SVABITE FROM CONTACT-METASOMATIC DEPOSITS OF

SIBERIA AND THE URALS[1]

S. V. Malinko, G. S. Rumyantsev and G. A. Sidorenko

All-Union Institute of Mineral Products; M. V. Lomonosov State
University, Moscow
(Presented by Academician D. S. Korzhinskiy, September 6, 1965)

Abstract: Svabite $(Ca_5[AsO_4]_3(OH, F, Cl))$ was detected in a contact-metasomatic copper deposit in the Urals in a slightly skarnified limestone. The presence of small grains of svabite in crystals of calciborite explains the appearance of a little arsenic in the chemical analyses of borates from this deposit. Definite similarities in mode of occurrence of svabite in the deposits of Siberia, the Urals and Central Asia are indicated.

Svabite $Ca_5[AsO_4]_3(OH, F, Cl)$, the arsenical counterpart of apatite, is an extremely rare mineral. Hitherto, it has been found only in three Swedish deposits (Jakobsberg mine, near Nordmarken; Harstig mine, Paisberg; Longban), in the Franklin deposit (New Jersey, USA) and in one skarn deposit in central Asia [1]. A study of two deposits in Siberia and the Urals has recently resulted in this mineral being detected here as well.

In the Siberian contact-metasomatic iron deposit, svabite is confined to zones of pyroxene-garnet and garnet-vesuvianite skarns heavily mineralized by sphalerite, where it was detected in a drill core from a depth of 41 to 254 m below the surface. In this rock svabite forms grains intergrown closely with pyroxene, vesuvianite, magnetite and later sphalerite (Fig. 1); svabite in places constitutes nearly the whole of the rock. Later alteration has resulted in the svabite being heavily szajbelyitized and brucitized.

The svabite crystals possess a prismatic habit and distinctive hexagonal outlines in cross section. Though usually colorless, they occasionally have a pale lilac tone. The specific gravity of the mineral is 3.53. In long ultraviolet and cathode rays svabite fluoresces reddish orange and pale pink, respectively. It is optically uniaxial and negative and shows straight extinction with respect to its elongation, which is negative. The refractive indices are: $\epsilon = 1.698 \pm 0.001$; $\omega = 1.716 \pm 0.001$, $\omega - \epsilon = 0.018 \pm 0.001$.

The X-ray study of svabite was performed solely by the powder method, for no single crystals of sufficient size for structural investigation could be found. The powder pattern was obtained in a RKU-14 camera ($FeK_{\alpha\beta}$ radiation, 35 kv, 12 ma). The film was measured with a geodetic ruler to within ± 0.05 mm; the relative intensity of reflections was estimated visually on the 10-point scale. A complete set of interplanar spacings for one specimen is given in Table 1. Because of its powder pattern the mineral can be assigned to the crystallochemical apatite group. Using structural type identification, it was possible to carry out comparative indexing and fix the dimensions of the hexagonal unit cell of the mineral, which proved to be typical of the As counterparts of apatite, namely: $a = 9.78 \pm 0.01$ kX, $c = 6.95 \pm 0.01$ kX, $c/a = 0.711$. The overestimated values of parameter a are due to the fact, established for the apatite-type structure, that the size of this parameter depends on the composition of the anionic part of the mineral when c is relatively constant; a increases with increasing ionic radius of the cation, be it a cation of the complex tetrahedral group or an additional anion (F, OH, Cl).

Chemical, spectral and thermal analyses were performed on the 3.35 to 3.6 S. G. fraction, isolated by centrifuging in heavy liquids a finely ground sample of svabite, sphalerite, diopside, magnetite, szajbelyite and brucite. The fraction thus isolated consisted almost entirely of svabite plus a little szajbelyite and calcite. The chemical analysis of svabite was made by K. A. Dorofeyeva and L. S. Abramova on a 2 g portion. The results of the analysis and the data of its recalculation are presented in Table 2.

