

Bannermanite, a new sodium-potassium vanadate isostructural with $\beta\text{-Na}_x\text{V}_6\text{O}_{15}$

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Abstract

Bannermanite, $(\text{Na,K})_x\text{V}_x^{4+}\text{V}_{6-x}^{5+}\text{O}_{15}$ ($0.90 > x > 0.54$), 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 $a = 15.413(7)$, $b = 3.615(2)$, $c = 10.066(8)\text{\AA}$, $\beta = 109.29(8)^\circ$, $Z = 2$, $D(\text{obs}) = 3.5 \pm 0.2 \text{ g/cm}^3$, and $D(\text{calc}) = 3.55 \text{ g/cm}^3$. 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 $(\text{Na,K})_x\text{V}_x^{4+}\text{V}_{6-x}^{5+}\text{O}_{15}$ has been discovered in the fumaroles in the summit crater of Izalco volcano, El Salvador, Central America ($13^\circ 49' \text{N}$; $89^\circ 38' \text{W}$). Identification of this mineral as the potassium-bearing analog of $\text{NaV}_6\text{O}_{15}$ 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. Co-type 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 ($\text{V}_6^{5+}\text{O}_{15}$), stoiberite ($\text{Cu}_3^{2+}\text{V}_2^{5+}\text{O}_{10}$), and ziesite ($\beta\text{-Cu}_2^{2+}\text{V}_2^{5+}\text{O}_7$).

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 $250 \mu\text{m}$ 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,

