RESEARCH PROGRAM, GEOCHRONOLOGY LABORATORIES
UNIVERSITY OF ARIZONA

By

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Geological sciences have been primarily concerned with three dimensional methodology in the study of the earth and its history; the fourth dimension, time, has been generally considered in a relative manner only. Allied sciences are adding a more definite time scale with which geologic phenomena can be correlated. The Geochronology Laboratories employ, or will employ shortly, many of the major "dating" methods developed by these allied sciences in attempts to supply a sharper focus on this fourth dimension. The methods used range from stratigraphic and paleontologic techniques, whereby events are merely placed in their correct relative position or sequence, to techniques in geochemistry and dendrochronology, whereby events are "dated" in terms of years. Research facilities available, plus those being planned and assembled, enable the Laboratories' personnel to study many varieties of temporal problems in historical field exercises.

The Geochronology Laboratories have their office, research library, paleontological, and palynological sections on Tumamoc Hill in buildings originally constructed and used by the Carnegie Institution for a desert laboratory. These buildings have been made available to the University by the Rocky Mountain Forest and Range Experiement Station, United States Department of Agriculture. The geochemical section of the Laboratories, including the Carbon 14 Age Determination Laboratory, are housed in the Geology Building on the University campus. The dendrochronological research is carried on in cooperation with the Laboratory of Tree-Ring Research, also housed on the campus. Research projects in the Laboratories are interdisciplinary and interdepartmental, the extent being dependent on the nature of the research. Four broad lines of approach to temporal problems are being followed. These include: 1, dendrochronology; 2, palynology; 3, paleontology; and 4, geochemistry.

I. DENDROCHRONOLOGY

Dendrochronology is limited in time and areal application. Nevertheless, it has been used in geological studies such as in rates of sedimentation and erosion, seasonal climatic changes, advance and retreat of glaciers, and the dating of recent geologic events. For example, Sunset Crater, an extinct cinder cone near Flagstaff, was known to have erupted in the recent past, although the exact time of the event could not be determined. When archaeologists discovered houses buried by the ash fall from that eruption, the idea of dating the eruption by the tree-ring method came to mind. The dating of this event has occupied a number of people at various times over the years. Tree-ring specimens from buried houses were dated and the dates ranged up to A.D. 1046. Houses constructed on top of the ash fall contained dated specimens which went back to A.D. 1071. This bracket of time, A.D. 1046-1071, had to be the period when the actual eruption took place. It was not until Paricutin erupted in 1943, however, that much credence could be placed on the interpretation of evidence remaining at Sunset Crater. Studies in archaeology, climatology, dendrochronology, ecology, and vulcanology were made on Sunset Crater remains,and, using Paricutin as a guide, tree-ring specimens from this area which grew through the bracket of time, A.D. 1046-1071, were restudied. An anomalous growth pattern, non-climatic in its characteristics, was found in a number of these specimens to have been laid down following August of A.D. 1064. It is believed that the eruption occurred during the fall, winter, or spring of A.D. 1064-5.

Another example of the use of tree-ring dating of geologic events is that of dating sediments recently deposited in the canyons and basins in northeastern Arizona, northwestern New Mexico, and elsewhere. The geologic dating of these sediments was dependent on a series of complex deductions based on climate and erosion. Considerable variation in interpretation exists among the individuals who have made such studies and their estimations of the time of deposition are great.

Numerous archaeological sites are located on the surface of these canyon bottoms, the latter having remained more or less stable since the time of construction of these sites. Tree-ring dates on material removed from these houses range from circa A.D. 900 up to historic times.

Arroyo cuts in the bottom sediments have revealed numerous earlier structures buried at varying depths in the sediments. Tree-ring dates have been determined on many of these buried structures, and the story of the deposition is gradually being determined through the use of archaeology, climatology, dendrochronology, palynology, and sedimentation. Present interpretation of available evidence indicates that following circa A.D. 650, changes in storm patterns (or some similar shift in climatic patterns) caused extensive erosion in the highlands and deposition in the areas where stream gradient changed enough to cause stream load to be deposited. This deposition, ranging up to thirty or so feet in places, continued until approximately A.D. 850, when it ceased except for local arroyo cutting and filling. For all practical purposes, however, there has been no subsequent deposition in such places as the Tsegi Canyon in Arizona and Chaco Canyon in New Mexico, the two areas wherein the time controls are best.

Research of this type is being carried on constantly in the field of dendrochronology, and often information on events of particular importance in other fields is to be had.

