

## DUTTONITE, A NEW QUADRIVALENT VANADIUM OXIDE FROM THE PEANUT MINE, MONTROSE COUNTY, COLORADO\*

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### ABSTRACT

Duttonite, a new quadrivalent vanadium oxide from the Peanut mine, Montrose County, Colo., has the formula  $\text{VO}(\text{OH})_2$ . The mineral occurs as crusts and coatings of pale-brown transparent platy crystals, as one of the first oxidation products of montroseite ore. It is associated with melanovanadite and abundant crystals of hexagonal native selenium. Duttonite is biaxial positive,  $2V$  is about  $60^\circ$ , dispersion is  $r < v$ , moderate;  $X = a$ , pale pinkish brown;  $Y = c$ , pale yellow-brown;  $Z = b$ , pale brown;  $\alpha = 1.810 \pm 0.003$ ,  $\beta = 1.900 \pm 0.003$ ,  $\gamma > 2.01$ . The hardness is about  $2\frac{1}{2}$ ; the calculated specific gravity is 3.24.

The chemical analysis shows, in per cent:  $\text{V}_2\text{O}_3$  2.6,  $\text{V}_2\text{O}_4$  75.3,  $\text{FeO}$  0.4,  $\text{H}_2\text{O}$  18.1, insoluble 4.2, total 100.6.

Duttonite is monoclinic,  $a_0 = 8.80 \pm 0.02 \text{ \AA}$ ,  $b_0 = 3.95 \pm 0.01 \text{ \AA}$ ,  $c_0 = 5.96 \pm 0.02 \text{ \AA}$ ,  $\beta = 90^\circ 40' \pm 5'$ . The space group is  $I2/c$ , ( $C_{2h}^6$ ); the cell contents are  $4[\text{VO}(\text{OH})_2]$ . The crystals are strongly pseudo-orthorhombic, and the structure departs only slightly from the space group  $Ibcm$ .

Duttonite is named for Captain Clarence Edward Dutton (1841-1912), early member of the U. S. Geological Survey.

### INTRODUCTION AND ACKNOWLEDGMENTS

A detailed study of the geology, geochemistry, and mineralogy of the vanadium-uranium ore at the Peanut mine, Montrose County, Colo., was begun early in 1954 by Carl H. Roach of the U. S. Geological Survey. A number of rare and new minerals were found in the ore and the study of these samples was undertaken by Mary E. Thompson. Duttonite is the first new vanadium mineral to be described from the Peanut mine. It is named for Captain Clarence Edward Dutton (1841-1912), who was one of the first geologists to work in the Colorado Plateau region and who was a member of the U. S. Geological Survey 1879-91.

We are indebted to the following members of the U. S. Geological Survey: K. V. Hazel for spectrographic analyses of duttonite, and M. E. Mrose and H. T. Evans, Jr., for measurement of the unit-cell constants. This work is part of a program being conducted by the U. S. Geological Survey on behalf of the Division of Raw Materials of the U. S. Atomic Energy Commission.

### OCCURRENCE

Duttonite has been found at the Peanut mine, in the Bull Canyon mining district, Montrose County, Colo. The Peanut mine is about 15 miles

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west of Naturita, Colo., in section 32, T. 46 N., R. 17 W. (Fig. 1). It is situated along the axis of the Dry Creek Basin syncline, which lies between the Paradox Valley and Gypsum Valley salt anticlines (Cater, 1954).

The vanadium-uranium ore at the Peanut mine occurs in the upper ore-bearing sandstone of the Salt Wash sandstone member of the Morri-

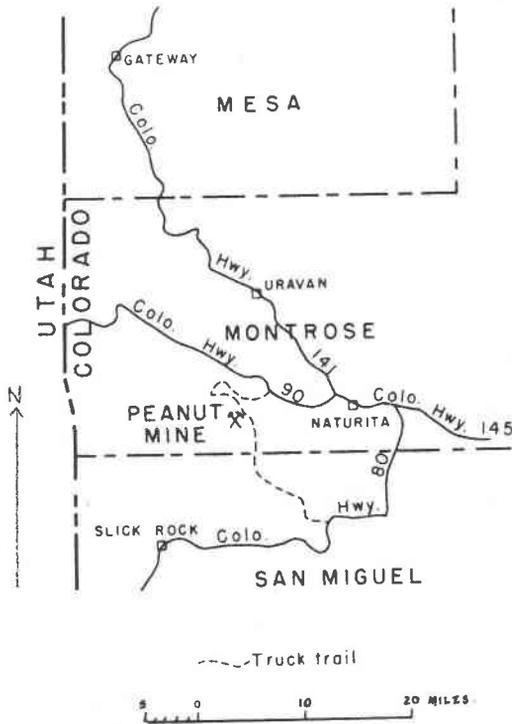


FIG. 1. Index map of the locality of duttonite—the Peanut Mine, Montrose County, Colorado.

son formation of Late Jurassic age. Ore bodies occur along the flanks of a buried channel and are localized by cross-bedding structures associated with the channel. The cross-bedding structures are called festoon cross lamination (Knight, 1930). The major festoon surfaces are relatively impermeable, and some have caused the formation of perched water tables. Most of the ore bodies are saturated with water which has prevented much oxidation of the ore minerals although the regional water table is several hundred feet below the ore horizon.

