

A CRYSTAL CHEMICAL STUDY OF THE VANADIUM OXIDE MINERALS, HÄGGITE AND DOLORESITE*

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ABSTRACT

Small, black vanadium oxide crystals obtained from a sandstone drill core taken near Carlile, Wyoming, were found by single-crystal x -ray diffraction techniques to consist of two monoclinic phases. Crystal structure analysis showed one phase to be a new mineral, häggite, having the following crystallographic properties: space group $C2/m$; cell dimensions, $a=12.17 \text{ \AA}$, $b=2.99$, $c=4.83$, $\beta=98^\circ 15'$; cell contents, $H_5V_4O_{12}$. The second phase ("phase B") was found to have crystallographic properties identical with those of the previously described doloresite: space group, $C2/m$; cell dimensions, $a=19.64 \text{ \AA}$, $b=2.99$, $c=4.83$, $\beta=103^\circ 55'$; cell contents, $H_5V_6O_{16}$ or $H_{10}V_6O_{16}$. The presence of the hydrogen atoms was established by recognizing hydrogen bonds from oxygen-oxygen distances and vanadium-oxygen bond distributions. To obtain the best interatomic distance data, the structures of both phases were refined by least squares analysis.

Häggite, phase B, and duttonite (H_2VO_3) are considered to be members of a homologous series of general composition $H_{2n-2}V_nO_{3n-2}$, with $n=4, 6$ and ∞ , respectively.

The problem of the chemical nature of doloresite was solved with information obtained from a study of the Carlile crystals. Doloresite is invariably twinned on (100) on a submicroscopic scale, producing pseudo-orthorhombic x -ray patterns. The x -ray intensities of the twin composite reflections are well accounted for in terms of the crystal structure found for phase B. Phase B is not twinned, but is intergrown with häggite in parallel orientation (b and c axes coincident) on a submicroscopic scale. The structural relationships and modes of occurrence of these minerals lead to the hypothetical conclusion that doloresite ($H_5V_6O_{16}$) is metastable and is formed by solid state oxidation of phase B ($H_{10}V_6O_{16}$), which is formed by metasomatic replacement of montroseite. The häggite and phase B from Carlile appear to have been directly crystallized from the primary mineralizing solutions. The mechanisms whereby these processes may have taken place are described.

INTRODUCTION

After montroseite and paramontroseite, the most frequently encountered vanadium oxide mineral in the Colorado Plateau ore deposits is doloresite. This new mineral, easily recognized and characterized petrographically, for a long time resisted definitive study because of its variable chemical composition, anomalous crystallography and intimate association with other vanadium oxide minerals. It is fibrous in character, and it was readily established that the structural spacing along the fibre direction is 3.0 \AA , thus suggesting a relationship to montroseite. We made extensive efforts without success in the earlier stages to determine the essential nature of the mineral through crystal structure analysis based on single-crystal intensity data of limited range and quality. Failure was certain because the crystals are twinned and the analysis was

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made in terms of an incorrect orthorhombic cell, as described in a later section.

After nearly a year of diligent effort, the doloresite problem was set aside for awhile and attention turned to another vanadium oxide mineral which came from Carlile, Wyoming. Of this material we had available a number of small crystals extracted from a sandstone matrix. X-ray patterns of these crystals revealed the presence of two separate phases, both monoclinic, intergrown in parallel orientation on a microscopic scale. One of these, it was discovered, by applying a simple twin law, could be made to account for both the geometry and intensities of the diffraction patterns of doloresite. The crystal structures of both phases in the Wyoming crystals were readily solved from Patterson projections, and this result led directly to the solution of the doloresite problem. Following these developments, the description of the mineral doloresite was completed and published by Stern, Stieff, Evans and Sherwood (1957). A preliminary description of the structures of häggite (one of the Wyoming phases) and doloresite has been given previously (Evans and Mrose, 1958). A detailed description of the analysis and interpretation of the crystal structures of these minerals is the objective of this paper.

THE CARLILE, WYOMING CRYSTALS

In 1956 we received a sample of a black vanadium oxide in the form of several small crystals (maximum size, 0.1 mm.) which had been worked out of a sandstone matrix by M. E. Thompson of the Geological Survey. The sample was taken from a drill core at a depth of 180–181 feet in drill hole TR-713, which is in the NE $\frac{1}{4}$ SE $\frac{1}{4}$ sec. 27, T. 52 N., R. 66 W., Crook County, Wyoming. This horizon is in a highly mineralized, unnamed siltstone member of the Lakota formation (Lower Cretaceous age), about 13 feet below the base of the Fuson member.* Spectrographic tests showed the presence only of vanadium and a minor amount of iron, and an x-ray powder diagram revealed a pattern hitherto unknown for a natural mineral. There was no possibility of making a chemical analysis of the mineral, and the only hope of discovering its constitution was through x-ray single-crystal studies. Fortunately, the crystals gave excellent Buerger precession patterns, at least in comparison with those usually given by vanadium oxide minerals. The outstanding feature of these patterns was the presence of a short crystallographic axis of 3.0 Å, as in montroseite and doloresite. The diffraction net normal to this axis gave a clearly resolved pattern of sharp spots as shown in Fig. 1a. This pattern consists of perfectly straight rows of spots, with an inter-row spacing

* The information concerning this core was kindly supplied by Miss Darlene N. Peacock of the Atomic Energy Commission.

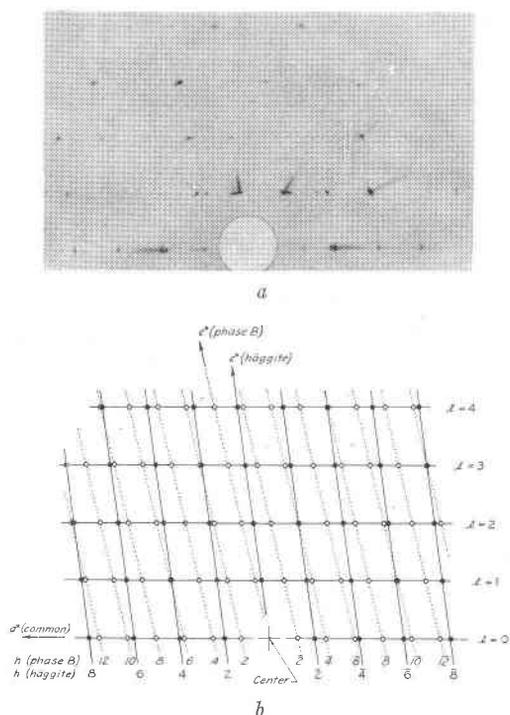


FIG. 1. *a*. Buerger precession photograph of $(h0l)$ net of a crystal from Carlile, Wyoming (MoK α radiation). *b*. Interpretation of *a*: full circles, full lines, haggite reciprocal lattice; open circles, dotted lines, phase B lattice.

