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THE SYNTHESIS AND SOLUBILITY OF CARBONATE FLUORAPATITE*

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ABSTRACT. The solubility of laboratory synthesized carbonate fluorapatite (CFAP) was determined from supersaturated and undersaturated initial conditions. A constant composition technique was used to synthesize the CFAP resulting in solids that appear to be homogeneous, crystalline, and of accurately known stoichiometry. The CFAP dissolves incongruently when exposed to solutions that differ greatly from that in which the solid formed. By analogy to solid solution systems, the results from undersaturation are extrapolated to congruent dissolution conditions.

The IAP's from undersaturated and supersaturated conditions are similar with an offset of $\sim 10^{2.3}$. This may be caused by not obtaining equilibrium fully in one or both of the procedures used. The results unequivocally demonstrate, however, that the solubility of apatite increases dramatically with increasing carbonate content. The seawater phosphate concentration in equilibrium with carbonate fluorapatite containing 1.4 carbonate ions per unit cell is 90 to 100 times greater than that that would be in equilibrium with pure fluorapatite. Extending the dependence of the measured ion activity product on the solution carbonate activity to natural apatites may provide an explanation for the differences reported by previous workers. These experiments also suggest that fluorapatite of relatively high carbonate content is the thermodynamically stable apatite phase in high carbonate solutions such as seawater.

INTRODUCTION

By far the most abundant authigenic phosphate phase in marine sediments is francolite (McConnell, 1973), a highly substituted form of fluorapatite. Carbonate is the major substituting ion in francolite with lesser amounts of sodium, magnesium, and sulfate present as well. To evaluate the importance of francolite in the oceanic system, we must establish the saturation state of seawater and pore waters with respect to this mineral.

The determination of the solubility of apatite has been clouded by arguments concerning: (1) the congruent or incongruent nature of apatite dissolution; (2) the assurance that the solubility determination was performed on a single homogeneous crystalline phase; and (3) the effect of foreign ions on the measured solubility constant.

A significant portion of the early literature reports that the dissolution of hydroxyapatite is incongruent (Levinskas and Neumann, 1955) or that a surface complex of the formula $Ca_2(HPO_4)(OH)_2$ controls the aqueous

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activity of calcium and phosphate ions in a water/hydroxyapatite system (La Mer, 1962; Rootare, Dietz, and Carpenter, 1962; and Dietz, Rootare, and Carpenter, 1964). Others, however, have described the dissolution of hydroxyapatite with a thermodynamic constant (Bell, Mika, and Kurger, 1978; McDowell, Gregory, and Brown, 1977; Mika, Bell, and Kurger, 1976; Chuong, 1973; Avnimelech, Moreno, and Brown, 1973; Wier, Chien, and Black, 1971; Moreno, Gregory, and Brown, 1968; Valyashko, Kogako, and Khodarkovskiy, 1968; Clark, 1955).

Most of the studies concerning the substitution of carbonate into apatite have concentrated on the nature and formation of carbonate apatite (Blumenthal, Betts, and Posner, 1975; McConnell, 1973; Ferguson and McCarty, 1971; Simpson, 1967, 1966, 1965, 1964; Ames, 1959). The effect of carbonate substitution on the dimensions of the apatite unit cell has been reported by McConnell (1973), Gulbrandson (1970), McClellon and Lehr (1969), Smith and Lehr (1966), and Le Geros and others (1969). Doi and others (1980) and Tochon-Danguy, Geoffroy, and Baud (1980) report that in aqueous systems most of the carbonate ions occupy former phosphate sites in the crystal.

Gron and others (1963) reported that substituting carbonate ions into the hydroxyapatite lattice had no effect on the solubility of the solid. Other work on the solubility of carbonate containing apatites is restricted to the studies of natural materials (MacKnight, 1978; Atlas and Pytkowicz, 1977; Chien, 1972; Roberson, 1966; Kramer, 1964). It is currently difficult to interpret these data quantitatively, because the stoichiometry of the solids was not precisely known, and multiple phases may exist.

This paper reports the results of an investigation of the solubility of synthetic carbonate fluorapatite. To minimize uncertainties caused by variations in the solid phase composition or crystal structure, carbonate fluorapatite was synthesized via a modified constant composition procedure similar to that reported by Tomson and Nancollas (1978). The synthesis of the carbonate fluorapatite and ancillary analyses that were performed to characterize the solid are discussed first. The results of the solubility experiments from both supersaturated and undersaturated starting solutions are then presented. The final section discusses the oceanographic implications of these results.

METHODS

The heart of the experimental apparatus used for apatite synthesis is a reaction vessel initially containing ~ 1800 ml of a 0.1M KNO_3 solution maintained at 70°C (fig. 1). Reagents, in the form of a ~ 0.2M $Ca(NO_3)_2$ and a ~ 0.12M K_2HPO_4 with 0.048M KF solution, were added to the chamber via a peristaltic pump at a rate of ~ 8 ml/hr. The actual reagent concentrations varied slightly with each experiment. The PCO_2 of the system was held constant at either 0 or 0.1 atm by continuously bubbling nitrogen gas or a 10 percent CO_2/90 percent N_2 gas mixture through the system. A Brinkman/Metrohm pH stat held the pH constant using 1N KOH as titrant. Dramatic variations in the ionic strength were avoided by using a 0.1M KNO_3 solution as the reaction medium. KNO_3 was used because these ions substitute into apatite to a much lesser extent than NaCl (Simpson, 1964).

The strategy behind this experimental procedure is to poise the system such that the removal of ions from solution via precipitation of apatite is exactly balanced by the rate at which reagents are pumped into the chamber. If this situation is achieved, for every ion that enters, one will be removed, and the solution composition will remain constant. The advantages of the approach are: (1) Once the growth phase has started, the solid is formed under a fixed degree of supersaturation (and, hence at a single point on the stability diagram) which significantly reduces the possibility of forming multiple phases; (2) by sampling the system at discrete time intervals, the homogeneity of the material formed (with respect to elemental composition) may be assessed; (3) the stoichiometry of the solid formed can be calculated very accurately; and (4) by repeating this procedure at different pH and PCO_2 values, apatites of differing carbonate contents may be synthesized. At the end of each experimental run, the solid was collected, oven dried at approx 60°C, and saved for analysis and solubility experiments.

