REFINEMENT OF THE CRYSTAL STRUCTURE OF LEUCOPHANITE

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ABSTRACT

The crystal structure of leucophanite [$CaNaBeSi_2O_6F$, *a* 7.401(2), *b* 7.412(2), *c* 9.990(2) Å, orthorhombic, $P2_12_12_1$, $Z = 4$], was refined using 926 observed ($I > 2.5\sigma I$) reflections collected with $MoK\alpha$ X rays and a crystal from Mont Saint-Hilaire, Quebec; a similar refinement of a crystal from Stokkoy, Norway gave nearly identical results. The structure is similar to that previously determined, but required a shift in origin ($+ \frac{1}{4}$, $+ \frac{1}{4}$, $+ \frac{3}{4}$) and an interchange of the *x* and *y* coordinates. The revised structure refined to $R = 3.0$ and $R_w = 2.7\%$ based on 926 observed reflections, as compared with $R \sim 20\%$ for the same data and the previous model. Leucophanite is a shell structure based on the 2-dimensional net ($5_1^3 5_1^4$) that is also the basis of the melilite-group minerals. The lower symmetry and different cation-ordering patterns in leucophanite as compared with the melilite-group minerals are mainly dictated by the local bond-valence requirements of F, which is required by stoichiometry in the leucophanite structure.

Keywords: leucophanite, Mont Saint-Hilaire, structure, cation ordering, nets.

SOMMAIRE

Nous avons affiné la structure cristalline du leucophane [$CaNaBeSi_2O_6F$, *a* 7.401(2), *b* 7.412(2), *c* 9.990(2) Å, orthorhombique, $P2_12_12_1$, $Z = 4$], en utilisant un échantillon du mont St-Hilaire et 926 réflexions observées ($I > 2.5\sigma I$) avec rayonnement $MoK\alpha$. Un affinement semblable, réalisé avec un cristal de Stokkoy (Norvège), a donné des résultats presque identiques. La structure, qui ressemble à celle qui avait été déterminée, requiert un déplacement de l'origine ($+ \frac{1}{4}$, $+ \frac{1}{4}$, $+ \frac{3}{4}$) et une permutation des axes *x* et *y*. L'affinement a atteint un résidu $R = 3.0\%$ et $R_w = 2.7\%$ pour les 926 réflexions observées, comparé à un résidu d'environ $R \sim 20\%$ avec les mêmes données et le modèle structural précédent. Ce minéral possède une structure en coquille calquée sur la maille bidimensionnelle ($5_1^3 5_1^4$), qui est aussi celle des minéraux du groupe de la mélilite. La symétrie plus faible et les agencements ordonnés différents parmi les cations du leucophane, en comparaison des membres du groupe de la mélilite, résultent des exigeances locales en valences des liaisons impliquant le fluor, dont la présence est imposée par la stoechiométrie.

(Traduit par la Rédaction)

Mots-clés: leucophane, mont St-Hilaire, structure, mise en ordre des cations, mailles.

INTRODUCTION

The crystal structure of leucophanite was reported by Cannillo *et al.* (1967). These authors used crystals from Brevig, Norway to measure intensity data using multiple Weissenberg films and a microdensitometer. With 586 observed reflections, they were able to refine the structure to a residual of $R = 9.4\%$.

We obtained leucophanite crystals from the Desourdy quarry, Mont Saint-Hilaire, Rouville County, Quebec (specimen number NMNS 53455) and from Stokkoy, Vestfold County, Norway (NMNS 46861). The Saint-Hilaire leucophanite was analyzed by Chao (1967) and determined to be $Ca_{0.85}Na_{0.95}(Be_{0.89}Al_{0.02})Si_{2.07}O_6(F_{0.97}OH_{0.12})$, almost pure end-member leucophanite, $CaNaBeSi_2O_6F$. The analytical data given by Brøgger (1890) for the Norwegian material also correspond to nearly end-member leucophanite. The structures determined on crystals from both localities confirm their chemical purity.

