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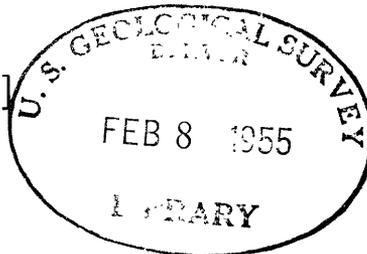
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SUMMARY OF THE RESEARCH WORK
OF THE TRACE ELEMENTS SECTION
GEOCHEMISTRY AND PETROLOGY BRANCH
FOR THE PERIOD JULY 1-SEPTEMBER 30, 1951

By
John C. Rabbitt

This preliminary report is released without editorial and technical review for conformity with official standards and nomenclature, to make the information available to interested organizations and to stimulate the search for uranium deposits.

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INTRODUCTION

This report summarizes the research work of the Trace Elements Section, Geochemistry and Petrology Branch, for the period July 1 - September 30, 1951. Earlier summaries, with similar titles, have been issued in this same series under numbers 148-A (June 1951), 151 (May 1951), and 167 (September 1951).

The research work of the Section consists of the following laboratory and related field studies:

1. Mineralogic, petrologic, and geochemical investigations of radioactive rocks, minerals, ores, and waters.
2. Investigations of chemical methods of analysis for uranium, thorium, and other elements and compounds in radioactive materials, and related chemical problems.
3. Investigations of spectrographic methods of analysis for a wide variety of elements in radioactive materials.
4. Investigations of radiometric methods of analysis as applied to radioactive materials.

Much of the work in progress is in the nature of investigations supporting field appraisal of known uraniferous deposits. A program of fundamental research in the geochemistry of uranium, recently approved by the Division of Research of the U. S. Atomic Energy Commission, is now getting started, and some of this work is described in this report.

Special thanks are due members of the Section who supplied material for this summary and who are referred to in the text.

MINERALOGIC AND PETROLOGIC INVESTIGATIONS

Introduction

The mineralogic and petrologic investigations of the Section, under the direction of Theodore Botinelly, are organized in the following projects:

1. The phosphate project
2. The Colorado Front Range project
3. The Colorado Plateau carnotite project
4. The properties of uranium minerals project
5. The lignite project
6. Miscellaneous projects

The laboratory work is supplemented by field work by members of the Section, and it is closely coordinated with the work of the resident field geologists in the areas studied.

The phosphate project

In the continuing study of the Florida phosphate deposits by Z. S. Atlschuler field examination indicates that the "Pleistocene" sands grade into the underlying leached-zone material of the Bone Valley formation. In addition unleached material equivalent to leached material underlying the "Pleistocene" sands shows a high content of quartz. A size-analysis study of the sands and underlying leached material was made to show whether the sands are related to the leached material. The analyses so far completed show a striking similarity in size and sorting characteristics of the basal "Pleistocene" sands and the underlying leached-zone material. It is probable that the basal sands were derived from the Bone Valley formation by weathering which removed all of the material except the quartz. Further size analyses and heavy-mineral studies will be made to determine how much of the "Pleistocene" sands have been derived from the Bone Valley formation by weathering.

Samples were collected during May from representative localities in the "hardrock" phosphate belt of Florida for mineralogic study. All but two of the samples were collected from abandoned phosphate pits and mine workings. Radiometric determinations show a range in percent equivalent uranium from 0.000X to 0.014; most of the samples fall in the range 0.002 to 0.006. Three samples (HR4a, b, and c) from near Floral City, Citrus County, run 0.014, 0.010, and 0.010 percent equivalent uranium, respectively. The samples consist of hard quartzose phosphatic clay. The following minerals have been

identified in these samples: apatite, montmorillonite, quartz, and wavellite. Quartz comprises about 40 percent of the rock and it is probable that the phosphatic material contains 0.02 to 0.03 percent equivalent uranium.

Altschuler spent one month of the quarter doing field work on the northwest phosphates. Samples were collected for studies of areal variations in lithology of the Phosphoria formation and for studies of weathering and depositional features. Work on size variation and chemical composition of phosphate pellets from the Phosphoria was temporarily suspended during the assignment of M. E. Thompson for the summer months in Alaska to mineralogic work for the Alaskan Trace Elements project. A report on the study by Robert S. Jones of the absorption of uranium by apatite in Phosphoria phosphate pellets is still in preparation.

Due to the resignation of Sol Silverman and Jeanne Weiser (now Mrs. Sol Silverman) work on the synthesis of apatites has been temporarily suspended. A summary of the work on differential thermal analysis as applied to Phosphoria material is being prepared by Mrs. Silverman.

Bottom samples in the Gulf of Mexico collected in the vicinity of Sarasota, Florida, by the U. S. Fish and Wildlife Service have been made available to Altschuler for study. The depths at which the samples were collected range from 2 to 100 fathoms.

The material is calcareous and quartzose; most of the samples contain shell fragments. Three of the samples contain detrital apatite nodules similar to those found on the beaches near Sarasota and to the nodules in the Hawthorn limestone. No phosphate minerals

were identified in any of the other samples. The uranium content of all the samples is 0.001 percent or less. The P_2O_5 content ranges from 0.06 percent to 0.21 percent. No areal distribution pattern of P_2O_5 is evident.

