

# STIBIOCLAUDETITE



## A NEW MINERAL FROM TSUMEB, NAMIBIA

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*Stibioclaudeite, the antimony analog of claudetite, has been found at the Tsumeb mine, Namibia, in bladed crystals to 6 mm association with leiteite, ludlockite, smithsonite and quartz. Previously identified specimens of claudetite from Tsumeb may well be stibioclaudeite instead.*

### ABSTRACT

Stibioclaudeite is a new mineral species with ideal chemistry  $\text{AsSbO}_3$ . The symmetry is monoclinic,  $P2_1/n$ , with  $a = 4.5757(4)$  Å,  $b = 13.1288(13)$  Å,  $c = 5.4216(5)$  Å,  $\beta = 95.039(4)^\circ$ ,  $V = 324.44(5)$  Å<sup>3</sup>,  $Z = 4$ , and  $d_{\text{calc}} = 5.009$  g/cm<sup>3</sup>. The strongest X-ray lines (calculated) are 3.512 (100), 3.282 (82), 3.238 (71), 2.279 (34), and 4.995 (32). The average of ten microprobe analyses is 45.15%  $\text{As}_2\text{O}_3$  and 55.77%  $\text{Sb}_2\text{O}_3$ , total 100.92, corresponding to  $\text{As}_{1.088}\text{Sb}_{0.912}\text{O}_3$ . Stibioclaudeite forms adamantine, colorless transparent bladed crystals to 6 mm, bound by {010}, {110}, {111}, and  $\{\bar{1}01\}$ . The mineral is flexible with perfect cleavage on {010}. The hardness is <2 and has refraction indices >2.00. Stibioclaudeite occurs with leiteite, ludlockite, smithsonite and quartz in a vug within massive tennantite from the Tsumeb mine, Tsumeb, Namibia. Stibioclaudeite is isostructural with claudetite, specifically an Sb-substituted ordered analog, and the name denotes the relationship. The crystal structure consists of corrugated sheets of corner-sharing  $\text{AsO}_3$  and  $\text{SbO}_3$  trigonal pyramids arranged in an ordered, alternating pattern. Raman spectra of stibioclaudeite, claudetite, and leiteite are presented and compared.

### INTRODUCTION

Mineral dealer David W. Bunk obtained an unusual Tsumeb specimen containing a well-formed leiteite ( $\text{ZnAs}_2\text{O}_4$ ) blade, red fibrous ludlockite, quartz, and an undetermined mineral occurring as colorless crystals to 6 mm in length. *In situ*, non-destructive examination of the unknown mineral with Raman spectroscopy failed to match its pattern from a large Raman spectral database that the Department of Geosciences at the University of Arizona is currently constructing. Raman spectroscopy confirmed that three separate crystals are of the same unknown. Similarities to the Raman spectrum of leiteite indicated an  $\text{As}^{3+}$ -bearing structure, and preliminary electron-dispersive spectroscopy (EDS) on an SEM indicated the presence of As, Sb and O (and no other elements with  $Z < 8$ ). Since no known mineral contained only As, Sb and O, the authors initiated a full characterization of the material.

Crystal structure determination (Origlieri *et al.*, 2007) and quantitative electron-probe microanalysis identified this phase as natural occurring  $\text{AsSbO}_3$ . Bodenstein *et al.* (1983) studied synthetic  $\text{AsSbO}_3$ , which they demonstrated to be isostructural with claudetite ( $\text{As}_2\text{O}_3$ ) (Pertlik, 1978). The crystal structure of this new mineral



