MELIPHANITE, LEUCOPHANITE AND THEIR RELATION TO MELILITE

BY

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1. Introduction.

In a previous paper[1] published some time ago I considered the chemical composition of the two minerals Meliphanite (Melinophan) and Leucophanite (Leukophan) on the basis of our modern knowledge of the mechanism of isomorphous substitution. My interpretation of the analyses is given in table 2. It leads definitely to the following formulae:

· Meliphanite: $(Ca, Na)_2 Be(Si, Al)_2(O, F)_7$
Leucophanite: $(Ca, Na)_2 BeSi_2(O, OH, F)_7$

For comparison the formulae derived by W. C. BRØGGER[2] will be given:

Meliphanite: $Ca_4 Na_2 Be_4 Si_6 O_{20} F_2$
Leucophanite: $Ca_8 Na_8 Be_8 Si_6 O_{18} F_8$

2. X-ray Examination.

I have examined Meliphanite and Leucophanite by means of the Laue-, the powder- and the oscillation methods.

The Laue-photographs of Meliphanite showed full tetragonal symmetry. This observation combined with the development of the crystal faces places the mineral in the tetragonal-scalenohedral class (D_{2d}). The Leucophanite photographs possessed definitely orthorhombic symmetry, although with very great approximation to tetra-

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[1] Zs. f. Krist. 74, 226, 1930.
[2] Zs. f. Krist. 16, 1890.

gonal symmetry as one should expect. The unit cells of the two minerals have the following dimensions:

Meliphanite: a=10.58±0.02 Å   c=9.88±0.02 Å c/a=0.933

Leucophanite: a= 7.38±0.02 Å   b=7.38±0.02 Å c=9.96±0.02 Å

with a : b : c=1 : 1 : 1.349

BRØGGER found the axial ratios c/a=0.6584 for Meliphanite and a/b/c=0.9939 : 1 : 0.6722 for Leucophanite. The axial ratio which I have found for Meliphanite is very nearly 0.6584√2 (0.933 instead of 0.931), showing that the direction of the correct a-axis makes an angle of 45° with the axial direction chosen by BRØGGER.

Table 1. *Chemical Analyses of Meliphanite and Leucophanite.*[1]

	Meliphanite	Leucophanite
K₂O	0.23	.
CaO...................	29.56	22.94
Na₂O	7.98	12.42
MgO	0.16	0.27
BeO...................	9.80	10.03
Al₂O₃	4.61	0.45
SiO₂...................	43.60	48.50
H₂O...................	.	1.08
F	5.73	5.94
	101.37	101.63
O eq. 2 F.............	— 2.27	— 2.48
	99.09	99.15

Table 2. *Atomic Ratios and Interpretation of the Analyses.*

	Meliphanite		Leucophanite	
K	5		-	
Ca	529	789 : 1.98	410	812 : 2.00
Na	255		402	
Mg............................	4		7	
Be	390	394 : 1.00	398	405 : 1.00
Al............................	90		9	
Si	727	817 : 2.05	801	810 : 2.00
OH	-		120	
F	284	2784 : 7.00	311	2846 : 7.00
O	2500		2415	

[1] Analyses by BÄCKSTRÖM by BRØGGER, l. c.

Table 3. *Powder Photographs of Meliphanite and Leucophanite.*[1]

Meliphanite				Leucophanite			
Int.	$\sin^2 \Theta$		hkl	Int.	$\sin^2 \Theta$		hkl
	obs.	calc.			obs.	calc.	
				w	.00352	.00356	101
vvw	.00454	.00448	200	vw	.00447	.00460	110
vw	.00511	.00514	002	w	.00495	.00505	002
				vvw	.00571	.00585	111
vw	.00745	.00738	112	vvw	.00725	.00735	102
w	.00691	.00688	211				
m	.00969	.00962	202	ms	.00947	.00965	112
				w	.01027	.01046	201
vw	.01129	.01120	310	vw	.01123	.01150	210
				vw	.01249	.01276	211
				w	.01361	.01367	103
m	.01416	.01410	222	ms	.01409	.01425	202
s	.01637	.01634	312	vs	.01637	.01655	212
w	.01795	.01792	400	w	.01818	.01840	220
vw	.02051	.02055	004				
m	.02314	.02306	402	s	.02332	.02345	222
m	.02547	.02530	332	m	.02556	.02575	302

It will further be noticed that the true c-axis for Leucophanite is doubled with respect to BRØGGER'S.

The determination of the unit cell is an excellent check on the chemical formulae, since the unit cell must contain an integral number of molecules.

BRØGGER'S formulae do not give integral numbers, while the formulae derived by me give exactly 8 molecules for Meliphanite and exactly 4 molecules for Leucophanite. The interpretation of the chemical analyses given in my previous paper is thus correct.

The X-ray photographs show some interesting features. In the Meliphanite diagrams no reflexion is observed for which $h+k+l$ is odd, showing that the cell is bodycentered. However, even for reflexions with even index sum we find large number of reflexions missing. The following regularity exists: Reflexions for which $h+k$ is odd, or for which l is odd occur with very weak intensity or are completely missing. If we thus disregard these weak reflexions, the remaining ones can be indexed according to a pseudo cell containing only two molecules. This cell will have the following dimensions:

$$a = 7.48 \text{ Å} \quad c = 4.94 \text{ Å} \quad c/a = 0.660$$

[1] Mo kα radiation. w = weak. m = medium. s = strong.

