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

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ABSTRACT

A uranous silicate that 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 Plateaus province, in several localities peripheral to this province, and in association with uraninite in vein deposits in the Copper King mine, Larimer County, Colorado. It is also associated with asphaltic pellets from sediments in Texas and Oklahoma.

In many Colorado Plateau mines coffinite and uraninite are the main uranium minerals in the unoxidized ore. In hand specimen coffinite is black; many of the samples have an adamantine luster resembling that of a high-rank coal. On the Plateau, coffinite occurs as replacements of organic material, as disseminations in sandstone, and in association 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; they 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 in Mesa County, Colorado, has $a_0 = 6.94 \text{ \AA}$, $c_0 = 6.31 \text{ \AA}$, $a_0:c_0 = 1:0.909$. Coffinite is best identified by its x -ray diffraction powder pattern.

Owing to its fine-grained nature and its association with uraninite and low-valence vanadium minerals, coffinite could not be completely purified. The specific gravity of coffinite-bearing material is variable, with a measured maximum of 5.1. Chemical analyses on carefully selected and concentrated but impure material indicated 46.37 to 68.29 per cent uranium (UO_2) and 5.20 to 8.50 per cent 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 1 N 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 that of thorogummite, $\text{Th}(\text{SiO}_4)_{1-x}(\text{OH})_{4x}$. The proposed chemical formula for coffinite is $\text{U}(\text{SiO}_4)_{1-x}(\text{OH})_{4x}$.

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INTRODUCTION AND ACKNOWLEDGMENTS

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" 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. This ore contained a new mineral, coffinite, 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 U. S. Geological Survey on its regional geophysical studies on the Colorado Plateaus province.

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 showed more than 20 per cent uranium and about 10 per cent vanadium. In August 1951 L. B. Riley, L. R. Stieff, and T. W. Stern examined 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 authors, 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) 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 of the U. S. Geological Survey. Besides those credited directly in this paper, they include A. D. Weeks, who identified and submitted samples of coffinite; R. G. Coleman, who made polished section studies; J. M. Schopf, who made a study of associated organic material; and F. S. Grimaldi, who gave advice on chemical leaching studies. H. R. Hoekstra, of the Argonne National Laboratory, discussed with us the chemical aspects of the problem and suggested the application of infrared analysis.

Professor Clifford Frondel, of Harvard University, furnished specimens of thorite and thorumite that he had previously studied and gave advice on many aspects of the problem. Professor J. W. Gruner, of the University of Minnesota, discussed the coffinite problem on several occasions.

This report concerns work done on behalf of the Divisions of Research and Raw Materials of the U. S. Atomic Energy Commission.

OCCURRENCE OF COFFINITE

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 (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, Cal Uranium, and Homestake mines, 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 vein occurrence might be used to support the hypothesis that the source of the metals in the Plateau ores is 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 variable; 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 formations and localities shown in Table 1.

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 (H. T. Evans, Jr., oral communication). 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 positive 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: (1) small pale-brown to dark-brown isotropic grains with opaque inclusions, and (2) grains that are opaque except on thin edges, where they 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.

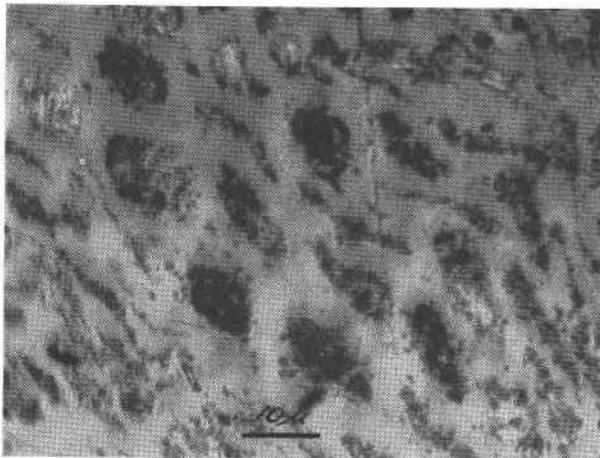
Coffinite in polished section presents even greater difficulties than in balsam mounts. Polished sections were made of the most intensely radio-

