

SIDPIETERSITE, $\text{Pb}^{2+}_4(\text{S}^{6+}\text{O}_3\text{S}^{2-})\text{O}_2(\text{OH})_2$, A NEW THIOSULFATE-BEARING MINERAL SPECIES FROM TSUMEB, NAMIBIA

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ABSTRACT

Sidpietersite, ideally $\text{Pb}^{2+}_4(\text{S}^{6+}\text{O}_3\text{S}^{2-})\text{O}_2(\text{OH})_2$, is triclinic, $P\bar{1}$, with unit-cell parameters refined from powder data: a 7.447(4), b 6.502(4), c 11.206(4) Å, α 114.30(3), β 89.51(4), γ 89.04(6)°, V 494.4(5) Å³, $a:b:c$ 1.1453:1:1.7235, Z = 2. The strongest eight lines of the X-ray powder-diffraction pattern [d in Å(hkl)] are: 10.13(100)(001), 5.93(50)(010), 4.401(35)(011), 3.414(100)(003), 3.198(80)(022), 2.889(35)(023,211), 2.805(35)(211,014) and 2.622(40)(213). The mineral occurs on a single specimen collected from the 40th to 44th levels of the Tsumeb mine, Tsumeb, Namibia, as ill-formed, almost warty, nodular masses and crystal groups, as earthy masses and, rarely, as free-standing to radiating bladed-crystal aggregates. Masses, groups and aggregates never exceed 3 mm in longest dimension. It is the last mineral to form in an assemblage that includes smithsonite, zincite, galena, sphalerite, and very minor quartz and greenockite. Individual subhedral to almost euhedral crystals are bladed, elongate [011], with a length-to-width ratio of approximately 4:1 and not exceeding 0.2 to 0.3 mm in maximum length. Forms are {001} major, and possible very thin {100} and {011} minor. Cleavage is perpendicular to [011]. The mineral is opaque (masses) to transparent (crystals), beige-cream to off-white to colorless (crystals), with a cream to off-white streak, and a vitreous (crystals) to earthy (masses) to pearly luster. Sidpietersite is sectile, with an uneven fracture, and is nonfluorescent; H (VHN load 25 g) 57–67, H (Mohs) 1–2; D (calc.) 6.765 g/cm³ for the idealized formula. In polished section, sidpietersite is light grey in plane-polarized reflected light in air, with ubiquitous brilliant white to yellow-brown internal reflections; the phase is birefractant and perhaps slightly pleochroic. Averaged results of electron-microprobe analyses yield PbO 89.55, S⁶⁺O₃ 7.58, S²⁻ 3.035, H₂O [1.79], sum 101.955, less O = S²⁻ –1.51, total [100.45] wt.%. The empirical formula, derived from results of the crystal-structure analysis and electron-microprobe analyses, is $\text{Pb}^{2+}_{4.09}(\text{S}^{6+}_{0.97}\text{O}_{2.90}\text{S}^{2-}_{0.97})\text{O}_{2.09}(\text{OH})_{2.03}$, on the basis of O + S²⁻ = 8 and with (OH) = 2.00. The infrared-absorption spectrum shows bands for structural (OH) and thiosulfate. The mineral name honors Sidney Pieters, Windhoek, Namibia, for his outstanding contributions to Namibian mineralogy over the last fifty years.

Keywords: sidpietersite, new mineral species, lead hydroxide–oxide–thiosulfate, X-ray data, electron-microprobe data, infrared spectroscopy, Tsumeb mine, Tsumeb, Namibia.

SOMMAIRE

La sidpietersite, dont la formule idéale serait $\text{Pb}^{2+}_4(\text{S}^{6+}\text{O}_3\text{S}^{2-})\text{O}_2(\text{OH})_2$, est triclinique, $P\bar{1}$; elle possède les paramètres réticulaires suivants, affinées à partir d'un spectre obtenu sur poudre: a 7.447(4), b 6.502(4), c 11.206(4) Å, α 114.30(3), β 89.51(4), γ 89.04(6)°, V 494.4(5) Å³, $a:b:c$ 1.1453:1:1.7235, Z = 2. Les huit raies les plus intenses du spectre de diffraction X

