

The crystal chemistry of sherwoodite, a calcium 14-vanadoaluminate heteropoly complex

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Abstract

The crystal structure of sherwoodite (tetragonal, space group $I4_1/amd$; $a = 28.06$, $c = 13.56$ Å) has been determined from 848 counter-measured intensity data (MoK α radiation). Difficulties with disorder and variability of crystal water as well as poor crystal quality prevented refinement below $R = 0.22$, but the essential structure is clearly revealed. Aluminum is found to play an essential role as the nucleus atom in the heteropoly complex molecule found in the structure: 14-vanadoaluminate, $(AlV_{14}O_{36})^{n-}$. There are 8 molecules in the unit cell joined by Ca²⁺ ions into chains along body diagonals, cross-linked to form an open framework of zeolitic character. The remaining Ca atoms and H₂O molecules could not be resolved and are presumably in disordered array in the intermolecular channels. The vanadium is partially reduced, and the ideal formula that best fits the determined structure and chemical analysis is $Ca_{4.5}(AlV_{12}V_2^VO_{40}) \cdot 28H_2O$. The molecule has $4/mmm$ symmetry and consists of 14 VO₆ octahedra condensed by edge-sharing around the central AlO₆ octahedron. The V-O distances vary from 1.58 to 2.36 Å.

Introduction

In 1958, Thompson *et al.* published a description of a new calcium vanadate mineral which was found at the Peanut Mine, Montrose County, Colorado. This rare species occurs as soft, greenish-black, tetragonal crystals up to 1 mm on fracture surfaces in Colorado Plateau sandstones bearing partially-oxidized vanadium minerals. The discrete nature of the mineral species was clearly established by its characteristic physical and crystallographic properties, but a wholly satisfactory chemical description could not be given. The best formula that could be derived from a microchemical analysis and crystallographic studies was $Ca_3V_8O_{22} \cdot 15H_2O$. The analysis also showed minor amounts of Al, Fe, and Mg. Thompson *et al.* (1958) recognized that the true chemical nature of sherwoodite could only be learned from a crystal structure analysis.

Such a structure determination has now been undertaken. Although still incomplete, it has clearly revealed that sherwoodite contains isolated molecules of a 14-vanadoaluminate heteropoly complex. The mineral is the first known occurrence in nature of this type of chemical complex. Although experimental difficulties have prevented full refinement of the

structure of this mineral to a degree that is nowadays considered desirable, the results obtained at this point are considered to be sufficiently noteworthy to warrant making this preliminary report.

Experimental procedure

A flat, square fragment of a euhedral crystal $0.07 \times 0.06 \times 0.025$ mm in size (from the Peanut Mine) was used for structure analysis. Precession photography confirmed the earlier space-group determination, given as $I4_1/amd$ (No. 141). Careful measurement of the 20.0.0 and 0.0.12 reflections in the plus and minus 2θ regions on the Picker automatic diffractometer using MoK α radiation gave cell constants $a = 28.06(3)$ and $c = 13.56(2)$ Å for this crystal. Intensities were measured for all allowed independent reflections with $2\theta < 45$ degrees; of 1783 measured, 848 had $F > 3\sigma$ based on counting statistics, and were used for the structure analysis.

The reflection 962 was used to monitor the primary beam during the run, and the intensity of this reflection showed somewhat greater than expected variation. As a consequence (and because of difficulties encountered in the structure refinement) the data set was measured a second time, but with no apparent

