THE AMERICAN MINERALOGIST

JOURNAL OF THE MINERALOGICAL SOCIETY OF AMERICA

Vol. 42 SEPTEMBER–OCTOBER, 1957 Nos. 9 and 10

DOLORESITE, A NEW VANADIUM OXIDE MINERAL FROM THE COLORADO PLATEAU*

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ABSTRACT

Doloresite, $H_8V_6O_{16}$ or $3V_2O_4 \cdot 4H_2O$, named for the Dolores River in southwestern Colorado, has been identified from 11 mines on the Colorado Plateau. Very fine fragments under oil immersion are reddish brown to yellow red in transmitted light with a mean index of refraction of about 1.90. The mineral has parallel extinction and exhibits weak absorption. In polished section doloresite is gray, variable in color along the elongation of the crystals, and shows selective absorption in plane polarized light. Under crossed nicols doloresite appears strongly anisotropic. Lamellar twinning, twin plane (100), is almost universal on a submicroscopic scale. The unit cell is monoclinic, space group $C2/m$ with $a = 19.64$ Å, $b = 2.99$ Å, $c = 4.83$ Å, $\beta = 103°55'$, and one formula per cell. The measured specific gravity is 3.27 to 3.33, and calculated specific gravity is 3.41.

OCCURRENCE

Doloresite, $3V_2O_4 \cdot 4H_2O$, named for the Dolores River, a major stream of the Colorado Plateau, was first collected by L. B. Riley, L. R. Stieff, and T. W. Stern in 1951 at the La Sal No. 2 mine at the head of Lumsden Canyon about 3½ air miles southwest of Gateway, Mesa County, Colo. At the La Sal No. 2 mine, doloresite occurs intimately associated with coffinite, $U(SiO_4)_{1-x}(OH)_{4x}$ (Stieff, Stern, and Sherwood, 1956), and carbonaceous matter. In this mine these minerals have formed several black concretionary masses about 1 foot by 2½ feet in cross section. The core of these masses contains large amounts of uranium and vanadium. Doloresite is found in the central part of these masses. The sandstone immediately adjacent to this heavily mineralized area contains small amounts of tyuyamunite.

Additional specimens have been collected by A. D. Weeks, M. E. Thompson, R. G. Coleman, T. W. Stern, and L. R. Stieff from the following mines: Corvusite, Matchless, Arrowhead, Black Mama, and Lumsden No. 2 in Mesa County, Colo.; Golden Cycle, J. J., and Peanut in Montrose County, Colo.; Mi Vida in San Juan County, Utah; and

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

Monument No. 2 in Apache County, Ariz. All of the Colorado mines listed above are in the Salt Wash sandstone member of the Morrison formation (Upper Jurassic). The Mi Vida mine is in the Chinle formation (Upper Triassic), and the Monument No. 2 mine is in the Shinarump member, the basal member of the Chinle formation. The mineral also occurs in sec. 33, T. 12 N., R. 9 E., Valencia County, N. Mex. in the Todilto limestone (Upper Jurassic). Doloresite is found in relatively unoxidized vanadium-uranium ores and is associated with coffinite, uraninite, clausthalite, montroseite, paramontroseite, and other vanadium oxides.

PHYSICAL AND CHEMICAL PROPERTIES

Doloresite is nearly black, with submetallic luster and greenish black streak. The material normally shows a dark bronzy tarnish. Many specimens of doloresite form radiating groups in bands or veinlets, locally penetrating mineralized wood. Exposed bands show botryoidal surfaces.

In polished section doloresite is gray, variable along the elongation of the crystals, and shows selective absorption in plane polarized light. Under crossed nicols doloresite appears strongly anisotropic. Paramontroseite is commonly present as remnant slivers scattered throughout the doloresite mass in varying amounts (Fig. 1). The mode of occurrence of the paramontroseite indicates that the doloresite has formed as a secondary replacement of a primary mass of montroseite.

Doloresite is fine grained and opaque except for very small fragments, which under an oil immersion objective are nonopqaue. The optical properties could not be determined in detail, but the mean index of refraction is about 1.90. The grains show a fibrous cleavage with parallel extinction and are reddish yellow in very thin flakes. No distinct interference figure could be observed, presumably because of the lamellar submicroscopic twinning that was observed in the *x*-ray study.

