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Fluorine Concentration Profiles in Archaeological Bone: An Application of a Nuclear Microprobe

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ABSTRACT

The nuclear microprobe at the Institute of Nuclear Sciences was applied to the measurement of radial concentration profiles of fluorine, in transverse slices of archaeological bone from humans, moas and other animals. A beam of 2.5 MeV protons was focused to a rectangular spot 250μm by 50μm, traversed along a radial line 3mm long, and gamma rays of 5–7 MeV from the reaction $^{19}F(p,\alpha\gamma)^{16}O$ were detected in a large sodium iodide crystal. Bombardment caused no detectable loss of fluorine from the bone.

Measured profiles display a wide variety of shapes and maximum concentrations. In bones which had been exposed to ground water the fluorine concentration usually increases from the centre towards the surface, sometimes by as much as a factor of eight. The concentration at the surface is usually in the range 0.2 to 1%, though in moa bone from a limestone cave it is only 0.025%. Once a quantitative method of analysis has been developed, based on the shape of the profile rather than its magnitude, these profiles might be useful for dating bone. In the meantime, they could be used to distinguish bones of different ages from a common site.

Keywords: FLUORINE, FLUORINE PROFILE, BONE DATING, MOA BONE, NUCLEAR MICROPROBE.

INTRODUCTION

A nuclear microprobe, which employs focused beams of protons or deuterons rather than electrons, has one special advantage over the electron probe: by applying a variety of nuclear reactions and several types of radiation detectors it is possible to detect trace levels of most of the light elements, in particular lithium, beryllium, boron, carbon, nitrogen, oxygen and fluorine. This is in addition to its capability for detecting all elements with $Z > 10$ via characteristic X-rays, with lower background and higher sensitivity than the electron probe. The beam spot is larger, but this is compensated for to some extent by reduced transverse scattering of the beam inside the specimen.

The original nuclear microprobe at Harwell, England, was first described in 1970 and about fifteen others are now in operation worldwide, including two in the Southern Hemisphere (Melbourne and Lower Hutt). The existing instruments and published applications, which are mainly in metallurgy, geology and biology, have been reviewed by Cookson (1979).

The Institute of Nuclear Sciences' microprobe was developed between 1977 and 1979 though the first projects were begun in 1978. We looked first for projects in which we could exploit the capability for detection of light elements, particularly fluorine, for which nuclear methods were well established (Bewers and Flack 1969, Jarjis 1978). A paper by Eisenbarth and Hille (1977) described work in Europe, in which fluorine and nitrogen concentrations in excavated bone were measured by fast neutron activation; they claimed that the measured ratio of the two elements could be used to date the bone. Only the average ratio could be determined, and it seemed to us that if concentration profiles of these elements could be measured the method could be tested

more thoroughly. Such a dating method might be very useful in New Zealand, where man had arrived relatively recently. There are problems in deriving reliable radiocarbon dates from bone and a supplementary method, even if the useful range proved to be only a few thousand years, could be valuable as a check.

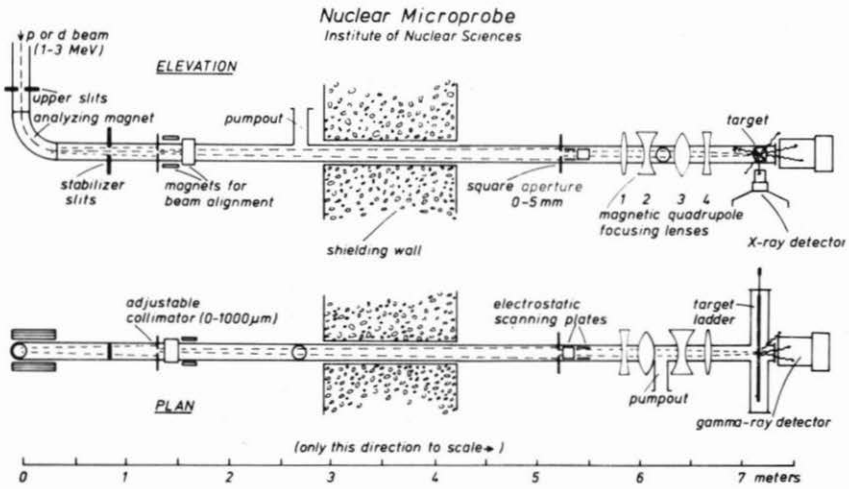


Figure 1: Schematic plan and elevation of the INS nuclear microprobe, with only the horizontal direction drawn to scale. Each magnetic quadrupole lens is represented by its function rather than its appearance.

