ON SYNADELPHITE AND PLUMBOSYNADELPHITE

CORNELIUS S. HURLBUT, JR., *Harvard University, Cambridge, Mass.*

IDENTITY OF SYNADELPHITE AND ALLODELPHITE

Synadelphite, essentially a hydrous arsenate of manganese and aluminum, was described as a new species from Nordmark, Sweden, by Sjögren (1884 A). The description of the new species was extended and modified by Sjögren (1884 B; 1885) and Hamberg (1889), the crystal system being variously given as tetragonal, monoclinic and orthorhombic.

Recently Quensel and von Eckermann (1930) described a mineral from Långban, Sweden, which they regarded as a new species and named allodelphite in allusion to the recognized similarity to synadelphite. According to the published descriptions, the two minerals are similar in color, luster and specific gravity; they agree in habit and form; both have slightly oblique extinction; and on x-ray powder photographs Aminoff (Quensel and von Eckermann, 1930, p. 643) found that "the lines on the photograms were identical both regarding position and intensity." Chemically the Långban mineral differed from the Nordmark material mainly in carrying 6.23 per cent of silica, which constituent was not reported in the older species; and it was principally on this difference that allodelphite was believed to be a distinct species.

To test this chemical difference an analysis was made by F. A. Gonyer on material from the collection of Långban minerals made by Flink (1926) and acquired some years ago by the Harvard Mineralogical Museum. The specimen used bears Flink's unidentified species number 325, the same number as that attached to the material analyzed as allodelphite by Almström (Quensel and von Eckermann, 1930).[1] The new analysis, as given and discussed later, shows only 1.45 per cent SiO_2. Thus the principal ground for regarding allodelphite as a distinct species proves to be false, and we are forced to conclude that the material to which the later name was attached agrees in all essentials with the described characters of synadelphite. This conclusion is confirmed by an examination of several specimens of typical synadelphite from Nordmark which showed crystallographic, physical and optical properties identical with those of the Långban material.

[1] Dr. Quensel has been kind enough to send a specimen of the Långban mineral described as allodelphite. It has arrived just as this paper is about to go to press. Examination of it shows that it agrees in all particulars with the material in the Harvard collection bearing Flink's No. 325.

Synadelphite from Långban

Several years ago Professor Palache measured some crystals (Flink's No. 325) from Långban, and found them to agree in form with allodelphite of Quensel and von Eckermann (1930). A microscopic examination of the crystals by Dr. Berman disclosed the fact that, instead of being homogeneous, they were made up of a nearly colorless interior with a red coating, which appears to be a variety of the material forming the central core. Because this fact had apparently been overlooked by Quensel and von Eckermann, a more complete study of the mineral was undertaken.

Morphology. The Långban crystals are small (1–3 mm.), short, striated prisms of orthorhombic appearance with simple terminations. A typical crystal (Fig. 1) has exactly the appearance of the crystal of synadelphite figured by Sjögren (1884 B; 1885). Taking the vertical prism as $\{110\}$ and the domatic prism as $\{011\}$, the observed forms are $b\{010\}$, $m\{110\}$, $d\{011\}$, $p\{121\}$, of which m and d are habitually large, b and p narrow. Two-circle measurements on ten crystals are summarized in Table 1; these lead to the elements and calculated angles given in Table 2.

Table 1. Synadelphite: Two-Circle Measurements of Ten Crystals

Forms	No. of faces	Measured ϕ	Measured ρ	Mean ϕ	Mean ρ	Calculated ϕ	Calculated ρ
b 010	13	—	89°57′–90°05′	0°00′	90°01′	0°00′	90°00′
m 110	25	61°39′–63°11′	89°57′–90°05′	62°01′	90°02′	61°56′	90°00′
d 011	10	0 00 – 0 01	29 31 –30 29	0 00	30 30	0 00	30 20
p 121	28	43 08 –43 41	57 40 –58 07	43 21	57 58	43 13	58 02

Table 2. Synadelphite: Angle-Table

$a:b:c=0.5333:1:0.5851$ $\quad p_0:q_0:r_0=1.0970:0.5851:1$

$q_1:r_1:p_1=0.5333:0.9598:1$ $\quad r_2:p_2:q_2=1.7094:1.8751:1$

Forms	ϕ	$\rho=C$	ϕ_1	$\rho_1=A$	ϕ_2	$\rho_2=B$
b 010	0°00′	90°00′	90°00′	90°00′	—	0°00′
m 110	61 56	90 00	90 00	28 04	0°00′	61 56
d 011	0 00	30 03	30 30	90 00	90 00	59 30
p 121	43 13	58 02	49 30	54 30	42 12	51 51

