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SUMMARY OF THE RESEARCH WORK OF THE TRACE ELEMENTS SECTION,
GEOCHEMISTRY AND PETROLOGY BRANCH, FOR THE
PERIOD JANUARY 1 - MARCH 31, 1951

by

John C. Rabbitt

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INTRODUCTION

This report summarizes the research work of the Trace Elements Section, Geochemistry and Petrology Branch for the period January 1 - March 31, 1951. Work before that is summarized in an earlier report, "Summary of the research work of the Trace Elements Section, Geochemistry and Petrology Branch, for the period April 1, 1948 - December 31, 1950," by John C. Rabbitt (U. S. Geol. Survey Trace Elements Investigations Rept. 148, January 1951). This report will be referred to as TEIR 148. In TEIR 148 the purpose of each project was described and it is not thought necessary to repeat that material.

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

1. Mineralogic and petrologic investigations of radioactive rocks, minerals, and ores.
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.

It should be emphasized that the work undertaken so far is almost entirely in the nature of investigations supporting the field appraisal of known uraniferous deposits. A program of more fundamental research, particularly in the mineralogy and geochemistry of uranium, is now being drawn up and will be submitted for approval soon.

This report does not deal with the routine analytical work of the Section nor the public-sample program. The analytical work will be summarized in a report to be issued after the end of fiscal year 1951, and a report on the public-sample program is in process.

Special thanks are due members of the Section who are engaged in the research work and who have supplied material for this report, to Earl Ingerson, Chief of the Geochemistry and Petrology Branch for his critical review, to Jane Titcomb of the editorial staff of the Section for editing the report, and to Virginia Layne of the same staff, for typing the manuscript and the multilith mats.

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 accompanied by field work by members of the Section, and it is closely coordinated with the work of the resident field geologists.

The phosphate project

In past reports the Section's work on phosphate deposits has been described under the headings "Florida phosphate project" and "Northwest phosphate project." It seems desirable to combine these headings under one, "The phosphate project."

Results of investigations

One of the principal aims of the work on the Florida deposits in recent months has been to find stratigraphically equivalent leached and unleached material in the Bone Valley formation because it is only by knowing the characteristics of the unleached rock that a full comprehension of the subsequent leaching can be obtained. This goal has now been attained by the study described in "The stratigraphy of the upper part of the Bone Valley formation and its relation to the leached zone," by Z. S. Altschuler, Elizabeth B. Jaffe, and Edward Dwornik (U. S. Geol.

Survey Trace Elements Memorandum Rept. 237, in preparation). The abstract follows:

The two topmost zones of the Bone Valley formation at the Homeland mine are a phosphate-cemented quartz sandstone and an underlying pebbly and clayey quartz and phosphate sand characterized by graded bedding. This sequence is found in every other area of the land-pebble field. Therefore, these zones are considered to be stratigraphic units and the transition between them to be a key horizon.

The leached zone of the Bone Valley formation encompasses either the upper or both of these units. As a result, rock from the leached zone has two different aspects. The upper unit is not obviously porous and in places has the appearance of a pure quartz sand. The lower unit develops large cavities during leaching. It is emphasized that the leached zone is a single secondary feature produced in two different stratigraphic units which respond differently to leaching and that it is not inherently composed of two subzones.

With the establishment of this marker horizon a chemical study is in progress comparing stratigraphically equivalent leached and unleached material. Also, field work in Florida during March carried forward a study of the leached zone and its relation to the overburden sands. There are many places where the overburden sands seem to grade into one another. The questions raised by these occurrences concern the original thickness of the leached zone and the overburden sands, their origins, and the amount of material originally available for the concentration of the uranium in the present leached zone. Samples have been collected for the investigation of these problems.

Work in the synthesis of apatite by Sol Silverman, Jeanne Weiser, and Ruth Fuyat continued. Studies of the products of synthesis are being made concurrently by chemical, mineralogic, spectrographic, X-ray diffraction, electron microscope, and differential thermal analysis methods.

Differences in the X-ray diffraction powder patterns of fluor- and hydroxyl-apatite and "carbonate"-fluorapatite have been reported by many observers and have been questioned by others. In order to test the possibility of real differences in the patterns a series of pure crystalline apatites (natural and synthetic) were examined in such a way as to minimize possible instrumental errors. Samples of these pure apatites (fluor- and hydroxyl-apatite and "carbonate"-fluorapatite) were ground to minus 400 mesh. The X-ray powder patterns of each specimen were made on the same machine, with the same camera, and with film from the same lot. Identifiable differences in the patterns were detected. Although small, these differences are distinctive and it is thought that by their use visual comparison of X-ray powder patterns is sufficient to identify relatively pure end members in the apatites.

Mixtures of the same types of apatites were X-rayed to determine whether the differences were due to individual specimens rather than to differences in composition. These mixtures showed no line broadening or any other differences in the powder patterns.

Mixtures of different types of apatites were X-rayed; the resulting patterns showed line broadening and, in some patterns, continuous merging of some lines to form a band. This indicates that structural distinctions exist among varieties of apatites.

Previously, staining methods had indicated that much of the carbonate of phosphorites is present as free calcite. Additional methods (solubility and differential thermal analysis) were used to test this possibility.

To establish a quantitative measure of the amount of carbonate held structurally, differential solubility tests were performed on the phosphorite material, using 0.5 molar triammonium citrate as a solvent. The solubility of calcite in this solvent is about 47 times that of pure fluorapatite and about 55 times that of pure "carbonate"-apatite (an optically homogeneous apatite containing 3.1 percent CO_2). Checks on laboratory mixtures of pure carbonate-free apatite and calcium carbonate indicate that this solubility relationship holds for calcite in the presence of apatite. The amount of CO_2 present as free calcite can be measured by this method to a precision of ± 0.1 percent.

