Sarabauite, a new oxide sulfide mineral from the Sarabau mine, Sarawak, Malaysia

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Abstract

Sarabauite, $CaSb_{10}O_{10}S_6$, is a new mineral found at the Sarabau mine, about 40 km SW of Kuching, Sarawak, Malaysia. It occurs as small realgar-like masses in vein-like mineral aggregates composed of quartz, calcite, wollastonite, stibnite, and minor senarmontite in an altered limestone. It is probably a product of primary hydrothermal mineralization. The mineral is monoclinic, space group $C2/c$, $a = 25.37(2)$, $b = 5.654(1)$, $c = 16.87(1)$A, $\beta = 117.58(4)°$, and $Z = 4$. The strongest X-ray powder lines are $3.215(100)(\overline{5}14)$, $2.817(88)(020,512,\overline{4}06,800)$, $3.466(78)(312)$, $3.182(60)(511)$, $3.164(50)(\overline{8}02)$, $4.227(42)(\overline{6}02)$, $2.583(40)(\overline{4}21)$. It has a realgar-like carmine-red color, resinous luster, and orange streak. Cleavage is not observed. Vickers microhardness (20 g load) is 272 ± 6 kg/mm². Specific gravity is 4.8 (meas.) and 4.99 (calc). Under the ore microscope it is gray with brownish to purplish pleochroic colors and has strong reddish-orange internal reflections. The reflectances are: 486 nm, 25.8–20.1 percent; 546 nm, 24.7–19.7 percent; 589 nm, 23.5–19.1 percent; 656 nm, 20.0–14.0 percent for maxima and minima respectively. Electron microprobe analysis gave Ca 2.43, Sb 74.89, O 9.61, S 11.91, total 98.84 percent, corresponding to $Ca_{0.99}Sb_{10}O_{9.76}S_{6.04}$. It is readily soluble in conc. HCl with evolution of H_2S and slowly in conc. NaOH and dilute HNO_3 solutions. Single crystals of sarabauite were synthesized under hydrothermal conditions: 500°C, 1000 kg/cm².

Introduction

A realgar-like carmine-red mineral was found in hydrothermal ore deposits of the Sarabau mine, Sarawak, Malaysia. After microprobe analysis and synthetic work, the mineral proved to be a new species having the ideal chemical formula $CaSb_{10}O_{10}S_6$. This is the second naturally occurring oxide sulfide mineral, kermesite (Sb_2S_2O) being the first.

The mineral is named sarabauite after the locality. The mineral and the name have been approved by the Commission on New Minerals and Mineral Names, IMA.
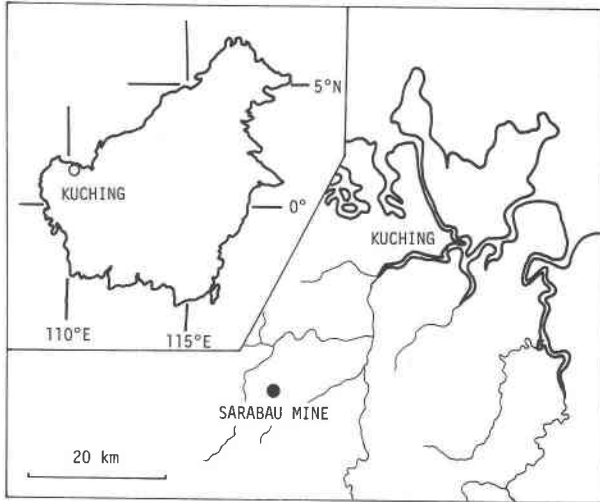
Fig. 1. Location map of the Sarabau mine, Sarawak, Malaysia.

Description

The ore deposits of Sarabau mine are located near Bau, about 40 km SW of Kuching, Sarawak (Fig. 1), where limestone, shale, chert, sandstone, and conglomerate belonging to the Bau Series of Upper Jurassic to Cretaceous are exposed. They are locally intruded by microdiorite, microtonalite, dacite, and quartz–andesite of late Tertiary age, and the volcanic activity is considered to be responsible for the mineralization of gold, silver, antimony, and mercury found in the rocks of the Bau Series (Wilford, 1955); very probably the formation of the Sarabau deposits was due to the same geologic event.