Studies were made on the apatite-free samples to determine the mode of occurrence of the phosphorus. Blackened limestone crusts present in most samples were found to contain minute black inclusions that are similar to glauconite as determined by optical and spectrographic means. Residues from these black crusts obtained by leaching with dilute HCl and triammonium citrate solutions contain compact black inclusions containing about 5 percent P_2O_5 . X-ray patterns of these compact black inclusions show the presence of only aragonite and calcite.

The study of these and other bottom samples from the Gulf of Mexico will continue.

The Colorado Front Range project

Work on this project in previous summary reports has been described under three headings:

1. Relation of pitchblende deposition to radioactive bostonite dikes in the Central City district, Colorado
2. The radioactivity of fluorite from the Blue Jay mine, Jamestown, Colorado
3. The use of the Ra/U ratio of pitchblende as a quantitative measure of the recent leaching

The studies in this project have now been broadened to other areas in the Front Range and the headings above will be dropped.

George Phair and Kiyoko Onoda (now Mrs. Tetsuo Shimamoto) did field work during most of the summer in the following areas in Colorado: Central City and Blackhawk, Gilpin County; Idaho Springs, Clear Creek County; Fort Collins, Larimer County; and Boulder, Boulder County.

Samples of porphyry dikes and larger intrusive porphyry masses were collected and field radiometric counts were made at each outcrop studied. Radiometric and chemical analyses are now being made of these samples and mineralogic work is in progress.

Samples were collected from the mine dumps in the Quartz Hill area near Central City. These mines have produced small amounts of uraninite and the mine dumps have local areas that show high radioactivity. This high radioactivity is thought to be due to residual concentrations of radium. The samples are being studied to check this assumption.

Samples of hard and of sooty uranium ores were collected from the stockpiles of the Copper King mine in Larimer County. This mine produces zinc ore and uraninite. Samples of the wall rock, country rock, and different types of ore were collected for mineralogic study.

Samples of purple fluorite were collected from the dumps of the Chase, War Dance, and Iroquois mines, south of Central City. At these mines the fluorite occurs as a gangue mineral with pyrite and tellurides. The samples will be studied in connection with the continuing study of radioactive fluorite in the Front Range.

Samples were collected from the radioactive cerite deposits in the pre-Cambrian Silver Plume granite near Jamestown, Colorado. Laboratory work by Shimamoto was started on these samples in September. Heavy-liquid and magnetic separates of the samples gave a final concentrate running 0.46 percent equivalent uranium. The minerals of

this separate have been tentatively identified as bastnaesite and the cerian hydroxylapatite, called britholite, which is supposed to have the formula $3(\text{Ca,Ce})_3(\text{Si,P})_2\text{O}_8\text{Ca}(\text{OH})_2$. This mineral has not been previously reported from North America. The Jamestown britholite (?) gives an apatite X-ray powder pattern with spacings close to those of a britholite specimen from Narijasik, Greenland, and a lessingite ($\text{H}_2\text{Ca}_2\text{Ce}_4\text{Si}_3\text{O}_{15}$) specimen from Kychtyn, Ural Mountains, U.S.S.R. According to Goddard and Glass,^{1/} an isomorphous series exists between cerite and lessingite; a similar series may exist between cerite and britholite. Spectrographic analysis of the Jamestown britholite (?) shows:

Ce > 10 percent
 Si, Ca, P = 1.0 - 10 percent
 Gd, La, Nd, Y, Th, Al, Eu, Mn, Pb, U = 0.1 - 1.0 percent
 Fe = 0.01 - 0.1 percent

Si is greater than or equal to 10 percent; Ca is slightly less than 5 percent; P is close to 2 percent. Chemical analysis for P shows 2.7 percent.

Optical data for britholite are inconclusive; it is variously reported as uniaxial and as biaxial with a small 2V. The indices are approximately $n_0 = 1.777$ and $n_E = 1.772$. The optical properties of the Jamestown mineral agree with these data.

The bastnaesite of the Jamestown deposit has been identified by X-ray study. It is variable in color from yellow green to dark red brown and is extremely fine grained. The X-ray patterns give some

^{1/} Goddard, E. N., and Glass, J. J., Deposits of radioactive cerite near Jamestown, Colo.: Am. Mineralogist, vol. 25, pp. 381-404, 1940.

indication that the material may be partly metamict. Further work will be done on these minerals.

The Colorado Plateau carnotite project

The report being prepared by Lorin Stieff and T. W. Stern, "A preliminary report on the lead-isotope ages of the Colorado Plateau carnotite ores," is being enlarged to include data resulting from work done during the quarter in the field and laboratory and also work to be done in the next quarter. It is hoped to have an interim report on this subject ready by January 1952.

Study of Salt Wash material and several specimens from the Shinarump conglomerate suggested the need for greatly enlarging the representation of Triassic ores in the isotope investigations. This followed from the similarity in lead-uranium ratio ages and in the isotopic composition of the extracted lead, the appreciable difference in age of the enclosing sediments, and because of the rapidly growing economic importance of the Triassic deposits. The summer's field work was planned to include many of the more important pre-Morrison uranium deposits on the Colorado Plateau.

Mill-pulp samples representing hundreds of tons of ore from individual deposits and splits of ore samples from the same deposits were collected.