The solubility of apatite was estimated in two ways. After approx 3 g of apatite had formed, the addition of reagents via the peristaltic pump was stopped, and the pH stat system was allowed to react for an additional 24 hrs. Samples were removed periodically, and the final concentrations were used to estimate the solubility product. From undersaturated conditions, the solubility was estimated via simple batch experiments. Approx 0.1 to 0.2 g of solid was mixed with 20 ml of a 0.1M KNO_3 solution, and the pH and carbonate ion activities were adjusted to the desired level via small additions of a 0.02M K_2CO_3 in 0.1M KNO_3 solution and/or 1N HNO_3. After approx 10 days, the pH was measured, and 5 ml of liquid was removed, filtered, and stored for analysis. Care was taken to remove as little of the solid as possible during sampling. The

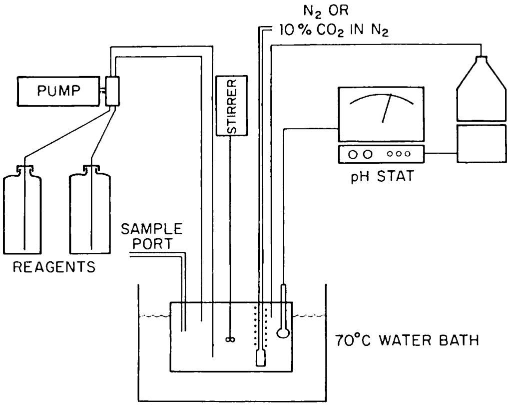

Fig. 1. Experimental apparatus used in the pH stat experiments.

volume in the vial was then restored to 20 ml by addition of KNO_3 solution, and the entire experiment repeated. For each solid, nine sequential dissolution experiments were performed at 25°C, five were performed at 4°C, three were performed at 70°C, and one was performed at 45°C. Since the apatite particles are generally greater than 20μ in length, surface energy effects are not important.

The samples were analyzed by standard analytical methods which will not be discussed in detail. Phosphate was measured via the reduction of the phosphomolybdate complex (Strickland and Parsons, 1972) to a precision of 2 percent. Fluoride was determined in most of the samples by alizarin complexone (Greenhalgh and Riley, 1961) to a precision of 2 percent. The fluoride content of samples from a few of the early pH stat experiments was measured by ion specific electrode to ± 10 percent. There was no detectable difference in accuracy between these methods as determined by comparing the results of common samples. The pH was determined by glass electrode which had been standardized against N.B.S. buffers to a precision of ± 0.01 pH units in the dissolution experiments and ± 0.05 pH units in the pH stat experiments. The carbonate ion activity was calculated from the PCO_2 and pH using the dissociation constants and Henry's Law constant reported by Harned and Scholes (1941) and Harned and Davies (1943). Potassium was measured in the solid by dissolving a known quantity of apatite in dilute acid and measuring the potassium concentration by flame atomic absorption. The carbon (assumed to be carbonate) and nitrogen (presumably as nitrate) content of the apatite were determined by Carlo Erba C:H:N analyzer.

RESULTS AND DISCUSSION

Synthesis and characterization of carbonate fluorapatite.—For brevity, a complete listing of the raw data will not be presented but may be obtained by writing the author or through University Microfilms (Jahnke, ms). I will first discuss the apatite synthesis. Although there is significant variation between the individual pH stat experiments, each has three general features exemplified in figure 2 for experiments 9 and 10. Initially, there is an unstable period, usually several hours in duration, representing the time required to supply enough reagents to the chamber to exceed the critical supersaturation value. An uncharacterized Ca-PO_4 phase initially precipitates and is followed by a period of steady state conditions during which the solid particles are growing at a rate commensurate with the rate of reagent addition. It is only this steady state period that approximates the constant composition procedure. Because the rate at which reagents are added to the system is constant, the amount of the solid produced during the unstable and growth periods is directly proportional to the duration of each. Generally, one to two times as much material was produced during the growth period as during the unstable period. At the time marked by the arrows (fig. 2), reagent addition was stopped, and the concentrations decreased as the system approached equilibrium.

The precision with which the stoichiometric ratios may be determined via this procedure is illustrated by comparing the results of runs 9 and 10 (fig. 2). In run 9, the Ca:PO_4:F ratio of the reagents was 5:3:1.39 and that of the precipitate was 5:2.88:1.28 (table 1). The difference in these ratios is demonstrated by the increase in phosphate and fluoride and decrease in calcium concentrations during the growth phase of the experiment. The ratios in the solid were calculated by determining a linear regression line for the growth phase concentration data and correcting the reagent ratios for the change observed in solution. Reagents were then prepared which had the same molar ratios as the solid produced in run 9, and the experiment was repeated (run 10, fig. 2B). The solution concentrations in the growth phase of this run are essentially constant with no detectable change in calcium or phosphate and only a slight increase in fluoride. One can see that the difference between the reagent and solid elemental ratios of runs 9 and 10 (table 1) were easily detected even

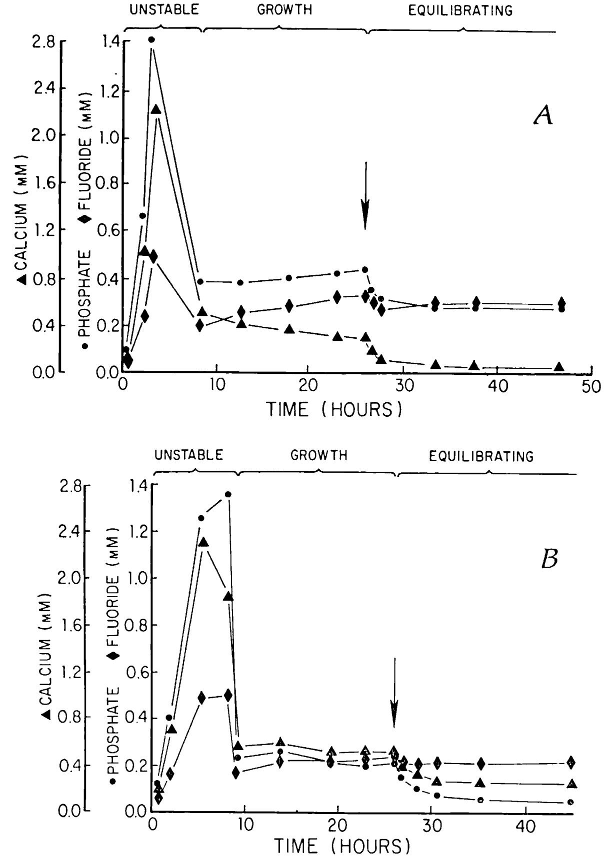

Fig. 2. Results of the pH stat experiments #9(A) and 10(B). The arrow indicates the cessation of reagent addition.

though these differences were only 4 and 8 percent of the total concentration of phosphate and fluoride, respectively. Also, one should note that useful solids are obtainable even when the solution concentrations do vary slightly (fig. 2A) as long as the changes are linear with time.