EXPERIMENTAL

The crystal structure of leucophanite was refined for crystals from both Mont Saint-Hilaire, Quebec and Stokkoy, Norway; only the experiment for the Saint-Hilaire sample will be described in detail as the techniques and results are very similar for both structure determinations.

The Saint-Hilaire crystal chosen for data collection was ground to an ellipsoid that measures 0.23 × 0.23 × 0.13 mm. X-ray-diffraction spots on precession photographs are sharp and intense. These photographs indicate orthorhombic symmetry and systematic extinctions consistent with the unique space-group $P2_12_12_1$ (#19). Intensity data were collected on a Nicolet *R3m* automated four-circle diffractometer using the method of Grice & Ercit (1986). The data relevant to the structure refinement are given in Table 1.

STRUCTURE REFINEMENT

The initial starting parameters for the atoms were those of Cannillo *et al.* (1967). These parameters

refined with isotropic temperature-factors to an R of 20.2% but would not refine further. It is interesting to note that even at this R index, the atomic coordinates had high, but not unreasonable, standard deviations of approximately ± 0.001 for the cations and ± 0.002 for anions. These standard deviations are in the order of those recorded by Cannillo *et al.* (1967); of course, these atomic parameters gave rise to the same reasonable polyhedra and bond lengths. The magnitudes of the temperature factors were not considered to be fully satisfactory, but most were believable. However, the residual index indicated a serious error in the model.

To find the correct structure, E-maps were calculated from a set of normalized structure-factors. With a set of starting coordinates for the heavier atoms, a series of refinements with difference-Fourier maps was run, and the structural model completed.

The final R values in Table 1 are for refinement with anisotropic temperature-factors, and the weighting scheme incorporated an isotropic, primary-extinction correction. The final positional parameters and equivalent isotropic temperature-factors are given in Table 2, and the anisotropic temperature-factors are given in Table 3. Bond lengths and angles are given in Table 4, and an empirical bond-valence summation is shown in Table 5. The observed and calculated structure-factors have been submitted to the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Canada K1A 0S2.

Leucophanite from Stokkøy, Norway gave almost identical results, with a slightly improved R of 2.6%. The very close similarity to the Saint-Hilaire material establishes the structure reported here as the correct one; the results for this second structure also have been deposited in CISTI.

DISCUSSION

Comparison of the atomic coordinates for the leucophanite structure as determined by Cannillo *et al.* (1967) to those reported here may be made by taking the coordinates in Table 2, interchanging x and y and adding ¼ to each and adding ¾ to z. The shift in origin involves one of 64 possible origins in space group $P2_12_12_1$, but only 16 of these possibilities lead to changes in the phases. The interchange of the x and y coordinates reflects the close proximity of this structure to tetragonal symmetry. The structure is in fact closely related to the tetragonal structure of melilite, $Ca_2MgSi_2O_7$. The lowering of symmetry from tetragonal to orthorhombic for the leucophanite structure results from the ordering of Ca and Na at two distinct sites, as opposed to the single Ca site in melilite (Smith 1953). The occupancy for these two sites refined to 1.043(4) for Ca and 0.996(9) for Na, indicating complete order.

The most prominent feature of the leucophanite structure (Fig. 1) is the tetrahedral $[BeSi_2O_6F]$ sheet perpendicular to [001]. This strongly bonded structure module is linked into a 3-dimensional structure by more weakly bonding alkali and alkaline earth cations, and thus is a sheet structure in the terminology of Hawthorne (1985, 1986). If we consider the sheet as a 2-dimensional net (*e.g.*, Smith 1977, Hawthorne & Smith 1986), it is represented by the general symbol $(5_2^3 5_1^4)$; this signifies that there are two 3-connected vertices and one 4-connected vertex in the net, and that all the shortest circuits from each vertex are pentagonal.