II. PALYNOLOGY

Research in palynology is progressing rapidly and numerous projects are underway. A major project is being directed toward a study of the postglacial pollen sequence in southeastern Arizona. The pollen grains and spores are extracted from various sediments in the intermontane basins in which archaeological materials have been found. The use of archaeological stratigraphy as a stratigraphic control gives assurance against any time lapse of long duration, at least, in the sequence. This study should yield information on the climatic change, as revealed by wind pollinated species, which has taken place in this area since the last glaciation. The use of Carbon 14 dating techniques on materials taken from the various archaeological horizons will give a time scale in terms of years with which the pollen sequence can be correlated. This study will be coupled with archaeological data and, through this combination, the biostratigraphic sequence of fine detail will be worked out for this area. This will be of aid in interpreting older phenomena in which such controls are lacking.

Numerous tests have been made on various sediments found over the State in order to determine if pollen grains and spores are present. These organic microfossils have been found in limestone, mudstone, shale, sandstone, and sand dunes; in fact, they have been found in most sediments where no oxidation has occurred. Oxidation is the only chemical action that is known to destroy the exine of the grains; the exine being immune to decomposition by the action of any known acid.

Results of these tests have been so encouraging that an intensive program in palynological stratigraphy is being planned and organized for the Cenozoic, Mesozoic, and Paleozoic eras. A large reference collection of materials from key beds will have to be made before any concrete results can be expected, however, and this will take time and effort. The Laboratories will test any sediment submitted, providing the donor can give exact location of the sample in the stratigraphic column within the section.

Species identification of grains is not essential for such stratigraphical work, the application being similar to the use of conodonts in that respect. Morphological characteristics are important, however, because it is essential that variations of the same type of grain caused by mechanical injury, such as erosion, be recognized. Considerable work in this type of application has been conducted by commercial industry personnel, but no publication of any consequence has been made on that research. Thus it will be necessary to duplicate much of the work.

III. PALEONTOLOGY

Concentrated effort is now being made to study vertebrate fossils found in the State, particularly those belonging to the Cenozoic era (studies on Mesozoic and Paleozoic materials will not be completely shunned while this work is being carried out, but the concentration of effort will center on the Cenozoic). Vertebrate paleontology is the only method now capable of furnishing a definite geologic time scale for the period, hence it must serve as the center around which other geochronological studies pertaining to this period will be integrated. A specific study of the Cenozoic materials is now getting underway. The study has three major objectives: 1, to establish a chronological time scale of geologic and biologic usefulness; 2, to determine the environment and life forms; and 3, to relate past climate and ecologic phenomena to the chronologic sequence.

A statewide program of collecting, preparing, and study of specimens from known localities will commence in the summer. Particular attention will be given to collect as complete an assemblage of fossil specimens as possible from each locality, and ample matrix will be included on which palynological and geochemical tests will be conducted. Many of these localities have already yielded pollen grains in preliminary testing. It is hoped that with the information derived by fossil fauna and flora, basic research in geochemical methodology will yield information on the "chemical" climate which could then, in turn, be applied elsewhere. This integrated approach should yield information on the climate and sedimentational history of the area, as well as on the evolutionary patterns of the flora and the fauna. Geologic mapping of the localities investigated will be beyond the facilities of the Laboratories; however, it is hoped that other agencies can be induced to cooperate on that phase of the study.

Once the biostratigraphic sequence is determined from known localities wherein control situations exist, extrapolation of these data can be made into other areas which lack such controls.

IV. GEOCHEMISTRY

By

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I. INTRODUCTION

A number of geochemical dating techniques are now available which extend dating over the entire range of geologic time with the possible exception of the late

Pliocene - early Pleistocene epochs. These methods are the C^{14} method (0 -40,000 years), the Ionium method (0 -500,000 years), the potassium-argon method (Present lower limit, "P.L.L.", 1.5 million years for mica), the rubidium-strontium method (P.L.L. 50 million years for glauconite), the alpha-helium method (P.L.L. = ?), the chemical-lead method (P.L.L. = 25 million years), and the various isotopic lead methods (P.L.L. = 50 million years).

