NATIONAL BUREAU OF STANDARDS REPORT

9920

Progress Report

on

STOICHIOMETRIC COMPOSITION OF WHITLOCKITE

NBS

U. S. DEPARTMENT OF COMMERCE

NATIONAL BUREAU OF STANDARDS

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STOICHIOMETRIC COMPOSITION OF WHITLOCKITE

By

Betty M. Wallace* and Walter E. Brown**

* Research Associate, American Dental Association Research Div., National Bureau of Standards, Washington, D.C. 20234

** Director, Research Associate Program of the American Dental Association, Dental Research Section, National Bureau of Standards, Washington, D. C. 20234

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STOICHIOMETRIC COMPOSITION OF WHITLOCKITE

ABSTRACT

X-ray studies have shown that the mineral whitlockite is identical with the salt known as β-tricalcium phosphate (Ca/P = 3/2). The exact stoichiometry of whitlockite is in doubt because arguments have also been presented for a molar Ca/P ratio of 10/7. Samples of dicalcium phosphate dihydrate, octacalcium phosphate and mixtures of anhydrous dicalcium phosphate with $CaCO_3$ were ignited to give the products calcium pyrophosphate and whitlockite. The empirical Ca/P ratio and the % phosphorus present as pyrophosphate in the ignited material were used to calculate the molar Ca/P ratio of the whitlockite product, giving a mean value of 1.506 ± 0.015. This value differs from 3/2 by less than the standard error of the mean and indicates that the formula for whitlockite is $Ca_3(PO_4)_2$.

INTRODUCTION

X-ray studies have shown that the mineral whitlockite is identical with the salt known as β-tricalcium phosphate (Ca/P=3/2). It is a material of biological significance[1] as a constituent of dental calculi and urinary tract concretions. However, the exact stoichiometry of whitlockite is now in doubt because arguments have been presented for molar calcium-to-phosphorus ratio of 10/7. Frondel[2] first described the mineral whitlockite as anhydrous tricalcium phosphate containing small amounts of magnesium and iron (both Fe^{++} and Fe^{+++}). Its apparent unit-cell contents, $Ca_{21}P_{14}O_{56}$, agree reasonably well with the measured density 3.12; however its space group $R\bar{3}c$ would not permit an odd number of cations, and Frondel suggested that some calcium ions are missing and are partly replaced by ferric ions. Mackay[3] concluded that the space group of whitlockite is R3c and investigated the inconsistency between cell contents and space groups without coming to a definite conclusion.

Keppler[4] noted that the space groups for $Sr_3(PO_4)_2$ and $Ba_3(PO_4)_2$, $R\bar{3}m$, indicate the presence of a three-fold inversion axis so that there is no inconsistency between the unit-cell contents and the indicated space group. He then proposed the formula $3Ca_3(PO_4)_2 \cdot M^{II}HPO_4$ for whitlockite, with M^{II} representing a divalent cation with smaller ionic radius than calcium (e.g., Fe or Mg), which has a 10/7 cation/anion ratio. Keppler[5] mentioned the isotypy of whitlockite to that of the mineral cerite[6] (a rare earth silicate of cerium and lanthanum $(RE)_8(Ca, Mg, Fe)_2(SiO_4)\cdot 3H_2O$) which also has a 10/7 ratio.

Welch and Gutt[7] report a phase diagram showing a region of solid solution between $2CaO\cdot P_2O_5$ and $3CaO\cdot P_2O_5$. Their data points indicate ratios between 1.39 and 1.42 at 1,000° and 1,050°C, respectively (i.e., Ca/P $\cong$ 10/7).

The work of Fowler, Moreno and Brown[8] on the infrared spectra of the products of pyrolysis of octacalcium phosphate showed that whitlockite and calcium pyrophosphate are the products formed between 650 and 900°C. Their work suggested a means of determining the stoichiometric composition of whitlockite by measuring the per cent conversion of orthophosphate to pyrophosphate; a Ca/P ratio of 10/7 would yield a smaller amount of pyrophosphate than if the ratio were 3/2.

EXPERIMENTAL SECTION

Materials--Samples used were: (a) dicalcium phosphate dihydrate (DCPD)[9], ($CaHPO_4 \cdot 2H_2O$); (b) three preparations of octacalcium phosphate (OCP)[10], ($Ca_8H_2(PO_4)_6 \cdot 5H_2O$); (c) mixtures of DCPD with $CaCO_3$; and (d) mixtures of commercial anhydrous dicalcium phosphate (DCPA), $CaHPO_4$, with $CaCO_3$. A sample of the compound or mixture was slurried in ethyl alcohol, ground in an agate mortar, and air dried before ignition.

Ignition conditions--Loosely covered platinum foil boats containing 0.2 g samples with Ca/P ratios in the range 1.0 to 1.5 were heated in an electric muffle furnace at 700° and 900°C for either 24 or 96 hours.