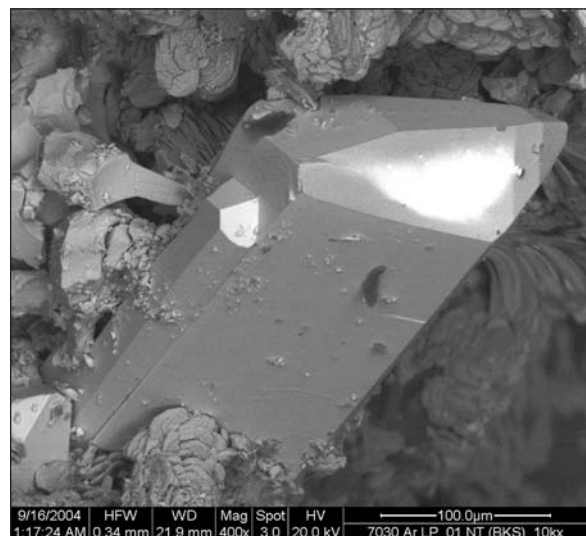
**Figure 1.** The largest cluster of crystals of stibioclaudeite, 6 mm across, in a vug of massive tennantite with quartz crystals. This is the holotype specimen. D. W. Bunk specimen, now in the W. W. Pinch collection.

**Figure 2.** Scanning electron photomicrograph of stibioclaudeite, showing the terminal morphology of the crystals.

consists of corrugated sheets of corner-sharing  $\text{AsO}_3$  and  $\text{SbO}_3$  trigonal pyramids, with sheets stacked along [010]. The Commission on New Minerals, Nomenclature and Classification (CNMNC) of the International Mineralogical Association approved the mineral (proposal IMA2007-028) and mineral name before publication. We have deposited type material at the United States National Museum of Natural History (Smithsonian Institution) in Washington, D.C. under catalog number 174550. The mineral name, stibioclaudeite, denotes the structural relationship with claudeite, as an ordered Sb-substituted analog.

Strunz *et al.* (1958) first reported claudeite from Tsumeb as gypsum-like platelets. Strunz (1959) further elaborated, describing 1–3 mm colorless to white crystals with unit cell dimensions  $a = 5.3 \text{ \AA}$ ,  $b = 13.0 \text{ \AA}$ ,  $c = 4.56 \text{ \AA}$ , and  $\beta \sim 94^\circ$ . He sublimated the mineral in a closed glass tube and condensed minute octahedral crystals. This microchemical behavior is consistent with the known behavior of claudeite, which condenses into octahedral crystals (i.e. arsenolite). However, these tests are not sufficient to distinguish claudeite from stibioclaudeite.  $\text{AsSbO}_3$  is also known to have a cubic modification with the same crystal structure as  $\text{As}_2\text{O}_3$  (arsenolite) (Hayek *et al.*, 1963). Consequently, sublimation of either claudeite or stibioclaudeite would produce octahedral crystals. The unit cell reported by Strunz (1959) lacks the precision required to reliably distinguish stibioclaudeite from claudeite. Keller *et al.* (1979) reported another occurrence of claudeite from Tsumeb in association with warikhanite, unfortunately without specifying the identification method. The original identification of claudeite from Tsumeb could be in error; therefore Tsumeb specimens labeled “claudeite” warrant re-examination.

Hayek *et al.* (1963) showed that cubic  $\text{As}_2\text{O}_3$  (arsenolite) and cubic  $\text{Sb}_2\text{O}_3$  (senarmontite) are miscible, forming a complete solid solution series. Consequently, ordinary solid solution between arsenolite and senarmontite might yield cubic  $\text{AsSbO}_3$  without structural ordering of As and Sb atoms. In that case, a cubic dimorph of stibioclaudeite would simply be an intermediate of the arsenolite-senarmontite series, and would not qualify as a new mineral species. The ordering of Sb into a single As position of the claudeite structure is apparently unique to the claudeite and stibioclaudeite structure (Origlieri *et al.*, 2009). A literature search failed to locate any report of monoclinic  $\text{Sb}_2\text{O}_3$ , however an orthorhombic phase which bears the mineral name valentinite is well known.



