Redetermination of despujolsite, $Ca_3Mn^{4+}(SO_4)_2(OH)_6 \cdot 3H_2O$

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The crystal structure of despujolsite [tricalcium manganese bis(sulfate) hexahydroxide trihydrate], the Ca/Mn member of the fleischerite group, ideally $Ca_3Mn^{4+}(SO_4)_2(OH)_6 \cdot 3H_2O$, was previously determined based on X-ray diffraction intensity data from photographs, without H-atom positions located [Gaudefroy *et al.* (1968). *Bull. Soc. Fr. Minéral. Crystallogr.* **91**, 43–50]. The current study redetermines the structure of despujolsite from a natural specimen, with all H atoms located and with higher precision. The structure of despujolsite is characterized by layers of CaO_8 polyhedra (*m..* symmetry) interconnected by $Mn(OH)_6$ octahedra (32. symmetry) and SO_4 tetrahedra (3.. symmetry) along [001]. The average Ca—O, Mn—O and S—O bond lengths are 2.489, 1.915, and 1.472 Å, respectively. There are two distinct hydrogen bonds that stabilize the structural set-up. This work represents the first description of hydrogen bonds in the fleischerite group of minerals.

Related literature

For the previous determination of the despujolsite crystal structure, see: Gaudefroy *et al.* (1968). For background to fleischerite, see: Otto (1975). For the crystal structures of sulfate minerals with split O sites, see: Hill (1977); Jacobsen *et al.* (1998). For TLS (translation, libration, and screw motions) rigid-body analysis, see: Downs (2000). Parameters for bond-valence analysis were taken from Brese & O'Keeffe (1991).

Experimental

Crystal data

$Ca_3Mn(SO_4)_2(OH)_6 \cdot 3H_2O$	c = 10.8094 (9) Å
M_r = 523.40	V = 682.81 (8) Å^3
Hexagonal, $P\bar{6}2c$	Z = 2
a = 8.5405 (5) Å	Mo $K\alpha$ radiation

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μ = 2.49 mm^{-1}
T = 293 K

$0.07 \times 0.06 \times 0.04$ mm

Data collection

Bruker APEXII CCD area-detector diffractometer	6018 measured reflections
	871 independent reflections
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2008*a*)	758 reflections with $I > 2\sigma(I)$
T_{min} = 0.845, T_{max} = 0.907	R_{int} = 0.051

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.024	$\Delta\rho_{max}$ = 0.45 e Å^{-3}
$wR(F^2)$ = 0.048	$\Delta\rho_{min}$ = -0.30 e Å^{-3}
S = 1.06	Absolute structure: Flack (1983), 305 Friedel pairs
871 reflections	Flack parameter: 0.0 (9)
49 parameters	
All H-atom paramters refined	

Table 1
Selected bond lengths (Å).

Mn—O*H3*^{i}	1.9149 (11)	Ca—O*W4*	2.578 (9)
Ca—O2^{ii}	2.3465 (11)	Ca—O*W4*^{iv}	2.690 (9)
Ca—O*H3*^{i}	2.456 (5)	S—O2	1.4697 (11)
Ca—O*H3*^{iii}	2.518 (5)	S—O1	1.4806 (18)

Symmetry codes: (i) $-x + y + 1, -x + 1, z$; (ii) $x, y, -z + \frac{1}{2}$; (iii) $x - 1, y, -z + \frac{1}{2}$; (iv) $-x + y, -x + 1, z$.

Table 2
Hydrogen-bond geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O*H3*—H1$\cdots$O2^v	0.75 (2)	2.11 (2)	2.8193 (16)	158 (3)
O*W4*—H2$\cdots$O1^{vi}	0.77 (2)	2.10 (2)	2.7892 (18)	150 (3)

Symmetry codes: (v) $-x + 1, -x + y, -z$; (vi) $y, x, -z$.

Data collection: *APEX2* (Bruker, 2003); cell refinement: *SAINT* (Bruker, 2005); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008*b*); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008*b*); molecular graphics: *XtalDraw* (Downs & Hall-Wallace, 2003); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008*b*).