TABLE 1. COFFINITE LOCALITIES LISTED BY MINE OR PROPERTY NAME AND GEOLOGIC FORMATION

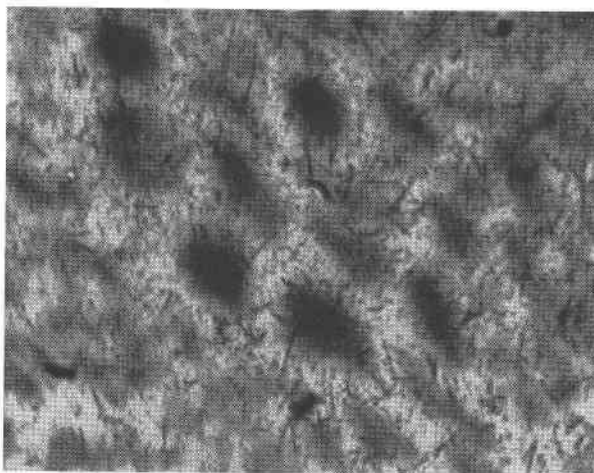
Formation	Mine or district	County	State
Browns Park formation (Miocene)	Poison Basin claims ¹	Carbon	Wyo.
Wind River formation (Eocene)	Vitro Uranium mine	Fremont	Wyo.
	Lucky Mc mine	Fremont	Wyo.
Fort Union formation (Eocene)	Kell Roy No. 3 mine ¹	Johnson	Wyo.
Vein deposit (Tertiary)	Copper King mine	Larimer	Colo.
Laramie formation (Cretaceous)	Old Leyden mine ²	Jefferson	Colo.
Mesaverde formation (Cretaceous)	La Ventana	San Doval	N. Mex.
	Arrowhead mine	Mesa	Colo.
	Black Mama mine	Mesa	Colo.
	La Sal No. 2 mine	Mesa	Colo.
	Matchless mine	Mesa	Colo.
	Small Spot mine ¹	Mesa	Colo.
	Shattuck Denn shaft	Montrose	Colo.
	Virgin No. 2 mine	Montrose	Colo.
	Wild Steer mine	Montrose	Colo.
	Oversight mine	Montrose	Colo.
Morrison formation (Jurassic)	J. J. mine ³	Montrose	Colo.
	Peanut mine ³	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 ¹	Valencia	N. Mex.
	Poison Canyon mine ¹	Valencia	N. Mex.
	Mesa Top mine ¹	Valencia	N. Mex.
	Mi Vida mine	San Juan	Utah
	Cal Uranium mine	San Juan	Utah
Chinle formation (Triassic)	Homestake mine	San Juan	Utah
	Ruth group mine ¹	Navajo	Ariz.
	Stinking Spring Mountain ¹	Navajo	Ariz.
Shinarump conglomerate (Triassic)	Denise No. 1 mine	Emery	Utah
Dolores formation (Triassic)	Robinson property, near Placerville ²	San Miguel	Colo.
Cutler formation (Permian)	Weatherly property, near Placerville ²	San Miguel	Colo.
Garber formation (Permian)	J. B. Smith farm, sec unit 1, Saddle Mountain ²	Kiowa	Okla.
San Andres formation (Permian)	Sec. 63, block 47, H. and T. C. Survey ²	Potter	Texas
Dripping Spring quartzite (Precambrian)	Workman No. 1 mine	Gila	Ariz.
Vein (unknown age)	Little Mo mine (Arrowhead No. 1) ¹	Fremont	Wyo.

¹ Identified by J. W. Gruner and D. K. Smith, Jr., University of Minnesota.² Identified by A. J. Gude, 3d., U. S. Geological Survey.³ Identified by M. E. Thompson, U. S. Geological Survey.

active fragments of mineralized wood. This wood shows cellular structure, and coffinite fills the cell cavities (pl. 1). The most easily recognizable minerals in the polished sections are montroseite, paramontroseite, new low-valence vanadium minerals, and uraninite. The organic material



(A) Cell cavities, some showing deformation, are replaced by coffinite. The light-colored areas of high reflectance are carbonaceous materials.



(B) Alpha-particle tracks (short dark lines) in nuclear-track film overlying the polished section shown in (A). Note radial arrangement of alpha tracks around cells filled with radioactive coffinite.

PLATE 1

Photomicrographs of polished section of radioactive ore from La Sal No. 2 mine, Mesa County, Colorado. Magnification approximately 900 \times .

in stringers and in the cell walls is anisotropic and has a moderately high yellowish reflectance. The use of high-resolution autoradiographic stripping-film techniques made it possible to localize the most radioactive phase—coffinite. Even under the highest magnifications (1000 \times) 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. Some deformation of the veinlets evidently 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 2 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 USiO₄.

