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THE ACID SOLUBILITY OF TOOTH ENAMEL AS AFFECTED BY VANADATE IONS

by

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In accordance with other bone-seeking ions, as *e.g.* P, Ca, Sr, and F, also vanadate was found in considerable concentration in the zones of rapid bone and tooth growth (*Söremark & Ullberg,* 1961, *Söremark, Ullberg & Appelgren,* 1962). *Rygh* (1949) found that the mineralization of teeth and bones of rats during the period of development was promoted by vanadium as well as by strontium. He also found the largest number of carious teeth in animals fed a vanadium and strontium deficient diet. No carious teeth appeared when the amount of the elements in question was increased in the synthetic diet employed. Later, the caries inhibiting effect in hamsters was tested by adding only 0.04—0.08 mg V_2O_5 daily to a caries-producing diet, and a pronounced inhibiting effect on the enamel and dentinal caries was found (*Geyer,* 1953). On the other hand, it has been found that hamsters receiving V_2O_5 in the drinking water in the high concentration of 10 p.p.m. developed higher caries scores than did the control animals (*Hein & Wisotzky,* 1955). Neither did *Muhler* (1957) find any reduction in the dental caries of a large number of rats, which had received vanadium pentoxide (10—40 μg/ml) in their drinking water. He found that V_2O_5 solution had a

highly toxic effect on the experimental animals. Recently, *Shaw & Griffiths* (1961) reported no significant influence on the dental caries incidence of caries-susceptible rats fed vanadium pentoxide and vanadyl sulphate. Vanadium pentoxide was given in the drinking water at levels of 18 and 36 p.p.m. or in the diet at 18 p.p.m. They found a higher rate of growth of the vanadium-supplemented rats; this seems to be in agreement with the observation by *Rygh* (1949). A significant reduction of dental caries was found in humans consuming drinking water which contained 0.07—0.22 p.p.m. vanadium (*Tank & Storvick*, 1960).

From theoretical considerations it has been suggested that vanadium replaces phosphorus in the hydroxy apatite crystals, and incorporated in enamel and dentine it could increase the hardness of the hydroxy apatite as well as the cohesion between the organic and inorganic matter (cf. the review by *Underwood*, 1956). V_2O_5 and some other vanadium compounds have been reported to be active in reducing the acid solubility of enamel (*Manly & Bibby*, 1949). However, recently the solution rate of synthetic hydroxy apatite was studied in 0.2 M acetate buffers, pH 4.2, 5.2, and 6.0, containing some foreign ions in concentrations of 0.1 mM or less (*Speirs, Spinelli & Brudevold*, 1961). The solution rate was determined by estimating the weight loss of the solid and the release of Ca and P. Of the ions studied only F, Zn, and Pb reduced the solution rate of the synthetic hydroxy apatite; VO_3 or SeO_3^{2-} or $Mo_7O_{24}^{6-}$ did not depress the solution rate.

In the present paper the acid solubility of human tooth enamel (intact surfaces and powdered) after exposure to solutions containing various concentrations of some vanadium compounds has been studied.

MATERIALS AND METHODS

For each series of tests four caries-free, intact bicuspids were used. The teeth were washed in physiological saline and buffed slightly with a cotton wheel to remove debris. The crowns were separated from their roots with a diamond wheel, and then halved longitudinally in a bucco-lingual direction. The cut areas of the teeth were covered with wax leaving only surface enamel

exposed. Each tooth and its halves were labelled and placed in test tubes. Five ml 0.2 M acetate buffer solution pH 5.0 were added to each tube after which the tubes were stoppered and shaken gently for 2 hours. The solution of each test tube was analyzed for calcium+magnesium using an EDTA-Eriochrome Black titration method, and phosphorus using a molybdenum blue method. To obtain evenly matched experimental and control sets, the crown-halves were grouped so that the sum of Ca+Mg and P concentrations, respectively, of four halves equalled, as closely as possible, the other four halves.

The eight crown-halves were washed in distilled water, after which the experimental set of four halves were subjected to shaking in a solution containing vanadate ions (pH = 7), while the corresponding controls were shaken in physiologic saline. Following this procedure the teeth were rinsed in distilled water and shaken again for two hours in the acetate buffer which was analyzed for Ca + Mg and P concentrations. These figures were tabulated.

In each of the fifteen series run the vanadium-containing solution was different, or the concentration was different, or the time of shaking in the solutions was varied.

Table 1.

Dissolution from intact enamel surfaces (mM/l). The control halves were shaken in physiologic saline solution.

