GEOLOGISKA FÖRENINGENS

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STOCKHOLM

FÖRHANDLINGAR

FYRTIOANDRA BANDET

(ÅRGÅNGEN 1920)

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STOCKHOLM 1921
KUNGL. BOKTRYCKERIET. P. A. NORSTEDT & SÖNER
200380

Armangite, a new arsenite from Långbanshyttan.

By

G. Aminoff and R. Mauzelius.

The mineral, which is described in this note, occurs on a few specimens, obtained at Långbanshyttan by dr. G. Flink in the summer 1919. The examination proved it to be a new mineral with a surprising chemical composition, it being an arsenite of manganese. Hitherto only two arsenites are known as minerals, viz. the chloro-arsenite ecdemite from Långbanshyttan and Harstigen and the mineral trippkeite from Copiapo, which, according to a qualitative analysis by Damour, is an arsenite of copper. It is remarkable, that two other arsenites are recently found at Långbanshyttan. The result of the investigation of these two minerals is to be published by G. Flink.

The below described mineral has recieved the name *armangite*, phonetically alluding to its chief chemical components.

The crystallographical investigations have been carried out at Stockholms Högskola, the chemical analysis in the laboratory of the Geol. Survey of Sweden.

Mode of occurence. Armangite belongs to the associations of the »calcite-fissures». It occurs in a coarse-crystalline mixture of calcite and baryte, which contains the following minerals:

1. Calcite. Coarse-crystalline; also scalenohedra.
2. Baryte. » ; also crystals, thin tabular after {001}.

3. Fluorite. Large, pale green octahedra with drusy faces.

4. Hæmatite. Small, black rhombohedra.[1] Two grey-black crystals, measuring about 5 *mm*, are possibly also hæmatite. The visible side of them is flat conical without any smooth faces, a mode of development, which is sometimes observed on hæmatite crystals.

5. A brown, lamellar mineral. Optically uniaxial and negative. Exhibits some resemblance to a type of pyroaurite, occurring at Nordmarken. Of this mineral there is not material enough for a chemical analysis.

6. A sulphur-yellow, orthorhombic (?) mineral. Of this mineral extremely little occurs, but apparently the same mineral has been found later in a quantity, which may be sufficient for an analysis. The mineral resembles somewhat ecdemite.

Moreover there occur in extremely small quantity one or two other, white minerals.

The succession is difficult to determine. The earliest crystallised minerals, however, are baryte and calcite. Later than these, hæmatite and the brown, lamellar mineral have crystallised. The yellow mineral seems to be older than baryte and calcite, but younger than hæmatite and the brown, lamellar mineral. Armangite occurs partly as crystals, directly imbedded in the mixture of calcite and baryte, partly in druses in this matrix. The crystal described below is broken and afterwards cemented by calcite. The crystallisation period of armangite seems to extend over the crystallisation of all the minerals, which are associated with it.

Colour. Armangite is black with brown streak. In microscopical slices brown to yellow.

Crystal form. The mineral is generally crystalline. A few crystals, however, have been found. The best crystal, about 4 *mm* in the direction of the c-axis, was measured. Some measurements were also made on a few smaller crystals. The

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[1] Geol. För. Förh. 40 (1918), p. 427.

crystals belong to the rhombohedral-hemihedral class of the hexagonal system. The following forms were observed

		c	b	p	f
G_2	pq =	0	∞	$+1$	$+\frac{1}{2}$
	Bravais =	0001	$11\bar{2}0$	$11\bar{2}1$	$11\bar{2}2$

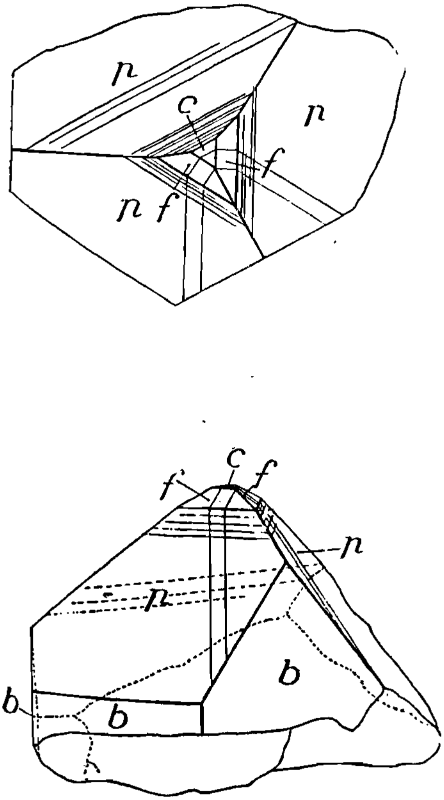

Fig. 1.

