

The crystal structure of vuagnatite, $\text{CaAl}(\text{OH})\text{SiO}_4$

ELIZABETH MC NEAR,¹ MICHAEL G. VINCENT AND ERWIN PARTHÉ

Laboratoire de Cristallographie aux Rayons X
Université de Genève, 24 Quai Ernest-Ansermet
CH-1211 Geneva 4, Switzerland

Abstract

The new orthorhombic mineral vuagnatite, $\text{CaAl}(\text{OH})\text{SiO}_4$ ($P2_12_12_1$, $a = 7.055(6)$, $b = 8.542(7)$, $c = 5.683(5)\text{Å}$, $Z = 4$) is isotypic with conichalcite, $\text{CaCu}(\text{OH})\text{AsO}_4$. From counter diffractometer data corrected for absorption [$\mu(\text{MoK}\alpha) = 22.5\text{cm}^{-1}$] the structure was refined anisotropically to a final R value of 0.043 for 974 reflections ($F > 3\sigma$). Vuagnatite is characterized by $\text{AlO}_4(\text{OH})_2$ octahedra sharing edges to form chains linked by isolated SiO_4 tetrahedra and CaO_7OH polyhedra. The Donnay-Allmann empirical method of recognizing O^{2-} , $(\text{OH})^-$, and H_2O in crystal structures indicates the presence of only one hydroxyl group, creating a hydrogen bond between the tetrahedral oxygen O(2) and the octahedral oxygen O(5). The position of the hydrogen atom was confirmed from a difference Fourier synthesis and successfully refined. The bond distance O(5)-H (the hydroxyl group) is $0.94(5)\text{Å}$ and the O(2)-O(5) distance is $2.530(3)\text{Å}$ with a value of $178(6)^\circ$ for the angle O(2)···H-O(5). Two oxygen atoms of each AlO_6 octahedron are hydroxyl groups. The crystal chemical formula of vuagnatite is therefore $\text{Ca}^{18}\text{Al}^{6}(\text{OH})\text{Si}^4\text{O}_4$.

Introduction

Vuagnatite, $\text{CaAl}(\text{OH})\text{SiO}_4$, is a new silicate mineral found in a metasomatic rodingite from Bögürtlercik Tepe in southwest Turkey. Its mineralogical data have been reported in the preceding article (Sarp *et al.*, 1976). This paper reports its crystal structure, with particular emphasis on determining the role of hydrogen, since by classical methods it was impossible in this material to quantify either the total water content or its role as $(\text{OH})^-$ or H_2O .

Experimental

Single crystals from crushed rock samples (containing predominantly hydrogarnet and chlorite (clinocllore) and minor amounts of prehnite and vesuvianite) were isolated and oriented for X-ray study by their optical ellipsoids on a spindle stage. Reciprocal-lattice explorer and Weissenberg films of four crystals indicated an orthorhombic unit cell. Systematic absences of the type h odd for $h00$, k odd for $0k0$ and l odd for $00l$ lead uniquely to space group $P2_12_12_1$.

Intensities of an anhedron crystal (approximately

$0.14 \times 0.10 \times 0.06$ mm) were measured on a Philips PW1100 computer-controlled four-circle diffractometer using $\text{MoK}\alpha$ radiation ($\lambda = 0.71069\text{Å}$), graphite monochromator, in the $\theta/2\theta$ scan mode. Data were collected in one octant of reciprocal space from $\theta = 3$ to 38° . A total of 1084 nonequivalent reflections was measured out to $\sin \theta/\lambda = 0.866\text{Å}^{-1}$ of which 974 had F_{obs} greater than 3σ . Absorption correction was applied to the data using the program CAMEL JOCKEY (Flack 1974, 1975). For this, eight families of eight equivalent planes were additionally measured using the ψ scan method. The least-squares refinement, using the program LATTIX (Gvildys, 1965), of $1/d$ values of 23 families of parallel planes yielded the following cell parameters (e.s.d.'s at the 3σ level): $a = 7.055(6)$, $b = 8.542(7)$, $c = 5.683(5)\text{Å}$.