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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-5 | 0 | | H-1 | 1 | | H | 0 | 2 | H | -4 | 4 | H | -4 | 4 | H | -2 | 5 |
| 1 | 88* | 45 | -19 | 520 | 429 | -14 | 573 | 566 | 4 | 245 | 244 | -4 | 1486 | 1488 | -20 | 88* | 47 |
| 3 | 277 | 237 | -17 | 343 | 292 | -12 | 123 | 131 | 6 | 227 | 225 | -2 | 563 | 535 | -18 | 625 | 609 |
| H-4 | 0 | | -15 | 218 | 168 | -10 | 1679 | 1581 | 6 | 227 | 225 | 0 | 289 | 273 | -16 | 368 | 348 |
| 2 | 489 | 431 | -13 | 675 | 611 | -8 | 1157 | 1169 | H-3 | 4 | | 2 | 168 | 123 | -14 | 368 | 369 |
| 4 | 277 | 290 | -11 | 172 | 156 | -6 | 373 | 371 | H-3 | 4 | | 4 | 1076 | 1035 | -12 | 126* | 124 |
| 6 | 152 | 91 | -9 | 1046 | 1020 | -4 | 243 | 212 | -17 | 411 | 445 | 6 | 178 | 249 | -10 | 492 | 558 |
| 8 | 191 | 234 | -7 | 1020 | 1031 | -2 | 119 | 1031 | -15 | 209 | 272 | 8 | 408 | 424 | -8 | 571 | 584 |
| 10 | 125* | 145 | -5 | 129 | 152 | 0 | 940 | 851 | -13 | 701 | 780 | 10 | 285 | 287 | -6 | 38* | 48 |
| 12 | 176 | 101 | -3 | 256 | 231 | 4 | 849 | 843 | -11 | 195 | 224 | 12 | 0* | 59 | -4 | 92* | 228 |
| H-3 | 0 | | -1 | 1739 | 1675 | 4 | 227 | 223 | -9 | 206 | 160 | 14 | 371 | 319 | -2 | 449 | 444 |
| 1 | 104* | 35 | 6 | 923 | 1013 | 6 | 790 | 743 | -7 | 150 | 107 | H-1 | 5 | | 0 | 1607 | 1509 |
| 3 | 475 | 466 | 3 | 652 | 627 | 8 | 1128 | 1118 | -5 | 472 | 434 | H-1 | 5 | | 2 | 1039 | 1087 |
| 5 | 607 | 618 | 5 | 174 | 41 | 10 | 842 | 819 | -3 | 96* | 114 | 4 | 225 | 242 | 4 | 225 | 242 |
| 7 | 320 | 334 | 7 | 333 | 361 | 12 | 502* | 150 | -1 | 215 | 224 | 6 | 177 | 184 | 6 | 177 | 184 |
| 9 | 359 | 446 | 9 | 1062 | 996 | 14 | 656 | 621 | -1 | 92* | 117 | -19 | 180 | 133 | 8 | 441 | 427 |
| 11 | 135* | 234 | 11 | 265 | 262 | 16 | 201 | 181 | 3 | 381 | 417 | -17 | 246 | 240 | 10 | 371 | 331 |
| 13 | 440 | 535 | -14 | 927 | 824 | 18 | 76* | 60 | 5 | 626 | 749 | -15 | 0* | 8 | 14 | 391 | 392 |
| 15 | 117* | 99 | -12 | 814 | 807 | H-4 | 3 | | 9 | 360 | 482 | -13 | 538 | 547 | 14 | 391 | 392 |
| H-2 | 0 | | 2 | 282 | 252 | -10 | 339 | 329 | 11 | 214 | 267 | -11 | 437 | 451 | H-4 | 7 | |
| 2 | 786 | 789 | 19 | 205 | 188 | -12 | 56* | 121 | 13 | 141* | 68 | -9 | 1335 | 1285 | -10 | 39* | 4 |
| 4 | 452 | 493 | H | 0 | 1 | -8 | 151* | 174 | H-2 | 4 | | -5 | 750 | 680 | -8 | 383 | 386 |
| 6 | 76* | 72 | -20 | 212 | 221 | -6 | 377 | 411 | -18 | 443 | 446 | -7 | 924 | 972 | -6 | 268 | 252 |
| 8 | 359 | 431 | -18 | 366 | 352 | -4 | 846 | 822 | -16 | 294 | 267 | -1 | 128 | 17 | -4 | 370 | 275 |
| 10 | 167 | 259 | -16 | 240 | 150 | 0 | 215 | 119 | -14 | 301 | 228 | 3 | 234 | 218 | -2 | 278 | 104 |
| 12 | 77* | 125 | -14 | 927 | 824 | 2 | 312 | 249 | -12 | 147* | 90 | 5 | 151 | 115 | 0 | 130 | 194 |
| 14 | 98* | 76 | -12 | 814 | 807 | 4 | 193 | 168 | -10 | 611 | 602 | 7 | 627 | 676 | 2 | 98* | 48 |
| 16 | 51* | 30 | -10 | 84* | 17 | 6 | 415 | 482 | -8 | 560 | 887 | 9 | 621 | 559 | 4 | 368 | 401 |
| 18 | 448 | 525 | -8 | 102* | 30 | 8 | 6* | 75 | -6 | 277 | 272 | 11 | 315 | 315 | 13 | 394 | 435 |
