

SIMPLOTITE, A NEW QUADRIVALENT VANADIUM  
MINERAL FROM THE COLORADO PLATEAU\*M. E. THOMPSON, C. H. ROACH, AND ROBERT MEYROWITZ *U. S. Geological Survey, Washington 25, D. C.*

## ABSTRACT

Simplotite,  $\text{CaV}_4\text{O}_9 \cdot 5\text{H}_2\text{O}$ , is a new calcium tetravanadate that has been found in five vanadium-uranium mines on the Colorado Plateau. It occurs as dark-green micaceous plates and as hemispherical aggregates of plates, coating fracture surfaces in sandstone impregnated by relatively unoxidized vanadium and uranium minerals. Simplotite represents an early stage in the oxidation sequence of the vanadium ore. It is associated with duttonite, melanovanadite, abundant crystals of hexagonal native selenium, and an undescribed vanadium oxide.

Simplotite is biaxial negative,  $2V$  about  $25^\circ$ , dispersion  $r > v$ , weak and crossed,  $\alpha = 1.705 \pm 0.002$ ,  $\beta = 1.767 \pm 0.002$ ,  $\gamma = 1.769 \pm 0.002$ .  $X = b$  yellow,  $Y$  green,  $Z \wedge c \sim -58^\circ$  green. The measured specific gravity is  $2.64 \pm 0.002$ .

A chemical analysis of material from the Peanut mine showed, in per cent:  $\text{CaO}$ , 11.6;  $\text{V}_2\text{O}_5$ , 67.7;  $\text{V}_2\text{O}_6$ , 0.5;  $\text{H}_2\text{O}$ , 18.4; insoluble, 0.5; total, 98.7.

Simplotite is monoclinic, pseudotetragonal; the space group is  $A2/m(C_{2h}^3)$ ,  $Am(C_s^3)$  or  $A2(C_2^3)$ ;  $a = 8.39 \pm 0.03$  A,  $b = 17.02 \pm 0.05$  A,  $c = 8.37 \pm 0.03$  A,  $\beta = 90^\circ 25' \pm 5'$ ;  $a:b:c = 0.4929:1:0.4918$ ; cell contents  $4[\text{CaV}_4\text{O}_9 \cdot 5\text{H}_2\text{O}]$ ; calculated specific gravity 2.65.

The new mineral is named for J. R. Simplot of the J. R. Simplot Mining Company of Boise, Idaho, former owner of the Peanut mine.

## INTRODUCTION AND ACKNOWLEDGMENTS

Simplotite was first recognized in a sample from the Sundown Claim, San Miguel County, Colo. The sample was submitted by L. B. Riley to A. D. Weeks (both of the U. S. Geological Survey) for identification in 1952. The mineral was recognized to be new, but there was only enough for determination of optical properties, x-ray powder patterns, and qualitative spectrographic analysis.

Early in 1954, simplotite was found in the Peanut mine, Montrose County, Colo., by C. H. Roach, who was making an intensive study of the mineralogy, geology, and geochemistry of the deposit. This study included detailed sampling of the ore and made possible the collection of enough material for determination of the physical properties and chemical composition of the new mineral. A preliminary description of simplotite was published in *Science* (Thompson, Roach, and Meyrowitz, 1956a).

Simplotite has since been found in three other mines: the Shattuck-Denn lease on Club Mesa, Montrose County, Colo., by C. A. Rasor of the U. S. Atomic Energy Commission; the J. J. mine in Paradox Valley, Montrose County, Colo., by D. P. Elston of the U. S. Geological Survey;

\* Publication authorized by the Director, U. S. Geological Survey.

and the Vanadium Queen mine at La Sal Creek, San Juan County, Utah, by W. D. Carter of the U. S. Geological Survey.

The study of the mineralogy of these samples was made as a part of the U. S. Geological Survey's program on behalf of the Division of Raw Materials of the U. S. Atomic Energy Commission.

Simplotite is named for J. R. Simplot of the J. R. Simplot Mining Company of Boise, Idaho, former owner of the Peanut mine. Mr. Simplot graciously permitted the detailed mine study which resulted in the finding of enough of the mineral for this description.

#### OCCURRENCE

The five mines in which simplotite has been found are all in vanadium-uranium ore deposits in the Salt Wash sandstone member of the Morrison formation of Late Jurassic age. The locations of these mines are shown on the index map, Fig. 1.

