

BOBJONESITE, $V^{4+}O(SO_4)(H_2O)_3$, A NEW MINERAL SPECIES FROM TEMPLE MOUNTAIN, EMERY COUNTY, UTAH, U.S.A.

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ABSTRACT

Bobjonesite, $V^{4+}O(SO_4)(H_2O)_3$, is a new mineral species from Temple Mountain, Emery County, Utah, U.S.A. It occurs as blue-green crusts and efflorescences in fractures in a fossil (Triassic) tree; individual crystals are $\ll 1$ mm and are intimately intergrown. Bobjonesite hydrates very easily, and is unstable in all but the driest atmosphere. Its structure was determined on a crystal of bobjonesite; however, the physical properties, optical properties and X-ray powder-diffraction pattern were recorded on the synthetic equivalent, and an electron-microprobe analysis was not possible. Bobjonesite has a pale blue streak, a vitreous luster and no observable fluorescence under ultraviolet light. It has no cleavage or parting. The Mohs hardness is ~ 1 , and the calculated density is 2.28 g/cm^3 . Bobjonesite is biaxial positive, with $\alpha 1.555(2)$, $\beta 1.561(1)$, $\gamma 1.574(2)$, $2V(\text{obs.}) = 72(1)^\circ$, $2V(\text{calc.}) = 69^\circ$; it is non-pleochroic, $X = b$, $Y \approx a$, $Z \wedge c \approx 19^\circ$ (in β obtuse). Bobjonesite is monoclinic, space group $P2_1/n$, cell dimensions from single-crystal data: $a 7.3940(5)$, $b 7.4111(3)$, $c 12.0597(9) \text{ \AA}$, $\beta 106.55(1)^\circ$, $V 633.5(1) \text{ \AA}^3$, $Z = 4$. The strongest seven lines in the X-ray powder-diffraction pattern [d in $\text{Å}(hkl)$] are as follows: $5.795(100)(002)$, $3.498(90)(112)$, $3.881(48)(\bar{1}03)$, $5.408(37)(101)$, $4.571(20)(012)$, $6.962(11)(\bar{1}01)$ and $6.254(11)(011)$. The chemical formula was derived from crystal-structure analysis; the end-member formula is $V O(SO_4)(H_2O)_3$. The crystal structure of bobjonesite was refined to an R index of 3.6% for 1105 observed ($|F_o| > 5\sigma F$) reflections measured with an automated four-circle X-ray diffractometer using $MoK\alpha$ X-radiation. There is one V site occupied by V^{4+} and surrounded by three O atoms and three (H_2O) groups in an octahedral arrangement, with one short vanadyl bond (1.577 \AA), four similar equatorial bonds ($< 2.022 \text{ \AA}$), and one longer $V-O$ bond (2.278 \AA) *trans* to the vanadyl bond. The structure consists of isolated $[V^{4+}_2 O_2 (H_2O)_6 (SO_4)_2]$ clusters linked by hydrogen bonds.

Keywords: bobjonesite, new mineral species, crystal structure, minasragrite, orthominasragrite, anorthominasragrite, vanadate, Temple Mountain, Utah.

SOMMAIRE

Nous décrivons ici la bobjonesite, $V^{4+}O(SO_4)(H_2O)_3$, nouvelle espèce minérale découverte au mont Temple, comté d'Emery, au Utah. On la trouve en croûtes bleu-vert et en efflorescences le long de fissures dans un arbre fossilisé d'âge triassique. Les cristaux sont sub-millimétriques et intimement enchevêtrés. La bobjonesite est facilement hydratée, et donc instable sous conditions ambiantes sauf les plus arides. Nous en avons déterminé la structure; toutefois, les propriétés physiques et optiques et le spectre de diffraction ont dû être enregistrés en employant l'équivalent synthétique. Une analyse à la microsonde électronique n'a pas été possible. La bobjonesite a une rayure bleu pâle et un éclat vitreux, et ne montre aucune fluorescence en lumière ultraviolette. Elle est sans clivage ou plan de séparation. La dureté de Mohs est d'environ 1, et la densité calculée est 2.28 g/cm^3 . La bobjonesite est biaxe positive, avec $\alpha 1.555(2)$, $\beta 1.561(1)$, $\gamma 1.574(2)$, $2V(\text{obs.}) = 72(1)^\circ$, $2V(\text{calc.}) = 69^\circ$; elle est non-pleochroïque, $X = b$, $Y \approx a$, $Z \wedge c \approx 19^\circ$ (dans l'angle β obtus). Elle est monoclinique, groupe spatial $P2_1/n$, avec les dimensions