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(méthode des poudres) [d en Å($D(hkl)$)] sont: 10.13(100)(001), 5.93(50)(010), 4.401(35)(011), 3.414(100)(003), 3.198(80)(022), 2.889(35)(023,211), 2.805(35)(211,014) et 2.622(40)(213). Le minéral a été découvert sur un seul échantillon prélevé entre le quarantième et le quarante-quatrième niveau de la mine de Tsumeb, en Namibie. Il se présente en masses mal formées, presque verruqueuses ou nodulaires, en groupes de cristaux et en masses terreuses, et, plus rarement, en agrégats de cristaux lamellaires isolés ou radiés. Les masses, groupes et agrégats ne dépassent pas 3 mm en longueur maximale. Il s'agit du dernier minéral à s'être formé d'un assemblage qui comprend smithsonite, zincite, galène, et sphalérite, avec quartz et greenockite accessoires. Les cristaux individuels sont sub-idiomorphes à presque idiomorphes, lamellaires, allongés sur [011], avec un rapport longueur à largeur d'environ 4:1 et ne dépassant pas 0.2 à 0.3 mm en longueur maximale. Les formes observées sont {001} majeure, possiblement {100} très mince, et {011} mineure. Le clivage est perpendiculaire à [011]. Le minéral est opaque (masses) à transparent (cristaux), beige-crème à blanchâtre à incolore (cristaux), avec une rayure crème à blanchâtre et un éclat vitreux (cristaux) ou terreux (masses) à nacré. La sidpietersite est sectile, avec une fracture inégale, et non fluorescente; sa dureté (VHN mesuré avec une masse de 25 g) va de 57 à 67, et la dureté sur l'échelle de Mohs est de 1 à 2. La densité calculée est 6.765 g/cm³ selon la formule idéale. En lame polie, la sidpietersite est gris pâle en lumière polarisée dans l'air, avec des réflexions internes brillantes ubiquistes blanches à jaune brunâtre. Elle pourrait être légèrement pléochroïque. Une moyenne des résultats d'analyses obtenues avec une microsonde électronique donne PbO 89.55, S⁶⁺O₃ 7.58, S²⁻ 3.035, H₂O [1.79], total 101.955, moins O = S²⁻ -1.51, égal à 100.45% en poids. La formule empirique, dérivée des résultats d'une ébauche de la structure cristalline et d'analyses par microsonde électronique, serait Pb²⁺_{4.09} (S⁶⁺_{0.97}O_{2.90}S²⁻_{0.97}) O_{2.09}(OH)_{2.03}, sur une base de O + S²⁻ = 8 et (OH) = 2.00. Le spectre d'absorption infra-rouge contient des bandes typiques du groupe (OH) et du thiosulfate dans la structure. Le nom honore Sidney Pieters, de Windhoek, en Namibie, et signale ses contributions extraordinaires à la minéralogie de la Namibie au cours des cinquante dernières années.

(Traduit par la Rédaction)

Mots-clés: sidpietersite, nouvelle espèce minérale, thiosulfate et oxyde de plomb hydroxylé, données de diffraction X, données de microsonde électronique, spectroscopie infra-rouge, mine de Tsumeb, Namibie.

INTRODUCTION

The Tsumeb mine, Tsumeb, Namibia (lat. 19°S, long. 18°E) has been a prolific source of new mineral species. Here we describe yet another new phase, sidpietersite, from this classic mineral locality. Megascopically identified as a potentially new species by one of us (C.L.K.), the nondescript phase occurs on and is associated with pale pink to colorless crystals of smithsonite; this sample had been acquired from a local miner in 1991. This particular specimen was deemed unusual and worthy of further study for two reasons: (1) the smithsonite crystals are coated with an unidentified (at that time) opaque tan-colored crust, and (2) the smithsonite crystals grew on a crystalline galena-sphalerite matrix. The combination of smithsonite with a sulfide-bearing matrix at Tsumeb is, historically, a strong indicator that additional rare and unusual phases may be in close association. This particular specimen was one of countless samples of smithsonite collected in the early 90s from the 40th to 44th levels of the Tsumeb mine. Subsequent X-ray powder diffraction, coupled with scanning electron microscopy (SEM) and energy-dispersion analyses, proved that this nondescript phase is indeed new to science.

