Leiteite: a new mineral from Tsumeb

by

Fabien P. Cesbron*, Richard C. Erd, Gerald K. Czamanski**, and Hélène Vachey***

***Laboratoire de Mineralogie-Cristallographie associe au CNRS, Université P. et M. Curie, 75230 Paris Cédex 05 France**

****U.S. Geological Survey, 345 Middlefield Road, Menlo Park, California 94025**

ABSTRACT

Leiteite ("lā'-tīt") is a new zinc arsenite found associated with tennantite, chalcocite, smithsonite, and schneiderhöhnite at Tsumeb (Southwest Africa). It occurs as cleavable masses to 7 cm in greatest dimension, colorless to brown and transparent; the Mohs hardness is 1½ - 2 and the observed density is 4.3(1). The cleavage lamellae on {100} are flexible but inelastic and have a pearly luster. Leiteite is optically biaxial positive with $\alpha = 1.87(1)$, $\beta = 1.880(5)$, $\gamma = 1.98(1)$, and $2V = 26\frac{1}{2}(1)°$; $X \wedge a = 11°$, $Y = b$, $Z \wedge c = +10°$; $r < v$, very strong. X-ray diffraction shows space group $P2_1/a$ with $a = 17.645(5)$Å, $b = 5.019(2)$, $c = 4.547(2)$, and $\beta = 90°\ 59(4)'$. The most intense powder diffraction lines (in Å) are **3.133** (100) (211), **3.163** (76) ($\bar{2}11$), **1.685** (49) (911), **3.320** (39) ($\bar{1}11$), **3.302** (32) (111), **4.833** (31) (110), but strong preferred orientation due to perfect cleavage can change this order. Wet chemical analysis yields the formula $(\mathbf{Zn_{0.98}Fe_{0.02}})\mathbf{As_2O_4}$ with four formula units in the cell. The name is for Luis Teixeira-Leite, mineralogist, of Pretoria, Republic of South Africa.

INTRODUCTION

The new mineral leiteite was discovered some years ago by Luis Teixeira-Leite among specimens from Tsumeb (Southwest Africa); unfortunately it is impossible to determine from the miners the exact location in this deposit from which the specimens were obtained. The leiteite was found as a single specimen, 7 x 4 x 0.3 cm, which was subsequently divided into several pieces for mineralogical studies and museum specimens (one of these is shown as figure 1). Parts of the original specimen have been deposited in the Smithsonian Institution (National Museum of Natural History), Washington, D.C., in the British Museum (Natural History), London, and in the Mineralogical Collection of the P. and M. Curie University, Paris. Leiteite (pronounced "lā' tīt") is named in honor of its discoverer.

The name and species have been approved by the Commission on New Minerals and Mineral Names, I.M.A.

OCCURRENCE

Leiteite occurs as colorless to brown cleavable masses; one of the larger fragments of the single known specimen is shown as Figure 1. Although the study of leiteite did not begin until after it had been brought from the mine and broken into several pieces, we can make some fairly good guesses as to its location in the mine and its paragenesis based on the minerals associated with it. Almost all of the fragments we examined were leiteite only, but on one piece we found platelets of leiteite with smithsonite on a matrix of tennantite. Most fortunately, at a later date, Peter Embrey sent us a description of the leiteite specimen in the Mineralogical Collection of the British Museum (Natural history) "Specimen B.M. 1976,235. Several bruised and cleaved crystals 4 to 10 mm across, near 6 mm and smaller cleaved black grains of schneiderhöhnite on a matrix of mixed sulfides, mainly chalcocite. No morphology is observable." Schneiderhöhnite, $8(Fe_{0.96}Zn_{0.03}Ge_{0.01})O{\cdot}5As_2O_3$, is a rare arsenite known so far only from a single occurrence in the Tsumeb mine (Otteman *et al.*, 1973). It was discovered here a few metres below the 29 level (908 m) in a small druse in the dolomite-chert breccia near its contact with pseudo-aplite in the "deep oxidation zone." The schneiderhöhnite was associated with chalcocite and zincian stottite with traces of relict pyrite, tennantite, and galena as accessory minerals. According to Otteman *et al.* (1973) schneiderhöhnite is a secondary mineral which probably formed at a temperature of 40°C. Thus, while the schneiderhöhnite found on the leiteite specimen in the British Museum may be a second occurrence of the mineral at Tsumeb, it seems likely that it came from the vicinity of the original discovery and that leiteite formed under the same conditions. It is worth noting that the zinc orthoarsenite, reinerite, $3ZnO{\cdot}As_2O_3$, was found in cavities about 10 metres below the 29 level associated with bornite and chalcocite (Geier and Weber, 1958).