corresponding to 4.83 \AA ; but the spots within the rows appeared to be irregularly arranged. It was found that the pattern could be accounted for in all detail in terms of two superimposed monoclinic lattices with equal and common b and c axes, but different a axes and β angles. Measurement of Buerger precession photographs of the $(hk0)$, and $(h0l)$ and $(h1l)$ nets gave the following dimensions for the two lattices, designated as shown:

Space group	Phase A	Phase B
	both $C2/m$, Cm or $C2$	
a	$12.17 \pm 0.05 \text{ \AA}$	$19.64 \pm 0.06 \text{ \AA}$
b	2.99 ± 0.01	2.99 ± 0.01
c	4.83 ± 0.02	4.83 ± 0.02
β	$98^\circ 15' \pm 5'$	$103^\circ 55' \pm 5'$
Vol.	173.9 \AA^3	275.3 \AA^3

The explanation of the $(h0l)$ net shown in Fig. 1*a* is shown graphically in Fig. 1*b*. The powder pattern of these crystals gave the data listed in

Table 1 wherein the identity of each line in terms of the lattice of phase A or B is indicated.

For the purpose of structure analysis, the intensities of the ($h0l$) reflections were measured on Weissenberg patterns by means of visual comparison with a calibrated strip made with one of the x -ray reflections. For phase A, 58 independent data were collected, and for phase B, 63 data. In only nine cases did reflections from the two lattices overlap seriously enough to prevent individual measurement. The pattern of phase A was always considerably stronger than that of phase B, presumably owing to its predominance in the crystal, so that it was expected that the data of phase A were the more reliable. These data were suitably corrected for the Lorentz and polarization factors, but not for absorption.

CRYSTAL STRUCTURE ANALYSIS OF HÄGGITE (PHASE A)

Unit cell contents and structure

The geometry of the unit cells of phases A and B places severe limits on the contents of the unit cells. Of the chemistry, it was known only that the major constituents were limited to vanadium, oxygen and hydrogen. By analogy to montroseite and similar oxides (Evans and Mrose, 1955), it seemed proper to associate with the 3.0 Å spacing a structure consisting of chains of octahedra stretched along the b axis by sharing edges. In such a structure all atoms readily lie on mirror planes normal to the chain axis, so, partly for this reason, the space group was assumed to be $C2/m$. The volume of the cell will accommodate exactly 12 oxygen atoms of specific volume 17.4 Å³. (In montroseite, the specific volume is 17.2 Å³; Evans and Block, 1953.) In the space group $C2/m$, there must be an even number of atoms in the unit cell. In addition, the average valence of vanadium was assumed to be between three and four. With these restrictions, the following formulations of the unit cell contents are allowed:

I. H ₁₄ V ₂ O ₁₀	V. H ₄ V ₄ O ₁₀
II. H ₁₂ V ₂ O ₁₀	VI. H ₂ V ₆ O ₁₀
III. H ₈ V ₄ O ₁₀	VII. V ₆ O ₁₀
IV. H ₆ V ₄ O ₁₀	

The structure of phase A was readily determined from the Patterson map, which is shown in Fig. 2a. In this map all the vectors characteristic of the double zig-zag octahedral chain (Fig. 2b) are easily recognized. With the knowledge of the presence of this structural feature and its orientation in the structure, it was soon determined, mainly from geometrical considerations, that the zig-zag chains are joined through the apices of the octahedrons into sheets extending parallel to the (001) plane. Structure factors for such an arrangement gave good agreement

TABLE 1. POWDER X-RAY DIFFRACTION DATA FOR BLACK VANADIUM OXIDE CRYSTALS FROM CARLILE, WYOMING

CuK α radiation; camera diameter 114.6 mm.; min. obs. $d=12 \text{ \AA}$.
 $d(\text{calc.})$ given for haggite to 1.500 \AA ; for phase B to 2.50 \AA

Phase B		Haggite (phase A)		Carlile crystals	
<i>hkl</i>	<i>d</i> (calc.)	<i>hkl</i>	<i>d</i> (calc.)	<i>d</i> (obs.)	I
200	9.52	200	6.02	6.04	4
		001	4.78	4.80	100
400	4.70			4.73	3
001	4.69				
201	4.68	201	4.04	4.05	50
201	3.85			3.87	3 (brd)
401	3.83	201	3.51	3.51	12
600	3.17	400	3.01	3.18	2
401	3.00			3.02	25
110	2.95				
601	2.95	110	2.90	2.91	3
111	2.54	401	2.73	2.74	6
021	2.52	111	2.52		
		111	2.443	2.44	25
		401	2.398		
		310	2.398		
		002	2.390	2.39	3
		202	2.340		
		311	2.221	2.22	3
		202	2.120	2.12	4
		311	2.073	2.071	3
		402	2.018		
		600	2.007	2.010	3
		601	1.954	1.959	18
		112	1.877	1.878	4
		510	1.875		
		511	1.817		
		112	1.814	1.815	12
		312	1.770	1.788	4
		601	1.763		
		402	1.754		
		511	1.684	1.686	6
		602	1.659	1.662	4
		312	1.625		
		203	1.598	1.600	3
		003	1.593		
		512	1.563	1.567	4
		800	1.505		
		403	1.500		
				1.492	12
				1.419	2
				1.400	3
				1.378	6
				1.347	3
				1.291	6
				1.199	3
				1.172	4

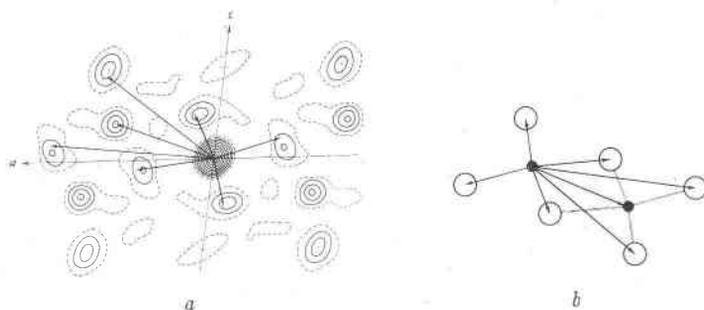


FIG. 2. *a.* Patterson projection on (010) of häggite. *b.* Vectors of the double octahedral chain of montroseite.

with the observed amplitudes, and with three repeated calculations, the final electron density shown in Fig. 3 was obtained.

