny inclusions occur parallel to the cleavage traces.

SPECIFIC GRAVITY

The molecular weight for the unit of structure of hydroxylapatite is 1004.69, while fluorapatite is 1008.68, a difference of only about 0.4%.

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[10] Bianchi, A., Apatite di Val Devero (Ossola): *Atti. Soc. Ital., Soc. Nat.*, **58**, 306–333 (1919).

[11] McConnell, D., and Gruner, J. W., The problem of the carbonate-apatites: Part III, *Am. Mineral.*, **25**, 157–167 (1940).

[12] Larsen, E. S., and Berman H., The Microscopic Determination of the Non-opaque Minerals: *U. S. Geol. Surv., Bull.* **848**, 2nd ed., (1934).

[13] Trömel, G., and Schneiderhöhn, H., Beiträge zur Kenntnis des Systems Kalziumoxyd-Phosphorpentoxyd. Mikroskopisch optische Untersuchungen der Schmelzen: *Mitt. Kaiser Wilhelm Inst. für Eisen-Forsch.* Düsseldorf, Band **14**, 25–36 (1932).

[14] Pardee, J. T., Glass, J. J., and Stevens, R. E., Massive low-fluorine topaz from the Brewer Mine, South Carolina: *Am. Mineral.*, **22**, 1058–1064 (1937).

[15] Wasastjerna, J. A., Über die Refraktionsäquivalente der Ionen und den Bau der zusammengesetzten Ionen: *Soc. Sci. Fenn. Comm. Phys. Math.*, **1**, #37 (1923); also, Über den Bau der Atome und Moleküle im Licht der Dispersionstheorie: *Zeits. Physikalische Chemie*, **101**, 193–218 (1922).

It has been previously pointed out that the lattice dimensions of the two minerals are almost indistinguishable. On the basis of these data one would necessarily conclude that the specific gravity of hydroxylapatite and fluorapatite are almost identical. The specific gravity was determined by the standard method using the analytical balance. The values obtained were corrected for the thin platinum wire-suspension and temperature. These are given in Table 2 with values from the literature.

TABLE 2. SPECIFIC GRAVITY DATA

Mineral	Locality	This Paper	Burri et al.[5]	Larsen & Berman[9]	Calculated*
Hydroxylapatite	Georgia	3.21	—	—	3.17
Fluor-hydroxylapatite	Swiss	3.21	3.076	—	
Fluorapatite				3.2	3.18

* $a=9.37$ Å, $c=6.88$ Å.

The value obtained by Burri et al. is surprisingly low and not in agreement with the supplementary crystal structure data. Moreover, the investigations of Kind[16] on various magmatic apatites exhibiting quite a range of substitutions does not support so low a specific gravity as that reported by Burri et al.

CHEMISTRY

Analytical data

Analyses were made according to the standard methods used in the Bureau of Plant Industry for the analysis of phosphates. Fluorine was determined by a modification of the Willard-Winter method.[17]

The frequently used etching test for fluorine has proven to be untrustworthy and it is desirable to base statements concerning the absence of fluorine upon quantitative analyses.[18]

For this reason the fluorine and water contents of the Swiss material, kindly furnished by Dr. W. F. Foshag of the National Museum, were redetermined. The value for the ignition loss, namely 1.77%, checked very well with 1.73% found in the original analysis. Fluorine determinations were, however, in complete disagreement, with 1.01% fluorine present whereas Burri et al. found none by a qualitative test. Their optical data also indicate an error in their fluorine determinations; for the birefringence and refractive indices are considerably lower than those for pure hydroxylapatite. Accordingly, the fluorine analysis from this work is used with the remainder of the analysis by Burri and his coworkers, although it is realized that the material might show considerable variation in composition.

The ignition loss of 1.73% is in excess of the expected value for an apatite containing 1.0% fluorine. Determination of water in apatites, however, is subject to exacting requirements. It is necessary to heat the sample to about 1400°C. in a current of dry air. Possible loss of halogens must be taken into account and corrections made. The material from Switzerland used in this work contains small but microscopically detectable amounts of a carbonate; a crystal dropped in cold 1:1 HCl gave slight effervescence.

Spectrographic analysis of the Georgia hydroxylapatite and fluorhydroxylapatite, kindly made by Dr. B. C. Brunstetter and Mr. A. T. Myers of the Bureau of Plant Industry, showed that calcium and phosphorus were the major constituents; that manganese, magnesium, iron, and aluminum were present in very small amounts; and that mere traces of copper, vanadium, boron, sodium, and potassium were present.

Formulas for the several apatites computed from the data in Table 3 are summarized in Table 4. Molal values are adjusted to make the (PO_4) value exactly 6.00; which is the number of (PO_4) groups in the unit of structure of a carbonate-free apatite. The total number of positive ions, S, exceeds the theoretical value, 10.00, by about 1.5% in samples 1, 2, and 4. This might be due in part to the usual analytical error. It could also be explained by the presence of some (CO_3^{--}) groups substituting for $(PO_4)^{---}$; the 1.5% excess would require 0.4% CO_2. Similarly the (OH, F) value exceeds 2.00, the theoretical maximum, in samples 1 and 3. This is probably due to water being occluded or adsorbed to a minor extent and not present as hydroxyl.

The material, analysis No. 4, that Bianchi described as "oxyapatite" is apparently hydroxylapatite. He failed to determine the water content—a very common error in apatite analyses. Damour's sample, No. 5, is probably fluorapatite and the large amount of water given in the analysis was evidently present as such.

Color of synthetic hydroxylapatite

Colorless hydroxylapatite can be synthesized but generally the prod-

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[16] Kind, Alfred, Der magmatische Apatit, seine chemische Zusammensetzung und seine physikalischen Eigenschaften: *Chem. der Erde*, Band **12**, Heft 1, 50–82 (1938).

[17] Reynolds, D. S., and Hill, W. L., Determination of fluorine with special reference to the analysis of natural phosphates and phosphatic fertilizers: *Ind. & Eng. Chem.*, Anal. Ed., **11**, 21–27 (1939).

[18] Hillebrand, W. F., and Lundell, G. E. F., Applied Inorganic Analysis, John Wiley & Sons, Inc., New York, 595–596 (**1929**).

TABLE 3. CHEMICAL ANALYSES

	1	2	3	4	5	6
	Hydroxyl-apatite. Holly Springs, Cherokee County, Georgia	Fluor-hydroxyl-apatite. Holly Springs, Cherokee County, Georgia	Fluor-hydroxyl-apatite. Kemmleton, Hospenthal Kt. Uri, Switzerland U.S.N.N. #7708 Roebling Coll.	Hydroxyl-apatite. Rossa, Val Devero, Italy	Damour's Hydro-apatite	Theoretical Hydroxyl-apatite
P_2O_5	42.05	41.96	42.19	41.63	40.00	42.40
V_2O_5	0.00	—	—	0.90 Fe_2O_3 Al_2O_3	—	—
CaO	55.84	55.90	55.47	55.25	52.35	55.81
MgO	0.10	0.05	—	0.29	—	—
MnO	0.07	0.10	0.06	—	—	—
H_2O	1.86**	1.33**	1.73**	0.32	5.30	1.79
F	0.16	0.84	1.01	trace	3.36	—
Cl	trace	0.06	—	0.95	—	—
Insol.	0.15*	0.15*	0.60*	1.30	—	—
	100.23	100.39	101.06	100.64	101.01	100.00
Less O=F O=Cl	0.07	0.36	0.43	0.21	1.42	—
Total	100.16	100.03	100.63	100.43	99.59	100.00
$\frac{P_2O_5}{CaO}$			0.761		0.764	0.760
Analyst	D. S. Reynolds	D. S. Reynolds	J. Jakob[7] with fluorine by D.S.R.	A. Bianchi[11]	A. A. Damour[2]	

* Insoluble in acid. Identified as talc. See Figs. 4 and 5.

** Ignition loss, corrected for small amount of fluorine volatilized.

ucts are various shades of pink. Gabriel[19] first reported this observation on bone heated to redness in contact with air, which is closely related to hydroxylapatite. He thought that it might be due to the presence of rare earths but was unable to prove the point. Bassett[5] observed simi ink colors in synthetic hydroxylapatite, the color varying greatly in shade and uniformity. He showed that the color could be intensified by the addition of copper salts during the course of the synthesis.

