

APPLICATION OF NEUTRON ACTIVATION ANALYSIS TO THE STUDY OF ELEMENT CONCENTRATION AND EXCHANGE IN FOSSIL BONES

E. BADONE,** R. M. FARQUHAR*

**Department of Physics, University of Toronto, Toronto (Canada)*

***Department of Anthropology, University of Toronto, Toronto (Canada)*

(Received July 7, 1981)

It has long been known that a variety of elements are introduced into voids in the structure of bone during fossilization. Visual examination of the cross-section of many bones in the early stages of fossilization reveal a staining which is most intense near the outer surface. This suggests that concentration gradients must exist for elements entering the bone. To investigate this possibility quantitatively, we have determined elemental concentrations in such bones as a function of depth below the outer surface. Using a SLOWPOKE reactor, we have analysed a number of samples of bone taken from secondary deposits of river sediments in the Old Crow region of the Yukon Territory, Canada. Our preliminary work indicates the decrease in concentration with depth into the cortex for previously recognized post-mortem elements such as U, F, Ba, Mn and Fe. Our measurements show that V, Sc, and Co also vary in this way and can be included in this group. As the hollow central shafts of bones are approached, concentrations increase again. Bones found in the Old Crow region display a variety of surface staining ranging from almost white through red to brown and black. There is a strong correlation between Fe and less positive relations between F and Ba, and staining. Highest Mn concentrations occur at the surfaces of light-coloured bones in which the staining is restricted to the outer 1 mm. Because of the wide range of concentrations which exist among post-mortem elements in these bones, correlations among these elements can be studied. Manganese and barium, for example, are correlated within each bone, but the correlation patterns differ from bone to bone. These relationships must reflect the nature of the chemical processes associated with the deposition of the elements within the bones. A comparison of these patterns show that some of the bones have been exposed to more than one set of environmental conditions. This data thus provides a way of studying these processes in bones in which the introduction of elements from the environment has not completely and uniformly filled all the available voids.

Introduction

The fossilization of bones is a process which involves not only the degradation of organic constituents but also significant exchanges of inorganic compounds with the environment. These exchanges have been studied

*Present address: Department of Anthropology, U.S.C., Berkeley, Calif., USA.

by a number of authors, notably TOOTS and PARKER and their coworkers^{1,2,3,4,1} using a variety of analytical techniques. About twenty-five elements have been identified as having been introduced into buried bone from the surrounding environment. Many of these elements occur in trace amounts and quantitative measurements of their concentrations have not been made. In fact the number of elements which have been introduced into fossilizing bones is probably much larger than this. Even the most compact phases of bone are porous, containing many microscopic cracks and voids. As the breakdown of the organic components of bone proceeds, more internal voids are generated, and complex organic acids are produced which may catalyze the precipitation of inorganic minerals from solutions which enter the bone from the exterior.⁵

In spite of its sensitivity and rapidity, neutron activation analysis (N.A.A.) does not appear to have been widely used to determine the chemical constitution of fossil bones. Neither have studies been made of the progressive character of fossilization. Because this would require multiple analyses, N.A.A. is again an attractive alternative to other established techniques. The process of bone mineralization is a gradual one and presumably any bone in an intermediate stage of fossilization will not be likely to contain a homogeneous distribution of those elements entering it from the environment. In fact we might expect that elemental concentrations within fossilizing bones would respond to changing external conditions as long as pathways into the bones' interiors remain open.

As a preliminary test of this hypothesis we have used N.A.A. to determine the concentrations of several elements as a function of depth in a number of bones in which the process of fossilization does not yet appear to be complete. The samples studied have been selected from materia

collected in the Old Crow basin of the Yukon Territory, Canada, during the course of the Northern Yukon Research Program (NYRP).^{6,11} This region is of anthropological importance because it remained unglaciated during the most recent ice age, and was a refugium for many species (including man) during that time. The most abundant and accessible source of skeletal material is in secondary deposits exposed on the banks of the Old Crow river; the material we have analysed is mainly from two such localities and consists of leg bones of herbivorous mammals such as bison, and mammoth. Although the bones have spent a significant portion of their burial history at temperatures below 0 C (the basin is now underlain by permafrost), they have also been in contact with ground water, and as a result they have been variously stained, superficially and internally, by the deposition of minerals.