For a preliminary estimate of the lattice stoichiometry, I have assumed that the sum of negative charges in the unit cell equals 20 equivalents. Neglecting the possible incorporation of OH^- into the apatite lattice, the fluoride content was calculated via the following expression:

$$20\text{eq} = 2(CO_3{}^{2-}) + X + 3XY$$

where: Y is the PO_4:F ratio

X is the fluoride content of the unit cell

$CO_3{}^{2-}$ is the carbon content of the unit cell.

The Ca^{2+} and $PO_4{}^{3-}$ contents were then calculated directly from the ratios presented in table 1. Potassium was measured independently and simply added to the final composition.

A summary of the final stoichiometry is given in table 2. The calcium content is relatively constant at a value generally below the theoretical value of 10 ions/unit cell. The potassium content is low considering that the experiments were performed in a 0.1M KNO_3 solution reflecting the reluctance of the large potassium ion to fit into the apatite lattice. The final column of table 2 represents the residual charge of the unit cell. Since the unit cell contains 20 equivalents of charge, the majority of the samples are balanced to ± 1 percent, and the worst case (expt. #8) is only 3 percent from zero net charge. The fact that there is not a large residual net charge implies that all major constituents of the solid have been accounted for supporting the assumption that hydroxide is not an important constituent of these solids.

The calculated stoichiometries were checked by directly measuring the phosphate content of each solid. In all cases, there was no statistical difference between the calculated and measured values.

TABLE 1

Summary of pH stat experimental conditions and molar ratios of reagents and precipitates

Run #	pH	PCO_2 (atm)	Ca:PO_4:F (reagents)	Ca:PO_4:F (precipitate)
6	5.38	0.0	5:3.00:1.14	5:2.99:1.15
8	5.85	0.0	5:3.00:1.39	5:3.03:1.35
9	6.15	0.1	5:3.00:1.39	5:2.88:1.28
10	5.99	0.1	5:2.89:1.29	5:2.89:1.24
11	6.93	0.0	5:2.88:1.34	5:2.93:1.24
13	6.55	0.0	5:3.05:1.42	5:2.98:1.33
14	6.76	0.1	5:3.00:1.39	5:2.88:1.28
24	7.25	0.1	5:2.59:1.09	5:2.61:1.09
25	7.89	0.1	5:2.59:1.09	5:2.55:1.07
30	7.07	0.1	5:2.75:1.15	5:2.71:1.13
31	7.77	0.1	5:2.59:1.09	5:2.48:1.03

Preliminary X-ray diffraction analyses were performed to confirm the mineralogy, assess the crystallinity, and evaluate changes in the unit cell dimensions of the material produced. X-ray diffractograms of four representative synthetic apatites ranging from 0 to 1.33 carbonate ions per unit cell are shown in figure 3. It is important to note that there is no detectable loss of crystallinity with increasing carbonate content. A summary of the peak position and relative intensities along with those reported for a naturally occurring apatite (Lucas, Pervot, and Lamboy, 1978) are given in table 3. There is an excellent correspondence between the natural francolite and the synthetic apatite of both the peak position and the relative intensities. One should also note, that with the exception of two minor peaks observed for expt. 9 (parentheses), every peak observed in these diffractograms is accounted for by the apatite structure. Thus, the presence of other phases seems unlikely.

A comparison of the variation in the position of the X-ray diffraction peaks (represented by the angular difference between the 004 and 410 peaks) and the carbonate content of each sample is presented in figure 4. Because the difference between closely positioned peaks is used instead of the absolute values, nearly all the variability that could be caused by changes in the goniometer reproducibility is eliminated. There is good correlation between the angular distance between these peaks and the carbonate content of the sample. Also included in figure 4 is a regression line reported by Gulbrandson (1970) for 74 naturally occurring phosphorites analyzed by McClellan and Lehr (1969). The regression line reported by Gulbrandson (1970) is very similar to the results obtained here suggesting that the carbonate ion alone is responsible for nearly all the change in unit cell dimensions observed in natural apatites.

As an additional check for the formation of minerals other than fluorapatite in the pH stat experiments, ion activity products of other solid phases that potentially could form were calculated (table 4). The ion pairing model used to calculate the individual ion activities was

TABLE 2

Summary of the stoichiometries calculated for the apatites synthesized in the pH stat experiments. The units are ions/unit cell except net charge which is in equivalents/unit cell

Run #	Ca	K	PO_4	CO_3	F	Net charge
6	9.88	0.27	5.91	n.d.	2.29	+0.03
8	9.57	0.23	5.80	n.d.	2.54	−0.63
9	9.86	0.08	5.68	0.22	2.52	−0.20
10	9.88	0.04	5.71	0.22	2.53	−0.20
11	9.97	0.13	5.84	n.d.	2.47	+0.07
13	9.63	0.33	5.74	0.12	2.56	−0.41
14	9.75	0.03	5.61	0.33	2.50	−0.47
24	10.06	0.04	5.25	1.03	2.19	+0.16
25	9.94	0.06	5.07	1.33	2.13	−0.05
30	10.07	n.d.	5.46	0.67	2.02	+0.14
31	10.10	0.07	5.01	1.45	2.02	+0.27

checked by comparing the calculated activities with those measured by ion selective electrode (Ca^{2+} and F^- only). There were no significant differences suggesting that all the important aqueous species have been included. None of the experiments becomes supersaturated with respect to CaF_2, β-$Ca_3(PO_4)_2$, or $Ca_4H(PO_4)_3 \cdot 3H_2O$. The results for hydroxyapatite are less conclusive. The four highest pH experiments (24, 25, 30, and 31) appear to be supersaturated. However, if hydroxyapatite were forming in these experiments, one would calculate a large charge imbalance for these solids. As shown in table 2, this is not observed.

