THE AMERICAN MINERALOGIST, VOL. 50, SEPTEMBER, 1965

A STUDY OF "CALCIUM-LARSENITE" RENAMED ESPERITE[1]

PAUL B. MOORE AND PAUL H. RIBBE[2] *Department of Geophysical Sciences, University of Chicago, Chicago, Illinois.*

ABSTRACT

Single crystal studies of "calcium-larsenite," (Ca, Pb)$ZnSiO_4$, from Franklin, New Jersey show that it is not directly related to larsenite, $PbZnSiO_4$, although both are tecto-zincosilicates. It is monoclinic with $a=2\times 8.814$, $b=8.270$, $c=2\times 15.26$ Å, $\beta=90°$. The space group of the basic unit cell is $P2_1/n$; but superlattice reflections, presumed due to Ca/Pb ordering, effectively double the a- and c-axes, making the superstructure B-face centered.

Marked structural similarities to beryllonite and trimerite are observed and an ordering scheme is proposed. Luminescence and decomposition with heating are of particular interest. "Calcium-larsenite" has been renamed *esperite* for Prof. Esper S. Larsen, Jr.

INTRODUCTION

"Calcium-larsenite" $(Pb, Ca, Zn)_2SiO_4$ was named by Palache (1928) in the course of his classic studies of Franklin, New Jersey paragenesis. Since single crystals were not found, it was tentatively classified with larsenite ($PbZnSiO_4$) as an olivine type structure. Recent single-crystal studies by Layman (1957) indicated, however, that larsenite is not related to the olivines. A partial structure analysis of larsenite by Prewitt (priv. comm., 1964) further showed that the SiO_4 tetrahedra are not insular, but are linked in infinite array with ZnO_4 tetrahedra; *i.e.*, larsenite is a tecto-zincosilicate. Our study has shown that "calcium-larsenite" is also a tecto-zincosilicate, but that it is not related to larsenite. We have renamed the mineral esperite for Prof. Esper S. Larsen, Jr.

"Calcium-larsenite," now esperite, has only been found at Franklin, New Jersey associated with replaced ores, as characteristic greasy white masses which usually darken superficially to a dirty grayish white upon exposure to air. Apparently it was a moderately abundant mineral, associated with large masses of franklinite, orange streaks of zincite, some green willemite and more rarely with native copper and glaucochroite. Larsenite occurs only in veins (Palache, 1935), usually with clinohedrite, and is far less abundant than esperite: only rarely are the two found together.

The material used in this study came from a 3″×4″ mass containing translucent esperite, brown andradite ("polyadelphite"), green willemite and traces of leucophoenicite. The esperite is transparent in small grains.

---

[1] Change approved by the Commission on New Minerals and Mineral Names, I.M.A.

[2] Present address: Department of Geology, University of California, Los Angeles 24, California.

It exhibits distinct (010), (100) and poor (101) cleavages, and its hardness is 5+.

A complete chemical analysis was made with an ARL electron microprobe. The microprobe data were corrected for absorption, fluorescence and atomic number effects using a program for the IBM 7094 by Dr. J. C. Ruckledge. The atomic ratios of Ca:Pb and Zn:Si in our specimen are very close to 3:1 and 1:1, respectively, suggesting the formula $Ca_3Pb(ZnSiO_4)_4$. The calculated density of $Ca_3Pb(ZnSiO_4)_4$ is 4.25. The measured density of 4.28 is in excellent agreement. The "calcium-larsenite" analyzed by Bauer (Palache, 1935) has a Ca:Pb ratio of 2.35:1, and its observed density of 4.421 confirms that it contains substantially more Pb than our specimen. The Mn in our specimen varies as much as ±20% from spot to spot over an analyzed area of 1 cm^2.[3] No Fe was detected at the 0.01% level, nor were any elements other than those listed found to be present in amounts greater than 0.03%.

TABLE 1. CELL DATA OF ESPERITE AND LARSENITE

	Esperite	Larsenite (Layman, 1957)
a	2× 8.814±0.002 Å	8.23 Å
b	8.270±0.003 Å	18.94 Å
c	2×15.26 ±0.01 Å	5.06 Å
β	90°	90°
volume	4×1123 Å^3	789 Å^3
Z	$4\times3Ca_3Pb(ZnSiO_4)_4$	$8PbZnSiO_4$
ρ_{obs}	4.28	5.90
ρ_{calc}	4.25	6.14
space group	$P2_1/n$ (subcell)	$Pna2_1$ (Prewitt, priv. comm.)

CRYSTALLOGRAPHIC DATA

Unit cell parameters. Using a variety of single crystal x-ray photographs, the unit-cell parameters and space group of "esperite" were determined. The data are compiled in Table 1 together with those of larsenite by way of contrast. It is interesting to note that $a_{esp} \simeq \frac{1}{2}b_{lars}$; $b_{esp} \simeq a_{lars}$; $c_{esp} \simeq 3c_{lars}$; when referring to the esperite $P2_1/n$ subcell as mentioned in the following paragraph. No doubt there is close, but distinct, structural relationship between the two minerals.