PHYSICAL AND OPTICAL PROPERTIES

Leiteite exhibits no crystal forms, but a perfect {100} cleavage was observed. The cleavage lamellae are flexible, inelastic, and somewhat sectile. The mineral has hardness between 1½ and 2 (Mohs). Density, measured with a pycnometer on an uncrushed 500 mg sample, was 4.3(1); the value is slightly low due to air entrapped between cleavage surfaces.

Leiteite is colorless to pale brown and transparent, with a pearly luster on the cleavage. Optically it is biaxial positive. Accurate determination of indices of refraction with high immersion media is difficult as the mineral is slowly attacked by these liquids. Leiteite is nonfluorescent. Optical data and orientation are given in table 1 and figure 2.

X-RAY DIFFRACTION STUDY

A small cleavage fragment, carefully squeezed between two glass slides to flatten it, was examined by precession techniques using MoK α ($\lambda = 0.7107$ Å) radiation. Leiteite is monoclinic, pseudo-orthorhombic, and systematic absences show the space group to be $P2_1/a$.

Unit cell parameters, after least-squares refinement of the powder diffraction data, are $a = 17.645(5)$ Å, $b = 5.019(2)$, $c = 4..547(2)$, and $\beta = 90°\ 59(4)'$. The calculated density with $4[(Zn_{0.98}Fe_{0.02})As_2O_4]$ is 4.61 g/cc.

A powder diffraction pattern was obtained using a Nonius Guinier camera and quartz as the internal standard. Relative intensities were obtained by measuring the film with a Joyce microdensitometer. X-ray powder data for leiteite are given in table 2. Because of its perfect {100} cleavage, diffractometer traces of leiteite show strong preferred orientation; the diffractometer intensities (I_D) are compared in table 2 with those measured from the Guinier film (I_G).

CHEMICAL COMPOSITION

Leiteite was analyzed by two different methods. **(1)** Samples were analyzed with an ARL EMX-SM electron microprobe using an accelerating voltage of 15 KV and a specimen current

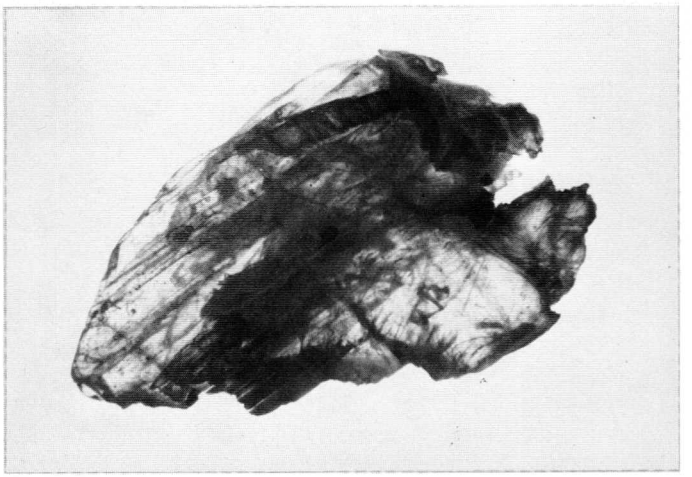
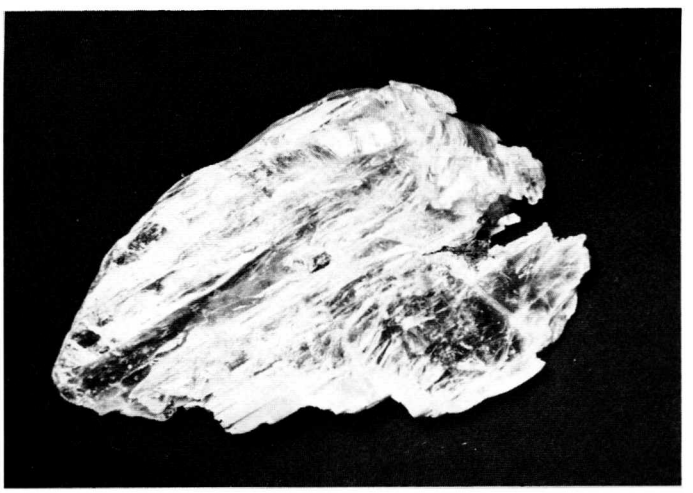