It is of interest to consider the substitution of cations on the basic melilite-type $(5_2^3 5_1^4)$ net. The melilite minerals may be written as $X_2 YZ_2O_7$, where $X = $ Ca, Na(+Ba, Sr . . .), $Y = $ Mg, Al, Zn, Be (+Co, Fe, Ni . . .), $Z = $ Si, Al; Y cations occupy the

TABLE 1. LEUCOPHANITE: STRUCTURE-REFINEMENT DATA

Ideal Formula:	CaNaBeSi₂O₆F	a(Å):	7.401(2)
Space Group:	P2₁2₁2₁	b(Å):	7.412(2)
Z:	4	c(Å):	9.990(2)
Radiation/Mono:	Mo/graphite	No. of Fo:	958
μ:	16.0 cm⁻¹	No. of Fo>2.5σ(I):	926
Min. transmission:	0.619	Final R:	3.0%
Max. transmission:	0.685	Final Rw:	2.7%

$$R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$$

$$R_W = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}, \; w = \sigma^{-2}(F_o)$$

TABLE 2. LEUCOPHANITE: POSITIONAL AND THERMAL PARAMETERS

Site	x	y	z	U(eq)X10⁴Å²
Ca	0.0788(1)	0.6462(1)	0.7599(1)	99(2)
Na	0.1021(2)	0.6782(2)	0.2465(2)	200(5)
Be	0.1200(6)	0.3592(6)	0.5307(4)	28(10)
Si1	0.1000(1)	0.3580(1)	0.0241(1)	76(3)
Si2	0.2371(2)	0.9917(2)	0.9994(1)	78(2)
O1	0.0912(4)	0.3548(4)	0.8645(2)	105(7)
O2	0.1483(4)	0.1580(4)	0.0895(3)	100(7)
O3	0.0986(4)	0.9136(4)	0.4111(3)	101(7)
O4	0.0800(4)	0.9129(4)	0.9030(3)	98(7)
O5	0.1769(4)	0.1626(4)	0.5935(3)	97(7)
O6	0.2553(4)	0.5076(4)	0.5892(3)	101(6)
F	0.1216(3)	0.3526(4)	0.3729(2)	159(7)

TABLE 3. LEUCOPHANITE: ANISOTROPIC TEMPERATURE-FACTORS (X10⁴Å²)

Site	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ca	116(3)	89(3)	91(3)	25(3)	6(3)	21(3)
Na	180(9)	250(10)	171(9)	-64(8)	45(8)	52(7)
Be	30(18)	4(15)	49(18)	0(0)	0(0)	0(0)
Si1	66(4)	73(4)	91(5)	-2(4)	0(4)	0(4)
Si2	68(4)	69(4)	98(4)	-5(4)	-11(4)	3(4)
O1	129(12)	96(11)	90(11)	3(11)	17(11)	11(14)
O2	124(12)	67(11)	110(11)	1(12)	13(10)	9(11)
O3	77(12)	116(11)	109(12)	0(11)	8(12)	-9(11)
O4	65(12)	114(11)	116(12)	-29(11)	-15(12)	-8(12)
O5	115(12)	66(12)	110(12)	-14(12)	31(10)	10(11)
O6	99(11)	104(11)	101(12)	20(12)	28(11)	-6(10)
F	162(12)	191(12)	123(11)	-18(11)	1(9)	-3(12)

TABLE 4. LEUCOPHANITE: SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (°)

Ca square anti-prism				Be tetrahedron			
Ca-O1	2.401(4)	O1 -Ca-O5b	79.0(1)	Be-O5	1.642(6)	O5 -Be-O6	108.1(3)
Ca-O4	2.440(4)	O5b-Ca-O4	66.6(1)	Be-O6	1.598(6)	F -Be-O5	110.6(3)
Ca-O6	2.381(4)	O4 -Ca-F c	74.2(1)	Be-F	1.577(5)	F -Be-O6	112.5(3)
Ca-O1d	2.349(4)	F c-Ca-O1	76.8(1)	Be-O4d	1.670(5)	O4d-Be-O5	106.7(3)
Ca-O2e	3.014(4)	O6 -Ca-O4d	61.4(1)	mean	1.622	O4d-Be-O6	104.3(3)
Ca-O4d	2.650(4)	O4d-Ca-O1d	82.4(1)			O4d-Be-F	114.3(3)
Ca-O5b	2.396(4)	O1d-Ca-O2e	75.1(1)			mean	109.4
Ca-F c	2.488(4)	O2e-Ca-O6	55.6(1)				
mean	2.515						