Only one specimen showing the mode of occurrence of sarabauite was found. All descriptions and studies were made on this material. It is a piece of gray fine-grained limestone cut by a sarabauite-bearing vein-like body more than 5 cm in width. The mode of occurrences of sarabauite and the associated minerals including stibnite, wollastonite, quartz, calcite, and minor senarmontite are depicted in Figure 2.

Sarabauite forms long tabular crystals elongated along the b axis, and the maximum length reaches 1 mm. A well-developed external shape was only occasionally observed under the ore microscope; however, even so, the morphology could not be determined.

The close association of stibnite, senarmontite, and sarabauite suggests the absence of any stable phases with intermediate compositions between $CaSb_{10}O_{10}S_6$–Sb_2S_3–Sb_2O_3 under the conditions of sarabauite formation, which excluded the formation of kermesite.

Physical and optical properties

Sarabauite has a realgar-like carmine-red color, resinous luster, orange streak, and no visible cleav-

age. The habit is tabular and prismatic parallel to the b axis. The specific gravity measured by Berman balance is 4.8, while the calculated value from the theoretical formula is 4.99. Vickers microhardness is 272 ± 6 kg/mm^2 (load 20 g). The mineral is not brittle but is to some extent sectile.

Under the ore microscope it is gray-white with discernible reflection pleochroism changing from a brownish to a purplish tint. Internal reflections are quite remarkable with reddish-orange color. No polishing cleavage is observed. The reflectances are: 486 nm, 25.8–20.1 percent; 546 nm, 24.7–19.7 percent; 589 nm, 23.5–19.1 percent; 656 nm, 20.0–14.0 percent for maxima and minima respectively. These figures may be affected due to internal reflections.

Owing to its extremely strong absorption, very limited optical properties for transmitted light were obtained. The samples used were synthetic $CaSb_{10}O_{10}S_6$. It is optically biaxial negative with $2V$ about 90°, $b = Y$, and the pleochroism is from reddish-yellow ($\| Y$) to brownish-red ($\| Z'$).

X-ray crystallography

The precession and Weissenberg photographic studies showed the mineral to be monoclinic with possible space group either Cc or $C2/c$. The latter is preferred according to the results of a structural analysis (Nakai et al., 1977). The unit-cell parameters refined with a four-circle automatic diffractometer ($MoK\alpha_1 = 0.709258A$) are $a = 25.37(2)$, $b = 5.654(1)$, $c = 16.87(1)A$ and $\beta = 117.58(4)°$.

In the sarabauite structure (Nakai et al., 1977), the

Fig. 2. Sketch of the studied sarabauite-bearing specimen. Sa: sarabauite; Sb: stibnite (with minor senarmontite); Wo: wollastonite; Ct: calcite.

Sb atoms are coordinated by three O and/or S atoms to form trigonal pyramids of SbO_3, SbS_3 and SbS_2O. The SbO_3 pyramids compose 4-membered and 8-membered Sb–O rings. These two rings link by sharing a corner O atom to form a chain parallel to [001]. On the other hand, two SbS_3 and two SbS_2O pyramids form an 8-membered Sb–S ring. Moreover the 8-membered Sb–O and Sb–S rings link by sharing a corner O atom to form a chain parallel to [101]. As a whole, those linkages of ring structures give rise to a two-dimensional network parallel to (010). The Ca atom is sandwiched between the two 8-membered Sb–O rings and forms a CaO_8 polyhedron. Thus the Ca atoms link the networks in the b-axis direction.

Kermesite (Sb_2S_2O) is the only mineral which is compositionally related to sarabauite. However, kermesite contains no cation other than antimony, and this gives a certain difference between the two structures. The kermesite structure (Kupčík, 1967) has a similar network composed of Sb, S, and O atoms parallel to (100). As mentioned above, in sarabauite the nets are linked by the Ca atoms to form a three-dimensional structure, whereas in kermesite the nets are stacked in the a axis direction and linked by weak Sb–S and Sb–O bonds. The average bond distances are: Ca–O 2.467, Sb–O 2.000 and Sb–S 2.465A. Similar values are observed in kermesite as well as in other oxides and sulfides.

