THE PROBLEM OF THE CARBONATE-APATITES; A CARBONATE OXY-APATITE (DAHLLITE).

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ABSTRACT.

A number of investigations have been concerned with the carbonate-apatites and the results are contradictory in some cases. The existence of carbonate-apatites has been questioned as well as the existence of oxy-apatites.

Gruner and McConnell investigated francolite through the use of chemical and X-ray methods and arrived at some entirely new conclusions regarding the structural conformity of this substance with fluor-apatite. Their conclusions were based on a single analysis and, for this reason, it seems desirable to extend the investigation to dahllite.

The conclusions regarding the existence of CO_4-groups are further substantiated. The water of this compound bears a rather complex relationship to the other constituents. There can be no further doubt regarding the existence of the carbonate-apatite or oxy-apatite molecules, although neither of these molecules exists as an ultimate end-member but is dependent upon complex inter-relationships with one another or with other apatite molecules. The isomorphism in these compounds is extremely complex.

INTRODUCTION.

An investigation of the problems concerning carbonate-apatites was begun several years ago as an integral part of a more general study of the isomorphism of the apatite group. The carbonate-apatites are of more than passing interest because there has been considerable debate as to their existence. Those who have participated in the discussion have arrived at two entirely different conclusions:

(1) That all CO_2 associated with phosphatic materials is to be accounted for as contaminating carbonate minerals (calcite or aragonite), or

(2) That the CO_2 is an essential constituent of certain special members of the apatite group.

One phase of the investigation of the carbonate-apatites, which was a collaboration, has appeared (1). This work demonstrated that the CO_2 could be accounted for in terms of the crystal structure of apatite and recorded a most complete analysis of a pure homogeneous crystalline mineral which contained 3.36 weight per cent of CO_2. This amount of CO_2 cannot possibly be accounted for in terms of a contaminating carbonate mineral, and there was no microscopic evidence of

contamination of any sort. This work permitted certain conclusions regarding the structural position of the *C*-ions within the structure.

TABLE I.

Chemical Analysis of Dahllite, from Mouillac, France.

	1 Weight % of oxides	2 Ionic ratios		3 Number of ions in cell	4 Weights of ions
P_2O_5	38.57	P	5.430	5.300	164.4
SO_3	0.05	S	.006	.006	0.2
SiO_2	0.40	Si	.067	.065	1.8
Al_2O_3	0.44	Al	.086	.084	2.3
CO_2	4.46*	C	1.014	.990	11.9
CaO	53.16	Ca	9.481	9.254	370.8
Na_2O	0.77	Na	.248	.242	5.6
K_2O	0.28	K	.060	.059	2.3
F	0.19†	F	.100	.098	1.9
Cl	0.02	Cl	.006	.006	0.2
$H_2O+300°$	0.51‡	OH	.567	.553	9.4
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$H_2O(110°\text{-}300°)$	0.21‡		.233		
$H_2O—110°$	0.48‡		.533		
Fe_2O_3	0.34				
	99.88			O = 25.343	405.5
Less O	0.08				
	99.80			42.000	976.3

* CO_2 determined on a different sample by Dr. R. B. Ellestad gave 4.35%.
†Determined by Dr. W. D. Armstrong.
‡ Determinations on a different sample by Dr. R. B. Ellestad gave: $H_2O+300°$, 0.50%; $H_2O(110°\text{-}300°)$, 0.50%; $H_2O—110°$, 0.61%.

The oxy-apatite [voelckerite] molecule also has been a matter of some controversy and a number of writers have debated its existence because its structure could not be satisfactorily accounted for (2) and the pure material could not be synthesized although mixtures containing as much as 60-70 per cent of this molecule were obtained (3). The oxy-apatite molecule undoubtedly does exist (4 and 6), however, and the writer has obtained a partial explanation, at least, resulting in a new formula, $(Ca, X)_{10}O_2(PO_4)_6$, where X represents an ion with a positive charge greater than two. It has been postulated that this ion may be carbon in some instances (4). In a later work the writer has given an alternate formula: $Ca_{10}O_2(P, X)_6O_{24}$ where X is an ion with a positive charge greater than five (5).

In view of the apparent interest in these earlier conclusions it has seemed desirable to resolve the problem further in terms of a new and rather complete analysis which has been obtained. The sample used in this study was obtained through the kindness of Dr. A. Lacroix, of the Muséum National d'Histoire Naturelle, Paris. It is labelled dahllite from Mouillac, France, and, although it is somewhat different from the original type material analysed by H. Bäckström (7), nevertheless, dahllite is probably the most satisfactory name that can be applied to it.

This investigation was made possible through a grant by the Committee on Research and Publications, The University of Texas. The writer wishes to acknowledge the kindness of Dr. R. B. Ellestad in furnishing several analytical determinations and of Dr. W. D. Armstrong in furnishing a determination of fluorine using a method developed by him (8).