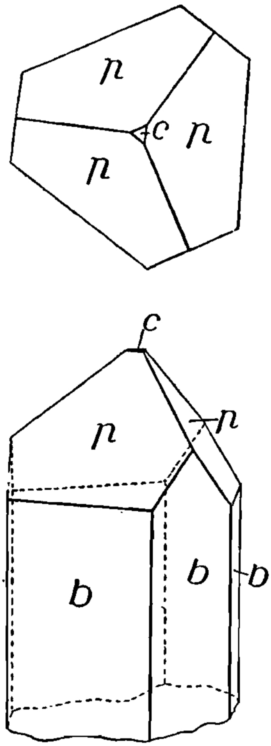

Fig. 2.

The habit is more or less pronounced prismatic. $p = +1$ is larger than $f = +\frac{1}{2}$. Fig. 1 shows the above mentioned, large crystal. Fig. 2 is a somewhat schematic drawing of one of the smaller crystals (about 1 *mm*).

For the calculation of p_0 two measurements were used from $f = + \frac{1}{2}$ on the large crystal, these measurements appearing to be the best ones. From the mean value, or $\varrho = 37° 08'$, is calculated:

$$p_0 = 0.8744$$
$$c = 1.3116$$

The reflections of $f = + \frac{1}{2}$ on the large crystal were good; the form $p = + 1$, however, the faces of which were striated || [b, p], yielded extended reflections with two stronger nodes, none of these, however, well corresponded to the angle ϱ, which is calculated from $f = + \frac{1}{2}$.

Table 1 contains the calculated angles of the observed forms.

Table 1.

Armangite. Hexagonal. Rhombohedral-hemihedral.

$c = 1.3116$	$\log c = 0.11780$	$\log a_0 = 0.12076$	$\log p_0 = 9.94171$	$a_0 = 1.3206$	$p_0 = 0.8744$

(G_1)

No.	Letters	Symb.	Miller (Bravais)	φ	ϱ	ξ_0	η_0	ξ	η	x Prisms (x : y)	y	d = tg ϱ
1	c	0	0001	—	0° 00	0° 00	0° 00	0° 00	0° 00	0	0	0
2	b	∞	$11\bar{2}0$	30° 00	90 00	90 00	90 00	30 00	60 00	0.5773	∞	∞
3	p	+ 1	$11\bar{2}1$	»	56 34	37 08	52 4$\dot{0}$	24 3$\dot{9}$	46 1$\dot{6}$	0.757$\dot{2}$	1.3116	1.5145
4	f	$+ \frac{1}{2}$	$11\bar{2}2$	»	37 08	20 44	33 1$\dot{5}$	17 34	31 3$\dot{1}$	0.3786	0.6558	0.757$\dot{2}$

The calculated and observed angles on the large crystal are given in table 2.

Table 2.

	Measured		Calculated	
	φ	ϱ	φ	ϱ
$b = 11\bar{2}0$	29° 56′	90° 04′	30° 00′	90° 00′
	88 58	89 57	90 00	»
	$\overline{29}$ 59	89 58	$\overline{30}$ 00	»
$p = 11\bar{2}1$	30 02	58 10	30 00	56 34
	30 20	53 55		
	150 42	58 39	150 00	»
	«	52 20		
	$\overline{88}$ 41	58 16	-90 00	»
	»	51 31		
$f = 11\bar{2}2$	29 36	37 00	30 00	37 08
	$\overline{88}$ 17	37 16	$\overline{90}$ 00	»

On two minute crystals we obtained for $p = +1$:

$$\left.\begin{array}{r}\varrho = 56^\circ\,07' \\ 56\ \ 49\end{array}\right\}\ 56^\circ\,28'\ (56^\circ\,34'\ \text{calc.})$$

The bad agreement between calculated and measured φ-angles in table 2 is due to the above mentioned fact, that the large crystal is broken and cemented by calcite-matrix.

Twins. On the large crystal one can observe a striation, which on the p-faces runs || the edge [b, p], on the f-faces ⊥ the zone [p, f, c] and on the face c || an edge [c, p]. The striation should be explained as lamellar twin-growth parallel — 1.

Cohesion. Hardness about 4, Cleavage, not very pronounced, parallel $c = \{0001\}$.

Optical properties. Optically uniaxial and negative. Refraction indices very high, higher than solutions of sulphur in methylene iodide (∾ 1.79), but lower than amorphous sulphur (= 1.93). Birefraction weak. No pleochroism.

Spec. gravity. (On analysed material) 4.23.

Chemical composition. The analyses (by R. MAUZELIUS) gave the following result:

Table 3.