Structure solution and refinement

Chemical formula, space group, and axial ratios a/b and c/b suggest an isotopy to the conichalcite [$\text{CaCu}(\text{OH})\text{AsO}_4$] structure studied by Qurashi and Barnes (1963). The calculated powder pattern based on conichalcite atomic positions shows a close fit to the observed powder intensities² (Table 3, Sarp *et al.*,

¹ Also attached to Département de Minéralogie, Université de Genève.

² Close also to those of a sample from Japan (A. Kato, 1975, private communication).

TABLE 7. Vuagnatite. Observed and calculated structure factors*

H,0,0			H,7,0					
2	454	478	6	125	123	1	66	41
4	808	840	7	358	369	2 L	55	7
6	242	253	8	125	134	3	528	539
8	552	572	9	341	345	4	125	122
10	116	125	10	93	87	5	324	324
12	170	167	11 L	0	6	6 L	38	35
14	81	75	H,4,0			7	77	80
16	76	67	0	153	148	8	122	114
18	32	24	1	596	551	9 L	47	15
H,1,0			2	277	287	10 L	0	11
1	193	198	3	244	240	H,8,0		
2	97	102	4	362	370	0	627	534
3 L	20	20	5	238	243	1	204	178
4	72	81	6	213	215	2	221	209
5	459	482	7	165	166	3	141	138
6	151	159	8	74	73	4	609	619
7	170	177	9	100	103	5	148	154
8	85	85	10 L	29	32	6	43	34
9	53	47	11	61	76	7	155	158
10	33	40	H,5,0			8	116	118
11	140	134	1	174	154	9 L	0	4
12	139	133	2	34	35	10	114	114
H,2,0			3	585	605	H,9,0		
0	139	111	4	174	182	1	542	476
1	64	58	5	329	326	2	275	256
2	295	294	6	223	222	3	114	119
3	454	460	7 L	35	24	4 L	37	35
4	856	893	8	282	279	5	161	164
5	169	174	9	34	7	6	266	265
6	364	378	10	67	66	7	123	119
7	224	228	11	102	104	8 L	30	31
8	183	185	H,6,0			9	314	302
9	31	38	0	698	605	H,10,0		
10 L	0	15	1	152	140	0	236	195
11	177	172	2	295	295	1 L	48	33
12	170	163	3 L	29	3	2	124	126
H,3,0			4	238	249	3	129	124
1	792	808	5	185	182	4	71	68
2	840	851	6	39	18	5	128	121
3	130	132	7 L	0	5	6	146	140
4	59	56	8	453	451			
5	129	128	9	79	84			
			10	211	207			
			11 L	0	3			

* Table of The Crystal Structure of Vuagnatite $\text{CaAl}(\text{OH})\text{SiO}_4$, Mc NEAR, E., M.G. VINCENT and E. PARTHE (1976) Am. Mineral.

The columns are h, L (less than 3 σ), $10F_{\text{obs}}$ and $10F_{\text{calc}}$.

The scale factor is $F_{\text{obs}} \times 2.140(6) = F_{\text{rel}}$ (shift/error: 0.009).

h	10F _O	10F _C	h	10F _O	10F _C	h	10F _O	10F _C
	H,10,0		2	939	978	4	327	334
7	86	87	3	124	122	5	319	329
8	116	122	4	62	59	6	151	159
	H,11,0		5	44	41	7	353	361
1 L	0	21	6	730	762	8	195	199
2	590	529	7	143	150	9	176	177
3	266	250	8	125	128	10	56	51
4 L	0	12	9	142	144	11	203	203
5	272	266	10	298	303		H,4,1	
6	281	277	11 L	31	3	0	46	29
7 L	0	10	12 L	0	6	1	289	287
8 L	0	21		H,1,1		2	177	188
	H,12,0		0	51	24	3	137	140
0	374	305	1	296	287	4	137	131
1 L	54	25	2	160	159	5	188	189
2	153	137	3	160	166	6	181	185
3	131	126	4	162	164	7	109	106
4	50	9	5	194	203	8	84	84
5	66	52	6	200	202	9	138	144
6 L	36	52	7	197	199	10	120	114
7	69	68	8	133	133	11	77	63
	H,13,0		9	56	61		H,5,1	
1	61	62	10	179	181	0	472	406
2	151	123	11	140	131	1	324	326
3 L	0	18	12	58	52	2	124	133
4	117	103		H,2,1		3	373	391
5	178	169	0	171	165	4	111	108
	H,14,0		1 L	59	39	5	210	208
0	163	129	2	599	611	6	120	118
	H,16,0		3	214	213	7	197	201
0	182	143	4	64	67	8	130	123
	H,18,0		5	193	193	9	211	207
0	123	109	6	193	196	10	176	171
	H,0,1		7	116	115	11	115	113
1	40	33	8	41	32		H,6,1	
			9	148	148	0	122	102
			10	155	155	1	265	249
			11	198	194	2	565	589
			12	94	90	3	155	161
				H,3,1		4	94	94
			0 L	0	16	5	156	153
			1	602	641	6	251	248
			2	102	100	7	203	200
			3	594	605			