The X-ray powder pattern obtained by the diffractometer method using Ni-filtered Cu radiation is given in Table 1. The indexing was made on the basis of single-crystal data. There is good agreement between intensities of the X-ray powder and single-crystal data.

Table 1. X-ray powder diffraction data for sarabauite*

hkl	d calc	d obs	I/I₀	hkl	d calc	d obs	I/I₀
200	11.24	11.33	20	10.0.2	1.922	1.922	16
$\bar{2}$02	8.224	8.276	6	$\bar{8}$26	1.888	1.890	22
111	4.970	4.979	6	$\overline{10}$.2.3	1.888		
$\bar{3}$12	4.452	4.462	36	026	1.869	1.872	18b
$\bar{6}$02	4.224	4.227	42	623	1.869		
$\bar{1}$13	3.915	3.924	30	804	1.869		
$\bar{5}$12	3.751	3.748	15	$\bar{1}$18	1.834	1.830	16b
600	3.748			$\bar{6}$27	1.826		
004	3.738			132	1.805	1.808	7
312	3.461	3.466	78	$\overline{13}$.1.6	1.791	1.791	12
$\bar{3}$14	3.379	3.386	10	$\bar{1}$33	1.780	1.783	13
$\bar{5}$14	3.207	3.215	100	516	1.756	1.756	7b
511	3.179	3.182	60	317	1.751		
$\bar{8}$02	3.156	3.164	50	624	1.730	1.731	8
$\bar{7}$12	3.050	3.052	6	531	1.692	1.694	18
$\bar{7}$13	3.007	3.011	5	$\overline{12}$.2.5	1.675	1.673	7b
$\bar{7}$11	2.970	2.970	6	$\bar{7}$32	1.672		
020	2.827	2.817	88	823	1.671		
512	2.816			$\bar{7}$33	1.665	1.666	5
$\bar{4}$06	2.811			$\bar{7}$34	1.638	1.640	2
800	2.811			$\overline{10}$.0.4	1.623	1.620	8
$\bar{2}$21	2.752	2.753	20	$\bar{5}$.1.10	1.601	1.603	9
$\bar{2}$06	2.713	2.718	28	318	1.578	1.580	8b
$\bar{7}$15	2.639	2.644	9	$\overline{12}$.0.10	1.578		
404	2.606	2.607	18	716	1.572	1.571	6b
$\bar{4}$21	2.580	2.583	40	$\overline{15}$.1.7	1.569		
$\overline{10}$.0.4	2.507	2.503	14	$\overline{15}$.1.2	1.559	1.560	11
006	2.492	2.498	15	$\bar{9}$35	1.526	1.524	7b
$\bar{7}$16	2.401	2.409	5	$\overline{10}$.2.9	1.512	1.515	5b
$\bar{9}$15	2.361	2.365	9	$\overline{13}$.1.10	1.483	1.483	8
712	2.327	2.329	6	$\bar{5}$18	1.448	1.450	6
910	2.285	2.281	20	$\overline{17}$.1.4	1.433	1.432	3
10.0.0	2.249	2.251	5	041	1.407	1.407	5b
604	2.188	2.187	4b**	$\bar{4}$41	1.379	1.379	4b
$\bar{7}$17	2.170	2.174	4b	734	1.377		
$\bar{8}$22	2.106	2.108	16	14.2.1	1.341	1.342	9
025	2.054	2.058	29	$\bar{6}$42	1.340		
$\overline{11}$.1.1	2.021	2.023	5	718	1.326	1.328	2
$\overline{11}$.1.6	2.001	2.004	5	$\overline{13}$.3.1	1.308	1.310	6
820	1.993	1.995	5	2.0.12	1.306		
$\bar{5}$18	1.973	1.976	5	$\bar{1}$39	1.269	1.270	5
$\bar{2}$26	1.957	1.960	12	$\overline{18}$.2.7	1.252	1.250	5
$\overline{10}$.0.8	1.947	1.952	13	$\overline{10}$.4.3	1.235	1.236	4