Hydrogen atoms

This result restricts the formulation to III, IV and V, leaving only the question of the number of hydrogen atoms present. This must, of course, be found by an indirect approach. The first indication comes from the presence of six short oxygen-oxygen distances of about 2.7 Å across the interlayer region of the structure. Crystal chemical principles require that such distances as these be associated with hydrogen bonds, so that we may thus account for six hydrogen atoms. To decide whether there are other hydrogen atoms present not involved in hydrogen bonding, we must attempt to estimate the distribution of electrons among the several vanadium-oxygen bonds. For this purpose, we may begin by dividing the three or four electron pairs associated with vanadium equally among the six oxygen ligands. This approach would lead us to suspect that O_1 is a hydroxyl group. Before accepting this conclusion, we must examine the vanadium-oxygen bond lengths to determine whether or not the bonding in the octahedron is actually uniform.

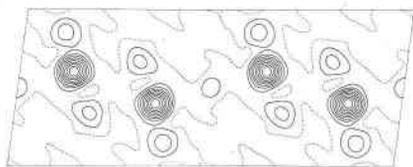


FIG. 3. Electron density projection on (010) of häggite. Dotted contour, zero electrons/Å²; contour interval, 5 electrons/Å².

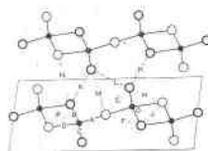


FIG. 4. Interatomic distances in häggite.

TABLE 2. STRUCTURE PARAMETERS FOR HÄGGITE (PHASE A)

Space group: $C2/m$, Int. Tab. No. 12

Atoms	x	y (cycles)	z	B (\AA^2)
4 V in (<i>i</i>)	0.1378 ± 0.0005	0	0.3967 ± 0.0012	4.16 ± 0.13
2 O ₁ in (<i>c</i>)	0	0	$\frac{1}{2}$	5.87 ± 0.98
4 O ₂ in (<i>i</i>)	0.6094 ± 0.0018	0	0.133 ± 0.004	4.90 ± 0.59
4 O ₃ in (<i>i</i>)	0.3026 ± 0.0019	0	0.346 ± 0.004	5.14 ± 0.59

Crystal structure refinement

To obtain the best measurement of the bond lengths in phase A, the structure was refined by the method of least squares analysis. This calculation was carried out by hand methods in the early stages, and completed with a program written for the Burroughs 205 digital computer. The approximation was used in which the nondiagonal terms of the normal equations are neglected, as described in the case of montroseite (Evans and Mrose, 1955). The weighting factor was chosen according to the absolute value of F , as follows:

$$\begin{aligned} \text{for } |F(\text{obs})| > 4 |F(\text{min})|, & \quad \sqrt{w} = 4 |F(\text{min})| / |F(\text{obs})|; \\ \text{for } |F(\text{obs})| < 4 |F(\text{min})|, & \quad \sqrt{w} = |F(\text{obs})| / 4 |F(\text{min})|. \end{aligned}$$

Each atom was assigned an individual isotropic temperature factor. By this route, the reliability factor was reduced to $R=0.143$. The observed and calculated structure amplitudes, $F(\text{obs})$ and $F(\text{calc})$, show good agreement.*

The final coordinates, temperature factors and corresponding standard deviations are given in Table 2. The interatomic distances, illustrated in Fig. 4, are listed in Table 3.

Vanadium-oxygen bonds

The six vanadium-oxygen bonds in the octahedron, as shown by Table 3, vary in length from 1.82 to 2.06 \AA . This range must correspond to a considerable variation in bond number. In a discussion of the structure of vanadium pentoxide, Byström and Wilhelmi (1951) have shown that an approximation of the bond number of a vanadium-oxygen bond may be obtained from the empirical relation of Pauling (1947):

$$D_n - D_1 = -2k \log n$$

in which the constants $D_1 = 1.77 \text{\AA}$ and $k = 0.39$. (For metals Pauling uses $k = 0.300$.)

* A copy of the $F(\text{obs})$ and $F(\text{calc})$ values may be obtained from the authors.

TABLE 3. INTERATOMIC DISTANCES IN HÄGGITE (PHASE A)
(SEE FIG. 4)

Atoms	Vector	Distance Å	Atoms	Vector	Distance Å
V-O ₁	A	1.82 ± 0.02	O ₁ -O ₂	E	2.80 ± 0.03
V-O ₂	B	1.97	O ₁ -O ₃	F	2.84
V-O ₃	C	2.01	O ₂ -O ₃	G	2.59
V-O ₃	D	2.06	O ₂ -O ₃	H	2.85
			O ₃ -O ₃	J	2.58
			O ₂ -O ₃	K	2.69
V-V	P	3.15 ± 0.01	O ₂ -O ₂	L	2.79
			O ₁ -O ₂	M	3.49
			O ₃ -O ₃	N	3.72

Evans (unpublished work) has found that for certain metavanadates whose structures are well refined, better consistency is obtained with $D_1 = 1.81$ Å. Applying this law to the vanadium-oxygen octahedron in phase A, the following distribution is obtained:

	D_n	n
V-O ₁	1.82 Å	0.98
V-O ₂ (2)	1.97	0.63
V-O ₃ (2)	2.01	0.55
V-O ₃	2.06	0.48
Total n		3.82

From this result it is unsafe to deduce directly the valence of vanadium because of the large accumulative errors in n . The indication is clear, on the other hand, that the V-O₁ bond is close to a full single bond. Since O₁ receives two of these bonds, we may conclude that it cannot carry a hydrogen atom, and therefore does not represent a hydroxyl group.

Constitution of häggite

The distribution of bonds over the oxygen atoms is consistent with the hydrogen bonds located earlier, but does not admit the presence of any other hydrogen atoms in the unit cell. We are thus led to the unique formulation for phase A of IV above:



Further arguments in support of this composition are given in a later section. Phase A is thus established as a new mineral species. In honor of Professor Gunnar Hägg of the University of Stockholm and his inestimable contributions to our knowledge of crystal chemistry, we propose the name häggite for this mineral. It will be referred to by this name in the remainder of this paper.

