Meetings

Geochronology of Marine and Fluvial Sediments

For more than 100 years, scientists have been trying to develop methods to determine the onset and duration of the Pleistocene epoch. Analysis of continental deposits is not reliable for this purpose because such disturbances as faulting, erosion, and glaciation leave only discontinuous records. Deep sea sediments, however, offer a possibility of determining sedimentation rates and absolute ages of recent geological periods. The extremely slow deposition of minerals under the protective layer of thousands of meters of sea water makes these sediments suitable material for dating. Included in the techniques for dating marine sediments are the micropaleontological method [*Science* **139**, 728 (1963)], and a method based on the radioactive decay of members of the two uranium families in the sea. The former method depends upon the characterization and distribution of foraminifera as a function of depth within the sediments. The appearances of foraminifera are related to the temperature of their environment and are correlated stratigraphically. The latter method is based on the concept that uranium is soluble in sea water; the daughters Th^{230} and Pa^{231} are insoluble and are concentrated in the sediments in a distribution which is not in equilibrium with their respective parents, U^{234} and U^{235}. Still another method, which is sometimes useful for obtaining sedimentation rates, is the ratio of Th^{230} to Th^{232}. Here, Th^{232} decays very slightly during the Pleistocene epoch, while Th^{230} decays with a 76,000 year half-life. After deposition this ratio is assumed to vary only because of the shorter half-life of Th^{230}.

Although these methods are used in many laboratories in the United States and abroad, many controversial issues exist, such as problems of sample collection and preparation, counting techniques, and the interpretation of results. A conference on the Geochronology of Marine and Fluvial Sediments was held at the Oak Ridge Institute of Nuclear Studies, 17–19 October 1963, with the purpose of discussing these questions, in order to establish items of agreement, to seek explanations of points of disagreement, and to discuss the validity of the basic assumptions on which various dating methods rest. The meeting, limited to 50 participants, was dedicated to Hans Pettersson (Goteborg, Sweden) who was in attendance. In 1937 he suggested that Th^{230} is precipitated (unsupported by its parent uranium) from the ocean onto the bottom, thus laying the cornerstone for thorium dating of the sediments. Emphasis was put on discussions and free intercourse of ideas. Six invited papers and 15 contributed papers were presented by scientists from leading institutions in this field.

The method of dating by the ratio of Th^{230} to Pa^{231} is based on the assumption that Th^{230} (commonly called ionium) and Pa^{231} are removed simultaneously from sea water soon after formation (authigenic materials) and are thus separated from their respective parents, U^{234} and U^{235}. In the sediments, each isotope decays with its own half-life of 76,000 years and 32,500 years, respectively. Provided the ratio of the uranium parents in sea water has remained constant for at least several hundred thousand years, the ratio of Th^{230} to Pa^{231} can be used for estimating deposition rates over periods of at least 200,000 years. The validity of this method rests on a few assumptions which were considered by the participants.

The longest and most involved discussions centered around the problem of separating authigenic thorium and protactinium isotopes from those isotopes of allogenic origin. It is obvious that some of these isotopes originate from allogenic minerals, such as volcanic ash, meteorites and continental detritus. E. D. Goldberg (Scripps Institution of Oceanography) presented data on samples prepared by leaching with $6N$ HCl and compared these results with those obtained by bringing the whole sample into solution by fusion methods. He found that the ratios of Th^{230} to Th^{232} were higher in the leached than in the fused samples. This is an indication that a harsher treatment brings the detrital thorium into solution. F. F. Koczy (Marine Laboratory, Miami) and most of the other participants believed that leaching (even mild leaching) dissolves some detrital thorium. Paul Antal (Marine Laboratory, Miami) found that Th^{230} was more refractory to acid leaching in deeper segments of a sediment core. He attributed this to a diagenetic induration, a process in which amorphous precipitates are converted into chemically resistant minerals. If this diagenesis causes a reduced leaching yield of Th^{230}, a large error in dating will result. Less leaching indicates apparently older ages for the sample.

The detrital contribution of thorium is most serious if ratio of Th^{230} to Th^{232} is used for sedimentation rates; the detrital contribution of Th^{230} is hard to assess. Goldberg showed, however, that dating methods with the ratios of Th^{230} to Pa^{231} and Th^{230} to Th^{232} gave the same results if proper geological considerations are observed. Sackett has shown, however, that the ratio of Pa^{231} to Th^{230} in the top of the cores is seldom equal to the predicted ratio. He attributes this result to the mixing of the sediments, which would upset the ratio of Th^{230} to Th^{232}, but less seriously affect the ratio of Th^{230} to Pa^{231}.