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de la maille suivantes, déterminées sur cristal unique: a 7.3940(5), b 7.4111(3), c 12.0597(9) Å, β 106.55(1)°, V 633.5(1) Å³, Z = 4. Les sept raies les plus intenses du spectre de diffraction (méthode des poudres) [d en Å(hkl)] sont: 5.795(100)(002), 3.498(90)(112), 3.881(48)($\bar{1}03$), 5.408(37) (101), 4.571(20)(012), 6.962(11)($\bar{1}01$) et 6.254(11)(011). La formule chimique a été dérivée à partir des résultats de l'ébauche de la structure; le pôle possède la formule $V O (SO_4) (H_2O)_3$. Nous en avons affiné la structure cristalline jusqu'à un résidu R de 3.6% en utilisant 1105 réflexions observées ($|F_o| > 5\sigma F$) mesurées avec un diffractomètre automatisé à quatre cercles et un rayonnement $MoK\alpha$. La structure contient le V^{4+} dans le site V , entouré de trois atomes d'oxygène et trois groupes (H_2O) dans un agencement octaédrique, avec une liaison vanadyle courte (1.577 Å), quatre liaisons équatoriales semblables (<2.022 Å>), et une liaison $V-O$ plus longue (2.278 Å) en position *trans* par rapport à la liaison vanadyle. La structure contient des groupements $[V^{4+}_2 O_2 (H_2O)_6 (SO_4)_2]$ isolés, interliés par des liaisons hydrogène.

(Traduit par la Rédaction)

Mots-clés: bobjonesite, nouvelle espèce minérale, structure cristalline, minasragrite, orthominasragrite, anorthominasragrite, vanadate, mont Temple, Utah.

INTRODUCTION

The Temple Mountain region of Utah contains some novel vanadium sulfate minerals associated with fossil trees of Triassic age. Systematic examination of these assemblages has led to the identification of several new minerals, and we have recently reported on orthominasragrite (Hawthorne *et al.* 2001). As a result of the successful solution and refinement of the crystal structure, we have identified bobjonesite as a new mineral species from this locality. Bobjonesite is unstable in all but the driest atmospheres, rapidly hydrating on exposure to air. Consequently, the physical properties were measured partly on the synthetic equivalent. The name honors Robert (Bob) Jones (born 1926) of Cave Creek, Arizona, for his enormous contributions to the mineralogical community through writing, lecturing and editing books, magazines and videos on minerals and their occurrence. The new mineral and mineral name were approved by the Commission on New Minerals and Mineral Names of the International Mineralogical Association, IMA# 2000-045. The holotype specimen of bobjonesite is stored in the collection of the Canadian Museum of Nature, Ottawa, Canada, catalogue number CMNMC 83759.

LOCALITY

The Temple Mountain mining district, in Emery County, Utah, had its initial mining claims staked in 1898. Most of the uranium–vanadium ore occurs in collapse structures, altered rocks, and widely separated stratigraphic units of the Shinarump conglomerate member of the Triassic Chinle Formation. A “considerable” amount of the ore was produced between 1914 and 1920. Between 1920 and 1948, only a small amount was produced. More profitable processes of extraction for uranium and vanadium from asphaltic ores were developed by 1948, which led to an acceleration of ore production in the district. From 1948 through 1956, the district produced about 237,000 tonnes of uranium ore that contained about 584,000 kilograms of U_3O_8 and

1,723,000 kilograms of V_2O_5 (Hawley *et al.* 1965). Production continued until 1965.

The North Mesa Mine Group is located on the southwestern end of the Calyx bench, in the southwest 1/4 of section 35, and on the adjacent eastern edge of section 34, Township 24 South, Range 11 East. Ore occurs in lenses of conglomeratic sandstone, scattered nodules in the sandstone, and in massive layers in the conglomerate near its contacts with other rocks. Near the base of the Shinarump conglomerate, high-grade asphaltic ore, with galena and sphalerite, occurs in silicified and calcified logs (in the North Mesa 5 mine) that host four blue vanadium sulfate minerals.

On March 11, 2002, the Utah Mined Land Reclamation Program started field supervision of a three-month construction program to close off most of the shafts and adits in the district; the North Mesa 5 mine is now closed.