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supporting information

Redetermination of despujolsite, $Ca_3Mn^{4+}(SO_4)_2(OH)_6\cdot 3H_2O$

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S1. Comment

Despujolsite, ideally $Ca_3Mn^{4+}(SO_4)_2(OH)_6\cdot 3H_2O$, is a member of the fleischerite group of minerals, which includes fleischerite, $Pb_3Ge(SO_4)_2(OH)_6\cdot 3H_2O$, mallestigite, $Pb_3Sb(SO_4)(AsO_4)(OH)_6\cdot 3H_2O$, and schauerteite, $Ca_3Ge^{4+}(SO_4)_2(OH)_6\cdot 3H_2O$. Thus far, only the structures of despujolsite and fleischerite (from a synthetic sample with the O1 site split) in this group have been determined (Gaudefroy *et al.*, 1968; Otto, 1975), both of which were based on X-ray diffraction intensity data measured from photographs, without H atom positions located. An *R*-factor of 0.162 was obtained for the structure model of despujolsite (Gaudefroy *et al.*, 1968). In our efforts to understand hydrogen bonding environments in general and the relationships in the hydrogen bonding schemes in the minerals of the fleischerite group in particular, we noted that the structural information of despujolsite needed to be improved.

The structure of despujolsite consists of layers of CaO_8 polyhedra (*m*.. symmetry), interconnected by $Mn(OH)_6$ octahedra (32. symmetry) and SO_4 tetrahedra (3.. symmetry). The average Mn—O bond length is 1.915 Å (Table 1). Calculations of bond-valence sums using the parameters from Brese & O′Keeffe (1991) yield 3.86 (v.u.) for Mn, indicating that the assigned valence of 4+ for Mn is consistent with the structure. The average S—O bond length is 1.472 Å. Ca atoms are eight coordinated with 4 (OH)⁻ ions, 2 H_2O molecules, and 2 O atoms. The average Ca—O bond length is 2.489 Å. There are two distinct hydrogen bonds: OH3—H1···O2 and OW4—H2··· O1 (Table 2).

The isostructural mineral fleischerite was previously modeled (Otto, 1975) with a split site for the O1 position. Similarly, studies of the sulfate mineral, barite $BaSO_4$, refined the O atoms that lie on special positions with a split atom model (Hill, 1977). However, Hill notes that there are no significant improvements in the refinement with a split-site model over the symmetry-constrained model. Further structure refinement with significantly better data by Jacobsen *et al.* (1998) led to a TLS (translation, libration, and screw motions) rigid body analysis (Downs, 2000) of the sulfate group. The results indicated that the SO_4 group behaves as a rigid body with significant translational and librational motions, demonstrating that the O atom sites are not split and that the large sizes of the displacement parameters are due entirely to thermal motion.

In contrast to the fleischerite study, our refinement of despujolsite did not indicate a split site. A TLS analysis of the displacement parameters indicate that the SO_4 group in despujolsite behaves likewise as a rigid body with a translational amplitude of 0.72 Å and a large libration angle of 7.95°. The libration angle for the SO_4 group in despujolsite, which is consistent with the 7°-8° range found in celestine, anglesite, and barite, indicates that the S–O bond lengths are ~0.009Å longer than their apparent values. If the libration angle is also large in fleischerite, then this may account for the effectiveness of splitting the O1 site, but our study indicates that the O1 site in fleischerite may not actually split.

S2. Experimental

The despujolsite specimen used in this study is from N′Chwaning III mine, Kalahari Manganese field, Northern Cape Province, South Africa and is in the collection of the RRUFF project (deposition No. R100208; http://rruff.info). The

composition was determined with a CAMECA SX100 electron microprobe (http://rruff.info) on a single-crystal from the same parent sample as the crystal used for the collection of X-ray diffraction intensity data. Electron microprobe analysis (15 points) with a 15 K eV accelerating voltage, 20 nA beam current, and a 5 μm beam size yielded an empirical chemical formula $Ca_{3.45}Mn^{4+}_{0.86}(S_{0.96}O_4)_2(OH)_6 \cdot 3H_2O$ (based on 11 O atoms). Because despujolsite crystals are not stable under the electron beam, which has also been observed by Gaudefroy *et al.* (1968), the electron microprobe data were used only for the estimation of cation ratios. The actual composition was determined by a combination of microprobe and X-ray structural analyses. Details of the sample chemistry and structural formula calculations can be found on the RRUFF Project website (http://rruff.info/R100208).

S3. Refinement

The H atoms were located from difference Fourier maps and their positions were refined with isotropic displacement parameters. The final refinement assumed an ideal chemistry, as the overall effects of the trace amount of Fe and Si on the final structure results are negligible. The highest residual peak in the difference Fourier maps was located 0.66 Å from O1, and the deepest hole was located 0.40 Å from Mn.

