American Mineralogist, Volume 59, pages 582–586, 1974

Crystal Structures and Mineral Chemistry of Hydrated Ferric Sulfates. IV. The Crystal Structure of Quenstedtite

JIMMY N. THOMAS, PAUL D. ROBINSON, AND JEN H. FANG

Department of Geology, Southern Illinois University
Carbondale, Illinois 62901

Abstract

Quenstedtite [$Fe^{3+}{}_2(H_2O)_9(SO_4)_3 \cdot 2H_2O$] is triclinic, space group $P\bar{1}$ with $a = 6.184(5)$; $b = 23.60(2)$; $c = 6.539(5)$ Å; $\alpha = 94.18(8)$; $\beta = 101.73(8)$; $\gamma = 96.27(8)°$ and $Z = 2$. Intensities were collected by a computer-controlled Buerger–Supper 2-circle goniometer (Weissenberg geometry). The structure was partially solved by the symbolic addition procedure and completed by locating the zeolitic water molecules by a difference Fourier synthesis. Full-matrix least-squares refinement using isotropic temperature factors and 1103 reflections yielded an R-index of 0.085. The water content was found to be 11 H_2O rather than 10 H_2O as previously reported in the literature. The dominant structural features are two types of isolated clusters of Fe octahedra-S tetrahedra. The two cluster types have formulae of $[Fe(H_2O)_4(SO_4)_2]^{1-}$ and $[Fe(H_2O)_5(SO_4)]^{1+}$, respectively. The individual clusters form layers parallel to the (010) cleavage plane. The zeolitic waters are situated between layers. The SO_4 tetrahedra have mean S–O distances of 1.46, 1.44, and 1.45 Å, while the Fe–(O, Ow)$_6$ octahedra have mean Fe–(O, Ow) distances of 1.99 and 2.00 Å.

Introduction

The mineral quenstedtite $Fe_2(SO_4)_3 \cdot 11\ H_2O$ is one of five known secondary sulfates with the general formula $Fe_2(SO_4)_3 \cdot nH_2O$. Papers I and II of this series dealt with a pair of polytypic minerals with $n = 9$, coquimbite (Fang and Robinson, 1970) and paracoquimbite (Robinson and Fang, 1971), while paper III elucidated the crystal structure of the $n = 7.25$ hydrate, kornelite (Robinson and Fang, 1973). Future papers will deal with the crystal structure of the remaining species, lausenite ($n = 6$) and the Al analogue of the ferric system, alunogen $Al_2(SO_4)_3 \cdot 11\text{–}18\ H_2O$. Later work will attempt to explain structural relations and mechanisms of dehydration. This paper describes the crystal structure of the mineral quenstedtite and clarifies the question of the water content, previously reported by Cesbron (1964) and others as 10 H_2O.

Data Collection and Reduction

Quenstedtite crystals were kindly supplied by Professor Cesbron of the Laboratoire de Mineralogie et de Cristallographie de la Sorbonne, Paris, France. The sample is of Chilean origin, but the exact locality is unknown. The crystal selected was tabular in shape, its dimensions being 0.10 × 0.26 × 0.30 mm. The short dimension is roughly parallel to the b axis on which the crystal was rotated during data collection. The unit cell parameters, from precession photographs, are $a = 6.184(5)$; $b = 23.60(2)$; $c = 6.539(5)$Å; $\alpha = 94.18(8)$; $\beta = 101.73(8)$; $\gamma = 96.27(8)°$; $Z = 2$ and space group $P1$ or $P\bar{1}$.

Intensity data were collected by a computer (PDP-8/e) controlled, Buerger-Supper equi-inclination goniometer. Mn-filtered Fe$K\alpha$ radiation was used to collect 1187 raw intensities. Scan speed was varied directly with the intensity of the peak being scanned in order to minimize variations in counting statistics. The stability of the system was periodically checked, under computer control, during the collection of individual reciprocal lattice levels. Between levels, preselected standard reflections were checked manually. Software for the system was kindly provided by Professor H. C. Freeman of the Crystal Structure Laboratory, School of Chemistry, University of Sydney, Sydney, Australia. A user's manual, written by Guss, Nockolds, and Wood (1970), is also available.

All data were corrected for Lp and absorption ($\mu = 115.02\ \text{cm}^{-1}$) using the ACAC program of Prewitt (Wuensch and Prewitt, 1965).

Structure Determination

The structure was solved by the symbolic addition method using a modified version of the program of

Long (1965), known as SAYREEQN. Normalized structure factors (E's) were calculated using the WILNORM program of Fang and Robinson (1969). The E-statistics strongly indicated centrosymmetry so the space group $P\bar{1}$ was adopted. The three origin-determining reflections and the four reflections used for the starting set were selected by manually applying the symbolic addition procedure to the 30 largest E's. The purpose of this procedure is to produce a superior starting set which insures that the starting reflections have a large number of interactions which extend into all classes of reflections. Our experience has shown that program-selected starting sets are often fallible. The information thus derived was then given to SAYREEQN and automated sign prediction was initiated. Of the resulting 16 possible solutions, three appeared promising and one seemed best, based on a combination of indicators built into the SAYREEQN program. Calculation of an E-map, based on the signs of this set, yielded all of the non-hydrogen atomic positions with the exception of the free H_2O molecule(s).

Location of nine of the expected 10 H_2O molecules showed them to be ligands of the Fe^{3+} cations. The tenth was expected to be a "free" water molecule. A difference Fourier was calculated in order to locate the remaining H_2O; however, somewhat to our surprise, two areas of high electron densities emerged. Since we had no reason to suspect that the H_2O content reported in the literature was incorrect, we proceeded under the assumption that these two positions could be explained by assuming half occupancy for the two new sites.

