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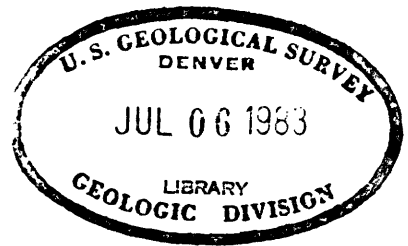
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COFFINITE, A URANOUS SILICATE WITH HYDROXYL SUBSTITUTION:  
A NEW MINERAL\*

By

L. R. Stieff, T. W. Stern, and A. M. Sherwood

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## COFFINITE, A URANOUS SILICATE WITH HYDROXYL SUBSTITUTION:

## A NEW MINERAL

By L. R. Stieff, T. W. Stern, and A. M. Sherwood

## ABSTRACT

A uranous silicate which shows substitution of  $(\text{OH})_4^{-4}$  for  $(\text{SiO}_4)^{-4}$  has been identified as a new mineral. This new mineral, coffinite, named for Reuben Clare Coffin, has been found in more than 25 uranium deposits in the sedimentary rocks of the Colorado Plateau province and in association with uraninite in vein deposits in the Copper King mine, Larimer County, Colorado. It also is associated with asphaltic pellets from sediments in Texas and Oklahoma.

In many Colorado Plateau mines coffinite and uraninite are the major uranium minerals in the unoxidized ore. In hand specimen, coffinite is black, and many of the samples have an adamantine luster resembling that of a high-rank coal. On the Plateau, coffinite occurs as replacement of organic material, as disseminations in sandstone and is associated with low-valence vanadium minerals, uraninite, clay, quartz, and organic material. In transmitted light the smaller particles of coffinite-bearing material are pale brown to very dark brown on thin edges and contain numerous opaque inclusions. The optical properties of coffinite could not be determined. The mineral is very fine grained as evidenced by its apparent isotropy and by the broadened lines of its X-ray diffraction powder pattern.

X-ray diffraction powder studies indicate that coffinite is tetragonal and isostructural with zircon; material from the Arrowhead mine, Colorado, has  $a_0 = 6.94$  A,  $c_0 = 6.31$  A;  $a_0:c_0 = 1:0.909$ . Coffinite is best identified

by its X-ray diffraction powder pattern.

Due to its fine-grained nature and association with uraninite and low-valence vanadium minerals, coffinite could not be completely purified. The specific gravity of coffinite-bearing material is variable and ranges up to 5.1. Chemical analyses on carefully selected and concentrated (but not pure) material indicated from 46.37 to 68.29 percent uranium ( $UO_2$ ) and from 5.20 to 8.50 percent silica. Heating, leaching, and alpha-plate studies have demonstrated that vanadium, aluminum, and arsenic, which are present in many samples and could substitute for silicon, are not essential constituents of coffinite. Oxidation-potential measurements on a suspension of coffinite in  $1N$   $H_2SO_4$  indicate that most of the uranium is in the quadrivalent state. Infrared studies on coffinite show that there are hydroxyl as well as silicon-oxygen bonds in the tetrahedral groups, and in this respect its infrared absorption spectrum resembles thorogummite,  $Th(SiO_4)_{1-x}(OH)_{4x}$ . The proposed chemical formula for coffinite is  $U(SiO_4)_{1-x}(OH)_{4x}$ .

#### INTRODUCTION AND ACKNOWLEDGMENTS

V. E. Goldschmidt (1954, p. 563) wrote, "The entrance of quadrivalent uranium into minerals of the thorite group (e.g., uranium entering into  $ThSiO_4$  in replacement of thorium ions) suggests the possibility of an unknown compound  $USiO_4\dots$ " This prediction was fulfilled with the discovery of a black highly radioactive ore from the La Sal No. 2 mine, Mesa County, Colorado, which gave a zircon-type X-ray diffraction powder pattern. The new mineral coffinite is named in honor of Reuben Clare Coffin for his outstanding geologic studies in southwestern Colorado. His report on the uranium-vanadium deposits (1921, p. 1) is a major contribution. Mr. Coffin has been with the Stanolind Oil and

Gas Company for many years and is also a consultant to the Geological Survey on its regional geophysical studies on the Colorado Plateau.

