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PIRETITE, $Ca(UO_2)_3(SeO_3)_2(OH)_4 \cdot 4H_2O$, A NEW CALCIUM URANYL SELENITE FROM SHINKOLOBWE, SHABA, ZAIRE

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ABSTRACT

Piretite, ideally $Ca(UO_2)_3(SeO_3)_2(OH)_4 \cdot 4H_2O$, is a new mineral from the Shinkolobwe uranium deposit in Shaba, Zaire, that occurs as crusts in association with an orange masuyite-like U–Pb oxide on the surface of uraninite samples. The crystals are lemon-yellow in color with a pearly luster; they do not fluoresce under ultraviolet light. Cleavage: {001} good. D_{meas} = 4.00 g/cm^3 and D_{calc} = 3.87 g/cm^3 (empirical formula), 3.93 g/cm^3 (idealized formula); H_{Mohs} = 2.5. Optically biaxial negative, $2V = 33(5)°$, α 1.54(calc.), β 1.73(1) and γ 1.75 (1), with optical orientation $X \parallel c$, $Y \parallel a$, $Z \parallel b$. The dispersion $r > v$ is weak, and the crystals are nonpleochroic. Piretite is orthorhombic, space group $Pmn2_1$ or $Pmnm$, with the following unit-cell parameters refined from powder data: a 7.010(3), b 17.135(7), c 17.606(4) Å, V 2114.8(1) Å^3, a:b:c 0.409:1:1.027, Z = 4. The forms recognized are {100} {010} {001}, tenacity is weak, and the fracture is uneven. The strongest ten reflections of the X-ray powder pattern [d(in Å)(I)hkl] are: 8.79(80)002, 8.56(40)020, 5.57(20)013, 4.43(20)130, 4.30(30)131, 3.51(100)200, 3.24(40)220, 3.093(50)115, 3.032(100)151 and 1.924(40)237. Electron-microprobe and thermogravimetric analyses gave: CaO 3.57, UO_3 72.00, SeO_2 19.29, H_2O 8.00, total 102.86 wt.%. The empirical formula is $0.76\ CaO \cdot 3.02\ UO_3 \cdot 2.09\ SeO_2 \cdot 5.33\ H_2O$. Piretite results from the alteration of uraninite and primary selenium-bearing sulfides such as penroseite, in the presence of Ca derived from the host rocks. The name is chosen to honor the Belgian crystallographer Paul Piret. Holotype material is deposited in the mineralogical collection of the Royal Belgian Institute of Natural Sciences, Brussels, Belgium.

Keywords: piretite, new mineral species, calcium uranyl selenite, Shinkolobwe, Shaba, Zaire.

SOMMAIRE

La piretite, de formule idéale $Ca(UO_2)_3(SeO_3)_2(OH)_4 \cdot 4H_2O$, est un nouveau minéral du gîte uranifère de Shinkolobwe, Shaba, Zaïre. Le minéral se présente en croûtes à la surface d'échantillons d'uraninite associée à un oxyde orange d'U–Pb semblable à la masuyite. La couleur des cristaux est jaune citron avec un éclat nacré; il n'y a aucune fluorescence aux rayons ultraviolettes. Le clivage {001} est bon. D_{mes} = 4.00 et D_{calc} = 3.87 (formule empirique), 3.93 (formule idéale); H_{Mohs} = 2.5. Optiquement biaxe négative $2V = 33(5)°$, α 1.54(calc.), β 1.73(1) et γ 1.75(1), avec orientation optique $X \parallel c$, $Y \parallel a$, $Z \parallel b$. La dispersion $r > v$ est faible, et les cristaux sont non pléochroïques. La piretite est orthorhombique, groupe spatial $Pmn2_1$, ou $Pmnm$, avec les paramètres de la maille a 7.010(3), b 17.135(7), c 17.606(4) Å, V 2114.8(1) Å^3, a:b:c 0.409:1:1.027 pour Z = 4. Les formes des cristaux sont: {100} {010} {001}; la tenacité est faible, et la cassure, irrégulière. Les dix raies les plus intenses du spectre de diffraction X (méthode des poudres) [d (en Å)(I)hkl] sont: 8.79(80)002, 8.56(40)020, 5.57(20)013, 4.43(20)130, 4.30(30)131, 3.51(100)200, 3.24(40)220, 3.093(50)115, 3.032(100)151 et 1.924(40)237. Les analyses à la microsonde électronique et thermogravimétriques ont donné: CaO 3.57, UO_3 72.00, SeO_2 19.29, H_2O 8.00, total 102.86%. La formule empirique est $0.76\ CaO \cdot 3.02\ UO_3 \cdot 2.09\ SeO_2 \cdot 5.33\ H_2O$. Le minéral résulte de l'altération de l'uraninite et de séléniures primaires, tel que la penroséite; le calcium provient de la gangue du gîte uranifère. Le nom est à l'honneur du cristallographe belge Paul Piret. Le minéral est enregistré dans la collection minéralogique de l'Institut royal des Sciences naturelles de Belgique, à Bruxelles, Belgique.