h	10F _O	10F _C	h	10F _O	10F _C	h	10F _O	10F _C
H,6,1			0 L	42	55	6	112	110
8	75	82	1 L	39	66	7	31	14
9	111	112	2 L	46	27	8	111	114
10	182	178	3	100	95	9	111	112
11	132	129	4	58	49	10	82	74
H,7,1			5	79	76	11	52	56
0	91	70	6	61	53	H,1,2		
1	67	65	7	74	78	0	129	113
2	102	105	8	74	82	1	731	688
3	220	239	H,11,1			2	676	638
4	94	100	0	343	278	3	410	402
5	108	108	1	260	214	4	173	172
6	116	114	2	103	87	5	124	125
7	92	96	3	172	166	6	129	131
8 L	30	33	4	342	342	7	232	234
9	62	63	5	149	143	8	133	135
10	133	122	6	69	82	9	284	291
H,8,1			7	98	105	10	52	50
0 L	49	39	8	267	257	11	43	44
1	275	247	H,12,1			H,2,2		
2	360	349	0 L	0	20	0	126	148
3	122	131	1	89	70	1	361	321
4 L	0	34	2	173	147	2	402	398
5	272	274	3	169	142	3	101	105
6	379	377	4	100	103	4	135	131
7	92	93	5	78	89	5	282	287
8	53	48	6	158	166	6	184	186
9	165	171	7	57	48	7	131	129
10	173	172	H,13,1			8	312	316
H,9,1			0	175	147	9	88	85
0	380	319	1 L	0	10	10	140	136
1	257	225	2 L	50	39	11	144	134
2	93	85	3	78	72	H,3,2		
3	187	192	4	100	96	0	202	195
4	169	180	5	107	102	1	498	469
5	126	137	H,0,2			2	300	292
6	101	103	0	782	761	3	932	940
7	234	236	1 L	47	5	4	158	161
8	113	118	2	404	393	5	728	741
9	40	49	3	111	107	6 L	25	24
H,10,1			4	786	792	7	142	146
			5	130	134	8	148	148
						9	187	189

h	10F _O	10F _C	h	10F _O	10F _C	h	10F _O	10F _C
	H,3,2			H,7,2		8	116	127
10	50	42	0	169	145		H,11,2	
11	160	153	1	225	229	0	58	10
	H,4,2		2	147	153	1	333	301
0	701	685	3	120	123	2	329	323
1	48	50	4	88	89	3	89	56
2	420	412	5	202	208	4 L	37	26
3	139	143	6	97	101	5	68	61
4	126	122	7	144	136	6	120	129
5	69	71	8	103	110	7	237	231
6	114	113	9	81	76		H,12,2	
7	35	12	10 L	34	28	0	229	187
8	208	208		H,8,2		1	116	84
9	165	162	9	741	645	2	63	82
10	189	183	1	312	249	3	137	127
11 L	40	14	2	181	190	4	312	316
	H,5,2		3	284	300	5	77	80
0 L	31	28	4	100	97	6	155	152
1	798	820	5	156	159		H,13,2	
2	47	45	6	206	212	0 L	53	32
3	347	341	7	212	210	1	86	77
4	160	160	8	199	204	2 L	44	32
5	133	128	9	42	41	3	270	254
6	151	150		H,9,2		4	72	81
7	394	394	0	95	81	5 L	48	32
8	176	177	1	56	22		H,0,3	
9	259	261	2 L	0	13	1	249	245
10	91	94	3	185	186	2	668	651
11	69	67	4	75	93	3	237	229
	H,6,2		5	315	324	4	92	92
0 L	35	37	6	138	135	5	54	53
1	417	437	7	62	66	6	520	520
2	158	161	8	77	82	7	99	100
3	253	262	9	95	96	8	38	36
4	527	534		H,10,2		9	166	163
5	311	312	0	386	334	10	291	285
6	357	359	1 L	44	43	11	125	122
7	156	160	2	193	190		H,1,3	
8	167	166	3	127	134	0	125	116
9	103	105	4	27	26	1	416	389
10	91	85	5	124	125			
			6	94	94			
			7	117	110			