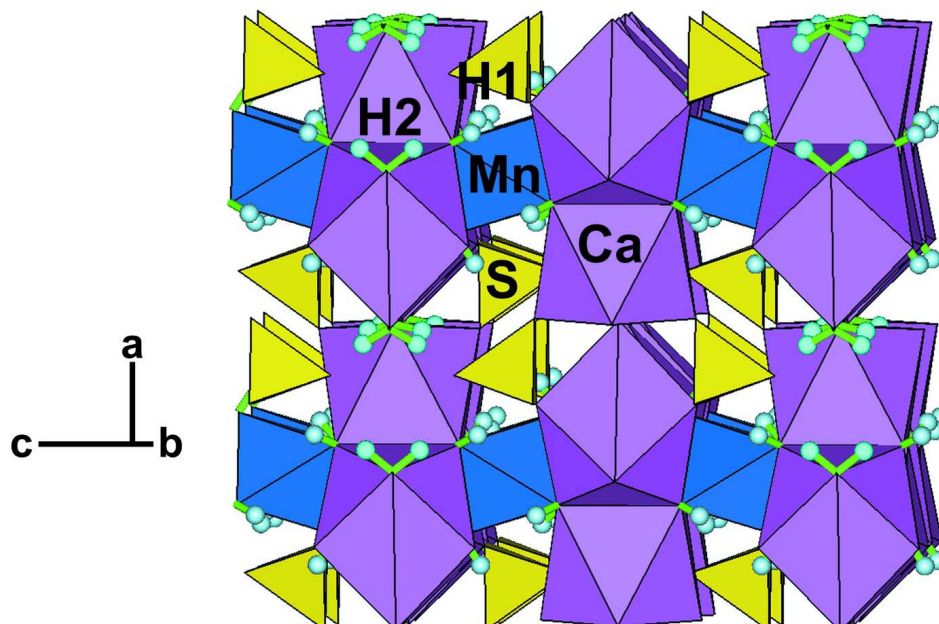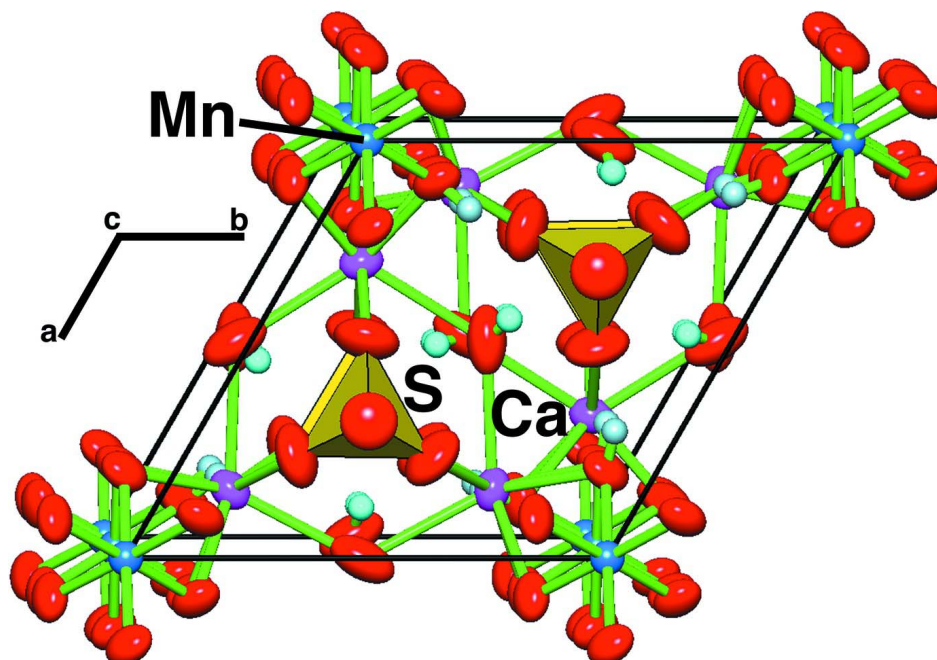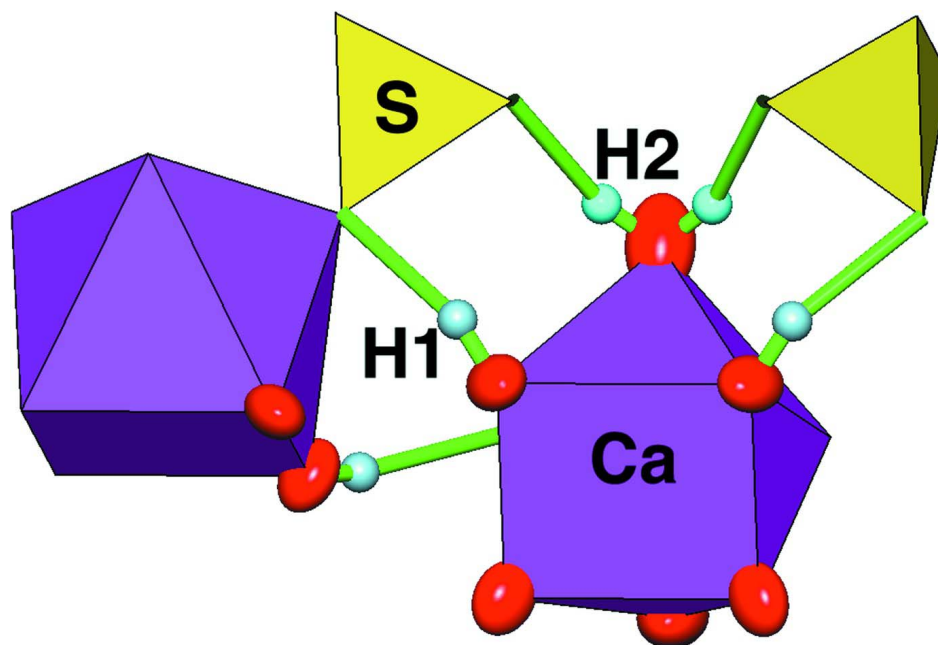**Figure 1**