The structural analogy of svabite with apatite makes it necessary to reduce the crystallochemical formula of the mineral being studied to A_5X_3Y, the form adopted for apatite, where A = Ca, Mn, Na, TR, Pb, etc., X = $(PO_4)^{5-}$, $(AsO_4)^{3-}$, $(SiO_4)^{4-}$, etc., and Y = O, OH, F, Cl, i.e., to calculate the formula from chemical data on the basis that X = 3. Since chemical analysis shows some of the arsenic to be trivalent, the general formula of the mineral can be written as:

---

[1]Translated from: Svabit iz kontaktovo-metasomaticheskikh mestorozhdeniy Sibiri i Urala. Doklady Akademii Nauk SSSR, 1966, Vol. 166, No. 5, pp. 1195-1198.
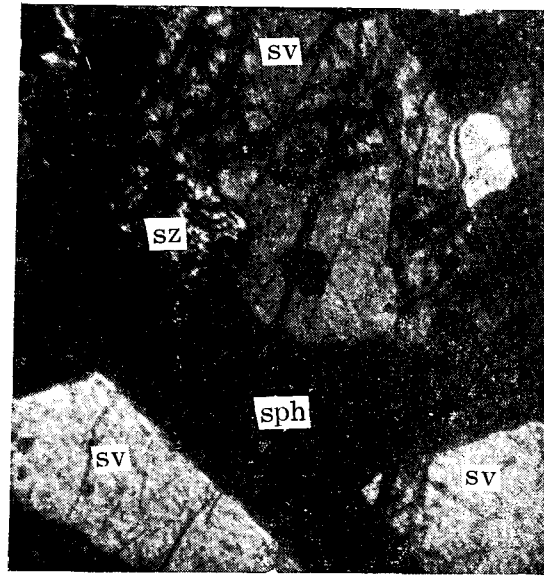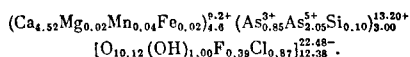
Fig. 1. Relationships between grains of svabite (sv) and sphalerite (sph). sz) szajbelyite. 72 x. Nicols +.

Table 1

hkl	Svabite from Siberia I	Svabite from Siberia d_α, kX	Svabite from central Asia I	Svabite from central Asia d_α, kX	Svabite from the Urals I	Svabite from the Urals d_α, kX
10$\bar{1}$0	4	8.414				
	1	7.312				
10$\bar{1}$1	2	5.281	1	5.28		
11$\bar{2}$0	3	4.892	2	4.88	2	4.93
11$\bar{2}$1β	3	(4.399)				
11$\bar{2}$1	7	3.983	5	3.98	7	3.997
					3	3.86
0002β	2	(3.773)				
2021	1	3.618				
1230β	1	(3.519)	4	3.53		
0002	6	3.425	5	3.44	7	3.47
12$\bar{3}$0+β	6	(3.207)			5	(3.18)
11$\bar{2}$2	4	(3.112)	4	(3.12)	4	(3.13)
21$\bar{3}$1	10	2.904	10	2.91	10	2.897
11$\bar{2}$2	9	2.834	10	2.84	10	2.82
30$\bar{3}$0	9	2.814	1	2.76		
20$\bar{2}$2	7	2.662	4	2.68	6	2.689
					1	2.59
					1	(2.46)
13$\bar{4}$1β	1	(2.450)				
13$\bar{4}$0	2	2.350	1	2.37	2	2.359
			1	2.33		
13$\bar{4}$1	5	2.226	4	2.25	5	2.21
23$\bar{5}$1β	2	(2.050)				
40$\bar{4}$1	1	2.030	3	2.07	3	2.06
22$\bar{4}$2	6	1.995	6	1.993	6	1.995
13$\bar{4}$2	2	1.949	3	1.953	2	1.940
23$\bar{5}$1	8	1.867	9	1.871	9	1.872
13$\bar{4}$3β—1124β	2	(1.810)	6	1.811		
			1	1.772		
			3	1.731	5	1.729
	3	(1.716)				
23$\bar{5}$2	5	1.696	4	1.702	6	1.690
			1	1.678		
13$\bar{4}$3, 11$\bar{2}$4	4	1.643	4	1.651	3	1.649

hkl	Svabite from Siberia I	Svabite from Siberia d_α, kX	Svabite from central Asia I	Svabite from central Asia d_α, kX	Svabite from the Urals I	Svabite from the Urals d_α, kX
42$\bar{6}$0	1	1.610				
	1	1.591				
	3	1.587	1—2	1.567	3	1.560
12$\bar{3}$4	5	1.525	4	1.528	4	1.520
	3	1.494	1	1.496		
15$\bar{6}$1; 33$\bar{6}$2	4	1.471	3	1.471	5	1.474
15$\bar{6}$3	2	(1.396)	1p	(1.395)	2	(1.395)
60$\bar{6}$1	2	1.372	1	1.369	2	1.360
25$\bar{7}$1	4	1.318	3	1.319	2	1.316
60$\bar{6}$2	2	1.295	3	1.293	3	1.297
	2	1.275				
15$\bar{6}$3	4	1.269	4—5	1.268	4	1.263
			1	1.239		
	1	1.212	1—2	1.215	2	1.211
	2	1.196	2p	1.197	2	1.195
70$\bar{7}$1; 42$\bar{6}$4	2	1.173	3	1.178	2	1.180
			2	1.152		
	4	1.147	2	1.144	3	1.145
	2	1.128	2	1.129	3	1.128
	3	1.117	3	1.119	1	1.115
	1	1.103	2	1.106		
	1	1.090				
	1	1.079				
	1	1.073				
	1	1.066	1	1.071		
	2	1.048	1	1.048	1	1.050
	2	1.040	1	1.040	1	1.043
			1	1.030	1	1.029
	5	1.025	3	1.024		
	1	1.002				
	1	0.9953				
	2	0.9913				
	1	0.9893				
	3	0.9832				
	1	0.9810				
	1	0.9788				

