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AN INVESTIGATION OF THE AMOUNT AND DISTRIBUTION OF URANIUM IN SULFIDE MINERALS IN VEIN ORE DEPOSITS

Annual Report for July 1, 1955 to March 31, 1956

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H. D. Wright
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College of Mineral Industries
Pennsylvania State University
University Park, Pennsylvania

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ABSTRACT

Material has been collected from 40 deposits in Idaho, Utah, Arizona, New Mexico, and Colorado for a study of the uranium content and distribution in galena, sphalerite, pyrite, and chalcopyrite associated with pitchblende in vein deposits. Variation in uranium content of each sulfide is studied relative to variation in ore grade from uranium-rich to uranium-poor portions of a deposit, and level of uranium content of each sulfide is compared between uraniferous and non-uraniferous deposits and districts.

Routine procedures have been developed for concentrating the sulfides by heavy liquid separations, froth flotation, and microscopic picking, and for cleaning the concentrates of surface uranium contamination by hydrochloric acid leaching. Uranium determinations are made by scintillation alpha counting, and samples from each deposit are checked for equilibrium using uranium and radium determinations by New Brunswick Laboratory, AEC. Fluorimetric determinations are used to spot-check the alpha-count determinations, and probably will be used on all samples in the future.

Distribution of uranium in each sulfide sample is studied with alpha autoradiographs. Uranium which entered the sulfide during crystallization, in solid solution or defects, is indicated by a random scattering of tracks, in contrast to clusters of tracks from uranium in inclusions or replacement bodies of pitchblende, or coatings on grain surfaces, fractures, or cleavages. Comparison of autoradiographs of uncleaned and cleaned sulfides shows that the cleaning procedure is effective in removing surface uranium.

Paragenesis studies are made to determine the age relationship between sulfide deposition and uranium mineralization, since the uranium content of the sulfides is significant only if the pitchblende and sulfides were deposited by the same solution.

Uranium determinations have been made on 91 sulfide samples from 19 deposits. The values generally lie between less than one part per million and several hundred ppm, with occasional samples over one thousand ppm. Sulfides concentrated from ore in barren portions of uranium-bearing mines generally contain less than 10 ppm uranium. The data obtained thus far show a rough correlation between uranium content of the sulfides and radioactivity of the ore at the sampling site. Not enough data are yet available to compare level of uranium content in different sulfides occurring together, or level of uranium content in a given sulfide between deposits and districts.

INTRODUCTION

This report summarizes the results of research for the first year on the amount and distribution of uranium in base metal sulfide minerals - especially galena, sphalerite, pyrite, and chalcopyrite - in pitchblende- and non pitchblende-bearing vein deposits. The purpose of this study is to determine whether uranium is present in abnormal concentration in sulfides coexisting with pitchblende, and whether the level of uranium content in the sulfides bears a systematic relation to uranium ore grade, or to proximity to uranium ore.

It seems probable that sulfide minerals crystallizing from an ore solution sufficiently rich in uranium to deposit pitchblende would incorporate an abnormal amount of uranium in their crystal lattice. Although considerations of ionic size and valence differences between uranium and the base metals, as well as the non-occurrence of uranium sulfides, would suggest little likelihood of extensive substitution of uranium in the base metal sulfides, as little as a part per million is readily measurable by fluorimetry or alpha-counting. Besides any small amount in solid solution, some uranium could be expected to be trapped in lattice defects. These considerations suggest the possibility of using determinations of the low level uranium content of sulfides as an indication of the uranium concentration in the solution from which the deposit formed.

The laboratory investigations which have been undertaken in connection with this research are the following: (1) measurement and comparison of the uranium content of galena, sphalerite, pyrite, and chalcopyrite in uranium-rich and uranium-poor deposits, (2) determination of the variation in uranium content of a given sulfide systematically collected with respect to uranium-rich and uranium-poor portions of the same deposit, (3) comparison of the uranium content of the different sulfides occurring together, (4) determination of the location and state of uranium in the sulfides - whether in grain coatings, fracture fillings, inclusions, or replacement bodies, or in solid solution, (5) determination of the associated trace elements, and (6) synthesis of sulfide minerals in the presence of uranium to determine experimentally the amount of uranium which can be taken into the crystal lattice.

The ultimate practical aim of these studies is to evaluate the possibility of using determinations of the low-level uranium content of the sulfides as an indicator of favorable environment for the occurrence of uranium in ore-grade concentrations. It is hoped that it may be possible to establish an approximate level of uranium concentration in each of the sulfides studied, above which uranium ore generally is found in association.

The emphasis in the first year's work has been placed on the development of satisfactory routine procedures for sample preparation, and on the uranium determinations of sulfides. Supporting

studies have included chiefly paragenetic studies to establish contemporaneity of sulfide deposition and uranium mineralization, and alpha autoradiograph studies of the distribution of uranium in the sulfides. The determination of trace element assemblages and experimental study of uranium solid solution in sulfides have been deferred to the second year.

COLLECTION OF SAMPLES

During July and August, 1955, samples of base metal sulfides were collected from deposits in Idaho, Utah, Arizona, New Mexico, and Colorado. A total of 181 samples were collected from 40 deposits in 14 mining districts. The localities for sampling were selected with the help of Dr. Donald Everhart of the Denver office, AEC, and were chosen to give broad coverage of a variety of vein uranium deposits containing base metal sulfides and sufficiently developed to permit collection of fresh material.