CRYSTAL STRUCTURE ANALYSIS OF PHASE B

Unit cell contents and structure

The crystal structure of phase B was worked out in the same way as that of haggite. The unit cell volume will just accommodate 16 oxygen atoms of specific volume 17.2 \AA^3 . Again assuming the space group to be $C2/m$ and the same restrictions to apply as for haggite, the possible formulations for phase B are the following:

VIII. $\text{H}_{20}\text{V}_4\text{O}_{16}$	XIV. $\text{H}_8\text{V}_6\text{O}_{16}$
IX. $\text{H}_{18}\text{V}_4\text{O}_{16}$	XV. $\text{H}_8\text{V}_8\text{O}_{16}$
X. $\text{H}_{16}\text{V}_4\text{O}_{16}$	XVI. $\text{H}_6\text{V}_8\text{O}_{16}$
XI. $\text{H}_{14}\text{V}_6\text{O}_{16}$	XVII. $\text{H}_4\text{V}_8\text{O}_{16}$
XII. $\text{H}_{12}\text{V}_6\text{O}_{16}$	XVIII. $\text{H}_2\text{V}_8\text{O}_{16}$
XIII. $\text{H}_{10}\text{V}_6\text{O}_{16}$	XIX. V_8O_{16}

The Patterson map for phase B, shown in Fig. 5, again shows the vectors of the double octahedral chain. Geometrical considerations based on this chain oriented as shown by the Patterson function quickly lead to the conclusion that there are also present single octahedron chains, with which the double chains are linked alternately by sharing octahedral apices as in haggite, to form sheets extending parallel to the (001) plane. Structure factor calculations indicated that such a model is a valid one, and finally led to the electron density map shown in Fig. 6. In this way the formulation of phase B was restricted to XI, XII, XIII or XIV. The electron density map shows the presence of 10 short inter-layer oxygen-oxygen distances or hydrogen bonds. This evidence leads to formula XIII for phase B, unless evidence for the presence of additional hydrogen atoms not involved in hydrogen bonds is found.

Crystal structure refinement

The 63 ($h0l$) data for phase B were refined by the method of least squares analysis, just as for haggite. The final reliability factor was $R=0.164$. The structure parameters are given in Table 4. The interatomic distances, as shown in Fig. 7, are listed in Table 5. As expected the errors

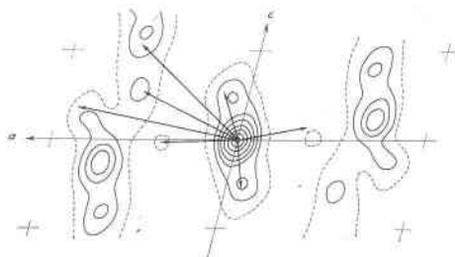


FIG. 5. Patterson projection of (010) of phase B.

TABLE 4. STRUCTURE PARAMETERS FOR PHASE B AND DOLORESITE

Space group: $C2/m$, Int. Tab. No. 12

Atoms	x	y (cycles)	z	B (\AA^2)
2 V_1 in (c)	0	0	$\frac{1}{2}$	2.26
4 V_2 in (i)	0.1766 ± 0.0007	0	0.3680 ± 0.0028	2.43
4 O_1 in (i)	0.470 ± 0.003	0	0.248 ± 0.012	5.47
4 O_2 in (i)	0.095 ± 0.004	0	0.427 ± 0.015	10.17
4 O_3 in (i)	0.665 ± 0.003	0	0.095 ± 0.012	5.17
4 O_4 in (i)	0.286 ± 0.003	0	0.362 ± 0.011	4.31

in these distances are larger than those obtained for häggite, because of the poorer quality of the measured data, but they are sufficiently small to permit some useful estimates of bond number to be made.

Vanadium-oxygen bonds

Applying Pauling's relation to this structure, the following bond distributions are found:

	D_n	n
$V_1-O_1(4)$	1.93 \AA	.70
$V_1-O_2(2)$	1.98	.60
	Total n	4.00
V_2-O_2	1.70 \AA	1.39
$V_2-O_3(2)$	1.97	.62
$V_2-O_4(2)$	2.01	.56
V_2-O_4	2.13	.39
	Total n	4.14

As in häggite, the oxygen atom which links the chains in the a -axis direction is joined to two vanadium atoms which supply it with a total valency of 1.99. It seems most probable that O_2 is not a hydroxyl group.

Constitution of phase B

By arguments similar to those used for häggite, it is concluded that the number of hydrogen atoms in the unit cell is 10, as a maximum. Thus, formulation XIII is the most probable composition of phase B:



In this case, we must recognize the possibility that the number of hydrogen atoms is less, or 8 as a minimum. Phase B would then be identical with doloresite which corresponds to formula XIV, as described in the



FIG. 6. Electron density projection on (010) of phase B. Contours as in Fig. 3.

next section. The relationship between phase B and doloresite is discussed in a succeeding section.

Possible ordering of hydrogen bonds

In both haggite and phase B, it will be noted that one of the hydrogen bonds is bisected by a symmetry center. This bond cannot in fact be centrosymmetric, so that the formal definition of the structure must be qualified to account for this anomaly. It is certain that any one chain of hydrogen bonds, 3 in the chain in haggite, and 5 in phase B, must be polarized with all the hydrogen bonds oriented in one direction or the other along this chain. Following this postulate, two further relations among the hydrogen bonds may occur: (1) the polarizations of the separate hydrogen bond chains are oriented at random throughout the structure; and (2) the polarizations are oriented in a parallel or some anti-parallel array. In the first case, the structure symmetry will be truly $C2/m$, and the structure parameters will be an average of the local positions assumed according to the orientation (instantaneous or permanent)

TABLE 5. INTERATOMIC DISTANCES IN PHASE B AND DOLORESITE
(SEE FIG. 7)

