TRN NZ8600356

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INSTITUTE OF NUCLEAR SCIENCES

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LOWER HUTT, NEW ZEALAND

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Institute of Nuclear Sciences INS-R--330.

DIFFUSION PROFILES OF FLUORINE IN ARCHAEOLOGICAL BONES AND TEETH: THEIR USE AS A POSSIBLE DATING METHOD

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June 1984

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ABSTRACT

Measurements of radial fluorine profiles in bone and teeth sections with a nuclear microprobe show that the distribution is due to diffusion of fluoride ions inward from any exposed surface. Assuming simple diffusion and constant environment, the profile shape depends only on the parameter Dt/a^2 (D = diffusion constant, t = time, a = radius of bone/teeth).

Three computer programs have been written to allow visual comparison of data with theoretical diffusion curves. Use of these programs has shown that experimental profiles follow closely the predictions of simple diffusion theory. (Although the diffusion constant <u>may</u> depend on concentration and species to a lesser extent.) A preliminary value of D $(2.74 \pm 0.4) \times 10^{-4}$ mm^2/y was deduced from radiocarbon dated Moa bones (age 400-16,200 yr B.P.). Preliminary investigations indicate that the diffusion constant in tooth dentine is approximately the same as in bone.

These results indicate that a dating method using the computer programs should be possible for bones ranging in age from a few years to perhaps millions of years and that dating teeth should also be possible.

KEYWORDS

FLUORINE
BONES
TEETH
PROFILES
DEPTH
DIFFUSION
COMPUTER PROGRAMS
ARCHAEOLOGY
ABSOLUTE AGE

INTRODUCTION

The mineral component of bone(3), tooth enamel and dentine is calcium hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$, which has a strong affinity to fluorine ions; these replace the OH^- ions along channels parallel to the c axis of crystal, which are defined by triangles of calcium ions. The apatite crystals in bone are extremely small, about 60 nm by 4 nm, so that the total area of surface is high. The fluorine content in fluorapatite is 3.77%, but only in a special environment and over a long period would complete conversion take place.

The gradual uptake of fluorine from groundwater into buried bones has been known since 1840, and many attempts have been made to use this as a method for dating fossil bones, or at least for relative dating at a single site. The techniques available, chemical analysis and X-ray powder diffraction, could only provide the average fluorine content of a piece of bone. The investigators assumed that the distribution was uniform throughout the bone and increased linearly with time. Without a method of analysis which could separate the effects of bone environment and bone geometry from those of age it appears in hindsight that "fluorine dating" more often misled the worker than provided him with useful information.

The situation changed in 1981 when Coote and Sparks(1) showed that by means of a technique based on a nuclear accelerator the radial distribution of fluorine in a cross-section of a bone could be measured accurately in a few minutes. A focussed beam (about 100 μm by 100 μm) of 2.5 MeV protons from a Van de Graaff accelerator was stepped under computer control in a linear or two-dimensional pattern, and 6-7 MeV gamma rays from fluorine were detected in a large sodium iodide crystal. From a variety of excavated Moa and human bones they reached the following conclusions:

fluorine was securely held in bone and did not migrate even under prolonged irradiation

the surface concentration was usually in the range 0.2 to 1% by weight

the concentration decreases inwards from the surface, sometimes very sharply

bone from an arid site or a limestone cave contained very low levels (<0.05%) and there was no evidence for inward migration.

They proposed that the shape of the diffusion profile (as distinct from its magnitude) be investigated as a dating method, as it would change with time as predicted by the mathematical theory of diffusion.

Coote and Holdaway(2) reported further developments including a larger range of profile shapes, with the duration of burial ranging from a few years to 1.75 million years (in the Olduvai Gorge); the same bone had the largest surface concentration (3.2%), which was reasonable as the soil there is rich in fluorine from volcanic ash. The sharp "spikes" in the distributions were shown to arise from high F concentration in the walls of Haversian canals, through which blood had flowed; they were therefore relics of the living animal rather than features which formed during burial. The spikes are most obvious in bones of low fluorine content, and in ancient bone they have disappeared by outward diffusion. Bone which had been burnt before burial was apparently sealed to the inward migration of fluorine. It had become evident that because diffusion slows with time, a dating method based on these profiles would have a working range from a few years to a few million years. This paper contained the first radial profiles of an excavated tooth. Although fluorine was absorbed by the enamel (to a concentration of 1.3%) it had been unable to penetrate into the dentine - in effect the tooth was sealed by the enamel (although not by the cementum). However, it was discovered that, carried by groundwater, F had penetrated the pulp cavity whence it diffused symmetrically outward through the dentine; as there are no Haversian canals in tooth dentine the profiles were smoother than those in bone. The authors suggested that a proper mathematical treatment of such profiles could lead to a method for dating teeth.

Coote and Nelson(3) reported the first comparison of a measured profile with that predicted by diffusion theory. A computer program was written to compare the measured profiles of bones with the solution of the diffusion equation for a solid cylinder of radius $\underline{a}$.

$$\frac{\partial C}{\partial t} = \frac{1}{r}\frac{\partial}{\partial r}\left(r\, D\frac{\partial C}{\partial r}\right)$$ - diffusion equation in cylindrical co-ordinates

- assuming concentration C is a function of radius r and time t only.