It was shown that nitrogen could be detected in bone by means of the $^{14}N(d,p\gamma)^{15}N$ reaction, but it escaped very readily under bombardment by even minute currents (a few nanoamperes of 1.4 MeV deuterons). However, the distributions did appear to be relatively uniform and measurements of average concentrations using a defocused beam may be performed later. Fluorine, however, was so firmly fixed in the bone that bombardment by 20 nA of protons caused no detectable loss.

THE NUCLEAR MICROPROBE

The main features of the Institute of Nuclear Sciences' microprobe are illustrated in Figure 1. The four magnetic quadrupole lenses, which focus the proton or deuteron beam, are operated as an inner and an outer pair. The beam spot is rectangular, with its size and shape controlled by the collimator openings and the currents through the lenses. The adjustable square aperture before the first lens has little effect on the size of the spot but is used to control the current on the target, which is set between 1 and 20 nA, depending on the nature of the specimen and the radiations being detected. Two pairs of electrostatic steering plates deflect the beam in the horizontal and vertical directions. An unusual feature of our microprobe is that beam steering precedes focusing; this appears to cause no deterioration in the beam spot and makes more space available near the target. With care the beam can be focused to a spot 10μm square, but 50μm was sufficiently small for the present measurements.

Figure 2 illustrates a number of devices which are arranged inside or around the aluminium target box. By means of the 45° mirror and a zoom stereo microscope the specimen can be observed during bombardment, illuminated through a glass window by a microscope lamp outside the chamber. A target of glass or quartz, which is included among the specimens, fluoresces when struck by high energy particles;

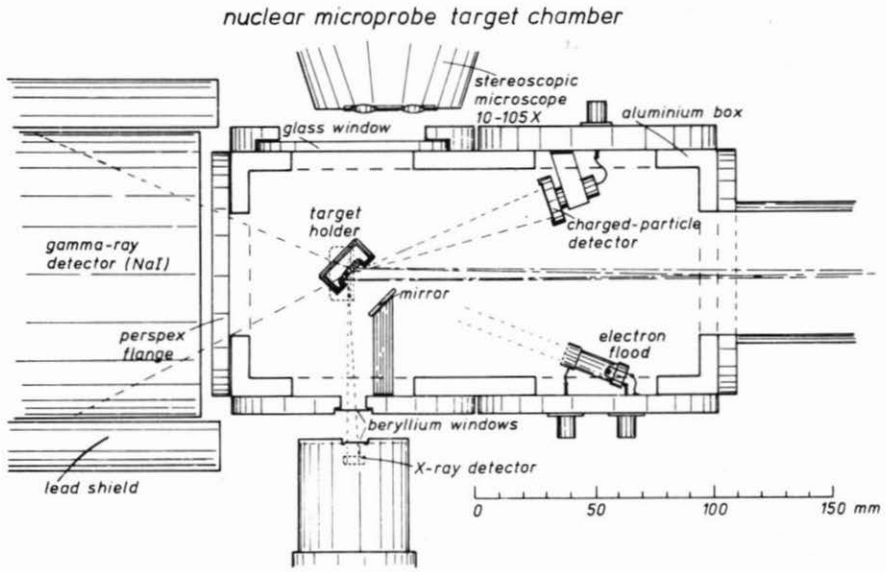


Figure 2: Target chamber of the microprobe, with associated radiation detectors. The target is set at 45° to the beam for X-ray measurements but at 90° for γ-ray and charged-particle detection.