The crystal structure of despujolsite. Yellow tetrahedra represent SO_4 groups. Blue octahedra and purple polyhedra represent $Mn(OH)_6$ groups and $Ca(O,OH,H_2O)_8$ groups, respectively. Light blue spheres represent H1 and H2.

Figure 2

Atoms in despujolsite with corresponding ellipsoids at 99% probability. SO$_4$ groups are treated as rigid bodies and shown as yellow tetrahedra. Blue, purple, and red ellipsoids represent Mn, Ca, and O atoms, respectively. Hydrogen atoms are shown as light-blue spheres.

Figure 3

H-bonding interactions in despujolsite. Yellow tetrahedra represent SO$_4$ groups. Purple polyhedra represent Ca(O,OH,H$_2$O)$_8$ groups. Red ellipsoids and blue spheres represent O and H atoms, respectively.

tricalcium manganese bis(sulfate) hexahydroxide trihydrate

Crystal data

$Ca_3Mn(SO_4)_2(OH)_6 \cdot 3H_2O$	$D_x = 2.546$ Mg m^{-3}
$M_r = 523.40$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hexagonal, $P\bar{6}2c$	Cell parameters from 1145 reflections
Hall symbol: P -6c -2c	$\theta = 2.8-32.0°$
$a = 8.5405$ (5) Å	$\mu = 2.49$ mm^{-1}
$c = 10.8094$ (9) Å	$T = 293$ K
$V = 682.81$ (8) Å^3	Euhedral, yellow
$Z = 2$	$0.07 \times 0.06 \times 0.04$ mm
$F(000) = 530$	

Data collection

Bruker APEXII CCD area-detector diffractometer	6018 measured reflections
Radiation source: fine-focus sealed tube	871 independent reflections
Graphite monochromator	758 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.051$
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2008a)	$\theta_{max} = 32.6°$, $\theta_{min} = 2.8°$
$T_{min} = 0.845$, $T_{max} = 0.907$	$h = -12 \rightarrow 11$
	$k = -12 \rightarrow 12$
	$l = -16 \rightarrow 15$

Refinement

Refinement on F^2	Hydrogen site location: difference Fourier map
Least-squares matrix: full	All H-atom parameters refined
$R[F^2 > 2\sigma(F^2)] = 0.024$	$w = 1/[\sigma^2(F_o^2) + (0.0113P)^2 + 0.2266P]$
$wR(F^2) = 0.048$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.06$	$(\Delta/\sigma)_{max} < 0.001$
871 reflections	$\Delta\rho_{max} = 0.45$ e Å^{-3}
49 parameters	$\Delta\rho_{min} = -0.30$ e Å^{-3}
0 restraints	Extinction correction: *SHELXL97* (Sheldrick, 2008), Fc*=kFc[1+0.001xFc$^2\lambda^3$/sin(2θ)]$^{-1/4}$
0 constraints	
Primary atom site location: structure-invariant direct methods	Extinction coefficient: 0.0142 (11)
Secondary atom site location: difference Fourier map	Absolute structure: Flack (1983), 305 Friedel pairs
	Absolute structure parameter: 0.0 (9)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}
Mn	0.0000	0.0000	0.0000	0.00846 (12)
Ca	0.1521 (3)	0.30348 (5)	0.2500	0.01085 (10)
S	0.3333	0.6667	0.02544 (5)	0.00936 (12)

