

The quest for an absolute chronology in human prehistory: anthropologists, chemists and the fluorine dating method in palaeoanthropology

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Abstract. By the early twentieth century there was a growing need within palaeoanthropology and prehistoric archaeology to find a way of dating fossils and artefacts in order to know the age of specific specimens, but more importantly to establish an absolute chronology for human prehistory. The radiocarbon and potassium–argon dating methods revolutionized palaeoanthropology during the last half of the twentieth century. However, prior to the invention of these methods there were attempts to devise chemical means of dating fossil bone. Collaborations between Emile Rivièrè and Adolphe Carnot in the 1890s led to the development of the fluorine dating method, but it was not until the 1940s that this method was improved and widely implemented by Kenneth Oakley to resolve a number of problems in palaeoanthropology, including the Piltdown Man controversy. The invention of the fluorine dating method marked a significant advance in the quest for absolute dating in palaeoanthropology, but it also highlights interesting problems and issues relating to the ability of palaeoanthropologists and chemists to bring together different skills and bodies of knowledge in order successfully to develop and apply the fluorine dating method.

The question of how long humans had existed on Earth rose to dramatic prominence in the 1860s, when it became generally accepted that humans had coexisted with the extinct animals of the Ice Age. Palaeontologists had excavated numerous sites where prehistoric flint artefacts were found associated with extinct mammal fossils from the Pleistocene. This meant that humans had lived at a geologically remote period of time.¹ But there was no certain means by which they could determine the exact age of these fossils or artefacts. Geologists and palaeontologists had devoted much of the early nineteenth century to working out the succession of geological strata and their associated fossils, thus creating a relative chronology where it was possible to know if one rock formation or group of fossils were older or younger than another, but estimates of the ages of various geological epochs varied widely.

The same situation prevailed in prehistoric archaeology. In the 1830s the Danish archaeologist Christian Jürgensen Thomsen proposed a relative chronology for human

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1 For an account of the problems involved in settling the question of the coexistence of humans with Pleistocene animals see D. K. Grayson, *The Establishment of Human Antiquity*, New York, 1983; and A. Bowdoin Van Riper, *Men among the Mammoths: Victorian Science and the Discovery of Human Prehistory*, Chicago, 1993.

prehistory that consisted of a Stone Age followed by a Bronze and then an Iron Age.² This three-age system offered a useful way of organizing artefacts chronologically, as well as a basic scheme for understanding the material and cultural development of early human civilization. However, there remained few ways to assign dates to these periods or to any specific artefact, unless some datable artefacts such as coins or inscriptions were also located. During the last half of the nineteenth century, palaeontologists and archaeologists excavated more sites containing stone artefacts associated with extinct Pleistocene animals. It became clear that even the Stone Age was not a single homogeneous period, but seemed instead to consist of a sequence of different stages. In his *Pre-historic Times* (1865) the archaeologist Sir John Lubbock divided the Stone Age into two periods, the Palaeolithic (Old Stone Age) followed by the Neolithic (New Stone Age). Lubbock's Palaeolithic was subjected to further subdivision by the French archaeologist Gabriel de Mortillet, who recognized that in many caves there was a stratigraphic sequence of distinct stone-tool types, some subsisting for long periods before apparently being replaced by new types later. On the basis of these discoveries de Mortillet divided the Palaeolithic into a series of successive cultures: the Chellean, Acheulean, Mousterian, Solutrean and Magdalenian.³

These relative chronologies were extremely useful because they allowed researchers to determine if one artefact or archaeological site were older or younger than another. But the real question that remained involved the exact age of prehistoric human fossils and artefacts. There were scientists such as the Canadian geologist and palaeontologist John W. Dawson who accepted the association of human and extinct mammal fossils, but argued that they could still be contained within a six-thousand-year biblical chronology.⁴ Most geologists realized that substantial quantities of time separated the Pleistocene world of early humans from the modern world. Quite different estimates were proposed for just how much time was involved; different methods were tried to obtain a rough calculation of the age of particular deposits or geological periods.

In 1864 the geologist Joseph Prestwich, involved in analysing evidence for human antiquity, remarked that the fact that 'we must greatly extend our present chronology with respect to the first existence of man appears inevitable; but that we should count by hundreds of thousands of years is, I am convinced, in the present state of the inquiry, unsafe and premature'.⁵ In 1868 Archibald Geikie proposed some means for estimating the age of recent geological periods.⁶ Soon thereafter Charles Lyell suggested that

2 The history of the three-age system is discussed in B. Gräslund, *The Birth of Prehistoric Chronology: Dating Methods and Dating Systems in Nineteenth-Century Scandinavian Archaeology*, Cambridge, 1987; M. A. Morse, 'Craniology and the adoption of the three-age system in Britain', *Proceedings of the Prehistoric Society* (1999), 65, 1–16; J. Rodden, 'The development of the three age system: archaeology's first paradigm', in *Towards a History of Archaeology* (ed. G. Daniel), London, 1981, 51–68; K. Skaare, 'Christian Jürgensen Thomsen-Grossereren som grunnla nordisk arkeologi', *Nordisk Tidskrift för Vetenskap, Konst och Industri* (1988), 64, 369–81.

3 G. de Mortillet, *Le Préhistorique: Antiquité de l'homme*, Paris, 1883.

4 J. W. Dawson, *Fossil Men and Their Modern Representatives*, London, 1880, 278.

5 J. Prestwich, 'Theoretical considerations on the conditions under which the (drift) deposits containing the remains of extinct mammalia and flint implements were accumulated, and on their geological age', *Philosophical Transactions of the Royal Society of London* (1864), 154, 303.

6 A. Geikie, 'On denudation now in progress', *Geological Magazine* (1868), 5, 249.

‘it must, I think, be conceded’ that the period separating the onset of the Ice Age and the subsequent retreat of the glaciers ‘required not tens but hundreds of thousands of years’.⁷ Estimates for the age of geological deposits containing human remains and artefacts were of great interest to prehistoric archaeologists. Lubbock referred to the research conducted in Switzerland by Charles Adolphe Morlot to calculate the age of a gravel cone, located at the spot where the Tinière river enters Lake Geneva, containing deposits built up at a regular annual rate and including artefacts from the Roman period and the Bronze and Stone Ages. From this research Morlot argued that the Bronze Age deposit had accumulated between three and four thousand years ago and that the Stone Age deposit remained from between five and seven thousand years ago.⁸ Lubbock also noted the work of Victor Gilliéron, who estimated that the prehistoric lake dwellings at Pont de Thièle in Switzerland were 6,750 years old.⁹

Given the evidence available, Lubbock expressed an opinion becoming generally accepted towards the end of the century that the facts gathered by geologists regarding the changes that had occurred since the appearance of the first humans

impress us with a vague and overpowering sense of antiquity. All geologists, indeed, are now prepared to admit that man has existed on our earth for a much longer period than was until recently supposed to have been the case. But it may be doubted whether even geologists yet realize the great antiquity of our race.¹⁰

Nor was Lubbock the only archaeologist who sought answers from geologists about the age of prehistoric sites. John Evans devoted a long section of the second edition of his *Ancient Stone Implements* to ways of determining the age of the Palaeolithic and Neolithic.¹¹ Between the late nineteenth century and the mid-twentieth, geologists and archaeologists continued to propose estimates for the age of geological epochs and archaeological sites, but these varied widely and the problem of the absolute chronology of human prehistory remained.

By the early twentieth century demand was growing for absolute dates for artefacts and fossil specimens. Eoliths were pieces of chipped flint believed to be the simplest stone tools, but were eventually shown to be naturally fractured stones, found in Pliocene and even Miocene geological deposits. They raised the controversial possibility that humans had existed in Europe far earlier than anyone had expected.¹² Moreover, the discovery of anatomically modern human skeletons in geologically early deposits

7 C. Lyell, *Principles of Geology*, 12th edn, 2 vols., London, 1875, i, 286.

8 J. Lubbock, *Pre-historic Times, as Illustrated by Ancient Remains, and the Manners and Customs of Modern Savages*, 4th edn, New York, 1887, 398–401.