PARAGENESIS

The host rock is the Shinarump conglomerate member of the late Triassic Chinle Formation. Bobjonesite occurs in a silicified tree, approximately 46 cm wide by 30 cm high by an undetermined length; there is a rim of coal 6–25 mm thick around the tree (Fig. 1). Pyrite has replaced part of the tree, and groundwater has reacted with the pyrite to produce various colorless, white and yellow iron sulfate minerals, including ferricopiapite, kornelite, rozenite, szomolnokite and an unidentified yellow-green hydrated Fe–V sulfate, accompanied by microscopic yellow crystals and yellow-to-green fine-grained aggregates of native sulfur. The iron sulfates generally occur in the outer rim of coal and in the adjacent conglomerate. There is dense submetallic to somewhat earthy, dull grey, radiating montroseite in the silicified tree, the probable source of the V that occurs in blue and green secondary vanadium sulfate minerals; these include bobjonesite, anorthominasragrite $V^{4+} O (SO_4) (H_2O)_5$ (Cooper *et al.*, in prep.), orthominasragrite and minasragrite, all of which are subtly different shades of blue.



FIG. 1. The silicified log and its coalified margin that hosts bobjonesite and other sulfate minerals. Bob Jones is shown for scale.

Specimens from the tree can leave a sticky resinous material on the fingers. Droplets of an Fe–V-rich liquid are, in some cases, present on fractures in freshly exposed fragments of tree. This liquid is acidic, destroying paper containers, and sometimes seeps from new fractures to evaporate and form native sulfur and sulfate minerals.

SYNTHESIS

Tudo (1965) gave a detailed description of the synthesis of vanadyl sulfates in different states of hydration. He showed that the ratio $\text{H}_2\text{SO}_4 : \text{V}_2\text{O}_5$ in solution determines the hydration state of the evaporation product: the pentahydrate, $\text{V O}(\text{SO}_4)(\text{H}_2\text{O})_5$, can be synthesized at an $\text{H}_2\text{SO}_4 : \text{V}_2\text{O}_5$ ratio of 3:1, and the trihydrate, $\text{V O}(\text{SO}_4)(\text{H}_2\text{O})_3$, can be synthesized at a value of 10:1. To reduce V^{5+} to V^{4+} , Tudo (1965) added gaseous (SO_2) until the color of the solution completely changed from orange to blue. Schneider *et al.* (1982) showed that with increasing temperature at constant $\text{H}_2\text{SO}_4/\text{V}_2\text{O}_5$, lower hydrates of vanadyl sulfates form. They also showed that between room temperature and 50°C , crystals of monoclinic $\text{V O}(\text{SO}_4)(\text{H}_2\text{O})_3$ precipitate, whereas from 50 to 130°C , the orthorhombic phase of $\text{V O}(\text{SO}_4)(\text{H}_2\text{O})_3$ forms.

Guided by these findings, we synthesized monoclinic $\text{V O}(\text{SO}_4)(\text{H}_2\text{O})_3$ at 40°C with $\text{V O}(\text{SO}_4)(\text{H}_2\text{O})_5$ and H_2SO_4 in a molar ratio of 1:6. After several weeks, large monoclinic crystals had formed. The powder-diffraction pattern of the sample was that of monoclinic $\text{V O}(\text{SO}_4)(\text{H}_2\text{O})_3$ with a small impurity of orthorhombic

$\text{V O}(\text{SO}_4)(\text{H}_2\text{O})_3$; there are no strong overlaps in these patterns [monoclinic $\text{V O}(\text{SO}_4)(\text{H}_2\text{O})_3$, PDF No. 27–950; orthorhombic $\text{V O}(\text{SO}_4)(\text{H}_2\text{O})_3$, JCPDS No. 36–651]. Thus, all peaks with relative intensities >5 were identified as peaks of the monoclinic $\text{V O}(\text{SO}_4)(\text{H}_2\text{O})_3$ powder pattern. Physical and optical properties were measured on synthetic crystals of $\text{V O}(\text{SO}_4)(\text{H}_2\text{O})_3$.

PHYSICAL PROPERTIES

Bobjonesite occurs as blue-green crusts and efflorescences; individual grains are $<<1$ mm. The grains are pale blue (paler blue than orthominasragrite), the streak is pale blue, and the luster, vitreous; no cleavage or parting was observed. The Mohs hardness is difficult to measure accurately, but it is approximately 1. The density could not be measured because of the instability of the mineral; the calculated density is 2.28 g/cm^3 .

Optical properties were measured with a Bloss spindle stage for the wavelength 590 nm using a gel filter. Bobjonesite is biaxial positive; the indices of refraction are α 1.555(2), β 1.561(1), γ 1.574(2), the calculated birefringence $\gamma - \alpha$ is 0.019, $(+2V(\text{meas.}) 72(1)^\circ$, $2V(\text{calc.}) 69^\circ$; orientation $X = b$, $Y \approx a$, $Z \wedge c \approx 19^\circ$ (in β obtuse); there is no pleochroism. Using the Gladstone–Dale relation, the calculated compatibility is poor (0.175). This is in accord with the compatibilities calculated for minasragrite, orthominasragrite and anorthominasragrite, and indicate that the Gladstone–Dale constant for VO_2 is not correct.