TABLE 4. OBSERVED FORMULAS OF THE VARIOUS APATITE MINERALS

Source	Formula		S	Excess Charge
1. Georgia	$(Ca_{10.10}Mg_{0.02}Mn_{0.01})$	$(PO_4)_{6.00}(OH_{2.09}F_{0.08})$	10.13	0.09
2. Georgia	$(Ca_{10.13}Mg_{0.01}Mn_{0.02})$	$(PO_4)_{6.00}(OH_{1.50}F_{0.45}Cl_{0.02})$	10.16	0.35
3. Switzerland	$(Ca_{9.99}Mn_{0.01})$	$(PO_4)_{6.00}(OH_{1.94}F_{0.54})$	10.00	−0.48
4. Italy	$(Ca_{10.10}Mg_{0.07})$	$(PO_4)_{6.00}(OH_{0.03}Cl_{0.02})$	10.17	2.18
5. France (Damour)	$Ca_{9.94}$	$(PO_4)_{6.00}(F_{1.88})$	9.94	0.00
6. Theoretical	$Ca_{10.00}$	$(PO_4)_{6.00}(OH_{2.00})$	10.00	0.00

Spectroscopic determination of copper in four synthetic samples of hydroxylapatite showed a correlation between intensity of pink color and adventitious copper. The pink color was easily observable in a sample containing about 0.003% Cu.

Dissociation of hydroxylapatite

Several years ago an attempt was made in the laboratory of the Bureau of Plant Industry[20] to measure the dissociation pressure of natural and synthetic hydroxylapatite. The experiments were not successful owing to the apparent irreversible character of the dissociation. It was found that this dissociation took place over an interval ranging from 1200°C. to 1500°C. These experiments also showed that if hydroxylapatite were heated so as to drive off almost one half of its water, the x-ray pattern of hydroxylapatite still persisted. However, if all the water were removed, a mixture of α-tricalcium phosphate and hilgenstockite (tetracalcium phosphate) resulted.

Another approach to this problem was made by Jacob, Reynolds, and Hendricks[21] who studied the "citrate solubility" of hydroxylapatite as a function of the heat treatment of the charge. They heated synthetic hydroxylapatite to various temperatures and determined the solubility of the phosphate in neutral ammonium citrate, according to the official method for available phosphate. It was found that at temperatures below

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[19] Gabriel, S., Chemical research on the mineral material of bone and teeth: *Zeits. Physiol. Chem.* **18,** 257 (1893).

[20] Nelson, R. A. Unpublished data, 1936.

[21] Jacob, K. D., Reynolds, D. S., and Hendricks, S. B. Unpublished data, 1936.

1200°C. the "citrate solubility" remained the same; at temperatures between 1200°C. and 1500°C. it was greatly increased; and that above 1500°C. it was the same as a mixture of α-tricalcium phosphate and hilgenstockite. These studies were in agreement with the accompanying x-ray investigations made on the same materials and with observations of Trömel.[13]

PETROLOGY

Microscopic examination

In thin section the Swiss apatite consists of subhedral and euhedral crystals in a coarsely foliated talc in which the foliae are more or less arranged in a parallel manner, with only occasional local areas exhibiting a decussate structure. The apatite has been invaded by talc crystals which occur as gash-like inclusions and narrow veinlets in the apatite. These talc areas usually behave as a unit. Tiny veinlets and irregular areas of carbonate were observed in some of the fluor-hydroxylapatite crystals. Excellently crystallized magnetite is scattered throughout the talc (see Fig. 4). The rock is an apatite-talc schist. A small portion of the associated steatite shows talc, magnetite, and chlorite. This chlorite is quite pleochroic, being pale emerald-green parallel to the cleavage and very pale yellow perpendicular thereto. The interference colors are anomalous, being a greenish-gray. The paragenetic sequence in the talc-schist is fluor-hydroxylapatite, talc, and magnetite.

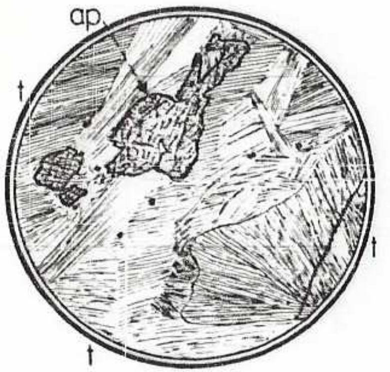

FIG. 4. Apatite-talc schist, Kemmleton, Hospenthal, Kt. Uri, Surtzerl, Switzerland. ap = apatite, t = talc, solid black areas = magnetite.

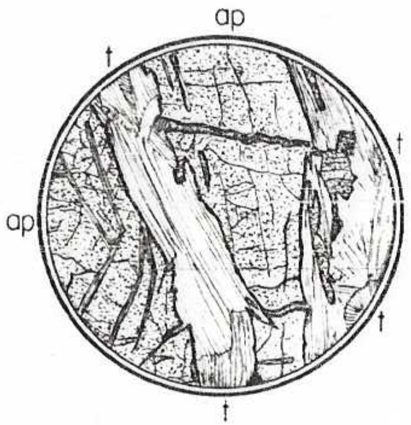

FIG. 5. Hydroxylapatite-talc schist from the old verde antique serpentine quarry near Holly Springs, Cherokee County, Georgia. ap = apatite (hydroxylapatite). t = talc.

The texture of the Georgia hydroxylapatite-talc schist is coarse. Long foliae of talc traverse the thin section and these are only rarely disturbed by small patches of talc cutting transversely across their length. Hydroxylapatite is subhedral and carries only long crystals of talc which are present as inclusions or as invading gash-like veinlets. These are to be seen in the camera lucida drawings in Fig. 5. The paragenetic sequence is hydroxylapatite, and talc.

Genesis

These talc schists, as judged by their accessory minerals (hydroxylapatite and magnetite), and the coarseness of the talc flakes, indicate metamorphism embodying hydrothermal reactions under dynamic stresses. They have arisen through the metamorphism of ultrabasic rocks. At the time of metamorphism a considerable amount of water was present to permit the formation of talc and hydroxylapatite. A definite upper temperature limit is set by the fact that at one atmosphere pressure talc dissociates into enstatite, a silica rich liquid, and water vapor between 800° and 840°C.[22] As was pointed out earlier, hydroxylapatite dissociates at a still higher temperature, namely, 1200° to 1500°C. The effect of non-uniform pressure would probably lower these dissociation temperatures significantly and thus set the upper limit of formation of these rocks at correspondingly lower temperatures.

Both of the hydroxylapatites carry some fluorine. Accordingly, talc of these rocks and a totally unrelated pure talc were analyzed for their fluorine content in order to ascertain whether there was any competition between the talc and hydroxylapatite for the available fluorine. The results of the analyses are given in Table 5. The talc used as reference was from Harford County, Maryland, U.S.N.M. #82519, and consists of clear transparent books about 7 cm. in diameter.

TABLE 5. FLUORINE CONTENT OF MINERALS OF THE HYDROXYLAPATITE-TALC SCHISTS

Locality	%F in Talc (Mineral)*	%F in Hydroxylapatite
Georgia	0.009	0.16%
Swiss	0.008	1.01%
Maryland	0.006	no associated apatite

* Optically the Georgia and Swiss talcs were similar in that 2V seems smaller than the value observed for the Maryland talc. Precise measurement of 2V on the scrapings of the talcs prepared for analysis was not possible.

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[22] Ewell, H. H., Bunting, E. N., and Geller, R. F., Thermal decomposition of talc: *Jour. Res. Natl. Bur. Stds.*, 15, 551–556 (1935).

The manner of formation of hydroxylapatite can partially be inferred from the observations discussed above. Minerals of the apatite group generally contain fluorine, even when formed in aqueous systems low in fluorine, such as the sea. Chlorine or hydroxyl are substituted for fluorine only under very unusual conditions, the former in some pegmatites and the latter in the presence of hydrous metamorphic minerals.

