THE CLASSIFICATION OF HUMAN BONE USING X-RAY FLUORESCENCE

by

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I. INTRODUCTION

Often archaeological excavations in the midwest yield cremated skeletal remains (Stewart, '79). Bone tissue upon reaching 800 degrees Celsius, shrinks, cracks, breaks, and in many cases disintegrates (van Vark in Stewart, '79). Important information such as the sex, age, and stature of the individual is usually lost due to the fact that present methods of analysis require measurements on intact bones which no longer exist or on morphological traits which if not lost entirely, may be remodeled to such an extent that analysis is not possible. Even less information can be gathered from excavations in which the cremated remains of many individuals are comingled. In the latter case the resulting fragments suggest only the maximum and minimun number of individuals interred at the site.

The use of trace-element analysis was proposed in the hope that the elemental make-up of an individual's skeleton might be: (1) homogeneously distributed throughout the skeleton, (2) not affected by temperatures such as those experienced in the cremation and (3) significantly unique as compared to other individuals. If the above could be shown to be true it would be possible to use trace-element analysis to classify particular fragments as belonging to a certain individual. Further studies as to the meaning of a given amount of a particular element might also lead to estimates as to age and sex.

A. An overview of previous literature.

The idea of using trace-element analysis for the classification of human and animal bone is not novel. Studies have been done using atomic absorption spectroscopy, neutron activation analysis and x-ray fluorescence for the purpose of establishing elemental concentrations in the skeletons of fossilized mammals (Toots and Voorhees, '65, Parker and Toots, '70; Boaz and Hampel, '78), modern human populations (Hodges et al., '50; Kulp et al., '57; Thurber et al., '58; Elias, '80) and archaic human populations (Brown, '73, '74; Gilbert,'75; Szpunar, 77; Wesson et al, 77; Schoeninger, '79; Geidel, '82; Sillen and Smith, '84).

The purpose of all but three of these experiments (Hodges et al., '50; Kulp et al., '57; Thurber et al., '58) was to reconstruct the diets of their subjects. The presence of certain levels of elements such as strontium, zinc, copper, manganese, and vanadium within the skeleton are thought to distinguish herbivores from carnivores, (Toots and Voorhees, '65; Underwood, '77) and weaned from unweaned children (Sullen and Smith '84). Such distinctions are then extrapolated to be evidence that can be addressed to theories on social status within a given population and shifts from hunting-gathering economies to agricultural ones. For example, work done by Schoeninger in '79 in analyzing the remains of skeletons excavated at Chalcatzingo (Morelos, Mexico) revealed good correlation between skeletons with low levels of strontium (indicating a more carnivorous diet) and "high" status

mortuary remains. She then conjectured that those persons of higher status had better access to meat.

There is, at present, much debate as to the conclusiveness and feasibility of using trace-element analysis for the classification of human bone. Approximately half of the authors of the articles cited above found the method to be adequate, the other half; did not. The problems which arose for these particular scientists and how they were met and/or interpreted have helped greatly in interpreting the results of the present experiment. The pages which follow use much of previous experience to help predict the success of establishing the three criteria stated above which are necessary for a positive thesis.

B. Considerations which will influence the interpetation of the data.

1. Consideration #1: The distribution of trace elements throughout the skeleton.

Bone mineral is made up of primarily hydroxyapatite, $Ca\ OH(PO\ )$ (Brown, '73). There are various other "trace" elements which have been found in bone and the reasons for their presence dictate the homogeneity of their distribution. Parker and Toots in 1970 used an electron microprobe to study the distribution of trace elements in fossil bone. The electron microprobe was used

to scan crossections of bone to determine which trace elements had become chemically incorporated into the apatite structure and which elements tended to fill small cracks and voids.

The trace elements which were found to have become part of the apatite structure were strontium, fluorine, sodium and perhaps chlorine and manganese. Of these, strontium and sodium were reported by Parker and Toots to have been incorporated only while the individual was living and not through ionic exchange with the environment.

No particular evidence was cited for sodium except a note that it had been found (no source cited) that sodium levels of modern versus fossilized specimens showed no obvious differences. From this one can hypothesize that the postmortem environment had no effect upon sodium levels and so the levels measured were indicative of those the specimens had in life.

Evidence which is said to support this conclusion for strontium includes the discovery that strontium content did not vary significantly between bone, dentine and enamel whereas high variability was observed in the amounts of chlorine, fluorine and other elements known to have been introduced by the postmortem environment. The significance of strontium's stable concentration comes from the idea that the enamel's higher density might make it both highly retentive of elements incorporated during life and relatively impervious to postmortem additions. Therefore, if more of a particular trace element is found in the environmntally more vulnerable tissues than in enamel one could conclude that this is an element which was introduced to the bone postmortem as well as through the individual's metabolic processes. In a later study

done by Boaz and Hampel in 1978, strontium was found to have an average coefficient of variance as high as .24 within the bone, dentine and enamel of a particular taxa. Such a coefficient of variance would be, by Parker and Toots' own standards, representative of a trace element introduced by the postmortem environment. In fact upon closer reflection, the data presented by Parker and Toots reveals similar variations between the number of ppm of strontium and those of yttrium and iron; elements which are considered to be introduced postmortem. Consequently, Boaz and Hampel concluded that strontium found in the skeleton could not be attributed entirely to the metabolic processes of the live individual.

The confirmation of strontium and other elements as dietary indicators and not as results of the environment in which the animal was fossilized or the human was interred is central to the success of the studies listed in the first paragraphs of this introduction. Whether or not a depositional environment has a detrimental effect for these studies and/or the one at hand depends upon the masking effect that an added amount would produce on the potentially unique amount of that element which would be characteristic of a particular population or individual.

Parker and Toots found that a number of elements filled cracks and voids once used for the transport of blood and nutrients to the bone (haversian canals and lacunae). These elements were silicon, manganese, iron and yttrium. Iron, yttrium and manganese were strictly confined to these areas suggesting that their presence was a direct result of additions from the postmortem environment.

The distribution of elements in the skeleton introduced by the environment is determined by that environment. Toots and Voorhees '65 and Schoeninger '79 both suggest that as long as the population analyzed was subject to the "same" post burial effects that distinctions in strontium amounts will remain measurable. Schoeninger, however, goes so far as to suggest that strontium content is virtually unchanged by the environment, a point denied by the evidence provided by Boaz and Hampel mentioned above. A distinction that must be made here is that Boaz and Hampel worked with fossilized material dated to the Pliocene-Pleistocene period (2-7 million years ago) and those scientists such as Schoeninger who claim their strontium amounts to be pristine worked with populations living less than 3,000 years before the present. It is possible that time (a point mentioned by Parker and Toots, '70) must be considered to understand the significance of the role of the postmortem environment. Boaz and Hampel did check fossils within various strata and found no evidence of changes in Sr content with respect to time. However, once again in comparing the interment period betweeen fossils and "modern" man the differences in time are still three orders of magnitude which cannot be denied possible significance.

The distribution of elements incorporated into the apatite during life is considered to be homogeneous [emphasis on strontium, (Hodges et al, '50, Thurber et al, '58, Wessen et al, '78)]. The preceeding articles are those cited by many authors in justifying the testing of only one bone of a particular skeleton as representative of the entire skeleton. Upon reading the articles however, one does not find evidence of homogeneity.

The data presented by Hodges et al. contain coefficients of variability between different bones of the body as high as .17, i.e. a 17% variation between different bones of a particular skeleton. Thurber et al. refer to an article which had not been written at the time. Wesson et al claim to have checked differences in samples taken from the same bone and between bones of a given skeleton but no statement or evidence was provided as to the outcome of these tests. In fact the only evidence located on the subject was presented in a paper written by Kulp, Eckelmann, and Schulert in '57. This article presents a single difference in strontium as great as 400% between two bones within the skeleton. This article does state that although the distribution of strontium was not found to be homogeneous the differences seemed to be consistent with respect to the type of bone with the skull containing the least amount and the vertebrae and sternum containing the most (long bones in between).

The above paragraphs taken together suggest that it may be possible that some elements are homogeneously distributed throughout the skeleton. The data are not conclusive, however, and demands that this experiment check for homogenaeity. Secondly, it appears that for archaeological specimens such as ours, an understanding of the depositional environment in which the individuals were interred is important. Finally a point that may hold important significance is the reaction of cremated bone to its environment. Perhaps the increase in density as a result

of shrinkage would be accompanied by a decrease in porosity and thus permeablilty with respect to the environment. If this were the case, it could be expected that the skeletal remains would be insignificantly affected by the environment.

2. Consideration #2: The response of bone tissue to cremation temperatures.

The response of bone tissue to heat was documented in Stewart's ESSENTIALS OF FORENSIC ANTHROPOLOGY. Stewart cites data from a study by G. N. van Vark in 1970 in which it was found that once a temperature between 500 - 800 degrees Celcius has been reached the bone will shrink, break and disintegrate. Microscopically, the bone shrinks to such an extent that lacunae (former sites of bone cells) are hardly visible. These lacunae were the sites where those elements noted by Parker and Toots in 1970 to be deposited by the postmortem environment were found. Work done by Wells, '60 and Gejvall '63 confirms that prehistoric cremations reached temperatures that remodel the bone sufficiently to cause such microscopic changes. If these voids are no longer available to be filled, it seems likely that for cremated tissue the postmortem environment will not play such a significant role as has been observed with non-cremated skeletons.

3. Consideration #3. The uniqueness of particular amounts of trace elements for a particular individual.

The uniqueness of the amount of a particular trace element may be the most difficult criterion of the three to meet. The word "trace", itself, describes the problem. A trace element is defined to be an element whose percentage of the entire bone mineral content is less that one tenth of one percent. For samples of the size used in this experiment, trace analysis implies the precise and accurate measurement of less than 100 micrograms of the element in question.

Schoeninger in 1979 presented evidence showing that within a given population of minks, all fed similar diets, the measured amount of strontium among individuals in the population presented a coefficient of variance of .19. She attributed this variance to the difference in metabolism of individuals. This and the studies by Boaz and Hampel, '78 suggest that there may be present within a given population a certain uniqueness to the amounts of this particular trace element within an individual's skeleton. Given sensitive equipment, careful technique, and if not a homogeneous, then a relatively predictable concentration of trace elements within the skeleton it may be possible to obtain a positive thesis.

II. THE PROCEDURE

A. The Use of X-ray Fluorescence.

The advantages of x-ray fluorescence over other methods of trace element analysis, such as atomic absorption spectroscopy and neutron activation analysis, are that it is a non-destructive method, that many elements may be analyzed both qualitatively and quantitatively at the same time, time for gathering data need not exceed ten minutes per sample, the operation of the equipment requires little expertise, and the maintenance of the equipment is neither costly nor involved.

The use of x-ray fluorescence involves the detection of photons of x-ray energy emitted from atoms in the sample. The energy of each x-ray photon is characteristic of a specific element. The number of x-rays detected which have this characteristic energy is an indication of what percent of the sample is made up of that element. In order for an atom to emit radiation with energies in the x-ray region it must be externally perturbed into what is called an "excited" state. The following paragraphs explain the physical processes which must occur to reach this unstable state and provide the reader with a general equation which connects the data gathered at the detector with the amount of a particular element in the sample

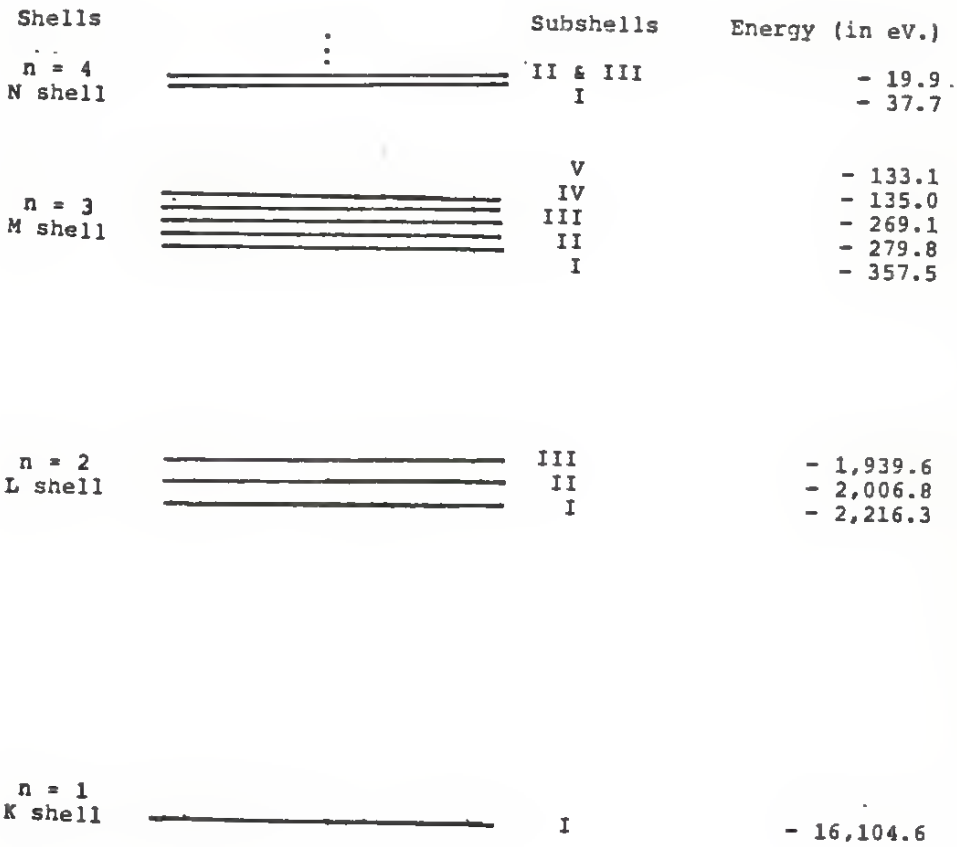
The stable atom consists of a nucleus around which

electrons move in specific orbits called shells. The nucleus is made up of two different types of nucleons called protons and neutrons, their major difference being that the neutrons have no charge and the protons have positive charge. The number of negatively charged electrons is the same as the number of protons so that the atom itself is neutral. The shells in which the electrons must orbit are labelled with numbers and letters. For example the innermost shell with principal quantum number n = 1 is also called the K shell, the second shell with principal quantum number n = 2 is called the L shell, from there the sequence continues: n = 3 is the M shell, n = 4 is the N shell etc. The maximum number of electrons per shell is given by $2n^2$. The K shell, therefore, can have 2 electrons, the L shell can have 8 electrons etc. The electrons in each shell have similar amounts of energy but the energies vary greatly from shell to shell, increasing with increasing principle quantum number. The energy "spacing" between shells is unique to every element and it is this uniqueness upon which elemental analysis using x-ray fluorescence is based.

Above it was mentioned that the electrons within a given shell have similar energies. They do not have exactly the same energies because within each shell there are (2n - 1) subshells. There are energy differences between different subshells just as there are between different shells. These energy differences are usually less than one percent of the energy differences between the major shells. In Figure 1 a schematic energy level diagram is shown for the first five shells, subshells and their respective energies for the element strontium.

EXPLANATION OF PLATE ONE: Figure 1 is a schematic energy level diagram of the K,L,M, and N shells of the strontium atom.

FIGURE 1: Schematic Energy Level Diagram for Strontium



If an electron is removed from one of the shells, the atom is in an unstable state. The electron may be moved to another shell within the atom but with x-ray excitiaton it is usually removed entirely, ionizing the atom. In order to remove the electon it must be given enough energy to break its bond with the nucleus. Usually it is provided with this amount of energy plus additional energy which is seen in the speed at which the electron leaves the atom. These energies are provided by a projectile which collides with the electron elastically giving up some or all of its energy to the electron. The projectile may be a massive particle such as a proton or it may be a quantum of electromagnetic energy; a photon. When photons are used, the photon's energy, given by hf (Planck's constant multiplied by the frequency), is completely lost to the electron. This is called the photoelectric effect.