Atoms	Vector	Distance Å	Atoms	Vector	Distance Å
V ₁ -O ₁	A	1.93 ± 0.07	O ₂ -O ₁	G	2.72 ± 0.10
V ₁ -O ₂	B	1.98	O ₂ -O ₁	H	2.81
V ₂ -O ₂	C	1.70	O ₁ -O ₁	J	2.44
V ₂ -O ₄	D	2.01	O ₄ -O ₄	K	2.60
V ₂ -O ₃	E	1.97	O ₄ -O ₂	L	2.77
V ₂ -O ₄	F	2.13	O ₂ -O ₃	M	2.79
			O ₃ -O ₄	N	2.82
			O ₄ -O ₃	P	2.57
V ₂ -V ₂	W	3.23 ± 0.02	O ₄ -O ₃	Q	2.62
			O ₃ -O ₁	R	2.79
			O ₁ -O ₁	S	2.88
			O ₂ -O ₃	T	3.52
			O ₂ -O ₁	U	3.53
			O ₄ -O ₄	V	3.75

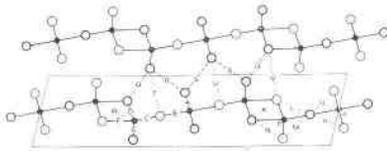


FIG. 7. Interatomic distances in phase B.

of the adjacent hydrogen bonds. The variations found in the temperature factors of the various oxygen atoms may be a result of this averaging process. In the second case, the space group symmetry of the structure would be lowered to Cm . Again, the observed temperature factors would be influenced by our procedure of refining the structure in terms of the more symmetrical space group. No attempt has been made to carry the refinement of the structures of häggite and phase B further in the space group Cm . Therefore, we cannot draw any conclusion as to which of the hydrogen bond arrangements, ordered or disordered, is actually present in these structures.

STRUCTURE OF DOLORESITE

Crystallography of doloresite

In the description of the brown, fibrous mineral doloresite by Stern, Stieff, Evans and Sherwood (1957), a brief account of the approach to the problem of chemical constitution and structure of this mineral has already been given. The crystal flakes give generally very poor diffraction patterns, partly because of their fibrous character, and partly because of the admixture of oriented paramontroseite. A specimen was finally obtained from the Monument No. 2 mine in Monument Valley, Arizona, which was relatively free of paramontroseite. A Buerger precession photograph of a net plane normal to the fibre axis (3.0 \AA spacing), made with a crystal fragment from this specimen, is shown in Fig. 8a. Although the reflections are still somewhat diffuse, an orthorhombic lattice is clearly indicated. Measurement of this and other patterns leads to the following data:

Space group: $Im2m$

$a = 19.11 \text{ \AA}$

$b = 2.98$

$c = 4.86$

Vol. = 277 \AA^3 .

This unit cell proved to be false at a later stage when it was discovered that the lattice could be exactly accounted for in terms of the monoclinic

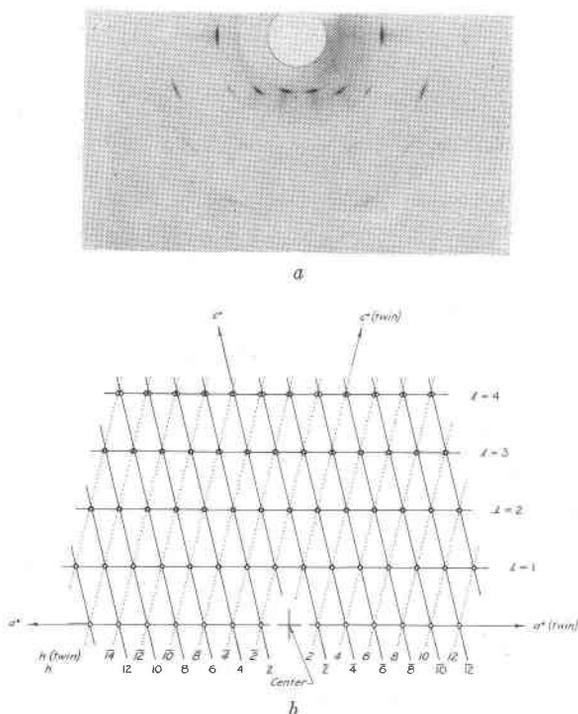


FIG. 8. *a*. Buerger precession photograph of $(h0l)$ net of doloresite, normal to fiber axis. *b*. Interpretation of *a*: full lines, primary reciprocal lattice; dotted lines, twin lattice. Note the orthorhombic symmetry of the photograph.

unit cell of phase B. If the phase B unit cell is transformed according to the matrix $101/010/00\bar{1}$, its dimensions* are:

Space group: $I2/m$

$$a = 19.07 \text{ \AA}$$

$$b = 2.99$$

$$c = 4.83$$

$$\beta = 90^\circ 18'$$

By twinning on (100) , the apparently orthorhombic lattice is produced, as shown in Fig. 8*b*.

Early attempts to interpret the "orthorhombic" structure

Until work was begun on the crystals from Carlile, Wyoming, the presence of twinning in doloresite was not suspected. As explained in the

* This setting of the unit cell is, in fact, the conventional setting of Donnay and Nowacki (1957). The unit cell used in this paper is retained in order to simplify the description of the structures and their interrelationships.

Introduction, a concerted effort was made to solve the structure in terms of the false orthorhombic unit cell. It may be of interest to describe this work briefly, in order to illustrate the extent to which a completely blind lead can be followed, especially in the use of the Fourier method of structure analysis.

Intensities were measured for the $(h0l)$ and $(h1l)$ reflections on Weissenberg films by visual estimate and corrected for Lorentz and polarization factors. These data were used to prepare the Patterson section $P(u0w)$ (spurious, because the intensities measured were all twinned composites). It was known from the unit cell volume that the cell contained 16 oxygen atoms, but the number of vanadium atoms was taken as 4, 6 or 8 in various trials. It was quickly found that no arrangement of octahedra was possible in the space group $Immm$, so the symmetry was assumed to be $Im2m$. Several trial arrangements of the vanadium atoms were evolved compatible with the "Patterson" function. Each led to a recog-

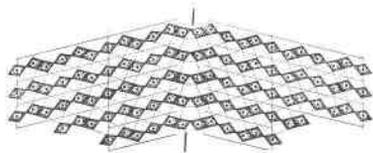


FIG. 9. Possible mechanism of twinning of doloresite, by a mirror operation.

nizable electron density projection. Only one showed any indication of oxygen atoms. This structure, the best of those tried, could not be refined to give a reliability factor lower than 0.35. The failure to find any structure that would refine beyond this point led us to abandon further work in this direction. Our experience with this problem provides a good example of the obliging nature of the Fourier method in crystal structure analysis, even when based on a completely erroneous crystallographic interpretation.