h	10F _O	10F _C	h	10F _O	10F _C	h	10F _O	10F _C
H,1,3			5	142	140	H,8,3		
2	113	111	6	137	138	0	108	108
3	150	147	7	162	162	1	190	200
4	129	123	8	185	184	2	277	287
5	232	231	9	104	106	3	130	130
6	170	165	10	52	57	4	176	184
7	128	130	11	36	16	5	238	236
8	108	102	H,5,3			6	313	310
9	139	139	0	201	200	7 L	31	56
10	119	125	1	304	296	8	65	59
11	102	101	2	61	49	9	163	158
H,2,3			3	357	355	H,9,3		
0	396	363	4	96	96	0	252	230
1	47	52	5	274	275	1	162	161
2	343	331	6	134	132	2	107	100
3	99		7	225	226	3	157	159
4	185	184	8	192	198	4	159	164
5	177	176	9	176	179	5	84	82
6	181	177	10	165	168	6	39	44
7	179	179	H,6,3			7	156	154
8	115	117	0 L	0	12	8	68	78
9	111	112	1	252	254	H,10,3		
10	96	95	2	443	434	0	303	265
11	156	151	3	222	219	1	88	88
H,3,3			4	62	56	2	113	121
0	63	70	5	165	165	3	74	83
1	563	515	6	217	217	4	83	98
2	144	145	7	177	184	5	60	63
3	516	508	8	86	83	6	52	51
4	233	229	9	89	87	7	126	124
5	306	311	10	158	158	8	135	124
6 L	27	8	H,7,3			H,11,3		
7	315	316	0	72	71	0	260	223
8	170	165	1	155	156	1	183	173
9	178	176	2	57	61	2	60	62
10	91	98	3	90	85	3	142	147
11	198	195	4	157	152	4	242	261
H,4,3			5	81	76	5	157	154
0	230	212	6	209	204	6	64	65
1	106	102	7	100	100	7	87	94
2	197	187	8	67	71			
3	152	148	9	107	105			
4	257	254	10	95	95			

h	10F _O	10F _C	h	10F _O	10F _C	h	10F _O	10F _C
H,12,3			1	167	157	8	179	172
0 L	0	3	2	294	279	9	58	60
1	161	143	3	173	163	10	85	83
2	174	168	4	561	556	H,6,4		
3	179	185	5	88	84	0	542	495
4	133	143	6	335	339	1	203	201
5	54	50	7	199	198	2	287	286
6	128	138	8	147	149	3	87	84
H,13,3			9	65	73	4	123	123
0	112	92	10	73	73	5	160	166
1	58	42	11	102	107	6	38	36
2	134	127	H,3,4			7 L	33	34
3 L	0	10	0	176	168	8	326	326
4 L	0	47	1	603	560	9	116	108
H,0,4			2	430	415	H,7,4		
0	1351	1382	3	95	98	0	216	211
1	67	64	4	192	196	1	140	134
2	174	177	5	65	73	2	109	110
3	175	171	6	207	211	3	357	361
4	529	533	7	283	281	4	89	89
5	187	191	8	74	80	5	231	230
6	211	204	9	244	243	6	55	44
7 L	28	3	10	94	91	7	157	156
8	453	449	H,4,4			8	123	122
9	108	111	0	171	164	9 L	0	38
10	113	117	1	323	301	H,8,4		
11 L	0	27	2	381	361	0	316	312
H,1,4			3	167	170	1	122	120
0	58	51	4	285	276	2	290	291
1	344	338	5	108	110	3	90	95
2	146	143	6	207	208	4	522	519
3	294	286	7	57	59	5	97	98
4	85	87	8	67	72	6	105	106
5	399	393	9	96	106	7	91	88
6	114	116	10	143	138	8	122	124
7	252	258	H,5,4			H,9,4		
8	104	103	0	132	122	0	66	65
9	48	56	1	175	167	1	291	293
10	121	118	2	132	128	2	220	220
11	139	128	3	454	447	3	73	81
H,2,4			4	180	181	4	168	166
0	119	121	5	227	229			
			6	97	94			
			7	75	69			