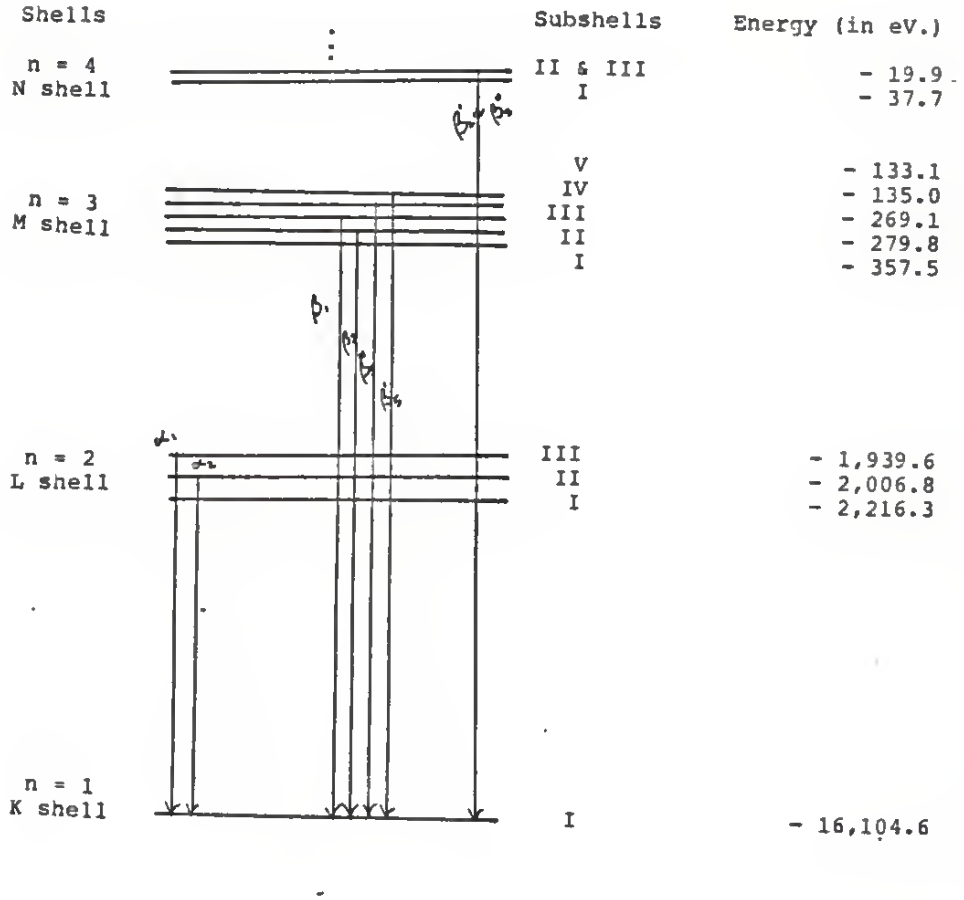
Once the vacancy has been created the unstable atom must in some way stabilize; it must fill the vacancy. What occurs is that an electron from a "higher" shell (a shell with a higher quantum number) drops into the lower shell to fill the vacancy. In doing so it goes from a higher to a lower energy state and the excess energy must be removed. The energy may be removed in two different ways. The excess energy may go into the removal of still another electron from the atom. This electron is called an Auger electron and the sum of its binding energy to the nucleus and its kinetic energy upon leaving the atom will equal the amount of excess energy released by the stablizing electron. The other way that this energy may be released is in the form of a photon. The photon's energy, given by hf, will also be equal to the energy

difference between the two shells. When the excess energy is released in the form of a photon the atom is said to fluoresce. If the energy of the photon is within the "x-ray" region of the electromagnetic spectrum then we have what is called x-ray fluorescence.

Exactly which electron in what higher shell will fill the vacancy is a matter of probability. For example a vacancy may be created in the innermost shell of an atom. It is entirely possible that an electron from the L-shell will fill the vacancy, or an electron from the M or N shells. In general it can be said that electrons from within the shell "closest" in energy to the vacant shell will be most likely to fill the vacancy. It is important to mention again that within each shell there are sub shells. Consequently, transitions of electrons from shell to shell also involve transitions between subshells. The probability of a transition occuring between two shells is now modified by another probability of transitions between certain subshells. Quantum mechanics provides selection rules which tell whether or not transitions between certain subshells are possible. In general, among possible transitions between different subshells the one or ones with the largest number of electrons in the higher subshell will be the most probable transition. Figure 2 shows the possible transitions for strontium with an inner shell vacancy. Transitions to the K-shell are called K transitions. A transition from the L shell to the K shell is called a K-alpha transition. A transition from the M shell - a K-beta transition. A transition from the third subshell of the L shell to the K shell is called the K-alpha-one transition. Note that there are subshells from

EXPLANATION OF PLATE TWO: Figure 2 shows the possible transitions of an electron from the L,M, and N shells to fill a vacancy in the K shell.

FIGURE 2: Schematic Energy Level Diagram for Stontium and Labelled K-transitions



which there are no transitions. These are prohibited by the selection rules mentioned above. Each possible transition has an energy unique to the element of interest.

The intensity or number of photons representing a particular element which eventually reach the detector is a function of the original intensity of projectiles produced at the source. That is, only a fraction of the source intensity will result in photons of energy representative of a particular element reaching the detector. The intensity is determined by 5 factors which are discussed in the paragraphs below. A mathematical equation relating these factor to the intensity of photons measured at the detector is developed in Appendix A.

In this particular experiment the projectiles were photons of energies sufficient to produce inner shell vacancies in the elements we were interested in; Calcium, Strontium, Zinc, Iron, and Yttrium. Of these original photons only a fraction will produce the photoelectic effect in a desired state. The probability for the photoelectric effect to occur is represented by the photoelectric cross section which increases with decreasing energy of incident photons and increasing atomic number of the target elements. There are two other competetive processes; elastic (Rayleigh) scattering , in which the photon, losing little energy, is scattered by the atom itself and ineleastic (Compton) scattering, where the photon loses some of its energy and changes direction by scattering off of a loosely bound electron.

The intensity is also a function of distance traveled into and out of the sample. It decreases exponentially with distance and included in the argument is the sum of the mass absorption

coefficients for the particular energies of the incoming photons and outgoing fluorescent photons and is dependent upon the elemental make-up of the sample itself. (The mass absorption coefficients can be obtained from Bracewell and Veigel, '71.) Mathematically what is done is to express the intensity as a total derivative which represents the intensity of photons in an infintesimal thickness at a certain distance within the sample. This equation is then integrated over the thickness or mass per unit cross sectional area of the sample. (The independent variable depends upon which parameter is easier to quantifiy in the experiment. In this experiment mass per unit area was used.)

Of the vacancies created only a fraction will be in the shell desired and of these only a fraction of the atoms will deexcite resulting in the emission of a photon. The intensity is, therefore, modified by two more factors. The first is included in the photoelectric cross section for a particular shell. The second, called the fluorescence yield, is the number of photons emitted divided by the number of vacancies created in the shell of interest. The fluorescence yield is a function of the atomic number and the shell of the atom in which the vacancy is created.

Finally, a fraction of the intensity is lost going in and out of the sample because of the geometrical arrangement of the source, sample, and detector. Figure 3 shows the geometry of the source and sample for this experiment. Note that only those photons which are directed such that they may travel through a cylindrical collimator in the holder and a Beryllium window will reach the detector to be counted. All other characteristic photons emitted from the sample are lost to the shield /holder.

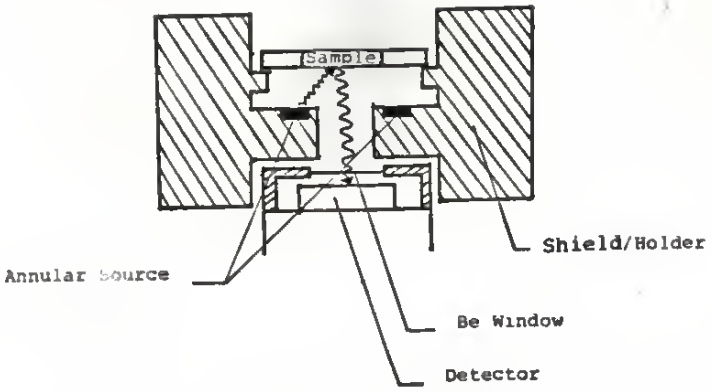


FIGURE 3: Cross Section of Arrangement of Source, Sample, and Detector

The final equation describing the intensity of photons measured at the detector for a certain transition in atoms of a particular element as a function the original intensity of photons from the source is given by:

$$I_n = \frac{g \tau_{Kn} \omega_{Kn} p_n I_o}{\mu_i + \mu_n} \left(1 - e^{-(\mu_i + \mu_n)x}\right)$$

where: g = the geometric factor determined by the sample, source, detector orientation.

ω_{Kn} = the fluorescence yield for a K-shell vacancy in a particular atom.

τ_{Kn} = the photoelectric cross section (probability per unit area of the creation of a K-shell vacancy by the absorption of a photon from the source.)

μ_i = the mass absorption coefficient of the incident photon's energy in the sample.

μ_n = the mass absorption coefficient of the fluoresced photon's energy in the sample.

x = the mass/unit cross sectional area of the sample.

FIGURE 4: Block Diagram of Electronics

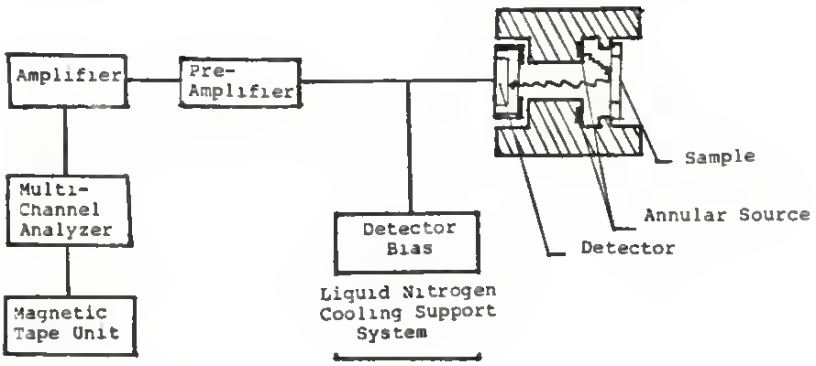


Figure 4 is a block diagram of the x-ray fluorescence apparatus used in our experiment. Beginning at the top of the drawing is a cross section of the source and sample holder. The source is an annular sample of radioactive Cadmium 109. The unstable Cadmium isotope undergoes K-capture. That is, the nucleus of the Cadmium atom captures an electron from its own K-shell (the innermost shell) the atomic number of the atom is now 47. The result is a Silver atom with a vacancy in its innermost shell. Electrons from higher energy shells (most probably the shell just "above" the K shell; the L shell) fill the vacancies. The energy change of these electrons is emitted with some probability (the fluorescence yield) in the form of photons of many energies the most intense of which has an energy equal to 22.2 KeV. These photons are then used to excite the elements of the sample for trace element analysis. Their energy makes it possible to create vacancies in the innermost shell for elements from atomic number 1; Hydrogen, up to atomic number 45; Ruthenium.

Thus characteristic x-rays and subsequently the amounts of these elements could be measured. It is also possible to create vacancies in the second shell, the L shell, in elements with higher atomic number than Ruthenium.

Once the sample is excited with the Cadmium source the photons emitted in the direction toward the detector, travel through the open center of the annular source and into the detector. The detector is a lithium drifted silicon detector, maintained at liquid nitrogen temperature to keep the lithium from diffusing. The absorption of a photon in this detector creates a charge pulse of magnitude proportional to the energy of the incident photon. This charge pulse travels to the pre-amplifier which converts the current pulse to a voltage pulse proportional to the charge pulse which is amplified at the amplifier. Having passed the amplifier, the voltage pulse is sent to the multichannel analyzer. The analyzer classifies the voltage pulse as having a voltage within a small range called a channel and records it as a one "count" in this channel. Since the voltages are proportional to the incident photon energy it is possible to determine the energy associated with each channel. Our particular analyzer's channel width was set at about .05 KeV. Photons of energies differing by more than .05 KeV are counted in different channels (hence the distinction multichannel analyzer). This energy width was small enough that x-rays characteristic of one element were easily distinguished from those of another element. Samples are usually "run" for a period of time which is long enough for the peaks representing counts of photons from particular elements to become statistically definite and distinct.

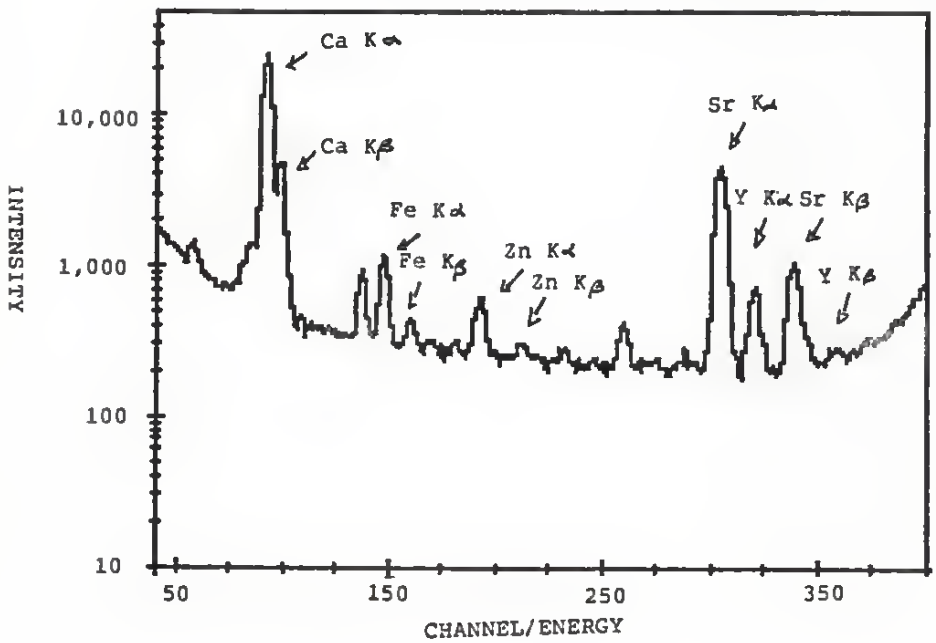
The multichannel analyzer displays the results on a cathode ray tube (See Figure 5). Such a distribution of x-ray intensities as a function of energy is called an x-ray spectrum. The abscissa is proportional to the photon energy with each channel representing an energy X +/- .025 KeV. The ordinate represents the number of photons counted (intensity). The peaks representing particular elements have a given width due to the resolution of the detector and they are observed in pairs. The pairs are intensities from K-alpha and K-beta transitions. In this particular experiment only the K-alpha peak was used to quantify the amounts of particular elements.

Once the data has been collected in the analyzer the spectral information is recorded on magnetic tape for future analysis.

EXPLANATION OF PLATE THREE: Figure 5 shows an example of the spectrum recorded by the multi-channel analyzer.

FIGURE 5: Example of Spectrum from Multi-Channel Analyzer

GD1034 #1 1983 IR



B. Sample Procurement and Preparation

Although this experiment was originally intended as an investigation of the properties of burnt bone, it was felt that not enough conclusive information had been gathered on unburnt bone. It was for this reason that the individuals from which samples were taken were of three types; archaeological, forensic and cadaverous. In comparing data from the three, the role of the post mortem environment could be investigated.

Four individuals (3 males and 1 female), American Indians from the Little Platte river valley, in Missouri were loaned to the experiment by Dr. Patricia O'Brien, Professor of Archaeology, Kansas state University. During life, circa 1100 AD, these persons were farmers growing corn, beans, squash and sunflower seeds. Another individual, also from Dr. O'Brien, was a protohistoric indian (protohistoric indicates that this individual lived around the 1700's) excavated in Missouri. The skeletons of seven individuals were loaned to us by Dr. Michael Finnegan, Professor of Physical Anthropology, also of Kansas State University. Four of the seven loaned by Dr. Finnegan were forensic specimens, The other three were cadaverous specimens. More specific data on the samples is given in Appendix A.

