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Summary of the Research Work of the Trace Elements Section, Geochemistry and Petrology Branch, for the Period April 1, 1948-December 31, 1950

Trace Elements Investigations Report 148

UNITED STATES DEPARTMENT OF THE INTERIOR
GEOLOGICAL SURVEY

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by

John C. Rabbitt

January 1951

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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

INTRODUCTION

This report summarizes the research work of the Trace Elements Section, Geochemistry and Petrology Branch, from the organization of the Section in April 1948 to December 31, 1950. The research undertaken thus far 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 thus far, described under the headings "Future work," is almost entirely in the nature of investigations supporting the field appraisal of known important uraniferous deposits. A comprehensive program of more fundamental research was submitted in April 1949 in a report entitled "Proposed program of desirable research in the geochemistry of uranium," but funds for this work have not been authorized. It is hoped, however, that funds to support basic research of the type indicated in that report may be available in the future.

This report does not cover the analytical work of the Section nor the public-sample program. The analytical work has been summarized for the fiscal year 1950 in the report, "Numerical summary of the analytical work of the Trace Elements Section, Geochemistry and Petrology Branch, for the fiscal year 1950," by John C. Rabbitt, U. S. Geol. Survey Trace Elements Memorandum Rept. 174, October 1950. A report on the public-sample program is in preparation.

Much of the material in this report has been paraphrased from reports prepared by members of the Section. My special thanks are due them; to Earl Ingerson, chief of the Geochemistry and Petrology Branch of the Survey, for his critical review; to my secretary, Marie Wholihan, for her aid in collecting material; and to Virginia Layne of the editorial staff of the Section for typing the manuscript and the multilith mats.

MINERALOGIC AND PETROLOGIC INVESTIGATIONS

Introduction

The mineralogic and petrologic investigations of the Section are organized in several projects. The work in each project is directed toward a given objective and the results of such work are covered by reports which may be descriptive of work on the project as a whole or on some of its separate parts. It should be kept in mind that the laboratory work has been accompanied by work in the field by members of the Section and that it has been tied in wherever possible with the work of the resident field geologists.

The Florida phosphate project

Purpose

Laboratory investigations of the Florida phosphate project were designed to meet three broad needs:

1. To supply mineralogic identification and petrographic description of the rocks composing the Bone Valley formation.
2. To determine the uranium content of the component minerals and to determine the relation of uranium to the physical and chemical properties of these minerals and to their occurrence in the field.
3. To gather new data on the occurrence of uranium in phosphates.

This project contributes to the over-all atomic energy program of the Survey as follows:

1. The mineralogy and petrography aid and supplement the work of field parties making economic studies as well

as make possible the presentation of a hypothesis explaining the geologic history of the Bone Valley formation.

2. The determination of uranium content of the minerals is a necessary prelude to the processing of raw material for uranium recovery.
3. Data on uranium occurrence in phosphates will aid in further exploration in phosphates or other sediments.

Results of investigations

The Bone Valley formation, which contains the minable phosphate in the Florida "land-pebble" field, rests unconformably on the Hawthorn formation, a phosphatic limestone. The Bone Valley consists of unconsolidated interbedded clays, clayey sands, sands, and conglomerates. Its clastic material is almost entirely apatite and quartz. Its clay is mainly montmorillonite; however, apatite also occurs in primary layers of clay-sized material. The apatite in the Bone Valley originated in at least three different ways, (1) as nodules reworked from the Hawthorn formation, (2) as fine-grained precipitates, and (3) as fragments of reworked precipitates. (See "A mineralogical and chemical study of the leached zone of the Bone Valley formation of Florida; a progress report," by Z. S. Altschuler and C. E. Boudreau, U. S. Geol. Survey Trace Elements Investigations Rept. 102, December 1949.)

A program of laboratory separation and testing early showed that there is no correlation in phosphorites between uranium content and magnetism, particle size, specific gravity, luster, color, or any other physical property that could be made the basis of separation. In addition, no uranium minerals (other than a very small amount of autunite) were found. However, some secondary redistribution of uranium in Bone Valley rock has been revealed by studies made of single pebbles which show a gradient in their uranium content and by finding a zone of secondary concentration at the base of leached rock in the topmost units of the Bone Valley formation. Detailed stratigraphic description and sampling show the widespread occurrence of this zone as well as its relations to the lithology.

The two topmost lithologic zones of the Bone Valley formation are a phosphate-cemented quartz sandstone and an underlying pebbly and clayey quartz and phosphate sand characterized by graded bedding. This sequence has been found in all the mines of the district and these zones are therefore considered to be stratigraphic units and the transition between them to be a valid and ubiquitous stratigraphic marker.

The leached zone 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 has in places the appearance of a pure quartz sand. The lower unit has developed large cavities during leaching. It is thus to be 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.

In the leached zone the original composition and texture of the Bone Valley formation have been modified. Apatite, the predominant phosphate mineral in the Bone Valley formation, is replaced in the leached zone by pseudowavellite and wavellite. These mineral transformations have given the rock as a whole a white color which, together with the coarse secondary porosity, distinguishes the leached zone from the rest of the Bone Valley formation. As leaching proceeded from the surface downward through the agency of groundwater, and as uranium was concentrated at the base of the leached zone, a general correlation can be observed among leaching, lime content, and uranium distribution. In the upper part of the leached zone residual concentration of the uranium occurred and the wavellite-quartz sands contain two to three times as much uranium as the unleached material. In the basal part of the leached zone leaching has not removed all of the apatite and an enrichment in uranium by preferential adsorption or by replacement in the crystal structure has occurred in the partially leached apatite pebbles.

A 13-foot section of well-developed leached zone at the Homeland mine has the following average percentage composition:

Quartz	58
Wavellite	24
Apatite	7
Pseudowavellite	5
Kaolinite, manganese wad, limonite, and accessory minerals	5

The average P_2O_5 content of this material is 15.0 percent and the average uranium content of the composite phosphatic material is 0.03 percent. The highest uranium content yet found in quartz-free phosphatic material from the leached zone is 0.164 percent. The phosphate fragments composing this section of leached zone range in size from pebbles 1 centimeter in diameter to clay-sized particles. The typical particle is of fine-sand size. (See Trace Elements Investigations Rept. 102.)

The secondary uranium mineral autunite, $Ca(UO_2)_2(PO_4)_2 \cdot 12H_2O$, was found in one outcrop of leached-zone material where it seems to be confined to a single layer, several inches thick. The autunite makes up less than 0.01 percent of the rock and accounts for less than 5 percent of the uranium present. Identification of the autunite was established, after tedious separation of pure grains, by chemical and X-ray means.

In view of the interest in any potential recovery of uranium from the large tonnages of washer-plant waste slimes, samples of such material selected on the basis of widespread distribution of both uranium content and geographic location were studied. The material of the slime ponds was found to be of the following two general types:

1. Simple, fine-grained mixtures of pure clastic apatite, quartz, and minor amounts of calcite and accessory minerals.
2. Fine-grained mixtures of clay-phosphate aggregates, phosphate mixtures (pseudowavellite and wavellite),

quartz, pure clay, pure apatite, and minor amounts of calcite and accessory minerals.

The uranium in the slimes was found to be dependent on the amount of apatite and other phosphate minerals present. (See "A progress report on the Geological Survey's work in determining the nature of the phosphate in the washer plant waste slimes from the Florida phosphate deposits," by Z. S. Altschuler, U. S. Geol. Survey Trace Elements Memorandum Rept. 98, January 1950.)

It is difficult to establish the role of uranium in apatite from a study of phosphorite alone because of the difficulty (if not impossibility) of separating completely pure apatite fractions of high enough uranium content. It is known from laboratory experience that complete separation of uranium from phosphate rock requires the complete solution of all apatite present. In addition, uranium in phosphorite is not associated preferentially with fine-size material, and in material from one section of leached-zone rock the uranium content varied directly with the calcium content. This suggests that uranium may be held within the apatite crystal structure, possibly proxying for calcium. Other possibilities, of course, are that the uranium is adsorped on the surface of the apatite and that it may be present as a uranium-mineral impurity in the crystal structure or on the surface. Except for its occurrence in autunite, the uranium in the Florida deposits seems to be preferentially associated with apatite. In the leached zone, as leaching proceeds, it will be preferentially associated with apatite as long as any apatite is present, then with the calcium-aluminum phosphate, pweudowavellite, and then with the aluminum phosphate, wavellite. How the uranium occurs in the wavellite and pseudowavellite is not known.

To answer some of these questions a program of synthesis studies of apatite has been undertaken. The literature on apatite synthesis has been summarized in "Abstracts of the literature on synthesis of apatites and some related phosphates," by E. B. Jaffe (C. E. Boudreau), U. S. Geol. Survey Trace Elements Investigations Rept. 132, December 1950.

Specimens and X-ray data have been collected. Alpha tricalcium phosphate has been synthesized hydrothermally and fluorapatite and chlorapatite have been synthesized by dry fusion. The chlor- and fluorapatites were made from stoichiometric mixtures containing 2 percent uranium and lacking an equivalent amount of calcium. The uranium was introduced in chlorapatite in the form of the water-soluble uranyl chloride (UO_2Cl_2) and the yellow insoluble hexafluoride; in fluorapatite the uranium was introduced as the green insoluble tetrafluoride. The resulting products (all yellow) contained more than one percent uranium. The chlorapatite prepared with the water-soluble uranium salt retained its uranium after washing. Because of the small size of the synthetic crystals and the presence of some glass and inclusions it is not yet possible to determine from these experiments whether uranium has been substituted for calcium in these apatite structures.

In addition to these syntheses, chemical experiments have established that free calcite in phosphate rock can be differentially leached with a solution of triammonium citrate. As such leaching does not remove all the carbonate from phosphorite it is believed that this procedure may be used to distinguish and measure the relative amounts of calcite and structurally held carbonate. This has a bearing not only on the nature of carbonate apatite but also on the problems of the quantitative petrography of phosphorites.

Future work

Because of the previous lack of stratigraphic control and the practical necessity of describing the petrography of the leached zone, it had not been possible to check the conclusions arrived at in the leached-zone study by comparison with unleached rock of the same original lithology. During the 1950 field season a suite of seven matched stratigraphic sections was sampled which exhibit the onset and progressive development of leaching. By comparing the mineralogy, chemistry, and petrography of these samples and by studying the relations of any changes to stratigraphic position, it is hoped that conclusive observations can be made on:

1. The nature and amount of uranium enrichment.
2. The time of uranium enrichment.
3. The effects of texture and composition on uranium enrichment.
4. The relations among erosion, post-depositional slumping, and leaching.

Future field work will be directed toward petrographic study of the unleached part of the Bone Valley formation and the Hawthorn formation.

The synthesis studies will be continued in efforts to get larger crystals and completely crystalline products from uraniferous melts. If this is possible it may be feasible to establish the role of uranium in apatite from X-ray diffraction and electron diffraction studies.

A study of the transition temperature for the $\alpha - \beta$ inversion of tricalcium phosphate is in progress. The inversion is a means of distinguishing hydroxyl apatite from tricalcium phosphate. The work is being checked by X-ray diffraction and electron microscope studies.

The northwest phosphate project

Purpose

The main objectives of the northwest phosphate project like those of the Florida phosphate project are (1) to describe the mineralogy and petrography of the rock, (2) to establish the facts of uranium associations within the rock, and (3) to present new data on the petrology of phosphorites and their contained uranium. The general problems of apatite mineralogy and the occurrence of uranium in phosphorites are common to both projects and the studies described in the preceding section apply equally to the Phosphoria formation of the northwest. However, there are specific differences between the Bone Valley and Phosphoria formations. In contrast to the Bone Valley the Phosphoria phosphorite has a high organic content; it is more or less uniform laterally; its phosphate nodules show little variation in size; its rocks are folded and minutely fractured; its minerals are not greatly altered; it is more indurated; in its rich phosphate facies it is of entirely marine origin; it has a much higher content of certain minor elements such as vanadium, chromium, nickel, and molybdenum.

Because of the pronounced original uniformity of this deposit and of its lack of large-scale post-depositional alterations the study of the distribution of its uranium has been most fruitfully pursued by a determination of variations in the chemical composition of many samples. Because of the dispersed impurities in the rock (quartz, silt, micas, clay, carbonates, and organic matter) the nature of the Phosphoria apatite has been studied partly in this manner.

Results of investigations

It is known from X-ray diffraction studies that apatite is the predominant phosphate mineral in the Phosphoria formation. Analyses for F, CO_2, and P_2O_5 indicate that the apatite is a fluor-carbonate-apatite. In several suites of samples analyzed for these constituents the F and CO_2 increase in almost constant ratio with increases in P_2O_5. Although it is true that some excess fluorine and probably some optically imperceptible calcite are present (also some free fluorite) it is hard to attribute the regular relationship shown by the analyses to adsorption of CO_2 by apatite particularly as adsorption would involve a competition between F and CO_2 for adsorption sites.

The nature of the organic matter in Phosphoria rock and its extraction as an aid in optical study present a many-sided petrographic problem. It has been possible to extract some of the organic matter from finely ground samples by washing in detergent solutions such as a 2-percent solution of the commercial detergent Tide. This peptizes the organic matter and an organic sol is formed which can be washed from the rest of the material in the sample. Analyses of material before and after this treatment show that little if any of the uranium present is carried in the organic matter.