Refinement

A full-matrix least-squares refinement was carried out utilizing the RFINE program of Finger (1969). The two free H_2O molecules were fixed at 1/2 occupancy. Of the 1187 raw intensities, 51 were considered to be "unobserved" and thus 1136 structure factors were used during refinement. Allowing positional parameters and isotropic temperature factors to vary reduced the R value to 0.135. However, the temperature factors of the two half-occupancy free water molecules had refined to nearly identical negative values, even though all other B's were behaving normally. It was thus apparent that these two atomic sites could not be considered half occupied and thus the chemical formula, with respect to the water content, was in error. It also seemed apparent that the two sites had nearly identical occupancy values since their temperature factors were essentially identical. The two sites were then set to full occupancy and all parameters varied. Convergence was obtained after two cycles at an R value of 0.096; all B's appeared to be normal.

To complete the refinement, 33 strong, low-angle reflections, obviously affected by extinction, were eliminated from the data. Two additional refinement cycles, varying all parameters, yielded the final R value of 0.085. Final atomic coordinates and temperature factors along with estimated standard deviations are presented in Table 1. The observed and calculated structure factors are given in Table 2.

Confirmation of Water Content

Several additional lines of evidence were obtained to confirm the H_2O content.

First, several additional least-squares refinement cycles were run where only the x, y, z coordinates and the temperature factors for the two waters were varied while the occupancy was changed every cycle in 0.1 increments from 0.5 to 1.0. The results of this test supported the hypothesis of 11 H_2O instead of 10 H_2O. The temperature factors of the two waters took negative values at 0.5 occupancy and increased

TABLE 1. Atomic Coordinates and Temperature Factors for Quenstedtite*

Atom	x	y	z	B($\AA^2$)
Fe(1)	.1411(6)	.1146(1)	.3365(5)	3.05(9)
Fe(2)	.4684(6)	.6182(1)	.2434(5)	3.05(9)
S(1)	.2633(8)	.2813(2)	.9573(8)	1.4(1)
S(2)	.1281(8)	.5732(2)	.7901(8)	1.3(1)
S(3)	.4462(8)	.0771(2)	.7623(8)	1.4(1)
O(1)	.084(2)	.3136(5)	.972(2)	2.3(3)
O(2)	.408(2)	.2843(5)	.164(2)	2.6(3)
O(3)	.186(2)	.2210(5)	.871(2)	2.5(3)
O(4)	.393(2)	.3072(5)	.810(2)	2.2(3)
O(5)	.229(2)	.5288(5)	.701(2)	2.7(3)
O(6)	.059(2)	.6112(5)	.637(2)	2.4(3)
O(7)	.051(2)	.4498(5)	.119(2)	2.0(3)
O(8)	.301(2)	.6071(6)	.960(2)	2.9(3)
O(9)	.334(2)	.0316(5)	.852(2)	2.8(3)
O(10)	.439(2)	.8790(5)	.072(2)	2.5(3)
O(11)	.400(2)	.9444(5)	.356(2)	2.5(3)
O(12)	.274(2)	.1022(5)	.620(2)	2.7(3)
Ow(1)	.052(2)	.1860(5)	.453(2)	2.4(3)
Ow(2)	.431(2)	.1533(6)	.292(2)	2.9(3)
Ow(3)	.010(2)	.1325(5)	.045(2)	2.0(3)
Ow(4)	.200(2)	.0390(5)	.210(2)	2.3(3)
Ow(5)	.160(2)	.9277(6)	.653(2)	2.8(3)
Ow(6)	.283(2)	.4228(5)	.817(2)	2.4(3)
Ow(7)	.232(2)	.6591(5)	.343(2)	1.8(3)
Ow(8)	.372(2)	.3699(5)	.449(2)	2.2(3)
Ow(9)	.333(2)	.5419(5)	.322(2)	2.7(3)
Ow(10)	.366(3)	.7854(6)	.370(3)	3.9(3)
Ow(11)	.179(3)	.7506(6)	.794(2)	3.6(3)

