tion; their members lead completely atypical lives and not infrequently have interests and views opposite to those of the majority of the people. Thus, it is easy for the visiting American to be seriously misled, unless he possesses suitable attributes and uses suitable methods of reaching a more adequate sample of people.

Behavioral scientists have no "miracle solutions" to problems of international relations, but they can help. Anthropologists and certain sociologists, for instance, have had much experience with the problems of attitude and methods just mentioned. A study of the practices, special problems, and views of the various government agencies involved must precede any detailed recommendations as to how the principles, facts, and techniques developed in behavioral sciences can be best used in international relations.

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Dating of Fossil Bones by the Fluorine Method

Fluorine analysis by indirect methods is not a reliable means of determining age.

Duncan McConnell

Attempts to determine the age of fossil bones from their fluorine contents seem to have first been made more than a century ago (*1*), although the method does not seem to have attracted considerable attention prior to the work of Carnot, in 1893 (*2*). Recent discussions on analytical methods are contained in papers by Baud (*3*) and Cook (*4*).

Some of the recently applied variations of the fluorine method suffer from all of the geochemical and geological uncertainties and, in addition, have introduced analytical procedures which depend upon elusive crystal-chemical and mineralogical principles.

I am concerned primarily with the x-ray diffraction methods for fluorine determination, as applied by Périnet (*5*), Gottardi *et al.* (*6*), van der Vlerk (*7*), and Niggli *et al.* (*8*). Before appraising these methods I shall review briefly what is known about the crystal chemistry (that is, the chemical composition and crystal structure) of bones and teeth of living vertebrates.

Crystal Chemistry of Bone

The chemical composition of the "mineral" component of bovine bone has been determined for all of the essential oxides, except water, through the diligent efforts of Armstrong (*9*). Compositional differences exist, depending upon the treatments utilized to free the mineral component from the organic matrix, but certain quantitative facts emerge which are of great significance: bone mineral (including dentin and dental enamel) is composed essentially of a calcium carbonate-phosphate containing much smaller, but measurable, amounts of sodium, potassium, magnesium, fluorine, and chlorine. Other inorganic consitutents are normally present merely as traces, except for water.

Table 1 shows the results of analysis of dry, fat-free, cortical, bovine bone, as recalculated in the form of oxides. It may be noted that about 28 percent, by weight, is not accounted for in the summation. This portion includes the chemically combined water of the mineral as well as all organic matter. The calcium-phosphorus ratio is 1.688 (atomic basis), which is above the theoretical value for hydroxyapatite (1.667); the ratio becomes still greater when equivalent amounts of sodium and magnesium are summed with the calcium.

However, in order that valid conclusions may be drawn concerning the mineral phase of bone, it is essential that the quantity of chemically combined water be known. Inasmuch as any treatment (such as the use of ethylenediamine) which will remove organic matter of bone is also capable of altering the amount of chemically combined water of the mineral phase, the problem of determining the amount of this water is best approached through consideration of fossil dental enamel. Not only is dental enamel comparatively free from organic matter but the fossilization process has stabilized the mineral composition and it has even further reduced the amount of organic matter.

Included in Table 1 are results of the analysis of the enamel portion of the tooth of a post-Wisconsin mastodon (*10*). This analysis was made by C. O. Ingamells, a highly qualified mineral analyst, using standard macro methods. Again, it may be noted that the calcium-phosphorus ratio (1.692) exceeds the theoretical value for hydroxyapatite (1.667), provided the magnesium and sodium are summed with the calcium. Many analyses made by reliable macro methods show that the calcium-phosphorus ratio exceeds 1.667 for bones and teeth (*11*), and this is true also for the minerals dahllite and francolite (*12*).

Dental enamel, dentin, and bone are composed of a single crystalline phase, a carbonate hydroxyapatite (dahllite), in which there is substitution within the crystal lattice of carbonate groups for phosphate groups. No other interpreta-

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tion will explain the various physical (including optical) and chemical data for these substances or for the minerals francolite and dahllite, which are essentially isostructural (*13*).

As has been indicated elsewhere (*12*), there is no simple relationship between the calcium-phosphorus ratio and the carbon dioxide content, nor is there an inverse relationship between the fluorine content and either the hydroxyl (water) content or the carbon dioxide content. According to my theory no such relationships would be expected, and none are observed.

Presently I shall give some details concerning crystallography and the x-ray diffraction method, but first I shall mention a few basic concepts.