The results of the solubility method have been checked by differential thermal analysis. Such an analysis of laboratory mixtures containing free calcite shows an endothermic peak in the temperature range of 780°C to 880°C . Pure "carbonate"-apatite (from Staffell, Germany, so-called staffellite) does not give a distinct peak but shows a general endothermic trend over a much wider temperature range. Furthermore, the area under the calcite peak is proportional to the amount of calcium carbonate present. The differential thermal analysis method can detect free calcite present in amounts greater than 1.6 percent.

Further checking has been done by X-ray means. X-ray studies of artificial mixtures of pure fluorapatite and calcite permit the detection of 3 percent or more of calcite. The basis for this is the appearance of three characteristic calcite lines (d-spacings of 3.038 Å, 2.089 Å, and 1.914 Å) in the powder patterns.

These three methods (solubility, differential thermal analysis, and X-ray) were used to establish the nature of the phosphate mineral in about 50 samples from Brazer Canyon and the Laketown district of Utah, from Coal Canyon, Wyo., and from the Conda mine and Trail Canyon in Idaho. These studies show that these phosphorites contain variable amounts of free calcite, but in all of them an appreciable part of the carbonate is present as "carbonate"-apatite. The results of these studies will be given in a report now in preparation by Sol Silverman, Jeanne Weiser, and Ruth Fuyat.

In addition to the synthesis of fluorapatite and chlorapatite by dry fusion (see TEIR 148, p. 15), a strontian chlorapatite, $3\text{Ca}_3(\text{PO}_4)_2 \cdot \text{SrCl}_2$, has been prepared during the quarter by the same method. All three apatites show typical apatite X-ray patterns. Chlorapatites containing 1.6 percent and 2.2 percent uranium had previously been prepared by dry fusion from a mixture of tricalcium phosphate, uranyl chloride, and calcium chloride; a fluorapatite containing 3.3 percent uranium had been prepared earlier by dry fusion from a mixture of uranium tetrafluoride, calcium fluoride, and tricalcium phosphate (see TEIR 148, p. 15). These products have now been X-rayed and show typical fluorapatite powder patterns. Apparently the presence in these apatites of the amounts of uranium mentioned above does not alter the fluorapatite X-ray pattern.

In an attempt to distinguish by X-ray means between hydroxylapatite and tricalcium phosphate it was found that the typical X-ray pattern given by hydroxylapatite was unaltered after heating the sample to 1200°C . Synthetic tricalcium phosphate, after heating to 800°C , showed significant deviations from the typical apatite pattern. The changes

do not fit the beta tricalcium phosphate pattern as established for whitlockite by Clifford Frondel of Harvard University. There is enough difference in the X-ray pattern of tricalcium phosphate after heat treatment to permit discrimination between this material and hydroxylapatite, which shows no alteration in powder pattern after being heated to 1200°C.

Studies of different apatites were also made by electron microscope methods. Polished surfaces were prepared on specimens of "carbonate"-apatite (Staffel, Germany); replicas were made of these surfaces by standard techniques and the replicas were studied under the electron microscope. The polished surfaces were then etched with triammonium citrate to leach selectively any calcite present, and replicas were made of the leached surface and studied under the microscope. This method might show the presence of calcite as inclusions too small to be detected under the optical microscope. No evidence of calcite inclusions was seen, but the study has not progressed far enough yet to rule out the presence of such inclusions.

The results of earlier work on the distribution of uranium and its relation to other constituents of the rich phosphate beds of the Phosphoria formation of the Northwest are reported in TEIR 148, pages 18 to 20. This work is further reported in "Distribution of uranium in rich phosphate beds of the Phosphoria formation," by M. E. Thompson (U. S. Geol. Survey Trace Elements Investigations Rept. 142, February 1951). The abstract follows:

Five sets of "close" samples were analyzed radiometrically for uranium, and chemically for P_2O_5 , CaO, organic matter, and loss on ignition. A Rosiwal analysis was made of thin sections

of one set of samples. The results of the analyses are plotted on graphs and on scatter diagrams, and coefficients of correlation are given for uranium with CaO , P_2O_5 , organic matter, and loss on ignition. Preliminary studies seem to indicate that the concentration of uranium in these samples is not due wholly to phosphate content, but may depend in part on organic matter or on other components. The correlations of uranium with P_2O_5 are poor in the groups of samples with smaller amounts of uranium but are good in the groups of samples containing more uranium.

Pellets from the Phosphoria are being studied for variations in size and chemical composition. Two samples from widely separated areas but from approximately the same stratigraphic position were found to have almost identical size characteristics. Spectrographic analyses of 10 samples from a single bed show that there is little lateral variation in elements reported spectrographically.

The adsorption of uranium by apatite in the pellets is being studied by immersing crushed and sized pellets in solutions of uranyl salts. The best results have been obtained by using uranyl sulfate in concentrations of 0.025 to 0.010 percent. It has been noted that marked increase in the uranium content of the pellets occurs and that the calcium content of the solutions is also increased. It is possible that this signifies the replacement of calcium ions in the apatite by uranium ions. This possibility is being tested further.

Future work

Field work in Florida was in progress at the end of March and the petrographic study of the leached zone will continue. Synthesis studies of the apatites will continue with particular reference to the problem of "carbonate"-apatite and the role of uranium in apatite. Search for

positive means of identifying the different apatites will continue.

Work will continue in the study of pelletal material of the Phosphoria formation and field work during the coming field season will supply new data and samples for this investigation.

The Colorado Front Range project

Relation of pitchblende deposition to radioactive bostonite dikes in the Central City district, Colorado

Results of investigations.---Mineralogical and chemical studies of the fine-grained radioactive bostonite and bostonite-porphphyry dikes of the Central City district, Colo., were continued by George Phair and Kiyoko Onoda in an effort to determine the radioactive constituents. It has not been possible so far to separate the radioactive constituents by means of heavy liquids or magnetic separations because (1) the small grain size of the groundmass necessitates crushing the material to minus 200, plus 325 mesh, and (2) the desired accessory minerals, although widely distributed, are scarce in these rocks.