O1	0.3333	0.6667	−0.11153 (15)	0.0167 (4)
O2	0.2419 (10)	0.47842 (15)	0.06891 (10)	0.0188 (3)
OH3	0.8945 (8)	0.0966 (8)	0.11070 (10)	0.0109 (3)
OW4	0.5006 (12)	0.4853 (12)	0.2500	0.0171 (5)
H1	0.836 (6)	0.125 (6)	0.076 (2)	0.026 (8)*
H2	0.521 (9)	0.445 (9)	0.193 (2)	0.046 (10)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Mn	0.00919 (15)	0.00919 (15)	0.0070 (2)	0.00460 (8)	0.000	0.000
Ca	0.0137 (10)	0.00918 (19)	0.00980 (16)	0.0058 (10)	0.000	0.000
S	0.01001 (16)	0.01001 (16)	0.0081 (2)	0.00501 (8)	0.000	0.000
O1	0.0213 (6)	0.0213 (6)	0.0075 (7)	0.0107 (3)	0.000	0.000
O2	0.027 (3)	0.0106 (5)	0.0170 (5)	0.008 (2)	0.004 (3)	0.0033 (4)
OH3	0.0084 (15)	0.0148 (19)	0.0107 (4)	0.0067 (6)	−0.0006 (16)	−0.0004 (16)
OW4	0.019 (2)	0.023 (2)	0.0136 (6)	0.0138 (12)	0.000	0.000

Geometric parameters (Å, º)

Mn—OH3[i]	1.9149 (11)	Ca—OH3[viii]	2.456 (5)
Mn—OH3[ii]	1.9149 (11)	Ca—OH3[iii]	2.518 (5)
Mn—OH3[iii]	1.9149 (11)	Ca—OH3[ix]	2.518 (5)
Mn—OH3[iv]	1.9149 (11)	Ca—OW4	2.578 (9)
Mn—OH3[v]	1.9149 (11)	Ca—OW4[x]	2.690 (9)
Mn—OH3[vi]	1.9149 (11)	S—O2[x]	1.4697 (11)
Ca—O2[vii]	2.3465 (11)	S—O2[xi]	1.4697 (11)
Ca—O2	2.3465 (11)	S—O2	1.4697 (11)
Ca—OH3[i]	2.456 (5)	S—O1	1.4806 (18)
OH3[i]—Mn—OH3[ii]	177.7 (4)	OH3[ii]—Mn—OH3[vi]	85.08 (5)
OH3[i]—Mn—OH3[iii]	85.08 (5)	OH3[iii]—Mn—OH3[vi]	96.5 (3)
OH3[ii]—Mn—OH3[iii]	93.4 (3)	OH3[iv]—Mn—OH3[vi]	177.7 (4)
OH3[i]—Mn—OH3[iv]	85.08 (5)	OH3[v]—Mn—OH3[vi]	85.08 (5)
OH3[ii]—Mn—OH3[iv]	96.5 (3)	O2[x]—S—O2[xi]	110.28 (5)
OH3[iii]—Mn—OH3[iv]	85.08 (5)	O2[x]—S—O2	110.28 (5)
OH3[i]—Mn—OH3[v]	96.5 (3)	O2[xi]—S—O2	110.28 (5)
OH3[ii]—Mn—OH3[v]	85.08 (5)	O2[x]—S—O1	108.65 (5)
OH3[iii]—Mn—OH3[v]	177.7 (4)	O2[xi]—S—O1	108.65 (5)
OH3[iv]—Mn—OH3[v]	93.4 (3)	O2—S—O1	108.65 (5)
OH3[i]—Mn—OH3[vi]	93.4 (3)		

Symmetry codes: (i) −x+y+1, −x+1, z; (ii) x−y−1, −y, −z; (iii) x−1, y, z; (iv) −y, x−y−1, z; (v) y, x−1, −z; (vi) −x+1, −x+y+1, −z; (vii) x, y, −z+1/2; (viii) −x+y+1, −x+1, −z+1/2; (ix) x−1, y, −z+1/2; (x) −x+y, −x+1, z; (xi) −y+1, x−y+1, z.

Hydrogen-bond geometry (Å, º)

D—H···A	D—H	H···A	D···A	D—H···A
O*H3*—H1···O2[xii]	0.75 (2)	2.11 (2)	2.8193 (16)	158 (3)

O*W*4—H2···O1[xiii]	0.77 (2)	2.10 (2)	2.7892 (18)	150 (3)

Symmetry codes: (xii) −*x*+1, −*x*+*y*, −*z*; (xiii) *y*, *x*, −*z*.