9 Lubbock, op. cit. (8), 401–2. Gilliéron published his ideas in *Notice sur les habitations Lacustres du pont de Thièle* (1862).

10 Lubbock, op. cit. (8), 431.

11 J. Evans, *The Ancient Stone Implements, Weapons and Ornaments, of Great Britain*, 2nd edn, London, 1897, Chapter 25.

12 The eolith controversy has been examined in some detail by R. de Bont, ‘The creation of prehistoric man: Aimé Rutot and the eolith controversy, 1900–1920’, *Isis* (2003), 94, 604–30; D. K. Grayson, ‘Eoliths, archaeological ambiguity, and the generation of “middle range” research’, in *American Archaeology Past and Future: A Celebration of the Society for American Archaeology 1935–1985* (ed. D. Meltzer, D. Fowler and J. Sabloff), Washington, DC, 1986, 77–133; F. Spencer, ‘Prologue to a scientific forgery: the British

seemed to suggest that humans had evolved at a geologically early period and only had a very remote ape ancestry. An anatomically modern human skeleton discovered at Galley Hill in geologically ancient deposits in 1895, following the original discovery of the skull in 1888, seemed to provide support for the presapiens hypothesis, which argued that modern humans had evolved very early and implied that the Neanderthals and other fossil hominids were not old enough to be the direct ancestors of modern humans.¹³ The excavation of human skeletons from equally early deposits at Ipswich in 1911 and at Swanscombe in 1935 seemed to add weight to the presapiens hypothesis, but some researchers were suspicious that all three skeletons were merely intrusive burials of relatively recent human remains into older geological layers. But with no means of actually determining the age of the bones the controversy continued. Similar problems existed over the interpretation of other hominid fossils and prehistoric artefacts from around the world. Most scientists recognized the need for some means of determining the age of fossil and archaeological specimens.

Remarkably little has been written about the history of the development of dating methods in palaeoanthropology.¹⁴ Tree-ring dating (dendrochronology) was one of the first techniques used to provide absolute dates for archaeological sites in the nineteenth century. Stephen Nash has recently written about the use of dendrochronology in America.¹⁵ Most historical research in this area has focused on the development of the radiocarbon (C14) dating method.¹⁶ This technique produced a revolution in archaeology, and when the potassium–argon (K–Ar) dating method was perfected in the late 1950s it quickly became indispensable in palaeoanthropological research. Other dating methods were developed during the last half of the twentieth century. Palaeoanthropologists and prehistoric archaeologists now readily obtain absolute dates for most of the specimens they discover.

The prevalence and great success of the C14 and K–Ar dating methods has overshadowed the efforts of scientists from various disciplines to devise a chemical method of dating fossil bone during the 1940s and 1950s. The most prominent of these was the fluorine dating method, originally proposed in the nineteenth century, which rose to

colithic movement from Abbeville to Piltdown', in *Bones, Bodies, Behavior: Essays on Biological Anthropology* (ed. G. Stocking), Madison, WI, 1988, 84–116.

13 On Galley Hill Man and the presapiens theory see F. Spencer, *Piltdown: A Scientific Forgery*, New York, 1990, 20–8; and R. G. Delisle, *Debating Humankind's Place in Nature 1860–2000: The Nature of Palaeoanthropology*, Upper Saddle River, NJ, 2007, 132–4.

14 For a general discussion of the history of dating methods in archaeology see M. J. Aitken, *Science-Based Dating in Archaeology*, London, 1990; S. Bowman, 'Questions of chronology', in *Science and the Past* (ed. S. Bowman), London, 1991, 117–40; S. Nash (ed.), *It's about Time: A History of Archaeological Dating in North America*, Salt Lake City, 2000.

15 S. Nash, *Time, Trees, and Prehistory: Tree-Ring Dating and the Development of North American Archaeology, 1914–1950*, Salt Lake City, 1999.

16 R. Burleigh, 'W. F. Libby and the development of radiocarbon dating', *Antiquity* (1981), 55, 96–8; G. Marlowe, 'W. F. Libby and the archaeologists, 1946–1948', *Radiocarbon* (1980), 22, 1005–14; G. Marlowe, 'Year one: radiocarbon dating and American archaeology, 1947–1948', *American Antiquity* (1999), 64, 9–32; R. E. Taylor, 'The beginnings of radiocarbon dating in American antiquity: a historical perspective', *American Antiquity* (1985), 50, 309–25; R. E. Taylor, A. Long and R. Kra, *Radiocarbon Dating after Four Decades: An Interdisciplinary Perspective*, New York, 1992.

some considerable prominence in the 1950s because of its role in disclosing the Piltdown Man as a forgery. In fact, almost all discussions of the fluorine dating method are within the context of the demise of the Piltdown fossils.¹⁷ This historiography ignores a much broader story. The fluorine dating method was a response to the need for a reliable dating method in palaeoanthropology and it was successfully used to solve several lingering problems in that discipline. This alone makes it an interesting historical subject, but there are other issues that this method raises and shares with later dating methods. The fluorine dating method was developed through the collaboration of anthropologists and chemists, and thus represents an interesting example of cooperation across scientific disciplines. But this cooperation possessed its challenges, since many anthropologists understood little of the chemical principles and techniques involved in obtaining an estimated age for a fossil, while the chemists were merely analysing fossil bone that held little meaning for them beyond its status as a material object. These fossils possessed geological, palaeontological and anthropological features that gave them meaning for palaeoanthropologists, whereas chemists viewed bone specimens as a material for chemical analysis yielding data to be interpreted so that the chemist could draw some conclusions about the age of the fossil. The anthropologists and the chemists involved in this novel dating technique had to develop trust in the methods and knowledge of the other group in order for each to feel secure about the results of their joint investigations. Equally importantly, the first practitioners of the fluorine dating method had to convince their anthropological colleagues of the validity and reliability of the new method. This paper explores the origins and development of the fluorine dating method, the anthropological questions it was meant to answer, the nature of the collaboration of the anthropologists and chemists involved, and the successes and failures of the method that eventually led to its almost complete disappearance in the face of newer dating methods based on radioactivity. While there was early optimism that the fluorine dating method would provide absolute ages for prehistoric fossil material, that hope was quickly shattered. Fluorine dating never provided absolute dates, but the development and eventual fate of the method are important elements in the general history of the quest for an absolute dating method.

Middleton, Carnot and the initial formulation of a fluorine dating method

The Italian chemist Domenico Morichini appears to have been the first to discover that fluorine was present in fossil bone. He analysed the chemical composition of a fossilized elephant tooth found by the Italian natural philosopher Carlo Lodovico Morozzo¹⁸ and published a paper in 1805 describing his results.¹⁹ The German chemist Martin Heinrich

17 On the discovery and controversy, and the process by which the Piltdown fossils were shown to be a forgery, see Spencer, *op. cit.* (13); C. Blinerman, *The Piltdown Inquest*, Buffalo, 1986; R. W. Millar, *The Piltdown Men*, New York, 1972.

18 C. Lodovico Morozzo, 'Sopra I denti fossili de un elephante trovato nelle vicinanze di Roma', *Memorie di Matematica e di Fisica della Società Italiana della Scienza (Modena)* (1803), 10, 162–71.