The mineral is named *sidpietersite* in honor of Sidney ("Sid") Pieters (b. 1920) of Windhoek, Namibia, for his outstanding contributions to Namibian mineralogy. Mister Pieters has been prospecting, mining, collecting, cutting, buying and selling the fabulous mineral treasures from this area for more than half a century, and a particularly fine tribute to him has been written by Key (1977). The mineral and mineral name have

been approved by the Commission on New Minerals and Mineral Names, IMA. Holotype material is housed in the Systematic Reference Series of the National Mineral Collection at the Geological Survey of Canada, Ottawa, Ontario, under catalogue number NMC 68076. The polished section used for the attempted reflectance study and for the Vickers microhardness determinations is preserved at The Natural History Museum, Great Britain, as BM1998, 36.

OCCURRENCE AND ASSOCIATED MINERALS

Sidpietersite was identified on a single sample that has been split for scientific study; the new mineral is rare, and we estimate that only 1–2 milligrams of pure sidpietersite are currently available. The matrix of the original piece consists of a mixture of fine-grained galena and sphalerite. Perched on the matrix, and by far the most visually striking mineral in the assemblage, are pale pink to colorless crystals of smithsonite, 7–8 mm in size, that have been partly coated by an opaque tan-colored crust of zincite. Minor greenockite and quartz also are present on and in the matrix. Sidpietersite is considered to be secondary after galena; masses have been observed both on the galena-sphalerite matrix and on the zincite-coated crystals of smithsonite, and it is obviously the last mineral to form in this environment. We postulate that thiosulfate formation occurred during an intermediate stage of oxidation as the assemblage moved toward complete oxidation and subsequent formation of sulfate after initial deposition of the sulfide. Sidpietersite is the first confirmed thiosulfate-bearing mineral known to occur at the Tsumeb deposit.

PHYSICAL PROPERTIES

Sidpietersite occurs as ill-formed, almost warty, nodular masses and crystal groups, as earthy masses and, rarely, as free-standing to radiating aggregates of bladed crystals (Figs. 1A, B). Masses, groups and aggregates never exceed 3 mm in maximum dimension, and most are typically much smaller. Individual bladed subhedral to euhedral crystals do not exceed 0.2 to 0.3 mm in maximum length, are elongate along $[01\bar{1}]$, and have a length-to-width ratio of approximately 4:1. Some crystals are platy on $\{001\}$. Cleavage is perpendicular to the elongation direction $[01\bar{1}]$. These crystals are too small to determine crystal forms by optical goniometry; single-crystal precession studies indicate that the dominant form is $\{001\}$, and other possible minor forms are $\{100\}$ and $\{01\bar{1}\}$. Twinning was not observed megascopically nor in X-ray single-crystal studies. The color of the mineral varies from beige-cream to off-white to colorless, depending on the nature of the material. Crystals

are colorless, and the streak is cream-colored to off-white. The luster varies from vitreous (for crystals) to earthy (for masses) to somewhat pearly. Crystals are transparent, whereas masses are opaque. Sidpietersite is sectile, with an uneven fracture, and is nonfluorescent under both long- and short-wave ultraviolet radiation. The density could not be measured because of the small size of available crystals and dearth of material. The calculated density, on the basis of the idealized formula and unit-cell parameters derived from an investigation of the crystal structure (Cooper & Hawthorne 1999), is 6.765 g/cm^3 . The mineral is very soft; crystals have an estimated Mohs hardness of 2 or less. Three Vickers microhardness indentations (25 g load) gave a range of 57–67 on composite grains used for the attempted study of reflectance; this translates to a Mohs hardness range of 1–2. These measurable indentations were perfect in shape and only slightly fractured. In dilute HCl, there is only an initial effervescence, after which the material turns to a chalky white color over a few minutes.

