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Bannermanite, a new sodium-potassium vanadate isostructural with β-$Na_xV_6O_{15}$

JOHN M. HUGHES[1]

Department of Earth Sciences, Dartmouth College, Hanover, New Hampshire 03755

AND LARRY W. FINGER

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

Abstract

Bannermanite, $(Na,K)_xV_x^{4+}V_{6-x}^{5+}O_{15}$ ($0.90 > x > 0.54$), a natural vanadium oxide bronze compound, occurs as black subhedral to euhedral crystals in the oxide zone of a fumarole at Izalco volcano, El Salvador, Central America. The mineral is associated with shcherbinaite, stoiberite, and ziesite. Bannermanite is monoclinic, space group $C2/m$, with a = 15.413(7), b = 3.615(2), c = 10.066(8)Å, β = 109.29(8)°, Z = 2, D(obs) = 3.5±0.2 g/cm^3, and D(calc) = 3.55 g/cm^3. The crystal structure of bannermanite has been refined to wR = 0.074 from the vanadium oxide bronze structure model. The structure consists of a clinolattice of VO_5 square-based pyramids and VO_6 octahedra. This array of V–O polyhedra forms rectangular tunnels in which Na and K ions occur. The vanadium ions are in two charge states, V^{4+} and V^{5+}, with the number of vanadium ions in the reduced state equal to the number of alkali ions in the tunnel sites; thus, charge balance is maintained.

Bannermanite transmits light on thin edges, with a mean index of refraction of 2.2, on the basis of the rule of Gladstone and Dale. The mineral has two cleavages, ($h0l$) and ($0kl$), and a dark gray-black streak. It is named in honor of the late Dr. Harold M. Bannerman.

Introduction

Naturally occurring $(Na,K)_xV_x^{4+}V_{6-x}^{5+}O_{15}$ has been discovered in the fumaroles in the summit crater of Izalco volcano, El Salvador, Central America (13°49′N; 89°38′W). Identification of this mineral as the potassium-bearing analog of NaV_6O_{15} is based on electron probe microanalysis and X-ray diffraction analysis. The new mineral is named bannermanite in honor of the late Dr. Harold M. Bannerman. Dr. Bannerman had a long and distinguished career in the field of geology and served in such posts as Chief of the Non-metalliferous Geology Section of the U.S. Geological Survey, Chief of the Division of Economic Geology of the U.S.G.S., and Professor of Geology, Dartmouth College. The type specimen of bannermanite is currently on deposit at the Department of Earth Sciences, Dartmouth College. Cotype specimens are on deposit at the Smithsonian Institution and the Geological Museum of Harvard University. The total amount of the mineral is a few milligrams. The mineral and mineral name have been approved by the Commission on New Minerals and Mineral Names of the International Mineralogical Association.

Locality and occurrence

Izalco volcano is a basaltic composite cone that has been intermittently active since its birth in 1770. The volcano rises to an altitude of 1965 m, with 650 m relief, and has an approximate volume of 2 km^3. The geology of the volcano is described by Meyer-Abich (1958), Rose and Stoiber (1969), and Stoiber *et al.* (1975).

Since 1963 the fumarolic gases and sublimate minerals of the summit crater have been extensively studied (Stoiber and Durr 1963; Stoiber and Rose, 1970, 1974; Stoiber *et al.*, 1975; Birnie and Hughes, 1979; Hughes and Birnie, 1980b). Vanadium was found to be a distinctive element in the minerals of the sublimate suite, which includes such vanadium minerals as shcherbinaite ($V_6^{5+}O_{15}$), stoiberite ($Cu_5^{2+}V_2^{5+}O_{10}$), and ziesite (β-$Cu_2^{2+}V_2^{5+}O_7$.

Bannermanite is found in the MR and L fumaroles (Stoiber *et al.*, 1975) at Izalco volcano as a black incrustation coating basaltic breccia fragments. The mineral occurs as subhedral to euhedral crystals up to approximately 250 μm in greatest dimension. It is intimately associated with shcherbinaite.

Introduction to oxide bronzes

The oxide bronzes are compounds of the class M_xTO_n, where M is an electropositive metal ion such as Na or K,

[1] Present address: Department of Geology, Miami University, Oxford, Ohio 45056.