Mots-clés : piretite, nouvelle espèce minérale, sélénite d'uranyle et de calcium, Shinkolobwe, Shaba, Zaïre.

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INTRODUCTION

Piretite, ideally $Ca(UO_2)_3(SeO_3)_2(OH)_4 \cdot 4H_2O$, is a new uranyl selenite mineral from Shinkolobwe, Shaba, Zaire. The Shinkolobwe uranium deposit has been exploited for uranium until 1960, and is world-famous for its rich association of secondary minerals. More than forty uranium-bearing species have been identified; twenty-seven were described for the first time from this deposit. This abundance of secondary uranium minerals is mainly due to two factors: (1) the large variety of primary sulfides, selenides and tellurides associated with uraninite, combined with the elements of the host rocks (calcium, barium, magnesium) provide complex chemistry, and (2) the exceptional thickness of the alteration zone, which locally reaches more than 100 meters.

The original sample of piretite was collected at the time of the activity of the mine, and was given to the authors by Gilbert Gauthier. The mineral and the mineral name were approved by the Commission on New Minerals and Mineral Names, IMA. The type specimen of piretite is stored as R.C. 4717 in the mineralogical collection of the Royal Belgian Institute of Natural Sciences, Brussels, Belgium. The mineral is named for Paul Piret, Professor of Crystallography, University of Louvain-la-Neuve, Belgium, who has been involved in the description of thirty-four new mineral species.

MORPHOLOGY, PHYSICAL PROPERTIES AND OCCURRENCE

Piretite occurs as elongate tablets lemon-yellow in color that possess an irregular outline. The streak is pale yellow. The crystals have a mean length of 2–3 mm and a width of around 1 mm, but some crystals are acicular prisms up to 5 mm in length. The mineral is transparent to translucent, with a pearly luster. The tablets are flattened on (001), have a good {001} cleavage, and are in some cases cracked and strongly striated parallel to the elongation. The forms of the crystals are {100}, {010} and {001}. The tenacity is weak, and the fracture is uneven. The photomicrograph (Fig. 1), taken by scanning electron microscopy (SEM), shows a typical association of stacked tablets of piretite. The crystals are generally of poor quality and occur as curved sheets. Figure 2 shows the acicular shape of a hollow crystal with rough faces. The Mohs hardness is 2.5. The density, measured by flotation in Clerici solution at 25°C, is 4.00 g/cm^3. The calculated density based on the empirical formula is 3.87 g/cm^3, and that based on the idealized formula is 3.93 g/cm^3. The higher value of the experimentally determined density may be explained by the presence of some micro-inclusions of uraninite in the crystals. The piretite found in the Shinkolobwe deposit results from the alteration of primary veins of uraninite associated with selenides, such as penroseite, or associated with