D is the diffusion constant, the boundary conditions used were:

$C = C_0 \quad r = a \quad t \geqslant 0 \quad C_0$ = concentration at surface

$C = C_1 \quad 0 < r < \underline{a} \quad t = 0 \quad C_1$ = initial concentration

the solution is

$$\frac{C - C_1}{C_0 - C_1} = 1 - \frac{2}{a} \sum_{n=1}^{\infty} \frac{\exp(-D\alpha_n^2 t)\, J_0(r\alpha_n)}{\alpha_n\, J_1(a\alpha_n)}$$

where α_n's are solutions of

$$J_0(a\alpha_n) = 0$$

and $J_0(x)$, $J_1(x)$ are the Bessel functions of the first kind of order zero and one respectively. The finite sum was approximated by truncating after 20 terms.

Since the spikes in the profile were deemed irrelevant the comparison of theory and experiment was made visually, instead of by a least squares fit. From use of the above program on a number of bones in which the profiles did not appear to be affected by the outward diffusion of fluorine from the inner surface of the bone, Coote reached the following conclusions:

the agreement in shape between experimental and theoretical profiles is remarkably good, considering that bone is not a uniform material and soil conditions could change over time, altering the equilibrium concentration at the surface;

there was no evidence of any process other than simple diffusion, with diffusion constant D;

an interim estimate of $D = 2.67 \times 10^{-4}$ mm^2/yr was proposed;

the edge of the bone as determined from the fluorine profile was consistent with the edge determined by a simultaneously measured calcium profile;

the mathematical treatment assumes cylindrical shape, which a bone is unlikely to have. But it was found that using the local radius for $\underline{a}$ or using an average radius has little effect on the analysis;

the method showed promise to serve to fill in the gap between present time and the minimum age which can be determined by C-14 dating (about 250 yr B.P. as a garden bone was dated at 4 ± 2 years (using $D = 2.67 \times 10^{-4}$ mm^2/yr);

although the precision of the dating method may never be high, the probable error as a fraction of age may stay roughly constant or even improve with the smoother profiles of older bones.

The above paper did not attempt to determine whether the calculated diffusion constant did in fact remain constant for a variety of bones, nor was diffusion in "hollow bones" (i.e. ones in which the F not only diffused inward from the outer surface of the bone, but also outward from the inner surface) or teeth compared quantitatively. The first investigations of this nature are described below.

METHOD

Three computer programs were written for the Institute of Nuclear Sciences PDP-11 computer with a graphics display, to compare experiment with the theory of diffusion into -

a solid cylinder with constant concentration at the outer surface (solid bone);

a hollow cylinder with constant (but perhaps different) concentrations at the inner and outer surfaces (hollow bone);

a hollow cylinder with constant concentration at the inner surface and with outer surface impermeable (teeth).

The analytical solution of the diffusion equation used in the previous work(3) was only applicable in the special case of a solid cylinder. Solutions for the above boundary conditions were found to be even more complicated(4) and proved difficult to approximate for numerical calculation. It was found that truncating the solution, for the solid cylinder, after 20 terms was not a satisfactory approximation for small times. For T near zero the "solution" developed oscillations in the concentration about $C = 0$ (i.e. giving negative values for C at some values of r), which is clearly unphysical.

Hence the analytical solutions were abandoned in favour of numerical solutions calculated using an explicit finite difference method outlined in Crank(4). The diffusion equation was transformed into the dimensionless variables R (scaled radius), T (scaled time) and c (scaled concentration):

$$R = r/a \qquad T = Dt/a^2 \qquad c = C/C_0$$

where a = outside radius of the bone or tooth, C_0 = concentration at r = a for bones, and r = b for tooth, where b = radius of pulp cavity for the tooth. Hence the diffusion equation becomes

$$\frac{\partial C}{\partial T} = \frac{1}{R}\frac{\partial}{\partial R}\left(R\frac{\partial C}{\partial R}\right) = \frac{\partial^2 C}{\partial R^2} + \frac{1}{R}\frac{\partial C}{\partial R} \quad .$$

This was approximated by the explicit finite difference formula

$$C_{i,j+1} = \frac{r}{2i}\left\{(2i+1)\, C_{i+1,j} + \left(\frac{2i}{r} - 4i\right) C_{i,j} + (2i - 1)\, C_{i-1,j}\right\} \qquad (1)$$

where $C_{i,j+1}$ = scaled concentration at radius $R = i\delta R$ and scaled time $T = j\delta T$ and $r = \delta T/(\delta R)^2$ for i and j integers.

The condition at R = 0 for a solid cylinder is

$$C_{o,j+1} = 4r\,(C_{i,j} - C_{o,j}) + C_{c,j} \quad . \qquad (2)$$

For a surface at $R = R_0 = k\delta R$ with constant scaled concentration C_0, the condition $C(R_0) = C_0$ becomes

$$C_{k,j+1} = C_0 = C_{k,j} \quad . \qquad (3)$$

For an impermeable surface at $R = 1 = n\delta R$ the condition $\left(\frac{\partial C}{\partial R}\right)_{R=1} = 0$ becomes

$$C_{n,j+1} = r\left\{\left(\frac{1}{r} - 2\right) C_{n,j} + 2\, C_{n-1,j}\right\} \quad . \qquad (4)$$

The numerical solution is built up from T = 0, i.e. j=0 from a given initial distribution. In all these cases this was assumed to be $C_{o,j}$ = C_1, (C_1 = background concentration) except at the exposed surfaces where $C_{o,k} = C_0$ (C_0 = the scaled concentration at the surface - assumed to be constant). The solution for $T = \delta T$ is then calculated using (1) at all internal grid points and the appropriate equations (2)-(4) at the surfaces. The solution for $T = 2\delta T$ is then calculated similarly. This procedure is repeated n times until the required T ($\simeq n\delta T$) is reached. This method is not without its disadvantages:

As only discrete values of time are calculated the time step δT must be small compared with the scaled age of the bone/tooth. Thus for very young bones δT needs to be $< 10^{-4}$. For the hollow bone program the radial step size δR needs to be small compared with a-b, so that a sufficient adjusting the magnitude of the data so that the concentration at the appropriate edge of the bone/tooth matches the theoretical value;

inputing (or changing) a value of the background concentration which is consistent with the data;

inputing or changing the inner scaled concentration.