To find out where the uranium is concentrated, hand-picked separates of the feldspar phenocrysts and of the groundmass from three samples taken from three different dikes were analyzed for uranium; the uranium content of the bulk samples was known from previous analyses to range from 0.004 to 0.007 percent. As was expected the results showed a two- to three-fold concentration of uranium in the groundmass as compared to the phenocrysts.

A sample of bostonite porphyry from the same region (Red Lyon Lodge, Idaho Springs, Colo.) had earlier been shown by Waldemar Schaller to have a ZrO_2 content of 0.11 percent and it seemed possible that much of the uranium and thorium in the bostonites under study might be tied up in zircon. Twenty samples (16 from the Central City district and 4 from bordering areas) were analyzed chemically for ZrO_2 . The results ranged from 0.02 percent to 0.22 percent ZrO_2 and showed that most of the bostonites are enriched in ZrO_2 , some highly so when compared to the average alkalic rock (alkalic rocks contain on the average much more ZrO_2 than do normal granitic rocks). The figure of 0.22 percent ZrO_2 represents a ZrO_2 content about 10 times that of the normal granitic rock.

The three bostonites highest in ZrO_2 came from the border of the Central City district and are abnormally low in uranium. If these are eliminated, the bostonites high in uranium tend to be high in ZrO_2 . They fall into two groups:

1. Of eight having ZrO_2 contents between 0.10 and 0.22 percent, seven have uranium contents ranging from 0.004 to 0.014 percent.
2. Of nine having ZrO_2 contents ranging from 0.02 to 0.07 per , eight have uranium contents ranging from 0.001 to 0.003 percent.

There is, however, no systematic relationship between ZrO_2 and uranium content within each group. The ZrO_2 contents, although high, are not high enough to account for more than a small part of the total uranium by solid solution in zircon even when the maximum allowance of

one percent uranium in zircon is invoked (as postulated by Professor E. S. Larsen, Jr., personal communication). It follows that most of the uranium in the rock is not in the zircon and therefore the ZrO_2 and most of the uranium are concentrated in separate mineral phases. This is compatible with the conception that these separate phases were formed by similar processes.

Study of thin sections and of heavy-mineral separates shows that interstitial fluorite is one of the most abundant accessory minerals in samples from the three bostonite dikes which exhibit the highest radioactivity. The high ZrO_2 content and the presence of interstitial fluorite in these dikes suggest that volatiles were active during the late stages of emplacement of the dikes. In this connection it is interesting to note that both ZrF_4 and UF_6 are volatile at only slightly elevated temperatures at atmospheric pressures. Moreover, uranium is associated with many fluorite deposits, including those at Jamestown, Colo., in the Thomas Range, Utah, and at Wölsendorf, Bavaria. The question as to the role of these postulated volatiles in uranium deposition in these rocks is under study.

Future work.—Laboratory work on the bostonites will be continued in an effort to determine:

1. The uranium and thorium minerals present.
2. The nature of the hydrothermal alteration.

During the coming field season investigations of the distribution of radioactive bostonites in the region surrounding the Central City district will be undertaken.

Additional sampling of the Tertiary intrusives of the Idaho Springs district and in the Central City district also is planned in order to complete the present data.

The radioactivity of fluorite from the
Blue Jay mine, Jamestown, Colorado

Results of investigations.--The work on hydrothermal uranothorite (see TEIR 148, pp. 27-29) is described in "Hydrothermal uranothorite in fluorite breccias from the Blue Jay mine, Jamestown, Boulder County, Colorado," by George Phair and Kiyoko Onoda (U. S. Geol. Survey Trace Elements Investigations Rept. 144, March 1951). The abstract follows:

In the course of thin-section and heavy-mineral studies of fluorite breccias from Jamestown, Colo., the mineral thorite, variety uranothorite, was identified on the basis of chemical, spectrographic, optical, and X-ray data. This uranothorite is compared with uranothorite from South Westland, New Zealand, described by Hutton (1950), and with similar material from an Alaskan placer sample studied by the writers. These uranothorites are in turn contrasted with the uranothorites described in the older literature all of which represent hydrated material. Thorium halos in fluorite are described, probably for the first time. The uranothorite associated with the fluorite breccias is clearly of hydrothermal origin--unlike all previously described thorites and uranothorites with one very doubtful exception.

The authors believe that uranothorite will prove to be a constituent of other hydrothermal veins now that the physical properties of the unaltered material are known.

No further work was done on this project during the last quarter.

Future work.--Further work is planned on the effects of radioactive emanations on the color of the Blue Jay fluorites. Studies will be made involving the range of alpha particles in thorium and uranium halos in

these fluorites in an attempt to use the widths of these halos as a means of identifying the radioactive elements causing them (uranium or thorium). Uranium halos have been studied before but thorium halos have not been previously reported in fluorites.

Additional studies will also be made on the causes of the photoluminescence in these fluorites.

The use of the Ra/U ratio of pitchblende as a quantitative measure of the recent leaching

Results of investigations.--No work was done on this project during the quarter. The results of earlier work will be given in a report now in preparation by George Phair.

Future work.--Additional equilibrium studies are planned to determine the extent to which the postulate of recent leaching of uranium is valid and in particular to get data on the origin of "sooty" pitchblende.

The Colorado Plateau carnotite project

Results of investigations

The continuing isotope studies by Lorin Stieff and Thomas Stern are involving a great amount of extended calculations. Preliminary calculations and graphs of the lead isotope data received from Oak Ridge indicate that the ratio of isotopes as determined by the mass spectrograph would be more useful than the usual form of reporting the

isotope abundances in percentages. Data in the new form have been supplied by Oak Ridge, have been transferred to index cards, and calculations are in progress.

