THE AMERICAN MINERALOGIST

JOURNAL OF THE MINERALOGICAL SOCIETY OF AMERICA

Vol. 56 MAY–JUNE Nos. 5 and 6

THE CRYSTAL STRUCTURE OF BUTLERITE

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ABSTRACT

The mineral butlerite is one of the two naturally occurring polymorphic modifications of the sulfate $Fe[SO_4](OH) \cdot 2H_2O$. Butlerite is monoclinic, space group $P2_1/m$. The cell dimensions are $a = 6.50(1)$ Å, $b = 7.37(1)$ Å, $c = 5.84(1)$ Å, $\beta = 108°23'(5')$. The reflection intensities were collected on a Weissenberg apparatus from $0kl$ to $4kl$ reciprocal lattice layers. The crystal structure was determined by interpretation of the Patterson function and refined to an R value 0.12 by least squares method. The atomic arrangement of butlerite consists of $[Fe(H_2O)_2(OH)_2O_2]$ coordination octahedra at inversion centers connected by opposite OH groups to form an infinite chain along the b axis. The SO_4 tetrahedra are in the chain too, making O–S–O bridges between two adjacent octahedra. The average Fe–O and S–O distances are 2.01 Å and 1.44 Å respectively. Connections between different chains occur through hydrogen bonds.

The atomic arrangement of butlerite is compared with that occurring in parabutlerite which represents the orthorhombic modification of $Fe[SO_4](OH) \cdot 2H_2O$.

INTRODUCTION

The structural determination of the mineral butlerite is a part of a crystallochemical study on iron sulfates undertaken in our laboratory: the present results follow those reported by the authors (1970) for roemerite; the crystal structure of copiapite is at present under investigation. Butlerite occurs in nature as monoclinic modification of the sulfate $Fe[SO_4](OH) \cdot 2H_2O$. A second modification, orthorhombic, is represented by parabutlerite. The two minerals are often found together as weathering products of more hydrated iron sulfates, resulting from the oxidation of pyritic ores.

Butlerite was first found at United Verde Mine, Jerome, Arizona, by Lausen (1928) who assigned it to the orthorhombic system. Later Bandy (1938) in his work on iron sulfates from Northern Chile, described the crystals as triclinic pseudoorthorhombic and twinned according to (100) in Lausen orientation. Gordon (1941) studied the morphology of butlerite from Argentina, assigned the mineral to the monoclinic system, and gave values for the axial ratios. Thermal and diffractometric data were reported by Cesbron (1964) who determined the possible space groups and the lattice parameters: butlerite crystallizes in the space group $P2_1/m$ or $P2_1$, and its cell dimensions are $a=6.44$ Å, $b=7.31$ Å, $c=5.87$ Å, $\beta=108°28'$.

EXPERIMENTAL

Some crystals of a sample of butlerite from the type locality of Jerome (Arizona), kindly supplied by Prof. P. B. Moore, were investigated with a Weissenberg apparatus. Because of the impossibility of selecting a single crystal, a fragment with polygonal irregular section elongated along the *a* axis, with dimensions 0.3×0.09×0.03 mm, was employed for collecting data. Twinning according to (101) was detected on the photographs. However it was possible to choose the points of the reciprocal lattice belonging to a single individual. Three-dimensional data from 0*kl* to 4*kl* were collected employing Cu Kα radiation. A total of 366 independent reflexions with intensity above the limit of observation were measured with the aid of a microdensitometer. Lorentz-polarization geometrical factors were introduced in the elaboration of data. Absorption correction for $\mu=265.7$ cm^{-1} was applied by means of a program written by De Meulenaer and Tompa (1965). The unit-cell constants of butlerite, redetermined from basal Weissenberg photographs, are $a=6.50\pm0.01$ Å, $b=7.37\pm0.01$ Å, $c=5.84\pm0.01$ Å, $\beta=108°23'\pm5'$. These values are in good agreement with those reported by Cesbron. The density calculated for two formula units per cell is 2.53 g.cm^{-3}, in agreement with the measured value 2.55 g.cm^{-3}. The space group $P2_1/m$, assumed at the beginning of this study, was confirmed by the structural analysis.