The adopted morphological lattice, which agrees with the structural lattice as determined later, is different from those chosen by the previous observers whose elements and symbols may be transformed to the new setting by the determinants:

Quensel & von Eckermann to Hurlbut: 010/200/001
Sjögren to Hurlbut: 001/200/010

Due, perhaps, to the similarity in the angles *mm*, *dd*, Sjögren's symbols are evidently in error in that the indices k and l require to be inter-

changed. The transformation given applies to Sjögren's uncorrected indices. The fundamental angles of the previous workers are compared with the new measurements in Table 3, which shows that the minerals named synadelphite and allodelphite are morphologically alike.

TABLE 3. SYNADELPHITE: MEASURED ANGLES

Sjögren		Quensel and v. Eckermann	Hurlbut
Original	Corrected		
$(100):(120)=(100):(102)=59°46\frac{1}{2}'$		$ao=(100):(102)=59°16'$	$bd=(010):(011)=59°40'$
$(100):(102)=(100):(120)=61°50'$		$ai=(100):(120)=62°13'$	$bm=(010):(110)=61°56'$

Physical Properties. Megascopically, synadelphite appears to be a red or dark brown mineral, and as such it has been described. However, examined microscopically one can distinguish a nearly colorless interior coated with a thin red film. The mineral, therefore, should be described as pale brown or colorless with a red coating of different material. An imperfect cleavage is present parallel to (010). The specific gravity of the mineral free of coating, as determined by suspension in Clerici solution, is 3.57.

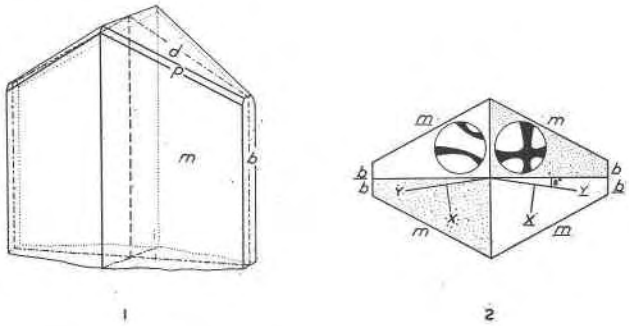

FIG. 1. Synadelphite. Pseudo-orthorhombic crystal of typical habit.

FIG. 2. Synadelphite. Basal section of a fourling twinned by reflection in (100) and (010). When one pair of parallel individuals are at extinction (stippled), the interference figures in a pair of twinned individuals are as indicated.

Optical Properties. Morphologically synadelphite appears to be orthorhombic, but in polarized light the crystals extinguish at a small angle against the vertical axis. Quensel and von Eckermann (1930, p. 640) state, "An angle of extinction in the zone of elongation not exceeding 2° to 3° has been observed in some crystals, but is generally wanting." Hamberg (1889, p. 223) also observed an extinction angle but, nevertheless, called the mineral orthorhombic. Basal sections observed in polarized light show that each crystal is made up of two individuals twinned by reflection in (100) and (010), thus giving a fourling in which the adjacent parts are in twinned relation, while the diagonally opposite

parts are in parallel position (Fig. 2). Hamberg (1889, p. 223) also noted such an appearance but did not recognize it as twinning. If one of the principal optical directions coincided with the vertical axis, the observed twinning would indicate a pseudo-orthorhombic monoclinic lattice with the chosen vertical axis as [010]. This is not the case, since on (100), $Z':c[001]=8°$ and on (010), $Z':c[001]=8°$. The lattice is therefore triclinic, twinned by reflection in the nearly rectangular axial planes (100), (010). The optical orientation is shown in the stereographic projection (Fig. 3). The eccentric nature of the interference figures obtained on a twinned basal section is shown in Fig. 2. Since the planes (011) and (010) show no sensible re-entrant angles, the triclinic axial angles cannot differ from 90° by more than a few minutes of arc.