(4) the lower bounding curve is then sought, and when a satisfactory* value is found, this is then stored.

(5) the upper bounding curve is found* and stored.

(6) the data and the "best fit" curve with its upper and lower bounds are then shown. The user then has the option of changing any of the three curves, or readjusting the data. This can be done repeatedly until the user is satisfied with the fit.

(7) the "real" and scaled averages are then displayed with the associated errors (taken as the maximum difference between the best fit curve and the bounds).

(8) the graphical information can then be written onto disk for later transferral to the Gracefield VAX to run a program written to plot the data and theoretical curves. A hard copy of the relevant information on the fit is printed for later interpretation.

* The theoretical curves are compared visually with the data to get the "best fit". This is a rather subjective method of comparison but least squares or similar method of selection for the "best fit" curve is impracticable due to the spiky nature of the data. To compensate for this the upper and lower bounding curves are also determined in a similar way, to give at least some indication of the uncertainty associated with the value obtained for T.

Full listings of the three programs (written in FORTRAN) are contained in an appendix.

RESULTS AND ANALYSIS

Three profiles from different sections of the same Moa bone (C-14 dated at 16,200 ± 300 yr B.P.) were "dated" using the solid and hollow bone programs. The scans were from the same bone used previously(3) for which a value of D (2.67×10^{-4} mm^2/yr) was deduced. This was done as a check of the new programs and to:

i) determine the consistency of the values for D obtained using different sections of bone;
ii) compare the results using local radius and the average radius;
iii) determine the effect of background concentration on D.

For profiles 0.211 and 0.133, the solid bone program was used. For profile 0.149, four runs were done; 1 and 3, with the local radius, 2 and 4 with average radius, and in 3 and 4 zero background concentration was used (see Table 1). A value of $(2.73 \pm 0.4) \times 10^{-4}\,\mathrm{mm}^2/\mathrm{yr}$ was obtained for D by averaging the first four values for D. The results show:

i) consistent values for D;
ii) the effects of choice of radii are negligible;
iii) that the background concentration has no affect on the value of D but only affects the accuracy of the fit (increasing the uncertainty in D).

<u>Table 1</u>: Results of "dating" three profiles from a single Moa bone

Scan*	Calculated D $\mathrm{mm}^2/\mathrm{yr}$	Outer radius (mm)	Inner radius (mm)	Scaled back-ground conc.	Conc. at inner surface
0.211	$(2.8 \pm 0.4) \times 10^{-4}$	24.0	14.0	0.07	-
0.133	$(2.3 \pm 0.9) \times 10^{-4}$	24.0	14.0	0.07	0.5
0.149/1	$(3.2 \pm 0.4) \times 10^{-4}$	24.0	5.0	0.10	-
0.149/2	$(2.6 \pm 0.8) \times 10^{-4}$	13.5	2.0	0.07	0.13
0.149/3	$(3.2 \pm 0.3) \times 10^{-4}$	24.0	5.0	0	0.50
0.149/4	$(3.4 \pm 0.6) \times 10^{-4}$	13.5	2.0	0	1.0

* the plots of the fits for all the profiles are contained in an appendix.

A variety of Moa bones of different ages, radii, and maximum concentrations were then compared (see Table 2) with diffusion theory and a value for D obtained for each bone. These values for D agree well with the value obtained in 1. above, except for the last three. Their inconsistency is attributed to large irregularities in the profiles 0.185, 0.163, and bad fitting of the theoretical curves near the outer edge in 0.183.

Table 2: Results of "dating" a variety of Moa bones

Scan	Age(7) (C-14)/y	Calculated D mm^2/y	Outer Radius (mm)	Inner Radius (mm)	Scaled back-ground conc.	Conc. at inner surface
0.171	658±59	$(2.4\pm1)\times10^{-4}$	11.0	6.0	0.02	0.23
0.177	1405±50	$(4.9\pm23)\times10^{-4}$	10.0	3.0	0	0.7
0.179	614±58	$(2.6\pm2)\times10^{-4}$	20.0	14.1	0.10	0.93
0.169	1060±70	$(0.8\pm3)\times10^{-4}$	21.0	11.0	0.15	0.15
0.187	400±500	$(4\pm6)\times10^{-4}$	10.0	8.0	0.01	-
0.163	11800±200	$(7\pm7)\times10^{-5}$	18.0	10.3	0.30	0.80
0.183	2590±70	$(8.7\pm37)\times10^{-4}$	15.0	-	0.12	-
0.185	7020±100	$(4\pm5)\times10^{-5}$	8.5	-	0.30	-

The hollow bone program was then tested on three scans that showed overlapping double profiles, the first from the Equus bone found in the Olduvai Gorge mentioned previously and dated at 1.75 million years(2). The second from a human tibia C-14 dated at 530±60 yr B.P.(7). This profile was not appropriate for this method as no diffusion curve was clearly defined (due to Haversian canals). The third was a human foot phalange of unknown age. As this is a Maori bone its age should be <1000 years. The Equus bone profile matched the theoretical solution well but the calculated diffusion constant was $(1.48\pm0.21)\times10^{-5}$ mm^2/y. This is smaller than the value in (1) for Moa bones by a factor of 10. This could be due to a number of effects: (1) the high F concentration 3.2% compared to 3.77% in fluorapatite (this high value is due to the high F content in the soil(2)). It is possible that diffusion slows down as the F concentration approaches that in fluorapatite, i.e. the diffusion constant may in fact be concentration dependent.