Initially it was thought that bone fragments could be mounted on a sample holder and placed in front of the source without any alteration of the samples whatsoever. This presented two problems. One, x-ray fluorescence demands the examination of

a constant surface area if different samples are to be compared. This criteria could not be met because too few of the bones of the skeleton had a constant surface over the one half inch diameter of our sample aperature. Secondly, the bones of the skeletons obtained in 1983 had suffered much damage (fragmentation, disintegration and staining) from exposure to the environment. Consequently, it seemed important to test areas of bone which had been exposed and areas which had not to establish some idea as to how the environment had affected the elemental make up of these bones.

What was done in the end for the 1983 samples was to grind off, using a tungsten carbide burr, a one square centimeter area of the periosteum of a particular bone and less than a millimeter in depth of the osseous tissue lying below this area. This sample was called an "outside" sample. Another sample called an "inside" sample was taken from approximately a millimeter's depth just below the area from which the outer sample was taken. The inner sample was taken to represent that part of the bone which had not been exposed to the environment.

The samples prepared in 1984 only contained that osseous tissue lying below the periosteum. The mass of each sample was measured and recorded. The samples were then placed between two sheets of mylar (1983, 2.5 microns thick) or polypropylene (1984, 6.4 microns thick) and pressed into the circular aperature of the sample holder. Neither mylar nor polypropylene gives rise to x-ray peaks in the energy range of the k-x-rays of the elements of interest in this study. The sample was held tightly in place by a polyethylene plastic ring whose outer diameter was equal to the

inner diameter of the sample holder. This procedure produced a circular disc of ground bone which had constant surface area and density; criteria which must be met for the accurate interpretation of data obtained through x-ray fluorescence.

The four individuals from Dr. O'Brien's specimens were tested during the fall of 1983 using a 7 year-old Cadmium - 109 radioactive source. Seven years time had reduced the activity of the source by a factor of .015. Consequently the samples tested had to be run for 12 hour periods to achieve good statistics. Three of these four individuals were tested again in 1984 along with those individuals provided by Dr. Finnegan, using a new source. The time to achieve good statistics was reduced by the aforementioned factor of .015 and results that previously required 12 hours of data collection were obtained in 10 minutes.

C. Treatment of the Data.

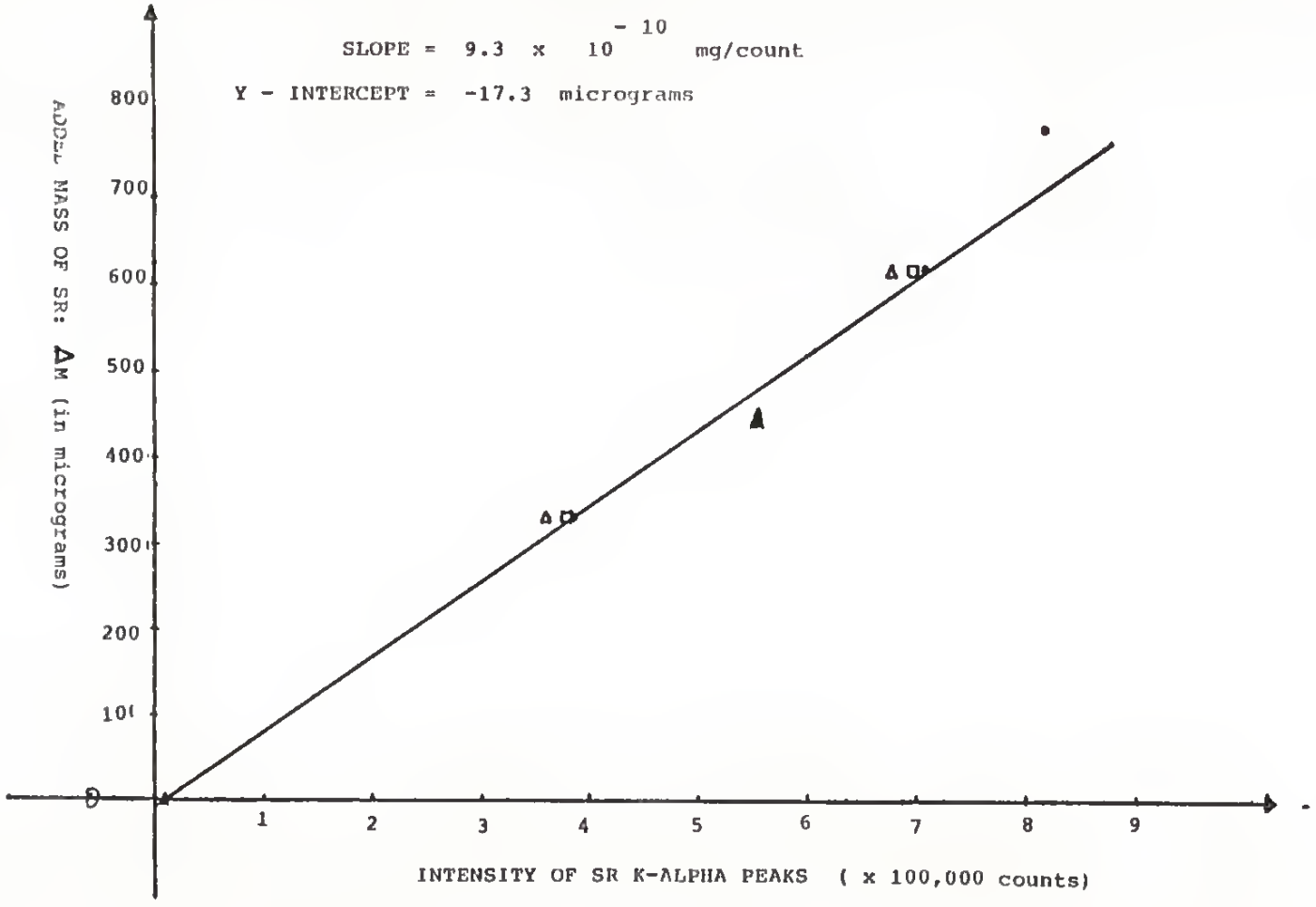
Once the spectrum was collected it was recorded on magnetic tape. This tape was copied on to a floppy disc which enabled the data to be analyzed on a DEC PDP 11 mini-computer. Referring once again to figure 5, the particular elements are represented by gaussian peaks (a normal distribution) and not lines in a single channel. All of the counts in a peak, unless it overlaps a second element, are representative of the amount of one particular element. It is, therefore, important to take into account the entire peak. In order to do this the area of the peak is computed. The area of the peaks in this experiment were

computed using a program called XRAYFT (a program created by Dr. James M. Hall of Kansas State University) which first used parameters of height, width and position of the peaks to fit a curve to the data and background. The computer was given initial estimates of the three parameters mentioned above for each peak in a portion of the spectrum and computed the best fit to the data by varying these parameters to minimize chi square. The subroutine is called "gradsearch" as it uses the gradient in the n-parameter space to minimize chi square (Bevington '69). Once the curve is fit, the area of each peak in the spectrum is calculated, the background noise subtracted and the statistical uncertainty calculated for a normal distribution

The area of a peak represents the number of K-alpha x-rays which is proportional to the relative amount of that particular element in the sample. In order to state the mass of a given element in the sample the apparatus must be calibrated. The apparatus was calibrated for calcium and strontium only. This calibration was done by making six samples of the same bone material (samples were taken from different bones and then mixed together to form six identical 80 mg samples), conducting analysis on these and then adding known amounts of calcium to three and known amounts of strontium to the other three and collecting x-ray fluorescence data on these. Four additions of Calcium Fluoride and five additions of Strontium Nitrate combined with Silicon Dioxide were analyzed. It was found that the area of the peaks increased linearly with the additions of both elements, $r = .982$ for the three Calcium samples and $r = .997$ for the three strontium samples. (See Figures 6 and 7.) Using these linear calibrations

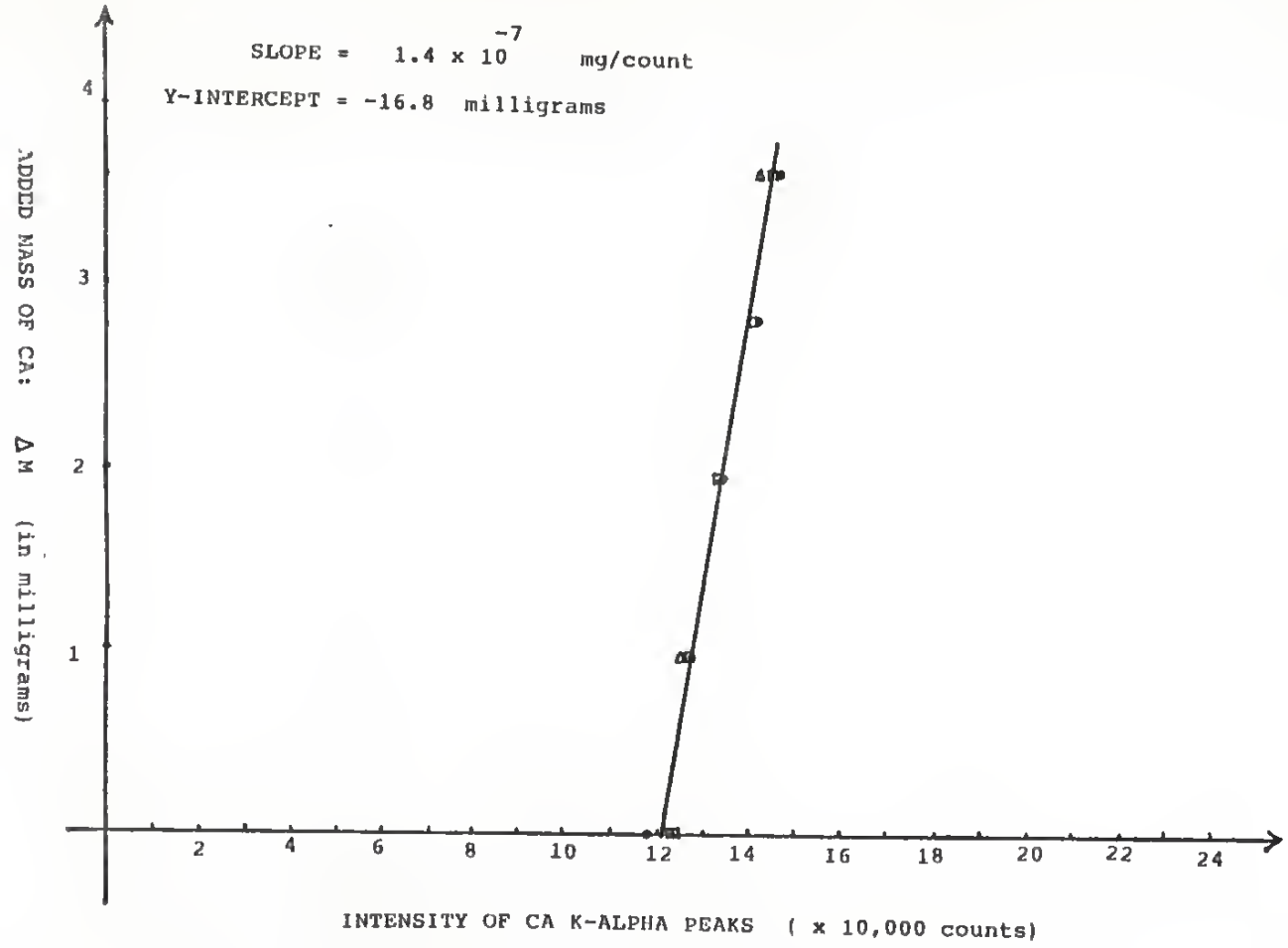
EXPLANATION OF PLATE FOUR: Figure 6 shows the calibration curve for strontium.

FIGURE 6: Sr Calibration Curve r = .977



EXPLANATION OF PLATE FIVE: Figure 7 shows the calibration curve for calcium.

FIGURE 7: CA CALIBRATION CURVE r = .982



it was possible to estimate the mass in grams of strontium and calcium in 80 mg samples.

Before the calibration curves could be used the data had to be corrected for the loss in the activity of the source ,for differences in mass and differences in run time. The loss of activity was accounted for by multiplying each area by an exponential funtion in which the product of the decay constant (CRC Handbook) and the time (in days) since the source was new (June 16, 1976 for 1983 data and August 1, 1984 for 1984 data) formed the argument. To correct for different masses each area was multiplied by a ratio of two exponential functions. The numerator of this ratio had an argument which contained the product of the total mass absorbtion coefficient estimated for the sample and the mass per unit cross sectional area of the sample being corrected. The denominator's argument consisted of the product between the same total mass absorption coefficient (Bracewell and Veigel. '71) mentioned above for the numerator and the mass per unit cross-sectional area of the 80 mg calibration samples. The final correction for differences in run time involved only the multiplication of the ratio of the corrected sample's run time to the calibration samples run time.

Approximately half of the data taken in 1983 was taken in two parts on much different dates and over different time intervals. Correction of this data required splitting the data into two parts and treating each separately using the methods outlined above.

After these corrections were made the calibration curves were used to interpolate the masses of strontium and calcium in 80

mg samples. For the elements not calibrated, iron, zinc, and yttrium, only relative ratios of their peak areas compared to the peak areas of calcium were calculated.

D. Estimation of Uncertainty.

The uncertainties in the data were estimated by combining the uncertainty given by the program XRAYFT in calculating the area of particular peaks in the spectrum and the propagation of error in the corrections for date, mass and run time. The propagation of error in the corrections was calculated using partial differentials of the intensity equation written to form a total differential which would represent the uncertainty produced by the correction calculations. (See Appendix B for expression of uncertainty.)

At least 75% of the uncertainty listed with the data came through the correction calculations for date, mass and run time. Although date is a parameter which might be difficult to keep constant, had the mass and run time been kept constant it can be shown that much of the uncertainty in the measurements would have been eliminated. Especially subject to great increases in uncertainty were the measurements of strontium and yttrium. Their high uncertainty is a result of their low total mass absorption coefficients which cause the numerator in the uncertainty calculation to be quite high. For that data taken in 1983, which had to be handled in two parts the uncertainty, in the mass correction alone amounted to 23%.

III. THE DATA

The data are organized in five sections in the order that it will be referred to in the results section. The first four parts present the ratios of areas of k-alpha peaks or intensities for strontium/calcium, iron/calcium, zinc/calcium and yttrium/calcium. (Only the fourth catagory has yttrium/calcium ratios.) The final part presents the absolute amounts of strontium, calcium, the ratio of strontium/calcium and the relative uncertainties in the values for 80 mg samples. All of the data have been corrected for date, run-time and mass differences. The data tables contain four columns. The first column identifies the sample using the designation of the individual skeleton, the bone and the site from which the sample was taken. (The individual is more clearly identified in Appendix B.) A key for abbreviations is given below. The second column gives the value for the specific ratio of K-alpha peaks. The third column gives the combined statistical and experimental uncertainty in this ratio and the fourth gives the percent uncertainty.

Abbreviations for sites on the skeleton from which samples were taken.

rf - cortical bone of right femoral diaphysis.

lf - cortical bone of left femoral diaphysis.

rt - cortical bone of right tibial diaphysis.*

lt - cortical bone of left tibial diaphysis.*

h - cortical bone of humeral diaphysis (not sided).*

rtem or rtm - cortical bone of the right temporal.

ltem or ltm - cortical bone of the left temporal.

lman or lmn - cortical bone of the left mandible.

rman or rmn - cortical bone of the right mandible.

r' - cortical bone of the radius (not sided).

r - cortical bone of the ramus of the mandible.

c - cortical bone of the cranium, specific bone not identified.

lb - cortical and hematogenous of long bone not specifically identified.

a - identifies the sample as being taken from an area located proximally on the diaphysis.

b - identifies the sample as being taken from an area located distally on the diaphysis.

i - sample taken from and below the osseous layer of the periosteum.

o - sample taken from the periosteum.

*In 1983 samples taken from these bones included both cortical and hematogenous bone.

DATA FOR SECTION ONE: Homogeneous distribution of elements between sites on the same bone.

