

Blossite, $\alpha\text{-Cu}_2^+\text{V}_2^{5+}\text{O}_7$, a new fumarolic sublimate from Izalco volcano, El Salvador

PAUL D. ROBINSON

Department of Geology, Southern Illinois University, Carbondale, Illinois 62901, U.S.A.

JOHN M. HUGHES

Department of Geology, Miami University, Oxford, Ohio 45056, U.S.A.

MARYANN L. MALINCONICO

Department of Geology, Southern Illinois University, Carbondale, Illinois 62901, U.S.A.

ABSTRACT

Blossite, $\alpha\text{-Cu}_2\text{V}_2\text{O}_7$, occurs as a fumarolic sublimate in the "Y" fumarole of Izalco volcano, El Salvador. The mineral is the natural analogue of the previously described synthetic phase, and is the low-temperature polymorph of ziesite, $\beta\text{-Cu}_2\text{V}_2\text{O}_7$, which was discovered at the same site. The crystals are orthorhombic, *Fdd2*, with $a = 20.676(6)$, $b = 8.392(3)$, and $c = 6.446(2)$ Å. The crystal structure was refined to $R = 0.047$. The atomic arrangement consists of (100) planes of $(\text{V}_2\text{O}_7)^{4-}$ anionic groups; adjacent planes along [100] are linked by Cu^{2+} in fivefold coordination. On the basis of previously determined atomic arrangements, the α - β (blossite-ziesite) phase transition is of the non-nearest-neighbor reconstructive type.

Blossite occurs as a equant, black anhedral crystals up to 150 μm in greatest dimension. The mineral has a metallic luster and a red-brown streak. The calculated density ($Z = 8$) is 4.051 g/cm^3 . Blossite is opaque, and white in blue-filtered white light in air, with weak to moderate bireflectance in shades of creamy-white, and a moderate anisotropy, from gray to creamy brown-gray. Minimum and maximum reflectance values (in air) are 481 nm, 14.6, 15.3%; 547 nm, 15.4, 16.6%; 591 nm, 14.8, 16.7%, and 644 nm, 14.5, 15.7%. The mineral is named in honor of Dr. F. Donald Bloss, past-President of the Mineralogical Society of America.

INTRODUCTION

Several high-temperature minerals have been discovered in the summit crater fumaroles of Izalco volcano, El Salvador, including shcherbinaite, bannermanite, stoiberite, fingerite, ziesite, and mcbirneyite. The latter four minerals crystallize in the $\text{CuO-V}_2\text{O}_5$ binary system and represent the natural analogues of compounds that were first discovered as synthetic compounds, although the naturally formed crystals have provided the only material suitable for single-crystal X-ray studies for two of the compounds. To these four copper vanadates is now added a fifth, $\alpha\text{-Cu}_2\text{V}_2\text{O}_7$, the low-temperature polymorph of ziesite ($\beta\text{-Cu}_2\text{V}_2\text{O}_7$). The authors are pleased to name the mineral blossite in honor of Dr. F. Donald Bloss, Virginia Polytechnic Institute and State University. Dr. Bloss has served the mineralogical community in numerous capacities, including as President of the MSA. His research in optical mineralogy is known to all mineralogists, and the honor of a mineral in his name is certainly overdue. Specimens of blossite have been deposited at the NMNH, Smithsonian Institution. The mineral and mineral name have been approved by the IMA Commission on New Minerals and Mineral Names.

LOCALITY AND OCCURRENCE

Izalco volcano, El Salvador, 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).

As part of a long-term study of fumaroles at active volcanoes, the fumarolic sublimate products of Izalco volcano were collected by R. E. Stoiber and colleagues throughout the 1960s. Analyses of fumarolic gas condensates collected simultaneously demonstrated that Cu and V were distinctive elements in the Izalco fumarolic gases. The first high-temperature V mineral, shcherbinaite, was first discovered at Izalco (Stoiber and Durr, 1963), and the existence of several unidentified copper vanadates in the fumarolic mineral suite was also noted (Stoiber and Rose, 1974).