STRUCTURE DETERMINATION AND REFINEMENT

According to the cell content and the space group symmetry, both iron and sulfur atoms must occupy special positions in the cell. From a three-dimensional Patterson synthesis it was possible to locate iron ions at the inversion centers 0, 0, 0 and 0, $\frac{1}{2}$, 0 and sulfur atoms on mirror planes at $\frac{1}{4}$ and $\frac{3}{4}$ *b*. Crystallochemical considerations and interpretation of the Patterson map led us to locate all the non-hydrogen atoms in the structure. Atomic coordinates were then refined by successive electron density maps to an *R* value (defined as $R=\Sigma||Fo|-|Fc||/\Sigma|Fo|$) of 0.19.

The further refinement of the structure was carried out by means of the least-squares method. A block-diagonal program written by Albano, Bellon, Pompa, and Scatturin (1963) for the IBM 1620 computer was employed; positional parameters and individual isotropic temperature coefficients were varied. Reflections were given weights according to the following scheme: $\sqrt{w}=1$ for reflections with $Fo\leq4F$ min.; $\sqrt{w}=4F$ min.$/Fo$ for $Fo>4F$ min.; unobserved reflections were excluded from the calculations. After five cycles, when the *R* index was 0.12, the refinement was stopped. No attempt to locate hydrogen atoms was made. Observed and calculated structure factors are listed in Table 1.[1] The atomic scattering factors given by Cromer and Waber (1965) for Fe^{3+}, S, and O were used.

DISCUSSION OF THE STRUCTURE

The clinographic view of the structure of butlerite is shown in Figure 1. Table 2 gives the atomic coordinates with their standard deviations in

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[1] To obtain a copy of Table 1, listing observed and calculated structure factors of butlerite, order NAPS Document 01380 from National Auxiliary Publications Service of the A.S.I.S., c/o CCM Information Corporation, 909 Third Avenue, New York, New York 10022; remitting $3.00 for microfiche or $5.00 for photocopies, in advance payable to CCMIC-NAPS.

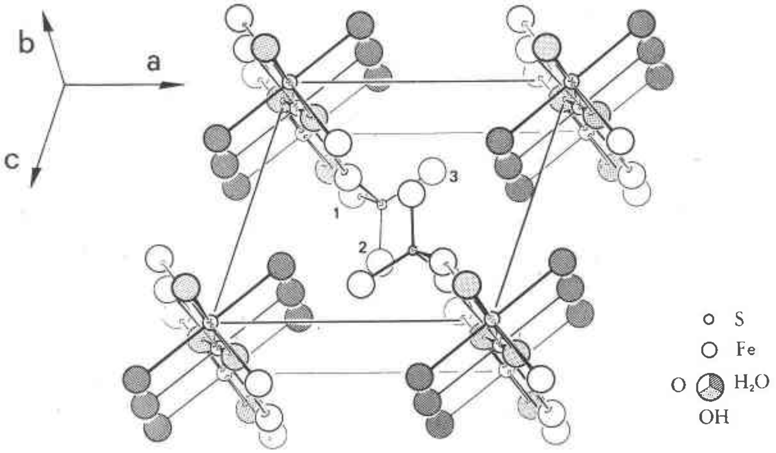

FIG. 1. Clinographic view of the structure of butlerite.

parentheses and the isotropic thermal parameters. Interatomic distances and angles are listed in Tables 3a and 3b respectively.

Ferric ion at the origin of the cell is octahedrally surrounded by two water molecules, two hydroxyl groups, and two oxygen atoms belonging to two different SO_4 groups. Fe–O distances involving water molecules are significantly longer (2.09 Å) than those connecting the cation to the oxygen atoms of SO_4 tetrahedra and the hydroxyl groups (both: 1.97 Å). The mean value of Fe–O distances, 2.01 Å, can be compared with that reported by Süsse (1968) for amarantite and by the authors (1970) for roemerite (respectively: 2.02 and 2.00 Å).

The SO_4 coordination polyhedra exhibit the usual tetrahedral shape with mean S–O distance 1.44 Å and regular angles. Concerning the S–O distances in butlerite, as in many other sulfates, it is observed that dis-

TABLE 2. FRACTIONAL ATOMIC COORDINATES WITH THEIR STANDARD DEVIATIONS IN PARENTHESES AND ISOTROPIC TEMPERATURE FACTORS.