In each district visited, the following general procedure in sample collection was used: (1) wherever possible, at least one deposit, usually the best developed, was selected for systematic sampling to obtain suites extending from the rich uranium ore centers outward into uranium-barren portions; (2) spot samples were taken to give wide areal distribution, and to represent all sulfides exposed; (3) samples of the same sulfides were collected from at least one uranium-barren deposit in the district, for comparison and control. Coarsely crystallized material was collected where possible because of easier concentration and cleaning. Evidence of a minimum of groundwater activity was desirable since the uranium of chief interest in this study is that deposited at the time of original sulfide crystallization, undisturbed by later reworking.

The districts sampled will be mentioned in the order visited, from Utah to Arizona, New Mexico, and Colorado.

Silver King Claims, Erickson mining district, Tooele County, Utah. Mineralized fractures in granite contain fluorite, specular hematite, manganese oxides, uraninite, pyrite, and copper sulfides. Development is new and exposures of suitable material are scanty - only a few samples were collected.

Marysvale, Utah. Four days were spent in the Marysvale area, chiefly in the three main VCA properties, the Freedom No. 2, Farmer John, and Prospector. Samples were also collected at the Deer Trail mine. Although reports on the district mention the common association of fine-grained pyrite with pitchblende, recognizable pyrite was not found abundantly in any of the

properties, and material suitable for our study was found in only a few places. Sulfides other than pyrite were not observed. Although it had been hoped that Marysvale would provide one of the best opportunities for detailed study of the relationship of uranium content of sulfides to uranium ore grade in various parts of a deposit, the sparseness of sulfides and the fine-grained nature of the pyrite eliminated this possibility. Successful use of the material collected will depend on the development of satisfactory techniques to concentrate and clean the fine pyrite.

Walapai District, Arizona. Good, coarsely crystallized galena, sphalerite, pyrite, and a little chalcopyrite, associated with strong radioactivity, were collected from the Detroit and De La Fontaine mines about 12 miles northwest of Kingman. Although the developments are small, the material was some of the best obtained during the trip, combining abundance and variety of sulfides, coarse crystallinity, and moderate to strong radioactivity. Samples of non-radioactive sulfide ore were obtained from the nearby Golconda mine.

Globe District, Arizona. Samples were collected from the Red Bluff mine, and from the Lucky Stop, Jon, Hope, and Little Joe deposits in the Workman Creek area. While the deposits are not of the vein type emphasized in our work, a hydrothermal origin appears probable and comparison of the uranium content of sulfides with vein deposits should be interesting. Pyrite, pyrrhotite, chalcopyrite, a little galena, and uraninite are disseminated through flat-lying beds of massive gray or coarsely recrystallized brown Dripping Spring quartzite. Sulfides for comparison were obtained from two non-radioactive deposits just west of Globe.

Silver City, Mogollon, and Truth or Consequences, New Mexico. A considerable variety of deposits was sampled in this area, and several of them provided good material for study. Most of the deposits visited in the Silver City area have inaccessible old workings, or are exposed by small recent developments, and systematic sampling was not possible. Some pyrite, sphalerite, galena, argentite, and cobalt-nickel sulfarsenides were collected from the Black Hawk and Alhambra mines, 21 miles west of Silver City. Sulfides were generally scarce or lacking in deposits of the White Signal district, about 20 miles south of Silver City.

Good pyrite-bearing vein material with moderate radioactivity in Tertiary volcanics was obtained at the Baby mine

in the Mogollon district, 70 miles northwest of Silver City. A few samples were taken from several deposits in the Caballo district, about 20 miles south of Truth or Consequences, and from some copper and uranium-bearing deposits in silicified limestone in the Iron Mountain district, about 40 miles northwest of Truth or Consequences.

Gunnison, Colorado. The Los Ochos mine, like the deposits in the Globe area, is a disseminated uranium deposit in sedimentary rocks but was included in our work because of its probable hydrothermal origin. Sulfides are poorly represented, but a suite of samples containing fairly well developed marcasite was obtained.

Front Range, Colorado. The Schwartzwalder mine, Ralston Creek district, was combed thoroughly for sulfides but only a few scattered showings of pyrite and occasional galena were noted, limiting the coverage to about ten samples. One suite extending from rich ore into nearly barren vein was collected.

In the Central City district, the Carroll mine provided vein material of low to moderate radioactivity containing abundant, well crystallized galena, and some sphalerite and pyrite. A few sulfide samples were obtained from the Wood-Calhoun deposit, where sulfides were abundant but few strongly radioactive showings were found. The Cherokee mine was inaccessible, but some good sulfide-bearing material with occasional pitchblende was collected from the dump.

Coeur d'Alene District, Idaho. Good suites of samples containing pyrite, galena, arsenopyrite, and freibergite were collected, extending over gradational sections from uranium concentrations into uranium-barren vein material. This mine provided the largest number of samples collected from one deposit.

Additional samples are available from a number of deposits in the Boulder batholith, Montana and the Colorado Front Range, collected in the course of previous studies. Further coverage, especially of non-uraniferous districts, will be provided by museum specimens.

LABORATORY INVESTIGATIONS

Most of the laboratory investigations during the first year

have been concerned with four major aspects of the problem. These are (1) the mode of occurrence, textural relations, and paragenesis of the sulfides, and their relationship to the uranium mineralization; (2) the amount, position, and state of uranium in the sulfides - chiefly pyrite, chalcopyrite, galena, sphalerite - in each deposit; (3) the distribution of uranium in each sulfide throughout a given deposit, and its relation to the distribution of pitchblende; and (4) the variation in range of uranium content in a given sulfide in a deposit as compared with other deposits in the same mining district, and with deposits in separate districts.