In the summer of 1951 a shipment of about five tons of high-grade uranium ore from the La Sal No. 2 mine was received at the U. S. Vanadium Company processing mill at Uravan, Colorado. The chemical assay on the ore shipment was over 20 percent uranium and about 10 percent vanadium. In August 1951 L. B. Riley, L. R. Stieff, and T. W. Stern went to examine the mine from which the high-grade black ore had come. Since August 1951 the new mineral first identified at the La Sal No. 2 mine has been found in more than 25 mines on the Colorado Plateau and in several other localities in the United States. Associated with coffinite is a new low-valence vanadium mineral which will be described later.

The writers, in 1953, wrote a preliminary description of coffinite which has been abstracted (Stern and Stieff, 1954). Weeks and Thompson (1954, p. 31), using data from the preliminary description, listed this mineral as "new black uranium mineral." Fleischer (1954, p. 1037) refers to this mineral as coffinite. Rosenzweig, Gruner, and Gardiner (1954, p. 356) made reference to "coffinite." A preliminary description of coffinite was published recently (Stieff, Stern, and Sherwood, 1955, p. 608). Gruner and Smith (1955, p. 16) in their annual report to the Atomic Energy Commission covering the period April 1, 1954 to March 31, 1955 discuss their work on coffinite. Many of their conclusions are similar to ours.

We gratefully acknowledge the assistance of many colleagues at the U. S. Geological Survey. Besides those credited directly in the report, these include: A. D. Weeks identifying and submitting samples of coffinite, R. G. Coleman polished section studies, J. M. Schopf study of associated organic material, and F. S. Grimaldi advice on chemical leaching studies. H. R. Hoekstra,

Argonne National Laboratory, discussed with us the chemical aspects of the problem and suggested the application of infrared analysis. Professor Clifford Frondel, Harvard University, furnished specimens of thorite and thorogummite which he had previously studied, and gave advice on many aspects of the problem. Professor John W. Gruner, University of Minnesota, discussed the coffinite problem on several occasions.

#### DESCRIPTION

Occurrence.--In hand specimen, coffinite is black, and many of the samples have an adamantine luster resembling that of a high-rank coal. On the Colorado Plateau coffinite occurs chiefly as replacements of organic material and to a lesser extent as disseminations in sandstone or as masses in which the original texture of the host material is no longer evident. In many localities on the Colorado Plateau the mineral is closely associated with fine-grained black low-valence vanadium minerals, with uraninite, and with finely disseminated black organic material. It is often impossible to distinguish between coffinite and uraninite in hand specimen, but in the laboratory coffinite can be identified by its X-ray diffraction powder pattern and by its infrared absorption spectrum. This mineral is tetragonal and gives a zircon-type X-ray pattern similar to that of thorite ( $\text{ThSiO}_4$ ), and its infrared absorption spectra show hydroxyl bonds as well as silicon-oxygen bonds in the tetrahedral groups.

Up to the present time most of the coffinite studied is from the black vanadium-rich ores of the Salt Wash sandstone member of the Morrison formation (Jurassic) in the Uravan mineral belt (Fischer and Hilpert, 1952, p. 1) on the Colorado Plateau. In this belt, coffinite and uraninite seem to be the most

abundant uranium minerals in the black ores. Only one sample of coffinite has been identified from the Shinarump conglomerate in the Denise No. 1 mine, Green River district, Emery County, Utah. The major uranium minerals in the Mi Vida mine, Monticello district, San Juan County, Utah, in the Chinle formation (Triassic) are uraninite and coffinite.

Although coffinite was first found in the uranium deposits in the sedimentary rocks of the Colorado Plateau, it has been found more recently with uraninite and pitchblende in the vein deposits of the Copper King mine, Prairie Divide, Larimer County, Colorado. The environment of deposition of the Plateau ores is not known, however, the Copper King occurrence might be used to support the hypothesis that the source of the metals in the Plateau ores is to be found at depth. The presence of low-valence vanadium minerals suggests that, in the sediments at least, reducing conditions were necessary for the deposition of coffinite.