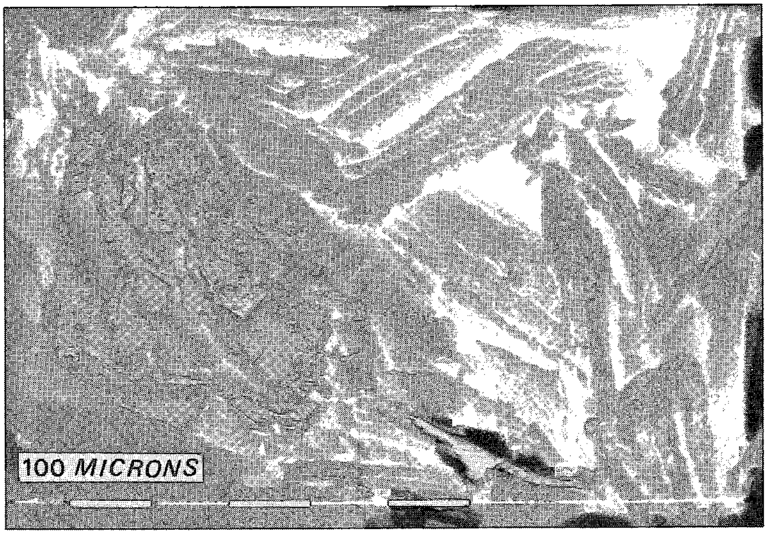

FIG. 1. SEM photomicrograph of piretite showing stacked curved tablets. Scale bar: 100 μm.

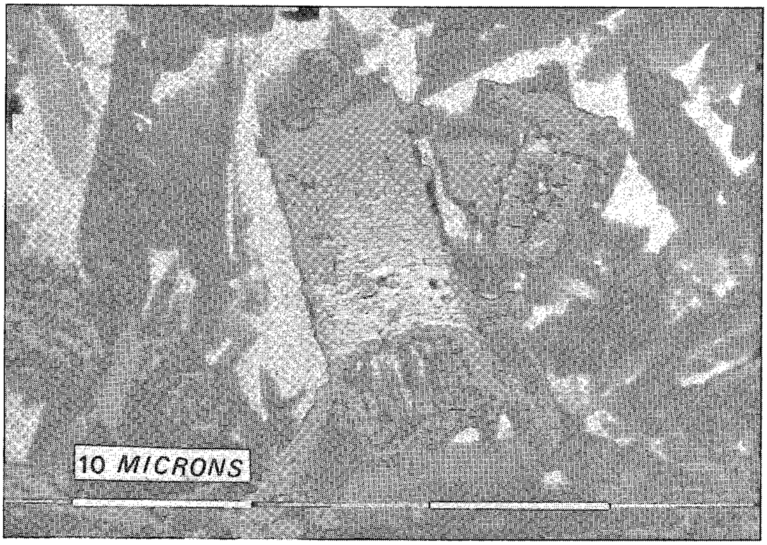

FIG. 2. SEM photomicrograph of a hollow acicular prism of piretite with rough faces. Scale bar: 10 μm.

selenium-containing sulfides such as linnaeite, siegenite, or vaesite, all in the presence of calcium from the dissolution of the upper Cambrian carbonaceous host-rocks of the Série des Mines. Piretite forms stacked aggregates on the surface of uraninite. An orange uranyl–lead oxide arranged in microcrystalline flecks and veinlets is the only associated uranyl mineral. Its X-ray powder pattern is very near to that of masuyite [$Pb_3U_8O_{27}{\cdot}10H_2O$] (PDF 13–408).

OPTICAL CHARACTERISTICS

The mineral is biaxial negative with a measured $2V$ value of 33(5)° (Tobi method). The indices of refraction were determined at 589 nm: α 1.54 (calc), β 1.73 (1) and γ 1.75 (1). The dispersion is weak, and the crystals are nonpleochroic. The optical orientation is $X \parallel c$, $Y \parallel a$ and $Z \parallel b$. Dispersion is weak, $r > v$.