In studying the uranium distribution in the Phosphoria, analyses were made of 123 closely spaced samples from several measured sections for CaO, P_2O_5, U, and organic matter. It was found that uranium and P_2O_5 bear a good positive correlation to each other in groups of samples containing more than an average amount of uranium, but the same correlation is poor in groups of samples with less than average uranium content. The only positive correlation between uranium and organic matter occurs in a group of samples with the lowest uranium content. The negative correlations between organic matter and uranium are poor for samples with low organic content and (understandably) good for samples with high uranium content.

Size studies of the grains composing the rocks used for chemical analysis do not show any significant correlation between uranium and absolute grain size or sorting (measured as quartile deviation).

The relation of carbonate to apatite in the Phosphoria has been studied petrographically as well as by differential leaching. Thin-section staining by successive treatment with silver nitrate and potassium chromate shows calcite dispersed in apatite nodules in discrete clumps that are either too small or too much masked by organic matter and apatite to be distinguished optically.

Evaluation of analyses of bulk Phosphoria rock for Al_2O_3 and Fe_2O_3 shows that these two constituents have a similar ratio to each other throughout many vertical sections of rock. The ratio can be explained by the presence of illite or an iron-rich montmorillonite.

A more detailed account of much of the preceding material will be found in "Distribution of uranium in rich phosphate beds of the Phosphoria formation," by M. E. Thompson (in preparation).

Future work

As most of the apatite in the Phosphoria formation is in pelletal material the uranium content, composition, size, shape, and internal structure of the pellets will be studied. In addition, the bulk rock and the pellets will be compared mineralogically and chemically from weathered and unweathered sections and from folded and relatively flat-lying sections in an effort to discern any secondary concentrations of uranium or secondary mineralogic alterations.

Samples of low-phosphate mudstones will be collected for a study of the mica and clay minerals of the Phosphoria and to establish more closely the role of alumina and iron in the rocks.

In chemical study of vertically close-spaced samples none of the correlations shown by any single suite of rocks was applicable to all of the suites. A possible explanation of this is an original variation in uranium deposition. By studying, in the same manner, closely spaced samples from the same stratigraphic layers, the factor of variation in conditions of deposition will be diminished. Therefore, several suites of samples will be collected for study of lateral variations in composition.

Future synthesis and other laboratory studies described in connection with the Florida phosphate project apply here as well. Carbonate studies should prove especially significant in the northwest project. The possibility of using differential thermal analysis methods as a means of distinguishing free calcite from CO_2 structurally held in apatite is being investigated.

The Colorado Front Range project

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

Purpose.--It has long been recognized that a genetic connection exists between the Colorado Front Range mineral belt and the Tertiary "porphyry" belt with which it is coextensive for more than 90 miles.

The Central City district lies in the northern half of this belt. The association of ore deposits and porphyry is also well known to the prospectors of the region who have learned from experience that altered porphyry is generally good ground for prospecting.

It seemed fruitful, therefore, to study the relationship between the pitchblende deposition and the Tertiary porphyry series in the Central City district with two specific objectives in mind:

1. To determine the degree to which uranium is concentrated in successive members of the porphyry sequence known to be radioactive locally.
2. To determine the extent to which particular members of the porphyry sequence, and particularly their uranium content, might serve as indicators of pitchblende ore.

The two objectives are inter-related by the obvious fact that residual solutions from uranium-rich magmas may be expected to be uranium-rich also. The tendency for uranium to concentrate in granitic pegmatites and other late-stage liquids has been pointed out so often by geologists that it needs no amplification here. It was hoped that the study not only would make possible the setting up of mineralogic and petrologic guides to prospecting but also would supply needed data on the geochemical behavior of uranium. The results of the study to date are definitely encouraging.

Results of investigations.--Results of the study to date follow:

1. Geochemical behavior of uranium

A magma initially somewhat enriched in uranium (monzonite stage) became highly enriched in that element during the succeeding bostonite stage. These rocks contain up to 50 times as much uranium and thorium as the average for granitic igneous rocks. The intrusion of bostonite in the Front Range was followed by the deposition of pitchblende during the pyritic stage (early stage) of Tertiary mineralization. Bastin and Hill (1917) noted that the deposition of pitchblende was followed by the introduction of nonuraniferous galena and sphalerite. The latest intrusives in the area, biotite latite and alkalic syenite (?), are "fresh" rocks unlike the earlier members of the sequence. Hot springs near Idaho Springs well up along a syenite contact and indicate that the intrusion is still cooling at depth (Bastin and Hill, 1917). The biotite latite, as noted by Spurr and Garry (1908), contains inclusions of ore in the Stanley mine and is definitely postmineralization. Although the analytical data at present are scanty the uranium content of both the syenite and latite seems to be low and suggests a magma, or magmas, depleted in uranium.

The analyses given by Bastin and Hill show that the bostonite stage was characterized by a maximum enrichment in K_2O. A similar co-enrichment in radioactive constituents and K_2O was found to hold for the rocks of the southern California batholith studied by Larsen and Keevil (1947).

In the present study chemical analyses of 12 bostonite samples from 3 dikes indicate ThO_2 contents that are abnormally high but that, unlike the uranium contents, are fairly constant. ThO_2 content ranges from 0.022 to 0.030 percent as compared to a range in uranium content of 0.004 to 0.016 percent for the same rocks. Like many similar igneous rocks the bostonites contain more thorium than uranium. Keevil's Th/U ratios (1938), determined on 12 granites, range from 1.75 to 4.05. The ratios in the 12 bostonites studied range from 1.5 to 6.5. The bostonites showing the lowest uranium content exceed Keevil's Th/U range by more than 50 percent. This fact suggests leaching of uranium.

2. The radioactivity of bostonite dikes as an indicator of pitchblende

(A) All 17 pitchblende occurrences in the Central City district reported up to June 1950 and verified on good authority lie in an area which formed a center for bostonite intrusion. This is not so in other members of the porphyry series but monzonites are extremely abundant in the surrounding area in which bostonites are very rare. Both the bostonite and monzonite areas have been intensively mined, principally for gold and silver. The same pyritic types of mineralized rock are found in the two areas.

(B) Within the area in which bostonite is extensive 16 out of 17 pitchblende deposits lie less than 500 feet from a "low-grade" dike (uranium content less than 0.004 percent).

(C) Fringing the center of bostonite intrusion and the associated pitchblende belt there is a partial frame of higher-grade bostonite dikes (uranium contents ranging from 0.004 to 0.016 percent). So far as is known no pitchblende is associated with these higher-grade dikes, with one significant exception. Pitchblende was found in quartz-hematite stringers cutting the high-grade dikes at one station on Nigger Hill. The bostonite at this point has been hydrothermally altered, bleached, and depleted in uranium (U is 0.003 percent). The same dike has been sampled at eight other places along its strike and it maintains a consistently high uranium content (U from 0.005 to 0.016 percent) for a distance of more than a mile.

Because the uranium content of the bostonites seems to decrease with an increase in hydrothermal alteration, and because all occurrences of pitchblende thus far reported are found near (very rarely actually in) low-grade rather than high-grade bostonite it is inferred, as a working hypothesis, that the uranium now found in the veins was leached from the bostonites by hydrothermal solutions during the earliest stage of mineralization. Calculations indicate that 0.002 percent of uranium was leached from the low-grade bostonites associated with the pitchblende belt. Presuming that such leaching operated to a depth of 1,500 feet, this would account for nearly 1.5 times the total uranium production of the district to date.

The results reported here are based on analyses of porphyries collected at 64 field stations in the district. At all stations both the interiors of the dikes and the contacts (where exposed) were sampled. From these bulk samples the least-weathered material was selected for analyses and for thin sectioning. Roughly 100 chemical analyses for uranium, 12 thorium determinations, 20 total iron and ferrous and ferric iron analyses, and more than 150 radiometric determinations by laboratory beta counts have been made on these samples. Every major bostonite dike in the district has been sampled at at least three places along the strike, and one (the most radioactive of all) has been sampled at nine stations. Between stations the equivalent uranium content of the dikes has been estimated in the field by gamma counting with a portable counter. The gamma counts obtained in the field were calibrated against laboratory beta counts made on samples from the same outcrop throughout the range of 0.001 to 0.030 percent equivalent uranium. The method as used at present gives good reproducibility and will detect differences in percent equivalent uranium as low as 0.004 percent for outcrops containing less than 0.01 percent equivalent uranium, and as low as 0.01 percent for outcrops containing 0.02 to 0.03 percent equivalent uranium.

Future work.--On the basis of the results described in this study certain recommendations can be made as to prospecting for uranium deposits in the Colorado Front Range mineral belt. Areas of pyritic mineralization characterized by the presence of both high- and low-grade bostonite dikes should be prospected for uranium. Within such areas the ground near low-grade dikes is believed to offer more promise than that near high-grade dikes. The presence of high-grade dikes is necessary to establish the fact that the bostonites in a particular area were initially enriched in radioactive constituents. The evidence of low-grade bostonites alone without associated high-grade dikes may also be indicative but at present is less compelling because it is not known that bostonites, developed outside the Central City district, were initially uranium rich. Investigations of the distribution of radioactive bostonites in the surrounding region, particularly in the Georgetown quadrangle, are planned for the field season of 1951. These studies will be carried on in cooperation with the field geologists of the Survey. Additional sampling of the Tertiary intrusives of the Idaho Springs district and in the

Central City district also is planned in order to fill in the present data.

Laboratory work on these fine-grained porphyries will be continued in an effort to determine:

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

Alpha-sensitive nuclear emulsions applied to uncovered thin sections should give useful information as to the radioactive constituents.

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

Purpose.--The fluorite breccia ores of the Blue Jay mine, Jamestown, Colo., were selected for detailed mineralogical study because earlier work by Goddard (1946) had indicated that they were among the most radioactive rocks in the Jamestown district. The work was undertaken at the request of Survey field geologists who were engaged in a reconnaissance field study of the uranium reserves of the fluorite mines in the district. R. U. King and H. C. Granger of the Survey cooperated with George Phair during the time that Phair spent in the field. Samples studied were from the second level of the Blue Jay mine.

Results of investigations.--Laboratory studies show that uraninite is the major source of the radioactivity in these breccias. The identification of the uraninite is described in "Verification of uraninite in fluorite breccias from the Blue Jay mine, Jamestown, Colorado," by George Phair and Kiyoko Onoda, U. S. Geol. Survey Trace Elements Memorandum

Rept. 173, November 1950. The identification was based on X-ray diffraction studies supplemented by optical, chemical, and spectrographic evidence. This confirms Goddard's (1946) earlier tentative identification based largely on autoradiographs. All fluorites from the Jamestown district tested by Phair and Onoda give excellent direct-contact pseudoautoradiographs regardless of the content of radioactivity or of the presence or absence of actual radioactive minerals. By the use of suitable filters this effect was shown to be due to ultraviolet autoluminescence invisible to the eye.

The report cited above (TEMR-173) gives data to show that uranium concentrates averaging 5 percent can be prepared from bulk ore initially averaging 0.02 percent uranium by successive heavy-liquid and magnetic separations under controlled conditions in the laboratory. Methods using more finely crushed material could be expected to give somewhat higher-grade concentrates. Chemical analyses of different parts of the breccia ores indicate that the uranium is distributed as follows, in order of decreasing abundance:

1. In finely crushed matrix.
2. In deep purple fluorite.
3. In light purple fluorite.

The finely curshed matrix consists chiefly of fluorite, carbonates, clay minerals, wall-rock fragments, and sulfides in variable proportions. Thin sections show that the fluorite in the matrix is generally deep purple but in hand specimens the general color of the highly radioactive matrix is much lighter (generally light purple to gray) as a result of the dilution of the fluorite color by the light-colored gangue minerals. The deepening of the fluorite color is caused by:

1. Content of uranium or thorium or both.
2. Contact with radioactive emanations.

Deepening of the purple color by emanations is shown in thin sections. Both uranium and thorium halos are well-developed in the Blue Jay fluorite. The dark color extends outward from such halos along radial cracks. In addition, large grains of light-purple fluorite that are not of themselves rich in uranium or thorium show deep-purple borders against the highly radioactive crushed matrix. These phenomena must be due to daughter products (emanations) rather than to alpha emission from uranium or thorium.

In the course of the work on these fluorites uranothorite, probably of hydrothermal origin, has been identified as inclusions in fluorite. Surrounding these inclusions are good thorium halos. Neither uranothorite nor thorium halos in fluorite have been previously described in the literature. A report on this phase of the work, "Hydrothermal uranothorite in fluorite breccias from the Blue Jay mine, Jamestown, Boulder County, Colorado," by George Phair and Kiyoko Onoda, is in preparation.

<u>Future work</u>.--Additional work is planned on the effects of radioactive emanations on the color of the Blue Jay fluorites. Studies will be made involving the measurement of 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 element 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

Purpose.--This study was undertaken to ascertain the facts concerning certain material on old mine dumps from the workings in pyritic pitchblende deposits and material from the oxidized zone of such deposits in which both the dump material and material from the oxidized zone are highly radioactive but contain relatively little uranium or thorium. In this type of material secondary uranium minerals are likely to be rare or absent.

