3. ON THE METHODS OF CHEMICAL ANALYSIS OF BONE AS AN AID TO PREHISTORIC CULTURE CHRONOLOGY

Robert F. Heizer

The Fact is so well known as to have become almost a cliché that the archaeologist turns to other sciences and their specialists for assistance in dating the artifacts and bones which he discovers. An astronomer, A. E. Douglass, is to be largely, though not exclusively, credited with devising the method of dendrochronology or tree-ring dating. Baron Gerard de Greer, a geologist, formulated the technique and determined the exact sequence of glacial varves in the Baltic region which has proved of highest importance in archaeological dating of the post-Paleolithic cultures in Northern Europe. Ernst Antevs in this country has counted varves, and all of the dates which he has deduced for archaeological sites are based directly upon his varve counts. The nuclear physisists have given us the dating method of radioactive carbon (C^{14}) which promises, at long last, to date some of the sites and cultures which have hitherto resisted all attempts aimed at determining their exact chronologic time placement. Mathematicians and astronomers such as Milankovitch, Spitaler and Soergel have accumulated data on solar radiation curves which have been applied in the dating of Pleistocene climates and archaeological remains in the Old World by the geochronologist, F. E. Zeuner. The field of chemistry promises to yield important assistance in our search for chronological techniques, and it is a review of some of the already developed methods of the chemistry of bone that I wish to outline here.

For the past three years, Dr. S. F. Cook of the Division of Physiology has been engaged in an extensive laboratory project entailing the quantitative analysis of human bones from archaeological sites in California and the American Southwest. This work has been supported by generous subventions from the Viking Fund Inc., and to some extent by contributions from the Committee on Research of this University. Of these investigations, one preliminary paper has been published,[1] another of somewhat broader scope is now on the point of being released in the Anthropological Record series,[2] and several more are in the process of being written. The essential point of this method is straight quantitative chemical analysis of series of uniform samples, generally femur and tibia sections which consist of dense and thick bone, and which come from prehistoric sites whose excavation has been adequately recorded so that the relative time position of each site is known in terms of local stratigraphic sequences. Analyses of bones from Northwestern, Central and Southern California have been made. The oldest bones exhibit the greatest degree of chemical alteration; those from more recent sites are less altered. The problem then becomes one of investing the course of fossilization, which is in itself a function of age, with the time factor in absolute terms. Considerable progress in this matter has been accomplished, though there still remain many x-factors and difficulties to be analyzed out before Dr. Cook and his collaborators will feel justified in proposing this as a chronological method of general applicability.

An Austrian chemist, Gangl, published in 1936 a method of calculating the age of fossil bones based upon the determination of the amount of organic fat remaining in the bone.[3] Attempts to utilize this method using bones from very late prehistoric sites in Central California have failed, and Gangl's method may be definitely excluded as a usable method in that region.

Dr. Austin F. Rogers of Stanford University published, in 1924, a valuable contribution entitled "Mineralogy and Petrology of Fossil Bone."[4] This work is important in providing information on the chemical properties characteristic of very ancient bone which has been undergoing fossilization for tens or hundreds of millenia. Individual contributions to the study of bone mineralization, often in the simple form of a listing of the chemical constituents of ancient bones, occur sporadically through the literature dealing with Old World and New World prehistory, and when these data are collected and analyzed they will help further in arriving at an understanding of the processes of bone fossilization.[5]

A still different age reckoning technique may be called the fluorine method. The earliest demonstration of the method was made by John Middleton, a British chemist who in 1844 published an article entitled, "On Fluorine in Bones, its Source and its Application to the Determination of the Geological Age of Fossil Bones."[6] In 1892 and 1893 a French mineralogist, Adolf Carnot, performed a large number of experiments and published his results in 4 important articles.[7] Carnot analyzed a large series of bones from different geological horizons and from these was able to show that their average fluorine content increased with their age.[8] Taking the fluorine-apatite ratio as equal to 1, Carnot found that the average fluorine content of Recent or Post-Pleistocene bones averages .058, those of Pleistocene animals average .360, and so on with increasing fluorine level in older specimens back to those from the Paleozoic era which average .993. Animal bones and teeth consist in large part of hydroxyapatite which is a form of calcium phosphate. This substance acts as a natural receptor or absorbent for erratic fluorine ions which occur naturally in most ground waters. Some waters contain a relative abundance of fluorine; in others this element is absent. With the addition of fluorine, the hydroxyapatite crystals become converted, one by one, to fluorapatite which happens to be an extremely stable mineral notably resistant to leaching, weathering, or other alteration. For this reason, fixed fluorine in the form of fluorapatite is not readily dissolved out, and therefore with the passage of time normally undergoes gradual quantitative increase. Carnot shows that the porosity of bone probably leads to a uniform rather than zonal alteration, so that any bone or part thereof may be expected to have a similar F-content providing the external conditions causing chemical alteration have been the same. Because the fluorine content of ground waters vary, the F-content of bones from different regions will therefore vary in relation to two factors: age, and fluorine level of ground water. Hence, no generalized dating curve based on F-content of bone can be established.

