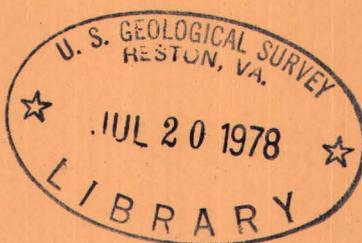# Duttonite, a new quadrivalent vanadium oxide from the Peanut mine, Montrose County, Colorado

By M. E. Thompson, C. H. Roach, and Robert Meyrowitz

Trace Elements Investigations Report 582

UNITED STATES DEPARTMENT OF THE INTERIOR
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PEANUT MINE, MONTROSE COUNTY, COLORADO*

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March 1956

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USGS - TEI-582

GEOLOGY AND MINERALOGY

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TEPCO, Denver	2
TEPCO, RPS, Washington, (including master)	2
	71

CONTENTS

ILLUSTRATIONS

TABLES

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

By

M. E. Thompson, Carl H. Roach, and Robert Meyrowitz

ABSTRACT

Duttonite, a new quadrivalent vanadium oxide from the Peanut mine, Montrose County, Colo., has the formula $VO(OH)_2$. 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°, 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 2.5; the calculated specific gravity is 3.24.

The chemical analysis shows, in percent: V_2O_3 2.6, V_2O_4 75.3, FeO 0.4, H_2O 18.1, insoluble 4.2, total 100.6.

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

Duttonite is named for Captain Clarence Edward Dutton (1841-1912).

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 from 1879-91.

We are indebted to the following members of the Geological Survey: K. E. Valentine 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 only at the Peanut mine, in the Bull Canyon mining district, Montrose County, Colo. The Peanut mine is about 15 miles west of Naturita, Colo., (fig. 1).

The Peanut mine is located 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 Morrison formation of Late Jurassic age. Ore bodies occur along the flanks of a buried channel
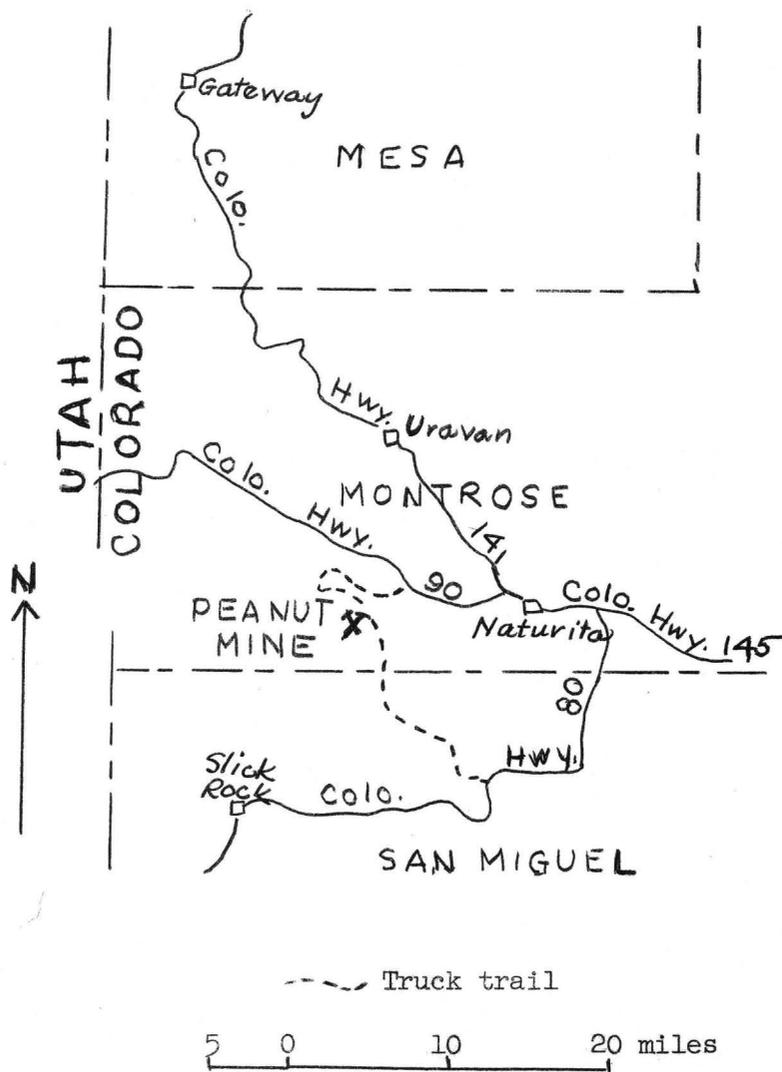
Figure 1.--Index map of the locality of duttonite, the Peanut mine, Montrose County, Colorado.

