CURRENT STATUS OF THE FLUORINE METHOD OF AGE DETERMINATION[1]

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As a result of Oakley's extensive use of fluoride incorporation as a dating index for archeological bone specimens, and with his unquestioned success in obtaining convincing RI, and, on occasion, RII data, the determination of this element in fossil bone is today a very popular tool. We felt that it was appropriate and advisable to examine more profoundly the limitations involved in the application of fluoride fixation to archeological work. In the course of this fairly systematic investigation and review of the uses of the method several interesting speculations presented themselves. Also, some pertinent questions arose regarding the objective validity of the method as it is employed at present.

Let us examine the chemistry of the procedure: in 1956 at Chicago, Oakley mentioned that his 1953 fluoride analyses presented an improvement in precision of the chemical procedure over his 1949 determinations. We were unable to find anywhere a published report by his chemists of this improvement in method, nor does he refer to such in any bibliography. However, the procedure used in 1949 was fully described by Hoskins and Fryd, Oakley's chemists, in the J. of Appl. Chem., 1955. The method is the classical one of Willard and Winters; a quantitative fluoride analysis which has been in use for the past 25 years. Hoskins and Fryd have utilized the micro adaptation of the original method, but even so, the lower limit exceeds quantitatively the range in which they found themselves working with archeologically recent bone specimens, so that they had to extrapolate the concentration curve of fluoride to zero and compensate for the introduction of interfering salts by a so-called "internal blank". This manipulation of the method, though not in itself without justification, is not the most satisfactory way of quantitatively determining trace amounts of chemicals or elements such as fluoride. It would be interesting to learn what the English laboratory has done to improve its procedures that have brought more precision to the 1953 data, as Oakley stated.

Wholly apart from Oakley's work the advent of radio isotopes leads to the possibility that new micro methods for the determination of traces of fluoride could be developed. The standard isotope dilution method would very likely be appropriate for use with such chemically heterogenous materials as bones and soils. However, the fact that the half-life of F^{18} is only 112 minutes means that ready access to the isotope as soon as it is formed would be necessary. Another method, activation procedure, would probably prove most straightforward and accurate. Possibly mass spectrography can offer a spectacular and simplified means of quantitating the small amounts of fluoride found in bones. However, the application of the mass spectrograph to bone analysis is hardly an hypothesis at this time. It might very well be that the mechanics involved would prohibit the application of this instrument for bone analysis.

Aside from isotope methods it has occurred to us, since fluoride is a specific enzyme inhibitor, that a biological assay technique could well be devised to quantitatively detect such limited amounts of fluoride as .01 of 1% by weight, or, in

absolute amounts, as little as 500 gamma.

Though not directly concerned with this paper we would like to state that when there is any consideration of methods based on F^{18}, such as those just mentioned, thoughts are directed, perhaps by association, to C^{14} dating. There is no particular tie-up between the two methods, nor is there any reason to assume that results of the two methods would in any way be related. To our knowledge, no C^{14} dating on bone material itself has ever been published, since it is obvious that both the inorganic C and organic C will be radioactive. Of course, as Oakley suggested in 1956, it would be relatively simple to remove the organic carbon from bone by hydrolysis and count it separately. How to get rid of the foreign invasion organic carbon would have to be kept in mind, since it has not yet been possible to remove the muccopolysaccharides, osseins and collagens intact from bone, fresh or fossil.

We may turn now to the mechanism of fluoride fixation in biological systems, especially bone. Oakley has stated in Anthropology Today the theoretical maximum fluoride content of fossil bones is 3.8%. We were unable to find his reference for this figure, and this led us to wonder whether it was derived empirically by laboratory investigations of the saturation curve of fossil bones in different soil - water concentrations of fluoride, or whether this figure is based on theoretical calculation assuming a one-for-one replacement of hydroxyl ion by fluoride ion in the apatite molecule. Other investigators in osseons systems, living and non-living, find a more complex situation exists than simple replacement of one ion for another. The relationship between the available apatite lattice surface area and the amount of fluoride affixed is of primary importance to understanding the mechanism. Initially it needs to be clearly and conclusively demonstrated by experimental investigation whether the organic phase of bone is or is not at all involved in fluoride fixation. P. C. W. Durbin in 1953 with in vivo studies on rats has shown by radioautographs the areas of deposition of fluoride in bone. The paths of vascularization, the periosteum and endosteum, marrow cavities and epiphysis are loci for concentration of fluoride. She found that the areas of compact bone in the long bone shafts have a meagre deposition of fluoride, and that this follows the Volkmann and Haversian systems closely. We may raise the question as to what happens to fluoride deposition in biologically inert material such as bone exposed to a foreign environment. We are not aware of much data on this subject. However, Band in 1956 investigated the crystallography of the mineral phase of bone saturated with fluoride and found that the amount of fluoride present is not a simple function of hydroxyl ion replacement, but that there is some othe process going on simultaneously which could not be defined by crystallographic methods. His work shows that saturated dead bone can contain more than 3.8% fluoride. In fact, what the real saturation limit of bone is, is not known. All this would lead us to conclude, in contrast to the classical point of view: firstly, the fluoride ion is not easily diffusible in bone, and secondly, the fluoride concentration is not necessarily the same throughout the diameter of a specimen. Very possibly there is a considerable gradation in the amount of fluoride fixed from the external surface progressively toward the interior of the bone. Neuman in 1950 showed that no calcium fluoride is formed in bone, and that fluoride does not compete with phosphate ion, but that it does compete with hydroxyl and bicarbonate ions on the crystal surface. In some archeological sites the ratio of environmental bicarbonate ion to hydroxyl ion on the crystal surface of the bone would be considerably different from that found in other sites. How could the variability in exposure to available bicarbonate from one fossil to another be controlled?

As far as RI dating is concerned, a relationship between the soil carbon dioxide (or pH) and the bone bicarbonate ion could be established. In addition to the carbon dioxide - bicarbonate ion relationships it is clear that numerous other chemical factors exist which will determine not only the mechanism, but the actual rate of fluoride uptake. This, in turn, will seriously influence the apparent age of the bone, providing that the latter is considered to depend upon quantity of fluoride found on analysis. Clearly, we must attack the problem of fluoride dating from the standpoint of the interaction between the soil environment and the fossil bone.

NOTES

1. This paper was delivered by Miss Ezra at the second Annual Kroeber Anthropological Society meetings in Berkeley, 1958.