The multiplicity of available methods has the advantage of allowing internal cross checks by different methods on different minerals which respond differently to the same perturbation. As an example of a concordant situation, in which there appears to be little perturbation after mineral genesis, we may take the results from the Keystone region of the Black Hills of South Dakota and contrast this with the results from the Huron Claim district of southwestern Manitoba (Table I). There appears to have been a geologic event subsequent to mineral genesis, in the case of the Huron Claim minerals, which resulted in lead loss from the uraninites and argon loss from the micas and feldspars. Strontium appears to have been quantitatively retained by the micas, but a slight loss is evident for the feldspar. It has been pointed out that the most probable age of the Huron Claim minerals is 2650± 40 million years, and that the discordancy could be explained by a moderate rise in temperature (ca. 200°C.) 500 million years ago lasting for a period of 1 million years (P.W. Gast, Absolute Age Determination from Early Precambrian Rocks, Columbia University Ph.D. thesis, 1957). The geology of the Huron Claim area is now being investigated to see if field evidence bears out this conclusion (F.D. Eckelmann, private communication).

It is important that geochemical dating be accompanied wherever possible by adequate geologic and mineralogic investigations. A single age derived from a dating method should be considered to be only an "apparent" geologic age. The "absolute" age in many cases can only be deduced from a thorough geochemical-geological-mineralogical investigation. For example, Schuermaun et. al. (Geol. en Mijnbuuw, V. 18, p. 312, 1956) processed two tons of the Lausitz granodiorite of Germany and found two distinct types of zircon (type A and B). According to the authors, type A gave an apparent geochemical age of 280 million years, whereas the apparent age of type B was 550 million years. The authors concluded that they were dealing with two distinct generations of zircon -- an allogenic and an authigenic variety. Similarly, G. Tilton of the Carnegie Geophysical Laboratory (private communication, 1957) found that the micas from the Baltimore gneiss gave consistent potassium-argon and rubidium-strontium ages of 350 million years, whereas the zircon lead isotopic ages were concordant at about 1000 million years. It is interesting that the Precambrian igneous rocks to the west in the Appalachians are also of Grenville Orogeny age (1000 million years). It is quite probable that the original sediments comprising this formation were derived from this Precambrian terrain. In this case the age of the rock (Baltimore gneiss) must be distinguished from the age of at least one of the mineral phases (zircon) of which the rock is comprised.

Mineralogic factors must be evaluated in order to interpret age relationships. For example, Tilton et. al. investigated both metamict and non-metamict zircon from the Wichita Mountains in Oklahoma (G. Tilton et. al., Trans. Amer. Geo. Union, V. 38, p. 360, 1957). The lead isotopic ages of these zircon ages agreed at 550 million years. On the other hand, the author (P. Damon and J. L. Kulp, Trans. Amer. Geo. Union, V. 38, p. 945) obtained an alpha-helium age (540 million years) for the non-metamict zircon which was in good agreement with the isotopic ages, but the apparent helium age of the metamict zircon was only 2 million years. This is not difficult to comprehend because it is known that helium can readily diffuse through the disordered (glassy) solid state.

Another example of a mineralogic factor which can result in a gross dating error is the ability of the beryl-like minerals to occlude volatiles and permanent gases within the "tunnels" formed by their six-membered silica tetrahedron rings. For example, 90% of the helium and 44% of the argon contained within cordierite schist from Gealkup in the Orange River Valley, South Africa, was occluded at the time of mineral genesis rather than being generated by radioactive decay within the mineral (P. Damon and J. L. Kulp, in press, Amer. Mineral, May, 1958). T. Hoering of the University of Arkansas (private communication) has also shown that this schist contains 720 ppm of nitrogen as compared to an average of 15 ppm for igneous rocks. Quite obviously this schist is not suitable for age determination by the potassium-argon method. On the other hand, it can be shown that potash micas, for example, do not occlude excess gases and retain the argon produced within them by the decay of potassium-40 (P. E. Damon and J. L. Kulp, Amer. Jour. of Sci., V. 255, p. 697, 1957).

In summary, if the available techniques are applied with discrimination, and, if adequate attention is given to the mineralogic and geologic factors involved, geochemical age determinations provide a powerful tool for the solution of geologic problems. On the other hand, a mechanical application of these techniques can lead to serious and even absurd errors.

The following geochemical research has been initiated or is planned:

1) Correlation and chronology of the igneous and metamorphic rocks of Arizona.
2) Correlation and chronology of ore deposits of Arizona.
3) Development and application of methods for the dating of sediments.
4) Development and application of methods for the dating of basalt flows.

II. DETERMINATION OF THE AGE OF IGNEOUS AND METAMORPHIC ROCKS OF ARIZONA

This work will consist of two parts. A cooperative investigation already in progress with Columbia University by the Rubidium-Strontium method, followed by Potassium-Argon and Alpha-Helium age determinations here at the University of Arizona upon the completion of the new geochemical laboratory.

The following are the specific objectives of this investigation:

1) To establish whether there is evidence for one or more than one major period of Precambrian orogeny in Arizona.

