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SIGLOITE, A NEW MINERAL FROM LLALLAGUA, BOLIVIA*

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Abstract

Sigloite, $(Fe^{3+}, Fe^{2+})Al_2(PO_4)_2(O,OH)\cdot 8H_2O$, is a new mineral formed as an oxidation pseudomorph after paravauxite at Llallagua, Bolivia. Triclinic; $a=5.26$, $b=10.52$, $c=7.06$ Å, $\alpha=106°58'$, $\beta=111°30'$, $\gamma=69°30'$; $a:b:c=0.4990:1:0.6711$; space group $P\bar{1}$. Color straw yellow. G=2.35 meas. 2.36 Calc., H=3. Optically biaxial (+), $\alpha=1.563$, $\beta=1.586$, $\alpha=1.619$, $2V=76°$, $r<v$. Optical orientation: X—$\phi 90°$ $\rho 32°$, Y—$\phi -144°$ $\rho 70°$, Z—$\phi -46°$ $\rho 66°$. Analysis gives P_2O_5 27.47, Al_2O_3 21.09, Fe_2O_3 13.53, FeO 2.76, MnO 0.24, MgO 0.87, Na_2O 0.44, K_2O 0.26, SiO_2 0.11, H_2O 33.55, total 100.32. Strongest x-ray powder lines are 9.69 Å (10) 6.46 (9), 4.86 (9). The name is from the Siglo XX mine, Llallagua.

Occurrence

In 1954 through the courtesy of Senor P. P. Zubrzycki, Chief Geologist, Corporacion Minera de Bolivia, the junior author collected the specimens used in the present study. On the 305-meter level of the Contacto vein, Siglo XX Mine, Llallagua, cavities were found filled with straw yellow intergrowths of crystals; in other cavities similar crystals were perched on wavellite overgrowths on quartz. Although the morphological appearance of these crystals was similar to paravauxite, the color was sufficiently different to attract attention. Chemical analysis confirmed the similarity and revealed the cause of the color difference. Most of the ferrous iron of paravauxite had been oxidized to the ferric state. The name, *sigloite*, taken from the Siglo XX mine, is given to the new mineral, an oxidation pseudomorph after paravauxite. Sigloite is apparently the mineral referred to by Bandy (1946, p. 56) as "hydrated paravauxite," a straw yellow alteration of paravauxite assumed to form by hydration.

The minerals associated with sigloite, in addition to wavellite and paravauxite, include metavauxite, crandallite, childrenite, and an unidentified reddish-brown phosphate. These and other phosphate minerals

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are found in open fractures cutting major cassiterite veins on all levels of the mine, and were considered of supergene origin by Ahlfeld (1931) and Gordon (1944). Turneaure (1935) indicated that vauxite is supergene but points out the unlikelihood of a supergene origin for the large amounts of wavellite. In later publications Bandy (1946) and Ahlfeld and Munoz (1943 and 1955) regard all of the phosphate minerals as belonging to the final phase of hydrothermal mineralization. Sigloite appears to be an exception. Its pseudomorphous nature indicates formation from paravauxite during a later supergene stage.

PHYSICAL AND OPTICAL PROPERTIES

The pale straw yellow to light brown color of sigloite is in marked contrast to that of paravuxite, which is colorless to pale green. The two minerals were observed together on only one specimen, and here most crystals were completely either one mineral or the other. However, a few showed a variation in color along their length and refractive index changes corresponding to the color differences. Although earlier suspected, it was this evidence that led the authors to the conclusion that the sigloite crystals are pseudomorphs after paravauxite.

The perfect {010} cleavage of paravauxite is preserved in sigloite, and in addition there is good {001} cleavage, traces of which are seen on {010}. On the reflecting goniometer sigloite crystals show distorted and curved faces which give continuous signals over a wide angular range. Although one cannot use the measurement for calculations they served to identify the following crystal forms: $c\{001\}$, $b\{010\}$, $a\{100\}$, $m\{110\}$, $M\{\bar{1}10\}$, $t\{\bar{1}20\}$, $k\{0\bar{1}1\}$, $r\{1\bar{1}1\}$, $h\{\overline{11}2\}$. Figure 1 shows the characteristic habit and form development.

The hardness of sigloite is 3. The specific gravity measured on the Berman balance is 2.35; 2.36 calculated.

The optical properties of sigloite are given in Table 1 with those of paravauxite for comparison. It will be noted that the oxidation of the iron has produced an appreciable rise in refractive indices and increase in the birefringence. Figure 2 shows diagramatically the optical orientation of sigloite. A comparison of the stereograms of Fig. 3 and 4 shows the marked difference in the optical orientation of paravauxite and sigloite.