CORRECTED SR/CA X-RAY RATIOS

SAMPLE	SR/CA	UNCERTAINTY	%UNCERTAINTY
#83 1984 rfa	.0935	.0175	18.72
#83 1984 rfb	.0997	.0182	18.25
#79-7 1984 rfa	.0531	.0121	22.79
#79-7 1984 rfb	.0418	.0083	19.86
#79-6 1984 rfa	.1102	.0218	19.78
#79-6 1984 rfb	.1136	.0231	20.30

CORRECTED FE/CA X-RAY RATIOS

SAMPLE	FE/CA	UNCERTAINTY	%UNCERTAINTY
#83 1984 rfa	.0168	.0011	6.55
#83 1984 rfb	.0192	.0011	5.73
#79-7 1984 rfa	.0167	.0016	9.58
#79-7 1984 rfb	.0133	.0014	10.53
#79-6 1984 rfa	.0152	.0012	7.84
#79-6 1984 rfb	.0143	.0011	7.95

CORRECTED ZN/CA X-RAY RATIOS

SAMPLE	ZN/CA	UNCERTAINTY	%UNCERTAINTY
#83 1984 rfa	.0497	.0025	5.03
#83 1984 rfb	.0513	.0019	3.70
#79-7 1984 rfa	.0171	.0018	10.52
#79-7 1984 rfb	.0137	.0009	6.57
#79-6 1984 rfa	.0203	.0017	8.37
#79-6 1984 rfb	.0201	.0014	6.74

DATA FOR SECTION TWO: Homogeneous distribution of elements between sites on the same bone and the reliability of the method.

CORRECTED SR/CA X-RAY RATIOS

SAMPLE	SR/CA	UNCERTAINTY	%UNCERTAINTY
#82 1984 rfa	.0606	.0118	19.47
#82 1984 rfb	.0659	.0130	19.73
#82 1984 rfb	.0643	.0125	19.44
#82 1984 rfb	.0629	.0128	20.30
#41 1984 rfa	.2347	.0435	18.53
#41 1984 rfa	.2340	.0434	18.55
#41 1984 rfb	.2351	.0423	17.99
#41 1984 rfb	.1899	.0317	16.69
#76 1984 rfa	.0706	.0138	19.55
#76 1984 rfa	.0721	.0138	19.14
#76 1984 rfb	.0692	.0131	18.93
#76 1984 rfb	.0666	.0123	18.47
#81-13 1984 rfa	.0451	.0088	19.51
#81-13 1984 rfa	.0540	.0105	19.44
#81-13 1984 rfb	.0562	.0107	19.04

CORRECTED FE/CA X-RAY RATIOS

SAMPLE	FE/CA	UNCERTAINTY	%UNCERTAINTY
#82 1984 rfa	.0155	.0013	8.39
#82 1984 rfb	.0156	.0012	7.69
#82 1984 rfb	.0181	.0013	7.18
#82 1984 rfb	.0190	.0015	7.95
#41 1984 rfa	.0300	.0019	6.33
#41 1984 rfa	.0270	.0018	6.67
#41 1984 rfb	.0288	.0018	6.25
#41 1984 rfb	.0228	.0015	6.58
#76 1984 rfa	.0192	.0009	4.69
#76 1984 rfa	.0223	.0022	9.87
#76 1984 rfb	.0190	.0011	5.79
#76 1984 rfb	.0172	.0011	6.40
#81-13 1984 rfa	.0145	.0007	4.83
#81-13 1984 rfa	.0335	.0020	5.97
#81-13 1984 rfb	.0170	.0014	8.24

CORRECTED ZN/CA X-RAY RATIOS

SAMPLE	ZN/CA	UNCERTAINTY	%UNCERTAINTY
#82 1984 rfa	.1309	.0056	4.28
#82 1984 rfb	.0977	.0041	4.20
#82 1984 rfb	.0913	.0041	4.49
#82 1984 rfb	.0924	.0053	5.73
#41 1984 rfa	.1062	.0046	4.33
#41 1984 rfa	.1021	.0040	3.92
#41 1984 rfb	.1012	.0041	4.05
#41 1984 rfb	.0750	.0034	4.53
#76 1984 rfa	.0354	.0019	5.37
#76 1984 rfa	.0365	.0014	3.83
#76 1984 rfb	.0341	.0016	4.69
#76 1984 rfb	.0319	.0016	5.02
#81-13 1984 rfa	.0155	.0011	7.10
#81-13 1984 rfa	.0427	.0020	4.68
#81-13 1984 rfb	.0230	.0016	6.96

DATA FOR SECTION THREE: Homogeneous distribution of elements between sites in the same skeleton.

CORRECTED SR/CA XRAY RATIOS

SAMPLE	SR/CA	UNCERTAINTY	%UNCERTAINTY
#1 1984 rf	.3199	.0547	17.10
#1 1984 lf	.3467	.0601	17.33
#1 1984 rt	.3100	.0580	18.71
#1 1984 lt	.3726	.0634	17.02
#1 1984 h	.2300	.0399	17.35
#6 1984 rtem	.3082	.0599	19.44
#6 1984 lman	.2656	.0490	18.45
#17 1984 lfa	.3256	.0609	18.70
#17 1984 lfb	.3612	.0671	18.58
#17 1984 rman	.2705	.0509	18.82
#17 1984 r'	.3297	.0623	18.90

CORRECTED FE/CA X-RAY RATIOS

SAMPLE	FE/CA	UNCERTAINTY	%UNCERTAINTY
#1 1984 rf	.0308	.0011	3.57
#1 1984 lf	.0267	.0011	4.12
#1 1984 rt	.0436	.0020	4.59
#1 1984 lt	.0858	.0017	1.98
#1 1984 h	.0329	.0012	3.64
#6 1984 rtem	.0428	.0021	4.91
#6 1984 lman	.0201	.0013	6.47
#17 1984 lfa	.0272	.0016	5.88
#17 1984 lfb	.0328	.0018	5.49
#17 1984 rman	.0912	.0034	3.73
#17 1984 r'	.0366	.0017	4.64

CORRECTED ZN/CA X-RAY RATIOS

SAMPLE	ZN/CA	UNCERTAINTY	%UNCERTAINTY
#1 1984 rf	.0231	.0010	4.33
#1 1984 lf	.0273	.0013	4.76
#1 1984 rt	.0143	.0008	5.59
#1 1984 lt	.0199	.0008	4.01
#1 1984 h	.0161	.0008	4.97
#6 1984 rtem	.0519	.0027	5.20
#6 1984 lman	.0176	.0013	7.39
#17 1984 lfa	.0437	.0025	5.72
#17 1984 lfb	.0361	.0026	7.20
#17 1984 rman	.0141	.0008	5.67
#17 1984 r'	.0269	.0016	5.95

DATA FOR SECTION FOUR: Homogeneous distribution of elements between sites in the same skeleton and the role of the environment in trace element analysis.

CORRECTED SR/CA X-RAY RATIOS

SAMPLE	SR/CA	UNCERTAINTY	%UNCERTAINTY
#6b 1984 ilmn	.1892	.0358	18.92
#6b 1984 olmn	.2131	.0397	18.63
#6b 1984 ilf	.2634	.0500	18.98
#6b 1984 olf	.2704	.0500	18.49
#6b 1984 irh	.2271	.0430	18.93
#6b 1984 orh	.2286	.0427	18.68
#6b 1984 iltm	.2266	.0427	18.84
#6b 1984 oltm	.2461	.0458	18.61
#1 1983 it	.4176	.1549	37.09
#1 1983 ot	.5457	.2117	38.79
#1 1983 ir	.2930	.1068	36.45
#1 1983 or	.3418	.1236	36.17
#1 1983 ic	.2652	.0940	35.43
#1 1983 oc	.3015	.1108	36.75
#1 1983 ilb	.3223	.1145	35.53
#1 1983 olb	.3658	.1348	36.85
#1 1983 ih	.5290	.1954	36.94
#1 1983 oh	.7816	.3278	41.94
#6 1983 ilb	.4754	.1710	35.97
#6 1983 olb	.4285	.2077	48.47
#6 1983 ir	.3997	.1942	48.59
#6 1983 or	.4226	.2067	48.91
#6 1983 ic	.4050	.1462	36.10
#6 1983 oc	.4264	.1512	35.46
#6 1983 ih	.3505	.1690	48.22
#6 1983 oh	.4134	.1457	35.24

CORRECTED SR/CA X-RAY RATIOS CONT.

SAMPLE	SR/CA	UNCERTAINTY	[illegible]
#17 1983 it	.1786	.0715	40.03
#17 1983 ot	1.0222	.5097	49.86
#17 1983 ir	.2074	.1042	50.24
#17 1983 or	.3602	.1724	47.86
#17 1983 ic	.2718	.1345	49.48
#17 1983 oc	.3556	.1861	52.33
#17 1983 ih	.3486	.1726	49.51
#17 1983 oh	.5149	.2122	41.21
#23 1983 ilb	.3346	.1184	35.39
#23 1983 olb	.3776	.1375	36.41
#23 1983 ir	.2179	.1019	46.76
#23 1983 or	.3335	.1709	51.24
#23 1983 ic	.2232	.0815	36.51
#23 1983 oc	.3254	.1176	36.14
#23 1983 ih	.3690	.1796	48.67
#23 1983 oh	.3795	.1886	49.70
#23 1983 iv	.2306	.1114	48.31
#23 1983 ov	.2639	.1304	49.41

CORRECTED FE/CA X-RAY RATIOS

SAMPLE	FE/CA	UNCERTAINTY	%UNCERTAINTY
#6b 1984 ilmn	.0174	.0015	8.62
#6b 1984 olmn	.0751	.0032	4.26
#6b 1984 ilf	.0128	.0010	7.81
#6b 1984 olf	.0494	.0021	4.25
#6b 1984 irh	.0163	.0009	5.52
#6b 1984 orh	.0514	.0019	3.70
#6b 1984 iltm	.0165	.0010	6.06
#6b 1984 oltm	.0641	.0029	4.52
#1 1983 it	.3655	.0658	18.00
#1 1983 ot	2.4065	.4486	18.64
#1 1983 ir	.0390	.0082	21.03
#1 1983 or	.1806	.0341	18.89
#1 1983 ic	.1732	.0311	17.98
#1 1983 oc	.0754	.0150	19.89
#1 1983 ilb	.1288	.0237	18.40
#1 1983 olb	.5720	.1005	17.57
#1 1983 ih	1.4177	.2475	17.46
#1 1983 oh	8.4277	1.5456	18.34
#6 1983 ilb	.2055	.0373	18.15
#6 1983 olb	.2348	.0667	28.41
#6 1983 ir	.1713	.0487	28.43
#6 1983 or	.2984	.0824	27.61
#6 1983 ic	.2438	.0454	18.62
#6 1983 oc	.2373	.0427	17.99
#6 1983 ih	.1783	.0506	28.38
#6 1983 oh	.2817	.0512	18.17

CORRECTIED FE/CA X-RAY RATIOS CONT.

SAMPLE	FE/CA	UNCERTAINTY	%UNCERTAINTY
#17 1983 it	.0741	.0212	28.61
#17 1983 ot	1.0879	.3085	28.36
#17 1983 ir	.1044	.0295	28.26
#17 1983 or	.8115	.2221	27.37
#17 1983 ic	.2446	.0686	28.05
#17 1983 oc	.7167	.1995	27.84
#17 1983 ih	.8890	.2461	27.68
#17 1983 oh	2.8402	.5186	18.25
#23 1983 ilb	.1051	.0200	19.03
#23 1983 olb	1.0522	.1899	18.05
#23 1983 ir	.0413	.0116	28.09
#23 1983 or	.1631	.0461	28.26
#23 1983 ic	.2056	.0373	18.14
#23 1983 oc	.2219	.0405	18.25
#23 1983 ih	.6235	.1675	26.86
#23 1983 oh	1.0522	.1899	18.05
#23 1983 iv	.6070	.1615	26.61
#23 1983 ov	1.1149	.2963	26.58

CORRECTED ZN/CA X-RAY RATIOS

SAMPLE	ZN/CA	UNCERTAINTY	%UNCERTAINTY
#6b 1984 ilmn	.0150	.0023	15.33
#6b 1984 olmn	.0360	.0017	4.72
#6b 1984 ilf	.0212	.0011	5.19
#6b 1984 olf	.0711	.0027	3.80
#6b 1984 irh	.0174	.0018	10.34
#6b 1984 orh	.0351	.0016	4.56
#6b 1984 iltm	.0108	.0013	12.04
#6b 1984 oltm	.0150	.0021	14.00
#1 1983 it	.0612	.0132	21.57
#1 1983 ot	.0906	.0231	25.50
#1 1983 ir	.0166	.0044	26.51
#1 1983 or	.0259	.0064	24.77
#1 1983 ic	.0164	.0046	27.93
#1 1983 oc	.0149	.0039	26.17
#1 1983 ilb	.0301	.0068	22.59
#1 1983 olb	.0433	.0102	23.56
#1 1983 ih	.0400	.0116	29.00
#1 1983 oh	.2377	.0624	26.25
#6 1983 ilb	.0284	.0067	23.59
#6 1983 olb	.0639	.0219	34.27
#6 1983 ir	.0309	.0112	36.25
#6 1983 or	.0570	.0200	35.09
#6 1983 ic	.0231	.0058	25.11
#6 1983 oc	.0319	.0076	23.82
#6 1983 ih	.0566	.0192	33.90
#6 1983 oh	.0300	.0074	24.67

CORRECTED ZN/CA X-RAY RATIOS CONT.

SAMPLE	ZN/CA	UNCERTAINTY	%UNCERTAINTY
#17 1983 it	.0333	.0128	38.44
#17 1983 ot	.1263	.0441	34.92
#17 1983 ir	.0159	.0061	38.36
#17 1983 or	.0369	.0143	38.75
#17 1983 ic	.0145	.0058	40.00
#17 1983 oc	.0241	.0101	41.91
#17 1983 ih	.0509	.0192	37.72
#17 1983 oh	.0850	.0265	31.18
#23 1983 ilb	.0445	.0098	22.02
#23 1983 olb	.1026	.0240	23.39
#23 1983 ir	.0314	.0104	33.12
#23 1983 or	.0486	.0177	36.42
#23 1983 ic	.0196	.0049	25.00
#23 1983 oc	.0249	.0064	25.70
#23 1983 ih	.0340	.0128	37.64
#23 1983 oh	.0616	.0262	42.53
#23 1983 iv	.0227	.0096	42.29
#23 1983 ov	.0394	.0163	41.37

CORRECTED Y/CA X-RAY RATIOS

SAMPLE	Y/CA	UNCERTAINTY	%UNCERTAINTY
#1 1983 it	.3496	.1659	47.46
#1 1983 ot	.5996	.2922	48.73
#1 1983 ir	.3140	.1444	45.89
#1 1983 or	.1301	.0620	47.65
#1 1983 ic	.0114	.0064	56.33
#1 1983 oc	.3344	.1544	46.18
#1 1983 ilb	.0460	.0230	49.98
#1 1983 olb	.2544	.1210	47.58
#1 1983 ih	.2147	.1045	48.69
#1 1983 oh	.4458	.2393	53.68
#6 1983 ilb	.1318	.0629	47.70
#6 1983 olb	.1440	.0829	57.54
#6 1983 ir	.1032	.0602	58.38
#6 1983 or	.1214	.0710	58.48
#6 1983 ic	.1418	.0675	47.61
#6 1983 oc	.1480	.0695	46.93
#6 1983 ih	.0643	.0379	58.94
#6 1983 oh	.0916	.0428	46.68
#17 1983 it	.1634	.0942	57.64
#17 1983 ot	.4200	.2553	60.78
#17 1983 ir	.0174	.0113	64.73
#17 1983 or	.2058	.1159	56.31
#17 1983 ic	.1399	.0810	57.90
#17 1983 oc	.3367	.2016	59.89
#17 1983 ih	.1933	.1126	58.26
#17 1983 oh	.3191	.1665	52.19

CORRECTED Y/CA X-RAY RATIOS CONT.