Physical properties.--The physical properties of coffinite-bearing material are quite variable because even the best concentrates consist of intimate mixtures in varying amounts of very fine grained carbonaceous substances, low-valence black vanadium minerals, clay or roscoelite, and uraninite. In general, coffinite is brittle, and the hardness of these coffinite-bearing specimens ranges from about 5 to 6. The typical hard massive variety shows no regular cleavage and has an irregular to subconchoidal fracture. The specific gravity of the most highly purified specimen is 5.1; however, we have obtained X-ray diffraction powder patterns of coffinite on material with a specific gravity of only 2.2. Coffinite does not fluoresce in either long or short wavelength ultraviolet radiation.



Coffinite has been identified from the following formations and localities:

Formation	Mine or district	County	State
Morrison formation (Jurassic)	Arrowhead mine	Mesa	Colo.
	Black Mama mine	Mesa	Colo.
	La Sal No. 2 mine	Mesa	Colo.
	Matchless mine	Mesa	Colo.
	Small Spot mine <u>1/</u>	Mesa	Colo.
	Shattuck Denn shaft	Montrose	Colo.
	Virgin No. 2 mine	Montrose	Colo.
	Wild Steer mine	Montrose	Colo.
	Oversight mine	Montrose	Colo.
	J. J. mine <u>2/</u>	Montrose	Colo.
	Peanut mine <u>2/</u>	Montrose	Colo.
	Little Muriel mine	San Miguel	Colo.
	Corvusite mine	Grand	Utah
	Grey Dawn mine	San Juan	Utah
	Jack Pile mine	Valencia	N. Mex.
	Woodrow Pipe mine	Valencia	N. Mex.
	Wind Whip mine <u>1/</u>	Valencia	N. Mex.
Poison Canyon mine <u>1/</u>	Valencia	N. Mex.	
Mesa Top mine <u>1/</u>	Valencia	N. Mex.	
La Ventana <u>1/</u>	San Doval	N. Mex.	
Mesaverde formation (Cretaceous)			
Shinarump conglomerate (Triassic)	Denise No. 1 mine	Emery	Utah
Chinle formation (Triassic)	Mi Vida mine	San Juan	Utah
Do.	Ruth Group mine <u>1/</u>	Navajo	Ariz.
Do.	Stinking Spring Mt. <u>1/</u>	Navajo	Ariz.
Wind River formation (Eocene)	Lucky Mack mine	Fremont	Wyo.
Dripping Spring quartzite (Precambrian)	Workman No. 1 mine	Gila	Ariz.
Tertiary vein deposit	Copper King mine	Larimer	Colo.
Dolores formation (Permian)	Robinson property, near Placerville <u>3/</u>	San Miguel	Colo.
Cutler formation (Permian)	Weatherly property, near Placerville <u>3/</u>	San Miguel	Colo.
Laramie formation (Cretaceous)	Old Leyden mine <u>3/</u>	Jefferson	Colo.
Garber-Wellington formation (Permian)	J. B. Smith farm, sec. unit 1, Saddle Mt. Creek area <u>3/</u>	Kiowa	Okla.
Big Lime (Lower Permian)	sec. 63, block 47, H. and T. C. Survey <u>3/</u>	Potter	Texas

1/ Identified by J. W. Gruner and D. K. Smith, Jr., University of Minnesota.

2/ Identified by M. E. Thompson, U. S. Geological Survey.

3/ Identified by A. J. Gude 3d, U. S. Geological Survey.

Optical properties.--The optical properties of coffinite cannot be determined because of the very fine grained nature and opacity of the material. Although X-ray studies indicate that coffinite is a tetragonal mineral, in balsam mounts of mineral separates the most abundant material is so fine grained that it appears isotropic. The broadening of the lines in its X-ray diffraction powder pattern suggests that the individual crystallites are approximately  $10^{-5}$  to  $10^{-6}$  cm in diameter (oral communication, H. T. Evans, Jr.). At high magnifications the smallest grains of the purest separates containing coffinite are pale brown to very dark brown and contain many minute opaque inclusions. The larger grains are usually opaque except on thin edges, which are dark brown. Examination of the balsam mounts of the purest coffinite separates showed the presence of at least four phases. Only the use of nuclear-track plates (alpha plates), sensitive to alpha particles (Stieff and Stern, 1952, p. 184), made possible the recognition of the radioactive coffinite.

