

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

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Abstract

Fingerite, $\text{Cu}_{11}\text{O}_2(\text{VO}_4)_6$, a new copper vanadate mineral, has been discovered in the summit crater fumaroles of Izalco volcano, El Salvador, Central America. The mineral, which occurs with thenardite and euchlorine, forms as a sublimate product from the volcanic gases. Fingerite occurs as euhedral, subhedral and anhedral crystals up to $150\ \mu\text{m}$ in greatest dimension.

Fingerite is triclinic, $P\bar{1}$, $a = 8.1576(6)$, $b = 8.2691(5)$, $c = 8.0437(7)\text{\AA}$, $\alpha = 107.144(5)$, $\beta = 91.389(7)$, $\gamma = 106.441(5)^\circ$ and $V = 493.84(6)\text{\AA}^3$. The five most intense lines on the Gandolfi pattern are $6.48(100; \bar{1}10, 01\bar{1})$, $3.894(60; 200, \bar{1}20)$, $3.042(80; 012, 120)$, $2.822(70; 1\bar{2}\bar{2}, 2\bar{1}\bar{2})$ and $2.025(70; 203)$.

Fingerite is black with a metallic luster and opaque. The calculated density of fingerite is $4.776\ \text{gm/cc}$, $Z = 1$. In reflected light in air, fingerite is medium gray, non-pleochroic and exhibits 2 extinctions per complete rotation of the stage. The reflectance of randomly oriented grains in blue-filtered white light in air is $21 \pm 2\%$.

Milligram amounts of the mineral exist. Type specimens are on deposit at the National Museum of Natural History, Smithsonian Institution and the Geophysical Laboratory, Carnegie Institution of Washington. The mineral is named in honor of Dr. Larry W. Finger, Geophysical Laboratory.

Introduction

Naturally occurring $\text{Cu}_{11}\text{O}_2(\text{VO}_4)_6$ has been discovered in the fumaroles in the summit crater of Izalco volcano, El Salvador, Central America ($13^\circ 49'\text{N}$; $89^\circ 38'\text{W}$). The authors are pleased to name the new mineral fingerite in honor of Dr. Larry W. Finger of the Geophysical Laboratory, Carnegie Institution of Washington. Dr. Finger is well known for his work in the fields of mineralogy, crystal chemistry and crystal physics, and has served both the Mineralogical Society of America and the International Mineralogical Association through his service on several committees.

Type specimens of fingerite have been deposited at the Geophysical Laboratory, Carnegie Institution of Washington and the National Museum of Natural History, Smithsonian Institution. The total amount of the new mineral on hand is a few milligrams. The mineral and mineral name have been approved by the Commission on New Minerals and Mineral Names, I.M.A.

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 $2\ \text{km}^3$. The geology of the volcano is described by Meyer-Abich (1958), Rose and Stoiber (1969) and Stoiber et al. (1975).

In 1963 the first-known, high-temperature vanadium mineral was discovered in the summit crater fumaroles of Izalco volcano. Since that time, the volcanic gases and sublimate minerals have been extensively studied. Several new vanadium minerals have been discovered at the site, including bannermanite $[(\text{Na},\text{K})_x\text{V}_x^{4+}\text{V}_{6-x}^{5+}\text{O}_{15}]$; Hughes and Finger, 1983a], shcherbinaite (V_2O_5 ; Hughes and Finger, 1983b), and three vanadates in the system $\text{CuO}-\text{V}_2\text{O}_5$. Fingerite is the fourth sublimate mineral in this chemical system, joining 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), and $\text{Cu}_3\text{V}_2\text{O}_8$ (Christian and Hughes, in

prep.). It has been demonstrated that the minerals formed as sublimates from a vanadium-bearing volcanic gas, at temperatures up to 760°C and oxygen fugacities of $10^{-3.5}$ bar (Hughes and Stoiber, 1985).

Fingerite is found in the "Y" fumarole (Stoiber et al., 1975, Fig. 1), one of five major fumaroles in the summit crater of Izalco. The mineral occurs as black grains up to 150 μm in greatest dimension. Fingerite was found in the outer sulfate zone of the fumarole, indicating a sublimation temperature between 100 and 200°C (Stoiber and Rose, 1974). The mineral is intimately associated with thenardite (Na_2SO_4) and euchlorine $[(\text{Na},\text{K})_7\text{Cu}_{10}(\text{SO}_4)_{10}(\text{OH})_7 \cdot 10\text{H}_2\text{O}]$; it is commonly intergrown with the latter.