The unit cell of a crystal lattice is the smallest dimensional unit that has the symmetry properties of the entire crystal. The fundamental periodicities of symmetrical repetition for the lattice, then, are a_o, b_o, and c_o, in the respective axial directions. (In the hexagonal case these are reduced to a_o and c_o, and in the cubic case to a_o.) These dimensions are customarily expressed in angstroms (1 angstrom $= 1 \times 10^{-8}$ cm).

Nevertheless, the unit-cell contents cannot represent the chemistry of the whole crystal because random (statistical) substitution of one atom for another can take place in some unit cells and not in others. For example, one sodium atom may substitute for a calcium atom in only one of every 57 unit cells. No qualitative change would take place in the diffraction effects as a consequence, but there would be quantitative changes in the interplanar spacings and intensities of the interference maxima, whether they are measurable or not.

The situation which involves ordered (regular) substitution of atoms is quite different. Here the substituted atoms form a regular array (lattice) of their own, and qualitative differences in the diffraction effects occur.

The crystal chemistry of bone and teeth gives no evidence of regular substitution of any of the minor constituents, or of a stoichiometric amount of carbonate substituting for phosphate. Thus, although measurable changes in the interplanar spacings reveal a change in a_o (depending upon the carbonate content, for example), the carbonate apatites can be treated as though they and ordinary fluorapatite were essentially isostructural (*10, 14, 15*).

The Fossilization Process

Dahllite and francolite are of fundamental interest with respect to the fossilization process inasmuch as bones and teeth are originally dahllite and are converted to francolite through interaction with fluorides contained in ground water, sea water, or connate water. The point of distinction between these two minerals (*14*) was arbitrarily set at a fluorine content of 1 percent, by weight, in accordance with the observation that most specimens would fall distinctly into one category or the other.

Apatite-like materials which are comparatively low in fluorine will extract fluoride ions from waters that contain only a few parts of fluorine per million. Such substances (including "bone char") have been used for defluoridation of drinking water (*16*), although there seem to be better practical methods. It has long been assumed that reduction in susceptibility to dental caries comes about through the interaction of fluoride ions and the outermost portions of the dental enamel.

In addition to a reduction in the amount of organic matter during the fossilization process, other changes can take place. Besides recrystallization, and a change in the fluorine content, changes in the apatite mineral can include (i) either an increase or a decrease in the carbon dioxide content, (ii) change in the amount of chemically combined water, (iii) increase in the chlorine content, and (iv) changes in the amounts of minor constituents (sodium, magnesium, and potassium). From the values in Table 1 it seems reasonably certain that there was an increase in the chlorine content of the dental enamel of the mastodon during fossilization, and there seems to have been a decrease in the carbon dioxide content.

Changes in the fluorine content during fossilization have always been assumed to be in the direction of increase, and indeed this may be true. Nevertheless, it may be noted that the fossil mastodon sample contains considerably less fluorine than the bovine bone.

Fluorine Contents of Apatite Minerals

Prior to the introduction of the distillation method, by Willard and Winter (*17*), in 1933, straightforward methods for making chemical analysis for fluorine were of highly dubious accuracy; hence, conclusions based upon these early fluorine determinations should certainly be reconsidered.

Recent analyses of francolite show amounts of fluorine appreciably in excess of the theoretical amount of fluorapatite (3.77 percent, by weight). The average for five such mineral specimens from widely separated localities is 4.05 (*15*), and the highest value is 5.60 (*18*). To be sure, there is no indication that fossil bones are likely to contain any such quantities of fluorine, but inasmuch as certain methods for age determination are based upon the relative amounts of fluorapatite and hydroxyapatite supposedly contained in the fossil bone, the amount of fluorine which is assumed to be present in the fluorapatite end member must be a matter of considerable significance.

In addition to excessive amounts of fluorine, these analyses of francolite show an average of 0.6 percent of chemically combined water, some of which was determined at temperatures above 300°C. From these data a major enigma arises if one is encumbered with obsolete concepts of crystal chemistry: not only could the calculated value for fluorapatite exceed 100 percent, but there would be an additional amount of hydroxyapatite (based on the amount of chemically combined water). There is a method for resolving this problem; one must reject the assumption that something intermediate between fluorapatite and hydroxyapatite is present.