The alpha plates of the mineral separates contained an opaque and a pale-brown birefringent nonradioactive phase. They also contained two radioactive components: small pale-brown to dark-brown isotropic grains with opaque inclusions, and grains opaque except on thin edges which are dark brown. The opaque nonradioactive grains and some of the opaque inclusions in the radioactive grains are believed to be low-valence vanadium minerals or organic material. The very fine grained birefringent material resembles a clay. The remaining isotropic pale-brown to opaque radioactive material is coffinite.

The recognition of coffinite in polished section presents even greater difficulties than the work with balsam mounts. Polished sections were made of the most intensely radioactive fragments of mineralized wood. This wood shows cellular structure and coffinite fills the cell cavities. The most easily recognizable minerals in the polished sections are montroseite,

paramontroseite, a new low-valence vanadium mineral, and uraninite. The organic material in stringers and in the cell walls is anisotropic and has a moderately high yellowish reflectance. Only by means of a high-resolution autoradiographic stripping-film technique was it possible to localize the most radioactive phase--coffinite. Even under the highest magnifications (1000 X), the mineral appears as grayish-black to brown aggregates of very fine particles. The reflectance of coffinite from the La Sal No. 2 mine, West Gateway district, Mesa County, Colorado, is low, and the mineral appears to be isotropic.

In the polished sections of La Sal No. 2 ore, coffinite is found both in the cell cavities and as veinlets. The veinlets of coffinite appear as thin elongated masses, oriented more or less perpendicularly to the walls of the vein. The coffinite masses are completely surrounded by carbonaceous material. There is evidence that some deformation of the veinlets occurred after emplacement as can be seen by the dispersal and rearrangement of elongated fragments of coffinite. In many other mines uraninite and coffinite are intimately associated. The reflective characteristics of uraninite are somewhat higher than those of coffinite but are otherwise similar.

X-ray diffraction.--Coffinite was first recognized as a new mineral by X-ray diffraction powder patterns. Its structure is of the zircon type. In table 1 the interplanar spacings of coffinite from the Arrowhead mine, Gateway mining district, Mesa County, Colorado, are compared with the calculated d-spacings, assuming the same reflections and orientation as for zircon. The c:a ratio for this specimen of coffinite is 0.909. The c:a ratio varies slightly from sample to sample. The similarity in X-ray diffraction powder patterns of thorite and coffinite originally suggested that this new mineral probably had the formula  $USiO_4$ .

Table 1.--X-ray diffraction powder data for coffinite from the Arrowhead mine, Gateway mining district, Mesa County, Colorado. Indexed assuming tetragonal zircon-type cell with  $a_0 = 6.94$  A,  $c_0 = 6.31$  A. Calculations by E. A. Cisney, U. S. Geological Survey (Cu/Ni radiation).

<u>I</u>	<u>d</u> meas., (A)	<u>d</u> calc., (A)	<u>hkl</u>
S	4.66	4.66	011
S	3.47	3.47	200
W	2.78	2.78	121
M	2.64	2.65	112
F	2.46	2.45	220
W	2.18	2.17	031
F	2.01	2.01	013
W	1.841	1.841	321
M	1.801	1.801	312
W	1.737	1.740 1.735	123 400
F	1.629	1.626	411
F	1.556	1.552	420
F	1.451	1.452	332
F	1.435	1.435	024

F = faint

W = weak

M = medium

S = strong

As has been mentioned, the X-ray diffraction powder lines show a broadening, indicating that the coffinite crystallites are extremely small, probably on the order of  $10^{-5}$  to  $10^{-6}$  cm in diameter. The very small size of the coffinite crystallites, and the association of coffinite with black very fine grained vanadium and uranium minerals, and with black organic material made it impossible to obtain pure separates of coffinite.

Chemical analyses.--The highest grade coffinite ores were hand picked to obtain a preliminary concentrate as low as possible in vanadium minerals, uraninite, and organic material. This preliminary concentrate was crushed, sieved, and a methylene iodide heavy-liquid separation was made. The separates which were heavier than methylene iodide (density 3.3) were used for the various chemical analyses. A series of separations with the Frantz isodynamic separator did not make any significant improvement in the concentration of the coffinite. The results of chemical analyses on three samples are given in table 2.