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 sat-
urated with water which has prevented much oxidation of the ore minerals al-
though the regional water table is several hundred feet below the ore horizon.

The principal ore minerals are montroseite, paramontroseite (Evans and
Mrose, 1955), vanadiferous 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 recements 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
on the longest dimension. Associated minerals are melanovanadite, abundant
crystals of native selenium (Thompson, Roach, and Braddock, in press), and
other undescribed vanadium minerals.

PHYSICAL AND OPTICAL PROPERTIES

Duttonite occurs as six-sided platy monoclinic crystals. The morpho-
logical elements (from X-ray measurements) are as follows:

Crystal class: monoclinic prismatic, $2/m$

$a:b:c = 2.228:1:1.509$, $\beta = 90°40'$

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

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
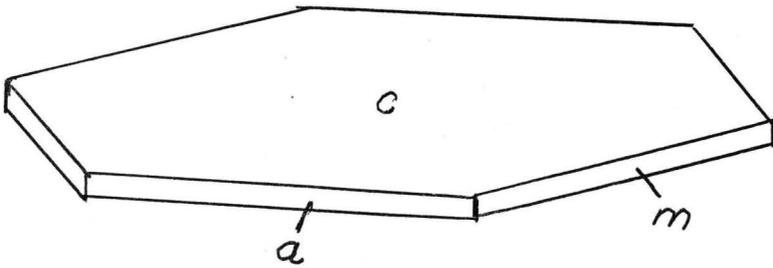the monoclinic symmetry is provided by the X-ray powder data. (See page 9.)

Figure 2.--Typical crystal habit of duttonite.

A pronounced cleavage is present parallel to (100). The hardness is about 2.5. 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°, 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. E. Valentine showed over 10 percent V, 0.1 to 0.5 percent Fe, and 0.05 to 0.1 percent 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 $\underline{N}$ standard potassium permanganate. The FeO content was determined spectrophotometrically 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-Bergkampf 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° C in a stream of oxygen.

The results of the chemical analysis are shown in table 1. The percentages, when recalculated to 100 percent after eliminating the insoluble fraction, agree well with the theoretical values for $V_2O_4 \cdot 2H_2O$. This result is

Table 1.--Chemical analysis of duttonite, in percent. (Robert Meyrowitz, analyst)

	Analysis of duttonite	Analysis, less insoluble, recalculated to 100 percent	$VO(OH)_2$
V_2O_3	2.6	2.7	
V_2O_4	75.3	78.1	82.2
FeO	0.4	0.4	
H_2O	18.1	18.8	17.8
Insoluble	4.2		
Total	100.6	100.0	100.0

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 CuKα 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: $a_0 = 8.80 \pm 0.02A$, $b_0 = 3.95 \pm 0.01A$, $c_0 = 5.96 \pm 0.02 A$, $\beta = 90° \pm 1$; 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 the pseudo-orthorhombic space group Imcm was at first 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 $\beta = 90°40' \pm 5$. 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.

Table 2.--Powder diffraction data for duttonite, CuKα radiation, 114.6-mm diameter camera. d (calculated) listed for monoclinic unit cell: $a_o = 8.80$ A, $b_o = 3.95$ A, $\bar{c}_o = 5.96$ A, $\beta = 90°40'$; space group $I2/c$.

hkl	d (calc.)	d (obs.)	I	hkl	d (calc.)	d (obs.)	I
200	4.401	4.402	100	004	1.491	1.491	4
110	3.604	3.609	85	420	1.470		
011	3.293	3.290	13	600	1.467	1.468	6
002	2.982	2.981	6	$\bar{5}12$	1.422	1.423	2
$\bar{2}11$	2.645	2.637	13	$\bar{2}04$	1.417		
211	2.629			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		
$\bar{3}10$	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		
$\bar{5}10$	1.610	1.611	3	404	1.228	1.229	1
$\bar{3}21$	1.578	1.580	6	$\bar{7}10$	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

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