The parent rocks which gave rise to the talc schists were of an ultra basic character and contained small, but unusually important quantities, of phosphatic compounds. During the period of metamorphism a continuous and significantly large quantity of water was probably present, since the principal mineral, talc, requires 4.8% H_2O as hydroxyl groups. Hence, in the absence of sufficient fluorine to combine with the available phosphate, or in the presence of water at high temperatures, hydroxyl, supplied by the water, was taken from the system and hydroxylapatite resulted. Analyses of the talc, as listed in Table 5, gave no experimental evidence of competition for the fluorine content of the system. Nevertheless, the talc, because of its far greater bulk, may have removed sufficient fluorine to prevent the re-formation of fluorapatite, if it had existed as such before reorganization set in. As was pointed out in the comments on the determination of the water content of apatites, the passage of heated water vapor over fluorapatite removes important quantities of fluorine for which the hydroxyl is substituted. This process, carried out over a long period of time, would reduce the fluorine content of a fluorapatite very decidedly. The operation of this process might lead to some variability in the fluorine content of unrelated masses of the hydroxylapatite, and some evidence of this fact was noted. The assemblage of minerals—talc, hydroxylapatite, and magnetite—and the coarse foliation of the talc indicate dynamothermal metamorphism. Temperature and non-uniform pressure were both critical factors in the formation of these talc schists. The system was undoubtedly closed, permitting the development or maintenance of a pressure suitable for the formation of hydroxylapatite.

The Italian hydroxylapatite is reported to occur in a diallage-serpentine rock mass. Other associates include rose-colored sphene, magnetite, fibrous hornblende, chlorite, and ilmenite. Although the exact field relations of this rock mass are not fully described, it is suggestive of the serpentine masses commonly associated with talc schists. Further field observation would be of interest to ascertain whether the apatite is associated with serpentine or talc.

The associated fluor-hydroxylapatite-chlorite schists

The talc deposits are related to the associated chlorite schists. Specimens of the chlorite schists examined consist principally of chlorite and fluor-hydroxylapatite, with talc in a few instances. The ω index of refraction was measured on the apatite of five different specimens and the value of each was found to be 1.645, which is significantly lower than ω of hydroxylapatite. Analyses of one sample, No. 2 in Table 3, showed the presence of 0.84% F and 0.06% Cl. This apatite occurs as masses resembling very oblate spheroids, as large as 5 cm. in diameter, which are embedded in a medium-grained chlorite schist. The measurements on the chlorite of the chlorite schist are given in Table 6.

TABLE 6. DATA ON THE CHLORITE FROM THE OLD VERDE ANTIQUE QUARRY NEAR HOLLY SPRINGS, CHEROKEE COUNTY, GEORGIA

Chemical Data	Spectroscopic Data	Optical Data
$P_2O_5=0.08$	Major Constituents: Mg, Al, Si, Fe	Biaxial (+) $2V=15°\pm$
$F=0.007$ H_2O at 100°C.=none H_2O at 600°C.=3.10%	Very Minor: Mn, K, Na, P	$r<v$ $\alpha=1.586\pm0.002$ $\gamma=1.595\pm0.002$
H_2O at 1000°C.=11.46% H_2O at 1200°C.=12.18% H_2O at 1400°C.=12.58% fused	Sought, but not found: Li, Ca, Sr	$\gamma-\alpha=0.009$

It is known from the researches of Doelter,[23] and Doelter and Dittler,[24] that chlorite dissociates to yield water vapor, glass and various crystalline phases. J. Orcel[25] found that a strong exothermic reaction, corresponding to the major loss of water, takes place in the range of 600°C.–800°C. for most of the chlorites that he examined. Analyses, Table 6, show that the chlorite studied in this work loses most of its water below 1000°C.

Chlorite resembles talc in being a very hydrous mineral, formed extensively by metamorphism in the presence of abundant water. Association of hydroxylapatite, or fluor-hydroxylapatite, with chlorite schists is thus similar to the association of these minerals with talc schists. From physicochemical considerations, the environment at the time of the metamorphism which produced the talc schists and the chlorite schists was nearly the same and permitted the contemporaneous development of

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[23] Doelter, C., Synthetische Studien: *Neues Jahrb. Min.* **1**, 3 (1897).

[24] Doelter, C., and Dittler, E., Über einige Mineralsynthesen: *Sitzber. Akad. Wiss. Wien*, **121**, 899–914, 1910 (1912).

[25] Orcel, J., L'analyse thermique des chlorités: *Compt. rend.*, **183**, 565–567 (1926).

both rocks. This agrees satisfactorily with the field evidence on the intimate association of talc and chlorite schists.

DESCRIPTION OF THE GEORGIA OCCURRENCE OF HYDROXYLAPATITE

The Georgia occurrence of hydroxylapatite crystals is in the serpentine quarry located about two miles southwest of Holly Springs in Cherokee County, about five miles north of the Cobb County line. The quarry is on a hill side in a rough, broken region near the head of one of the tributaries of Blanket Creek. McCallie[26] described the deposit and the early workings for talc and verde antique. He also described some of the structural and physical characteristics of the serpentine.

The area about the quarry is hilly country representing the foothills of the Appalachian Mountains. The country rock of this region and of all the piedmont and mountain regions of Georgia is of ancient origin, generally presumed to be pre-Cambrian or early paleozoic in age. There are very few recognizable sediments and most rocks of the crystalline area are igneous or metamorphic. The rocks comprising the largest distinguished group in this area of Georgia are those of the Carolina series, which vary from a hard biotite gneiss to mica schists, often cut by pegmatite dikes. A particular facies of the Carolina series is known as the Ashland schist. The serpentine quarry near Holly Springs is in a lenticular body of ultrabasic rock apparently intruded into the biotite gneiss and Ashland schist. The ultrabasic body is approximately 150 feet wide at the widest portion near the center and is approximately 600 feet long. The strike of the schistosity varies from N. 25° E. to N. 35° E., and averages around N. 30° E. The dip is 83 degrees to the southeast, although folding makes this value somewhat uncertain. Approximately five miles further southwest along the line of strike a similar body is said to outcrop.[27]

The ultrabasic rock-body now consists mainly of hard serpentine and dark green chlorite schist, both cut by veins of foliated talc of a light sea-green color. In places the talc is bordered by crusts of magnesite of an iron-bearing variety known as breunnerite.[28] It is probably to be assumed that the mass was intruded as a peridotite and has changed in place to serpentine, chlorite, talc, and magnesite. There has been considerable metamorphism as the talc varies in character from the beautiful green micaceous, or foliated variety, to twisted radially crystallized masses of lighter color, and in still other places to a dull gray mass filled with small crystals of magnetite and chromite. In some places magnetite crystals were noted which had been flattened by gliding of one face on the other. Some hardened talc was also noted, and this variety seemed to have a surface quite suggestive of slickensides. The apatite occurs in the micaceous talc, magnetite filled talc, and in the dark green chlorite schist. A crystal was noted which was formed squarely across the boundary of talc and chlorite. The apatite crystals are normally of a lemon yellow color, and usually of poorly developed crystal form, but some specimens were found having an apple-green color.

There are places in the quarry where thin layers of chlorite alternate with thin layers of talc, with the layers twisted and distorted by much local folding. Such a mass of interlayered talc and chlorite grades into serpentine of a hard, dark green variety. In some spots, the serpentine has a purplish cast. Surfaces were found where asbestiform serpentine had been developed.

Most ultrabasic rocks in the Georgia crystalline area, other than the trap dikes of Triassic age, are generally considered as part of the Roan gneiss, an ancient rock of somewhat doubtful age.[29] However, basic and dioritic rocks are fairly common over the crystalline area of Georgia. A dark green chlorite schist similar to that in the quarry is found as the country rock of the famous Little Bob pyrite mine, 25 miles southwest of the quarry. A basic injection into the pegmatite near Kennesaw Mountain, 15 miles south, has changed the feldspar there into a high-calcium plagioclase and has led to development of large hornblende crystals. Other instances of basic rocks in the vicinity are known, but a connection between them and the serpentine has not been established. No specimens of hydroxylapatite have been reported as found at other localities than in the quarry.

ACKNOWLEDGMENTS

W. L. Hill offered valuable suggestions during the course of the work and in the preparation of the manuscript. Dr. W. F. Foshag of the U. S. National Museum kindly supplied us with several specimens from the museum collections. We are indebted also to Dr. B. C. Brunstetter and A. T. Myers of the Bureau of Plant Industry for a number of spectroscopic analyses.