(ii) The theory also assumes that the external conditions at the time of excavation are representative of the conditions throughout the duration of burial, i.e. a dry spell(2) or change in pH(5) may account for the difference. For example, if $(2.7\pm0.4)\times10^{-4}$ mm^2/y is used for D an age of 96,000±20,000 years is obtained, which might indicate that the environment changed from low to high F concentration about 100,000 years ago (assuming that D is in fact constant).

(iii) Another possible explanation for the low D is that D depends on the exact crystalline structure of the bone which may vary with species and type of bone, but this is not thought to be a major factor.

Table 3: Results of "dating" three hollow bones

Scan	Age (yr)	Calculated D mm^2/y	Outer Radius (mm)	Inner Radius (mm)	Scaled back ground conc.	Conc. at inner surface
0.002	(1.75 0.1)x10^{6}	(1.48 0.21)x10^{-5}	15.0	5.0	0	0.96
0.181	530±60	(3 ± 4)x 10^{-3}	8.5	1.5	0.10	0.90
0.015	8000±2000	(1.48±0.21)x10^{-5}	5.0	2.0	0.06	0.40
0.015	400±160	(2.7 ±0.4)x10^{-4}	5.0	2.0	0.08	0.40

The profile for the human foot phalange (scan 0.015) again shows good agreement with the theoretical curves. This bone is undated, but was found in the Chatham Islands and hence is relatively young. Using 2 values for D gives two ages for the bone. The age using the D estimated from the Equus bone is clearly too large. The age 460±160 years determined using (2.7±0.4) x10^{-4} mm^2/y for D obtained in (1) appears to be reasonable.

Three different sections of the same tooth, excavated from the Taumako site(6) with an estimated age of $\sim$800 years, were analysed (see Table 4). All the profiles appear to agree well with the theory and the values for age agree well (using the value for D obtained in (1)). The age was estimated at 1000±300 years, using this value of D. This indicates that the diffusion constant in tooth dentine is approximately the same as that in Moa bone.

Table 4: Results of "dating" three sections of the same tooth

Scan	Estimated age	Outer radius (mm)	Inner radius (mm)	Scaled back ground conc.
0.076	940±700	2.59	0.57	0.09
0.077	1080±600	2.47	0.59	0.08
(0.090/1	960±300	2.99	0.87	0.04
(0.090/2	1000±400	3.11	0.87	0.03

(scans on opposite sides of the pulp cavity.

Fluorine profiles from three further teeth from the same burial site were analysed. The outer radii of these teeth were unavailable at the time of writing so that no comparison with (4) was possible. An outer radius of 1 was used and the inner radii were determined from the scan by comparing the distance from the centre of the profile to the enamel and to the edge of the pulp cavity (see Table 5).

The results indicate that the teeth are approximately the same age (assuming they have the same radii). It was noted that these profiles and those in (4) indicate that the enamel is not completely impermeable as was previously thought, but is semi-permeable (with D much lower than in the dentine). A comparison with diffusion into a hollow cylinder with constant concentrations at both edges was done (see tooth 0.131/HB) - this shows that the diffusion constant for enamel is much less than that in dentine.

Table 5: Results of "dating" three teeth of unknown age and radii

Scan	Estimated age (D=1)(a=1)	Inner radius (mm)	Scaled background conc.
0.120	0.025±0.005	0.21	0.07
0.131	0.035±0.005	0.14	0.10
0.133	0.025±0.005	0.31	0.07

DISCUSSION AND CONCLUSIONS

There is no evidence that simple diffusion theory is not appropriate for the modelling of the fluorine profiles in bones (except for the Haversian canals) or teeth. (Although the diffusion constant may be concentration dependent and the high background values in a few cases may be due to non-simple diffusion.) This is despite the fact that diffusion of fluorine into hydroxyapatite is not well understood and hydroxyapatite in bone and tooth dentine is not a uniform material.

The major assumption that is made in the theory is that the surface concentration is constant; this is unlikely to be the case. But as long as it does not vary greatly and the value at the time of excavation is representative, the method should be applicable.

The assumption of cylindrical geometry requires the values of the radii. It has been shown that the choice of local or average radius has little effect on the analysis. This assumption also requires that there be no diffusion along the direction of the axis of the cylinder. For this to be true the sections should be taken away from the ends of the bones and near the crown of the tooth. There was no evidence of non-radial diffusion in any of the profiles compared.

Fluorine distributions in bone.

From the rather limited applications of the above technique, the following conclusions can be drawn:

(1) Care must be taken to only use the method on bones which are relatively free of Haversian canals (and their associated spikes, caused by transport of fluorine along them), and are from non-acid sites.

(2) The theoretical profiles must be fitted with great care at the edges of the bones, as the slope at the edge is the major factor in the value of T obtained in the fit.

(3) Bearing in mind the above comments, constant values for the diffusion constant were obtained for the Moa bones, indicating that an absolute dating method might be possible.