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 that

TABLE 2. X-RAY DIFFRACTION POWDER DATA FOR COFFINITE FROM THE ARROWHEAD MINE, GATEWAY MINING DISTRICT, MESA COUNTY, COLORADO

Indexed assuming tetragonal zircon-type cell with $a_0=6.94 \text{ \AA}$, $c_0=6.31 \text{ \AA}$. Calculations by E. A. Cisney, U. S. Geological Survey (Cu/Ni radiation).

<i>I</i>	<i>d</i> meas., (\AA)	<i>d</i> calc., (\AA)	<i>hkl</i>
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	123
		1.735	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.

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 of three samples are given in Table 3.

As can be seen from the analyses in Table 3, 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 1 *N* 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 hexivalent amorphous uranium.

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.

TABLE 3. CHEMICAL ANALYSES OF COFFINITE-BEARING SAMPLES¹

	USiO ₄	La Sal No. 2 mine	Arrowhead mine	Arrowhead mine ²
UO ₂	81.80	68.29	46.37	58.60
SiO ₂	18.20	5.20	7.40	8.50
As ₂ O ₅		4.35	1.44	1.22
Al ₂ O ₃		3.87	6.80	10.12
V ₂ O ₅		2.85	18.90	3.25
Fe ₂ O ₃		1.24	1.57	4.44
P ₂ O ₅			2.69	
S			0.80	
Pb		0.12	0.52	0.15
CaO				2.00
Loss on ignition ³ 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
	100.00	94.41	96.53	102.28

¹ Analyses by A. M. Sherwood, U. S. Geological Survey.

² Sample prepared by M. E. Thompson, U. S. Geological Survey.

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

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 USiO₄ from melts at high temperatures without success. At the present time, July 1955, in spite of repeated attempts, USiO₄ has not been prepared by any of the workers mentioned above. Attempts to prepare coffinite from aqueous solution are being continued by the authors.

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 minute opaque inclusions had not been identified. 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, some heavier and some 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 was seen that the material 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) HNO₃. The total silica content of the two purest separates of coffinite was 6.0 to 7.0 per cent. The HNO₃ leach solutions of coffinite separates contained 4.50 and 1.25 per cent silica. The HNO₃ leach solutions from two thorogummite specimens contained 5.25 and 7.50 per cent silica. Originally these two thorogummite samples contained 19.00 and 37.50 per cent 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 per cent) to less than 0.0001 per cent.

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 4.

The Si/U ratios of the filtrates, F_1 and F_2 (Table 4), are 0.0536 and 0.0537, respectively. The theoretical Si/U ratio for USiO₄ is 0.1176. From these data, it would appear that this specimen of coffinite contains slightly less than half as much silica as the theoretical maximum. The similarities in the Si/U ratios of F_1 and F_2 support the oxidation-potential measurements in suggesting that amorphous uranium, readily soluble in H₂SO₄, 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

TABLE 4. RESULTS OF LEACHING EXPERIMENTS ON COFFINITE SAMPLE FROM LA SAL No. 2 MINE, GATEWAY DISTRICT, MESA COUNTY, COLORADO

	Original sample (per cent)	Treated with 1 N H ₂ SO ₄ for 1 hr.		R ₁ treated with 1 N HNO ₃ for 16 hr.	
		Filtrate, F ₁ (per cent)	Residue, R ₁ (per cent)	Filtrate, F ₂ (per cent)	Residue, R ₂ (per cent)
U	39.50	30.78	8.72 ¹	7.82	<0.0001 ²
Si	4.80	1.65	3.15 ¹	0.42	2.73 ¹
V	10.38	6.59	3.79 ¹	3.62	0.17 ¹
Al	1-10 ²		1-10 ²		1-10 ²
As	4.08	~4.08	0.1-1 ²		<0.0001 ²
Fe	1.83		0.1-1 ²		
H ₂ O--	2.87				
H ₂ O+	6.13				
H	0.63-0.73 ³				
C	5.89-5.94 ³				
Specific gravity	4.64		3.23		2.75
X-ray	coffinite		coffinite		no pattern

¹ By difference.

² Semiquantitative spectrographic analysis by C. S. Ansell, U. S. Geological Survey.

³ Analyses by R. T. Moore, U. S. Geological Survey.

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 residue from the H₂SO₄ and HNO₃ leaches show a number of marked changes. R₁, the residue of the H₂SO₄ leach, contains relatively few pale- to dark-brown isotropic radioactive grains compared with 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 HNO₃ leach, R₂, 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 silicon and aluminum reported in the analyses of the residues, R_1 and R_2 (Table 4).

