THE MINERALOGY AND GENESIS OF HYDROXYLAPATITE

LANE MITCHELL,
Department of Geology, Georgia School of Technology,
AND
G. T. FAUST, S. B. HENDRICKS, AND D. S. REYNOLDS,
United States Bureau of Plant Industry, Washington, D. C.

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 "hydroxylapatite" 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 hydroxy-apatite. This compound had been synthesized by Warrington,[4] in 1873,

---

[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).

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

---

[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 $(OH)^-$.

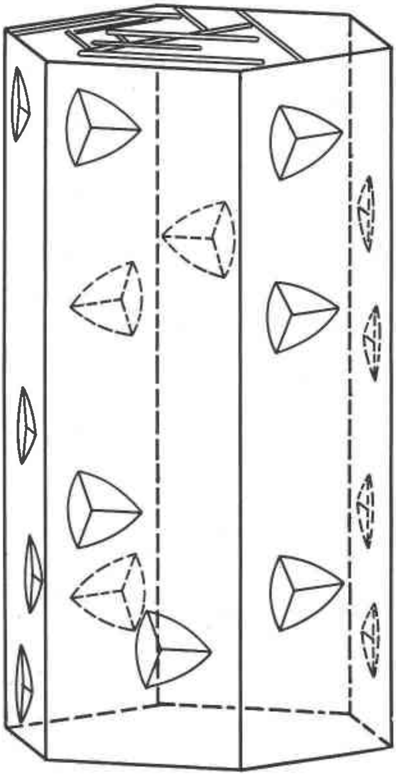


FIG. 1. Crystal forms and natural etching of the Georgia hydroxylapatite.

---

[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).

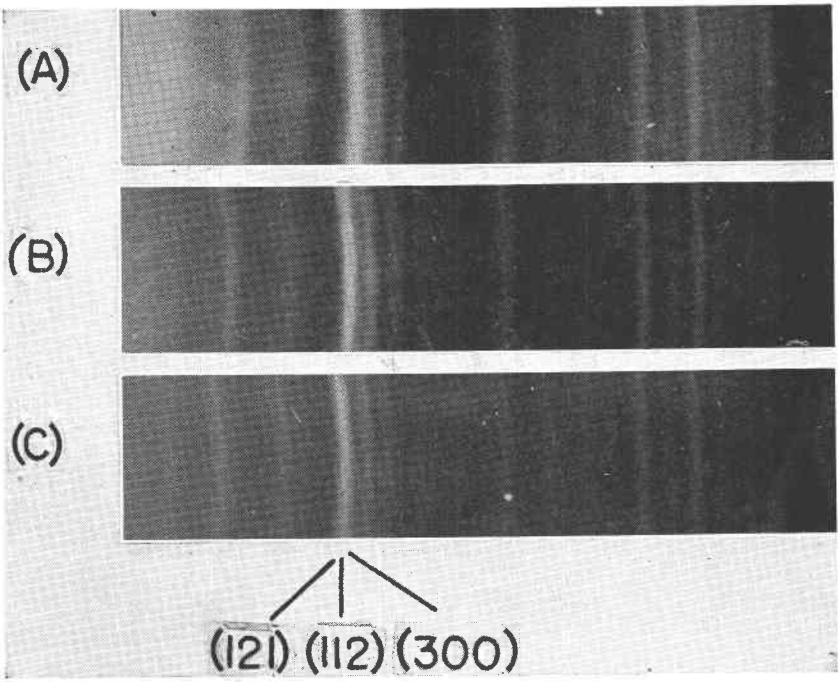


FIG. 2. X-ray powder diffraction patterns, Cu Kα radiation, of (A) synthetic hydroxylapatite (heated for one hour at 800°C.), (B) hydroxylapatite from Georgia, (C) fluorapatite.

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
$(\omega-\epsilon)_{\text{Na}}$	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, ($4CaO \cdot P_2O_5$), $\gamma_{\text{Na}} = 1.647$, $\alpha_{\text{Na}} = 1.643$. 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

---

[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 Molecüle im Licht der Dispersionstheorie: *Zeits. Physikalische Chemie*, **101**, 193–218 (1922).

