Occurrence, Pathological Aspects, and Treatment of Fluoride Waters*

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ADEQUATE proof that minute amounts of fluorine as fluorides in drinking water produce an imperfect enamel structure in the teeth during the formative period of the enamel has created a serious problem in water supply, not only throughout the nation, but throughout the world in general. Furthermore, the action of fluorine may not be confined to the teeth, but may have pathological effects upon other parts of the body structure. On the other hand, no proof has been brought forward to show that it is altogether a useless or harmful element rather than an element active and needed in minute quantities such as is the element of copper. That body well-being can be maintained on extremely minute quantities of fluorine as it can be on minute quantities of the essential element iodine is found in the fact that many waters contain only very small quantities of fluorine yet cause no outstanding apparent defects in body metabolism. Few waters can be found that do not show as much as 50 micrograms of fluorine per liter, which is the approximate amount of iodine required daily to prevent simple goiter.

The problem, without doubt, is to provide drinking water which contains a minimum amount of fluoride, since mottled enamel, which is produced at levels of at least 1 p.p.m. and above, is certainly evidence of definite ab-

Table I

Showing Relation of Fluoride to Incidence of Mottled Enamel in Children

City and State	Fluoride Content in p.p.m.	Composite of 9, 10, and 11 Year Old Children: Number of Children Examined	Composite of 9, 10, and 11 Year Old Children: Incidence per 100 Children
Junction City, Kans.	0.7	115	1.7
East Moline, Ill.	1.5	110	24.5
Webster City, Iowa	1.6	72	26.4
Clovis, N. M.	2.2	138	71.0
Plainview, Tex.	2.9	77	87.0
Amarillo, Tex.	3.9	229	89.5
Conway, S. C.	4.0	59	88.1
Lubbock, Tex.	4.4	164	97.6

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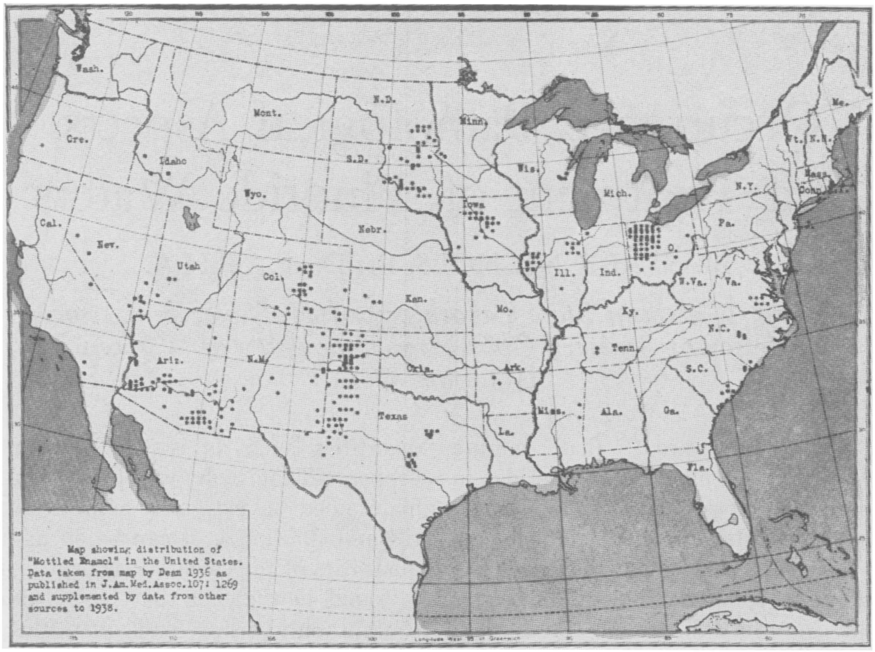


FIGURE I—Distribution of mottled enamel in the United States up to 1938

normal physiology, as proved by Dean, Dixon, and Cohen.[1]

In Table I, taken from report by Dean and Elvove,[27] are shown data for the incidence of mottled enamel in children correlated with the fluoride content of waters from widely separated cities in the United States. Such a correlation as shown is rather conclusive evidence that fluorides alone are responsible for the mottled enamel since the mineral content of these waters and the diets of the children examined from so many divergent localities are bound to be different.