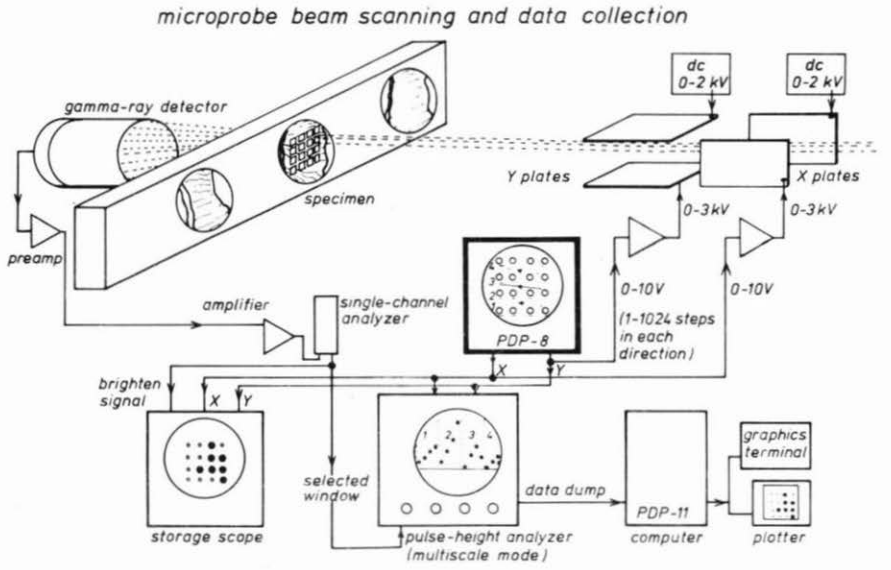


Figure 3: Composite drawing showing: beam steering plates and target holder; electronic equipment for steering the beam and storing data.

it is employed to monitor the beam focus and the shape and size of the scanned area. Ten specimens may be inserted into the chamber at one time and moved consecutively into position under the beam.

When X-rays are to be detected the target must be at 45° to the beam but an angle of 90° is better if only gamma rays or charged particles are to be detected. The electron flood device is one way of preventing the specimen from becoming charged during bombardment; if this is not done, electrons accelerated to it cause a high background in the X-ray detector. An alternative method we have used is to coat the specimen with a thin layer of carbon from an arc.

The beam is not moved continuously but in steps, under the control of a PDP-8 minicomputer, making use of the two digital-to-analog converters which normally control an X-Y oscilloscope display (Fig. 3). In either direction the number of steps selected can lie between 1 and 1024 and the dwell time at each position can be set between 0.1ms and 1 second. The complete scan is swept through automatically many times until sufficient accuracy is attained. The output dc levels, amplified by two hybrid amplifiers, drive the steering plates; they also control the collection of data by the pulse-height analyzer and the image which builds up on the screen of a storage oscilloscope. This image is valuable when the scan is being set up but only the digital data is recorded in permanent form.

The present electronic equipment is limited in that data can be collected from only one window in one spectrum at a time, though an alternative mode is to accumulate up to 16 spectra in sequence, for detailed analysis later. A more versatile system based on an LSI-11 microcomputer is almost completed; with this we will be able to collect gamma-ray and X-ray data simultaneously from a number of elements.

Once sufficient data has been collected it is dumped to the PDP-11 computer. A number of programs can then be brought into play for smoothing the data (if desired), plotting it in a suitable form, and storing it permanently on magnetic tape.

MEASUREMENT OF FLUORINE DISTRIBUTIONS

In Figure 4 we summarize the nuclear physics relevant to the detection of fluorine:

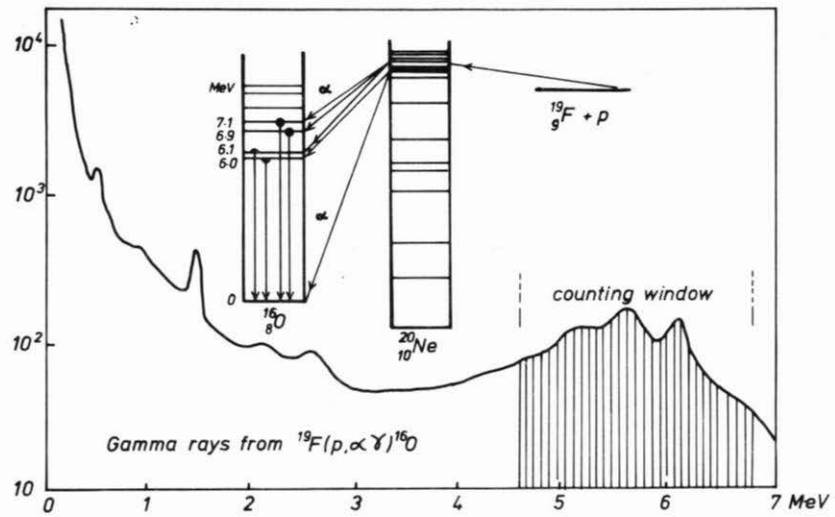


Figure 4: High energy gamma rays from the $^{19}F(P,\alpha\gamma)^{16}0$ reaction result from transitions in the residual nucleus $^{16}0$. The counting window in the sodium iodide spectrometer is set between 4.6 and 6.8 MeV.

the intermediate nucleus ^{20}Ne decays by alpha emission to four high-energy levels of ^{16}O, which decay directly to the ground state by emission of high energy gamma rays. The spectrum in a sodium iodide scintillation detector is a continuous distribution, but if a window is set as shown in the high-energy region the counting rate is almost entirely specific to fluorine, as the above reaction dominates all others which could occur.