METHODS OF STUDY

Mineral Association and Paragenesis

The determination of age relations between the various sulfides and pitchblende in a deposit is very important in interpreting the data on uranium content. If the uranium content of a sulfide is to be interpreted as reflecting the richness of uranium in the ore-forming solution, it is necessary to establish the co-existence of the sulfide with pitchblende. The relationship must be established for each sulfide individually. In districts, such as the Colorado Front Range, where deposition of sulfides took place in two or more epochs but uranium was introduced in only one of these, the importance of recognizing disparity in time of deposition is obvious. Since the criteria for determining paragenetic relationships seldom are clear-cut and definitive, conclusive results are not always possible and considerable caution must be used in correlating the results of uranium determinations with mineralogic paragenesis.

Determination of Uranium Content

Determinations of uranium in the pure sulfide fractions were made by thin-source alpha scintillation counting. The counter used is similar to that described by Kulp, J. L., et al, (1951) and utilizes a custom-made housing with an RCA #5819 photomultiplier and a Nuclear - Chicago #182A scaling unit. Using a three-inch disk and a sample thickness of 0.4-1.0 mg/cm^2, the method is sensitive to 0.1 ppm. The validity of uranium determinations by radiometric methods rests of course on the assumption of equilibrium. This would appear to be justified under the conditions applying to the samples under study, since the uranium of chief interest is that disseminated through the sulfide in lattice positions or in defects, and thus the uranium series elements should not be very accessible to leaching solutions capable of upsetting equilibrium.

A check on this distribution is provided by alpha autoradiographs, as discussed in a separate section below. In order to validate further the assumption of equilibrium, sulfides from each deposit studied are sent to AEC's New Brunswick Laboratory for radium and uranium analyses, and the determinations compared with the ratio required by equilibrium.

Thin source preparations have the advantage of negligible absorption (the ud term is of secondary importance in comparing emission rates from different materials) and maximum count yield. This is an important advantage in the present problem with the low level activity involved and the exorbitant time required for preparing even small amounts of sample. However, the difficulty of preparing uniform thin sources of the sulfides greatly restricts the counting precision obtainable. For this reason, all future counts will be made using thick source preparations. It is believed that the greater reliability of thick source counts will justify the additional expense involved in preparing larger samples.

Calibration of the counters is done externally with standards prepared by the National Bureau of Standards. In an attempt to standardize directly the sulfides analyzed, two samples have been submitted to Dr. J. L. Kulp at the Lamont Geological Observatory, Palisades, New York, for isotope dilution determinations with the mass spectrograph.

A proportional counter made by Nuclear Measurements Corporation is being set up and calibrated. This instrument is certified by the manufacturerfor a background of 1 cph, which should greatly extend the limit of sensitivity now permitted with the scintillation counter alpha background of 7-8 cph.

Fluorimetric determination of uranium is well adapted to the low levels involved in the sulfide determinations, and independent alpha and fluorimetric uranium analyses on all samples would be highly desirable. At the suggestion of Dr. Hans Adler of AEC, arrangements are being discussed with Dr. C. J. Rodden of the AEC's New Brunswick Laboratory for the fluorimetric analysis of all sulfide samples after they have been alpha-counted here. Both fluorimetric and alpha-count determinationswere made on a large group of samples on the Boulder batholith project, and good agreement was found in most cases. The use of two independent analytical methods serves to point up anomalous determinations which would otherwise escape notice. The validity of the conclusions to be made from the project studies will rest directly on the accuracy of the uranium determinations.

Distribution of Uranium in the Sulfides

In general, uranium in the sulfides falls into one of two

categories: (1) uranium incorporated during crystallization of the sulfide - in solid solution, crystal defects, or inclusions; and (2) uranium introduced after crystallization, in the form of grain coatings, fracture fillings, or replacement bodies. The uranium of greatest significance to this study is that which was emplaced in the lattice (including defects) at the time of crystallization, and therefore should reflect the concentration of uranium in the ore-forming solution.

Alpha autoradiographs are of particular usefulness in studying the distribution of uranium in the sulfides. That emplaced in solid solution or lattice defects during crystallization should be revealed by randomly distributed tracks in the emulsion. On the other hand, the amount of uranium in scattered inclusions of pitchblende would not bear as direct relation to the uranium concentration of the solution; these should show up in concentrations of tracks in clusters, unless the inclusions are extremely fine. All uranium introduced after the sulfide had crystallized should appear in concentrations of tracks, whether from grain coatings, fracture fillings, or replacement bodies. The form of the cluster may provide a clue as to the nature of the uranium concentration. Uranium in coatings along cleavages gives rise to tracks emanating from source points oriented along straight lines, while grain coatings of uranium show up as rings of tracks about the margin. If the autoradiographs show a considerable percentage of the uranium to be present in concentrations rather than disseminated through the sulfide, the uranium determinations can be interpreted accordingly, or thrown out altogether if the percentage is too high.

Analysis of Data on Uranium Content of Sulfides

The variation in uranium content of a given sulfide mineral is being studied on three general levels: (1) variation within a single deposit; (2) variation between deposits within a single mining district; and (3) variation between deposits in separate mining districts. Where two or more sulfides occur together fairly generally throughout a deposit, which is commonly the case, comparisons are made between the sulfides both as to absolute amount of uranium content, and any trends in variation of uranium content relative to uranium mineral concentration, ore grade, or level of radioactivity.

In order to gain some knowledge as to the range of values expectable, and to test some of the general ideas discussed above, the samples for analysis during the first year were selected to provide as broad coverage of districts and mines as possible. Some idea of the range of uranium content in the sulfides was necessary in order to select the most suitable sample preparation procedures and alpha-counting technique.