h	10F _O	10F _C	h	10F _O	10F _C	h	10F _O	10F _C
H,9,4			5 L	0	12	H,4,5		
5	127	125	6	408	404	0	231	211
6	187	190	7	177	175	1	105	99
7	107	102	8	49	21	2	88	73
8	52	65	9	123	118	3	127	123
H,10,4			10	238	237	4	294	287
0	210	200	H,1,5			5	130	133
1	125	122	0	91	102	6	121	119
2	178	189	1	292	294	7 L	33	25
3	78	84	2	156	154	8	126	126
4	66	51	3	247	242	9	119	122
5	112	119	4	172	165	H,5,5		
6	185	190	5	161	166	0	75	75
7	102	104	6	92	86	1	242	219
H,11,4			7	134	137	2	60	57
0 L	44	25	8	74	62	3	204	197
1 L	0	46	9	110	102	4	70	60
2	358	382	10	139	137	5	249	244
3	193	204	H,2,5			6	63	73
4	45	44	0	312	310	7	142	142
5	210	216	1	95	94	8	42	45
6	249	250	2	330	322	9	212	214
H,12,4			3	112	105	H,6,5		
0	218	201	4	170	175	0	93	89
1	82	82	5	98	93	1	74	66
2	99	99	6	206	206	2	294	283
3	110	120	7	115	116	3	137	135
4	55	34	8	133	142	4	54	37
5	157	149	9	64	64	5	119	121
H,13,4			10	110	122	6	200	205
0	136	112	H,3,5			7	245	245
1	122	111	0	211	201	8	92	95
2	83	89	1	271	254	9	98	99
3	72	77	2	174	172	H,7,5		
H,0,5			3	246	242	0 L	41	26
1	113	118	4	158	156	1	172	171
2	549	553	5	218	218	2	188	185
3	173	171	6	200	206	3	208	213
4	105	103	7	228	226	4 L	32	43
			8	169	171	5	186	193
			9	102	98	6	117	122
			10	72	66	7	134	147
						8	79	64

h	10F _O	10F _C	h	10F _O	10F _C	h	10F _O	10F _C
	H, 8, 5			H, 0, 6		9	89	68
0	156	163	0	91	93		H, 4, 6	
1	101	96	1	158	165	0	295	289
2	287	287	2	304	308	1 L	47	32
3	73	86	3 L	26	18	2	365	351
4	105	112	4	447	451	3	134	121
5	164	162	5	175	175	4	117	122
6	201	205	6	51	53	5	150	151
7	71	69	7 L	0	13	6	205	215
8	123	122	8	46	44	7	124	117
	H, 9, 5		9	192	191	8	142	138
0	183	184		H, 1, 6		9	86	86
1	164	171	0 L	29	14		H, 5, 6	
2	191	188	1	276	277	0 L	0	37
3	137	142	2	123	127	1	529	499
4	186	190	3	247	244	2 L	0	16
5 L	0	51	4	132	133	3	236	230
6	158	157	5	153	154	4	141	141
7	128	136	6	85	86	5	77	81
	H, 10, 5		7	217	214	6	60	58
0	94	96	8	95	79	7	286	290
1	147	139	9	225	219	8	39	51
2 L	0	37		H, 2, 6			H, 6, 6	
3	134	133	0	237	238	0	45	17
4	122	120	1	185	188	1	317	298
5	60	66	2	371	372	2	63	73
6	67	80	3	71	78	3	184	181
	H, 11, 5		4	132	131	4	228	225
0	260	260	5	170	168	5	187	185
1	219	220	6	233	228	6	211	214
2	111	111	7	114	112	7	63	69
3	106	110	8	193	195	8	49	52
4	209	205	9	112	115		H, 7, 6	
5	133	120		H, 3, 6		0	180	162
	H, 12, 5		0	208	211	1	269	252
0 L	0	5	1	157	156	2	55	36
1	126	127	2	140	131	3	226	224
2	43	49	3	451	444	4	176	179
3	102	110	4	171	172	5	211	214
			5	363	363	6	105	100
			6	88	90	7	153	156
			7	90	87			
			8	126	118			