* *Standard errors are in parentheses.*

TABLE 2. Observed and Calculated Structure Factors for Quenstedtite

H	K	L	F(OBS)	F(CAL)
0	0	-1	32.14	40.58
0	0	-2	109.39	-80.19
0	0	-3	42.59	35.72
1	0	-4	28.64	-23.11
1	0	-3	22.49	19.03
1	0	-2	25.70	-20.46
1	0	-1	21.91	-17.23
1	0	0	35.86	-36.55
1	0	1	18.27	20.87
1	0	2	137.35	112.85
1	0	3	23.60	20.96
1	0	4	47.29	-38.17
2	0	3	25.19	-25.63
2	0	2	23.80	-22.28
2	0	1	26.12	26.66
2	0	0	3.99	-16.62
2	0	-1	33.26	-38.34
2	0	-3	20.21	-20.48
2	0	-4	44.25	35.13
2	0	-5	36.14	-31.04
3	0	-3	34.37	32.31
3	0	-2	76.57	77.73
3	0	-1	50.60	47.92
3	0	0	39.18	-32.84
3	0	1	24.07	-25.99
3	0	2	73.61	70.74
3	0	3	32.11	-30.34
3	0	4	41.13	-33.68
4	0	1	41.54	39.16
4	0	-2	22.18	23.37
5	0	-4	36.29	-39.42
5	0	-3	19.32	-26.85
5	0	-2	28.60	27.13
-5	1	4	33.08	33.44
-5	1	3	21.86	16.63
-5	1	0	32.99	31.27
-5	1	-1	53.57	54.86
-4	1	-1	21.69	-23.80
-4	1	1	55.20	52.39
-4	1	2	23.68	22.61
-4	1	3	53.16	-50.62
-4	1	4	22.08	22.18
-4	1	5	50.87	47.93
-3	1	5	44.52	-45.28
-3	1	4	35.40	33.08
-3	1	2	70.60	-70.64
-3	1	-2	34.98	35.80
-3	1	-3	42.43	-43.30
-2	1	-5	31.73	-27.84
-2	1	-4	23.83	17.72
-2	1	-3	117.93	90.99
-2	1	-2	48.63	43.22
-2	1	-1	57.33	-41.99
-2	1	0	10.91	16.13
-2	1	1	77.97	70.48
-2	1	2	37.59	42.03
-2	1	3	22.61	-23.69
-2	1	4	27.77	-26.71
-2	1	5	12.74	14.93
-1	1	2	56.64	61.42
-1	1	1	47.04	-45.84
-1	1	0	44.44	45.62
-1	1	-1	60.31	46.99
0	1	-5	31.64	-28.37
0	1	-4	40.54	-34.74
0	1	-3	34.06	31.25
0	1	-2	23.79	-25.15
0	1	-1	48.59	-55.67
0	1	2	46.62	47.34
0	1	3	28.97	24.56
0	1	5	11.65	16.39
0	1	6	20.90	17.22
1	1	3	42.79	41.17
1	1	1	168.04	-128.87
1	1	0	58.39	-62.18
1	1	-1	68.41	62.03
1	1	-2	29.98	-21.12
1	1	-4	19.50	17.82
1	1	-6	35.51	30.59
2	1	-4	26.00	24.66
2	1	-2	30.21	-33.67
2	1	-1	76.34	78.60
2	1	1	39.19	-37.87
2	1	3	35.61	-41.43
2	1	4	20.39	23.75
2	1	5	10.83	14.31
3	1	2	33.94	-35.63
3	1	1	39.98	40.57
3	1	0	30.06	-31.78
3	1	-2	5.79	-19.53
3	1	-4	25.43	27.44
3	1	-5	20.10	26.21
4	1	-5	27.49	28.55
4	1	-4	14.55	-21.00
4	1	-3	37.69	-42.89
4	1	-1	26.15	-28.63
4	1	0	27.18	-30.10
4	1	1	30.20	31.28
5	1	1	18.64	19.18
5	1	0	16.10	17.20
5	1	-1	25.69	-26.43
5	1	-2	18.69	-19.63
5	1	-3	27.61	30.38
-5	2	3	24.73	22.58
-5	2	2	9.46	17.91
-5	2	1	19.54	-16.73
-4	2	-2	50.92	48.09
-4	2	0	35.29	-29.15
-4	2	5	22.19	-22.27
-3	2	5	41.30	-45.06
-3	2	4	39.27	43.62
-3	2	2	104.83	-105.58
-3	2	1	35.09	33.88
-3	2	-1	23.08	-20.71
-2	2	-5	27.15	23.18
-2	2	-4	19.89	-22.68
-2	2	-2	14.72	-19.89
-2	2	-1	22.41	-25.52
-2	2	0	56.58	47.37
-2	2	1	11.07	20.30
-2	2	2	43.08	48.22
-2	2	3	26.83	23.16
-2	2	4	26.16	-28.12
-1	2	6	17.72	16.18
-1	2	5	16.75	17.03
-1	2	3	19.15	-17.21
-1	2	2	14.25	-19.74
-1	2	1	23.44	-26.04
-1	2	0	73.79	73.85
-1	2	-1	25.97	-20.91
-1	2	-2	111.32	-79.07
-1	2	-3	63.28	49.75
0	2	-4	33.42	30.82
0	2	-3	35.53	-30.85
0	2	-2	110.36	-81.49
0	2	1	76.27	-77.80
0	2	2	34.63	-35.58
0	2	3	37.07	36.25
0	2	4	37.70	-35.78
1	2	4	45.11	-44.23
1	2	3	97.17	-91.11
1	2	2	32.44	26.00
1	2	1	49.16	43.56
1	2	0	75.31	-77.15
1	2	-1	13.79	23.32
1	2	-2	45.57	40.94
1	2	-3	28.27	27.19
1	2	-4	26.74	26.43
2	2	-6	43.10	-37.09
2	2	-4	19.85	20.67
2	2	-2	55.75	57.57
2	2	-1	76.66	79.32
2	2	0	52.18	-66.88
2	2	1	39.92	41.92
2	2	2	15.04	-18.83
2	2	4	34.03	32.25
2	2	5	17.39	-17.72
3	2	4	27.95	-27.57
3	2	2	20.01	23.75
3	2	1	61.83	68.54
