CHEMICAL STUDIES OF ARCHAEOLOGICAL BONES FROM INDIA

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The application of chemical analysis to material remains found in excavations is a recent development in modern archaeology. Chemical analysis of an archaeological bone can provide information about the fossilization process and the ecological conditions under which it was buried, and it can also give a clue to relative age. The progressive time-dependent chemical alteration of bone, subsequent to burial in sediments, also provides a valuable aid for establishing whether a particular bone is contemporary with other skeletal remains found in the same deposit (Oakley 1969).

However, detailed chemical analysis of fossils has rarely been attempted in India, though many studies have been done on materials from temperate regions. The fluorine content of bone has often been used for relative dating; this technique was first developed in the 19th century and was successfully applied to the Galley Hill skeleton and the Swanscombe skull by Professor Oakley in 1949. The results of fluorine and nitrogen analyses confirmed the antiquity of the Swanscombe skull, but the Galley Hill skeleton was found to be an intrusive burial since it contained low fluorine and high nitrogen.

The initially dense mass of fresh bone becomes, after burial, perforated with millions of extremely fine ramifying open spaces. This is because fats disappear rapidly, while proteins are lost at a slow and declining rate. Nitrogen content is an index of surviving organic matter, and it is often used to give a cross-check for fluorine dating. The changes in the inorganic phosphatic material, hydroxy apatite $Ca_{10}(PO_4)_6(OH)_2$, are of two kinds:

(a) Addition of new mineral matter involving a change in weight. When bone is desiccated, the inter-crystal spaces vacated by disappearing organic materials may become filled with foreign intrusive mineral precipitates such as calcium carbonate, silica and iron oxide, resulting in dense, heavy and hard fossils.

(b) Alteration of the phosphatic material without a change in weight, through the progressive substitution during burial of fluorine-forming fluorapatite, which is less soluble and more stable than hydroxy apatite. This process is irreversible, and with the passage of time bones in permeable deposits accumulate fluorine progressively.

The chemical changes in a buried bone depend upon the bone texture and chemical composition, and upon the environmental conditions under which it was buried. Other factors such as temperature, water circulation, and the pH and chemical composition of the surrounding groundwater also affect the process. Professor Oakley and other scientists relate the fluorine present not to the weight of total bone but only to the apatite contained in it. Since phosphorus is an integral part of the apatite crystal, the fluorine/phosphorus ratio serves this purpose, and this value is independent of the density of the bone. Cancellous or spongy tissue is liable to contamination by silt or other mineral matter, and in certain instances fossil bone can accumulate these minerals, heavily increasing apparent density and diminishing the observed percentage of fluorine by weight (Cook 1960). Therefore, when a comparison is made between the fluorine/phosphate ratios of different bones this complicating factor is eliminated. The ratio is usually expressed as $100F/P_2O_5$, and the theoretical maximum value of $100F/P_2O_5$ is 8.92.

RESULTS

Table 1 gives some of the results of chemical analyses of bones from Indian archaeological sites of different periods.

Site	Culture/ period	%F	%P	$\frac{100F}{P_2O_5}$	%N	$\%CaCO_3$
Inamgaon (18°35'N 76°35'E)	Chalcolithic	0.037	13.64	0.119	0.056	19.20
Ramapuram (15°05'N 78°05'E)	Chalcolithic	0.053	11.75	0.175	0.051	25.38
Vagad (22°19'N 71°51'E)	Chalcolithic	0.061	10.75	0.248	0.072	39:48
Burzahom (34°10'N 74°53'E)	Neolithic	0.076	9.37	0.471	0.053	14.12
Betamcherla (15°25'N 78°08'E)	E. Holocene	0.954	11.56	3.604	0.026	33.47
Devakachar (23°00'N 79°07'E)	U. Pleistocene	1.259	10.31	5.332	0.024	37.6
Burman Ghat (23°02'N 79°02'E)	U. Pleistocene	2.28	12.19	8.169	0.022	15.84
Pinjor (30°48'N 76°55'E)	Pleistocene	2.47	12.75	8.45	0.022	15.84

Table 1. Chemical analyses - sites of various periods.

It may be observed that fluorine content and the fluorine/phosphorus ratio both increase according to age. Nitrogen disappears as the age of the bone increases, but there is no such trend in the cases of phosphorus and calcium carbonate.

Table 2 gives the mean $100F/P_2O_5$ values of several bones from sites in different geographical regions of India.