X-RAY CRYSTALLOGRAPHY

Preliminary single-crystal precession photos of a crystal of sidpietersite showed that the symmetry is triclinic with space-group choices $P1$ or $P\bar{1}$. The crystal-

TABLE 1. X-RAY POWDER-DIFFRACTION DATA FOR SIDPIETERSITE

I_{est}	$d\text{\AA}_{(\text{meas})}$	$d\text{\AA}_{(\text{calc})}$	hkl		I_{est}	$d\text{\AA}_{(\text{meas})}$	$d\text{\AA}_{(\text{calc})}$	hkl
100	10.13	10.212	001					$\bar{2}13$
30	6.39	6.393	01 $\bar{1}$		10	2.062	2.074	014
50	5.93	5.924	010	*	3	1.915	1.914	222
30	5.02	5.023	01 $\bar{2}$	*	10	1.886	1.886	23 $\bar{2}$
5	4.81	4.818	1 $\bar{1}$ 1		20	1.856	1.861	400
* 35	4.401	4.398	011				1.858	23 $\bar{2}$
5	4.171	4.160	1 $\bar{1}$ 2				1.838	026
* 20	3.681	3.677	013	3	1.836	1.837	401	
* 20	3.513	3.517	201	*	10	1.816	1.817	214
* 100	3.414	3.404	003	* 15	1.784	1.784	$\bar{2}14$	
3	3.270	3.260	012	* 5	1.723	1.724	015	
* 80	3.198	3.196	02 $\bar{2}$	* 10	1.702	1.702	006	
* 30	3.118	3.121	$\bar{2}10$			1.674	036	
		2.994	21 $\bar{2}$	10b	1.665	1.665	$\bar{2}16$	
30b	2.976	2.962	020			1.661	235	
		2.904	02 $\bar{3}$			1.654	$\bar{2}35$	
35	2.889	2.875	211			1.649	216	
		2.809	$\bar{2}11$	10	1.648	1.645	226	
35	2.805	2.801	014			1.645	403	
		2.622	$\bar{2}13$			1.639	231	
* 40	2.622	2.622	$\bar{2}13$	*	3	1.630	1.630	024
* 20	2.580	2.575	021	* 3	1.618	1.618	42 $\bar{2}$	
* 20	2.557	2.553	004	*	3	1.618	1.611	04 $\bar{2}$
3	2.465	2.459	22 $\bar{1}$		3	1.606	1.610	$\bar{2}31$
1	2.401	2.409	22 $\bar{2}$				1.599	42 $\bar{2}$
* 5	2.343	2.343	220	3	1.592	1.598	044	
		2.298	22 $\bar{3}$				1.575	017
15b	2.295	2.293	$\bar{2}20$	* 5	1.575	1.575	1.562	423
		2.281	$\bar{2}23$				1.560	$\bar{2}20$
3	2.230	2.235	015				1.560	041
* 20	2.143	2.144	025	5	1.557	1.557	1.556	$\bar{2}14$
* 20	2.123	2.122	204				1.556	
5	2.092	2.089	$\bar{2}04$					

114.6 mm Debye-Scherrer powder camera employing Ni-filtered Cu radiation ($\lambda \text{ CuK}\alpha = 1.54178 \text{ \AA}$). Intensities estimated visually; b = broad line. Not corrected for shrinkage and no internal standard used; * = lines used for unit-cell refinement. Indexed on a 7.447(4), b 6.502(4), c 11.206(4) $\text{\AA}$, α 114.30(3), β 89.51(4), γ 89.04(6)°.

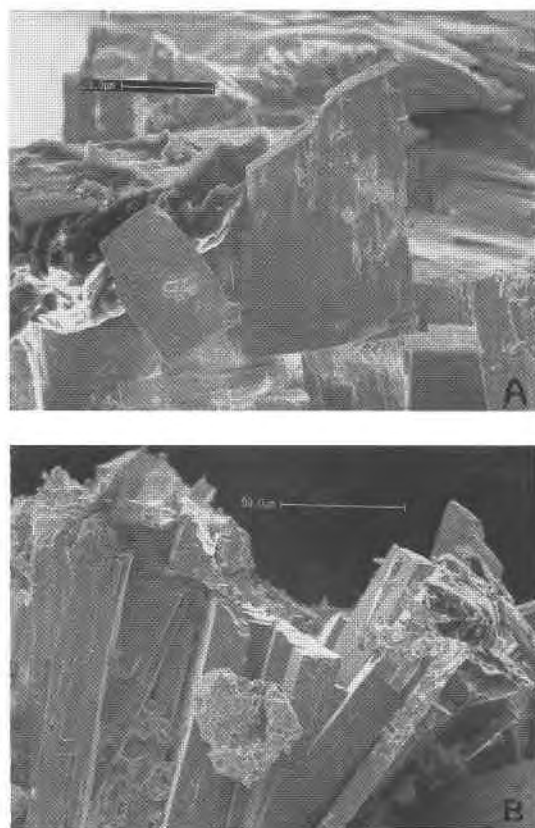


FIG. 1. A. SEM photomicrograph of a free-standing crystal of sidpietersite. Scale bar: 20 μm . B. SEM photomicrograph of an aggregate of sidpietersite crystals. Scale bar: 50 μm .