SAMPLE	Y/CA	UNCERTAINTY	%UNCERTAINTY
#23 1983 ilb	.1557	.0721	46.33
#23 1983 olb	.7192	.3296	45.83
#23 1983 ir	.0074	.0049	66.93
#23 1983 or	.2742	.1620	59.08
#23 1983 ic	.0158	.0089	56.80
#23 1983 oc	.0495	.0253	51.16
#23 1983 ih	.0976	.0573	58.69
#23 1983 oh	.1370	.0810	59.10
#23 1983 iv	.0235	.0149	63.52
#23 1983 ov	.0288	.0189	65.79

DATA FOR SECTION FIVE: Absolute amounts of strontium to calcium ratios in an 80 milligram sample.

CALIBRATED DATA
STRONTIUM (micrograms) AND CALCIUM (micrograms)

	Strontium		Calcium		Sr/Ca	
#83-9 1984						
rfa	9.40 +/-	19.03	15,051 +/-	538	.00062 +/-	.00128
rfb	9.16	19.03	13,755	427	.00067	.00141
#79-7 1984						
rfa	5.30	18.59	14,912	565	.00036	.00128
rfb	4.29	18.27	15,295	554	.00028	.00120
#79-6 1984						
rfa	10.60	19.29	14,469	537	.00073	.00136
rfb	11.57	19.45	15,320	560	.00076	.00131
#82 1984						
rfa	6.12	18.56	15,090	586	.00041	.00126
rfb	5.63	18.49	12,762	552	.00044	.00146
rfb	5.37	18.43	12,459	572	.00043	.00150
rfb	5.76	18.52	13,786	500	.00042	.00137
#41 1984						
rfa	19.35 +/-	20.56	12,365 +/-	565	.00156 +/-	.00173
rfa	19.35	20.57	12,401	561	.00156	.00173
rfb	19.94	20.72	12,855	568	.00155	.00168
rfb	14.57	19.83	12,727	445	.00114	.00156
#76 1984						
rfa	6.71	18.66	14,212	532	.00047	.00132
rfa	6.84	18.70	14,172	433	.00048	.00133
rfb	6.09	18.52	13,154	538	.00046	.00142
rfb	6.46	18.60	14,502	430	.00045	.00131
#81-13 1984						
rfa	4.56	18.29	15,052	566	.00030	.00121
rfa	4.99	18.36	13,802	555	.00036	.00134
rfb	5.79	18.48	15,380	546	.00037	.00119

CALIBRATED DATA
STRONTIUM (in micrograms) AND CALCIUM (in micrograms)

#1 1984

	Strontium		Calcium		Sr/Ca	
rf	34.00 +/-	22.77	15,958 +/-	355	.00213 +/-	.00147
lf	33.97	22.80	14,707	391	.00231	.00161
rt	33.42	22.80	16,186	557	.00206	.00148
lt	38.85	23.51	15,657	348	.00248	.00156
?h	25.81	21.57	16,848	352	.00153	.00131

#6 1984

rtm	28.61	22.16	13,934	601	.00205	.00167
lmn	28.86	22.12	16,308	505	.00177	.00141

#17 1984

lfa	36.69	23.34	16,920	550	.00216	.00144
lfb	40.47	23.95	16,825	525	.00241	.00150
rmn	28.86	22.17	16,012	524	.00180	.00144
?r	36.22	23.32	16,495	555	.00220	.00149

#6b 1984

ilmn	18.53	20.52	14,596	538	.00127	.00145
olmn	22.65	21.12	15,952	534	.00142	.00137
ilf	29.81	22.65	16,987	537	.00175	.00138
olf	29.28	22.17	16,251	491	.00180	.00142
irh	23.13	21.21	15,283	567	.00151	.00144
orh	22.71	21.15	14,907	524	.00152	.00147
iltm	24.02	21.38	15,905	541	.00151	.00140
oltm	23.17	21.24	14,124	513	.00164	.00156

#1 1983

it	23.93	23.99	8,599	1227	.00278	.00279
ot	12.51	20.99	3,436	969	.00364	.00611
ir	24.27	23.92	12,431	1,464	.00195	.00215
or	19.05	22.54	8,461	1,193	.00225	.00298
ic	17.61	22.09	9,957	1,250	.00177	.00244
oc	16.79	21.98	8,355	1,227	.00201	.00293
ilb	24.19	23.85	11,263	1,310	.00215	.00237
olb	19.67	22.86	8,077	1,169	.00244	.00319
ih	18.19	22.44	5,158	1,020	.00353	.00505
oh	9.42	20.47	1,803	851	.00522	.01381

CALIBRATED DATA
STRONTIUM (in micrograms) AND CALCIUM (in micrograms)

#6 1983

	Strontium		Calcium		Sr/Ca	
ilb	30.43	+/-25.52	9,610	+/-1,263	.00317	+/-.00308
olb	55.13	35.96	19,322	2,939	.00285	.00229
ir	53.35	35.62	20,045	2,977	.00107	.00087
or	46.68	33.51	16,589	2,504	.00281	.00244
ic	22.20	23.30	8,227	1,205	.00270	.00323
oc	25.48	24.11	8,969	1,209	.00284	.00269
ih	46.50	33.13	19,926	2,958	.00233	.00201
oh	24.17	23.74	8,774	1,189	.00275	.00307

#17 1983

it	28.10	26.82	23,614	3,512	.00119	.00131
ot	59.45	38.20	8,736	1,671	.00681	.00568
ir	31.16	28.64	22,550	3,341	.00138	.00147
or	30.93	27.84	12,892	2,056	.00240	.00254
iC	34.87	29.65	19,260	2,867	.00181	.00181
oc	33.97	30.33	14,341	2,232	.00237	.00248
ih	27.77	26.98	11,956	2,071	.00232	.00266
oh	9.54	20.48	2,772	899	.00344	.00850

#23 1983

ilb	24.56	23.85	11,013	1,323	.00223	.00243
olb	15.59	21.66	6,189	1,076	.00206	.00322
ir	36.11	29.26	24,882	3,661	.00145	.00139
or	35.38	30.47	15,927	2,422	.00222	.00225
ic	18.30	22.40	12,302	1,429	.00149	.00200
oc	14.63	21.40	6,740	1,095	.00217	.00353
ih	37.78	30.36	15,371	2,363	.00246	.00236
oh	25.77	26.56	10,191	1,782	.00253	.00305
iv	23.35	25.51	15,195	2,262	.00154	.00191
ov	18.12	23.90	10,298	1,753	.00176	.00262

IV. RESULTS AND CONCLUSIONS

These results and conclusions are organized in five sections, two of which overlap with other considerations and a final conclusion.

1) Homogeneous distribution of elemental ratios between sites on the same bone.

In 1984 samples were analyzed from individuals #83, #79-7, and #79-6 to check the homogeneity of the elements; strontium, iron, and zinc (yttrium was not found in any of the skeletons loaned to us by Dr. Finnegan) within the same bone. Two samples were taken from the right femoral diaphysis, one more distal than the other. All of the results show that for all three elements tested homogeneity existed within the right femur. Also to be noted is that no particular uniqueness existed in the ratios between individuals except that the Zn/Ca x-ray ratios in #83 were three times larger than the other two individuals.

2) Homogeneous distribution of elemental ratios between sites on the same bone and the reliability of the method.

In 1984 four other individuals; #'s 82, 41, 76, and 81-13

were tested in the same way as in Part One except added to that were tests of the method itself. For this part the identical sample was tested again to see if the same ratios would be measured. For each individual homogeneity was evident for the Sr/Ca and Fe/Ca x-ray ratios. In two cases however, #'s 82 and 81-13 the Zn/Ca values for two of the samples were 30 to 50 percent higher than the values measured in the other samples. In fact the Fe/Ca x-ray ratio for RFA from #81-13 is also statistically higher than the others. Because this sample was one tested for repeatability there seems to be a problem in this one sample. The only explanation which seems somewhat plausible is that a concentrated amount of iron and zinc was in the sample and shifted before the second sampling to an area which was more easily readable by the detector. This is only speculation. Consequently, at this time, no reason can be given for this discrepency which would allow for its elimination in future experiments. Turning back to the Sr/Ca x-ray ratios, #41 is the only individual whose ratios show any sign of statistically supported uniqueness with respect to any of the individuals mentioned thus far. This conclusion can be made easily by comparing Figures 8 and 9. These figures are graphical representations of the data for the Sr/Ca x-ray ratios of #41 and #82. #82 is a typical representation of the Sr/Ca x-ray ratios for individuals reported on so far. The abscissa is not an independent variable but identifies the particular sites on the skeleton from where samples were taken . (The abbreviations were defined in the beginning of the data section.) The ordinate presents the values of the ratios of the Sr/Ca K-alpha peaks.

EXPLANATION OF PLATE SIX: Figure 8 is a graphical representation of the Sr/Ca x-ray ratios for #41, 1984.

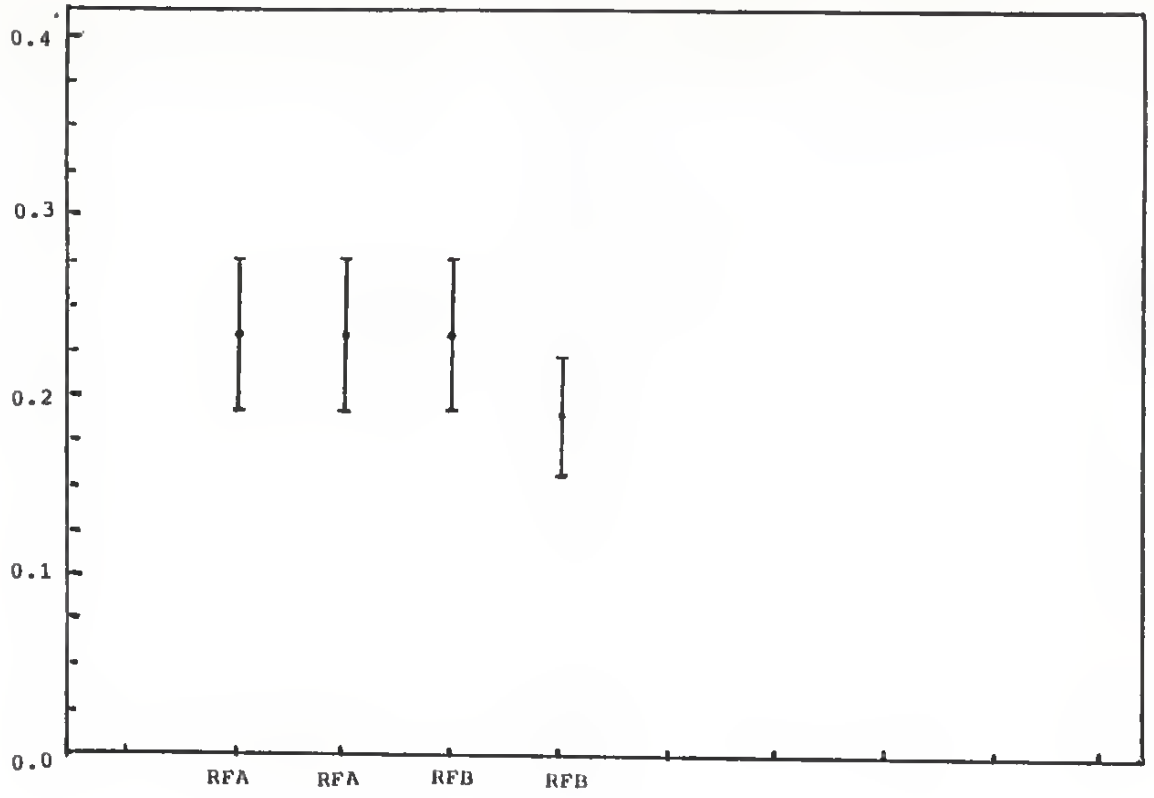


FIGURE 8: Graphical Representation of the Sr/Ca x-ray ratios for #41, 1984

EXPLANATION OF PLATE SEVEN: Figure 9 is a graphical representation for the Sr/Ca x-ray ratios for #82, 1984.

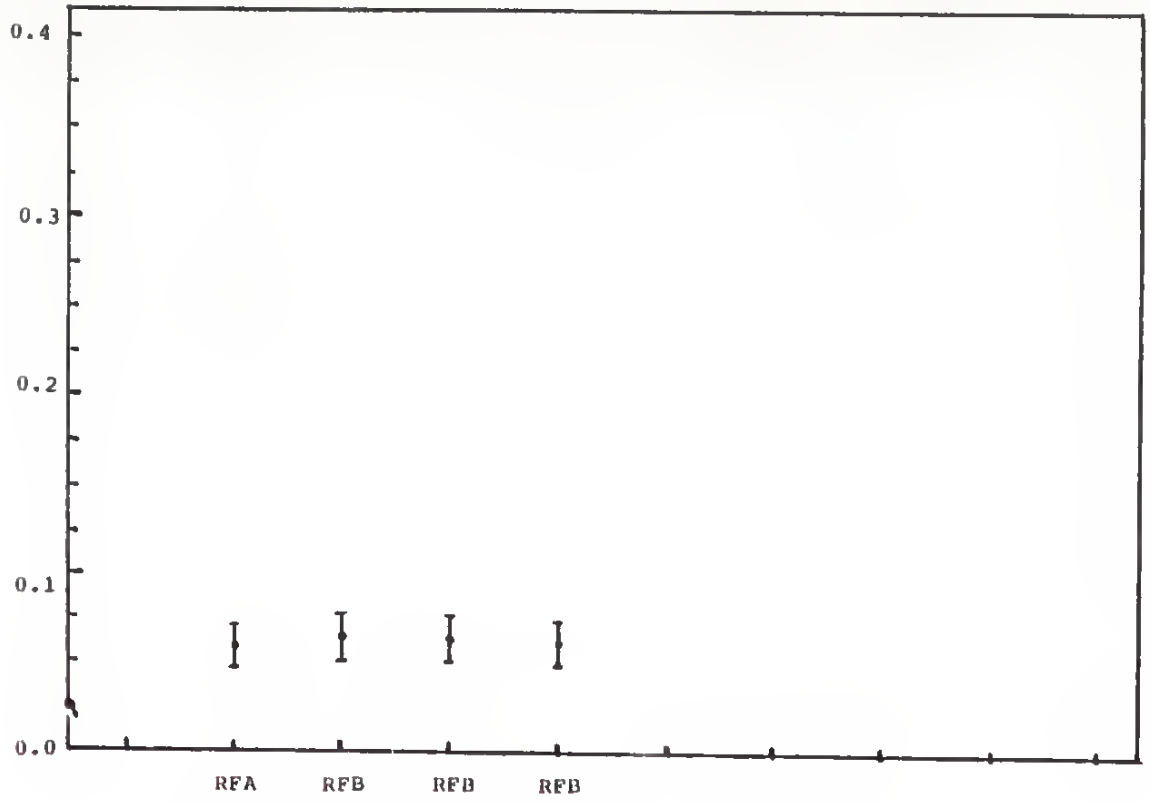


FIGURE 9: Graphical Representation of the Sr/Ca x-ray ratios for #82, 1984

3) Homogeneous distribution of elemental ratios between sites in the same skeleton.

Three individuals who had already been tested in 1983 were sampled again in 1984. The second sampling was done to see if experience that had been gained in that year might change the results found before. These samples were taken from those parts of the skeletons felt to be the cleanest and contained the most cortical bone. The test was performed to see if the Sr/Ca, Fe/Ca, or Zn/Ca x-ray ratios found to be somewhat homogeneously distributed in a single bone were homogeneously distributed throughout the skeleton. For these individuals it was found that the ratio of the Sr/Ca K-alpha intensities was constant in the different bones tested. The ratios of Fe/Ca and Zn/Ca do not show evidence of constancy in any individual skeleton. Although, occasionally, as shown in these values for individual #17, graphically represented in Figure 10, the ratios for two bones may be similar but the ratios measured in other bones are different. There is not within this set of data nor in any of the data which follows any indication of which bones will have the same values or which will have more than others. That is, not only do the Fe/Ca and Zn/Ca x-ray ratios appear nonhomogeneous but there is no predictable pattern to the non-homogeneity.

