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Stoiberite, $Cu_5V_2O_{10}$, a new copper vanadate from Izalco volcano, El Salvador, Central America

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Abstract

Stoiberite, $Cu_5V_2O_{10}$, a new copper vanadate mineral, occurs as black platy crystals in the oxide zone of a fumarole in Izalco volcano, El Salvador, Central America. It is monoclinic, space group $P2_1/n$, with $a = 15.654(15)$, $b = 6.054(4)$, $c = 8.385(11)$A, and $\beta = 102.29°(12)$. The mineral is opaque with a medium reflectivity less than that of galena. Its calculated density is 4.96 gm/cc. It is named after Dr. Richard E. Stoiber.

Introduction

Naturally-occurring $Cu_5V_2O_{10}$ 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 $Cu_5V_2O_{10}$ is based on (1) electron microprobe chemical analysis, and (2) X-ray diffraction analysis. The new mineral is named stoiberite (stoi′ · bər · īt) in honor of Dr. Richard E. Stoiber, Professor Emeritus of Geology at Dartmouth College, who is noted particularly for his studies of Central American volcanoes, fumarolic gases, and fumarolic mineral incrustations. Type specimens are deposited in the mineral collection of the Department of Earth Sciences, Dartmouth College and the National Museum of Natural History, Smithsonian Institution, Washington, D.C. (NMNH 144942). The total amount of the mineral on hand is a few milligrams. The mineral and mineral name have been approved by the Commission on New Minerals and Mineral Names, IMA.

Locality and occurrence

Izalco volcano is a 2-km^3 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. The geology of the volcano is described by Meyer-Abich (1958), Rose and Stoiber (1969), and Stoiber *et al.* (1975).

During its brief history, Izalco has had 55 eruptive periods, ranging from 9 years to less than one year in duration. Since 1958, the volcano has been inactive except for a small flank lava flow in 1966. During this repose period, the gases and minerals of the fumaroles in the summit crater have received extensive study (Stoiber and Dürr, 1963; Stoiber and Rose, 1970, 1974; Stoiber *et al.*, 1975). Copper and vanadium were found among the four distinctive elements in the Izalco fumarole mineral suite. Copper occurs in chalcocyanite ($CuSO_4$) and chalcanthite ($CuSO_4 \cdot 5H_2O$), while vanadium occurs in shcherbinaite (V_2O_5). The compound V_2O_5 was first noted at Izalco (Stoiber and Dürr, 1963) but not named. It was subsequently found in a fumarole at Bezymyanny Volcano, Kamchatka and named (Borisenko, 1972; Fleischer, 1973).

Stoiberite is found only in the "Y" fumarole, one of five major fumaroles at Izalco (Stoiber *et al.*, 1975, Fig. 1). In 1964, when the mineral was first discovered, the temperature of the fumarole was 450°C. The temperature of the fumarole in November, 1978, had fallen to 89°C, and only small amounts of stoiberite were found. The mineral occurs as a black incrustation in the oxide zone of the fumarole (fumarole zonation described by Stoiber and Rose, 1974). The crystals are less than 100 μm in greatest dimension and coat basaltic breccia fragments.

Chemistry

The synthesis of $Cu_5V_2O_{10}$ was first reported by Brisi and Molinari (1958). They observed that the compound melts incongruently at 800°C and is one of the five incongruently melting phases in the CuO–

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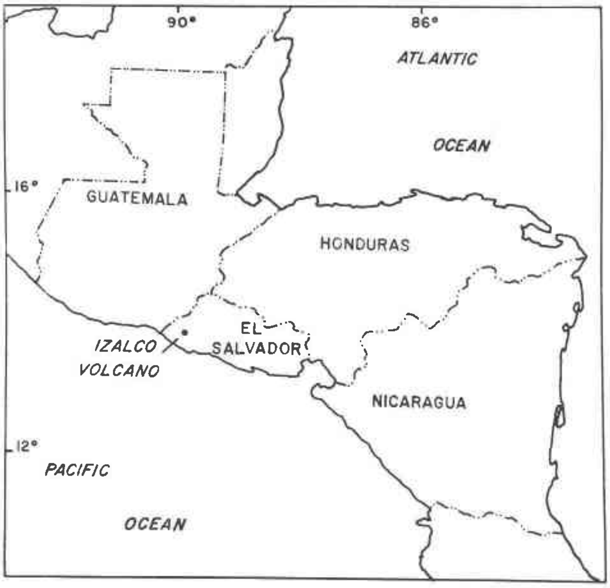

Fig. 1. Location of Izalco volcano, El Salvador.