Blossite was collected from the "Y" fumarole (Stoiber et al., 1975) in the summit crater of Izalco volcano. The mineral was found in the outer sulfate zone of the fumarole, indicating a sublimation temperature between 100 and 200°C (Stoiber and Rose, 1974). Associated copper

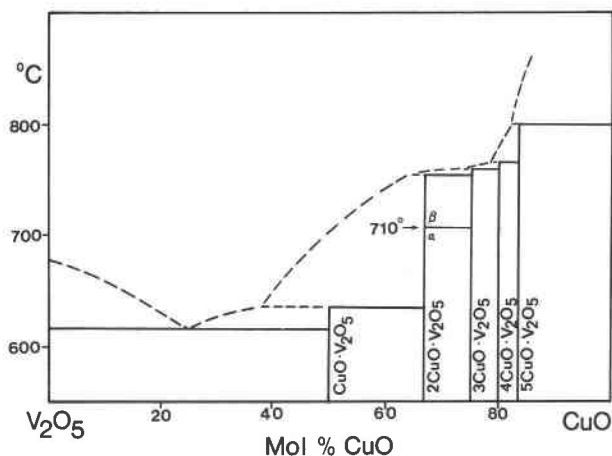


Fig. 1. Phase diagram of system $\text{CuO-V}_2\text{O}_5$ (after Brisi and Molinari, 1958).

vanadates in the fumarole include stoiberite ($\text{Cu}_5\text{V}_2\text{O}_{10}$; Birnie and Hughes, 1979), ziesite ($\beta\text{-Cu}_2\text{V}_2\text{O}_7$; Hughes and Birnie, 1980), fingerite [$\text{Cu}_{11}\text{O}_2(\text{VO}_4)_6$; Hughes and Hadidiacos, 1985] and mcbirneyite [$\text{Cu}_3(\text{VO}_4)_2$; Hughes et al., in prep.]. Only a few crystals of blossomite have been isolated to date, generally 100–150 μm in greatest dimension.

PREVIOUS WORK

The copper vanadates discovered at Izalco volcano are all natural analogues of compounds that crystallize in system $\text{CuO-V}_2\text{O}_5$ (Fig. 1), a binary system that was first studied by Brisi and Molinari (1958). Subsequent workers have undertaken studies on both specific compounds within the $\text{CuO-V}_2\text{O}_5$ system and phase relations among the various system compounds. Studies that are particularly germane to the present work are studies on ziesite, the high-temperature polymorph of $\text{Cu}_2\text{V}_2\text{O}_7$ (Hughes and Birnie, 1980; Mercurio-Lavaud and Frit, 1973a), as well as detailed structural studies on the synthetic analogue of blossomite presented by Mercurio-Lavaud and Frit (1973b) and Calvo and Faggiani (1975).

CHEMISTRY

A crystal of a blossomite-fingerite intergrowth was mounted and polished for electron-microprobe microanalysis. The crystal was estimated to be >80% blossomite from the Gandolfi pattern. A qualitative energy-dispersive analysis

TABLE 1. Unit-cell parameters of blossomite and synthetic $\alpha\text{-Cu}_2\text{V}_2\text{O}_7$

	1	2	3
a	20.676(6)	20.645(13)	20.68(1)
b	8.392(3)	8.383(7)	8.411(5)
c	6.446(2)	6.442(12)	6.448(5)

Note: Columns are (1) This study; (2) Calvo and Faggiani (1975); (3) Mercurio-Lavaud and Frit (1973). One estimated standard deviation of least units cited is given in parentheses.