Trial calculations have also indicated that a few of the analyses might be in error. Duplicate analyses of the samples involved have been obtained.

The calculations are far enough along so that a report summarizing the study of the isotopic composition of the carnotite leads will be started in the quarter ending June 30, 1951, by Lorin Stieff and Thomas Stern.

During the quarter 50 thin sections of material from the Colorado Plateau were covered with nuclear emulsion stripping film as part of the general survey of the radioactive minerals of the ores of the Plateau. Fifty companion alpha plates were also made. The technique for permanently mounting unsupported nuclear emulsions on uncovered thin sections has been studied in some detail. Completely satisfactory results have not been obtained yet but solution of the problems involved is in sight. Such mountings should provide high resolution for nuclear tracks and the use of such high resolution for low-grade material should conclusively demonstrate whether uranium is systematically distributed throughout the rock.

Mineralogic and petrographic studies continued. A black iron-vanadium mineral from Saskatchewan, Canada, sent in by Dr. H. V. Ellsworth, was compared with montroseite (see TEIR 148, p. 37), the new iron-vanadium mineral from Colorado. The Canadian material is similar but contains more iron and has a higher density.

About four grams of a red-brown iron-vanadium mineral from the Jo Dandy mine, Montrose County, Colo., was submitted to the Chemistry Unit for analysis. The mineral occurs with hummerite (see TEIR 148, p. 37) and pyrite in gray clay and is probably a new mineral.

Work on the clays underlying the carnotite ores continued. Earlier work was reported in TEIR 148, pages 40 to 41 and a report on this work is still in preparation by Alice Dowse Weeks.

A set of 50 clay and siltstone samples representing six members or formations from eight localities in western Colorado and eastern Utah are being studied. Briefly stated, the purpose of the work is to look for distinctive mineralogic features in each formation, and to detect regional differences and other evidence bearing on the origin of the clays and siltstones. It was agreed that size analyses would be done on the clay samples by R. A. Cadigan of the Mineral Deposits Branch in the sedimentation laboratory in Grand Junction, Colo.

Semiquantitative spectrographic analyses and X-ray diffraction powder pictures have been made on some of these fine clays and will be completed on the rest of the samples probably during April. Differential thermal analyses will be made on certain samples; one has been completed. Montmorillonite, kaolinite, and hydromica have been identified. Not until the X-ray patterns of the rest of the samples are completed can general conclusions be drawn concerning the distribution of the clay minerals in the different formations.

Heavy-mineral separations have been made on the sands in certain of these samples and barite and pyrite have been found in one sample;

detrital biotite, zircon, and tourmaline have been found in some; euhedral zircons, apatite, magnetite, and biotite have been found in others.

Only one sample contained fossils. These fossils seem to be the microscopic calcareous algae, Chara, and these have been submitted to the Paleontology and Stratigraphy Branch of the Survey for identification.

It is expected that work on these samples will be completed and a report prepared by June 1951. It is hoped that the distinctive mineralogic characteristics of each formation suggested by studies of the first samples will be borne out by the rest of the studies.

Future work

In general future work on this project will be so directed that, if possible, reliable ore guides based on a knowledge of the origin of the deposits can be developed within a reasonable time. To this end, the lead isotope studies will be expanded to provide a broader statistical foundation for any conclusions that might be drawn and to include suites of uranium ores that have been collected but not yet analyzed. The expansion, however, will be governed by whether evaluation of the data now in hand warrants such a course. The radium-equilibrium studies will continue and information from these studies will be combined with information obtained by the use of nuclear-track plates and stripping films in an effort to establish the radioactive equilibrium conditions in the deposits.

The mineralogic and petrologic studies and the synthesis work will continue as indicated. The whole project is closely tied in with the work of the field geologists and this cooperation assures a balanced program.

The properties of uranium minerals project

Results of investigations

Arrangements have been made with the U. S. National Museum so that George Switzer, Associate Curator of the Museum, is now devoting his full time to work on this project. This should aid immeasurably in accelerating the work on the preparation of a monograph on the properties of uranium minerals. Mr. Switzer is compiling abstracts of the literature on uranium mineralogy and they are being typed on Ozalid master cards so that duplicate sets can be made for interested workers. The following note has been prepared for early publication in the American Mineralogist. (It is given in full here so that it will have a preliminary distribution in this report.)

Monograph on the Properties of Uranium Minerals

The United States Geological Survey in cooperation with the United States National Museum on behalf of the United States Atomic Energy Commission is engaged in the preparation of "A Monograph on the Properties of Uranium Minerals." This monograph is to be a definitive work on the uranium minerals; it will contain all the data available in the literature and where this data is either incomplete or unsatisfactory new data will be obtained. The descriptions of the individual minerals will be more complete and more extensive than those in the seventh edition of the Dana System. Dr. Clifford Frondel of Harvard University who is engaged in the preparation of the new edition of the Dana System will cooperate in the preparation of the monograph.

The value of such a publication at the present time should be readily apparent. It is hoped that all persons engaged in research on the uranium minerals will contribute the data they have available or at least indicate that they are engaged in such research. Full credit will be given to all these contributors. We would like especially to find out what minerals are being worked on in order to avoid duplication of effort.

All inquiries and contributions of data should be addressed to John C. Rabbitt, Chief, Trace Elements Section, U. S. Geological Survey, Washington 25, D. C., or to George Switzer, Associate Curator of Mineralogy, U. S. National Museum, Washington 25, D. C.

It has been decided to work up the data for one of the uranium minerals in the form in which the data might appear in the monograph and to circulate this report among interested workers for comment and suggestions. Curite has been chosen for this preliminary form and work on it is in progress.

