STUDIES OF RADIOACTIVE COMPOUNDS: IX—SKLODOWSKITE

D. H. GORMAN

University of Toronto, Toronto, Canada

ABSTRACT

New *x*-ray data are presented for the uranium silicate, sklodowskite. The mineral is monoclinic, $C2/m$; $a = 17.28\text{Å}$, $b = 7.03$, $c = 6.56$; $\beta = 105°53'$. Isomorphism with uranophane is discussed. Conditions for the formation of this rare mineral are reviewed.

Of the several species of uranium silicate minerals, sklodowskite has the most limited geographical distribution, the only recorded occurrence being that at Shinkolobwe, Katanga, Belgian Congo. It was first described by Schoep (1924*a*). The analogy with uranophane was recognized by Schoep (1924*b*) who subsequently (1927) described its isomorphism with this mineral. Billiet (1936) obtained an *x*-ray powder pattern, and established cell dimensions and a symmetry based upon rotation photographs. As was the case with his work on uranophane, erroneous results were obtained owing to the non-amenability of the crystals to the *x*-ray technique employed.

In 1923 Schoep published two brief notes describing a new mineral species from the Shinkolobwe deposits, which he called chinkolobwite. However, in 1926 he wrote on the identity of chinkolobwite and the species which he had previously named sklodowskite. It was pointed out to Schoep by Buttgenbach that the name sklodowskite was the more appropriate for the species owing to the fact that the mineral does not actually occur at the village of Shinkolobwe, but at Kasolo Hill, and that the honor paid to Maria Sklodowska (later Madame Curie) should be perpetuated.

Physical Properties

Sklodowskite occurs as minute acicular crystals in tightly compacted parallel aggregates, often reticulate, radiating divergent or stellate. Exceedingly small crystals form velvety coatings on host rock. According to the several papers of Schoep it occurs as spherulites, and a massive earthy variety is very common.

The color of the crystals is a bright citron yellow, which resembles that of uranophane, but is distinctly lighter than that of the associated minerals kasolite and soddyite. The massive variety appears to be paler than the crystals. The lustre is adamantine to vitreous for the crystals, and earthy for the massive type. The writer has never observed the waxy lustre so common for uranophane. The hardness, difficult to estimate, is probably 2–3 on the Moh's scale. Crystals exhibit perfect (100) cleavage, comparable to uranophane and beta-uranophane in that the cleavage planes are parallel to the two shortest dimensions of the unit cell.

Schoep (1924*b*) gives specific gravities of 3.54 for the fibrous spherulitic type, and 3.74 for massive material. Billiet (1936), using Clerici solution, obtained a value of 3.776. By the same method the writer measured 3.64 for clean, idiomorphic crystals.

This value compares remarkably well with the value 3.638, calculated from the accepted formula and the writer's newly established cell dimensions. George (1949) records the fluorescence as negative to possibly faint green. The present writer found that the several specimens available to him did not fluoresce under either short or long wave ultra-violet excitation. All specimens were radioactive.

The optical properties of sklodowskite are well established, the values recorded in the literature being highly consistent. The optical constants are as follows.

$\alpha = 1.613$
$\beta = 1.635\text{–}1.642$
$\gamma = 1.657$
$Y = b =$ elongation

$X =$ colourless
$Y =$ yellow
$Z =$ pale yellow

negative
$2V$, very large
dispersion, high

The above measurements, made by the writer, are in complete agreement with published values, the only difference being that Y which is in the direction of the axis of elongation, is recorded as $Y = b$ instead of $Y = c$, where the c axis was erroneously considered to be the axis of elongation.

It is noted that the indices of refraction of sklodowskite are very much lower than those of the similar minerals, uranophane and beta-uranophane.

Crystallography

In all of his papers Schoep maintains that sklodowskite is orthorhombic, crystals being prismatic or prismatic-tabular, elongated in the *c*[001] direction. In 1927 he published a summary of his crystallographic data, which included a drawing of a prismatic crystal, with measured and calculated ϕ and ρ values for the forms {010}, {140}, {110}, {210}, {100}, {103}. The crystal, as drawn, shows a strong prismatic zone in [001] singly terminated by the form {103}. The axial ratio was calculated as $a:b:c = 0.3114:1:1.0554$.