(4) The low value of the diffusion constant in the Equus bone has at least three explanations -

i) the diffusion constant decreases as the fluorine concentration approaches its maximum value (3·77% in fluorapatite);

ii) the diffusion constant may vary with species;

iii) the soil conditions may have changed over time, e.g. a sharp increase in F concentration from ∿1% to 3.2% about 100,000 years ago would be consistent with the observed profile (with D = 2.7×10^{-4} mm^2/y). This is only one possibility and highlights the uncertainty in the assumption that the soil conditions are constant, especially for very old bones. In contrast to this if the age of the bone is known and if the properties of the diffusion "constant" are known, then information on changes in the environment might be deduced.

These three possibilities will need further investigation before the dating method can be used reliably.

The calculated age of the human foot phalange using the diffusion constant from the Equus bone is unrealistically high, indicating that (if human and Equus bone are of similar structure) the low diffusion constant obtained for the Equus bone is due either to the high F concentration or some change in the Equus bone's environment. Using the value for D obtained from Moa bones, a reasonable value for the age is obtained. Whether this is the correct age awaits C-14 dating of the bone.

Fluorine profiles in teeth.

The fluorine profiles in teeth, being smoother than those in bone, due to the absence of Haversian canals, show greater promise for use in dating, the fits being good and self-consistent. Due to the limited number of tooth profiles available, and the fact that they were from the same site and of unknown age, little can be concluded about the diffusion constant, except that it appears to be very approximately the same as that in bone! It was found that the enamel is not completely impermeable but is semi-permeable (this would not effect the dating of these "young" teeth, as the amount of fluorine diffused through the enamel was small). For older teeth this effect would need to be modelled, perhaps by an outer layer of lower diffusion constant.

A great deal more work is necessary before fluorine profiles can be reliably used for dating bones and teeth. But this preliminary investigation suggests that when the effects of concentration on the rate of diffusion are better understood, and when the variation of diffusion constant with species (and type of bone/tooth) is determined, a method of relative dating at one site (where the environment is the same for each bone/tooth) should be possible. An absolute dating method for bones/teeth excavated from sites whose soil conditions have changed little should also be possible. (Although the accuracy of the dates obtained in this way would probably never be high (errors $\gtrsim 10\%$)). Finally, for bones/teeth of known age, changes in the soil conditions might be deduced or at least confirmed.

ACKNOWLEDGEMENTS

The Institute of Nuclear Sciences is thanked for the use of their PDP-11 computer and its peripherals, and for access to the Gracefield VAX and the HP plotter.

Dr G.E. Coote is thanked for providing the fluorine profiles and for helpful discussions.

Dr M.R. Manning is thanked for writing the plotting program for the Gracefield VAX.

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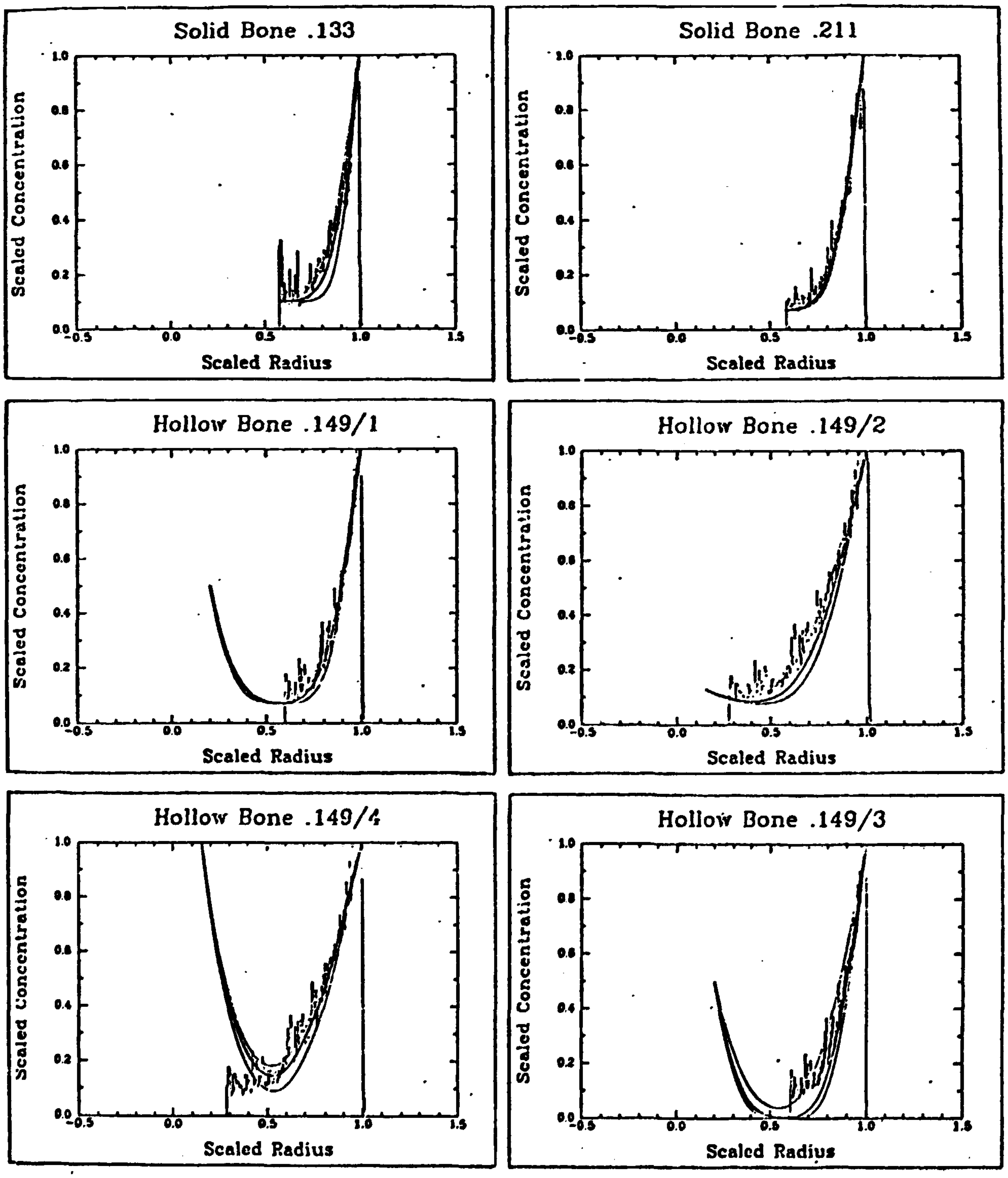