Results of investigations.--Two 5-pound samples from the weathered dump of the Wood mine, Central City district, Colo., the nation's second largest producer of pitchblende to date (production stopped about 20 years ago) show excessive quantities of radium. Two 5-pound samples from the "hot spot" (radioactively speaking) of the dump show Ra/U ratios that are nearly constant at 150 times the equilibrium value although the uranium contents differ by a 7-fold factor. The constant but excessive Ra/U ratio can be explained only by postulating the recent leaching of 99 percent of the uranium and fixation of the residual radium. Such differential leaching of uranium with respect to radium is to be expected in the highly acid oxidizing environment of pyritic dumps because of the extreme insolubility of $RaSO_4$ and the high solubility of UO_2SO_4.

Results of this work will be reported in "Some factors in the differential leaching of uranium and radium in pyritic mines and mine dumps," by George Phair, which is now in preparation.

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

References

Bastin, E. S., and Hill, J. M., 1917, Economic geology of Gilpin County and adjacent parts of Clear Creek and Boulder Counties, Colorado: U. S. Geol. Survey Prof. Paper 94.

Goddard, E. N., 1946, Fluorspar deposits of the Jamestown district, Boulder County, Colorado: Colorado Sci. Soc. Proc., vol. 15, no. 1, pp. 1-47.

Keevil, N. B., 1938, Thorium-uranium ratios of rocks and their relation to lead ore genesis: Econ. Geol., vol. 23, no. 7.

Larsen, E. S., and Keevil, N. B., 1947, Radioactivity of the rocks of the batholith of southern California: Geol. Soc. America Bull., vol. 58.

Colorado Plateau carnotite project

Purpose

The main purpose of the laboratory investigations of the carnotite deposits of the Colorado Plateau is the development of ore guides that can be used in the search for new deposits. The investigations are also designed to provide mineralogic data to metallurgists working on problems of ore beneficiation and to provide mineralogic and petrographic data to field geologists to aid them in their studies. Finally, the investigations will provide new data as to the occurrence of uranium in carnotite-like deposits and will contribute to the solution of problems of geologic age determinations involving radioactive disintegration.

Useful ore guides for the exploratory drilling program on the Colorado Plateau may be established empirically from statistical studies of drill cores and the environment of known deposits, from the use of geophysical exploration methods, or from laboratory and field studies of the origin of carnotite-like deposits. Ore guides developed from a knowledge of the origin of the deposits, in particular, should be applicable over wide areas as well as in the different beds in which the ore has been found.

Any hypothesis of the origin of the carnotite deposits that will give information useful in the search for new deposits must include a basic and unique estimation as to the time of ore deposition relative to the enclosing rocks. This critical estimation must then be checked by all field and laboratory methods at our disposal before the ore guides implied by the hypothesis can be practically applied. Geologic theories seldom can be conclusively established and it is not surprising, therefore, that a positive and unequivocal dating of the carnotite deposits by field methods alone has not yet been accomplished. It is expected, however, that, evidence established by studies of radioactive disintegration in the radioactive minerals of the Plateau deposits will contribute greatly to dating the ore deposition and, added to the backlog of field facts established by Fischer and others, will perhaps establish the origin of the deposits.

The work of the Section on this project consists of a broad study of radioactivity methods of dating the ore deposition and mineralogic and petrologic study of the deposits.

Results of investigations

The only strictly quantitative means available for dating the deposits depends on the regular processes of radioactive decay of uranium in the carnotite and related minerals and on the accumulation of predictable amounts of radioactive daughter products and the stable end products, Pb^{206} and Pb^{207}. Other methods can provide information that may broadly limit the time of deposition or at best provide relative information on the age of the carnotite. These methods depend on the roughly predictable mineralogic and petrologic relations of the ore minerals to each other, to the major rock-forming minerals, to the cementing materials, and to the microstructures in the host rock implicit in the estimated time of ore deposition. Further limits on the age of the deposits may be established from a study of the chemical and physical properties of the ore minerals and the chemical and physical conditions existing in the host rock at the estimated time of deposition of the ore.

Results of the geologic age studies of the carnotite are described in the report, "A preliminary report on methods of determining the age of Colorado Plateau carnotite," by L. R. Stieff, M. N. Girhard, and T. W. Stern, U. S. Geol. Survey Trace Elements Investigations Rept. 108, April 1950. I quote the abstract in part:

> Four methods of dating Colorado Plateau carnotite have been examined and evaluated: mineralogic methods, radioactive-equilibrium methods, lead-uranium-ratio methods, and lead isotope methods. The data on 12 high-grade samples, from a suite of 50 representative carnotite ores, are presented....
>
> Two of the 12 high-grade samples are approximately in radium-uranium equilibrium. One sample has a 5-percent excess of radium, and the remaining 9 samples are deficient in radium. The minimum radium-uranium age of the 2 samples in radium-uranium equilibrium is approximately 500,000 years. The maximum radium-uranium age of 2 essentially lead free samples not in radioactive equilibrium are 15,000 and 40,000 years. Samples which contain lead and which are not in radium-uranium equilibrium cannot be dated by this method. Near-surface occurrences of the predominantly crystalline samples have the greatest radium deficiencies. The only sample of crystalline carnotite found at depth, however, has a 5-percent excess of radium. Radium content of the 7 predominantly microcrystalline samples ranged from an excess of 2 percent to a deficiency of 20 percent.
>
> The 3 high-grade carnotites that are most nearly in radium-uranium equilibrium and that probably have been least disturbed have uncorrected lead-uranium-ratio ages that range from 21 to 77 million years. The age of the 3 predominantly crystalline samples that can be calculated by the lead-uranium-ratio method range from 30 to 35 million years.
>
> The Pb^{206}/U^{238} and Pb^{207}/U^{235} ratio age calculations corrected for common lead but uncorrected for the possible addition of radiogenic lead are essentially in agreement for each sample but range from 27 to 96 million years. The Pb^{207}/Pb^{206} ratio ages are in marked disagreement with the lead-uranium-ratio ages and range from 520 to 600 million years (late pre-Cambrian). Assuming correct analyses the paradox of late pre-Cambrian radiogenic lead in deposits whose maximum age is late Jurassic may be explained by (1) the loss of radon or (2) the introduction of old radiogenic lead. It is believed that the quantitative dating of these ores by the lead-uranium ratio and lead-isotope methods will be possible when mass-spectrographic analysis has established the source of the lead in the carnotite.

Stieff and his colleagues spent the field season of 1950 on the Plateau doing detailed mineralogic studies and carefully collecting samples in the area for isotope determinations. These samples were collected to provide data (1) on the carnotite from as many mines as possible, (2) on composite mill pulps representing about 5,000 tons of ore from many mines, (3) on the lead in the so-called "galena band", (4) on a suite of samples from one mine for detailed study, and (5) on the barren sandstone.

The lead from many of these samples has been extracted in the Survey laboratory, converted to lead iodide under carefully controlled conditions, and the lead iodide sent to Roger Hibbs at Oak Ridge for mass spectrometric isotopic analysis. Analyses of 45 samples have been received from Oak Ridge to date and these data are now being processed by the rather involved and lengthy calculations necessary to make them useful for age determinations. Chemical analyses on these and other samples for uranium are partly completed as are the necessary radiometric determinations. This work should show whether the loss of radon or the addition of old radiogenic lead is responsible for the anomalous isotopic compositions observed.

If the loss of radon has been a significant process in the history of the deposits, the corrected ratios of Pb^{207}/Pb^{206} would be expected to show wide variations with changes of grade of the ore. Likewise, the Pb^{207}/U^{235} ratio ages should be the most reliable and they should be nearly the same from sample to sample. The corrected Pb^{206}/U^{238}, Pb^{207}/U^{235}, and Pb^{207}/Pb^{206} ratio ages calculated would be expected to be in reasonably close agreement.

If significant amounts of old radiogenic lead have been added to the ores the corrected Pb^{207}/Pb^{206} ratio ages would be expected to show relatively small variations with changes in the grade of the ore and should not differ markedly from the Pb^{207}/Pb^{206} ratio ages of the samples representing large tonnages of ore. If this is so a quantitative dating of the deposits might not be possible, but the presence of relatively large amounts of old radiogenic lead in the carnotite ores would clearly indicate a Tertiary age for the deposits.

When the lead isotope studies have been put on a firm statistical basis it seems reasonable to expect that they will give important information on the geologic history of the lead associated with the carnotite and the age and origin of the deposits.

Radium-uranium equilibrium studies can be used to date carnotite ores only when the corrected Pb^{206} and Pb^{207} content of the ore is negligible or when it is certain that the radiogenic lead in the sample has been added. Two samples meeting the first condition have been studied and give radium-uranium ratio ages of 15,000 to 40,000 years. If the lead isotope studies indicate the addition of large amounts of old radiogenic lead the importance of the radium-uranium ratio age determinations will increase and samples containing radiogenic lead but not in radium-uranium equilibrium can be dated.

This whole study is providing a great amount of data which will be of the utmost significance to the large question of methods of geologic age-determination based on radioactive disintegration.

Mineralogic and petrologic studies have proceeded along with the age studies. Basic to these studies are the recognition and identification of the uranium- and vanadium-bearing materials found in the ores. In the course of this work new X-ray and optical data have been obtained on minerals incompletely described in the literature such as pascoite, hewettite, metahewettite, and vanoxite. Two new vanadium minerals, named hummerite and montroseite, have been recognized. They are described in an abstract presented at the annual meeting of the Geological Society of America in Washington in November 1950, under the title, "Hummerite and montroseite, two new vanadium minerals from Montrose County, Colorado," by Alice Dowse Weeks, Evelyn A. Cisney, and Alexander Sherwood, Geol. Soc. America Bull., vol. 61, no. 12, pt. 2, p. 1513, 1950. The abstract follows:

> Two new minerals, collected in the summer of 1949, are described and compared with previously known vanadium minerals from Colorado.
>
> Hummerite was first identified in bright-orange veins in gray clay at the Hummer mine of the Jo Dandy Group on the southwest side of Paradox Valley, Montrose County, Colorado, and later as a yellow efflorescence on sandstone at the North Star mine on the opposite side of Paradox Valley. It is translucent, water soluble, and similar in appearance to pascoite but has the composition hydrous magnesium vanadate. The X-ray powder pattern of crystals formed by evaporation of a water solution is the same as that of the original vein mineral. The recrystallized material is triclinic, pinacoidal class, and forms crystals elongated parallel to the c axis or tabular parallel to the b and c axes. It is optically negative, has strong dispersion, and nY = 1.81. The chemical analysis and morphologic and X-ray crystal data will be presented.
>
> Montroseite, in black microscopic bladed crystals, was found in the Bitter Creek mine on the northeast side of Paradox Valley, Montrose County, Colorado. It is orthorhombic, probably rhombic-dipyramidal class, opaque, and has the composition $2FeO \cdot V_2O_3 \cdot 7V_2O_4 \cdot 4H_2O$. Morphologic and X-ray crystal data are presented together with spectrographic and chemical analyses.

Studies in the synthesis of carnotite and related minerals have resulted in the report, "Hydration and base exchange properties of carnotite, tyuyamunite, and related compounds," by K. J. Murata, E. A. Cisney, L. R. Stieff, and E. V. Zworykin, U. S. Geol. Survey Trace Elements Investigations Rept. 107, March 1950, Geol. Soc. America Bull., vol. 61, no. 12, pt. 2, pp. 1489-1490, 1950. This was presented as an abstract at the Geological Society of America meeting mentioned above as follows:

> Hydrated uranyl vanadates of potassium, ammonium, thallium, calcium, strontrium, barium, sodium, copper, and zinc were synthesized as part of a mineralogic study of carnotite and tyuyamunite. Microscopic and electron-microscopic examination show the crystals to be diamond-shaped plates with micaceous cleavage.
>
> On the basis of x-ray powder patterns, these compounds may be classified into two structural types:
>
> Type I. Compounds of K, NH_4, and Tl
> Type II. Compounds of Ca,Sr,Ba,Na,Cu, and Zn
>
> The two types of compounds also differ greatly in the degree of hydration. Type I compounds contain about 1 molecule of water in the air-dried state; type II compounds, 5 to 9 molecules. The higher hydration of type II compounds may be correlated with the presence of low-angle, basal reflections in their x-ray powder patterns.
>
> The water molecules and the characteristic cations (K, NH_4, Ca, etc.) occur between uranyl vanadate layers, a condition analogous to that found in the clay mineral montmorillonite. There is a progressive decrease in the interlayer spacing of type II compounds as water is removed by heating.
>
> Type II compounds, when treated with solution of potassium salts, rapidly exchange their cations for portassium and are converted to carnotite. This entails a contraction of the interlayer spacing as the lower hydration characteristic of type I is assumed. The reverse process, the conversion of carnotite to compounds of type II, involves the expansion of interlayer spacing and takes place much less readily.

The main objective of these synthesis studies is to provide standard reference samples of carnotite, tyuyamunite, and related minerals for use in the identification and description of the natural material. These studies will also contribute greatly to a knowledge of the chemical and physical conditions that might control the deposition of carnotite and to the geochemistry of uranium.

The recognition of the different radioactive materials in thin section and as powders in mineral separates has required the modification or development of new techniques, particularly in the use of alpha-sensitive photographic emulsions. A useful technique is reported in "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 abstract follows:

> Some modifications of current techniques for preparing nuclear plates for mineralogical studies are described. A method of mounting nuclear-track stripping film on thin sections is given. Illustrations are presented of the application of these techniques to the study of radioactivity of powdered rocks, minerals, or thin sections.