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Bannermanite Final Structure Factors

FACTOR = 10.00

H	OBS	CALC	H	OBS	CALC	H	OBS	CALC	H	OBS	CALC	H	OBS	CALC	H	OBS	CALC	H	OBS	CALC
	H -5	0		H -1	1		H 0	2		H -4	4		H -2	5		H 0	6		H -2	8
1	88*	45	-19	520	429	-14	573	566	4	245	244	-4	1486	1488	-20	88*	47	-18	405	430
3	277	237	-17	343	292	-12	123	131	6	227	225	-2	563	535	-18	625	609	-16	329	337
			-15	218	168	-10	1679	1581				0	289	273	-16	368	348	-14	324	214
	H -4	0	-13	675	611	-8	1157	1169		H -3	4	2	168	123	-14	368	369	-12	86*	77
			-11	172	156	-6	373	371				4	1076	1035	-12	126*	124	-10	410	416
2	489	431	-9	1046	1020	-4	243	212	-17	411	445	6	178	249	-10	492	558	-8	779	776
4	277	290	-7	1020	1031	-2	119	43	-15	209	272	8	408	424	-8	571	584	-6	194	196
6	152	91	-5	129	152	0	940	851	-13	701	780	10	285	287	-6	38*	48	-4	328	321
8	191	234	-3	256	231	2	849	843	-11	195	224	12	0*	59	-4	92*	228	-2	269	275
10	125*	145	-1	1739	1675	4	227	223	-9	206	160	14	371	319	-2	449	444	0	328	275
12	176	101	1	923	1013	6	790	743	-7	150	107				0	1607	1509	6	187	181
			3	652	627	8	1128	1118	-5	472	434		H -1	5	2	1039	1087	8	126	121
	H -3	0	5	174	41	10	842	819	-3	96*	114				4	225	242	10	424	388
			7	333	361	12	502*	190	-1	215	224	-21	256	315	6	177	184			
1	104*	36	9	1062	996	14	656	621	1	92*	117	-19	180	133	8	441	427		H -1	8
3	475	466	11	265	262	16	201	181	3	381	417	-17	246	240	10	371	331			
5	607	618	13	529	519	18	76*	60	5	626	749	-15	0*	8	14	391	392	-19	66*	94
7	320	334	15	282	252				9	360	482	-13	538	547				-17	171	230
9	359	446	17	320	333		H -4	3	11	214	267	-11	437	451		H -4	7	-15	558	585
11	135*	234	19	205	188				13	141*	68	-9	1335	1285				-13	987	1012
13	440	535				-12	56*	121				-7	924	972	-10	39*	4	-11	437	436
15	117*	99		H 0	1	-10	339	329		H -2	4	-5	750	680	-8	383	386	-9	506	394
						-8	151*	174				-1	212	228	-6	268	252	-7	399*	59
	H -2	0	-20	212	221	-6	377	411	-18	443	446	1	128	17	-4	370	275	-5	186	206
			-18	366	352	-4	846	822	-16	294	267	3	234	218	-2	278	104	-3	356	368
2	786	789	-16	240	150	-2	215	119	-14	301	228	5	151	115	0	130	194	-1	51*	93
4	452	493	-14	927	824	0	312	249	-12	147*	90	7	627	676	2	98*	48	1	385	400