Esperite is monoclinic and has a well-developed superstructure involving a doubling of the a- and c-axes (Fig. 1). The space group, dis-

---

[3] The willemite associated with this esperite contains ~4% Mn substituting for Zn. It too has no detectable Fe or other elements.

counting the superlattice reflections and based on the unit cell $a \times b \times c = 8.8 \times 8.3 \times 15.3$ Å, is $P2_1/n$. When the superlattice reflections are included, the unit cell becomes B-face centered (h+l=2n) with doubled a- and c-axes and four times the volume of the basic cell. A new choice of unit cell to avoid B-centering is possible. However, we feel that it is important to retain the axial convention of the basic structure in order to maintain the simple and obvious structural classification of esperite with such minerals as beryllonite and trimerite (discussed below).

X-ray powder pattern. The powder pattern (Table 2) is indexed for the basic unit cell and superstructure. No superlattice reflections appear in the pattern.

Comparison with other minerals. A study of the h0l precession photograph of esperite shows its pronounced pseudo-hexagonal symmetry. In this respect it is very much like beryllonite and trimerite. In fact, the correlation of h0l reflections among these minerals is remarkable, considering the disparity in respective compositions: their precession photographs are shown in Fig. 2 for purposes of comparison. Table 3 compares the unit cell data of the three.

Of these, the only known crystal structure is that of beryllonite (Golovastikov, 1961). Its atomic coordinates were used to calculate structure factors for the dimensionally-expanded esperite by substituting (Ca, Pb) for Na, Zn for Be, and SiO_4 for PO_4. A rough comparison of I_{obs}

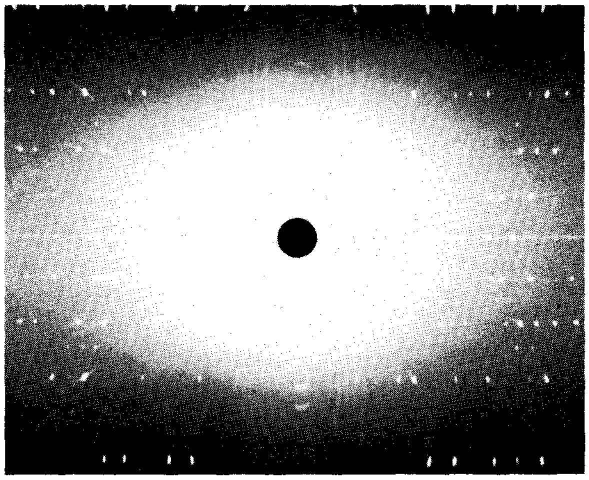

FIG. 1. An a-axis oscillation photograph of esperite showing superlattice reflections (h+l=2n). CuK_α radiation.

TABLE 2. X-RAY POWDER DIFFRACTION PATTERN OF "CALCIUM-LARSENITE", USING Cu/Ni RADIATION AND CaF_2 (a=5.463 Å) AS AN INTERNAL STANDARD

I/I_0	d_{obs}	d_{calc}	hkl	
			Basic cell	Superstructure
45	7.62	7.63	002, 101	004, 202
10	4.73	4.73	112	214
15	4.41	4.41	200, 103	400, 206
15	3.82	3.81	004, 202	008, 404
7	3.76	3.77	211	412
15	3.64	3.64	121, 022	222, 024
23	3.363	3.360	122	224
17	3.216	3.208	023	026
100	3.017	3.017	220	420
22	2.958	2.958	221	422
33	2.884	2.884	105, 204	2·0·10, 408
4	2.805	2.805	222	424
8	2.675	2.672	124	228
3	2.597	2.602	312	614
75	2.534	2.543	006	0·0·12
4	2.490	2.487	132	234
8	2.434	2.432	$3\bar{1}3$	616
40	2.367	2.366	224	428
4	2.314	2.310	231	432
4	2.237	2.240	314	618
4	2.205	2.207	400	800
8	2.169	2.169	323	626
4	2.145	2.145	225	4·2·10
8	2.118	2.118	402	804
13	2.051			
10	2.015			
4	1.994			
45	1.944			

and I_{calc} indicates that the structures of the two minerals are substantially the same. There is, of course, the notable difference of a superstructure in esperite which is presumed to be a consequence of Ca/Pb ordering. A superstructure is also evident in trimerite (Fig. 3); but superstructure notwithstanding, the basic or substructure of all three minerals is due to pseudo-hexagonal arrays of Na, (Ca, Pb), or (Ca, Mn) in the b-axis projection. Systematically strong reflections (indexed on the subcell for esperite and trimerite) are 600, 12·0·0; 303, 309, 3·0·15; 606, 6·0·12, 6·0·18; 903, 909; 006, 0·0·12, 0·0·18, etc. A selection of these is shown in Table 4 which lists structure factor calculations based on $\cos 2\pi(hx+lz)+\cos 2\pi hx \cos 2\pi lz$ of the coordinate species $Na_{1,2,3}$;