| H-1 | 0 | | -6 | 286 | 277 | 10 | 44* | 153 | -4 | 627 | 621 | 15 | 391 | 357 | 15 | 391 | 357 |
| 1 | 38* | 45 | 2 | 386 | 416 | H-3 | 3 | | 0 | 940 | 893 | H | 0 | 5 | -15 | 70* | 40 |
| 3 | 882 | 895 | 4 | 2150 | 2122 | 6 | 478 | 507 | 2 | 266 | 197 | -13 | 0* | 11 | -13 | 232 | 184 |
| 5 | 844 | 884 | 6 | 2056 | 1998 | -17 | 478 | 507 | 6 | 348 | 411 | -18 | 413 | 440 | -11 | 59* | 91 |
| 7 | 565 | 621 | 8 | 270 | 271 | -15 | 150 | 96 | 8 | 393 | 382 | -16 | 165 | 134 | -9 | 59* | 91 |
| 9 | 668 | 645 | 10 | 789 | 808 | -13 | 136 | 125 | 6 | 413 | 488 | -14 | 960 | 874 | -7 | 314 | 295 |
| 11 | 378 | 387 | -11 | 403 | 472 | -9 | 403 | 472 | 10 | 413 | 488 | -12 | 313 | 305 | -5 | 83* | 46 |
| 13 | 722 | 701 | -7 | 216 | 145 | -7 | 216 | 145 | 12 | 261 | 279 | -10 | 59* | 59 | -3 | 41* | 34 |
| 15 | 178 | 142 | -5 | 219 | 184 | -5 | 219 | 184 | 14 | 90* | 173 | -10 | 59* | 59 | -1 | 430 | 423 |
| 17 | 418 | 461 | -3 | 77* | 60 | -3 | 77* | 60 | H-1 | 4 | | -8 | 68* | 88 | 1 | 846 | 893 |
| 19 | 287 | 233 | -1 | 599 | 582 | -1 | 599 | 582 | 14 | 90* | 173 | -6 | 815 | 836 | 3 | 194 | 85 |
| H | 0 | 0 | -1 | 446 | 460 | -3 | 77* | 60 | 2 | 266 | 197 | -6 | 815 | 836 | 7 | 227 | 240 |
| 2 | 1435 | 1261 | -1 | 446 | 460 | -3 | 77* | 60 | 2 | 266 | 197 | -4 | 2005 | 2088 | 9 | 227 | 240 |
| 4 | 794 | 731 | -1 | 599 | 582 | -1 | 446 | 460 | 2 | 266 | 197 | -2 | 762 | 755 | 9 | 227 | 240 |
| 6 | 0* | 18 | -1 | 446 | 460 | -1 | 446 | 460 | 2 | 266 | 197 | -2 | 762 | 755 | H-2 | 7 | |
| 8 | 647 | 626 | 3 | 76* | 15 | 3 | 76* | 15 | -17 | 575 | 565 | 4 | 1335 | 1373 | -16 | 55* | 146 |
| 10 | 337 | 348 | 5 | 511 | 559 | -13 | 1025 | 1023 | -15 | 345 | 341 | 8 | 526 | 517 | -16 | 0* | 95 |
| 12 | 159 | 134 | 7 | 150 | 79 | -13 | 1025 | 1023 | -13 | 1025 | 1023 | 10 | 329 | 324 | -14 | 509 | 545 |
| 14 | 208 | 88 | 9 | 150 | 166 | -9 | 380 | 223 | -11 | 336 | 322 | 12 | 125* | 63 | -12 | 765 | 778 |
| 16 | 49* | 30 | 11 | 163 | 119 | -9 | 380 | 223 | -9 | 380 | 223 | 14 | 468 | 369 | -10 | 93 | 60 |
| | | | 13 | 232 | 302 | -7 | 21* | 97 | -7 | 21* | 97 | 16 | 149 | 134 | -8 | 555 | 577 |
| | | | H-2 | 3 | | -5 | 730 | 698 | -3 | 267 | 276 | -4 | 506 | 427 | -6 | 469 | 467 |
| | | | | | | -3 | 267 | 276 | 1 | 184 | 270 | H | 1 | 5 | -4 | 506 | 427 |
| | | | | | | 1 | 184 | 270 | 1 | 184 | 270 | -2 | 498* | 162 | -4 | 498* | 162 |
| | | | | | | 3 | 494 | 626 | 3 | 494 | 626 | 0 | 238 | 255 | 0 | 238 | 255 |
| | | | | | | 5 | 1035 | 1130 | 5 | 1035 | 1130 | 2 | 112 | 38 | 2 | 112 | 38 |
| | | | | | | 7 | 162 | 17 | 7 | 162 | 17 | 4 | 490 | 588 | 4 | 490 | 588 |
| | | | | | | H-4 | 6 | | H-4 | 6 | | H-3 | 9 | | -13 | 239 | 192 |
| | | | | | | | | | | | | | | | -11 | 136 | 194 |
| | | | | | | | | | | | | | | | -9 | 841 | 808 |

Table with multiple columns and rows of numerical data, including values like 20 15* 60, 4 127 77, 6 230 261, 10 576 514, etc. The data is organized in a grid-like structure with various numerical entries across the page.