6	76*	72	-12	814	807	2	193	168	-10	611	602	9	621	559	4	368	401	3	230	264
8	359	431	-10	84*	17	4	282	273	-8	660	887	11	315	315				5	564	548
10	167	259	-8	102*	30	6	415	482	-6	277	272	13	394	435		H -3	7	7	359*	76
12	77*	125	-6	286	277	8	68*	75	-4	627	621	15	391	357				9	516	568
14	98*	76	-4	731	654	10	44*	153	-2	754	751				-15	70*	40	11	412	429
16	51*	30	0	855*	697				0	940	893		H 0	5	-13	0*	11			
18	448	525	2	386	416		H -3	3	2	266	197				-11	232	184		H 0	8
			4	2150	2122				4	217	314	-20	102*	30	-9	59*	91			
	H -1	0	6	2056	1998	-17	478	507	6	348	411	-18	413	440	-7	314	295	-20	0*	46
			8	270	271	-15	150	96	8	393	382	-16	165	134	-5	35*	46	-18	417	481
1	38*	45	10	789	808	-13	136	125	10	413	488	-14	960	874	-3	41*	34	-16	403	402
3	882	895	12	260	187	-11	403	472	12	261	279	-12	313	305	-1	430	423	-14	346	248
5	844	884	14	403*	21	-9	313	402	14	90*	173	-10	59*	59	1	846	893	-12	77*	76
7	565	621	16	354	315	-7	216	145				-8	68*	88	3	194	85	-10	477	485
9	668	645	18	99*	18	-5	219	184		H -1	4	-6	815	836	7	227	240	-8	901	897
11	378	387				-3	77*	60				-4	2005	2088	9	55	45	-6	256	251
13	722	701		H -5	2	-1	599	582	-21	192	34	-2	762	755				-4	316	350
15	178	142				1	446	460	-19	371	329	2	199	178		H -2	7	-2	387	374
17	418	461	-3	489	446	3	76*	15	-17	575	565	4	1335	1373				0	365	319
19	287	233	-1	133*	149	5	511	559	-15	345	341	6	304	292	-18	55*	146	2	186	52
			1	198	183	7	150	79	-13	1025	1023	8	526	517	-16	0*	95	4	560	560
	H 0	0				9	150	166	-11	336	322	10	329	324	-14	509	545	6	201	210
				H -4	2	11	163	119	-9	380	223	12	125*	63	-12	765	778	8	109*	128
2	1435	1261				13	232	302	-7	217	97	14	468	369	-10	93	60	10	370	426
4	794	731	-12	64*	85				-5	730	698	16	149	134	-8	555	577	12	0*	15
6	0*	18	-10	689	730		H -2	3	-3	267	276				-6	469	467			
8	647	626	-8	526	578				-1	514	521		H 1	5	-4	506	427		H -3	9
10	337	348	-6	80*	102	-18	295	276	1	184	270				-2	498*	162			
12	159	134	-4	136	145	-16	122*	61	3	494	626	-3	0*	89	0	238	255	-13	239	192
14	208	88	-2	30*	5	-14	296	249	5	1035	1130				2	112	38	-11	136	194
16	49*	30	0	352	313	-12	72*	98	7	162	17		H -4	6	4	490	588	-9	841	808