Experimental

Table 1 lists a subset of the samples we have analysed, for which we are reporting concentration data here, together with a description of the colour and penetration of the staining. This subset has characteristics typical of the other samples for which we have data. In general those bones with pale external surfaces show only slight internal colouring, while bones with dark red to black exteriors are deeply and strongly stained internally, suggesting that within the latter, relatively large amounts of minerals have been deposited. For neutron activation analysis, samples of 50 - 300 mg were obtained by sequentially coring the bones radially using a set of end mills and a drill press, as shown in Fig. 1. The end mills, made of hardened steel, have flat ends, so that the depth of each sample was reasonably well defined. These depths were determined relative to the external surface of

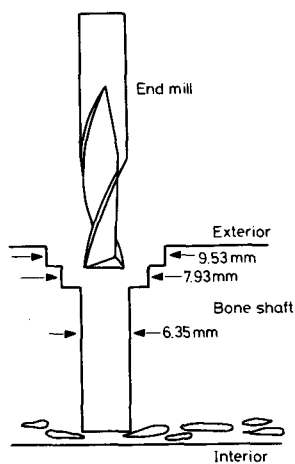


Fig. 1. Bone sampling procedure

Table 1
Listing of the subset of samples analysed

Sample No. and location	Bone Type	Characteristics of staining
M-1 Old Crow area	Modern Moose, long bone (fragment)	unstained, surface find
11-1-75-2, Old Crow River	Bison, right metacarpal (whole)	pale yellow, no visible penetration
11A-76-2784, Old Crow River	Proboscidea, long bone (fragment)	black, deep visible penetration
13-75-25, Old Crow River	Bison, right humerus, (whole)	yellow-brown, minor visible penetration
1175-3-3, Old Crow River	Bison, left humerus, (whole)	red-brown, moderate visible penetration
Big bluff 76-29 Porcupine River	Bison, right humerus, (part)	yellow-brown, minor visible penetration

each sample using a vernier caliper depth gauge. A number of measurements of each depth were made; in all the figures in which concentration-depth data are shown, the value of the depth for each sample point is plotted at the average mid-point of the cylindrical sample core relative to the exterior bone surface. The powdered bone samples obtained from each coring step were transferred to weighed polyethylene vials, weighed, and capped for neutron irradiation. The samples were not ashed to remove organic compounds and water.

Slow neutron irradiation took place in the University of Toronto's SLOWPOKE reactor.⁷ Three separate irradiations were used. The first, at a thermal neutron flux of approximately 10^{11} neutrons cm^{-2} s^{-1} for 10 s, was designed to activate fluorine to produce the 11.1 s gamma activity due to ^{20}F . The second irradiation at 10^{11} neutrons cm^{-2} s^{-1} for 6 m, activated predominantly short half-life isotopes in U, Ba, Sr, Na, V, Al, Mn, La, Eu, Sm and Ca.⁸ A 16 h irradiation at a flux of 2.5×10^{11} neutrons cm^{-2} s^{-1} was used to produce much longer lived activities in Fe, Co, Cr, Sc, and Th. After each of these irradiations, gamma activities of the samples were determined using a Li-drifted Ge detector coupled to a multi-channel analyser (Canberra Ltd., model 8100). The integrated gamma ray counts for each peak of interest, together with background, were output on a standard teletype printer. A simple computer program was used to make corrections for the decay of the various gamma activities in the interval between removal from the reactor and counting, and also to determine the concentrations of the elements activated using factors supplied by Dr. R.G.V. Hancock of the SLOWPOKE reactor laboratory, or determined by the authors using activation analysis of standards of known composition.

Results

Among the elements whose concentrations we have measured as a function of depth, Ca is the only major constituent which is clearly part of the original bone structure. Fig. 2 presents the Ca concentration distributions in three of the samples; the modern moose bone, a lightly stained bison metacarpal, and a heavily stained proboscidea fragment. There are fluctuations in Ca concentration with depth, but the data do not suggest that any progressive changes in this element exist. Sr and Na are like Ca in this regard. Fig. 3 is a plot of U concentration with depth in one of the samples of fossil bone. This Fig. indicates there are significant positive concentration gradients toward the exterior surface of the bone and also toward the interior surface. By comparison, the U content of the modern bone is below the detection limit (~ 0.2 ppm) almost throughout its interior.

The concentrations of U in Fig. 3 are expressed in $\mu\text{g}/\text{g}$ of raw bone, since the samples were not dried or ignited before analysis. Compensation for the presence of varying amounts of water and organic residues can be achieved by expressing the concentration of U relative to Ca, a major component of the hydroxy-apatite matrix of bone. Fig. 4 indicates how this ratio varies with depth in the same bone shown in Fig. 3. The concentration gradients are still evident.

The existence of these concentration gradients is a common feature of all but one of the fossil bones listed in Table 1, for a wide range of elements. Fig. 5 demonstrates this for Mn, and also compares the distribution of this element in samples taken from opposite ends (~ 25 cm apart) of a single fossil bone. The concentration gradient in a given bone may apparently be defined reasonably accurately by a set of measurements made at one point on the bone. Like Mn, Ba is more highly concentrated toward

