STIBIOCLAUDETITE

$AsSbO_3$

A NEW MINERAL FROM TSUMEB, NAMIBIA

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Stibioclaudetite 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 stibioclaudetite instead.

ABSTRACT

Stibioclaudetite is a new mineral species with ideal chemistry $AsSbO_3$. The mineral has monoclinic symmetry, $P2_1/n$, with a = 4.5757(4) Å, b = 13.1288(13) Å, c = 5.4216(5) Å, β = 95.039(4)°, V = 324.44(5) Å^3, Z = 4, and d_{calc} = 5.009 g/cm^3. 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% As_2O_3 and 55.77% Sb_2O_3, total 100.92, corresponding to $As_{1.088}Sb_{0.912}O_3$. Stibioclaudetite 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; indices of refraction are >2.00. Stibioclaudetite occurs with leiteite, ludlockite, smithsonite and quartz in a vug within massive tennantite from the Tsumeb mine, Tsumeb, Namibia. Stibioclaudetite 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 AsO_3 and SbO_3 trigonal pyramids arranged in an ordered, alternating pattern. Raman spectra of stibioclaudetite, claudetite, and leiteite are presented and compared.

INTRODUCTION

Mineral dealer David W. Bunk obtained an unusual Tsumeb specimen containing a well-formed leiteite ($ZnAs_2O_4$) 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 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.*, 2009) and quantitative electron-probe microanalysis identified this phase as naturally occurring $AsSbO_3$. Bodenstein *et al.* (1983) studied synthetic $AsSbO_3$, which they demonstrated to be isostructural with claudetite (As_2O_3) (Pertlik, 1978). The crystal structure of this