The results for calcite are also ambiguous. Experiments 24, 25, 30, and 31 appear to be saturated or supersaturated with respect to $CaCO_3$.

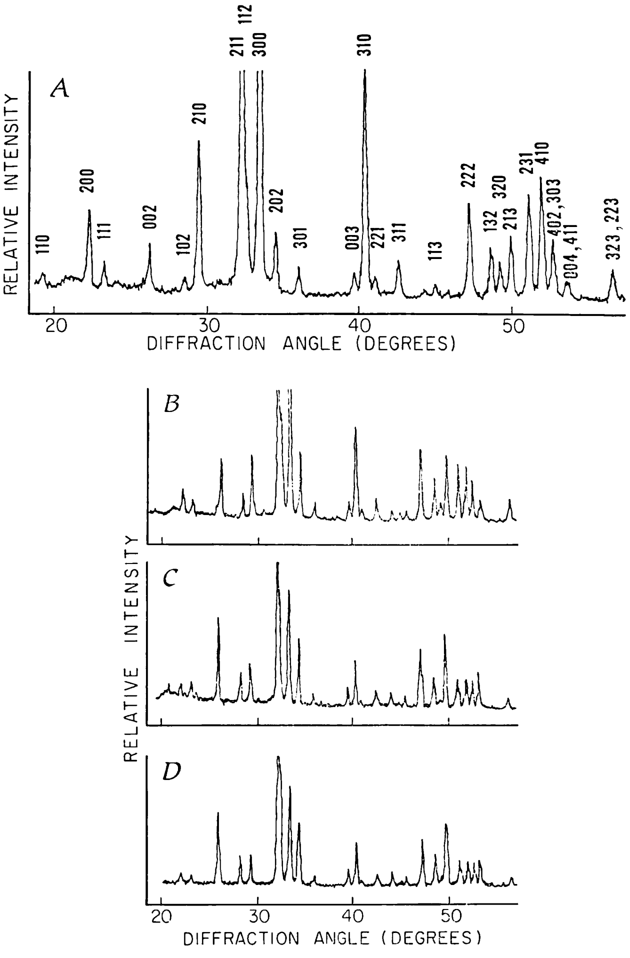

Fig. 3. X-ray diffraction patterns of representative synthetic apatites of varying carbonate content using CuKα X-ray source at 1° 2Θ/min. Sample 8 (A) contains no detectable carbonate, sample 9 (B) contains 0.33, sample 24 (C) contains 1.03, and sample 25 (D) contains 1.33 carbonate ions per unit cell.

However, the solid formed in experiment 31 would need to be 17 percent (wt/wt) $CaCO_3$ to account for all the carbonate present. Based on no observable $CaCO_3$ peaks in the X-ray diffraction data and the consistent variation between the carbonate content and the angular difference between the 004 and 410 peaks already discussed, I conclude that $CaCO_3$ was not produced in significant quantities. The experiments are everywhere supersaturated with respect to fluorapatite. The exact degree of supersaturation will be discussed in greater detail in the next section.

SOLUBILITY OF CARBONATE FLUORAPATITE

pH stat experimental results.—I will first present the solubility results of the final stage of the pH stat experiments. The advantages of estimating the solubility product in this manner are: (1) The system approaches equilibrium from supersaturated conditions which can be

Table 3

Summary of the X-ray diffraction data displayed in figure 5. For comparison, the date reported by Lucas, Prevot, and Lamboy (1978) is also presented

	North Spain		Sample 8		Sample 9		Sample 24		Sample 25	
hkl	dA	I/I_o	dA	I/I_o	dA	I/I_o	dA	I/I_o	dA	I/I_o
100	8.05	4	7.87	10	8.03	5	7.70	5	8.00	5
—	—	—	—	—	7.65	5	—	—	—	—
—	—	—	—	—	7.56	5	—	—	—	—
101	5.26	3	—	—	—	—	—	—	—	—
110	4.64	—	4.60	2	—	—	4.67	5	—	—
201	4.38	—	—	—	—	—	4.28	5	—	—
200	4.02	6	3.99	12	4.05	7	4.05	4	4.03	6
111	3.84	4	3.82	4	3.87	5	3.85	6	3.85	5
002	3.43	32	3.39	7	3.43	18	3.43	37	3.43	36
102	3.17	13	3.12	3	3.16	6	3.15	13	3.16	13
210	3.03	19	3.03	23	3.05	19	3.05	16	3.04	15
211	2.775	100	2.768	83	2.790	100	2.785	100	2.783	100
112	2.765	ind.	2.742	16	2.767	32	2.765	50	2.765	60
300	2.68	48	2.670	100	2.690	63	2.690	51	2.685	49
202	2.615	24	2.600	10	2.613	20	2.613	29	2.615	30
301	2.51	5	2.492	5	2.505	5	2.502	5	2.497	5
003	2.285	8	2.270	4	2.280	7	2.281	8	2.280	9
310	2.235	21	2.230	37	2.245	29	2.239	21	2.235	21
221	2.196	—	2.199	3	2.215	7	—	—	—	—
311	2.130	7	2.120	6	2.130	6	2.130	7	2.125	6
302	2.111	—	—	—	2.100	3	—	—	—	—
113	2.05	4	2.013	2	2.057	4	2.058	7	2.055	7
400	1.995	3	—	—	1.957	6	1.997	5	1.994	5
222	1.925	25	1.924	14	1.930	22	1.930	25	1.926	23
132	1.875	14	1.870	7	1.880	10	1.875	13	1.875	14
320	1.842	—	1.849	5	—	—	—	—	—	—
213	1.835	30	1.823	9	1.833	19	1.833	33	1.830	30
231	1.790	13	1.773	16	1.791	17	1.787	13	1.785	11
410	1.760	11	1.759	18	1.765	18	1.760	12	1.757	11
402, 303	1.740	9	1.736	9	1.743	12	1.740	12	1.738	11
004, 411	1.722	12	1.708	2	1.717	8	1.720	16	1.720	13
323, 223	1.629	—	1.627	4	1.633	5	1.631	5	1.628	5
313	1.516	—	—	—	1.602	2	1.602	3	—	—

compared to the results from undersaturation. (2) The solids have not been exposed to widely varying conditions such as drying nor have the concentrations of ions in solution differed greatly from those in which the solid formed. Thus, the possibility of forming surface layers that differ from the bulk phase is minimized. The major sources of error in this procedure are: (1) The reaction time was limited to ~ 24 hrs. Although it appears that the solution concentrations are not appreciably changing after this time period (see fig. 2), the proximity of the system to equilibrium is not rigorously known. (2) There is some uncertainty in the value of the third dissociation constant of phosphoric acid at 70°C. The heat of reaction for the dissociation of HPO_4^{2-} is -3.53 ± 1 kcal/mole (Truesdell and Jones, 1974) resulting in a value of pK_3 at 70°C of 12.1 ± 0.1 (assuming ΔH is independent of temperature at least between 25° and 70°C). This results in an overall uncertainty in the solubility product estimate of $10^{\pm 0.6}$. (3) As mentioned in the methods section, the pH was measured to a precision of only ± 0.05 pH units which results in an uncertainty in the I.A.P. of $10^{\pm 0.4}$.