Figure 1. **Leiteite fragment in *(above)* transmitted and *(below)* reflected light. The fragment is 22 mm long.**

Figure 2. (right) **Edge view of plate showing optical orientation for leiteite.**



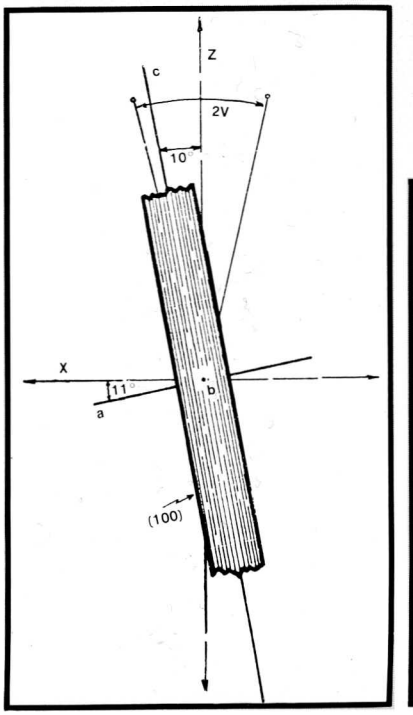


Table 1.
Optical properties of leiteite.

α	= 1.87(1)
β	= 1.880(5)
γ	= 1.98(1)
(+)2V	= 26½(1)°
X ∧ a	= +11°
Z ∧ c	= +10°
Y	= b

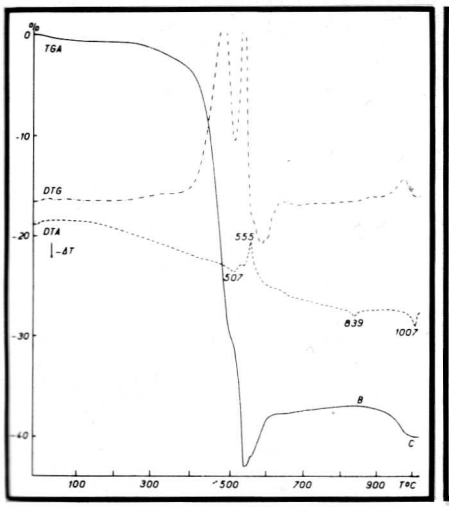
$r < v$, very strong
optic axial plane {010}
Indices determined in both sodium light and white light.

of 2 x 10^{-8} amperes on benitoite. The Kα lines of both As and Zn were analyzed using LiF crystals. (The Lα line of As, though exhibiting a better peak-to-background ratio as analyzed by an ADP crystal, encounters heavy absorption by Zn that is apparently overestimated by Heinrich (1966), and consequently overcompensated by FRAME, the theoretical data reduction program utilized.) Recrystallized reagent grade As_2O_3 and ZnO were used as standards. Because As_2O_3 is noticeably affected by even a defocussed beam, counts were taken on it with a beam 10 microns in diameter, whereas the fine-grained ZnO standard and micaceous plates of leiteite required a well-focussed beam. Two independent analyses of the new mineral were made, each relying on 10 counts of 10 seconds each for both the standards and the mineral. Count termination was made in the fixed beam current mode to compensate for possible fluctuation in beam energy. Count data were corrected by the computer reduction scheme, FRAME, of the U.S. National Bureau of Standards (Yakowitz *et al.*, 1973). Assigned error limits represent one standard deviation as determined from counting data on the new mineral. **(2)** Samples were also analyzed by wet chemical analysis. Arsenic, after oxidation with HNO_3, was determined by the molybdenum blue colorimetric method. Both zinc and iron were determined by atomic absorption spectrophotometry. Leiteite dissolves slowly in cold

