Nuclear and Chemical Dating Techniques

Interpreting the Environmental Record

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To the memory of
Willard Frank Libby
The source of much of the inspiration and insight
recorded in this volume

FOREWORD

The ACS SYMPOSIUM SERIES was founded in 1974 to provide a medium for publishing symposia quickly in book form. The format of the Series parallels that of the continuing ADVANCES IN CHEMISTRY SERIES except that in order to save time the papers are not typeset but are reproduced as they are submitted by the authors in camera-ready form. Papers are reviewed under the supervision of the Editors with the assistance of the Series Advisory Board and are selected to maintain the integrity of the symposia; however, verbatim reproductions of previously published papers are not accepted. Both reviews and reports of research are acceptable since symposia may embrace both types of presentation.

PREFACE

When I was invited to plan a symposium on nuclear dating, it immediately occurred to me to invite my former professor, Bill Libby, to present the keynote lecture. Libby's impact on the field had been enormous, with basic contributions ranging from cosmic ray physics to the history of modern man. His discovery of the first cosmogenic nuclide in nature followed by his development of the method of radiocarbon dating resulted in Libby's being awarded the Nobel Prize in Chemistry in 1960. Since publication of his classic volume on the subject ("Radiocarbon Dating," University of Chicago Press, 1952), bienniel or trienniel International Radiocarbon Conferences have taken place—the first in Andover, Massachusetts in 1954, and the most recent in Bern and Heidelberg in 1979. (These last proceedings are published in *Radiocarbon,* Volume 22, Numbers 2 and 3, 1980.)

Although Libby initially agreed to speak at the symposium, he was unable to attend for reasons of health, and Professor H. Oeschger kindly agreed to present the keynote. Following the meeting I informed Libby of my intention to dedicate this volume to him. He was pleased and graciously submitted the historical perspective that appears at the beginning of the volume. Libby passed on in September of 1980. We shall miss him, but we shall continue to be inspired by his enthusiasm, his insight, and his breadth of interest and knowledge.

The initial title for the symposium has had a twofold expansion, to incorporate *chemical* dating techniques and *interpretation* (or modeling). The relevance of chemical dating is clear when one considers the three kinds of geophysical "clocks"—those depending on (a) the rates of nuclear transformations, (b) the rates of chemical transformations or transport, and (c) natural cycles or accumulation processes (e.g., tree rings, ocean sediment). Also, the chemical properties of the nuclear species themselves are crucial in our approach to and the applicability of nuclear dating schemes, as Libby noted in his remarks with reference to ^{14}C and ^{187}Re.

With respect to interpretation, the existence of alternative dating techniques has made clear the necessity for and the difficulty of this step. That is, nature seldom provides ideal dating systems with fixed injection rates, negligible losses, and constant temperature. As a result, simple dates based upon observed isotopic ratios and nuclear half-lives, for example, frequently require cautious interpretation before they can serve as accurate measures of age; and in the absence of adequate models, alternative dating techniques will give discrepant results. The subject of this volume thus transcends dating. As put by H. Oeschger in his keynote lecture, a simple date (or observed radioisotope concentration) is but one factor to be considered in interpreting the current or past state of the environmental system. An adequate representation (model) of the system is required, as are sufficient isotopic and physicochemical data to yield reliable estimates for the parameters of the model. Thus, there is a dualism in that an accurate age cannot generally be deduced without a suitable environmental model, but simple dates help us to construct such models and to learn more about the state of the system than simply its age.

Isotopic and chemical patterns used in conjunction with absolute or relative dating techniques are also providing extremely interesting insights into the nature of geophysical or archaeological systems at various points in time. Such patterns may reflect physicochemically induced fractionation or composition variations indicative of natural or human activities [c][1]. Some of the examples explored herein include: ^{14}C production and carbon cycle perturbations [2,13], mixing of hydrological reservoirs [2,11], the history of climate [14,15], variations and sources of atmospheric dust [10,15], sources of ancient organic matter [19], an extraterrestrial cause of the Cretaceous extinction [20], and the identification of manufacturing sources in an ancient culture [21]. Geophysical modeling, chemical pattern recognition, and time series analysis make important contributions to such investigations; and one important outcome is chronological refinement.