The crystalline phase present is an isomorphic apatite intermediate which contains carbon dioxide. Indeed, I have never examined a fossil bone or tooth that has not vigorously liberated carbon-dioxide bubbles when placed in normal hydrochloric acid. In some specimens of fossil wood the amount of carbon dioxide is reported to be as high as 6.9 percent (*19*). This information should dispel the untenable view that carbonate groups can substitute for fluorine (one for two) to give $Ca_{10}CO_3(PO_4)_6$, because this hypothetical compound contains only 4.27 percent of carbon dioxide. Not only was the existence of such a compound disproved on the basis of structural principles by Gruner and me (*20*) but Ames (*21*) has produced synthetic carbonate apatite in which he finds that as much as 10 percent of carbonate may be present in the lattice of the apatite mineral.

Indirect Methods of Fluorine Determination

Several persons have cautiously presented correlations of age determinations and fluorine contents of fossil bones. Some recent fluorine determinations utilize x-ray diffraction results, with or without prior treatment of the specimens by calcination. Although it would be interesting to compare the fluorine contents thus determined with those determined by straightforward chemical methods, the latter data do not seem to be available.

In a recent study, Périnet (*5*) measured the ratio of c_o to a_o and thereby supposedly ascertained the fluorine content, inasmuch as the axial ratios (c/a) are different for fluorapatite and hydroxyapatite. He disregarded the influence of the carbonate content on the axial ratio, despite the fact that numerous investigators have found that a_o ranges from 9.30 to 9.36 angstroms in a series of carbonate apatites in which the variation appears to be caused primarily by variation in the carbonate content and *not* by variation in the fluorine content. Although he admits the existence of other opinions on the subject, Périnet apparently holds to the archaic belief that fluorine substitutes for carbonate groups (and vice versa) within the lattice of apatite.

Although Périnet's work is more recent than that of Niggli *et al.* (*8*), Gottardi *et al.* (*6*), and van der Vlerk (*22*), Périnet does not refer to the contributions of these workers. While all of their papers contain some interesting features—particularly concerning the supposed accuracy of such methods—the paper by Gottardi *et al.* is the only one which adequately considers the possible influence of the universally present carbonate constituent. The other authors predicate their methods on fallacies which are of such a nature as to make any correlations between the ages of the fossils and the x-ray diffraction measurements quite fortuitous.

Gottardi *et al.* decided that it should be possible to deduce the relative amounts of fluorapatite and hydroxyapatite if it were possible to convert the bone samples to something intermediate by removing the carbon dioxide through calcination. Périnet and Michaud (*23*) previously had measured c/a ratios after heating to 800°C and deduced that the value is greater than 0.732 for Tertiary bones but less for Quaternary bones. The principal difference between their work and that of Gottardi *et al.* is that the latter authors do not use the axial ratio c/a but merely use the a_o dimension. They assume that the three end members with which they are concerned have the following dimensions (all ± 0.002 angstroms):

	a_o	c_o	c/a
Hydroxyapatite	9.422	6.882	0.730
Fluorapatite	9.369	6.884	0.735
Chlorapatite	9.629	6.777	0.704

Inasmuch as c_o for hydroxyapatite and c_o for fluorapatite are identical within experimental error, these workers deduced that it is merely necessary to determine a_o. (Périnet and his coworkers and van der Vlerk and his coworkers did not make any absolute measurements but merely determined the angular separation necessary to give the relative value, c/a.)

Gottardi *et al.* found that calcination at 1100°C was fairly effective as a means of removing carbon dioxide and that an increase in a_o took place as a consequence. Périnet and Michaud (*23*) found that as a result of what was probably incomplete removal of carbon dioxide (that is, calcination at 800°C), c/a for bones and dentin increased, whereas c/a for dental enamel decreased. In the absence of any absolute measurements it can merely be pointed out that the results of Périnet and Michaud are not consistent with those of Gattardi *et al.*, which indicated an increase in a_o and a very minor change, if any, in c_o. Thus, a decrease in c/a may be expected for bones on calcination, according to Gottardi *et al.*, but an increase may be expected according to Périnet and Michaud.

Table 1. Compositions of apatites of organic origin.

Oxides	Bovine bone* (%, by weight)	Mastodon enamel† (%, by weight)
CaO	38.11	51.44
MgO	0.72	0.34
Na_2O	0.99	0.80
K_2O	0.07	0.05
P_2O_5	28.57	39.92
CO_2	3.48	2.72
H_2O	—	3.63
F	0.07	0.03
Cl	0.08	0.42
Others	—	0.14
Total	72.09	99.49

* Fat-free, cortical bone; the values have been recalculated as percent, by weight, of the dry sample [data from Armstrong (*9*)]. † Dental enamel fraction of tooth of post-Wisconsin mastodon from the vicinity of Bluffton, Ohio (*10*). Values for oxides included under "Others" are as follows: Al_2O_3, 0.07; Fe_2O_3, 0.03; and insoluble oxides, 0.04.