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 the Argonne National Laboratory, Dr. H. R. 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 furnished by Professor Frondel of Harvard University, 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 the Baringer Hill specimen of thorogummite. In general, the absorption band in the OH region was not as 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

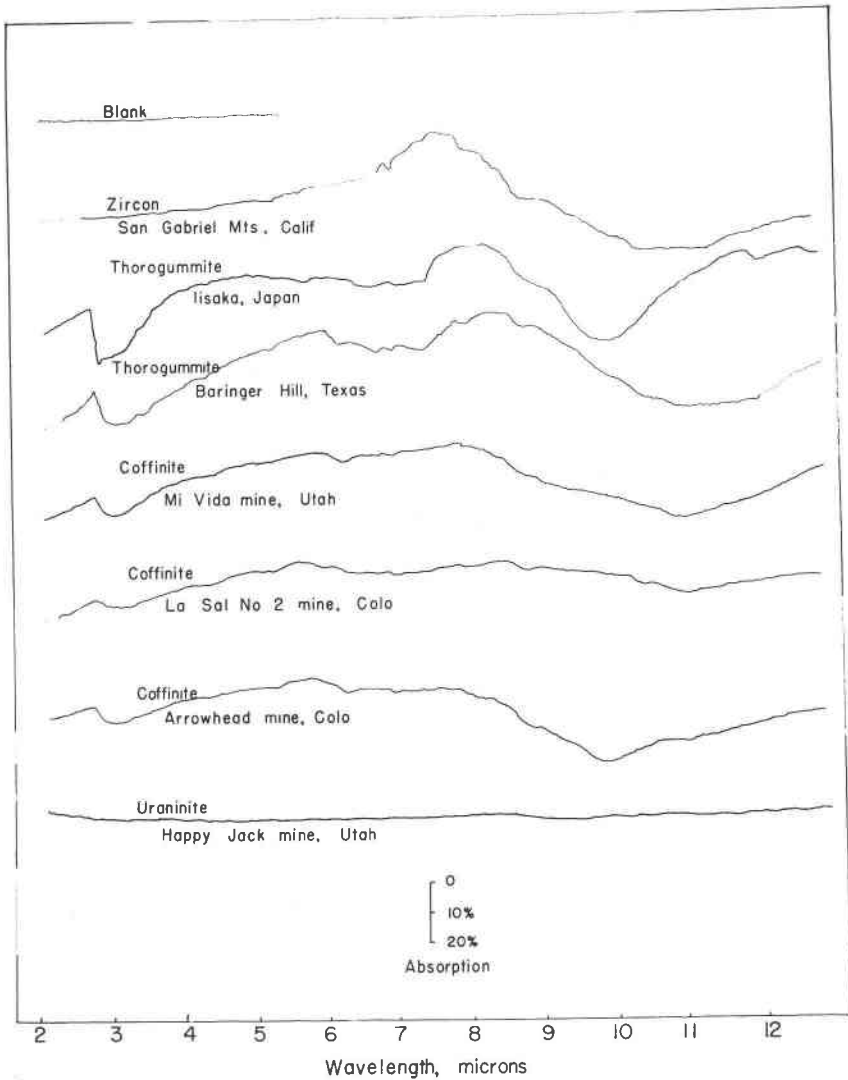


FIG. 1 Infrared absorption spectra of zircon, thorogummite, coffinite, and uraninite.

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 20 to 75 per cent of the total silica in the coffinite-bearing speci-

men. Amorphous sexivalent uranium is not present, and the uranium is in the quadrivalent state. Coffinite has a distinctive x -ray diffraction powder pattern of the zircon-type with $a_0=6.94 \text{ \AA}$ and $c_0=6.31 \text{ \AA}$. The close similarity of the infrared absorption spectra of thorogummite, $\text{Th}(\text{SiO}_4)_{1-x}(\text{OH})_{4x}$, 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 $\text{U}(\text{SiO}_4)_{1-x}(\text{OH})_{4x}$.

ADDENDUM

Since the preparation of this manuscript H. R. Hoekstra and L. H. Fuchs of the Argonne National Laboratory have synthesized coffinite using uranous chloride and sodium silicate. The oven-dried product gave an x -ray diffraction powder pattern which matched patterns of natural coffinite. The infrared absorption spectra showed the presence of bonded OH groups. A report of this work is published in *Science*, **123**, 105 (1956).

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