Mineralogist Sidney A. Williams identified hexagonal  $\text{AsSbO}_3$  among mine fire products from Nevada (Gibbs, 1985).

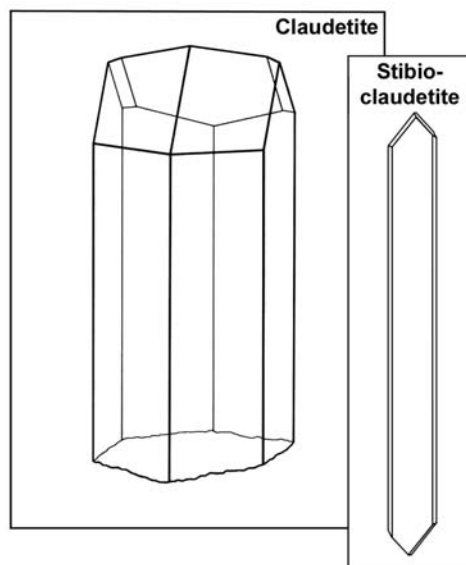
## OCCURRENCE AND PARAGENESIS

The new mineral occurs within a cavity in a massive tennantite sample ( $4 \times 5 \times 7 \text{ cm}$ ) from the Tsumeb mine at Tsumeb, Namibia. The cavity measures 3 cm across, and hosts quartz crystals to 3 mm, a single terminated leiteite blade 7 by 20 mm, red fibers of ludlockite, smithsonite and crystals of stibioclaudeite to 6 mm. Figure 1 shows a photograph of the largest group of stibioclaudeite crystals. Although we do not know the precise original location of the specimen within the Tsumeb mine, the association with leiteite leads to certain conclusions. Leiteite occurs in the second and third oxidation zones at the Tsumeb mine (Gebhard 1991, 1999). Type leiteite occurs with tennantite, chalcocite, smithsonite and schneiderhöhnite (Cesbron *et al.*, 1977). Our present leiteite sample occurs on tennantite matrix with quartz, ludlockite and smithsonite. This assemblage suggests that its specific origin within the Tsumeb mine may be distinct from other known leiteite occurrences.

Although antimony-dominant minerals are not typical of the arsenic-rich assemblages at Tsumeb, primary tennantite contains substantial antimony (Moritz, 1933). Previous investigators have

reported five mineral species from the Tsumeb mine with essential antimony: famatinite (Schneider, 1992), stibnite (Schneider, 1992), stibiconite (Schneider, 1992), nadorite (Schneider, 1992) and biehlite (Schlüter *et al.*, 2000). Schneider (1992) quantifies the 1988 production of NaSb(OH)<sub>6</sub> at the Tsumeb smelter at 156 metric tons. Oxidation of host tennantite could readily supply both the arsenic and antimony sufficient to form stibioclaudeite. Moritz (1933) further notes a substantial zinc content in Tsumeb tennantite, which could supply both the zinc and arsenic required to form leiteite (ZnAs<sub>2</sub>O<sub>4</sub>).

Monoclinic As<sub>2</sub>O<sub>3</sub> (claudeite) forms above 250° C, while cubic As<sub>2</sub>O<sub>3</sub> (arsenolite) has a melting point near 275° C (Schulman and Schumb, 1943). Hayek *et al.* (1963) report a melting point of 315° C for claudeite. In other words, claudeite remains stable at higher temperatures than arsenolite. Bodenstein *et al.* (1983) synthesized their monoclinic AsSbO<sub>3</sub> at temperatures near 347° C. These data conservatively bracket the formation of stibioclaudeite between 300° C and 400° C.



**Figure 3.** Crystal morphology of stibioclaudeite, showing forms {010}, {110}, {111}, and  $\bar{1}01$ . At left is claudeite from Imperial County, California, as illustrated by Palache (1934).