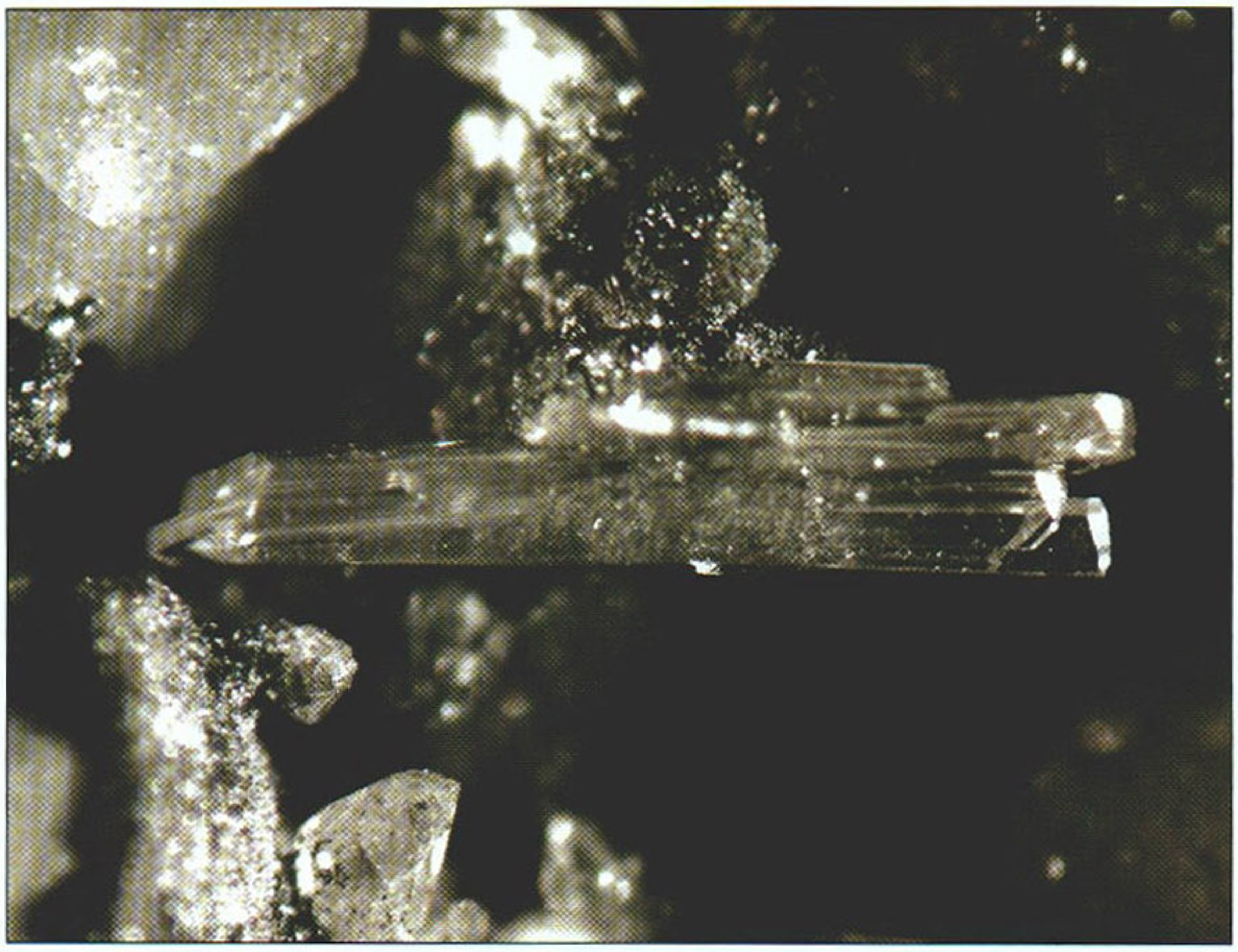

Figure 1. **The largest cluster of crystals of stibioclaudetite, 6 mm across, in a vug of massive tennantite with quartz crystals. This is the holotype specimen. D. W. Bunk specimen, now in the W. W. Pinch collection.**

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

new mineral consists of corrugated sheets of corner-sharing AsO_3 and 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, stibioclaudetite, denotes the structural relationship with claudetite, as an ordered Sb-substituted analog.

Strunz *et al.* (1958) first reported claudetite 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 Å, b = 13.0 Å, c = 4.56 Å, and $\beta \sim 94°$. He sublimated the mineral in a closed glass tube and condensed minute octahedral crystals. This microchemical behavior is consistent with the known behavior of claudetite, which condenses into octahedral crystals (i.e. arsenolite). However, these tests are not sufficient to distinguish claudetite from stibioclaudetite. Synthetic $AsSbO_3$ also has a cubic modification with the same crystal structure as cubic As_2O_3 (arsenolite) (Hayek *et al.*, 1963). Consequently, sublimation of either claudetite or stibioclaudetite would produce octahedral crystals. The unit cell reported by Strunz (1959) lacks the precision required to reliably distinguish stibioclaudetite from claudetite. Keller *et al.* (1979) reported another occurrence of claudetite from Tsumeb in association with warikhanite, unfortunately without specifying the identification method. The original identification of claudetite from Tsumeb could be in error; therefore Tsumeb specimens labeled "claudetite" warrant re-examination.

Hayek *et al.* (1963) showed that cubic As_2O_3 (arsenolite) and cubic Sb_2O_3 (senarmontite) are miscible, forming a complete solid solution series. Consequently, ordinary solid solution between arsenolite and senarmontite might yield cubic $AsSbO_3$ without structural ordering of As and Sb atoms. In that case, a cubic dimorph of stibioclaudetite 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 claudetite structure is apparently unique to the claudetite and stibioclaudetite structure (Origlieri *et al.*, 2009). A literature search failed to locate any report of monoclinic Sb_2O_3; however, an orthorhombic phase which bears the mineral name valentinite is well known.

Mineralogist Sidney A. Williams identified hexagonal $AsSbO_3$ among mine fire products from Nevada (Gibbs, 1985).

OCCURRENCE AND PARAGENESIS

The new mineral occurs within a cavity in a massive tennantite sample (4 × 5 × 7 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 stibioclaudetite to 6 mm. Figure 1 shows a photograph of the largest group of stibioclaudetite 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, stibnite, stibiconite and nadorite (Schneider, 1992), and biehlite (Schlüter *et al.*, 2000). Schneider (1992) quantifies the 1988 production of $NaSb(OH)_6$ at the Tsumeb smelter at 156 metric tons. Oxidation of host tennantite could readily supply both the arsenic and antimony sufficient to form stibioclaudetite. Moritz (1933) further notes a substantial zinc content in Tsumeb tennantite, which could supply both the zinc and arsenic required to form leiteite ($ZnAs_2O_4$).

Monoclinic As_2O_3 (claudetite) forms above 250° C, while cubic As_2O_3 (arsenolite) has a melting point near 275° C (Schulman and Schumb, 1943). Hayek *et al.* (1963) report a melting point of 315° C for claudetite. In other words, claudetite remains stable at higher temperatures than arsenolite. Bodenstein *et al.* (1983) synthesized their monoclinic $AsSbO_3$ at temperatures near 347° C. These data conservatively bracket the formation of stibioclaudetite between 300° C and 400° C.