V_2O_5 system. Fleury (1966, 1969; reported in Shannon and Calvo, 1973) conducted magnetic susceptibility measurements on synthetic $Cu_5V_2O_{10}$ and determined that the copper is divalent; therefore, the formula can be written as $5CuO \cdot V_2O_5$. Single crystals of $Cu_5V_2O_{10}$ have also been synthesized by Shannon and Calvo (1973) from a melt with the composition $5CuO{:}1V_2O_5{:}6KVO_3$ at 1000°C.

The ideal formula of stoiberite is $Cu_5V_2O_{10}$ (Table 1). Electron microprobe analysis of the mineral was carried out using the following standards: CuO (Cu metal); V_2O_5 (V_5O_5); CrO_3 (uvarovite). No other major elements were detected.

Table 1. Electron microprobe analyses of stoiberite. All values in weight percent

Oxide	(1)	(2)*	(3)*
CuO	68.62	68.0(4)	68.1(6)
V_2O_5	31.38	30.1(4)	30.3(5)
CrO_3	--	1.03(1)	1.0(1)
	100.00	99.13	99.4

*One standard deviation in parentheses

(1) Ideal stoiberite
(2) $\bar{X}$ of 3 analyses of type crystal
(3) $\bar{X}$ of 20 analyses of 10 crystals

formula (analysis (3)) on the basis of 10 oxygens:

$Cu_{4.98}(V_{1.94}Cr_{0.06})O_{10}$

ideal formula: $Cu_{5.00}V_{2.00}O_{10}$

An average of 3 mole percent chromium substitutes for vanadium. The quantification of the Cr substitution is difficult because of spectral interference by vanadium. The chromium is known to substitute for the vanadium because chromium increases in concentration with vanadium in more vanadium-rich copper vanadates associated with stoiberite. The oxidation state of the Cr is not known, but is assumed to be Cr(VI). This assumption is made because the Cr in stoiberite occupies the vanadium sites, which are all tetrahedrally coordinated (structure analysis by Shannon and Calvo, 1973). Cr(VI) is the more stabilized oxidation state in a tetrahedral crystal field, and Cr(III) is not known to occupy tetrahedrally-coordinated sites (Burns and Burns, 1975).

Evidence of the compatibility of Cr(VI) in the vanadium sites of stoiberite is given by the metal–oxygen bond lengths. Typical Cr(VI)–O_4 bond lengths are ~1.65A (Burns and Burns, 1975), and values between 1.54 and 1.81A have been reported (White and Roy, 1975). These values are consistent with the 1.72A V–O_4 bond lengths in synthetic $Cu_5V_2O_{10}$ (Shannon and Calvo, 1973).

The substitution of minor amounts of the hexavalent chromium ion for the pentavalent vanadium ion poses a neutrality problem in the formula calculation. Brisi and Molinari (1958) described solidus and sub-solidus oxidation–reduction reactions in copper vanadates. Oxidation reactions of the sort required to accommodate minor amounts of Cr(VI) in natural $Cu_5V_2O_{10}$ are known to take place in the oxide zone of volcanic fumaroles (Naboko, 1959), and it may be that the naturally-occurring $Cu_5V_2O_{10}$ has undergone a reaction of this type.

The presence of Cr in stoiberite is of interest because Cr-bearing fumarole minerals are rare, although not unknown (Naboko, 1959). Several other Cr-bearing phases have also been discovered at this fumarole by the authors (manuscript in preparation).

X-ray crystallography

An X-ray diffraction pattern of stoiberite was obtained from a polycrystalline grain mount in a 114.6 mm Gandolfi camera using CrKα radiation (2.2909A, V filter) in a helium atmosphere. Correction were made for film shrinkage, and intensities were visually estimated. Powder patterns of synthetic $Cu_5V_2O_{10}$ were published by Brisi and Molinari

(1958; JCPDS #16-418) and Shannon and Calvo (1973; JCPDS #27-1135). The diffraction pattern of stoiberite agrees with the patterns of the synthetic phase. The stoiberite pattern has been contributed to the Powder Diffraction File. The lattice constants measured from precession photographs (MoKα radiation, 0.7107A, Zr filter) and those refined from Gandolfi patterns are listed in Table 2.