The general consensus was that the best method is the dissolution of the total sample and subsequent correction for the isotopes of detrital origin. Different approaches for arriving at this correction were discussed. Elizabeth Rona *et al.* (Oak Ridge Institute of Nuclear Studies) are investigating the validity of using the ratio of Th^{230} to Pa^{231} for dating in the Gulf of Mexico. They reported on the analysis of samples (thorium, protactinium, and uranium) along the Mississippi River, the principal contributor of sediment material to the Gulf. Using the ratios Th^{230} to Th^{232} and Th^{230} to Pa^{231}, they hope to make corrections on the sediments of the open Gulf for terrestrial contributions of these isotopes. Thurber found activity ratios of Th^{230} to Th^{232} in the Mississippi and other Gulf Coast waters to be about one, although this ratio varied considerably in other bodies of water.

Aaron Kaufman (Lamont Geological Observatory) discussed this problem from a different aspect. He determined the isotopic ratios of thorium, radium, and uranium on 25 selected samples of the fluvial carbonate sediments in the Great Basin. These sediments were also dated by C^{14} age procedures. In nearly every case, in which the Ra^{226} and Th^{230} were in equilibrium, the data lead to the assumption that the initial activity ratio of Th^{230} to Th^{232} is 2.2. Thus, one can use the Th^{232} data for these selected samples to convert Th^{230} to authigenic Th^{230}. Applying this correction, the ages derived from the ratio of Th^{230} to U^{238} are found to be equal to 80 percent of the C^{14} ages.

Disequilibrium of members of the uranium family can be used to date fossil marine carbonates. The principle of the method is that uranium is in low, but measurable, concentrations in modern shells, whereas Th^{230} is below the limit of detection. As the shells get older, Th^{230} grows in them, and the ratio of Th^{230} to U^{238} is then a measure of the age of the fossil shell. Results of analysis of 12 fossil sediments were presented by Herbert Potratz (Washington University, St. Louis) and Richard Blanchard (U.S. Public Health Service). Ages, based on the ratio of Th^{230} to U^{234}, agreed in most instances with ages estimated on stratigraphy. Wallace Broecker (Lamont Geological Observatory) found that fossil coral without calcite shows uranium concentrations close to the level contained in living coral. However, recrystallized coral samples, compared to their living equivalents, are deficient in uranium. Broecker reported that unrecrystallized material could apparently be dated with reliability to 300,000 years, and by using the ratio of U^{234} to U^{238} even beyond this range.

Until recently, the ratio of U^{234} to U^{238} has been assumed to be equal to 1. Several cases of disequilibrium between these two isotopes have been reported recently. To assess the authigenic origin of Th^{230} and to correct for uranium-produced Th^{230}, the concentration of its parent U^{234} must be known. Deviation of the uranium ratio from 1.0 was discussed. Goldberg reported that the ratio for water from the Atlantic, Pacific, and Indian oceans is 1.14 ± 0.01; a Red Sea sample showed a ratio of 1.18 ± 0.01. Ratios of U^{234} to U^{238} were determined on lake and river samples by David Thurber (Lamont Geological Observatory). He found isotope fractionation resulted in activity ratios of U^{234} to U^{238} that were greater than 1, in nearly all cases being greater than 1.2 and ranging as high as 6.

Considerable isotope fractionation was reported by John Rosholt (U.S. Geological Survey, Denver) in roll features (uranium-bearing fluvial sandstone) in Shirley Basin, Wyoming. In these samples, the U^{234} is found to be deficient in altered ore sands by as much as 70 percent, while calcite ore sand shows only a slight deficiency. A small amount of uranium in unaltered sand, above and below the roll feature, do not show isotopic fractionation. The reasons for fractionation in the samples were discussed by Rosholt, and several mechanisms were proposed. Any environment which contains intimately mixed sediment and hydrological phases for a sufficient length of time may lead to the enrichment or depletion of U^{234} in one phase or another. Thurber suggested that the recoil of the nuclides during alpha decay makes the daughter U^{234} nuclide more available to weathering than the parent U^{238}. Subsequent preferential leaching leads to the deficiency or enrichment of U^{234}.