The most detailed study of the occurrence of simplotite was made at

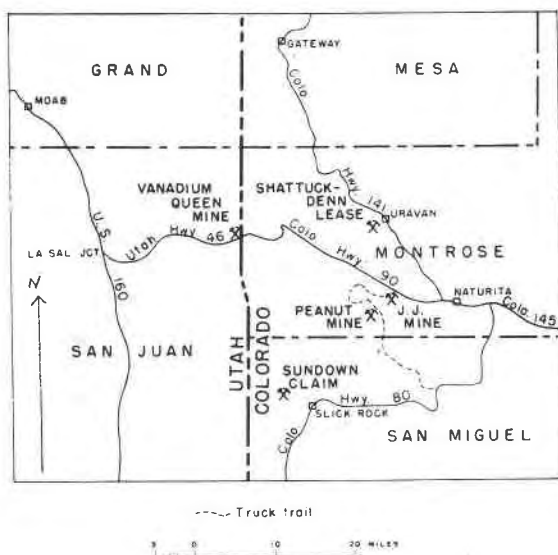


FIG. 1: Index map of parts of Colorado and Utah showing the localities of simplotite.

the Peanut mine (C. H. Roach and M. E. Thompson, written communication, 1955), which is very near the axis of the Dry Creek Basin syncline between the Paradox Valley and Gypsum Valley salt anticlines (Carter, 1954). The vanadium-uranium ore bodies occur in the upper ore-bearing sandstone of the Salt Wash member. Ore bodies are localized along the flanks of a buried channel by crossbedding structures known as festoon

cross-lamination (Knight, 1930). The main festoon surfaces are relatively impermeable and have caused the formation of perched water tables. Water saturates most of the ore bodies and oxidation of the ore minerals is related to a slowly falling water level.

Simplotite in samples from all five mines occurs as micaceous plates and as hemispherical aggregates of radiating books of platy crystals. It coats fracture surfaces in vanadium-uranium ore-bearing sandstone. The primary ore minerals impregnating the sandstone and replacing coalified wood in the sandstone are montroseite, vanadiferous silicates, uraninite, and coffinite. Montroseite,  $\text{VO}(\text{OH})$ , oxidizes readily to paramontroseite,  $\text{VO}_2$  (Evans and Mrose, 1955). Studies of polished sections of samples of fractured ore-bearing sandstone from the Peanut mine show that paramontroseite near the fracture surfaces grades into a thin massive coating of an undescribed vanadium oxide on which crystals of simplotite, duttonite— $\text{VO}(\text{OH})_2$ —(Thompson, Roach, and Meyrowitz, 1956b), melanovanadite, and hexagonal native selenium formed later.

The original sample of simplotite from the Sundown Claim has recently been re-examined by A. D. Weeks, who reports that the simplotite occurs coating a joint surface of dark sandstone ore with duttonite and native selenium. This marks a second occurrence of duttonite which has previously been recognized only from the Peanut mine.

#### PHYSICAL AND OPTICAL PROPERTIES

Simplotite is monoclinic, pseudotetragonal. It has a platy habit and a micaceous cleavage on  $\{010\}$ . Aggregates of simplotite are black or greenish black, but thin flakes of the mineral are yellow green. The color of the powdered mineral is brownish black. In color and habit simplotite is very much like sincosite,  $\text{CaV}_2\text{P}_2\text{O}_{10} \cdot 5\text{H}_2\text{O}$ , which is structurally related to simplotite.

Simplotite has a vitreous luster. The hardness is about 1, probably because of the very easy cleavage. The specific gravity, measured by immersing a few grains in a mixture of bromoform and acetone, is  $2.64 \pm 0.02$ .

In immersion simplotite appears as nearly square plates on  $\{010\}$ , commonly with two opposite corners (101) truncated at about  $45^\circ$ . It is biaxial negative,  $2V$  about  $25^\circ$ , dispersion  $r > v$ , weak and crossed. The optical orientation, pleochroism, and indices of refraction are as follows:

Orientation	Pleochroism	Indices of refraction
X=b	yellow	$\alpha$ 1.705 $\pm$ 0.002
Y	green	$\beta$ 1.767 $\pm$ 0.002
Z $\wedge$ c $\sim$ $-58^\circ$	green	$\gamma$ 1.769 $\pm$ 0.002

Mrs. Weeks' recent re-examination of the original sample of simplotite

(from the Sundown Claim, 1952) indicates that the mineral apparently dehydrates slowly in a dry atmosphere. The optical properties of the Sundown material, measured in 1952, gave data close to that obtained from the more recently collected material, but in June 1956 the Sundown sample had somewhat higher indices:  $\alpha$  (calculated from  $\beta$ ,  $\gamma$ , and  $2V$ ) is  $1.730 \pm 0.005$ ,  $\beta$   $1.781 \pm 0.003$ ,  $\gamma$   $1.807 \pm 0.003$ , and  $2V$  measured on a universal stage is  $40^\circ$ .