Table 2. Indexed powder pattern for leiteite (CuKα_1 radiation, λ = 1.5405981 Å).

hkl	$d_{calc.}$(Å)	$d_{obs.}$(Å)	$I_{(G)}$	$I_{(D)}$
200	8.818	8.808	--	32
110	4.828	4.833	31	6
400	4.409	4.405	4	100
011	3.369	3.369	4	--
$\bar{1}11$	3.318	3.320	39	--
111	3.302	3.302	32	6
$\bar{2}11$	3.162	3.163	76	18
211	3.135	3.133	100	21
600	2.941	2.940	26	400
$\bar{3}11$	2.940	--	--	--
311	2.908	2.908	10	--
510	2.887	2.884	--	19
$\bar{4}11$	2.695	2.694	8	2
411	2.661	2.660	3	1
020	2.510	2.510	19	1
$\bar{5}11$	2.452	2.452	3	2
220	2.414	2.414	19	3
002	2.273	2.273	18	1
$\bar{2}02$	2.210	2.211	9	--
202	2.192	2.193	17	3
420	2.181	2.180	26	5
112	2.053	2.053	7	--
321	2.053	--	--	--
$\bar{4}02$	2.035	2.034	14	2
402	2.007	2.006	10	2
811	1.856	1.856	2	7
811	1.835	1.835	2	8
10·0·0	1.764	1.761	--	22
911	1.685	1.685	49	3
022	1.685	--	--	--
130	1.666	1.665	7	--
10·1·0	1.666	—	—	
$\bar{1}31$	1.565	1.565	6	2
$\bar{2}31$	1.547	1.547	18broad	--

I(G). Intensity measured from Guinier film.
I(D). Intensity measured from diffractometer trace.



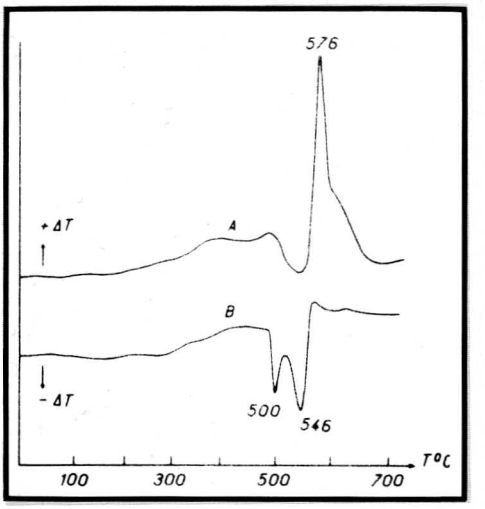


Figure 3. (far left) **Thermogravimetric (TGA), differential thermogravimetric (DTG), and differential thermo-analysis (DTA) curves for leiteite.**

Figure 4. (left) **DTA curves for leiteite in normal atmosphere ("A") and in nitrogen ("B").**

Table 3. Chemical analyses of leiteite.

Microprobe

	Analysis 1	Analysis 2	Calculated Composition for $ZnAs_2O_4$
Zn	23.6 ± 0.4 %	23.6 ± 0.3 %	23.41 %
As	53.7 ± 1.1	53.4 ± 1.7	53.84
O	—	—	22.75

Wet Methods

	Analysis	Molecular Ratios			Calculated Composition for $ZnAs_2O_4$
ZnO	28.5 %	0.3503	0.971	0.99	29.14
FeO	0.5	0.007	0.019		
As_2O_3	71.4	0.3609	1		70.86
Total	100.4				100.00

1:1 HCl. Analytical data are presented in table 3. The wet chemical analysis yields the formula $(Zn,Fe)O \cdot As_2O_3$ or $(Zn,Fe)As_2O_4$, with Zn:Fe = 98:2.