These techniques have aided in distinguishing microcrystalline carnotite from other fine-grained yellow minerals in the deposits and they have been used to show that some fine-grained green, brown, red, and opaque materials in the deposits also contain uranium. The identification and description of these materials are now in progress. These new methods of study have also shown that a colorless mineral, probably barite, in the deposits, contains colloidal concentrations of radium. A study of these radiocolloids should aid in evaluating the lead-uranium ratio age determinations and in interpreting the recent alteration of the deposits.

So far, petrologic studies of the ore suggest that carnotite was usually the last mineral deposited. Carnotite is apparently later than either the calcite or siliceous cements and many of the thin sections show quartz with highly irregular boundaries indicating partial solution of the quartz prior to or at the same time as the deposition of carnotite. Although the dating of the fracturing of the quartz grains is uncertain many of the fractures in the grains are filled with carnotite. Vugs, presumably young, have also been seen with crystals of carnotite projecting into them.

Work is in progress on the problem presented by the occurrence of red and gray clays associated with ore in the Salt Wash member of the Morrison formation and on the problem of the mineralogy of the Salt Wash clays as compared with the clays of the Brushy Basin, Burro Canyon, and Dakota formations lying stratigraphically above, and the Summerville formation lying stratigraphically below the Salt Wash.

In preliminary studies of the clays underlying the ore of the Morrison formation, chemical analyses show that the red clay contains more total iron and more ferric iron than the gray clay. Spectrographic analyses of minor constituents show no significant difference between the red and gray clays except in iron content. The chief clay mineral in the Salt Wash has been tentatively identified as hydrous mica and in the Brushy Basin as montmorillonite.

Work on the clays will be reported in "Red and gray clays underlying ore sandstone of the Morrison formation in western Colorado," by Alice Dowse Weeks (in preparation).

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.

Properties of uranium minerals project

Purpose

A study of the properties of uranium minerals was undertaken by the Section primarily to provide a means of identifying these minerals and to contribute to the knowledge of the geochemistry of uranium. A survey of the existing literature in the summer of 1948 showed that the nomenclature of the uranium minerals was in a confused state. It also showed that there were little or no data on the properties of many minerals of this group. It soon became apparent that many specimens in collections in the Survey, the National Museum, and elsewhere were mislabeled. Clifford Frondel at Harvard, who has been assembling data for the seventh edition of Dana's System of Mineralogy, had information about many unnamed uranium minerals assumed to be new. He offered to aid in this project, as did George Switzer at the National Museum, and both have been more than generous with their knowledge, help, and specimens from their collections.

It was decided to prepare first a glossary of uranium- and thorium-bearing minerals to bring some order out of the confusion of nomenclature. It was necessary to assemble a library of X-ray diffraction powder patterns and to assemble on index cards the data on d-spacings. Optical, chemical, and other properties had to be assembled from the literature, redetermined if faulty, or newly determined if not previously measured. A field manual for uranium-mineral identification had been requested by many field geologists. The problem of the metamict minerals was pressing. And finally, a monograph on the properties of uranium minerals was needed badly. The Section decided to undertake the preparation of such a monograph and to investigate these other problems.

Results of investigations

The glossary was assembed and published under the title, "A glossary of uranium- and thorium-bearing minerals," by Judith Weiss Frondel and Michael Fleischer, U. S. Geol. Survey Circular 74, April 1950. It has 325 entries representing 81 mineral species containing uranium and thorium as major constituents, 39 species containing small amounts of uranium and thorium, 29 species that should be tested for uranium and thorium, and 13 species that have been reported to contain impurities or intergrowths of uranium and thorium. This first edition, up to date as of March 1950, consisted of 2,500 copies and is nearly exhausted. A new edition with corrections and additions will be prepared during the summer of 1951, and further editions will be issued as new data are obtained.

A library of X-ray diffraction powder patterns was started as soon as the Section was organized and is constantly growing. In January 1951 it consisted of 75 standard patterns and about 600 patterns of duplicate material, unknown material, and material the data for which are incomplete. Specimens for these patterns were obtained from collections at the National Museum, the American Museum of Natural History, Harvard University, the Geological Survey, and miscellaneous sources. A card catalog of d-spacings for the patterns has been prepared and duplicates can be made available.

It was early decided in consultation with the Atomic Energy Commission that the Survey in cooperation with the National Museum would serve as a repository for data on the uranium minerals and would in turn serve as a source of X-ray patterns, X-ray spindles, data cards, and specimens for workers in the field of uranium mineralogy. The mechanism of cooperation in this field has been discussed at two conferences on uranium mineralogy sponsored by the Atomic Energy Commission, one held in the New York offices of the Commission in April 1950 and the other in the Section's Washington laboratory in November 1950. These conferences were attended by representatives of laboratories in Canada and the United States.

In order to make known to these representatives and others the X-ray patterns, spindles, and specimens in existence at Harvard, the National Museum, and the Geological Survey, a catalog has been prepared entitled, "A catalog of study material of radioactive minerals," by T. W. Stern, U. S. Geol. Survey Trace Elements Investigations Rept. 129, October 1950. This catalog, in addition to listing the material mentioned, gives the conditions under which specimens, patterns, and spindles can be obtained by interested workers. Additions to the catalog will be made as the work progresses.

A program of determining the optical properties, chemical composition, and other properties of those uranium minerals for which adequate information is lacking is in progress. In this field there is, of course, enough work to keep a score of laboratories busy, and duplication of work by other laboratories is avoided as much as possible. Mr. Donald

Everhart, Mrs. Muriel Mathez, and others of the Atomic Energy Commission circulate information among the cooperating laboratories, and the mechanism of cooperation and communication in this respect is constantly improving.

An example of studies in this field is the paper, "Studies of uranium minerals (IV): Zeunerite," by Judith Weiss Frondel, in manuscript, ready for publication in the American Mineralogist. This paper reports the results of work on synthetic zeunerite and natural zeunerite from Tintic, Utah.

A special problem in identification arises for those radioactive minerals that are metamict. This thorny problem has been discussed at both mineralogic conferences mentioned, and a resumé of the Survey's work in this field was given by Joseph Berman at the November meeting. Berman pointed out that:

> Minerals subject to metamictization are generally those that contain radioactive elements but not all minerals with radioactive elements necessarily become metamict. Conversely, some compounds with only minor amounts of radioactive elements (i.e. allanite) are often found in the metamict state. Examples of radioactive minerals usually found in the metamict condition are the thorites (including the uranothorites or orangites), some zircons, allanite, fergusonite-formanite series, pyrochlore-microlite series, euxenite-polycrase series, eschynite-priorite series, samarskite, betafite series, and many related minerals. Notable examples of radioactive minerals not as yet found in the metamict state are thorianite, monazite, and sphene. It is to be noted that with the possible questionable exception of uraninite, all of the metamict minerals are silicates and rare earth multiple oxides of columbium, tantalum, and titanium. Minerals of the columbite-tantalite series which contain no rare earths and which are free of radioactive elements have not been found in the metamict state.

Berman, in the course of his work, has found that:

> The metamict minerals heated in this laboratory assume a crystallinity that is not necessarily that of the original crystal. They definitely do not revert to a crystal with the original orientation but instead become microcrystalline rather than holocrystalline. However, empirical data disclose that controlled ignition of the metamict mineral and subsequent X-ray powder patterns of the ignited material yield a sufficient identity of patterns to be used for purposes of identification. For example, the metamict thorites and uranothorites (orangites) may readily be identified when ignited properly because they give a strong pattern of thorium oxide (when only very minor amounts of impurities are present) or a pattern equivalent to "huttonite", a monoclinic dimorph of thorite. Since no metamict thorianite is known, any metamict material properly ignited and giving an X-ray powder pattern of thorianite must necessarily be a metamict thorite. Care must be exercised in the method of ignition because other metamict minerals containing thorium give the anomalous thorianite pattern when improperly heated. Likewise, other metamict minerals show considerable variations in their patterns unless ignited under controlled conditions.

Studies are being made to establish the best heating conditions for metamict minerals. Experiments have been at controlled temperatures in an electric furnace in atmospheres both of air and of nitrogen. Reproducible results for identification purposes have been achieved by heating at 950°C ± 20°C for a period of 30 minutes. For some of the samples under this procedure slightly different patterns result. The difference is mainly in the presence of certain lines when the mineral is heated in air and a corresponding absence of these lines when the mineral is heated in nitrogen alone. The reason for this is not known definitely although the lines present only when the mineral is heated in air may be due to the formation of extraneous oxides. All samples are being heated in air and nitrogen at present.

Much of the scanty literature on metamict minerals is in foreign languages, and Theodore Botinelly is compiling a selected annotated bibliography on the subject. This bibliography will be made available for distribution when it is finished.

As work progresses in the Survey and elsewhere, the monograph on the properties of uranium minerals comes nearer fruition. A tentative outline for the monograph was distrubuted to those present at the November mineralogic conference and comments and suggestions have come in from Frondel at Harvard, Switzer at the National Museum, and others. It is agreed that each uranium mineral species should be represented by at least the following:

1. As good a chemical analysis as possible
2. Spectrographic analysis
3. Optical data
4. X-ray data
5. Description of physical properties
6. Distinguishing characteristics for identification
7. Occurrence

The outline goes into much more detail.

Where reliable information in these categories and others is not available in the literature it will be gathered by studies in the Geological Survey augmented by studies in other laboratories. For many rare species not enough material is available and synthesis of some of these is being attempted. The synthesis work is assuming an increasing importance in these studies and will contribute greatly to a knowledge of the formation of uranium minerals in nature.

Data collected for the monograph are being arranged for inclusion in a handbook for the field identification of uranium minerals. Many requests for such a handbook have come from geologists in the Survey, some of whom have sent in outlines of what they think would be useful to include in such a work from their experience in the field. Production of this handbook is under study.

Another aid would be a set of punch cards based on the properties of uranium minerals for identification (insofar as possible) in laboratories and field offices where X-ray data and equipment and chemical analyses are not available. This idea, too, is 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 black shale project

The goal of investigation of black shales, in particular those of the Chattanooga shale, was the same as that stated for the phosphate projects. Work on the shales has been very slight. It began when the Section was first organized when interest in the shales as a source of uranium was at its height. The work that was done was paralleled more or less by work done at Battelle Memorial Institute and in the laboratories of Y-12 at Oak Ridge, and the results were about the same in all three laboratories. In the Survey an annotated bibliography on the black shales was prepared (but not published), and the basic mineralogy of the shales was established.

For instance, the composite volumetric mineral composition of four samples of the shale from near Smithville, De Kalb County, Tenn., is as follows:

Mineral	Percent by volume
Quartz	20 - 30
Pyrite and marcasite	5 - 15
Calcite	2 - 10
Muscovite and sericite	2
Clay minerals	5 - 10
Kerogenous material	35 - 50

The clay minerals seem to consist largely of hydromica. Oil content by the Fischer method ranges from a trace to as much as 12 gallons per ton, but in roasting the shales a large amount of "off gases" is produced. Sulfide sulfur, sulfate sulfur, and organic sulfur are present up to as much as a total of 8 percent for many samples. In work to date, in the Survey and elsewhere, the manner of occurrence of uranium in the shales has not been determined.

As interest in the shales died down the project became dormant, and that is its status today. However, much groundwork has been laid as a starting point whenever it may become advisable to reactivate this project.

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 New York Atomic Energy Commission office, by Mr. Spelman of the Washington Atomic Energy Commission 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 by 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 studying 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. Progress in this project was reported in an abstract presented at the November 1950 meeting of the Geological Society of America in Washington, "Method of determining the age of igneous rocks using the accessory minerals," by E. S. Larsen, Jr., N. B. Keevil, and H. C. Harrison, Geol. Soc. America Bull., vol. 61, no. 12, pt. 2, p. 1480, 1950. The abstract follows:

> In the common igneous rocks most of the lead is concentrated in the potash minerals, and most of the radioactivity in the zircons and other accessory minerals. The lead in the potash minerals is believed to be mostly primary lead; that in the accessory minerals is probably chiefly radiogenic lead. By separating the accessory minerals of fresh igneous rocks, determining the lead with the spectrograph and the radioactivity by alpha counts, it was found that the age of the rocks could be determined with an error of approximately 10 percent. Basalts and gabbros may carry too few accessory minerals for satisfactory age determination by this method. Zircon is the most satisfactory mineral for this kind of determination and can be used for rocks as young as Miocene. Apatite from young rocks is too low in lead for accurate age determination, and sphene seems to give somewhat erratic results. By using very young rocks (Miocene) it was found that very little primary lead crystallizes with the zircon and apatite.

This study has been broadened considerably. Professor Larsen is cooperating with Harrison Brown and has sent him samples of accessory minerals on which to test Brown's "spiking" technique for the determination of lead isotopes which has been used with some success on samples of meteorites.

Professor Larsen also encouraged the start of a project in the Section on the development of new high-index liquids for the use of mineralogists and petrologists; progress in this study will be described in the section on chemical investigations. He also has a cooperative project with Professor Hurley of M.I.T. in which he has provided Hurley with selected samples of zircon for alpha counting.

Techniques used in investigations

Introduction

None of the research work described could be done without certain equipment and special techniques. The classic methods of mineralogic and petrologic research both in the field and laboratory have certain limitations,and therefore new techniques are constantly being devised to meet new problems and to solve old ones more rapidly or satisfactorily. These new techniques result in new types of instruments and the new instruments are revised as more new techniques in their use are developed. Many of the problems concerning radioactive materials demand new methods in their solution; this is particularly true when very fine-grained material like the phosphates are being investigated. Fortunately, the radioactive minerals exhibit characteristics that encourage the use of new and elegant methods of working on them; the use of nuclear emulsions to record and trace to their source alpha tracks from many of these minerals is an example. It is particularly important that information as to techniques used in a given laboratory be communicated to other laboratories so that all can benefit as new methods are developed. This section describes some of these methods (as well as older ones), and they will be the subject of reports in the Trace Elements Memorandum series from time to time.