Table 2, page 2

H, 4, 1			H, 9, 1			H, 17, 1		
5	301	-294	10	709	-510	22	149	-170
9	248	190	12	287	-216	H, 18, 1		
11	125	-81	14	153	161	21	252	-186
13	88	38	16	252	426	23	182	194
15	144	-129	18	88	-107	H, 19, 1		
19	120	61	20	301	257	20	142	-47
21	225	-117	22	96	111	H, 20, 1		
23	271	-211	24	184	-170	21	95	63
27	178	121	26	207	-172	H, 0, 2		
H, 5, 1			H, 10, 1			4	199	-209
8	210	-228	17	503	538	10	282	237
12	91	-42	23	94	89	12	88	-54
14	112	94	H, 11, 1			14	160	-170
16	263	-259	16	342	273	20	245	-221
22	99	-33	24	153	150	22	212	139
24	247	-231	28	143	-112	24	382	-302
H, 6, 1			H, 12, 1			26	427	367
9	411	354	15	156	111	28	154	-111
11	144	211	19	155	219	H, 1, 2		
13	160	-161	21	96	-90	3	168	-113
15	217	-189	23	255	-222	5	101	142
19	233	-217	H, 13, 1			7	195	175
23	139	-63	14	429	306	9	566	430
25	183	108	26	101	61	11	166	-182
29	116	26	H, 14, 1			15	258	231
H, 7, 1			17	224	130	19	206	-228
8	617	-535	21	287	-261	21	289	281
10	170	-154	H, 15, 1			23	107	-55
12	120	78	16	115	62	25	148	123
14	196	-178	H, 16, 1			27	119	83
18	472	382	17	136	16	H, 2, 2		
22	122	-117	19	219	-219	4	594	-415
26	97	-53	H, 17, 1			6	157	153
28	270	-224	17	136	16	8	288	209
H, 8, 1			19	219	-219	16	124	-132
11	86	110	H, 18, 1			18	100	-53
17	143	-125	17	136	16			
19	112	221	19	219	-219			
23	115	85						

Table 2, page 3

	H, 2, 2		24	93	48	17	374	309
			26	316	267	19	102	-138
20	85	-28	28	103	86	23	159	95
22	319	-228				27	168	-134
24	206	191		H, 7, 2				
	H, 3, 2		7	1002	-818		H, 12, 2	
			9	147	-104	14	289	-247
5	210	247	11	419	-362	16	125	163
7	521	471	13	268	-204	22	158	-176
9	305	230	15	149	-120			
11	79	128	17	283	198		H, 13, 2	
15	238	206	21	105	92	13	262	161
23	347	291	23	250	-223	15	135	55
25	138	129	25	95	-115			
29	145	119	27	111	-82		H, 14, 2	
			29	156	-131			
	H, 4, 2			H, 8, 2		16	120	-115
6	117	130	10	1092	962	22	158	-131
8	427	303	12	307	214			
10	93	54	18	258	161		H, 15, 2	
14	310	-283	20	163	-97	15	149	-124
16	130	107	24	175	181	21	171	-173
18	119	-110	26	174	129			
20	181	-161	28	161	116		H, 16, 2	
24	172	123				20	205	-212
26	184	140		H, 9, 2				
23	148	108	9	1395	-1279		H, 17, 2	
			11	339	-296			
	H, 5, 2		13	158	-132	19	172	-138
5	165	176	15	120	67			
7	188	178	19	309	302		H, 21, 2	
9	168	-158	23	130	-74			
11	95	63	25	149	-151	21	203	139
13	197	182	27	209	-201			
17	84	-74					H, 0, 3	
19	164	131				1	293	-259
23	155	-61		H, 10, 2		5	169	228
27	161	105	12	201	242	7	222	250
			16	196	173	9	219	251
	H, 6, 2		28	112	68	11	142	224
8	707	627				13	140	163
10	461	381		H, 11, 2		15	463	-425
14	106	80	11	635	-669	21	283	-229
16	82	-97	13	153	-135	23	100	-29
18	137	-121	15	360	308			
22	145	-23						

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H, 0, 3			8	125	218	11	445	367
25	421	310	10	99	-121	13	138	180
29	118	-2	12	160	112	15	513	-450
H, 1, 3			18	159	-131	17	209	150
6	188	210	20	147	101	21	110	-76
8	335	328	24	105	100	23	103	-68
14	165	194	26	94	104	25	168	136
20	101	-90	28	101	110	H, 11, 3		
22	186	134	H, 6, 3			12	104	-87
26	311	284	7	138	219	16	224	189
H, 2, 3			15	205	-149	18	155	-28
7	367	350	17	89	25	20	155	-126
9	149	201	19	87	-46	22	171	105
13	147	-187	21	161	-81	24	103	23
17	132	-125	25	184	150	H, 12, 3		
19	130	-54	29	114	15	13	169	-162
23	89	-15	H, 7, 3			15	276	198
27	384	281	8	83	-129	19	89	-59
29	117	-45	10	415	-403	21	144	-65
H, 3, 3			14	249	-245	23	118	95
6	515	561	20	118	26	25	157	71
8	133	208	22	89	-107	H, 13, 3		
12	91	9	24	97	-78	14	126	-53
18	121	-98	H, 8, 3			16	124	-132
20	117	-125	9	738	649	18	186	-155
22	184	150	11	252	215	24	121	96
24	310	217	13	230	-236	26	101	92
26	133	103	15	101	58	H, 14, 3		
28	139	126	17	226	-184	15	154	163
H, 4, 3			21	106	-91	23	99	40
7	166	186	23	88	-42	H, 15, 3		
11	259	-282	27	250	196	16	225	-215
13	170	-183	H, 9, 3			24	108	101
17	81	57	10	115	-82	H, 16, 3		
23	196	143	12	614	-537	17	185	180
25	314	184	14	238	256	19	232	153
29	101	3	16	221	-155	21	134	-122
H, 5, 3			18	169	109	H, 10, 3		
6	109	115	28	105	-103	H, 10, 3		