The solubility product calculated from the pH stat experiments for the stoichiometries listed in table 2 are tabulated in table 5. The error

Fig. 4

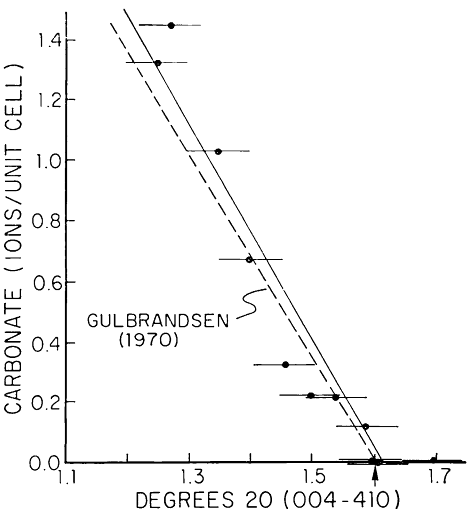

Fig. 5

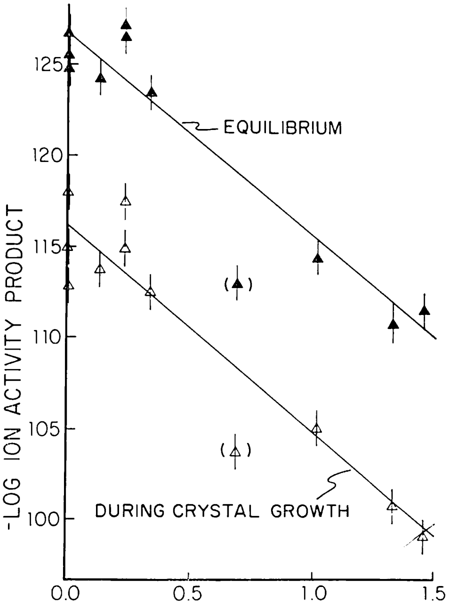

Fig. 4. The effect of carbonate substitution on the angular distance between the 004 and 410 X-ray diffraction peaks using Cu Kα X-ray source at 1/8° 2Θ/min. The dashed line is the relationship reported by Gulbrandsen (1970) for naturally occurring apatites, and the solid line is a linear regression of the data. The arrow indicates the value for pure apatite.

Fig. 5. Comparison of the ion activity product at equilibrium and during crystal growth at 70°C.

in this calculation is approx 1.2 log units. There is a dramatic increase (10^{14}) in the ion activity product with increasing carbonate content.

To check if surface layers had formed during the equilibration period of the pH stat experiments and interfered with the solubility determination, I have compared the concentration decrease at the end of each run to the calculated stoichiometry of the solid. Generally, the ratios are the same indicating no compositional difference between the solid formed during the growth phase and the equilibrium phase. However, the errors in this analysis are admittedly large, and subtle surface phases could go undetected.

To investigate this possibility further, the ion activity product during crystal growth is compared to the measured solubility product in figure 5. The reaction rate (pump rate) is nearly the same for all experiments. Since the kinetics of precipitation appear to be comparable between solids (concluded from the similar reaction times observed upon ceasing reagent addition), the degree of supersaturation in all runs should be nearly the same. This appears to be the case as the two sets of ion activity product data displayed in figure 5 parallel each other with an offset of $\sim 10^9$. Surface artifacts could not be important in controlling the ion

TABLE 4

Summary of the pI.A.P. for solids which could form in the pH stat experiments. The two data points listed for each experiment correspond to the first and last sample obtained during the growth phase of each experimental run. The column marked I.A.P. is the pI.A.P. calculated using the individual stoichiometries determined for each sample. Numbers in parentheses are reported solubility products for the solids

Sample	$Ca_{10}(PO_4)_6F_2$ (122.8)	$Ca_{10}(PO_4)_6(OH)_2$ (115.5)	$Ca_4H(PO_4)_3$ (46.9)*	β-$Ca_3(PO_4)_2$ (27.0)*	CaF_2 (10.5)*	$CaCO_3$ (8.42)†	I.A.P.
6	117.5	124.8	57.0	35.5	10.9	—	117.4
	118.5	125.3	57.2	35.7	11.4	—	118.4
8	116.5	123.0	56.8	35.2	11.1	—	114.8
	116.8	123.6	56.9	35.3	10.9	—	115.0
9	114.8	120.4	56.0	34.5	11.4	10.8	114.2
	116.2	121.3	56.6	35.0	11.2	11.0	115.5
10	117.6	123.4	57.2	35.4	11.5	11.1	117.4
	117.9	124.0	57.4	35.5	11.3	11.1	117.6
11	111.1	115.4	54.8	33.2	11.4	—	111.1
	114.6	119.3	56.6	34.5	11.1	—	114.5
13	113.9	119.3	55.9	34.3	11.1	—	112.7
	116.0	121.6	56.8	34.9	11.2	—	113.9
14	113.3	117.8	55.5	33.9	11.7	9.90	112.0
	114.4	119.3	56.0	34.3	11.5	10.2	112.9
24	106.8	110.2	53.0	31.8	11.4	8.58	105.1
	106.6	110.1	53.1	31.8	11.2	8.45	104.7
25	103.9	106.2	52.1	30.8	11.5	7.58	100.2
	104.8	107.2	52.4	31.1	11.6	7.74	101.2
30	105.3	109.0	52.5	31.4	11.1	8.54	103.4
	105.9	109.8	52.8	31.6	11.0	8.60	103.9
31	102.3	104.8	51.5	30.4	11.2	7.44	98.7
	102.7	105.4	51.6	30.5	11.2	7.60	99.3

* Data from Nancollas, Amjad, and Koutsoukos 1979.