Not enough data have yet been obtained to permit satisfactory analysis of the variation of uranium content of a given sulfide between deposits and districts.

From several deposits where satisfactory suites of samples could be collected from rich to barren sections, sufficient data have been gathered to permit tentative interpretation of some interesting trends in the uranium content of certain sulfides. These will be discussed later.

SAMPLE PREPARATION

Several months were required to develop and perfect routine procedures for purifying individual sulfides for uranium analysis. The main problems were 1) obtaining a pure sulfide fraction from an ore sample in a reasonable time, 2) removing surface contamination of uranium with minimum loss of sample, and 3) providing a satisfactory check on purity from contaminating uranium. Since uranium determination by highly sensitive alpha-count and fluorimetric methods is possible down to extremely low trace quantities - 0.1 to 0.01 ppm - the necessity for highly efficient concentration and cleaning procedures is obvious. The need for hundreds of determinations in the course of the research places a premium on efficient procedures requiring a minimum of labor.

Sample preparation time for uranium and spectrographic analysis has been reduced from 8-10 hours per sample during the first few months to about 2 1/2 hours per sample at present. It is doubtful that appreciable further savings in time can be achieved.

Concentration of Sulfides

The ore sample is washed and coarsely crushed, and sufficient material is picked to provide a minimum of one gram of pure concentrate of each sulfide present. Each sulfide fraction is crushed and screened to a 0.177 - 0.420 mm. size range. The next step is a gravity separation performed with bromoform or Clerici's solution, or both successively, depending on the kinds and amounts of contaminants identified by inspection under a binocular microscope. The separations made with these liquids on mineral associations involved in this work are shown in general form in table 1.

As may be seen from table 1, an appropriate combination of heavy liquid separations serves to concentrate each sulfide among the four of chief importance to this study - pyrite, chalcopyrite, galena, and sphalerite - except in ores where

Table 1. Heavy Liquid Separations

Agent	Sulfide minerals	Gangue minerals
		Feldspar (G. = 2.56-2.75)
		Quartz (G. = 2.65)
		Calcite (G. = 2.7)
Bromoform (G. = 2.84)		
		Siderite (G. = 3.83-3.88)
		Ferromagnesian minerals
		Most gangue-ore aggregates
Clerici's solution (G. = 3.9)		
	Chalcopyrite (G. = 3.5-4.0)	
	Sphalerite (G. = 3.9-4.1)	Remaining gangue-ore aggregates
Clerici's solution (G. = 4.3 @ 25° C.)		
	Pyrrhotite (G. = 4.58-4.64)	
Clerici's solution (G. = 4.65 at 50° C.)		
Further separation by	Pyrite (G. = 4.95-5.10)	
froth flotation or	Arsenopyrite (G. = 5.9-6.2)	
hydraulic elutriation.	Galena (G. = 7.4-7.6)	

pyrite and galena occur together. Galena is separated from pyrite by froth flotation, using cresylic acid as the frothing agent, ethyl xanthate to activate the pyrite and galena, and sodium cyanide to depress the pyrite.

The final step in the concentration process is picking under a binocular microscope, using a collecting bottle with tube and drawn glass nozzle to remove the remaining contaminants.

Leaching the Pure Concentrate

Tests were conducted to determine the optimum conditions of leaching time and acid concentration for removing surface uranium contamination from the sulfide concentrates with hydrochloric acid. The acid concentration was varied from 1N to 3N, and the leaching period from six minutes to 36 hours. The conditions yielding the best balance of high uranium removal (checked by alpha-counting) with relatively little sample loss was obtained with 1 normal HCl for 24 hours. The longer period permits some leaching of cleavages and fractures, of importance especially in galena and sphalerite.

Preparation of Grain Mounts for Check on Leaching

In order to check the effectiveness of the HCl leaching in removing uranium from surfaces, grain mounts in plastic are prepared from both the original uncrushed grains and the leached, crushed concentrate, and exposed to alpha-sensitive emulsions. The effectiveness of removal of uranium from the surface of grains (or from fracture or cleavage surfaces of crushed grains) may be determined by comparison of the unleached raw grains and the leached crushed grains. Since the grain mounts are ground down, yielding cross sections of the original grains, surface contamination of uranium gives a ring of alpha tracks. If the leaching is successful, this ring is missing in autoradiographs of the leached grains.

The grain mounts are prepared with Lakeside 70 plastic on a petrographic slide and ground to a flat surface with silica carbide and alumina abrasives until 90% of the grains have had a portion of their volume removed. The mounts are finished by polishing with levigated alumina on billiard cloth.

Alpha Autoradiographs

To determine the nature of the distribution of uranium in

the sulfide grains, and to check on the removal of uranium from grain surfaces, alpha autoradiographs are prepared. The emulsions are applied in one of two forms, Kodak type NTA nuclear emulsion plates, and Kodak experimental stripping film. The problem of obtaining satisfactory registration between the plates and grain mounts makes precise identification of source of radiation in the individual grains difficult. More satisfactory results have been obtained with the stripping film, which remains on the mount and does not require registration. The technique of floating the film onto the section assures a uniform close contact with the source. Stripping film emulsions of five micron thickness provide better resolution than thicker preparations, of great importance in this application since precise location of source of activity is the prime purpose rather than measurement of alpha energies or calculation of uranium content.