Vanadium compound tested	Concentration mM	Shaking time min	Quantities dissolved			
			Testhalves		Controlhalves	
			Ca + Mg	P	Ca + Mg	P
Vanadium pentoxide	0.5	2	4.11	5 15	3.87	5.67
»	»	5	2.96	1.76	2.86	1.66
»	0.05	2	3.54	2.21	3.79	2.11
»	»	5	3.69	2.42	3.57	2.54
»	»	10	3.00	1.23	3.86	2.72
»	»	15	3.46	4.03	3.73	4.59
»	»	30	3.35	3.54	3.49	3.02
»	0.005	5	3.95	2.38	3.76	2.17
»	»	10	4.35	2.37	4.89	2.91
»	»	15	5.44	3.57	5.45	4.02
»	»	30	6 40	3.90	6.26	3.43
Na-metavanadate	0.05	10	1.53	0.82	2.39	1.48
»	»	15	2.30	1.30	2.30	1.69
Na-orthovanadate	»	10	2.46	2.13	1.69	1.52
»	»	15	1.76	1.45	1.72	1.49

Table 2.

Dissolution from enamel powder (mM/l). 100 mg powder samples with particle size 40-100 mesh.

Compound tested	Concentration mM	Shaking time min.	Quantities dissolved Ca + Mg	mean	P	mean
Sodium chloride	0.3	5	2.50; 2.73; 2.61; 2.64	2.62	1.27; 1.23; 1.35; 1.30	1.29
»	»	10	2.15; 2.60; 2.25; 2.20	2.30	1.16; 1.20; 1.25; 1.10	1.18
Vanadium pentoxide	0.5	5	2.40; 2.56; 2.45; 2.60	2.50	1.16; 1.23; 1.14; 1.17	1.18
»	0.05	5	2.35; 2.30; 2.40; 2.62	2.42	1.17; 1.17; 1.20; 1.16	1.18
»	»	10	2.25; 2.35; 2.56; 2.50	2.42	0.97; 1.20; 1.11; 1.15	1.11
Na-metavanadate	»	5	2.26; 2.45; 2.30; 2.28	2.32	1.04; 1.16; 1.21; 1.13	1.14
»	»	10	2.25; 2.15; 2.16; 2.06	2.16	1.32; 1.26; 1.18; 1.20	1.24
Na-orthovanadate	0.5	5	2.60; 2.31; 2.55; 2.10	2.39	1.20; 1.26; 1.15; 1.32	1.23
»	»	10	2.33; 2.46; 2.35; 2.61	2.44	1.30; 1.41; 1.26; 1.18	1.29
»	0.05	5	2.23; 2.22; 2.31; 2.41	2.29	1.19; 1.28; 1.27; 1.14	1.22
»	»	10	2.66; 2.52; 2.46; 2.63	2.57	1.21; 1.29; 1.20; 1.36	1.27
Sodium fluoride	0.5	»	1.70; 1.41; 1.66; 1.59	1.59	0.70; 0.67; 0.74; 0.72	0.71
»	0.05	»	1.96; 2.00; 1.88; 2.07	1.98	0.90; 1.07; 1.00; 0.82	0.95

In eleven series of tests powdered enamel was used with 4 samples in each series; the above-mentioned method for obtaining matched groups of course does not apply to these series. For these tests 100 mg powdered enamel samples of particle size 40—100 mesh were used. The samples were shaken in 5 ml of various vanadium solutions at pH 7. The vanadium solutions tested were vanadium pentoxide, sodium orthovanadate, and sodium metavanadate, in concentrations of 0.5 mM, 0.05 mM, and 0.005 mM; the shaking periods were 5 and 10 minutes. For comparison, two series were subjected to 5 ml dilute (0.5 mM and 0.05 mM, pH = 7) NaF solutions. Two control series were shaken in 0.3 mM NaCl, 5 ml.

RESULTS AND DISCUSSION

At pH 7 and the concentrations and other conditions used in the present study it will seem that $H_2VO_4^-$ and $H_3V_2O_7^-$ ions are the most abundant, but also $H_2V_2O_7^{2-}$, $HV_2O_7^{3-}$ and VO_3^- ions are present in the test solutions.

From the tabulated concentrations of Ca + Mg and P the following observations were made. In some of the series there was

a slight decrease in the amounts dissolved by the acetate buffer from the vanadium-treated teeth as compared with the NaCl-treated teeth. In some other series, on the other hand, somewhat more Ca + Mg and P was found in the acetate buffer of the vanadium-treated teeth than in that of the controls. And again, in most of the test series no appreciable differences were observable.

The series of tests using powdered enamel instead of intact crowns showed no decrease in the acid solubility of the enamel after subjection to an environment of vanadate ions.