CHEMICAL COMPOSITION

A chemical analysis of sigloite, made on the same material used for optical and *x*-ray study, is given in Table 2 with an analysis of paravauxite. The analyses correspond closely except for the state of oxidation of the iron. In sigloite, to balance the excess positive charge of Fe''', there is assumed to be a concomitant substitution of oxygen for hydroxyl giv-

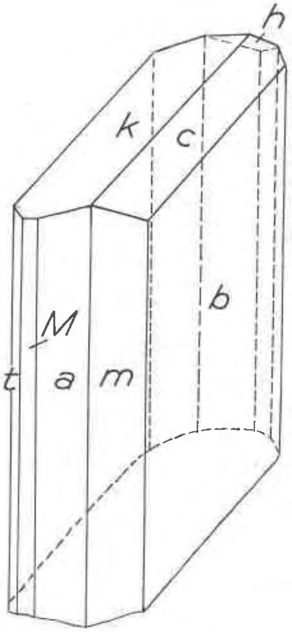

FIG. 1. Sigloite. Pseudomorph after paravauxite.

ing the formula $(Fe^{3+} Fe^{2+})Al_2 (PO_4)_2 (O,OH)_2 \cdot 8H_2O$. There is one formula weight per unit cell.

Differential thermal analysis curves of sigloite and paravauxite are given in Fig. 5. The differences in the marked endothermic peaks, between 100° and 300° C, resulting from the loss of water, indicate a difference in the role of water in the two minerals. After heating to 1000° C, both sigloite and paravauxite yield a red powder. An x-ray powder photo-

TABLE 1. OPTICAL PROPERTIES OF SIGLOITE AND PARAVAUXITE

Orientation				Indices (Na)	
		ϕ	ρ		
Sigloite	X	90°	32°	$\alpha=1.563$	Opt. +
	Y	−144	70	$\beta=1.586\pm0.001$	2V=76°
	Z	−46	66	$\gamma=1.619$	r<v strong
Paravauxite	X	61	56°	$\alpha=1.552$	Opt. +
	Y	180	55	$\beta=1.559\pm0.001$	2V=72°
	Z	−61	54	$\gamma=1.572$	r<v

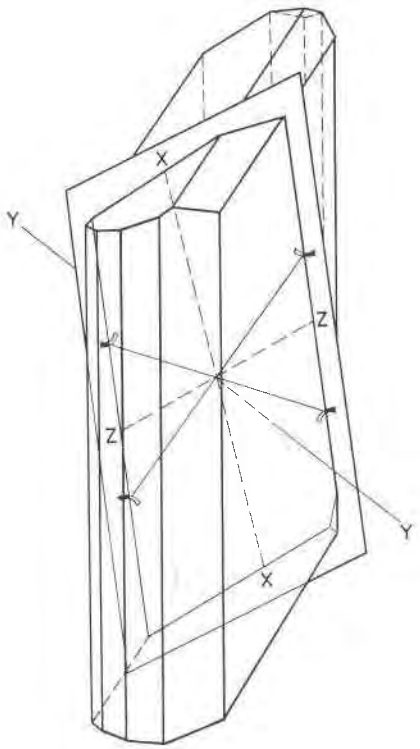

FIG. 2. Optical orientation of sigloite.

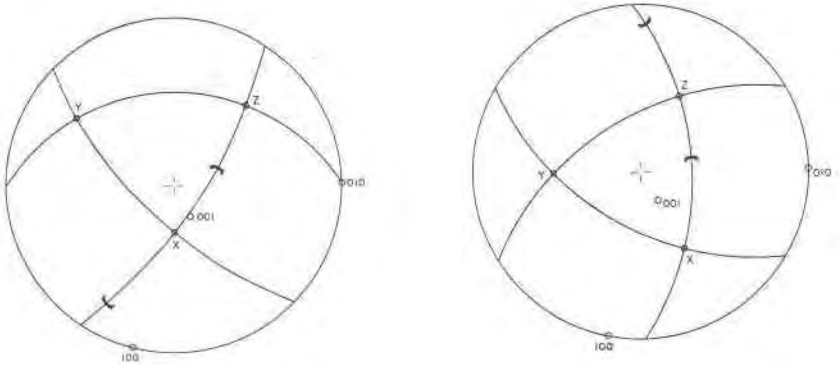

FIG. 3. Sigloite.

FIG. 4. Paravauxite.

Stereograms showing optical orientation.