Once again wih reference to the uniqueness of the Sr/Ca x-ray ratios, although these ratios are higher in these individuals than those donated by Dr. Finnegan, there is no particular uniqueness within the population itself.

EXPLANATION OF PLATE EIGHT: Figure 10 is a graphical representation of the Fe/Ca & Zn/Ca x-ray ratios for #17, 1984.

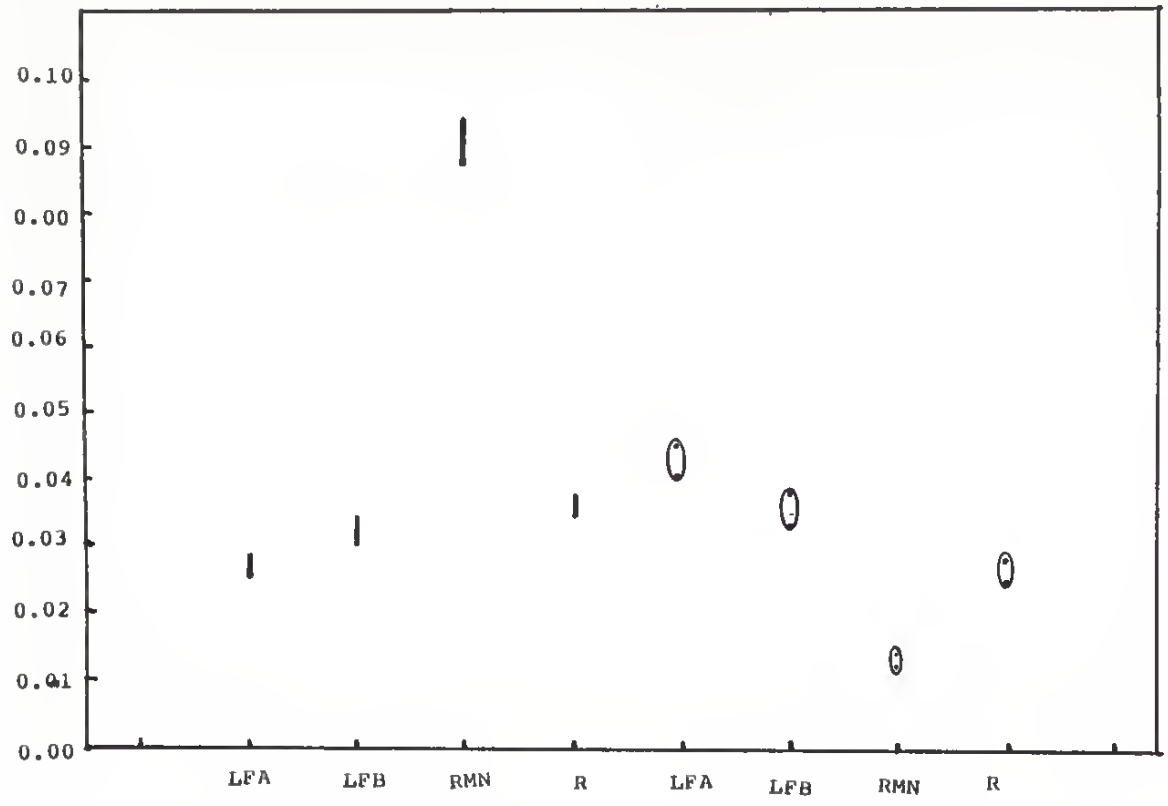


FIGURE 10: Graphical Representation of the Fe/Ca & Zn/Ca x-ray ratios for #17 1984

4) Homogeneous distribution of elemental ratios between sites within the skeleton and the role of the environment in trace element analysis.

In 1984 only one skeleton, #6b, which was checked for homogeneous distribution within the skeleton was also checked for contamination from the environment. In 1983, four individuals were tested for both of the considerations mentioned above. The role of the environment was checked by taking samples from the inner and outer layers of bone.

For the individuals tested in 1983, both cortical and hematogenous bone were sampled. For three of the four individuals this meant including in the outer samples visible amounts of earth. Since iron and yttrium are elements whose presence in bone is considered entirely to be a result of the depositional environment it comes as no suprise that the x-ray ratios for Fe/Ca and Y/Ca are the highest in these samples. In fact yttrium was only present in measureable amounts in the archaeological samples.

Taking a closer look at the data it is found that the Sr/Ca x-ray ratios are higher in the outer samples than in the corresponding inner samples. However, all of these Sr/Ca ratios show evidence of homogeneous distribution throughout the skeleton within the statistics of the data. Although some of the values within individual skeletons were higher than others, no uniqueness

was statistically supported.

In general an increase in the Fe/Ca x-ray ratios occurred in going from the inside of the bone to the outside. As can be seen in Figures 11 and 12 (graphical representaions of Fe/Ca x-ray ratios for '84-#6b and '83-#6) this increase was not statistically supported in all cases. The Fe/Ca x-ray ratios from the inner sample did not always turn out to be homogeneously distributed. Data from #1 (1983) gives an example of an erratic set of Fe/Ca x-ray ratios. (See Figure 13 for a graphical representation of the data.)

The Y/Ca x-ray ratios are also very erratic, showing a trend towards higher values in the outer samples. Something to note is that in certain inner samples the Y/Ca ratios would become almost non-existent. (See Figure 14.) Add to that, the fact that in the forensic and cadaverous samples no yttrium was ever observed in the spectrum and there appears to be good evidence that yttrium is an element whose presence is completely due to environmental comtamination.

The Zn/Ca x-ray ratios tend to be higher in value in the outer samples than in the corresponding inner samples. However, this is only a trend and is not supported statistically. The Zn/Ca ratios are somewhat homogeneous in the inner samples. Statistically the only skeleton which showed signs of nonhomogeneity was in #1 (1983) which is graphically represented in Figure 15.

To summarize this section, it was found that the x-ray ratios Sr/Ca and Zn/Ca show some signs of being distributed homogeneously throughout the skeleton. The eratic values of the

EXPLANATION OF PLATE NINE: Figure 11 is a graphical representation of the Fe/Ca x-ray ratios for #6b, 1984.

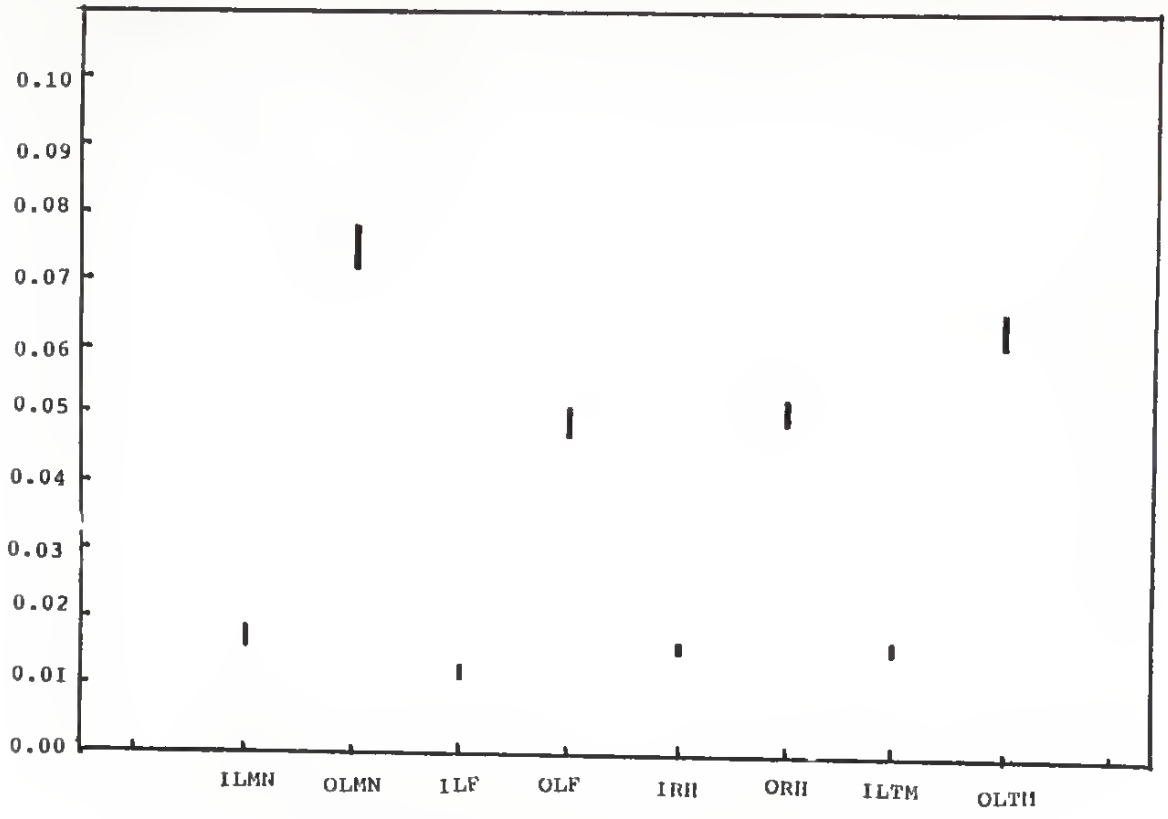


FIGURE 11: Graphical Representation of the Fe/Ca x-ray ratios for #6b, 1984

EXPLANATION OF PLATE TEN: Figure 12 is a graphical representation of the Fe/CA x-ray ratios for #6, 1983.

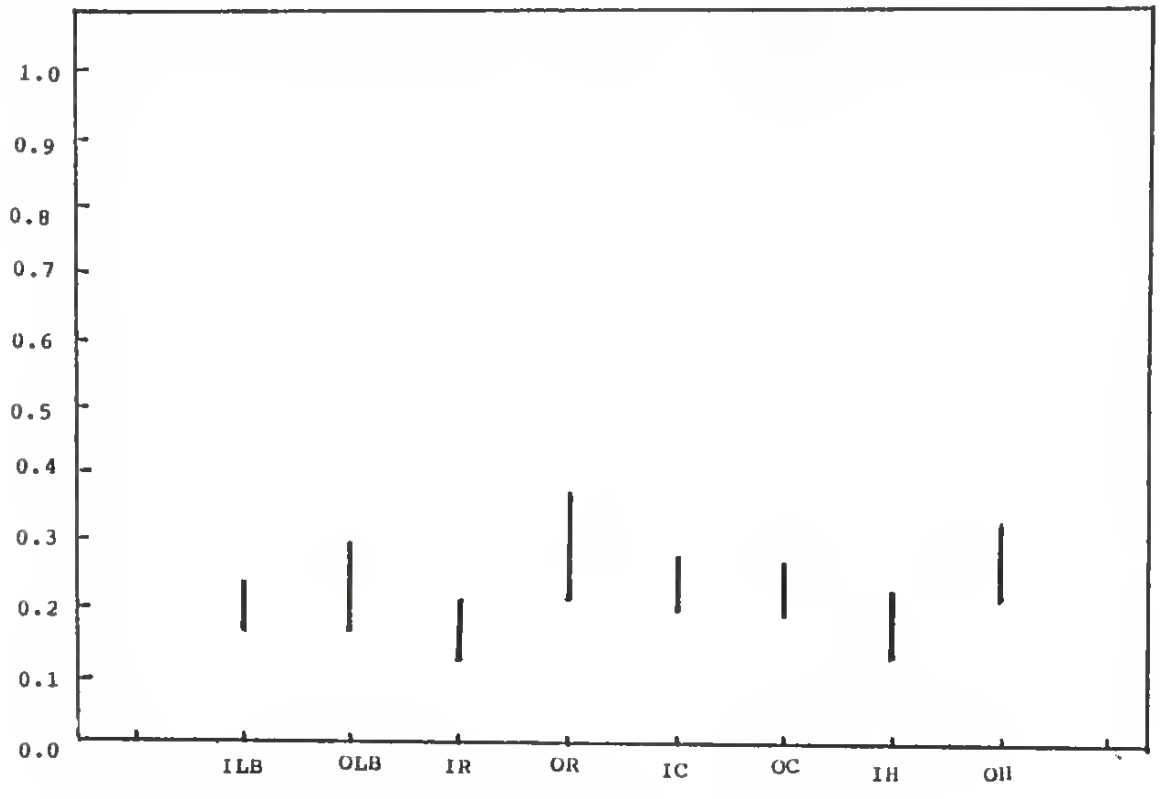


FIGURE 12: Graphical Representation of the Fe/Ca x-ray ratios for #6, 1983

EXPLANATION OF PLATE ELEVEN: Figure 13 is a graphical representation of the Fe/Ca x-ray ratios for #1, 1983.

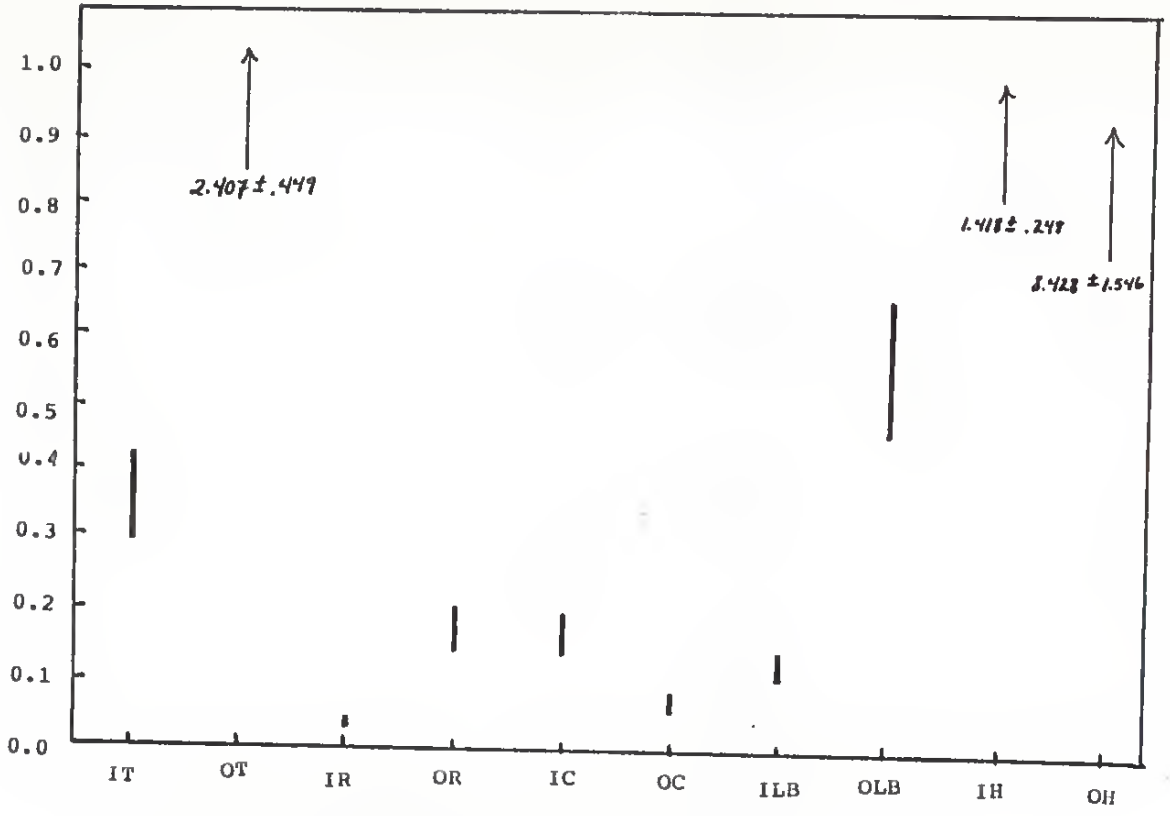


FIGURE 13: Graphical Representation of the Fe/CA x-ray ratios for #1, 1983

EXPLANATION OF PLATE TWELVE: Figure 14 is a graphical representation of the Y/Ca x-ray ratios for #23, 1983.

