

BONE FLUORINE AS A MEASURE OF ARCHÆOLOGICAL ANTIQUITY

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ABSTRACT

Relative dating of ancient cultures can be done by measuring the Fluorine content in the bones unearthed at archaeological excavations. Similarly later intrusion of bones can conveniently be shifted from the older ones. This method has advantage over others in comparison of antiquity, that can be made in not too old archaeological material also. In this paper the author establishes a time sequence of ancient cultures as indicated by the Fluorine content of the bones excavated at different sites.

INTRODUCTION

In 1802 an Italian chemist MRNICHINI (in MOORE, 1962) detected traces of fluorine in the tooth of a fossil elephant excavated in Rome. A question, therefore, arose as to how it entered the bone. GAY LUSSAC, a French scientist held that it was probably absorbed by the animal during its life time. Later on, it was discovered that this element was absorbed by the teeth during life, but a bone buried in the earth is likely to continue to absorb it if it is exposed to fluorine bearing waters. This led the scientists to consider whether or not the fluorine content is proportional to the age, and if so we may be able to lift the veil off from the face of antiquity.

It was in the year 1844 that JAMES MIDDLETON (in MOORE, 1962) claimed that fossil bones contain fluorine in proportion to their antiquity. He compared the fluorine content of some fossil bones with that of the bones of a Greek skeleton 2,000 years old. He also estimated the age of some Eocene beds in France as 24,000 years with the help of the fluorine content in the fossil bones.

CARNOT (in MOORE, 1962) supported the views of MIDDLETON (in MOORE, 1962) and further claimed that fluorine present in the soil water steadily accumulates in bones and teeth. CARNOT (in MOORE, 1962) went a step further and analysed a number of bones ranging from Palaeozoic to Recent eras. The fluorine content in the fossil bones in different geological eras as given by him are as follows:

RECENT	0.30 %
PLEISTOCENE	1.50 %
TERTIARY	2.30 %
MESOZOIC	3.40 %
PALAEOZOIC	3.70 %

The work of CARNOT (in MOORE, 1962) was entirely forgotten till OAKLEY (in MOORE, 1962) infused a new life in this research. OAKLEY (in MOORE, 1962) thought that though fluorine could not be used for absolute dating it could certainly be used for relative dating, e.g. animal or human bones which have been lying in a gravel bed for 2,00,000 years are likely to have accumulated more fluorine than a human skeleton entered in the same bed, 2,000 years ago.

The largely controversial Galley Hill skeleton was finally put to the fluorine test. This test was carefully executed and in addition to the samples taken from the Galley Hill bits, some other samples were taken from twenty two animal bones, which were found nearby. Galley Hill animal bones of Middle Pleistocene Period had 1.7 to 2.8% fluorine. Upper Pleistocene fossils from the same region had 0.9 to 1.4% fluorine and those from Holocene the percentage of fluorine was from 0.05 to 0.30%. OAKLEY (in MOORE, 1962) therefore, opined that the Galley Hill man was a recent burial. Further OAKLEY (in MOORE, 1962) dated the Swanscombe skull containing 1.9 to 2.0% fluorine as 1,00,000 years old.

As fluorine tests proved their significance in separating the old from the antiquity, hope grew that at last we might have fluorine as a time tool with which to date. In this context one of the most contested cases of determining the age of the Piltdown skull (*Eoanthropus dawsoni*) lay well within the field of fluorine dating. The fluorine content was only 0.2% and so OAKLEY (in MOORE, 1962) claimed that it could not have been in the gravel for too long.

For the Fontchevade skull OAKLEY (in MOORE, 1962) determined fluorine of bones discovered below and above the stalgmite layer and found the values as 0.5% and 0.1% respectively.

It is argued, as stated above, that fluorine dating is not a method for determining chronological order with any pretence to meticulous accuracy. OAKLEY (in MOORE, 1962) himself constantly warned that it could not be used to draw comparisons between ages of materials found in different parts of the world. He emphasized that its utility lay in comparing the ages of objects found at the same site and thus subjected to the same fluorine bearing waters but in his 1950 report to the Viking Fund he could not resist quoting some comparisons made by a Dutch scientist who had studied both the Swancombe and the Fontchevade materials. At Swancombe all the vole teeth examined by the Dutch scientist belonged to extinct species. At Fontchevade she failed to trace any extinct species among a fairly large collection. OAKLEY (in MOORE, 1962), therefore, announced that taking that fact into consideration with the new palaeontological data, the Swancombe skull certainly belonged to an earlier interglacial period than the Fontchevade skull and comparing the Piltdown man he concluded that the Piltdown and Fontchevade man appeared to be contemporary i.e. 50,000 years old. At Suffolk he found the fluorine content of human skull as 0.10% while in a horncore of a *Bos primigenius* he found the fluorine content as 1.50% and announced that the skull belonged to the Recent Period.