Water supplies low in fluorides must be obtained either by the selection of a suitable water free from excessive amounts of fluorides or treatment of unsuitable supplies to reduce the fluoride to the "safe" level. Waters known to contain excessive amounts of fluorides are widespread throughout the United States and evidence is fast accumulating that such waters are found widely distributed throughout the world. In Figure I is shown the distribution of areas known to have mottled enamel and in most cases the waters are known to contain excessive fluorides. The question naturally arises: From what stratum or source do these fluoride waters arise? McKay in 1918 [2] pointed out that the inhabitants of many endemic areas used artesian water. He also pointed out that the artesian waters of the great plains were obtained from the Dakota sandstone and that the original source of this water was the east side of the Rocky Mountain watershed. In general fluoride waters are derived from wells but not necessarily from sandstone. In Ohio [3] many of the fluoride waters appear to rise in the limestone. In the Colorado Springs area the surface water from Pike's Peak watershed seems to be the source of the fluoride, and such water entering the western outcrops of the Dakota sandstone and underlying sedimentary formations at the Rocky Mountains may furnish the

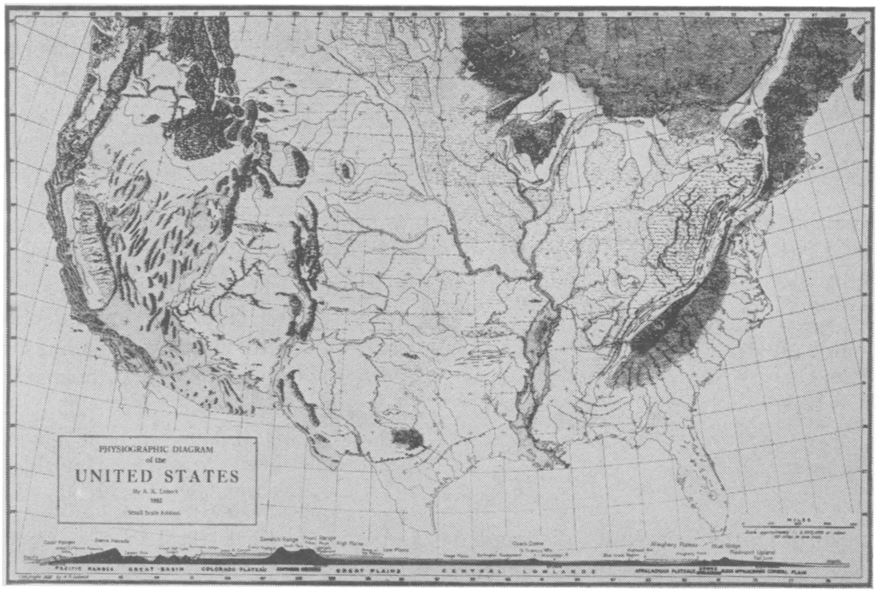


FIGURE II—Areas of igneous rocks (dark) with possible relationship to entrance of percolating fluoride waters

fluorides in many places in the western plains, including the large endemic area of northwestern Texas.

In Figure II a relief map of the United States shows the general geologic conditions. Note the Piedmont areas adjacent to the igneous protrusions into which drainage water from igneous formation percolates. The presence of mottled enamel in areas adjacent to Mt. Vesuvius in Italy appears to have been associated with waters which had their origin on the laval surfaces of that volcano. In gases from volcanoes and fumaroles fluorine compounds [5] have been found. Geologic data bearing on the probability of procuring fluoride-free ground water would provide assurance to the municipality that a given well development would probably be successful. That such data ever will permit of definite interpretation is by no means certain since fluoride compounds are very widely distributed in many types of rock formation.

Since fluorine is a very reactive element it is seldom found free in nature. Calcium fluoride, fluorite, CaF_2 and cryolite the double salt of sodium and aluminum with fluorine are two of the naturally occurring minerals which contain large quantities of fluorine. The origin of all fluorine bearing minerals is of course the igneous rocks underlying all sedimentary formations. Recorded analyses of several thousand igneous rock structures as compiled by Washington [6] and which give results for fluorine in about two hundred analyses, show this element to be present in about 85 per cent of the igneous rocks tested. The amount of fluorine contained in these rocks varied from 0.01 to 3.36 per cent, with an over-all average of 0.23 per cent.

