Radiocarbon Datability of Peat, Marl, Caliche, and Archaeological Materials

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IN DATING POSTGLACIAL ORGANIC REMAINS by measuring the radioactivity of residual carbon 14, there is an uncertainty about the probable composition of marl and *caliche* that must be kept in mind. To a less degree the same uncertainty may apply to peat subaqueously produced under conditions that approximate those under which marl may be deposited. Alternating layers of marl and peat are frequently produced in the same plant habitat, indicating an environment fluctuating through the narrow range of conditions that result, on one side, in precipitation of calcium as calcareous tufa or marl and, on the other, in deposition of calcareous (as opposed to fairly acid) peat. At the time of deposition an indeterminate amount (up to 50 per cent) of "dead" C^{12} derived from geologically ancient calcium carbonate may dilute the equilibrated mixture of C^{12} and C^{14} derived from atmospheric carbon dioxide.

In the formation of the marl beds and calcareous tufa deposits that overlie glacial till in the glaciated region, the available calcium was derived from more or less pulverized Paleozoic limestone and dolomite, in which radioactivity from C^{14} content would have approached extinction. Calcium carbonate containing only "dead" carbon, in contact with rain water saturated with atmospheric CO_2, would yield soluble calcium bicarbonate in which the C^{14} constituent could not exceed half that in atmospheric CO_2, because some amount less than half of all the carbon would initially have come from the ancient limestone and would be "dead." Escaping from a hillside spring, or seeping underground into a lake, pond, or river, the equilibrated system, water–carbon dioxide–carbonic acid–calcium bicarbonate, would yield CO_2 to submersed plants carrying on photosynthesis. As a result of the disturbed equilibrium, calcium carbonate would be deposited in or on the plants, as, for example, in *Chara,* or on *Potamogeton,* or within the gelatinous matrix of certain blue-green algae, which act as agents in the formation of marl concretions.

Assuming that calcium bicarbonate produces calcium ions as well as hydrogen ions by dissociation, no matter in how low a concentration, then the constant make and break of ionizing molecules in an equilibrated system would yield a marl or calcareous tufa with more than half the C^{14} radioactivity that would be expected if the marl were actually of organic origin. The possible error that would arise from considering a marl or tufa to be of "organic" origin would correspond to less than the half-life of C^{14}. One cannot assume full half, for dissolved atmospheric CO_2 also enters into the soil-water equilibrium, and its resulting product, carbonic acid, regardless of how little there may be, dissociates and serves as a means of equilibrated exchange of C^{14} for C^{12}.

In order not to take too much for granted, it is planned to determine the C^{14} radioactivity of calcium carbonate derived from a synthetic bicarbonate made from "dead" calcium carbonate and atmospheric CO_2 under conditions simulating those in nature. The results, however, can hardly fail to be in accordance with expectation. In the meantime, it will be well to take the precaution of eliminating calcium carbonate or other carbonates from "organic" materials to be dated by the radiocarbon method.

Superficial marls and calcareous tufas of postglacial origin in the glaciated region cannot be expected to give dates that will conform with those derived from peat, charcoal, or undecomposed plant material of the same age. The age will appear to be greater than it actually is, and it would be expected that even peat formed subaqueously in water containing considerable calcium bicarbonate would yield dates of dubious authenticity. To the extent that CO_2 used in photosynthesis is derived from the decomposition of dissolved calcium bicarbonate from limestone sources that are geologically old, it would be expected that aquatic plants would give rise to organic deposits deficient in radiocarbon, with the greatest possible deficiency always less than 50%. The actual deficiency would depend upon how much of the CO_2 used in photosynthesis had been derived by direct diffusion from the air and not by the breakdown of calcium bicarbonate. The contemporaneous atmospheric constituent would probably be much greater, for even in ground water calcium bicarbonate would be enriched in radiocarbon by equilibration with radioactive CO_2 directly from the air or produced by the respiration of animals and the underground parts of plants.

There are too many uncertain factors to make the dating of subaquatic calcareous deposits fully convincing. In order to appraise possible errors, the dating of peat with alternating marl or calcareous tufa must be undertaken. The only part of a calcareous sample used for dating in comparison with associated marl or tufa should be that part which is definitely organic (i.e., not a carbonate). This can best be secured by treatment of the mixed sample with hydrochloric acid, followed by thorough washing of the organic residue. The comparison of the carbonate and organic components should be checked, if possible, by contemporaneous charcoal or wood from the same deposit.