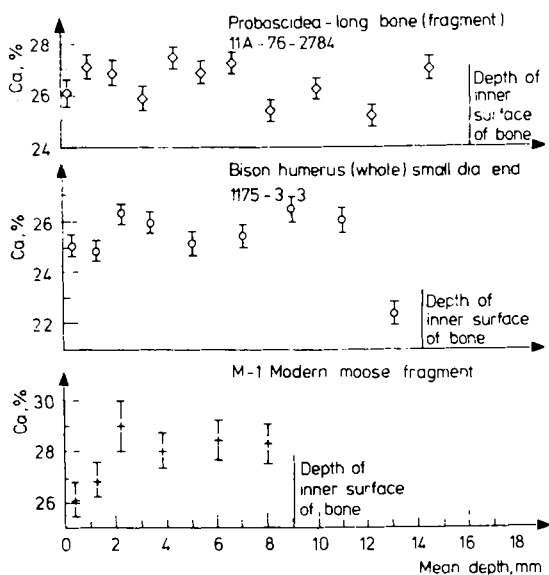


Fig. 2. Calcium concentration with depth in modern and fossil bones

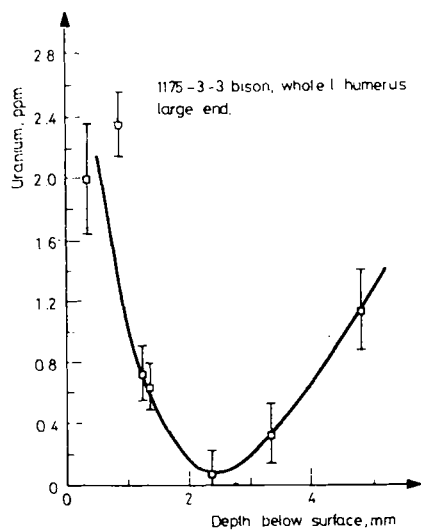


Fig. 3. Uranium variation with depth in fossil bone

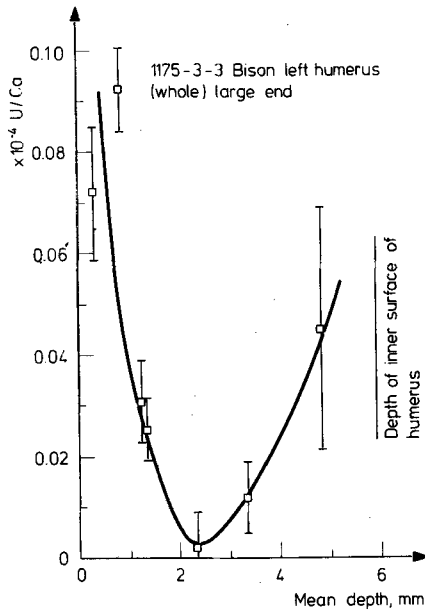


Fig. 4. Uranium/calcium ratio variation with depth in fossil bone

the bone surfaces, as shown in Fig. 6. The general level of Ba concentration differs greatly in bone from one locality compared to that from another, even though the exterior staining of the bones is similar. For V, on the other hand (Fig. 7) concentrations and concentration gradients are similar at the outer surfaces of two bones having great differences in staining, found at different localities. In contrast F in two bones of dissimilar staining, is quite differently distributed (Fig. 8) although still displaying higher concentrations toward the exterior surface. With the exception of Ba, the concentration of the above elements in modern bone M-1 is at or below the limit of detection.

The data on which Figs. 2-8 are based, are given in Table 2. Included in that table are concentration results for Fe, Co and Sc for a selected

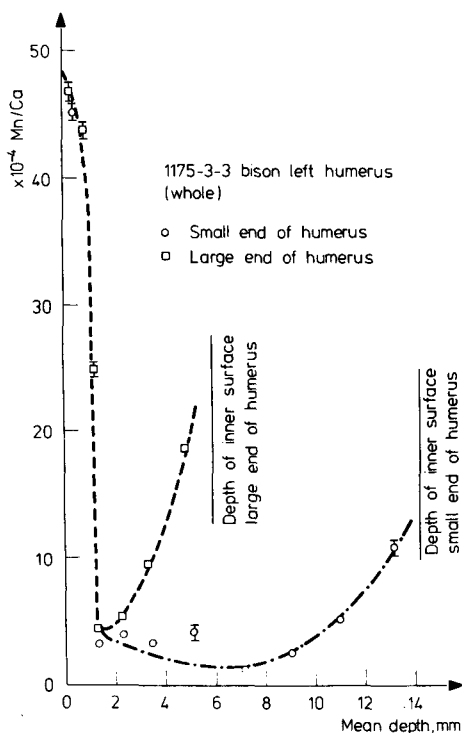


Fig. 5. Manganese/calcium ratio variations with depth in a single fossil bone

sub-set of the samples. It is not possible to draw "continuous" concentration-depth profiles for these elements, but the discrete data values for them suggest that in general they vary within the bones in a similar way to Mn, Ba, V, U and F. In a qualitative way our activation analyses also suggest that Al, Dy, La, Eu and Sm, are similarly distributed.