Among the samples obtained were two specimens of pure, hard, massive uraninite. One sample was taken from the Happy Jack mine, San Juan County, Utah, and the other from the Shinarump No. 1 claim, Grand County, Utah. It is believed that these two massive uraninite

samples are the first to be collected from the Shinarump conglomerate of the Colorado Plateau and identified and analyzed for Pb/U determinations. On the basis of Pb isotope abundance determinations made at Oak Ridge and chemical determinations for Pb and U made in the Washington Laboratory, ages calculated from the Pb^{206}/U^{238} and Pb^{207}/U^{235} ratios after tentative corrections for common lead range from 65 to 75 million years. A report summarizing this work is in process. The conclusions in the report are quoted here:

If the ages, calculated from the foregoing data, for the uraninites in the Shinarump conglomerate and similar ages for the carnotite deposits of the Salt Wash sandstone member of the Morrison formation (Upper Jurassic) are close to the true ages of these ores, then these uranium-bearing minerals were probably introduced into the sediments in early Tertiary time. This interpretation differs markedly from the earlier conclusions, based on field evidence, by Hess (1914, p. 687), Webber (1947), and Fischer (1950, p. 3), that the uranium minerals were introduced into the sandstones of the Colorado Plateau during or soon after deposition of the sandstones. Further careful evaluation of the apparent conflict between field and laboratory data and a search for additional critical evidence are needed to establish a satisfactory hypothesis of origin of these ores.

Work is in progress on additional uraninites and possible uraninites from the Todilto limestone of Upper Jurassic age collected near Grants, McKinley County, New Mexico; the Morrison formation, Gray Dawn mine, San Juan County, Utah, submitted by C. A. Razor of the Colorado Raw Materials Operations, A.E.C.; from the Shinarump conglomerate, Cato Sells mine, Tract 1, Apache County, Arizona, collected by Ralph Smith of the Climax Uranium Co.; from Monument No. 2 mine, Apache County, Arizona, collected by Donald Johnson of the Geological Survey; and from Garo, Park County, Colorado, collected by V. E. McKelvey of the Geological Survey.

Studies on samples from the Happy Jack mine by Stieff, Stern, and Alice Weeks show that the ores contain chalcopyrite, bornite, chalcocite, covellite, pyrite, galena, sphalerite, chalcantite, halotrichite, and zippeite as well as massive and sooty uraninite. This mineral assemblage suggests that this copper-uranium deposit may be of hydrothermal origin and has undergone supergene enrichment and surface weathering.

Ore from the Hideout No. 1 claim in the White Canyon area, Utah, contains bornite, chalcopyrite, malachite, and azurite; the uranium mineral (or minerals) has not been identified yet. Ore from the Scenic No. 4 claim in the same area contains jarosite and cobalt and aluminum sulfates.

The Monument No. 2 mine in the Monument Valley area, Utah-Arizona, contains both red and yellow rauvite ($\text{CaO} \cdot 2\text{UO}_3 \cdot 6\text{V}_2\text{O}_5 \cdot 20\text{H}_2\text{O}$), hewettite, and much black and reddish-black ore containing vanadium, uranium, and iron. X-ray powder patterns of separates from this material do not match any known iron-vanadium minerals.

The Skyline claim in this area contains a coarse arkosic sandstone with disseminated chalcopyrite. The feldspar of the sandstone has been considerably altered and many of the quartz grains show secondary growth. The open joints are coated with alunite presumably formed by the action of water from the sulfide ore on the potash feldspar in the arkose or on potash clay.

The new Whitney mine in Long Park in the Uravan mineral belt is of interest because it is deeper than the other mines in the vicinity and thus the ore has presumably undergone less alteration by surface water. The ore is black and contains montroseite, pyrite, carbonaceous

material, and several unidentified minerals. The pyrite is reported to contain gold. Work is in progress to identify the uranium minerals and to confirm the presence of gold in the pyrite as auriferous pyrite might be an indication of hydrothermal origin of the deposit.

In the Club group (Bitter Creek and Mill No. 1 mines) samples of the orange efflorescent minerals proved to be pascoite. Samples were collected in a number of mines in the group to determine the distribution of pascoite and hummerite.

Arsenic was found in a rich rauvite specimen from the Arrowhead mine. Arsenic has been reported in several widely separated areas in the deposits of the Plateau and the significance of its occurrence is under study.

As study of the mineralogy of all these ores progresses, the laboratory evidence indicating a hydrothermal origin for these deposits becomes stronger. Work is now in progress on the paragenesis of all these deposits and on the temperature of deposition of the ore minerals.

Charts showing the identification of water-soluble and clay minerals in the formations above and below the Morrison formation, prepared by Alice Weeks (as indicated in TEIR-167, p. 20) were distributed during the quarter to the field party in Grand Junction. The charts were discussed by Alice Weeks with members of the field party and a report on this phase of the work is in preparation.

Work is also in progress by Alice Weeks on wall-rock alteration in the Plateau deposits.

The properties of uranium minerals project

Writing of the monograph "The Mineralogy of Uranium" began during the quarter according to the plan described in TEIR-167, pp. 23-24. Clifford and Judith Frondel of Harvard, George Switzer of the National Museum, and Rabbitt and Botinelly of the Survey are cooperating in writing the monograph.