X-RAY POWDER DIFFRACTION

The powder-diffraction pattern was recorded with a Philips PW1729 powder diffractometer using Ni-filtered $\text{CuK}\alpha$ radiation. Table 1 shows the X-ray powder-diffraction data for bobjonosite, together with the unit-cell dimensions refined from the powder pattern. Unit-cell dimensions were also determined on a Siemens P4 automated four-circle diffractometer (Table 2).

SINGLE-CRYSTAL DIFFRACTION

A small crystal of the mineral was attached to a glass fiber and mounted on a Siemens P4 automated four-circle diffractometer equipped with a serial detector and $\text{MoK}\alpha$ X-radiation. Reflections were automatically aligned, and the cell dimensions and orientation matrix were determined by least-squares refinement of the setting angles; the values are given in Table 2. A total of 5972 reflections was measured out to $60^\circ 2\theta$. Data were corrected for Lorentz, polarization and background effects, and reduced to structure factors; of the 1839 symmetrically distinct reflections, 1105 were considered as observed ($|F_o| > 5\sigma F$).

TABLE 1. X-RAY POWDER-DIFFRACTION DATA FOR BOBJONOSITE

| d(obs) | d(calc) | l/l _o | h | k | l | d(obs) | d(calc) | l/l _o | h | k | l |
|--------|---------|------------------|---|---|---|--------|---------|------------------|---|---|---|
| 6.982 | 7.005 | 11 | 1 | 0 | 1 | 3.498 | 3.498 | 90 | 1 | 1 | 2 |
| 6.255 | 6.247 | 11 | 0 | 1 | 1 | 3.423 | 3.424 | 10 | 0 | 1 | 3 |
| 5.795 | 5.790 | 100 | 0 | 0 | 2 | 3.295 | 3.288 | 6 | 1 | 2 | 0 |
| 5.408 | 5.403 | 37 | 1 | 0 | 1 | 3.200 | 3.201 | 6 | 2 | 1 | 0 |
| 4.571 | 4.564 | 20 | 0 | 1 | 2 | 2.817 | 2.818 | 5 | 1 | 1 | 3 |
| 4.369 | 4.368 | 9 | 1 | 1 | 1 | 2.643 | 2.642 | 3 | 2 | 0 | 4 |
| 3.881 | 3.887 | 48 | 1 | 0 | 3 | 2.489 | 2.489 | 4 | 2 | 1 | 4 |
| 3.712 | 3.710 | 3 | 0 | 2 | 0 | 2.459 | 2.459 | 9 | 3 | 0 | 1 |
| 3.550 | 3.548 | 8 | 2 | 0 | 0 | 2.417 | 2.419 | 4 | 0 | 3 | 1 |

Diffractometer: Philips PW 1729, wavelength: $\text{CuK}\alpha$, (1.5406 Å), filter: nickel, external standard: SiO_2 (quartz). Lattice parameters refined from powder-diffraction data: a 7.404(3), b 7.420(3), c 12.080(7) Å, β 106.56(5)°. Values of d(obs) and d(calc) are expressed in Å.

TABLE 2. EXPERIMENTAL DATA FOR BOBJONOSITE

| Crystal system | monoclinic | Crystal size (µm) | 40 x 40 x 60 |
|---------------------|------------|----------------------|--------------------|
| Space group | $P2_1/n$ | Wavelength (Å) | $\text{MoK}\alpha$ |
| a (Å) | 7.3940(5) | No. of l | 5972 |
| b | 7.4111(3) | No. of unique F | 1839 |
| c | 12.0597(9) | No. of Fobs > 5σF | 1105 |
| β (°) | 106.55(1) | R _{int} (%) | 2.2 |
| V (Å ³) | 633.5(1) | R (%) | 3.6 |
| Z | 4 | wR (%) | 3 |

$$R = \Sigma(|F_o| - |F_c|) / \Sigma|F_o|$$

$$wR = \Sigma w(|F_o| - |F_c|)^2 / \Sigma F_o^2)^{1/2}, w = 1$$

STRUCTURE SOLUTION AND REFINEMENT

Scattering curves for neutral atoms were taken from the International Tables for Crystallography (Ibers & Hamilton 1992). R indices are of the form given in Table 1, and are expressed as percentages. The Siemens SHELXTL PLUS (PC version) system of programs was used for this work.