A principal reason for organizing the symposium at this particular time was the recent occurrence of significant advances in dating techniques. Enormous improvements have taken place in minimizing chemical contamination, and in both the measurement of extremely small differences in isotopic ratios [a], and the separation and measurement of tiny quantities of inorganic [15] and very similar organic species [19,d]. Important progress is taking place in the measurement of very small quantities of long-lived radionuclides by means of direct high-energy (accelerator) ion counting, high-sensitivity microprobe and noble gas mass spectrometry, and ultralow-level counting [Section III]. Among the most important benefits from these advances will be the ability to date samples that are quite rare or difficult to obtain (deep ice cores, precious artifacts, cometary dust, etc.) and an increase in the reliability or information content of the dates through high spatial, temporal, or chemical resolution. (The ability to date less than a milligram of carbon, for example, makes it interesting to

[1] Figures in brackets refer to chapter numbers; letters refer to Symposium papers abstracted in the ACS Book of Abstracts. The Appendix provides further notes and a classification of these references according to technique and application.

determine the radiocarbon age of individual amino acids in bone [23].) Additional information concerning accelerator mass spectrometry and selected chemical dating techniques is given in the Appendix.

Progress in the application of a multiplicity of advanced dating techniques to a given problem together with sophisticated modeling [2,11,18] promises to give us reliable information on the state and age of the system under consideration, as well as some extra degrees of freedom for model verification. When applied to natural archives [2; Section IV; c], such studies can provide vital insight concerning the present and past states of the environmental (geophysical) system; of critical importance may be information on the relative influence of man's activities and natural events on environmental contamination and climate. Finally, questions involving the history and prehistory of man and the evolution and extinction of life [Section V] are in many respects the most interesting to examine with these techniques, and they are certainly among the most challenging.

The efforts of all authors, reviewers, and other symposium participants are gratefully acknowledged. Special thanks are due Vic Viola, Juan Carlos Lerman, and Chet Langway for their assistance with the meeting. Credit for their excellent work in preparing the manuscripts for publication goes to Joy Shoemaker and Teresa Sperow of the Text Editing Facility of the Center for Analytical Chemistry, National Bureau of Standards.

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Nuclear Dating

An Historical Perspective

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I want to thank the symposium members and the Chairman, Dr. Lloyd Currie for the honor you do me.

During my work with nuclear dating in 1930, I built a Geiger Counter, and using air as a gas which is undoubtedly one of the worst possible gases, by brute force got it going using a string electrometer to detect the pulses. In a few months, however, we built a simple electronic circuit which detected and registered them on moving photographic paper using a tiny mirror glued to the needle of a microammeter. Our voltage supply was a motor-generator set and, needless to say, I several times found myself on the floor of the laboratory as a result of having touched the output electrodes. We take a great deal for granted today in electronics and voltage supplies and detection equipment. All this had to be developed, and development was initiated in this period of the early 1930's.

My professor, Wendell Latimer and I, decided that we would use the Geiger Counters to test for natural radioactivity in ordinary elements. We thought it would be a good idea to begin with the Rare Earths since as far as we could tell no one had looked at them. It had been known for many years that potassium was radioactive, as was rubidium. So the idea of radioactivity in the ordinary elements was hardly new. But a systematic search with as sensitive an instrument as the Geiger Counter seemed to be a good idea. We looked at the rare earths through the kindness of Herbert N. McCoy, who had been in the rare earth business in Chicago. Through him, we obtained samples of considerable purity of the various rare earths.

So, in the fall of 1931, spreading into 1932, we finally got going with the samples of the rare earth oxides. We built a counter with a screen instead of a solid cylinder as its wall to permit soft radiation to enter the counting volume.

The first sample we tested was samarium oxide, and we found it to be very radioactive. Now we know today that the radioactive isotope is samarium-147 with a half life of 105,000,000,000 years, and that the radiation is an emission of helium ions (alpha

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particles). It is a most remarkable radioactivity and now seems to be a useful tool in dating the earth.