Because of the very low level uranium content of most of the samples studied, exposure periods are long - generally two to four months. To avoid this undesirable delay, experimentation is being conducted in conjunction with another AEC project to develop a suitable technique for fission fragment radiography. The potential advantages of the method include, besides the possibility of greatly shortened exposure time, the ability to distinguish uranium from its daughters, and uranium from thorium. A disadvantage of alpha tracks as a means of detecting location of the uranium in sulfides is the possibility of migration of the daughters, especially radon, from primary uranium positions. Thus all alpha-emitting daughters below radon in the decay series would register locations in the radiographs which could not be easily distinguished from those of uranium. Procedures for preparation of the fission fragment radiographs have been developed which are satisfactory for high concentrations of uranium, but low levels (such as random distribution of a few ppm uranium through a sulfide lattice) cannot be satisfactorily handled as yet.

Preparation of Material for Alpha Counting

Thin sources of powdered sulfides are prepared by settling from distilled water onto a stainless steel or lucite disc. A suspension of sample in 150 ml. distilled water containing a drop of aerosol is poured rapidly onto the disc seated in a filter paper-lined Buchner funnel. Slow filtration provides a fairly uniform covering. The sample thickness used, 0.4 to 1.0 mg/cm^2, is well within thin-source range for the sulfides, but the difficulty of achieving absolutely uniform sources introduces appreciable error due to absorption. As mentioned previously, future alpha-count determinations will be made with thick-source preparations.

Polished Sections

Polished sections are prepared from all ore samples from which sulfides are concentrated and analyzed. Microscopic study of these sections provides information on the mineral association and paragenesis, and textural data important in setting up concentration and purification procedures. Alpha autoradiographs of the polished sections enable study of the distribution of uranium in the ore as a whole. Its distribution in individual sulfides may also be observed and compared with the distribution observed in the autoradiographs of the sulfide concentrates.

RESULTS

Most of the actual laboratory study, following development of suitable sample concentration and cleaning procedures, involved the preparation of pure sulfide concentrates and their study by alpha counting and by alpha autoradiographs. Supporting studies were given less emphasis; mineral association and paragenesis were studied in detail for only two districts, and the investigations of uranium solid solution in the sulfides and of sulfide trace element correlation with uranium content were deferred until the second year.

Paragenesis Studies

De La Fontaine Mine, Walapai District, Kingman, Arizona.

The ore minerals found in samples from the De La Fontaine mine, in order of abundance, are galena, sphalerite, pyrite, chalcopyrite, and pitchblende(?). Two varieties of sphalerite were distinguished on the basis of color, with a dark variety predominating. Some small dark gray grains with strong radioactivity were tentatively identified as pitchblende. The gangue minerals are rhodochrosite, calcite, and quartz.

Two stages of sulfide mineralization are represented, with the bulk of the sulfides belonging to the first stage. Pyrite, the earliest sulfide, was followed by dark sphalerite containing exsolution blebs of chalcopyrite, and galena. Although contemporaneous in part, much of the dark sphalerite preceded galena. Some pyrite crystallized with galena, and these were followed by light sphalerite.

The second stage was separated from the first by brecciation and quartz deposition in open space. Rhodochrosite and calcite were formed in abundance, and the carbonate gangue was accompanied by minor pyrite, galena, and sphalerite of fine grain size.

Although the small grain size of the pitchblende(?) suggests that it may be more closely related to the sulfides of the later stage, the pitchblende(?) grains are usually observed in the interstices between the coarse sulfide grains of the earlier stage. This suggests that the pitchblende(?) was introduced late in the first stage. There is no indication of appreciable difference in age between the two stages of sulfide deposition.

Uranium Content and Distribution Studies

Samples for the initial studies of uranium content and distribution were selected from those collected last summer on the basis of the following considerations:

(1) ease of concentration and cleaning (coarsely crystallized material better)
(2) representation of all levels of radioactivity
(3) association of two or more sulfides
(4) broad coverage of deposits sampled
(5) two or three sample suites giving detailed coverage from rich ore zones outward to barren ore.

For purpose of standardization, several samples permitting relatively easy concentration of a large amount of pure sulfide and representing a considerable range of radioactivity were selected. Splits of these were sent to the New Brunswick Laboratory, AEC, for fluorimetric uranium analysis and to Lamont Geological Observatory, Columbia University, for mass spectrograph (isotope dilution) uranium analysis. Besides serving as standards, these analyses provide direct checks on our alpha-count determinations. Additional samples are sent to New Brunswick Laboratory for fluorimetric uranium and radium determinations to provide checks on radioactive equilibrium.

Uranium Content of Sulfides

103 alpha counts have been made on 91 individual sulfide fractions. Some of these were subjected to more than one determination, for comparison of unleached and leached material and to spot-check counting reproducibility. The analyses represent 19 deposits in 10 mining districts, and include detailed studies of a sample section from uranium-rich to uranium-barren ore in two deposits.