Billiet (1936), on crystals 2 mm. long, measured,

(130):(010) = 37°46′
(101):(100) = 43°08′

and from these values calculated an axial ratio $a:b:c = 0.4303:1:0.4593$. The discrepancy between this ratio and Schoep's is almost certainly due to the fact that sklodowskite crystals are very small, and as admitted by Billiet, not amenable to accurate goniometric studies. Billiet further calculated an axial ratio from his *x*-ray data which is in very good agreement with that obtained from his goniometry. However, it appears to the present writer that a predilection to orthorhombic symmetry, and inadequate *x*-ray apparatus forced Billiet to draw erroneous conclusions.

The present writer was unable to obtain goniometric measurements from crystals available to him. However, he corroborates Schoep's description of sklodowskite crystals in that they are prismatic to prismatic-tabular, with a strong prismatic zone in the direction of elongation. The following crystallographic constants were calculated from *x*-ray measurements on sharp rotation and Weissenberg photographs of single crystals. Sklodowskite crystals are monoclinic,

$a:b:c = 2.548:1:0.934$ $\beta = 105°53'$
$p_2:q_2:r_2 = 0.423:1:1.111$ $\mu = 74°07'$
b = elongation

These values are in harmony with those of the similar minerals uranophane and beta-uranophane (Gorman & Nuffield, 1955) and unpublished data for cuprosklodowskite (Gorman).

The correlation between the forms, as described by Schoep (1927), and the newly established orientation and constants becomes evident if one draws a reciprocal lattice based on the new *x*-ray measurements, and plots the forms based on Schoep's angle table. In the new orientation the dominant forms become {001} and {100}, *i.e.* the basal and front pinacoids, with the pinacoid {301} in the same zone, and the terminating prism {011}. Two other minor forms described by Schoep could not be indexed.

It is significant that Schoep (1924*a*) notes that the crystals sometimes have a lozenge or rhombic cross section. This would arise from an equal development of the basal and front pinacoid, in the new orientation. Most of the confusion in the establishment of the symmetry based on goniometry arose from Schoep's interpretation of 72°–73°45′ (Schoep, 1927) as the angle between the side pinacoid and the prism {110}, rather than the angle between the basal and front pinacoids. That this is the angle between the pinacoids is evident from the *x*-ray data, where the μ value has been established as 74°07′.

In summary, crystals of sklodowskite are minutely prismatic to tabular-prismatic, monoclinic, elongated in the *b* direction, with a strong pinacoidal zone in this direction, terminated by the prism {011}.

Schoep, in his descriptions of sklodowskite, mentions no twinning. However, for chinkolobwite (= sklodowskite) he notes that lamellar crystals often show contact twinning. This twinning undoubtedly occurs with (001) or (100) as the twin plane. The present writer observed no twinning in crystals available to him.

X-ray Crystallography

Billiet (1937) produced a rather poor (by our present day standards) *x*-ray powder photograph of sklodowskite from Shinkolobwe. He also attempted single crystal work, and obtained the following orthorhombic cell dimensions based upon rotation photographs:

a 6.67 Å (probably kX)
b 15.50
c 7.12 = elongation

It is quite understandable that he arrived at results which are, in part, not compatible with those of the present writer, since it is an extremely difficult task to orient such minute crystals so that three axial rotation photographs might be obtained.

Several *x*-ray powder photographs were obtained from specimens of sklodowskite from Kasolo, by the present writer. All photographs were sharp and identical. An actual size print is shown in Fig. 1*b*. The powder data are presented in Table 1.

Sharp *x*-ray rotation and Weissenberg photographs were obtained from a single crystal rotated about the axis of elongation. The following monoclinic cell dimensions, with *b* as the axis of elongation, were obtained:

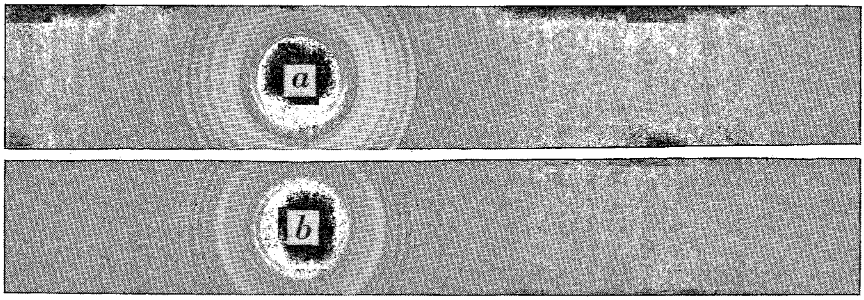

FIG. 1 (*a*) Uranophane, Kupferberg, Silesia; (*b*) sklodowskite, Kasolo, Belgian Congo. Cu/Ni radiation ($\lambda = 1.5418$ Å); camera diameter 57.3 mm; actual size prints.

