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Sulphosalts of the plagionite group

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SUMMARY. Three of the members of the plagionite group, fülöppite $Pb_3Sb_8S_{15}$, plagionite $Pb_5Sb_8S_{17}$, and semseyite $Pb_9Sb_8S_{21}$, show linear correlations of cell volume and density versus $PbS:Sb_2S_3$ mol ratios. This relationship can be used better to define the nature of the fourth member of the group, heteromorphite, $Pb_7Sb_8S_{19}$. The cell dimensions derived for heteromorphite are *a* 13·60, *b* 11·93, *c* 21·22 Å, β 90° 50′.

SULPHOSALTS are difficult minerals to study, partly because of their physical, compositional, and structural similarity. In detail, however, these similarities are potentially useful and have been exploited to show, for example, that the densities of most lead sulphantimonides and lead sulpharsenides vary linearly with changes in PbS/Sb and PbS/As ratios (Jambor, 1967). The plagionite group of lead sulphantimonides is particularly amenable to analysis of such group relationships because it contains three well-defined members and a fourth (heteromorphite), which alone has not been previously studied by single crystal methods.

The plagionite group. The three well-defined members of the group are fülöppite, $Pb_3Sb_8S_{15}$; plagionite, $Pb_5Sb_8S_{17}$; and semseyite, $Pb_9Sb_8S_{21}$. The fourth member, heteromorphite, is believed to have the composition $Pb_7Sb_8S_{19}$. The group thus shows a systematic variation in $PbS:Sb_2S_3$ values, that is, 3:4, 5:4, 7:4, and 9:4. Nuffield and Peacock (1945) noted that the specific gravities of the minerals increase in a roughly linear manner in keeping with the regular increment of PbS.

The minerals of the plagionite group are monoclinic, space group *C*2/*c*. For fülöppite, Nuffield (1946) obtained *a* 13·36, *b* 11·67, *c* 16·88 kX, β 94° 41′. From the same specimen (Nagybanya, Romania; ROM M19239), the present writer obtained the X-ray powder data given in table I. The cell dimensions, which were calculated from the powder pattern and are in excellent agreement with the earlier work, yield a cell volume of 2645 Å^3.

X-ray powder data for semseyite (Kisbanya; National Mineral Collection, Canada) and plagionite (Wolfsberg, Germany; National Mineral Collection, Canada) are given in tables II and III. Cell dimensions calculated from these patterns are in excellent agreement with the single crystal data of Nuffield and Peacock (1945).

The calculated cell volumes and the $PbS:Sb_2S_3$ ratios of fülöppite, plagionite, and semseyite vary linearly, as is shown in fig. 1. From the proposed chemical composition of heteromorphite and fig. 1, it is evident that the cell volume of this mineral should be approximately 3440 Å^3.

The measured and calculated densities of the plagionite group minerals are given in table IV. A direct linear relationship exists between composition and density as

shown in fig. 2. From this relationship, it is evident that heteromorphite should have a density of about 5·80 g/cm³; using the predicted cell volume of 3440 Å³, the calculated density is 5·86. Measured values given in Palache, Berman, and Frondel (1944) range from 5·59 to 5·73, and a new determination by Mozgova *et al.* (1967) gave 5·79 g/cm³.

TABLE I. *Fülöppite X-ray powder data; 114·6-mm camera,* Cu-*Kα radiation. Indexed with a* 13·41, *b* 11·71, *c* 16·90, *β* 94° 43′, *space group* $C2/c$, $V = 2645$ Å³

I	d_{meas}	d_{calc}	hkl	I	d_{meas}	I	d_{meas}
½	8·42 Å	8·42 Å	002	1	2·857	2	2·049
5	6·25	6·26	$\bar{1}12$	8	2·822	1	2·026
<½	5·96	5·93	112	7	2·749	<½	2·019
2	5·53	5·53	021	<½	2·727	3	1·991
2	4·85	4·86	$\bar{1}13$	2	2·686	<½	1·973
<½	4·32	4·32	$\bar{2}21$	2	2·662	½	1·941
<½	4·22	4·21	004	1	2·611	1	1·907
1	4·16	4·16	310	2	2·516	2	1·889
½	4·05	4·05	023	<½	2·453	1	1·865
<½	3·98	3·97	311	1	2·428	2	1·840
10	3·885	3·882	$\bar{1}14$	<½	2·406	½	1·814
½	3·813	3·818	222	<½	2·353	1	1·795
3	3·748	3·747	130	1	2·291	1	1·762
4	3·676	3·676	$\bar{1}31$		2·282	1	1·743
5	3·629	3·640	131	½	2·246	½	1·724
		3·623	312	½	2·232	<½	1·710
1	3·559	3·560	$\bar{2}23$	4	2·208	1	1·690
5	3·377	3·377	223	½	2·169		
7	3·227	3·227	313	1	2·148		
9	3·203	3·205	$\bar{1}15$	5	2·125		
5	3·131	3·130	$\bar{2}24$	<½	2·101		
<½	3·093	3·091	115	½	2·090		
2	2·965	2·964	224	½	2·063		
8	2·919	2·919	$\bar{3}31$				