The monograph will be prepared for publication as Monograph I in the new series of The Mineralogical Society of America.

The investigation of metamict minerals is continuing by Joseph Berman. Heat treatment has now been standardized and a file of X-ray patterns obtained from such treated minerals is now being built up.

In the standard method the mineral is heated in a Dietert tube furnace with sillimanite tubes in an atmosphere of water-free helium. A cylinder of helium feeds gas through a pressure-reducing valve and a U-tube filled with calcium chloride to provide a water-free inert atmosphere. The helium exhausts from the tubes in the furnace into a beaker partly filled with water which serves as a non-return valve to prevent air from entering the tubes.

The sample is placed in a sillimanite boat and the boat is placed in the furnace tube. The air in the tube is flushed out with helium and a constant flow of helium through the tube is maintained. The sample is then heated to the appropriate temperature depending on the mineral being studied. Duplicate samples are heated in air for comparison purposes. Temperatures used range from 850°C to 1200°C.

Variations in the heat treatment are necessary for certain minerals and certain anomalous results have been found, notably with thorites and related minerals.

At present standard X-ray patterns have been obtained on material heated by this method for thorite, huttonite, euxenite, fergusonite, brannerite, allanite, and samarskite. The mineral identifications have been checked carefully by spectrographic and other means and it is believed that these patterns can be used as standards for identification purposes.

Work is continuing by Theodore Botinelly on the compilation of a selected annotated bibliography on metamict minerals, and it is hoped to have it ready soon for distribution.

Production of a handbook for the field identification of uranium minerals is still under study.

Future work

The investigations leading to a monograph on the properties of uranium minerals are immediately practical for identification purposes and are of fundamental importance to a knowledge of the geochemistry of uranium. The studies embrace chemistry, physics, physical chemistry, crystal chemistry, and crystal optics as well as mineralogy and petrology, and the Section will continue the studies described under Results of investigations in as broad a manner as possible. Particular attention will be given to synthesis studies as they will prove most fruitful in answering the many problems in this field. It is apparent, for

instance, that the synthesis of metamict minerals will be necessary before much more progress can be hoped for in an understanding of metamictization. It is also apparent that the properties of many rare uranium minerals together with many complex ones for which adequate amounts of material are not available cannot be determined until these minerals have been synthesized and studies can be made of the pure compounds. This has been true, for instance, for carnotite and related minerals.

Efforts will be continued to improve cooperation and communication with other laboratories working in this field so that duplication of work can be avoided, and so that each laboratory will benefit by progress made in other laboratories.

The lignite project

Work started late in March by Maurice Deul on a study of the uraniferous lignites of the Dakotas. It is planned to investigate the lithologic and chemical composition of the material with particular reference to the manner of occurrence of the contained uranium. The possibility of adsorption of uranium by organic constituents in the lignites will be studied in close cooperation with Professor Farrington Daniels of the University of Wisconsin. Professor Daniels will be working on some aspects of this problem involving a study of the geochemistry of uranium in peat bogs and in their constituent plants. He will also investigate problems connected with the extraction of uranium from lignites. Mr. Deul is in close touch with Professor Daniels on this work.

The project has not proceeded far enough for a report on results as yet.

Miscellaneous projects

There are many small research projects in the mineralogy and petrology of radioactive materials in progress in the Section at any given moment. Many of these are "spot" research jobs on small suites of samples sent in, for example, by the field geologists of the Reconnaissance Program. Others are jobs on small samples sent in by Mrs. Mathez of the Atomic Energy Commission New York office, by Mr. Spelman of the Atomic Energy Commission Washington office, and by the public. The total of this work looms rather large in the over-all work of the Section. Part of it, of course, can be called service work, and scarcely can be dignified by the term "research," but much of it does entail investigations that can be called research.

The studies of Professor E. S. Larsen, Jr., are in a special category. He works in the Section as a special consultant and catalyst, especially in the mineralogic and petrologic work, and his advice is constantly sought in carrying on the research program. He is also making many investigations of his own. As an example, his studies on the determination of the geologic age of igneous rocks by investigating the radioactivity and lead content of the accessory minerals were started while he was still at Harvard, but the Survey has contributed to the work by supporting the project as soon as Larsen joined the

Section's staff. The results of some of his work are reported in TEIR 148, pages 51 and 52. Work is continuing by Harrison Brown and his colleagues and by Professor Hurley of M.I.T. on many of Professor Larsen's samples and the progress of this work will be described in the next summary report to be issued in July 1951.

Work is in progress by Z. S. Altschuler on a suite of samples of phosphate rock from Mona Island, B.W.I. The material occurs in limestone caves and it was desirable to know its uranium content and whether it is a residual product of weathered limestone or alterations of limestone related to guano accumulations. Eight samples were submitted to the Section for study, containing 11 different rocks: 2 fresh limestones, 4 weathered limestones, and 5 phosphorites. Chemical analyses were made for P_2O_5 , fluorine, and uranium, and it was found that the fluorine and uranium contents were extremely low for marine apatite. In addition a semiquantitative spectrographic survey of the samples did not show any significant enrichments of the minor or trace elements in the phosphates with respect to the limestones. This can be evaluated by comparing the normally less soluble or less active rock elements which accumulate lateritically such as Fe, Al, and Pb.

It was noted that some of the limestones that contain calcite oolites or fossils also contain phosphate. However, any attempt to decide whether the phosphate is undisturbed or replaced, and if replaced, whether the replacement is diagenetic or epigenetic and continental must await further work which is in progress.

Techniques used in investigations

Concentration and separation

Nothing basically new has been added to methods of concentration and separation during the quarter. It is expected that a report on the combined air scrubber and Cottrell precipitator (see TEIR 148, p. 54) will be completed by Lorin Stieff in the coming quarter.