TABLE 2. CHEMICAL ANALYSIS OF SIGLOITE

	1. Sigloite	2. Paravauxite
P_2O_5	27.47	27.64
Al_2O_3	21.09	21.00
Fe_2O_3	13.53	1.52
FeO	2.76	13.60
MnO	0.24	—
CaO	—	0.28
MgO	0.87	0.22
Na_2O	0.44	—
K_2O	0.26	—
SiO_2	0.11	1.20
H_2O	33.55	35.05
	100.32	100.51

1. Jun Ito, analyst.
2. E. V. Shannon analyst, in Gordon (1944).

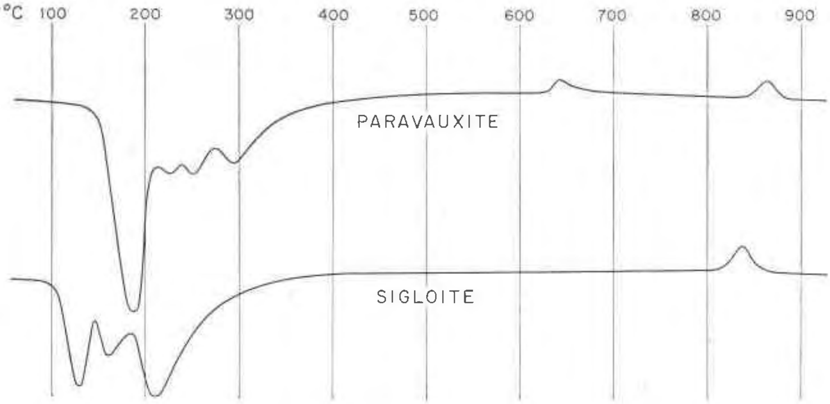

FIG. 5. Differential thermal analysis curves of paravauxite and sigloite.

TABLE 3. UNIT CELL DIMENSIONS OF SIGLOITE AND ISOSTRUCTURAL MINERALS

	Sigloite	Paravauxite	Gordonite	Laueite
a	5.26 Å	5.23 Å	5.24 Å	5.28 Å
b	10.52	10.52	10.49	10.66
c	7.06	6.96	6.96	7.14
α	106°58′	107°17′	107°25′	107°55′
β	111 30	111 24	111 04	110 59
γ	69 30	72 29	72 22	71 07
$a:b:c$	0.4990:1:0.6711	0.4971:1:0.6611	0.4990:1:0.6635	0.4953:1:0.6698
G	2.35	2.36	2.23	2.44–2.49
Ref.		Dana System 1951	Dana System 1951	Strunz 1954

TABLE 4. INDEXED *X*-RAY POWDER PATTERN OF SIGLOITE. Fe RADIATION, Mn FILTER. λ=1.9373 Å

d(meas.)	I	hkl	*d*(calc.)	*d*(meas.)	I	hkl	*d*(calc.)
9.69 Å	10	010	9.70	2.09 Å	2	$\bar{1}\bar{5}1$	2.10
6.46	9	001	6.45			$\bar{2}\bar{4}2$	2.10
5.83	2	$0\bar{1}1$	5.90			032	2.09
4.86	9	$\bar{1}\bar{1}1$	4.85			122	2.08
		020	4.85	2.04	2	211	2.03
4.79	3	110	4.78			201	2.03
4.68	4b*	100	4.70			$\bar{1}13$	2.03
3.91	4	120	3.96	1.952	3	$\bar{2}12$	1.959
3.83	3	$\bar{1}10$	3.84			$0\bar{5}1$	1.958
3.61	3	$\bar{1}11$	3.57			$\bar{1}40$	1.946
3.33	2	$\bar{1}\bar{1}2$	3.35	1.917	1	$\bar{2}20$	1.919
3.25	3	$0\bar{1}2$	3.25			$2\bar{1}1$	1.916
3.23	7	030	3.23	1.898	1	$1\bar{3}2$	1.903
		002	3.23			$\bar{2}03$	1.889
3.16	3	$0\bar{3}1$	3.13	1.868	1	231	1.870
3.09	4	130	3.08			$\bar{2}\bar{5}2$	1.870
		$1\bar{1}1$	3.08	1.806	½	$\bar{1}23$	1.808
2.99	3	$\bar{1}20$	2.99	1.761	1	051	1.765
2.89	2	012	2.90			$2\bar{2}1$	1.761
		121	2.89			$\bar{1}\bar{2}4$	1.761
2.82	6	$\bar{1}\bar{3}2$	2.81			$1\bar{1}3$	1.756
		$\bar{1}21$	2.79	1.750	2	151	1.752
		031	2.79			$\bar{1}\bar{6}1$	1.751
2.72	3	$\bar{1}12$	2.70			$\bar{1}\bar{1}4$	1.750
2.62	1	$1\bar{2}1$	2.64			250	1.747
		$\bar{2}\bar{1}1$	2.61	1.732	1	$\bar{3}\bar{2}1$	1.738
2.58	1	$\bar{2}\bar{2}1$	2.59			$\bar{3}\bar{2}2$	1.736
		$\bar{1}\bar{4}1$	2.59			$\bar{2}13$	1.733
2.56	5	$0\bar{3}2$	2.54	1.669	2		
2.39	2b	$\bar{2}\bar{1}2$	2.40	1.626	1		
		220	2.39	1.615	3		
		$\bar{1}\bar{4}2$	2.38	1.570	1		
2.34	2b	200	2.35	1.524	2		
		$\bar{1}\bar{1}3$	2.33	1.498	1		
2.27	3	$\bar{1}22$	2.28	1.464	½		
2.12	3	$0\bar{2}3$	2.12	1.407	½		
				1.358	½		
				1.292	½		