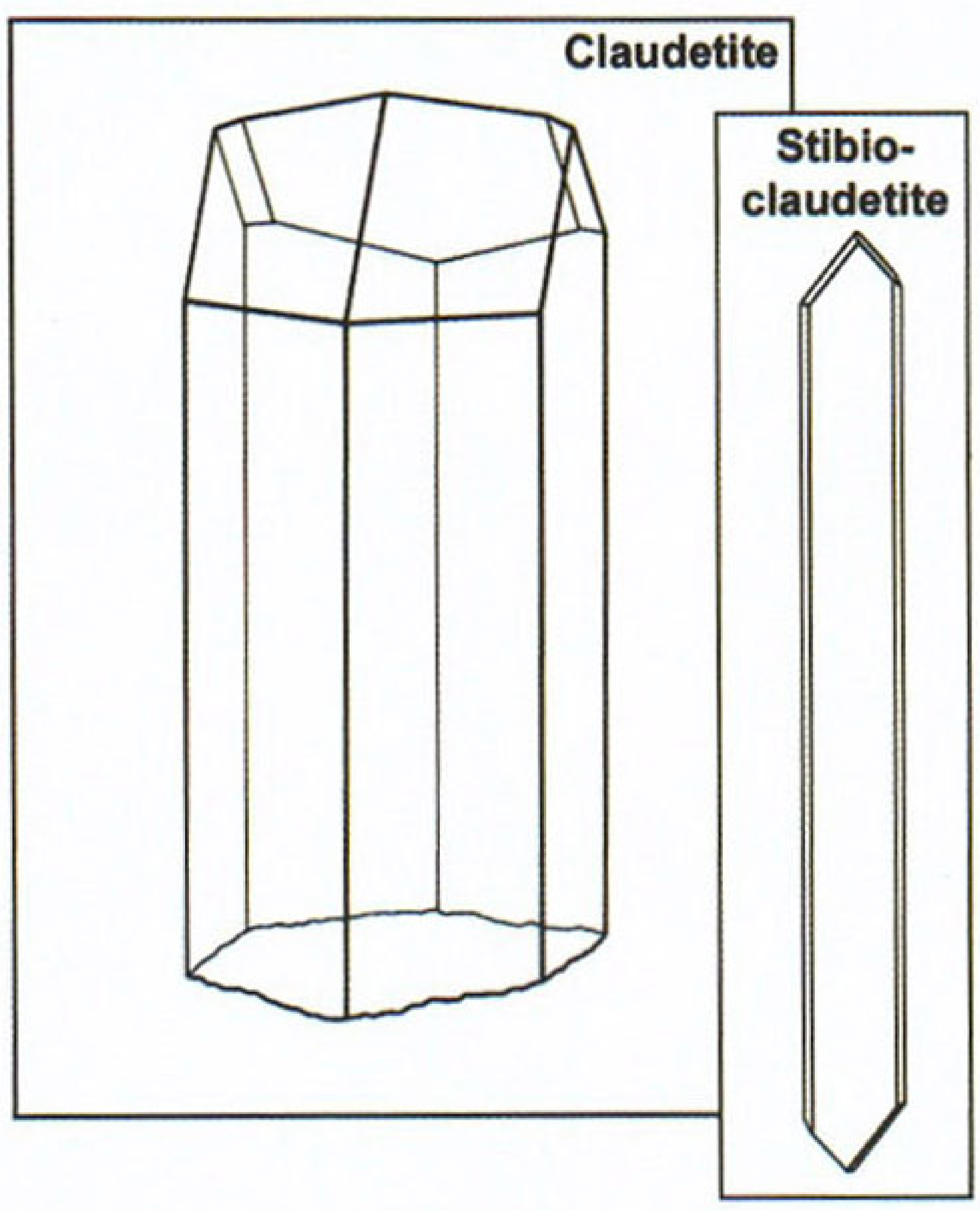

Figure 3. **Crystal morphology of stibioclaudetite, showing forms {010}, {110}, {111}, and {$\bar{1}$01}. At left is claudetite from Imperial County, California, as illustrated by Palache (1934).**

APPEARANCE AND PHYSICAL PROPERTIES

Stibioclaudetite forms bladed crystals to 6 mm bound by major {010}, major {110}, minor {111}, and very minor {$\bar{1}$01}. Stibioclaudetite 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 stibioclaudetite 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. Stibioclaudetite crystals mimic the morphology of claudetite from Imperial Valley, California as illustrated by Palache (1934), shown 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 stibioclaudetite attached to a glass disc. Qualitative WDS scans showed only As, Sb and O, and no other elements with $Z > 8$.