Discussion

The surface colouration, or staining of the fossil bones, noted in Table 1, is an optical phenomenon which results from chemical compounds distributed in layers no more than a few nm in thickness. Our analyses

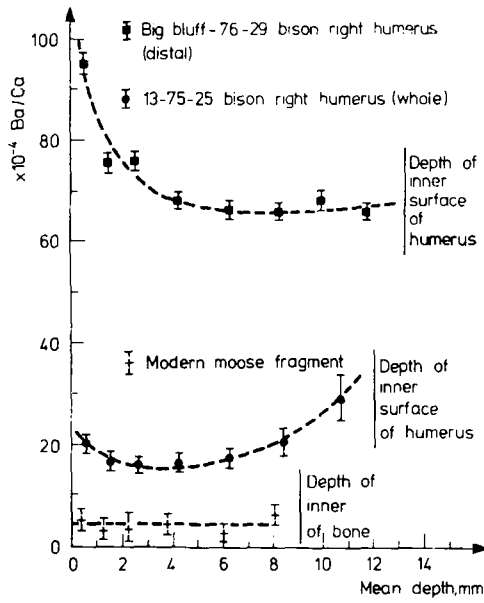


Fig. 6. Barium/calcium ratio variations with depth in fossil bones of similar colour from different locations

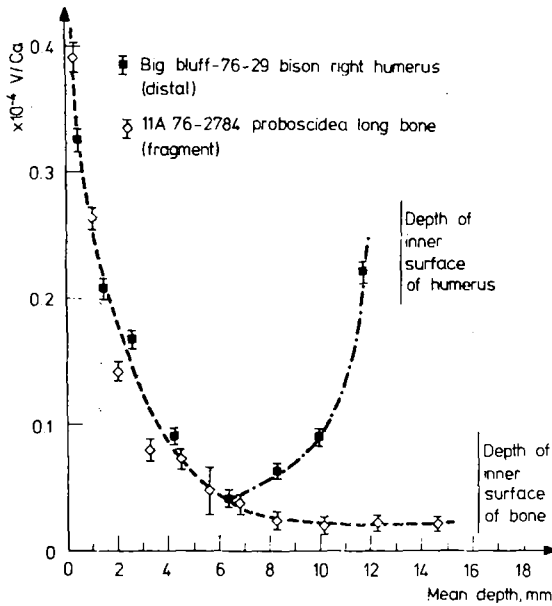


Fig. 7. Vanadium/calcium ratio variations with depth in fossil bones of different colour from different locations

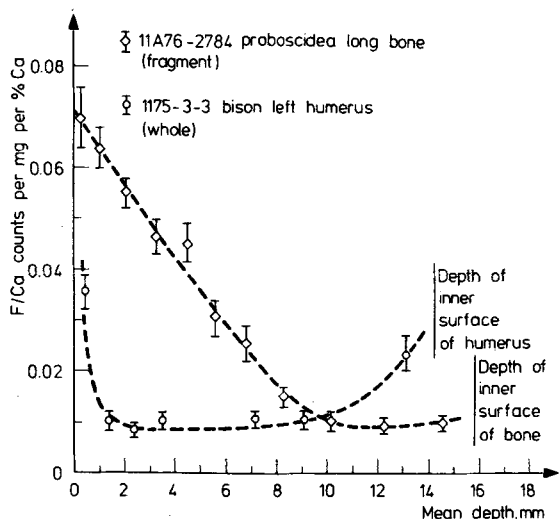


Fig. 8. Fluorine/calcium ratio variations with depth in fossil bones of different colour from different locations. Calibration factor for F is not available

of the elemental concentrations in the outer bone sections give averages over depths of 0.6 to 1.0 mm. The concentration gradients in these sections are large, and vary from sample to sample. Nevertheless there is a rough correlation between colour and the concentrations of Fe, Ba, F, and Mn, as Table 3 indicates. We have examined the staining-concentration relationship in more detail using a larger suite of bones, and find that the correlation between colour and outer-layer Fe concentration is a strong one. Mn, which has been identified by others^{12,13} as a staining agent of fossil bones, is less strongly correlated with colour, as are Ba and F. The data on which these observations are based will be presented and discussed in a separate publication. The larger suite of samples includes many which have been ¹⁴C dated. We observe weak correlations between age and the concentrations of Fe, Ba, F and Mn in those samples, and will discuss the details of these relationships in a later publication.