Joseph Berman continued his studies of metamict minerals. Most of the quarter was spent in checking and indexing X-ray powder patterns obtained so far in the investigation. A paper by Berman, "Studies of metamict minerals. I Methods and procedures" will be given at the November meeting of the Mineralogical Society of American in Detroit. The abstract follows:

Review of the literature reveals much confusion in the identification of metamict minerals and in interpretation of results obtained by X-ray powder studies. The need for standard methods of studying these minerals is urgent.

On the basis of X-ray powder patterns it is ascertained that many minerals containing radioactive elements show various degrees of "metamictization." Reproducible powder patterns are obtained after ignition of these minerals in certain gases under controlled temperatures. The current practice of heating a sample in a crucible over an open flame may lead to misinterpretation of resultant patterns.

Our studies have indicated that ignition of the noncrystalline specimens results in randomly oriented crystallized material. None of our samples recrystallized as single homogeneous crystals, although this phenomenon has been reported for gadolinite. The results also indicate that different gases have a marked influence on crystallization and on dissociation of some material.

The apparatus used for heating consists of a tube furnace that can be set up for heating in air or in any other atmosphere. The samples are first crushed and then heated at temperatures below their fusion points for a short time both in air and in uncontaminated helium. It was found that both helium and commercial nitrogen, which for a time was used as the inert gas, contain sufficient water to oxidize the specimen being heated.

The resulting X-ray powder patterns are strong with sharp diffraction lines indicating good crystallinity after ignition. Preliminary data on allanite, brannerite, davidite, fergusonite, samarskite, thorite, and zircon are given.

A selected bibliography on metamict minerals is nearing completion by Theodore Botinelly.

The lignite project

The field conference on the uraniferous lignites of the Dakotas met as scheduled in North and South Dakota and Montana the week of July 15, 1951. The conference, arranged by Maurice Deul of the Trace Elements Section, and conducted by Norman M. Denson, Fuels Branch Project Chief, was also attended by the following people:

Howard D. Zeller, Geologist in charge of core drilling
 James M. Schopf, Chief of the Fuels Branch Coal Geology Laboratory at Columbus, Ohio
 Theodore Botinelly, Acting Head, Mineralogy and Petrology Unit, Trace Elements Section
 Farrington Daniels, Department of Chemistry, University of Wisconsin
 Donald Peppard, Chemistry Division, Argonne National Laboratory

Most of the promising lignite exposures were visited. Denson pointed out the field relations of the lignites to associated sediments and explained his theory that the contained uranium was derived from the overlying sediments which are in part tuffaceous and are believed to be uraniferous.^{2/} A discussion was held on how the uranium might be held in the lignite. Simple absorption or the formation of a secondary

^{2/} Denson, N. M., Bachman, G. O., and Zeller, H. D., Summary of new information on uraniferous lignites in the Dakotas: U. S. Geol. Survey Trace Elements Memorandum Rept. 175, 1951.

uranium mineral was thought to be unlikely. Daniels and Peppard agreed that base exchange probably plays a part. This possibility will be studied.

Lignite outcrops were visited in North Dakota at Sentinel Butte, Medicine Pole Hills, Lodgepole Hills, Rhame, and north of Bowman; in Montana at Capitol Rock; and in South Dakota at Slim Buttes, Cove Hills, and Fossil Tooth Gulch. Samples were collected at these places by the party and scintillometer and beta-gamma meter readings were observed at each site.

All agreed that a broad-scale investigation of the lignites will require close coordination of the cooperating units and that no one unit has all the facilities to conduct satisfactorily an independent study of the whole problem. The problem involves coal petrology, paleobotany, adsorption studies, chemical, spectrographic, and radiometric analyses, mineralogic studies including nuclear emulsion techniques, mass spectrographic determination of organic compounds in the lignites, metallurgical investigations, X-ray studies, and other techniques of geologic and physico-chemical studies along with field geologic work. Hence it was agreed that certain studies could best be done by one or another of the cooperating units. Some overlapping of effort will be unavoidable but will be kept to a minimum by rapid dissemination of information as the work progresses.

A periodic report will be prepared by Deul and issued to all those concerned with the problem. The first report, now in preparation, will briefly review the development of the project and will summarize the data so far accumulated by the Trace Elements Section, the Fuels Branch

field party, the Coal Geology Laboratory, Farrington Daniels, and the analyses by the Bureau of Mines. In TEIR-167 it was said that "six selected samples of lignites were ashed and the ash analyzed both chemically and spectrographically. Results of this work will be given in the next quarterly report." Since then, chemical and spectrographic data have been obtained on many more samples of ash, and much of this data will be given in Deul's forthcoming report. It is therefore not thought necessary to include it here.

It has been impressed on all concerned that samples received for study should be lignites generally representative of minable material and that large homogeneous samples should be split into appropriate sizes for all the laboratories to study so that all are working on comparable materials. A large 1000-pound sample is being collected for metallurgical study.

A system has been set up in the Trace Elements Section Washington Laboratory for the orderly and routine analysis of the lignites and associated sediments for the different field parties of the Fuels Branch working on lignites, not only in the Dakotas but also in other States. By the end of the quarter more than 800 samples had been received. Many of these have been analyzed radiometrically and chemically and have been checked for 69 elements by the semiquantitative spectrographic method. The rest of the samples are in process.