3	2	0	30.72	-32.06
3	2	-1	28.77	-32.19
3	2	-2	83.01	85.87
3	2	-4	58.16	-69.99
3	2	-5	23.02	-22.59
4	2	-5	34.20	37.64
4	2	-4	19.16	24.21
4	2	-3	32.71	-33.70
4	2	-2	31.98	-35.86
4	2	0	16.11	20.66
4	2	1	13.27	-25.74
4	2	2	58.87	-73.30
5	2	1	22.48	26.32
5	2	0	17.73	-20.34
5	2	-2	46.98	56.44
5	2	-3	37.95	45.63
-5	3	3	46.75	-42.82
-5	3	2	40.60	-35.33
-5	3	0	16.45	-19.42
-5	3	-1	22.67	-19.19
-4	3	-3	27.79	26.13
-4	3	-1	17.25	-20.43
-4	3	1	22.31	20.93
-4	3	2	50.50	-51.03
-4	3	3	28.08	-29.17
-4	3	4	31.08	-29.89
-4	3	5	17.00	-19.81
-3	3	5	50.65	-51.50
-3	3	4	18.20	-22.85
-3	3	3	28.68	26.39
-3	3	2	26.77	25.86
-3	3	-1	23.44	24.17
-3	3	-2	31.19	29.27
-3	3	-3	22.41	23.67
-2	3	-5	44.18	-38.47
-2	3	-3	56.17	46.29
-2	3	-2	77.80	-61.95
-2	3	-1	53.10	-45.50
-2	3	1	38.24	42.64
-2	3	6	21.81	15.62
-1	3	6	18.76	-18.25
-1	3	4	56.40	-55.82
-1	3	3	23.27	18.32
-1	3	2	25.19	-34.60
-1	3	1	188.63	-139.08
-1	3	0	88.56	-83.66
-1	3	-1	85.34	63.89
0	3	-4	64.35	56.17
0	3	-3	30.84	28.19
0	3	-2	25.87	-26.69
0	3	-1	44.14	43.77
0	3	1	34.72	41.56
0	3	2	12.94	15.39
0	3	3	79.73	-74.57
0	3	5	43.16	40.43
1	3	4	19.48	23.28
1	3	3	82.87	77.94
1	3	2	39.51	37.67
1	3	1	73.60	-72.22
1	3	0	46.12	-45.37
1	3	-1	179.74	141.98
1	3	-2	50.75	43.98
2	3	-4	23.91	-19.42
2	3	-3	21.32	-23.90
2	3	-2	22.79	-25.41
2	3	-1	69.93	-71.22
2	3	0	15.65	-21.43
2	3	2	51.17	-52.39
2	3	3	36.13	-41.07
2	3	4	28.10	26.35
2	3	5	44.61	43.16
3	3	3	10.67	-18.40
3	3	2	45.88	-51.99
3	3	1	31.72	37.10
3	3	-1	49.70	-47.69
3	3	-2	25.02	23.95
3	3	-3	37.30	-40.29
3	3	-4	36.12	-43.31
3	3	-5	69.16	70.90
4	3	-4	44.22	48.39
4	3	-3	58.51	61.83
4	3	-1	74.47	-76.12
4	3	1	45.76	51.40
4	3	2	22.28	-29.11
5	3	1	25.93	-30.82
5	3	-2	11.42	-18.33
5	3	-4	15.46	-20.98
-5	4	4	12.45	13.59
-5	4	2	47.42	-46.95
-5	4	0	15.43	17.39
-4	4	-3	20.44	17.10
-4	4	-2	59.44	58.90
-4	4	-1	38.41	-33.76
-4	4	1	26.50	23.30
-4	4	3	69.87	66.02
-4	4	4	20.75	21.36
-4	4	5	19.35	-22.11
-3	4	4	22.28	22.58
-3	4	3	33.42	30.74
-3	4	2	71.37	-66.80
-3	4	1	16.83	-17.55
-3	4	0	57.63	50.22
-3	4	-2	84.61	-73.05
-3	4	-3	30.25	-26.03
-2	4	-5	13.29	-13.29
-2	4	-3	25.43	19.99
-2	4	-1	44.03	-39.87
-2	4	0	104.78	-99.24
-2	4	1	20.34	-20.38
-2	4	3	61.37	55.56
-2	4	4	63.60	-59.36
-2	4	5	33.26	31.83
-2	4	6	14.59	15.51
-1	4	6	27.62	-25.39
-1	4	5	19.00	16.45
-1	4	4	31.36	27.35
-1	4	3	12.14	-15.99
-1	4	2	27.12	-23.92
-1	4	1	2.75	10.45
-1	4	0	97.47	85.07
-1	4	-1	95.82	71.01
-1	4	-2	58.20	-49.43
-1	4	-3	42.39	-32.02
-1	4	-4	94.76	71.99
-1	4	-5	15.92	14.67
0	4	-5	32.58	-27.70
0	4	-3	59.39	-49.72
0	4	-2	4.53	13.36
0	4	-1	6.70	-16.02
0	4	1	103.44	90.30
0	4	2	46.61	35.89
0	4	3	45.70	-40.04
0	4	4	14.56	-17.11
0	4	5	31.27	27.92
1	4	5	13.40	-17.88
1	4	4	28.39	27.12
1	4	3	18.34	16.81
1	4	0	55.73	-50.91
1	4	-1	45.06	-43.07
1	4	-2	23.75	-22.88
1	4	-3	65.87	-59.63
1	4	-5	23.37	-19.41
1	4	-6	21.05	-17.02
2	4	-6	17.59	17.76
2	4	-5	18.39	17.60
2	4	-4	52.90	-50.69
2	4	-2	53.70	52.28
2	4	-1	86.38	-92.11
2	4	0	50.45	-47.37
2	4	4	35.45	-28.55
2	4	5	29.88	-26.53
3	4	5	46.17	47.59
3	4	0	17.68	20.57
3	4	-1	36.09	-32.62
3	4	-3	25.80	26.56
3	4	-5	25.08	-26.11
4	4	-3	42.67	-46.84
4	4	-1	27.56	31.01
4	4	1	38.47	-41.79
5	4	0	18.94	18.23
5	4	-1	10.00	-14.51
5	4	-2	27.05	-31.98
5	4	-4	27.01	-28.75
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-2	12	-3	19.33	19.11