† Data from Stumm and Morgan, 1981.

TABLE 5

Ion activity product results for the pH stat experiments corrected to 25°C

Sample	CO_3^{2-}/unit cell	pI.A.P.
6	N.D.	122.7
8	N.D.	121.6
9	.22	122.6
10	.22	123.2
11	N.D.	120.8
13	.12	120.3
14	.33	119.5
24	1.03	110.4
25	1.33	106.8
30	.67	109.1
31	1.45	107.6

activity product during the growth phase of the pH stat experiments. Based on the similarity of the trends in the ion activity products with increasing carbonate content, I conclude that the equilibrium ion activity product increases by approx 10^{14} over the range of carbonate contents used, and surface artifacts do not account for the observed trend.

Dissolution experiments.—If a mineral dissolves incongruently, surface layers that have a different composition and solubility than the bulk solid may form. Before presenting the results of the dissolution experiments, therefore, the congruency of apatite dissolution will be evaluated.

Initial batch experiments were performed within a pH range of ~ 5.5 to 6.5. For each equilibration, the net Ca:PO_4 and PO_4:F ratios of the dissolving material were calculated and compared to the compositions listed in table 2 (figs. 6, 7, and 8). To avoid surface artifacts that may have formed during drying and handling, the results of the first equilibration are not considered. Also, the 45°C data are not considered here, because only one equilibration was performed at this temperature.

The 4°C samples (fig. 6) appear to dissolve congruently. The PO_4:F ratio and Ca:PO_4 ratios are generally within 30 percent of the stoichiometric value. The large error bars on the values result from the small amount of dissolution that occurs compared to the standing stock of ions in solution at the start of the experiment. At 25°C (fig. 7), the results are mixed. The PO_4:F ratio for all samples appears to equal the stoichiometric value as does the Ca:PO_4 ratio for the low carbonate materials. However, the high carbonate apatites are dissolving with a larger Ca:PO_4 ratio than the solid. At 70°C (fig. 8), dissolution of the high carbonate apatites appears to be highly incongruent, with Ca:PO_4 ratios nearly 100 times the stoichiometric value of solid and PO_4:F ratios approximately a factor of 20 less. (Note the scale change for the 70°C data, fig. 8.)

The high carbonate apatites, therefore, appear preferentially to release calcium to solution relative to phosphate (at least at 25° and 70°C). To maintain electroneutrality, either H^+ or K^+ must be incorporated into the solid during dissolution or CO_3^{2-} must be preferentially released to solution. Since the aqueous activities of H^+ and K^+ in these experiments do not differ significantly from the pH stat experiments in which the solid formed, the most likely explanation for this phenomena is the preferential release of carbonate ions from the surface. This mechanism is supported by the fact that the final aqueous carbonate activity in these dissolution experiments is a factor of 10^5 lower than when the mineral formed.

The formation of a carbonate depleted surface layer would also provide an explanation for the different results obtained at the different temperatures. Since diffusion coefficients within a solid increase significantly with temperature, the thickness of a surface phase that may form would also increase resulting in a greater release of Ca^{2+} and CO_3^{2-} ions to solution. If this temperature trend is valid, one may expect that the high carbonate apatites are dissolving incongruently even at 4°C, but that the surface layer formed is so thin that the solution concentrations were not measurably affected.

It is presently not possible to predict accurately under what conditions carbonate apatites will dissolve congruently. The extent of substitution of a foreign ion into a solid depends on: (1) the solubility product ratio of the individual pure phases; (2) the solution activity ratio of the ions competing for the same sites in the solid; and (3) the ratio of the activity coefficients of the competing ions in the solid phase (Stumm and Morgan, 1981; Gresens, 1981; Lippmann, 1977). It is not possible to apply these concepts directly to the substitution of carbonate into fluorapatite.

Fig. 6

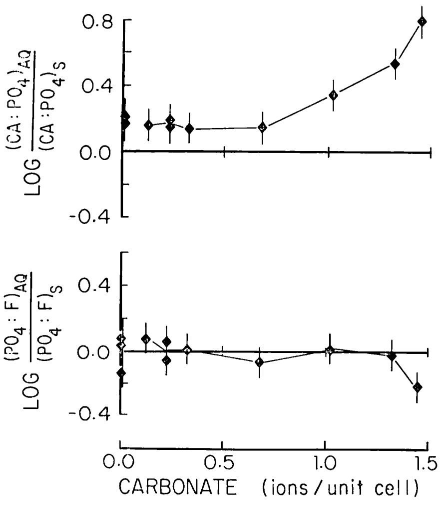

Fig. 7

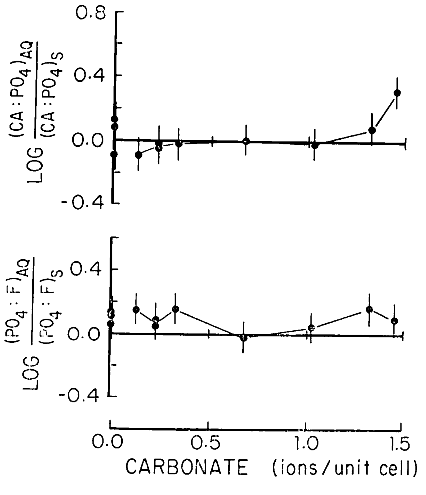

Fig. 6. A test of the congruency of dissolution for the 4°C dissolution experiments as a function of the carbonate content. The numerator of the ordinate is the elemental ratio of the ions released to solution. The denominator is the stoichiometric ratio of the ions in the solid calculated from the pH stat experiments.

Fig. 7. A test of the congruency of dissolution for the 25°C dissolution experiments. The axes are the same as in figure 6.

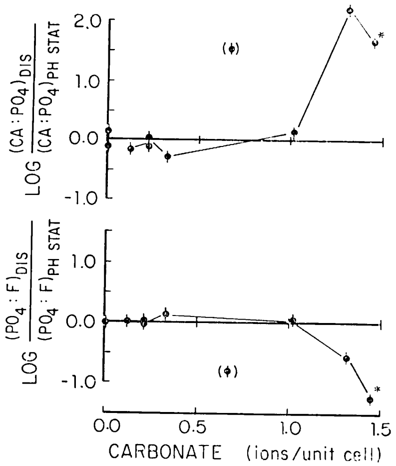

Fig. 8. A test of the congruency of dissolution for the 70°C dissolution experiments. * These values were calculated from the results of all three 70°C equilibrations.