At the present time there are only a few age determinations available which indicate that the intrusion of some pegmatites and granites into the Vishnu and Yavapai schists took place approximately contemporaneously at 1400 million years before Present. It has been assumed by most geologists, but not proven, that the Yavapai, Vishnu, and Pinal schists are the essentially contemporaneous products of the Mazatzal orogeny. These schists cover large areas ranging from the northwestern to the southeastern corner of Arizona. It will be sufficient here to show that they are or are not contemporaneous in their type localities.

2) To establish whether or not the granitic rocks which are intrusive into the Precambrian terrain are invariably either Precambrian or post-Paleozoic.

It is believed that, in addition to the Precambrian Mazatzal orogeny, there was possibly Nevadan and certainly Laramide-Tertiary orogenies in Arizona but no orogenesis during the Paleozoic. This belief has led to the assumption that an intrusive into the Precambrian metasediments in the extensive regions where there are no

Paleozoic sedimentary rocks must either itself be Precambrian or post-Paleozoic. An attempt is made to distinguish between these two supposed alternatives on the basis of appearance alone (e.g. weathering). For example, in the Wallapai Mining District, Cerbat Mountains of Mohave County, the Chloride granite is Mesozoic-Tertiary according to Thomas (B. E. Thomas, Economic Geology, V. 44, no. 8, p. 663, 1949) and Precambrian according to Dings (Geol. Survey Bull., 978E, 1951). A similar situation exists in the Harcuavar Mountains.

3) To establish whether or not there is geochemical evidence in the post-Paleozoic igneous and metamorphic terrains for both the Nevadan and Laramide orogenies, or whether as some believe, there is Laramide-post-Laramide orogenesis but no evidence for Nevada orogeny.

It has not yet been proven that there are any Nevadan age ore deposits, although the Bisbee and Ajo districts have been tentatively (although with much opposition) listed as Nevadan. These areas will be investigated.

4) To settle the question of the age of certain key formations concerning which the disagreement is so great as to leave doubt as to whether or not they are Precambrian or post-Paleozoic.

The best example of this is the Catalina gneiss of the Santa Catalina Mountains. Much of the geologic interpretation of this area hinges upon the solution of this critical problem.

III. CORRELATION AND CHRONOLOGY OF ORE DEPOSITS

Hurley (Nuclear Geology, J. Wiley & Sons, N.Y., H. Faul editor, 1954) has reviewed the status of the helium method of age determination up to 1953. It was quite apparent at that time that most minerals and rocks did not yield reliable helium ages. In general a minimum age is obtained as a result of the leakage of helium from minerals. Thus the helium age method which had been widely and somewhat uncritically accepted has tended to become discredited by recent workers.

The deflation of stock in the helium age method has tended to obscure certain potentialities which have not yet been fully exploited. Several minerals commonly appeared to give fairly reliable results with occasional anomalies. It is far from certain that the anomalies are not due in most cases to experimental inaccuracies and in other cases to fallacious geologic interpretation. For example, a younger-than-expected age can be due to recrystallization. In this case a definite geologic event is being dated. Several examples can be given where a supposedly incorrect helium age determination has later been found to be correct after subsequent reinterpretation of the geology.

The author has reinvestigated the helium ages of several minerals which appeared most promising. A source of discrepancy in the helium ages for zircons was found to be the incomplete recovery of helium from the mineral (P. E. Damon and J. L. Kulp, Determination of Radiogenic Helium in Zircon by Stable Isotope Dilution Technique, Trans. Amer. Geo. Union, V. 38, p. 945, 1957). Errors in the determination of the alpha activity were also discovered in the older work. The results of this reinvestigation have shown that a helium age method is still possible for zircon.

Magnetite shows greater promise than zircon for the helium age method. In 1943 Hurley and Goodman (P. M. Hurley and C. Goodman, Helium Age Measurement. I. Preliminary Magnetite Index, Bull. Geol. Soc. Amer., V. 54, p. 305) made a series of measurements on 81 samples of magnetite and sulfide minerals - 70 were in reasonable agreement with geologic expectation, 5 were anomalously high and 6 anomalously low.