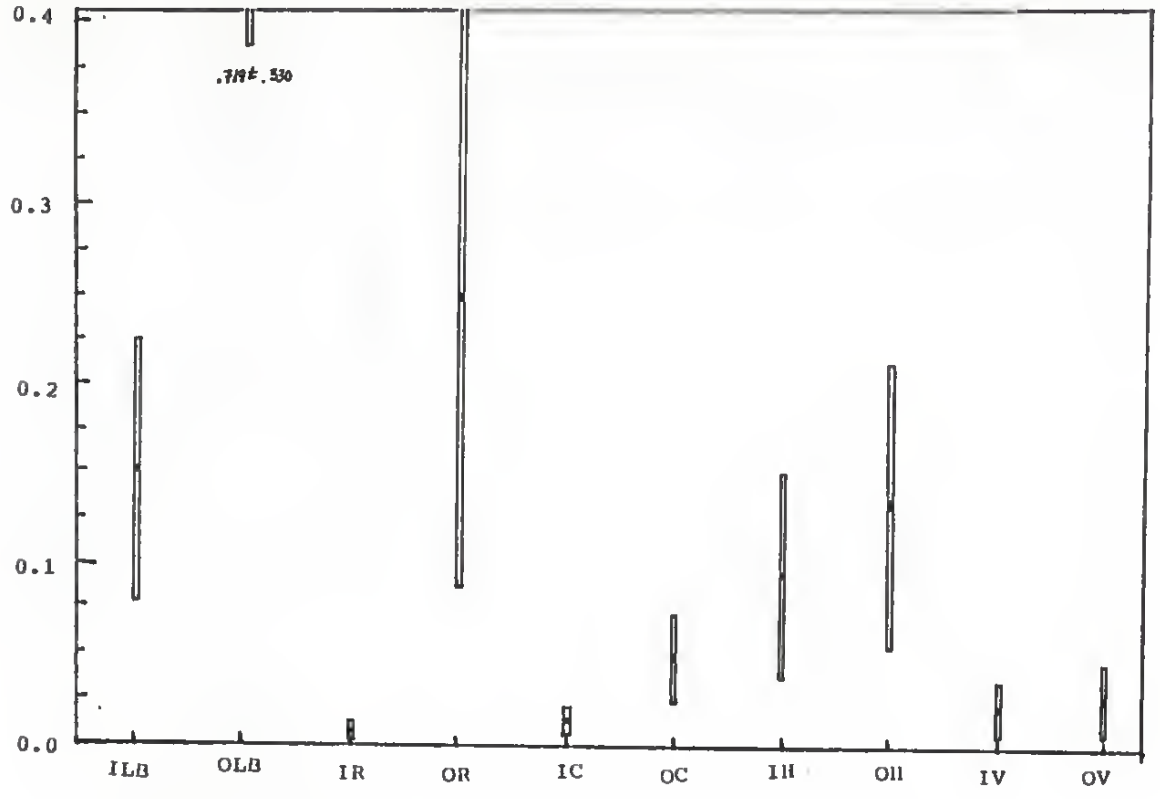


FIGURE 14: Graphical Representation of the Y/CA x-ray ratios for #23, 1983

EXPLANATION OF PLATE THIRTEEN: Figure 15 is a graphical representation of the Zn/Ca x-ray ratios for #1, 1983.

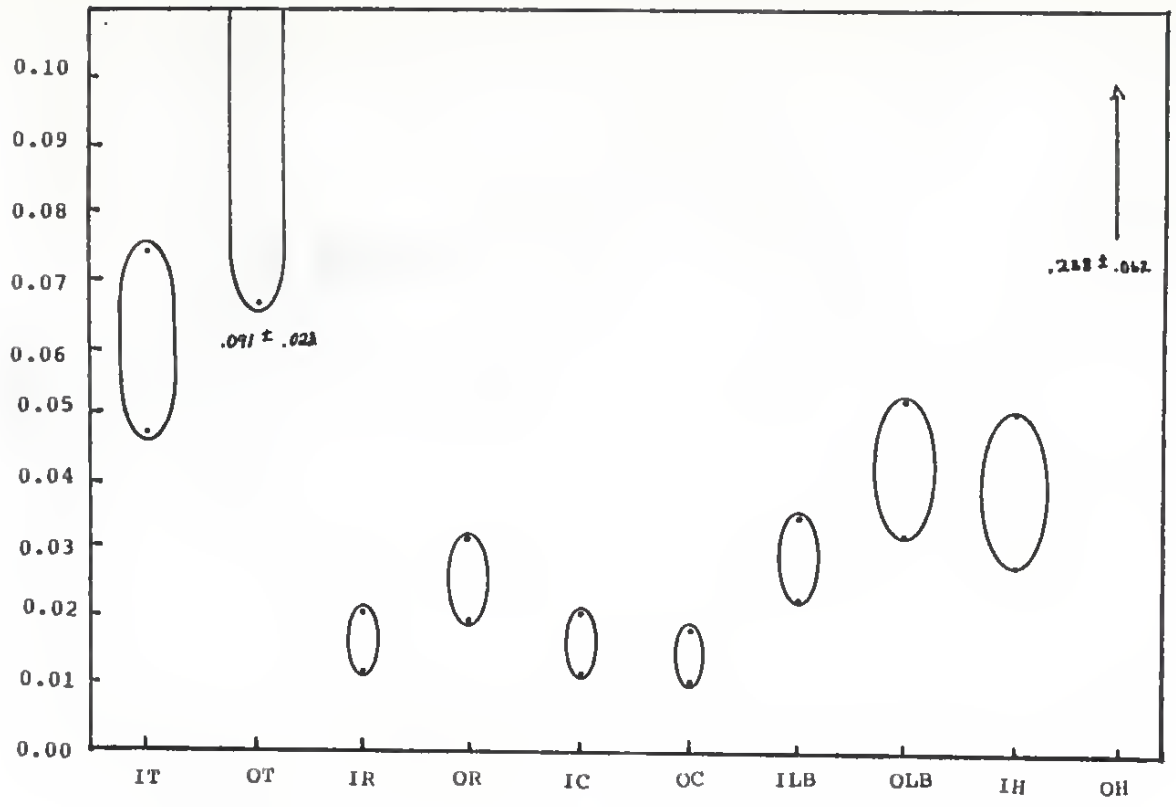


FIGURE 15: Graphical Representation of the Zn/CA x-ray ratios for #1, 1983

Fe/Ca and Zn/Ca x-ray ratios seem to indicate that those elements are probably deposited by the environment. Again it is important to note that quantities of yttrium were only found in those skeletons which had been buried for a period of years. This is not to say, however, that all skeletons having been buried for a number of years will have traces of yttrium in them. For example, in skeleton #6b, the protohistoric indian, there were no measurable amounts of yttrium. Yet this individual had been buried for approximately 200 years.

5) Absolute amounts of strontium to calcium ratios in 80 mg samples.

The absolute amounts of strontium and calcium were interpolated from the calibration curves shown previously in Figures 6 and 7 in Part II-c entitled "Treatment of the data". The interval of error which had to be added due to using these curves was equal to approximatedly 17 micrograms for strontium. This amount of error when trying to measure amounts in a range of 5 to 40 micrograms caused the total uncertainty in the measurement to be at times more than 100 percent. Figure 16 is a graphical representation of the Sr/Ca mass ratios for #1 (1984). The error bars which are filled in represent the additional error added in using the calibration curves. All of the mass ratios overlap with each other, demonstrating what may be a false conclusion of homogeneity without uniqueness for all of the individuals tested.

The interval of error from strontium was by far the major contributor to this possible masking effect on the data. The calibration curve for strontium had a linear calibration coefficient of .997. It appears that the data indicates that the use of absolute mass values to classify human bone using x-ray fluorescence and the curent technique is not possible. However, graphical representations of the x-ray ratios and mass ratios have the same pattern (Compare Figures 16 and 17.) In fact, mathematically the two sets of data vary only by a constant. This implies that comparing the x-ray ratios of various bones and individual skeletons will give the same conclsions as comparing the mass ratios. More conclusive results can then be made because the uncertainty is much less in the x-ray ratios.

Final Conclusions.

In this experiment we set out to validate three criteria which, if found to be valid, would serve as a foundation on which a means of unique identification of an individual skeleton could be made. These three criteria were that the elemental make up of an individual skeleton would be: (1) homogeneously distributed or predictably distributed throughout the skeleton, (2) not affected by temperatures experienced during cremation, and (3) if homogeneously distributed then measurably unique between individuals of a given population.

Only the first and third criteria were directly addressed by this experiment. The second criterion can be deduced to be

EXPLANATION OF PLATE FOURTEEN: Figure 16 is a graphical representation of the Sr/Ca mass ratios for #1, 1984.

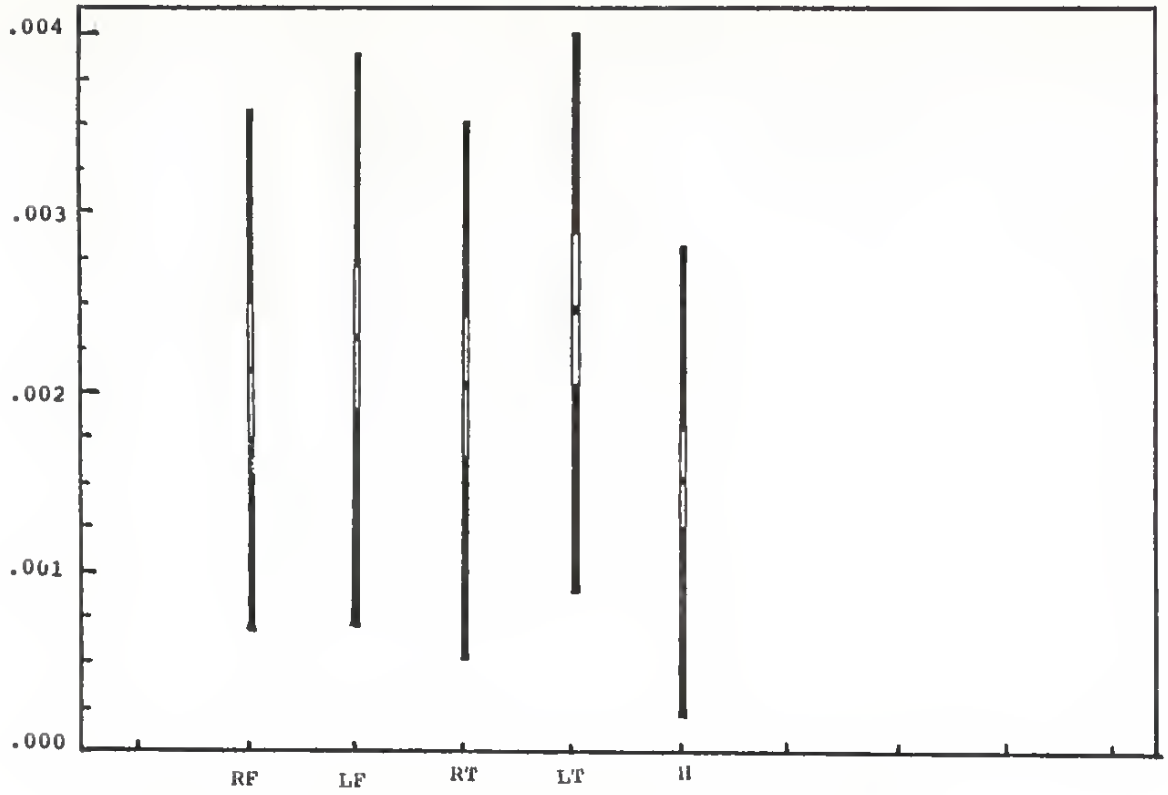


FIGURE 16: Graphical Representation of the Sr/Ca mass ratios for #1, 1984

EXPLANATION OF PLATE FIFTEEN: Figure 17 is a graphical representation of the Sr/Ca x-ray ratios for #1, 1984

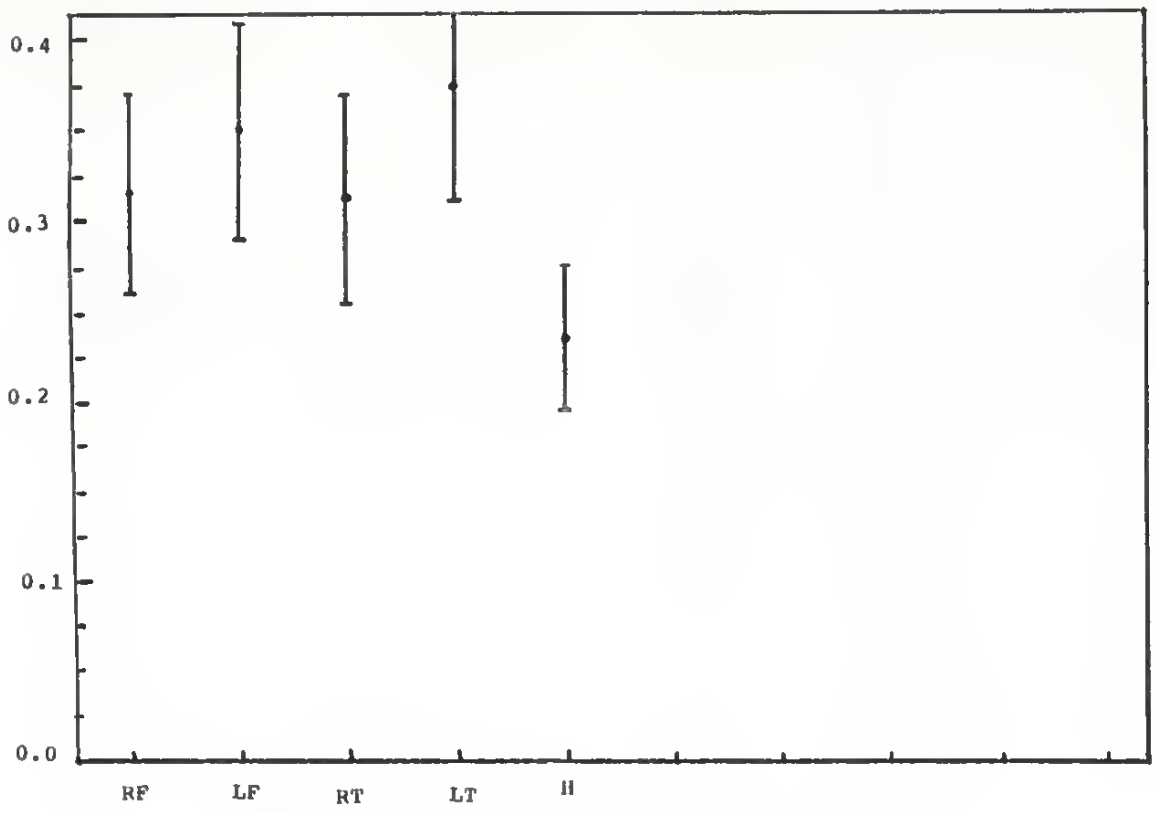


FIGURE 17: Graphical Representation of the Sr/Ca x-ray ratios for #1, 1984

valid since there is evidence that the temperatures reached during cremation may drive out water but are not sufficient to break down much of the apatite molecular structure.

Looking at what has been discovered about the first criterion, it appears that the x-ray ratios of Sr/Ca, Fe/Ca, and Zn/Ca are homogeneously distributed within a single bone which has not been exposed to the environment for more than 2 months. The ratios of Sr/ca were found to be homogenously distributed in archaeological specimens. The x-ray ratios of Zn/Ca may be homogeneously distributed but this conclusion was not always statistically supported (Refer to sections 2 and 3.) Finally, neither the Fe/Ca nor Y/Ca ratios showed any consistent evidence of homogeneity.

The third and final criteria could only pertain to the Sr/Ca ratios since these were the only ones found to be homogeneously distributed throughout the skeleton within the uncertainty of the measurements. Although the values ranged greatly the uncertainty in the measurement was never small enough for any one individual to stand out as having a unique ratio of strontium to calcium.

Concerning the method of x-ray fluorescence itself, there appeared only one measurement which seemed irregular. (Refer to section 2 of the results.) The large uncertainty introduced when calculating absolute amounts of strontium and calcium diminished the conclusions which could be made from the data. However, the calibrated data differed from the x-ray ratio data only by a constant. This indicated that conclusions taken from the x-ray ratio data, which has much lower uncertainty, were no different

than those taken from absolute values with better uncertainty.