The distribution of effort in this project by the different cooperators is described in TEIR-167, pp. 25-27.

Miscellaneous projects

Professor E. S. Larsen, Jr., spent some time in the field during the quarter on the Colorado Plateau and in the Colorado Front Range. On his return to Washington he began investigation of the distribution of uranium in igneous rocks by subjecting samples from the southern California batholith to a weak HCl leach to determine the effect of such leaching on the radioactivity. It was found that for many samples the radioactivity was reduced as much as 90 percent by such treatment and studies are in progress to determine the manner of occurrence of the radioactive material in these samples. This investigation will involve a careful determination of the radioactivity in the separate minerals and in the different size fractions as well as chemical uranium determinations, nuclear emulsion studies, and X-ray and electron microscope and electron diffraction studies to find a solution to this fundamental problem which is basic to all future work on this project.

Work done by Larsen on the determination of the geologic age of igneous rocks by the application of isotope-dilution techniques developed by Harrison Brown and his colleagues at the Institute of Nuclear Studies, University of Chicago, is described in an abstract to be given at the Detroit meeting of the Mineralogical Society of America in November, entitled "Isotopic composition of lead and the ages of minerals in a pre-Cambrian granite," by Harrison Brown, Mark G. Inghram, Esper S. Larsen, Jr., Claire Patterson, and George Tilton. The abstract follows:

Techniques have been devised for the analysis of micro quantities of lead and uranium in granitic materials using isotopic tracers. The general method consists of equilibrating known micro amounts of lead or uranium highly enriched in a single isotope with known amounts of the sample, chemically isolating the element, and measuring the change in the isotopic composition of the tracer. Chemical procedures, which progressed from a macro to a micro scale, and surface ionization techniques in a mass spectrometer of a very high sensitivity were used. The concentration and isotopic composition of lead and uranium in mineral separates of a Canadian granite have been studied. These data have given the lead-uranium and lead-lead ages of the minerals. The data have also given the isotopic composition of a non-ore lead of known pre-Cambrian age, and the isotopic composition of non-ore uranium.

No work was done during the quarter by Z. S. Altschuler on further studies of phosphate rock from Mona Island, B. W. I.

A study was undertaken during the quarter by John B. Lyons and Elizabeth B. Jaffe on the crystallography of attapulgite by electron diffraction methods. Single-crystal and powder patterns were photographed and measured, and the effects of heating and of high vacuum (as used in the electron diffraction unit) on the diffraction patterns were determined. A report on this work is in preparation.

CHEMICAL INVESTIGATIONS

Methods of analysis project

Fluorimetry

Work continued in fluorimetry in the Washington Laboratory by Irving May and Mary H. Fletcher consisting of making minor modifications to existing instruments to make them more compact, stable, and versatile.

Methods of uranium and thorium analysis

Work continued by Mary H. Fletcher and F. S. Grimaldi in the investigation of colorimetric and fluorimetric reagents for the rapid determination of thorium. Six additional reagents were thoroughly tested which, on the basis of earlier tests, had shown some promise. None of these reagents proved desirable. During September work was started on the synthesis of a few organic compounds which, on the basis of their structure and previous information on similar structures, may give sensitive tests for thorium.

The study by J. J. Rowe of the effect of possible interference of arsenate ion in the volumetric determination of uranium was completed, and a report on the conclusions reached is in process. The tentative abstract of the report is as follows:

Arsenate ions in sulfuric acid solution do not interfere in the volumetric determination of uranium when zinc amalgam reductors are used. Tests on zinc reductors amalgamated with 2 percent, 3 percent, and 10 percent by weight of mercury indicate that the arsenate ion is reduced slightly but this interference is overcome during the aeration of the solutions after passage through the reductors and prior to titration.

An investigation of the fluorimetric determination of uranium in saline and nonsaline waters was begun in September by Audrey Pietsch and F. S. Grimaldi. Two methods of concentration were studied:

1. Precipitation of uranium with ammonium hydroxide, using aluminum as a carrier
2. Precipitation of uranium as the phosphate, using aluminum phosphate as a carrier

Procedure 2 was found to be better in every respect and the results obtained on preliminary experiments indicate good recovery. Procedure 2 is now being tested thoroughly and no difficulties in its successful application are anticipated.

Methods of analysis for aluminum and phosphorus

The investigation by Henry Mela, Jr., of the molybdenum blue method for the determination of micro amounts of P_2O_5 in the presence of As and Si in sea water continued. Tests were made to determine the efficacy of As^{+5} reduction with formic acid, potassium iodide, sodium nitrite, and sodium meta bisulfite. Potassium iodide proved to be the best in the suppression of As activity up to about 20 micrograms; higher quantities were not tested. Tests for the suppression of Si interference at varying acidities were not encouraging. Results indicate that As can be controlled successfully by reduction to As^{+3} with potassium iodide but that Si, which is expected to be in excess over As in sea water, will interfere. Tests will be made to determine the possibility of eliminating Si interference by combining the Si as H_2SiF_6 .