Concentration and separation

Concentration and separation of pure mineral phases are basic to mineralogic and petrologic research. They are major headaches in much of the work on radioactive materials. The subject has been discussed at the two mineralogic conferences mentioned, and the conclusion has been that much work needs to be done in this field.

Use of the Superpanner and Infrasizer has been found to be particularly helpful in the clay studies of the Colorado Plateau carnotite project and also on the phosphate projects, both of which deal with material in sub-sieve sizes. The Superpanner has not been used in working with carnotite-bearing samples as the carnotite would contaminate it beyond further use with other materials.

Lorin Stieff has devised a combined air-scrubber and Cottrell precipitator which has been used successfully in producing high-grade carnotite concentrates. The scrubber part consists of a bowl-like receptacle containing air jets. The sample is put into the bowl and agitated by air from the jets. This sets up a scrubbing action of the sand grains in the sample, and the fine-grained carnotite is set free. An outlet at the top of the bowl leads to a glass cylinder enclosing a copper cylinder and an axial copper wire which forms a Cottrell precipitator when connected to a high-voltage source. The fine-grained material containing the carnotite set free in the air-scrubber is blown up into the cylinder and a variable precipiation of the fine-grained particles (as fine as 10 microns in size) on the inner wall of the copper cylinder can be achieved by varying the air velocity and the voltage. This is essentially a size separation and high-grade carnotite separates are possible in this manner because much of the carnotite is in certain size fractions. A report on this instrument is in preparation.

The Franz Isodynamic magnetic separator, the induced-roll magnetic separator (Carpco model), and high-intensity hand magnets are used constantly. An electrostatic separator (Carpco type) has recently been put in operation and should increase the scope of separation in the laboratory.

Heavy-liquid separation is used extensively and is based on the use of methylene iodide, Clerici solution, bromoform, and acetone. Alcohol-free bromoform is preferred to acetylene tetrabromide because of its greater liquidity, but it is more expensive. Mixtures of the two have been used to advantage. It is possible that as a by-product of the study of high-index liquids new heavy liquids may be developed.

A laboratory-size Wilfley table is on order and should prove useful in rough concentration of large volumes of material. For example, it will be used on Professor Larsen's age determination project to make rough preliminary concentrations of the accessory minerals in large samples of igneous rocks. Laboratory-size flotation cells are also being made, and collections of a wide variety of flotation reagents have been obtained free from a number of companies making these reagents. Flotation has long since proved its usefulness in many types of laboratory separations and much more can be done in this field, especially in dealing with small samples.

For many samples it is necessary to resort to hand-picking methods under the microscope. For those uranium minerals that fluoresce hand-picking is done under lights of appropriate wave-length. This can be done under both the petrographic and stereoscopic microscopes or under large magnifiers.

Simple gold-panning and vanning techniques are used on some samples and simple vibration of a sample on a sheet of paper works well for many platy minerals.

The use of ultrasonic methods of concentration seems to have possibilities and is under study.

A Burgess "Vibra-Tool" (essentially a small vibrating chisel) has been used to advantage in scraping off thin films of minerals from the surface of samples. The action of the tool can be controlled so that relatively pure samples can be collected in this manner.

Most concentration is preceded by some form of crushing and grinding of the sample and methods are more or less standard. However, for much of the work with radioactive materials contamination is a serious problem and particular care must be used to keep high- and low-grade material separate. This is done by having separate facilities for the different grades and where extreme care must be used (such as in separating accessory minerals for age determination) the grinding is done by hand on hardened steel plates under a hood.

For many studies with small samples a small tumbling mill has been developed consisting of a glass bottle holding about 25 grams of material and rotated by a small air motor. This can be called a ball mill without a foreign grinding medium.

Nuclear emulsions

The use of nuclear emulsions to record alpha tracks has proved of great importance. The development of new techniques of using stripping films has been described (TEIR-127) in the section on the Colorado Plateau carnotite project. The stripping films are used on thin sections and form permanent mounts. Studies are in progress using unsupported emulsions on thin sections to make permanent mounts, and results are encouraging. Backed nuclear emulsions have been found useful in isolating radioactive minerals in powdered samples. In the work with nuclear emulsions Herman Yagoda of the National Institute of Health has aided with advice and suggestions.

Electron microscopy

The Section's electron microscope laboratory, equipped with an RCA electron microscope, an RCA electron diffraction unit, and an evaporation unit is in constant use for work on fine-grained materials such as the phosphates, carnotite, clays, and the fine-grained products of the synthesis studies. In preparing sample mounts it is hard to get a proper dispersal of the mineral powder and this has been a serious problem in electron microscope laboratories. Edward Dwornik has solved this problem for many samples by dispersing the mineral powder in a Waring blender. For very small samples he has devised a miniature Waring blender based on having a proper-sized bit of a Handee tool, rigidly mounted, rotate in a small vial of 5- to 10-ml capacity which contains the sample and dispersing medium.

The electron diffraction unit produces electron diffraction patterns from material that is too fine-grained to give recognizable X-ray diffraction patterns. It is also used for patterns from single grains seen in the electron microscope. It is theoretically capable of producing patterns from small grains in polished sections, but in practice the method is not simple and is now under study. A particular advantage of the electron beam is its small diameter (about 1/1000 of an inch) and it can form a pattern of a contaminant which may be present in such small amounts (less than 2 percent) that it will not be detected by the X-ray beam. The electron beam has a low penetrating power and therefore has found great use in work in metallurgical laboratories on surface films on metals. It should therefore be useful in studying surface films on minerals in polished section. This possibility is also under study.

Problems in interpretation are presented by all the patterns attained, and it is obvious that a library of standard patterns is necessary. Such a library has been started and now consists of about 150 patterns.

The evaporation unit is used for "shadow casting" techniques. It is also used for other purposes such as the preparation of standards for alpha-plate work in which films of uranium of known thickness and area are deposited on glass slides. These slides are then used as standard sources in alpha-plate studies.

Mass spectrography

In the spring of 1950 the Survey bought the necessary materials with Survey funds to build a mass spectrometer after designs furnished by Roger Hibbs of K-25, Oak Ridge. The Survey is now building this instrument, and it will be set up in the Section's Washington laboratory. It will then be available for determinations of lead isotope abundances, for example, of the type that are now being made for the Survey at Oak Ridge. It will also be available for many types of isotope abundance determinations.

In connection with the isotope work the Survey is making arrangements to prepare lead isotope standards and will distribute these to appropriate laboratories. These standards will be useful for instrument calibration and as a check on determinations made in different laboratories.

Optical spectrography

The aid of chemical analysis and radiometry in mineralogic and petrologic investigations of radioactive materials is obvious. Spectrographic analysis, however, has not been used as widely as it should be. It has been found indispensable in the Section's work. The qualitative, semiquantitative, and quantitative determination of both minor and major elements in minerals under study often result in producing the deciding evidence in problems of identification in conjunction with X-ray and optical evidence. The rapidity with which tests can be made and the small amount of sample that can be used are two of this method's decided advantages. The spectrographers, therefore, work closely with the mineralogists in much of the mineralogic work.

Differential thermal analysis

At present a portable differential thermal analysis unit (made by Eberback and Son, Ann Arbor, Mich.) is in use in the northwest phosphate project. The portable instrument was designed by Reuben Nelson of the Survey after an idea furnished by Sterling Hendricks of the Department of Agriculture. A recording instrument designed by George Faust of the Survey is available in the investigations Section of the Branch and has been used in a preliminary way on some of the red and gray clays from the Colorado Plateau. It is planned to expand the use of this very useful method on many of the materials under study.

Miscellaneous techniques

The development by the Section of new high-index liquids for refractive index work is of great importance and has excited the interest of many geologists throughout the country and abroad. This study is a joint mineralogic and chemical study, and, as mentioned, will be described in the section on chemical investigations.

A thin-section laboratory is now partially in operation. Methods of mass production of thin section as developed by Charles Meyer of the Anaconda Copper Mining Company will be used.

Flux tests for the detection of radioactive mineral grains in powdered samples are in constant use. This test employs a sodium fluoride-sodium carbonate flux similar to that used in the fluorimetric method of uranium analysis. The grain in question is fluxed and examined under a light of the proper wave length. A field method for the estimation of uranium content on samples in field offices, using this same flux, has been devised for the use of the mineralogists by the chemists of the Section. In practice this method employs standard flux disks of known uranium contents in the desired range; these disks are prepared in the laboratory. In the field office a given weight of sample is prepared as a flux disk, and its fluorescence under an appropriate lamp is compared to the fluorescence of the standard disks. Good estimations of uranium can be obtained in this way on many materials, such as phosphates.

CHEMICAL INVESTIGATIONS

Introduction

Chemical research in the Section has been broad and varied. Much of it has been concerned with improving known methods of analysis for uranium, thorium, and other elements and compounds, modifying existing methods for particular applications, and devising new methods. In the analytical work of the Section a wide variety of radioactive rocks, minerals, ores, and synthetic materials are handled; during the fiscal year 1950 nearly 45,000 samples were received. It is necessary, therefore, to employ analytical methods that are rapid and reasonably accurate. Much of the material handled is very low-grade in terms of uranium, and it is therefore necessary to use highly sensitive analytical methods. Conversely, some materials require the very highest accuracy, and standard methods that can be used with high accuracy for one material will not be applicable to other materials. Finally, the precision and accuracy of analytical methods are hard to determine, and it is necessary to investigate continually the quality of analyses performed.

Before the organization of the Section and during the time that the atomic energy work of the Survey was conducted on behalf of the Manhattan District and later on behalf of the Atomic Energy Commission the Survey contributed significantly in devising methods of analysis for uranium and thorium. Examples of some of this early work are given in the following reports (papers 1 through 6 appear as chapters in U. S. Geol. Survey Trace Elements Investigations Rept. 31, July 1946, under condensed titles):

1. Methods for the complete decomposition of rock and ore samples to be analyzed for very small amounts of uranium and thorium, by M. D. Foster, R. E. Stevens, F. S. Grimaldi, W. G. Schlect, and Michael Fleischer.

2. The U.S.G.S. cupferron precipitation-extraction method for the determination of very small amounts of uranium in naturally occurring materials, by F. S. Grimaldi.

3. The U.S.G.S. carbonate-phosphate-peroxide method for the determination of very small amounts of uranium in naturally occurring materials, by M. D. Foster and R. E. Stevens.

4. Elimination of interference by nickel in the determination of uranium by means of zinc amalgam reductors, by F. S. Grimaldi.

5. The U.S.G.S. phosphate-fluoride-iodate method for the determination of very small amounts of thorium in naturally occurring materials, by F. S. Grimaldi and J. G. Fairchild.

6. The U.S.G.S. carbonate-iodate-iodine method for the determination of small amounts of thorium in naturally occurring materials, by J. J. Fahey and M. D. Foster.

7. The determination of thorium in high grade and low grade ores, by F. S. Grimaldi and Charlotte A. Marsh (U. S. Geol. Survey Trace Elements Investigations Rept. 44, AECD-2818, September 1947).

All of the problems described here together with related ones are under constant study.

Methods of analysis project

Fluorimetry

Purpose.--In the fluorimetric analysis for uranium, instrumentation has been an important field of research. The Model R fluorimeter developed at Oak Ridge was early made available to the Survey and other laboratories, and each laboratory, including that of the Survey, has modified the instrument to suit its own needs. The Survey's goal in research in fluorimetry has been to modify existing instruments for better ease of operation and to design new instruments as the need for them arises.

Results of investigations.--In the latter half of 1948 the Model R fluorimeter was modified, with the following advantages over the original model:

1. Greater sensitivity.
2. Increased electrical stability.
3. Greater flexibility, by which a wider range of fluorescence can be measured.

The modifications are described in the report, "An improved fluorimeter for the determination of uranium in fluoride melts," by Mary H. Fletcher and Irving May, U. S. Geol. Survey Trace Elements Investigations Rept. 120, June 1950. This instrument is now being superseded to a large extent by a more recently developed transmission fluorimeter, but it is still a very useful tool for many types of analysis.

Fluorimeters in use in uranium analysis have been of the reflection type, that is, ultraviolet light is allowed to fall on the flux disk and the resulting fluorescence is reflected into the light-gathering part of the instrument. In this arrangement much scattering of light results and, the component parts of the instrument being fixed in position, the sensitivity cannot easily be changed. These difficulties and others led to the design of a fluorimeter based on transmission of light rather than reflection of light.