Cell dimensions of heteromorphite. Although there is a direct relationship of cell volume versus composition for the group, the individual parameters contributing to the cell volume do not vary linearly with composition. As can be seen from the data in table V, there is nevertheless a general increase in *a*, *b*, and *c* with increasing proportion of lead. Thus, heteromorphite would be expected to have $a \approx 13{\cdot}4$, $b \approx 11{\cdot}9$, and *c* less certain, but ≈ 22 Å. Although *β* does not show a consistent trend, the parameter $c \sin \beta$ appears to change with more regularity and can be predicted to be about 21·3 Å for heteromorphite.

The above *a*, *b*, and $c \sin \beta$ values yield a volume of 3432 Å³, comparable to the 3440 Å³ obtained from fig. 1. Cell dimensions for hypothetical members of the plagionite group, not yet known as minerals, can be derived in the same manner.

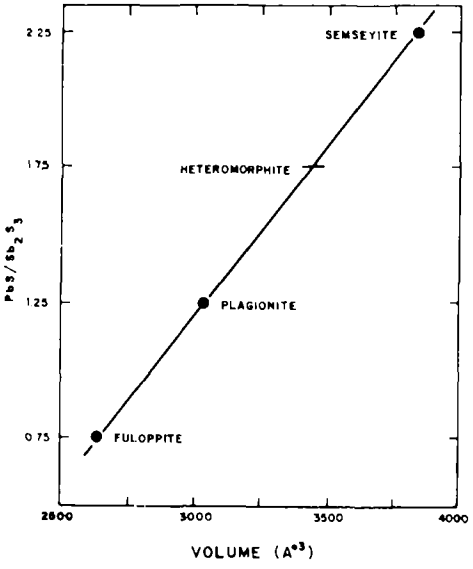
Natural heteromorphite. The difficulties surrounding the earlier X-ray work on the enigmatic species heteromorphite are summarized in Palache *et al.* (1944). An X-ray powder pattern of heteromorphite was recently published by Mozgova *et al.* (1967),

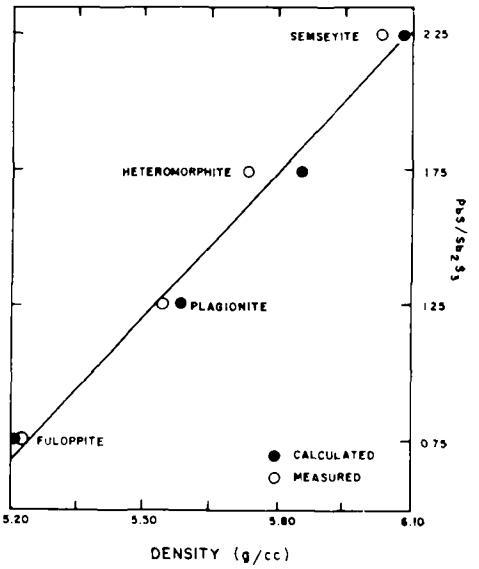
TABLE II. *Plagionite X-ray powder data;* 114·6-*mm camera,* Cu-*K*α *radiation. Indexed with a* 13·47, *b* 11·82, *c* 19·99 Å, *β* 107° 20′, *space group* $C2/c$, $V = 3038$ Å^3