Na square anti-prism				Si1 tetrahedron			
Na-O3	2.398(4)	F -Na-O2d	71.3(1)	Si1-O2	1.659(3)	O1a-Si1-O2	112.9(2)
Na-F	2.729(4)	O2d-Na-O3	65.3(1)	Si1-O1a	1.596(3)	O3e-Si1-O2	105.0(2)
Na-O1e	2.569(4)	O3 -Na-O1e	76.4(1)	Si1-O3e	1.658(4)	O3e-Si1-O1a	110.9(2)
Na-O2d	2.479(4)	O1e-Na-F	69.9(1)	Si1-O6d	1.601(3)	O6d-Si1-O2	104.6(2)
Na-O3e	2.921(4)	O6d-Na-F	76.5(1)	mean	1.628	O6d-Si1-O1a	116.2(2)
Na-O5e	2.530(4)	O3e-Na-O2d	86.3(1)			O6d-Si1-O3e	106.2(2)
Na-O6d	2.341(4)	F a-Na-O3	86.7(1)			mean	109.3
Na-F a	2.461(4)	O5e-Na-O1e	75.6(1)				
mean	2.553						

Si2 tetrahedron			
Si2-O4	1.618(3)	O2b-Si2-O4	107.8(2)
Si2-O2b	1.662(3)	O3g-Si2-O4	111.3(2)
Si2-O3g	1.658(3)	O3g-Si2-O2b	105.3(2)
Si2-O5d	1.612(3)	O5d-Si2-O4	112.0(2)
mean	1.638	O5d-Si2-O2b	111.5(2)
		O5d-Si2-O3g	108.7(2)
		mean	109.4

5^4 vertex, and Z cations occupy the 5^3 vertex; this type of vertex occupancy seems to be the norm for incorporation of divalent cations into polymerized tetrahedral modules. Notably, gugiaite contains Be at the 5^4 vertex. This contrasts strongly with leucophanite, in which Be occupies a 5^3 vertex and Si occupies a 5^4 vertex. Thus we have the question of why leucophanite is orthorhombic (and not tetragonal), and also why the different ordering scheme in the tetrahedral sheet is different.

One notable aspect of leucophanite is that it has both Na and Ca in equal amounts as intramodule cations, and that these are ordered in the structure. By itself, this cannot be the determinative factor for the orthorhombic symmetry, as synthetic "soda-melilite", $NaCaAlSi_2O_7$ (Louisnathan 1970), is tetragonal with the melilite structure, and has Na and Ca disordered at a single site. The occurrence of Be in the sheet cannot be the primary reason gugiaite, $Ca_2BeSi_2O_7$ (Kimata & Ohashi 1982), has the tetragonal melilite structure. Zachariasen (1930) suggested that the presence of F in leucophanite causes the orthorhombic symmetry. This is probably the case, but does not address the reaons(s) for the different ordering schemes of the leucophanite and melilite sheets. Furthermore, it is not clear why F could not disorder within a tetragonally symmetrical sheet.

In a gugiaite-composition melilite-like sheet, F cannot occupy any of the bridging anion positions in the sheet because of local bond-valence constraints. Only a single nonbridging anion position is left to accommodate the F. This nonbridging anion (O2 in the nomenclature of Smith 1953) is bonded to one Si and three Ca atoms; hence it also cannot be replaced by F, again because of local bond-valence restrictions. However, if the Be occupies a 5^3 vertex, then the local environment of the O_2 anion (one Be and three Ca atoms) is ideal for the incorporation of F. Thus we see that the determinative factor for the difference in the ordering scheme among tetrahedra in leucophanite is the need to incorporate F into the sheet and to satisfy its local bond-valence requirements.