TABLE 1. SKLODOWSKITE, $MgO.2UO_3.2SiO_2.6H_2O$: X-RAY POWDER DATA
Monoclinic, $C2/m$; $a = 17.28$; $b = 7.03$; $c = 6.56Å$; $\beta = 105°53'$; $Z = 2$

I(Cu)	d (meas)	hkl	d (calc)	I**(Cu)	d (meas)**	I(Cu)	d (meas)	I(Cu)	d (meas)
10	8.04	200	8.29	10	8.42	2	2.87	3	1.540
2	6.27	001	6.27	2	6.37	4	2.72	4	1.491
5	5.78	$\bar{2}01$	5.86	5	5.91	3	2.50	3	1.442
1/2*b	5.37	—	—	—	—	4	2.33	2	1.403
3	4.79	$\bar{1}11$	4.75	4	4.82	5	2.24	5	1.357
—	—	310	4.35	1	4.51	5	2.10	1	1.311
5	4.25	111	4.26	4	4.33	4	1.971	3	1.292
10	4.08	400	4.09	8	4.19	5	1.913	1	1.272
2	3.95	$\bar{4}01$	3.95	5	4.00	3	1.764	1	1.234
8	3.51	020	3.52	6	3.52	1	1.732	3	1.224
		220	3.25			2	1.693	2	1.195
9	3.23	311	3.25	7	3.27	3	1.640	2	1.174
		$\bar{2}02$	3.23			5	1.609	3	1.158
9	2.96	—	—	6	3.00	½	1.589	1/2	1.136

I(Cu)	d (meas)	I(Cu)	d (meas)	I(Cu)	d (meas)	I(Cu)	d (meas)
1/2	1.115	1	0.971	1/2	0.861	1	0.795
1/2	1.091	1/2	0.957	2	0.841	1	0.792
2	1.082	1	0.940	1/2	0.836	1	0.788
1/2	1.051	3	0.928	1/2	0.830	1	0.787
1/2	1.036	1	0.911	2	0.824	2	0.783
1/2	1.025	2	0.898	1	0.816	1	0.781
1	1.011	1/2	0.875	3	0.809	1/2	0.779
1/2	0.990	1/2	0.871	2	0.801		

Cu$K\alpha$ = 1.5418Å, Ni filter, camera diameter 57.3 mm.

*A weak diffuse line on an otherwise sharp photograph, possibly not due to sklodowskite.

**Intensities and spacings from Frondel, Riska and Frondel (1956) for sklodowskite from Katanga district, Cu$K\alpha$, Ni filter, camera diameter 114.6 mm.

a 17.28 Å $\beta = 105°53'$
b 7.03 space group $C2/m$
c 6.56

A second crystal was subjected to identical analysis with identical results. The first ten lines of the powder photograph were indexed, using the above constants. Measured and calculated spacings were in excellent agreement, and the conditions of the space group ($h+k$ even) corroborated (Table 1).

Chemistry and Cell Contents

In Table 2 are shown the existing published analyses of sklodowskite. All analyses were made by Schoep, and from these he derived the formula $MgO.2UO_3.2SiO_2.7H_2O$. Billiet (1936) modified this to $MgO.2UO_3.2SiO_2.6H_2O$ in view of the analogy with uranophane whose formula had been more precisely established.

TABLE 2. SKLODOWSKITE—CHEMICAL ANALYSES

	I	II	III	IV
SiO_2	13.49	12.53	14.28	13.2
UO_3	67.25	66.33	64.72	69.3
MgO	1.91	3.96	3.74	3.4
CaO	2.57	—	—	—
Na_2O+K_2O	—	—	1.97	—
PbO	—	1.17	—	—
NiO	—	Trace	0.20	—
CoO	1.27	—	—	—
TeO_3	—	2.64	1.08	—
H_2O	13.33	14.27	13.41	14.2
TOTAL	99.82	100.90	99.40	100.1
S.G.	3.54	3.74	3.54	

I —Sklodowskite; fibrous, spherulites; Anal. Schoep (1924*b*)
II —Sklodowskite; compact, granular; Anal. Schoep (1924*b*)
III—Sklodowskite; crystals; Anal. Schoep (1924*a*)
IV—Sklodowskite; compact, spherulitic; Anal. Schoep (1926) after deducting 10% wulfenite and other impurities.