* b=broad.

Table 5. Sigloite *d*-Spacings Compared with Isostructural Minerals.
1 and 4—Fe Radiation, Mn Filter; 2 and 3—Cu Radiation, Ni Filter

1. Sigloite		2. Paravauxite		3. Gordonite		4. Laueite	
d	I	*d*	I	*d*	I	*d*	I
9.69 Å	10	9.82 Å	10	9.78 Å	10	9.91 Å	10
6.46	9	6.38	9	6.32	5	6.57	7
5.83	2	5.92	1	4.86	3	6.17	2
4.86	9	4.91	4	4.76	5	4.95	8
4.79	3	4.20	9	4.50	1	4.27	1
4.68	4b*	4.15	½	4.15	1	4.15	1
3.91	4	3.91	3	3.94	3	4.02	5
3.83	3	3.61	2	3.85	2	3.93	5
3.61	3	3.25	1	3.61	2	3.70	2
3.33	2	3.18	8	3.17	8	3.42	3
3.25	3	3.08	4	3.07	5	3.28	9
3.23	7	2.85	6	3.01	2	3.12	5
3.16	3	2.70	2	2.94	1	3.07	3
3.09	4	2.58	5	2.83	7	2.93	1
2.99	3	2.47	2	2.56	6	2.88	6
2.89	2	2.38	1	2.45	3b	2.77	1
2.82	6	2.35	1	2.39	4	2.62	5
2.72	3	2.27	2	2.33	2	2.54	1
2.62	1	2.12	1	2.27	3	2.51	2
2.58	1	2.01	2	2.11	3	2.47	2b
2.56	5	1.973	1	1.997	4	2.43	1
2.39	2b	1.937	1	1.964	2	2.40	4
2.34	2b	1.807	1b	1.929	2	2.34	1b
2.27	3	1.758	1	1.797	1b	2.18	3
2.12	3	1.736	1	1.742	1b	2.15	1
2.09	2	1.665	1b	1.653	1b	2.12	2
2.04	2	1.635	1	1.624	4	2.09	3
1.952	3	1.567	1	1.587	2b	2.02	4
1.917	1			1.563	2	2.00	1
1.898	1			1.538	2	1.969	2b
1.868	1			1.487	1	1.897	1b
1.806	½			1.442	1	1.848	3
1.761	1			1.389	1	1.805	2
1.750	2			1.356	1	1.769	1
1.732	1			1.334	1	1.746	1
1.669	2			1.303	2	1.717	1b
1.626	1			1.284	1	1.687	2b
1.615	3			1.249	1b	1.649	2b
1.570	1					1.620	2b

* b = broad.

graph of this material shows it to be dominantly hematite but with smaller amounts of berlinite, $AlPO_4$. The berlinite was confirmed by optical examination.

X-RAY STUDY

Precession and Weissenberg *x*-ray photographs taken of sigloite crystals rotating about the *a* and *c* axes yielded the data given for that mineral in Table 3. Data for the following isostructural minerals are also given in the table:

Sigloite, $(Fe^{3+}Fe^{2+})Al_2(PO_4)_2(O, OH)_2 \cdot 8H_2O$
Gordonite, $MgAl_2(PO_4)_2(OH)_2 \cdot 8H_2O$
Paravauxite, $Fe^{2+}Al_2(PO_4)_2(OH)_2 \cdot 8H_2O$
Laueite, $MnFe_2^{3+}(PO_4)_2(OH)_2 \cdot 8H_2O$

Table 4 lists the indexed *x*-ray powder pattern of sigloite, with calculated *d*-spacings from the parameters determined by single crystal techniques. Powder data for the isostructural minerals are listed in Table 5 for comparison. Similarities between the patterns of all four minerals are apparent, but wide differences are present in *d*-spacings, line intensities, and in omission of some lines.

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