X-RAY CRYSTALLOGRAPHY

The X-ray powder-diffraction data were recorded with a Guinier–Hägg camera using monochromated Cu$K\alpha_1$ radiation (λ = 1.5406 Å) operated at 40 kV and 20 mA. Synthetic fluorphlogopite (SRM–675) was used as a calibrant for the lower θ-values, and silicon powder (SRM–460) was used for the higher θ-values. The relative intensities of the diffraction lines were measured with a Carl Zeiss Jena MD–100 microdensitometer. The pattern is unique and could not be matched with that of any phase in the ICDD Powder Diffraction File.

Single crystals of piretite were examined using Weissenberg methods employing filtered Cu-radiation. Film data of the 0, 1 and 2 levels for a crystal mounted along the c axis indicate orthorhombic symmetry. Systematic absences give the space groups $Pmn2_1$ or $Pmnm$. The refined unit-cell parameters are: a 7.010(3), b 17.135(7), c 17.606(4) Å, V 2114.8(1) Å^3, a:b:c 0.409:1:1.027, Z = 4; they were obtained using the d-values of 32 powder-diffraction lines. The indexing of these lines is conformable with single-crystal Weissenberg data. The program PIRUM (Werner 1969) was used for unit-cell refinement. Figure of merit values are $M(20)$ = 8, $F(20)$ = 14 (0.0214,70). A fully indexed powder pattern is given in Table 1.

CHEMICAL COMPOSITION

Crystals of piretite were chemically analyzed using a Cameca SX–50 electron microprobe with a beam size of 2 μm operating at 15 kV and a beam current of 20 nA. Except for the major components, no peaks of elements with an atomic number of 6 or greater were significantly above the detection limit, indicating that piretite is essentially a pure Ca–U–Se phase. The

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

hkl	d_{obs} (Å)	d_{calc} (Å)	*I*
011	12.30	12.28	10
002	8.79	8.80	80
020	8.56	8.57	40
021	7.73	7.70	5
101	6.52	6.51	5
022	6.15	6.14	20
013	5.57	5.55	20
130	4.43	4.43	20
131	4.30	4.29	30
132	3.96	3.96	5
024	3.92	3.92	10
200	3.51	3.50	100
015	3.45	3.45	5
142	3.38	3.38	5
220	3.24	3.24	40
115	3.093	3.095	50
151	3.032	3.033	100
125	2.952	2.954	20
016	2.895	2.892	20
223	2.841	2.839	5
062	2.715	2.716	10
145	2.535	2.536	5
017	2.487	2.488	5
171	2.291	2.291	5
073	2.257	2.259	5
330	2.162	2.163	10
156	2.124	2.124	10
236	2.093	2.093	5
038	2.053	2.054	10
075	2.009	2.010	5
237	1.924	1.924	40
228	1.821	1.821	5

Guinier-Hägg camera, Cu*K*α_1 radiation. Intensities measured with Carl Zeiss Jena MD-100 microdensitometer.

following standards were used: wollastonite (Ca), synthetic UO_2 (U), Analytical Reagent selenium (Se). H_2O content was determined thermogravimetrically. A thermogravimetric analysis (TGA) reveals a total weight-loss of 8.00 wt.%. Five electron-microprobe analyses carried out on each of five different crystals yield the proportion (wt.%) of major components: CaO 3.57 [3.07–4.07], UO_3 72.00 [70.60–73.40], SeO_2 19.29 [18.60–20.20]. The oxide formula calculated on the basis of 14 O atoms is: $0.76\ CaO{\cdot}3.02\ UO_3{\cdot}2.09\ SeO_2{\cdot}5.33\ H_2O$. The empirical formula, taking into account electroneutrality, is: $Ca_{0.76}(UO_2)_{3.02}(SeO_3)_{2.09}(OH)_{3.38}{\cdot}3.64H_2O$. The ideal formula is: $Ca(UO_2)_3(SeO_3)_2(OH)_4{\cdot}4H_2O$. Piretite is soluble in dilute HCl without effervescence.

