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Ziesite, β-$Cu_2V_2O_7$, a new copper vanadate and fumarole temperature indicator

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Abstract

Ziesite, β-$Cu_2V_2O_7$, a new copper vanadate mineral, occurs as anhedral black crystals in the oxide zone of a fumarole at Izalco volcano, El Salvador, Central America. The mineral is associated with stoiberite and other unnamed copper vanadates. It is monoclinic, space group *A2/a*, with $a = 10.094(15)$, $b = 8.020(13)$, $c = 7.711(10)$Å, $\beta = 110.43(9)°$, $Z = 2$, and $D_{calc.} = 3.87$ g/cc. It has metallic luster and a red-brown streak. No cleavages were observed and the mineral shows no fluorescence in short- or long-wave UV radiation. The mineral is opaque and exhibits class C reflectivity. The phase relations between ziesite and other copper vanadates indicate a temperature of formation between about 760° and 770°C. The mineral is named in honor of Dr. Emanuel G. Zies.

Introduction

Naturally-occurring β-$Cu_2V_2O_7$ has been discovered in a fumarole in the summit crater of Izalco volcano, El Salvador, Central America (13°49′ N; 89°38′ W) (Fig. 1). Identification of this mineral as the analog of synthetic β-$Cu_2V_2O_7$ is based on (1) electron microprobe chemical analysis and (2) X-ray diffraction analysis. The new mineral is named ziesite (zēs · īte) in honor of Dr. Emanuel G. Zies of the Carnegie Institution of Washington. Dr. Zies is noted particularly for his classic papers on the Valley of Ten Thousand Smokes, Alaska. The type specimen of ziesite is deposited in the collection of the Geophysical Laboratory, Carnegie Institution of Washington. The mineral and mineral name have been approved by the Commission on New Minerals and Mineral Names of the IMA.

Locality and occurrence

Izalco volcano is a basaltic composite cone which has been intermittently active since its birth in 1770. The volcano rises to an altitude of 1965 m, with 650 m relief. It 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 minerals of the summit crater have received extensive study (Stoiber and Durr, 1963; Stoiber and Rose, 1970, 1974; Stoiber *et al.*, 1975; Birnie and Hughes, 1979). Copper and vanadium are distinctive elements in the minerals of the fumarolic suite. The mineral suite includes chalcocyanite ($CuSO_4$), chalcanthite ($CuSO_4 \cdot 5H_2O$), shcherbinaite (V_2O_5), and stoiberite ($Cu_5V_2O_{10}$).

Ziesite is found only in the "Y" fumarole, one of five major fumaroles at Izalco volcano (Stoiber *et al.*, 1975, Fig. 1). The mineral occurs as equant black anhedral crystals less than 200 μm in greatest dimension. The grains are found as an incrustation coating basaltic breccia fragments about 1 m below the surface. The mineral is associated with stoiberite and two other undescribed copper vanadates ($Cu_3V_2O_8$; $Cu_4V_2O_9$).

Chemistry

Ziesite was analyzed on the Massachusetts Institute of Technology automated MAC5 electron microprobe. The instrument was operated at 15 kV accelerating voltage and 300 nA beam current on the flag. The counting time was 30 seconds for samples and standards, and corrections were made for detector dead time and current drift. Cu, V, and Cr were analyzed using Cu metal (Cu), V_2O_5(V) and Cr metal (Cr) as standards. No Cr was detected above background. Mineral analyses were calculated using the MAGIC-4 correction program. These analyses are summarized in Table 1 and give an ideal formula for ziesite of $Cu_2^{2+}V_2^{5+}O_7$.

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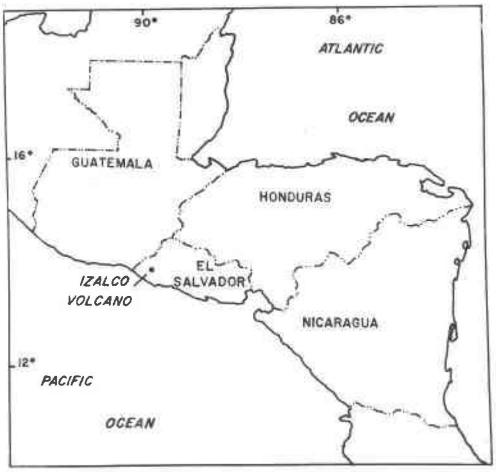

Fig. 1. Location of Izalco volcano, El Salvador.

X-ray crystallography

Ziesite was first identified by comparison of its diffraction pattern with that of synthetic β-$Cu_2V_2O_7$ (JCPDS 26-569). The pattern was obtained using a 114.6 mm Gandolfi camera, Cr*Kα* radiation (2.2909Å, V filter), and a helium atmosphere. Intensities were visually estimated, and corrections were made for film shrinkage. The indexed diffraction pattern of ziesite agrees with the pattern of the synthetic phase. The ziesite pattern has been submitted to the Powder Diffraction File.