System $\text{CuO-V}_2\text{O}_5$

The first study of compounds in the $\text{CuO-V}_2\text{O}_5$ binary system was undertaken by Brisi and Molinari (1958), who identified five incongruently melting compounds between the CuO and V_2O_5 end members (Fig. 1). The phases reported by Brisi and Molinari have $\text{CuO}:\text{V}_2\text{O}_5$ molar ratios of 1:1, 2:1, 3:1, 4:1 and 5:1 (stoiberite). Subsequent studies have been undertaken on both specific compounds within the binary system and phase relations among the various compounds. For example, Mercurio-Lavaud and Frit (1973) demonstrated that a high temperature polymorph of the 2:1 phase (ziesite, $\beta\text{-Cu}_2\text{V}_2\text{O}_7$) exists above 712°C. Fleury (1966, 1969) redetermined the phase relations within the system and was able to reproduce all of the compounds except $\text{Cu}_4\text{V}_2\text{O}_9$ reported by Brisi and Molinari.

Fingerite was first identified as a new mineral by

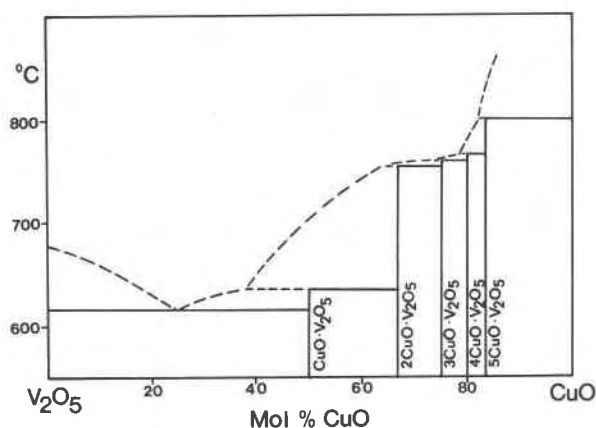


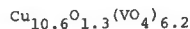
Fig. 1. Phase diagram of the system $\text{CuO-V}_2\text{O}_5$ (after Brisi and Molinari, 1958). Similar diffraction patterns of fingerite ($\text{Cu}_{11}\text{V}_6\text{O}_{26}$, $3.67\text{CuO}:\text{V}_2\text{O}_5$) and the $\text{Cu}_4\text{V}_2\text{O}_9$ (4 $\text{CuO}:\text{V}_2\text{O}_5$) phase of Brisi and Molinari suggest that their determination of phase composition is in error. The high-temperature polymorph of the $2\text{CuO}:\text{V}_2\text{O}_5$ phase ($\beta\text{-Cu}_2\text{V}_2\text{O}_7$, ziesite) was not recognized in the Brisi and Molinari study. The phase $5\text{CuO}:\text{V}_2\text{O}_5$ ($\text{Cu}_5\text{V}_2\text{O}_{10}$) = stoiberite.

Table 1. Microprobe chemical analyses of fingerite

	1*	2*	3
CuO	59.3(13)	59.53(33)	61.59
V_2O_5	39.65(40)	39.67(18)	38.41
Total	98.95	99.20	100.00

1. \bar{X} of 7 analyses of type crystal for chemical analyses.

2. \bar{X} of 15 analyses of 3 crystals. Formula (O=26):



3. Ideal $\text{Cu}_{11}\text{O}_2(\text{VO}_4)_6$.

* One standard deviation in parentheses.

comparison of its diffraction pattern with that of $\text{Cu}_4\text{V}_2\text{O}_9$ (JCPDS 16-420; note that the most intense peak of JCPDS 16-420 is listed as 3.52Å, whereas the original publication lists the peak as 3.59Å). The similar patterns suggested that fingerite is the natural analog of $\text{Cu}_4\text{V}_2\text{O}_9$. As shown subsequently the formula of fingerite is $\text{Cu}_{11}\text{V}_6\text{O}_{26}$. Brisi and Molinari (1958), however, never analyzed the reaction products in their study of system $\text{CuO-V}_2\text{O}_5$. Their proposed chemical formulas were derived from the ratio of the system components at which the most intense powder diffraction peaks of each product was observed. This error in chemical formula perhaps explains the inability of Fleury (1966, 1969) to synthesize the $\text{Cu}_4\text{V}_2\text{O}_9$ phase of Brisi and Molinari.

The formulation $\text{Cu}_{11}\text{O}_2(\text{VO}_4)_6$ is preferred for fingerite to emphasize the fact that it is a member of the class of vanadates based on tetrahedral VO_4 groups, in contrast to the vanadium bronzes such as bannermanite, which have sheet structures based on linked, distorted VO_6 octahedra. All the compounds in Figure 1 are tetrahedral types: $\text{Cu}(\text{VO}_3)_2$ (metavanadate, probably tetrahedral chains); $\text{Cu}_2(\text{V}_2\text{O}_7)$ (divanadate); $\text{Cu}_3(\text{VO}_4)_2$ (orthovanadate); $\text{Cu}_{11}\text{O}_2(\text{VO}_4)_6$ (fingerite); and $\text{Cu}_5\text{O}_2(\text{VO}_4)_2$ (stoiberite).