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H, 20, 3			H, 4, 4			15	307	480
21	119	-108	12	266	-375	17	208	-276
H, 0, 4			14	83	54	21	106	-17
0	75	63	16	302	355	H, 10, 4		
2	285	-327	18	171	183	16	253	-306
4	474	482	20	131	-149	24	137	-162
6	429	-354	22	179	212	26	163	149
10	268	221	28	94	-67	H, 11, 4		
12	139	152	H, 5, 4			13	286	345
14	539	-426	11	83	86	15	185	-300
16	327	252	13	106	-113	17	160	196
18	220	-235	15	117	-146	19	132	-72
20	136	137	17	156	-167	25	261	178
22	186	-147	19	114	-111	H, 12, 4		
28	178	126	H, 6, 4			16	230	228
H, 1, 4			8	100	98	20	265	-220
3	502	-459	10	103	-178	24	211	101
5	281	249	12	151	-208	H, 13, 4		
7	91	60	14	162	154	25	169	91
13	153	147	16	221	174	H, 14, 4		
15	460	-378	18	125	86	14	232	137
17	338	317	20	139	130	H, 15, 4		
19	340	-327	26	116	54	17	321	-378
25	257	191	H, 7, 4			23	158	73
H, 2, 4			11	179	-224	H, 16, 4		
2	97	107	13	185	262	16	221	247
4	289	-240	15	244	-286	H, 17, 4		
6	98	123	17	105	67	19	358	-297
		108	25	143	147	H, 18, 4		
1		-94	H, 8, 4			18	265	320
16		-131	8	190	-211	H, 9, 4		
18	261	256	12	92	141	13	155	-258
22	125	-139	14	331	-429			
26	178	132	16	161	196			
28	118	-26	18	160	95			
H, 3, 4			22	206	-257			
5	124	-144	26	126	-25			
7	257	308	H, 9, 4					
13	146	-101						
17	404	-404						
27	175	174						

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	H, 19, 4		15	263	299		H, 11, 5
			17	275	335		
21	237	-121				12	84 78
	H, 0, 5			H, 5, 5		14	103 65
			14	90	33	16	119 -73
1	306	-285	16	164	-164	24	204 -159
5	178	103	24	133	57	26	150 110
7	465	-601					H, 12, 5
9	94	145				15	112 -69
13	245	-177				21	151 -168
17	165	-179	9	136	-113	23	102 10
19	174	200	11	140	-87	25	119 114
21	242	-158	15	204	334		H, 13, 5
23	153	-155	17	273	341	16	108 -30
			19	159	197	20	117 -112
	H, 1, 5		21	128	101		H, 14, 5
2	290	-214	23	140	-86	17	100 47
4	288	337	25	128	-121		H, 15, 5
6	218	-379				22	119 -22
8	187	206				24	175 117
14	124	-136					H, 16, 5
16	112	138	14	112	175	19	115 161
18	230	-319	20	156	149	21	106 21
20	159	106	22	335	265		H, 17, 5
			24	187	-149	18	198 -216
			26	111	71		H, 18, 5
	H, 2, 5					19	148 153
3	112	-195				21	147 36
5	239	-279					H, 19, 5
9	166	-89				20	118 -96
17	204	247					H, 10, 5
27	155	-25				13	89 -148
						15	163 136
	H, 3, 5						
6	146	197					
8	138	-160					
10	127	-48					
12	124	184					
16	200	-259					
22	125	-136					
26	167	37					
28	220	67					
	H, 4, 5						
7	100	121					
11	119	-240					