Leiteite is a zinc metaarsenite; the compound was first synthesized by Avery (1906) and has some industrial importance as a wood preservative. Chemically it can be related to trippkeite, $CuAs_2O_4$, but trippkeite is tetragonal (Zemann, 1951). As noted above, zinc orthoarsenite, $Zn_3(AsO_3)_2$, reinerite, is also found at Tsumeb and apparently formed under similar conditions.

THERMAL BEHAVIOR

The thermal behavior of leiteite is shown in figure 3 by the thermogravimetric (TGA), differential thermogravimetric (DTG), and differential thermo-analysis (DTA) curves presented. At first there is a major loss of As_2O_3, followed by the oxidation of a part of the remaining As_2O_3 to As_2O_5; the A position on the TGA curve corresponds to the temperature (507°C) where the increased weight induced by oxidation equilibrates the loss of weight due to sublimation of As_2O_3.

When oxidation is complete (position B, 839°C), the composition $Zn_3(AsO_4)_2$ is obtained, following the reaction

$$3\,ZnAs_2O_4 + O_2 \rightarrow Zn_3(AsO_4)_2 + 2\,As_2O_3\uparrow$$

A chemical analysis of the resulting product gave (wt. %): As_2O_5 47.9, Fe_2O_3 0.84, and ZnO 49.9; this, disregarding the Fe_2O_3, yields the formula $2.94ZnO.As_2O_5$ or $Zn_3(AsO_4)_2$.

Between 900° and 1000°C, incongruent melting occurs with additional loss of As_2O_3 due to partial reduction; a chemical analysis of the sample at position C (1007°C) gave (wt. %): As_2O_5 42.8, Fe_2O_3 1.18, and ZnO 56.2.

The endothermic peak (507°C) on the DTA curve corresponding to the loss of As_2O_3, is very small and suggests that oxidation (exothermic) begins earlier than expected; when oxidation becomes preponderant, it gives a large exothermic peak (555°C). There is a small endothermic peak at 839°C and a more important one at 1007°C, corresponding to the melting point.

The DTA curves of figure 4 represent behavior in normal and inert atmosphere. Curve "A" shows the thermal behavior of leiteite in normal atmosphere: the large exothermic peak at 576°C corresponds to the oxidation of As_2O_3. Curve "B" shows the behavior of leiteite in an inert atmosphere (nitrogen); the two definite endothermic peaks at 500° and 546°C corresponding to the loss of As_2O_3: oxidation does not occur.

ACKNOWLEDGMENTS

We are grateful to Miss M. C. Sichère for her help in making the thermal analyses. The manuscript has benefitted from the helpful criticism of Howard T. Evans, Jr., and Mary E. Mrose, U.S. Geological Survey. Some of the specimens studied were supplied by A. L. McGuinness and P. Bariand. We thank Peter Embrey for the information concerning the British Museum specimen.

REFERENCES

AVERY, S. (1906) The constitution of Paris green and its homologues. *J. Amer. Chem. Soc.*, **28**, 1155-1164.

GEIER, B. H. and WEBER, K. (1958) Reinerit, $Zn_3(AsO_3)_2$, ein neues Mineral der Tsumeb Mine Sudwestafrika. *Neues Jahrb. Mineralogie, Monatsh.*, **1958**, 160-167.

HEINRICH, K. F. J. (1966) *X-ray absorption uncertainty in the electron microprobe.* New York, John Wiley and Sons: 296-377.

OTTEMANN, J., NUBER, G., and GEIER, B. H. (1973) Schneiderhöhnit, ein naturliches Eisen-Arsen-Oxid aus der tiefen Oxidationszone von Tsumeb. *Neues Jahrb. Mineralogie, Monatsh.*, **1973**, 517-523.

YAKOWITZ, H., MYKLEBUST, R. L., and HEINRICH, K. F. J. (1973) FRAME: an on-line correction procedure for quantitative electron probe analysis. *U.S. Dept. Commerce, Natl. Bur. Standards, NBS Tech. Note* **796**, 46 pp.

ZEMANN, J. (1951) Formel und Kristallstruktur des Trippkeits. *Tscherm. Mineralog. Petr. Mitt.*, **2**, 417-423.