The structure was solved by direct methods. Two cation sites were identified by a combination of site-scattering values and local stereochemistry. All anions were assumed to be oxygen atoms ($Z = 8$), and the cation scattering indicated that the two cation sites are occupied by V ($Z = 23$) and S ($Z = 16$); the local stereochemistry is in accord with this interpretation. The structure refined rapidly to an R index of ~4% for a model with anisotropic-displacement factors at all non-hydrogen atoms. At this stage, a difference-Fourier map allowed identification of H-atom sites. These were added to the refinement with the soft constraint that O-H be approximately equal to 0.98 Å. Full-matrix least-squares refinement of all atoms (with fixed isotropic-displacement factors on all the H atoms) converged to an R index of 3.6%. Positional and displacement parameters for the constrained refinement are given in Table 3, selected interatomic distances are listed in Table 4, and bond-valences are given in Table 5. Observed and calculated structure-factors are available from The Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A 0S2, Canada.

DESCRIPTION OF THE STRUCTURE

Bobjonosite is isostructural with synthetic V^{4+} O (SO_4) $(\text{H}_2\text{O})_3$, the crystal structure of which was reported by Tachez & Theobald (1980); however, details of the hydrogen bonding are somewhat different.

Coordination of the cations

There is one S site, occupied by S and surrounded by four O atoms in a tetrahedral arrangement with a <S-O> distance of 1.470 Å, close to the grand <S-O> distance of 1.473 Å reported for sulfate minerals by Hawthorne *et al.* (2000). There is one V site, occupied by V and surrounded by six O atoms in an octahedral arrangement. There is one very short V-O distance of 1.577 Å, four intermediate length V-O bonds in the range 2.002–2.048 Å and approximately orthogonal to the short V-O bond, and one long bond of 2.278 Å *trans* to the short V-O bond. The short V-O bond is a *vanadyl* bond, the intermediate-length bonds are *equatorial* bonds, and the long bond is a *trans* bond. This geometry is characteristic of $^{[6]}\text{V}^{4+}$, as discussed by Schindler *et al.* (2000).

TABLE 3. POSITIONAL COORDINATES AND ANISOTROPIC-DISPLACEMENT PARAMETERS FOR BOBJONESITE

| | x | y | z | U_{11} | U_{22} | U_{33} | U_{23} | U_{13} | U_{12} | U_{eq} |
|------|------------|------------|-------------|------------|------------|------------|-------------|------------|-------------|------------|
| V | 0.56808(9) | 0.28298(9) | -0.12525(5) | 0.0122(3) | 0.0172(3) | 0.0153(3) | 0.0047(2) | 0.0044(2) | 0.0009(2) | 0.0148(2) |
| S | 0.2291(1) | 0.3590(1) | -0.01264(7) | 0.0118(4) | 0.0120(4) | 0.0158(4) | 0.0014(4) | 0.0047(4) | 0.0001(3) | 0.0130(2) |
| O(1) | 0.4478(4) | 0.4063(5) | -0.2260(3) | 0.0245(17) | 0.0556(23) | 0.0290(17) | 0.0193(14) | 0.0089(14) | 0.0137(14) | 0.0361(12) |
| O(2) | 0.7577(4) | 0.1028(3) | 0.0128(2) | 0.0165(14) | 0.0196(15) | 0.0229(14) | -0.0043(11) | 0.0030(11) | 0.0023(11) | 0.0202(9) |
| O(3) | 0.4416(4) | 0.0398(4) | -0.1696(2) | 0.0259(17) | 0.0340(16) | 0.0219(14) | -0.0116(12) | 0.0122(13) | -0.0145(13) | 0.026(1) |
| O(4) | 0.7614(4) | 0.2042(4) | -0.2081(2) | 0.0167(13) | 0.0331(15) | 0.0211(13) | -0.0019(12) | 0.0087(11) | -0.0019(11) | 0.024(1) |
| O(5) | 0.7627(4) | 0.4573(4) | -0.0356(2) | 0.0163(14) | 0.0170(14) | 0.0427(18) | -0.0075(12) | 0.0121(13) | -0.0022(11) | 0.026(1) |
| O(6) | 0.4230(3) | 0.3012(4) | -0.0086(2) | 0.0124(12) | 0.0220(14) | 0.0210(13) | -0.0008(10) | 0.0066(10) | 0.0038(10) | 0.018(1) |
| O(7) | 0.1576(4) | 0.2350(3) | 0.0596(2) | 0.0198(13) | 0.0188(14) | 0.0220(13) | 0.0024(10) | 0.0102(11) | -0.0002(10) | 0.021(1) |
| O(8) | 0.1073(4) | 0.3574(4) | -0.1310(2) | 0.0174(14) | 0.0378(16) | 0.0167(13) | 0.0063(12) | 0.0045(11) | -0.0015(12) | 0.025(1) |
| H(1) | 0.880(3) | 0.152(5) | 0.057(3) | 0.0200* | | | | | | |
| H(2) | 0.803(6) | -0.012(3) | -0.009(3) | 0.0200* | | | | | | |
| H(3) | 0.354(5) | -0.001(5) | -0.127(3) | 0.0200* | | | | | | |
| H(4) | 0.915(4) | 0.512(4) | 0.253(3) | 0.0200* | | | | | | |
| H(5) | 0.726(5) | 0.226(5) | -0.2917(6) | 0.0200* | | | | | | |
| H(6) | 0.889(2) | 0.251(5) | -0.172(3) | 0.0200* | | | | | | |