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[26] McCallie, S. W., The marbles of Georgia, 2nd ed.: *Geol. Survey Ga., Bull.* **1**, 114–116 (1907).

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Significant Precision in Crystal Structural Details: Holly Springs Hydroxyapatite

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The degree to which physically significant precision in crystal-structural details can be obtained with selected routine procedures has been assessed and some illustrative applications to analyses of bonding effects and of impurity substitutions have been made. Least-squares refinements with X-ray data for three single crystals of mineral hydroxyapatite and with neutron diffraction data for a fourth of the same origin yielded $R \simeq 2\%$ in each case (≥ 40 parameters adjusted and > 500 reflections). Seemingly minor extinction corrections improved the mutual agreement among separate measures of some parameters from 4σ to the final 1σ (typically $< 5\%$) found for all, even anisotropic thermal, parameters in the X-ray cases. Final results were insensitive to reasonable changes in the weighting scheme. Comparisons of X-ray and neutron results, which generally agreed within 2σ, showed systematic differences associated with the oxygen atoms bonded to phosphorus in the phosphate group. Analysis of the final R-value also suggested (1) real differences, among the crystals, smaller than the σ's associated with individual parameters and (2) either a systematic inadequacy of the refinement model, or similar residual systematic errors (such as thermal diffuse scattering contributions), in both neutron and X-ray data. Direct refinement for the degree of fluorine substitution for OH in $Ca_{10}(PO_4)_6(OH)_2$ led to the same result, 8 at.% substitution, with both X-ray and neutron data. Analysis of the decrements found with both X-ray and neutron data in the apparent site-occupancy factors for the Ca atoms showed that a simple substitution of Mg^{2+} for Ca^{2+} at the same site is not in itself a sufficient substitutional model for this case.

Introduction

The precision ordinarily obtained in crystal structure refinements, even 'precision structure refinements,' is far less than that which would seem to be intrinsically available with present single crystal diffractometers used in a well-chosen routine fashion. The ACA Single Crystal Intensity Data Project (Abrahams, Alexander, Furnas, Hamilton, Ladell, Okaya, Young & Zalkin, 1967) has shown how well several experimental groups, each interested in routine precision measurements of intensities, agreed on the measurements of the same reflections from the same crystal (generally 3 to 5%). An I.U.Cr. project of similar name undertook to determine how well a greater variety of research groups, operating in approximately their normal fashion, agreed on the measurements of intensities from crystals from the same batch. As recently reported (*Commission on Crystallographic Apparatus*, 1966), the agreement in this second project is presently much poorer, *e.g.* no better than approximately 7% within a sub-set of most-similar results. Since X-ray apparatus is, presumably, stable to greater than 1%, and since counting statistical errors can also be small, it is clear that there must be very significant differences in the details of the techniques (and, in the I.U.Cr. project case, perhaps the crystal sizes, shapes, and states of twinning) used by the various groups. In the context provided by these projects, it is of interest to investigate how well a particular group can reproduce its own results in a series of independent experiments using different specimens as nearly identical as possible in composition (and, hence, in structural details) but not necessarily in size or mosaic spread.

A more important reason for the assessment of precision is that a number of questions of far reaching importance in the physics and chemistry of solids appear to lend themselves to study by precision crystallography. These include (1) anharmonicity in thermal motions (Willis, 1963, 1965), (2) actual electron wave functions in crystals (McWeeny, 1951, Freeman, 1959), (3) character, degree of direction and electron content of bonds (Dawson, 1964; McWeeny, 1951; Brill, 1950; Coppens, 1968*a*, *b*), and (4) structural location and role of impurity atoms in real crystals. In brief, precision crystallography should be expected to provide detailed determinations of structural features of real crystals, as opposed to those of the idealized crystals.

It now appears that Zachariasen's (1963, 1967) extinction-correction method has removed one of the major barriers to a reasonably successful reduction of intensities to $|F|^2$ values for many crystals. Newly useful comparisons of $|F|^2$ values from different crystals can thus be made, permitting examination of the real precision in physically significant quantities such as the coordinate parameters, temperature factors, and atom multipliers obtained from least-squares refinements. Physical interpretations may then be based on differences lying outside the limits of this demonstrated precision. With these limits established, bonding and impurity studies, for example, may then proceed both directly and indirectly, the latter through determination of the differences among specimens in

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respect to distortions of both actual and apparent thermal motions. Significant precision in anisotropic temperature factors is, therefore, not only a good test of refinement precision but also a practically useful tool. Finally, the values obtained by X-ray means for the various physical quantities studied may be compared with those obtained from neutron diffraction, in which many of the systematic errors would be different, for some indication of their possible accuracy. The question of significance in the apparent precision, and something of accuracy, has been attacked here through comparison of results from X-ray studies of three distinct specimens and neutron studies of a fourth specimen, all of the same origin. The question of permissible physical interpretations has then been partially explored in an effort to determine further the potential value of precision crystallography.

No studies strictly comparable to the present one have been found in the literature. A somewhat similarly conducted assessment of precision has been made by Abrahams for X-ray studies of NaCl (Abrahams, 1964; Abrahams & Bernstein, 1965). The only adjustable parameters were the two isotropic temperature factors and the agreement among the results for the five single crystals studied was, generally, within about 5σ, where σ was about 4% of the quantity being determined. Both X-ray and neutron studies of lithium tantalate have been made by Abrahams, and coworkers (Abrahams & Bernstein, 1967; Abrahams, Hamilton & Sequeira, 1967), who found the positional coordinates agreed to within about one σ ($\sim 0{\cdot}003$) while the thermal parameters disagreed by as much as 50% ($\sim 2\sigma$). Thorium pentahydrate has been independently analyzed by neutron diffraction (Taylor, Mueller & Hitterman, 1966) and by X-ray diffraction (Ueki, Zalkin & Templeton, 1966) with the result that coordinate parameters agreed within about 0·003 ($\sim 3\sigma$) while the agreement for the thermal parameters was poorer. Calcium tungstate has been studied both by X-ray diffraction (Zalkin & Templeton, 1964) and by neutron diffraction (Kay, Frazer & Almodovar, 1964) with the result that the three independent coordinate parameters agreed within σ ($\sim 0{\cdot}001$) while some of the temperature factors disagreed by more than 25% ($\sim 4\sigma$). Finally, both Trueblood (1967) and Coppens (1968*a*, *b*) have recently reported that the temperature factors obtained from X-ray data consistently exceed those from neutron data, especially for the light atoms in organic crystals.

Experimental technique

For the X-ray studies three spherical single-crystal specimens of 0·17, 0·21, and 0·18 mm radius, respectively, were separately prepared from the same Holly Springs source of mineral hydroxyapatite. For this previously studied material the space group is $P6_3/m$ (Kay, Young & Posner, 1964; Posner, Perloff & Diorio, 1958). The values $a=9{\cdot}424$ and $c=6{\cdot}879$ Å were found to be satisfactory for predetermination of X-ray reflection angles and, hence, are probably correct to within 0·004 Å for these specimens. Intensity data were collected with a punched-tape controlled single-crystal diffractometer and filtered Mo $K\alpha$ radiation. The scanning range required had been determined previously by a brief manual survey. A survey run was then made under automatic control at the rate of ~ 700 reflections per day. This survey provided information from which the final data-collection program was prepared with scanning speeds and background counting ranges adjusted to yield $\sim 1\%$ counting statistics in the net intensity, subject to a maximum scanning time of 14 minutes. Those reflections which showed obviously abnormal character on the strip-chart recording, used for 100% visual monitoring of the data, were discarded.

Single-filter 2θ scans were used in the range $25° \le 2\theta \le 100$. For one specimen (X–23–4), 60 reflections were measured with balanced-filter ω-scans in the range $2\theta < 25°$. In the 2θ-scans, backgrounds were measured only on the high-angle side for $2\theta < 60°$ and on both sides of the peak for larger 2θ. In the ω-scans, four measures were required to establish the background (Young, 1965). A particular 'standard' reflection was remeasured every two or three hours. If two such successive measures did not agree within 1% the intervening data were discarded. Experience over several years with the reproducibility of intensities of various reflections from many specimens of Holly Springs hydroxyapatite has indicated that no radiation damage effects, from the incident beam, should be expected in the data. Thus, only one reflection was ordinarily used as standard.