19 D. Morichini, 'Analisi dello smalto di un dente fossile di elefante e dei denti umani. Memoria di Domenico Morichini presentata da Giachino Pessuti', *Memorie di Matematica e di Fisica della Società*

Klaproth was one of the first scientists to examine Morichini's discovery,²⁰ and soon thereafter the Swedish chemist Jöns Jakob Berzelius confirmed the presence of fluorine in living and fossil bone.²¹ Edmond Frémy, professor of chemistry at the Muséum national d'histoire naturelle in Paris, conducted a more extensive series of studies on the chemical composition of fossil bone in the 1850s. He confirmed the presence of fluorine, but the quantities were small and extremely difficult to measure.²² The idea that the fluorine content of fossil bones could be used as a means of dating them was first suggested by James Middleton, professor at University College London and fellow of the Geological Society of London. Middleton was drawn to this question by reading Berzelius's studies of the fluorine content of fossil and recent bone. Early in 1844 he began a series of experiments on the subject. Middleton started from the observation that fossil bone appeared to contain a greater quantity of 'fluoride of calcium' than recent bone. Chemists disagreed, however, about the means by which fluorine was absorbed by bone. Middleton came to suspect that fluorine was present in groundwater. If that were the case then 'its accumulation in fossil bones would be found to be the result of infiltration'.²³ In order to test his hypothesis, Middleton looked for fluorine in a water pipe from a coal mine, a stalactite, the deposits left in a tea kettle used to boil water, and several other objects. In all cases fluorine was found, in differing quantities, but this sufficed to convince Middleton that the source of the fluorine in fossil and living bone was groundwater.²⁴

Middleton realized that if fluorine were absorbed by bone from groundwater then the amount of fluorine in a bone should increase over time. This idea prompted him to undertake a series of experiments designed to ascertain 'the law by which fluoride of calcium becomes augmented or developed in fossil bones, as, should this be established, an important step would, I conceived, be thereby made towards the ascertainment of geological time'. The fluorine content of fossil bone might be used as a means of determining the relative, if not the absolute, age of fossils. This supposition led Middleton to investigate the amount of fluorine present in certain aqueous geologic deposits of different ages. He found that fluorine was present in all cases 'from the most recent deposit down to the old red sandstone, and that it is present in the older in larger proportion than in the newer beds'.²⁵ From this discovery Middleton concluded that he

Italiana della Scienza (Modena) (1805), 12, 73–88. This paper also appeared in the *Journal für die Chemie und Physik* (1806), 2, 177–87.

20 M. Heinrich Klaproth, 'Recherches sur l'acide fluorique contenu dans un dent fossile d'éléphant', *Mémoires de l'Académie royale des sciences de Berlin* (1804), 136–9.

21 J. Jakob Berzelius, 'Extrait d'une lettre de M. Berzelius à M. Vauquelin', *Annales de chimie* (1807), 61, 256; *idem*, 'Untersuchungen über die Flußspathsäure und deren merkwürdigste Verbindungen', *Poggendorff's Annalen der Physik und Chemie* (1824), 77, 1–48; J. Jakob Berzelius, A. J. L. Jourdan and M. Esslinger, *Traité de chimie*, 8 vols., Paris, 1829–33.

22 E. Frémy, 'Recherches chimiques sur les os', *Annales de chimie et de physique* (1855), Ser. 3, 43, 47–107.

23 J. Middleton, 'Comparative analysis of recent and fossil bones', *Philosophical Magazine* (1844), 25, 14.

24 Middleton, *op. cit.* (23), 14–15. See also J. Middleton, 'On fluorine in recent and fossil bones, and the sources from whence it is derived', *Philosophical Magazine* (1844), 25, 261–2.

25 J. Middleton, 'On fluorine in bones, its source, and its application to the determination of the geological age of fossil bones', *Proceedings of the Geological Society (London)* [1843–45] (1846), 4, 432.

might be able to show ‘that the relative geological age of rocks may be estimated by the proportion of fluoride of calcium which they contain’.²⁶

Middleton then used fossil specimens from different geological ages to see if their fluorine content increased with their geological age. He obtained horse, camel and alligator fossils from the geologist Hugh Falconer, who had excavated the fossils from the Siwalik Hills in India. He also examined the bones of an Iguanodon, a Miocene sea urchin, a two-thousand-year-old human skull found in Greece (the age of the skull was known from a coin placed in its mouth) and the skull of an Egyptian mummy. In a paper published in the *Philosophical Magazine* Middleton gave the quantities of fluoride of calcium, as well as other chemicals, found in each specimen, but drew few conclusions from these results, although the quantity of fluorine in each specimen was generally proportionally greater the older the specimen.²⁷ However, in a paper read before the Geological Society of London, Middleton gave the results for recent bone, the ancient Greek skull, the Siwalik fossils and a fossil *Anoplotherium* bone (a mammal from the Eocene period), showing how the amount of fluorine in each specimen increased according to its geological age. Moreover, as the age of the Greek skull was known to be two thousand years, Middleton boldly used the relative ratios of fluorine in each specimen to estimate their absolute ages. Thus he suggested that the Siwalik fossils should be 7,700 years old and the *Anoplotherium* 24,200 years old.²⁸

Middleton’s research was the first to suggest a means by which bone absorbed fluorine and from this to establish the basic principles of a method to date fossil bone. Moreover, Middleton recognized the significance of his work in relation to one of the pre-eminent problems of geology and palaeontology in his day. He proclaimed before the Fellows of the Geological Society of London that the ‘accumulation of fluoride of calcium in fossil bones constitutes a very interesting and important subject of inquiry in reference to Geology, since it seems to involve the element of *time*, so interesting in all geological investigations’. Knowing the significance of this problem, Middleton began his experiments ‘to ascertain the proportion of fluoride of calcium in bones that had been preserved for various periods, with a view to infer, if possible, from the mineral condition, the relative ages of the specimens’.²⁹ Yet Middleton did not expand upon his initial researches and published no further papers on the subject. The basic concepts that Middleton outlined for the use of fluorine to date fossil bone were not developed further until half a century later.

Middleton’s research attracted little attention and it appears that no further efforts were devoted to using the fluorine content of fossil bones to determine their ages until the 1890s, when the French archaeologist Emile Rivière resurrected the technique. During the 1870s and 1880s Rivière excavated a number of Neolithic and Palaeolithic sites in France that in some cases produced stone artefacts in association with the fossil remains of mammoths and other Pleistocene fauna. This was an exciting time in French prehistoric archaeology: Louis Lartet had discovered the fossil remains of Cro-Magnon

26 Middleton, op. cit. (25), 432.

27 Middleton, op. cit. (23), 15–18.

28 Middleton, op. cit. (25), 432–3.

29 Middleton, op. cit. (25), 431; original emphasis.

Man at Les Eysies in 1868 and Neanderthal fossils were discovered at Spy in Belgium in 1886. Rivière's excavations were part of a widespread effort by European archaeologists to uncover prehistoric artefacts, and especially human fossil remains, from the Ice Age or earlier. It was generally accepted that the approximate age of human artefacts or skeletal remains could usually be judged from the animal fossils with which they were found associated when excavated. But it was also recognized that such associations could be deceptive, since there were natural mechanisms, such as floods, that could mix objects from different stratigraphic layers and different geological ages. Moreover, the custom of burying the dead also led to human remains being accidentally mixed with the bones of much older animal fossils.