Table 2
Concentration and depth data for bone samples

Sample	Ca %	Mn ppm x10 ²	Ba ppm x10 ²	V ppm	U ppm	F cts/mg	Fe %	Co ppm	Sc ppm	Mean Depth mm
Modern Moose M-1	26.1±.8	<.05	1.5±.5	n.d.	.3±.2	n.d.	.04±.04	4.3±.7	8±3	.39
	26.8±.8	<.06	.9±.5	n.d.	<.4	.05±.05	-	-	-	1.27
	29.0±.9	<.08	1.1±.9	n.d.	.4±.4	n.d.	-	-	-	2.25
	28.0±.6	n.d.	1.3±.4	<.2	.3±.2	<.05	<.03	1.1±.3	<2	3.83
	28.4±.6	n.d.	.8±.4	n.d.	<.3	.09±.04	-	-	-	6.07
	28.3±.9	<.05	1.9±.5	.8±.2	.5±.2	<.11	.06±.02	1.7±.3	3±1	8.03
11-1-75-2	23.7±.3	.90±.04	4.1±.3	1.6±.1	.5±.1	.26±.04	.729±.010	1.4±.1	22.7±.9	.61
	25.1±.6	.07±.04	3.8±.3	0.8±.2	.5±.1	.21±.04	-	-	-	1.78
	25.9±.8	.15±.06	4.5±.6	0.8±.3	1.2±.3	.23±.07	-	-	-	3.01
	24.8±.8	.54±.08	4.0±.8	4.1±.5	1.6±.4	.47±.11	-	-	-	4.70
	24.1±.8	.4±.1	3.3±1.3	4.9±.7	3.8±.6	.70±.15	<.012	3±1	32±6	7.20
	24.7±.8	.4±.1	4.0±1.5	10.3±.9	3.0±.7	.9±.2	-	-	-	9.55
23.4±.7	.4±.1	5.5±1.5	6.0±.9	3.3±.7	.54±.15	-	-	-	11.32	
26.6±.8	.4±.1	7.0±1.4	6.5±.8	1.5±.6	.41±.15	.18±.06	5±1	33±5	13.40	

Table 2 (cont.)

Sample	Ca %	Mn ppm $\times 10^2$	Ba ppm $\times 10^2$	V ppm	U ppm	F cts/mg	Fe %	Co ppm	Sc ppm	Mean Depth mm
13-75-25	25.5±.3	4.17±.07	5.3±.3	.9±.1	1.8±.1	.61±.05	.49±.01	1.4±.1	41±1	.55
	27.7±.6	.68±.05	4.7±.4	.4±.1	.5±.1	.43±.06	-	-	-	1.58
	27.8±.6	.52±.05	4.5±.3	.5±.2	.3±.1	.39±.05	-	-	-	2.66
	25.9±.6	.45±.05	4.4±.4	.2±.1	.2±.2	.30±.06	-	-	-	4.23
	26.3±.6	2.13±.06	4.7±.3	1.3±.2	.3±.1	.32±.04	.25±.01	1.2±.1	8.1±.7	6.27
	24.7±.5	4.8 ±.1	5.2±.6	6.9±.4	1.1±.2	.40±.06	-	-	-	8.40
Big Bluff-76-29	21.5±.6	7.3 ±.2	6.3±1.2	25.7±.9	1.7±.5	.63±.13	.98±.03	4.5±.4	129±3	10.70
	23.7±.3	4.48±.08	22.6±.5	7.7±.2	.6±.2	1.42±.08	2.07±.03	6.7±.3	439±3	.50
	25.7±.6	3.15±.08	19.5±.5	5.3±.2	<.2	1.00±.07	-	-	-	1.50
	24.6±.5	2.36±.06	18.7±.4	4.1±.2	<.2	.74±.06	-	-	-	2.59
	24.2±.3	2.21±.05	16.6±.3	2.2±.1	.4±.1	.34±.03	-	-	-	4.25
	24.7±.3	1.97±.06	16.5±.4	1.1±.1	<.2	.47±.05	2.15±.02	1.3±.1	6.4±.9	6.35
	26.6±.3	2.16±.06	17.6±.4	1.7±.1	<.1	.51±.05	-	-	-	8.22
	25.8±.6	2.39±.07	17.6±.5	2.4±.2	.3±.1	.57±.06	-	-	-	9.92
	25.4±.6	3.67±.08	16.8±.4	5.6±.2	.4±.2	.81±.06	2.28±.02	2.4±.2	46±1	11.74

E. BADONE, R. M. FARQUHAR: APPLICATION OF NEUTRON ACTIVATION

Table 2 (cont.)

Sample	Ca %	Mn ppm x10 ²	Ba ppm x10 ²	V ppm	U ppm	F cts/mg	Fe %	Co ppm	Sc ppm	Mean Depth mm
11-75-3-3 Small end	25.1±.6	11.4±.1	8.3±.5	1.4±.2	2.2±.2	.90±.07	.31±.01	1.7±.2	32±1	.43
	24.9±.5	.83±.05	4.2±.3	<.2	.3±.1	.26±.05	-	-	-	1.34
	26.4±.3	1.05±.05	3.2±.3	.2±.1	.2±.1	.23±.03	-	-	-	2.37
	26.0±.6	.84±.04	4.4±.3	n.d.	.2±.1	.27±.04	-	-	-	3.48
	25.2±.6	1.07±.05	4.4±.4	.7±.2	.4±.1	-	-	-	-	5.13
	25.5±.6	.30±.04	4.3±.3	<.5	.4±.1	.28±.04	.17±.01	.8±.1	3.4±.8	7.17
	26.5±.6	.69±.05	4.4±.4	.3±.1	.3±.1	.29±.04	-	-	-	9.06
	26.1±.6	1.37±.06	4.8±.4	2.0±.2	.4±.2	-	-	-	-	11.03
	22.4±.5	2.47±.08	4.4±.6	9.0±.4	1.1±.2	.53±.07	.92±.02	2.8±.2	78±2	13.13
	27.7±.9	13.0±.2	12.1±.9	4.3±.4	2.0±.4	1.16±.12	2.05±.04	3.3±.4	78±3	.34
11-75-3-3 Large end	25.5±.6	11.2±.1	7.1±.5	2.6±.2	2.4±.2	.68±.06	-	-	-	.86
	23.6±.5	5.9±.1	7.4±.5	.8±.2	.7±.2	.57±.07	-	-	-	1.24
	26.6±.6	1.20±.06	4.6±.4	.1±.1	.6±.2	.38±.05	-	-	-	1.33
	26.2±.6	1.44±.06	4.8±.4	.1±.1	<.2	.30±.05	-	-	-	2.33
	27.7±.6	2.67±.09	5.3±.5	<.2	.3±.2	.62±.08	.99±.02	1.2±.2	22±10	3.32
	25.4±.6	4.8±.1	6.7±.6	5.3±.4	1.1±.3	.71±.08	1.51±.03	3.0±.4	42±2	4.79