Analyses--Calcium and phosphorus contents were determined on the samples before and after ignition, and the pyrophosphate content after ignition. Calcium was measured by atomic absorption using 2 ppm of strontium as the chloride in both standards and samples to suppress interference by phosphate. Values for the amount of phosphorus in pyrophosphate form were obtained by the difference between the amounts of orthophosphate present before and after hydrolysis in perchloric acid[11].

RESULTS

The pyrophosphate contents in the ignited samples are shown in Table 1.

TABLE 1

Pyrophosphate Formation on Ignition

Sample	Ignition Temp. °C.	Empirical Ca/P Ratio[d] n	%P as pyrophosphate 100x	Calculated Ca/P Ratio for whitlockite, m
DCPD	700[c]	0.999 ± .014	97.8 ± 1.4	0.955 ± .910[e]
	900[c]	0.988 ± .015	98.5 ± 1.4	0.200 ± 1.500[e]
DCPA +$CaCO_3$	900[a]	1.150 ± .017	76.8 ± 1.3	1.646 ± .127
	900[a]	1.218 ± .	57.2 ± 1.2	1.509 ± .062
	900[a]	1.213 ± .018	47.1 ± 1.2	1.403 ± .052
	900[a]	1.336 ± .019	38.8 ± 1.2	1.549 ± .048
OCP#1	700[c]	1.318 ± .019	29.8 ± 1.3	1.453 ± .042
	900[c]	1.337 ± .020	30.0 ± 1.3	1.481 ± .043
DCPD +$CaCO_3$	900[b]	1.359 ± .019	33.1 ± 1.2	1.537 ± .044
OCP#2	700[c]	1.324 ± .019	26.8 ± 1.3	1.443 ± .042
	900[c]	1.356 ± .020	26.4 ± 1.3	1.484 ± .041
OCP#3	700[c]	1.366 ± .019	29.8 ± 1.3	1.521 ± .042
	900[c]	1.333 ± .019	29.0 ± 1.3	1.469 ± .041

Sample	Ignition Temp. °C.	Empirical Ca/P Ratio[d] $\underline{n}$	%P as pyrophosphate 100$\underline{x}$	Calculated Ca/P Ratio for whitlockite, $\underline{m}$
DCPA +$CaCO_3$	900[b]	1.399 ± .020	21.1 ± 1.3	1.506 ± .039
	900[b]	1.478 ± .022	10.4 ± 1.4	1.533 ± .037
	900[b]	1.468 ± .021	7.3 ± 1.4	1.505 ± .035
	900[b]	1.541 ± .022	1.2 ± 1.4	1.548 ± .035
			Mean value	1.506 ± .015[f]

[a]heated 24 hours

[b]heated 96 hours

[c]average of 2 ignitions, 1 for 24 and 1 for 96 hours

[d]after heat treatment

[e]omitted from calculation of the mean

[f]standard error of the mean

Corresponding data at 24 and 96 hours indicated that pyrophosphate formation was essentially complete at 24 hours, and eight of the values are averages of the data for the two ignition times. Probable errors were calculated with an estimated 1% error in the calcium and phosphorus measurements.

DISCUSSION

The empirical composition of the heated sample may be expressed as $Ca_{\underline{n}}H_{(3-2\underline{n})}PO_4$, and the pyrolysis reaction may be written in terms of the coefficients for calcium or phosphorus:

$$Ca_{\underline{n}}H_{(3-2\underline{n})}PO_4 = \frac{\underline{x}}{2}\, Ca_2P_2O_7 + \frac{\underline{n}-\underline{x}}{\underline{m}}\, Ca_{\underline{m}}H_{(3-2\underline{m})}PO_4$$

$$= \frac{\underline{x}}{2}\, Ca_2P_2O_7 \pm (1-\underline{x})\, Ca_{\underline{m}}H_{(3-2\underline{m})}PO_4$$

Here $\underline{n}$ represents the empirical ratio of calcium to phosphorus in the sample, $\underline{m}$ is the ratio of calcium to phosphorus in the whitlockite product, and $100\underline{x}$ is the % phosphorus in pyrophosphate form. Equating coefficients gives:

$$\underline{m} = \frac{\underline{n}-\underline{x}}{1-\underline{x}}$$

It is assumed that the calcium pyrophosphate formed is stoichiometric and that whitlockite is the only other product. As shown in the table the calculated mean value of $\underline{m}$ is 1.506 ± 0.015.

The above calculation of $\underline{m}$ breaks down when $\underline{n}$ approaches one because it involves small differences between large numbers. For this reason, the first two values were omitted in obtaining the mean value of m. The value 1.506 differs from 3/2 by less than the standard error of the mean. It is concluded that the formula for whitlockite is $Ca_3(PO_4)_2$ under the conditions of these experiments.

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