FIGURE 1 (See Table 1).

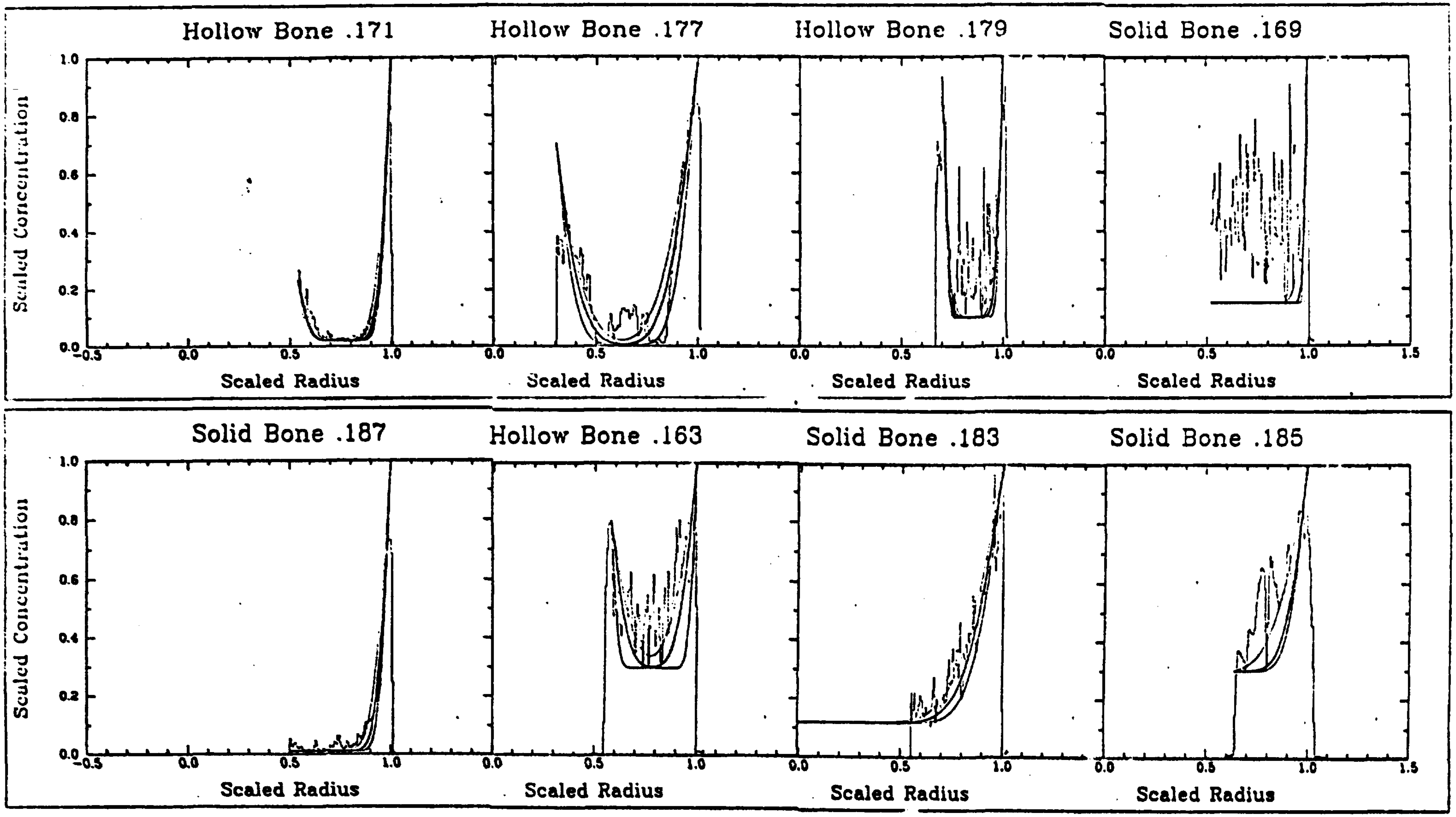

FIGURE 2 (See Table 2)