-2	12	-1	10.29	10.39
-2	12	0	15.06	-14.67
-2	12	1	62.25	-59.71
-2	12	2	10.43	-11.08
-2	12	3	28.61	29.71
-1	12	3	19.14	15.38
-1	12	1	54.05	-51.10
-1	12	0	72.96	70.88
-1	12	-1	29.79	27.01
-1	12	-3	10.39	10.28
0	12	-5	16.05	16.23
0	12	-4	16.03	-14.05
0	12	-3	54.09	-49.77
0	12	-1	23.73	21.41
0	12	0	81.97	-74.46
0	12	1	48.75	-47.64
0	12	2	16.90	-17.79
0	12	4	38.20	37.20
1	12	3	69.86	-65.05
1	12	2	33.26	-39.71
1	12	1	58.77	57.38
1	12	0	25.02	-25.37
1	12	-1	42.61	-41.34
1	12	-4	46.00	44.85
1	12	-5	14.81	12.81
2	12	-5	41.01	40.18
2	12	-4	12.21	12.62
2	12	-2	19.71	20.77
2	12	-1	50.11	51.65
2	12	0	7.59	-10.48
2	12	2	16.41	17.03
2	12	3	8.27	-11.38
3	12	1	79.50	87.73
3	12	-1	45.77	-49.10
3	12	-2	18.12	-20.54
3	12	-3	15.23	17.25
3	12	-4	8.58	12.46
4	12	-3	10.54	-11.99
4	12	-1	25.54	-30.63
4	12	0	18.24	-23.14
4	12	1	26.33	-33.24
-5	13	1	14.65	-9.79
-4	13	-2	30.34	-27.92
-4	13	-1	27.82	-26.59
-4	13	0	18.37	21.75
-4	13	2	44.19	-46.93
-3	13	4	15.96	-20.43
-3	13	3	16.84	16.93
-3	13	2	23.23	24.13
-3	13	0	26.49	27.55
-3	13	-3	44.59	44.14
-2	13	-4	42.29	36.22
-2	13	-2	95.73	-82.24
-2	13	-1	30.90	29.60
-2	13	0	51.68	53.64
-2	13	1	14.26	-11.23
-2	13	2	30.74	37.25
-2	13	3	9.83	-12.37
-2	13	4	18.31	20.29
-1	13	4	46.56	-47.70
-1	13	2	75.56	73.06
-1	13	1	10.40	-10.16
-1	13	0	80.17	-76.99
-1	13	-2	18.94	20.40
-1	13	-3	8.35	11.13
-1	13	-4	43.87	-39.68
-1	13	-5	25.31	-23.06
0	13	-4	47.30	40.91
0	13	-2	34.49	-33.05
0	13	-1	13.59	12.27
0	13	1	7.49	-13.48
0	13	2	16.02	-15.40
0	13	4	8.31	10.77
1	13	3	8.64	11.67
1	13	2	44.32	47.06
1	13	1	63.74	65.72
1	13	0	44.27	-43.24
1	13	-1	18.12	15.43
1	13	-2	94.41	88.46
1	13	-4	61.76	-60.90
2	13	-5	19.15	22.29
2	13	-4	36.11	-38.25
2	13	-3	17.17	-19.66
2	13	-2	32.08	-29.07
2	13	-1	23.14	-24.30
2	13	0	57.67	59.28
2	13	1	28.12	34.02
2	13	2	54.02	-59.33
2	13	3	26.43	28.94
3	13	1	7.59	-13.12
3	13	0	16.53	-19.15
3	13	-1	27.49	-26.50
3	13	-3	19.76	-20.88
3	13	-4	28.84	-34.30
4	13	-1	22.68	25.89
4	13	0	16.49	23.32
-4	14	-2	19.21	15.72
-4	14	1	33.40	34.79
-4	14	2	13.20	11.28
-3	14	4	17.06	13.46
-3	14	3	41.53	45.75
-3	14	2	24.69	29.27
-3	14	1	27.90	-24.45
-3	14	0	13.36	16.08
-3	14	-1	57.61	56.43
-3	14	-2	6.93	-14.04
-3	14	-3	29.31	-29.21
-2	14	-3	13.90	12.43
-2	14	-2	27.18	-28.64
-2	14	-1	26.27	24.31
-2	14	0	26.03	-23.93
-2	14	3	32.31	-30.44
-1	14	4	9.64	10.16
-1	14	3	18.33	16.46
-1	14	2	23.43	-24.89
-1	14	1	23.16	-23.92
-1	14	0	9.45	-8.61
-1	14	-1	59.14	51.53
-1	14	-2	20.54	18.24
-1	14	-3	58.64	-51.40
0	14	-4	21.02	18.67
0	14	-1	12.02	-10.46
0	14	0	10.87	-5.69
0	14	1	59.41	60.33
0	14	3	49.84	-48.91
1	14	3	13.02	16.89
1	14	1	30.56	29.10
1	14	0	25.26	-25.12
1	14	-3	24.22	-25.66
2	14	-3	14.72	15.23
2	14	-2	18.17	-19.05
2	14	-1	67.81	-67.50
2	14	0	17.12	15.16
2	14	1	12.45	16.60
2	14	2	19.38	-19.46
3	14	2	9.41	-10.58
3	14	1	23.35	-28.45
3	14	0	8.73	-11.82
3	14	-1	14.39	-17.36
3	14	-3	30.59	35.74
4	14	-2	19.17	23.59
4	14	-1	29.41	34.74
-4	15	-1	14.09	-14.23
-4	15	1	15.18	11.61
-4	15	2	29.79	32.08
-3	15	1	6.72	-9.03
-2	15	-4	12.29	12.14
-2	15	-3	21.14	-17.67
-2	15	-2	28.63	26.56
-2	15	-1	31.57	32.41
-2	15	1	29.62	-29.13
-2	15	2	18.51	16.59
-2	15	3	35.33	-34.01
-2	15	4	32.53	-31.36
-1	15	2	21.59	20.02
-1	15	1	78.97	73.11
-1	15	0	5.96	7.27
-1	15	-1	20.84	-16.68