Culture/ Period	Jammu & Kashmir	Gujarat	Madhya Pradesh	Mahara-shtra	Andhra Pradesh
Historic	Gufkral 0.158 Semthan 0.120	Tarsang 0.308	-	-	-
Chalcolithic	-	Vagad 0.295 Lothal 0.216 Jekhada 0.505	Eran 0.144 Navdatoli 0.106 Runeja 0.175	Daimabad 0.135 Inamgaon 0.125 -	Ramapuram 0.21 - -
Neolithic	Burzahom 0.206 Gufkral 0.178 Semthan 0.210	-	-	-	Betamcherla 0.34
Mesolithic	-	Tarsang 2.76	-	-	-
Palaeolithic	Sombur 5.076	-	Burmanghat 7.945	Inamgaon 5.40	Betamcherla 3.022

Table 2. Mean $100F/P_2O_5$ values - sites of several periods and regions.

From these two tables it will be clear that there are marked differences in fluorine contents of bones from Chalcolithic/ Neolithic and Palaeolithic sites. $100F/P_2O_5$ values are below 0.5 in bones from Chalcolithic/Neolithic sites in all regions, while they are above 3.0 in the Palaeolithic sites. However, after analysing several bones from Inamgaon (Chalcolithic), it was observed that the method is of limited value for distinguishing

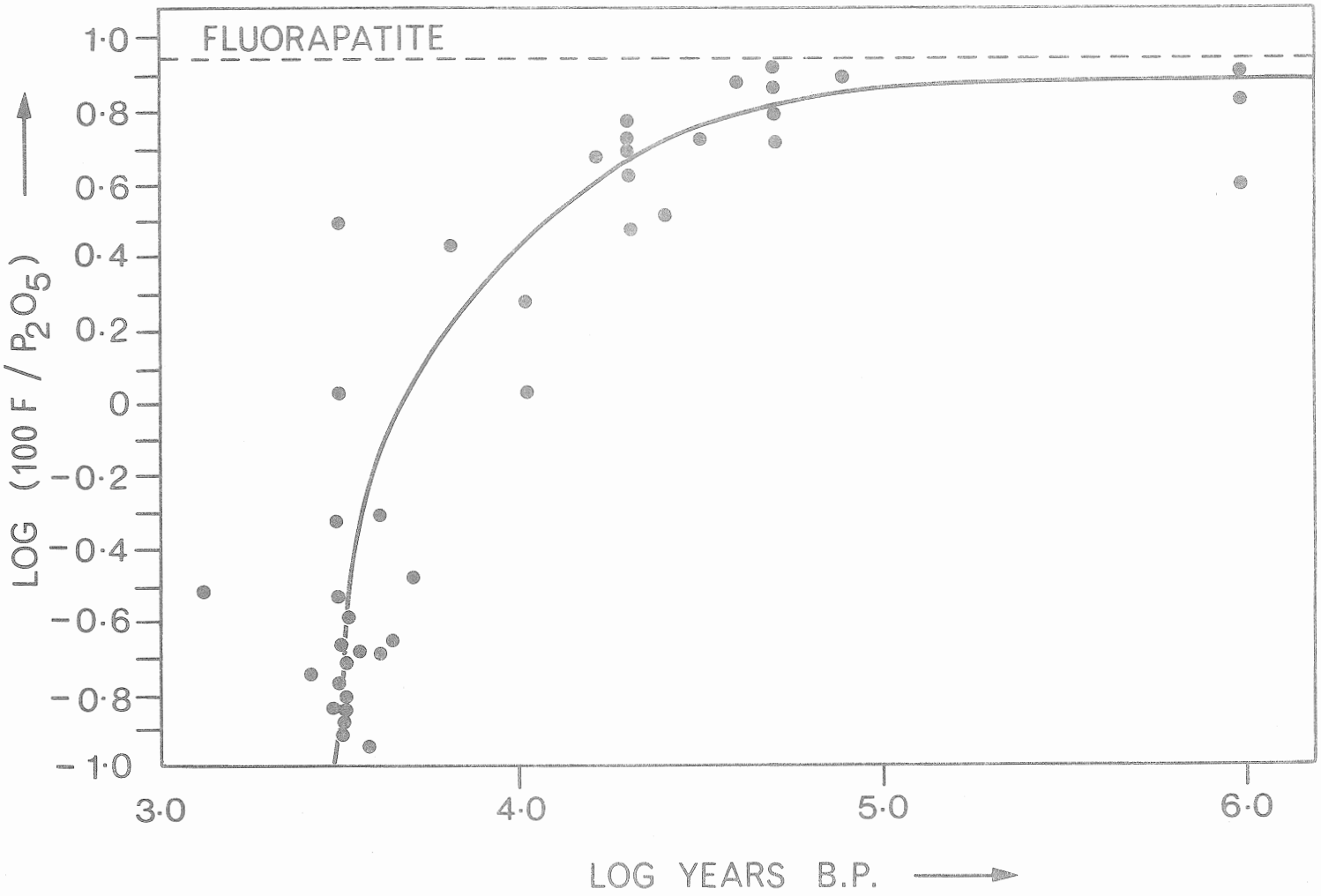

Figure 1. Fluorine/Phosphate Ratios of Fossils from India.

short sub-stages of occupation of less than 1000 years duration. Differences in $100F/P_2O_5$ ratios in different regions for the same time period may be attributed to differences in the fluorine contents of the surrounding soils and groundwaters. Therefore, interpretation of results must take account of environmental differences.