#### APPEARANCE AND PHYSICAL PROPERTIES

Stibioclaudeite forms bladed crystals to 6 mm bound by forms major {010}, major {110}, minor {111}, and very minor  $\bar{1}01$ . Stibioclaudeite is colorless and transparent with an adamantine luster and a white streak. The mineral does not show fluorescence under ultraviolet radiation. Figure 1 is a close-up of the largest stibioclaudeite crystals on the holotype, and Figure 2 shows the terminal morphology in a scanning electron micrograph. Figure 3 is a line drawing of the ideal morphology. Stibioclaudeite crystals mimic the morphology of claudeite from Imperial Valley, California as illustrated by Palache (1934), shown in the inset in Figure 3. Hardness is ~2. The mineral has perfect cleavage on {010}, readily obtained. Cleavage plates are flexible, and deform similarly to gypsum. The mineral shows strong relief under  $n=2.00$  index fluids, indicating an index of refraction above 2.00.

#### CHEMISTRY

We conducted electron probe microanalysis on a cleavage plate of the stibioclaudeite attached to a glass disc. Qualitative WDS

**Table 1.** Electron probe microanalysis data for stibioclaudeite with corresponding atomic compositions normalized to three oxygen atoms. The average of these ten analyses, with standard deviations is 45.15(0.95)% As<sub>2</sub>O<sub>3</sub>, 55.77(1.07)% Sb<sub>2</sub>O<sub>3</sub>, total 100.92%. Normalized to three oxygen atoms, the average composition is As<sub>1.088</sub>Sb<sub>0.912</sub>O<sub>3</sub>. Ideal AsSbO<sub>3</sub> contains 40.43% As<sub>2</sub>O<sub>3</sub> and 59.57% Sb<sub>2</sub>O<sub>3</sub>.

% As <sub>2</sub> O <sub>3</sub>	% Sb <sub>2</sub> O <sub>3</sub>	Total	Composition
45.66	55.03	100.69	As <sub>1.100</sub> Sb <sub>0.900</sub> O <sub>3</sub>
44.57	55.46	100.02	As <sub>1.084</sub> Sb <sub>0.916</sub> O <sub>3</sub>
44.82	56.39	101.22	As <sub>1.079</sub> Sb <sub>0.921</sub> O <sub>3</sub>
43.95	55.64	99.59	As <sub>1.076</sub> Sb <sub>0.924</sub> O <sub>3</sub>
44.30	56.13	100.43	As <sub>1.075</sub> Sb <sub>0.925</sub> O <sub>3</sub>
46.62	56.33	102.95	As <sub>1.099</sub> Sb <sub>0.901</sub> O <sub>3</sub>
44.54	56.77	101.31	As <sub>1.072</sub> Sb <sub>0.928</sub> O <sub>3</sub>
46.75	56.76	103.51	As <sub>1.097</sub> Sb <sub>0.903</sub> O <sub>3</sub>
45.50	53.16	98.67	As <sub>1.116</sub> Sb <sub>0.884</sub> O <sub>3</sub>
44.74	56.05	100.80	As <sub>1.081</sub> Sb <sub>0.919</sub> O <sub>3</sub>

scans showed only As, Sb and O, and no other elements with  $Z > 8$ . Standardized quantitative WDS analysis employed a Cameca SX-50 electron microprobe at the Lunar and Planetary Sciences Department, University of Arizona. Operating conditions were 15 kV and 30 nA with a beam diameter of 1.5  $\mu$ m. Enargite (As) and stibiotantalite (Sb) served as standards. Data reduction and correction followed the PAP method (Pouchou and Pichoir, 1984).