We were quite elated, and it appeared that it was a rich field. Now, fifty years later, I must say that it wasn't as rich as we thought. But we have over the years discovered half a dozen natural radioactive elements, and two of these, the samarium-147 with its decay to neodymium-143 and rhenium-187 with its decay to osmium-187, prove to be of use in Nuclear Dating. The importance of rhenium is that it is iron soluble while the other radioactivities are insoluble in metallic iron. In fact, the best half life we have for rhenium-187 was obtained by measuring the osmium-187 to rhenium-187 ratio in iron meteorites which had been dated by other methods. This work was started many years ago by Dr. Herr and others in Germany. The half life is 43,000,000,000 years.

The other natural activities such as indium-115, which has a half life of 10^{15} years, are interesting in their nuclear properties but are too long-lived to be useful in Nuclear Dating. Rhenium-187 in radioactive decay has the least energetic of all known nuclear transformations – its total disintegration energy is not known but it is probably in the range of 2 to 3 kilovolts. If the electronic binding energies were not included the transformation might not occur, hinting strongly that there is a close connection between nuclear transformations and the external electrons in the atom.

In the 1930's we began a search for carbon-14 to fill an obvious blank in the isotope table, for the reason that carbon is so very important in biology – a radioactive carbon isotope longer lived than a few minutes would be very valuable as a tracer. Due to an error in theoretical judgment we failed to find carbon-14. It was later discovered by Samuel Ruben working with Martin Kamen. An interesting point about the failure was that we, Kamen, Ruben, and I, guessed the half life to be about three months. As you all know, it is 5730 years. This meant that we did not make enough of it to detect it. Kamen and Ruben bombarded graphite with a deuteron beam – a sledge hammer approach – and found it.

This development was interrupted by World War II. We resumed work on it in about 1945 at the end of the war when we went to the University of Chicago. Again, we used the screen wall counter together with a new trick to shield the mesons. We surrounded the dating counter with a cylindrical shield consisting of Geiger counters, perhaps a dozen, some two inches in diameter; this arrangement is electronically connected so that if a cosmic ray meson triggers one of the shielding counters, the dating counter is turned off. The carbon radiation is so very weak there is no possibility that it could itself trigger the shielding counters. This whole bundle was put inside a massive iron shield, and in this way we were able to measure the natural radiocarbon and to measure the radiocarbon age.

The generation process for radiocarbon in the atmosphere makes CO_2 which enters the biosphere; because of the long lifetime the mixing is essentially perfect. We assumed the rate of production to be constant which turns out to be somewhat incorrect. Variations of about 10 percent can be seen back in time to early Egyptian periods and before. The earth's magnetic field was apparently weaker then as the cosmic rays delivered to the surface and the atmosphere were more intense.

Now we have many tens of thousands of radiocarbon dates from many laboratories throughout the world and the results continue to proliferate.

One of the most interesting of the geophysics results from radiocarbon dates is the history of the sun. Apparently, it is registered in fluctuations of the cosmic ray intensity. These are fluctuations of rather short duration in terms of the radiocarbon lifetime, perhaps a century or so, and apparently they are caused by variations in the solar wind due to long-term changes in the solar emissions. This idea has been developed in some detail recently by Dr. Lal and his collaborators. It promises to give us a way of watching the history of the sun over tens of thousands of years. This fine structure on the curve of calibration was discovered by Dr. Suess and others.

In archaeology there are many applications. They are very gratifying and successful.

We have seen the development recently of a new method of measuring radioactive isotopes which promises to evaluate smaller samples than we needed before. The present method requires perhaps 10 g of wood, oil, or charcoal or whatever the material is. The newer method of measuring the carbon-14 is by direct counting of the carbon-14 atoms instead of its decays. This should allow us to use only a few milligrams. This is a wonderful development which may allow us to make major advances in many important areas where the available samples were previously too small. One important case is the organic matter in sea cores. (Many investigators think the organic matter is more reliable for dating than shell.) Measurements of variations in the carbon-14 concentration in this organic matter may allow evaluation of the history of the solar fluctuations. Other small samples of special interest are works of art and religious artifacts which are too valuable to date by the conventional method. They may be datable now.

Nuclear dating has been most helpful in establishing the history of the earth and of the moon and of the meteorites. The fact is, there is no other way of measuring their ages. Prior to the discovery of natural radioactivity in the late 19th century, indirect methods were used to estimate the age of the earth, but there were no real answers until the radioactivity of thorium, uranium, and potassium were discovered and we began to understand atomic structure and to realize that nuclear transformation was essentially independent of the chemical form.