The specific gravity of two doloresite samples from La Sal No. 2 mine determined by means of the Berman balance, ranges from 3.27 to 3.33. The specific gravity of doloresite calculated from the unit cell and proposed chemical formula is 3.41.

Microchemical reactions of doloresite have been determined on small fragments. The mineral is slowly soluble in 1:1 HCl, yielding a green solution. A blue solution is produced by 1:1 HNO_3. No reaction is observed with 1:1 NH_4OH, but the mineral is slightly soluble in 40 per cent KOH. No reaction was observed with either 20 per cent KCN or 20 per cent $FeCl_2$.

It is apparent from the optical observations described above, and also the *x*-ray studies, that doloresite is almost always mixed with other vanadium oxide minerals. The most common impurity is montroseite or paramontroseite (Evans and Mrose, 1955) or both. *X*-ray powder patterns made on numerous samples always show admixed paramontroseite (montroseite transforms rapidly to paramontroseite in air) in proportions varying from predominant to subordinate. Other unidentified phases are also present in some samples. The chemical analysis, specific-gravity determinations, and optical characteristics must be interpreted with due allowance made for the prevalence of admixed impurities.

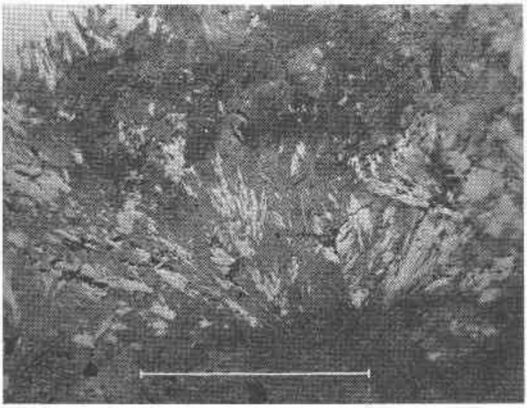

FIG. 1. Photomicrograph of polished section of specimen from the Mi Vida mine, San Juan County, Utah, showing doloresite (gray) replacing paramontroseite (white). Bar indicates 0.1 mm. Photograph courtesy of R. G. Coleman, U. S. Geological Survey.

Only one specimen has been found, obtained from Monument No. 2 mine in Apache County, Ariz., that contains a small seam of doloresite that is relatively pure. This material is in chocolate-brown, bladed masses showing satinlike cleavage surfaces. The metallic luster characteristic of the common impure doloresite is absent. The *x*-ray powder pattern shows only traces of the strong paramontroseite lines. Fragments of this material were used for single-crystal *x*-ray studies, but unfortunately there was insufficient material for any chemical tests.

Chemical analysis

Two samples of doloresite from La Sal No. 2 mine were analyzed quantitatively in the following manner. A part of the sample was dissolved in H_2SO_4 in a covered platinum crucible and titrated with $K_2Cr_2O_7$. In this treatment, V_2O_3 is oxidized to V_2O_4 and FeO to Fe_2O_3. A second part was dissolved in H_2SO_4 and titrated with $KMnO_4$. By this titration V_2O_3 and V_2O_4 are oxidized to V_2O_5 and FeO to Fe_2O_3. A third and fourth portion of the sample were used to determine total V and Fe separately. From these data, the proportions of V_2O_3, V_2O_4, and FeO were calculated. The analyses are given in table 1.

As explained above, these analyses must be interpreted as a mixture of doloresite with montroseite ($V_2O_3 \cdot H_2O$), paramontroseite (V_2O_4), and other impurities. The SiO_2, MgO, Al_2O_3, UO_3, As_2O_3, and Pb can be subtracted as mineral impurities extraneous to the vanadium oxides, but at least part of the FeO is probably present as a result of solid solution in the original montroseite (Weeks, Cisney, and Sherwood, 1953). Analysis no. 2 can be accounted for on a hypothetical basis in terms of 53 per cent doloresite, 44 per cent paramontroseite, and 3 per cent montroseite, assuming that the latter two minerals contain 10 mole per cent Fe replacing V.