Table 2 (cont.)

Sample	Ca %	Mn ppm x10 ²	Ba ppm x10 ²	V ppm	U ppm	F cts/mg	Fe %	Co ppm	Sc ppm	Mean Depth mm
11A-76-2784	26.1±.6	9.1±.1	31.1±.7	10.2±.3	.9±.2	1.8±.1	4.76±.07	16.3±.7	948±8	.31
	27.1±.6	8.3±.1	23.1±.6	7.1±.3	2.1±.2	1.7±.1	-	-	-	1.06
	26.8±.6	7.3±.1	20.3±.5	3.8±.2	.8±.2	1.49±.08	-	-	-	2.07
	25.9±.6	5.69±.09	18.8±.5	2.1±.2	.7±.2	1.21±.08	-	-	-	3.28
	27.5±.8	5.7±.1	17.7±.7	2.0±.2	.6±.2	1.3±.1	-	-	-	4.49
	26.9±.7	5.8±.1	14.5±.7	1.3±.3	<.4	.83±.09	2.55±.06	3.6±.5	16±2	5.60
	27.3±.6	5.2±.1	14.4±.6	1.0±.2	.9±.2	.70±.09	-	-	-	6.80
	25.4±.6	4.86±.09	12.6±.5	.6±.2	.2±.2	.39±.05	-	-	-	8.28
	26.3±.6	4.76±.09	12.5±.4	.5±.1	.7±.2	.27±.04	-	-	-	10.14
	25.2±.3	4.47±.07	11.5±.3	.6±.1	.4±.1	.24±.03	-	-	-	12.27
	27.1±.3	5.22±.08	12.6±.4	.6±.1	.5±.1	.28±.03	2.26±.02	1.1±.1	4.4±.7	14.61

Table 3
Surface colours and outer layer mean concentrations

Bone Sample	Surface Colour	Fe/Ca	Ba/Ca $\times 10^{-4}$	F/Ca cts/mg/%Ca	Mn/Ca $\times 10^{-4}$
Modern Moose M-1	White	<.003	5 \pm 2	0	.2 \pm .2
11-1-75-2	Pale Yellow	.0307 \pm .0001	17 \pm 1	.011 \pm .002	3.8 \pm .2
13-75-25	Yellow-Brown	.0191 \pm .0004	21 \pm 1	.024 \pm .002	16.3 \pm .3
Big Bluff-76-29	Yellow-Brown	.0874 \pm .0012	95 \pm 2	.060 \pm .003	18.9 \pm .3
1175-3-3 (small end)	Red-Brown	.0123 \pm .0004	33 \pm 2	.036 \pm .003	45.4 \pm .5
(large end)	Red-Brown	.0742 \pm .0014	44 \pm 3	.042 \pm .004	47.0 \pm .8
11-A-76-2784	Black	.183 \pm .002	119.4 \pm .3	.070 \pm .004	34.9 \pm .5

Since none of the bones described in Table 1 have been dated, we cannot examine the relation of age to element concentration and distribution. Time certainly plays a role in the mineralization process, as previous studies have shown.^{9,14} In our analyses, time is probably one of the parameters which determines the magnitude of the concentration gradients for U, F, Mn, Ba and V shown in Figs. 3-8. The simplest explanation for the existence of these gradients is that they are associated with the gradual mineralization of bone buried in environments containing relatively large concentrations of these elements (as well as V, Fe, Co and Sc) dissolved in ground water. As many authors^{10,15,4,16,17} have remarked, mineralization is a complex function of bone type, mineralizing solution chemistry, temperature and time, and we are not likely to be able to entirely separate the effects of these variables even by greatly increasing our sample data base. If