Chemistry

Energy dispersive chemical analyses of fingerite were performed with a JEOL SEM/Microprobe. The analyses showed that among elements with $Z > 9$, only Cu and V are present. Quantitative wavelength dispersive analyses of fingerite were performed with JEOL 35 and MAC400 electron microprobes. Cu metal and V metal were used as standards. The results of the analyses are summarized in Table 1.

Calculation of the empirical formula suggested that the $\text{Cu}_4\text{V}_2\text{O}_9$ ($\text{CuO}:\text{V}_2\text{O}_5 = 4:1$) formula of Brisi and Molinari (1958) was incorrect. On the basis of density, volume/oxygen atom, and the empirical formula, a formula of $\text{Cu}_{10}\text{V}_6\text{O}_{25}$ ($\text{CuO}:\text{V}_2\text{O}_5 = 3.33:1$) was proposed for the new mineral. A subsequent structure determination, de-

scribed in the following paper (Finger, 1985), demonstrated that the correct formula for fingerite is $Cu_{11}V_6O_{26}[Cu_{11}O_2(VO_4)_6]$. Analysis 2 in Table 1 is thus in error by -3.8% and $+2.8\%$ of the amount present for CuO and V_2O_5 , respectively.

X-ray crystallography

Diffraction patterns of fingerite in vacuo were obtained with a 114.6 mm Gandolfi camera with Ni-filtered, Cu radiation. Intensities were visually estimated. The indexed Gandolfi pattern, together with the pattern calculated from the crystal structure, is presented in Table 2.

After definition of the reduced lattice by precession methods, precession photographs were taken with Zr-filtered, Mo radiation. Cone-axis and precession photographs of the 0, 1 and 2 levels were taken along *a*, *b*, and *c*. The axial parameters were refined using 2θ values from the Gandolfi pattern, and these values were subsequently confirmed in the structure work by Finger to be reported in the subsequent report. Because of the higher precision of Finger's data, those parameters are reported here. The axial parameters were refined from the positions of 20 independent observations with $39^\circ \leq 2\theta \leq 54^\circ$ measured on a four-circle diffractometer by the eight-reflection centering method of King and Finger (1979). The refined unit cell parameters of the all-ortho normal representation of the unit cell are $a = 8.1576(6)$, $b = 8.2691(5)$, $c =$

$8.0437(7)\text{\AA}$, $\alpha = 107.144(5)^\circ$, $\beta = 91.389(7)^\circ$, $\gamma = 106.441(5)^\circ$ and $V = 493.84(6)\text{\AA}^3$.

Precession photographs demonstrated that fingerite is triclinic, space group $P1$ or $P\bar{1}$. The structure study by Finger to be reported subsequently demonstrates that fingerite crystallizes in space group $P\bar{1}$.

Physical properties

Fingerite occurs as euhedral, subhedral and anhedral crystals up to approximately $150\ \mu\text{m}$ in greatest dimension. The mineral is black with a metallic luster. The streak of fingerite is dark reddish brown, similar to the streak of hematite.

Crystals of fingerite grow in both plate-like and equant habits. Figure 2 is an SEM micrograph of a twin intergrowth of two plate-like twin members and one equant twin member; the figure shows the relationship between morphology and principal axes of the plate-like habit. The two plate-like twin members are related by a 180° rotation about [010].

No cleavages were observed in optical or SEM examination of fingerite crystals.

The calculated density of fingerite (MW = 1420.65 gm/mol) is 4.776 gm/cc, $Z = 1$. Sample scarcity prohibited direct measurement of the density. Crystals of fingerite were observed to sink rapidly in methylene iodide (S.G. = 3.32 gm/cc). The density and volume/oxygen atom