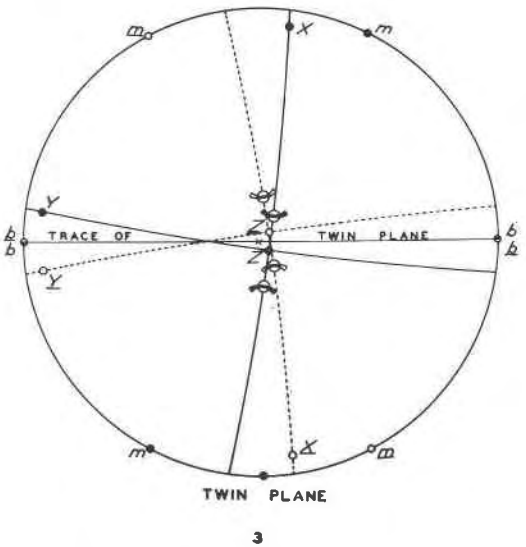

FIG. 3. Synadelphite. Triclinic optical orientation.

The optical elements of synadelphite are as follows:

	Orientation		n(Na)	
	ϕ	ρ		
X (colorless)	− 8°	86°	1.750	Positive
Y (colorless)	−172°	86°	1.751	2V=37°
Z (light brown)	42°	7°	1.761	$r>v$

Quensel and von Eckermann obtained their values for the refractive indices by the method of minimum deviation, which no doubt accounts for the lack of agreement with those given above. In using a crystal in this manner, the light would pass first through the red coating into the synadelphite, then from one twin individual into the other, and finally

emerge through the coating. Any value thus obtained would be false.

X-Ray Measurements. With the knowledge that all of the crystals of synadelphite are twinned, great care was taken in breaking out a portion of a single individual for x-ray study. A rotation photograph and Weissenberg photographs of the zero and first layer lines were made with c[001] as the axis of rotation. Similar photographs were also taken using a twin crystal; these were found to be indistinguishable from those of the single individual. The two sets of x-ray photographs confirm the morphological conclusion that the crystal lattice is sensibly orthorhombic, since there is no visible separation of the x-ray diffractions due to twinning.

The dimensions of the unit cell are:

$$a_0 = 9.91\text{Å},\ b_0 = 18.70\text{Å},\ c_0 = 10.65\text{Å}$$

giving $a_0 : b_0 : c_0 = 0.5321 : 1 : 0.5695$, which compares with the morphological axial ratio: $a : b : c = 0.5333 : 1 : 0.5851$. The volume of the unit cell is 1962 cubic Å. The density of synadelphite free of the red coating is 3.57. Hence the molecular weight of the unit cell $M = 4246$.

Composition. The existing analyses of synadelphite and allodelphite are listed below, together with a new analysis of synadelphite from Långban.

TABLE 4. SYNADELPHITE AND ALLODELPHITE ANALYSES

	1	2	3	4
SiO_2	—	—	6.23	1.45
As_2O_5	29.31	32.43	21.91	26.89
As_2O_3	—	—	0.62	—
Sb_2O_5	—	—	0.15	—
Mn_2O_3	11.79	—	—	—
Al_2O_3	6.16	—	1.50	1.41
Fe_2O_3	1.23	—	0.98	0.86
FeO	—	0.17	—	—
MnO	35.71	56.43	50.30	53.10
CaO	3.76	0.28	1.10	1.55
MgO	2.19	—	6.22	4.62
PbO	—	—	0.39	—
K_2O	—	—	0.74	0.79
Na_2O	—	—	0.53	0.62
H_2O	11.39	11.33	8.82	8.52
Insol.	—	0.19	—	—
	101.54	100.83	99.49	99.81

1. Synadelphite, Nordmark, Sweden; anal. A. Sjögren, in Sjögren (1885).

2. Synadelphite, Nordmark, Sweden; anal. Blix, in Quensel and von Eckermann (1930).

3. Allodelphite, Långban, Sweden (Flink's No. 325); anal. Almström, in Quensel and von Eckermann (1930).

4. Synadelphite, Långban, Sweden (Flink's No. 325), fresh interior of crystals; anal. F. A. Gonyer.

Analyses 1 and 2 were presumably made on the same material; 3 and 4 were made on samples bearing the same specimen number. Since the results all differ considerably, it would appear that the values given were somewhat influenced by impurity of material and analytical difficulties. The most notable difference lies in the SiO_2 values in the two analyses of material from Flink's Långban specimens. We are obliged to conclude that the high value reported by Almström is an error and that, therefore, the main chemical difference between synadelphite and allodelphite is fictitious.