Figure 5 shows that a useful way of presenting a two-dimensional scan is as a perspective view, with concentration plotted vertically. As an aid to interpretation the distribution can be viewed from different vantage points, as shown. An alternative approach is a gray-scale plot (Fig. 6); this can be valuable when the distributions of two or more elements are to be compared.

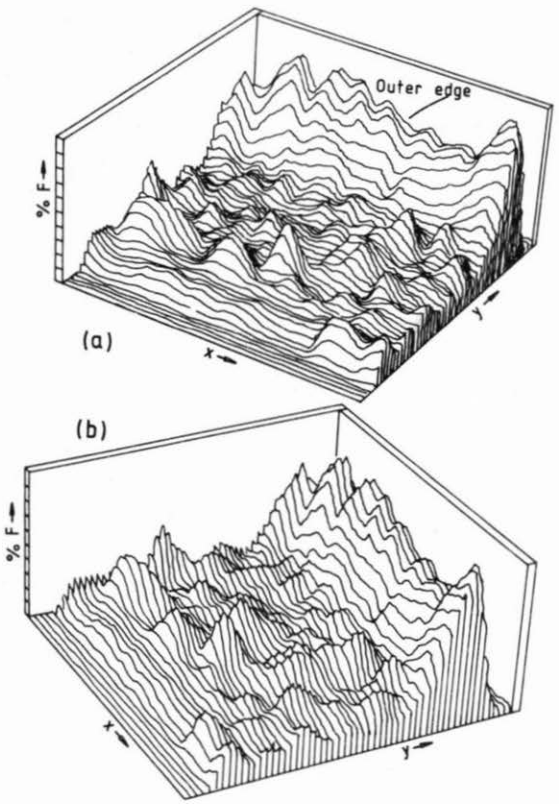


Figure 5: Perspective plot of fluorine concentration in a 2mm by 2mm area of a hand phalanx, Waihora, Chatham Islands. The proton beam traversed 56 steps in each direction. a. Viewed at 30° to the y axis; b. Viewed at 60° to the axis.

A radial line scan was adopted as providing adequate data for the present purpose, with the beam spot sufficiently long perpendicular to the scan direction to provide some data smoothing. Fluorine concentration was then plotted against radial distance from the surface. Another possibility would be several line scans in parallel, which could be averaged later if desired.

The standard for fluorine concentration was an artificial form of mica (fluorphlogopite) with a fluorine concentration of 9.0 ± 0.3% (Kohn and Hatch 1955).

Figure 6: Gray-scale plot of fluorine distribution in a polished section of rock, (2mm square). Small dark areas represent grains of apatite, containing 1% fluorine.

PREPARATION AND IRRADIATION OF BONE SPECIMENS

The bones which were available for initial experiments had been sent to INS for other purposes, such as radiocarbon dating or trace element analysis. Using a small hacksaw, with a blade used for no other purpose, a transverse slice about 2mm thick was cut from a bone. If the cross section was very large the slice was cut into segments small enough to fit into the target holder. The present holder takes specimens up to 18mm wide and 100mm long but a redesigned holder could accept specimens 50mm wide. One surface was lapped on silicon carbide paper (grades 240, 400 and 600) until it was flat and smooth – this took only a minute or two. No water was used and care was taken that a fresh area of the paper was used for each specimen, to avoid any possible contamination of one bone by another. The target holder was a strip of aluminium with eight 10mm holes in a row. Each specimen was stuck to the back with cyanoacrylate glue so that an outer edge of the bone was approximately vertical. A gold foil behind the specimens ensured that protons which missed the specimen generated minimal background.

The beam of 2.5MeV protons was focused to a spot 250μm by 50μm and scanned in 64 steps along a horizontal distance of 3mm. Because the bone fluoresces slightly under the beam the position of the line scan can be observed in the microscope and adjusted until it is satisfactory. A black line which appears after a few minutes of bombardment (presumably due to radiation damage or heating) provides a useful permanent record, though it can be easily lapped away later if desired. A line scan takes about five minutes running time, but a detailed scan of an area (usually 64 points each way) requires an hour or more. The target chamber is insulated from ground to serve as a Faraday cup, so the total charge striking the specimen can be measured by a beam-current integrator. Irradiations are stopped automatically once a set amount of charge has been collected so that the fluorine calibration for each profile is the same.