The basic design of this so-called transmission fluorimeter is described in the report, "A transmission fluorimeter for use in the fluorimetric method of analysis for uranium," by Mary H. Fletcher, Irving May, and Morris Slavin, U. S. Geol. Survey Trace Elements Investigations Rept. 104, August 1949. The abstract follows:

> A fluorimeter has been built which measures fluorescence by transmission rather than by the usual 'reflection' methods. The consequence of the adoption of this new principle is a large gain in simplicity, compactness, ruggedness, sensitivity, cheapness of construction, and efficient use of light energy.
>
> When used with an uncooled 1P12 photomultiplier tube operated at 45 volts per stage and a D.C. amplifier, the instrument has a sensitivity of one scale division equivalent to 1.7×10^{-10} grams of uranium in 1.5 grams of flux. However, in practice the lower limit is set by the blank readings. As a consequence of compactness and compartmentalization, stray light, which contributes to this blank reading, is reduced to a very small amount.
>
> Reproducibility is such that a few thousandths of one percent of uranium can be determined on a 0.05-mg sample with an error of about 10 percent of the amount present.
>
> If desired, the much simpler Photovolt Electronic Photometer (Model 512) with the C search unit can be substituted for the more elaborate photomultiplier tube and D.C. amplifier. Efficiency of light use is so great that still simpler measuring devices may prove adequate.

This early model has continued to be improved and new models have been designed. The latest model is described, and working drawings are included, in the report, "The design of the Model V transmission fluorimeter," by Mary H. Fletcher, Irving May, and Joseph W. Anderson, U. S. Geol. Survey Trace Elements Investigations

Rept. 133, December 1950.

Another development in fluorimetry has been the design of a battery-powered fluorimeter for use in field offices, mobile units, and laboratories. Although there are a number of fluorimeters in general use which employ battery-powered current-amplifying and measuring devices, they all require house current as a source of power for the ultraviolet light source. The main problem in designing a completely battery-powered fluorimeter resolved itself into finding a suitable ultraviolet lamp that could be operated with batteries. This problem was solved by using a 3-watt RP-12 lamp as the ultraviolet source. The instrument as designed is sufficiently sensitive for the determination of 0.001 percent uranium in a 0.4-mg sample and should be most useful in connection with a field method for the estimation of uranium content described below.

The battery-powered instrument is described in the report, "A battery-powered fluorimeter for the determination of uranium," by Irving May and Mary H. Fletcher, U. S. Geol. Survey Trace Elements Investigations Rept. 135, December 1950.

Other laboratories have shown some interest in the Model V fluorimeter and sets of working drawings of the instrument have been sent to the Industrial Hygiene Field Station of the Federal Public Health Service in Salt Lake City, to Farrington Daniels of the Department of Chemistry, Wisconsin University, to the chemistry laboratory of the Port Hope Refinery in Port Hope, Canada, and to the Canadian Government through Mr. John Hall of the Atomic Energy Commission Washington office.

The fluorimetric method of analysis for aluminum has been investigated, and there has been a need for a completely self-contained fluorimeter for use with solutions and with which any of many different phototubes and measuring devices could be used. The usual method of measuring the fluorescence of solutions is to use the fluorimetric attachment for the Beckman spectrophotometer. The self-contained unit would give greater flexibility in measurement and would allow for the substitution of measuring units much less expensive than the Beckman instrument. Such an instrument has been designed and will be applicable, also, in the fluorimetric determination of beryllium and other elements.

Future work.--It is now apparent 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 of simplifying present instruments to make them more compact, stable, versatile, and less expensive, and designing new instruments for special applications. Fluorimeters for the measurement of fluorescence in solutions can be greatly improved, and this problem will be kept under study.

Methods of uranium and thorium analysis

Purpose.--As stated in the introduction to this section methods of uranium analysis are under continual study designed to improve existing methods and to devise new methods.

Results of investigations.--Much of the routine uranium analysis conducted by the Survey is based on a method described in the report, "A preliminary report on the rapid fluorimetric determination of uranium in low-grade ores," by F. S. Grimaldi and Harry Levine, U. S. Geol. Survey Trace Elements Investigations Rept. 47, April 1948, AECD-2824, April 1950. The abstract in part follows:

> A simple and very rapid fluorimetric procedure is described for the determination of uranium in low-grade shale and phosphate ores. The best working range is from 0.001 percent to about 0.04 percent U. The procedure employs batch extraction of uranium nitrate by ethyl acetate, using aluminum nitrate as the salting agent, prior to ...fluorimetric estimation. The procedure is especially designed to save reagents; only 9.5 g of aluminum nitrate and 10 ml of ethyl acetate being used for one analysis. ...After fusion the sample is immediately extracted without removing silica and other hydrolytic precipitates. Aluminum nitrate very effectively ties up fluoride and phosphate, thus eliminating steps required for their removal.

This method has been continually improved and has been modified for application to special materials. Such a modification is described in the report, "Short routine direct method for the determination of uranium in phosphate rocks," by F. S. Grimaldi and Norma Guttag, U. S. Geol. Survey Trace Elements Investigations Rept. 134, December 1950. The abstract follows:

> A short routine direct fluorimetric procedure for the determination of up to 0.06 percent uranium in phosphate rocks is described. The procedure employs a simple acid leach for preparing the sample, and the uranium is determined directly on a 1.8 mg aliquot. The results obtained by using this simple procedure on several thousand samples are discussed. The quenching of the uranium fluorescence by foreign elements was found to be negligible, for all practical purposes, and results on western phosphates (as contrasted to those on Florida phosphates, J.C.R.) may be corrected by using an empirically determined quenching factor.

Paralleling these developments was the study of a method that could be used in the field for the determination of small amounts of uranium. The methods most commonly used for the field had been chiefly physical. Radiometric techniques using portable Geiger counters do not discriminate between the radioactivity due to uranium and that due to other radioacitve elements. Therefore, it was most desirable to supplement the radiometric methods with an independent technique, preferably one specific for uranium. The investigation of this problem led to the development of the so-called direct fluorimetric method, described in the report, "A direct quantitative fluorimetric method for the determination of small amounts of uranium in the field and laboratory," by Frank Grimaldi, F. N. Ward, and Ruth Kreher, U. S. Geol. Survey Trace Elements Investigations Rept. 98, June 1949, AECD-2825, April 1950. The method has been applied to shales, phosphates, low-grade carnotite-bearing samples, and plant ash. The procedure involves a direct fusion of 3.75 mg of powdered sample with 3 g of the standard sodium-fluoride sodium-carbonate flux in a platinum container. The fluorescence of the resulting flux disk can then be measured with the battery-powered fluorimeter or compared visually with standard flux disks. Columbium and other elements tested do not give any fluorescence of their own in this procedure.

Continuing study of fluorimetric methods of analysis for uranium resulted in the report, "A study of critical factors in the direct fluorimetric determination of uranium," by Mary H. Fletcher (in preparation). The abstract follows:

> A study was made of the important factors in the "direct" fluorimetric determination of uranium in the range 0.0005 to 0.08 microgram of uranium, and a modified procedure based on these results is given. Detailed time-temperature studies showed that the sensitivity of the fluorescent method decreased rapidly when the fusion temperature was greater than 650°C., and that at temperatures above 650°C. the sensitivity decreased with increased time of heating. Inhomogeneity of the carbonate fluoride flux led to erratic results.
>
> Highly reproducible results were obtained by fusing at 650°C. for 25 minutes, using a carbonate fluoride flux that had been fused and then ground. Phosphors prepared by this procedure are reproducible to about 5 percent day after day, thus allowing the use of a permanent standard curve. Standard samples are unnecessary once the standard curve has been prepared.

An important analytical problem was the pressing need for a method of thorium analysis that was much more rapid than those in current use. Thorium analyses have always been slow and tedious, and the results have been none too certain. One of the worst problems the analyst has to face is to determine thorium, as he if often asked to do, on black-sand concentrates and related materials. An investigation of the problems involved led to the development of the mesityl oxide method, described in the report, "Application of mesityl oxide to the determination of thorium," by Harry Levine and F. S. Grimaldi, U. S. Geol. Survey Trace Elements Investigations Rept. 105, February 1950. The abstract follows:

> Thorium nitrate is quantitatively extracted by mesityl oxide from solutions saturated with aluminum nitrate even in the presence of relatively large amounts of phosphate. Uranium is the only other element extracted quantitatively by a single extraction. Zirconium is largely extracted, whereas yttrium and vanadium are extracted to a small extent. Cerium in both valence states is extracted only to a very slight degree, ceric cerium being reduced probably by the olefinic bond in the solvent. Mesityl oxide thus is useful not only for the concentration of uranium and thorium but also for the

separation of thorium from the rare earths, the separation taking about 10 minutes per sample.

The mesityl oxide procedure for the determination of thorium has been applied to a wide variety of thorium ores such as monazite, black sands, thorianite, thorite, euxenite, and eschynite.

This method has been most useful for obtaining more rapid thorium analyses. However, thorium analysis is far from being put on a routine basis and the problem is being intensively studied.

Polarographic methods of analysis for uranium have been studied to the point where a modified procedure has been worked out, using a new-type calomel electrode, and trial runs were made on selected samples early in 1950. Good results were obtained with some samples but were erratic with others, and it is believed that the erratic results were due to troubles in the preparation of the samples. The investigation was left in this state because of more pressing work.

Future work.--The many papers on thorium and uranium analysis produced by the Survey are being edited for inclusion in a proposed Survey bulletin which is tentatively entitled, "Collected papers on U. S. Geological Survey methods of analysis for uranium and thorium," edited by F. S. Grimaldi. 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 applications in the Section's work, and investigations will be made in this field.

Methods of analysis for aluminum and phosphorus

Purpose.--The Section has been called on to analyze some thousands of samples for aluminum and phosphorus, particularly samples of phosphates, and studies have been made in this field to develop more rapid methods that are reasonably accurate.

Results of investigations.--The investigation of methods of aluminum analysis has led to the development of a fluorimetric method, described in the report, "The fluorimetric determination of aluminum in phosphate rock with 8-hydroxyquinoline," by F. S. Grimaldi and Harry Levine, U. S. Geol. Survey Trace Elements Investigations Rept. 60, August 1950. The abstract follows:

> A method is described whereby aluminum in phosphate rock is determined by the fluorescence of aluminum hydroxyquinolate in chloroform solution. The procedure is designed to determine from 0.01 to 3 percent Al_2O_3 with a 0.1 mg sample of rock. The accuracy is better than 5 percent. No element, in the percentages commonly occurring in phosphate rock, interferes with the procedure.

It is probable that this method is also applicable to silicate and carbonate rocks. It has made possible the analysis of thousands of samples for aluminum in a reasonable length of time.

Phosphorus analysis, particularly in western phosphates, presents many problems despite intensive research in and out of the Survey. One of the problems in connection with the western phosphate is the presence of more than trace amounts of vanadium. A method has been developed for such material, described in the report, "The determination of phosphorus in rocks containing vanadium," by R. B. Randolph and F. S. Grimaldi, U. S. Geol. Survey Trace Elements Investigations Rept. 99, July 1949. The abstract follows:

> This paper describes a rapid routine procedure for the determination of phosphorus in the presence of vanadium. Vanadium is reduced with formic acid prior to precipitation of phosphorus as ammonium phosphomolybdate and the ammonium phosphomolybdate is weighed as such. Ratios of V_2O_5 to P_2O_5 of 100 to 1 (the highest tested) give no interference. P_2O_5 in amounts from 0.1 mg to 0.2 g of P_2O_5 may be determined with no change in conditions or quantity of reagents. The separation of molybdic acid is prevented and the molybdate precipitate has a constant composition.

Future work.--Research work will continue 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

Purpose.--In the fiscal year 1950 about 17,000 chemical determinations out of a total of 43,000 were made of elements and compounds other than uranium and thorium on a wide variety of material. Determinations were made of such elements and compounds (besides Al_2O_3 and P_2O_5) as V_2O_5, CaO, Fe_2O_3, F, Au, Ag, Cu, Pb, Se, Zn, Ash content, oil content, and many others. The Chemistry Unit of the Section is called on to do analytical work in the whole field of inorganic analysis and performs certain organic analyses as well. The Section therefore investigates analytical methods in these fields.

Results of investigations.--Studies of the application of flame photometry to the determination of Ca, K, Na, Cs, Rb, Li, and Ba in many different materials have been undertaken. These methods have been studied extensively in other laboratories and also in the Investigations Section of the Survey's Geochemistry and Petrology Branch. Most laboratories have developed their own modifications and special applications of flame photometric methods.

The Denver laboratory of the Section has successfully applied this method for the rapid determination of CaO in many thousand samples of carnotite-bearing material from the Colorado Plateau. A similar method is used in such industrial laboratories as those of the American Smelting and Refining Company.

Procedures have been developed in the Washington laboratory by which reproducible working curves have been established for K, Ca, Na, Rb, Cs, Li, and Ba. Standard samples of phosphates have been run successfully for Na, K, and Ca and the same elements have been successfully determined in standard carnotite samples. The possibility of using a high-temperature volatilization method for separating the alkalies for determination with the flame photometer has been investigated to the point where it is apparent that it has good possibilities. Other work has been more pressing but this work will be resumed.

The problem of the determination of organic matter in such materials as black shales and western phosphates is under sporadic investigation. The term "organic matter" is vague and such determinations by different laboratories are usually not comparable. A standard method of determination is badly needed.

A preliminary procedure has been tested on about 40 western phosphate samples. This procedure consists of the following steps:

1. The sample is dried at 280°C to free loosely held water. This high temperature is necessary because in many materials the loosely held water is not given up at lower temperatures.

2. Organic matter is ignited at a controlled temperature of 460°C. At this temperature none of the fixed water is lost nor is CO_2 lost from carbonates and thus the loss in the range 260° to 460°C should represent organic matter.

The results obtained by this method seemed to be too low, most likely because some organic matter (probably graphitic) did not burn off. Study of this and other possible procedures will be continued.