In the Leucophanite diagrams similarily reflexions for which l is odd are missing or very weak, so that we again have a pseudo cell with two molecules and the following dimensions:

$$a = 7.38 \text{ Å} \quad c = 4.98 \text{ Å} \quad c/a = 0.675$$

Corresponding reflexions in Meliphanite and Leucophanite occur with very similar intensity, showing that the crystal structures are nearly identical. Only by means of a complete structure determination would we be able to tell quite definitely why Leucophanite and Meliphanite do not have exactly the same structure. It seems reasonable, however, to ascribe the small difference in structure to the larger content of univalent anions in Leucophanite.

Meliphanite and Leucophanite as Members of the Melilite Group.

The crystal structure of Melilite has been determined by B. E. WARREN.[1] The tetragonal unit cell has the dimensions:

$$a = 7.73 \text{ Å} \quad c = 5.01 \text{ Å} \quad c/a = 0.648$$

(The a-axis of the true unit cell is at 45 to that ordinarily used by crystallographers). This cell contains two molecules of the composition (Ca, Na)$_2$ (Mg, Al) (Si, Al)$_2$O$_7$, this formula being derived by BERMAN[2] and WARREN. As an end member of the isomorphous series we have: Ca$_2$MgSi$_2$O$_7$. This compound can be compared with Ca$_2$ZnSi$_2$O$_7$, being the composition of the rare mineral Hardystonite from Franklin Furnace, N. J. I pointed out this relation, meaning that Hardystonite really was to be considered as a Zink-Melilite. An X-ray investigation by WARREN and TRAUTZ[3] showed my suggestion to be correct, since Hardystonite was found to have the same structure as Melilite. The unit cell of Hardystonite has dimensions:

$$a = 7.83 \text{ Å} \quad c = 4.99 \text{ Å} \quad c/a = 0.637$$

Now Melilite and Hardystonite have formulae quite analogous to that of Meliphanite, they are all tetragonal crystals and even the axial ratios agree very well. In my previous paper I therefore con-

1 Zs. f. Krist. 74, 131, 1930.

2 Amer. Min. 14. 11, 389.

3 Zs. f. Krist. 75, 525, 1930.

sidered it highly probable that Meliphanite has Melilite structure (Leucophanite a deformed Melilite structure). The X-ray examinations presented in this paper show that my hypothesis is not quite correct. The true unit cells of Meliphanite and Leucophanite do not correspond to that of Melilite, so the crystal structures are not the same. There is, however, in spite of that a very close relation. The pseudo cells of the two Beryllium minerals agree with that of Melilite and Hardystonite as the following table shows:

Table 4.

Compound	a	c	c/a
Melilite	7.73	5.01	0.648
Hardystonite................	7.83	4.99	0.637
Meliphanite	7.48	4.94	0.660
Leucophanite	7.38	4.98	0.675

Even in the intensities of reflexion there is some resemblance for the four minerals (taking into account the scattering powers of the different atoms). We may therefore consider it to be above any doubt that Meliphanite and Leucophanite have deformed Melilite structures, the deformation presumably being due to the content of fluorine and hydroxyl.

Summary.

The correct chemical formulae for the two minerals Meliphanite and Leucophanite are: $(Ca, Na)_2 Be (Si, Al)_2 (O, F)_7$ and $(Ca. Na)_2 BeSi_2 (O, OH, F)_7$ respectively. The formulae were checked by means of the dimensions of the unit cells. Meliphanite has 8 molecules of the above composition in the tetragonal unit cell: $a = 10.58$ Å $c = 9.88$ Å; whereas Leucophanite has 4 molecules in the orthorhombic cell: $a = b = 7.38$ Å $c = 9.96$ Å.

Both Meliphanite and Leucophanite have pseudo cells containing only two molecules. These small cells have the dimensions: $a = 7.48$ Å $c = 4.94$ Å for Meliphanite and $a = 7.38$ Å $c = 4.98$ Å for Leucophanite. The close similarity in all observations proves that the two minerals have very nearly the same crystal structure.

There is also a close relation to the Melilite structure as indicated in the following table.

Melilite $(Ca, Na)_2 (Mg, Al) (Si, Al)_2 O_7$	$a = 7.73$ Å	$c = 5.01$ Å	$c/a = 0.648$
Hardystonite $Ca_2ZnSi_2O_7$	$a = 7.83$ Å	$c = 4.99$ Å	$c/a = 0.637$
Meliphanite $(Ca, Na)_2 Be (Si, Al)_2 (O, F)_7$ $\frac{1}{2}\sqrt{2}$	$a = 7.48$ Å	$c = 4.94$ Å	$c/a = 0.660\sqrt{2}$
Leucophanite $(Ca, Na)_2 BeSi_2 (O, OH, F)_7$ ...	$a = 7.38$ Å	$\frac{1}{2}c = 4.98$ Å	$c/a = 0.675 \cdot 2$

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