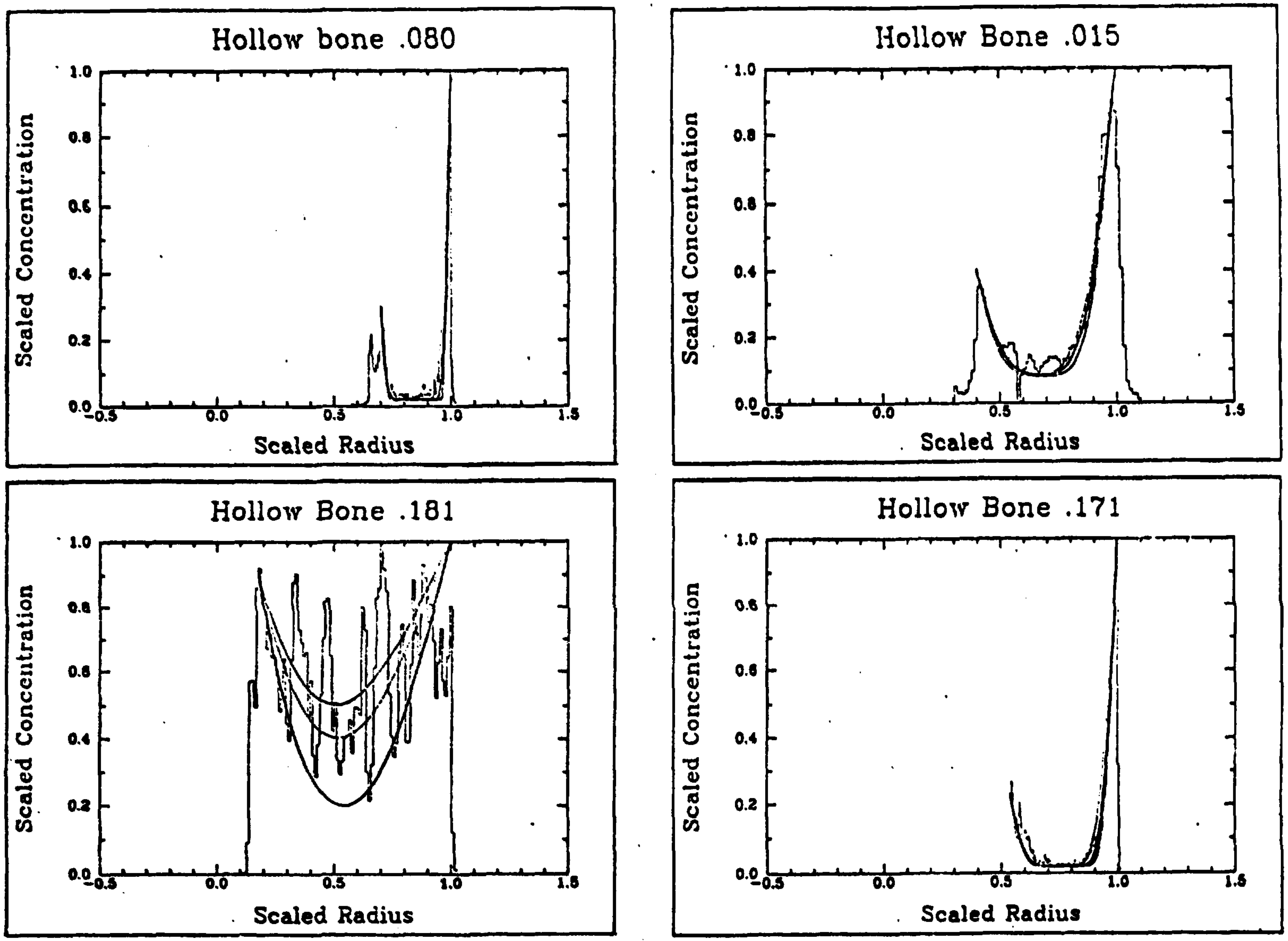

FIGURE 3 (See Table 3)