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H,0,6			13	85	-123	12	143	157
			17	212	205	14	137	-126
4	398	-369	19	159	100	16	117	-39
6	449	522	21	142	150	20	117	30
8	243	-406	23	236	206	22	157	-183
10	158	199	27	103	-79	24	179	211
12	108	-145	H,6,6			H,11,6		
16	194	-195	8	187	-183	11	213	-324
20	118	-175	16	229	235	13	88	123
26	137	86	18	303	358	15	146	-172
H,1,6			20	170	118	23	207	-214
1	211	-209	26	128	-95	H,13,6		
3	115	-50	H,7,6			13	203	-243
5	411	557	7	86	93	H,14,6		
7	492	-735	11	243	-293	20	127	-55
15	195	-251	13	274	301	H,15,6		
17	133	146	H,9,6			15	208	242
21	108	4	9	219	-280	23	105	31
23	116	-112	H,7,6			H,16,6		
H,2,6			17	123	169	18	209	273
4	127	103	19	134	165	H,17,6		
6	292	-357	21	310	378	17	324	361
8	191	283	H,8,6			21	127	92
12	171	-236	10	83	59	H,18,6		
16	173	197	12	209	-310	20	130	88
26	183	86	16	147	221	H,19,6		
H,3,6			18	131	182	19	120	205
9	150	-217	20	92	66	H,0,7		
13	107	73	22	144	155	5	180	-243
17	178	-208	24	219	-216	7	526	794
19	197	262	H,9,6			9	309	343
23	186	-128	11	155	239	H,5,6		
H,4,6			13	187	-220	5	112	-113
6	94	-86	19	158	235	H,10,6		
10	93	-123	23	112	73			
16	183	262	H,10,6					
18	167	164						
20	144	97						
H,5,6								
5	112	-113						

Table 2, page 8

H, 0, 7			H, 6, 7			H, 14, 7		
11	95	72	7	84	-166	17	117	116
13	115	-83	13	301	-318			
15	192	269	17	122	116	H, 15, 7		
17	96	-177	21	135	-61	16	226	229
19	205	-159	23	130	34	20	114	84
23	111	132				H, 17, 7		
25	116	133	H, 7, 7					
H, 1, 7			10	109	-174	18	239	298
			12	253	255			
2	75	-98	16	123	127	H, 0, 8		
8	199	-356	18	110	91	4	178	-158
16	95	-190	22	148	141	6	220	263
22	130	-130				8	626	713
H, 2, 7			H, 8, 7			10	406	432
			9	98	91	12	189	132
5	121	218	11	208	-265	14	133	27
9	298	439	13	85	73	16	122	180
11	177	209	17	85	91	18	233	-243
13	100	-32				24	234	221
15	167	-189	H, 9, 7					
17	141	177	10	263	284	H, 1, 8		
25	164	228	12	203	-240	7	233	-217
H, 3, 7			14	119	104	9	168	-124
			16	114	54	11	246	-248
4	87	14	20	107	44	13	104	-123
6	82	-118	22	104	82	19	197	-184
8	255	-276	24	133	-69	21	178	223
10	149	-60				25	108	-136
12	117	-203	H, 10, 7					
15	118	47	11	197	215	H, 2, 8		
18	111	61	13	90	-123	2	221	-230
24	117	-154				4	87	60
H, 4, 7			H, 11, 7			8	369	419
			12	129	132	10	366	389
7	78	10	16	142	-203	12	184	209
19	105	130				14	112	-120
H, 5, 7			H, 12, 7			16	99	-32
			15	173	-149	18	125	-18
6	157	-175	23	130	-91	20	144	-158
10	87	-122				22	117	-12
16	110	125						
20	196	172						
26	120	-87						