Methods of analysis for miscellaneous elements and compounds

Work continued by Henry Mela, Jr., and Claude Waring on the chemical-spectrographic determination of small amounts (0.001 percent and more) of individual rare earths in phosphate rocks. The first phase of the work was described in preceding summary reports. The second phase of the work consisted of the chemical concentration of the rare earths prior to their incorporation in an Al_2O_3 matrix for

spectrographic analysis. The concentration procedure was first tried on several levels of yttrium and cerium concentrations and good recoveries were made in spectrographic analysis. As little as 0.02 mg of each rare earth (the smallest quantity tested) was satisfactorily recovered. The concentration method was also tested on several concentration levels of Pr, Gd, Nd, Sm, La, Dy, Eu, Yb, and Th, and the spectrographic recoveries were satisfactory. The third and final phase of the investigation is now under way and consists of the following steps:

1. Careful determination of what rare earths occur in phosphate rocks
2. Quantitative analysis for rare earths of a selected series of phosphate rocks by the proposed procedures
3. Spiking of these samples with different amounts of rare earths and determining if the amounts added are quantitatively recovered.

The study of a volumetric method for the estimation of oil yield in oil shales was completed by Frank Cuttitta and a report on the subject is in process. A tentative abstract of this report is as follows:

A method is presented for the volumetric estimation of the oil yield of oil shale. The oil shale is distilled in a closed test tube and the oil extracted with ethyl acetate. The ethyl acetate is volatilized on a steam bath, and the oil residue is centrifuged in a graduated tube at 1500 rpm while still hot. The volume of the oil yield is read directly off the calibrated stem of the centrifuge tube. The method yields much the same results as the Fischer assay in a much shorter time. It is applicable to shale and phosphatic shale.

No work was done during the quarter on the determination of small amounts of lead (0.1 to 10 ppm) by microchemical methods.

A volumetric method for the determination of fluorine was set up and tested in the Denver Laboratory by Lewis Rader and his associates. A separation is made by distillation from perchloric acid, essentially by the Willard and Winter method except for the addition of steam rather than water to the distilling flask to control the temperature. The titration is with standard thorium nitrate at a controlled pH (method of Matuszak and Brown) to the end point of alizarin. Steps have been taken to have a specially designed, all-glass apparatus built. Temperature is controlled in this apparatus by a thermoregulator in addition to the steam distillation. The design was furnished by E. J. Fox, U. S. Department of Agriculture, Beltsville, Md. In connection with the method it has been found that a more accurate standardization of the thorium nitrate solution can be made by determining the thorium content rather than by standardizing by titrating sodium fluoride.

Quality of analysis project

No work was done on this project during the quarter beyond making many chemical checks for the Spectrography Unit.

High-index liquids project

The primary goal of the high-index liquids project, the development of complete series of liquids with indices from 1.72 to 2.00, has been attained. Additional work will be done from time to time with major emphasis on the development of end-member liquids with indices above 2.00. A series of papers on the liquids work is being prepared for publication in the American Mineralogist. The first of these

"Immersion liquids of high refractive index," by Robert Meyrowitz and E. S. Larsen, Jr., appeared in volume 36, September-October 1951, of that journal, pp. 746-750.

SPECTROGRAPHIC INVESTIGATIONS

The coverage of the semiquantitative method has been increased to 69 elements by the addition of Ru, Rh, Pd, Os, and Ir to the 64 elements previously covered. A list of the 69 elements and the sensitivity of the method for each element is given in table 1. This list will be revised from time to time as sensitivities are improved. Experiments with this method have shown that calcium phosphate, or calcium, or phosphorus, have an enhancing effect on the gallium spectral lines. The extent of this enhancement is not known at present; probably gallium results given at the bottom of one percentage bracket should be near the top of the next lower bracket when phosphate rocks are analyzed. A few chemical checks were made and the results were lower than the spectrographic results by about one-half of a percentage bracket. However, chemical analysis for gallium is not too reliable for trace amounts. Further investigation of this problem will be made.

Development by Jules Stich of the so-called single-grain method continued. Standard plates for 55 elements have been prepared so far for use with the Gaertner prism spectrograph, thus making the method semiquantitative rather than qualitative. This method is particularly useful for the analysis of small mineral grains and X-ray powder spindles.

In connection with the study of the spectrographic determination of trace amounts of lead by Claude Waring and Helen Worthing, additional

Table 1.--Standard sensitivities for the elements determined by the semiquantitative spectrographic method.

Note: It is possible to detect some elements below the values listed, as the standard reference plates were prepared on the basis of 10 percent increments.