Calculation of the Gladstone–Dale relationship using the constants of Mandarino (1981) yields a "good" compatibility index between physical and chemical data using the measured density [$1 - (K_P/K_C) = 0.0567$].

THERMAL STABILITY

The thermal stability of piretite was studied with a TGA 2950 thermogravimetric analyzer, TA Instruments, with a heating rate of 5°C/min and a constant N_2-flow of 50 mL/min. The TGA curve shows that dehydration and dehydroxylation do not take place in distinct steps.

INFRARED SPECTROSCOPY

The infrared spectrum was recorded using the KBr dispersion technique (1 mg sample in 300 mg KBr) with an Ati–Mattson Genesis Fourier transform infrared spectrometer, which covers the range 400–4000 cm^{-1}. The infrared spectrum, presented in Figure 3, is characterized by the vibrations of H_2O molecules, OH, UO_2 and SeO_3 groups. The absorption bands at about 3303 and 1623 cm^{-1} are due to H_2O, and correspond to stretching and deformation modes, respectively. The assignment of the absorption bands is summarized in Table 2.

RELATIONSHIPS TO OTHER SPECIES

In addition to guilleminite, piretite is the second uranyl selenite to be found at Shinkolobwe. Selenium in southern Shaba is mainly concentrated in the Musonoi copper deposit, which also contains localized uranium mineralization. This deposit, located 200 km east of Shinkolobwe, is the type locality for four of the five known secondary uranyl selenites previously described: demesmaekerite [$Pb_2Cu_5(UO_2)_2(SeO_3)_6(OH)_6{\cdot}2H_2O$] (Cesbron *et al.* 1965), derriksite [$Cu_4(UO_2)(SeO_3)_2(OH)_6{\cdot}H_2O$) (Cesbron *et al.* 1971), guilleminite [$Ba(UO_2)_3(SeO_3)_2O_2(H_2O)_3$]] (Cooper & Hawthorne 1995) and marthozite [$Cu(UO_2)_3(SeO_3)_3(OH)_2{\cdot}7H_2O$] (Cesbron *et al.* 1969). The last secondary

TABLE 2. INFRARED ABSORPTION BANDS OF PIRETITE

Wavenumber (cm^{-1})	Assignment
3303 (s,b)	$\nu_1\ H_2O$ *
2927 (w)	$\nu_2\ H_2O$ *
1623 (s)	$\delta\ H_2O$ **
1483 (w)	$\delta\ H_2O$ **
898 (s)	$\nu_2\ UO_2$ *
815 (w)	$\nu_1\ SeO_3$ *
732 (s)	$\nu_3\ SeO_3$ *
468 (m)	$\nu_2\ SeO_3$ *

s: strong, m: medium, w: weak, b: broad
* Khandelval & Verma (1976); ** Morris *et al.* (1991).