Table 2. Calculated and observed powder patterns of fingerite*

d(obs)	d(calc)	I(obs)	I(calc)	h k l	d(obs)	d(calc)	I(obs)	I(calc)	h k l
-	7.770		3.8	1 0 0	-	2.574		31.3	1 2 1
-	7.633		7.6	0 0 1	2.525	2.540	40	55.3	2 3 1
7.53	7.528	10	2.5	0 1 0		2.521		64.2	1 1 3
6.48	6.479	100	13.7	1 1 0	6 lines,				
	6.474		93.2	0 1 1	2.52-2.36				
5.80	5.796	10	15.8	1 0 1		2.486		46.2	0 3 2
4.738	4.735	50	56.1	1 1 0		2.466		47.1	3 2 1
3.894	3.885	60	20.5	2 0 0		2.456		17.7	2 2 1
	3.882		14.4	1 2 0		2.447		39.1	1 2 3
3.617	3.639	60	44.1	2 0 1		2.419		28.9	1 2 2
	3.612		23.1	1 1 1		2.368		25.7	2 2 0
	3.598		20.2	2 1 1	2.332	2.337	20	10.6	0 2 2
	3.597		59.0	1 0 2		2.328		13.2	3 2 1
3.293(d)	3.309	60	51.3	2 0 1		2.313		11.8	1 3 1
	3.277		47.6	1 0 2	2.287	2.281	40	64.3	3 1 1
3.192	3.187	10	13.8	2 2 1		2.271		69.1	3 0 2
3.108	3.116	10	15.8	2 1 1		2.209		29.9	0 1 3
	3.091		32.3	2 1 0	2.070	2.064	50	84.3	1 4 1
3.042	3.044	80	26.4	1 2 0	2.025	2.022	70	77.4	2 0 3
	3.040		69.9	0 1 2	1.946	1.941	30	12.1	2 4 0
	3.020		42.9	0 2 1	1.720	1.717	30	26.1	3 0 3
2.901	2.898	40	84.8	2 0 2	1.688	1.686	20	14.8	1 4 3
2.822	2.830	70	21.5	1 2 2		1.588		33.1	2 4 4
	2.820		78.1	2 1 2	1.531	1.532	20	48.0	4 4 1
2.753	2.747	40	88.7	1 3 1	1.523	1.523	20	19.1	2 4 3
2.716	2.716	40	80.2	3 1 0		1.489		52.9	5 0 1
	2.716		38.5	2 1 2		1.486		29.1	3 4 4
2.668(d)	2.694	40	100.0	2 1 2		1.481		51.0	2 0 5
	2.680		63.0	0 1 3		1.462		29.1	1 5 1
	2.666		47.1	2 1 1		1.410		35.7	4 2 4
	2.643		29.2	0 3 1	1.358	1.357	40	28.5	3 4 3
	2.633		20.8	1 3 0	1.343	1.343	20	5.4	4 5 1

*Observed data obtained from 114.6 mm Gandolfi camera, Ni-filtered Cu radiation, vacuum, visual intensity estimates. Calculated data obtained from the crystal structure.

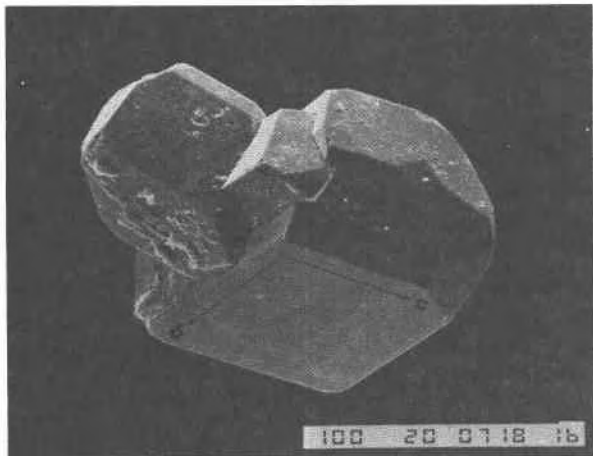


Fig. 2. SEM photomicrograph of a multiply-twinned crystal of fingerite, denoting *b* and *c* axes of the dominant twin member. Both the {100} and {010} pinacoidal forms are present on the dominant twin member. Scale bar represents 100 microns.

(18.99\AA^3) of fingerite are both within the range of other copper vanadates.

Fingerite is opaque in transmitted light. In reflected light in air, fingerite is medium gray. The mineral is non-pleochroic and randomly oriented grains exhibit 2 extinctions per complete rotation of the stage.

Determination of quantitative reflectance values was hampered by the small grain size of fingerite and the extensive plucking that resulted from polishing. Reflectance in blue-filtered white light in air was determined by comparison with standards. Randomly oriented grains of fingerite were found to have a reflectance indistinguishable from that of magnetite. Thus the reflectance of fingerite is estimated at $21 \pm 2\%$.

The mean index of refraction of fingerite, calculated by the rule of Gladstone and Dale with the specific refractivity values given by Mandarino (1976), is 2.124.

Sample scarcity and size prohibited measurements of hardness. The mineral does not fluoresce in short- or long-wave ultraviolet radiation.

Acknowledgments

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