Table 5 gives the atomic content of the unit cell of synadelphite from the new analysis (anal. 4, Table 4, reduced to 100 per cent) and the molecular weight, $M = 4246$.

TABLE 5. SYNADELPHITE: CONTENT OF THE UNIT CELL

		Molecular Ratio		Atoms per Unit Cell	
SiO_2	1.45	0.0241	Si	1.0	1.0
As_2O_5	26.94	0.1172	As	10.0	10.0
Al_2O_3	1.41	0.0138	Al	1.2	1.7
Fe_2O_3	0.86	0.0054	Fe'''	0.5	
MnO	53.20	0.7500	Mn	31.8	
CaO	1.56	0.0278	Ca	1.2	
MgO	4.63	0.1148	Mg	4.9	39.4
K_2O	0.79	0.0084	K	0.7	
Na_2O	0.62	0.0100	Na	0.8	
H_2O	8.50	0.4744	H	40.3	40.3
	100.00		O	88.4	

Neglecting SiO_2 as an impurity, the numbers in the last column give the content of the unit cell as: $R''_{40}(AsO_4)_{10}(OH)_{50}$ or $10[R''_4(AsO_4)(OH)_5]$, where R = Mn, Ca, Mg, K, Na, Fe''', Al. The composition thus written assumes more water than was found, but it appears to be demanded by valency considerations. From analysis 3, Table 4, Quensel and von Eckermann obtained a similar molecular ratio and attempted to balance the formula by recalculating all the arsenic as trivalent and part of the manganese as trivalent. Since these elements are not found in that state, this does not seem as reasonable as assuming more water. Moreover, from the analysis given by Quensel and von Eckermann, Machatschki (1931) in a discussion of allodelphite and synadelphite likewise assumed additional water to obtain a balanced formula.

PLUMBOSYNADELPHITE

As previously mentioned, a red material of variable thickness is to be found coating the crystals of synadelphite from both Nordmark and Långban. On examination, the coating proved to be a new variety, to

which the name plumbosynadelphite is given. This mineral has a high luster, a hardness of 4 and a density of 3.79.

The optical elements of plumbosynadelphite are as follows:

	n(Na)	
X (light brown)	1.851	Positive
Y (brown)	1.864	$2V = 40°$
Z (dark red-brown)	1.894	

Due to the lack of crystals the crystal system and optical orientation were not obtainable.

It is found that the above-listed optical properties are in good agreement with those given for synadelphite by Larsen and Berman (1934). The specimen of synadelphite, No. 84331 of the U. S. National Museum, on which Larsen originally worked out the optics, was loaned to the writer through the courtesy of Dr. Wm. F. Foshag. Examination of it showed that the synadelphite is covered by an extremely thick layer of plumbosynadelphite, and it was apparently on this coating material that the published optical data were obtained.

X-ray powder photographs of both synadelphite and plumbosynadelphite were taken and a comparison of them shows considerable differences, although several of the stronger lines are similar in both position and intensity.

Enough plumbosynadelphite was separated for a chemical analysis. Because of the extremely fine grinding necessary to separate it from the synadelphite, the separation was not complete, and it is estimated that the sample analyzed had 10% synadelphite as an impurity.

Analysis of Plumbosynadelphite by F. A. Gonyer

SiO_2	0.63
As_2O_5	26.18
Fe_2O_3	0.48
MnO	52.27
CaO	1.25
MgO	5.89
PbO	3.24
K_2O	0.70
Na_2O	0.59
H_2O	8.74
	99.97

The above analysis is very similar to that of synadelphite, the only important difference being the presence of 3.24% PbO. Since in specific gravity, optical properties, and structure, as shown by x-ray powder photographs, the coating is different from synadelphite, the variety name plumbosynadelphite is proposed for it. With no lead present in

the synadelphite itself, it is reasonable to assume that the coating is not merely a surface oxidation of the manganese, as suggested by Sjögren (1885, p. 155), but an alteration accompanied by the deposition of material. Another explanation of the universal coating on synadelphite may be a zoning similar to that found in the plagioclase feldspars, the solutions toward the end of the period of deposition having been richer in lead.

Acknowledgments

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