Of interest was that the powdered enamel treated with 0.5 mM NaF solution showed a pronounced decrease in its acid solubility. This is in accordance with previous investigations (cf. *Brudevold,* 1962).

From the results of this study no support can be derived for the theory that enamel becomes less soluble in weak acids after subjection to solutions containing vanadate ions.

SUMMARY

The solubility of human tooth enamel (intact surfaces and powdered) in 0.2-M acetate buffer pH 5.0 was studied after exposure of the enamel to neutral solutions containing vanadium pentoxide, sodium orthovanadate or sodium metavanadate of 0.5-mM, 0.05-mM or 0.005-mM concentration. Neither the intact surfaces nor the enamel powder showed any reduction of the solubility after treatment with these vanadium compounds, as compared to saline-treated controls. Treatment of the enamel powder with 0.5-mM sodium fluoride solution substantially reduced the acid solubility.

RÉSUMÉ

EFFET DE COMBINAISONS VANADEUX SUR LA SOLUBILITÉ D'ÉMAIL DENTAIRE EN ACIDE

Après avoir exposé de l'émail dentaire humain (pulvérisé et surfaces intactes) à des solutions neutres contenant du pentoxyde de vanadium ou de l'orthovanadate ou métavanadate de sodium, en concentration 0,5-, 0,05- ou 0,005-millimolaire, ou étudia la solubilité de l'émail dans une solution tampon d'acétate de pH 5,0.

Ni les surfaces intactes, ni l'émail pulvérisé ne montrèrent aucune réduction de la solubilité après le traitement avec ces combinaisons de vanadium. Un traitement de l'émail pulvérisé avec une solution 0,5-millimolaire de fluorure de sodium reduisit considérablement la solubilité de l'émail pulvérisé dans la même solution tampon.

ZUSAMMENFASSUNG

EINWIRKUNG VON VANADIUMVERBINDUNGEN AUF DIE SÄURELÖSLICHKEIT DES ZAHNSCHMELZES

Die Löslichkeit menschlichen Zahnschmelzes (intakter Flächen und pulverisierter Substanz) in 0,2-M Azetatpuffer pH 5,0 wurde untersucht, nachdem der Schmelz mit Vanadinpentoxyd, Natriumorthovanadat oder Natriummetavanadat in 0,5-mM, 0,05-mM oder 0,005-mM neutraler Lösung behandelt worden war. Weder die intakten Schmelzflächen noch das Schmelzpulver zeigten eine deutliche Herabsetzung der Löslichkeit nach der Einwirkung von diesen Vanadiumverbindungen. Schütteln mit 0,5-mM Natriumfluoridlösung reduzierte dagegen erheblich die Säurelöslichkeit desselben Schmelzpulvers.

REFERENCES

Brudevold, F., 1962: Fluorides in prevention of dental caries. Dent. Clin. N. Am. p. 397.

Geyer, C. F., 1953: Vanadium, a caries-inhibiting trace element in the Syrian hamster. J. dent. Res. *32*, 590.

Hein, J. W. & J. Wisotzky, 1955: The effect of a 10 ppm vanadium drinking solution on dental caries in male and female Syrian hamsters. J. dent. Res. *34*, 756.

Manly, R. S. & B. G. Bibby, 1949: Substances capable of decreasing the acid solubility of tooth enamel. J. dent. Res. *28*, 160.

Muhler, J. C., 1957: The effect of vanadium pentoxide, fluorides, and tin compounds on the dental caries experiences in rats. J. dent. Res. *36*, 787.

Rygh, O., 1949: Importance of trace elements in nutrition. Research, suppl. 2—7, 340.

Shaw, J. H. & D. Griffiths, 1961: Developmental and postdevelopmental influences on incidence of experimental dental caries resulting from dietary supplementation by various elements. Arch. oral. Biol. *5*, 301—322.

Speirs, R. L., M. Spinelli & F. Brudevold, 1961: Solution rate of hydroxyapatite in acetate buffers containing low concentrations of foreign ions. J. dent. Res. *40:* 704.

Söremark, R. & S. Ullberg, 1961: Distribution and kinetics of vanadium pentoxide in mice. Proceedings of the IAEA Conference in Mexico City, p. 103.

Söremark, R., S. Ullberg & L.-E. Appelgren, 1962: Autoradiographic localization of vanadium pentoxide ($V_2{}^{48}O_5$) in developing teeth and bones of rats. Acta odont. scand. *20,* 225.

Tank, G. & C. A. Storvick, 1960: Effect of naturally occurring selenium and vanadium on dental caries. J. dent. Res. *39,* 473.

Underwood, E. J., 1956: Trace elements in human and animal nutrition. Academic Press, New York.

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