The evidence gatnered together in this thesis indicates that it is not possible to determine that a certain group of bones came from a particular skeleton. This indication is not conclusive. More work will have to be done. Two things, in particular, should be done to arrive at more conclusive results. First of all, if the samples' masses, run-times and dates of measurement could be held as constant as possible, as stated earlier in section V, this would cut the uncertainty in half. In addition to saving a great deal of time that would otherwise be spent doing calculations to estimate uncertainty. Second, archaeological samples from different sites should be checked for both homogeneity of Sr/Ca x-ray ratios within particular bones and throughout the skeleton. Likewise, the forensic samples should be checked for both types of homogeneity. (Note: in this experiment only the archaeological samples where used to test the homogeneity of ratios throughout the skeleton and only one archeological skeleton was checked for homogeneity within a single bone.)

It is entirely possible that the range implied in the measurements of "trace" elements is not sufficient to provide unique classification of human bones belonging to a particular skeleton. Indeed this thesis indicates that this is the case. However, until the sample handling technique is improved so that the uncertainty in the measured x-ray ratios is reduced, it shall remain only an indication.

Of the trace elements tested only the strontium/calcium x-ray ratios were found to be homogeneously distributed within the experimental uncertainty in both a single bone and throughout the skeleton. The apparatus was then calibrated in order to obtain absolute amounts of strontium and calcium in each 80 milligram sample. Interpolating mass values from the resulting calibration curves added approximately 75% uncertainty to the ratios and information on the possible uniqueness of the individual was lost. The x-ray ratios differed from the mass ratios by a constant which indicated that analysis of the x-ray ratios could be used yielding the same conclusions as the mass ratios but with far less uncertainty. However, using the Sr/Ca x-ray ratios it was found that no individual skeleton contained a unique level of strontium which distinguished its bones as belonging only to that individual. It may be possible in future experiments to hold certain parameters constant thereby eliminating the need for corrections which introduce large levels of uncertainty. These large levels of uncertainty generated by the present technique made it impossible to conclude with confidence that unique amounts of trace elements between individuals do not exist.

APPENDIX A

The following derivation describes the measured intensity of fluoresced x-rays counted by a detector as a function of the initial intensity of the source and of the mass per unit area of the sample.

As soon as the photons are incident on the sample their numbers begin to attenuate due to absorption by the sample. This attenuation can be described by the equation

$$I_i(x) = I_o e^{-\mu_i x}$$

where: I_o = the intensity of x-rays from the source.

X = the mass/unit area.

μ_i = the total mass absorption coefficient for the absorption of x-rays of the ith kind of energy by the sample.

I_i = the intensity of the source x-rays at x.

The total mass absorption coefficient for an x-ray of ith energy in a sample of many elements is found by

$$\mu_i = \sum_{j=1}^{N} \rho_j \mu_{ij}$$

where: ρ_j = the fraction mass of the jth element in the sample

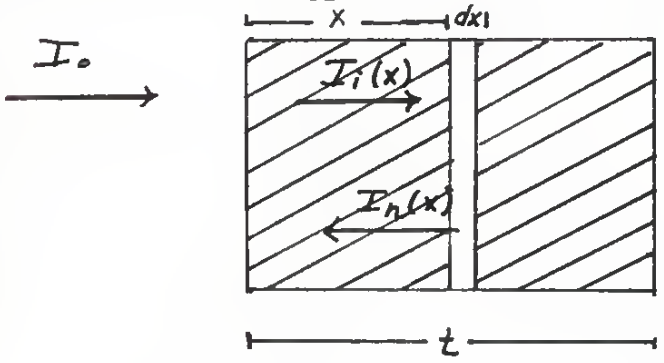
and $$\sum_{j=1}^{N} \rho_j = 1$$

μ_{ij} = the mass absorption coefficient for the ith energy by

manner as is was for the source x-rays. For characteristic x-rays produced by the nth element:

$$\mu_n = \sum_{j=1}^{N} \rho_j \mu_{nj}$$

where: μ_{nj} = the mass absorption coefficient for the nth energy by the jth element.



The intensity of characteristsic K-x-rays produced by the nth element of the sample in a thickness dx at a distance x in the sample is given by:

$$dI_n(x) = g\sigma_{kn}\omega_{kn}I_o e^{-\mu_i x} e^{-\mu_n x} \rho_n dx$$

The intensity measured at the detector produced by the entire sample of thickness (mass per unit area), t, is then:

$$I_n = \int_o^t g\sigma_{kn}\omega_{kn}I_o e^{-\mu_i x} e^{-\mu_n x} \rho_n dx$$

$$= g\sigma_{kn}\omega_{kn}\rho_n I_o \int_o^t e^{-(\mu_i+\mu_n)x} dx$$

$$= g\frac{\sigma_{kn}\omega_{kn}\rho_n I_o}{(\mu_i+\mu_n)} \left(1 - e^{-(\mu_i+\mu_n)t}\right)$$

In the equation I_o is constant for the source, g is

the jth element.

N = the total number of elements in the sample.

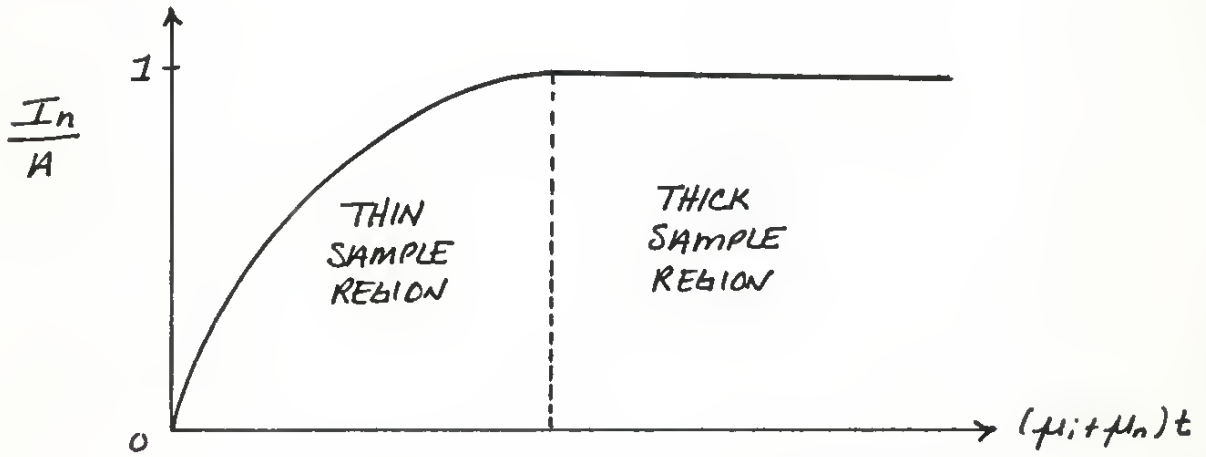
Thus, in order to calculate μ_j the elemental composition of the samples had to be approximated. Bone is primarily made up of $Ca_5OH(PO_4)_3$ and water. The water content was approximated by baking extra samples in a ceramic crucible until their masses stabilized. The mass difference (before and after baking) represented the amount of water in the samples. By definition, the trace elements contribute less than one tenth of one percent to the mass of the sample. This definition was used to approximate the masses of strontium, iron, zinc and yttrium in the samples.

Only a fraction of the photons absorbed create an inner shell vacancy which results in the emission of a characteristic K-x-ray from the element of interest designated as n. This fraction is equal to the product of the photoelectric cross section for k-shell ionization, σ_{Kn}, and the fluorescence yield for a K shell vacancy, ω_{Kn}.

In order for the characteristic x-ray to be detected it must travel back through the sample to the detector. Because the fluoresced x-rays are emitted isotropically only a fraction, g, will be emitted in a direction such that they may be able to reach the detector. Travelling back through the sample the x-rays are attenuated just as they were travelling into the sample.

The total absorption coefficient, μ_λ, is calculated in the same

constant for the source, sample and detector geometry, σ_{Kn}, ω_{Kn}, are constant for a specific transition by the element of interest, the sum $(\mu_i + \mu_n)$ is constant with respect to the sample composition and the element of interest, and ρ_n for the sample composition. If we let all of these constants be called "A", then the intensity of the fluoresence of the nth element divided by A is represented by the function $(1 - e^{-(\mu_i + \mu_n)t})$. This function varies from zero to one as a function of mass per unit area and the sum of the mass absorption coefficients for the source x-rays and the x-rays of the fluorescing element as shown in the figure below.



In the experiment the mass of the samples varied so each measurement was corrected to a mass of 80 milligrams was made in order to be able to use the calibration curves and compare samples. For the elements calcium, iron and zinc the mass absorption coefficients were such that the samples could be considered thick samples. The thick sample region can be seen in the graph above. As the argument goes to infinity the intensity does not change significantly. Therefore, calcium, iron and zinc intensities changed little when the mass correction was made.

The mass absorption coefficients of strontium and yttrium, however, were small and their measured intensities fell within that part of the graph designated as the thin sample region. The mass correction was necessary for these measurements.

The correction equation for differences in mass, run-time and date is shown below. This equation was used to correct all samples to a mass of 80 milligrams, a run time of 600 seconds and back to the date when the cadmimum sources were new.

$$I_n' = I_n \left\{ \frac{1 - EXP[-(\mu_i + \mu_n)\Delta x'}{1 - EXP[-(\mu_i + \mu_n)\Delta X} \right\} * e^{\lambda t'} \times \frac{600}{t}$$

where: I_n' = corrected intensity.

I_n = measured intensity.

$\Delta x'$ = mass of sample.

ΔX = .08 grams.

λ = decay constant for cadmium 109 source.

t' = days from when source was new.

t = run time in seconds.

The fractional uncertainty introduced when this equation is used is found by calculating the total differential of the correction equation the result is shown below.

$$\frac{dI_n'}{I_n'} = \frac{dI_n}{I_n} + \frac{d\Delta x' (\mu_i + \mu_n) EXP[-(\mu_i + \mu_n)\Delta x']}{1 - EXP[-(\mu_i + \mu_n)\Delta x']} + \lambda dt'$$

$$+ \frac{d\Delta x (\mu_i + \mu_n) EXP[-(\mu_i + \mu_n)\Delta x]}{1 - EXP[-(\mu_i + \mu_n)\Delta x']} + \frac{dt}{t} + t' d\lambda$$

where: $\frac{d\Pi_n}{I_n}$ = factional uncertainty in the intensity from XRAYFT.

APPENDIX B

#1	archaeological specimen	male
#6	archaeological specimen	male
#6b	archaeological specimen	male
#17	archaeological specimen	female
#23	archaeological specimen	male

With the exception of #6b these American indians lived circa 1100 AD. For more information on these specimens see O'Brien '77, '82. For more information on #6b see O'Brien & Hart '72.

#81-13	forensic case	male
#79-6	forensic case	male
#79-7	forensic case	male
#83-9	forensic case	male

#82	cadaver	female
#41	cadaver	female
#76	cadaver	female

The forensic and cadaver specimens are part of the comparative collection in the osteology laboratory at Kansas State University.

Bevington, Philip R.
Data reduction and error analysis for the physical sciences.
New York: McGraw-Hill. 1969.

Boaz, N. T., and J. Hampel
Strontium content of fossil tooth enamel and diet in early hominids.
J. Paleont. , 52:928-933, 1978.

Bracewell, B. L. and Veigel, W. J.
Tables of x-ray mass attenuation coefficients for 87 elements at selected wavelengths.
Developments in Applied Spectroscopy , vol. 9. New York: Plenum Press. 1971.

Brown, A. B.
Bone strontium as a dietary indicator in human skeletal populations.
Doctoral dissertation, Univ. of Mich., Ann Arbor, 1973.

Brown, A. B.
Bone strontium as a dietary indicator in human skeletal populations.
Contrib. Geol. , 13: 47-48, 1974.

Elias, M.
The feasibility of dental strontium analysis for diet- assesment of human populations.
Am. J. Phys. Anthro. , 53: 1-4, 1980.

Geidel, R. A.
Trace element studies for Mississippian skeletal remains: findings from neutron activation analysis.
MASCA J. , 2:1, 1982

Gejvall, N.
Cremations.
In: Science in Archaeology. Eds., D. Brothwell and E. H. Higgs. New York: Praeger. 1963.

Gilbert, R. I.
Trace element analysis of three skeletal Amerindian populations at Dickson Mounds.
Doctoral dissertation, U. of Mass., Amherst, 1975.

Hodges, R. M., et. al.
Strontium content of human bones.
J. Biol. Chem. , 185: 519-524, 1950.

Kulp, J. L., et. al.
Strontium - 90 in man.
Science , 125: 3241, 1957.

O'Brien, P. and Hart B.
The Utlaut Site (23SA162W): An Oneota-historic Missouri burial site.
Mo. Archaeologist , 34, Nos 1-2: 48, 1972.

O'Brien, P.
Cultural resources survey of Smithville Lake, Missouri.
Report submitted to the U.S. Army Corps of Engineers; K.C. District, Vol. 1; Archaeology, 1977.

O'Brien, P.
Steed-Kisker: A cultural interpretation.
Mo. Archaeologist , 42: 97, 1982.

Parker, R. B., and H. Toots
Trace elements in bones as paleobiological indicators.
In: Fossils in the making. Eds., S. K. Behrensmeyer and A. P. Hill. Chicago: University of Chicago Press. 1980.

Schoeninger, M. T.
Diet and status at Chalcatzingo: some empirical and technical aspects of strontium analysis.
Am. J. Phys. Anthrop. , 51: 295-310, 1979.

Sillen, A. and P. Smith
Weaning patterns are reflected in strontium - calcium ratios of juvenile skeletons.
J. Archeological Sciences. , 11: 237-245, 1984.

Stewart, T. P.
Essentials of forensic anthropology.
Springfield: Thomas. 1979.

Szpunar, C.
Atomic absorption analysis of archaeological remains: human ribs from Woodland Mortuary sites.
Doctoral dissertation, 1977, Northwest U., Evanston.

Thurber, D. L., et. al.
Common strontium content of the human skeleton.
Science , 128: 256-257, 1958.

Toots, H. and M. R. Voorhies
Strontium in fossil bones and the reconstruction of food chains..
Science , 149: 854-855, 1965.

Underwood, E. J.
Trace elements in human and animal nutrition, 56(Cu), 170(Mn), 196(Zn), 308(V), 445(Sr).
New York: Academic Press. 1977.

Van Vark in Stewart, T. D.
Chapter 5: Burned bones; Firing temperatures.

Wells, C.
A study of cremation.
Antiquity , 34: 29-37, 1960.

Wessen, G.
Characterization of archaeological bone by neutron activation analysis.
Archaeometry , 19: 200-205, 1977.

THE CLASSIFICATION OF HUMAN BONE USING X-RAY FLUORESCENCE

by

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ABSTRACT

The classification of human bone using trace element analysis has contributed much to anthropological theories on the diet of given populations of prehistoric peoples. This experiment was begun with the hope that differences in levels of certain trace elements might not only be seen between certain status groups but also between individuals. If the levels were measurably unique, trace elemental analysis could be used as a means of identifying a number of bones as belonging to one and only one skeleton. Such a tool would be of particular help in classifying fragements of bone excavated in cremation burial sites. In these sites the fragments are commingled and only an estimate of the number of individuals interred can be obtained. If the levels of trace elements are unique, the fragments could be grouped according to individuals and different types of analysis might be applied to obtain more information.

X-ray fluorescence was used to measure elemental x-ray ratios of strontium to calcium, iron to calcium, zinc to calcium and yttrium to calcium in samples of ground bone taken from various sites on a skeleton. The sample sites were chosen to check for degree of homogeneity of the ratios within a single bone, and within the skeleton itself. Samples from inner and outer layers of bone from archaeological specimens were taken to establish the role of the depositional environment. Also results from archaeological samples were checked against those of samples from forensic and cadaverous specimens in order to determine the role of the environment.