In Table II are given results showing that there were only 40 rocks of the 172 that contained more than the average amount of fluorine and that of these there were only 8 which contained the element in amounts above 1.0 per cent. Fluorine was found in not only many different kinds of rocks but it

TABLE II

Showing Distribution of Fluorine Content as Found by Analyses of 172 Igneous Rocks from Different Parts of the World

Content of F. Per cent Incl.	Number of Different Rock Specimens Showing F.	Per cent of Total Numbers of Rocks Showing F.
0.01 to 0.05	57	33.2
0.06 to 0.09	35	20.3
0.1 to 0.23	40	23.3
0.24 to 0.50	19	11.0
0.51 to 1.00	13	7.6
1.01 to 3.36	8	4.6
Above 3.36	None	
Total	172	100.0

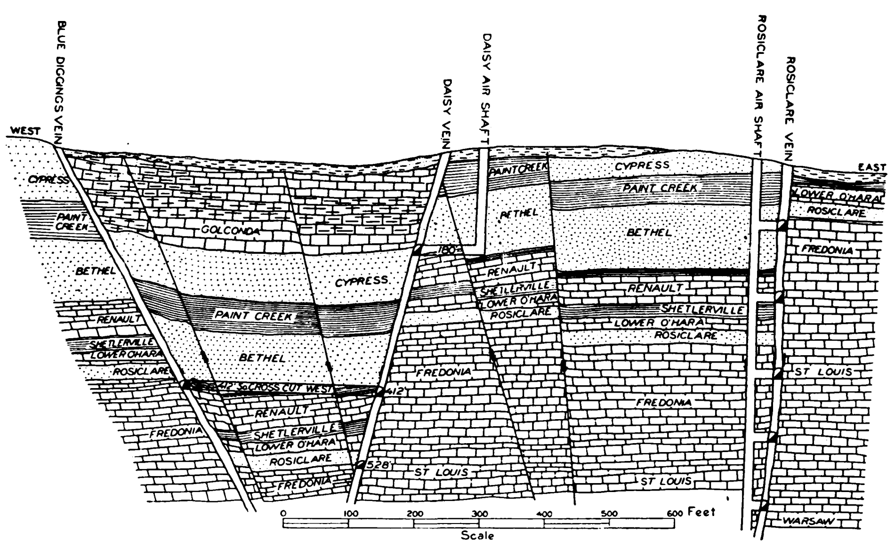
was also rather evenly distributed among the various classes of igneous rocks. The occurrence of fluorides in sedimentary formations seems to be still more erratic than that in primitive rocks.

A study of the fluorspar deposits of southeastern Illinois and northwestern Kentucky shows that these were laid down along fault and fissure lines as shown in Figure III, which is taken from work by Bastin.[7] Note that the fluoride is laid down vertically and horizontally as a vein mineral in these deposits. According to Fohs [8] these deposits of fluorspar were depositions resulting from thermal waters laden with fluorides or fluorsilicates arising in the igneous rock formations, ascending and spreading laterally through these fissures which developed along the faults in the sedimentary formations. He states:

> These several deposits occur both filling open cavities and as replacement of adjacent rock . . . Likewise they occur in tabular deposits, filling vertical or inclined faults or fissures, as horizontal deposits along bedding planes, faults or replacing bedded strata and filling stock works: hence irregular in outline.

There is in these findings an indication that faults and fissures which extend upward from primary rock strata are important geologic signs of fluoride bearing waters. Near the location of the fluoride water area in northeastern

FIGURE III—Faults and fissures in sedimentary formations permitting thermal magmatic fluoride bearing waters to ascend and spread laterally (*Drawing from Bastin*)



Diagrammatic cross-section showing stratigraphic and structural relations in the vicinity of Rosiclare.

Wisconsin are known to exist faults, and their proximity suggests a possible cause for these few fluoride waters of that state. A similar condition exists in the fluoride area between Moline and Peoria, Ill. The derivation of fluorspar deposits suggests also that no particular limestone strata can be held responsible for fluoride waters but that any of the sedimentary formations could be interspersed with fluoride deposits. It appears, however, that replacement deposits as well as deposits filling cavities are more likely to occur in limestone formations since these are known to be subject to channel formations which are favorable to depositions as well as re-solution.

Sundstrom and McKee [10] show by means of well packers that fluoride in amounts of about 2.0 p.p.m. is present in both limestone and sandstone water from a well drilled 916 feet to granite in Wisconsin's fluoride area.

Fluorapatite, $Ca_5(PO_4)_3F$, is another mineral which may be responsible for the presence of fluorides in natural waters, as it is a rather common constituent of all classes of rocks—igneous, metamorphic, and sedimentary, and forms the source of fluorine in the phosphate rock deposits of Florida, Tennessee, Virginia, Idaho, and Montana. The fluorine content of these materials varies from practically zero to 4 per cent, and the presence of this element in these products, which are used both for fertilizer, as a supplementary mineral in stock feeding, and as a source of phosphate in baking powders, has occasioned much experimentation on the physiological effect of fluorine on both animal and plant life.