I	d_{meas}	d_{calc}	hkl	I	d_{meas}	d_{calc}	hkl	I	d_{meas}
2	9·55 Å	9·54 Å	002	9	2·911	2·906	$\bar{4}21$	½	2·127
1	7·37	7·38	111	½	2·877	2·875	$\bar{4}23$	½	2·080
½	6·25	6·27	$\bar{2}02$	2	2·792	2·801	026	2	2·034
4	5·87	5·87	112			2·785	331	2	2·000
½	5·66	5·65	021	1	2·771	2·768	$\bar{4}24$	½	1·971
<½	4·60	4·59	$\bar{1}14$	1	2·688	2·685	240	1	1·947
<½	4·44	4·44	$\bar{2}21$			2·680	043	<½	1·919
3	4·33	4·33	023	6	2·622	several possibilities		2B	1·896
1B	4·18	4·19	$\bar{3}11$	<½	2·584	2·591	$\bar{5}11$	2	1·866
<½	4·07	4·07	221	<½	2·575	2·573	$\bar{3}35$	½	1·844
<½	3·99	3·99	$\bar{2}23$			2·571	135	<½	1·824
<½	3·936	3·939	$\bar{3}13$	½	2·548	several possibilities		½	1·809
8	3·870	3·867	114	2	2·490	2·490	$\bar{2}08$	1	1·786
7	3·771	3·767	130	<½	2·367	2·370	243	½	1·771
½	3·717	3·712	024			2·363	$\bar{3}18$	½	1·756
5	3·613	3·618	$\bar{3}14$			2·362	423	<½	1·740
		3·613	$\bar{1}32$			2·337	$\bar{2}45$	<½	1·726
½	3·400	3·404	132	½	2·338	2·337	045	1B	1·698
1	3·366	3·365	$\bar{4}02$			2·332	136	½	1·680
3	3·303	3·295	223	1	2·226	several possibilities			1·669
9	3·263	3·265	$\bar{3}15$	½	2·203	2·202	$\bar{5}31$	<½	1·646
		3·263	$\bar{2}06$			2·199	$\bar{4}43$	<½	1·633
		3·261	115	1	2·164	2·167	046	½B	1·608
10	3·211	3·215	400			2·163	$\bar{1}19$	<½	1·585
½	2·966	2·958	$\bar{3}31$	4	2·141	2·143	600		
4	2·934	2·934	224			2·136	$\bar{1}54$		

TABLE III. *Semseyite X-ray powder data;* 114·6-*mm camera,* Cu-*K*α *radiation. Indexed with a* 13·64, *b* 11·96, *c* 24·46 Å, *β* 105° 52′, *space group* $C2/c$, $V = 3838$ Å^3

I	d_{meas}	d_{calc}	hkl	I	d_{meas}	d_{calc}	hkl	I	d_{meas}	I	d_{meas}
2	11·69 Å	11·76 Å	002	4	3·025	3·023	314	½	2·064	<½	1·560
<½	8·85	8·84	110	<½	2·988	2·990	040	2	2·053	<½	1·550
1	7·80	7·81	111	9	2·949	2·950	227	½	2·026	<½	1·533
3	6·53	6·56	200			2·942	$\bar{3}33$	1	2·001	<½	1·514
		6·51	112	8	2·857	2·853	334	½	1·971	<½	1·499
2	5·37	5·39	113	4	2·770	2·776	421		1·962	½	1·482
		5·37	$\bar{1}14$			2·763	315	3	1·915		1·477
<½	5·13	5·13	$\bar{2}04$	2	2·727	2·721	240	1	1·889	<½	1·463
2	4·52	4·51	$\bar{1}15$			2·719	$\bar{2}42$	1	1·857	<½	1·452
4	4·22	4·23	$\bar{3}11$	4	2·690	2·687	$\bar{2}28$		1·850	<½	1·442
6	3·88	3·88	311	½	2·650	2·651	422	<½	1·828	½	1·430
9	3·81	3·81	130	<½	2·587	2·587	242	1	1·808	½	1·412
3	3·72	3·72	131	<½	2·523	2·524	045	½	1·790	<½	1·399
3	3·58	3·58	223	<½	2·489	2·485	243	1	1·767	<½	1·390
	3·55	3·55	132	3	2·449	2·446	208	<½	1·741	<½	1·370
		3·54	$\bar{1}33$	½	2·361	2·365	$\bar{5}17$	1	1·723	½	1·359
2	3·408	3·410	$\bar{4}02$	4	2·251	2·248	$\bar{5}33$	½	1·709	<½	1·343
7	3·351	3·354	$\bar{1}17$	3	2·226	2·227	153	1	1·688	½	1·325
2	3·306	3·306	313	<½	2·185	—	—	1B	1·634	<½	1·310
10	3·260	3·270	$\bar{4}04$	5	2·152	2·151	154	½	1·600	<½	1·288
		3·257	224	1	2·096	2·093	$\bar{6}21$	½	1·578	½	1·281





FIGS. 1 and 2: Fig. 1 (left). Relationship of unit cell volume and PbS/Sb_2S_3 mol ratios of the members of the plagionite group. Fig. 2 (right). Relationship of density and PbS/Sb_2S_3 mol ratios of the members of the plagionite group.