Methods of chemical separation of nuclides in dating were discussed in some detail. Two approaches to the determination of the ratio of Th^{230} to Pa^{231} were presented. William Sackett (Lamont Geological Observatory) used a direct chemical separation of protactinium and thorium. Goldberg in a few experiments and Ronas group in all experiments used an indirect method which involves separating thorium chemically and then counting the Po^{215}, a daughter of Th^{227}. This isotope (Po^{215}) can be well characterized by its alpha emission of 7.35 Mev energy in alpha spectroscopy. In both cases, a thorough knowledge of thorium and protactinium chemistry is necessary. Harold Kirby (Monsanto Research Corporation, Miamisburg, Ohio) discussed the chemical similarities and differences of these two elements; the latter far outnumbered the former. Protactinium can be separated from thorium by the hydrolysis of protactinium in strong hydrochloric acid, in which process the thorium remains in solution. There different behavior in ion exchange and solvent extraction techniques is also exhibited. Kirby concluded by stating that the wet chemical behavior of thorium and protactinium denies the existence of an actinide series of elements because protactinium and thorium have little in common with each other or with the elements of higher atomic number, from uranium on. This dissimilarity of the chemistry of thorium and protactinium raises the speculation as to whether the two isotopes, once reaching the ocean bottom, behave in the same way in the sediments. Richard Ku suggested that uranium and possibly thorium may migrate in the sediments.

The use of isotopes as tracers for yield determinations was also discussed, and it was pointed out that the lack of exchange between the tracer and the isotope, whose yield has to be determined, may lead to serious errors.

All the participants used either gridded ionization chambers or solid-state detectors for determining the alpha spectra of their samples. Equally good results were obtained with both detectors provided that infinitely thin and homogenous samples were available. The method of choice for the preparation of thin samples is usually electrodeposition. Stephen Kim (Oak Ridge Institute of Nuclear Studies) discussed how he used dilute hydrochloric acid and ethanol as an electroplating solution. He varied temperature, *p*H, current, and time of electrodeposition and found that under the best conditions very thin samples can be prepared with a yield of 80 to 100 percent for uranium, thorium, and protactinium.

It is apparent that dating of marine sediments by the ratio of Th^{230} to Pa^{231} cannot be extended beyond a few hundred thousand years. Peter Deines (Pennsylvania State University) outlined a program in which Be^{10} is used. It is formed in the atmosphere by cosmic rays and has been detected in deep-sea sediments through its β activity. It has an approximate half-life of 2.7×10^6 years. The change in concentration of this isotope in profiles of cores whose age fell beyond the limit of Th^{230} measurement can be used to date sediments with ages ranging to millions of years. The concentration of Be^{10} in the sediments is very low, and it is obvious that methods of ultrahigh sensitivity have to be used. Deines described a mass spectrograph now under construction that is designed to reach this sensitivity. With this instrument determination of Be^{10} will be 10 to 1000 times as great as is possible by measurement of its radioactivity and dating sediments of ages up to 20 million years may be possible.

The conference was stimulating, ideas were exchanged, and information shared. Some of the controversial issues

—the use of whole sample versus leaching techniques, correction for allogenic thorium and protactinium, and the need for determinations of isotope fractionation in dating the samples—were clarified. Among the problems that still remain unsolved are the varying results obtained in similar samples and sample preparation by different methods and measurement. It was generally agreed that it may be possible to clarify controversial issues by the preparation and inter-laboratory distribution of samples, such as red clay marine carbonates and marine limestones. These samples will be distributed among laboratories which are active or interested in dating marine sediments. Results of these investigations should be presented at a later date, possibly at a conference to be convened as a follow-up of this meeting.

ELIZABETH RONA

Oak Ridge Institute of Nuclear Studies, Oak Ridge, Tennessee

Gas Chromatography

Advances in gas chromatography were the subject of an international symposium held in Houston, Texas, 23–26 March 1964. The foreign countries represented were Canada, West Germany, Holland, Israel, Italy, South Africa, Switzerland, the United Kingdom, and Russia.