Verification of the true structure of doloresite

It has been noted that the geometry of the doloresite lattice corresponds to a phase B lattice twinned on (100) . It was further found that the intensities of the $(h0l)$ reflections of doloresite, measured as indicated above, could be fully accounted for if it was assumed that each was the sum of the intensities of two reflections of the phase B lattice superimposed by the twin operation. After the refinement of phase B was completed, a set of structure factors was calculated using the final structure parameters obtained for phase B, but with an overall temperature factor of $B=4.0 \text{ \AA}^2$ instead of the individual temperature factors shown in Table 4. By combining these calculated F^2 values appropriately for the

twin composites and taking square root for comparison with the measured doloresite "F" values, a reliability factor of 0.098 was obtained. An attempt to refine the structure further in terms of the doloresite data did not lead to any significant change in the phase B structural parameters. The calculated and observed structure factors are in good agreement.

CRYSTAL CHEMICAL RELATIONSHIP BETWEEN MONTROSEITE AND DOLORESITE

Twinning in doloresite

A universal property of the mineral doloresite is its submicroscopic lamellar twinning on (100). No crystals have ever been found which do not give perfect pseudo-orthorhombic diffraction patterns. It is of considerable interest to examine this twinning in terms of the crystal structure of doloresite, and its mode of origin. The usual mechanism of twinning makes use of some element in the structure which can play a common role in the original crystal and in the twinned counterpart which is related to it by some symmetry operation. In this case, as shown in Fig. 9, we may use the O_2 atoms as a twin "bridge" by passing a mirror plane through them parallel to the c axis. Such a mechanism is feasible, especially if a hydrogen bond is invoked to join oxygen atoms O_3 (distance 2.57 Å) across the twin plane. Such a fusion may actually be accomplished in several ways, to join two single octahedron chains, two double chains, or a single and a double chain, at the composition plane (which may or may not be a mirror plane).

Another mechanism is equally feasible, and is actually more plausible in light of the relationship of doloresite to its parent, montroseite. In Fig. 10 is shown an arrangement in which the double chain of one sheet in one crystal is joined to double chains in two sheets in the twin component.

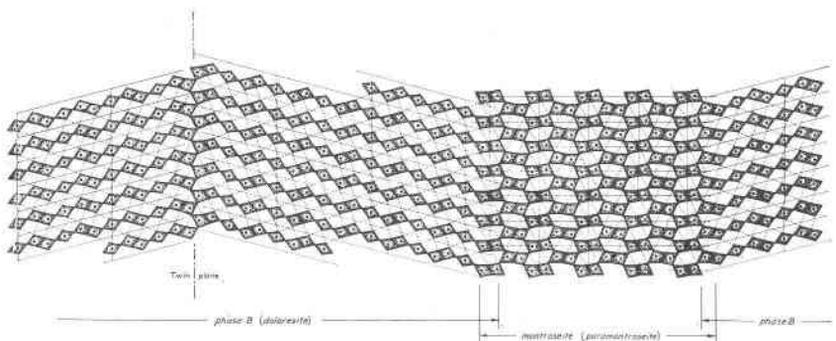


FIG. 10. Probable mechanism of twinning of doloresite, by a diagonal glide operation, shown at the left. Coalescence of the montroseite structure with the doloresite structure is shown in the two possible orientations at the right.

The two structures fit almost exactly in this way without strain. In fact, the arrangement of chains at the composition plane is almost identical with that found in the montroseite structure, illustrated to the right of Fig. 10. It can be derived by means of a diagonal glide plane parallel to the *b* and *c* axes in the twin composition plane, such as is characteristic of the montroseite structure parallel to the *a* and *c* axes.

Origin of doloresite

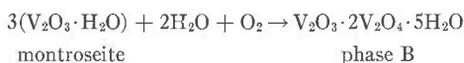
Doloresite is commonly found intimately associated with paramontroseite, and single-crystal photographs show that the two crystals are always in parallel orientation. The *b* and *c* axes of doloresite are found to be parallel to the *c* and *a* axes of paramontroseite, respectively. If the slab of structure at the composition plane (see Fig. 10) is considered to constitute a montroseite structure, its orientation is just that found for paramontroseite with respect to the two doloresite twin components. It follows, of course, that the doloresite structure will coalesce with the montroseite structure, as shown in Fig. 10.

On the basis of the information gained from the structure studies so far, a mode of origin of doloresite may be proposed, as described below.

1. Doloresite, as shown by Stern *et al.* (1957), is derived by secondary replacement of primary montroseite.

2. On exposure to ground waters containing oxygen, montroseite is altered to phase B.

3. The alteration mechanism, unlike that of montroseite to paramontroseite, is partially reconstructive, and involves a shifting of positions of vanadium, oxygen and hydrogen atoms and introduction of new atoms, according to the reaction:



4. In spite of the reconstructive nature of the alteration, structural control is maintained between montroseite and phase B, as shown in Fig. 10.

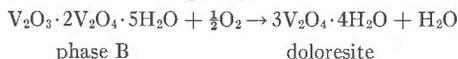
5. As in the case of paramontroseite (Evans and Mrose, 1955), the formation of phase B is nucleated on a very fine scale throughout the mass of the montroseite crystal.

6. With respect to the original montroseite crystal, the phase B nucleus may form with equal probability in either of two orientations.

7. When two adjacent nuclei in opposite orientations grow toward each other and finally consume the intervening montroseite, they may be joined at the contact in a manner shown in Fig. 10. It is also possible that there will be no coherent structural boundary, since the twin orientations were determined by the original montroseite structure and not by a direct structural relation between the twins themselves at the composition plane.

8. The size of the twin crystallites or lamellae of phase B, as suggested by the diffuseness of the single-crystal patterns, is of the order 10^{-5} cm.

9. When the alteration of montroseite to phase B is halted, perhaps by exposure to air, it is rapidly altered to doloresite according to the reaction:



10. At this stage, the remaining unreacted montroseite is converted to paramontroseite, according to the mechanism proposed by Evans and Mrose (1955).