PATHOLOGICAL ASPECTS OF FLUORIDES

De Eds [11] and McClure [12] have recently made excellent reviews of the subjects up to 1933. Of the vast amount of material avaliable in this literature of nearly 150 articles, only a few outstanding points can be given here. Fluorine as fluorsilicates, sodium fluoride, rock phosphate, and calcium fluoride show toxicity to the animal body in the order given and in comparatively small amounts. Leake in 1928 [13] showed 87.5 mg. of sodium fluoride per kg. when given intravenously to be fatal for rabbits in about 40 minutes. Many cases of fluoride poisoning of humans are to be found in the literature and as little as 4 gm. has proved fatal when taken by stomach.

The chronic poisoning by fluorides is an entirely different matter. Here the changes in body tissue are gradual and adjustments to the fluoride intoxication are made so that pathological evidence of toxicity is difficult to gather. Interpretation of animal toxicity experimentation in terms of human reaction is frequently difficult. It is a well known fact that the dose of certain drugs for dogs is 15 times as much as for man on an equivalent weight basis. Differences in life span and age at chemical maturity as well as species tolerances of adverse environment need be given their proper value when transposition of experimental results are made. Thus, Smith, Lantz, and Smith [14] noted in their preliminary experiments on St. David water (F. from 4.2 to 7.1 p.p.m.) that "No destructive effect of the St. David water on the teeth of the rats was noticed when the diet was adequate in all respects." However, when rats were given this same water concentrated by evaporation to 10 times the original mineral content (F. 42 to 71 p.p.m.) gross defects (mottled enamel) occurred in the teeth within 1 month's time. While on the other hand, children using the unconcentrated St. David water developed mottled enamel practically 100 per cent. Such a result is explained on the basis of the rapidity of growth of the tooth structure of the rat as compared to humans.

Evidence has also been obtained that

the fluoride in some tissue may be present as an immobilization phenomenon since analyses have shown it to be present in all tissues. In muscle it is found present from 0.4 to 4.6 p.p.m.; from 1,180 to 1,800 p.p.m. in dental enamel, with a value of 700 p.p.m. for bone calculated to a dry basis. Normal results for fluorine in tissue is difficult to ascertain since all foodstuffs have been found to contain fluorine in varying amounts depending upon the locality of production. Analyses show an average of over 5 p.p.m. for fluoride in 32 edible food substances and 26.5 p.p.m. for 63 plant products with more fluoride in leaves than in stems and in skin of fruit than in pulp.[12]

Phillips, Hart, and Bohstedt [15] found that an intake of 2 to 3 mg. per kg. of body weight per day (1.5 gm. of fluoride per cow) was the upper limit of tolerance for dairy cows. Even at this level toxic changes are manifest in the teeth and bones as seen from photographs by these authors. The fluorine content of the bones and teeth of these same dairy cows as reported by Chang, Phillips, Hart, and Bohstedt [16] showed a great increase (10 to 20 times, depending upon the amount of fluoride fed), but liver, muscle, hair, and hoof remained practically unchanged. The thyroid glands, however, increased in fluorine content from 125 to 240 times the normal. Data by Evans and Phillips [17] just published (1938) show fluoride content of the thyroid gland in hyperthyroidism to vary from 1.5 to 95 p.p.m. and all those containing more than 20 p.p.m. of this element were associated with a high basal metabolic rate, with one exception.

Sharpless and McCollum [18] in answer to the question, "Is fluorine an indispensable element in the diet?" state in part that: "No difference could be noted between these and the control rats which were fed fluorine" (an amount equivalent to that taken on a normal diet). "The rats on the low fluorine diet looked very well, were quite fat, and on the whole appeared normal." The teeth of these low fluorine rats were free of fluorine as far as could be determined, yet showed no gross deficiency or defect. From the description of the diet and methods of analyses used by these authors their low fluorine diet contained less than 1.0 p.p.m. F.

Ellis and Maynard [19] used rats and fed sodium fluoride or bone meal equivalent in fluorine content to the extent of from 8 to 14 p.p.m. in a diet which contained 3.0 p.p.m. fluorine. They noted deposition of fluorine in bones and teeth with a lightening of the enamel in the teeth of those fed the diet plus added fluorine. No lightening occurred in those eating basal diet with 3.0 p.p.m. fluorine.

While no definite knowledge is yet available to show that fluorine is necessary for body function, there is much definite evidence that it is a toxic poison whose intake should be reduced to the lowest limit possible. Mention should be made of the recent finding of Dean,[20] however, that the dental caries attack rate is only about one-half as great in those children using fluoride waters and having mottled enamel as in children using water low in fluorides.