TABLE 1.—CHEMICAL ANALYSES OF DOLORESITE
A. M. Sherwood, analyst

Constituent	1	2	3	4
V_2O_4	68.53	78.00	86.7	86.8
V_2O_3	10.30	1.89	2.1	2.2
FeO	3.53	3.83	4.2	4.0
SiO_2	2.04	.30		
MgO	1.12	3.98		
Al_2O_3	2.46	1.33		
UO_2	1.34			
		3.88		
UO_3	3.47			
As_2O_3	.73	.30		
H_2O-	.48	.37		
H_2O+	4.72	6.33	7.0	7.0
Pb	.08	.07		
Total	98.80	100.28	100.0	100.0

1. Sample 1 from La Sal No. 2 mine, Mesa County, Colo. Specific gravity 3.27.
2. Sample 2 from La Sal No. 2 mine. Specific gravity 3.33.
3. Analysis of column 2 with V_2O_4, V_2O_3, FeO, and H_2O recalculated to 100 per cent.
4. Theoretical composition for a mixture of 53 per cent doloresite ($3V_2O_4 \cdot 4H_2O$), 44 per cent paramontroseite (V_2O_4) and 3 per cent montroseite ($V_2O_3 \cdot H_2O$), with 10 mole per cent FeO in solid solution in the paramontroseite and montroseite.

X-RAY CRYSTALLOGRAPHY

Early attempts to obtain single-crystal patterns of doloresite were unsuccessful because of the extremely poor quality of the crystal fragments and the oriented admixture of paramontroseite. Specimens from the Monument No. 2 mine mentioned above gave relatively clean Buerger precession photographs, with only traces of a paramontroseite pattern, although the doloresite pattern was still somewhat diffuse. The patterns conformed to a body-centered orthorhombic lattice, but the lattice constants derived on this basis could not be made to account adequately for the powder pattern. Also, the most diligent efforts to find an orthorhombic crystal structure for doloresite were fruitless. The key to the crystallography of doloresite was finally provided by *x*-ray studies on a new vanadium oxide mineral from Carlile, Wyoming, which proved to be monoclinic with the space group $C2/m$, $a = 19.64$ Å, $b = 2.99$ Å, $c = 4.83$ Å and $\beta = 103°55'$. The close relationship between this crystal and doloresite can be appreciated if the above monoclinic cell is transformed to a setting for which the space group would be written $I2/m$, and which is strongly pseudo-orthorhombic in dimensions with $\beta' = 90°18'$. In fact, it was found that the orthorhombic intensity distribution found for doloresite from Monument No. 2 mine could be reconciled with the monoclinic patterns of the mineral from Carlile by taking account of the superposition of spots that would arise by twinning the monoclinic lattice on (100) as the twin plane. Finally, the monoclinic lattice was found to give a satisfactory explanation of the powder pattern, as shown in Table 2.

The crystal structure of the monoclinic crystal was readily determined. The unit cell contains one formula and the unit-cell volume of the Carlile crystal and of doloresite is just sufficient to accommodate 16 oxygen atoms with a specific volume of 17.2 Å^3 per atom. This value of the specific volume is entirely consistent with that found for other vanadium oxides; for example, 17.2 Å^3 for montroseite, $V_2O_3 \cdot H_2O$ (Evans and Block, 1953) and 17.1 Å^3 for duttonite, $V_2O_4 \cdot 2H_2O$ (Evans and Mrose, personal communication). The crystal-structure analysis of the Carlile crystal indicates the presence of 6 vanadium atoms, but the number of hydrogen atoms, in the absence of a chemical analysis, must be determined by an indirect method. Thus, the unit-cell content of the Carlile mineral, and consequently of doloresite, is established as $H_nV_6O_{16}$. The crystal structure will not permit n to be greater than 10, and if the oxidation state of vanadium is not greater than 4, n cannot be less than 8. The chemical analyses strongly indicate that doloresite is essentially an oxide of quadrivalent vanadium, and therefore the ideal formula $H_8V_6O_{16}$, or $3V_2O_4 \cdot 4H_2O$, is proposed for this mineral.

It has not yet been established with certainty whether the Carlile mineral is doloresite ($H_8V_6O_{16}$) or a more reduced phase ($H_{10}V_6O_{16}$). In the absence of any possibility of chemical analysis of the Carlile mineral,

TABLE 2.—*X*-RAY POWDER DATA FOR DOLORESITE FROM MONUMENT NO. 2 MINE, APACHE COUNTY, ARIZ.

