

Fingerite, $\text{Cu}_{11}\text{O}_2(\text{VO}_4)_6$, a new vanadium sublimate from Izalco volcano, El Salvador: crystal structure

LARRY W. FINGER

*Geophysical Laboratory, Carnegie Institution of Washington
Washington, D. C. 20008*

Abstract

Fingerite, $\text{Cu}_{11}\text{O}_2(\text{VO}_4)_6$, is triclinic with $a = 8.1576(6)$, $b = 8.2691(5)$, $c = 8.0437(7)\text{\AA}$, $\alpha = 107.144(5)^\circ$, $\beta = 91.389(7)^\circ$, $\gamma = 105.441(5)^\circ$, $Z = 1$, and space group $P\bar{1}$. The crystal structure has been solved and refined to a weighted R of 0.044 from 2875 intensities measured on a four-circle diffractometer. The structure consists of vanadium in tetrahedral coordination and copper in octahedral and trigonal bipyramidal coordination with Jahn-Teller distortions typical for Cu^{2+} . The octahedra form a sheet with holes and are cross-linked by vanadium tetrahedra and copper trigonal bipyramids.

Introduction

Fingerite, $\text{Cu}_{11}\text{O}_2(\text{VO}_4)_6$, a fumarolic mineral from Izalco volcano, El Salvador, is described in the preceding paper (Hughes and Hadidiacos, 1985). It is a double honor to have the mineral named after me and to have the opportunity to solve and present its crystal structure.

Experimental

A crystal of fingerite, $0.09 \times 0.09 \times 0.15$ mm, was mounted on a four-circle diffractometer, and the orientation matrix and reduced unit cell were determined by an automatic indexing algorithm similar to that suggested by Jacobson (1976). The cell proposed by Hughes and Hadidiacos (1985) was confirmed. In the final orientation the axis of crystal rotation was approximately parallel to $[3\bar{8}2]$. Unit-cell and orientation parameters were refined from the positions of 20 independent observations with $39^\circ \leq 2\theta \leq 54^\circ$ measured by the eight-reflection centering method of King and Finger (1979). The unit cell and other crystal data are listed in Table 1.

The intensity data for one hemisphere ($l \geq 0$) of the triclinic mineral were measured to $60^\circ 2\theta$ with omega step scans and Nb-filtered Mo radiation. The resulting data were integrated by application of the Lehmann and Larsen (1974) technique for optimum background selection. In accordance with the suggestions of Gabo (1980), the inner edge of the background region was selected two steps outside the point corresponding to the minimum in σ/I . Integrated intensities were corrected for Lorentz-polarization and absorption effects ($\mu_1 = 143.2 \text{ cm}^{-1}$) with the program of Burnham (1966). A total of 2875 intensities were measured. Of these, 2257 had values greater than twice the standard deviation.

Solution of the crystal structure was accomplished through use of the tangent formula as implemented in MULTAN-80 and associated programs (Main et al., 1980). Pseudosymmetry of the copper and vanadium atoms resulted in some difficulty in the solution (cf. Hai-Fu et al., 1983). In addition, the formula as derived from electron microprobe analyses was thought to be $\text{Cu}_{10}\text{V}_6\text{O}_{25}$. Despite these difficulties, successive cycles of

Fourier syntheses revealed the positions of all atoms, the correct stoichiometry and confirmation of the space group ($P\bar{1}$).

Program RFINE4 (Finger and Prince, 1975) was used to refine the structure. Effective standard deviations, σ' , used to calculate least-squares weights, were calculated from the formula $\sigma'^2 = \sigma^2 + (0.012F)^2$, where σ is the standard deviation derived from counting statistics and F is the structure factor. All structure-factor calculations were performed with neutral atom scattering curves selected from the data of Cromer and Mann (1968). Anomalous dispersion coefficients were taken from *International Tables for X-Ray Crystallography, Vol. IV* (1974). The refined structure converged to an R factor of 7.6% with isotropic temperature factors and an isotropic secondary extinction coefficient. After conversion to anisotropic temperature factors, the structure converged to a weighted R of 4.4% and an unweighted R of 4.6%. The anisotropic refinement is significantly better than the isotropic calculation (Hamilton, 1965). Robust/resistant techniques (Prince, 1982) were employed in the final stages of the refinement. Final observed and calculated structure factors are listed in Table 2.¹ Refined atomic coordinates and equivalent isotropic temperature factors are listed in Table 3.