-1	15	-2	26.35	23.88
0	15	-4	11.83	-10.59
0	15	-2	26.31	21.52
0	15	-1	10.99	-10.41
0	15	3	61.30	58.65
0	15	4	12.17	12.98
1	15	2	12.70	-13.56
1	15	1	7.65	-9.80
1	15	0	8.22	-9.48
1	15	-1	69.10	-64.56
1	15	-2	20.36	21.60
1	15	-3	10.26	13.24
1	15	-4	41.53	-38.25
2	15	-1	28.81	27.88
2	15	0	66.92	68.86
2	15	1	16.75	-19.28
2	15	2	43.78	-48.16
3	15	1	22.04	23.63
3	15	0	13.13	15.86
3	15	-1	20.84	23.21
3	15	-2	27.80	27.78
-4	16	1	10.61	-12.87
-4	16	0	29.64	-30.95
-4	16	-1	10.72	13.57
-3	16	-2	29.17	28.33
-3	16	-1	52.44	50.74
-3	16	0	7.54	-11.12
-3	16	1	29.12	-30.52
-2	16	3	29.15	-30.84
-2	16	1	45.42	42.29
-2	16	0	55.48	53.42
-2	16	-1	24.70	21.40
-2	16	-2	11.56	11.01
-1	16	-4	13.66	-13.81
-1	16	-3	40.68	-37.85
-1	16	-2	18.09	18.64
-1	16	-1	24.78	23.03
-1	16	0	20.20	-19.80
-1	16	2	9.09	9.28
-1	16	3	20.18	21.48
0	16	3	47.97	-46.59
0	16	2	24.22	-25.78
0	16	1	27.61	27.98
0	16	0	19.93	18.28
0	16	-1	53.26	-51.18
0	16	-3	34.12	34.27
0	16	-4	26.44	25.27
1	16	-4	7.43	-8.85
1	16	-3	41.69	44.68
1	16	-2	17.86	17.94
1	16	0	38.66	38.84
1	16	1	23.16	-27.97
1	16	3	11.85	14.68
2	16	2	14.65	15.99
2	16	1	13.86	17.39
2	16	0	52.10	56.65
2	16	-1	13.28	-10.95
2	16	-2	13.85	-16.79
2	16	-3	56.72	65.18
2	16	-4	18.32	20.66
3	16	-3	14.27	-17.31
3	16	-2	16.35	19.33
3	16	-1	16.98	22.57
3	16	0	32.29	-36.21
3	16	1	39.38	-43.00
-4	17	0	4.69	-9.01
-4	17	1	18.65	22.13
-3	17	2	13.54	11.98
-3	17	1	17.47	21.26
-3	17	0	13.34	15.35
-2	17	-2	75.74	76.29
-2	17	-1	33.13	-32.85
-2	17	0	71.17	-71.75
-2	17	1	45.47	47.08
-2	17	2	32.67	34.13
-1	17	3	32.83	31.64
-1	17	2	51.61	-52.51
-1	17	1	45.88	-46.36
-1	17	0	7.73	6.29
-1	17	-1	14.59	-9.98
-1	17	-3	23.72	-22.30
0	17	-4	17.56	-15.43
0	17	-2	45.69	41.79
0	17	-1	11.10	-9.37
0	17	0	4.93	-5.56
0	17	1	15.02	-14.89
0	17	2	25.44	28.64
1	17	2	32.90	-35.23
1	17	1	24.23	-21.20
1	17	0	43.63	43.79
1	17	-1	35.08	36.62
1	17	-2	23.12	-20.93
1	17	-3	10.80	-10.97
1	17	-4	10.29	11.11
2	17	-3	25.15	-27.64
2	17	-2	26.21	-29.22
2	17	-1	13.96	-12.06
2	17	0	10.02	12.60
3	17	0	17.01	-17.04
3	17	-2	41.06	-46.28
-3	18	2	25.05	-26.18
-3	18	1	21.93	21.35
-3	18	0	14.30	15.42
-3	18	-1	25.49	-27.74
-3	18	-2	20.41	-20.80
-2	18	-3	23.66	-22.39
-2	18	-2	7.47	-7.65
-2	18	0	6.72	6.99
-2	18	1	25.06	-24.97
-2	18	2	40.77	-40.07
-2	18	3	12.73	-10.12
-1	18	3	40.76	-37.74
-1	18	2	13.58	-15.21
-1	18	1	32.52	33.13
-1	18	-1	38.32	-32.68
-1	18	-2	7.37	-6.87
-1	18	-3	32.91	33.23
0	18	-3	51.25	46.19
0	18	0	26.14	19.15
0	18	2	16.06	13.03
1	18	2	16.47	19.36
1	18	1	40.31	-36.99
1	18	-1	14.55	15.95
1	18	-2	23.57	-21.78
2	18	-3	5.41	-7.53
2	18	-2	28.57	-30.10
2	18	0	19.92	-18.90
2	18	1	8.03	-10.26
-3	19	1	20.35	-17.23
-3	19	0	35.37	-31.12
-3	19	-1	30.83	-25.99
-2	19	-2	25.34	23.91
-2	19	2	8.68	-9.51
-1	19	1	14.92	-16.35
-1	19	0	12.92	13.28
-1	19	-1	49.47	41.55
-1	19	-2	14.00	-13.21
-1	19	-3	12.40	-10.59
0	19	-3	5.24	8.27
0	19	-2	36.74	-35.17
0	19	-1	23.51	-18.83
0	19	1	14.15	-12.87
0	19	2	9.86	9.68
1	19	1	13.21	-17.58
1	19	-1	31.98	30.91
1	19	-2	46.22	-46.06
1	19	-3	26.72	-28.59
2	19	-2	18.29	18.89
2	19	-1	16.20	-19.25
2	19	0	21.16	-21.05
-2	20	-1	1.65	5.61
-2	20	0	15.82	17.61
-1	20	2	3.96	6.65
-1	20	1	19.96	19.91
-1	20	0	14.91	10.92
-1	20	-1	31.05	-27.82
-1	20	-2	35.54	-36.59
0	20	0	47.00	-41.77
0	20	1	24.72	-24.97
1	20	-1	26.89	27.11