As can be seen from the analyses in table 2, there is no simple relation between uranium, silicon, vanadium, arsenic, and aluminum. The low silica content of the samples reduced the possibility that coffinite had the simple formula  $USiO_4$ . The presence of amorphous uranium, or the substitution of hydroxyl, arsenic, vanadium, and aluminum for silicon was a distinct possibility. On the basis of the chemical analyses alone, however, coffinite could not be adequately characterized.

Oxidation-potential measurements by A. M. Pommer and J. C. Chandler on a suspension of coffinite in  $1N$   $H_2SO_4$  indicated that most of the uranium was in the quadrivalent state. These Eh measurements also ruled out the possibility of the presence of sexivalent amorphous uranium.

Table 2.--Chemical analyses of coffinite-bearing samples.<sup>1/</sup>

	USiO <sub>4</sub>	La Sal No. 2 mine	Arrowhead mine	Arrowhead mine <sup>2/</sup>
UO <sub>2</sub>	81.80	68.29	46.37	58.60
SiO <sub>2</sub>	18.20	5.20	7.40	8.50
As <sub>2</sub> O <sub>5</sub>		4.35	1.44	1.22
Al <sub>2</sub> O <sub>3</sub>		3.87	6.80	10.12
V <sub>2</sub> O <sub>5</sub>		2.85	18.90	3.25
Fe <sub>2</sub> O <sub>3</sub>		1.24	1.57	4.44
P <sub>2</sub> O <sub>5</sub>			2.69	
S			0.80	
Pb		0.12	0.52	0.15
CaO				2.00
Loss on igni- tion <sup>3/</sup> at 110° C		1.68	0.44	
110-450° C		6.81	9.60	
450-800° C		0	0	
250° C				6.00
250-500° C				6.80
500-850° C				1.20
	<u>100.00</u>	<u>94.41</u>	<u>96.53</u>	<u>102.28</u>

<sup>1/</sup> Analyses by A. M. Sherwood, U. S. Geological Survey.

<sup>2/</sup> Sample prepared by M. E. Thompson, U. S. Geological Survey.

<sup>3/</sup> Results of loss on ignition are not a direct indication of water content because of the presence of carbonaceous material.

Synthesis.--The impurity of the natural coffinite-bearing concentrates immediately suggested that the uncertainties concerning the chemical composition could be overcome if coffinite could be synthesized. The problem of synthesis was undertaken at the Geological Survey laboratories, by Dr. George W. Morey at the Geophysical Laboratory of the Carnegie Institution of Washington, and by Prof. Clifford Frondel at Harvard University. Previously Dr. S. M. Lang of the National Bureau of Standards had attempted to obtain  $USiO_4$  from melts at high temperatures without success. At the present time, July 1955, in spite of repeated attempts,  $USiO_4$  has not been prepared by any of the workers mentioned above. Attempts to prepare coffinite from aqueous solution are being continued at the Geological Survey.

Alpha-plate and leaching studies.--The complete failure of the synthesis studies and the ambiguous results of the chemical analyses made it necessary to use several indirect techniques to arrive at the composition of coffinite. In addition, the identity of the minute opaque inclusions had not been established. It also remained to determine if the vanadium, aluminum, and arsenic were essential. The presence of bonded hydroxyl groups in the structure of coffinite could not be established by chemical analyses of the natural material, and the relatively low silica content of the samples raised legitimate doubts as to whether the silicon was essential, present in quartz, or present in amorphous silica.

Representative samples of the coffinite-bearing material, both heavier and lighter than methylene iodide, were heated in closed tubes, and heated under controlled atmospheres. The sample highest in arsenic, on heating in a closed tube, produced an arsenic mirror. The X-ray diffraction powder pattern of the heated material showed that coffinite was still the only major crystalline material present. This experiment suggests that arsenic is not

essential to coffinite.