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h	10F _O	10F _C	h	10F _O	10F _C	h	10F _O	10F _C
H, 8, 6								
0	328	305	1	238	251	4	57	27
1	158	153	2	49	56	5	257	251
2	148	143	3	158	164	6	64	48
3	146	155	4	40	42	7	169	168
4	83	86	5	212	217	H, 6, 7		
5	95	105	6	115	119	0 L	39	11
6	180	185	7 L	38	45	1	171	167
7	91	90	8	128	124	2	127	132
H, 9, 6			H, 2, 7			3	229	225
0	230	220	0	245	265	4	48	65
1	104	115	1 L	29	15	5	115	122
2	53	48	2	56	63	6	97	94
3	112	121	3	100	97	7	153	163
4	166	161	4	261	267	H, 7, 7		
5	190	192	5	80	83	0 L		4
6	79	73	6	113	110	1	197	192
H, 10, 6			7	148	144	2	165	156
0	168	169	8	179	179	3	100	96
1	99	106	H, 3, 7			4	68	58
2	167	171	0	94	94	5	139	140
3	113	124	1	200	198	6	145	154
4 L	0	23	2	167	169	H, 8, 7		
5	129	131	3	203	201	0	181	168
H, 11, 6			4	132	135	1	74	75
0 L	36	21	5	158	160	2	138	138
1	194	199	6	59	50	3	73	66
2	140	144	7	148	141	4	190	188
3	127	120	8	116	117	5	126	131
H, 0, 7			H, 4, 7			H, 9, 7		
1	146	155	0	358	357	0	76	70
2	225	227	1	156	163	1	63	46
3	158	162	2	40	46	2	132	135
4	72	75	3	119	119	3	62	60
5	52	40	4	265	271	4	97	98
6	138	130	5	81	82	H, 10, 7		
7	56	53	6	52	51	0	238	220
8	85	87	7	142	150	1	101	106
H, 1, 7			H, 5, 7			2	50	66
0	40	15	0	55	49			
			1	184	187			
			2 L	34	51			
			3	176	171			

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h	10F _O	10F _C	h	10F _O	10F _C	h	10F _O	10F _C
	H,0,8							
0	422	460	6	200	202	5	130	117
1	41	56		H,3,8			H,6,8	
2	48	38	0	92	98	0	183	190
3	69	69	1	204	211	1	107	101
4	190	198	2	165	173	2	169	169
5	157	157	3 L	34	48	3	144	137
6	157	155	4	191	196	4 L	36	50
7 L	33	6	5	60	66	5	161	166
	H,1,8		6	181	193		H,7,8	
0	145	164		H,4,8		0	126	132
1	251	275	0	131	135	1	151	145
2	158	167	1	176	177	2	94	97
3	244	261	2	254	262	3	229	220
4 L	37	33	3 L	43	49	4	101	96
5	193	193	4	96	94		H,8,8	
6	109	108	5	100	87	0	133	120
7	230	230	6	228	239	1 L	39	63
	H,2,8			H,5,8		2	250	244
0 L	0	23	0	45	57		H,0,14	
1	97	102	1	140	139	0 L	36	51
2	249	270	2	91	99			
3 L	0	32	3	228	222			
4	221	220	4	106	103			
5	43	52						

To compare vuagnatite and conichalcite, the transformations are :

$$\underline{a}_v = \underline{a}_c$$

$$x_v = x_c + 1/4$$

$$\underline{b}_v = \underline{c}_c$$

$$y_v = z_c + 1/4$$

$$\underline{c}_v = -\underline{b}_c$$

$$z_v = y_c - 1/4$$