<u>Percent</u>	<u>Percent</u>
Ag - 0.001	Mo - 0.001
Al - 0.0001	Mn - 0.001
As - 0.1	Na - 0.001 <u>1/</u> (0.1)
Au - 0.01	Nd - 0.01
B - 0.001	Ni - 0.001
Ba - 0.0001	Os - 0.1
Be - 0.0001	P - 0.1
Bi - 0.001	Pb - 0.01
Ca - 0.001	Pr - 0.01
Cb - 0.01	Pt - 0.01
Cd - 0.01	Rb - 0.01 <u>1/</u> (10.0)
Ce - 0.1	Rd - 0.01
Co - 0.01	Re - 0.1
Cr - 0.001	Rh - 0.01
Cs - 0.1 <u>1/</u> (1.0)	Ru - 0.01
Cu - 0.0001	Sb - 0.01
Dy - 0.01	Sc - 0.1
Eu - 0.01	Si - 0.0001
Er - 0.01	Sm - 0.1
F - 0.1 <u>2/</u>	Sn - 0.01
Fe - 0.001	Sr - 0.01
Ga - 0.01	Ta - 0.1
Gd - 0.01	Tb - 0.01
Ge - 0.001	Te - 0.1
Hf - 0.1	Th - 0.1
Hg - 0.1	Ti - 0.001
Ho - 0.01	Tl - 0.1
In - 0.001	Tm - 0.01
Ir - 0.1	U - 0.1
K - 0.01 <u>1/</u> (1.0)	V - 0.01
La - 0.01	W - 0.1
Li - 0.0001 <u>1/</u> (0.1)	Y - 0.001
Lu - 0.01	Yb - 0.0001
Mg - 0.0001	Zn - 0.01
	Zr - 0.001

1/ A second exposure is required for the high sensitivity listed.

2/ A third exposure is required for the fluorine estimation.

work is planned to determine the effect of aqua regia on the lead content of zircon. Previous tests showed that some zircons contained the same amount of lead before and after treatment. Other zircons lost considerable amounts of lead when acid treated, but most of these zircons seemed to have a geologic age close to the expected age, after the loss of lead, suggesting the presence of impurities containing lead.

No work was done during the quarter on the determination of thorium in samples high in uranium (by Claude Waring, Charles Annell, and Helen Worthing) pending the receipt of a special thermometer which is on order. Similarly, no work was done during the quarter on the determination of impurities in uranium as a means of handling complex refractory oxides with complex spectra (by Annell and Worthing) and on the detection of trace amounts of thorium without prior chemical concentration (by Waring, Annell, and Worthing).

Work continued on the automatic scanning of the semiquantitative plates and progress will depend on the successful solution of mechanical difficulties.

In the continuing evaluation of spectrographic analyses 100 chemical check analyses were made on samples on which routine semiquantitative determinations were made. Borderline anomalies were found for phosphorus in some samples and for aluminum and iron in others but in general the results were good. A comparison of semiquantitative analyses made on splits of 99 samples in both the Denver and Washington Laboratories is now under study.

A report by Tennyson Myers and Paul R. Barnett of the Denver Laboratory on contamination in grinding, under the title "Contamination

of rock samples during grinding as determined spectrographically," is in process. Further investigation of contamination in grinding is in progress. Large samples of five suitable rocks (massive quartz, Table Mountain basalt, Golden - Boulder Creek granite, quartzite, and Silver Plume granite) have been collected for use in tests on new or modified grinding machinery. Rock powders have been prepared by (1) heating, quenching in distilled water, grinding in agate mortar, (2) reduction in jaw crusher, grinding in agate mortar, and (3) reduction in the usual grinding machinery. These samples will be analyzed spectrographically.

RADIOMETRIC INVESTIGATIONS

The characteristics of the apparatus set up for the determination of absolute alpha activities of low orders of magnitude are still being studied by Jim Bracken and William R. Champion. The emanation properties of zircon are also under study in connection with the work of Professor Larsen on the radioactivity of the accessory minerals of igneous rocks.

A system for the identification of radioactive isotopes is being designed by Bracken and Champion. The system will consist of a linear detector, pre-amplifier, and amplifier feeding into an oscillograph. A photograph of the cathode-ray tube face can then be analyzed for pulse height and density, thus giving the energy of the emitter and its concentration. Long exposures will be possible for samples of low activity.

Bracken and Champion of the Washington Laboratory and John W. Rosholt of the Denver Laboratory cooperated in installing in the Denver Laboratory two radon-counting units. A plan is under way by Rosholt

to determine thorium and Pb^{210} (RaD) simultaneously from aliquot portions of samples prepared for radium analysis. In practice such determinations, together with chemical determination of uranium, should allow calculation of the component strength of all the long-lived isotopes of the uranium and thorium series. By assuming that the short-lived elements are in equilibrium with their long-lived parents, it may thus be possible to get a complete analysis of the source of the radioactivity.

Work continued on the development of a rapid radiochemical method for the determination of uranium and thorium in monazite by Francis J. Flanagan, Jesse Warr, and F. S. Grimaldi. A study was made of more rapid methods of taking the sample into solution and precipitating the radium isotopes. Two procedures were tried:

1. Fluxing with a sodium peroxide - sodium carbonate mixture and eventual precipitation (using barium as a carrier) as the sulfate. The ignited precipitate is counted 25 hours after precipitation which is taken as time zero (T_0).
2. Fluxing with a sodium fluoride-potassium pyrosulfate mixture and direct precipitation as the sulfate from a diluted solution of the melt and counting the ignited precipitate as above.

Procedure 2 seems to give the better results. The activity of the precipitates was checked as a function of time, and it was found that there is no increase in counts when the precipitate was filtered and counted after standing 16 hours.