RESULTS FROM BONE SCANS

MOA AND OTHER ANIMAL BONES

Figure 7 shows a selection of measured profiles, so arranged that for each the yield from the bone surface is plotted towards the left-hand edge, with common scales for fluorine concentration and radial distance. There is not only a wide range in the maximum concentrations of fluorine, as would be expected from the diverse environments from which the bones were collected, but a variety of profile shapes. The remarkably low level (0.025%) of profile *e* is still ten times the background level; the highest level (1.6%) is found in the 1 million year bone from Europe (profile *h*). The fluctuations about a smooth curve originate in three ways: statistical variations, which are about 1.5% at the 1% fluorine level (which corresponds to 5000 counts per channel); imperfections in the multi-channel analyzer which lead to systematic variations in channel width; and inhomogeneity of the bone. There appears to be a qualitative relationship between the age of the bone and the steepness of the profile, and it will be our task in future work to attempt to make this quantitative.

HUMAN BONES

Profile *d* in Figure 8 is typical of bone found in a dry cave; the fluorine level is low and irregular and does not increase near the surface. In contrast, most of the remaining profiles have their maximum concentration near the surface with a relatively steep decline towards the centre. The smoothest and most striking profiles are found in finger and toe phalanges (*h, i, j*). Because ground water can pass to a lesser extent into the medullary cavity (either through foramina or because of inevitable minor damage to the surface of the cancellous bone ends), the profiles rise towards the inner surface as well as the outer, though to a reduced concentration.