structure determination (Cooper & Hawthorne 1999) indicated that $P\bar{1}$ is the correct space-group. The unit-cell parameters, given below, are for the same orientation as in the structural study.

Unit-cell parameters, a 7.447(4), b 6.502(4), c 11.206(4) Å, α 114.30(3), β 89.51(4), γ 89.04(6)°, V 494.4(5) Å³, $a:b:c$ 1.1453:1:1.7235, and $Z = 2$, were refined from 22 powder reflections representing d values between 4.401 and 1.575 Å for which unambiguous indexing was possible on the basis of the calculated intensities derived from the crystal structure. A fully indexed powder pattern is presented in Table 1. The powder data are not similar to any other inorganic phase listed in the Powder Diffraction File. Sidpietersite is the second confirmed thiosulfate found in nature, the first being bazhenovite (Chesnokov *et al.* 1987).

CHEMISTRY

Sidpietersite crystals were analyzed with a Cameca SX-50 electron microprobe, utilizing an operating voltage of 15 kV, a beam current of 20 nA, and a beam 5 µm in diameter. Natural galena was used as a standard for both Pb and S. An energy-dispersion scan indicated

the absence of any other elements with atomic number greater than 9 except those reported here. Ca and Cl were sought, but are below detection limits. Data were corrected using the PAP procedure of Pouchou & Pichoir (1984, 1985). The valence states for both Pb and S, as well as the number of O atoms, were determined by crystal-structure analysis (Cooper & Hawthorne 1999) prior to final interpretation of the electron-microprobe results. The paucity of pure material prevented quantitative determination of H₂O. However, the presence of H as (OH) was confirmed both by crystal-structure analysis and powder infrared-absorption study; the formula was therefore calculated to give 2(OH). The average of five determinations (and standard deviations) gave Pb 83.13(1.12) and S 6.07(0.10) wt. %. After converting Pb to PbO, partitioning S to S⁶⁺ and S²⁻ in a 1:1 ratio, converting S⁶⁺ to S⁶⁺O₃, and calculating H₂O to give 2(OH), the analyses gave: Pb 89.55, S⁶⁺O₃ 7.58, S²⁻ 3.035, H₂O [1.79], sum 101.955, less O = S²⁻ -1.51, total [100.45] wt. %. With O + S²⁻ = 8, the empirical formula for this lead hydroxide-oxide-thiosulfate is Pb²⁺_{4.09}(S⁶⁺_{0.97}O_{2.90}S²⁻_{0.97})O_{2.09}(OH)_{2.03}. The ideal formula, Pb²⁺₄(S⁶⁺O₃S²⁻)O₂(OH)₂, requires PbO 88.66, S⁶⁺O₃ 7.95, S²⁻ 3.18, H₂O 1.79, sum 101.58, less O =