Rivière encountered just such an instance in the course of excavating at Billancourt, on the outskirts of Paris, where he discovered the bones of Quaternary animals along with Palaeolithic artefacts and portions of two human skeletons. However, Rivière noted that the fossils' appearance, as well as their density and general physical characteristics, differed greatly from the animal bones found with them. These facts convinced Rivière that the human remains were undoubtedly much younger in age.³⁰ Several prominent archaeologists and palaeontologists disagreed with Rivière's conclusion, most notably Jean Louis Armand de Quatrefages, professor of anthropology at the Muséum national d'histoire naturelle. There was no clear way to settle the debate and the dispute continued for the next ten years. Rivière faced the opposite problem in 1892, when he unearthed two human skeletons from a cave at Baoussé-Roussé near Menton. He had been excavating there since 1870 and found numerous animal fossils dating from the late Quaternary period along with Solutrean, Mousterian and Magdalenian flint tools.³¹ Because the deposits in the cave showed no evidence of being disturbed, Rivière was adamant that the animal fossils and the human artefacts and skeletons were deposited in the cave at the same time and were therefore of very great age.³² He suggested that the human skeletons belonged to the race of Cro-Magnon,³³ but once again there were sceptics, notably the anthropologist René Verneau, who rejected this conclusion and suggested that the human remains dated from the Neolithic and were therefore not so ancient.³⁴ Rivière vigorously defended the late Quaternary age of the human remains based upon the geological evidence, but had already taken steps to discover a way of determining with certainty the ages of the Billancourt and Baoussé-Roussé skeletons.³⁵

In October 1885 Rivière deposited a *pli cacheté* with the Académie des sciences regarding his opinion about the human skeletons found at Billancourt, with instructions

30 E. Rivière, 'Le Gisement quaternaire de Billancourt (Seine)', *Association française pour l'avancement des sciences, Comptes rendus* (1882), 376.

31 E. Rivière, 'Sur l'âge des squelettes humains des grottes des Baoussé-Roussé, en Italie, dites grottes de Menton', *Association française pour l'avancement des sciences, Comptes rendus* (1892, part 2), 349.

32 Rivière, op. cit. (31), 348–53.

33 Rivière, op. cit. (31), 354.

34 Rivière, op. cit. (31), 357.

35 Rivière, op. cit. (31), 358.

that it should be opened at the completion of some new investigations he was about to start on the chemical composition of fossil bones of different ages from various geological deposits.³⁶ He got this idea from reading works published in 1860 on this subject by Alphonse Milne-Edwards and Achille-Joseph Delesse. In order to carry out the chemical analysis of the Billancourt bones, Rivière enlisted the assistance of Adolphe Carnot, professor of chemistry at the Ecole des mines. Carnot was an ideal choice in many ways, since he was a chemist and mining engineer with experience in geology. Carnot immediately focused on the fluorine content of the fossils as the subject of his investigations, in part from reading Edmond Frémy's 1855 work on the subject.³⁷

Carnot, who gives no indication of having read Middleton, undertook a much more extensive study of fossils of different geological age than had the London professor, obtaining many of his fossil specimens through the assistance of Albert Gaudry, professor of palaeontology at the Muséum.³⁸ The procedures of chemical analysis and knowledge of palaeontology and geological strata had all expanded considerably since Middleton's time, and Carnot made good use of this new knowledge. He began by chemically analysing more than fifty fossil bones (the oldest fossils belonging to the Silurian period) and twenty modern bones, then compared the proportion of 'phosphoric acid' (PhO₅) to fluorine in each fossil. Carnot described in some detail the procedures he followed to isolate and measure the quantity of fluorine and other substances of interest in each specimen, clearly a laborious and demanding process.³⁹

One objective of these investigations was to compare the chemical composition of modern and fossil bone in order to determine the chemical processes that caused fossilization – processes not then well understood.⁴⁰ This was important for the interpretation of the cause and significance of the presence of fluorine and other chemicals in fossil bones. Carnot gave charts listing the amounts of various chemicals found in fossils from each geological period, with a clear implication that while the chemical composition of fossils could vary greatly, the amount of fluorine generally increased with the age of the fossil.⁴¹ Carnot explained the presence of fluorine and some other chemicals in fossils by suggesting these chemicals existed in groundwater and gradually infiltrated the bone buried in these sediments. To test this hypothesis, Carnot conducted several experiments where he immersed modern bone in a fluorine solution and tested

36 E. Rivière, 'Détermination par l'analyse chimique de la contemporanéité ou de la noncontemporanéité des ossements humains et des ossements d'animaux trouvés dans un même gisement', *Association française pour l'avancement des sciences, Comptes rendus* (1892, part 2), 379.

37 A. Carnot, 'Recherche du fluor dans les os modernes et les os fossiles', *Comptes rendus hebdomadaires des séances de l'Académie des sciences* (1892), 114, 1189.

38 A. Carnot, 'Sur la Composition des ossements fossiles et la variation de leur teneur en fluor dans les différentes étages géologique', *Comptes rendus hebdomadaires des séances de l'Académie des sciences* (1892), 115, 244.

39 A. Carnot, 'Recherches sur la composition générale et la teneur en fluor des os modernes et des os fossiles des différents âges', *Annales des mines* (1893), 3, 159–64.

40 Carnot, *op. cit.* (39), 166, 170–1.

41 Carnot, *op. cit.* (39), 173–81; see also *idem*, *op. cit.* (38), 244–5.

the amount of fluorine absorbed by the bone at regular intervals, which showed that fluorine was indeed absorbed by bone.⁴² From this he drew the significant conclusion that similar continuous action over a very long period could result in much greater concentrations of fluorine in bone, exactly what his analysis of fossilized bones indicated.⁴³

There was, however, one problem with the use of fluorine to determine the age of a fossil. Carnot noted that the amount of fluorine in fossils of the same geological age but taken from different geographical localities showed 'very great variation'.⁴⁴ He attributed this to differences in the chemistry of the local groundwater and soil.⁴⁵ Yet this had profound consequences for the usefulness of any fluorine dating method, since it meant that no general method could be formulated to assign a geological age to a fossil solely on the basis of its fluorine content because that quantity would vary from place to place.⁴⁶ Carnot's investigations did nevertheless have immediate practical consequences for prehistorians, because the significant difference in fluorine content between modern bone and Pleistocene bone meant that it should be possible to identify modern bones that had become accidentally mixed with older animal fossils, as long as both sets of fossils came from the same location.⁴⁷ Carnot was now ready to address the issue of the human and animal fossils encountered by Emile Rivière at Billancourt. Carnot analysed two fragments of animal bone from Billancourt, as well as a human tibia sent to him by Rivière. The results were dramatic and convincing. The animal fossils contained much more fluorine than the human bone. The amount in the animal bones corresponded very well with other Quaternary fossils while the human bone was consistent with modern bone. From this Carnot concluded that the human remains were much younger than the animal fossils, thus their association in the geological deposits at Billancourt was accidental, just as Rivière had asserted all along.⁴⁸

Carnot argued that 'this new method of control may often be useful in the examination of problems relative to the antiquity of man' since human and animal bones buried in the same deposits at the same time should always contain the same amounts of fluorine, but if fossils of different ages had become mixed in alluvial deposits or in caves then this would be shown by the differences in their fluorine content.⁴⁹ Both Carnot and Rivière published accounts of these investigations, but while Carnot gave details of his chemical analysis and its results, he did not discuss the geological or archaeological details of the Billancourt fossils, although he did discuss the potential application of his method to prehistoric research. Rivière only mentioned the most

42 Carnot, *op. cit.* (39), 183–5.

43 Carnot, *op. cit.* (39), 186, 190.

44 Carnot, *op. cit.* (39), 181.

45 Carnot, *op. cit.* (39), 191.

46 Carnot, *op. cit.* (39), 192.

47 Carnot, *op. cit.* (39), 192; *idem*, *op. cit.* (38), 245–6.

48 Carnot, *op. cit.* (39), 193–4. See also *idem*, 'Sur une application de l'analyse chimique pour fixer l'âge d'ossements humains préhistorique', *Comptes rendus hebdomadaires des séances de l'Académie des sciences* (1892), 115, 337–9.