Nuclear emulsions

The use of nuclear emulsions in the mineralogic and petrologic work of the Section is becoming increasingly important. New work with these emulsions by Lorin Stieff and Thomas Stern has been described under the Colorado Plateau project.

Electron microscopy

An application of electron microscopy by Edward Dwornik to the synthesis studies on apatite has been described under the Phosphate project. Additions of about 30 patterns have been made to the library of standard electron diffraction patterns.

Mass spectroscopy

The Survey's mass spectrometer, now under construction, is well along and it will be set up in the Section's Washington laboratory when completed. No accurate prediction can be made as to when the instrument will be in operation but it is hoped that it will not be later than next fall.

Optical spectrography

Progress in research in this field in the Section during the quarter is described under Spectrographic investigations.

Differential thermal analysis

The differential thermal analysis apparatus in use in the Washington laboratory (see TEIR 148, p. 59) has been modified by many changes in the past three months. Chief among these has been the substitution of Pt-Pt,Rh thermocouples for the chromel-alumel thermocouples formerly in use. This has greatly improved the reproducibility of results. The construction of a recording instrument for use in the Washington laboratory is now under study.

CHEMICAL INVESTIGATIONS

Methods of analysis project

Fluorimetry

Results of investigations.--Work has been done on the design of a fluorimeter for solutions and the instrument is described in "A fluorimeter for solutions," by Mary H. Fletcher and E. Ray Warner (in preparation). The abstract follows:

A description of and complete drawings for the construction of a fluorimeter for the measurement of fluorescence of solutions are given. The instrument is rugged and versatile. It may be used with various phototubes and measuring devices. It is constructed so that phototubes and filters may be changed readily. Sensitivity is controlled easily over a wide range by limiting the size of either the ultraviolet or fluorescent light beam with standard apertures.

Future work.--It cannot be emphasized too strongly that present fluorimeters used in the analysis for uranium are adequately sensitive and it is not necessary to expend research effort in improving sensitivity. Future work will consist in simplifying present instruments to make them more compact, stable, versatile, and less expensive, and in designing new instruments for special applications.

Methods of uranium and thorium analysis

Results of investigations.--A study of separations obtainable with sodium carbonate for application to the analysis of uranium by fluorimetric procedures in shales and lignites was made during the quarter, resulting in a report, "Fluorimetric determination of uranium in shales, lignites, and monazites after alkali carbonate separation," by Norma S. Guttag and F. S. Grimaldi (in preparation). The abstract follows:

Comparative data are presented on separations of microgram amounts of uranium from milligram amounts of various metal ions with $\text{Na}_2\text{CO}_3\text{-K}_2\text{CO}_3$, $\text{Na}_2\text{CO}_3\text{-K}_2\text{CO}_3\text{-H}_2\text{O}_2$, and $\text{Na}_2\text{CO}_3\text{-NaClO}$. The $\text{Na}_2\text{CO}_3\text{-K}_2\text{CO}_3$ separation procedure is applied to the analysis of shales, lignites, and monazites. This method will determine as little as 0.001 percent uranium in shales and lignites and 0.01 percent uranium in monazites.

Future work.--The many papers on thorium and uranium analysis produced by the Survey are being edited for inclusion in a proposed Survey 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 which was tentatively referred to in TETR 148 as, "Collected papers on U. S. Geological Survey

methods of analysis for uranium and thorium." This collection will not include any classified papers.

Research will continue in this whole field. It is planned to continue the interrupted studies in polarographic analysis.

Ion-exchange methods of analyses have been studied and can be useful for certain special application in the Section's work, and investigations will be made in this field.

Methods of analysis for aluminum and phosphorus

Results of investigations.--No new developments occurred during the quarter.

Future work.--Research work will continue from time to time on methods for the analysis of aluminum and phosphorus. There is still much to be done in developing new rapid methods; improvements in phosphorus analysis are needed particularly when standard methods have to be applied to special materials for which the methods may not be well suited.

Methods of analysis for miscellaneous minerals and compounds

Results of investigations.--Work was started during the quarter by Henry Mela, Jr., and Claude Waring on the chemical-spectrographic determination of small amounts (0.001 percent and up) of individual rare earths in phosphate rocks. Consultation among the chemists and spectrographers resulted in agreement that the best approach to the determination of individual rare earths in phosphate rocks is a combined chemical

concentration and spectrographic determination and the investigation is thus a cooperative one. So far, (1) 10 rare-earth salts have been obtained and their high purity tested by spectrographic analysis and (2) Al_2O_3 is being tested as a possible base material and internal standard for the spectrographic determination of the rare earths. For this purpose different levels of concentration of each rare earth in Al_2O_3 have been prepared (about 49 samples) and given to the spectrographers for selection of the spectral lines that can be used for these levels. In addition, these samples will give data on the spectral behavior of the rare earths in Al_2O_3 . As part of this project an annotated bibliography of the analytical chemistry of the rare earths is being prepared and it will be distributed to interested workers upon completion.

A report on the new rapid estimation of oil content of shales and phosphates, based on the optical density of toluene solutions of the oil (see TEIR 148, pp. 75-76) has been prepared by Frank Cuttitta and is being edited.

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

Future work.—Work will continue in this field as indicated in this report and in TEIR 148. The goal is for the Section to be prepared to perform analyses of any sort that are required on many different kinds of material and to do the work as rapidly as possible, with an accuracy sufficient to meet the needs of the problem at hand.

Quality of analyses project

Results of investigations

Out of 427 samples of Florida phosphates previously studied statistically 10 samples showed discrepancies between the radiometric and chemical results and these discrepancies persisted on re-analysis. These 10 samples were made the subject of further study to determine whether the differences were due to natural causes (lack of radioactive equilibrium) or to analytical errors. Six chemical determinations were made on each sample, three using the usual routine method and three using one of the most refined methods available. The samples were also counted radiometrically with the samples shielded for longer periods of time after special attention was paid to the preparation of the sample. The results by the two chemical methods were in complete agreement. Nine out of the ten differences between the previous chemical and radiometric measurements were resolved and were found to be due to analytical error (about half chemical, half radiometric).