Now it is unlikely that any part of western North America will yield human skeletal remains or animal bones in sufficient amount and of wide enough temporal range so that a gradient curve of fluorine content with a considerable spread can be established. That is, the fluorine method will probably not yield an absolute time curve with which skeletal or cultural remains can be dated. But the fluorine method does have one outstanding potential application, and this is in those instances where bone tools or human remains are recovered in apparent association with the bones of extinct, and therefore, indubitably ancient, animals. In many such instances, the human bones are not recovered under conditions where it is possible to make the necessary stratigraphic observations so that it cannot be said definitely that the bones lay in a stratum whose immediately superincumbent layers were unbroken by an intrusive grave pit. This is exactly the situation which still faces the proponents of the Tepexpan and Minnesota skeletons as dating from

Pleistocene times. When dealing with human skeletal remains, particularly when these comprise complete or nearly complete skeletons whose bones lie in normal anatomical articulation, one must always suspect that the skeleton is that of a person who was deliberately buried. Interment is so widely practiced as a means of disposal of the dead, and is so ancient in human history, that the chance discovery of a skeleton will prove, in nine times out of ten, to be that of an individual whose body was intentionally deposited in a dug hole. According to my observations, California Indians usually buried the dead in a grave between two and three feet deep, sometimes less, but rarely more. In many situations a pit two or three feet deep will be intrusive into alluvial deposits of Pleistocene age. Under ordinary circumstances we find burials in obvious association with other cultural remains such as refuse deposits containing discarded food bones of animals, charcoal from hearths, fire broken stones, and the like, where no reasonable doubt exists as to the nature and time of deposition of the skeleton. But in rare instances the chance association of a human skeleton with bones of Pleistocene animals may occur, and it may be difficult either to prove or disprove contemporaneity of the two lots of bone. The fluorine method may solve just such doubtful instances of association as these.

In California we have, ready at hand, what might be called a **laboratory example** in the form of the Los Angeles skeleton found near the intersection of Moynier Lane and Figueroa Street in Los Angeles in 1936 at a depth of 13 to 14 feet (site LAn-172). A prehistoric human burial deposited in a dug grave 13 feet deep is to be ruled out on logical grounds. Dr. Ivan Lopatin and Professor Thomas Clements of the University of Southern California both believe that the human skeleton and the skull of an imperial elephant (Archidiskodon imperator) found some distance away and at the same level are contemporaneous. If the two finds could be proved to be contemporaneous, we should then have one of the clearest and best documented instances of the association of man himself and extinct animals in the New World, all other discoveries being, as this one is at present, beset by lack of proof of contemporaneous association.

It is unfortunate that presumed stratigraphic association must be forever plagued by the possibility that the human artifacts or bones may have been intrusive into the lower and more ancient deposits which produce the paleontological remains. In such instances where a sufficient time has elapsed since the Pleistocene animal was buried in the soil, the fluorine test should prove sufficiently strong in quantitative terms, to either prove, indicate strongly, or disprove outright the question of contemporaneity of the human and animal remains. Carnot, the man who developed this method of relative dating, saw this clearly when he said (1893:192), "Perhaps it will be possible to make profitable use of the observation that modern bones show a significantly lesser proportion of fluorine than Quaternary bones in order to assist in establishing the true age of certain human bones which are found in the vicinity of Quaternary animal bones, but in deposits which have perhaps been disturbed." He then gives details (1893:192-193) of the chemical investigation of the controversial Billancourt skeleton discovered in France in 1882 in association with bones of Quaternary animals among which were those of Elephas, Cervus, and Rhinoceros. He was able to show, by fluorine content of the bones, that those of the human were recent, and those of the animals were very ancient, and concluded that the two were non-contemporaneous.

It is possible that some of the materials recovered by Cressman in southern Oregon and northern California, or some of Haury's Ventana Cave materials, or the Sandia Cave remains reported on by Hibben could be analyzed with a view to gaining some idea of the range of fluorine content exhibited by recent and ancient bones in these areas. With a file of such data for reference, new discoveries, or older one such as the Calaveras skull, the Tranquillity site remains, and the Angeles Mesa find referred to above. Very recently M. F. Ashley Montagu and K. P. Oakley[9] have applied the fluorine test to the Galley Hill skeleton and have concluded that this cannot be assigned to second interglacial gravels in which it lay, but rather to the postglacial period. Intrusion from upper levels is therefore proved in the absence of actual stratigraphic evidence of such intrusion. The Piltdown skull has likewise been shown to date from the end of the Pleistocene, rather than early Pleistocene, as formerly believed by many students of fossil man. The Swanscombe skull, on the other hand, has been verified as dating from the second interglacial period as a result of fluorine content analysis.[10]

The potential value of this method for the New World appears to lie in enabling us to reach some objective conclusion on the general antiquity or recency of skeletal remains. As such I feel it should be recognized and applied.