In Table 3 are shown the cell contents calculated from the new cell dimensions and a measured gravity of 3.64. In explanation of Tables 2 and 3, it should first be pointed out that the values for SiO_2, UO_3 and water are fairly consistent considering the amount of material with which the analysts worked, and the difficulty of obtaining homogeneous material. This difficulty became evident to the present writer when he tried, unsuccessfully, to collect enough clean material for a quantitative analysis. Secondly, it is admitted by Schoep that the tellurium, cobalt

TABLE 3. CELL CONTENTS OF SKLODOWSKITE

	I	II	III	IV	V
SiO_2	3.80	3.48	4.02	3.70	4
UO_3	3.97	3.86	3.83	4.06	4
MgO	.80	1.64	1.57	1.42	2
CaO	.86	—	—	—	
Na_2O+K_2O	—	—	.43	—	
PbO	—	.87	—	—	
NiO	—	—	.05	—	
CaO	.29	—	—	—	
TeO_3	—	.25	.10	—	
H_2O	12.48	13.19	12.58	13.25	12

I–IV—Calculated from analyses 1–4 in Table 2, using newly established cell dimension and S.G. 3.64.

V —Theoretical values based on $2[MgO.2UO_3.2SiO_2.6H_2O]$.

and nickel appearing in the assays are probably not essential constituents of sklodowskite, in that these elements are abundant in the Kasolo area, and appear in the analyses of many minerals.

Out of respect for the above factors, no attempt is made here to manipulate the values listed in Tables 2 and 3. It appears reasonable to attribute the formula $2[MgO.2UO_3.2SiO_2.6H_2O]$ to sklodowskite.

SKLODOWSKITE AND URANOPHANE

From chemical and crystallographic data Schoep (1927) concluded that sklodowskite and uranophane were isomorphous, with magnesium and calcium interchangeable. Billiet (1936) concurred, adding to the argument the weight of his *x*-ray data. In view of the existing chemical analyses of uranophane and sklodowskite the present writer is of the opinion that there may be some substitution between magnesium and calcium. But in assessing the *x*-ray data it is apparent that, although the minerals have certain features in common, notably the lengths of the *b* and *c* axes, and almost certainly possess similar if not identical units of structure, nevertheless there are differences which preclude complete isomorphism. These differences are clearly seen from Table 4. The dissimilarity of the powder photographs is evident from Fig. 2. A further discussion of the similarities and differences among the uranium silicate minerals will be included in a forthcoming paper by the writer on cuprosklodowskite.

Occurrence

According to Schoep (1936) the sklodowskite at Shinkolobwe occurs in fractures in a talcose, siliceous breccia. Crystals occur as cross fibres in

TABLE 4. COMPARISON OF SKLODOWSKITE AND URANOPHANE

SKLODOWSKITE	URANOPHANE
$2[MgO.2UO_3.2SiO_2.6H_2O]$	$2[CaO.2UO_3.2SiO_2.6H_2O]$
S.G. 3.85 calc.	S.G. 3.638 calc.
Space Group $C\,2/m$	Space Group $P2/a$ or $P2/a$
a 17.28 Å	a 15.87 Å
b 7.03 elongation	b 7.05 elongation
c 6.56	c 6.66
β 105°53′	β 97°15′
Low indices of refraction	Much higher indices

the fissures, as spherulites or velvety coatings on the walls. The massive variety is most common, and is frequently cut by kasolite. Other associated minerals are soddyite and wulfenite. Vaes & Derriks (1955) note the association of sklodowskite with uranophane and saléeite.

As regards the genesis of the mineral, it is well known (Thoreau, Neve) that it occurs in the silicate zone where minerals formed later than the uranium oxides and hydroxides, but before the phosphates. Although Schoep (1936) favors in general the theory that most secondary minerals in the Shinkolobwe deposits have been formed from ascending juvenile waters, he believes that some minerals, including sklodowskite, have been formed by the alteration of pitchblende by supergene solutions charged with magnesia and silica. Vaes & Derriks (1955) note that sklodowskite is formed near pitchblende as a direct alteration product of it. They advocate supergene solutions.