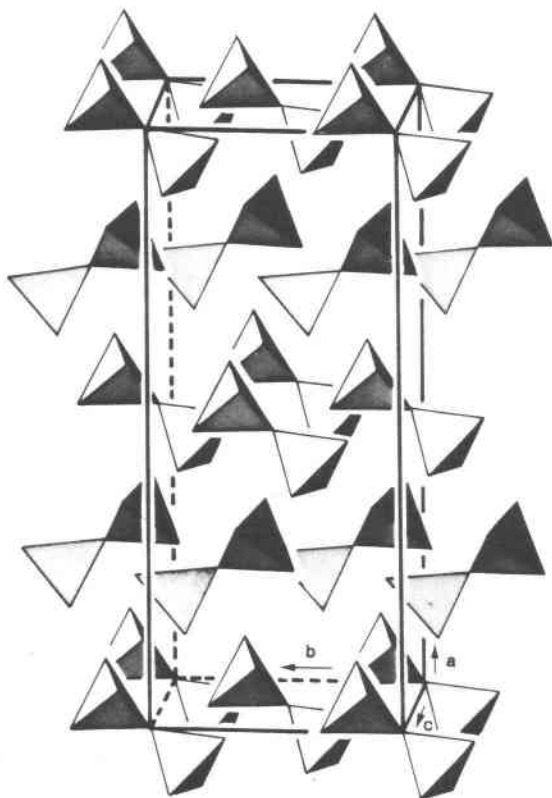


Fig. 2. Arrangement of $[\text{V}_2\text{O}_7]^{4-}$ anionic groups in blossomite. Adjacent (100) planes of tetrahedra are linked by Cu atoms in fivefold coordination with oxygen. Cu atoms not shown.

showed that of elements with $Z \geq 10$, only Cu and V were present.

Quantitative analyses were performed on an ETEC Autoscan microprobe operating at 20 kV. Cu and V metal were used as standards, and the results give 46.49(.07) wt% CuO, 53.28(.27) wt% V_2O_5 (the deviation of analyses from the mean in parentheses). Ideal $\text{Cu}_2\text{V}_2\text{O}_7$ has 46.66 wt% CuO and 53.34 wt% V_2O_5 .

X-RAY CRYSTALLOGRAPHY

Blossite was first identified by comparison of its diffraction pattern to that of JCPDS 26-566, the pattern of synthetic $\alpha\text{-Cu}_2\text{V}_2\text{O}_7$. The pattern was obtained with a 114.6-mm Gandolfi camera, Ni-filtered Cu radiation, *in vacuo*. Several extra lines were noted, but these were attributable to contamination of the crystals of blossomite with either mcbirneyite or fingerite.

A single-crystal precession study of blossomite was undertaken utilizing unfiltered Mo radiation. The available data on the synthetic analogue allowed rapid orientation of the crystal. Cone-axis and precession photographs of the 0, 1, and 2 levels along the a and b axes were taken which displayed systematic extinctions consistent with space group $Fdd2$ (43).

The lattice parameters of blossomite were refined from diffraction angles obtained from the Gandolfi photo-

graphs and indices obtained from the precession suite as well as Calvo and Faggiani (1975). The parameters were in agreement with those obtained by those authors. The lattice parameters were also refined using 22 diffraction angles measured on a four-circle diffractometer (Table 1).

CRYSTAL STRUCTURE

To further confirm that blossite is the natural analogue of synthetic α - $\text{Cu}_2\text{V}_2\text{O}_7$, a structure refinement of the natural phase was undertaken. However, the structure refinement was not completely successful. The only crystal large enough for data collection was an intergrowth of blossite and fingerite, and thus not completely suitable. Apparent overlap in intensities caused one oxygen atom to refine nonpositive definite when anisotropic temperature factors were used. The structure ultimately refined to $r = 0.047$ with anisotropic temperature factors for all metal atoms and isotropic temperature factors for all oxygen atoms. Our refinement serves to confirm the previously determined structure. Because of the higher quality of the previous determinations, however, the reader is referred to those works for atomic coordinates and anisotropic temperature factors. A description of the structure is given below.