Table 2

Constituent	Wt.% in svabite	Molecular quantities				Wt.%, in svabite		Molecular quantities in svabite on conversion to 100%	Atomic quantities in svabite	
		total	in impurities		in svabite	after deduction of impurities	on conversion to 100%		cations	oxygen
			calcite	szaj-bel-yite						
Al_2O_3	Traces not. det.	—			—					
TiO_2	not. det.									
SiO_2	1.10	0.018			0.018	1.10	1.12	170	170 ⎫	340
As_2O_3	14.05	0.071			0.071	14.05	14.24	705	1410 ⎬ 4948	2115
As_2O_5	38.22	0.166			0.166	38.22	38.74	1684	3368 ⎭	8420
CaO	41.67	0.743	0.01		0.733	41.11	41.68	7432	7432 ⎫	7432
MgO	0.63	0.015		0.012	0.003	0.12	0.12	30	30 ⎪	30
MnO	0.41	0.006			0.006	0.41	0.42	59	59 ⎬ 7547	59
Fe_2O_3	0.21	0.001			0.001	0.21	0.21	13	26 ⎭	39
P	0.45	0.024			0.024	0.45	0.46	242		242
Cl	1.88	0.053			0.053	1.88	1.91	538		538
H_2O+	1.21	0.067		0.006	0.061	1.10	1.12	617		617
H_2O-	not. det.	—								
CO_2	0.41	0.01	0.01							
B_2O_3	0.45	0.006		0.006						
	100.59					98.65	100.00			19832
$-O = Cl_2$	0.42									
$-O = F_2$	0.19									
	99.93									

$$(Ca_{4.52}Mg_{0.02}Mn_{0.04}Fe_{0.02})^{9.2+}_{4.6}(As^{3+}_{0.85}As^{5+}_{2.05}Si_{0.10})^{13.20+}_{3.00}$$
$$[O_{10.12}(OH)_{1.00}F_{0.39}Cl_{0.87}]^{22.48-}_{12.38} .$$

The visible deficit of ions in group A does not modify the valency balance, which gives $(9.2 + 13.2)^+ - 22.48^- = \Delta = 0.08$ and may be due to the low precision of the coefficients for each element in the formula. Noteworthy in the formula of the mineral is: 1) the deficit of cations (instead of a cation total of 5, we have one of 4.6); 2) the presence of As^{3+} together with As^{5+}; 3) the distinct shortage of oxygen, the amount of which must be taken as 12 if the As-Si tetrahedra alone are to be constructed. However, all three compositional features appear to be interdependent.

In the first place, the position of As^{3+} in the structure of the mineral should be considered. Proceeding from the size of the ionic radii²

r^{3+}_{As} (0.58), r^{4+}_{As} (0.46 and r^{2-}_{O} (1.32), it can be supposed that As^{3+} is typified by a coordination number of 6 ($r_x:r_a = 0.44$) and by an octahedron as the standard polyhedral form. This is also observed in As_2O_3, the simplest compound of trivalent arsenic (although there is the arsenate trippkeïte, $CuAs_2O_4$, where the coordination number of As^{3+} equals 3). For As^{5+} $r_x:r_a$ = 0.35, so the element surrounded tetrahedrally by oxygen ions. The isomorphous replacement of As^{5+} by As^{3+} would appear to be impossible. However, previous work [3] has shown the isostructural nature of two lead arsenates:

	a. kX	c. kX	System	c/a	z
$Pb_5(AsO_4)_3Cl$	10.01	7.28	Hexagonal	0.727	2
$Pb_5(AsO_3)_3Cl$	10.21	6.98	"	0.683	2

²The ionic radii are taken from Ahrens [2].