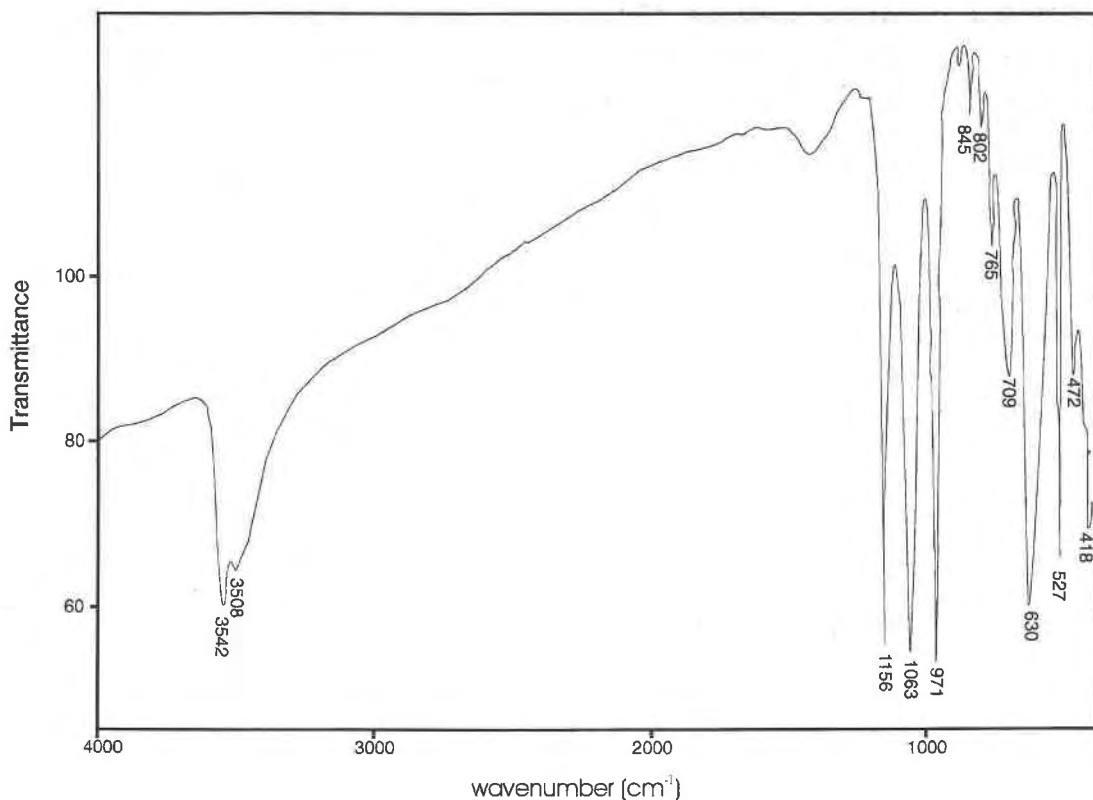


FIG. 2. Infrared-absorption spectrum for sidpietersite.

S^{2-} –1.58, total 100.00 wt. %. Further details regarding the thiosulfate topology are addressed in the companion crystal-structure paper (Cooper & Hawthorne 1999). It is, however, without doubt that this new mineral would have been described as a sulfate and not a thiosulfate if not for the structural and infrared-absorption results; this is another example of the use of crystal-structure analysis to determine the exact chemical formula of a complex mineral species (*cf.* Hawthorne & Grice 1990).

INFRARED SPECTROSCOPY

The procedures for acquiring the infrared-absorption spectrum for sidpietersite are identical to those used to obtain the spectrum of mcalpineite (Roberts *et al.* 1994) and are not repeated here. The sample was analyzed using a Bomem Michelson MB-100 FTIR spectrometer equipped with a wide-band mercury-cadmium telluride detector. The transmittance spectrum (Fig. 2) shows a medium strong, somewhat broad and asymmetric band that has peaks at 3508 and 3542 cm^{-1} attributable to O–H stretching in the hydroxyl groups. Characteristic bands for thiosulfate are strong to medium strong, sharp, and are centered at 1156, 1063, 971, 709, 630 and 527 cm^{-1} .

OPTICAL PROPERTIES

In polished section, the mineral forms compact clusters of elongate crystals (aspect ratio 1:8 to 1:12), the largest individuals of which are about $5 \times 40 \mu\text{m}$ in plane section. The cluster polished for optical study is $0.2 \times 0.4 \text{ mm}$. Its specular reflectance (low, about 12–14% and n about 2) is almost entirely “swamped” by brilliant white internal reflections. Its surface reflectance is light grey. Also present, where the cluster of crystals is thickest, are yellow-brown internal reflections. It is impossible, because of the internal reflections, to obtain reliable reflectance data with the crystals available. Measurements were made in air and in oil as a matter of routine but, as expected, there were substantial discrepancies between the refringences in the two media. This proved that a substantial component of diffuse reflectance was contributing to the measurements, and that this component was greater for the immersed specimen. Because of the above, we have chosen not to publish

the erroneous reflectance data. The mineral is bireflectant and perhaps slightly pleochroic (uncertainty due to the possible directional contribution from internal reflections).

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