with each increment of the occupancy to expected values at full occupancy. The *R* value gave a similar indication by decreasing steadily from $R = 0.092$ at half occupancy to $R = 0.085$ at full occupancy.

Second, density was calculated using the unit cell volume and *Z* determined previously by trying both 10 H_2O and 11 H_2O in the formula weight. The density calculations, when compared to our measured density of 2.14 gm/cm^3 (obtained by the sink-float method), supported the existence of 11 H_2O.

Finally, Cesbron (1964) reported a water loss (Penfield's method) of 33.4 percent by weight. Theoretical calculations, using 10 H_2O and 11 H_2O, yield weight loss values of 31.06 percent and 33.14 percent, respectively. This again indicates 11 H_2O for the crystal under study (see paragraph 3 under "Description and Discussion of the Structure").

Description and Discussion of the Structure

According to the structural classification of ferric sulfates proposed by Süsse (1971), quenstedtite would be considered as an isolated *M-T* cluster type. Actually there are two types of isolated *M-T* clusters in quenstedtite, as can be seen in Figure 1. The first cluster type (which will be herein referred as type "A") is composed of the Fe(2) octahedron sharing two of its corners with the S(1) and S(2) tetrahedra to form a cluster of composition $[Fe^{3+}(H_2O)_4(SO_4)_2]^{1-}$. The second cluster (designated as type "B") is made up of the Fe(1) octahedron sharing a corner with the S(3) tetrahedron to yield a cluster of composition $[Fe(H_2O)_5(SO_4)]^{1+}$. Except for hydrogen bonding, these two cluster types are completely isolated. Figure 1 shows that the clusters form discernible layers parallel to the (010) plane, individual layers containing type "A" or type "B" clusters. The stacking sequence of the layers is ...AABBAA... and the zeolitic water molecules Ow(10) and Ow(11) are situated only between the "A" and the "B" layers. The perfect (010) cleavage is a result of the layering, with breakage probably occurring most often between layers of like composition, since a relative paucity of hydrogen bonding in these areas would be expected.

Selected interatomic distances and angles are presented in Table 3. The three independent SO_4 tetrahedra have mean S-O distances of 1.46, 1.44, and 1.45 Å, in agreement with all other ferric sulfate hydrates. As in previous studies in this system, we note the increase in S-O distances when the oxygens involved are also shared by an Fe octahedron. This is illustrated by S(1)-O(4), S(2)-O(8), and S(3)-O(12). Fe(1) has five Ow ligands and one oxygen ligand [mean Fe(1)-(O, Ow) distance = 1.99 Å] while Fe(2) is bonded to four Ow atoms and 2 oxygen atoms [mean Fe(2)-(O, Ow) distance = 2.00 Å]. As expected, the Fe-O distances are significantly shorter than those of Fe-Ow.

The variable H_2O content of quenstedtite merits further discussion. As previously stated, Cesbron's weight loss data supports full occupancy of the zeolitic sites while half occupancy is indicated by the analyses of Linck and Ungemach who obtained values of 31.35 percent and 31.69 percent respectively

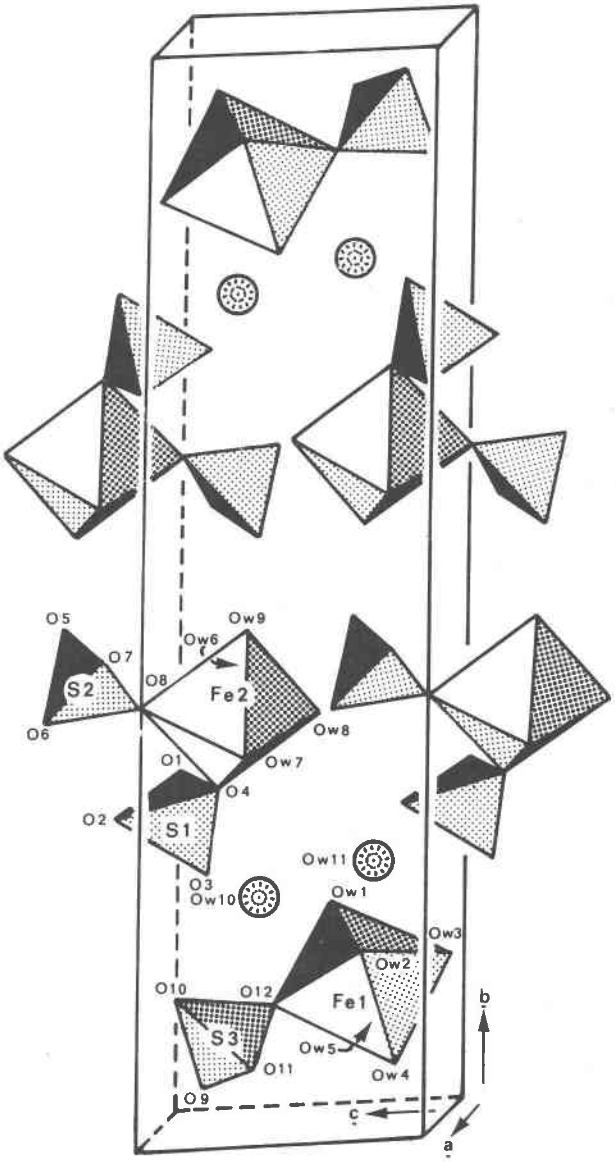

FIG. 1. Polyhedral representation of the quenstedtite structure.