Atom	x	y	z	B(Å^2)
Fe	0	0	0	0.95
S	0.3809 (12)	$\frac{1}{4}$	0.3530 (10)	1.12
O(1)	0.2476 (22)	0.0885 (16)	.2697 (19)	1.63
O(2)	0.4559 (32)	$\frac{1}{4}$	.6098 (29)	1.71
O(3)	0.5587 (42)	$\frac{1}{4}$	.2630 (39)	3.53
OH	0.1023 (32)	$\frac{3}{4}$	.0886 (28)	1.51
H_2O	0.1844 (25)	0.0133 (21)	.7647 (24)	2.95

TABLE 3. SELECTED INTERATOMIC DISTANCES AND ANGLES.

(I)	x, y, z	(IV)	$-x, -y, 1-z$
(II)	$-x, 1-y, -z$	(V)	$1-x, 1-y, 1-z$
(III)	$x, y, z-1$	(VI)	$x, \frac{1}{2}-y, z$

a) Bond lengths with their standard deviations		
Fe(I)	-O(1)(I)	1.97±0.01 Å ×2
	-OH(II)	1.97±0.01 ×2
	-H_2O(III)	2.09±0.01 ×2
S(I)	-O(1)(I)	1.46±0.01 Å ×2
	-O(2)(I)	1.42±0.02
	-O(3)(I)	1.41±0.03
H_2O(I)	-O(2)(I)	2.83±0.02 Å
	-O(3)(IV)	2.60±0.02
OH(I)	-O(2)(V)	2.86±0.03
b) Bond angles with their standard deviations		
O(1)(I)–Fe(I)	-OH(II)	91.3±0.6°
	-H_2O(III)	91.0±0.5°
OH(II)–Fe(I)	-H_2O(III)	90.0±0.7°
O(1)(I)–S(I)	-O(1)(VI)	109.0±0.8°
	-O(2)(I)	108.7±0.6°
	-O(3)(I)	110.2±0.7°
O(2)(I)–S(I)	-O(3)(I)	110.1±1.3°
O(2)(I)–H_2O(I)–O(3)(IV)		87.9±0.7°

tances between sulfur and oxygen atoms linked to the cation are significantly longer than those involving sulfur and unbonded oxygen atoms. This can be ascribed to a decrease of effective negative charge on oxygen atoms coordinated by the cations, which causes a lower coordinative π-effect. The water molecule in the unit-cell is distant 2.83 Å and 2.60 Å from two oxygen atoms of two different SO_4 groups, with an angle O–O(w)–O of 87°51′. These two distances have been ascribed to hydrogen bonds. Another hydrogen bond (2.86 Å long) connects the oxygen atom of the hydroxyl group with O(2). As in roemerite, only the oxygen atoms belonging to the sulfate group, and not coordinated to the ferric ion, function as proton acceptors in the system of hydrogen bonds. Table 4

TABLE 4. BALANCE OF ELECTROSTATIC VALENCES FOR OXYGEN ATOMS.

	Fe^{3+}	S	–H··	··H–	TOTAL
O(1)	$\frac{1}{2}$	$\frac{3}{2}$			2
O(2)		$\frac{3}{2}$		$3\times\frac{1}{4}$	$2+\frac{1}{4}$
O(3)		$\frac{3}{2}$		$2\times\frac{1}{4}$	2
O(h)	$2\times\frac{1}{2}$		$\frac{3}{4}$		$2-\frac{1}{4}$
O(w)	$\frac{1}{2}$		$2\times\frac{3}{4}$		2

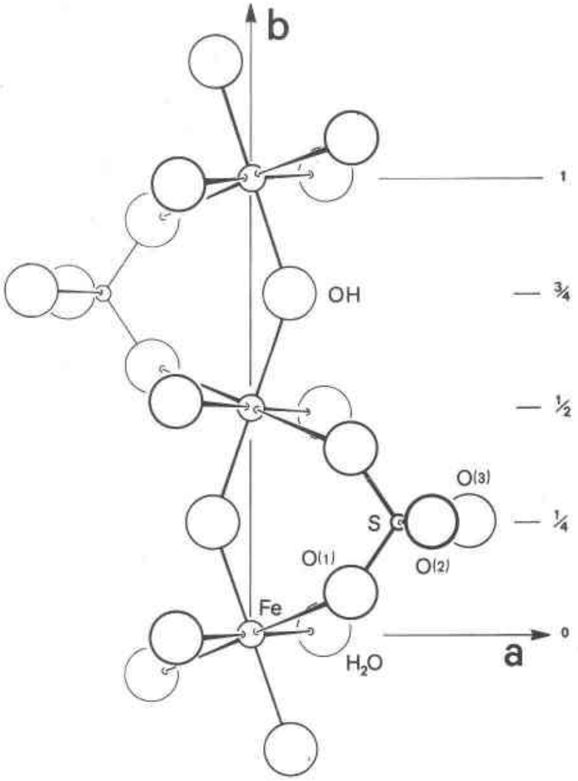

FIG. 2. Projection of a single chain on *ab* plane.

shows a scheme of balance of electrostatic valences for oxygen atoms in butlerite derived on the assumption that each hydrogen contribution is distributed between two oxygen atoms as $+\frac{3}{4}$ for the bonded one and $+\frac{1}{4}$ for the unbonded atom.