Since sklodowskite has such a limited distribution, the present author can only draw his conclusions as to its formation from an assessment of facts written by those who have seen the Shinkolobwe deposits. It does seem obvious that for the formation of sklodowskite an abundance of magnesium is necessary. This condition is certainly fulfilled at Shinkolobwe where, according to the several authors cited above, and Mr. Franc Joubin,[1] the magnesitization in this area has been intense. In this respect it is unusual that sklodowskite has not been found at the Nicholson Mine, Saskatchewan, where pitchblende is associated with a siliceous dolomite. From this deposit Hogarth (1951) identified several of the rare species of uranium minerals that occur at Shinkolobwe, and emphasized the similarity in zoning of the two deposits, but failed to identify sklodowskite.

It appears to the present writer to be significant that Vaes & Derriks (1955) note that sklodowskite does not appear below the 57 level at Shinkolobwe, and yet uranophane is abundant. Moreover, Hacquaert

---

[1] Private communication (1956)

(1927) briefly describes uraninite cubes with centers altered to sklodowskite. These two factors indicate that intense alteration seems to be necessary for the formation of sklodowskite. This would explain its absence at Nicholson where Arctic conditions prevail.

In summary, it appears that sklodowskite is formed by the supergene alteration of pitchblende. The solutions must be charged with magnesia and silica, and oxidizing conditions must be intense.

Acknowledgments

The writer wishes to thank the several curators of museums who loaned the fragile and valuable specimens which made this study possible. Appreciation is expressed to Professor E. W. Nuffield of the University of Toronto, for his critical reading of the manuscript. Portions of the foregoing study were completed while the author was receiving financial assistance from the National Research Council of Canada. Thanks are extended to the Council both for that financial assistance and permission to publish.

REFERENCES

Billiet, V. (1936): Uranotiel en Sklodowskiet, *Natuur. Tijd. Gent* No. **8**, 284.

Frondel, C., Riska, D., & Frondel, J. W. (1956): *X*-ray powder data for uranium and thorium minerals, *U.S. Geol. Survey*, Bull. 1036-G, 133.

George, D. (1949): Mineralogy of uranium and thorium bearing minerals, *U.S. Atomic Energy Commission* report RMO-563, 186.

Gorman, D. H. & Nuffield, E. W. (1955): Studies of radioactive compounds VIII Uranophane and beta-uranophane, *Amer. Min.*, **40**, 634.

Hacquaert, A. (1927): Over Pseudomorphosen in radioactive Mineralen van Katanga, *Natuur. Tijd. Ant.* **9**, 34.

Hogarth, D. D. (1951): Meta-zeunerite, uranophane, kasolite, cupro-sklodowskite in Canada, *Amer. Min.* **36**, 411.

Schoep, A. (1923): Sur la chinkolobwite, nouveau minéral uranifère du Katanga, *Bull. Soc. Belge Geol. Brux.* **23**. 87. *Bull. Soc. Chim. Belge* **32**, 345.

——— (1924a): La sklodowskite, nouveau minéral radioactif, *Compt. Rend. Acad. Sci. Paris*, **19**, 413.

——— (1924b): Sur la sklodowskite, nouveau minéral uranifère, ses analogies avec l'uranotile, *Bull. Soc. France Min.* **47**, 162.

——— (1926): Sur l'identité entre la chinkolobwite et la sklodowskite, *Ann. Soc. Geol. Belge* **48**, B303.

——— (1927): Isomorphie van Sklodowskiet met Uranofaan, *Natuur. Tijd. Ant* **9**, 30.

——— (1936): Sur les associations à cuprosklodowskite du Katanga, *Bull. Soc. Belge de Geol.* **56**, 298.

Thoreau, J. & Trieu de Terdonck, R., du (1934): Le gite d'uranium de Shinkolobwe-Kasolo (Katanga), *Inst. Roy. Col. Belge*, Tom **2**, Fasc 1.

Vaes, J. & Derriks, J. (1955): Le gite d'uranium de Shinkolobwe, A/Conf/8/P/1105, Belgique, Conférence Internationale sur l'utilization de l'énergie atomique à de fins pacifiques.