* Fixed during refinement

TABLE 4. SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (°) IN BOBJONESITE

| | | | |
|------------------|----------|------------------|----------|
| V-O(1) | 1.577(3) | S-O(5) | 1.475(3) |
| V-O(2) | 2.278(2) | S-O(6) | 1.484(3) |
| V-O(3) | 2.031(3) | S-O(7) | 1.465(3) |
| V-O(4) | 2.048(3) | S-O(8) | 1.455(2) |
| V-O(5) | 2.006(3) | <S-O> | 1.470 |
| V-O(6) | 2.002(3) | | |
| <V-O> | 1.990 | | |
| H(1)-O(2) | 0.98(2) | H(3)-O(3) | 0.98(3) |
| H(1)...O(7) | 2.13(2) | H(3)...O(2) | 1.95(3) |
| H(2)-O(2) | 0.98(3) | H(4)-O(3) | 0.98 |
| H(2)...O(7) | 1.81(2) | H(4)...O(8) | 1.73(3) |
| H(1)-O(2)-H(2) | 97(3) | H(4)-O(3)-H(3) | 113(2) |
| O(2)-H(1)...O(7) | 148(3) | O(3)-H(3)...O(2) | 164(3) |
| O(2)-H(2)...O(7) | 169(3) | O(3)-H(4)...O(8) | 168(3) |
| H(5)-O(4) | 0.98(3) | H(5)-O(4)-H(6) | 110(2) |
| H(5)...O(7) | 1.74(7) | O(4)-H(5)...O(7) | 179(1) |
| H(6)-O(4) | 0.98(2) | O(4)-H(6)...O(8) | 170(3) |
| H(6)...O(8) | 1.74(2) | | |

The O(2)-H(1), O(2)-H(2), O(3)-H(3), O(3)-H(4), O(4)-H(5) and O(4)-H(6) bond lengths were softly constrained to the value 0.98 Å.

Topology of the structure

The structure of bobjonesite consists of $(V\phi_6)$ ($\phi = O, H_2O$) octahedra and (SO_4) tetrahedra linked together by sharing corners to form a four-membered ring of alternating octahedra and tetrahedra of the form $[V_2(SO_4)_2 O_2 (H_2O)_6] = [M_2(TO_4)_2 \phi_8]$ (M : octahedrally coordinated cation, T : tetrahedrally coordinated cation) (Fig. 2). These clusters are linked by hydrogen-bonding

TABLE 5. BOND-VALENCE* (ν) TABLE FOR BOBJONESITE

| V | S | Σ | H(1) | H(2) | H(3) | H(4) | H(5) | H(6) | Σ |
|----------|------|----------|------|------|------|------|------|------|----------|
| O(1) | 1.96 | 1.96 | | | | | | | 1.96 |
| O(2) | 0.22 | 0.22 | 0.8 | 0.8 | 0.2 | | | | 2.02 |
| O(3) | 0.47 | 0.47 | | | 0.8 | 0.8 | | | 2.07 |
| O(4) | 0.45 | 0.45 | | | | | 0.8 | 0.8 | 2.05 |
| O(5) | 0.51 | 1.51 | 2.02 | | | | | | 2.02 |
| O(6) | 0.52 | 1.44 | 1.96 | | | | | | 1.96 |
| O(7) | 1.51 | 1.51 | 0.2 | 0.2 | | | 0.2 | | 2.12 |
| O(8) | 1.55 | 1.55 | | | | 0.2 | | 0.2 | 1.95 |
| Σ | 4.13 | 6.03 | 1 | 1 | 1 | 1 | 1 | 1 | |

* Bond-valence curves from Zachariasen (1978) ($V^{*}-O$) and Brown & Altermatt (1985).

between the H-atoms of the (H_2O) groups and O atoms of the cluster.