49 Carnot, *op. cit.* (39), 194–5.

basic results of the chemical analysis conducted by Carnot and focused instead on showing how these results confirmed his earlier conclusions about the Billancourt fossils based on his palaeontological and archaeological interpretation of the human and animal remains.⁵⁰

Both Carnot and Rivière saw the potential for this method to resolve a common problem in prehistoric archaeology. However, despite publication of the results of their investigations in prominent scientific journals, only a few other archaeologists utilized Carnot's method. In Mexico the biologist Alfonso Luis Herrera had a human mandible discovered on the shore of Lake Chalco and a fossil horse skull from the same deposit tested for their fluorine content. The tests showed that the 'Xico mandible' and the extinct horse were contemporaneous.⁵¹ Two years later, Thomas Wilson, curator of the Department of Prehistoric Anthropology at the Smithsonian Institution, announced the results of his analysis of the controversial 'Natchez Man' specimen discovered in 1845 by Montroville Wilson Dickeson, a physician and amateur archaeologist. Dickeson discovered the human pelvis near Natchez, Mississippi in geological deposits that also contained numerous extinct Pleistocene animal fossils. Dickeson presented this remarkable collection to the Academy of Natural Sciences of Philadelphia in 1846, noting that the human bone was found directly below the animal fossils and was also clearly fossilized.⁵² Considerable debate surrounded the question of whether this was evidence that humans were present in America along with the mastodon and other Ice Age mammals. Wilson saw Carnot's fluorine analysis as a possible way to settle the question. Wilson obtained samples of the Natchez fossils and gave them for analysis to Robert Lawrence Packard, a mineralogist at the Smithsonian. Although the amount of fluorine was somewhat less in the human bone, Wilson believed they were about the same age, dating from a period midway between the present and the Quaternary period.⁵³ Wilson and Packard also published an English translation of Carnot's 1893 paper, thus making his means of analysing fossil bone accessible to American scientists.⁵⁴

The Dutch chemist Jakob Maarten van Bemmelen also used Carnot's method of fluorine analysis to test the famous *Pithecanthropus erectus* fossils discovered on Java by Eugène Dubois between 1891 and 1892. From the anatomy of the fossils and the apparent late Pliocene or early Pleistocene geology of the site, Dubois was convinced that *Pithecanthropus* represented the intermediate link between apes and humans. Many of Dubois's colleagues were sceptical of this interpretation of the fossils. One

50 Rivière, op. cit. (36), 379–82. See also *idem*, 'Fossilisation et analyse chimique des os', *Bulletins de la Société d'anthropologie de Paris* (1893), 4, 309–15.

51 A. L. Herrera, 'El hombre prehistórico de México', *Memorias de la Sociedad Científica Antonio Alzate* (1893), 7, 31–4.

52 The announcement of this discovery appeared in a note published in the *Proceedings of the Academy of Natural Sciences of Philadelphia* (1848), 3, 106–7. The discovery and debate over Natchez Man is examined by J. Cotter, 'Update on Natchez Man', *American Antiquity* (1991), 56, 36–9.

53 T. Wilson, 'On the presence of fluorine as a test for the fossilization of animal bones', *American Naturalist* (1895), 29, 719–25.

54 T. Wilson, 'On the presence of fluorine as a test for the fossilization of animal bones', *American Naturalist* (1895), 29, 307–17, 439–56.

problem was Dubois's assertions about their geologic age.⁵⁵ As a result, Dubois despatched a fragment of *Stegodon* bone found in the same deposits as the *Pithecanthropus* fossils, to test its fluorine content so that it could be compared with those of European fossils given by Carnot. The amount of fluorine present in the *Stegodon* bone was consistent with late Pliocene fossils from Europe.⁵⁶ Yet this analysis had little impact on the debate over the *Pithecanthropus* fossils. Indeed, despite the promise and the apparent success of Carnot's fluorine dating method in the cases of the Billancourt, Xico and Natchez human fossils, the method never became widely used and fell into relative oblivion during the early decades of the twentieth century.

Kenneth Oakley and the modern fluorine dating method

The fluorine dating method had all but disappeared as a tool in palaeoanthropological research during the early decades of the twentieth century. The British geologist and palaeoanthropologist Kenneth Oakley almost single-handedly revived the method in the 1940s and transformed it into a useful and widely used technique. Oakley studied geology and anthropology at University College London and in 1935 became assistant keeper of palaeontology at the Natural History Museum. During the Second World War Oakley was attached to the Geological Survey of Great Britain, where he conducted research on the use of phosphates in fertilizer as well as the impact of fluorine on dental health. This latter project brought Oakley into contact with Adolphe Carnot's research.⁵⁷ The first occasion Oakley had to apply Carnot's method of analysing fossil bone arose from the First Pan-African Congress on Prehistory, held in Nairobi in 1947. Oakley had discussed the fluorine dating method; Louis Leakey, organizer of the congress, realized that Oakley might have the solution to a long-standing problem. Leakey had discovered two partial human crania at Kanjera near Lake Victoria and a human mandible at another site, Kanam, in 1934. Both were remarkably modern in their anatomy but came from very old geological deposits. Leakey took these fossils to be evidence that anatomically modern humans had evolved very early in Africa, but many of his critics viewed the fossils with suspicion.⁵⁸ Since animal fossils had been found in the deposits containing the human skull and mandible, the fluorine test might determine if they were of the same age or if the human fossils were recent intrusive burials, as some believed.

Leakey provided Oakley with a sample from a Kanjera skull, along with animal specimens from the same deposit, as well as a late prehistoric human bone from the

55 On Dubois's discovery and the debate over the evolutionary status of *Pithecanthropus erectus* see B. Theunissen, *Eugène Dubois and the Ape-Man from Java: The History of the First 'Missing Link' and Its Discoverer*, Dordrecht, 1989.

56 J. M. van Bemmelen, A. Simon Thomas and E. A. Klobbie, 'Sur le Teneur en fluorure de calcium d'un os d'éléphant fossile de l'époque tertiaire', *Archives néerlandaises des sciences exactes et naturelles* (1900), 229–30.

57 K. P. Oakley, 'The fluorine-dating method', *Yearbook of Physical Anthropology* (1949) (1951), 5, 44.

58 L. S. B. Leakey, 'Fossil human remains from Kanam and Kanjera, Kenya Colony', *Nature* (1936), 138, 643; P. G. H. Boswell, 'Human remains from Kanam and Kanjera, Kenya Colony', *Nature* (1935), 135, 371. The controversy over the fossils is examined in J. Reader, *Missing Links: The Hunt for Earliest Man*, 2nd edn, New York, 1988, 139–42.

same region. Oakley submitted these samples to Henry James Walls of the Home Office Forensic Science Laboratory in Bristol for chemical analysis. Unfortunately, Walls found that the Kanjera fossils were all saturated with fluorine, the result of the extremely high concentrations of the element found in the Kanjera deposits due to their volcanic origin.⁵⁹ While this first attempt to use the fluorine dating method was unsuccessful, Oakley was convinced of its potential value to palaeoanthropology. In fact, he already had two candidates for fluorine analysis in mind, the Galley Hill skeleton and the troublesome Piltdown Man fossils.⁶⁰

The Galley Hill skeleton, already mentioned above in the context of the presapiens hypothesis, was discovered in 1895 in Kent in Pleistocene geological deposits. The skull of Galley Hill Man had been found seven years earlier. The skeleton was interesting because of its apparent great age and the fact that it was anatomically modern. The palaeontologist Edwin Tulley Newton, member of the Geological Society of London, published an account of the skeleton in 1895 in which he argued for the antiquity of the Galley Hill skeleton on the basis of the geological strata in which it was found and the stone implements excavated in the same strata. Newton also emphasized certain morphological features of the skull that indicated it might be very old.⁶¹ There was, however, suspicion concerning the supposed age of the skeleton from the very beginning. John Evans, a respected and influential prehistoric archaeologist who had participated directly in the geological debate over the coexistence of humans and Ice Age mammals, doubted it was as old as Newton claimed. This view was shared by others who suspected it might be a relatively recent skeleton buried in a much older deposit.⁶² The debate over the age of the Galley Hill skeleton grew during the early decades of the twentieth century. Prominent figures such as Arthur Keith supported its antiquity while other eminent scientists such as Wynfrid Laurence Henry Duckworth concluded it was a more recent intrusive burial.⁶³ Oakley saw the fluorine dating method as a means of settling the debate. In 1948 he and Wilfred Norman Edwards, keeper of geology and palaeontology at the Natural History Museum, approached the Department of the Government Chemist in London seeking assistance in conducting a chemical analysis of the Galley Hill skeleton and the Pleistocene animal fossils from the same deposit. Three chemists – R. H. Settle, C. Randall Hoskins and E. C. W. Maycock – agreed to join the investigation.⁶⁴

59 K. P. Oakley, 'Fluorine and the relative dating of bones', *Advancement of Science* (1948), 4, 336. See also *idem*, op. cit. (57), 45.