The low values are probably due to recrystallization and can yield valuable information. However, the high values, if correct, present an obstacle to the method. For this reason the author reinvestigated magnetite from the Sudbury, Ontario area. Four of the five anomalously high magnetite samples measured by Hurley and Goodman were from the Sudbury region. The most anomalous magnetite sample was a separate from the Levack norite at Sudbury. Significantly, their sample was not pure, containing less than 50% magnetite. A pure sample, separated from the norite by the author, failed to yield the anomalously high age obtained by Hurley and Goodman. However, an investigation of ferromagnesian minerals by the author has disclosed that the amphiboles commonly give anomalously high helium and potassium-argon ages. This can be readily comprehended from the structure of the amphiboles. It is well known that in the ideal tremolite structure the alkali cation position is completely vacant and only partially filled in the hornblende structure. It can thus be concluded that the anomalous result obtained by Hurley and Goodman was not due to excess gas in the magnetite but was rather from amphibole impurity which had not been quantitatively removed from the separate.

Thus there appears to be no valid objection to the general applicability of the helium age method to magnetite and the sulfide minerals providing that: (1) care is taken to separate the pure species, (2) experimental errors are kept to a minimum, (3) the geological factors are correctly interpreted.

The helium method makes possible much more extensive investigation of the age of ore deposits than is possible if work is limited solely to the isotopic or chemical dating of uranium ores. It is expected that a proper application of the helium method combined with other geological investigations can lead to a reliable correlation of ore deposits.

The initial stage will consist of an investigation of magnetite and sulfide minerals from typical ore deposits where the geology has been most thoroughly investigated. The experience gained from this work will then be applied to ore deposits where the geology is unknown or doubtful.

The experimental technique for magnetite has already been worked out and applied by the author. Helium will be released directly by decomposition and fusion in an R.F. induction furnace. The gases will be thoroughly purified and measured by isotope dilution technique. For this purpose an all metal trochoidal mass spectrometer capable of being degassed at 450°C. will be constructed. The helium will be determined by the static rather than the flow method, thus greatly increasing the sensitivity. The helium production rate will be determined directly by alpha counting using specially designed low level alpha counters. Adequate care will be taken to separate pure mineral species rather than to deal with the impure separates which has made for difficulties in the past.

IV. DEVELOPMENT AND APPLICATION OF METHODS FOR THE DATING OF SEDIMENTS

During the last decade it has become increasingly apparent that supposedly high temperature minerals may grow under low temperature conditions in the presence of sufficient water. Thus the potash micas, feldspars, garnet, and even magnetite and zircon, have been claimed to exist as authigenic minerals in sediments. Geochemical dating techniques afford a tool for determining whether or not a mineral is authigenic or allogenic, and when adequate mineralogic criteria are available to clearly demonstrate the authigenic origin of a mineral the sediment itself may be directly dated by geochemical methods.

So little is known about this subject that it is best to start with a review of the literature followed by field and laboratory petrographic and mineralogic investigation before initiating the geochemical phase of the work. An area suitable for the initial stages of this work is being sought at the present time.

V. DEVELOPMENT AND APPLICATION OF METHODS FOR THE DATING OF BASALT FLOWS AND TUFF BEDS

Virtually no work has been done on the geochemical dating of basalt flows and tuff beds. However, there are methods which could be applied to the correlation and chronology of volcanic sequences. Several possible methods which have occurred to the author are as follows:

(1) Age determination of recent flows by measuring the ratio of radium to barium in plagioclase phenocrysts resulting from the diadochic replacement of calcium by these cations.
(2) Carbon 14 measurements on carbonaceous material in buried soils between basalt flows and tuff beds.
(3) Alpha-helium determinations on zircon and magnetite extracted from flows.
(4) Potassium-argon measurement of biotite separated from flows.

The radium and Carbon 14 method would cover and time region from present to 40,000 years. The helium might possibly be successful throughout the Pleistocene and the potassium-argon method can be applied to pre-Pleistocene beds.

It is expected that this work will be initiated in the summer of 1958 in the Flagstaff volcanics by Mr. Bruno Sabels as a doctoral dissertation. Sabels will initiate the work with a thorough chemical and petrologic study of the flows. An attempt will be made to correlate the flows by chemical composition, mineralogical composition, and paleomagnetism as well as by the geochemical dating methods outlined above.

Table I. Example of concordant and discordant age relationships (age in millions of years).

Locality	238/206	235/207	207/206	Pb/U	K/A	Rb/Sr
Black Hills	1615 (u)	1615 (u)	1622 (u)	1610 (u)	1620 (m)	1690 (l)
Huron Claim	1860 (u)	2170 (u)	2505 (u)	--------	2330 (m)	2650 (m)
					2440 (l)	2680 (l)
					834 (f)	2340 (f)

u = uraninite, m = muscovite, l = lepidolite, f = microcline feldspar

All results from Lamont Geological Observatory, Palisades, New York.