NEW ZEALAND ARCHAEOLOGICAL ASSOCIATION NEWSLETTER

FLUORINE ANALYSIS IN NEW ZEALAND ARCHAEOLOGY

Michael M. Trotter and R. S. Malthus

Bones recovered from archaeological sites generally show some physical or chemical changes which have taken place during their interment. Workers in New Zealand frequently refer to 'mineralised', 'fossilised' or 'sub-fossil' bone, particularly with reference to moa species, but very little analytical work has been done here to determine the significance of these changes, and whether they can be used to provide information of use to archaeologists. In other countries various relative dating methods have been evolved to determine the contemporaneity or otherwise of bone specimens; to place them, or associated deposits, in relation to an established sequence; or in some cases, in the establishment of a chronological sequence at one site or locality (see for instance Cook 1960, and Oakley 1963). The establishment of the bogus nature of the Piltdown Skull in 1953 is perhaps the best known example of the application of relative dating techniques. Most methods are based on the assumption that chemical or physical changes of a similar nature will take place in bones buried in the same site, or the same area, if they have been subjected to similar conditions.

Once buried, certain organic constituents, such as fat, are usually lost quite quickly while others, like collagen (protein), disappear much more slowly. (This latter material has proved useful for radiocarbon dating as it is not subject to contamination by atmospheric carbon dioxide as is bone carbonate (Rafter 1965-67). Under good conditions of preservation collagen can survive for tens of thousands of years, but as the rate of decomposition is fairly uniform under the same conditions an assessment of the amount remaining in a sample can be used for purposes of comparison. This is commonly done by determining the nitrogen content of the bone.

The mineral component of the bone is also altered by time in the ground and this takes place in two ways, both dependent on the composition and amount of percolating ground water. Materials may be deposited in the pores of the bone and can be determined in thin section under a microscope or by chemical analyses - for instance, there may be an increase in the amount of calcium carbonate as compared with fresh bone. This causes an increase in the weight of the bone and is what most people mean by 'fossilisation', 'petrification' or 'mineralisation', and it can be quite misleading as an index to the relative (or the chronometric) date.

Of much more use is the invisible, weightless alteration of the hydroxy-apatite constituent of the bone by substitution of the hydroxyl ions with those of fluorine, the latter occurring in the form of soluble fluorides in trace quantities in nearly all ground water.

Fluorine analysis is used, often in conjunction with other methods such as nitrogen (collagen) or uranium analysis, to show the contemporaneity or otherwise of bone samples which seem to be from the same level. Its value lies mainly in that when fluorine ions have been absorbed, replacing the hydroxyl ions of the hydroxy-apatite constituent to form fluor-apatite, they are not readily dissolved out. Judging from published results, which include confirmation by chronometric dating methods such as radiocarbon analysis, fluorine would appear to be the most reliable and tested relative dating method available. Factors which could adversely affect the reliability of the results would apply equally (or to a greater extent) to methods based on the intake of other substances from ground water. or on the loss of original constituents.

During the past few months the authors have worked on this and other methods as part of a general research programme into the chemical and physical properties of archaeological bone. Through the courtesy of Mr John Linzey, differential thermal analyses (see Trotter 1966 for a description of the process) were made of bone samples of modern (present day), archaeological (500 years) and pre-human (3,000 years) age. The results are shown in Fig. 1.

