

AN X-RAY STUDY OF ROEMERITE¹

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ABSTRACT

Roemerite is triclinic *P*1 with *a* 6.48, *b* 15.26, *c* 6.27 Å, α 90° 04', β 100° 48', γ 85° 28'. The orientation of the structural cell corresponds to Wolfe's normal setting based on the morphology. The cell contains $1[\text{Fe}''\text{Fe}_2'''(\text{SO}_4)_4 \cdot 14\text{H}_2\text{O}]$. X-ray powder data and a list of associated minerals are included. The paper gives two tables for the re-orientation of oblique cells to the normal setting.

INTRODUCTION

Roemerite, $\text{Fe}''\text{Fe}_2'''(\text{SO}_4)_4 \cdot 14\text{H}_2\text{O}$, was first identified in 1858 by Grailich, on material from the Rammelsberg mine, in the Harz district of Germany. The first adequate crystallographic work on the mineral was carried out by Blaas (1884), who studied crystals from Persia and obtained triclinic elements. These were adopted with minor corrections by Goldschmidt in the Index (1891). This was the beginning of a series of studies of the morphology of this mineral which have left us at present with nearly as many settings for roemerite as there are publications concerning it. Linck (1889), Dana (1892), Scharizer (1913), Doelter (1927), Ungemach (1935) and most recently Wolfe (1937), have all presented varying settings or elements. However no structural data are available for roemerite, and consequently the mineral offered an interesting study, and an opportunity to determine if the "normal" setting advanced by Wolfe corresponds to the structural cell defined by the three shortest non-coplanar identity periods in the lattice.

We were fortunate in obtaining from the Royal Ontario Museum a well-crystallized specimen (ROM 14699) from the locality of Island

TABLE 1. ROEMERITE: OPTICAL OBSERVATIONS

	1	2	3
α	1.524	1.519	1.520
β	1.571	1.570	1.578
γ	1.583	1.580	
	} ± 0.003		} ± 0.002

1. Atacama, Chile (Larsen, 1921). 2. Tierra Amarilla, Chile (Larsen, 1921). 3. Island Mountain, California (this paper).

¹Extracted from a thesis for the M.A. degree, University of Toronto.

Mountain, Trinity County, California. This specimen is composed of massive, clove-brown roemerite, with well-developed crystal faces on the free surface. The identity of the material was checked by a determination of the major indices of refraction using immersion oils. Table 1 shows that the optical constants agree reasonably well with corresponding published data on roemerite from other localities.

MORPHOLOGY

Several of the best-formed crystals were selected for examination on the Goldschmidt two-circle goniometer. The material had probably undergone slight re-resolution at some time. This was evidenced by occasional rounding of crystal faces, hopper development and oriented pits and etch surfaces in some of the crystals. Perhaps because of this no single clear reflections could be obtained from the faces, but rather multiple or blurred images. Nevertheless, the most prominent zone was easily recognized as Wolfe's $c[001]$ crystallographic axis, and used as the rotation axis on the goniometer. The morphological elements determined here are not so highly accurate as might be desired, because of the quality of the crystals, but the agreement between the angles measured on the best crystal and Wolfe's calculated angles (Table 2) shows that the morphology of the study crystal was correctly interpreted in terms of Wolfe's setting. A drawing of this crystal is shown in Fig. 1 while a drawing of the simpler and more common habit is shown in Fig. 2.

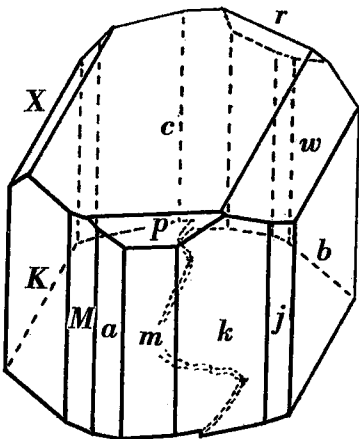


FIG. 1

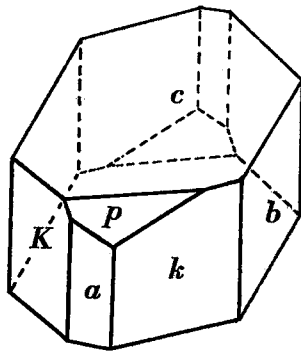


FIG. 2

- FIG. 1. Roemerite-Drawing of crystal showing all forms observed.
 FIG. 2. Roemerite from Island Mountain, California. Drawing of crystal showing most common habit.