The next problem is more difficult: why is leucophanite ordered and orthorhombic rather than disordered and tetragonal? The 5^3 vertices are occupied by ½ Be + ½ Si, suggesting the possibility of ordering and a lowering of symmetry. Gehlenite, $Ca_2Al(AlSi)O_7$, has ½Al + ½Si occupying the 5^3 vertices and yet is tetragonal (Louisnathan 1971). However, Louisnathan (1971) also remarked on the occurrence of optically biaxial gehlenite, and the presence of very fine-scale twinning in some gehlenite, suggesting that incipient ordering occurs on a very fine scale. In beryllosilicates, Be rarely if ever disorders with Si. This being the case, the occurrence of Be at the 5^3 vertex in the melilite-like sheet will require these two vertices to be symmetrically distinct, lowering the symmetry of the structure. Given the opportunity, the Ca and Na also order to produce

TABLE 5. BOND-VALENCE SUMMATION* FOR LEUCOPHANITE

	Ca	Na	Be	Si(1)	Si(2)	Σ
01	0.290 0.326	0.139		1.072		1.827
02	0.085	0.162		0.908	0.901	2.056
03		0.187 0.080		0.910	0.910	2.087
04	0.266 0.170		0.458		1.011	1.905
05	0.293	0.149	0.490		1.027	1.959
06	0.303	0.207	0.548	1.057		2.115
F	0.198	0.084 0.131	0.454			0.867
Σ	1.931	1.139	1.950	3.947	3.849	

* Brown (1981).
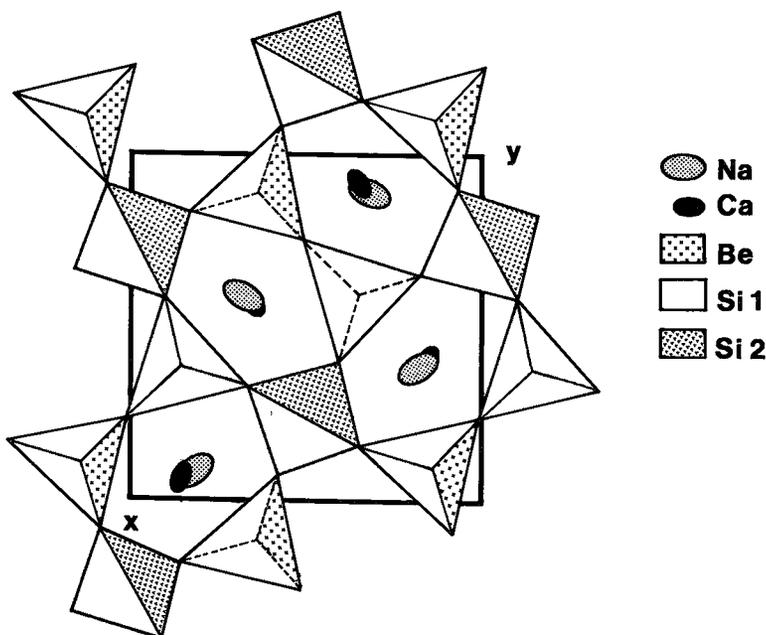
FIG. 1. A Z-axis projection of the leucophanite structure showing only the upper sheet of tetrahedra within the unit cell. The lower tetrahedra, consisting of the same topological 2-dimensional net ($5_2^3 5_1^4$) is offset slightly in x and y coordinates.

the final structure. However, the determinative factor for the existence of leucophanite is the local bond-valence requirements around the F that *must* be incorporated into the structure for overall electroneutrality.

Examination of the bond-valence values for leucophanite (Table 5) shows that the deviations from regularity in the various coordination polyhedra can be ascribed to local bond-valence requirements. In particular, the Si–O bond lengths to the Si–O–Si bridging anions are lengthened to allow for the additional bonding to the intramodule Ca and Na. Note also how the relative ordering of Ca and Na has occurred such that Ca can form more and stronger bonds to those anions that are most underbonded in the tetrahedral sheet [the nonbridging O(1) and the Si–O–Be bridging O(4), O(5) and O(6) anions], whereas Na forms more than one bond to those anions that are most strongly bonded in the tetrahedral sheet [the Si–O–Si bridging O(3) anion]. The control of this local connectivity and geometry is the local bond-valence requirements, around both Ca and Na. Thus leucophanite can be thought of as a cation-ordered derivative of the melilite-type structure, the determining factor for the existence of which is dependent on the stoichiometric need to incorporate F into the structure.

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