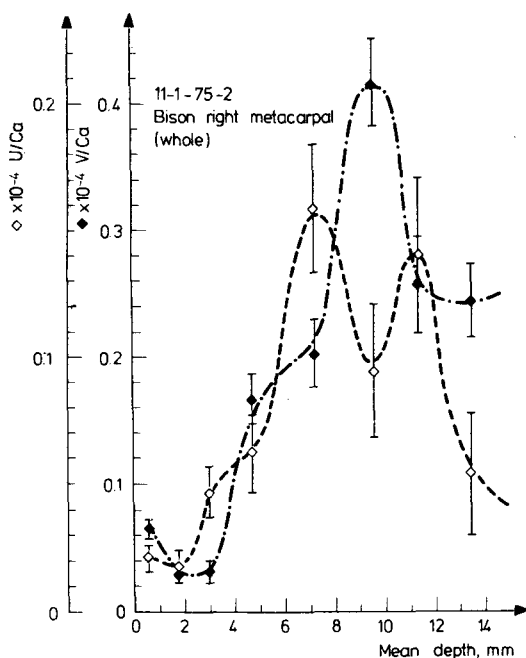


Fig. 9. Vanadium/calcium and uranium/calcium ratios in fossil bone from locality 11-1-75-2

the negative gradients in Figs. 3-8 are the result of movement into the bones, then the distributions for U and V in 11-1-75-2 (Fig. 9) could result from a reversal of this process. This effect has been reported¹⁸ for fossil bovid teeth. The relatively large interior concentrations would thus be the residue of a previous episode of mineralization altered by immersion in a second environment.

Most of the bones in the present study are found in secondary deposits and have certainly been in contact with at least two ground water systems. Although the effects of these systems seem clearly evident in bison metacarpal 11-1-75-2, there is less obvious evidence for several of the other bones that the concentrations of the elements deposited in them have been

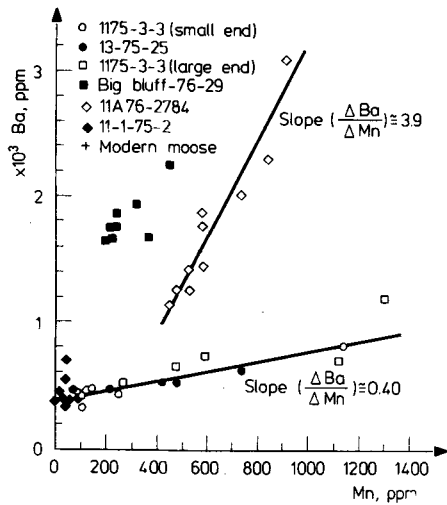


Fig. 10. Barium concentrations against manganese concentrations for all fossil bones. Linear segments are least squares fitted to data

determined by exposure to more than one set of environmental conditions. Fig. 10 is a plot of the concentrations of Ba against Mn, for all the samples in Table 2. This graph indicates that there are strong correlations between Ba and Mn for 11A-76-2784, for Big Bluff-76-29 and for the remaining bones, and that these correlations are quite different from each other. There are similar types of correlations between V and Mn (Fig. 11) and F and Mn (Fig. 12). The correlations suggest that within each bone the Ba/Mn, V/Mn and F/Mn ratios are roughly constant, but that these ratios differ greatly from bone to bone. The slopes of the lines which best fit the distributions give average values for these ratios (Ba/Mn \sim 3.9 for 11A-76-2784; \sim 0.4 for 1175-3-3 and 13-75-25; V/Mn \sim 0.018 for 11A-76-2784; \sim 0.030 for Big Bluff-76-29). The ratios reflect those in the mineralizing solutions or the nature of the minerals deposited in the bones. Little is known about the mineralogical nature of the compounds which precipitate

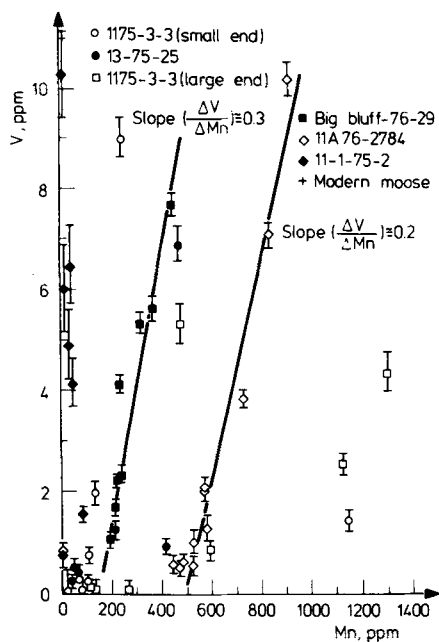


Fig. 11. Vanadium concentrations against manganese concentrations for all fossil bones. Linear segments are least squares fitted to data