Table 2 presents the results of the alpha-count measurements calculated to uranium equivalent in ppm on the assumption

Table 2. Alpha-count Determinations of Uranium Content of Galena, Sphalerite, Pyrite and Chalcopyrite

District and Mine	Sample No.	Location, where part of a sample section (distance in feet from "0" point)	Field count, mr/hr	Uranium in Sulfide, ppm			
				Galena	Sphalerite	Pyrite	Chalcopyrite
Coeur d'Alene District, Idaho							
Sunshine Mine	D-1	0 - 3100 level, west "U" drift	9.8			264	
	D-4	10' NW of D-1	Bkgrnd			3.3	
	D-5	14' NW of D-1	Bkgrnd			2.6	
	D-6	19' NW of D-1	Bkgrnd			6.3	
	D-7	25' NW of D-1	Bkgrnd			1.4	
	D-8	31' NW of D-1	Bkgrnd			.8	
	D-10	———	4.8			21.2	
	D-11	———	Bkgrnd			8.0	
	D-13	———	0.4			1.2	
	D-14	———	0.35			4.5	
	D-17	———	1.7			93.2	
	D-18	———	14-20			303	
	D-19	———	4			99.2	
	D-31	———	1.2			6.0	
	D-38	———	2-5			35.3	
Boulder Batholith, Montana							
Josephine Mine	9300	Dump	(cold)	1.6		.1	
	9302	Dump	2	10.8		23.6	
Comet Mine	1575	Dump	3	37.2			
Bullion Mine	1573	Dump	(cold)		.0		
Liverpool Mine	9497	Dump	.2	2.3			
Free Enterprise Mine	34872		?	735			

Table 2. (Cont'd) Alpha-count Determinations of Uranium Content of Galena, Sphalerite, Pyrite, and Chalcopyrite

District and Mine	Sample No.	Location, where part of a sample section (distance in feet from "0" point)	Field count, mr/hr	Uranium in Sulfide, ppm			
				Galena	Sphalerite	Pyrite	Chalcopyrite
Central City District, Colorado							
Carroll Mine	B-45	0-53' E of shaft	0.1		23.6	1.7	
	B-46	7' E of B-45	7.6	64.9		14.5	
	B-47	112' E of B-45	Bkgrnd	1.5		4.7	
	B-48	188' E of B-45	Bkgrnd	9.7	9.0	.7	
	B-49	194' E of B-45	Bkgrnd	3.3		.1	
	B-50	———	Bkgrnd	2.6			
	C-1	———	4.6	216			
	C-2	———	0.6		95.5		
	C-3	Dump	———			4.0	
Calhoun Mine	C-5	———	4.9			49.5	41.8
Caribou Mine	9373	———	3.2	23.3			
	9350	———	14	96.1			
Globe District, Arizona							
Little Joe Mine	B-6	Dump				2.7	
Dominion Mine	B-7	———				15.7	
Hanover District, New Mexico							
Empire Mines,	B-20	———	Bkgrnd		1.5		
Buckhorn Quarry	B-23	———	Bkgrnd	12.6			

Table 2. (Cont'd) Alpha-count Determinations of Uranium Content of Galena, Sphalerite, Pyrite, and Chalcopyrite

District and Mine	Sample No.	Location, where part of a sample section (distance in feet from "0" point)	Field count, mr/hr	Uranium in Sulfide, ppm			
				Galena	Sphalerite	Pyrite	Chalcopyrite
Mogollon District, New Mexico							
Baby Mine	B-25		.15			3.1	
	B-28		3.0			398	
Walapai District, Kingman, Arizona							
De La Fontaine Mine	A-26	0.-Adit level, 45' west of shaft	1.2	204	243		
	A-27	85' E of A-26	0.2	19.7			
	A-25	150' E of A-26	Bkgrnd	2.4			
	A-24	———	5.5	3.3			
	A-23	———	Bkgrnd	3.3	4.5		
	A-28	———	4.6	475			
	A-29	———	0.2		7.8	2.4	
Detroit Mine	A-30	0.-Adit level, 12' south of slope	Bkgrnd			2.3	
	A-31	21' S of A-30	1.0		50.0		
	A-34	21' S of A-30	1.0			3.9	
	A-32	32' S of A-30	0.2		2.9		
	A-33		0.8			16.9	
Golconda Mine Dump	A-36				4.4		4.9
Marysvale District, Utah							
Freedom No. 2 Mine	A-10		15			74	
Deer Trail Mine	A-9		1			34	

of equilibrium (now being verified by uranium and radium determinations). For comparison, the geiger count value in mr/hr obtained at the sampling site in the mine is shown with the uranium equivalent (alpha count) determination. The data are arranged by districts, mines within districts, and individual sulfides in each mine. Relative sample locations are shown for groups of samples closely related in space.

To permit easier comparison of the alpha-count uranium determinations with field radiometric counts at sample locations, the alpha count data have been arranged in table 3 in four groups representing different levels of radioactivity in the field. The arbitrary groups used are (1) <0.1 mr/hr, (2) 0.1-0.5 mr/hr, (3) 0.6-2.5 mr/hr, and (4) >2.5 mr/hr. Each group represents a range greater than the next lower by a factor of 5.

Table 4 presents a further breakdown of the data of table 2, using the same ranges of field activity, but presenting values by individual sulfides, with values for different mines thrown together. Table 5 shows a breakdown of the determinations by individual mines, where sufficient determinations were available for comparison, but with data for individual sulfides thrown together.

Discussion. As may be seen from table 3, the equivalent uranium content of the sulfides bears a rough correlation with level of radioactivity at the sampling site. There is little difference between the averages for the <0.1 mr/hr and 0.1-0.5 mr/hr groups - 4.2 ppm and 6.6 ppm. A marked difference is apparent between the averages for the 0.1-0.5 mr/hr and 0.6-2.5 mr/hr groups - 6.6 ppm and 74 ppm, and between the averages for the 0.6-2.5 mr/hr and >2.5 mr/hr groups - 74 ppm and 140 ppm. A large range in equivalent uranium values is seen in the two "hotter" groups, and occasional values in the other groups are much greater than the average values. Thus the ranges of equivalent uranium values overlap considerably among the four groups.