CHEMISTRY OF ABSORPTION OF FLUORINE IN BONES

According to MELLOR (1923) liquid from which the bones are deposited in animal tissues is very nearly neutral and although complicated by the presence of additional salts, the conditions are probably similar, so far as calcium salts are concerned, to those of the simpler ternary system, $\text{CaO-P}_2\text{O}_5\text{-H}_2\text{O}$. Hydroxyapatite is the stable phase in solution with the degree of acidity characteristic of animal tissues. BASSETT (in MELLOR, 1923) calculated the data given in table 1 below by S. GABRIEL (in MELLOR, 1923), and showed that the mineral constituent of bones is mainly hydroxyapatite— $(\text{Ca}_3\text{P}_2\text{O}_8)_3 \cdot \text{Ca}(\text{OH})_2$ or $3 \text{Ca}_3(\text{PO}_4)_2 \cdot \text{Ca}(\text{OH})_2$ is mixed with a certain amount of calcium carbonate. In addition to these chief constituents, there are small amounts of the bicarbonates of magnesium, sodium, and potassium, which appear to be merely absorbed by the aggregate of phosphate and carbon. Several other investigators namely AEBY (in MELLOR, 1923), HEINTZ (in MELLOR, 1923), MULLER (in MELLOR, 1923) and ERLEUMEYER (in

MELLOR, 1923) suggested that teeth contain basic calcium phosphate. AEBY (in MELLOR, 1923) found the composition of bone phosphate to be $6 \text{ Ca}_3(\text{PO}_4)_2\text{Ca}(\text{OH})_2 \cdot 2 \text{ H}_2\text{O}$ or $3 \text{ Ca}_3(\text{PO}_4)_2\text{Ca}(\text{OH})_2 \cdot 2 \text{ H}_2\text{O}$, similar to that of hydroxyapatite.

Table. I— S. Gabbriel's Analyses of Bone Phosphate

Ingredients	Human bone	Goose bone	Ox bone	Ox teeth	Ox teeth	
					Enamel	Re- mainder
Calcium Oxide	51.53	51.01	51.28	50.70	51.98	50.36
Magnesium Oxide	0.77	1.27	1.05	1.52	0.53	1.83
Potassium Oxide	0.32	0.19	0.18	0.20	0.20	0.14
Sodium Oxide	1.04	1.11	1.09	1.16	1.10	0.80
Water of crystallisation	2.46	3.05	2.33	2.21	1.80	2.90
Phosphorous penta-oxide	36.65	38.19	37.46	38.88	39.70	38.60
Carbondioxide	5.86	4.11	5.06	4.09	3.23	3.97
Chlorine	0.01	0.06	0.04	0.05	0.21	0.03
Water of constitution	1.32	1.07	1.37	1.27	1.17	1.25
Total	99.74	100.06	99.86	100.08	99.92	99.88

BASSETT (in MELLOR, 1923) added that the range of acidity or alkalinity in most ordinary soils comes well within the range over which hydroxyapatite is the stable calcium phosphate, and it seems certain that it is the only phosphate that can exist permanently in the soil. Any other phosphate added to the soil will be converted into hydroxyapatite with greater or lesser readiness according to circumstances. It has long been recognised that calcium hydroxyapatite added to the soil in the form of superphosphate very quickly ceases to be present as such, although it is generally stated that it reverts to normal calcium phosphate. By adding the phosphate in the form of a superphosphate, the hydroxyapatite is obtained in a finely divided state, which is important due to its sparing solubility. Under conditions which have led to the accumulation of phosphate deposits, a certain amount of replacement of the hydroxyl of the hydroxyapatite by fluorine has occurred, owing certainly to the action of saline solution.

MELLOR (1923) says that BASSETT (in MELLOR, 1923) found hydroxyapatite to be $3 \text{ Ca}_3(\text{PO}_4)_2\text{Ca}(\text{OH})_2$ which is chemically calcium hydroxyhexaphosphate. The region of this compound is fairly extensive, and reaches very nearly to the point representing the solubility of calcium hydroxide; the solubility curve extends from markedly acid, through neutral, to markedly alkaline solution. Of all the calcium phosphates this is the only one not decomposed by water; it can dissolve unchanged in water, but the saturated solution is very dilute. WARINGTON (in MELLOR, 1923) showed that by repeatedly extracting normal calcium phosphate with boiling water, a product is finally contained with analyses corresponding closely with hydroxyapatite. BUCH's (in MELLOR, 1923) experiments on the action of

been preserved under comparable conditions. Fortunately the fluorine content of burried bones increases at about the same rate in gravel, sand and clay as claimed by BROTHWELL *et al* (1969, p. 40). The failure of fluorine and uranium to circulate in calcarious cave deposits is an established fact according to BROTHWELL *et al* (1969, p. 43) and one may not be surprised of low fluorine content of bones of high antiquity.

THE PRESENT WORK

To this end were analysed for the first time in the history of the archaeological research in this country, bones excavated at different places for their fluorine contents with a view to establish a time sequence (Table No. II). The results are self explanatory. This work is in progress and it will be reported subsequently. Consequently the discussion and conclusion on bone fluorine as a measure of archaeological antiquity will be sent for publication when more bones are analysed.

Table. II

Serial number	Site	Fluorine %
1	Kotia	0.005
2	Bilawali	0.03
3	Lakhania	0.03
4	Ujjain	0.05
5	Lekhania	0.05
6	Kausambi	0.12
7	Nagarjunakonda	0.12
8	Kakoria	0.12
9	South Andaman	0.15
10	Lothal	0.21

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