Description of the structure

The anion arrangement of $\text{Cu}_{11}\text{O}_2(\text{VO}_4)_6$ may be described as essentially a close-packed array of oxygen. Octahedrally coordinated copper ions form a sheet with holes (Fig. 1). These edge-shared polyhedra have Jahn-Teller distortion typical for Cu^{2+} (Shannon and Calvo, 1973). Each octahedron has four equatorial oxygen ions at distances approximately equal to 2\AA (Table 4) and two apical oxygens at greater distances. For Cu3 and Cu4, the

¹ To receive a copy of Table 2, order Document AM-85-258 from the Business Office, Mineralogical Society of America, 2000 Florida Avenue, N.W., Washington, D. C. 20009. Please remit \$5.00 in advance for the microfiche.

5	707	719	632	626	115*	146	247	210	940	976	1377	1370	30*	79
6	482	499	145	121	147	129	341	335	1951	1519	347	357	350	374
7	253	255	284	294	460	464	27*	89	486	462	240	225	624	647
8	117*	71	H 10	0	171	188	735	765	1447	1382	598	581	243	291
9	327	293	0	0	219	289	491	521	224	232	118*	108	178	200
H 4	0	0	328	317	197	138	882	979	338	339	603	624	0	1467
-11	440	418	144	150	1079	1067	374	370	653	650	200	169	1	258
-10	792	778	203	183	2012	2033	200	195	695	694	409	397	2	79*
-9	926	939	256	236	626	667	82*	34	547	567	108*	12	3	216
-8	32*	17	29*	14	31*	120	1201	1158	61*	71	87*	57	4	929
-7	237	265	657	643	145	87	131	119	285	289	H -8	2	5	336
-6	1015	1063	88*	143	1115	1227	157	116	26*	43	H -8	2	6	614
-5	304	341	641	648	611	659	492	483	H 6	1	-4	11	7	1092
-4	151	154	30*	83	325	353	753	748	206	239	27*	36	8	30*
-3	83*	24	H 11	0	586	596	560	519	307	302	506	556	9	171
-2	987	989	154	116	280	292	365	338	427	415	179	175	10	286
-1	427	414	398	409	631	638	658	627	280	325	625	672	11	390
1	890	863	154	116	32*	94	H 1	1	170	168	0	127*	H -2	2
2	218	219	305	281	55*	64	182	147	479	464	1204	1220	-10	125
3	444	441	52*	64	H -4	1	352	322	144	130	2	1042	-9	563
4	978	975	H-11	1	183	159	27*	31	479	464	82*	54	-8	161
5	378	364	45*	48	348	400	577	579	28*	357	387	427	-7	525
6	461	460	461	428	332	319	1262	1194	372	357	97*	125	-6	97*
7	230	253	72*	72	530	529	30*	45	48*	22	94*	92	-5	132
8	115	100	134	83	108*	127	883	908	212	199	721	747	-4	621
H 5	0	0	101*	166	175	184	239	256	684	669	326	294	-3	453
-11	194	211	101*	166	188	164	445	466	259	256	180	168	-2	113
-10	152	132	H-10	1	371	418	446	464	190	180	H -7	2	-1	839
-9	522	527	284	308	325	325	64*	14	265	223	182	219	0	163
-8	913	940	468	469	1050	2344	761	718	H 7	1	174	167	1	149
-7	130*	89	232	231	27*	35	108*	78	330	323	101*	81	2	120
-6	460	485	468	485	901	935	162	142	269	281	209	185	3	944
-5	176	181	250	267	30*	54	276	274	254	268	519	504	4	198
-4	453	485	480	477	566	565	769	750	100*	62	276	284	5	504
-3	351	367	480	477	483	483	458	423	184	208	188	176	6	29*
-2	581	584	185	178	260	250	458	423	385	394	914	931	7	93*
-1	1387	1331	432	428	27*	54	485	464	542	509	103*	76	8	926
0	501	495	301	283	101*	108	126*	131	542	509	409	397	9	233
1	229	244	536	570	253	241	10	131	168	157	402	401	10	614
2	608	587	258	268	0	0	987	928	1069	1024	520	543	11	28*
3	246	246	8	8	967	930	967	930	967	930	444	455	-10	86*
4	434	430	8	8	987	928	987	928	987	928	115*	86	-9	432
5	83*	106	106	106	106	106	106	106	106	106	106	106	H -1	86
6	163	501	-10	51*	53	548	303	303	182	141	484	140	-4	53*
7	452	501	H	0	542	515	151*	112	140	110	193	130	-3	53*
8	358	398	H	0	541	299	320	320	321	344	453	430	-2	53*
9	890	888	H	0	541	583	583	583	583	583	583	583	-1	53*