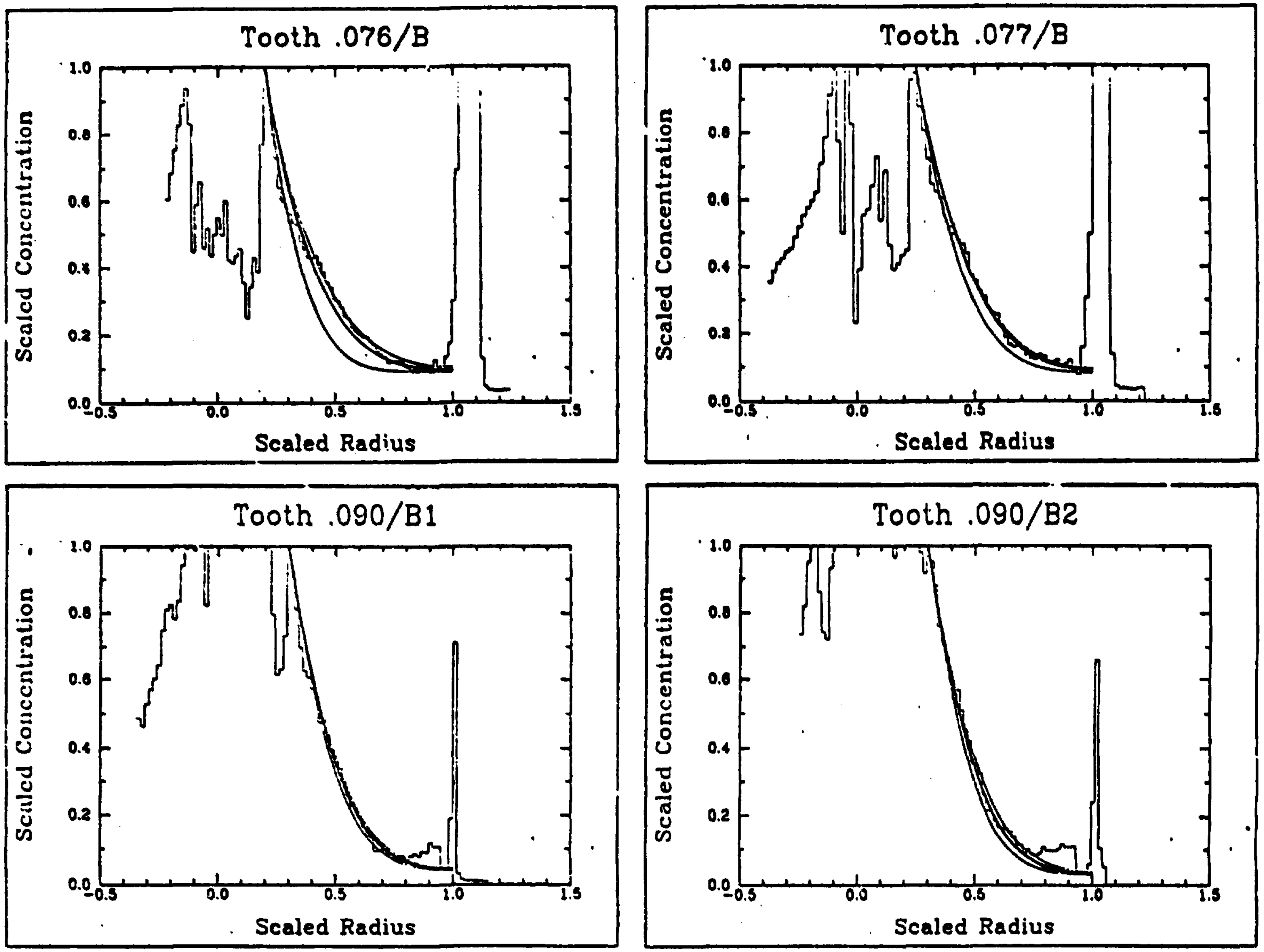

FIGURE 4 (See Table 4)

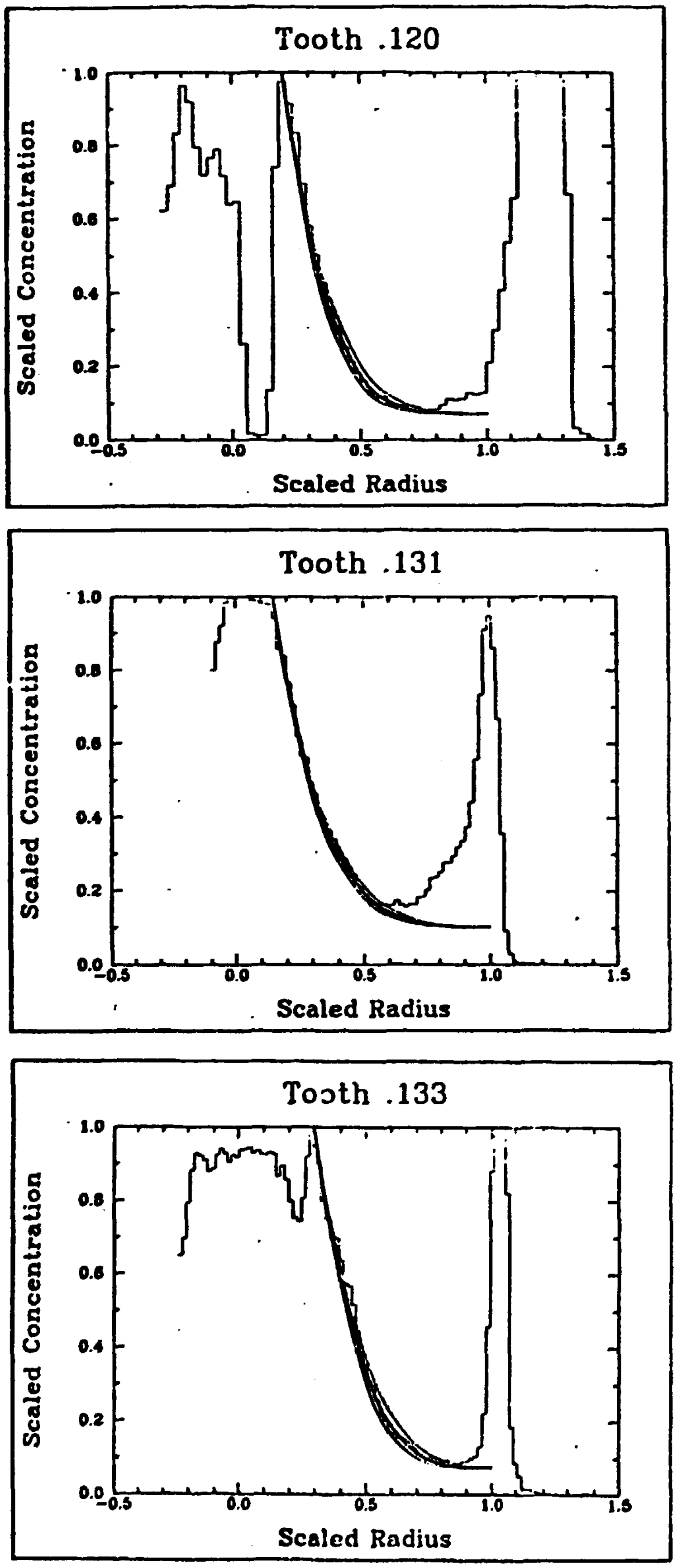

FIGURE 5 (See Table 5)