The form $b\{010\}$ was best developed of all in every crystal studied. The form $c\{001\}$ was large in every case, but rather poorly developed, and invariably gave blurred reflections. The form $m\{110\}$ gave the next best reflections after $\{010\}$, but the remaining forms were all poorly developed.

X-RAY MEASUREMENTS

Because of the greater simplicity in orienting the crystal in the various positions necessary for obtaining the structural elements, the precession method of M. J. Buerger was employed in examining roemerite. Initial orientation was carried out on the two-circle goniometer and then x -ray photographs were obtained of the three zero-level reciprocal planes normal to Wolfe's crystallographic axes. Table 3 gives the reciprocal elements provided by the films, together with the calculated direct cell elements in Wolfe's setting.

TABLE 2. ROEMERITE:
MEASURED AND CALCULATED ANGLES

Form	This paper (meas.)		Wolfe ¹ (calc.)	
	ϕ	ρ	ϕ	ρ
$c(001)$	88° 00'	11° 25'	87° 24½'	10° 30'
$b(010)$	0 00	90 00	0 00	90 00
$a(100)$	95 40	[90 00]	94 19½	90 00
$j(130)$	40 40	"	40 29	90 00
$k(120)$	51 40	"	52 55	90 00
$m(110)$	72 16	"	71 13	90 00
$M(\bar{1}\bar{1}0)$	117 32	"	116 10	90 00
$K(1\bar{2}0)$	132 47	"	132 12½	90 00
$w(011)$	24 40	24 05	23 26½	24 57½
$X(0\bar{2}1)$	165 38	42 12	167 24½	40 24½
$p(111)$	73 52	50 35	73 36	51 11
$r(\bar{1}\bar{1}1)$	-56 43	46 37	-58 31½	43 56½

$$^1a:b:c = 0.4214:1:0.4174, \alpha 91^\circ 17', \beta 100^\circ 30', \gamma 85^\circ 31'$$

TABLE 3. ROEMERITE:
DIRECT AND RECIPROCAL CELL ELEMENTS

Reciprocal elements		Direct elements	
a^*	0.1576	a	6.48 Å
b^*	0.066	b	15.26
c^*	0.1624	c	6.27
α^*	90° 48'	α	90° 04'
β^*	79 12	β	100 48
γ^*	94 36	γ	85 28

The direct elements fit the convention of the normal setting (Peacock, 1937) whereby the cell is defined by the three shortest non-coplanar identity periods in the lattice, $c[001]$ is the axis of the main zone of the crystal and a is less than b . Table 4 compares the structural axial ratios with the morphological ratios of Wolfe and those derived in this study from measurements of Island Mountain roemerite. On the whole, the structural elements are in somewhat better agreement with Wolfe's values than are the new morphological elements. This is probably, as mentioned earlier, a result of the quality of the crystals studied.

TABLE 4. ROEMERITE: COMPARISON OF AXIAL RATIOS

	1	2	3
$a : b : c =$	0.424 : 1 : 0.410	0.4452:1:0.4211	0.4214 : 1 : 0.4174
α	90° 04'	91° 32'	91° 17'
β	100 48	100 34	100 30
γ	85 28	84 14	85 31

1. Structural cell; this paper. 2. Morphological cell; this paper.
3. Morphological cell; Wolfe.

It is clear from the present study that roemerite represents another case where the morphological development is a clear expression of the conventional structural cell.

The morphology of roemerite gives every indication of the presence of a centre of symmetry, and therefore roemerite is placed in the space group $P\bar{1}$. Table 5 gives the usual powder data for the mineral.

TABLE 5. ROEMERITE:
X-RAY POWDER DATA;
Fe/Mn Radiation, $K\alpha = 1.9373 \text{ \AA}$

I	d (meas.)	I	d (meas.)	I	d (meas.)
$\frac{1}{2}$	7.94Å	$\frac{1}{2}$	3.26Å	3	2.38Å
$\frac{3}{2}$	6.33	2	3.16	$\frac{1}{2}$	2.21
5	5.05	1	3.04	$\frac{3}{2}$	2.11
10	4.79	$\frac{1}{2}$	2.94	1	1.990
1	4.22	1	2.84	2	1.907
9	4.03	2	2.62	1	1.812
1	3.66	1	2.55	$\frac{1}{2}$	1.740

COMPOSITION AND CELL CONTENTS

Table 6 gives a representative number of published analyses of roemerite together with the cell contents calculated with the aid of the relationship $MW \times Z = V \times G / 1.66$, where G is 2.18, the average of two specific gravity determinations—2.174 (Tschermak in Grailich, 1858) and