When the heated coffinite was dispersed on alpha plates, it had changed in several aspects. The transparent moderately radioactive grains had changed from brown to a gray color. The edges of the opaque highly radioactive grains appeared to be more granular, and only a few showed a reddish-brown color on thin edges. Hence, heating the coffinite separates had also visibly reduced the amount of organic material in the samples.

Chemical analyses for soluble silica and total silica were made on four samples of coffinite and two samples of thorogummite. The soluble silica was determined on the solutions obtained by treating the mineral concentrates with (1+3)  $\text{HNO}_3$ . The total silica content of the two purest separates of coffinite was 6.0 to 7.0 percent. The  $\text{HNO}_3$  leach solutions of the coffinite separates contained 4.50 and 1.25 percent silica, respectively. The  $\text{HNO}_3$  leach solutions from two thorogummite specimens contained 5.25 and 7.50 percent silica. Originally, these two thorogummite samples contained 19.00 and 37.50 percent total silica. The coffinite residue did not give an X-ray diffraction pattern, and the uranium content of the residue dropped from that of a major constituent ( $> 10$  percent) to less than 0.0001 percent.

Following these preliminary leaching studies a more detailed series of experiments were undertaken on coffinite from the La Sal No. 2 mine to establish, if possible, the relation of the soluble silica to the uranium content, the form of the insoluble silica, and the role of vanadium. The results of these experiments are summarized in table 3.

The Si/U ratios of the filtrates,  $F_1$  and  $F_2$  (table 3), are 0.0537 and 0.0535, respectively. The theoretical Si/U ratio for  $\text{USiO}_4$  is 0.1176. From this, it would appear that this specimen of coffinite contains slightly less than half as much silica as the theoretical maximum. The similarities in the



Table 3.--Results of leaching experiments on coffinite sample from La Sal No. 2 mine, Gateway district, Mesa County, Colorado.

Original sample (percent)	Treated with 1N H <sub>2</sub> SO <sub>4</sub> for 1 hr		R <sub>1</sub> treated with 1N HNO <sub>3</sub> for 16 hr	
	Filtrate, F <sub>1</sub> (percent)	Residue, R <sub>1</sub> (percent)	Filtrate, F <sub>2</sub> (percent)	Residue, R <sub>2</sub> (percent)
U	30.78	8.72 <u>1/</u>	7.82	< 0.0001 <u>2/</u>
Si	1.65	3.15 <u>1/</u>	0.42	2.73 <u>1/</u>
V	6.59	3.79 <u>1/</u>	3.62	0.17 <u>1/</u>
Al	1 - 10 <u>2/</u>	1 - 10 <u>2/</u>		1 - 10 <u>2/</u>
As	4.08	0.1 - 1 <u>2/</u>		< 0.0001 <u>2/</u>
Fe	1.83	0.1 - 1 <u>2/</u>		
H <sub>2</sub> O-	2.87			
H <sub>2</sub> O+	6.13			
H	0.63 - 0.73 <u>3/</u>			
C	5.89 - 5.94 <u>3/</u>			
Specific gravity	4.64	3.23		2.75
X-ray	coffinite	coffinite		no pattern

1/ By difference.  
2/ Semiquantitative spectrographic analysis by C. S. Annell, U. S. Geological Survey.  
3/ Analyses by R. T. Moore, U. S. Geological Survey.

Si/U ratios of  $F_1$  and  $F_2$  support the oxidation-potential measurements in suggesting that amorphous uranium, readily soluble in  $H_2SO_4$ , was not present and that the U and Si are combined in a single phase. In contrast, the V/U ratios of the filtrates  $F_1$  and  $F_2$  are 0.214 and 0.463, respectively. The large difference suggests that the V was not an essential constituent of the uranium mineral. This interpretation was strengthened by the study of the polished sections of La Sal ore which showed numerous intergrowths of montroseite,  $VO(OH)$ , and other low-valence vanadium oxides with coffinite.

Comparative alpha-plate studies of the original La Sal ore and residues from the  $H_2SO_4$  and  $HNO_3$  leaches show a number of marked changes.  $R_1$ , the residue of the  $H_2SO_4$  leach, contains relatively few pale- to dark-brown isotropic radioactive grains compared to the original sample. The number of brown birefringent nonradioactive grains appeared greater. Most opaque radioactive grains were not transparent on thin edges, and the grain boundaries were irregular. The alpha activity of the opaque grains appeared somewhat reduced. Radiocolloids were abundant.