Coordination octahedra around the iron ions share opposite vertices through the hydroxyl groups; furthermore, two adjacent octahedra are linked by SO_4 tetrahedra. The resulting chain, running along the *b* axis, is sketched in Figure 2. The crystal structure of butlerite may be described as built up by these chains; each chain is connected to the six nearest chains by hydrogen bonds to form a three-dimensional framework.

RELATIONSHIP TO PARABUTLERITE

When this study on butlerite was nearly completed, the crystal structure of parabutlerite was published by J. Borène (1970). Close analogies may be observed in the cell dimensions of the two modifications. The *B*-centered non-primitive cell of butlerite built on the diagonals in the *ac* plane is approximately orthorhombic with the following parameters: $a'=10.01$ Å, $b=7.37$ Å, $c'=7.24$ Å, $\beta=96°28'$. These values are comparable with those of parabutlerite by doubling a' and changing suitably the symbols of the axes. In fact, the lattice parameters of parabutlerite determined by Cesbron (1964) and assumed for his investigation by Borène are: $a=7.38$ Å, $b=20.13$ Å, $c=7.22$ Å. The symmetry group is *Pmnb*. The unit-cell vectors of parabutlerite expressed in terms of those of butlerite are represented by the following square matrix $(010/\bar{2}02/101)$.

There are remarkable similarities in the atomic arrangement of the two minerals corresponding to the analogies observed in the cell parameters.

Coordination octahedra in parabutlerite exhibit the same configuration as in butlerite. In both structures the Fe–H_2O distances are significantly longer than the other mean Fe–O distances in the octahedron (2.06 Å against 1.97 Å in parabutlerite; 2.09 Å against 1.97 Å in butlerite).

Each octahedron shares two opposite hydroxyl groups with the neighboring octahedra. Additional connections between adjacent octahedra occur through SO_4 tetrahedra. The resulting structural motif of parabutlerite consists of chains of the same kind as in the monoclinic polymorph running along the *a* axis (corresponding to *b* in butlerite). Distances between one chain and the six nearest analogous chains surrounding it, represented by Fe–Fe distances in the plane (100), are only slightly different from those occurring in butlerite. The two distances of 7.22 Å along the *c* axis correspond to the two distances of 7.24 Å in butlerite directed along the short diagonal in the *ac* plane, while the four closer distances (5.88 Å, 6.20 Å (×2), 6.52 Å) may be compared with the values of Fe–Fe separations along *a* and *c* axes in butlerite, 5.84 Å (×2) and 6.50 Å (×2).

The essential difference in the two structures consists in the reciprocal array of these chains. In parabutlerite we may consider that half of them are shifted a $\frac{1}{2}$ period along the *a* axis. It follows that, while in butlerite each Fe-octahedron has the four closest Fe-octahedra of the four nearest chains showing its own orientation, in parabutlerite only two Fe-octahedra exhibit the same orientation in contrast to the other two which exhibit a mirror orientation with respect to a plane parallel to (100). Notwithstanding the different array of the chains, the system of hydrogen bonds connecting a chain to the six nearest chains remains practically unchanged. As it was pointed out by Borène, the crystal structures of butlerite and parabutlerite are closely related to that determined by Johansson (1961) for $In[SO_4](OH)\cdot 2H_2O$, space group $P2_1/m$, $a=6.05$,

$b = 7.89$, $c = 12.66$ Å, $\beta = 107.5°$. In this compound, with unit cell volume doubled in respect of that of butlerite, there are two nearly identical types of chains built by corner-sharing $In(H_2O)_2(OH)_2O_2$ octahedra running parallel to the b axis and lying at $\frac{1}{2}$ c from each other. The resulting arrangement is very similar to that in butlerite.

ACKNOWLEDGMENT

This study was supported by the Italian Consiglio Nazionale delle Ricerche.

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Manuscript received, July 31, 1970; accepted for publication, November 4, 1970.