#### CHEMICAL ANALYSIS

About 150 mg. of simplotite was handpicked from samples collected from the Peanut mine for the chemical analysis. A semiquantitative spectrographic analysis of this material was made by C. S. Annell of the U. S. Geological Survey and showed that Si was the only impurity present in amount over 0.1 per cent. The complete analysis is given in Table 1.

The chemical analysis was made by Robert Meyrowitz; the results, which yield the formula  $\text{CaV}_4\text{O}_9 \cdot 5\text{H}_2\text{O}$ , are shown in Table 2. The  $\text{H}_2\text{O}(-)$  content is equivalent to four of the five water molecules.

TABLE 1. SEMIQUANTITATIVE SPECTROGRAPHIC ANALYSIS OF SIMPLOTITE FROM THE PEANUT MINE  
C. S. Annell, analyst

Per cent	Elements
Over 10	V
5-10	—
1-5	Ca
0.5-1	—
0.1-0.5	Si
0.05-0.1	Al
0.01-0.05	Fe Mg
0.005-0.01	Sr Ti
0.001-0.005	Mo Cr Ba Sc

A sample weighting 36 mg. was used for the determinations of  $\text{H}_2\text{O}(-)$ , silica plus insoluble, CaO, and total vanadium. The sample was dried to constant weight at  $110^\circ \pm 5^\circ \text{C.}$ , and silica and insoluble were separated by dehydration in a nitric acid solution. The CaO was determined as the sulfate after separation as the oxalate from the filtrate resulting from the separation of the silica and insoluble. Total vanadium was determined spectrophotometrically using the hydrogen peroxide procedure on an aliquot of the filtrate from the CaO determination after the oxalate had been destroyed by boiling with nitric acid.

The  $\text{V}_2\text{O}_4$  was determined by dissolving 15 mg. of the mineral in (1+3)

TABLE 2. CHEMICAL ANALYSIS OF SIMPLOTITE FROM THE PEANUT MINE

Robert Meyrowitz, analyst

	Analysis of simplotite	Analysis recalculated to 100 per cent <sup>1</sup>	CaV <sub>4</sub> O <sub>3</sub> · 5H <sub>2</sub> O
CaO	11.6	11.8	11.7
V <sub>2</sub> O <sub>4</sub>	67.7	69.0	69.5
V <sub>2</sub> O <sub>5</sub>	0.5	0.5	—
SiO <sub>2</sub> plus insoluble	0.5	—	—
H <sub>2</sub> O(+)	3.9	4.0	3.8
H <sub>2</sub> O(-)	14.5	14.7	15.0
Total	98.7	100.0	100.0

<sup>1</sup> After subtraction of SiO<sub>2</sub> plus insoluble.

sulfuric acid and titrating with approximately 0.03*N* standard potassium permanganate, and V<sub>2</sub>O<sub>5</sub> was calculated by difference.

Total water was determined in a sample weighting 17 mg. by use of a modified microcombustion train of the type used for the determination of carbon and hydrogen in organic compounds. The sample was decomposed by ignition at 900° C. in a stream of oxygen.

#### X-RAY DATA

Because of its very easy micaceous cleavage and relatively large unit cell, simplotite does not give very good *x*-ray diffraction patterns. The powder pattern whose *d*-spacings are given in Table 3 was prepared by M. E. Mrose of the U. S. Geological Survey, using a Debye-Scherrer camera of radius 114.59 mm. and nickel-filtered copper radiation. To make a spindle that would produce a powder pattern with this many lines it was necessary to crush the mineral very gently, to make the spindle as dense as possible, and to increase the *x*-ray exposure to about 20 hours.

The intensities given for the diffraction lines in Table 3 were measured by direct comparison with a set of carefully calibrated intensities registered on a strip of film. Such a scale is linear in total *x*-ray energy and not logarithmic as is commonly used. Intensities estimated in terms of apparent density of diffraction lines exaggerate the weaker reflections and would give the three strongest lines as follows:

<i>d</i> (Å)	<i>I</i> (density)
8.51	10
3.14	6
2.62	8

TABLE 3. X-RAY DIFFRACTION DATA AND UNIT-CELL CONSTANTS OF SIMPLOTITE

Indexed on monoclinic unit cell: probable space group,  $A2/m$ ;  $a=8.39\pm 0.03$  Å,  $b=17.02\pm 0.05$  Å,  $c=8.37\pm 0.03$  Å,  $\beta=90^\circ 25' \pm 5'$ .  $\text{CuK}\alpha$  radiation,  $\lambda=1.5418$  Å; camera diameter 114.6 mm;  $d(\text{obs.})$  cutoff 14.0 Å.