The structure was not fully interpreted by these authors, but their analysis did suggest that there was limited isomorphism between $(AsO_4)^{3-}$ and $(AsO_3)^{3-}$.

Reverting to the crystallochemical formula of the svabite being investigated it should be noted that if there is statistical replacement of $(AsO_4)^{3-}$ by $(AsO_3)^{3-}$ and $(SiO_4)^{4-}$ the average ionic radius of the cation of the complex will be 0.494 at the As^{3+}, As^{5+} and Si^{4+} contents found. This gives $r_k:r_x = 0.374$ and thus ensures that the cation is tetrahedrally surrounded by oxygen ions.

If the tetrahedron is to be constructed and the charge maintained, the ion As^{3+} will have to be surrounded by atoms of both oxygen and hydroxyl. This would account for the high (OH) content of the mineral. However, calculations show that hydroxyl, which is able to create hydrogen bonds in the structure and can be built into the apatite structure adopted, is clearly insufficient. F can then be substituted for it, and this will isolate the anionic tetrahedra from the cation, thus decreasing their number and producing a deficit of cations. Having built F into the tetrahedra, we limit the number of Y anions to one that is quite appropriate for the apatite structure, i.e., to the number of large Cl ions available, and by the same token explain to some extent the unusual nature of the crystallochemical formula of this mineral.

The heating curve of svabite from the Siberian deposit is defined between 20 and 1000° by a total lack of thermal effects and testifies to the thermal inertia of the mineral in the interval in question. In this connection, it must be noted that the endothermal reaction at 450° on the heating curve given by G. M. Utekhin [1] and ascribed by him to svablite actually appears to belong to another mineral, probably to a hydrous arsenate developed from svabite.

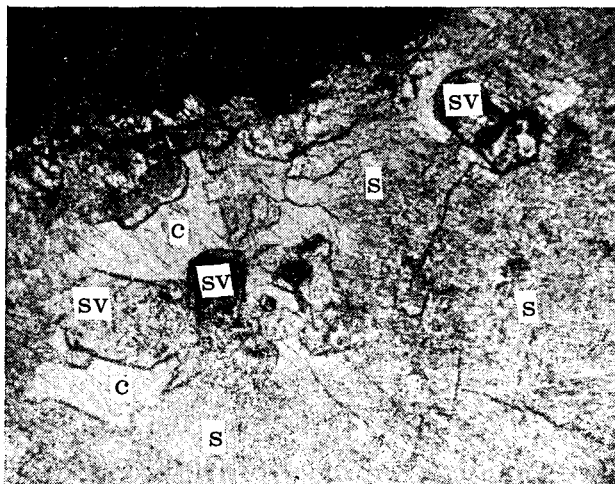In the contact-metasomatic copper deposit of the Urals, svabite was detected in weakly

Fig. 2. Crystals of svabite (sv) in calciborite (c). s) si-
birskite. 72 x. Nicols +.

skarnified limestone with rich mineralization, at
a depth of 250 to 300 m from the surface [4].
Here, the fact that small idiomorphic grains of
svabite up to 0.15 mm in size, with prismatic and
hexagonal outlines, occur sporadically in crystals
of calciborite (Fig. 2) explains the appearance of
a little arsenic in the chemical analyses of bor-
ates from this deposit [5].

The X-ray powder photographs of Ural svabite
show a diffraction pattern analogous to that ob-
tained for specimens of svabite from Siberia and
central Asia (Table 1). The refractive indices of
Ural svabites are: ϵ = 1.696 ± 0.001, ω = 1.710
± 0.001, ω - ϵ = 0.014 ± 0.001. The specific
gravity is 3.502.

The definite analogy in the mode of occurrence
of svabite in the deposits of Siberia, the Urals
and central Asia is noteworthy. Svabite is always
observed near zones of garnet-diopside skarn,
in direct association with borates, and is itself

heavily replaced by them. The question of the
interrelation of arsenic and boron in this process
requires special study.

Received September 6, 1965

REFERENCES

1. Utekhin, G. M. Zap. Vsesoyuzn. min. obshch.,
90, fasc. 6, 1961.
2. Ahrens, L. H. Geochim. et Cosmochim. Acta,
8, No. 1/2, 1955.
3. Aminoff, G. and A. L. Pargas. Geol. Fören.
i Stockholm Förhandl., 49, 438, 1927.
4. Malinko, S. V. Geol. rudn. mestorozhd.,
No. 6, 1963.
5. Malinko, S. V., N. N. Kuznetsova et al. Zap.
Vsesoyuzn. min. obshch., 92, fasc. 6, 1963.