Absorption corrections were based on the tabular data in *International Tables for X-ray Crystallography* (1959). The polarization factor for the kinematic case only was used in the initial data reduction.

Multiple-reflection errors were directly assessed in two ways and are thought not to be serious. The intensities of each of 30 reflections for which, finally, $||F_o|^2 - |F_c|^2| \ge 3\sigma$ were monitored as the crystal was rotated $\sim 20°$ about the particular diffraction vector. Generally, the visible multiple-reflection effects were not strong, though in one case (112) a 5% decrease in intensity was noted at the approximate orientation used for data collection. A second test was made by re-collection, with differing specimen orientation about the diffraction vector, of 65 reflections of mixed strong and weak character. Using subscripts to indicate the data set, we found $(I_1 - I_2)/(\sigma_1^2 + \sigma_2^2)^{1/2} \ge 3$ for 7 cases but $< 5{\cdot}3$ for all. Finally, comparisons of $|F_o|^2$ and $|F_c|^2$ show no consistent excess of $|F_o|^2$ over $|F_c|^2$ for the weak reflections, as might have been expected if multiple reflection effects were an important source of error.

Progress of structure refinements

Table 1 shows the weighted and non-weighted R values at different stages of refinement. X–23–4, X–23–6, and

X-23-10 refer to the X-ray data collected on three different crystals. For all but the final cycles, least-squares refinements on $|F|^2$ and an additional cycle on $|F|$ were carried out with an Algol version (Gallaher & Kay, 1964) of the full-matrix Busing, Martin & Levy (1962) program. For the X-ray cases, the hydrogen parameters were kept fixed at the values given by neutron diffraction. Atomic scattering factors for Ca^{2+}, P^{+} and O^{-} were taken from *International Tables for X-ray Crystallography* (1962). For these refinement cycles the Ca^{2+} values were modified by the real part of the anomalous dispersion term given in the same Tables. The various R values used are defined as

$$R_n=\Sigma\,||F_o|^n-s^n|F_c|^n|/\,\Sigma\,|F_o|^n\,,$$
$$wR_n=\{\Sigma\,[w^{1/2}(|F_o|^n-|F_c|^n)]^2/\Sigma\,[w^{1/2}|F_o|^n]^2\}^{1/2}\,, \qquad (1)$$

where n is either 1 or 2 and w is the reciprocal variance, as discussed later. After several cycles of refinement the R_2 values were those shown in the 'Before extinction correction' columns of Table 1. At this stage the observed structure factors were corrected for secondary extinction with Zachariasen's approximate method (Zachariasen, 1963).

The mutual agreement factors, R_M, between sets of optimally-scaled extinction-corrected $|F|^2$ values for the different crystals were then found to be about 3% where

$$R_M=\sum_H\,||F_{H1}|^2-|F_{H2}|^2|/\sum_H\,|F_{H1}|^2 \qquad (2)$$

and where $|F_{H1}|^2$ and $|F_{H2}|^2$ refer to the same reflections, with indices indicated by H, as observed with X-rays from two different crystals. In view of this good agreement (in $|F|^2$, *not* I), those reflection data seriously compromised by erratic instrument performance (*e.g.* a scaler digit being dropped in the read-out) were culled out by requiring that the various mutually-scaled and extinction-corrected measures of the same $|F^2|$ value agree to within 5σ, or the data for that reflection be discarded [σ given by equation (3)]. After the culling, which removed 6 reflections and changed the R_2 value by 0·1%, the extinction corrections were applied with the results shown in the 'After extinction correction' column of Table 1.

Since mineral apatites invariably show foreign ion substitution, atomic multiplying factors were also refined. Only the multipliers for Ca, O(H) and H showed shifts, from stoichiometric values, greater than one standard deviation. In subsequent refinements the other multipliers were therefore kept fixed at their stoichiometric values.

Various chemical analyses (Smith, 1967; Kay, Young & Posner, 1964; Mitchell, Faust, Hendricks & Reynolds, 1943) of Holly Springs hydroxyapatite have indicated the presence of fluorine to the extent of, variously, 0·16 to 0·28 wt.%. Other impurities, such as Mn and Mg were reported to be present in much smaller amounts. Hence fluorine was introduced in the refinement model at $0,0,\frac{1}{4}$, *i.e.* in the same position as in fluorapatite. Strong correlation between the multiplying factor for this F and the O(H) thwarted their simultaneous refinement with the X-ray data. Since it was expected that F^- was substituted for OH^-, the O(H) multiplier and all other variable parameters were successively refined with the F multiplier fixed at each of several values. With the F multiplier corresponding to 0·32 wt.%, wR_2 was effectively minimized and the sum of the multipliers of O(H) and F equalled the stoichiometric value for O(H). Further, and perhaps more significantly, the O(H) multipliers agreed for the X-ray and the neutron cases and, in the neutron case, essentially the same value was independently obtained for the multipliers of both O(H) and H.

Finally, one last refinement cycle was carried out for each X-ray specimen with the Johnson (1966) version of the Busing, Martin & Levy program incorporating both real and imaginary parts of the anomalous dispersion terms for Ca and P. The effect of this incorporation of the additional anomalous dispersion terms was very small, changing less than one third of the parameters by as much as one unit in the fourth significant figure and none of them by as much as one standard deviation. Although the non-weighted R value was reduced in each case (from 3·3 to 3·1% in the largest case, X-23-4) the weighted R_2 value was not changed by this final cycle.

Results of refinements

As Table 1 shows, the final weighted R_1 values (*i.e.* those based on $|F|$) for the three crystals were about 2%. Structure factor values are provided in the Appendix.

Table 1. *Reliability factors at various stages*

		wR_2 (%)				R_2 (%)				
Specimen	Number of reflections	Before extinction correction	After extinction correction	Final	R_1 (%) Final	Before extinction correction	After extinction correction	Final	R_1 (%) Final	Extinction parameter, C
X-23-4	725	4·9	4·6	3·9	2·0	3·8	3·6	3·1	2·3	0·0027
X-23-6	703	6·2	4·9	3·7	1·9	5·4	3·5	3·1	2·2	0·0030
X-23-10	500	5·1	4·8	4·2	2·2	3·6	3·5	3·3	2·8	0·0036
Neutron	253	11·8	4·8	4·5	2·5	16·5	4·4	4·1	2·8	0·0012

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Table 2 gives the final determinations of the various atomic parameters for each of the four crystals. For the three X-ray cases, all of the separate determinations of the same parameter agree within one standard deviation, even for the cross-terms of the temperature factors. This excellent agreement of the parameters confirms that the estimated standard deviations, though small, are of correct magnitude.

The neutron diffraction data collected by Kay, Young, & Posner (1964) were here corrected anew for extinction by means of Zachariasen's expression with appropriate modifications, and the positional and thermal parameters and the atomic multipliers were refined. In comparing the neutron and X-ray results given in Table 2, one finds agreement within one standard deviation for all the positional parameters except that of the hydroxyl oxygen, O(H), for which the agreement is still within three standard deviations. Of the 26 independent thermal parameters, 20 agree within one standard deviation, three agree within two standard deviations and the remaining three agree within three standard deviations. However, even these small disagreements seem to show some systematic character that is physically reasonable, as will be discussed later.

Possible contributions to *R*

Although the final R values are 'good', one may legitimately ask why, with 1% statistics as the experimental goal for most reflections, the R_2 values were not still lower. Further, the question of the physical significance of differences in R values at this level arises. We therefore estimate the known contributions to R_1 and R_2; the balance must be the result of uncorrected short-term variations in overall performance of the diffraction instrument, inadequacy of the model and other unknown systematic errors.