Future work

These studies will continue and multiple analyses will be made for uranium and other elements and compounds on different types of material, and the results will be analyzed statistically. The work will constitute a continuing and expanding program of evaluating the quality of Survey analyses.

High-index liquids project

Results of investigations

Additional sets of high-index liquids were prepared (see description in TEIR 148, pp. 81-83) and distributed, mainly in the Survey. A new series of liquids ranging in refractive index from 1.66 to 2.02 has been prepared by Robert Meyrowitz, and the stability of these solutions is being determined. All of them contain arsenic bromide, α -bromonaphthalene, precipitated sulfur, and arsenic disulfide.

Future work

This study will continue and the dispersion, phase relations, and related properties of these and other possible liquids will be investigated. There is some hope that this work may also produce new heavy liquids, but the possibility is none too good. Reports on these investigations will be written from time to time for publication.

SPECTROGRAPHIC INVESTIGATIONS

Results of investigations

During the quarter eight elements were added to the list of elements determined in the semiquantitative method in one arcing of a 10-mg sample, thus bringing the total to 64.

Work was done during the quarter by Charles Annell and Helen Worthing on the determination of impurities in uranium as a means of handling

complex refractory oxides with complex spectra. The so-called carrier distillation method is being investigated whereby gallium oxide is used to carry the impurities in uranium into the arc without exciting the uranium atoms. This study uses 100-mg samples of U_3O_8 prepared from $(UO_2)(NO_3)_2 \cdot 6H_2O$, and pitchblende to which 2 percent of Ga_2O_3 has been added. It has been found that the lines of the impurities in uranium were enhanced and those of the uranium were suppressed at 5-6 amperes, 260-270 volts, interrupted d-c arc. Moving-plate studies indicated that the above conditions lasted about two minutes before the uranium entered the arc stream. A 10-second preburn is necessary as uranium oxide is swept into the stream by the ignition spark. Further work indicated that the Ga_2O_3 carrier was not essential for the suppression of the uranium lines when the following arcing conditions were used: 25 ohms, 5-6 amperes, 260-270 d-c volts. Mg and Si, as impurities, showed more sensitivity in material with the carrier added but Ca, U, and Ti showed more sensitivity without the carrier. Additional work will be done before any definite conclusions are reached.

Work is in progress by Annell and Worthing on the detection of trace amounts of thorium in samples without prior chemical concentration, the determination of thorium in samples of high uranium content, and the detection of trace amounts of lead. These investigations are continuing, and it is expected that the work will have proceeded far enough to be described in the next summary report.

Development by Jules Stich of the so-called single-grain qualitative method (see TEIR 148, pp. 85-86) continued. At present the procedure is

being adapted from use in the 3-meter Baird spectrograph for use in the Gaertner prism spectrograph. This transfer will make more lines of the elements available for inspection on one plate due to the wider wavelength coverage. When this transfer is completed, the method should be ready for formal description in a separate report.

During the quarter, 7¹/₄ check analyses of routine semiquantitative determinations were made and no serious disagreements were noted. As part of a continuing evaluation of the spectrographic results, a project was started by Tennyson Meyers in the Section's spectrographic laboratory in Denver to determine contamination of samples handled by ordinary grinding procedures. Six auger-drill samples (sand, silt, and clay) from the Lost Creek schroeckingerite deposit in Wyoming were selected for study. Treatment of the samples was as follows:

1. All samples had previously been ground in the Denver grinding laboratory. This operation consisted of grinding the samples in a jaw crusher to minus 1/4 inch, and then mixing the samples in a rotating mixing cylinder, and splitting them in a mechanical splitter. The samples used for experiment were one-quart splits from this operation. None of the original untreated rock was available for testing.
2. Each sample was hand rolled on wrapping paper in stages of 100 rolls per splitting operation, using a small Jones splitter. Two representative splits, about 4 oz each, of each sample were obtained.

3. The splits from stage (2) above were treated as follows:

- A. Samples, called "A" samples, were pulverized in the grinding laboratory.
- B. Samples, called "B" samples, were pulverized in the spectrographic laboratory, largely in an agate mortar.

The "A" and "B" samples were then analyzed spectrographically. Mo, Ni, and Cu were added to all of the "A" samples as compared to the "B" samples; and Cr, Co, and Mn were added to some of the "A" samples. However, for 15 other elements determined there was no apparent contamination. This work is part of a thorough investigation now in progress on the subject of contamination in the preparation of samples for spectrographic analysis.

Future work

Work will continue in the investigation of methods of analysis with the goal of increasing the rapidity and accuracy of the analyses and adapting methods to special materials. Such work will include studies of qualitative, semiquantitative, and quantitative analysis. Fundamental studies such as those mentioned and others will be continued and expanded.

A study is being made of the application of infrared spectroscopy to the problems of the whole program, and recommendations in this matter will be forthcoming.

The mass spectrometer (as described) when built will be situated in the spectrographic laboratory in the Section's Washington quarters.

RADIOMETRIC INVESTIGATIONS

Results of investigations

In the continuing study by Jim Bracken and William R. Champion of phosphors for use in scintillometers the behavior of anthracene in xylol as an internal phosphor was investigated. The results were unsatisfactory.

A high-gain linear amplifier and power supply was designed and constructed for use with an ionization chamber for the study of absolute alpha activity of low orders of magnitude. The characteristics of this apparatus are now under study.