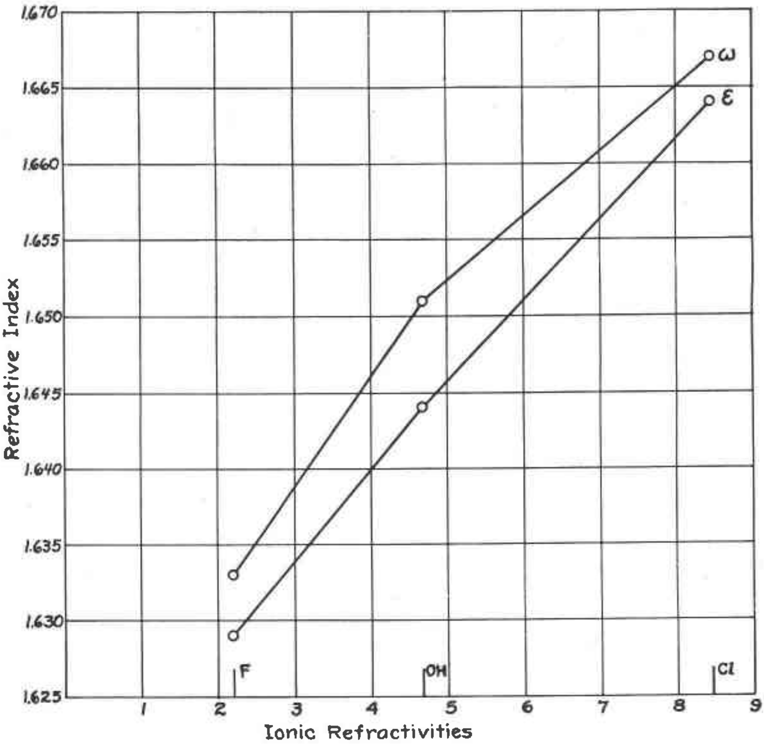


FIG. 3. Refractive indices of fluorapatite, hydroxylapatite, and chlorapatite as functions of ionic refractivities.

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]

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%.

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.[6]	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 ot 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 determina-

---

[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).

tions 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 co-workers, 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 fluor-hydroxylapatite, 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-

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	—	—	$0.90\left\{\begin{matrix}Fe_2O_3\\Al_2O_3\end{matrix}\right.$	—	—
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 $\left\{\begin{matrix}O=F\\O=Cl\end{matrix}\right.$	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

---

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

earths but was unable to prove the point. Bassett[5] observed similar pink 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	$(Ca_{10.10}\,Mg_{0.07})\ (PO_4)_{6.00}\,(OH_{0.03}\,Cl_{0.03})$	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

---

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

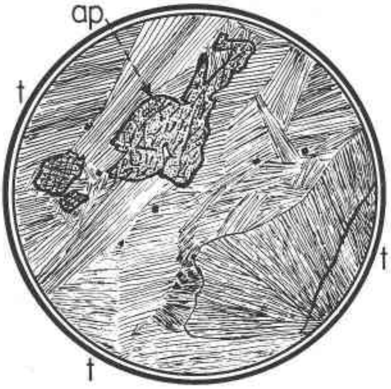
[21] Jacob, K. D., Reynolds, D. S., and Hendricks, S. B. Unpublished data, 1936.

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.



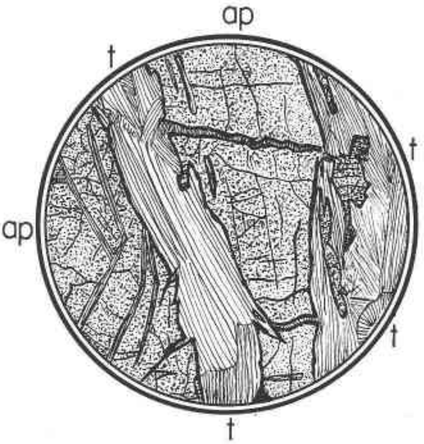


FIG. 4. Apatite-talc schist, Kemmleton, Hospenthal, Kt. Uri, Surtzerl, Switzerland, ap = apatite, t = talc, solid black areas = magnetite.

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.

---

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

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

[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

---

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

[27] Crickmay, G. W., The geology of the crystalline rocks, geologic map of Georgia: *Georgia Division of Mines, Mining, and Geology,* Atlanta (**1939**).

[28] Foshag, W. F. Personal communication to F. A. Daniel, December 13, 1939.

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.

---

[29] Crickmay, G. W., Status of the Talledega series in southern Appalachian stratigraphy: *Bull. Geol. Soc. Am.*, **47**, 1371–1392 (1936).