20	15*	60	4	127	77	-8	210	221	11	351	337	-12	161	129	8	0*	7
			6	230	261	-6	565	564	13	0*	65	-10	369	330	12	61*	91
	H 2 0		10	576	514	-4	1430	1448	15	90*	35	-8	364	336			
						-2	400	240	17	89*	236	-6	70*	40		H -1 7	
0	3382	3030		H -3 2		0	560	488				-4	131*	86			
						2	365	327		H 0 4		-2	205	195	-19	502	527
	H -5 1		-17	103*	40	8	108	147				0	797	694	-17	816	818
			-15	200	294	10	183	193	-20	262	270	2	566	567	-15	71*	68
-3	0*	85	-13	416	463	12	0*	65	-18	508	493	4	86*	170	-13	72*	28
-1	488	453	-11	264	247	14	423	509	-16	329	298	6	131	154	-11	259	230
1	324	265	-9	293	271				-14	405	294				-9	189	151
3	226	162	-7	323	166		H -1 3		-12	76	102		H -3 6		-7	375	378
			-5	384	358				-10	813	802				-5	131	119
	H -4 1		-3	815	777	-21	399	343	-8	1161	1176	-17	0*	33	-3	97	18
			-1	181	201	-19	445	440	-6	447	486	-15	281	325	-1	500	534
-12	329	415	1	283	271	-17	646	622	-4	875	872	-13	166	90	1	1232	1299
-10	130*	78	5	469	472	-15	72*	131	-2	1152	1166	-11	412	413	3	114	92
-8	84*	7	9	422	396	-13	164	164	0	1058	1066	-9	185	174	5	669	711
-6	45*	97	11	317	306	-11	705	738	2	367*	192	-7	48*	12	7	366	322
-4	266	261	13	398	310	-9	721	591	4	325	340	-5	1121	1046	9	178	62
-2	272	147				-7	377	251	6	531	552	-3	836	823	11	87*	133
0	322	293		H -2 2		-5	426	426	8	523	500	-1	249	225	13	0*	14
2	166	143				-3	79*	74	10	559	581	1	448	454			
4	876	901	-18	128	109	-1	867	948	12	338	322	3	56*	72		H 0 7	
6	708	763	-16	76*	50	1	329	431	14	84*	178	5	127	103			
8	212	208	-14	441	480	3	0*	41	16	76	15	7	226	207	-20	250	250
10	305	372	-12	100*	112	5	710	848				9	133	7	-14	625	629
12	51*	78	-10	1156	1197	7	169	161		H -4 5		11	83*	27	-12	935	942
			-8	860	914	9	222	170							-10	137	104
	H -3 1		-6	251	239	11	126	177	-12	207	208		H -2 6		-8	705	731
			-4	199	190	13	321	373	-10	87*	43				-6	597	636
-15	74*	157	-2	79	17	15	318	282	-8	71*	9	-18	532	534	0	279	285
-13	462	442	0	638	563	17	388	381	-6	399	346	-16	300	315	2	90	17
-11	105*	102	2	540	587				-4	863	849	-14	260	334	4	666	714
-9	616	675	4	69*	139		H 0 3		-2	336	307	-12	129	128	6	676	663
-7	551	572	12	302	156				0	235	213	-10	496	475	8	53*	7
-3	15*	112	14	457	546	-20	213	225	2	123*	65	-8	479	486	10	575	563
-1	867	826	16	127	152	-18	325	323	6	151	183	-6	64*	6	12	124*	106
1	552	521				-16	208	60				-4	132	169	14	197	239
3	282	303		H -1 2		-14	386	280		H -3 5		-2	313	327			
5	66*	108				-12	43*	59				0	1169	1141		H -4 8	
7	264	245	-19	20*	87	-10	637	629	-17	0*	186	2	706	856			
11	201	215	-17	174	78	-8	238	247	-15	136	8	4	161	214	-8	575	576
13	324	378	-15	345	353	-6	576	620	-13	389	406	6	145	178	-6	142*	116
15	168	218	-13	698	686	-4	2003	2057	-11	286	279	8	316	365	-4	209	264
			-11	449	438	-2	398	366	-9	932	904	12	258	211	-2	0*	160
	H -2 1		-9	440	344	0	798	756	-7	655	633				0	250	200
			-7	667*	313	4	670	617	-5	509	417		H -1 6				
-18	299	336	-5	176	252	6	1048	1019	-3	0*	12					H -3 8	
-16	215	123	-3	1346	1349	8	204	208	-1	164	195	-21	469	417			
-14	758	710	-1	287	274	10	196	221	1	0*	31	-19	0*	63	-15	400	456
-12	607	645	1	400	434	12	69*	54	3	136	174	-15	370	421	-13	744	780
-10	45*	42	3	2*	109	14	647	576	5	87*	53	-13	97*	101	-11	336	314
-8	71	8	5	645	807	16	238	14	7	491	420	-11	648	676	-9	425	294
-6	138	199	7	405*	197	18	578	542	9	403	451	-9	396	236	-7	215	19
-4	445	459	9	566	621				11	215	239	-7	89*	20	-5	118	113
-2	405*	220	11	442	436		H -4 4					-5	1677	1661	-3	294	257
0	571	463	13	353	357					H -2 5		-3	1240	1309	-1	139	87
2	237	266	15	517	496	-12	147	67				-1	324	337	1	280	283
4	1242*	1537	17	311	308	-10	336	376	-18	406	401	1	597	638	3	148	191
8	203	255				-8	510	539	-16	83*	97	3	89*	126	5	321	450
10	452	619		H 0 2		-6	117	97	-14	819	734	5	197	172	7	159*	78
12	127	138				-4	388	380	-12	259	272	7	311	309			
14	255	25	-20	253	154	-2	392	377	-10	93	59	11	104	31			
16	257	281	-18	123	115	0	687	601	-8	112	49	13	441	434			