(1) *Counting statistics*

The standard deviation, σ, in each net intensity due to errors in counting statistics was calculated with the relation

$$\sigma = C_1 + C_2|F|^2 \tag{3}$$

where C_1 is a constant representing the minimum detectable intensity and for the 2θ scan case (Young, 1965)

$$C_2 = \left[\frac{1+(1+t)/\mathcal{S}}{I_N}\right]^{1/2} \tag{4}$$

here I_N = net intensity measured, t = ratio of the time pent in measuring the peak intensity to that spent on ckground, and $\mathcal{S}$ = signal-to-noise ratio. For the lanced filter ω-scans the relation

$$C_2 = [I_1 + I_2 + (I_{b1} + I_{b2})t^2]^{1/2}/I_N \tag{5}$$

s used. I_1 and I_2 are the gross peak intensities while and I_{b2} are the background intensities (sampled at th sides of the peak) for ω-scans made with the first and second filter, respectively. The net intensity is given by $I_N = I_1 - I_2 - (I_{b1} - I_{b2})t$.

To find the possible contribution to R_2 from counting statistics we calculated the R_2 values to be expected as a result of an intensity measurement error of one standard deviation, *i.e.* $(\Sigma\sigma)/(\Sigma\,|F_o|^2)$ for the unweighted, and $(N^{1/2})/[\Sigma\, w(|F_o|^2)^2]^{1/2}$ for the weighted, case where N is the number of observations and w is the weight for each observation. Table 3 gives these calculated values, which indicate the most probable values of nonweighted and weighted R_2 factors that could be expected even if the model described the real structure perfectly and the data were free of all systematic errors.

(2) *Absorption correction*

The crystals used were ground to approximate spheres of radii 0·17, 0·21 and 0·18 mm with respective μR values of 0·49, 0·62, and 0·52. The maximum deviation of the crystal radii from the spherical value was approximately 0·01 mm. For these values of μR, uncertainty in the absorption correction due to a variation in the radii of approximately 0·01 mm is less than 0·6% in the worst case, and is therefore certainly less than 0·3% on the average.

Treating the components of R_2 in Table 3 as independent random variables indicates that in each case a substantial contribution to R_2 remains unaccounted for by the known random errors. Presumably the quantities in the 'Remaining component' columns in Table 3 are then due in large part to the combined effects of erratic machine operation (thought to be <0·5%, as assessed by separate reproducibility tests), the degree to which the model fails to represent the real crystal by reason of oversimplification, and residual systematic errors common to both the X-ray and neutron cases. An obvious source of such systematic error is the thermal diffuse scattering (TDS) contribution to apparent Bragg intensities (Young, 1965; Nilsson, 1957, 1959). Although it is clearly needed, no correction for TDS contribution has been undertaken in the present work.

Sensitivity of *R* and parameters to various factors

Weighting scheme

So much has been written about weighting schemes that one tends to feel the choice must be important, perhaps even in the final stages of refinement. The weight for each reflection was estimated from the calculated standard deviation and the function minimized was $\Sigma w(|F_o|^2 - |F_c|^2)^2$. In all cases $\Sigma w(\Delta|F|^2)^2/(m-n)$ was found to be more than 2·5, where $\Delta|F|^2 = |F_o|^2 - |F_c|^2$, m is the total number of observations and n the number of parameters varied. As a check on the weights used, the complete set of $|F_o|^2$ values was divided into 12 ranges in $|F_o|^2$ and the average values of $w(|F_o|^2 - |F_c|^2)$ in each range were plotted against the corresponding average values of $|F_o|^2$. The plot was concave upward. The standard deviation for each observation was then revised to

$$\sigma' = C_1 + C_2|F|^2 + C_3 + C_4|F|^2 , \qquad (6)$$

where the constants C_3 and C_4 were assigned values such that the revised weights gave a 'fairly good' straight line of zero slope for the plot $w(|F_o|^2-|F_c|^2)_{av}$ *versus* $|F_o|^2_{av}$. In subsequent least-squares refinements with the altered weights it was found that the shift in the parameters was less than one standard deviation. There was no change $>0{\cdot}1\%$ in the unweighted R_2 values but the weighted R_2 factors increased, in the worst case, from 4·6% to 5·0% and $\Sigma\, w(\Delta|F|^2)^2/(m-n)$ was finally found to be between 1·4 and 1·6. The change in weighting was, in general, different for each reflection. However, since the unweighted R_2 values were not changed significantly, some kind of 'average' fractional change in weights is indicated by the change in $\Sigma w(\Delta|F|^2)^2/(m-n)$, *i.e.* ~40%. The results reported in Table 2 came from refinements based on the standard deviations calculated with equation (3).

Extinction corrections

The secondary extinction correction, though seemingly slight [*i.e.* changing $R_2(|F|^2)$ from 5·4% to 3·5% in the worst case] was important to the excellent agreement finally found; prior to application of the extinction correction some of the temperature parameters differed by more than four standard deviations. Table 4 shows explicitly the relatively large effect which small corrections had on some of the independent parameters, the hydroxyl oxygen being chosen for the example because it exhibited the largest effects.

Since the extinction correction differed among the crystals, yet iterative application of it brought about agreement among previously differing measures of the same parameters, the correction may be accounted successful, necessary, and correctly applied here.

Sensitivity of R to parameter differences

In view of the small R values, a natural question is to what extent are improvements in R associated with significant changes in parameters. The final parameters for cases X–23–6 and X–23–4 were interchanged and the R_2 value recalculated with the result that R_2 increased from 3·2% to 4·0% and 3·4% to 4·2% – rather large changes in the present context. By Hamilton's (1965) R-ratio test these changes would be significant at more than the 99·5% level. Thus it seems probable that some real differences do exist, probably both in the crystals themselves and in the systematic errors associated with each, and these are indicated in Table 2, even though their effects on the parameters are smaller than the statistical standard deviations in the individual refinements.

Physical interpretations of results

It is evident from Table 2 that the atoms are consistently located and the thermal parameters are consistently determined with precision by this set of structure refinements. That accuracy as well as precision has been approached with these X-ray analyses is suggested by the agreement between X-ray and neutron results; however, corrections for TDS and any other sources of systematic error common to both techniques would have to be made before accuracy could be claimed. Nonetheless, the precision obtained and the fraction of the final R *not* due to statistical factors would seem to be possibly sufficient to support further examination of the thermal motions for anharmonic character such as has concerned Willis (1963, 1965) in UO_2 and CaF_2. Possible asymmetry of form factors might also be investigated by way of an apparent anharmonic contribution to the thermal parameters (Dawson, 1964). However, no such examinations have been undertaken here, one reason being that for such purposes the data could usefully be made still better by the use of longer counting times.

An apparent effect of bonding character does occur in Table 2. First, one notices that the thermal parameters of the oxygen atoms in the phosphate group are consistently measured larger with X-rays than with neutrons, whereas for the other atoms there does not appear to be a consistent pattern of difference. Since the P–O bonds are the only ones present which would be expected to have substantial covalent character, it is in the thermal parameters of these oxygen atoms, in particular, that one might then expect most easily to see neutron *vs.* X-ray differences due to the redistribution and probable anisotropy of the electron density associated with bonding. Conversion of the temperature factors of the oxygen atoms to thermal ellipsoids was done with an Algol version (Gallaher & Taylor, 1964) of the Busing, Martin & Levy (1964) *Function and Error Program*. The principal-axis data are given in Table 5. For all three atoms the smallest principal axis lies along the P–O bond direction, as expected. However, both X-ray and neutron refinements yield essentially the same lengths for this principal axis. The X-ray *vs.* neutron differences shown in the β_{ij} values of O_{III} in Table 2 therefore actually arise from differences in the real or apparent thermal vibrations perpendicular to the P–O bond. For these directions the individual X-ray *vs.* neutron principal-axis results differ by $1{\cdot}4\sigma$ in one case, $\sim 2{\cdot}5\sigma$ in two cases and $\sim 4\sigma$ in three cases. Statistical significance of these differences is strongly enhanced by the fact that they are all in the same direction with an average difference of about 3σ.

This excess of apparent thermal motion perpendicular to the P–O bond in the X-ray case may occur because some experimental error has enlarged the apparent X-ray temperature factors or decreased the apparent neutron temperature factors, but it is not obvious why the oxygen atoms should be preferentially so affected. It seems more probable that this apparent excess may be physically interpretable in terms of crystal-field effects or bonding effects, as described above, on the atomic wave functions. However, a thorough investigation of that point is left for future work in which the comparisons can be based on sets of data for which internal consistency of several sets has also been shown for the neutron data, as it has been here for the X-ray data. It does appear that, compared to neutron results, this excess in the X-ray determined thermal parameter of the lighter atoms may become commonly observed, as both Trueblood (1967) and Coppens (1968*a*, *b*) have noted similar differences occurring for some organic crystals.