Evans and Garrels (1959) have determined the conditions of formation and stability of many vanadium minerals in aqueous environments in terms of acidity (pH) and oxidation potential (E_h). In Fig. 11 we have suggested how their diagram may be further modified to include the new oxide phases described in this paper. The sequence of events described above is shown by means of arrows. This diagram also shows the relation

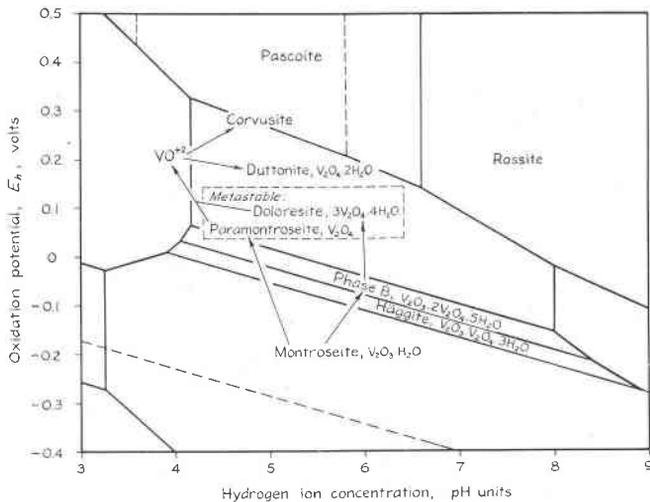


FIG. 11. Alteration sequences of montroseite to doloresite and higher oxides, shown on equilibrium diagram of Evans and Garrels (1959).

of these minerals to duttonite (Thompson, Roach and Meyrowitz, 1957) as it occurs at the Peanut mine, and to higher valence oxides ("corvusite") as it is found at most other localities.

It is important to remember in following the arguments set forth above that conclusive proof is not obtainable for every step. The weathering mechanism postulated and represented by the diagram presents what we feel is the most probable one in terms of all the accumulated evidence. The most uncertain aspect of the process is the change from phase B to doloresite. This question will be further discussed below.

ORIGIN OF HÄGGITE AND PHASE B

Intergrowth of häggite and phase B

As explained earlier, apparently single crystals from Carlile, Wyoming, were found to be an intimate intergrowth of two vanadium oxide phases, häggite and phase B. This situation is reminiscent of montroseite and

paramontroseite (Evans and Mrose, 1955), which were also found to be intergrown on a fine scale. In that case, the x -ray pattern for montroseite was found to be sharp, and for paramontroseite, diffuse. This was taken as evidence, together with other considerations, that the latter had been derived from the former by a solid state oxidation process. In the case of häggite and phase B, both superposed x -ray patterns are sharp. It is believed that a wholly different explanation must be sought for the existence of these two minerals.

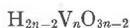
Stability of häggite and phase B

An understanding of the mode of formation of the various oxides requires a knowledge of the stable phases under the various environments of oxidation potential and acidity. On the equilibrium diagram of Evans and Garrels (1959), only two lower-valence oxides appear as stable phases: montroseite ($V_2O_3 \cdot H_2O$) and duttonite ($V_2O_4 \cdot 2H_2O$). Paramontroseite was said by Evans and Mrose (1955) to be metastable, because of its unique mode of origin and the fact that it is unknown as a synthetic product. It is entirely possible, of course, that stable phases exist that have not previously been identified. Many such intermediate type phases have recently been discovered in the molybdenum-tungsten-oxygen system (Magnéli, 1956) and the titanium-oxygen system (Anderson, Collén, Kuylenstierna and Magnéli, 1957). Most of these phases have been proved by crystal structure study to be members of groups termed by Magnéli "homologous series," in which the average valence of the metal atom is slightly altered from one phase to the next. Thus, in the titanium-oxygen system, the homologous series denoted by the formula



is represented by known phases for which $n = 4, 5, 6, 7, 8, 9, 10$ and ∞ .

Häggite and phase B have structures which suggest the existence of a homologous series of the type:



In this series, häggite has $n = 4$, phase B has $n = 6$ and duttonite has $n = \infty$. For structural reasons, n must be even and cannot be less than 4, and montroseite is not a member of the series. The structural basis of this series is the combination in varying ratios of single and double octahedron chains (ratio = $n/2 - 2$) to form sheet structures as explained in the section on the structure of phase B. The relationship among these structures is shown in Fig. 12. In duttonite (Evans and Mrose, 1958) only single octahedron chains are present, and these are subject to distortions.

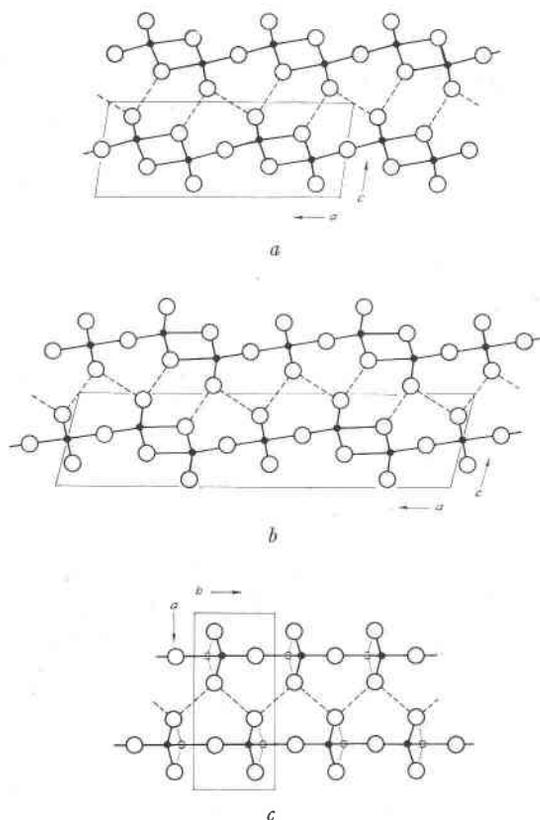


FIG. 12. Structures of the homologous series, (a) haggite, (b) phase B and (c) duttonite. Note hydrogen bond chains (dashed lines): 3 bonds (a), 5 bonds (b), and infinite (c) in length.

tions in the octahedral environment which have not been found in haggite and phase B.

Formation of haggite and phase B

It seems most probable that both haggite and phase B were formed as primary minerals in the sandstones at Carlile, Wyoming, from the mineralizing solutions. These oxides undoubtedly represent stable phases with narrow ranges in the oxidation potential variation between montroseite and duttonite. The minerals in this occurrence show no paramorphic relationship to other oxides such as montroseite. It may be imagined that the crystals grew in an environment in which the oxidation potential oscillated over a narrow interval bridging the stability ranges of haggite

and phase B. Under these conditions, the crystal may be expected to grow in an oscillatory manner, producing a crystal edifice consisting of fine lamellae of alternating häggite and phase B regions. These lamellae coalesce structurally at the interface in a natural way, as shown in Fig. 13, in a manner to produce a relative orientation just as found in the x -ray photographs.