THE TREATMENT OF FLUORIDE WATERS

In those geographic areas in which excessive amounts of fluorides (1.0 p.p.m.) are present in the water supply the authority has three courses of action from which a choice need be made. (1) Remove the fluoride from the supply then in use. (2) Sink other wells in a different locality or stratum as advised by a competent geologist with the hope of procuring a safe and satisfactory supply low in fluorides. (3) Develop any available surface water supply which is found to be low in fluoride, adequate in quantity, and capable of treatment by ordinary purification procedures so that a safe and suitable water may be obtained.

In many areas removal of fluoride seems to be the only method available since no surface supplies are obtainable and all ground waters show fluorides. Such a situation is reported to be present in the Texas " Panhandle " fluoride area which, according to Dean, Dixon, and Cohen,[1] constitutes the largest mottled-enamel area in the United States. Laboratory and semi-plant scale experimentation on the removal of fluorides followed rather slowly the discovery that fluorides in amounts above 1.0 p.p.m. was the cause of mottled enamel in teeth. Boruff [21] published the first results on removal and came to the conclusion that treatment of water with alum (10 gr. per gal.) would reduce the artificially prepared sodium fluoride waters from 5.0 p.p.m. to less than 1.0 p.p.m. Activated alumina was found efficient in reducing the fluoride content from 5.0 p.p.m. down to from 0.5 to 2.3 p.p.m., depending upon the rate of filtration and quantity of water treated. He also reported a 60 per cent reduction by lime softening.

Swope and Hess [22] carried out tests with Defluorite (activated alumina at that time) on Chetopa, Kans., water with a resulting reduction in fluoride content from 6.2 to less than 1.0 p.p.m., but such a process, to the author's knowledge, has not been employed by any municipality.

Scott, Kimberly, Van Horn, Ey, and Waring [3] have found that fluorides may be removed by lime treatment at high pH values provided the water contains sufficient magnesium. Such treatment to be effective required removal of 91 p.p.m. magnesium in order to reduce the fluoride from 3.0 to 1.0 p.p.m., the safe level.

Elvove [23] has reported that fluorides can be removed from water with the aid of tricalcium phosphate, magnesium oxide, or magnesium hydroxide, but states that the question of cost must be solved before it can be applied on a practical basis. MacIntire and Hammond [24] and Adler, Klein, and Lindsay [25] nearly simultaneously, have published experiments on fluoride removal by means of tricalcium phosphate with similar success but the latter authors appear to have pointed to a rather practical means of application of the treatment, that is, by using it as a filtering material. It is of interest to note that these authors prepared their chemical from commercial phosphoric acid of high purity and milk of lime of such proportions that a mixture of hydroxy apatite $3Ca_3P_2O_8Ca(OH)_2$ and tricalcium phosphate $Ca_3P_2O_8H_2O$ results and constitutes the material now sold as Defluorite.

Regeneration of the bed with 1 per cent sodium hydroxide followed by washing, neutralization of residual alkali with dilute HCl and subsequent washing was practised but about 3.0 per cent of bed was lost per regeneration. They found this chemical to have more than twice the capacity of activated alumina used by Swope and Hess or 1.8 gm. of fluoride per kg. of filter bed. The initial cost of this removal material, the fact that 3 per cent of the bed was lost with each regeneration, besides the cost of chemicals for regeneration, have militated against any notable installations of the process.

Recently, Behrman and Gustafson [26] have improved the method of regeneration of Adler, Klein, and Lindsay [25] by the use of carbon dioxide in place of hydrochloric acid for the neutralization of residual alkali and have shown that the filter bed of chemical can be used indefinitely without any loss of filtering material. Moreover, it is possible to employ ordinary materials of construction and equipment when carbon dioxide is the neutralizing agent. The improvement is covered by a patent application. Since only a very small fraction of a water supply is used for drinking and cooking, individual household units have been proposed which will treat a stated quantity of water of certain fluoride content, but if these are not controlled, a false sense of security will prevail at times when the capacity of the unit is spent.

Experimental work done in this laboratory with softening a water containing a total hardness of 240 p.p.m. with a fluoride content of 2.8 p.p.m. reduced the fluorides to 1.3 p.p.m. This water when treated with 10 grains of alum per gallon and filtered shows 50 per cent removal of fluorides. Neither ferric hydroxide nor hydrated manganese dioxide had any sorptive effect upon the fluorides.

Many phases of the fluoride problem are still unsolved and with the results of extended experimentation into the physiological effects of minute amounts of fluorides may come a demand upon both the chemist and geologist for fluorides lower than the present permissible limit of 1.0 p.p.m.

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