TABLE 3. Selected Interatomic Distances and Angles for Quenstedtite*

		Tetrahedral coordination around S			
		O(1)-O(2)	2.34(2)Å	O(1)-S(1)-O(2)	108.5(8)°
S(1)-O(1)	1.43(1)Å	O(1)-O(3)	2.42(2)	O(1)-S(1)-O(3)	112.9(8)
S(1)-O(2)	1.45(1)	O(1)-O(4)	2.38(2)	O(1)-S(1)-O(4)	109.0(8)
S(1)-O(3)	1.48(1)	O(2)-O(3)	2.42(2)	O(2)-S(1)-O(3)	110.9(8)
S(1)-O(4)	1.50(1)	O(2)-O(4)	2.41(2)	O(2)-S(1)-O(4)	109.0(8)
		O(3)-O(4)	2.39(2)	O(3)-S(1)-O(4)	106.6(8)
MEAN	1.46Å	MEAN	2.39Å	MEAN	109.5°
		O(5)-O(6)	2.33(2)Å	O(5)-S(2)-O(6)	110.2(8)°
S(2)-O(5)	1.42(1)Å	O(5)-O(7)	2.36(2)	O(5)-S(2)-O(7)	111.3(8)
S(2)-O(6)	1.42(1)	O(5)-O(8)	2.35(2)	O(5)-S(2)-O(8)	107.8(8)
S(2)-O(7)	1.43(1)	O(6)-O(7)	2.37(2)	O(6)-S(2)-O(7)	112.3(8)
S(2)-O(8)	1.49(1)	O(6)-O(8)	2.34(2)	O(6)-S(2)-O(8)	106.8(8)
		O(7)-O(8)	2.37(2)	O(7)-S(2)-O(8)	108.3(8)
MEAN	1.44Å	MEAN	2.35Å	MEAN	109.4°
		O(9)-O(10)	2.36(2)Å	O(9)-S(3)-O(10)	109.6(8)°
S(3)-O(9)	1.44(1)Å	O(9)-O(11)	2.38(2)	O(9)-S(3)-O(11)	111.1(8)
S(3)-O(10)	1.45(1)	O(9)-O(12)	2.34(2)	O(9)-S(3)-O(12)	107.2(8)
S(3)-O(11)	1.45(1)	O(10)-O(11)	2.39(2)	O(10)-S(3)-O(11)	111.1(8)
S(3)-O(12)	1.47(1)	O(10)-O(12)	2.38(2)	O(10)-S(3)-O(12)	108.7(8)
		O(11)-O(12)	2.38(2)	O(11)-S(3)-O(12)	109.2(8)
MEAN	1.45Å	MEAN	2.37Å	MEAN	109.5°
		Octahedral coordination around Fe^{3+}			
		O(12)-Ow(1)	2.70(1)Å	O(12)-Fe(1)-Ow(1)	87.5(6)°
		O(12)-Ow(2)	2.82(2)	O(12)-Fe(1)-Ow(2)	91.8(6)
		O(12)-Ow(4)	2.90(2)	O(12)-Fe(1)-Ow(4)	94.7(6)
Fe(1)-O(12)	1.92(1)Å	O(12)-Ow(5)	2.89(2)	O(12)-Fe(1)-Ow(5)	93.7(6)
Fe(1)-Ow(1)	1.98(1)	Ow(1)-Ow(2)	2.91(2)	Ow(1)-Fe(1)-Ow(2)	94.0(5)
Fe(1)-Ow(2)	2.01(1)	Ow(1)-Ow(3)	2.82(2)	Ow(1)-Fe(1)-Ow(3)	89.9(5)
Fe(1)-Ow(3)	2.01(1)	Ow(1)-Ow(5)	2.83(2)	Ow(1)-Fe(1)-Ow(5)	89.6(5)
Fe(1)-Ow(4)	2.01(1)	Ow(2)-Ow(3)	2.74(2)	Ow(2)-Fe(1)-Ow(3)	86.2(5)
Fe(1)-Ow(5)	2.03(1)	Ow(2)-Ow(4)	2.87(2)	Ow(2)-Fe(1)-Ow(4)	91.0(5)
		Ow(3)-Ow(4)	2.80(2)	Ow(3)-Fe(1)-Ow(4)	88.1(5)
		Ow(3)-Ow(5)	2.82(2)	Ow(3)-Fe(1)-Ow(5)	88.5(5)
		Ow(4)-Ow(5)	2.74(2)	Ow(4)-Fe(1)-Ow(5)	85.2(5)
MEAN	1.99Å	MEAN	2.82Å	MEAN	90.0°
		O(8)-O(4)	2.74(2)Å	O(8)-Fe(2)-O(4)	89.9(6)°
		O(8)-Ow(6)	2.87(2)	O(8)-Fe(2)-Ow(6)	94.6(6)
		O(8)-Ow(7)	2.84(2)	O(8)-Fe(2)-Ow(7)	92.3(6)
Fe(2)-O(8)	1.92(1)Å	O(8)-Ow(9)	2.91(2)	O(8)-Fe(2)-Ow(9)	94.2(6)
Fe(2)-O(4)	1.96(1)	O(4)-Ow(6)	2.88(2)	O(4)-Fe(2)-Ow(6)	93.7(5)
Fe(2)-Ow(6)	1.99(1)	O(4)-Ow(7)	2.77(2)	O(4)-Fe(2)-Ow(7)	88.0(5)
Fe(2)-Ow(7)	2.02(1)	O(4)-Ow(8)	2.86(2)	O(4)-Fe(2)-Ow(8)	91.6(5)
Fe(2)-Ow(8)	2.03(1)	Ow(6)-Ow(8)	2.81(2)	Ow(6)-Fe(2)-Ow(8)	88.5(5)
Fe(2)-Ow(9)	2.05(1)	Ow(6)-Ow(9)	2.78(2)	Ow(6)-Fe(2)-Ow(9)	87.0(5)
		Ow(7)-Ow(8)	2.73(2)	Ow(7)-Fe(2)-Ow(8)	84.5(5)
		Ow(7)-Ow(9)	2.90(2)	Ow(7)-Fe(2)-Ow(9)	90.9(5)
		Ow(8)-Ow(9)	2.74(2)	Ow(8)-Fe(2)-Ow(9)	84.2(5)
MEAN	2.00Å	MEAN	2.82Å	MEAN	90.0°

* *Standard errors are in parentheses.*

(Palache, Berman, and Frondel, 1951). Thus, if we accept the occupancy limits to be as indicated by the analyses, the structural formula for quenstedtite should be written as

$$[Fe(H_2O)_4(SO_4)_2]\cdot[Fe(H_2O)_5(SO_4)]\cdot 1\text{–}2\ H_2O.$$

High temperature work is needed to define the lower zeolitic limit, thereby establishing the range of the H_2O content. However, it is clear that past confusion over water content in hydrated sulfate minerals stems predominantly from varying occupancies in the zeolitic water sites.

Acknowledgments

The authors are grateful to Professor F. Cesbron for providing the crystals used in this study. We are also indebted to the late Mr. Y. Ohya for his technical assistance throughout the course of the work. This work was supported by NSF Grant GA-19688.

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Manuscript received, December 3, 1973; accepted for publication, February 15, 1974.