The principal ore minerals are montroseite, paramontroseite (Evans

and Mrose, 1955), vaniferous silicates, uraninite, and coffinite. The primary ore minerals impregnate sandstone and replace coalified wood. Along fractures in the ore-bearing sandstone there is commonly a thin massive coating of an undescribed vanadium oxide which partially re-ements the fractures.

On this coating duttonite occurs as crusts of randomly oriented six-sided platy crystals which range in size from extremely minute to about 0.5 mm. for the longest dimension. Associated minerals are melanovanadite, abundant crystals of native selenium (Thompson *et al.*, 1956*a*), simplotite (Thompson *et al.*, 1956*b*), and other undescribed vanadium minerals.

Duttonite has also been found in association with native selenium and simplotite at the Sundown claim, Slick Rock mining district, San Miguel County, Colorado (A. D. Weeks, written communication, 1956).

#### PHYSICAL AND OPTICAL PROPERTIES

Duttonite occurs as six-sided platy monoclinic crystals. The morphological elements (from *x*-ray measurements) are as follows:

Crystal class: monoclinic prismatic,  $2/m$

$a:b:c=2.228:1:1.509$ ,  $\beta=90^{\circ}40'$

$p_0'=0.677$ ,  $q_0'=1.509$ ,  $x_0'=0.012$

Forms:  $c\{001\}$ ,  $a\{100\}$ ,  $m\{110\}$

The crystals are flattened parallel to  $c\{001\}$ , and are strongly pseudo-orthorhombic in aspect (Fig. 2). In fact, the only positive evidence for

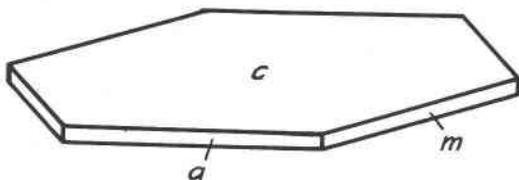


FIG. 2. Typical crystal habit of duttonite.

the monoclinic symmetry is provided by the *x*-ray powder data. A pronounced cleavage is present parallel to (100). The hardness is about  $2\frac{1}{2}$ . The specific gravity was not measured directly, but the mineral sinks in bromoform of specific gravity 2.9 and floats on methylene iodide of specific gravity 3.3. The specific gravity calculated from the *x*-ray data is 3.24.

The optical properties of duttonite are consistent with the pseudo-orthorhombic symmetry. It is biaxial positive,  $2V$  about  $60^{\circ}$ , dispersion

$r < v$ , moderate. The indices of refraction, pleochroism, and optical orientation are summarized as follows:

Orientation	$n$	Pleochroism
X = $a$	$\alpha = 1.810 \pm 0.003$	pale pinkish brown
Y = $c$	$\beta = 1.900 \pm 0.003$	pale yellow-brown
Z = $b$	$\gamma > 2.01$	pale brown

#### CHEMICAL ANALYSIS

Duttonite occurs as aggregates of tiny platy crystals, altering from another undescribed vanadium oxide and intermixed with tiny crystals of hexagonal native selenium. The sample used for chemical analysis was prepared by hand-picking a number of aggregates of crystals and crushing each aggregate between glass slides. The crushed material was examined with a binocular microscope. The other vanadium oxide appeared as formless opaque blobs; the tiny acicular selenium crystals were not easily seen. Only the purest of the aggregates were saved, and by this means about 25 mg. was accumulated for the analysis.

A microqualitative spectrographic analysis by K. V. Hazel showed over 10 per cent V, 0.1 to 0.5 per cent Fe, and 0.05 to 0.1 per cent Si, Al, and Ca. The blue-green color of a solution of the mineral in concentrated HCl and the structure determination by Evans and Mrose indicate that the mineral is an oxide of  $V^{4+}$ .

The selection of the procedures used for the chemical analysis was based upon the qualitative spectrographic analysis.  $V_2O_3$  and  $V_2O_4$  were calculated using the values obtained for the following determinations: (1) total reducing ability of the mineral, (2) total vanadium, and (3) FeO.

The total reducing ability was determined by decomposing the mineral in boiling (1+3) sulfuric acid and titrating with approximately 0.03  $N$  standard potassium permanganate. The Fe content was determined spec-

TABLE 1. CHEMICAL ANALYSIS OF DUTTONITE, IN PER CENT  
(Robert Meyrowitz, analyst)

	Analysis of duttonite	Analysis, less insoluble, recalculated to 100 per cent	VO(OH) <sub>2</sub>
V <sub>2</sub> O <sub>3</sub>	2.6	2.7	
V <sub>2</sub> O <sub>4</sub>	75.3	78.1	82.2
FeO	0.4	0.4	
H <sub>2</sub> O	18.1	18.8	17.8
Insoluble	4.2		
Total	100.6	100.0	100.0

TABLE 2. POWDER-DIFFRACTION DATA FOR DUTTONITE

CuK $\alpha$  radiation, 114.6-mm diameter camera.  $d$  (calculated) listed for monoclinic unit cell:  $a_0=8.80$  Å,  $b_0=3.95$  Å,  $c_0=5.96$  Å,  $\beta=90^\circ40'$ ; space group  $I2/c$ .