Gottardi *et al.* admit that entry of chlorine into the apatite lattice almost vitiates the use of the x-ray diffraction method, and that it does is readily apparent from comparisons of a_o and c_o given above. Such factors as the sodium, potassium, and magnesium contents of the fossil bones have not been considered, although introduction of appreciable amounts of these elements unquestionably would alter a_o, c_o, and c/a.

One of the principal sources of error in fluorine dating has long been recognized to be the extremely diverse conditions which might exist in the different strata of burial. These differences include (i) textural and structural characteristics (including porosity and permeability); (ii) composition (including acidity or alkalinity) and rate of percolation of the connate water, as well as its alteration by additions from the surface, from thermal springs, and so on; and (iii) the mineralogical composition of the sediment itself (the presence of large or small quantities of bones, the presence of carbonates, the presence of clay minerals with high exchange capacities, and so on).

To be sure, the rate of alteration of cortical bone would be expected to differ from that of cancellous bone, and both types of bone would alter more rapidly than dental enamel because of significant structural and textural differences among these hard tissues. Consequently, even in comparative studies (for relative dating of fossils from the same deposit), where it can be assumed that both the geochemical and the geological conditions are comparable, it is not permissible to compare gross tooth samples, for example, but only permissible to compare carefully differentiated samples of dental enamel or of dentin.

Summary and Conclusions

In the light of the discussion presented here, we may conclude that fluorine dating is subject to many uncertainties. While the geochemical and geological uncertainties have been recognized (*24*), numerous crystal-chemical concepts concerning the nature of the carbonate-apatite minerals have been almost completely disregarded.

Even straightforward chemical methods can hardly be expected to give consistent age determinations. The x-ray diffraction method involves measurements which can be attributed to at least three compositional variables, and consequently the method is incapable of producing a reliable analytical determination of fluorine, either with or without calcination of the sample. In passing it should be noted that use of the fluorine-phosphorus ratio introduces still another variable inasmuch as the carbonate content of the apatite mineral is also likely to change with time and the phosphate content is inversely related to the carbonate content.

Because the x-ray diffraction method is unreliable for determining the fluorine content, fluorine analysis that depends upon it is unreliable as a means of dating fossils. Hence, age correlations obtained by measuring either a_0 or c/a (with or without calcination) must be regarded as fortuitous in view of present knowledge of the crystal structure of bone.

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News and Comment

Atomic Power: Cinderella Is Slipping Back into the Kitchen

The government will spend about $240 million this year on research and development applicable to the goal of economically competitive atomic power plants. Private businesses in the atomic field seem satisfied with this level of investment, but the Joint Committee on Atomic Energy is unhappy with the way things are going and is likely to remain unhappy for at least the next year or so. This leaves the Administration more or less allied with business interests against the liberal Democrats who dominate the Joint Committee.

The sore point is a $60-million item for beginning several new prototype power reactors which the AEC explains was originally included in its estimates but was deleted by the Bureau of the Budget. With this deletion the funding for prototype power reactors runs rather steadily downhill to a point where it can go down no further: For fiscal 1958, $150 million; 1959, $25 million; 1960, $45 million; 1962 (the last Eisenhower budget), $12 million; 1963, nothing. The Joint Committee, which had been badgering the Eisenhower Administration for letting atomic power slide, now finds that so far as the prototype reactor program is concerned things could not possibly be worse under a Republican Administration than they are now under Kennedy. The AEC argues that it is misleading to draw conclusions about its support for atomic power by picking out one part of the program, the building of prototype plants; it is, after all, still spending a great deal of money on work relevant to atomic power, and this will be augmented next year with the return of some money for prototype plants. But the Joint Committee is not satisfied, and indeed the zero figure for prototypes this year does reflect a change in the place of atomic power plants in national priorities.

What has happened, most briefly, is that the glamour has gone out of atomic power. Space has taken over most of the position that atomic energy so recently held as a field to be pursued, quite aside from its intrinsic value, as a symbol of national prestige and technological supremacy. Accordingly, the goal of economically competitive nuclear power, once talked about almost in the way the race to the moon is discussed now, has lost much of its sense of urgency. You spend money in quite different ways when you shift from trying to develop a technology as rapidly as possible to merely trying to develop the technology. In particular you are less interested in going in for large-scale, necessarily expensive, prototypes when you do not see much return either in showing off these projects to the world for their prestige value or in pay-