It cannot be hastily assumed that wood or charcoal imbedded in a deposit is not actually either much older (charcoal) or much younger (wood) than the matrix. A wise precaution, therefore, in dating peat or organic material in archaeological deposits would consist in the mechanical sorting-out of possibly intrusive organic material. Thousands of years after an organic deposit had been initially laid down it could continue to be "diluted" and apparently made younger by new organic material introduced in the form of plant roots and burrowing animals. Among the least readily humified constituents of plant debris are pollen grains and leaf cuticles. Among the most readily humified under some conditions is wood. If the latter has been well preserved, however, it should be picked out. If too rotten for mechanical separation it may be removed, with other humified material, by acidification of the sample with dilute hydrochloric acid, washing by repeated decantation, treatment with ammonium hydroxide, and washing until all soluble humus has been removed. Washing the remaining detritus through a fine screen will permit detection of exuviae of insects and crustaceans, which may or may not be later and intrusive. If microscopic examination shows only cuticular debris with pollen and other spore exines, these, of all material in a deposit, are least likely to be intrusive and to be the best part for dating. Masses of wood from large tree roots may possibly be hundreds or thousands of years later than the peat in which they are imbedded, and if rotten are especially likely to dilute old material with young constituents. Intrusive organic materials from a recent surface might conceivably get into an old deposit by the filling of holes left by the rotting of dead trees, or by the activity of burrowing animals. The role of earthworms in turning over the soil is not to be forgotten, and the metabolic activities and final death underground of hundreds of thousands of generations of burrowing creatures may not be a negligible factor in radiocarbon dating.

The problem of determining the age of *caliche* deposits in arid regions poses great uncertainties. The redeposition of calcium carbonate from solution is more complicated in arid areas with strongly alkaline soils than in most of our northern glaciated regions, because the soil-water equilibria involve sodium carbonate and bicarbonate, as well as the two calcium carbonates, carbonic acid and carbon dioxide. Caution would lead one to use for dating no sample in an area of *caliche* from which carbonates had not been removed, and only constituents built as products of photosynthesis remained. Unless *caliche* were known from its geological relations to be so old as to be undatable by the radiocarbon method, there would be some question as to whether any carbon radioactivity detected in it might be wholly the result of secondary enrichment by infiltration of old "dead" *caliche* with young bicarbonates. A desirable precaution in dating buried organic materials in regions where *caliche* forms is the removal of all carbonates by thorough acid extraction.

The problems of dating mollusk shells, eggshells, bone, and horn are varied. Specimens from dry caves may be unimpeachable; those that may have been subjected to replacements of original substance by carbonates from the soil solution may be extremely dubious material for dating. The possibility of replacement of original substance (such as phosphate) in shells by carbonate must be judged from the conditions of preservation. The original carbonate content of shells, precipitated from calcium compounds in body fluid by the shell gland, would doubtless at the time of deposition have the maximum radioactivity that would be expected from newly synthesized organic material. Later addition of carbonate might conceivably increase or decrease the C^{14} content, depending upon circumstances. The same is true for bone. Horn and ivory might have enough organic material left in them, even after burial, so that they could be decalcified for dependable dating.

The object of this article is to put enthusiasts for the radiocarbon dating of postglacial and prehistorical events on their guard against assuming that the method will have no gross sources of error quite independent of laboratory procedure in the measurement of radiation. Even charcoal from alkaline regions should be acid-treated and washed to remove carbonate. Marl should not carelessly be assumed to be of organic origin. It may be partly so, to the extent that it is made of shells, but the greater part of most marl is formed incidentally through the agency of submersed plants, which disturb a complex equilibrium by removal of CO_2 used in photosynthesis and thus bring about precipitation of calcium carbonate from material that never entered into their biochemical structure. It has merely been chemically deposited, even if found in the sheaths or cell walls of algae. Except under thoroughly understood conditions, marl cannot be considered datable. Neither can *caliche*. Even peat found in close association with marl or calcareous tufa is somewhat doubtful and should be used with caution, after removal of carbonates and mechanical and chemical separation of possibly late intrusive organic constituents. The dating of peat in acid bogs is likely to be safe, if intrusive material is guarded against. Wood or charcoal found in marl or *caliche,* if decalcified, will be dependably datable, for its organic carbon will have come only from photosynthesis, but it need not be of the same age as the matrix. Precautions must be taken to detect possibilities not only of materials having had their carbon radioactivity diminished by entry of "dead" carbon, but also of having been enriched in radiocarbon content by physical and chemical processes that are constantly taking place.

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