First, a pure carbonate apatite endmember does not exist. Secondly, although the ion activities in solution are known, it is difficult to assess the activity ratio of the competing ions. Even though carbonate ions predominantly substitute for phosphate, the replacement of fluoride and perhaps the filling of lattice vacancies also occur. Therefore, the potential for the incorporation of carbonate ions into the apatite lattice may not be described by a single activity ratio. Finally, the activity coefficients of the ions in the solid are not known. Since the extent of substitution reaches significant levels, (1.45 CO_3^{2-} ions/unit cell) one cannot assume ideality.

I have attempted to determine empirically conditions under which carbonate apatite dissolves congruently. Additional dissolution experiments were performed at 25°C in the pH range of ~ 6 to 8. The aqueous carbonate activity varies appreciably over this pH range and at the higher pH's approaches the same activities as were present in the pH stat experiments.

The congruency of dissolution was evaluated in the last of the additional experiments. Although the errors are large, the high carbonate apatites appear to dissolve nearly congruently under these conditions. It appears that the congruency of dissolution changes as the aqueous carbonate ion activity varies. By analogy to solid solution systems, therefore, I assume that carbonate apatites dissolve congruently when the carbonate activity in the dissolution experiment equals that of the pH stat experiment in which the mineral formed.

To estimate the solubility of the synthetic apatites, I have separated them into two groups. One group is comprised of the apatites that were synthesized in a CO_2 free system (6, 8, 11, and 13). These solids appear to have dissolved congruently in the initial experiments of low carbonate ion activity, and their solubility may be estimated directly by averaging

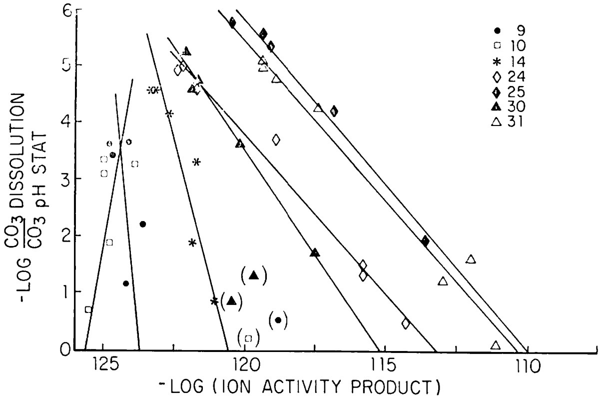

Fig. 9. A comparison of the equilibrium ion activity products calculated from the dissolution experiments as a function of the ratio of the aqueous carbonate ion activity in the dissolution experiment to the pH stat experiment in which the solid formed. The lines represent linear regressions of the data.

the results. The other group is those apatites formed under a 0.1 atm partial pressure of CO_2. To estimate the solubility of these solids, I extrapolate the dissolution experiment results to conditions at which these materials most likely dissolve congruently.

The variations in the solubility products and carbonate ion activities of the second group of apatites are shown in figure 9. A linear regression for each data set was calculated and extrapolated to the point at which the carbonate activity in the dissolution experiment equals that of the pH stat experiment. The ion activity product at this point is considered the best estimate of the solubility product.

The dissolution and pH stat experimental results are compared in figure 10. The differences in the values obtained by the two methods, with the exception of pH stat expt. #30 (shown in parentheses) averages approx $10^{2.3}$. The offset may be caused by not achieving equilibrium fully in one or both of the procedures. The offset may also be caused by consistent errors in extrapolating the dissolution experiment results to the appropriate carbonate ion activities or in correcting the pH stat results from 70° to 25°C. Although there is some scatter, the trend clearly indicates a large increase in the solubility product as the carbonate content of the solid increases.

From the phosphate and fluoride compositional variations shown in table 2, the stoichiometry of the synthesized carbonate fluorapatite may be approximated as:

$$Ca_{10}(PO_4)_{5.83-0.57X}(CO_3)_X F_{2.52-0.3X}$$

where X is the carbonate content.

Using the linear regression line displayed in figure 10 to represent the variation in solubility product, the free energy of formation, ΔG_{CFAP}, may be calculated via the following equation:

$$\Delta G_{CFAP} = 10\Delta G_{Ca} + [5.83\text{-}0.57X]\Delta G_{PO_4} + X\Delta G_{CO_3} + [2.52\text{-}0.3X]\Delta G_F + RTlnK.$$

where: X = carbonate content per unit cell
T = temperature °K
R = gas constant
K = solubility product
ΔG_y = free energy of formation of species y

Using the free energy data of Rossini and others (1952), for the individual aqueous ions, the free energy of formation of carbonate fluorapatite is calculated to vary linearly from −3086 kcal/mole with no carbonate present to −3015 kcal/mole at a carbonate content of 1.45 CO_3^{2-} ions/unit cell.

IMPLICATIONS

The purpose of the final section is to discuss the implications of the carbonate effect on apatite solubility for understanding the seawater/francolite system. It must be pointed out that the behavior of naturally occurring apatites may differ from the laboratory material due to compositional and crystallographic differences. However, it is hoped that the

Fig. 10

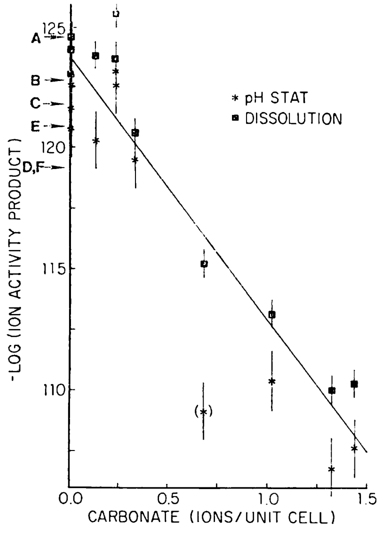

Fig. 11

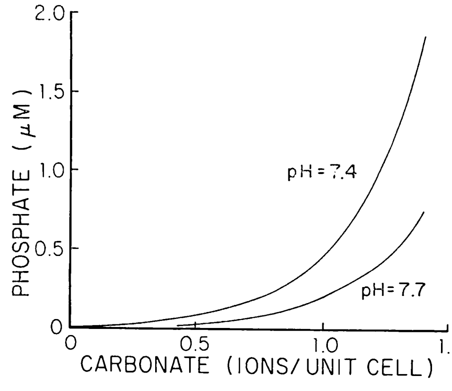

Fig. 10. Ion activity product of carbonate fluorapatite as a function of the carbonate content determined in the pH stat and dissolution experiments. The line is a linear regression of the data omitting the value obtained for sample 30 from the pH stat experiment (in parentheses). The arrows indicate previously reported solubility products for pure fluorapatite (A — Smirnova, Illarionov, and Vol'fkovich, 1962; B — Stauffer, 1982; C — Farr and Elmore, 1962; E — Valyashko, Kogarko, and Khodarkovskiy, 1968; F — McCann, 1968; and D — Hagen, 1975).