NOTES

[1]Cook, S. F. and R. F. Heizer. 1947. The Quantitative Investigations of Aboriginal Sites: Analyses of Human Bone. Amer. Journ. Phys. Anthro. n.s. 5:201-220.

[2]Heizer, R. F. and S. F. Cook. 1950. The Archaeology of Central California: Chemical Analysis of Human Bone from Nine Sites. UC-AR 12, No. 2.

[3]Gangl, I. 1936. Alterbestimmung Fossiler Knochenfunde auf Chemischen Wege. Oester. Chem. Zeitschr. 39:79-82.

[4]Rogers, A. F. 1924. Mineralogy and Petrology of Fossil Bone. Bull. Geol. Soc. Amer. 35:535-556.

[5]Fremy, E. 1855. Recherches Chimiques sur les os. Paris, Compt. Rend. Acad. Sci. 39:1052-1060.

Girardin, and Preisser. 1843. Memoire sur les os anciens et fossiles. Annales de physique et Chemie.

Hawley, F. G. 1937. A Criticism of a Chemical Method for Determining the Antiquity of Bones. Amer. Anthrop. 39:725-726.

Hrdlicka, A. 1918. Recent Discoveries Attributed to Early Man in America. BAE-B, 66, (pp. 61-63).

Jenks, A. E. 1936. Pleistocene Man in Minnesota. Univ. Minnesota Press.

Tanabe, G. 1944-46. Kalzium- und phosphorgehalt der Menschenknochen aus den steinzeitlichen Muschelhafen von Hobi. Prov. Mikawa. Journ. Anthrop. Soc. Japan (Zinruigaku Zassi) 59:1-5.

Barber, H. 1939. Untersuchungen über die chemische Veränderung von Knochen bei der Fossilisation. Paleobiol. 7:217-235.

Rees, G. O. 1838. On the Proportions of Animal and Earthy Matter in the Different Bones of the Human Body. Med. Chir. Soc. Trans. 21:406-413.

Klaproth, M. H. 1804. Recherches sur l'acide fluorique contenu dans une dent fossile d'éléphant. Berlin, Mem. Acad. 136-139.

Morichini, D. 1804. Analisi dello smalto di un dente fossili de elefante e dei denti umani. Modena, Soc. Ital. Mem. 12, Part 2:73-88.

Other contributions may be found by consulting the following author's names in the Royal Society Catalogue: Phipson, Lassaigne, John, Merat-Guillot, Chevrevl, Boussingault, Marchand, Valentin, Bibra, Fourcroy, Fourcroy and Vauquelin, Fremy.

[6]Middleton, J. 1844. On fluorine in bones, its source and its application to the determination of the geological age of fossil bones. Proc. Geol. Soc. London 4:431-433.

1843-45. On Fluorine in Recent and Fossil Bones, and the Sources from which it is Derived. Chem. Soc. Mem. 2:134-35. (Also in Phil. Mag. 25:260-62, 1844; Edinb. New Phil. Journ. 38:116-119, 1845.)

1844. Comparative Analysis of Recent and Fossil Bones. Phil. Mag. 25:14-18. (Also Edinb. New Phil. Journ. 37:285-88, 1844.)

[7]Carnot Ad. 1892a. Recherche du fluor dans les os modernes et les os fossiles. Acad. Science, Compt. Rend. 114:1189-1192, Paris. (Also in Journ. Pharm. 26:124-125, 1892.)

1892b. Sur une application de l'analyse chimique pour fixer l'âge d'ossements humains préhistoriques. Acad. Sci., Compt. Rend. 115: 337-339, Paris.

1892c. Sur la composition des ossements fossiles et la variation de leur teneur en fluor dans les différents étages géologiques. Acad. Sci., Compt. Rend. 115:243-246, Paris.

1893. Recherches sur la composition générale et la teneur an fluor des os modernes et des os fossiles des différents ages. Annales des Mines, Memoires, Ser. 9, Vol. 3:155-195, Paris.

[8]Carnot's analytical method is given in "Nouvelle Méthode pour le dosage du fluor," Annales des Mines, Memoires, Ser. 9, Vol. 3:130-147.

[9]Montagu, M. F. A. and K. P. Oakley. 1949. The Antiquity of Galley Hill Man. Amer. Journ. Phys. Anthrop. n.s. 7:363-380. (pp. 367-69).

[10]Oakley, K. P. 1948. Fluorine and the relative dating of bones. The Advancement of Science 4:336-337.