Table 1. **Electron probe microanalysis data for stibioclaudetite with corresponding atomic compositions normalized to three oxygen atoms. The average of these ten analyses, with standard deviations is 45.15(0.95)% As_2O_3, 55.77(1.07)% Sb_2O_3, total 100.92%. Normalized to three oxygen atoms, the average composition is $As_{1.088}Sb_{0.912}O_3$. Ideal $AsSbO_3$ contains 40.43% As_2O_3 and 59.57% Sb_2O_3.**

% As_2O_3	*% Sb_2O_3*	*Total*	*Composition*
45.66	55.03	100.69	$As_{1.100}Sb_{0.900}O_3$
44.57	55.46	100.02	$As_{1.084}Sb_{0.916}O_3$
44.82	56.39	101.22	$As_{1.079}Sb_{0.921}O_3$
43.95	55.64	99.59	$As_{1.076}Sb_{0.924}O_3$
44.30	56.13	100.43	$As_{1.075}Sb_{0.925}O_3$
46.62	56.33	102.95	$As_{1.099}Sb_{0.901}O_3$
44.54	56.77	101.31	$As_{1.072}Sb_{0.928}O_3$
46.75	56.76	103.51	$As_{1.097}Sb_{0.903}O_3$
45.50	53.16	98.67	$As_{1.116}Sb_{0.884}O_3$
44.74	56.05	100.80	$As_{1.081}Sb_{0.919}O_3$

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 µm. 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_2O_3, 45.15(0.95)% As_2O_3; total 100.92%. Normalized to three oxygen atoms, the average composition is $As_{1.088}Sb_{0.912}O_3$. The composition remained homogeneous over the sampled regions. In the solution of the crystal structure, use of the idealized formula $AsSbO_3$ produced a smaller residual error than the empirical electron probe formula (Origlieri *et al.*, 2009). The crystal structure analysis indicates that $AsSbO_3$ more accurately represents the chemistry of stibioclaudetite 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 MoKα radiation generated at 50 kV and 35 mA. A cleavage fragment of 30 × 70 × 220 µm produced diffraction spots with streaking along constant 2θ. 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° 2θ, and Bruker Shelxtl 6.14 to determine the space group. Table 3 compares the unit cell parameters for stibioclaudetite and claudetite (Origlieri *et al.*, 2009) in Table 3.

RAMAN SPECTROSCOPY

Raman spectroscopy provides a nondestructive and rapid means to distinguish claudetite from stibioclaudetite. Samples compared include the stibioclaudetite fragment from our X-ray study; claudetite 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 Yvon Spex HR 460 spectometer equipped with a liquid nitrogen cooled Princeton Instruments 1152 × 256 pixel CCD detector.

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

d	*I/I₀*	*h*	*k*	*l*
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
2.6450	24	0	1	2
2.2790	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
1.8720	21	2	4	0
1.8223	8	–2	0	2
1.8096	6	–2	4	1
1.8050	5	–2	1	2
1.7344	16	1	7	0
1.7305	7	2	4	1
1.7270	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 claudetite and stibioclaudetite.**

	Stibioclaudetite	*Claudetite**
idealized formula	$AsSbO_3$	As_2O_3
space group	$P2_1/n$	$P2_1/n$
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) Å³	314.83(5) Å³
Z	4	4
calculated density	5.009 g/cm³	4.174 g/cm³

*Origlieri *et al.* (2009)

Table 4. **Principal Raman peak positions (shifted cm⁻¹) of stibioclaudetite, claudetite, and leiteite.**

Stibioclaudetite	*Claudetite*	*Leiteite*
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