A second aspect which invites physical interpretation is the matter of deficiencies in certain ions as indicated by the final atom-multiplying factors, shown in Table 6. It is encouraging that the X-ray and neutron results agree so well. Yet, since the scattering powers of atoms differ for X-rays and neutrons in an irregular way, complete agreement among the multipliers would be physically realistic only in cases in which the correct ions in the correct proportions have been included in the refinement model. Such a situation would occur naturally only for the stoichiometric case. It can be produced in the non-stoichiometric case by explicit introduction of impurity ions, at their proper locations, into the refinement model, as was done here for F substitution for O(H). But even without explicit substitution in the model, the expected X-ray *vs.* neutron differences make possible some consistency tests of substitutional models postulated to account for specific deficiencies such as, in this case, the apparent Ca deficiency. A test may be devised as follows. In the refinement of the neutron data, consider the effect on the multiplier of atom 1 if a fraction, x, of its sites are filled instead with atom 2, the scattering lengths being b_1 and b_2, respectively. It is necessary that

Table 2. *Positional coordinates and thermal parameters of Holly Springs hydroxyapatite*

Values × 10^4, standard deviations given in parentheses for parameters varied.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
$\mathrm{O_I}$									
X-23-4	3284 (2)	4848 (2)	2500	39 (2)	30 (1)	54 (2)	27 (1)	0	0
X-23-6	3282 (2)	4846 (2)	2500	37 (2)	29 (2)	55 (2)	25 (1)	0	0
X-23-10	3282 (2)	4847 (2)	2500	40 (2)	29 (1)	54 (2)	26 (1)	0	0
Neutron	3282 (2)	4846 (1)	2500	35 (1)	28 (1)	44 (2)	24 (1)	0	0
$\mathrm{O_{II}}$									
X-23-4	5873 (2)	4651 (2)	2500	20 (1)	26 (1)	96 (3)	9 (1)	0	0
X-23-6	5871 (2)	4649 (2)	2500	18 (1)	28 (2)	97 (2)	10 (1)	0	0
X-23-10	5872 (2)	4652 (2)	2500	19 (1)	28 (2)	102 (3)	11 (1)	0	0
Neutron	5876 (1)	4652 (1)	2500	20 (1)	24 (1)	89 (2)	9 (1)	0	0
$\mathrm{O_{III}}$									
X-23-4	3437 (2)	2579 (1)	702 (2)	92 (2)	42 (1)	49 (2)	45 (2)	−41 (2)	−27 (1)
X-23-6	3434 (2)	2579 (2)	704 (2)	89 (2)	43 (2)	53 (2)	44 (2)	−38 (2)	−26 (1)
X-23-10	3438 (2)	2581 (2)	704 (2)	87 (2)	45 (2)	53 (2)	44 (2)	−42 (2)	−24 (2)
Neutron	3433 (1)	2579 (1)	704 (1)	84 (1)	39 (1)	44 (1)	43 (2)	−34 (2)	−21 (1)
P									
X-23-4	3987 (2)	3685 (1)	2500	19 (1)	17 (1)	25 (1)	10 (1)	0	0
X-23-6	3985 (2)	3684 (1)	2500	18 (1)	17 (1)	27 (1)	10 (1)	0	0
X-23-10	3987 (2)	3685 (1)	2500	20 (1)	17 (1)	27 (1)	11 (1)	0	0
Neutron	3983 (1)	3683 (1)	2500	18 (1)	20 (1)	26 (2)	9 (1)	0	0
$\mathrm{Ca_I}$									
X-23-4	3333	6667	15 (1)	31 (1)	β_{11}	18 (2)	$\beta_{11}/2$	0	0
X-23-6	3333	6667	14 (1)	31 (1)	β_{11}	21 (2)	$\beta_{11}/2$	0	0
X-23-10	3333	6667	14 (1)	32 (1)	β_{11}	22 (2)	$\beta_{11}/2$	0	0
Neutron	3333	6667	13 (1)	33 (1)	β_{11}	24 (2)	$\beta_{11}/2$	0	0
$\mathrm{Ca_{II}}$									
X-23-4	2468 (2)	9934 (1)	2500	21 (1)	23 (1)	28 (1)	10 (1)	0	0
X-23-6	2465 (1)	9933 (1)	2500	21 (1)	21 (1)	31 (1)	10 (1)	0	0
X-23-10	2468 (2)	9934 (1)	2500	21 (1)	24 (1)	30 (1)	10 (1)	0	0
Neutron	2465 (1)	9931 (1)	2500	24 (1)	25 (2)	30 (2)	12 (1)	0	0
O(H)									
X-23-4	0	0	1950 (7)	25 (2)	β_{11}	102 (8)	$\beta_{11}/2$	0	0
X-23-6	0	0	1960 (6)	26 (3)	β_{11}	95 (7)	$\beta_{11}/2$	0	0
X-23-10	0	0	1955 (8)	26 (3)	β_{11}	98 (8)	$\beta_{11}/2$	0	0
Neutron	0	0	1978 (7)	25 (2)	β_{11}	101 (8)	$\beta_{11}/2$	0	0
H									
X-23-4	0	0	608	129	β_{11}	104	$\beta_{11}/2$	0	0
X-23-6	0	0	608	129	β_{11}	104	$\beta_{11}/2$	0	0
X-23-10	0	0	608	129	β_{11}	104	$\beta_{11}/2$	0	0
Neutron	0	0	608 (14)	129 (8)	β_{11}	104 (12)	$\beta_{11}/2$	0	0

$$(1-x)b_1+xb_2=(1-y)b_1\,, \qquad (7)$$

where y is the fractional decrement in the multiplier of atom 1. (Note that y could be negative.) Then

$$x=y/[1-(b_2/b_1)]\,. \qquad (8)$$

A somewhat similar relation must hold for the X-ray results, but here b_2 and b_1 must be replaced by $\langle f_2\rangle$ and $\langle f_1\rangle$, the effective values of the atomic scattering factors f_2 and f_1 properly weighted and averaged over the $\sin\theta/\lambda$ range used in the experiment.

According to the chemical analyses, some Mg is present in Holly Springs hydroxyapatite. As one example of how data of the type obtained from these refinements may be used to assess substitutional models, we test for the substitution of Mg for Ca at the same site. The scattering lengths are $b_{\rm Ca}=0{\cdot}49\times10^{-12}$ cm and $b_{\rm Mg}=0{\cdot}35\times10^{-12}$ cm. The arithmetic-mean value of the multiplying factor measured with X-rays is 0·3246 for $\rm Ca_I$ and 0·4828 for $\rm Ca_{II}$. Over the range $0{\cdot}2\le\sin\theta/\lambda\le0{\cdot}9$ the ratio $f_{\rm Mg^{2+}}/f_{\rm Ca^{2+}}$ runs from 0·65 to 0·40. For the sake of our, thus necessarily rough, calculation, we will use 0·5 for the effective average value of this ratio for our data. Table 7 shows the results for the degree of substitution as calculated from equation (8).

Table 3. *Apparent components of R_2 and wR_2 values*

	From counting statistics			Observed final values		Remaining component	
Specimen	$\Sigma\sigma/\Sigma\|F\|^2$ (%)	$\sqrt{N}/\sqrt{\Sigma w(\|F\|^2)^2}$ (%)	From absorption (%)	R_2 (%)	wR_2 (%)	R_2' (%)	wR_2' (%)
X-23-4	2·0	2·1	0·3	3·1	3·9	2·3	3·3
X-23-6	1·2	1·2	0·3	3·1	3·7	2·8	3·5
X-23-10	1·9	2·0	0·3	3·3	4·2	2·7	3·7

Table 4. *Effect of small corrections as shown in independent parameters of* O(H)

	Parameters (σ) × 10^4						
Refinement*	x	y	z	β_{11}	β_{33}	R_2 (%)	wR_2 (%)
X-23-6*A*	0	0	2037 (39)	19 (4)	462 (16)	5·4	6·2
X-23-6*B*	0	0	2028 (8)	29 (3)	100 (1)	3·6	4·6
X-23-6*C*	0	0	1969 (6)	26 (3)	94 (7)	3·2	3·7

* *A* No extinction correction.
B Extinction correction applied.
C Extinction correction applled, F impurity (0·32 wt %) introduced at fixed position, multipliers of Ca and O(H) varied.