The relationship between equivalent uranium of sulfides and the field counts persists when broken down by individual sulfides (table 4) and by individual mines (table 5), though rather few data are available for some of these comparisons. As yet, not enough data have been gathered to permit breakdown by individual sulfides within individual mines. Table 4 shows no significant difference for pyrite between the averages of the two lower groups, but large differences between these and the 0.6-2.5 mr/hr group, and between the 0.6-2.5 mr/hr and >2.5 mr/hr groups. The data for galena are sparser but tend to bear out the same relationship, with little apparent difference, however, between the averages for the two hotter groups (113 ppm and 131 ppm).

Table 3. Uranium Content in ppm of Pyrite, Galena, and Sphalerite Grouped by Level of Radioactivity at Sampling Site

<0.1 mr/hr	0.1-0.5 mr/hr	0.6-2.5 mr/hr	>2.5 mr/hr
2.6 ppm	2.6 ppm	124 ppm	264 ppm
6.3	3.3	11	21
1.5	1.2	24	101
.8	4.5	96	74
8.0	3.1	34	216
1.5	1.7	204	15
9.7	23.6	243	50
3.3	19.7	50	37
2.6	7.8	4	3
4.7	2.4	17	475
.7	2.9	6	65
.1			398
9.0	Average:	Average:	303
2.4	6.6	74	99
3.3			23
4.5			96
2.4			
12.6			Average:
1.5			140
15.7			
2.7			
.1			
.0			
Average:			
4.2			

Table 4

Uranium Content in ppm of Individual Sulfides from Various Mines Grouped by Level of Radioactivity at Sampling Site

Pyrite

<0.1 mr/hr	0.1-0.5 mr/hr	0.6-2.5 mr/hr	>2.5 mr/hr
2.4	2.4	4	15
4.7	1.7	17	50
.7	3.1	34	398
.1	3.3	96	74
2.6	1.2	24	264
6.3	4.5	6	21
1.5			101
.8	Average:	Average:	303
8.0	2.7	30	
15.7			Average:
2.7			153
.1			
Average:			
3.8			

Galena

<0.1 mr/hr	0.1-0.5 mr/hr	0.6-2.5 mr/hr	>2.5 mr/hr
2.4	19.7	204	3
3.3	2.6	124	475
1.5		11	65
9.7	Average:		216
3.3	11.2	Average:	23
2.6		113	96
12.6			37
Average:			Average:
5.1			131

Sphalerite

<0.1 mr/hr	0.1-0.5 mr/hr	0.6-2.5 mr/hr	>2.5 mr/hr
4.5	7.8	243	
9.0	2.9	50	
1.5	23.6		
.0		Average:	
	Average:	147	
Average:	11.4		
3.8			

Table 5. Uranium Content in ppm of Pyrite, Galena, and Sphalerite from Individual Mines Grouped by Level of Radioactivity at Sampling Site

Walapai District, Kingman, Arizona

De La Fontaine Mine

<0.1 mr/hr	0.1-0.5 mr/hr	0.6-2.5 mr/hr	>2.5 mr/hr
2.4	19.7	204	3
3.3	7.8	243	475
4.5	2.4		
Average: 3.4	Average: 10.0	Average: 224	Average: 239

Central City District, Colorado

Carroll Mine

<0.1 mr/hr	0.1-0.5 mr/hr	0.6-2.5 mr/hr	>2.5 mr/hr
1.5	1.7		65
9.7	23.6		216
3.3			15
2.6	Average: 12.7		
4.7			Average: 99
.7			
.1			
9.0			
Average: 4.0			

Coeur d'Alene District, Idaho

Sunshine Mine

<0.1 mr/hr	0.1-0.5 mr/hr	0.6-2.5 mr/hr	>2.5 mr/hr
2.6	3.3	96	264
6.3	1.2		21
1.5	4.5		101
.8			303
8.0	Average: 3.0		99
Average: 3.8			Average: 158

Table 5 brings out similar relationships for determinations on all sulfides in the De La Fontaine mine, Walapai District, Arizona; the Carroll mine, Central City, Colorado; and the Sunshine mine, Coeur d'Alene district, Idaho. The data are too few, and the raw values (considered without reference to the various factors discussed below) spread over too wide a range, for careful comparison of range within different sulfides in the same deposit, or between different deposits for the same sulfide. No tentative differences are suggested by these preliminary comparisons. When more values are available, careful statistical analysis will be necessary.

It should be pointed out that there are a number of factors which could be expected to work against a close correlation of uranium content of sulfides with field counts. These are:

(1) Lack of precision of the field radiometric counts.
(2) Presence in the purified sulfide of small inclusions of pitchblende, or concentrations of uranium in grain coatings, fracture fillings, replacement bodies.
(3) Difference in time of sulfide deposition from that of uranium introduction.
(4) If uranium concentration in the sulfides is related to its concentration in the depositing solution, uranium in the sulfides might be expected to be constant at all places where the depositing solution was saturated (or solubility product exceeded), while amount of uranium deposition (as pitchblende) would not be limited - hence field count would not be.

On the other hand, even if no uranium at all went into the sulfide lattice, association with surrounding radioactive material would probably cause the sulfide to gain some uranium by contamination, and the amount of contamination would depend to some extent on the concentration of uranium in the surrounding rock. This factor would tend in the direction of a closer apparent correlation between present uranium content of sulfides and the activity of the surrounding material than there would be between original uranium in the sulfide and field activity.