Hawthorne (1983) showed how a combination of graph theory and combinatorial topology can be used to derive the number of graphical and geometrical isomers for a specific stoichiometry of a cluster, and applied this approach to clusters of the general form $[M_2(TO_4)_2\phi_n]$. There are 1216 distinct graphical isomers; this reduces to 28 graphical isomers if tetrahedra do not share faces or edges with constituent polyhedra, and only 14 of these isomers are completely connected. These 14 graphical isomers give rise to 38 stereochemically reasonable geometrical isomers (*i.e.*, clusters without interpenetrant polyhedra). Hawthorne (1983) conjectured that the most common clusters in structures and the most stable clusters in solution will be those that have their local bond-valence requirements most closely satisfied, and identified four such clusters. The $[M_2(TO_4)_2\phi_8]$ cluster in bobjonesite is one of these clusters. This cluster also occurs in the structure of the minerals of the rozenite group: aplowite, boyleite, ilesite,

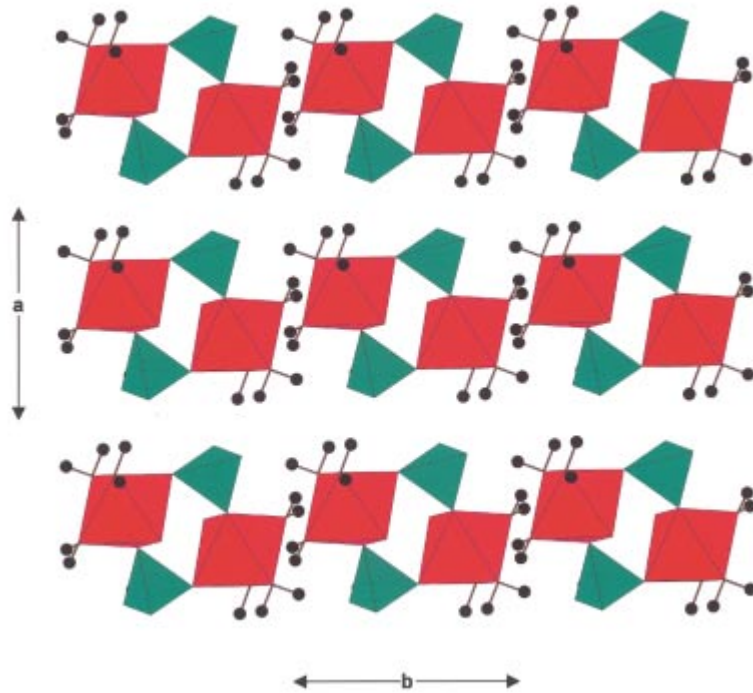


FIG. 2. The crystal structure of bobjonesite projected onto (001); ($V\Phi_6$) octahedra are red, (SO_4) tetrahedra are green, H atoms are shown as small black circles.

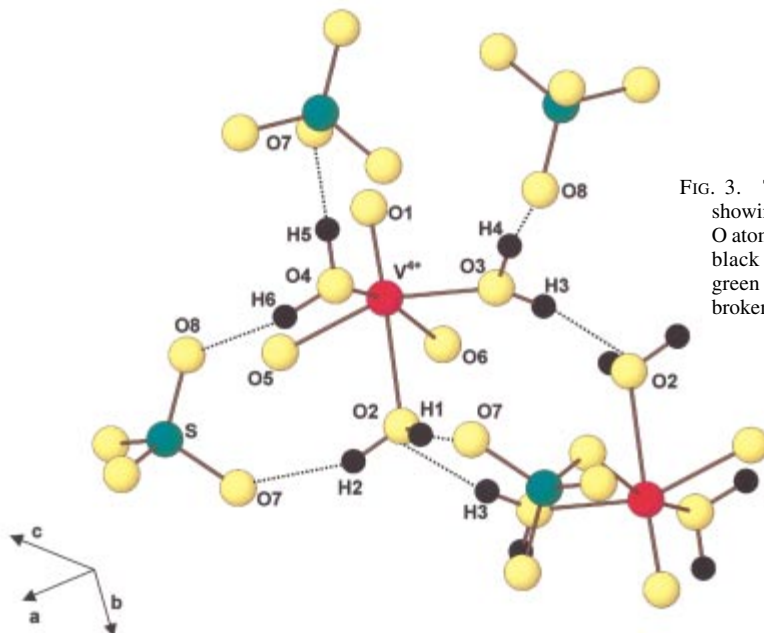


FIG. 3. The crystal structure of bobjonesite showing the details of the hydrogen bonding; O atoms: large yellow circles; H atoms: small black circles, V atom: red circle; S atom: green circle; hydrogen bonds are shown as broken lines.

rozenite and starkeyite: $[M^{2+}_2(SO_4)_2(H_2O)_8]$, $M = Co, Zn, Mn^{2+}, Fe^{2+}, Mg$.