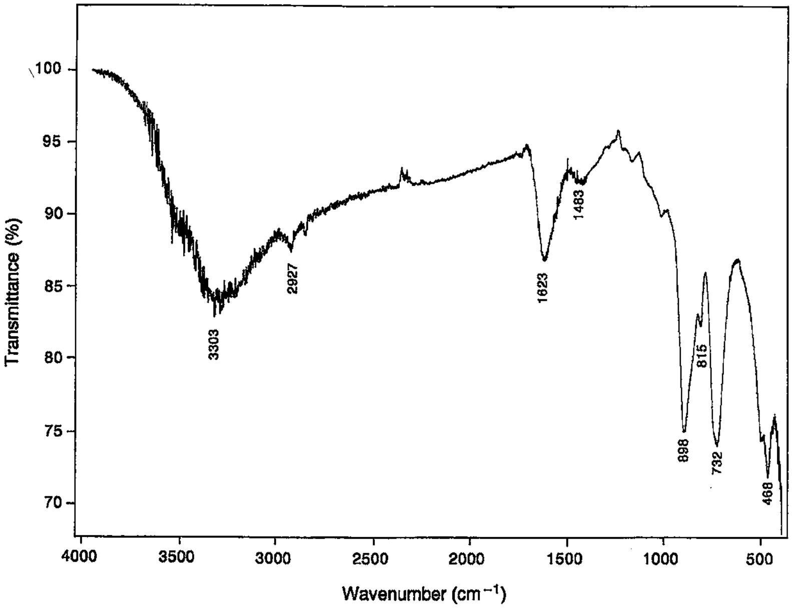

FIG. 3. Fourier-transform infrared spectrum of piretite from 400 to 4000 cm^{-1}.

uranyl selenite described is haynesite [$(UO_2)_3(SeO_3)_2(OH)_2 \cdot 5H_2O$] (Deliens & Piret 1991) from the Repete mine, in Utah. Piretite differs from the other yellow secondary uranium minerals at the Shinkolobwe deposit by its stacking of striated tablets and its pearly luster. Guilleminite, the other uranyl selenite known from Shinkolobwe, occurs as microcrystalline or powdered amber-yellow-colored crusts on uraninite. The yellow uranyl selenite, haynesite, whose morphology and state of aggregation of crystals resembles that of piretite, has a vitreous luster and is only known from a uranium deposit hosted by the Morrison Formation in Utah, of Upper Jurassic age (Deliens & Piret 1991).

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REFERENCES

CESBRON, F., BACHET, B. & OOSTERBOSCH, R. (1965): La demesmaekerite, sélénite hydraté d'uranium, cuivre et plomb. *Bull. Soc. fr. Minéral. Cristallogr.* **88**, 422-425.

________, OOSTERBOSCH, R. & PIERROT, R. (1969): Une nouvelle espèce minérale: la marthozite, uranyl-sélénite de cuivre hydraté. *Bull. Soc. fr. Minéral. Cristallogr.* **92**, 278-283.

________, PIERROT, R. & VERBEEK, T. (1971): La derriksite, $Cu_4(UO_2)(SeO_3)_2(OH)_6 \cdot H_2O$, une nouvelle espèce minérale. *Bull. Soc. fr. Minéral. Cristallogr.* **94**, 534-537.

COOPER, M.A. & HAWTHORNE, F.C. (1995): The crystal structure of guilleminite, a hydrated Ba–U–Se sheet structure. *Can. Mineral.* **33**, 1103-1109.

DELIENS, M. & PIRET, P. (1991): La haynesite, sélénite hydraté d'uranyle, nouvelle espèce minérale de la mine Repete, comté de San Juan, Utah. *Can. Mineral.* **29**, 561-564.

KHANDELVAL, B.L. & VERMA, V.P. (1976): Liquid–liquid distribution, spectrophotometric, thermal, IR and Raman studies on selenite uranylates. *J. Inorg. Nucl. Chem.* **38**, 763-769.

MANDARINO, J.A. (1981): The Gladstone–Dale relationship. IV. The compatibility concept and its application. *Can. Mineral.* **19**, 441-450.

MORRIS, R.E., HARRISON, W.T.A., STUCKY, G.D. & CHEETMAN, A.K. (1991): The synthesis and crystal structure of two novel aluminum selenites, $Al_2(SeO_3)_3 \cdot 6H_2O$ and $AlH(SeO_3)_2 \cdot 2H_2O$. *J. Solid State Chem.* **94**, 227-235.

WERNER, P.E. (1969) : Refinement of unit cell. *Arkiv Kemi* **31**, 513-516.

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