Stoiberite is monoclinic, uniquely determined as space group $P2_1/n$. Precession photographs show extinctions $h + l \neq 2n$ for $(h0l)$ reflections. Also in Table 2 are the lattice constants reported for synthetic $Cu_5V_2O_{10}$. Shannon and Calvo (1973) originally reported an unreduced cell that conforms to the nomenclature in the *International Tables* for space group $P2_1/c$. The axial parameters of the unreduced cell are related to those of the proposed reduced cell by $a_{\text{unred}} = [101]_{\text{red}}$; $b_{\text{unred}} = [0\overline{10}]_{\text{red}}$; $c_{\text{unred}} = [00\overline{1}]_{\text{red}}$. Shannon and Calvo's cell parameters are comparable to the unreduced cell parameters if Shannon and Calvo's a and c axes are reversed to conform with the convection $a > c$ in monoclinic crystals.

The crystal structure of synthetic $Cu_5V_2O_{10}$ was solved by Shanon and Calvo. They describe the structure as a network of chains of $Cu{-}O_6$ octahedra and $Cu{-}O_5$ trigonal dipyramids linked by edge-sharing of the octahedra and corner-sharing of the $V{-}O_4$ tetrahedra.

Physical properties

Stoiberite occurs as polycrystalline aggregates <100 μm in greatest dimension. The mineral is black with a metallic luster and a reddish-brown streak similar to the streak of hematite.

Shannon and Calvo (1973) report both plate-like and needle-like habits in synthesized $Cu_5V_2O_{10}$. Only the plate-like habit is observed in the naturally-occurring analog. The plates represent the front pinacoid {100}. Figure 2 is an electron microscope image of a well-formed crystal of stoiberite. The orientation of the principal axes was determined from precession photographs of the crystal pictured. Scanning electron microscope examination of numerous crystals showed that euhedral grains are rare and polycrystalline aggregates are common. Some images also reveal parallel striae on the (100) face which intersect the b and c axes at intercepts proportional to the respective axial lengths. The a axial intercept could not be determined. These striae may represent an $\{h11\}$ cleavage trace.

Table 2. Unit-cell parameters of stoiberite and synthetic $Cu_5V_2O_{10}$

	a(A)*	b(A)*	c(A)*	β(deg.)*	V(A³)
(1)	15.69	6.06	8.32	102.3	773
(2)	15.654(15)	6.054(4)	8.385(11)	102.29(12)	776
(3)	15.712	6.068	8.389	102.34	781

*esd's in parentheses

(1) Measured from precession photographs

(2) Least-squares refinement using 16 d values from Gandolfi pattern (refined using LCLSQ program, Charles W. Burnham, Harvard University).

(3) Reduced parameters reported on JCPDS #27-1135 (reduced from data of Shannon and Calvo, 1973).

The calculated density of ideal stoiberite and the natural Cr-bearing analog is 4.96 g/cc. This was calculated using the X-ray cell volume and assumed $Z = 4$. Due to the small amount and size of the naturally-occurring material, density was not measured. Shannon and Calvo (1973), however, report a measured density of 5.0 g/cc in the synthetic analog; they obtained $Z = 4$ from refined crystal structure data.

Stoiberite transmits light only on thin edges. The color of this transmitted light is "moderate reddish-brown" (similar to 10 R 46, Goddard *et al.*, 1963). Extremely weak absorption of unknown direction is observed. In reflected light in air, stoiberite exhibits a weak anisotropy. The colors are not unlike "very light gray" (N8, Goddard *et al.*, 1963). A slight bluish-white pleochroism is present (estimated at 5 B 9/1 to 5 B 8.5/1, Goddard *et al.*, 1963). The mineral has a medium reflectivity, less than that of galena.

Stoiberite does not fluoresce in either short- or long-wave ultra-violet radiation. It is soluble in dilute H_2SO_4.

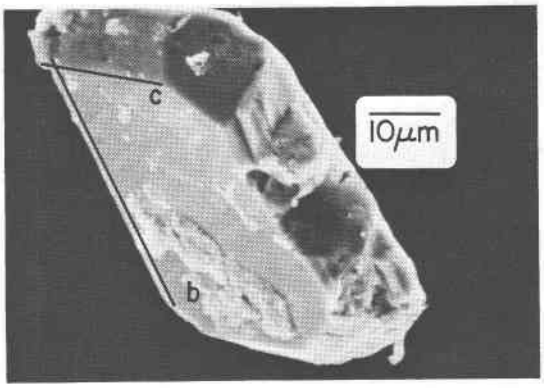

Fig. 2. Scanning electron microscope image of a well formed crystal of stoiberite. The plane surface is (100) and on it are marked the b and c axial directions. The a axis makes an angle (β) of 102.29° with c.

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