60 Oakley, op. cit. (59), 336–7.

61 E. Tulley Newton, 'On a human skull and limb-bones found in the Palaeolithic terrace-gravel at Galley Hill, Kent', *Quarterly Journal of the Geological Society of London* (1895), 51, 505–27.

62 Evans, op. cit. (11), 607.

63 A. Keith, *Ancient Types of Man*, London, 1911, 28–45; W. H. L. Duckworth, 'The problem of the Galley Hill skeleton', in *Essays and Studies Presented to William Ridgeway on his Sixtieth Birthday, 6 August, 1913* (ed. E. C. Quiggin), Cambridge, 1913, 458–73.

64 K. P. Oakley and M. F. A. Montague, 'A re-consideration of the Galley Hill skeleton', *Bulletin of the British Museum (Natural History). Geology Series* (1949), 1, 42. See also K. P. Oakley, 'Some applications of the fluorine test', *Archaeological Newsletter*, 1949, 1.

In order to ensure the reliability of the results of their analysis of the fluorine content of the Galley Hill collection, they first needed to

establish the probable range of fluctuation in fluorine content of a pilot series of fossil bones undoubtedly contemporary with the particular bed from which the specimen of questionable age has been derived, and to show also what deviation is to be expected through local differences in matrix.⁶⁵

A series of twenty-two bone samples from the Galley Hill site were then chosen for analysis, including fossils from the Lower Pleistocene deposits where the human skeleton was found, as well as more recent fossils from Upper Pleistocene deposits taken from nearby gravel pits and samples from a Saxon skeleton from historic times.⁶⁶ It was then necessary that the chemists obtain a 'representative sample' of bone for analysis from each specimen. In order to achieve this, the chemists drilled holes about five millimetres deep from three or four widely separated spots on each bone and the powder produced from each drill hole was then mixed together.⁶⁷

Once samples had been obtained in this way from each specimen of bone they were subjected to analysis. The chemical procedures used to isolate and measure fluorine had advanced significantly from the techniques used by Carnot and Middleton. When Henry Walls had examined the Kanjera fossils he had used a new method of determining fluorine content devised by R. F. Milton, H. F. Liddell and J. E. Chivers.⁶⁸ To determine the fluorine content of the Galley Hill fossils, Settle, Hoskins and Maycock used a slightly different method developed by Hobart Willard and O. B. Winter in 1933.⁶⁹ Both methods were extremely time-consuming and exacting, severely limiting the number of specimens that could be reasonably and affordably analysed. This point was emphasized by Oakley, who remarked that 'in order to be used accurately this method requires considerable technical experience'.⁷⁰ Unlike the Kanam and Kanjera analysis, that of the Galley Hill fossils produced very good results. The fluorine content of the specimens showed conclusively that the Galley Hill human skeleton did not date from the Pleistocene, but was instead a recent burial.⁷¹

The validity of the fluorine method was strengthened when another fossil, a human skull found in 1935 at Swanscombe in Kent, was also tested. The Swanscombe skull was found in association with Acheulean flint tools, thus placing it in the Lower Middle Pleistocene. The fluorine analysis of the skull showed that it was consistent with this early period.⁷² The success of the fluorine dating method in resolving the Galley Hill

65 Oakley, *op. cit.* (57), 46.

66 Oakley, *op. cit.* (64).

67 Oakley, *op. cit.* (57), 46.

68 Oakley, *op. cit.* (57), 46. This new method was described in R. F. Milton, H. F. Liddell and J. E. Chivers, 'A new titrimetric method for the estimation of fluorine', *Analyst* (1947), 72, 43–7.

69 Oakley, *op. cit.* (57), 46. This method was published in H. H. Willard and O. B. Winter, 'Volumetric method for determination of fluorine', *Industrial Engineering and Chemistry: Analytic Edition* (1933), 5, 7–10.

70 Oakley, *op. cit.* (57), 47.

71 Oakley and Montagu, *op. cit.* (64), 43–5. See also Oakley, *op. cit.* (64), 1.

72 Oakley, *op. cit.* (64), 1.

debate and in confirming the antiquity of the Swanscombe skull led Oakley to think that it might finally resolve one of the most debated problems in human palaeontology, the age and validity of the Piltdown Man specimen. Between 1908 and 1912 Charles Dawson, a solicitor and amateur archaeologist, had discovered fragments of a modern-looking human skull along with a portion of a very ape-like mandible in a gravel pit in Piltdown Common in Sussex. The geologist Arthur Smith Woodward and anatomist Arthur Keith believed that the skull and jaw belonged to a species of early human they called *Eoanthropus dawsoni*. Some anthropologists believed that the skull and jaw fragments belonged to two separate creatures, whilst other scientists were sceptical of the supposed Lower Pleistocene age of the fossils.⁷³ A further complication was introduced in 1946 when Alvan T. Marston, a London dentist with extensive experience in Palaeolithic archaeology, suggested that the Piltdown skull and jaw might not be of the same age. Oakley had discussed the use of the fluorine dating method for the Piltdown fossils in 1947 at the Dundee meeting of the British Association for the Advancement of Science: the success of the method with the Galley Hill and Swanscombe fossils prompted Oakley and his collaborators at the Department of the Government Chemist to submit the Piltdown fossils to fluorine analysis.⁷⁴

In October 1948 Wilfred Norman Edwards authorized analysis of all the Piltdown fossils as well as animal fossils from the Piltdown gravels and nearby deposits. The oldest animal fossils were from the Lower Pleistocene and Villafranchian, while the remaining fossils were from the Middle to Late Pleistocene. Samples were taken from the broken or worn edges of each specimen in order not to damage the fossils. A dental drill was used to extract about twenty milligrams of powder from each specimen.⁷⁵ In this case Randall Hoskins conducted the chemical analysis. The Lower Pleistocene animal fossils contained two to three per cent fluorine and the remaining animal fossils contained less than 1.6 per cent fluorine. The Piltdown Man fossils, however, all contained only about 0.2 per cent of fluorine.⁷⁶ From these results Oakley concluded first that the skull bones and the mandible were the same age, which resolved Marston's doubts. It was also clear that *Eoanthropus dawsoni* could not date from the Lower Pleistocene and provisionally Oakley dated it to the last interglacial period (the Riss-Würm) or

73 Some of the key papers on the discovery are C. Dawson and A. Smith Woodward, 'On the discovery of a Palaeolithic human skull and mandible in a flint-bearing gravel overlying the Wealden (Hastings Beds) at Piltdown, Fletching (Sussex)', *Quarterly Journal of the Geological Society of London* (1913), 69, 117–51; A. Keith, 'The Piltdown skull and brain cast', *Nature* (1913), 92, 107–9, 197–9, 292, 345–6; G. E. Smith, 'The controversies concerning the interpretations and meaning of the remains of the dawn-man found near Piltdown', *Nature* (1913), 92, 468–9. A considerable literature exists on the Piltdown affair. The circumstances surrounding the discovery and interpretation of the fossils and the debate over them is discussed in detail in F. Spencer, *op. cit.* (13); C. Blinderman, *The Piltdown Inquest*, Buffalo, 1986; Millar, *op. cit.* (17); M. Hammond, 'A framework of plausibility for an anthropological forgery: the Piltdown Case', *Anthropology* (1979), 3, 47–58.