The alpha plate of the residue from the  $HNO_3$  leach,  $R_2$ , contained only pale-brown birefringent nonradioactive grains, weakly radioactive opaque grains, and scattered radiocolloids. The opaque grains were lacy in appearance showing abundant evidence of the removal of material by the nitric acid leach. This evidence suggested that many of the opaque inclusions noted in the radioactive brown isotropic grains were carbonaceous, and that the opacity of many of the radioactive particles was due to carbonaceous material. The fine-grained birefringent phase most resembled a clay. The presence of a clay mineral would account for the silica and aluminum reported in the analyses of the residues,  $R_1$  and  $R_2$  (table 3).

Infrared analyses.--Although the experiments described above suggested that arsenic and vanadium are not essential and that coffinite does contain some silica, the total silica content of the coffinite concentrates was not sufficient to allow a formula of the type  $USiO_4$ . McConnell (1950, p. 166) proposed the substitution of  $(OH)_4^{-4}$  for  $(SiO_4)^{-4}$  in montmorillonite. Frondel (1953, p. 1007) has shown that hydroxyl substitution exists in thorogummite. During the authors' visit at Argonne National Laboratories, Dr. Henry Hoekstra suggested that the presence of bonded hydroxyl groups in the coffinite structure might be established by infrared analyses. Following his suggestion, specimens of coffinite, thorogummite, zircon, and uraninite were ground to pass through a 400-mesh sieve, vacuum dried in an Abderhalden drying pistol, and analyzed in an infrared spectrometer for hydroxyl and silicon-oxygen bonds by R. G. Milkey of the Geological Survey.

Figure 1 shows the results of infrared absorption studies on zircon, thorogummite, coffinite, and uraninite. The silicon-oxygen bonds in the tetrahedral groups in zircon,  $ZrSiO_4$ , show absorption from wavelengths of about 10.2 to 11.2 microns. This is the region where Launer (1952, p. 770) has shown that silicates with isolated tetrahedra, such as zircon, will absorb strongly. He has also shown that zircon has an absorption at a shorter wavelength band, approximately 9.7 microns. The thorogummite from Iisaka, Japan, and Baringer Hill, Llano County, Texas, showed absorption in the 9.7 and 11.2 micron region. In addition, these samples showed strong absorption in the region between 2.8 and 3.1 microns. The latter absorption is characteristic of bonded OH groups with some unbonded OH present.

Coffinite from three localities on the Colorado Plateau showed absorption spectra closely resembling either the Iisaka or Baringer Hill specimens of thorogummite. In general, the absorption band in the OH region was not as