$hkl$	$d$ (calc.)	$d$ (obs.)	$I$	$hkl$	$d$ (calc.)	$d$ (obs.)	$I$
200	4.40	4.40	100	004	1.491	1.491	4
110	3.60	3.61	85	420	1.470		
011	3.29	3.29	13	600	1.467	1.468	6
002	2.98	2.98	6	$\bar{5}12$	1.422	1.423	2
$\bar{2}11$	2.65	2.64	13	$\bar{2}04$	1.417		
211	2.63			512	1.409		
$\bar{2}02$	2.482	2.480	15	204	1.407	1.407	2
202	2.455	2.454	15	$\bar{4}13$	1.389		
310	2.361			$\bar{1}14$	1.380	1.380	3
$\bar{1}12$	2.303			114	1.375		
112	2.292			413	1.375		
400	2.201	2.202	7	$\bar{6}11$	1.343		
020	1.975	1.974	14	611	1.337		
$\bar{3}12$	1.857	1.860	5	$\bar{6}02$	1.322		
312	1.840			$\bar{4}22$	1.322	1.324	3
$\bar{1}21$	1.835			422	1.314	1.314	2
$\bar{4}11$	1.835	1.838	21	602	1.310	1.309	1
121	1.832			130	1.302		
411	1.824			031	1.286	1.285	3
220	1.802	1.801	3	$\bar{5}21$	1.286		
$\bar{4}02$	1.780	1.779	7	521	1.281		
013	1.776			$\bar{3}14$	1.265		
402	1.761	1.759	6	314	1.254	1.258	1
$\bar{2}13$	1.653	1.656	2	$\bar{4}04$	1.237		
022	1.647			$\bar{2}31$	1.235	1.235	3
213	1.641	1.639	2	231	1.233		
510	1.610	1.611	3	404	1.228	1.229	1
$\bar{3}21$	1.578	1.580	6	710	1.199	1.199	3
321	1.573			$\bar{1}32$	1.194		
$\bar{2}22$	1.545	1.542	3	132	1.193		
222	1.539			620	1.178	1.179	2

trophotometrically by the *o*-phenanthroline procedure and calculated as FeO. A 5-cm absorption cell was used. The total vanadium was determined spectrophotometrically by the hydrogen peroxide procedure using a separate sample which was dissolved by boiling with (1+1) nitric acid. Orthophosphoric acid was used to mask the iron.

The insoluble material was determined by boiling the sample with (1+3) sulfuric acid in a weighed Schwarz-Bergkampff microfilter beaker. The residue was filtered and washed with water and dried to constant weight at  $110^\circ \pm 5^\circ$  C. These weighings were made with a microbalance.

An  $x$ -ray powder pattern of the insoluble material by George Ashby of the U. S. Geological Survey showed it to consist of hexagonal selenium and quartz.

Water was determined 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  $900^{\circ}$  C. in a stream of oxygen.

The results of the chemical analysis are shown in Table 1. The percentages, when recalculated to 100 per cent after eliminating the insoluble fraction, agree well with the theoretical values for  $V_2O_4 \cdot 2H_2O$ . This result is in agreement with the composition which has been predicted for Duttonite by Evans and Mrose on the basis of a crystal structure study now in preparation.

#### X-RAY DATA

An  $x$ -ray diffraction powder pattern of duttonite was taken with a Debye-Scherrer camera (114.6-mm diameter) using  $CuK\alpha$  radiation. The measured powder data are listed in Table 2. M. E. Mrose has determined the unit cell of duttonite by the Buerger precession method as follows:  $a_0 = 8.80 \pm 0.02 \text{ \AA}$ ,  $b_0 = 3.95 \pm 0.01 \text{ \AA}$ ,  $c_0 = 5.96 \pm 0.02 \text{ \AA}$ ,  $\beta = 90^{\circ} \pm 1^{\circ}$ ; space group  $I2/c$  ( $C_{2h}^6$ ); unit-cell contents,  $4[VO(OH)_2]$ . Because of the poor quality of the crystals, the monoclinic angle could not be detected in the single-crystal study, and at first the orthorhombic space group  $Imcm$  was assigned to the mineral. H. T. Evans has shown, however, that the orthorhombic lattice accounts for the powder spacings only approximately, and that a good fit of calculated and observed spacings can be obtained only by assuming monoclinic symmetry with  $\beta = 90^{\circ}40' \pm 5'$ . His interpretation of the powder pattern is shown in Table 2. The crystal structure study of duttonite carried out by Evans and Mrose will be published at a later date.

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