Hydrogen bonding

All H atoms in the structure were located in the final stages of refinement, and their positions are in accord with those reported by Tachez *et al.* (1982). Cooper *et al.* (in prep.) show that the bond-valence parameters for V^{4+} -O bonds presented by Brown & Altermatt (1985) give bond valences that are too low for the *vanadyl* bond, whereas the curve of Zachariasen (1978) gives values more in accord with the valence-sum rule (Brown 1981). Here we use the curve of Zachariasen (1978) for V^{4+} -O bonds and the curves of Brown & Altermatt (1985) for the remaining bonds. The bond-valence table (Table 5) indicates that the V^{4+} cation bonds to three (H_2O) groups. The O(1) atom receives 1.96 *vu* from the central V atom, and hence the anion must be an O atom. The O(5) and O(6) atoms each bond to both V^{4+} and S, with incident bond-valence sums of ~ 2.00 *vu* from these cations (Table 5); hence O(5) and O(6) are O atoms. There are two other anions in the structure, O(7) and O(8), that bond to S with associated bond-valences of ~ 1.5 *vu*; these anions also act as bond-valence acceptors (Table 5), and hence are O atoms. The bond-valence sums from V and S at O(2), O(3) and O(4) are $\ll 1$ *vu* and hence these "anions" must be (H_2O) groups. This assignment is in accord with the locations of the H atoms.

Details of the hydrogen-bonding scheme are given in Tables 4 and 5, and Figure 3. The H(1) and H(2) atoms are linked to the O(2) atom. The H(1) atom hydrogen-bonds to O(7) with a H-acceptor distance of 2.13 Å, and an O-H...O angle of 148°; the H(2) atom hydrogen-bonds to O(7) with a H-acceptor distance of 1.81 Å. The H(3) and H(4) atoms are linked to the O(3) atom, and hydrogen-bond to the O(2) and O(8) anions with H-acceptor distances of 1.95 and 1.73 Å, respectively, and O-H...O angles of 164 and 168°. The H(5) and H(6) atoms are linked to the O(4) atom, and hydrogen-bond to the O(7) and O(8) anions, with H-acceptor distances of 1.74 and 1.74 Å, respectively, and O-H...O angles of 179 and 170°. These values are typical for normal hydrogen bonds.

CHEMICAL COMPOSITION

Crystals could not be analyzed with an electron microprobe because of their instability. The chemical composition was established by crystal-structure solution and refinement (Hawthorne & Grice 1990). This method establishes the relative scattering from various sites in the structure. Stereochemical examination allows assignment of the anionic (and neutral) parts of the structure, and leads to site-scattering values on an absolute basis; the cations can then be identified by the number of electrons at the cation sites (Hawthorne *et al.* 1995).

The crystal-chemical characteristics provide a check on the chemical composition assigned from the crystal-structure refinement.

As noted above, the observed site-scattering values are in accord with the presence of the cations V and S in this structure. The tetrahedral coordination of S and the $\langle S-O \rangle$ distance of 1.470 Å are in accord with hexavalent S (Hawthorne *et al.* 2000). The octahedral coordination of V, together with the presence of one *vanadyl* bond (1.577 Å), four *equatorial* bonds (2.002–2.048 Å) and one *trans* bond (2.278 Å), are completely diagnostic of tetravalent V (Schindler *et al.* 2000). Examination of the bond-valence table for bobjonesite (Table 5) shows that the bond-valence sums incident at three of the anions from the cations (V^{4+} and S^{6+}) are $\ll 1.0$ *vu*. The bond-valence sum rule (Brown 1981, Hawthorne 1994, 1997) indicates that these anions must be (H_2O); the remaining anions have incident bond-valence sums from the V^{4+} and S^{6+} that are $\gg 1.0$ *vu*, and hence these anions must be O^{2-} . Thus the composition derived from this analysis is $V^{4+} O (SO_4) (H_2O)_3$, and in accord with the electroneutrality principle. The ideal chemical composition is as follows: VO_2 38.21, SO_3 36.88, H_2O 24.91, total 100 wt. %.

RELATED MINERALS

Anorthominasragite (Cooper *et al.*, in prep.), orthominasragite (Hawthorne *et al.* 2001) and minasragite (Schaller 1917, Smith & Marinenko 1973) are triclinic, orthorhombic and monoclinic, respectively, and are polymorphs. Three polymorphs of $V O (SO_4) (H_2O)_5$ were identified by Ballhausen *et al.* (1968), one monoclinic structure and two orthorhombic structures. The monoclinic structure corresponds to minasragite and one of the orthorhombic structures corresponds to orthominasragite. We have found no sign of another orthorhombic $V O (SO_4) (H_2O)_5$ structure, and Ballhausen *et al.* (1968) did not report a triclinic phase.

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