Fingerite after Cycle 26

FACTOR = 10.00

10	117*	116	363	353	431	94*	1582	7	211	171	254	326	332
	H 2	2	493	431	146	0	1673	4	382	378	202	8	516
-11	276	286	122*	146	9	1	1705	5	783	781	244	9	129
-10	26*	8	25*	119	-3	2	330	6	216	244		10	541
-9	147	129	110*	115	-4	3	1001	4	128	119			561
-8	32*	108	346	397	-3	4	422	5	422	417			
-7	82*	94	734	754	-2	5	29*	6	29*	20			
-6	440	456			-1	6	204	7	613	607			
-5	127	119	H 8	2	0	7	176	8	26*	30			
-4	321	372	364	378	1	8	590	9	273	291			
-3	693	721	811	828	2	9	286	10	497	507			
-2	200	229	167	196	3	10	289						
-1	1234	1203	619	641	4		289						
0	808	761	409	334	5		113*						
1	295	264	344	423	6		343						
2	1215	1147	283	274	7		30*						
3	112	20	227	201	8		406						
4	895	852	340	321	9		417						
5	124*	123	359	341	10		299						
6	857	841	235	218			H -5						
7	305	307	750	763			233						
8	28*	30	39*	26			97*						
9	367	365	H 9	2			711						
	H 3	2	333	337			206						
-11	397	376	874	892			1126						
-10	123	145	208	203			469						
-9	195	206	302	336			444						
-8	39*	34	223	217			164						
-7	1105	1131	82*	17			762						
-6	50*	75	837	808			735						
-5	26*	27	193	84			998						
-4	351	380	547	549			593						
-3	394	391	27*	47			317						
-2	484	484	350	341			624						
-1	479	466	H 10	2			591						
0	914	861					26*						
1	124	137					536						
2	1056	1009	56*	69			743						
3	1029	975	344	344			H -4						
4	637	605	337	332			314						
5	235	249	269	254			429						
6	237	257	417	436			142						
7	110*	36	294	266			114						
8	37*	50	H -11	3			142						
9	27*	11					297						
	H 4	2	403	422			297						
-11	102*	102	32*	26			2046						
-10	145	60	845	887			1229						
-9	71*	115	243	231			195						
-8	445	469	101*	130			401						
-7	286	272	186	160			192						
	H 4	2	375	329			542						
0	451	408	100*	45			36*						
-1	452	410	545	5345			21*						
-5	1128	1535	620	131			491						

