AN INVESTIGATION OF THE METHOD OF FLUORINE REMOVAL BY TRICALCIUM PHOSPHATE

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SUMMARY

It has been shown that both adsorption and ion exchange play a part in the reaction of calcium phosphate with very dilute solutions of sodium fluoride. The ratio of Ca to P in a distilled water solution of tricalcium phosphate is taken as the basis for calculating the degree of chemical reaction taking place.

Ever since Adler, Klein and Lindsay (1938) reported the use of tricalcium phosphate as a material for fluorine removal from water, a number of papers have appeared on the subject. The mechanism of removal, however, does not seem to have been dealt with exhaustively. Adler, *et al.* "assume that the removal of fluorides takes place by adsorption and that it is also possible, in view of the composition of tricalcium phosphate, that the removal of fluorides is due to the formation of a complex compound such as fluorapatite". The mechanism of fluorine removal by materials like dentine, enamel, bone and hydroxyapatite, has been investigated by means of radioactive isotopes (Volker, J. F., Wilson, H. J., and Van Voorlis, S. N., 1940) and shown to be a process of adsorption. The mechanism of fluorine deposition in bones has been investigated by means of isotopic exchange, ion competition and column techniques (Neuman, W. F., Neuman, M. W., Main, E. R., O'Leary, J., Mulryan, B. J. and Smith, F. A., 1950) and it is suggested that bone ash and synthetic apatatites behave as reversible exchange adsorbents of fluorides.

These studies on the mechanism of fluorine removal by tricalcium phosphate were undertaken in the hope of clarifying our ideas on the subject.

EXPERIMENTAL

200 c.c. of a solution of sodium fluoride in the laboratory tapwater were shaken with varying quantities of powdered "tricalcium phosphate" (B.D.H.) for one hour in a reciprocating shaker. Fluorides were estimated in the initial solution and in the filtrates by a modification of the method of Sanchis (1934), while phosphates were estimated by the method of Fiske and Subbarow (1925).

RESULTS AND DISCUSSION

The influence of the final concentration on the adsorption of fluorine by tricalcium phosphate is shown in the results presented in Table I and in the Graph. It will be seen that the points obtained by plotting log (dF) against log (final F) fall on a straight line, thus satisfying the Freundlich's equation.

TABLE I

Solution	Initial F (p.p.m.)	Final F (p.p.m.)	F removed (dF)	Phosphate as P in 200 c.c. (mg.)	Phosphate liberated as P in 200 c.c. (mg.)
0·5 g. Cal. phosphate +Dist. Water	0	0	..	1·4634	1·4634
,, +2 ppm. NaF	1·95	0·20	1·75	4·6604	3·1970
,, +2·25 ppm. NaF	2·30	0·25	2·05	4·5714	3·1080
,, +2·5 ppm. NaF	2·45	0·30	2·15	4·5714	3·1080
,, +2·75 ppm. NaF	2·65	0·35	2·30	5·0526	3·5892
,, +3·0 ppm. NaF	2·80	0·40	2·40	6·0000	4·5366
,, +4·0 ppm. NaF	4·20	0·70	3·50	5·7143	4·2409
,, +4·5 ppm. NaF	4·50	0·80	3·30	5·8253	4·3519
,, +5·0 ppm. NaF	4·80	0·80	4·00	6·1258	4·6614
,, +6·0 ppm. NaF	6·15	0·95	5·20	6·1460	4·6828
,, +7·0 ppm. NaF	6·80	1·50	5·30	6·5937	5·1303
,, +8·0 ppm. NaF	7·75	1·80	5·95	6·7168	5·2534

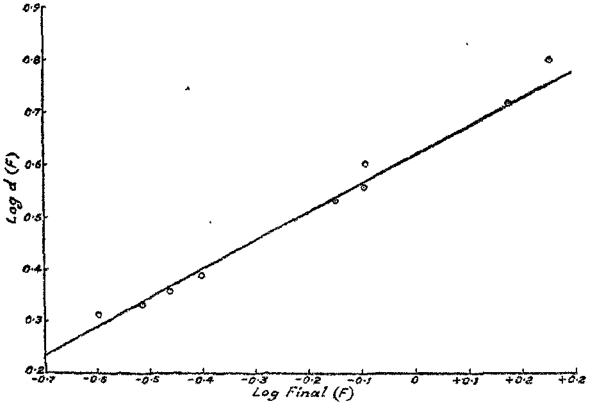

FIG. 1. Freundlich's Equation for Calcium Phosphate

Contrary to the findings of Behrmann and Gustafson (1938), we found significant amounts of phosphates in the filtrates. This difference may perhaps be due to the fact that they adopted a percolation technique and that the material used by them was also different. As can be seen from the results presented in Table I, the amount of phosphate released into solution increased regularly as the initial concentration of fluorine was increased, thus suggesting that the reaction is one of anion exchange.