74 Oakley, *op. cit.* (59), 337; *idem*, *op. cit.* (64), 1.

75 K. P. Oakley and C. Randall Hoskins, 'New evidence on the antiquity of Piltdown Man', *Nature* (1950), 20, 380.

76 K. P. Oakley, 'Relative dating of the Piltdown skull I', *Advancement of Science* (1950), 6, 343–4; also Oakley and Hoskins, *op. cit.* (75), 381.

Upper Pleistocene.⁷⁷ Oakley admitted, however, that the amount of fluorine in the Piltdown Man specimens was so low as to be comparable with modern bone, a fact that ‘requires some explanation’, although it could only serve ‘to emphasize the probably enormous time-gap’ separating the Piltdown Man remains from the Lower Pleistocene.⁷⁸ This small matter would become of considerable importance just a few years later. In the interim, Oakley felt confident in asserting that the fluorine results had not only settled the question of the age of *Eoanthropus dawsoni* but had also ‘considerably increased the probability that the mandible and the cranium represent a single creature’.⁷⁹

The fluorine dating method had clearly shown its value to palaeoanthropology. Oakley now turned his attention to other human fossils that were of doubtful antiquity. He and Hoskins examined human skull fragments found in 1882 at Westley, near Bury St Edmunds. Although the fragments were found associated with Acheulean hand axes in Middle Pleistocene deposits, fluorine analysis proved that they were from a recent intrusive burial.⁸⁰ The next specimens to be analysed were the human skulls excavated from the French Palaeolithic site of Fontéchevade in 1947 by Germaine Henri-Martin. The Fontéchevade skulls were at the centre of a debate over the validity of the pre-sapiens hypothesis because, like the Swanscombe and Piltdown fossils, they seemed to be similar in their structure to modern human skulls but were from very old geological deposits.⁸¹ At the request of Henri-Martin, Oakley had the skulls tested. While the results did not definitively settle the question of their age, they were consistent with the supposed Tayacian age of the deposits where the skulls had been found.⁸² From this examination, Oakley also learnt that the fluorine dating method ‘only yields conclusive results when the age-difference between the groups under comparison is sufficiently great. Thus, it is unsuitable in all but the most favourable circumstances for the differentiation of, say, Mousterian from Upper Palaeolithic, Upper Palaeolithic from Mesolithic.’⁸³ This did not undermine the validity of the method, but it did imply that it had its limits and that this should be realized by palaeoanthropologists.

Fluorine analysis also showed that fragments of a modern human skull found in association with a horn from the extinct aurochs (*Bos primigenius*) in Suffolk were modern and that a human skull found along the banks of the Thames in deposits containing stone tools of the Levalloisian type was not contemporaneous with those tools. The notorious Moulin Quignon jaw, found in Abbeville in 1863 in deposits containing numerous Palaeolithic implements, also succumbed to the fluorine dating

77 Oakley and Hoskins, op. cit. (75), 381–2.

78 Oakley and Hoskins, op. cit. (75), 381.

79 Oakley, op. cit. (76), 344.

80 D. F. W. Baden-Powell and K. P. Oakley, ‘Report on the re-investigation of the Westley (Bury St. Edmunds) skull site’, *Proceedings of the Prehistoric Society* (1953), 18, 1–20.

81 On the debate over the Fontéchevade fossils see E. Trinkhaus and P. Shipman, *The Neanderthals: Changing the Image of Mankind*, New York, 1993, 305–10.

82 Oakley, op. cit. (57), 47–8; K. P. Oakley and G. Henri-Martin, ‘Application du test de la fluorine aux crânes de Fontéchevade (Charente)’, *Anthropologie* (1951), 55, 239–47.

83 Oakley, op. cit. (57), 48.

method.⁸⁴ Oakley received permission to analyse the famous fossil from the Musée de l'homme in Paris and the results showed with certainty that the jaw was not from the Palaeolithic.⁸⁵ Within just a few short years Oakley and his colleagues at the Department of the Government Chemist had resolved doubts about more than half a dozen fossils, indicating that several were not at all prehistoric while strengthening the ancient status of several others. Moreover, they had demonstrated the power of the fluorine dating method to solve problems that had resisted solution in any other way.

Oakley's investigations using the fluorine dating method attracted the attention of Paul Fejos, director of research of the Wenner-Gren Foundation (originally the Viking Fund), while Oakley was lecturing on this research in New York City in 1950. Fejos and the Wenner-Gren Foundation provided financial support for many types of anthropological and archaeological research and Fejos offered Oakley funds to allow for the expanded use of the fluorine dating method. Oakley discussed this offer with Wilfrid Norman Edwards of the Natural History Museum and the Department of the Government Chemist, which quickly led to an agreement on a long-term collaborative project between the two institutions to apply the fluorine dating method to much larger numbers of fossils from around the world. Oakley and his colleagues received their first grant from the Wenner-Gren Foundation in 1952 to purchase equipment and allow for travel abroad.⁸⁶ It is significant that Fejos not only supported Oakley's fluorine dating investigations, but was also among the first to recognize the potential value of American physical chemist Willard Frank Libby's radiocarbon (carbon-14) dating method and he encouraged the foundation to fund that research as well.⁸⁷ These two dating methods quickly began to transform the study of prehistory.

The fluorine dating method, still relatively little known among anthropologists, suddenly made its dramatic mark in 1953 as a result of a new series of investigations of the Piltdown Man fossils. Oakley had analysed the fossils in 1949 but the research had not resolved all the questions surrounding the Piltdown specimen. Renewed doubts and suspicions about the fossils finally prompted Joseph Sidney Weiner, professor of physical anthropology at Oxford University, to inspect the fossils anew during the summer of 1953. Weiner enlisted the assistance of Oakley and the Oxford anatomist Wilfrid Le Gros Clark; they were soon obtaining some very interesting results. Oakley once again had the skull fragments and the mandible subjected to fluorine analysis. On this occasion Charles Frederick Fryd of the Department of the Government Chemist used a new and much more sensitive technique. A startling difference in the fluorine content now appeared, not achievable with the original technique used in 1949. Oakley and Fryd found that the Piltdown skull fragments contained about 0.1 per cent of

84 Trinkhaus and Shipman, *op. cit.* (81), 90–125, offer an informative account of the discovery and controversy surrounding the Moulin Quignon jaw.

85 Oakley, *op. cit.* (57), 48–9.

86 K. P. Oakley, 'Relative dating of the fossil hominids of Europe', *Bulletin of the British Museum (Natural History)* (1980), 34, 53.

87 See R. E. Taylor, 'The beginnings of radiocarbon dating in American antiquity: a historical perspective', *American Antiquity* (1985), 50, 311–12; G. Marlowe, 'W. F. Libby and the archaeologists, 1946–1948', *Radiocarbon* (1980), 22, 1005–14. On the impact of the radiocarbon dating method in archaeology see D. Wilson, *The New Archaeology*, New York, 1974, Chapters 4–6.

fluorine while the mandible only contained 0.03 per cent.⁸⁸ This meant that the skull could still be prehistoric, but the mandible was certainly modern. Other chemical analyses and a close inspection of the fossils provided further evidence not only that the skull and mandible were not the same age and were not very old, but also that they were not what they appeared to be. Weiner, Oakley and Le Gros Clark found convincing evidence that the jawbone had been tampered with and that the Piltdown fossils were an elaborate forgery.⁸⁹

The disclosure that the Piltdown fossils were a fraud created an uproar and attracted huge attention, because of the prominence of the Piltdown fossils and half-century of often acrimonious debate that surrounded them. There was also a great deal of interest in the means employed to uncover the fraud. Many of the chemical methods used were relatively new, at least in their application to anthropological problems, but they clearly showed the power of chemical analysis and especially of the fluorine dating method for resolving problems in palaeoanthropology. Because of the Piltdown affair, many palaeoanthropologists learnt of the fluorine dating method and its possible uses. With substantial funding from the Wenner-Gren Foundation to expand their research and the pivotal role that the fluorine dating method played in solving the Piltdown problem, the way was prepared for its widespread application.