Blossite is a member of that class of vanadates that crystallizes with V^{5+} in tetrahedral coordination with oxygen. The VO_4 tetrahedra in blossite dimerize in $[\text{V}_2\text{O}_7]^{4-}$ groups, and thus the structure is closely related to that of the thortvetite-group compounds. The atomic arrangement is also found in many other $\text{M}^{2+}(\text{V}_2\text{O}_7)$ compounds, as noted by Calvo and Faggiani (1975).

In blossite, the $[\text{V}_2\text{O}_7]^{4-}$ anionic units are arranged in planes parallel to (100) (Fig. 2). The bridging oxygen atoms (O_B) in the coplanar divanadate units are in special positions that contain the diad and are all coplanar (100). In successive $[\text{V}_2\text{O}_7]$ planes along [100], however, the divanadate units are staggered such that the V-O_B -V vector is oriented parallel to [120] in one plane and parallel to $[\bar{1}20]$ in the adjacent plane. The divanadate tetrahedra are bonded by Cu atoms (not shown) in fivefold coordination, sharing oxygen atoms with the VO_4 tetrahedra in adjacent planes along [100], thus effectively linking the $[\text{V}_2\text{O}_7]$ layers.

The α - β (blossite-ziesite) phase transition in the copper vanadate dimorphs has been found to occur at 710°C (Mercurio-Lavaud and Frit, 1973b). The crystallographic relationships between the two polymorphs have been given by Calvo and Faggiani (1975). In both phases the VO_4 tetrahedra are dimerized in $[\text{V}_2\text{O}_7]^{4-}$ groups, and the copper is five-coordinated in a distorted trigonal dipyramid (Mercurio-Lavaud and Frit, 1973a, 1973b). In both structures the Cu-O trigonal dipyramids are polymerized by edge-sharing to form infinite chains. The phases differ, however, in the symmetry relationships between the divanadate groups. In ziesite, the double V_2O_7 tetrahedra are related by a two-fold rotation axis, whereas in blossite they are related by a d glide. Calvo and Faggiani (1975) also noted that in the atomic rearrangement during the

phase transition, three Cu-O bonds must be broken and reformed, although the final coordination polyhedra are identical. Thus, the phase transition is of the non-nearest-neighbor reconstructive type; according to Buerger (1961), activation energies are high for this type of transformation, and reactions are typically sluggish. The fumarole mineral suite from Izalco therefore contains ziesite, which formed stably and persists metastably, and also blossite, which formed when the fumarole temperatures dropped below the inversion temperature of 710°C.

PHYSICAL PROPERTIES

Blossite occurs as equant, black anhedral crystals up to 150 μm in greatest dimension. The mineral has a metallic luster. The crystals of blossite isolated to date are intergrown with other fumarolic copper vanadates or sulfates, although several crystals are essentially pure blossite.

Blossite has a red-brown streak, as determined from the natural material and also noted by Mercurio-Lavaud and Frit (1973b). The mineral does not fluoresce in ultraviolet radiation. The calculated density of blossite ($Z = 8$; $\text{FW} = 340.97$) is 4.051 g/cm^3 . Density values of 3.95 (Mercurio-Lavaud and Frit, 1973b) and 3.969 g/cm^3 (Calvo and Faggiani, 1975) have been reported for the synthetic analogue. No distinct cleavages were observed in blossite, although the anhedral, often-polycrystalline nature of the mineral grains prohibits good observations of cleavage.

Blossite is opaque to transmitted light. In blue-filtered white light in air, blossite is white. A single grain of unknown orientation was found to exhibit weak-to-moderate birefractance in shades of creamy white. Red-brown internal reflections were noted. Blossite displays moderate anisotropy (nicols 5–7° from crossed), from gray to creamy brown-gray. Reflectance values were measured in air using a SiC standard. Average values for minimum and maximum reflectivity values were determined at four wavelengths: 481 nm, 14.6, 15.3%; 547 nm, 15.4, 16.6%; 591 nm, 14.8, 16.7%; and 644 nm, 14.5, 15.7%. The mean index of refraction of blossite, calculated by the rule of Gladstone and Dale with the specific refractivity values given by Mandarino (1976), is 2.05.