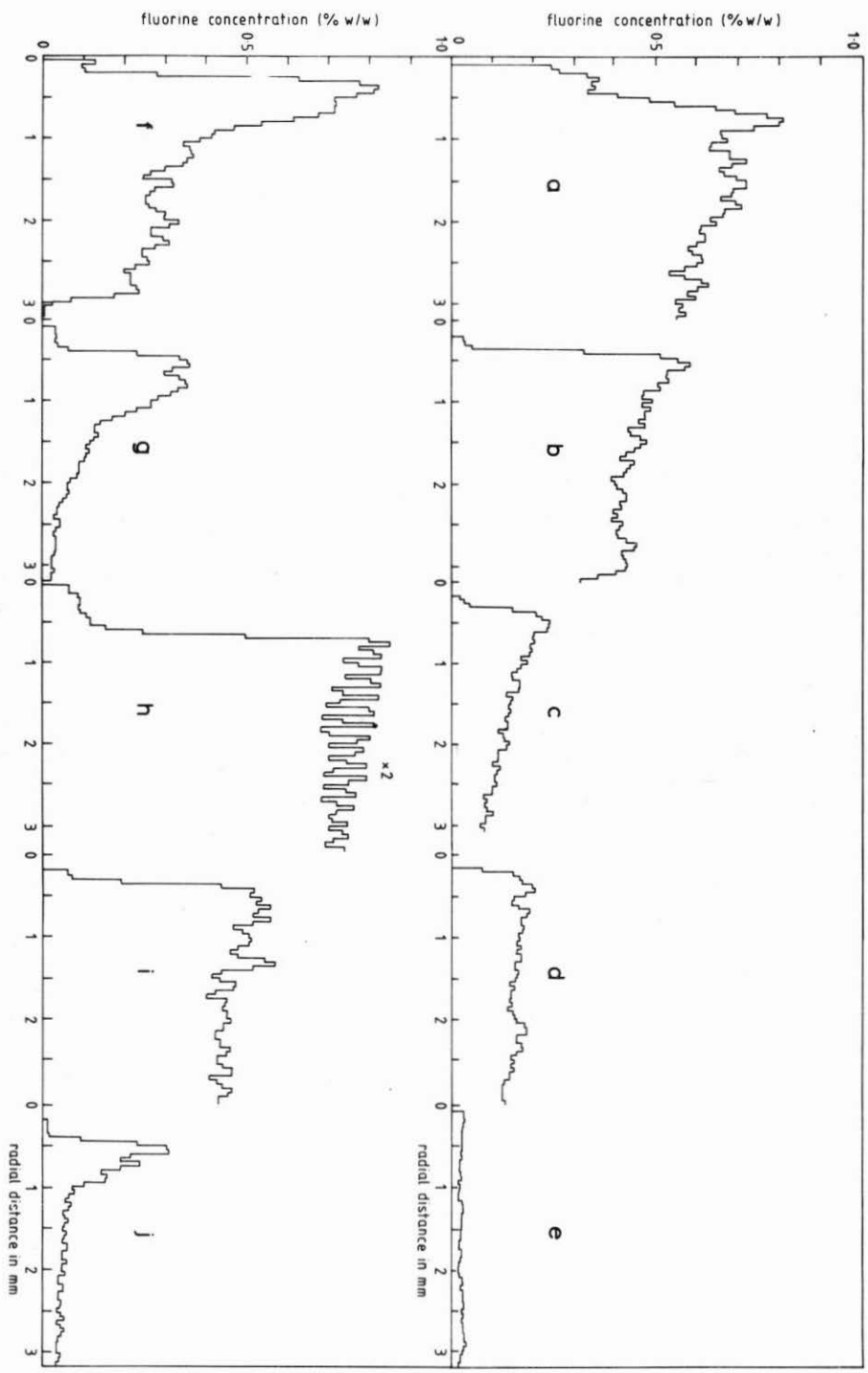
DISCUSSION

It appears that, although it has been accepted for many years that fluorine migrates from groundwater into bone, no quantitative theory has been proposed. The present results show that the penetration distance is very large – several millimetres – whereas the maximum penetration of water or fluorine into obsidian, for example, is only a few μm (Leach 1977). But the results also show that the time required for the bone to become saturated is quite long – ten thousand years or more. The porous nature of bone is clearly important but that in itself is no reason why a simple diffusion model should not be tested as a first approximation, though the diffusion constant obtained will be much larger than for a non-porous material.

As the simplest possible approximation we can regard a bone as a semi-infinite homogeneous solid, buried at time $t=0$ (Fig. 9). Fluorine concentration c_0 at the outer surface is maintained constant by ground water, water soaks into the bone and fluorine migrates slowly so that after time t the concentration profile follows a distribution $c(x,t)$. This problem is analogous to one of heat conduction, and has the solution shown which involves the error function erf(x) (Carslaw and Jaeger 1947). The curves in Figure 9 illustrate the evolution of the calculated profile as the parameter Dt increases. Analysis of the profiles of bones of known ages should show whether such a simple approach has some validity. We need to know if a sensible diffusion constant D can be extracted and how much this varies with the type of bone and the conditions of a site, particularly the average temperature.

More realistic treatments will recognize that, as bone is a polycrystalline material, diffusion will involve two inter-related processes: rapid diffusion along grain boundaries followed by a slower movement from the surface of each crystal into the lattice. The subject of "high-diffusivity paths" is treated by Shewmon (1963), though only with reference to metals. The most complete mathematical treatment, that of Levine and MacCallum (1959), appears to be a sound base on which to build.

The essential feature of a fluorine profile is not the maximum or average concentration, dependent as this is on the concentration in ground water, but the shape of the


fluorine concentration (% w/w)
fluorine concentration (% w/w)
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radial distance in mm
radial distance in mm

profile, which changes with time following burial in a way whose general features should be predictable. Deviations about the predicted curves, which arise from the composition of a given piece of bone, could well be important, and will have to be investigated by comparing different sections of the same bone and different bones from the same site. Some comparisons of this type can already be made, for example Figure 8 (*a* and *b*) and (*g-j*). An approach which might prove useful would be to compare the fluorine profile with those of other elements, for example calcium or phosphorus.

SOME POSSIBLE APPLICATIONS

A possible dating technique?

As mentioned above we should analyze profiles in bones dated by radiocarbon to see if a valid mathematical treatment of the diffusion process in bone can be devised and valid parameters extracted. The method could be applied only if the bone had been in continuous contact with ground water with an approximately constant fluorine content, and the average temperature of the site would have to be allowed for. The useful range would probably be a few thousand years.

As an aid to radiocarbon dating

This might take two forms: as a survey method used to select bones suitable for dating, or as a check on the validity of a date since different components of bone sometimes provide markedly different dates.

To quickly separate bones of different ages

The most likely application would be as a quick means of distinguishing bones of different ages which have become mixed together in a site. Chemical determinations of fluorine content have been used in this way previously, but the new technique provides extra information and should be more reliable.