Table 5. *Thermal ellipsoid axes*

r.m.s. values and (σ) in Å × 10^3.

	Axis parallel to P–O		Axis along **z**		Axis ~ perpendicular to P–O and Ca–O		Remaining axis	
	X-ray	Neutron	X-ray	Neutron	X-ray	Neutron	X-ray	Neutron
$\rm O_I$	68 (3)	67 (3)	114 (2)	103 (2)			120 (2)	113 (2)
$\rm O_{II}$	82 (3)	82 (3)	153 (2)	146 (2)			101 (2)	96 (3)
$\rm O_{III}$	73 (3)	76 (3)			192 (2)	180 (2)	101 (2)	90 (2)

Table 6. *Structural models for substitutions*

Multiplying factors (σ) × 10^4

	$\rm Ca_I$		$\rm Ca_{II}$		O(H)	
Specimen	Before refinement	After refinement	Before refinement	After refinement	Before refinement	After refinement
X-23-4	3333	3234 (11)	5000	4852 (14)	1666	1525 (20)
X-23-6		3216 (13)		4870 (18)		1494 (24)
X-23-10		3259 (18)		4837 (24)		1515 (28)
Neutron		3226 (13)		4817 (14)		1541 (13)

Table 7. *Consistency check of substitutional model*

	Neutron case			X-ray case		
	$y(\%)$	b_2/b_1	$x(\%)$	$y(\%)$	$\langle f_2\rangle/\langle f_1\rangle$	$x(\%)$
Ca I	3·21	0·715	11 ± 2	3·01	0·5	6·0
Ca II	3·66		12 ± 2	2·96		5·9

However, even though very generous estimates of possible error in Table 7 are made, the X-ray-based and neutron-based estimates of x disagree. This failure of the consistency check is itself informative, for it may therefore be concluded that the observed Ca-

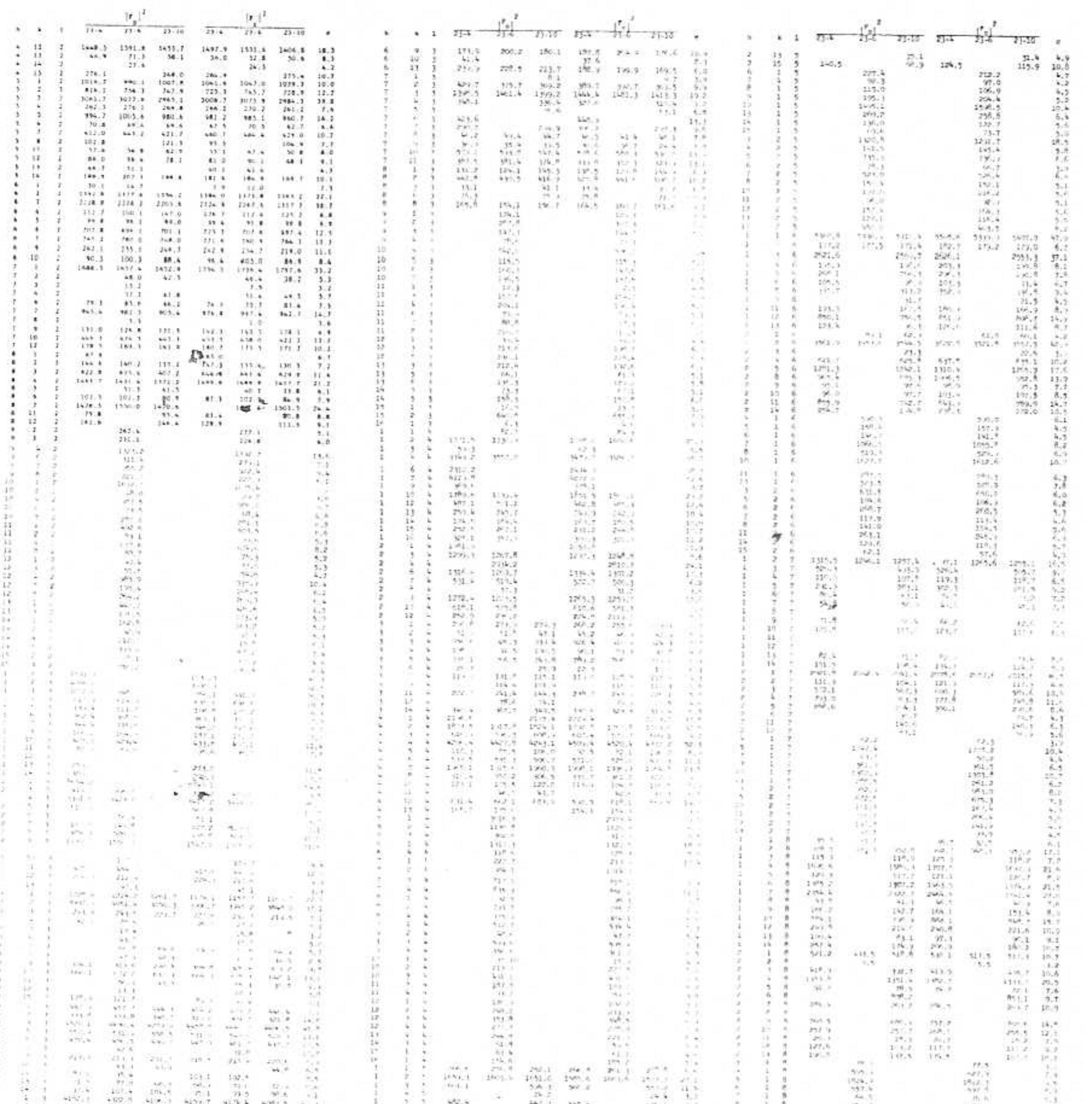
APPENDIX

Squares of structure amplitudes (X-ray)

Specimens to which the values refer are identified by numbers at the head of each column.

[illegible]

APPENDIX (*cont.*)



multiplier decrements do not arise from a simple substitution of Mg for Ca. While there may be some substitution of Mg for Ca at the same site, it is clear that other substitutions, perhaps at other sites, and probably of other atoms or even vacancies, must also exist in these specimens.

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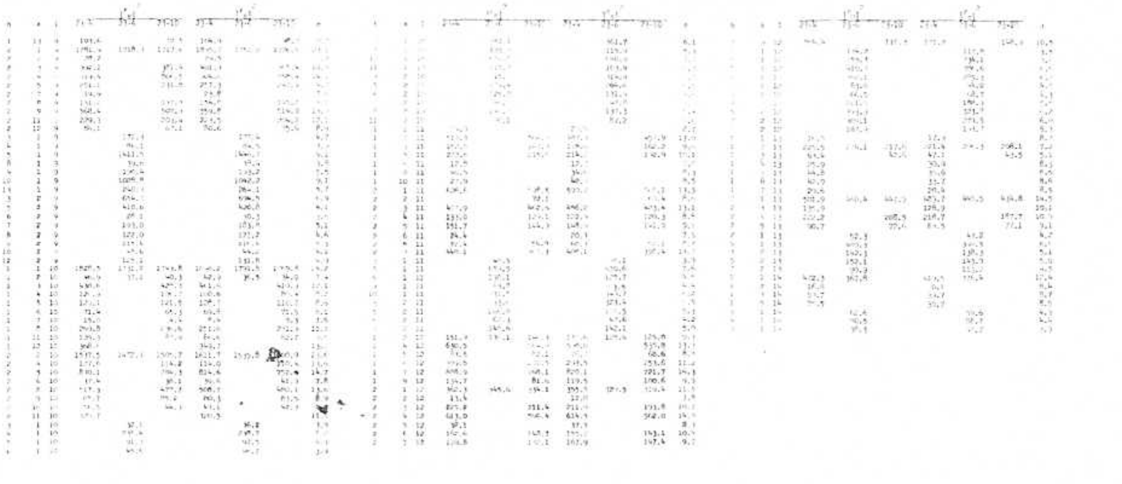
APPENDIX (*cont.*)



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