Mercurio-Lavaud and Frit (1973a) determined that synthetic β-$Cu_2V_2O_7$ is monoclinic, space group *C*2/*c* (15). Precession photographs of ziesite were taken, using unfiltered Mo radiation in a helium atmosphere. These photographs confirm that its symmetry is consistent with space group *C*2/*c* (15). The *a* and *c* axes of ziesite are reversed from those of Mercurio-Lavaud and Frit (1973a) to conform with the convention of $a > c$ in monoclinic crystals, and thus the space group is reported as *A*2/*a*. The refined unit-cell parameters of synthetic β-$Cu_2V_2O_7$ and ziesite are given in Table 2. The parameters were refined on the basis of 17 *d* values from the Gandolfi pattern, using a least-squares refinement program (CPLSQ, B.A. Wechsler, SUNY Stony Brook; translated from MAXI-BASIC level 1.2 to BASIC by senior author).

Table 1. Electron microprobe analyses of ziesite. All values in wt.%

	(1)	(2)*	(3)+
CuO	46.66	45.0(4)	45.37(17)
V_2O_5	53.34	53.4(8)	52.82(78)
	100.00	98.4	98.19

(1) Ideal ziesite

(2) $\bar{X}$ of 6 analyses of 3 cotype crystals

(3) $\bar{X}$ of 2 analyses of holotype crystal

formula (analysis (3)) on the basis of 7 oxygens:

$Cu_{1.97}V_{2.01}O_7$

ideal formula: $Cu_{2.00}V_{2.00}O_7$

*One standard deviation in parentheses
+Deviation of analyses from mean in parentheses

The crystal structure of synthetic β-$Cu_2V_2O_7$, determined by Mercurio-Lavaud and Frit (1973a), is based on 931 independent reflections. The vanadium in the structure is tetrahedrally coordinated and occurs in $(V_2O_7)^{4-}$ groups. The Cu is five-coordinated by oxygen in a distorted trigonal dipyramid.

Phase relations

The CuO–V_2O_5 binary system has been studied by Brisi and Molinari (1958) and Fleury (1966, 1969). Brisi and Molinari found five incongruently-melting phases between the CuO and V_2O_5 end members. These phases have CuO:V_2O_5 ratios of 1:1, 2:1, 3:1, 4:1, and 5:1 (stoiberite) (Fig. 2). These authors first synthesized the low-temperature copper pyrovanadate phase, α-$Cu_2V_2O_7$. They suspected the existence of a polymorphic inversion at approximately 660°C, but were unable to isolate the high-temperature polymorph. Mercurio-Lavaud and Frit (1973a,b) isolated the high-temperature (β) and low-temperature (α) $Cu_2V_2O_7$ phases and studied the $\alpha \rightleftarrows \beta$ transition. They found that the transition is reversible and occurs at 712°C. The transition occurs less readily in the cooling direction of $\beta \rightarrow \alpha$, particularly when the compound has been heated to fusion (780°C) before cooling.

The metastability of the β phase (ziesite) results from the nature of the phase transformation, which involves a non-nearest-neighbor reconstruction. In

Table 2. Unit-cell parameters of ziesite and synthetic β-$Cu_2V_2O_7$

	a(Å)*	*b*(Å)*	*c*(Å)*	*β*(deg.)*
(1)	10.094(15)	8.020(13)	7.711(10)	110.43(9)
(2)	7.685	8.007	10.09	110.27

*esd's in parentheses

(1) Unit cell parameters of ziesite refined on the basis of 17 d values from Gandolfi photographs.

(2) Unit cell parameters of synthetic β-$Cu_2V_2O_7$ (Mercurio-Lavaud and Frit, 1973).

both the α and β phases the vanadium is four-coordinated by oxygen in a tetrahedron, and the copper is five-coordinated by oxygen in a distorted trigonal dipyramid (Mercurio-Lavaud and Frit, 1973a,b). In both structures, the Cu–O trigonal dipyramids are polymerized by edge-sharing and form infinite chains. Furthermore, in both structures the V–O tetrahedra are polymerized in pairs by sharing an oxygen and form $(V_2O_7)^{4-}$ units. This polymerization classifies both as thortveitite structure types. In ziesite, the planes formed by the V–O–V polymerizing bonds are parallel and are related by a 2-fold screw axis. However, in the α phase, there are two non-parallel sets of these planes which are related by a diamond glide. These different symmetries result from the non-nearest-neighbor reconstructive phase transformation. According to Buerger (1961), activation energies are high for this type of transformation and reactions are typically sluggish. Thus ziesite was preserved metastably as the fumarole cooled below the inversion temperature.

Fumarole thermometry

In situ temperature measurements of the Izalco fumaroles have been made intermittently since 1964 with a thermocouple 50 cm below the surface. At no time have temperatures greater than 520°C been measured (Stoiber *et al.*, 1975).