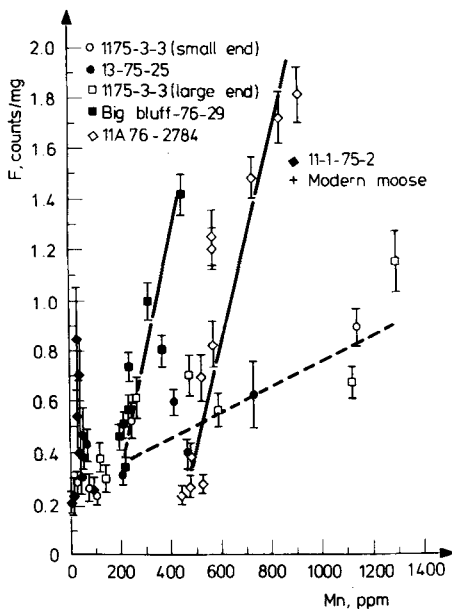


Fig. 12. Fluorine concentrations against manganese concentrations for all fossil bones

in bones during fossilization, but PARKER and TOOTS⁵ have identified a manganese-containing mineral (hollandite-coronadite) in fossil bone with which Ba is often associated. Whatever the nature of the factors controlling the Ba/Mn and V/Mn ratios in 11A-76-2784, examination of Fig. 11 indicates that the additions of V and Mn took place in a bone which already had an internal concentration of 450-500 p.p.m. Mn. The data for the Big Bluff-76-29 sample suggests that its Mn concentration must have been 180-200 p.p.m. prior to the additions of V and Mn which produced the correlated distribution for that bone. Referring to Fig. 10, 11A-76-2784 must also have contained 1050-1250 p.p.m. Ba, when Ba and Mn were added in a ratio of $\sim 3.9:1$, while Big Bluff-76-29 must have contained 1400-1600 p.p.m. Ba when the second-stage additions of Ba and Mn took place. These initial levels of Mn and Ba are significantly higher than those measured for modern bone from the Old Crow area (Mn ~ 0 ; Ba ~ 100 p.p.m.), and seem unlikely to have been incorporated into the samples through bone growth processes.

Conclusions

Neutron activation analysis of samples of fossil bone taken at a sequence of increasing depths into the bone cortex provide data which enable us to identify a variety of elements which have entered the bone since its burial. The range of concentrations encountered within the bone is often sufficiently large so that it becomes possible to define correlations among elements. These correlations in turn may assist us in deciding whether the bone has been exposed to a change in ambient conditions such as that which might accompany physical transportation to a new environment, or a change in the chemical nature of the surrounding

ground water. There are correlations between surface colour and the concentration of some elements (Fe, Mn, Ba and F) in the Old Crow region samples we have analysed. Further work will be necessary to determine whether the concentration gradients observed near the outer and inner surfaces of the bones can provide any useful information about the time interval during which the bones have been exposed to the various mineralizing environments.

*

We wish to thank W. N. IRVING, and B. BEEBE for advice in sample selection and identification and NINA BREGMAN and R. G. HANCOCK for assistance in making the analyses. Support for this project was received from the University of Toronto and The Natural Sciences and Engineering Research Council.

References

1. H. TOOTS, *Contr. Geol.* 2 (1963) 69.
2. H. TOOTS, M. R. VOORHIES, *Science*, 149 (1965) 854.
3. R. S. HOUSTON, H. TOOTS, J. C. KELLY, *Contr. Geol.*, 5 (1966) 1.
4. R. B. PARKER, H. TOOTS, *Geol. Soc. Amer. Bull.*, 81 (1970) 925.
5. R. B. PARKER, H. TOOTS, *Amer. Mineral.*, 57 (1972) 1527.
6. W. N. IRVING, in: *Early Man in America from a Circum-Pacific Perspective*; A. L. BRYAN (Ed.), Dept. of Anthropology, Univ. of Alberta, Occ. papers 1, 1978, p. 96.
7. R. E. KAY, P. D. STEVENS-GUILLE, J. W. HILBORN, R. E. JERVIS, *Inter. J. App. Radiation Isotopes*, 24 (1973) 509.
8. R. G. V. HANCOCK, *Anal. Chem.*, 48 (1976) 1443.
9. K. P. OAKLEY, *Phys. Anthrop. Yearbook*, 5 (1950) 44.
10. R. B. PARKER, H. TOOTS, in: *Fossils in the Making Vertebrate Taphonomy and Paleoecology*, A. K. BEHRENSMEYER, A. P. HILL (Eds), Univ. Chicago Press, 1980, p. 197.
11. W. N. IRVING, C. R. HARRINGTON, *Science*, 179 (1973) 335.
12. R. GRADZINSKI, *Paleontol. Polonica*, 21 (1969) 147.
13. K. K. TUREKIAN, R. L. ARMSTRONG, *Geol. Soc. Amer. Bull.*, 72 (1961) 1817.
14. K. P. OAKLEY, in: *Science in Archaeology*, D. BROTHWELL (Ed.), Thames and Hudson, 1963, p. 24.
15. R. B. PARKER, J. W. MURPHY, H. TOOTS, *Archaeometry*, 16 (1974) 98.
16. D. McCONNELL, *Science*, 136 (1962) 241.
17. S. F. COOK, R. F. HEIZER, *Amer. J. Phys. Anthropol.*, 17 (1959) 109.
18. M. G. SEITZ, R. E. TAYLOR, *Archaeometry*, 16 (1974) 129.