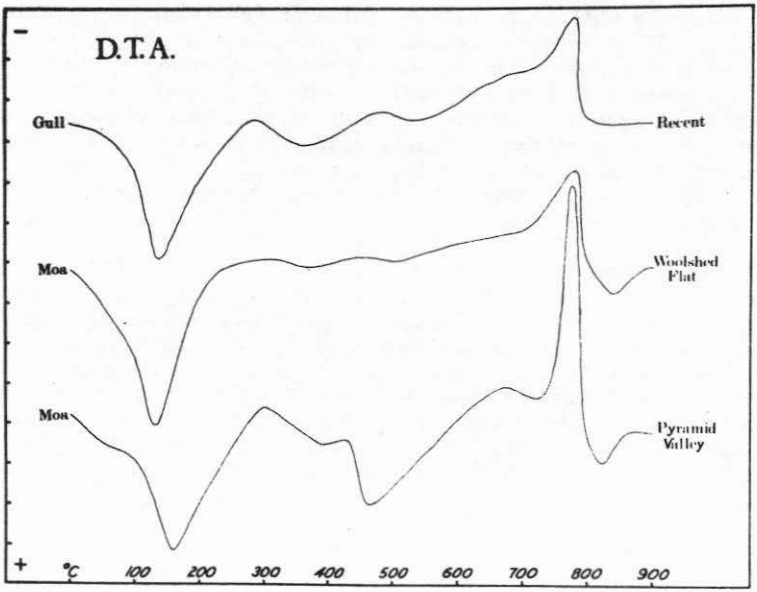

Fig. 1

There are some obvious chemical differences in the three bones which were: recent Black-backed Gull from Aromoana Beach; Eurapteryx from a Moa-hunter site at Aviemore (S.117/3); and Dinornis from Pyramid Valley swamp. The first downward peak, an endotherm, at 130°-160°C. represents the evolution of hydroscopic moisture. (A temperature of about 100°C. will expel a certain amount of water which is gradually reabsorbed from the atmosphere if the sample is then allowed to return to room temperature. At higher temperatures, however, more water is extracted but irreversibly.) At between 360° and 390°C. the three samples show another, but smaller, endotherm, and there is a major exotherm at about 780°C., probably representing the crystallisation of apatite. The Pyramid Valley sample has large endotherms at 460°C. and 730°C. not shown markedly by the other samples, and both moa bone samples have endotherms at 820°-840°C. not shown by the gull. To obtain more detailed information the differential thermal analyses are being followed up by chemical analyses of a number of samples ranging in age up to about a quarter of a million years, and also with a carefully controlled experiment to measure the short term uptake of fluorine in bones of various species and ages by immersing samples in fluoride solutions of different strengths for periods of up to two years.

Preliminary results for the fluorine analyses have been obtained. Samples of different species from different types of sites and of different ages were collected in the field by Trotter (Canterbury Museum) and analysed for fluorine content by Malthus (Nutrition Research Department, Otago Medical School). The method used was to take samples weighing between 0.4 and 1.0 gram from the bone specimen and to isolate the fluoride by steam distillation from perchloric acid (the standard Willard-Winter distillation). Two hundred millilitres of distillate were collected, and as the method of estimation used in the laboratory was designed for a few micrograms of fluoride, it was necessary to dilute a volume of between 5 ml. and 0.5 ml. (based on preliminary trials) of the distillate to 50 ml. with distilled water, and 9 ml. of this was taken for estimation. To it was added 1 ml. of Zr-SPADNS reagent (see Wharton 1962: 1296-98). The absorbance of solutions was measured at 598 mu against a reference solution of dye, and compared with the absorbance of standard solutions.

Details of samples, sites and results are as follows - in most cases separate analyses were made of different parts of each bone.

Specimen A. Moa toe from Shag River Moa-hunter camp site (S.155/5), charcoal from which has been radiocarbon dated to early twelfth century (D. Simmons, personal communication). A sample from the surface of the bone contained 0.67% fluorine and a sub-surface sample 0.51%.

Specimen B.	Moa tibia from Shag Point Intermediate age site (S.146/5). Estimated age of site about 300 years before present, though the moa is probably not contemporaneous. Two samples contained 0.33% and 0.36% respectively.
Specimen C.	Heat-stained moa tibia from Shag Point site, as Specimen B. Two samples contained 0.16% and 0.18%.
Specimen D.	Dog jaw from Shag Point site, as Specimen B. Four samples contained 0.25%, 0.27%, 0.25% and 0.35% fluorine.
Specimens E & E1.	Two pieces of sea bird bone (probably shag) from Shag Point site, as Specimen B. 0.68% and 0.54%.
Specimen F.	Moa tibia from Tai Rua Moa-hunter camp site (S.136/1, see Trotter 1965: 349). Collagen from other moa leg bones from the same layer gave radiocarbon dates of mid-fifteenth century. Three samples of cortical bone contained 0.20%, 0.19% and 0.24% fluorine, and one sample of cancellous bone contained 0.20%.
Specimen G.	Moa tibia from a loess deposit at Bakers Clay Pit, Halswell. Age 10,000 to 100,000 years before present. Three samples contained 1.50%, 1.88% and 1.90% fluorine.
Specimen H.	Moa rib from a swamp deposit in Scaifes Lagoon, Wanaka. Radiocarbon age 2,000 years before present. Three cross-section samples contained 0.97%, 0.80% and 0.77% fluorine.
Specimens I and I1.	Two pieces of moa femur (from the same bird) from lower (pre-human) levels of Moa-bone Point Cave near Christchurch (S.84/77). Estimated age 2,000-3,000 years before present. Two samples from one specimen contained 0.48% and 0.42% fluorine, and from the other a sample of the outer layer 0.47%, two cancellous samples 0.39% and 0.25% and two mixed (cancellous and cortical) samples 0.30% and 0.32%.

Specimen J. Moa tibia from the occupational levels of Moa-bone Point Cave (S.84/77). Estimated age 500-800 years before present. Three samples contained 0.12%, 0.11% and 0.07%.

For convenience these figures are show diagrammatically and in order of approximate age of sites in Fig. 2. The scale is logarithmic and the white portion of each bar indicates the difference between minimum and maximum figures.