* Cu/Ni radiation, diffractometer method, 0.5° min⁻¹ in 2θ.
**b: broad

Table 2. Electron microprobe chemical analysis of sarabauite

	1.	2.	molecular quotient	mole number (basis Sb=10)	ideal number	3.
Ca	2.43	2.46	0.0614	0.99	1	2.49
Sb	74.89	75.77	0.6223	10	10	75.62
O	9.61	9.72	0.6075	9.76	10	9.94
S	11.91	12.05	0.3759	6.04	6	11.95
Total	98.84	100.00				100.00

1. Sarabauite, Sarabau mine, Sarawak, Malaysia.
2. Sarabauite, normalized to 100%.
3. Theoretical $CaSb_{10}O_{10}S_6$.

Chemical composition and properties

The electron microprobe analysis using JXA-5A analyser gave the results shown in Table 2. Wavelength scans disclosed only Ca, Sb, O, and S in major amounts and other elements were not found. The standards used were stibnite, kermesite, valentinite, and wollastonite. Measurements were made at 25 kV for Ca, Sb, and S, and 15 kV for O. The result calculated on the basis of Sb = 10 leads to the empirical formula $Ca_{0.99}Sb_{10}O_{9.76}S_{6.04}$. From the measured specific gravity, $Z = 4$.

The mineral decomposes readily in conc. HCl with evolution of H_2S and very slowly in conc. NaOH and dilute HNO_3 solutions.
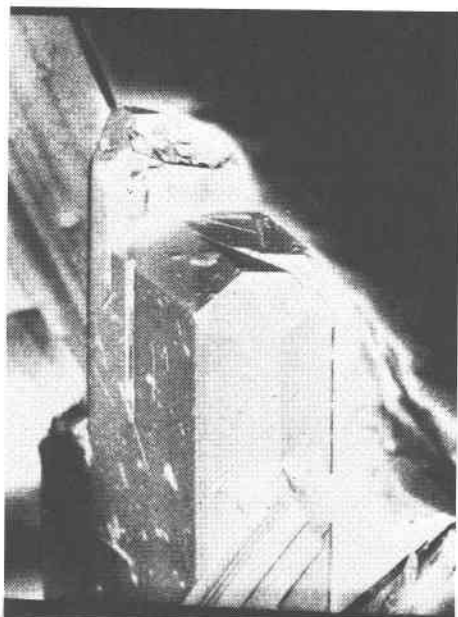
Fig. 3. Scanning electron micrograph of synthetic $CaSb_{10}O_{10}S_6$.

Thermal study

Thermal analyses were performed with a heating rate of 2.5°C/min. The DTA and TGA curves are characterized by a strong exothermic peak at about 420° with a weight loss and a weak one at about 490°C. The corresponding peaks for synthetic $CaSb_{10}O_{10}S_6$ are found at 410° and 490°C, respectively. X-ray powder study of the product after thermal treatment at 490°C revealed that it consists of a mixture of cubic Sb_2O_3, Sb_2O_4, and $CaSb_2O_6$. The latter two compounds survive in the product at 1000°C.

Synthesis

Stoichiometric $CaSb_{10}O_{10}S_6$ was hydrothermally synthesized from $CaO : Sb_2S_3 : Sb_2O_3 = 1:2:3$ mixture in both cold-seal stellite bombs and silica tubes at temperatures from 230 to 560°C under pressures from 30 to 1500 kg/cm². The reaction rate is so rapid that the formation requires only one hour at 500°C and 1000 kg/cm². Although it includes small fractions of recrystallized acicular Sb_2S_3 and polygonal Sb_2O_3 (either cubic or orthorhombic) in some runs, the product, including single crystals up to 3 mm elongated along the b axis, consists of aggregates of carmine-red tablets having the same appearance, habit, and luster as the natural mineral. A scanning electron micrograph of the synthetic crystal is given in Figure 3.

Synthetic $CaSb_{10}O_{10}S_6$ is made up of at least two morphologically different crystals, columnar and tabular. They are elongated along the b axis like the natural crystals, and the latter are characterized by a well-developed {100} form.

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