-5	392	274						
-3	379	361						
-1	105*	117						
1	147	159						
3	60*	154						
5	103*	126						
	H -2 9							
-18	119	186						
-16	0*	4						
-14	341	185						
-12	138	154						
-10	107*	138						
-8	41*	76						
-6	302	312						
-4	654	662						
-2	322	295						
0	484	479						
2	213	246						
4	49*	26						
6	47*	137						
8	322	323						
	H -1 9							
-19	166	102						
-17	319	325						
-15	150	106						
-13	238	226						
-11	166	230						
-9	1060	1033						
-7	513	496						
-5	443	361						
-3	489	513						
-1	221	178						
1	161	173						
3	192	218						
5	142	132						
7	266	250						
9	349	312						
	H 0 9							
-20	270	317						
-18	168	199						
-16	77*	16						
-14	372	209						
-12	218	174						
-10	205	187						
-8	0*	88						
-6	398	371						
-2	330	328						
0	577	567						
2	294	276						
4	68*	15						
6	174	175						
8	370	351						
10	276	243						
	H -3 10							
-13	504	507						
-11	316	271						
-9	310	276						

18 52* 22 -16 65* 52 2 162 167 -6 603 595 15 170 221 -7 182 90

Bannermanite Final Structure Factors FACTOR = 10.00

H	OBS	CALC	H	OBS	CALC	H	OBS	CALC	H	OBS	CALC	H	OBS	CALC	H	OBS	CALC	H	OBS	CALC
H -3 10			H -1 10			H -2 11			H 0 11			H 0 12			H 0 14					
-5	546	518	7	201	212	-6	126	141	2	166	175	-8	716	680	-10	83*	47			
-3	474	470				-4	222	218	4	351	364	-6	130	183	-8	135	140			
-1	260	253	H 0 10			-2	285	264	6	300	330	-4	589	545	-6	237	199			
1	406	384				0	173	192				-2	204	120	-4	122*	107			
3	207	231	-18	553	614	2	181	143	H -2 12			0	0*	20						
			-16	470	498							2	282*	286						
H -2 10			-14	0*	16	H -1 11			-12	202	209	4	175*	192						
			-12	398	419				-10	314	319									
-16	436	455	-10	0*	29	-17	270	318	-8	588	602	H -2 13								
-14	67*	28	-8	118	106	-15	107*	140	-6	185	150									
-12	371	352	-6	257	244	-13	223	200	-4	464	483	-8	0*	108						
-10	59*	33	-4	0*	148	-11	199	211	-2	199	118	-6	64*	25						
-8	35*	90	-2	205	201	-9	582	603	0	71*	21									
-6	190	205	0	746	681	-7	723	734				H -1 13								
-4	0*	113	2	249	278	-5	83*	81	H -1 12											
-2	207	170	4	227	230	-3	298	353				-13	343	354						
0	678	591	6	490	478	-1	416	446	-15	210	292	-11	0*	94						
2	146*	250	8	59*	9	1	469	508	-13	523	549	-9	479	492						
4	197	215				3	92*	133	-11	153	115	-7	220	138						
6	464	424	H -3 11			5	352	373	-9	399	259	-5	303	303						
									-7	204	210	-3	122	156						
H -1 10			-9	508	493	H 0 11			-5	533	503	-1	116*	135						
			-7	569	557				-3	653	659									
-15	146	146	-5	192	76	-18	248	252	-1	0*	19	H 0 13								
-13	652	642	-3	338	285	-16	100*	185	1	293	274									
-11	311	316	-1	338	354	-14	631	617	3	73*	87	-14	45*	57						
-9	381	370				-12	686	670				-12	237	186						
-7	216	157	H -2 11			-10	0*	99	H 0 12			-10	255	242						
-5	642	628				-8	253	275				-8	105*	106						
-3	569	576	-14	517	544	-6	255	168	-16	299	296	-6	86*	35						
-1	303	332	-12	549	610	-4	298	278	-14	262	91	-4	480	470						
1	474	484	-10	61*	86	-2	258	287	-12	273	222	-2	65*	92						
3	346	319	-8	194	257	0	249	225	-10	303*	364	0	406	372						