Indexed on monoclinic unit cell; space group *C*2/*m*,
$a=19.64$ Å, $b=2.99$ Å, $c=4.83$ Å, $\beta=103°55'$
CuKα radiation; camera diameter 114.6 mm; *d*(obs.) cutoff at 12 Å

hkl	*d*(calc.) (Å)	*d*(obs.) (Å)	*I*
200	9.52		
400	4.76		
001	4.69	4.70	100
$\bar{2}01$	4.68		
201	3.85		
$\bar{4}01$	3.83	3.83	50
600	3.17	3.16	42
401	3.00	2.98	15
110	2.95		
$\bar{6}01$	2.95	2.93	6
$\bar{1}11$	2.54		
021	2.52		
111	2.458		
$\bar{3}11$	2.454	2.45	50
$\bar{2}02$	2.415		
800	2.380		
601	2.376		
$\bar{8}01$	2.364		
002	2.344		
$\bar{4}02$	2.338		
311	2.245	2.23	3
$\bar{5}11$	2.185		
202	2.159	2.153	3
$\bar{6}02$	2.148		
511	1.987	1.985	5
$\bar{7}11$	1.981		
801	1.942		
$\overline{10}.9.1$	1.933	1.933	25
402	1.927		
802	1.916		
10.0.0	1.903	1.901	2
$\bar{1}12$	1.871		
312	1.869	1.864	7
112	1.804		
512	1.799	1.799	21
711	1.740		
911	1.735	1.732	9
602	1.700		
$\overline{10}.0.2$	1.690	1.692	6
312	1.688		
712	1.682		
10.0.1	1.632		
$\overline{12}.0.1$	1.626		
$\bar{2}03$	1.605		
$\bar{4}03$	1.604	1.604	2
12.0.0	1.586	1.584	3
003	1.563		
$\bar{6}03$	1.558		
512	1.549		
$\bar{9}12$	1.542		
911	1.526		
803	1.522		
$\overline{11}.1.1$	1.522	1.518	4
802	1.499		
020	1.495	1.490	15
$\overline{12}.0.2$	1.491		
203	1.486	1.485	11
220	1.477		
420	1.426		
$\bar{2}21$	1.424		
$\bar{3}13$	1.418	1.417	4
712	1.408		
12.0.1	1.404		
$\bar{1}13$	1.403		
$\bar{5}13$	1.401		
$\overline{11}.1.2$	1.401	1.400	4
		1.385	2
		1.344	5
		1.293	5
		1.224	2

the final decision rests on the detailed refinement of its crystal structure. The detailed description of the crystal-structure analysis of doloresite and of the vanadium oxides from Carlile will be given in another paper.

SUMMARY

A new vanadium oxide mineral from the Colorado Plateau is described and named doloresite after the Dolores River in Colorado. The mineral is very widespread in slightly oxidized vanadium ores and, because of the complexity of the V_2O_4-V_2O_5 hydrate weathering system, is almost always intimately mixed with other oxide minerals, especially paramontroseite, which it replaces. When pure, the mineral is dark brown, massive with radiating botryoidal structure and a fibrous, flaky cleavage. When mixed with paramontroseite it is opaque with a submetallic luster, taking on a dark bronzy tarnish. Optically it is nonopaque, reddish yellow with a mean refractive index near 1.90; in polished section it appears gray and strongly anisotropic. Single crystal *x*-ray study shows that doloresite is monoclinic with space group $C2/m$, $a=19.64$ Å, $b=2.99$ Å, $c=4.83$ Å, $\beta=103°55'$. Lamellar twinning is practically universal on a submicroscopic scale, with twin plane (100). Crystal structure and chemical evidence indicate that the formula is $H_8V_6O_{16}$ or $3V_2O_4 \cdot 4H_2O$. The mineral is best identified by its *x*-ray powder pattern.

This work is part of the program conducted by the U. S. Geological Survey on behalf of the Divisions of Research and of Raw Materials of the U. S. Atomic Energy Commission.

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Manuscript received March 12, 1957.