2.185 (Buehrer in Lausen, 1928). The ferric iron and SO_3 contents are fairly consistent in all the analyses and closely approximate 2 and 4 respectively. The divalent metal content and water, however, are much less constant. Zinc apparently substitutes for ferrous iron in roemerite from the Harz. The sum $\text{Fe}'' + \text{Zn}$ is very close to 1 in four of the six analyses. The water content varies from 12.55 to 14.93 molecules but is close to 14 in four analyses. The calculations confirm the generally accepted composition and indicate that the cell contents are

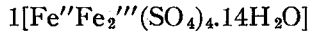


TABLE 6. ROEMERITE: SELECTED ANALYSES AND CELL CONTENTS
Cell Volume = 608.8 \AA^3

	1	2	3	4	5	6	7
FeO	6.26	5.80	8.71	6.94	7.01	8.78	8.94
ZnO	1.97	3.06					
MgO		0.25				0.14	
CaO	0.58					0.62	
Na ₂ O					0.88		
Fe ₂ O ₃	20.63	19.77	20.11	20.60	20.84	19.55	19.86
Al ₂ O ₃					2.55	1.45	
SO ₃	41.54	39.71	39.79	38.30	39.34	38.40	39.83
H ₂ O	28.00	31.17	30.99	33.40	31.33	30.98	31.37
TOTAL	98.98	99.76	99.60	99.24	101.95	99.92	100.00
Fe''	0.71	0.65	0.97	0.78	0.77	0.98	} 1
Zn	0.20	0.30					
Mg		0.05				0.03	
Ca	0.08					0.14	
Na					0.22		
Fe'''	2.08	1.98	2.02	2.08	2.04	1.96	} 2
Al					0.38	0.22	
SO ₃	4.20	3.99	3.98	3.85	3.85	3.84	4
R''	0.99	1.00	0.97	0.78	0.88	1.15	1
R'''	2.08	1.98	2.02	2.08	2.42	2.18	2
H ₂ O	12.55	13.83	13.81	14.93	13.64	13.76	14

1. Rammelsberg, Harz; anal. Tschermak, in Grailich (1858)
2. Rammelsberg, Harz; anal. Scharizer (1903)
3. Tierra Amarilla, Chile; anal. Scharizer (1903)
4. Island Mountain, California; Landon (1927)
5. United Verde Mine, Jerome, Arizona; anal. Buehrer in Lausen (1928)
6. Pfaffenreuth, Bavaria; anal. Gossner and Drexler, (1935)
7. $\text{Fe}''\text{Fe}_2'''\text{(SO}_4)_4\cdot 14\text{H}_2\text{O}$ and ideal cell contents.

ASSOCIATED MINERALS

Two other distinct minerals were observed on the specimen of roemerite. Copiapite, $\text{Fe}''(\text{OH})_2\text{Fe}_4'''\text{(SO}_4)_6\cdot 20\text{H}_2\text{O}$, was present as very tiny, equant crystals and masses of a lemon-yellow to yellow-green

mineral scattered over the surface. Kornelite, $\text{Fe}_2'''(\text{SO}_4)_3 \cdot 7\text{H}_2\text{O}$, occurs as an extensive alteration over the surface of the roemerite. It is an earthy, finely pulverulent mineral with a pale cream-brown colour. Pyrrhotite is associated with the roemerite, and in fact, many of the roemerite crystals contain inclusions of this sulphide. At Island Mountain, the roemerite has formed by the alteration of pyrrhotite.

THE RE-ORIENTATION OF OBLIQUE CELLS

Many crystallographers, among them Peacock (1937) and Buerger (1942), have pointed out that with a right-handed co-ordinate system, there are twenty-four ways of orienting an oblique cell. Yet nowhere in the literature are the possible combinations of the elements presented in a simple form. We have prepared a tabulation of these combinations as an aid in examining various orientations of wire models representing triclinic cells. The data, in the form of two tables, have proved useful in this laboratory, and it is hoped, will aid others in the problem of re-orienting triclinic cells.