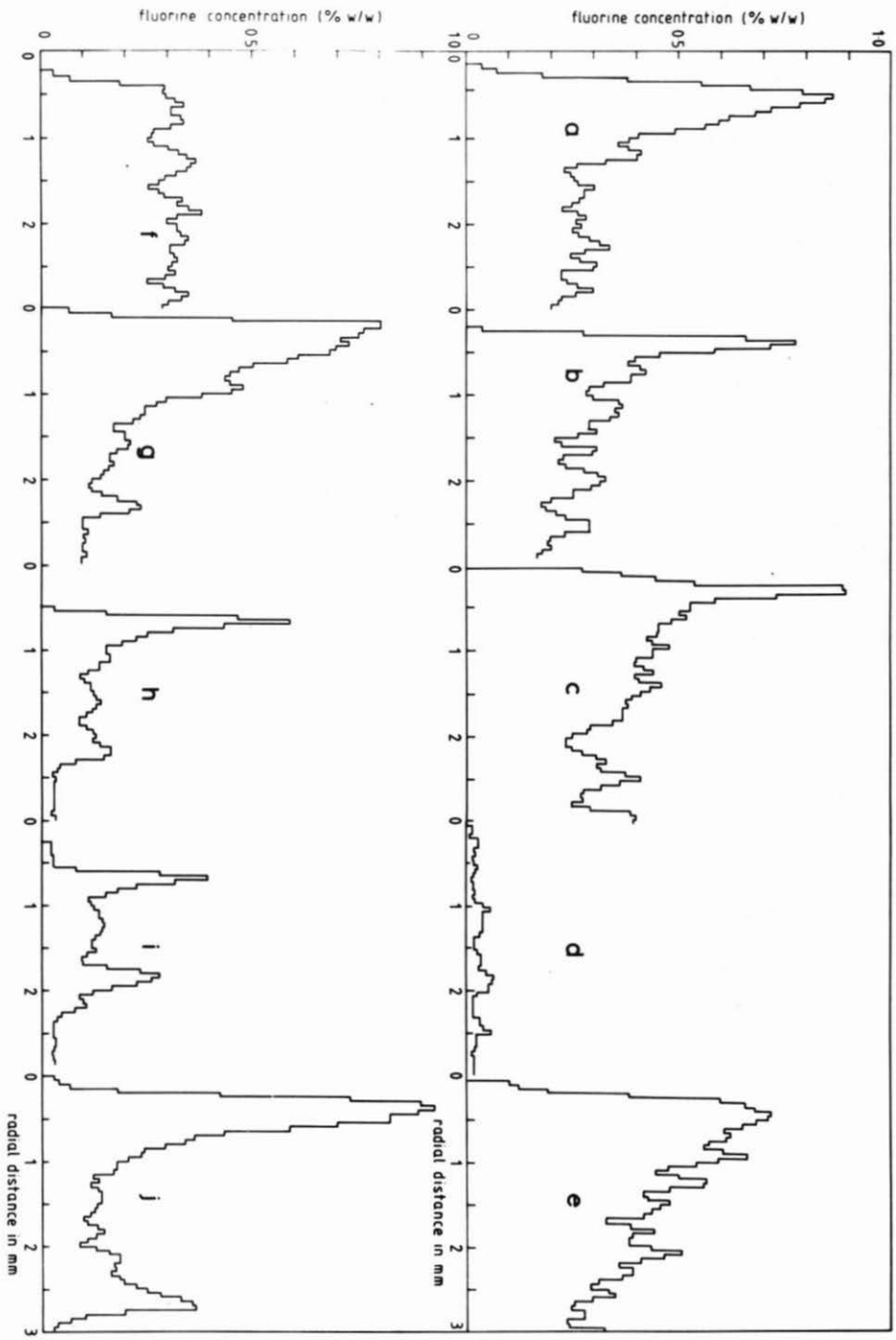
To show whether damage to a bone was contemporaneous with or later than the original burial

Bones are sometimes found which have been notched or otherwise damaged by human hand. The profile at a notch could be compared with that at an undamaged portion, to show if the bone was worked on at a later date than the burial.

Figure 7: Radial profiles of fluorine in moa bone and some animal bone from Europe.

a. Moa bone, Foxton Beach (Palmer Collection), N148/1. 400–600 B.P. (McFadgen 1978). (2)
b. Moa bone, Tom Bowling Bay, North Cape. 2130 ± 130 B.P., R5756/9, P. R. Millener. (3)
c. Moa bone, Henderson Bay, Northland. 2670 ± 110 B.P., R5708, J. C. Coster and G. Johnston. (3)
d. Moa bone, Tom Bowling Bay, Northland. 6040 ± 690 B.P., R5756/8, P. R. Millener. (3)
e. Moa bone, Martinborough Caves, Wairarapa. 1470 ± 50 B.P., M. M. Trotter, pers. comm. (2)
f. Moa bone, Cape Maria van Diemen, Northland. 1190 ± 70 B.P., R5756/1, P. R. Millener. (3)
g. Moa bone, Paremata, Wellington. Site N160/50. 400–500 B.P. (McFadgen 1980). (2)
h. "Animal" bone, Europe. 1 million years B.P. (4)
i. "Animal" bone, Europe. 12 000 years B.P. (4)
j. "Animal" bone, Europe. 1 600 years B.P. (4)