For several years it has been predicted that gas chromatography will become an analytical routine of established technique and instrumentation. The discussions indicated that this stage has still not arrived. The most noticeable current trend is the resurgence of gas-adsorption chromatography after a period of eclipse by gas-liquid chromatography. A. V. Kiselev (University of Moscow) reported studies of the adsorption of vapors on silica gels of differing porosity and water content. He found that the heats of adsorption of alkenes or ethers, or other polar adsorbates, varied with pore size and water content of the silica in a way that differs from the variation for alkanes or nonpolar adsorbates. This finding illustrates the role of specific physicochemical interactions between the surface and different chemical groupings in the adsorbate. It is the existence of such specific interactions between solutes and variously chosen stationary liquids that has given gas-liquid chromatography its recent dominance. It appears that adsorbents might also be manufactured to provide similar specificity.

Capillary columns have recently been used for gas-adsorption chromatography. H. Bruderreck (Scholven-Chemie, Germany) described capillary columns coated with graphitized carbon black, which could be used to separate hydrocarbons from C_1 to C_8 in groups according to carbon number. Many of the effects of surface nonhomogeneity—for example, peak tailing—can be removed by impregnating the graphite with a small proportion of nonvolatile liquid. G. P. Cartoni (University of Rome) described how glass capillary tubes can be used as adsorbent columns if they are first etched with sodium hydroxide solution; this etching produces a large hydroxylated surface area.

L. B. Rogers (Purdue University) reported on the use of adsorbents that had been prepared by careful elimination of water or other volatile ligands from various inorganic salts and complexes—for example, $Cu(Py)_2(NO_3)_2$. The resulting adsorbents all have a very small capacity but provide specific separations of mixtures not otherwise easily separated—for example, 2- and 3-alkanones of the same carbon number. Rogers emphasized that the recent development of gas-adsorption chromatography has been possible only because of the previous development of detectors (such as the flame ionization detector) sensitive enough to handle the minute concentrations of vapor required to keep within the linear region of the adsorption isotherms of low-capacity adsorbents. Also, it is becoming apparent that the curvature of adsorption isotherms on most of the adsorbents used in gas chromatography is due far more to heterogeneity of the surface than to incipient saturations, as described by the Langmuir isotherm.

Discussions on the development of detectors dealt with ways of making them easier to calibrate, or responsive only to selected groups of compounds, so that they could be used for limited qualitative identification. Bruderreck classified detectors into those sensitive to concentration (such as the catharometer) and those sensitive to the rate of flow of the mass of vapor through them (such as the flame ionization detector). At fast flow rates, detectors of the second class are more sensitive, but at very slow flow rates of carrier gas it may be that a concentration-sensitive detector of what is normally regarded as low sensitivity (for example, the catharometer) is more responsive than an ionization detector sensitive to mass flow.

J. E. Lovelock (University of Houston) described the construction of an ionization cross-section detector with a volume of only 10 microliters. A. Karmen (Johns Hopkins University School of Medicine) reported on a device by which the flame ionization detector could be made sensitive to halogen compounds. Metal gauze covered with sodium hydroxide is placed in the flame; halogens cause increased volatilization of the metal, and the ions of the metal are detected in a second flame above the first. The principles of the device were demonstrated by an impressive set of colored slides of apparatuses in which bunsen burners were used as the flames. Also discussed was a detector which depends on changes in the velocity of ultrasound, and one in which the vapors to be detected exchange with nonvolatile radioactive material in the column, after which the radioactivity of the exchanged material is detected in the effluent stream.

Several papers indicated a renewal of interest in the factors that produce the dispersion of chromatographic peaks in packed columns. In this connection, the theoretical work published by J. C. Giddings (University of Utah) in the last few years has clearly been a stimulus. Giddings discussed the "C-term," a quantity whose magnitude is relevant in determining the resolution secured in chromatography at fast flow rates of the mobile phase, and thus relevant in studying how to perform analyses in the minimum time. It has been concluded that the part of the "C-term" which is attributable to slow lateral diffusion of vapor in the gas phase is of primary importance in determining the performance of preparative columns. It also appears that flow turbulence may well be relevant in gas chromatography at fast flows. Previously, it had been thought that the Reynolds number for flow in gas-chromatographic columns is so small that all flow is laminar, but it was pointed out that in packed beds of irregular particles, turbulence may occur at quite small Reynolds numbers. Evidence for turbulence in pipelines carrying natural gas at high pressure and high speed was presented by regarding these pipelines as giant capil-