The effect of Ra^{226} has been evaluated by precipitating out this isotope from a standard uranium ore with a barium carrier. It was found that the Ra^{226} added 160 cpm/0.1 percent uranium to the counts

obtained from the radium isotopes from the thorium series at the time of counting (25 hours). Preliminary calibration charts have been established for both the Ra²²⁶ and for a series of chemically analyzed monazites. It was found that the radium isotopes from monazites (corrected for Ra²²⁶) will give about 500 cpm for each percent of thorium with the apparatus used. Chemical recovery of the barium sulfate is better than 98 percent. Recovery of the radium isotopes, when known amounts are added to solutions containing the equivalent of 50 mg of barium sulfate, must be checked.

At present the method will work for thorium in 28 hours if a chemical fluorimetric determination is made of the uranium content and the count equivalent of the uranium present is subtracted from the counts obtained from the radium - barium sulfate precipitate. Work is contemplated using alpha counts to discriminate between the uranium and thorium series in the precipitate.

Flanagan is designing several types of tube-and-sample holders for pin-based and non-pin-based tubes in order to cut down the mortality of the Geiger tubes used in routine beta-gamma counting.

In the Denver Laboratory, Lewis Rader and his associates have prepared 16 AX-size cores, in one-foot lengths, and containing four different amounts of uranium for use as standards in the scanning of drill cores at Grand Junction, Colorado. Fine quartz sand, quartz flour, cement, and uranium ore were mixed with a minimum amount of water and the mass allowed to set in forms. Radiometric and chemical tests of the completed cores indicate that segregation found in previously prepared cores has been largely overcome. However, the problem of preparing core sections that are uniformly smooth has not been solved.

Flanagan has compiled data for southeast phosphates on the comparison between radiometric and chemical uranium determinations made in both the Denver and Washington Laboratories, and the data are being statistically analyzed. Similar compilations and studies are planned for the analytical results for shales and for the northwest phosphates.

REPORTS

Reports issued from July 1, 1951, to September 30, 1951, in the U. S. Geological Survey's Trace Elements Investigations Report and Trace Elements Memorandum Report series are as follows:

<u>TEIR</u>	<u>Title and author</u>	<u>Date</u>
118	The quantitative determination of calcite associated with carbonate-bearing apatites, by Sol R. Silverman, Ruth K. Fuyat, and Jeanne D. Weiser (also submitted for publication in American Mineralogist)	August
153	The fluorimetric determination of uranium in shales, lignites, and monazites after alkali carbonate separation, by Norma S. Guttag and F. S. Grimaldi	August
167	Summary of the research work of the Trace Elements Section, Geochemistry and Petrology Branch, for the period January 1 - June 30, 1951, by John C. Rabbitt	September
<u>TEMR</u>		
149	Physical and chemical comparison of modern and fossil tooth and bone material, by Elizabeth B. Jaffe and A. M. Sherwood	August
250	Numerical summary of the analytical work of the Trace Elements Section, Geochemistry and Petrology Branch, for fiscal year 1951, by John C. Rabbitt	August

<u>TEMR</u>	<u>Title and author</u>	<u>Date</u>
305	Further uranium determinations on sea water samples by Gerta Koczy, translated by John B. Lyons	September
312	An outline of a research program on the cosmic abundances of nuclear species, by Hans E. Suess	September

The following reports were approved for publication by the Director of the Geological Survey:

Strontian apatite, by E. S. Larsen, Jr., Mary H. Fletcher, and E. A. Cisney, approved for publication in the American Mineralogist.

Hydrothermal uranothorite in fluorite breccias from the Blue Jay mine, Jamestown, Colorado, by George Phair and Kiyoko O. Shimamoto, approved for publication in the American Mineralogist.

The following report was published:

Immersion liquids of high refractive index, by Robert Meyrowitz and E. S. Larsen, Jr., Am. Mineralogist, vol. 36, nos. 9 and 10, pp. 746-750, 1951.

The following reports were in process as of September 30, 1951:

1. Bibliography of metamict minerals, by T. Botinelly
2. Some factors in the differential leaching of uranium and radium in pyritic mines and mine dumps, by George Phair
3. USGS Bulletin--Contributions to Geochemistry: Methods of analysis for uranium and thorium developed by the U. S. Geological Survey, edited by F. S. Grimaldi, Irving May, and Jane Titcomb
4. Further studies of the distribution of uranium in rich phosphate beds of the Phosphoria formation, by M. E. Thompson
5. Absorption of uranium by pelletal phosphate, by R. S. Jones
6. Contamination of rock samples during grinding as determined spectrographically, by A. T. Myers and Paul R. Barnett
7. The spectrographic determination of trace amounts of lead in zircon and other minerals, by C. L. Waring and Helen Worthing

8. A semiquantitative spectrographic method for the analysis of minerals, rocks, and ores (II), by C. L. Waring and C. S. Annell
9. Summary of uranium mineralogy related to deposits studied by the Geological Survey through 1950, by T. Botinelly
10. Summary of current U. S. Geological Survey chemical methods of uranium and thorium analysis, by F. S. Grimaldi
11. A method of determining the age of igneous rocks using the accessory minerals, by E. S. Larsen, Jr., N. B. Keevil, and H. C. Harrison.
12. Noninterference of the arsenate ion in the volumetric determination of uranium using the Jones reductor, by J. J. Rowe
13. A volumetric method for the estimation of the oil yield of oil shale, by Frank Cuttitta and F. S. Grimaldi

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