In addition, other exciting and interesting approaches such as fission track dating and dating by means of chemical reactions occurring under proper conditions are rapidly developing. Of course, there may be as yet undiscovered techniques of great importance.

Once again, I want to thank the members of this symposium and the Chairman, Dr. Lloyd Currie.

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The Contribution of Radioactive and Chemical Dating to the Understanding of the Environmental System

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Radioactive and chemical dating methods are yielding most valuable information on the history of the earth and the planetary system. In this paper mainly methods using cosmic ray produced isotopes are discussed.

During the recent past, fluctuations in radioisotopes produced by cosmic radiation in the earth's atmosphere have been observed, the most convincing example being the fluctuations of the $^{14}C/C$-ratio observed in tree-ring samples. Such fluctuations complicate the interpretation of radioactive ages in terms of absolute ages, and their interpretation asks for the development of models considering not only isotope production variations but also the geochemical behavior of the isotopes of the different elements. For this purpose, it is useful to distinguish between noble gas radioisotopes (e.g., ^{39}Ar, ^{81}Kr), radioisotopes which get incorporated in molecules of gases and vapors (^{14}C, ^{3}H), and radioisotopes of solids (^{10}Be, ^{36}Cl) which get attached to aerosol particles and are deposited with precipitation.

In polar ice sheets air gets continuously trapped, and ice cores obtained by drilling through the ice caps therefore constitute a continuous set of ancient air samples. $^{39}Ar/Ar$ and $^{81}Kr/Kr$ measurements on these samples primarily reflect the production rates of these radioisotopes averaged over a few half-lives.

It is expected that due to the short residence time of Be and Cl in the atmosphere, ^{10}Be and ^{36}Cl measurements on ice cores will directly reveal isotope production variations. Due to dilution in the CO_2 exchanging system the atmospheric $^{14}C/C$-ratio shows a dampened response to ^{14}C production rate variations. In contrast to the noble gas radioisotopes the size of the effective dilution reservoir – atmosphere plus parts of the ocean and biosphere – depends on the characteristic

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times of the production rate variations. In addition, $^{14}C/C$ variations in atmospheric CO_2 may be caused by variations in the CO_2 exchange dynamics, as indicated by the observation of changes in the atmospheric CO_2 concentration in ice cores.

Finally a strategy for the study of the environmental system and its history is proposed. Dating methods provide the time scale for ancient system states, and fluctuations in the parameters used for dating point to important changes in system processes. Recent developments in field and analytical methods as well as model calculations promise accelerated progress regarding a quantitative understanding of processes determining our environment. This is badly needed in view of possible natural and/or anthropogenic changes with effects on society.

Radioactive and chemical dating methods have not only provided unique information on the history of man and his environment, but also on processes in the solar system and their history. It has been found however that the assumptions on which these dating methods were based are only partly fulfilled. During recent years strong emphasis has been given to studies of some deficiencies of these dating methods and their causes. They have yielded most valuable results on natural processes; an example is the ^{14}C-variations which are attributed to variations in the isotope production rate by cosmic rays on the one hand and to fluctuations in the global CO_2 exchange on the other.

During the last several decades the natural systems have been disturbed by human activities. Natural and anthropogenic disturbances of the environmental system are discussed in terms of models, and answers regarding possible negative consequences of human interactions with natural processes are searched for.

Again the atmospheric $^{14}C/C$ ratio is an excellent example. Man-induced disturbances of the environmental system lead to changes in the $^{14}C/C$ ratio which are of the order of magnitude of the natural fluctuations or even larger: the emission of ^{14}C-free CO_2 from fossil energy consumption leads to a decrease, and the emission of man-made ^{14}C from nuclear weapons testing, to an increase of the atmospheric $^{14}C/C$ ratio.

In this article, we first discuss basic dating principles and then studies based on isotopes produced by cosmic radiation in extraterrestrial matter and in the earth's atmosphere. The discussions are intended to illustrate how analytical physical and chemical studies contribute to the understanding of processes in the environmental system and their history.