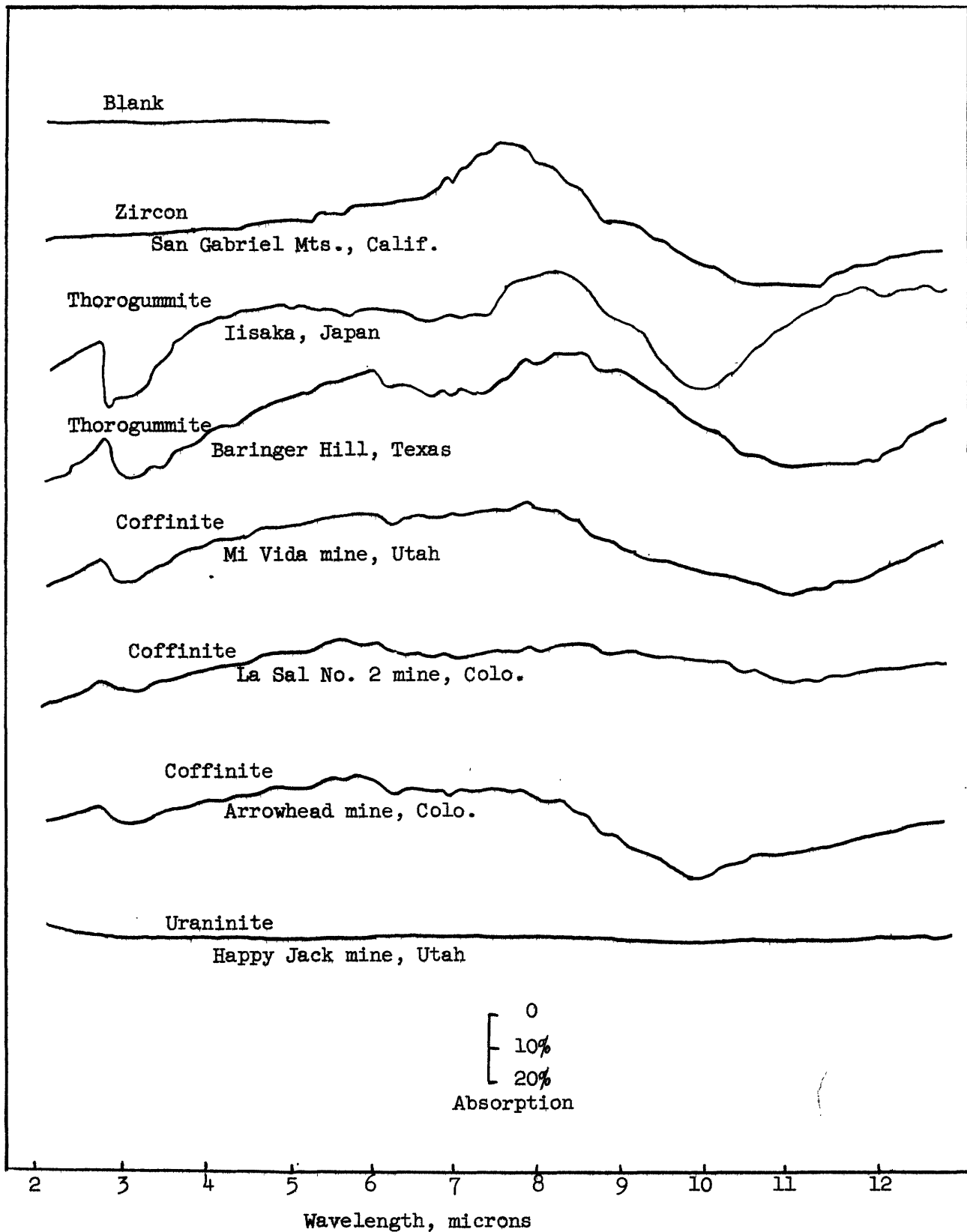


Figure 1.--Infrared absorption spectra of zircon, thorogummite, coffinite, and uraninite.

sharp as that obtained for thorogummite. In contrast, the infrared absorption pattern for very pure uraninite, essentially  $UO_2$ , from the Happy Jack mine, San Juan County, Utah, did not show any significant absorption throughout the region from 2 to 14 microns. The infrared analyses strongly suggest that coffinite, like thorogummite, does contain bonded OH.

### CONCLUSIONS

Difficulties in obtaining pure coffinite concentrates and the complete failure of repeated attempts to synthesize  $USiO_4$  made it necessary to use a combination of indirect techniques in order to arrive at the chemical composition of coffinite. Heating, leaching, and alpha-plate studies combined with X-ray and semiquantitative spectrographic analyses strongly suggest the following: Silica to uranium ratios are constant but insufficient to satisfy the formula  $USiO_4$ , arsenic and vanadium are not essential constituents of coffinite, the phase soluble in  $HNO_3$  contains most of the uranium and from 20 to 75 percent of the total silica in the coffinite-bearing specimen. Amorphous hexivalent uranium is not present, and, finally, the uranium is in the quadrivalent state. The close similarity of the infrared absorption spectra of thorogummite,  $Th(SiO_4)_{1-x}(OH)_{4x}$ , and coffinite indicated that coffinite contains silicon-oxygen bonds in tetrahedral groups as well as bonded hydroxyl groups. Although no single line of evidence is sufficient to establish the identity and composition of this important uranium mineral of the unoxidized ores of the Colorado Plateau, all of the evidence taken together strongly supports the idea that coffinite is tetragonal with a zircon-type structure and has the formula  $U(SiO_4)_{1-x}(OH)_{4x}$ .

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