Oblique cells may be classified into two types on the basis of whether two of the solid angles have 1) three obtuse or 2) three acute plane (interaxial) angles. The cells are respectively obtuse or acute parallelepipeds (Balashov, 1956). In the first case the remaining six solid angles each consist of two acute and one obtuse plane angles, and in the second

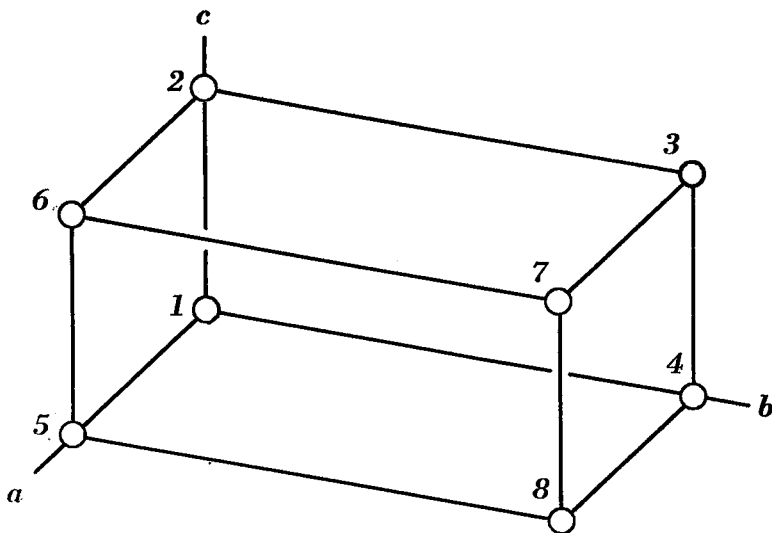


FIG. 3. Triclinic unit cell, key to tables 7 and 8.

case, one acute and two obtuse plane angles. Two tables, covering the twenty-four orientations for the two types of cells are presented.

Most crystallographers choose a setting in which α and β are taken obtuse (for example the normal setting of Peacock). Thus if γ is obtuse, the cell is an obtuse parallelepiped, and if acute, an acute parallelepiped. The orientation $c < a < b$ is most popular, and this condition, together with α and β obtuse heads the list in each table. The numbers 1, 2, etc. refer to the corners of the cell according to the scheme of Fig. 3. When each of these is in the origin position (lower rear left-hand corner of cell), the three possible arrangements of its interaxial angles and axes are indicated by the letters A, B and C after the number. Axes are written in ascending order of magnitude. Thus $c a b$ signifies $c < a < b$.

To place a cell into the conventional orientation (α, β obtuse, $c < a < b$), locate first the existing orientation in the tables. For example the elements

$$\begin{array}{ll} a & 6.48 & \alpha & 89^\circ 56' \\ b & 15.26 & \beta & 100 \ 48 \\ c & 6.27 & \gamma & 94 \ 32 \end{array}$$

TABLE 7. THE TWENTY-FOUR ORIENTATIONS OF ACUTE PARALLELEPIPEDS

Corner	α	β	γ	Axes
1 A	Obtuse	Obtuse	Acute	c a b
B	A	O	O	a b c
C	O	A	O	b c a
2 A	A	A	A	b a c
B	A	A	A	c b a
C	A	A	A	a c b
3 A	O	O	A	a b c
B	A	O	O	b c a
C	O	A	O	c a b
4 A	A	O	O	b a c
B	O	A	O	c b a
C	O	O	A	a c b
5 A	O	A	O	a c b
B	O	O	A	b a c
C	A	O	O	c b a
6 A	O	O	A	b c a
B	A	O	O	c a b
C	O	A	O	a b c
7 A	A	O	O	a c b
B	O	O	A	c b a
C	O	A	O	b a c
8 A	A	A	A	c a b
B	A	A	A	a b c
C	A	A	A	b c a

TABLE 8. THE TWENTY-FOUR ORIENTATIONS OF OBTUSE PARALLELEPIPEDS

Corner	α	β	γ	Axes (ascending order of magnitude)
1 A	O	O	O	c a b
B	O	O	O	b c a
C	O	O	O	a b c
2 A	A	O	A	b a c
B	A	A	O	c b a
C	O	A	A	a c b
3 A	A	O	A	a b c
B	O	A	A	c a b
C	A	A	O	b c a
4 A	A	A	O	b a c
B	O	A	A	c b a
C	A	O	A	a c b
5 A	A	O	A	c b a
B	A	A	O	a c b
C	O	A	A	b a c
6 A	A	O	A	c a b
B	O	A	A	b c a
C	A	A	O	a b c
7 A	O	O	O	c b a
B	O	O	O	a c b
C	O	O	O	b a c
8 A	A	O	A	b c a
B	A	A	O	c a b
C	O	A	A	a b c

fit condition 6B in Table 7. The corner which marks the origin in this orientation is now moved to the number 6 position (Fig. 3), and maintained here while the cell is rotated until the longest axis is left and right. The cell is then in the conventional orientation (1A) and in our example the elements become

$$\begin{array}{ll}
 a & 6.48 & \alpha & 90^{\circ} 04' \\
 b & 15.26 & \beta & 100 48 \\
 c & 6.27 & \gamma & 85 28
 \end{array}$$

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