ACKNOWLEDGMENTS

J.M.H. would like to acknowledge Richard E. Stoiber of Dartmouth College for his collection of the fumarolic sublimates from Izalco Volcano and his long-standing contributions to fumarole mineralogy. J.M.H. would also like to acknowledge the NSF for continuing support of the fumarole mineral studies through Grants EAR-8410707, EAR-8418135, and CHE-8418897. The manuscript was improved through reviews by Howard T. Evans, Jr., and Paul H. Ribbe.

REFERENCES CITED

- Birnie, R.W., and Hughes, J.M. (1979) Stoiberite, $\text{Cu}_5\text{V}_2\text{O}_{10}$, a new copper vanadate from Izalco volcano, El Salvador, Central America. *American Mineralogist*, 64, 941–944.
- Brisi, C., and Molinari, A. (1958) Il sistema ossido ramicoanidride vanadica. *Annali di Chimica. Roma*, 48, 263–269.
- Buerger, M.J. (1961) Polymorphism and phase transformations. *Fortschritte der Mineralogie*, 39, 9–24.

- Calvo, C., and Faggiani, R. (1975) α cupric divanadate. *Acta Crystallographica*, B31, 603–605.
- Hughes, J.M., and Birnie, R.W. (1980) Ziesite, β - $\text{Cu}_2\text{V}_2\text{O}_7$, a new copper vanadate and fumarole temperature indicator. *American Mineralogist*, 65, 1146–1149.
- Hughes, J.M., and Hadidiacos, C.G. (1985) Fingerite, $\text{Cu}_{11}\text{O}_2(\text{VO}_4)_6$, a new vanadium sublimate from Izalco volcano, El Salvador: Descriptive mineralogy. *American Mineralogist*, 70, 193–196.
- Mandarino, J.A. (1976) The Gladstone-Dale relationship. Part I. Derivation of new constants. *Canadian Mineralogist*, 14, 498–502.
- Mercurio-Lavaud, D., and Frit, M.B. (1973a) Structure cristalline de la variété haute température du pyrovanadate de cuivre: $\text{Cu}_2\text{V}_2\text{O}_7$. *Comptes Rendus de l'Académie des Sciences, Paris, ser. C.*, 277, 1101–1104.
- (1973b) Structure cristalline de la variété basse température du pyrovanadate de cuivre: $\text{Cu}_2\text{V}_2\text{O}_7$, α . *Acta Crystallographica*, B29, 2737–2741.
- Meyer-Abich, H. (1958) Active volcanoes of Guatemala and El Salvador. In *Catalogue of active volcanoes of the world including solfataras*, Part VI, Central America, p. 39–105. International Association of Volcanology, Rome, Italy.
- Rose, W.I., and Stoiber, R.E. (1969) The 1966 eruption of Izalco volcano, El Salvador. *Journal of Geophysical Research*, 74, 3229–3130.
- Stoiber, R.E., and Durr, F. (1963) Vanadium in the sublimates, Izalco volcano, El Salvador (abs.). *Geological Society of America Special Paper* 76, 159.
- Stoiber, R.E., and Rose, W.I. (1974) Fumarole incrustations at active Central American volcanoes. *Geochimica et Cosmochimica Acta*, 38, 495–516.
- Stoiber, R.E., Rose, W.I., Lange, I.M., and Birnie, R.W. (1975) The cooling of Izalco volcano (El Salvador) 1964–1974. *Geologisches Jahrbuch*, 13, 193–205.

MANUSCRIPT RECEIVED MAY 30, 1986

MANUSCRIPT ACCEPTED NOVEMBER 20, 1986