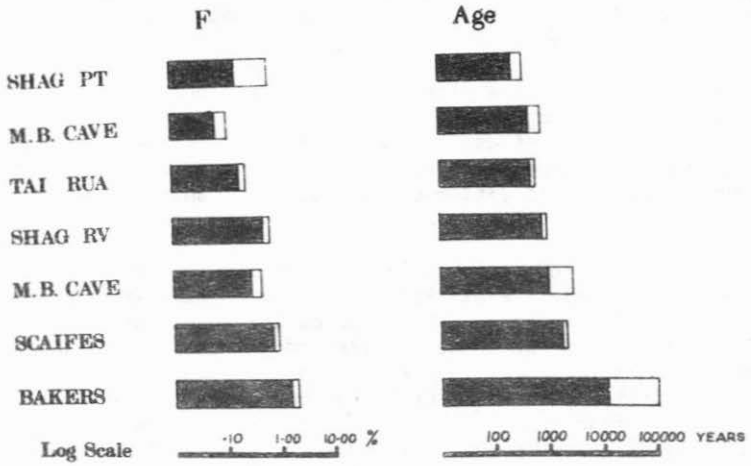

Fig. 2

Several points are immediately apparent. There is in general, as expected, a gradual increase in the amount of fluorine absorbed as the samples become older, but the wide variation between individual samples from one site immediately throws doubt on the value of fluorine analysis as a relative dating method. This is particularly the case with the ten Shag Point samples which vary from 0.16% to 0.68%. A possible source of the relatively high amount of fluorine in the bird bone is from fish bone digested by marine birds. Fluorine levels in fresh fish bone are generally similar to those in mammal bones but sea birds that digested hard fish tissue could accumulate fluorine from this source in addition to that which would normally occur in their bones. Although dogs eat bones they apparently digest very little, and fish bones are commonly found in archaeological dog faeces. Simons (1965: 571-605) gives a table summarising "normal" fluorine concentrations in hard tissues of various species at death, from which it would appear that the bones react

similarly and that levels found depend on intake and on length of time of exposure. There may be other factors involved here and more work will be required before we definitely know the answer. The low level in the heat stained moa bone from Shag Point (Specimen C) is surprising, especially as burnt bone meal is often used as an efficient filter to remove fluorine from fluoridated drinking water. There is no evidence that moa was used for food at Shag Point (see Trotter 1965: 352); the moa bone found in the midden has presumably been salvaged from an earlier natural or Moa-hunter deposit. If this is the case it would be expected to contain a higher level of fluorine than the 0.33% and 0.36% of Specimen B, which is comparable to that of the only other land animal analysed, the dog of Specimen D (0.25% to 0.35%).

The generally low fluorine percentage for moa bones from both lower (pre-human) and upper (occupational) levels of Moa-bone Point Cave (Specimens I and J) are doubtless due to the dryness of the cave. In limestone caves and shelters there is often a low level of fluorine uptake due to the more rapid calcification of the bone, but this is not the case here where the cave is of volcanic origin.

From these figures and from similar results obtained recently by other workers (Cook 1966) it would appear that by itself fluorine analysis is of somewhat doubtful value as a tool for dating unless the factors causing the variations can be better understood and their effects applied to the results of analyses (cf. Zeuner 1960: 333). This is particularly the case in the limited time scale of human occupation in New Zealand. Where it is used, comparisons should be confined to one type of bone, and made on the basis of a statistically valid mean for each level - whether the number of determinations required to do this is warranted, considering the limited accuracy and value of the results, would appear to be debatable.

REFERENCES

Cook, S. F. 1960 "Dating Prehistoric Bone by Chemical Analysis" in The Application of Quantitative Methods in Archaeology, edited by Heizer and Cook. Chicago.

1966 Private correspondence.

Oakley, K. P. 1963 "Analytical Methods of Dating Bones" in Science in Archaeology, edited by Brothwell and Higgs. Thames and Hudson.

Rafter, T. A. 1965-67 Private correspondence.

Simons, J. H. 1965 "Fluorine Chemistry", Vol. IV. Academic Press.

Trotter, Michael M. 1965 "The Barbed Fish-hook: its place in the Murihiku Cultural Sequence". Journal of the Polynesian Society, 74 (3).

1966 "Consolidated Ash from North Otago Archaeological Sites", N.Z. Archaeological Assn. Newsletter 9 (2): 48-52.

Wharton, H. W. 1962 "Analytical Chemistry", 34.

Zeuner, F. E. 1960 "Advances in Chronological Research" in The Application of Quantitative Methods in Archaeology, edited by Heizer and Cook. Chicago.

AN EXCAVATION AT OPITO BAY

C. J. Murdock and R. G. W. Jolly

In the vicinity of Opito Bay and along its shores there exist many places ideally suited to Polynesians who lived mainly by fishing and fowling. At present though no-one can be sure of the length of time that has elapsed from first settlement to the Classic Maori phase, evidence is gradually being discovered of all stages. On Opito Bay evidence for many of these stages has already been recorded ranging from the dominant pa (N 40/15) at the south-eastern end of the Bay to early middens with evidence of moa-hunting and archaic artifacts in several sites at the north-western end of the beach (Green 1963: 57-64). Among those sites previously reported is N 40/2, where on the dunes fronting the beach an investigation had been carried out (Jolly and Green 1962: 42). The consolidated state of the dune inland from the area previously investigated would suggest, perhaps, that