	I	II	III	IV	Mean value	Mol. ratio
As_2O_3	43.10	—	42.74	—	42.92	0.207
Sb_2O_3	0.41	—	0.39	—	0.40	.001
PbO	0.35	—	0.30	—	0.32	.001
FeO	2.07	2.39	2.11	—	2.19	.030
MnO	45.23	44.76	45.15	—	45.06	.635
CaO	2.69	2.88	2.92	—	2.83	.051
MgO	0.46	0.50	0.51	—	0.49	.012
H_2O	—	—	—	0.71	0.71	.039
CO_2	5.08	—	—	—	5.08	.115
Insuluble	—	0.16	0.25	—	0.20	
					100.20	

To the analysis 0.5—0.8 *gr* were used.

The mineral dissolves without difficulty in hydrochloric acid, separating arsenic trioxide, which on adding water and heating is completely dissolved.

By the determination of water according to BRUSH-PENFIELD the mineral first changed its colour into grey and by higher temperatur fused to a greyish-black, porous glass.

An attempt was made to determine quantitatively the degree of oxidation of the arsenic. According to GYÖRY[1] arsenic trioxide can be determined in a solution, containing HCl by volumetric analysis with $\frac{n}{10}$ bromate of potassium and by using methyl-orange as indicator. This method, however, has never been tested in presence of other metals than alkali metals. It now proved to be necessary, by the presence of manganese, to add a considerable excess of bromate of potassium before

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[1] Zeitschr. f. anal. Chemie 32 (1893), p. 415.

the pigment was destroyed. The solution was then strongly coloured by bromine. By adding to this solution KJ and determining the free iodine with the aid of thiosulphate of natrium, values, however, were obtained, which proved to be useful for the purpose. Thus, about 0.2 *gr* in two tests gave 41.4 and 40.8 % and in a third test (on other material) 41.8 % As_2O_3.

Concerning the quality of the analysed material, the following must be said. The material was selected by the use of a pocket lens to a size of the grains of 0.5 — 0.2 *mm*. Hereby a material was obtained, which at the first sight seemed rather satisfactory. Microscopically tested, howevor, after being crushed, the material was shown to contain a considerable amount of calcite or a calcite-like mineral, often in so small dispersion that a further separation by heavy liquids seemed to be impossible. The portion of the material, which by crushing had become smaller than 0.2 *mm*, was also separated by methylene iodide of sp. grav. 3.33. Hereby much calcite was separated, but the heavier material still contained a great deal of a calcite-like mineral, also in small grains. Repeated separation did not improve the result.

The analysis shows an amount of 5 % CO_2 in the analysed material. Does any part of this enter in the composition of the mineral?

From the material, which was analysed, some tens of grains (about 0.5 *mm*) were selected under a pocket lens and were put into hydrochloric acid one after another. Hereby doubtful grains developed richly carbon dioxide and were divided into smaller grains, which afterwards were dissolved. Other grains, however, which seemed to be quite homogeneous, developed CO_2 from some corners and edges and also, as the decomposition advanced, from their inner parts, while the chief part of the grain seemed to dissolve without any development of CO_2. No grain, however, was found, which did not develope some bubble of CO_2.

From these tests the conclusion has been drawn, that the chief part of the material does not contain any amount of CO_2 worth mentioning. The amount of CO_2, however, is greater than corresponds to the amounts of CaO and MgO. Thus, the material must contain besides calcite some carbonate of manganese (and iron?). This conclusion is to some extent supported by the behaviour to methylene iodide, which indicates the presence of a carbonate with higher sp. grav. than calcite.

Concerning the degree of oxidation of the iron no attempt has been made to determine it on account of the presence of arsenic trioxide. The iron has been supposed to be present as ferrous iron. A small part of it, however, may be present as ferric iron, the solution of the mineral in HCl already from the beginning being yellow. This fact may be connected with the presence of the grumsy parts, which sometimes are to be seen in the microscopical slices.

According to what has been said above, the analysis is calculated as follows:

$$As_2O_3 : RO : CO_2 = 0.208 : 0.768 : 0.115$$

If a quantity of RO, corresponding to CO_2, is subtracted, there remains:

$$As_2O_3 : RO = 0.208 : 0.653 = 1 : 3.14,$$

or, neglecting the amount of water,

$$As_2O_3 : RO = 0.208 : 0.614 = 1 : 2.95$$

Judging from the character of the material, undoubtedly at least a part of the water must belong to the mineral, but a part of it can also with some probability be considered to originate from the above mentioned, grumsy portions, which occur in fissures and possibly consist of hydrate of ferric iron. Thus we can put:

$$As_2O_3 : RO = 1 : 3$$

and the mineral can be considered as an ortho-arsenite of manganese, $Mn_3(AsO_3)_2$, with a small part of the manganese substituted by hydrogene.

The carbonate, or better the mixture of carbonates, which is found in the analysed material, according to this interpretation is composed of

MnO	3.69
CaO	2.83
MgO	0.49
CO_2	5.08
	12.09

Mineralogical institute of the University of Stockholm. Aug. 1920.