DOLORESITE AND PHASE B ("PROTODOLORESITE")

Although doloresite and phase B have crystal structures so nearly identical that the difference between them cannot be detected, they have been treated in the previous sections as though they were distinct phases.

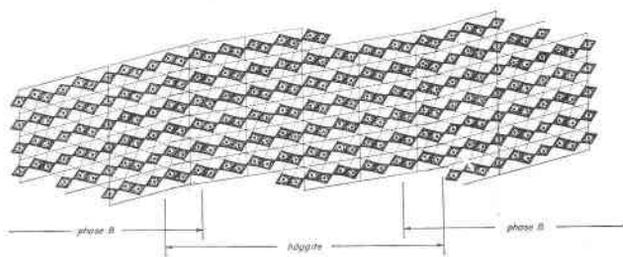


FIG. 13. Structural mechanism of intergrowth of häggite and phase B.
Note parallelism of c axes of the two phases.

The reasons for this practice are partly structural, partly morphological and partly chemical in nature.

Definition of doloresite

As described in the section above on the structure of doloresite, the number of hydrogen atoms in the formula $H_nV_6O_{16}$ will have a maximum of 10, and a minimum of 8. In the description of doloresite by Stern *et al.* (1957), it was shown that chemical analyses of carefully prepared samples showed that V_2O_3 was present in insignificant amount. Mainly for this reason, the formula given for doloresite was $H_8V_6O_{16}$ or $3V_2O_4 \cdot 4H_2O$. On the other hand, other analyses made on doloresite have shown the presence of appreciable amounts of V_2O_3 , but these samples were considered to contain admixed montroseite.

Hydrogen bonds and stable phases

There are sufficient hydrogen bond sites in the structure of doloresite to account for 10 hydrogen atoms in the formula. This formulation is that given to phase B, which, as explained in a previous section, is believed to be a member of a homologous series, and therefore, a stable

phase with a very narrow stability range. In doloresite, which is not a member of the postulated series, two of the ten possible hydrogen bonds are not occupied. No structural adjustments could be found tending to lengthen any of the oxygen-oxygen distances, but if the vacancies were distributed randomly over the ten hydrogen bonds, the corresponding structural changes would probably be so small as to escape detection by means of the limited diffraction data available.

We believe that doloresite is a metastable phase and bears the same relation to phase B as paramontroseite does to montroseite. It seems unreasonable that a stable tetravalent oxide hydrate phase could exist with such a complex structure, requiring as it does some special dispensation of the hydrogen atoms through disorder or other means. This reasoning is strengthened by evidence of the existence of this same structure with fully occupied hydrogen bonds as a stable phase. On the other hand, it is entirely reasonable to expect that phase B might undergo solid state oxidation by the loss of two hydrogen atoms per unit cell by a process of diffusion out of the structure, leaving the original structural framework intact. In the weathering diagram shown in Fig. 11, the transformation of phase B into doloresite would, therefore, be of the same type as that of montroseite into paramontroseite.

Phase B as a mineral species

Although we believe, as a result of the arguments given above, that phase B and doloresite are separate minerals, it is apparent that the evidence for their existence as distinct species is entirely circumstantial. Therefore, we are not in a position to define phase B as a valid species. If it should be possible at some later time to prove its existence, it would be proper to give it a name which indicates its relationship to doloresite, such as "protodoloresite."

SUMMARY

A detailed crystal chemical study of the vanadium oxide hydrate minerals doloresite and häggite has been made. In this study, the following facts have been established:

1. In crystals from Carlile, Wyoming, two vanadium oxide minerals are intimately intergrown on a microscopic scale. These minerals have closely related monoclinic lattices which are oriented with respect to each other so that their *b* and *c* axes are parallel.
2. The crystal structure of both these intergrown phases has been determined. Application of crystal chemical principles has led to a formulation of their chemical constitution.
3. One of these phases is established as the mineral häggite. The

structure consists of double octahedron chains linked by octahedron corner-sharing into sheets parallel to the (001) plane, the sheets being tied together by hydrogen bonds.

4. The crystallography and crystal structure of the second phase (phase B) have been determined and found to be identical with that of doloresite within the limits of experimental error. The structure consists of double octahedron chains linked alternately with single octahedron chains in sheets parallel to (001), the sheets being tied together by hydrogen bonds.

From these facts and other associated information, the relationships among the various vanadium oxide hydrates (montroseite, paramontroseite, häggite, phase B, doloresite and duttonite) have been studied and interpreted. The following significant conclusions have been arrived at:

1. Häggite, phase B and duttonite form a homologous series of the type: $H_{2n-2}V_nO_{3n-2}$, with $n=4, 6$ and ∞ respectively. These phases are probably thermodynamically stable.

2. Doloresite is probably different from phase B, and has the formula $H_8V_6O_{16}$, corresponding to a pure quadrivalent oxide hydrate. It is believed to be metastable, like paramontroseite, and formed from phase B through the loss of two hydrogen atoms per unit cell.

3. Doloresite, was formed originally as phase B by secondary replacement of montroseite. This process is reconstructive but evidently occurs under the structural control of montroseite. Thus, any phase B nucleus formed is constrained to have one of two possible orientations with respect to the original montroseite crystal. The twinning of doloresite on a submicroscopic scale is thereby accounted for.

4. The lamellar intergrowth, with no evidence of twinning, of häggite and phase B in crystals from Carlile, Wyoming, is believed to be the result of oscillatory growth of the crystals from the original mineralizing solutions under conditions in which the oxidation potential varies over a narrow critical range.

ACKNOWLEDGMENTS

Many persons have contributed to the accomplishment of the work described in this paper, which has extended over a period of several years. We wish especially to mention the assistance of A. D. Weeks, M. E. Thompson and T. W. Stern in acquiring and characterizing the materials on which the study was made. We are especially grateful to D. E. Appleman for assistance with the least squares analysis involving the use of the Burroughs 205 computer. All the work has been supported by the Division of Raw Materials and Division of Research of the U. S. Atomic Energy Commission.

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