TABLE IV. *Compositions, cell volumes, and densities of the members of the plagionite group*

	$PbS:Sb_2S_3$	V	Density		Ref. for measured density
			from *V*	obs.	
Fülöppite	3:4	2645 Å³	5·21	5·22	Nuffield (1946)
Plagionite	5:4	3038	5·58	5·54	Nuffield and Peacock (1945)
Heteromorphite	7:4	3440*	5·86	5·73	Palache *et al.* (1944)
Semseyite	9:4	3838	6·08	6·03	Nuffield and Peacock (1945)

* From fig. 1.

TABLE V. *Cell dimensions of the plagionite group, with estimated parameters of heteromorphite*

	a	*b*	*c*	*β*	*c* sin *β*
Fülöppite	13·41 Å	11·71	16·90	94° 43′	16·8
Plagionite	13·47	11·82	19·99	107° 20′	19·1
Heteromorphite	13·54	11·9	22	—	21·3
Semseyite	13·64	11·96	24·46	105° 52′	23·5

who reported a new occurrence, the Kara Kamar deposit, Tadzhik S.S.R. In addition, the present writer has identified heteromorphite intimately intergrown with plagionite and semseyite in a polished section of material labelled 'plagionite' from Wolfsberg, Germany (National Mineral Collection, Canada). The X-ray powder pattern of a minute amount of material dug from the section is given in table VI, and give *a* 13·60, *b* 11·93, *c* 21·22 Å, β 90° 50′, *V* 3443 Å^3, in good agreement with the predicted values cited above.

TABLE VI. *Heteromorphite, Wolfsberg, Germany;* 114·6-*mm camera,* Cu-*K*α *radiation. Indexed with a* 13·60, *b* 11·93, *c* 21·22 Å, β 90° 50′, *space group C*2/*c*, *V* = 3443 Å^3

I	d_{meas}	d_{calc}	*hkl*	*I*	d_{meas}	d_{calc}	*hkl*	*I*	d_{meas}	*I*	d_{meas}
1	10·59 Å	10·61 Å	002	8	3·25	3·25	$\bar{4}02$	2	2·281	½	1·859
1	6·89	6·88	$\bar{1}12$	<½	3·15	3·16	$\bar{2}06$	3	2·234	½	1·847
2	5·58	5·58	$\bar{1}13$	7	3·097	3·097	$\bar{2}25$	6	2·135	<½	1·817
½	4·58	4·58	$\bar{1}14$	3	3·068	3·068	225	<½	2·127	<½	1·795
<½	4·41	4·40	$\bar{2}21$	7B	2·970	2·964	$\bar{3}31$	<½	2·098	1	1·767
1	4·23	4·24	310	7	2·884	2·885	$\bar{3}32$	2	2·074	½	1·753
<½	3·96	3·96	024	2	2·838	2·836	422	1	2·065	1	1·725
½	3·92	3·92	312	4	2·794	2·790	$\bar{2}26$	2B	2·020	<½	1·705
6	3·85	3·85	$\bar{1}15$	3	2·763	2·764	$\bar{3}33$	2B	1·975	½	1·685
4	3·82	3·82	130	½	2·722	2·731	240	½	1·911		
7	3·75	3·75	131	5	2·710	2·711	$\bar{2}41$	1	1·892		
1	3·59	3·59	132			2·707	241	3	1·884		
½	3·44	3·44	$\bar{2}24$	1	2·523	2·522	$\bar{2}27$				
8	3·40	3·40	400	<½	2·499	2·500	227				
10	3·30	3·30	$\bar{1}16$	3	2·460	2·459	208				

Conclusions. Sulphosalts of the plagionite group show systematic variations in densities and unit cell volumes that are linearly related to variations in the mol ratios of $PbS:Sb_2S_3$. This phenomenon can be used to predict the general nature of hypothetical members of the plagionite group, and has been utilized here to more firmly define heteromorphite. The data indicate that minerals in the plagionite group have the generalized formula $4[nPbS{\cdot}4Sb_2S_3]$.

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