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H, 3, 8			H, 9, 8			H, 1, 9		
5	217	-157	11	228	224	6	107	-93
7	152	-217	13	90	7	10	307	-343
9	418	-377	17	177	-128	16	149	47
11	313	-288	21	122	-86	18	137	-58
13	169	-159				20	172	144
15	89	-34	H, 10, 8			H, 2, 9		
17	126	45	10	371	425	5	119	-101
21	168	-168	12	91	-105	7	104	-97
25	97	-19	16	158	165	9	369	371
H, 4, 8			20	141	-95	13	93	-23
4	242	-258	H, 11, 8			19	131	-134
10	229	279	15	88	-96	21	99	119
12	86	-15	H, 12, 8			23	115	-40
14	111	-88	16	201	-246	H, 3, 9		
16	208	-233	H, 13, 8			6	132	-156
20	106	-62	17	110	-20	8	216	-226
22	99	-86	H, 14, 8			10	191	-213
24	116	-83	14	226	-229	14	120	-147
H, 5, 8			H, 15, 8			16	143	209
9	225	-218	17	101	48	20	92	-25
13	91	13	H, 16, 8			H, 4, 9		
H, 6, 8			16	164	147	5	148	-155
10	213	268	18	117	-94	9	130	92
12	143	-161	H, 0, 9			11	91	95
14	151	-165	1	212	243	15	92	-154
24	151	40	3	225	-169	23	119	-84
H, 7, 8			5	137	-126	H, 5, 9		
9	371	353	7	312	379	6	102	46
11	90	36	9	120	72	8	94	-12
21	135	71	11	258	235	10	95	-107
23	117	17	15	93	83	14	93	109
H, 8, 8			19	189	186	18	115	25
8	477	469	21	185	-218	20	106	17
10	207	-226	H, 6, 9			7	139	133
12	94	119						
14	92	12						
16	142	53						
22	112	9						

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H, 6, 9

13	88	-67
19	132	107

H, 7, 9

10	259	327
12	93	99
14	97	-131
16	148	-143

H, 8, 9

9	264	346
11	125	-152
13	109	36
15	132	153
17	127	195
21	162	151

H, 9, 9

12	92	8
18	181	-259
22	131	-71

H, 10, 9

11	92	23
15	158	129
19	140	215
21	153	-149

H, 11, 9

14	151	-165
18	115	-120
20	141	-172

H, 12, 9

17	126	71
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H, 13, 9

14	110	107
16	139	-127

H, 14, 9

19	153	-45
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H, 0, 10

2	545	566
8	191	-220
10	200	306
12	196	-368
14	125	179
16	153	271
18	205	288

H, 1, 10

1	267	286
3	194	-199
5	146	74
7	138	194
9	214	-245
19	132	99

H, 2, 10

4	144	79
10	128	-216
18	100	191

H, 3, 10

3	233	253
13	119	5
15	144	212
17	120	152
21	129	129

H, 4, 10

6	162	-242
14	96	-187
16	149	118
20	116	31

H, 5, 10

5	102	83
11	144	74
13	108	51

H, 6, 10

12	102	-163
14	97	-5

H, 7, 10

15	134	-158
19	111	68

H, 8, 10

12	97	36
16	107	21
18	157	248

H, 9, 10

13	136	-125
17	151	-137
19	262	-271

H, 10, 10

12	190	-242
16	151	218

H, 11, 10

11	166	-146
15	96	-21
17	113	-76

H, 12, 10

14	88	-111
18	180	179

H, 0, 11

1	113	113
3	185	274
7	126	-138
11	132	-32
15	238	222
17	223	227
19	145	186

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H, 1, 11			H, 9, 11			7	160	-83
2	183	180	16	215	-114	11	105	-68
10	199	248				15	98	-1
12	249	-322	H, 10, 11			H, 6, 12		
14	211	221	11	122	-56	6	126	237
16	104	67	15	102	136	14	91	-48
H, 2, 11			H, 11, 11			H, 7, 12		
9	101	-75	16	134	122	11	92	-68
17	175	187	H, 12, 11			H, 8, 12		
19	129	95	13	136	-44	10	93	134
H, 3, 11			H, 0, 12			H, 10, 12		
4	130	-58	0	250	-226	10	143	7
6	144	123	4	90	-42	H, 0, 13		
10	128	-61	8	111	-111	1	93	-161
12	95	70	10	132	-167	H, 1, 13		
16	142	86	12	175	175	4	97	-13
H, 4, 11			14	178	-253	H, 2, 13		
9	109	116	H, 1, 12			H, 5, 13		
11	100	-52	13	104	-128	10	115	88
15	107	52	H, 2, 12			12	106	-82
17	111	83	2	133	-160	H, 2, 14		
H, 5, 11			8	134	71	4	104	-55
6	143	-167	12	135	-152	H, 3, 14		
10	103	-112	H, 3, 12			5	96	31
18	130	76	13	159	74	H, 4, 14		
H, 6, 11			H, 4, 12			6	100	4
7	111	111	4	127	-202			
15	96	-13	6	120	128			
H, 7, 11			8	150	235			
16	115	78	10	142	213			
H, 8, 11			16	96	7			
9	87	42	H, 5, 12					
15	158	-158						
17	118	136						