While these results suggest that both adsorption and ion-exchange reactions play a part, it has yet to be shown whether fluorine is not taken up by a process of total molecular adsorption as NaF. This was sought to be studied by estimation of both Na and F ions in the filtrates. 400 c.c. of a solution (equivalent to 5 parts per million F) of sodium fluoride in distilled water were shaken for one hour with 2 gm. of tricalcium phosphate and the filtrate analyzed for F, PO_4, Na and Ca. A control experiment was conducted under identical conditions with distilled water and the same amount of tricalcium phosphate. Sodium was estimated by precipitation with zinc uranyl acetate and comparing the golden yellow colour on addition of sulphosalicylic acid and sodium tungstate to the dissolved precipitate (Darnell, M. C., Jr., and Walker, B. S., 1933). Calcium was estimated as oxalate (Murmann, E., 1910). The results of these experiments (Table II) suggest that molecular adsorption also plays a part since the content of Na is diminished.

TABLE II

Solution	Na (mg.)	F (mg.)	Ca (mg).	P (mg.)
Sod. fluoride solution ..	0·558	0·5	Nil	Nil
Sod. fluoride+cal. phosphate ..	0·359	0	1·92	1·56
Dist. water+cal. phosphate ..	Nil	Nil	1·50	1·04

Comparison of the figures for Ca in the filtrates from the experiments where sodium fluoride solution and mere distilled water were used shows that there is a greater release of Ca into solution when sodium in a solution of sodium fluoride is replacing the Ca of the calcium phosphate.

We may assume that the phosphate in the filtrate from the sodium fluoride experiment exists partly as sodium phosphate and partly as calcium phosphate, whereas in the experiment with distilled water, it would all be as calcium phosphate. Since the Na content of the filtrate in the experiment was 0·359 mgm., it accounts for 0·25 mgm. P (on the basis of Na_2HPO_4) leaving 1·56 minus 0·25, or 1·31 mg. to be accounted for as calcium phosphate, as against only 1·04 mg. present in the control experiment. This excess of phosphate should, therefore, be a measure of the Ca released from calcium phosphate by cation exchange. An idea of the calcium so released is obtained as follows:—

In solution of calcium phosphate + dist. water, 1·04 mg. P = 1·5 mg. Ca
Hence, for excess of 0·27 mg. P .... = 0·42 mg. Ca

When the figure (for Ca so released) thus obtained is compared with the actual figures for Ca as estimated in the experiment and control (1·92 and

1·50 mg. giving an excess of 0·42 mg. of Ca in the former), it is seen that the agreement is indeed very satisfactory.

Experiments in which calcium phosphate was shaken up with a solution of calcium fluoride also showed a good reduction of fluorides. The content of Ca in the filtrate was less than that which could be expected, indicating molecular adsorption (Table III).

TABLE III

Solution	Ca (mg.)	F (p.p.m.)
Calcium phos.+dist. water ..	2·8026	Nil
Solution of calcium fluoride ..	1·5570	2·6
Total Ca expected ..	4·3596	..
Cal. fluoride solution+dist. water	3·0102	1·1
Reductions ..	1·3494	1·5

It would thus appear that the reaction of tricalcium phosphate with fluorides in very dilute solutions such as are met with in natural waters is not simple. There appears to be suggestive evidence that fluorine removal may be due partly to the adsorption of the entire molecule of sodium fluoride or calcium fluoride and partly to the replacement of PO_4 of the $Ca_3(PO_4)_2$ by the F in solution. In addition to the above, there also appears to be evidence to suggest that the Ca in tricalcium phosphate can be replaced by the Na of the sodium fluoride.

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