Prior to the discovery of ziesite at Izalco, the only phase in the Izalco fumarolic suite that could be used as a temperature indicator was metathenardite, a high-temperature polymorph of thenardite (Na_2SO_4). Temperatures must exceed 241°C for thenardite to invert to the high-temperature polymorph (Kracek and Gibson, 1930). This polymorph is normally not stable below 241°C, but may be stabilized as metathenardite by fusion with greater than 0.1 mole % Na_2CO_3 (JCPDS #1-0990; Ramsdell, 1939). The occurrence of metathenardite at Izalco was reported by Stoiber and Rose (1974); its presence, therefore, indicates temperatures must have exceeded 241°C.

The existence of a metastable high-temperature polymorph of $Cu_2V_2O_7$ also allows it to be used as a fumarole geothermometer. Using the inversion temperature determined for the synthetic system and assuming this is valid for the natural phase, the minimum temperature of formation of ziesite must have been 712°C (Mercurio-Lavaud and Frit, 1973a).

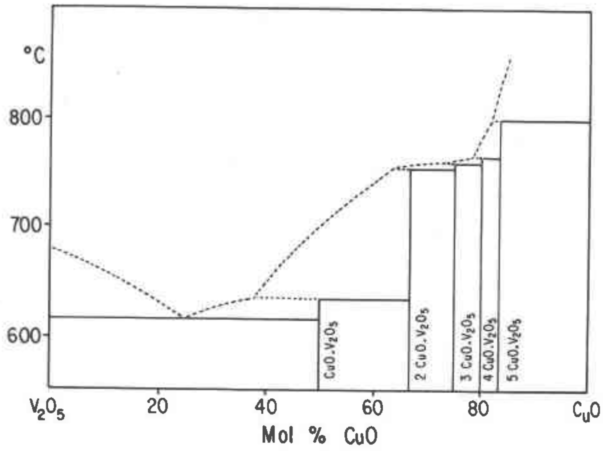

Fig. 2. Phase diagram of system CuO–V_2O_5 (after Brisi and Molinari, 1958).

Electron microprobe and X-ray diffraction analyses indicate that crystals of ziesite are intergrown with the copper vanadate $Cu_4V_2O_9$, an undescribed mineral. This phase was originally synthesized by Brisi and Molinari (1958), but Fleury (1966, 1969) was unable to synthesize it. The intergrowths are in the ratio of approximately 80% ziesite to 20% $Cu_4V_2O_9$. If they grew together in equilibrium, this intergrowth of the two phases demonstrates the existence of a previously unknown two-phase region (β-$Cu_2V_2O_7$ and $Cu_4V_2O_9$) in the natural CuO–V_2O_5 system. The stable region for coexisting β-$Cu_2V_2O_7$ and $Cu_4V_2O_9$ must lie above the solidus temperature of the intermediate copper vanadate $Cu_3V_2O_8$ and below the solidus temperature of $Cu_4V_2O_9$. According to the phase diagram of Brisi and Molinari (1958, Fig. 1), these temperatures are 760° and 770°C, respectively. If the natural system is reproduced by the experiments in the CuO–V_2O_5 binary system, the temperature of formation of ziesite must have been between 760° and 770°C; thus, 760°C is the lower limit of the "Y" fumarole's highest temperature. The intermediate copper vanadate $Cu_3V_2O_8$, an undescribed mineral, is found in samples from the same location, presumably formed at temperatures below 760°C. The data of Fleury (1966, 1969) suggest that the temperature of formation of ziesite is between 780° and 784°C, but we consider his data less relevant because his experiments do not produce the naturally-occurring phase $Cu_4V_2O_9$. In either case, the temperature difference is of little significance.

Physical properties

Ziesite occurs as anhedral black grains 200 μm in greatest dimension. The mineral has a metallic luster and a reddish-brown streak similar to the streak of hematite.

The calculated density of ziesite is 3.87 g/cc, assuming Z = 2. The measured density of synthetic β-

$Cu_2V_2O_7$ is 3.86 ± 0.05 g/cc and Z = 2 (Mercurio-Lavaud and Frit, 1973a). It was not possible to measure the density of ziesite due to sample scarcity and mineral intergrowths.

Ziesite transmits light on very thin edges. The color of this transmitted light is between moderate and dark reddish brown (10 R 3.5/5, Goddard *et al.*, 1963). Ziesite exhibits weak absorption of unknown orientation. The mean index of refraction, calculated by the rule of Gladstone and Dale, is 2.055. In reflected light in air, ziesite is white and non-pleochroic. The mineral exhibits a moderate to strong anisotropy and gives two observable extinctions per complete stage rotation. Individual grains are often composed of several optically discontinuous regions. Ziesite exhibits moderate reflectivity in air, with the mean value of the uniradial reflections between those of acanthite and tetrahedrite. This corresponds to class C reflectivity of Short (1940).

No cleavages were observed in ziesite. The mineral does not fluoresce in short- or long-wave UV radiation.

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