Table 3 gives the results of chemical analyses of Pleistocene fossils from different regions of India. At present the subdivisions of the Pleistocene in India are ordered by taking into consideration the faunal materials found in association with Stone Age implements. However, it is difficult to recognise clear-cut subdivisions exclusively on the basis of fauna, since the same species often occur in deposits containing implements of different industries. Therefore, we wish to see whether fossils of different periods can be distinguished by their fluorine contents.

It is observed that the $100F/P_2O_5$ ratio for Pleistocene fossils from India varies from 3 to 8.5. Morphologically, the fauna from the Narmada valley appears to be older than that recovered from the Ghod and Manjra valleys. Also, the fauna from the Kurnool caves near Betamcherla in south India appears to be younger than that recovered from the Deccan river valleys, and belongs to the terminal Pleistocene (Badam 1979). The chronological sequence of Indian Pleistocene fossils worked out faunistically by Dr Badam and the corresponding fluorine/phosphate ratios are thus comparable:

Narmada	5.3 to 8.1
Ghod & Godavari	4.0 to 6.0
Kurnool Caves	3.6

The ratio for the fossils from Hunsgi is higher (6.7 to 8.3), and almost reaches the saturation value (8.92).

There is much variation in the calcium carbonate content of fossils from different regions. It is low in the fossils from Narmada and the Siwaliks, but high in those from the Ghod, Manjra, and Godavari valleys. It rises to about 75% in one fossil specimen from Manjra, and this is the highest value noted in the present study. Nitrogen is less than 0.1% in all fossils.

Figure 1 gives a graphical representation of the fluorine/phosphate ratios of fossils from India, plotted against their approximate stratigraphic ages. The theoretical maximum of this ratio is reached by approximately the Lower Palaeolithic stage. The ratios for Hebbal Buzurg (8.387) and Pinjor (8.45) are similar, although the Siwalik specimens are likely to be older than those from Hunsgi.

X-ray diffraction studies of some bone specimens from Chalcolithic and Pleistocene Inamgaon confirmed the hydroxy apatite structure of the inorganic parts of the bones, the gradual conversion of hydroxy apatite to fluorapatite with increasing age,

Region & State	%F	P_2O_5	100F/P_2O_5	%$CaCo_3$	%N
Kashmir Karewas					
Sombur	1.525	30.04	5.076	14.55	0.068
Siwalik					
Mirzapur	1.45	21.75	6.66	27.73	0.026
Paramandal	1.02	25.46	4.01	11.44	0.017
Pinjor	2.47	29.20	8.45	15.84	0.026
Narmada Valley					
Burmanghat	2.28	28.62	8.169	18.16	0.022
Devakachar U.Pl.	1.259	23.61	5.332	37.60	0.024
Devakachar M.Pl.	1.757	30.04	5.850	20.68	0.022
Devakachar L.Pl.	1.807	22.33	8.08	42.30	0.017
Godavari Valley					
Kalegaon	1.116	18.6	6.00	42.24	0.026
Manjra Valley					
Dhanegaon	0.307	6.00	5.11	74.61	0.022
Ganjur	0.400	8.29	4.825	65.96	0.026
Tadula	0.456	14.59	3.125	43.65	0.051
Wangdari	0.931	20.75	4.487	45.55	0.038
Ghod Valley					
Chandoli	0.642	16.03	4.001	58.08	0.026
Inamgaon	0.983	28.62	5.588	48.70	0.011
Hunsgi Valley					
Hebbal Buzurg	0.902	10.76	8.387	55.29	0.062
Kaldevanhalli	1.116	16.60	6.720	48.50	0.053
Kupi	0.807	10.76	7.513	63.05	0.027
Kurnool Caves					
Betamcherla	0.954	26.47	3.604	33.47	0.038
Coastal region					
Uran	1.14	22.90	4.978	29.10	0.038

Table 3. Chemical analyses of Pleistocene fossils from various regions of India.

and the non-existence of carbonate-apatite in any of the specimens. Therefore, there is no substitution of carbonate for phosphate groups, as was once thought, and hence the fluorine/phosphate ratio holds good for the comparisons.

CONCLUSIONS

The fluorine technique seems to be useful for studying fossilization processes in ancient bones from the Indian environment. To some extent it can also be used for relative dating, but there are limitations. The method gives fairly good results when there are long time differences between samples. It is now necessary to build up complete sequences of results for bones from different periods and from different environments. With this information it should be possible to assign an age to a bone of unknown stratigraphic context when no other means of dating are available.

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