Also under study are the merits of magnetic, electrostatic, and differential pulse height alpha analyzers with respect to possible geologic applications such as half-life determinations, abundance ratios, and U/Th ratios. Different published circuits for differential pulse analyzers are being evaluated.

A windowless Geiger-Muller tube was constructed so that a sample can be inserted directly into the tube, thus affording minimum absorption. The tube was also designed for minimum backscattering and nearly 2π geometry. Experiments are in progress with different combinations of counting gases to obtain the best plateau. This tube will be used for absolute β -counting.

Control charts for the Tracerlab automatic counter are still in preparation.

During the quarter work was started by Francis J. Flanagan and Jesse Warr on a project involving the development of a rapid radiochemical

method for the determination of uranium and thorium in monazite. This method involves the chemical separation of the radium isotopes in monazite by sulfate precipitation, using barium as a carrier. The half lives of the two radium isotopes of the thorium series are short as compared to radium in the uranium series, and equilibrium with their daughter products is reached in about 25 hours as compared to 30 days for the radium in the uranium series.

The radium isotopes precipitated in the procedure are Ra^{223} , Ra^{224} , Ra^{226} , and Ra^{228} . The effect of Ra^{223} on the count may be neglected and it is assumed (this remains to be confirmed) that the radium from the U^{238} series does not contribute appreciably to the β - γ count in the time required for the operation of the method. Preliminary separations on monazites supplied by John B. Mertie of the Survey indicate that a practical maximum (probably not absolute) in the growth curve of the isotopes from monazite occurs at about 25 hours after precipitation of the sulfates. Test runs seem to confirm this idea.

The method is further based on the assumptions that (1) Ra^{226} does not yield, in the amounts found, an appreciable β - γ count in the time required and (2) that it is possible to obtain 100-percent chemical recovery of BaSO_4 in the method. These assumptions are being checked.

If this method proves to be sound, its application to monazites will be most useful. Possibly uranium and thorium could be determined in about 28 hours of elapsed time, with only about three hours being spent in work on the sample; whereas, with present chemical methods of determining these two elements directly in monazite, about three to four days are required.

Future work

Research in methods of radiometry will continue. Contacts with other laboratories are maintained and frequent conferences are held with experts at M.I.T., the Bureau of Standards, Oak Ridge, and elsewhere. The voluminous literature in this field is followed closely.

REPORTS

Reports written by members of the Section, or on behalf of the Section by other members of the Survey up to December 31, 1950 are listed in TEIR 148, pages 93 to 96.

Reports issued during the quarter of the U. S. Geological Survey's Trace Elements Investigations Reports and Trace Elements Memorandum Report series are as follows:

<u>TEIR</u>	<u>Title</u>	<u>Date</u>
130	A study of the critical factors in the "direct" fluorimetric determination of uranium, by Mary H. Fletcher.	October 1950 transmitted February 1951
142	Distribution of uranium in rich phosphate beds of the Phosphoria formation, by M. E. Thompson.	March 1951
143	A semiquantitative spectrographic method for the analysis of minerals, rocks, and ores, by C. L. Waring and C. S. Annell.	March 1951
144	Hydrothermal uranothorite in fluorite breccias from the Blue Jay mine, Jamestown, Boulder County, Colorado, by George Phair and Kiyoko Onoda.	March 1951
148	Summary of the research work of the Trace Elements Section, Geochemistry and Petrology Branch, for the period April 1, 1948 - December 31, 1950, by J. C. Rabbitt.	March 1951

<u>TEMR</u>	<u>Title</u>	<u>Date</u>
236	Preliminary notes on the minor-metal content of Florida phosphate rock, by V. E. McKelvey, J. B. Cathcart, and Helen Worthing.	January 1951

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

1. Immersion liquids of high refractive index, by Robert Meyrowitz and Esper S. Larsen, Jr., approved March 1951 for publication in The American Mineralogist.
2. Chapter on Geochemistry in National Research Council's Review of Nuclear Science for 1950, by Michael Fleischer and John C. Rabbitt, approved March 1951 for publication.

The following report was placed on open file in the Survey, and approval (by the Director of the Survey) for its publication is being sought:

The preparation of nuclear-track plates and stripping films for the study of radioactive minerals, by L. R. Stieff and T. W. Stern, U. S. Geol. Survey Trace Elements Investigations Rept. 127, August 1950.

The following report was published:

Studies of uranium minerals VII: Zeunerite, by Judith Weiss Frondel: Am. Mineralogist vol. 36, nos. 3 and 4, pp. 249-255, 1951.

The following reports were in process as of March 31, 1951:

1. Red and gray clays underlying the ore-bearing sandstone of the Morrison formation in western Colorado, by Alice Dowse Weeks.
2. The phosphorite facies and genesis of natural phosphates, by A. V. Kazakov, translated by E. B. Jaffe.

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. (Previously referred to as Collected papers on U. S. Geological Survey methods of analysis for uranium and thorium.)
4. A fluorimeter for solutions, by Mary H. Fletcher and E. Ray Warner.
5. Bibliography of metamict minerals, by T. Botinelly.
6. Some factors in the differential leaching of uranium and radium in pyritic mines and mine dumps, by George Phair.
7. The stratigraphy of the upper part of the Bone Valley formation and its relation to the leached zone, by Z. S. Altschuler, E. B. Jaffe, and E. Dwornik.
8. Fluorimetric determination of uranium in shales, lignites, and monazites after alkali carbonate separation, by Norma Gutttag and F. S. Grimaldi.
9. Further studies of the distribution of uranium in rich phosphate beds of the Phosphoria formation, by M. E. Thompson.
10. A photometric method for the estimation of the oil yield of oil shale, by Frank Cuttitta.
11. Physical and chemical comparison of modern and fossil tooth and bone material, by E. B. Jaffe and A. M. Sherwood.
12. A summary report of public samples received 1949-1950, by Maurice Deul.