After learning of Oakley's application of the technique to the Galley Hill skeleton, the University of California–Berkeley archaeology professor Robert Fleming Heizer and Sherburne Friend Cook, professor of physiology, had already begun to apply the fluorine dating method to palaeoindian sites in California.⁹⁰ Throughout the 1950s they used the fluorine dating method, along with other chemical methods they were developing to date fossil bone, to resolve doubts about human fossils that were of uncertain age.⁹¹ From 1953 into the 1960s Oakley oversaw the fluorine dating of numerous specimens including the Broken Hill, Florisbad and Saldanha human fossils from Africa, as well as a number of European fossils.⁹² Other anthropologists also began to adopt the method. The American anthropologist Carleton Stevens Coon used the fluorine dating method in 1951 to test bones collected during excavations at Hotu

88 J. S. Weiner, W. E. Le Gros Clark and K. P. Oakley, 'The solution of the Piltdown problem', *Bulletin of the British Museum (Natural History) (Geology)* (1953), 2, 139–46; J. S. Weiner and K. P. Oakley, 'The Piltdown fraud: available evidence reviewed', *American Journal of Physical Anthropology* (1954), 12, 1–7; J. S. Weiner, *The Piltdown Forgery*, Oxford, 1955, Chapter 4.

89 A full discussion of the evidence and the means employed by the team led by Weiner and Oakley to uncover the Piltdown hoax is provided in Weiner, op. cit. (88); Spencer, op. cit. (13), Chapter 6.

90 R. F. Heizer, 'On the methods of chemical analysis of bone as an aid to prehistoric culture chronology', *Reports of the University of California Archaeological Survey* (1950), 10–14; R. F. Heizer and S. F. Cook, 'Fluorine and other chemical tests of some North American human and fossil bones', *American Journal of Physical Anthropology* (1952), 10, 289–303; S. F. Cook and R. F. Heizer, 'The present status of chemical methods for dating prehistoric bone', *American Antiquity* (1953), 18, 354–8.

91 I plan to explore the research of Heizer and Cook as well as the application of their methods by Oakley in a separate paper.

92 Oakley's later applications of the fluorine dating method are recorded in K. P. Oakley, 'Relative dating of the fossil hominids of Europe', *Bulletin of the British Museum (Natural History) (Geology)* (1980), 34, 1–63.

Cave in Iran, but also submitted samples of charcoal from the site to be tested using the new radiocarbon (carbon-14) dating method.⁹³

This juxtaposition of dating methods is significant, because the fluorine dating method flourished only for a brief period, while the carbon-14 dating method continued to grow in importance. Indeed, the fluorine dating method had all but disappeared by 1970, although it continued to be used in specific situations where other methods could not be applied.⁹⁴ A noteworthy indication of the fading importance of the fluorine dating method by 1970 is the fact that while a chapter devoted to the technique appeared in the 1963 edition of Don R. Brothwell and Eric S. Higgs's *Science in Archaeology*, it was not even mentioned in the 1970 edition. The major reason for the decline of the fluorine dating method was the fact that it did not provide absolute dates for the specimens analysed, but could only show whether or not a group of fossils were contemporaneous. Developed at the same time as the refinement by Oakley and his colleagues of the fluorine dating method, the carbon-14 technique could provide absolute dates for organic specimens and excavation sites (if organic material was present), if those specimens were less than about fifty thousand years old. However, by 1958 the potassium–argon (K–Ar) dating method had been developed. This approach provided absolute dates for prehistoric specimens and sites millions of years old, as long as these were located in volcanic deposits. The successful application of the carbon-14 and potassium–argon dating methods to prehistoric artefacts and sites meant that the fluorine dating method was no longer needed, except under very specific conditions.

Yet between 1949 and 1969 the fluorine dating method was used to analyse a substantial number of human fossil specimens from around the world and made a significant contribution to palaeoanthropology by finally settling doubts about the antiquity of a large number of specimens. As apparent in the case of Rivière, the ability to distinguish truly prehistoric human fossils from recent intrusive burials was becoming a major problem by the late nineteenth century, when substantial numbers of archaeologists excavated sites seeking human bones or artefacts dating from the Pleistocene or earlier. Intrusive burials and the accidental association of bones of different ages through the disturbance of geological deposits created doubts about many supposed Palaeolithic human remains. The fluorine dating method devised by Carnot was the only available means that definitively resolved such cases. The method was also important in the history of palaeoanthropological research because it was a significant advance in the search for an absolute dating method. For the first time, the stratigraphic method used to obtain relative dates for archaeological and geological sites was supplemented by an entirely new chemical means to date fossil specimens. Although the

93 C. S. Coon, 'Excavations in Hotu Cave, Iran, 1951, a preliminary report', *Proceedings of the American Philosophical Society* (1952), 96, 231–49.

94 Examples of the recent use of the method can be found in R. T. Callaghan, 'Analysis of the fluoride content of human remains from the Gray Site, Saskatchewan', *Plains Anthropologist* (1986), 31, 317–28; A. Haddy and A. Hanson, 'Nitrogen and fluorine dating of Moundville skeleton samples', *Archaeometry* (1982), 24, 37–44; S. B. Lal, 'Bone fluorine as a measure of relative chronology at Piprahwa', *Current Anthropology* (1978), 19, 150–1.

fluorine dating method could not provide the absolute dates desired by palaeoanthropologists, the search for chemical or physical means of dating bones or artefacts did not end and was eventually successful, first with the carbon-14 dating method and later with other methods.

Moreover, the collaboration that this kind of research required, between anthropologists or archaeologists and chemists or physicists, so essential to the successful development and application of archaeological dating methods and the correct interpretation of their results, was already apparent in the relationship between Rivière and Carnot. It is even more visible in the close cooperation that arose between Oakley and chemists such as Hoskins and Fryd at the Department of the Government Chemist. Oakley brought his knowledge of palaeontology and geology to the interpretation of human fossil remains. Hoskins and Fryd applied their expertise and knowledge as chemists to exacting and difficult chemical analyses of fossils bones to produce numbers that had to be interpreted chemically before the results could give an understanding of the relative ages of the fossils under investigation. Oakley had to trust the skills and results of the chemists with whom he worked, while the chemists sometimes had to revise and improve the methods they employed to obtain the results anthropologists desired from them. Chemistry also benefited from this relationship. Hoskins and Fryd were able to publish a paper on a refined method for measuring quantities of fluorine in fossil bone that they had developed for the second round of Piltdown analyses.⁹⁵ This kind of collaboration between scientists of different disciplines in palaeoanthropological research would become important not only with the development of new dating methods but also as modern palaeoanthropological expeditions and research teams became increasingly multidisciplinary in the 1970s. The development of the fluorine dating method, now a largely forgotten episode in the history of palaeoanthropology, not only was influential because of the results of its application in such cases as the Galley Hill skeleton and the Piltdown fossils, but also marks the beginning of significant changes in the way palaeoanthropological research would be conducted in the last half of the twentieth century. It reflects some of the challenges and rewards introduced by this new type of research.

⁹⁵ C. Randall Hoskins and C. F. M. Fryd, 'The determination of fluorine in Piltdown and related fossils', *Journal of Applied Chemistry* (1955), 5, 85–7.