As an aid in the work on geological age determinations by radioactivity methods work has been done in the microchemical laboratory of the Section on the determination by microchemical methods of very small amounts of lead (0.1 to 10 ppm.). The goal is to establish a procedure for the precise determination of less than 0.5 micrograms of lead by a method that will not be too slow and tedious. Purification of reagents to be used in the study have been made, and a literature search has been completed. Lead standards have been prepared and calibrated. Preliminary determinations on lead standards indicate that a method can be devised which will allow for the determination of lead to the nearest 0.1 microgram. New micro absorption cells for use in the Beckman spectrophotometer as a part of the procedure are being adjusted. It is obvious that the reagent blanks will more or less determine the lower limit of lead detection, and work is being done to reduce this blank. This work is in active status.

The Section is called on from time to time for determinations of oil content in many samples of material such as the black shales and recently on western phosphates. The standard method is the Modified Fischer Assay and this is a satisfactory quantitative method, used in many laboratories. However, when thousands of samples need to be run for oil content it is desirable to use a screening method which is simple and rapid but will give reliable semiquantitative results. The Fischer method calls for 100 grams of sample ground to not much less than one-eighth inch in size, and such samples are not always available.

The Section has recently developed a method which employs a small sample of powdered material and which gives good semiquantitative results. It is based on a relationship which has been found to exist (in working with oil shales) between the oil yields of shales determined by the Fischer method and the color of a toluene solution of the oil. This was made the basis of the new method. The procedure follows:

A 0.500-gram sample of the dry shale ground to minus 80-mesh is placed in a 25-ml glass-stoppered test tube. The lower third of the tube is then heated in a small tube furnace of special design at 480°-500°C for 11-14 minutes. The exposed upper two-thirds of the stoppered tube acts as an air condenser. The oil evolved is extracted with toluene, filtered, and diluted to a volume of 25 ml. The optical density of the toluene solution is read on a Model 400-A Lumetron colorimeter, using a blue filter transmitting light of 420 mu wave length.

The percentage of oil obtained is read from a graph relating oil yields by the Fischer assay to optical densities. This graph is prepared by running 50 to 100 samples by both methods and plotting a standard curve. This curve will then be applicable for similar material. In practice it has been found that the results obtained by the new method agree with those of the Fischer method on the same material to $\pm$ 0.5 percent of oil.

In studies establishing the new method it was found that the time of heating, the temperature of heating, and the solvent used are critical. It was also found that the stability of the color of the oil solution depends on the solvent used. The best time and temperature seem to be those given, and toluene seems to form a stable solution as regards color.

This procedure should prove useful in determining the oil content of shales and phosphates. A report on the method is being prepared.

Future work.--Work will continue in this field as indicated. The goal is for the Section to be prepared to perform analyses of whatever sort 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

Purpose

A group of closely related continued studies are concerned with methods of checking the precision and accuracy of the analytical work of the Section. This question is of the highest importance, and it presents some of the most difficult problems in the whole field of analytical work. The same problem is found in spectrographic and radiometric analysis although it is not so serious in radiometry.

Results of investigations

The Section makes continuous check analyses on samples interchanged between its two laboratories. Standard samples are prepared and used in the many analytical procedures. Early in the work homogeneous samples of black shale, Florida phosphate, western phosphate, carnotite ore, and black-sand concentrate were prepared. Splits of the samples were sent to such laboratories as those at Battelle Memorial Institute, M.I.T., Y-12 at Oak Ridge, Dow Chemical Company, and the National Bureau of Standards, and each laboratory analyzed the samples radiometrically and chemically in a routine way by fluorimetric, colorimetric, and other methods in general use. The results were collected and analyzed by the Atomic Energy Commission, and it was shown that the methods in general use in these laboratories, such as the fluorimetric and colorimetric, were generally reproducible from laboratory to laboratory.

Detection and elimination of gross errors in analysis are under constant study. Such errors are, of course, embarrassing to a laboratory, but they cannot be completely eliminated; they can, however, be reduced to a minimum consistent with the human factor involved. Their detection and elimination depend mainly on (1) alertness and care by the chemist, (2) alertness and care in those who handle the analytical reports, (3) reducing subjectivity so far as possible in analytical methods, and (4) making the chemist as familiar as possible with the nature of the samples he is analyzing. These and related problems are subjects of research in the Section. The fourth item is being fulfilled by conferences between the chemists and geologists on mutual goals and by educational talks in the Section at regular intervals designed to acquaint the non-geologists with the geologic setting of samples handled and to acquaint the geologists with the facts of chemical, spectrographic, and radiometric analysis. A program is now in being whereby the chemists (a few at a time) of each of the two laboratories will spend some time in the other laboratory working with the men in that laboratory so that in the course of about a year all of the chemists of the Section will be acquainted with each other and with the variations in methods used in Denver and in Washington. This will assure uniform methods of analysis in the Section. Visits to laboratories outside the Survey help in keeping the chemists alert to these problems, and plans are being studied to improve this type of communication among the laboratories within the Branch.

The application of statistical methods to an evaluation of the precision and accuracy of chemical analytical work is not easy, mainly because most methods of analysis are highly complex, and it is hard to determine whether errors are random. In order to clear up certain erroneous notions about error in chemical analysis, William Schlecht of the Survey at the request of the Section prepared some time ago a draft discussion entitled, "The probable error of a chemical analysis." Copies of this were circulated to different laboratories and were sent to the Atomic Energy Commission for further circulation, and comments and suggestions were invited. Many meetings have been held in the Washington laboratory in which this and related questions have been discussed among the chemists and geologists. At the suggestion of the Atomic Energy Commission a meeting was held with Dr. A. E. Brandt of the Atomic Energy Commission, who has consulted with many groups on statistical matters, on November 12, 1950. Those attending were Brandt, Everhart, Hosted, and Mathez of the Atomic Energy Commission and Fink, Flanagan, Grimaldi, Larsen, Rabbitt, and Schlecht of the Survey. At this meeting a general discussion was held on the application of statistical procedures to the analytical problems of the Survey, and Brandt, as a statistician, explained some statistical procedures in general. Following this meeting a formal project was set up in the Section to provide for a continuing study of this problem. As a first venture, multiple uranium analyses (chemical and radiometric) were made on some hundreds of samples of Florida phosphates, and these were submitted to Brandt for statistical interpretation December 20, 1950, in a meeting in the New York Atomic Energy Commission offices attended by Brandt and Mathez of the Atomic Energy Commission and Flanagan, Grimaldi, and McKelvey of the Survey. Brandt explained the different methods of statistical interpretation and demonstrated the calculations involved. Preliminary results of the statistical study tend to show that:

1. There is no significant difference in the results obtained on Florida phosphate samples (with the probable exception of certain slimes) between the present chemical method and the present radiometric method used for uranium analysis in the Washington laboratory.

2. Results on a sample of Florida phosphate by both radiometric and chemical analysis differing by 0.003 percent uranium may or may not be due to chance variation.

3. The odds are very much against differences greater than 0.003 percent being due to chance variation. Differences of that order of magnitude indicate that factors other than chance are operating.

The results are being evaluated further and a report will be written on the results. This will form the basis for any needed change in the number of samples of Florida phosphates analyzed chemically as contrasted with those analyzed radiometrically.

Future work

The statistical studies will be continued 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.

This will be accompanied by other activities as mentioned in a continuing and expanding program of evaluating the quality of Survey analyses.

High-index liquids project

Purpose

For many years there has been a wide need for better liquids for the measurement of high refractive indices, mainly in the immersion method of determining the refractive index of mineral grains. This need is particularly keen in research involving uranium, thorium, and rare earth minerals. Liquids, such as the phosphorus liquids, exist for this purpose, but most of them have serious drawbacks. The problem of developing more satisfactory liquids has never been undertaken in a systematic fashion. Such a fashion would entail a chemist of experience and training and a mineralogist or petrologist of experience and training working in cooperation in a systematic study of the problem. The Section has undertaken the study in this desired way.

Results of investigations

Some results of this work were presented in abstract form at the Geological Society of America meeting in Washington in November under the title, "Immersion liquids of high refractive index," by Robert Meyrowitz and Esper S. Larsen, Jr., Geol. Soc. America Bull. vol. 61, no. 12, pt. 2, p. 1486, 1950. The abstract follows:

> A study of inorganic, organic and metal-organic compounds that might be employed in the preparation of high refractive index liquids has been undertaken.
>
> Mixtures of arsenic tribromide and precipitated sulfur yielded a series of clear yellow liquids (mixture A), stable at room temperature. An index of 1.829 was obtained. After a period of 12 weeks, the maximum change in index was 0.003. The mixing curve of mixture A with methylene iodide (n = 1.74 to 1.81) deviated considerably from a straight line.
>
> At room temperature, mixture A and arsenic disulfide formed a series of clear green-yellow to green-amber liquids (B) whose indices range from 1.876 to 1.952. The maximum change in index after a period of 12 weeks was 0.004 for those liquids below 1.92 and 0.007 for those above 1.92. When the temperature was raised during preparation, liquid B was obtained with n = 2.006. The mixing curve of A and B is a straight line (n = 1.81 to 2.01).
>
> Red mercuric sulfide added to mixture B gave a clear yellow and very viscous liquid whose index was 2.035.
>
> Black selenium added to mixture B gave a clear, light-red semiviscous liquid whose index was 2.017.
>
> Arsenic tribromide, arsenic disulfide, and black selenium formed a very dark-red, viscous liquid whose index was 2.008.
>
> All the liquids described give an acid reaction and decompose some minerals.

The liquids (B) seem to be satisfactory. Stock solutions have been prepared and sets can be made available to appropriate people in and out of the Survey as soon as a policy is agreed upon as to how such distribution should be undertaken.

Further study has resulted in a series of solutions containing alpha-bromonaphthalene, arsenic bromide, and precipitated sulfur. The end members of this series are alpha-bromonaphthalene and 10 percent sulfur in arsenic bromide. The mixing curve of these liquids (n = 1.66 - 1.81) deviates slightly from a straight line.

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

Purpose

Research in spectrography is designed, much like that in chemistry, to investigate known methods of analysis, and to devise new ones. Such studies may lead to research in all aspects of spectrography ranging from fundamental principles to instrumentation.

In Survey work the spectrographers are called on to analyze a wide variety of material. This results in a situation different than that found in many industrial spectrographic laboratories. In them the work is likely to be routine; for example, aluminum may be analyzed day after day for eight impurities. A method can be devised for doing such analysis routinely, and once in operation can be kept in operation with ease.

In Survey work the situation is different. Each analytical request could easily become a research project of its own, but balanced against this is the imperative need to perform thousands of determinations as rapidly as possible. To devise a method or methods to fulfill this need requires much preparatory work in making standards, experimenting with methods of "arcing" the samples, and in general devising a procedure that will be as universally applicable as possible. The solution of this problem has been paramount in the Section's work in this field.

Results of investigations

It has been found in consultation with many of the field geologists that a semiquantitative method of analysis, covering as many elements as possible, and giving results in powers of ten, would be the most satisfactory method for general work. Such a method would be rapid and therefore many samples could be handled in a reasonable time; it would screen out those samples not needing further quantitative spectrographic and chemical treatment, and it would provide a maximum amount of information for the effort expended.

After a long period of preparation a semiquantitative method has been developed that meets the specifications mentioned. The method is described in a report entitled, "A semiquantitative spectrographic method for the analysis of minerals, rocks, and ores," by C. L. Waring and C. S. Annell (in preparation). The abstract follows in part:

> ... The semiquantitative method described determines 56 elements in one arcing of a 10-mg sample, requires a minimum of sample handling thus reducing the chances of contamination, detects low concentrations of elements, and is rapid. The method has been used to complete 15,000-20,000 determinations during a nine-month period. Of these determinations 304 have been checked chemically and indicated approximately 10 disagreements, in the magnitude of the 1-10-percent bracket.

The method has been applied to the analysis of phosphates, clays, sandstone, limestones, slags, coal ash, sulfur "ore", sphene, allanite, apatite, zircon, microlite, galena, idocrase, carnotite, hewettite, sphalerite, thorite, vanoxite, uranothorite, brannerite, davidite, miscellaneous precipitates, tap- and mine-water residues, leach products, phosphoric acid, among many other materials.

Work is in progress on a so-called single-grain qualitative method. In much of the mineralogic and petrologic work a single grain or at most a few small grains are all of a given mineral available for study. Spectrographic examination may be needed of such grains as an adjunct to X-ray diffraction and other tests to establish the identity of the material. It is therefore desirable to develop a method that will detect in such grains the presence or absence of as many elements as possible in a single arcing of the grain. It is also desirable to make such a method as quantitative as possible; probably the best that can be hoped is that such a method will be nearly semiquantitative.

The method being developed involves the preparation of standards in groups of 10 elements to a standard plate up to about 60 elements based on the arcing of a 1-mg sample. If the grain being arced is close to one mg in weight the results will be nearly semiquantitative; however, grains down to 0.1 mg in weight can be used, but the method will then be qualitative although an estimation of the amounts of the elements present can be given. The small Gaertner prism instrument, in which a region of 2,000 to 10,000 angstroms is covered on one plate, is used in this method. Fortunately the alkalies are also covered in the one exposure.

This procedure has been used on many single-grain samples (using the 3-meter Baird spectrograph), and in its full development it will prove to be of inestimable help in the work of the Section. Details of the procedure are nearing completion, and a report on the method will be issued.