Table 1 lists the results of ten separate electron probe spot analyses. The average of these weight percent analyses with standard deviations is: 55.77(1.07)% Sb<sub>2</sub>O<sub>3</sub>, 45.15(0.95)% As<sub>2</sub>O<sub>3</sub>; total 100.92%. Normalized to three oxygen atoms, the average composition is As<sub>1.088</sub>Sb<sub>0.912</sub>O<sub>3</sub>. The composition remained homogenous over the sampled regions. In the solution of the crystal structure, use of the idealized formula AsSbO<sub>3</sub> produced a smaller residual error than the empirical electron probe formula (Origlieri *et al.*, 2009). The crystal structure analysis indicates that AsSbO<sub>3</sub> more accurately represents the chemistry of stibioclaudeite than the empirical electron microprobe chemistry given in Table 1. (Origlieri *et al.*, 2009).

#### X-RAY CRYSTALLOGRAPHY

We obtained single-crystal X-ray diffraction data using a Bruker X8 Apex diffractometer equipped with a 4K Apex II CCD detector. We used monochromatic MoK $\alpha$  radiation generated at 50 kV and 35 mA. A cleavage fragment of 30  $\times$  70  $\times$  220  $\mu$ m produced diffraction spots with streaking along constant  $2\theta$ . Despite the poor appearance of the data, the reflections yielded a merged  $R_{int}$  value of 3.08%. A data collection strategy resulted in the acquisition of 1863 frames in 6 scans, from which the Bruker software generated the calculated powder pattern given in Table 2. We used Bruker Saint 7.16b to fit the unit cell parameters from the positions of 6609 reflections collected to 82°  $2\theta$ , and Bruker Shelxtl 6.14 to determine the space group. Table 3 compares the unit cell parameters for stibioclaudeite and claudeite (Origlieri *et al.*, 2009) in Table 3.

#### RAMAN SPECTROSCOPY

Raman spectroscopy provides a nondestructive and rapid means to distinguish claudeite from stibioclaudeite. Samples compared include the stibioclaudeite fragment from our X-ray study; claudeite from Jachymov, Czech Republic (University of Arizona Mineral Museum 16128; RRUFF R050313); and leiteite from Tsumeb, Namibia (RRUFF R040011). We collected Raman spectra with a benchtop 100 mW Ar-ion laser centered at 514.532 nm and a Jobin

**Table 2. Calculated X-ray powder diffraction data for stibioclaudeite.**

<i>d</i>	<i>I/I</i> <sub>0</sub>	<i>h</i>	<i>k</i>	<i>l</i>
4.995	32	0	1	1
3.645	11	-1	0	1
3.512	100	-1	1	1
3.400	18	0	3	1
3.342	14	1	0	1
3.282	82	0	4	0
3.238	71	1	1	1
3.157	24	1	3	0
2.8048	39	0	4	1
2.8006	31	-1	3	1
2.7003	23	0	0	2
2.6559	28	1	3	1
2.645	24	0	1	2
2.279	34	2	0	0
2.2692	8	-1	2	2
2.2454	5	2	1	0
2.1401	5	-2	1	1
2.1304	9	-1	5	1
2.1188	8	1	2	2
2.0853	17	0	4	2
2.0646	13	1	5	1
1.8825	10	0	5	2
1.872	21	2	4	0
1.8223	8	-2	0	2
1.8096	6	-2	4	1
1.805	5	-2	1	2
1.7344	16	1	7	0
1.7305	7	2	4	1
1.727	5	-1	0	3
1.6649	7	0	3	3
1.6574	6	2	1	2
1.6263	7	1	0	3
1.6064	6	-1	3	3
1.5932	6	-2	4	2
1.5702	17	0	8	1
1.4876	7	-3	1	1
1.4572	7	1	4	3
1.3087	7	-2	8	1