Bones were contributed by: (1) P. Houghton, Otago Medical School; (2) B. McFadgen, New Zealand Historic Places Trust; (3) Institute of Nuclear Sciences Radiocarbon Laboratory; (4) P. Eisenbarth, Austria.


fluorine concentration (% w/w)
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radial distance in mm
fluorine concentration (% w/w)
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radial distance in mm

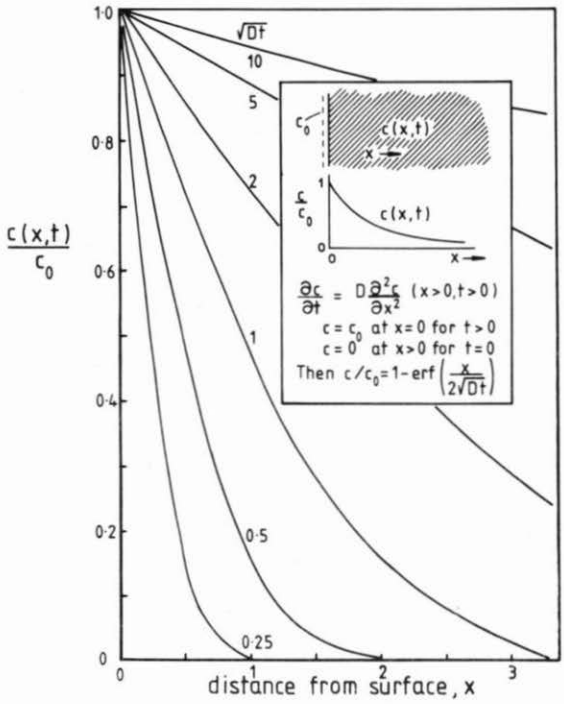

Figure 9: Mathematical theory of diffusion into a semi-infinite body, when the external concentration c_0 of diffusant remains constant in time; erf(x) is the error function.

Figure 8: Radial profiles of fluorine in human bone.
a. Femur, Chatham Islands. 620 ± 70 B.P., R5750/2, D. G. Sutton. (3)
b. Another section of the same bone as a.
c. Cortical bone from femur, Otago Peninsula. (1)
d. Cortical bone from fibula, Cape Wanbrow, Oamaru. (1)
e. Tibia, Takahanga Pa, Site S49/135. 540 ± 70 B.P., R5742. M. M. Trotter. (3)
f. Cortical bone from femur, Efate, New Hebrides. (1)
g. Cortical bone from fibula, Waihora, Chatham Islands. (1)
h. Hand phalanx, Waihora, Chatham Islands. (1)
i. A second hand phalanx, Waihora, Chatham Islands. (1)
j. Foot phalanx, Waihora, Chatham Islands. (1)
N.B. The bones g, h, i and j were all from the same Waihora burial.
Bones were contributed by: (1) P. Houghton, Otago Medical School; (2) B. McFadgen, New Zealand Historic Places Trust; (3) Institute of Nuclear Sciences Radiocarbon Laboratory; (4) P. Eisenbarth, Austria.

New applications

With further experience in interpreting profiles some new applications might be found, e.g. a suitable profile might provide a record of ground-water variations at a site over a long period, and there could be uses in forensic science.

CONCLUSIONS

We have shown that with the nuclear microprobe we can measure in a few minutes the radial profile of fluorine in a bone, with minimal preparation of the specimen and with adequate sensitivity and spatial resolution for any likely application.

As expected, absolute concentrations of fluorine at the surface vary widely but so do the shapes of the profiles. Even at this early stage the method could probably be applied to distinguish bones of different ages from a common site, or to select bones suitable for carbon dating. Further measurements on dated specimens and study of the mathematics of diffusion in bone may lead to a new dating method. Systematic studies, with groups of bones selected to test particular aspects of the method, will be needed before the full potential and limitations of this new technique can be established.

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Mr G. J. McCallum brought to our attention the work of Eisenbarth and Hille (1977) and suggested we try to develop it further. P. Houghton, B. McFadgen, P. Eisenbarth and C. McGill supplied the bone samples which allowed this project to get "into the ground". J. West, P. Pohl and C. Purcell made important contributions to the development of the microprobe. Dr B. F. Leach made helpful comments on a draft of this paper.

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