MEGASCOPIC AND MICROSCOPIC DESCRIPTION.

The color of the dahllite is creamy white to milky white [bluish] but the mineral contains, within numerous interconnecting cavities, a superficial iron staining [limonite?]. The specimen is composed of a complex system of radial fibers. It is very tenacious rather than brittle when struck with a hammer.

In thin section the material appears slightly cloudy and not completely colorless. This cloudiness may be caused by air spaces or extremely small quantities of impurities between the fine fibers. If any impurity is present in addition to the iron staining, it is probably a very small amount of kaolinite or a related mineral.

There is no evidence of the presence of any impurity which might contain CO_2 and it can be concluded with certainty that calcite and aragonite are entirely absent, because no mineral with high birefringence is present in quantities capable of detection under the microscope and the x-ray powder diagrams did not show lines of calcite or aragonite. To account for the CO_2 obtained in the analysis it would be necessary for about ten per cent of the material to be $CaCO_3$. If this amount of impurity were present it could certainly be detected by one or the other or both of these methods.

The refractive indices are slightly variable, the highest observed value being about 1.628 and the lowest about 1.619 for yellow light (Wratten filter no. 90). Although the bire-

fringence is probably not as great as the difference between these values, nevertheless, it is somewhat greater than that of ordinary fluor-apatite.

The density was obtained by several determinations using a fused silica pycnometer and tetrahydronapthalene, and by using Thoulet's solution and an electric centrifuge. It was not possible to check duplicate determinations using the same method and the two methods yield values which do not satisfactorily agree. Because most reliable checks have been obtained by duplicate determinations and determinations made by both of these methods on other substances, it can safely be concluded that the difficulty lies in the nature of the material. Probably the best value was obtained by the pycnometer method and this is 2.93. This value is probably too low because of water or air spaces which were included within the very fine fibrous texture of the mineral, in spite of the fact that the determinations were made on powder retained on a 100-mesh screen.

CHEMICAL AND X-RAY DATA

A chemical analysis of material from the same locality, and supposedly similar, was made by F. Pisani (9, p. 1390) with the following results:

CaO	P_2O_5	CO_2	$Al_2O_3 + Fe_2O_3$	H_2O	F	Sum
53.65	38.40	5.30	0.57	2.10	trace	100.02

A new analysis was obtained from Ledoux and Company, New York, New York, which differs somewhat—most notably with regard to the water content and CO_2. The results of the determinations are given in column 1 of Table I.

As mentioned above the mineral is contaminated by iron oxide. For this reason the Fe_2O_3 has been deducted from the analysis for the purpose of the computations. The possibility of a very small amount of contamination by a clay mineral has been mentioned but the Al_2O_3 and SiO_2 have not been deducted from the analysis because these oxides can occur in the phosphate mineral and because the assignment of Al^{3+} and Si^{4+} to the phosphorus positions makes certain conclusions regarding the carbon more valid than they would otherwise seem, were these ions to be disregarded. The probability of the existence of alkali-apatites has been demonstrated (5) and there is no evidence that the alkalies are present in the form of impurities. Consequently the alkalies are used in the calculations.

The number of ions relegated to the 42 ionic positions of fluor-apatite is indicated in column 3. Column 4 contains the weights used to ascertain the molecular weight of the unit cell.

The interplanar distances obtained by the powder method using FeK_α have been given elsewhere (5). These measurements yield lattice dimensions: $a_0 = 9.41$Å; $c_0 = 6.88$Å; $c = 0.731$. Using 976 for the molecular weight the theoretical density,

$$\rho = \frac{976 \times 1.649}{528} = 3.048$$

The agreement of this value with the measured value 2.93 is not satisfactory by virtue of the difficulties which attend the experimental determination of the density and which have been mentioned.

The most interesting hypothesis advanced by Gruner and McConnell (1) and by the writer (4) is that concerning the tetrahedral configuration of carbon in the structure of francolite and ellestadite. The present investigation offers further support of this hypothesis, because, even when all of the aluminum and silicon ions are assigned to phosphorus positions, it is necessary to assume that a significant number of the phosphorus positions are vacant or occupied by carbon. The improbability of vacancies in these positions has been discussed (1) and will not be considered further here.

Vernadsky (10) has extended some of the writer's conclusions (4) to alumino-phosphates and alumino-sulfates and has presented an interesting question regarding the probability of the existence of alumino-carbonates [having CO_4-groups analogous to the SiO_4-groups of alumino-silicates]. Although the implications to be drawn from an hypothesis stipulating a tetrahedral configuration for carbon are interesting, to be sure, it must be recalled that this configuration is not the most stable one (1) and probably does not exist except to a limited extent in certain special sorts of compounds, Furthermore, it is to be remembered that, although this is the third compound for which such a configuration has been postulated, the proof is indirect and has not been demonstrated except for members of the apatite group.