Fig. 11. The equilibrium phosphate concentration in seawater as a function of the carbonate content of apatite.

overall influence of the carbonate ion on the stability of francolite in seawater can be demonstrated.

The importance of including the effect of carbonate substitution on the solubility of fluorapatite in seawater is displayed in figure 11. The curves represent the phosphate concentration in equilibrium with fluorapatite as a function of carbonate substitution. These calculations were performed for the following conditions:

$[Ca^{2+}] = 0.01$ moles/kg

$\gamma_{Ca} = 0.2$

$[F^-] = 70\ \mu$moles/kg

$\gamma_F = 0.33$ (Miller and Kester, 1976)

Titration alkalinity = 2.4 meq/kg

$\gamma_{CO_3} = 0.024$ (Berner, 1965)

The apparent dissociation constants of phosphoric acid in seawater at 5°C reported by Atlas (1975) were used.

There is a dramatic increase in the equilibrium phosphate concentration as the extent of carbonate substitution increases. For a carbonate content of 1.4 ions/unit cell, the equilibrium phosphate concentration is 90 to 100 times that which would be in equilibrium with pure fluorapatite under the same conditions. McArthur (1978) has concluded that freshly precipitated marine apatite contains ~ 1.5 CO_3^{2-} ions/unit cell.

Previous studies of marine apatite solubility have indicated that francolite is more soluble than pure fluorapatite (Kramer, 1964; Roberson, 1966; Chien, 1972; and Atlas and Pytkowicz, 1977). However, the solubility products reported by these workers vary significantly. In light of the work presented here, several points must be considered.

The previous investigations have been performed entirely on natural apatites. Because of this, the exact compositional stoichiometry is unknown, and the solid may, in fact, consist of more than one phase. Therefore, it is not possible to assess the congruency of the dissolution of these materials. The solubility products reported by these investigators are based nearly totally on dissolution experiments and are, therefore, susceptible to the formation of surface layers during incongruent dissolution. Such phases would interfere with the solubility determination as demonstrated in figure 9 for the synthetic apatites.

To examine the suspected carbonate effect further, I have replotted Chien's (1972) data against the calculated carbonate ion activity in solution (fig. 12). I have assumed that the experimental solutions were in equilibrium with atmospheric CO_2 and had an average ionic strength of 0.1. This interpretation of his results was restricted to apatites that had not been previously extracted to avoid low carbonate surface layers that may form via such a procedure. There is a very consistent trend toward larger ion activity products at higher carbonate ion activities. This relationship is directly analogous to the one previously discussed for the synthetic carbonate fluorapatites.

I would like to suggest that the "best guess" of the ion activity product of francolite in marine systems from Chien's study is the value of the regression line shown in figure 12 which corresponds to the carbonate activity of the waters bathing the solid. For example, if the aqueous carbonate ion activity is 10^{-6} and Chien's (1972) stoichiometry for a carbonate rich francolite is used $Ca_{9.54}Na_{0.33}Mg_{0.13}(PO_4)_{4.8}(CO_3)_{1.2}F_{2.48}$, the solubility product is $10^{-99.7}$. I must caution the reader that the reinterpretation of Chien's data is speculative and demands further work before strong conclusions are made concerning the thermodynamics of the francolite/seawater system.

One should also note that a similar trend in the solubility product with the aqueous carbonate ion activity is observed in the majority of the data presented by Atlas (ms). However, Atlas also presents the results of an experiment in which he compares the solubility results obtained from equilibrations performed in atmospheric and zero CO_2 partial pressures and reports no difference. This contradicts the findings presented here. One potential explanation for this contradiction is the pretreatment procedure used by Atlas. All the solids used in these experiments were first soaked in HCl, followed by distilled water, and then seawater. If a low carbonate surface layer was formed during this pre-treatment which was not removed during the column equilibrations, the solids may appear to be insensitive to the carbonate activity (similar to the low carbonate solids #9 and 10 shown in fig. 9). Also of interest is Atlas' observation that "alkalinity changes (in the equilibrating solution) depend on the pH of prior equilibrations." Future work will be required to resolve this discrepancy.

Several important conclusions can be drawn from this work. The substitution of carbonate into fluorapatite significantly alters the chemical

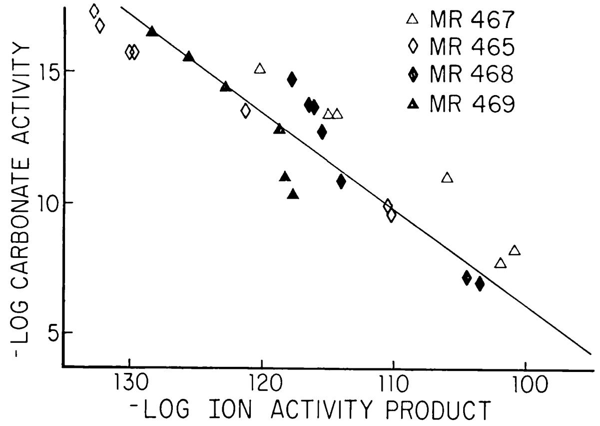

Fig. 12. The solubility data reported by Chien (ms) as a function of the aqueous carbonate activity.

stability of fluorapatite. If imagined as a solid/solution, carbonate fluorapatite is the thermodynamically stable apatite phase in high carbonate solutions such as seawater. Therefore, all marine apatites should contain similar amounts of carbonate when they form and should retain this carbonate as long as the apatite remains in seawater. A loss of carbonate from the lattice should occur only when the solid is exposed to low carbonate solutions. This is in agreement with the findings of McArthur (1978).

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