$hkl$	$d(\text{calc.})$ Å	$d(\text{obs.})$ Å	I	$hkl$	$d(\text{calc.})$ Å	$d(\text{obs.})$ Å	I
020	8.51	8.51	100	260	2.35	2.35	3
011	7.51			062	2.35		
120	5.98			340	2.34		
11 $\bar{1}$	5.61			071	2.33		
111	5.58			302	2.33		
031	4.70	4.71	3	302	2.32		
040	4.26	4.26	9	21 $\bar{3}$	2.31		
200	4.19			213	2.29		
002	4.19			162	2.26	2.26	3
13 $\bar{1}$	4.11			162	2.26		
131	4.09	4.10	3	17 $\bar{1}$	2.25		
140	3.80			171	2.25		
10 $\bar{2}$	3.76			322	2.25		
220	3.76			322	2.24	2.23	1
022	3.76			053	2.16	2.15	1
102	3.73			23 $\bar{3}$	2.16		
21 $\bar{1}$	3.67			233	2.14		
211	3.65			080	2.13		
12 $\bar{2}$	3.44			35 $\bar{1}$	2.10	2.10	2
122	3.42	3.42	6	400	2.10		
051	3.15	3.14	18	004	2.09		
23 $\bar{1}$	3.13			351	2.09		
231	3.12			15 $\bar{3}$	2.09		
240	2.99			153	2.09		
042	2.98			180	2.06		
20 $\bar{2}$	2.97			262	2.05	2.05	2
15 $\bar{1}$	2.95			262	2.05		
151	2.95	2.96	3	420	2.04		
202	2.95			27 $\bar{1}$	2.04		
060	2.84	2.84	9	024	2.03		
14 $\bar{2}$	2.82			41 $\bar{1}$	2.02		
142	2.81			411	2.02		
22 $\bar{2}$	2.81					1.998	1
222	2.79					1.882	5
013	2.75					1.866	5
160	2.69						
320	2.66					1.832	3
31 $\bar{1}$	2.63						
311	2.62	2.62	25			1.696	1
11 $\bar{3}$	2.62						
113	2.61					1.617	1
251	2.52	2.52	5			1.606	1
25 $\bar{1}$	2.52					1.567	1
033	2.50					1.548	1
24 $\bar{2}$	2.44					1.503	1
242	2.43					1.439	1
33 $\bar{1}$	2.41					1.342	2
331	2.40					1.324	2
13 $\bar{3}$	2.40					1.308	2
133	2.40					1.176	2

The powder pattern was indexed using the unit-cell constants measured by H. T. Evans, Jr., and M. E. Mrose from single crystal  $x$ -ray precession photographs as follows:

Monoclinic, space group  $A2/m(C_2^3h)$ ,  $Am(C_2^3)$  or  $A2(C_2^3)$

$a = 8.39 \pm 0.03 \text{ \AA}$

$b = 17.02 \pm 0.05$

$\beta = 90^\circ 25' \pm 5'$

$c = 8.37 \pm 0.03$

$a:b:c = 0.4929:1:0.4918$

Cell contents:  $4[\text{CaV}_4\text{O}_9 \cdot 5\text{H}_2\text{O}]$

Specific gravity: calc., 2.65; meas.,  $2.64 \pm 0.02$

The pseudotetragonal nature of simplotite is shown clearly by the selected area electron diffraction spot pattern (Fig. 2) taken by Malcolm