In order to obtain a more direct measure of the relationship between sulfide uranium content and uranium in the surrounding ore, laboratory beta-gamma counts with a scaler are now being made on the bulk rock of each sample from which sulfides are concentrated. The uranium content of the sulfides will then be compared with the equivalent uranium content calculated from the beta-gamma count on the sample itself. This will obviate the difficulties in correlation with field counts

due to variable background, lack of precision with survey meter, and influence of rock other than that sampled. The greater sensitivity of laboratory counting furthermore will permit measurements on rock lumped by field counts in the group "not above background".

The presence of introduced or contamination uranium may be detected in the autoradiographs as described below, and, under some circumstances, its effect cancelled by applying a factor obtained by comparing the amount of tracks randomly distributed through the sulfide with those in clusters indicating contamination.

Paragenetic studies, as mentioned previously, will in some cases indicate sulfides which are unrelated in time to the introduction of uranium in the hydrothermal solutions. The uranium content of these sulfides should be very low, and in hot samples would contrast with the high field activity or laboratory beta-gamma counts on the sample itself.

Two general conclusions may be stated from the analysis of the preliminary alpha count uranium determinations on sulfides:

1. There is a rough correlation between equivalent uranium in sulfides and the radioactivity of the surrounding ore. To evaluate the degree of this correlation for the different sulfides, in different districts, and to determine the factors contributing to the correlation and those affecting the correlation adversely, will require much more data and careful statistical analysis.

2. To develop the potential use of uranium determinations on sulfides in indicating deposits formed by solutions high in uranium and therefore favorable for uranium prospecting, more sensitive and more precise means of uranium determination are required. The method would have its greatest usefulness in showing abnormally high uranium content in sulfides from rock samples with radioactivity below the sensitivity of field counters. The data presented above indicate that the uranium content of the sulfides in barren vein material deposited near pitchblende concentrations and contemporaneously with them is on the order of a few ppm, and is uncommonly more than 10 ppm even where slight radioactivity can be detected with a field counter. The lower limit of sensitivity of uranium determinations by alpha counting is of the order of 0.1 ppm, and the precision decreases rapidly approaching this limit. As mentioned above, thick source sample preparations are now being counted rather than thin source, to provide better precision.

In order to establish the significance of the uranium determinations on the order of one to several ppm, a number of determinations will need to be made on sulfides from non-uraniferous deposits. It is thought that the use of fluorimetric determinations and a proportional counter with alpha background of 1 cph should provide sufficient sensitivity and precision for this very low level work.

Distribution of Uranium in Sulfides

Alpha track distribution has been studied in autoradiographs of both uncleaned and cleaned sulfide grains from the De La Fontaine and Detroit mines, Walapai district, Arizona, and the Carroll mine, Central City district, Colorado.

For each grain mount, the pattern of distribution and the density of the alpha tracks are studied and tabulated. In general, where the tracks are not simply distributed randomly over the polished sections of grains, they are in concentrations along grain margins or cleavages, or occasionally in irregular areas in the interior. In addition to the overall pattern of distribution, a notation is made of the relative amount of tracks in clusters radiating from a point, compared with individual tracks. The presence of abundant clusters indicates that much of the uranium is concentrated in discrete grains of a uranium mineral rather than distributed in atomic form through the sulfide lattice.

Track density is classified by number per unit length in the case of linear concentrations, as those along grain boundaries and cleavages. In non-linear concentrations, the density is classified by number per unit area, counted with the aid of a Whipple grid. The following arbitrary groups are used:

1. Along grain boundary or cleavage
   a. "light" - 0-50 tracks per mm.
   b. "medium" - 51-500 tracks per mm.
   c. "dense" - more than 500 tracks per mm.

2. In grain interior
   a. "sparse" - less than 12 tracks per $mm.^2$
   b. "light" - 12-60 tracks per $mm.^2$
   c. "medium" - 61-6000 tracks per $mm.^2$
   d. "dense" - more than 6000 tracks per $mm.^2$

The data on track distribution are recorded as in the following examples:

Sample no.	Mineral	U, ppm from alpha count	Percent of grains	Density	Orientation
A-27	Galena (cleaned)	26.0	20	sparse	random tracks
A-29	Sphalerite (cleaned)	12.2	50+	light	random stars
			10	sparse	random tracks
			40	light	random tracks
A-29	Sphalerite (uncleaned)	———	61	dense	clusters on grain borders and along cleavage
			46	medium	tracks on borders and along cleavage
			54	dense	"
			61	medium	multi-track clusters over interior
			29	dense	random tracks

The distribution of tracks was studied in grain mounts of 29 sulfides, most of them cleaned, from the De La Fontaine, Detroit, and Carroll mines. Comparison of the autoradiographs of cleaned and uncleaned material showed that the cleaning procedure was quite effective in removing contamination from grain surfaces. In no sample of cleaned material were concentrations of tracks observed along grain boundaries.

A great majority of the cleaned samples showed a random distribution of individual tracks, generally in the "sparse" and "light" density groups, as in the first example above (A-27). For the purpose of this study, this is the most desirable distribution as it is the one which would be expected to result from uranium introduced during crystallization of the sulfide. Occasional samples, as the second example above (A-29, cleaned sphalerite), even after cleaning, show a large percentage of tracks in concentrations or oriented in radiating clusters. It is clear in such cases as this that the uranium determination cannot be relied upon as an indication of the amount of uranium which entered the sulfide during crystallization. The third example (A-29, uncleaned sphalerite) shows a large percentage of tracks in clusters along grain boundaries and cleavages. Although this sample showed an unusual degree of contamination, most autoradiographs of uncleaned material revealed some contamination along grain boundaries, confirming the need for cleaning the sulfide concentrates prior to determination of their uranium content.

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