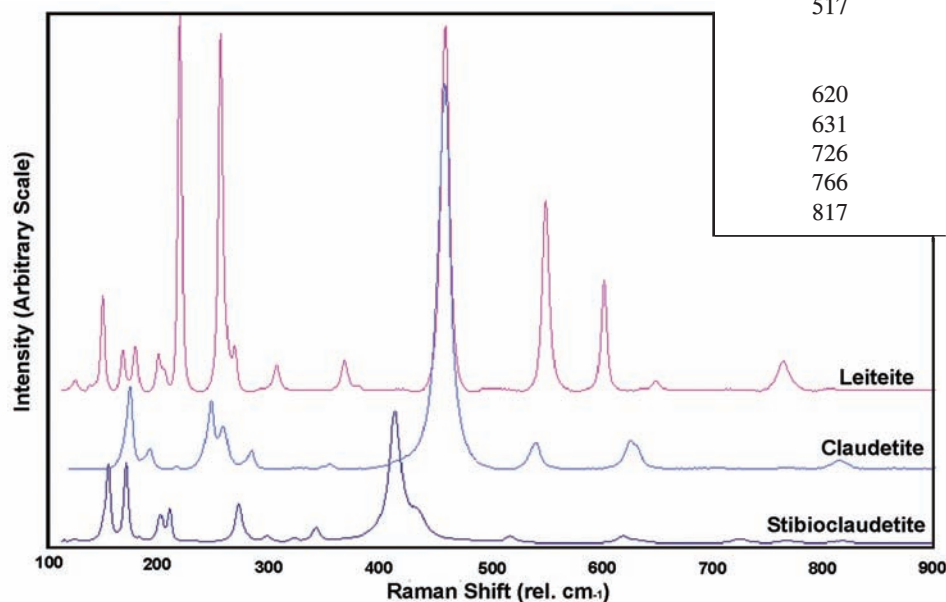
**Table 3. Comparison of the unit cells of claudeite and stibioclaudeite.**

	<i>Stibioclaudeite</i>	<i>Claudeite</i> *
idealized formula	AsSbO <sub>3</sub>	As <sub>2</sub> O <sub>3</sub>
space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>
a	4.5757(4) Å	4.5460(4) Å
b	13.1288(13) Å	13.0012(14) Å
c	5.4216(5) Å	5.3420(5) Å
β	95.039(4)°	94.329(2)°
V	324.44(5) Å <sup>3</sup>	314.83(5) Å <sup>3</sup>
Z	4	4
calculated density	5.009 g/cm <sup>3</sup>	4.174 g/cm <sup>3</sup>

\*Origlieri *et al.* (2009)

**Table 4. Principal Raman peak positions (shifted cm<sup>-1</sup>) of stibioclaudeite, claudeite, and leiteite.**

<i>Stibioclaudeite</i>	<i>Claudeite</i>	<i>Leiteite</i>
115		
125		125
		138
155		150
		168
171	175	179
183		
	193	201
202		205
210	218	220
	248	256
232	259	269
273	284	
298		307
	354	368
323	356	379
342		
414		
430		
468	459	459
477		
517		
	541	550
		603
620	626	649
631	632	
726		
766		764
817	814	806



**Figure 4. Comparison of Raman spectra of stibioclaudeite, claudeite, and leiteite. Table 4 lists the peak positions for these spectra.**

Yvon Spex HR 460 spectrometer equipped with a liquid nitrogen cooled Princeton Instruments 1152 × 256 pixel CCD detector. Using a 1200 grooves mm<sup>-1</sup> grating centered at 530.4 nm and Roper Instruments Winspec/32 software, we collected the shifted region from 113 to 1016 cm<sup>-1</sup>.

Figure 4 compares the Raman spectra of stibioclaudeite, claudeite and leiteite, all in unknown orientations. The stibioclaudeite spectrum shows 22 vibrational modes. Raman selection rules for the claudeite and stibioclaudeite structures allow for 15 A<sub>g</sub> modes and 15 B<sub>g</sub> modes, not all of which may be visible. Table 5 lists the principal Raman peak positions for stibioclaudeite, claudeite and leiteite. Additionally, Raman spectroscopy in the region between 3000–4000 rel cm<sup>-1</sup> showed no active Raman modes of greater significance than background, demonstrating that the mineral is nominally anhydrous.

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