Although one could readily advance the supposition that CO_3-groups enter the apatite lattice in the fluorine positions on

the basis of the ionic ratios obtained here (Table I), this is not tenable for several other reasons which have been given by Gruner and McConnell (1) and by the writer (5).

The mineral is a carbonate-apatite, to be sure, but it does not contain sufficient water to fill the fluorine positions of the apatite structure. It is necessary, on this account, to assume that the oxy-apatite molecule is present also. Even if all the water found (H_2O—110°, H_2O+110°, H_2O+300°) were assumed to enter the structure as hydroxyl ions there would still be a significant deficiency which would have to be accounted for in terms of the oxy-apatite molecule.

The determinations of CO_2, H_2O+300° and H_2O—110° by the two analysts show excellent agreement, but the determinations of water between 110° and 300° differ by slightly more than 100 per cent.[1] This lack of agreement possibly could be interpreted as error on the part of one of the analysts but the writer does not hold to this opinion. Because the water determinations were not made on the same sample, these differences seem to bear out certain suppositions which arose from previous experiences with the liberation of water from fibrous minerals of this sort. A most plausible explanation is as follows:

(1) The water above 300° is present as OH-groups in the apatite lattice and this amount is rather stable, showing little if any variation below 300° C.

(2) The amount of hygroscopic water below 110° is somewhat variable, to be sure, but does not vary greatly with different samples of the same material which have been allowed to approach equilibrium with the atmosphere. Furthermore, the amount of this water does not vary greatly under normal humidity conditions.

(3) The water liberated between 110° and 300° depends to a considerable extent upon the texture of the mineral material and is appreciably altered by the method used to prepare the sample. This water is very firmly held by superficial forces but probably is not present as OH-groups in the crystal

[1] Water was determined by different methods by the two analysts. Ledoux and Company determined the water between 300° and 1000° by electrically heating the specimen in a silica tube and weighing the water. Dr. Ellestad determined the total water by Penfield's method using a lead oxide flux. The moisture was determined as loss in weight at 108° C. after heating for 3 hours and again after heating for 17 hours. The water between 108° and 300° was determined as loss in weight on heating in an electric oven for 18 hours.

lattice. This supposition could account for the significant differences in the total water as determined by the three analysts: Ledoux and Company, 1.20; R. B. Ellestad, 1.61 and F. Pisani, 2.10. The first two of these analysts have already been shown to agree remarkably well on water determined outside of this temperature range.

Quite admittedly the selection of 300° as the optimum temperature for distinguishing between the water present as *OH*-groups in the structure and the water of the third sort, is an arbitrary one and has no particular theoretical justification, but the mere fact that it is possible to obtain checks at temperatures above 300° but apparently not possible to obtain checks below this temperature is believed to be significant.

The reasons given above are the basis on which the water below 300° is excluded from the calculation of the statistical distribution of the ions in the 42 theoretical positions of apatite. This distribution is as follows:

$$\begin{aligned} 10\ \mathrm{Ca} &= 9.25\ Ca + .24\ Na + .06\ K + .45\ C \\ 6\ P &= 5.30\ P + .01\ S + .08\ Al + .07\ Si + .54\ C \\ 2\ F &= .10\ F + .01\ Cl + .55\ OH + 1.34\ O \\ 24\ O &= 24\ O \end{aligned}$$

CONCLUSIONS.

The name dahllite should be extended in its connotation to include a carbonate oxy-apatite as well as a carbonate hydroxy-apatite. A detailed account of the study of a specimen of dahllite has been presented in order further to substantiate evidences already reported for other carbonate-apatites, but many of the more detailed considerations have not been included here.

On the basis of this study all of the conclusions previously set down seem increasingly justifiable with one notable exception. The specimen of dahllite considered here was previously considered by the writer (5) to be a carbonate hydroxy-apatite on the basis of Pisani's analysis. Although Pisani's analysis is essentially correct in some of its constituents, it is sufficiently wanting in others to have resulted in this erroneous conclusion. Possibly this demonstrates the futility of basing detailed considerations upon analyses which have not been made according to more recent procedures, even though produced by quite reliable analysts at a somewhat earlier date. On the other hand it may indicate that similar samples from the same locality,

although supposedly identical, may differ as greatly as the determinations by Pisani and Ledoux and Company. The former of these propositions seems the more reasonable in this case.

The hypothesis, previously advanced, which requires a tetrahedral configuration for carbon in compounds of this type, has received additional support through this investigation. The occurrence of CO_4-groups is interesting but this supposition cannot be extended to other structures by way of analogy without the use of most complete and reliable analytical data, because no method is available at present for the direct location of carbon ions in structures of this complexity.

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