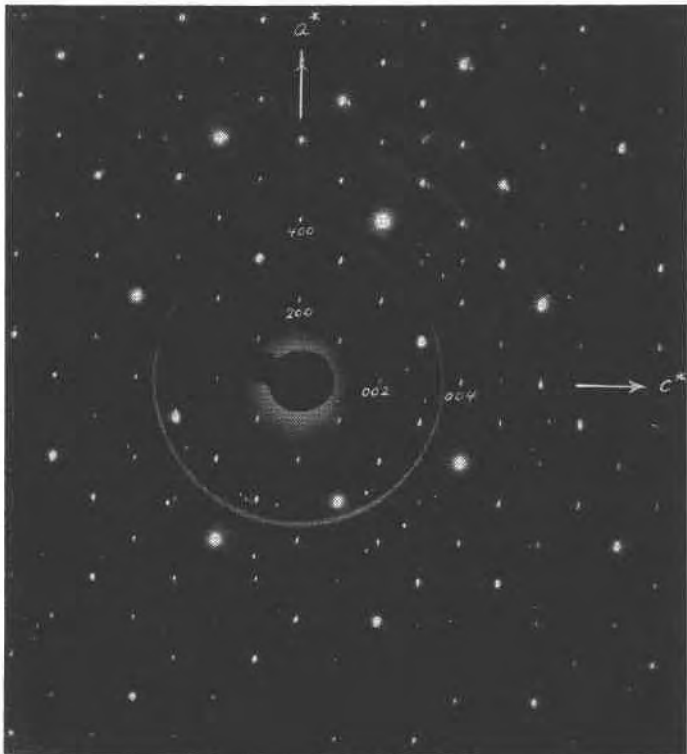


FIG. 2. Electron diffraction spot pattern of simplotite representing the  $a^*-c^*$  reciprocal net plane superimposed on an aluminum ring pattern.

Ross of the U. S. Geological Survey. The photograph shows the  $a^*-c^*$  reciprocal net and the included  $\beta$  angle. The mount was lightly shadowed with aluminum to provide an internal standard for purposes of measure-

ment; the aluminum produced the superimposed ring pattern. Measurements of electron diffraction patterns of simplotite give cell constants in good agreement with those determined by x-rays.

To correlate the optical, morphological, and x-ray orientations, one crystal was mounted on a goniometer head and studied with the two circle goniometer, polarizing microscope, and Buerger precession camera. The results are shown in Fig. 3. The habit of the crystal is square, with

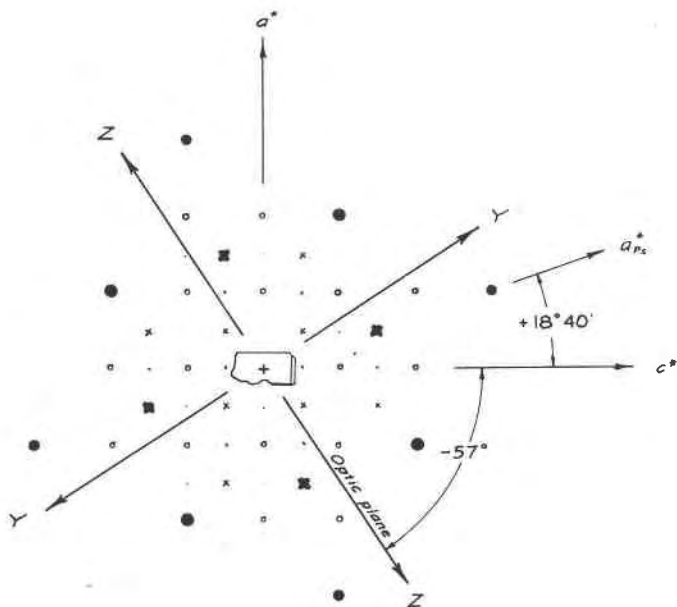


FIG. 3. Schematic drawing showing relation between the reciprocal lattice, optical orientation, and habit of simplotite. Circles represent reciprocal lattice points with  $k=0$ , crosses those with  $k=1$ . (See Fig. 2.) Sketch shows approximate appearance of the crystal on which correlative measurements were made (longest dimension 1 mm.).

edges parallel to  $[100]$  and  $[001]$  and beveled by an undetermined prism form. Opposite corners are truncated by  $(101)$  in some crystals. In both the electron diffraction and x-ray precession photographs of the net normal to  $[010]$  the reflections for which  $k=0$  and  $k=1$  are not easily distinguished. In Fig. 3, the  $k=0$  reflections are indicated by circles, the  $k=1$  reflections by crosses. The patterns show, in the intensity distribution, a pronounced pseudotetragonal cell of small size inclined to the monoclinic axes. The pseudo-cell is body centered with  $a_{ps}=2.6\text{\AA}$  and  $c_{ps}=17\text{\AA}=b_m$ . The pseudotetragonal  $a$ -axis is inclined at  $+18^\circ40'$  to the monoclinic  $c$ -axis. The  $\beta$  angle and the  $a$  and  $c$  axial lengths are diffi-



cult to measure accurately because of the poor quality of the crystals. The best key to the absolute orientation of the simplotite lattice, therefore, is through the relation between the pseudotetragonal lattice and the optic directions to the true monoclinic lattice.

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*Manuscript received May 20, 1957.*