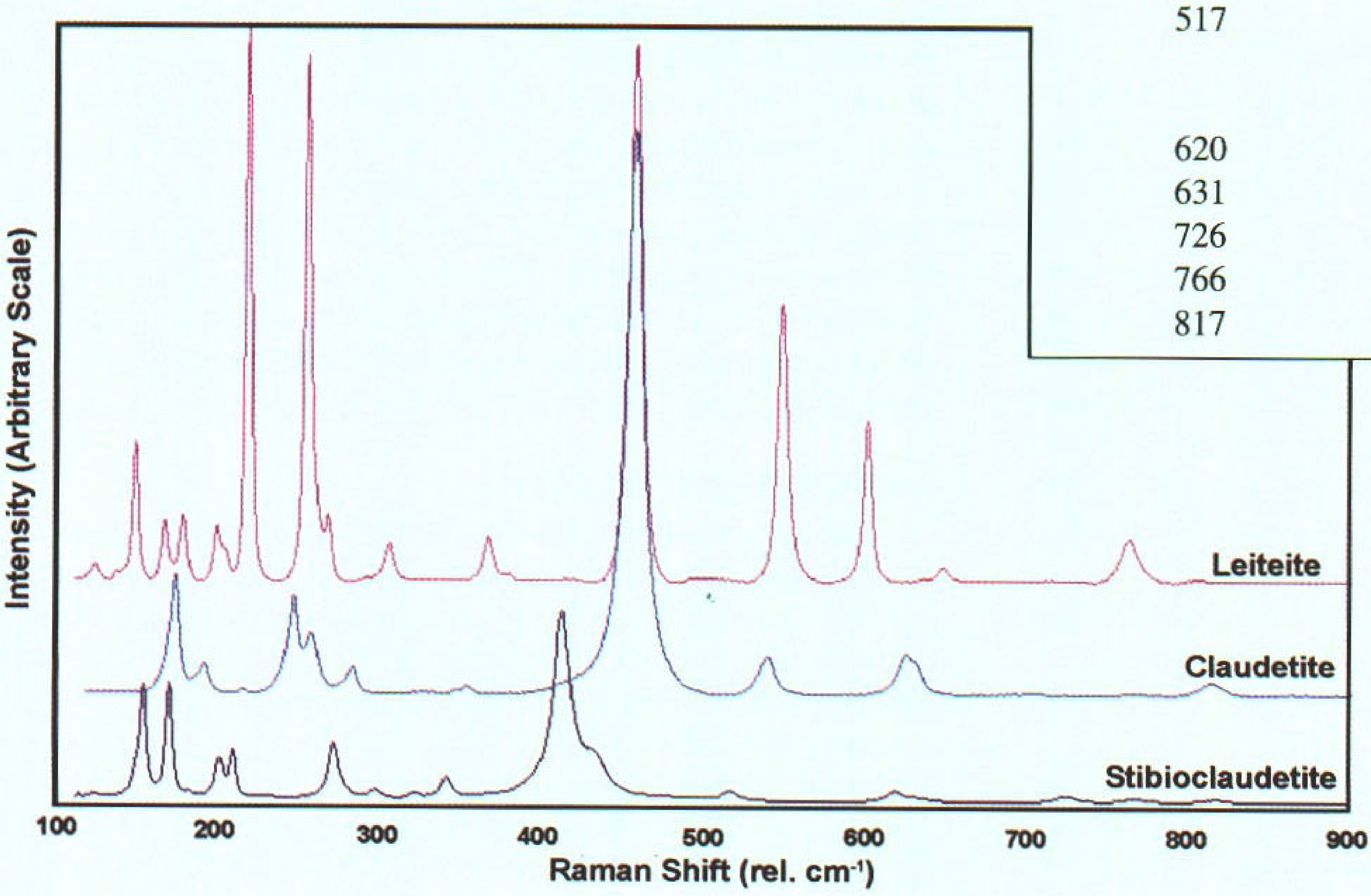

Figure 4. **Comparison of Raman spectra of stibioclaudetite, claudetite, and leiteite. Table 4 lists the peak positions for these spectra.**

Using a 1200 grooves mm^{-1} grating centered at 530.4 nm and Roper Instruments Winspec/32 software, we collected the shifted region from 113 to 1016 cm^{-1}.

Figure 4 compares the Raman spectra of stibioclaudetite, claudetite and leiteite, all in undetermined orientations. The stibioclaudetite spectrum shows 22 vibrational modes. Raman selection rules for the claudetite and stibioclaudetite structures allow for 15 A_g modes and 15 B_g modes, not all of which may be visible. Table 4 lists the principal Raman peak positions for stibioclaudetite, claudetite and leiteite. Additionally, Raman spectroscopy in the region between 3000–4000 rel cm^{-1} showed no active Raman modes of greater significance than background, demonstrating that the mineral is nominally anhydrous.

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