Aside from research on methods of analysis, investigations are in progress on such problems as the detection of trace amounts of thorium in samples without prior chemical concentration and detection of very small amounts of lead (less than 1 p.p.m.). These studies have not progressed beyond preliminary stages, and there has been opportunity to work at them only sporadically. Many of the problems connected with these studies and with the investigation of methods of analysis involve fundamental work with excitation sources, controlled atmospheres, and related matters. Work is in progress sporadically on some of these matters.

Quantitative spectrographic analysis is performed according to well-established standard methods.

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.

Spectrographic work is becoming increasingly important not only as a producer of analytical results for the field geologist but as a companion tool in all the work of the Section. Efforts will continue in encouraging and assuring cooperation of the spectrographers with other workers in the Section and with the field geologists.

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

Purpose

Radiometric research is designed to improve methods of radiometry so that the tens of thousands of samples received by the Section yearly can be handled more rapidly and with increasingly reliable results. Radiometric determinations are of different kinds: routine determination of percent equivalent uranium by beta-gamma counting; radon determination by alpha counting; alpha and beta-gamma counting with scintillation counters; alpha counting with parallel-plate chambers; and others. Methods of making these determinations are under continuous investigation.

Radiometric determinations made in the Section fall into two broad categories, (1) the routine determination of percent equivalent uranium on nearly all samples received, and (2) a variety of determinations made on some samples for special purposes. In the first category the determinations are made (1) to screen out many samples so that chemical analysis for uranium will not be necessary for such samples, (2) to serve as a check on the chemical results for those samples assumed to be in equilibrium, and (3) to provide data for equilibrium studies. Determinations in the second category are made for many special purposes such as to determine the radioactivity of water residues and waters in terms of curies, to determine alpha production in certain mineral grains and other small mineral samples, to determine the radioactivity in chemical precipitates, and other purposes.

It is therefore necessary, for reasons similar to those applying to the research work of the chemists and the spectrographers, that methods of making these determinations be constantly improved, and that new methods be developed.

Results of investigations

Routine beta-gamma counting was originally done in the Section by the use of horizontal lead chambers by standard and well-established methods. These were soon found to be too slow, because of the tremendous load of samples, and have been displaced by a special adaptation of coaxial sample holders.

In this method a thin-walled beta-gamma Geiger tube is placed coaxially inside a glass tube (the space between the two tubes acting as a sample holder) and arranged with appropriate rubber corks, swivel clamps, and ring stands so that the assembly can be filled with and emptied of the powdered sample very rapidly. The tube being completely surround by the sample, counting time per sample for this arrangement is reduced to one minute. The sample holder is not cleaned between each sample as significant contamination will not occur when long runs of samples of the same kind (phosphates, for example) are being made. Counting is done by conventional scalers, and the results are given in terms of percent equivalent uranium. The tubes are calibrated by the use of appropriate standards.

This method is rapid, as one operator can handle about 150 samples per working day. The results are reliable enough for what is needed. (See pp. 79-80.)

A special modification was made of the Tracerlab Automatic Scaler in order to utilize its mechanism for large low-grade samples. This is described in "Modification to Tracerlab automatic sample changer," by F. J. Flanagan, J. M. Nelson, and J. J. Warr, Jr., U. S. Geol. Survey Trace Elements Memorandum Rept. 142, June 1950, Ra-Det vol. 3, no. 7, July 1950.

The Tracerlab instrument is used as an adjunct in routine determinations and for many special purposes. In order to test statistically the reliability of its results special runs of samples were started with it some time ago and are being continued at intervals so that a statistical control chart can be established for it. A report on this chart will be prepared when the chart is completed.

Scintillation counting engaged the attention of the Section late in 1948 as a means of making alpha counts on a variety of mineral samples, water residues, chemical precipitates, and similar materials. This method seemed to possess many advantages such as high counting efficiency, low background, fair geometry, insensitivity to microphonics, and little or no need for external amplification. The combination of these advantages made a scintillation counter of the proper design more useful for many purposes than the parallel-plate chamber which was in use.

After thorough investigation of different phosphors, photomultiplier tubes, and electronic arrangements a very simple instrument was developed which serves the purposes of the program admirably. This instrument employs a ZnS-Ag phosphor (R.C.A. 33F20), and a No. 5819 photomultiplier tube, hooked up to a scaler (originally designed for use with G-M tubes) with the addition of only a cathode follower.

Several units were built and have been in operation for about two years. They operated for some time at a background count of four to five counts per hour at 25 percent geometry with a 10-cm^2 sample area. The background has increased owing to contamination in the chamber and in the laboratory.

These instruments are cheap and rugged and have been used on many different kinds of samples.

At the time the scintillation counters were built anthracene crystals (for use as phosphors in beta-gamma counting) were not easily available. In fact, after repeated contacts at Oak Ridge and elsewhere they were not available to the Section. Unrefined anthracene was therefore obtained, a large cylinder of alundum for use as a furnace core was sent from the Norton Company through the help of John Sullivan of Battelle Memorial Institute, and a furnace for growing anthracene crystals was built. The anthracene was purified and after a few trial runs adequate anthracene crystals were produced. These have been used when the need arose.

Different phosphors have been investigated for use as beta-gamma detectors, among them being NaI, KI, $CaWO_4$, and naphthalene, and the literature on the subject has been followed closely. The characteristics of many phosphors, including those mentioned, have long since been established in other laboratories, and the Section has used some of them for special purposes. For example, a study has been made of anthracene used in conjunction with a No. 5819 photomultiplier tube to determine the U/Th ratio in minerals like zircon and monazite. The results, wholly preliminary, are encouraging.

The determination of radon early became a pressing need. A "radon counting unit" was built some time ago and used on many samples. Need for more units soon arose and a 5-unit apparatus was completed and put in operation in November 1950. The basic unit is similar to the Bureau of Standards model, but the Section designed its own electronic circuits for the amplifiers, preamplifiers, and power supply.

In use the units operate at 90-95 percent efficiency. Pushed to the limit and with an efficiency of 85-90 percent the units have a background of 1 count per minute, but in normal use at an efficiency of 90-95 percent the background is 1.5 counts per minute. The limit of detection for these units (about at background) is 10^{-13} curies. The units are being used on liquid samples, but they can be used on solid samples and will soon be so used.

Many other types of counters are used. Modifications of existing instruments and adaptations of standard methods for special sizes and kinds of mineral samples are undertaken. When any of these modifications and adaptations seem important enough they will be reported.

Members of the Radioactivity Unit contributed to the design, assembly, and installation of the instruments used in the Survey's airborne detection program.

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, are listed here. The lists cover the period April 1, 1948 - December 31, 1950, inclusive. List 1 contains papers in the U. S. Geological Survey Trace Elements Investigations Reports series. List 2 contains papers in the U. S. Geological Survey Trace Elements Memorandum Reports series. List 3 contains all papers not in these two series. List 4 contains papers in process. An asterisk after the report number means that a condensed version of the paper was presented at the Raw Materials Conference in London, September 1949.

List 1

TEIR No.	Title	Date
47	The rapid fluorimetric determination of uranium in low-grade ores: a preliminary report, by F. S. Grimaldi and Harry Levine.	April 1948 (declassified April 1950)
60	The fluorimetric determination of aluminum in phosphate rock with 8-hydroxyqyinoline, by F. S. Grimaldi and Harry Levine.	August 1950
91	Preliminary report on transmission fluorimeter, by Mary H. Fletcher and Irving May.	December 1948
98	A direct quantitative fluorimetric method for the determination of small amounts of uranium in the field and laboratory, by Frank Grimaldi, F. S. Ward, and Ruth Kreher.	June 1949 (declassified April 1950)
99	The determination of phosphorus in rocks containing vanadium, by R. B. Randolph and F. S. Grimaldi.	July 1949

TEIR No.	Title	Date
101	First annual report of the Trace Elements Section for the Fiscal Year 1949, by J. C. Rabbitt.	September 1949
102	A mineralogical and chemical study of the leached zone of the Bone Valley formation of Florida, by Z. S. Altschuler and C. E. Boudreau (Confidential).	December 1949
103	A glossary of uranium- and thorium-bearing minerals, by Judith Weiss Frondel and Michael Fleischer; issued as U. S. Geol. Survey Circular 74.	April 1950
*104	A transmission fluorimeter for use in the fluorimetric method of analysis for uranium, by M. H. Fletcher, Irving May, and Morris Slavin.	August 1949
*105	Application of mesityl oxide to the determination of thorium, by Harry Levine and F. S. Grimaldi (Confidential).	February 1950
*106	Study of radioactive equilibrium in carnotite ores of the Colorado Plateau, by L. R. Stieff, M. N. Girhard, and T. W. Stern.	August 1949
*107	Synthesis, base exchange, and photosensitivity of carnotite, tyuyamunite, and related minerals, by K. J. Murata, E. A. Cisney, L. R. Stieff, and E. V. Zworykin, Geol. Soc. America Bull., vol. 61, no. 12, pt. 2, pp. 1489-1490, 1950.	March 1950
108	A preliminary report on methods of determining the age of Colorado Plateau carnotite, by L. R. Stieff, M. N. Girhard, and T. W. Stern.	April 1950 (released Aug. 1, 1950)
120	An improved fluorimeter for the determination of uranium in fluoride melts, by Mary H. Fletcher and Irving May.	June 1950
127	The preparation of nuclear track plates and stripping films for the study of radioactive minerals, by L. R. Stieff and T. W. Stern.	August 1950

TEIR No.	Title	Date
128	An introduction to the geochemistry of gadolinium, by Michael Fleischer.	September 1950
129	A catalog of study material of radioactive minerals, by T. W. Stern.	October 1950
132	Abstracts of the literature on synthesis of apatites and of some related phosphates, by Elizabeth B. Jaffe.	December 1950
133	The design of the Model V transmission fluorimeter, by Mary H. Fletcher, Irving May, and J. W. Anderson.	December 1950
134	A short routine direct method for the fluorimetric determination of uranium in phosphate rocks, by F. S. Grimaldi and Norma Guttag.	December 1950
135	A battery-powered fluorimeter for the determination of uranium, by Irving May and Mary H. Fletcher.	December 1950

List 2

TEMR No.	Title	Date
57	Carnotite mineralogical research, by L. R. Stieff.	April 1948
68	Progress report on some methods of study of the mineralogy of the Colorado Plateau carnotites, by L. R. Stieff.	September 1948
74	Use of isotopes in geological investigations, by L. R. Stieff.	March 1949
89	Progress on Florida phosphate mineralogy, by Z. S. Altschuler.	December 1949
90	Progress on carnotite mineralogy, by L. R. Stieff.	December 1949
94	Progress report: Northwest phosphate mineralogy, by T. Botinelly.	January 1950

TEMR No.	Title	Date
95	Progress report: Shale mineralogy, by T. Botinelly.	January 1950
98	A progress report on the Geological Survey's work in determining the nature of the phosphate in the washer plant waste slimes from the Florida phosphate deposits, by Z. S. Altschuler.	January 1950
142	Modification to Tracerlab automatic sample changer, by F. J. Flanagan, J. M. Nelson, and J. J. Warr, Jr., Ra-Det, vol. 3, no. 7.	June 1950 July 1950
173	Verification of uraninite in fluorite breccias from Blue Jay mine, Jamestown, Colorado, by George Phair and Kiyoko Onoda.	October 1950
174	Numerical summary of the analytical work of the Trace Elements Section, Geochemistry and Petrology Branch, for the fiscal year 1950, by John C. Rabbitt.	October 1950

List 3

Immersion liquids of high refractive index, by Robert Meyrowitz and Esper S. Larsen, Jr., Geol. Soc. America Bull., vol. 61, no. 12, pt. 2, p. 1486, 1950.

Methods of determining the age of igneous rocks using the accessory minerals, by E. S. Larsen, Jr., N. B. Keevil, and H. C. Harrison, Geol. Soc. America Bull., vol. 61, no. 12, pt. 2, p. 1480, 1950.

Hummerite and montroseite, two new vanadium minerals from Montrose County, Colorado, by Alice Dowse Weeks, Evelyn A. Cisney, and Alexander M. Sherwood, Geol. Soc. America Bull., vol. 61, no. 12, pt. 2, p. 1513, 1950.

List 4

Distribution of uranium in rich phosphate beds of the Phosphoria formation, by M. E. Thompson.

Red and gray clays underlying ore sandstone of the Morrison formation in western Colorado, by Alice Weeks.

The phosphorite facies and genesis of natural phosphates, by A. V. Kazakov (translated by E. B. Jaffe).

Collected papers on U. S. Geological Survey methods of analysis for uranium and thorium, F. S. Grimaldi, editor.

A fluorimeter for the measurement of fluorescence of solutions, by Mary H. Fletcher and E. Ray Warner.

Abstracts of the literature on metamict structure, by T. Botinelly.

Some factors in the differential leaching of uranium and radium in pyritic mines and mine dumps, by George Phair.

A semiquantitative spectrographic method for the analysis of minerals, rocks, and ores, by C. L. Waring and C. S. Annell.

Hydrothermal uranothorite in fluorite breccias from the Blue Jay mine, Jamestown, Colorado, by George Phair and Kiyoko Onoda.

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. J. Dwornik.

A study of the critical factors in the "direct" fluorimetric determination of uranium, by Mary H. Fletcher.

Studies of uranium minerals (IV): Zeunerite, by Judith Weiss Frondel.