Fingerprint after Cycle 26

FACTOR = 10.00

H	DBS	CALC	H	DBS	CALC	H	DBS	CALC	H	DBS	CALC	H	DBS	CALC	H	DBS	CALC			
-8	115	71	-9	305	290	-7	188	240	5	492	445	2	337	325	-7	277	255	-9	707	684
-7	1895	1918	-8	219	190	-6	117	11	5	129	81	3	158	104	-6	114*	17	-8	93*	90
-6	166	181	-7	121	136	-5	187	181	5	374	385	4	482	503	-4	353	385	-7	770	764
-5	442	484	-6	63*	56	-4	165	155	8	264	250	5	108*	147	-3	752	746	-6	195	165
-4	396	391	-5	150	126	-3	28*	30	9	112*	100	5	108*	147	-2	1272	1252	-5	431	443
-3	573	568	-4	474	475	-2	28*	29	9	112*	100	5	108*	147	-1	363	371	-4	137	148
-2	1235	1189	-3	96*	70	-1	111*	71	5	206	207	2	337	325	0	97*	125	-3	152	89
-1	441	443	-2	120	104	0	30*	66	5	206	207	2	337	325	1	776	748	-2	200	221
0	880	791	-1	358	346	1	637	632	5	206	207	2	337	325	2	257	241	-1	349	360
1	155	128	0	374	357	2	305	300	5	206	207	2	337	325	3	334	321	0	508	489
2	306	313	1	188	158	3	78*	33	5	206	207	2	337	325	4	171	175	-1	474	428
3	1035	997	2	510	590	4	30*	86	5	206	207	2	337	325	5	880	873	1	28*	66
4	145	54	3	545	578	5	660	642	5	206	207	2	337	325	6	484	513	2	272	276
5	178	173	4	348	343	6	473	462	5	206	207	2	337	325	7	484	513	3	103*	24
6	45*	632	5	215	230	7	580	570	5	206	207	2	337	325	8	433	430	4	135	208
7	637	632	6	45*	632	8	206	196	5	206	207	2	337	325	9	148	145	5	708	719
8	358	351	7	637	632	9	29*	94	5	206	207	2	337	325	10	148	145	6	135	208
9	199	216	8	115*	493	10	137	193	5	206	207	2	337	325	11	148	145	7	604	629
H	1	4	H	7	4	H	-5	5	5	206	207	2	337	325	H	-4	6	H	2	6
-10	565	550	-8	515	493	-8	725	692	5	206	207	2	337	325	-8	430	404	-9	138	134
-9	26*	81	-7	183	182	-6	381	378	5	206	207	2	337	325	-7	18*	1	-8	620	629
-8	116	105	-6	455	457	-5	102	47	5	206	207	2	337	325	-6	226	258	-7	229	214
-7	108*	123	-5	495	483	-4	152	84	5	206	207	2	337	325	-5	227	198	-6	620	629
-6	281	261	-4	283	293	-3	192	84	5	206	207	2	337	325	-4	477	495	-5	229	214
-5	800	822	-3	271	264	-2	712	725	5	206	207	2	337	325	-3	207	224	-4	620	629
-4	872	881	-2	510	542	-1	393	425	5	206	207	2	337	325	-2	477	495	-3	229	214
-3	610	592	-1	302	309	0	244	253	5	206	207	2	337	325	-1	332	344	-2	620	629
-2	597	563	0	58*	11	-1	924	948	5	206	207	2	337	325	0	28*	62	-1	337	310
-1	250	243	1	417	417	0	1112	1085	5	206	207	2	337	325	-1	128	120	-2	560	540
0	581	586	2	417	417	1	585	578	5	206	207	2	337	325	-2	234	240	-3	217	229
1	1178	1132	3	417	417	2	197	193	5	206	207	2	337	325	-3	1575	1516	-4	345	341
2	34*	19	4	417	417	3	53*	534	5	206	207	2	337	325	-4	345	341	-5	213	204
3	315	308	5	330	387	4	137	129	5	206	207	2	337	325	-5	109*	1038	-6	849	839
4	28*	36	6	70*	104	5	228	185	5	206	207	2	337	325	-6	773	768	-7	291	305
5	477	489	7	292	289	6	544	570	5	206	207	2	337	325	-7	345	341	-8	845	805
6	217	216	8	357	357	7	23*	33	5	206	207	2	337	325	-8	109*	90	-9	291	305
7	61*	101	9	518	548	8	639	646	5	206	207	2	337	325	-9	773	771	-10	849	839
8	379	385	10	28*	88	9	367	376	5	206	207	2	337	325	-10	109*	90	-11	291	305
9	284	285	11	67*	23	10	206	221	5	206	207	2	337	325	-11	109*	90	-12	291	305
H	2	4	H	9	4	H	-4	5	5	206	207	2	337	325	H	-3	6	H	3	6
-10	38*	67	-8	108*	63	-7	140	140	5	206	207	2	337	325	-8	26*	10	-9	177	173
-9	230	240	-7	140	140	-6	1012	1017	5	206	207	2	337	325	-7	340	346	-8	222	213
-8	239	253	-6	429	406	-5	429	406	5	206	207	2	337	325	-6	134	143	-7	455	443
-7	194	182	-5	142	121	-4	136	120	5	206	207	2	337	325	-4	30*	99	-6	237	231
-6	346	339	-3	636	650	-2	636	650	5	206	207	2	337	325	-3	28*	19	-5	499	509
-5	951	948	-2	140	112	-1	140	112	5	206	207	2	337	325	-1	78*	86	-4	572	591
-4	106*	30	-1	450	452	0	450	452	5	206	207	2	337	325	0	351	330	-3	572	591
-3	464	465	0	224	223	0	224	223	5	206	207	2	337	325	0	58*	68	-2	550	343