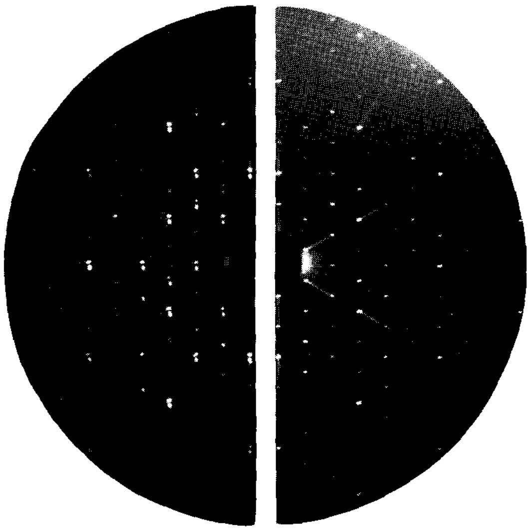

FIG. 2. The h0l precession photographs of trimerite, beryllonite and esperite. The left half of the plate is a superposition of the trimerite (upper set of spots) and beryllonite (lower set of spots) diffraction patterns. The right half of the plate is the esperite pattern slightly enlarged and reversed to allow easy visual comparison of relative spot intensities across a vertical "mirror" plane. MoK_α radiation.

$Be_{1,2,3}$; and $P_{1,2,3}$ using Golovastikov's beryllonite coordinates. The systematically strong reflections show relatively large magnitudes and like signs for each of the atomic species, and in all probability these would dominate the overall structure factor amplitudes of any beryllonite-type structure.

Ordering in esperite: a structural model. Since the superlattice reflections

TABLE 3. COMPARISON OF UNIT CELL DATA FOR BERYLLONITE, ESPERITE AND TRIMERITE

	Beryllonite ($NaBePO_4$)	Esperite ($Ca_3Pb(ZnSiO_4)_4$)	Trimerite[1] ($CaMn_2(BeSiO_4)_3$)
a	8.16 Å	2×8.814 Å	2×8.07 Å
b	7.79 Å	8.270 Å	7.62 Å
c	14.08 Å	2×15.26 Å	2×13.96 Å
c/a	1.725	1.731	1.730
β	90°	90°	90°09′
Z	12	4×3	4×4
Space group:	$P2_1/n$	$P2_1/n$ (subcell)	$P2_1/n$ (subcell) (this study)
Reference:	Wehrenberg (1954)	This study	Aminoff (1926)

[1] Trimerite has a superlattice somewhat analogous to the intermediate plagioclases with "split-'b'" reflections (Brown and Gay, 1958; see Fig. 3). This will be treated elsewhere in some detail.

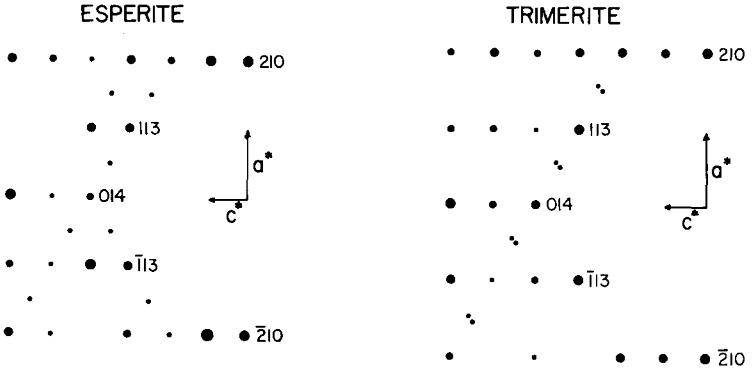

Fig. 3. Schematic of part of the esperite and trimerite h1l precession photographs indexed on the $P2_1/n$ subcell. Notice the "split" super-lattice reflections of trimerite.

in esperite require doubled *a*- and *c*-axes, it is presumed that Ca and Pb must have an ordered distribution. Figure 4 is a schematic *b*-axis projection of a possible ordering scheme, showing four beryllonite-like subcells with Pb substituted in the Na_1 site—that with the largest average sodium-oxygen bond distances—in one subcell and (Ca, Pb) in the Na_1 site of the immediately adjacent subcells. Ca everywhere substitutes

Table 4. Selected Beryllonite Structure Factor Calculations

(x, z) coordinates	*Na*		*Be*		*P*	
	Na_1	(.248, .248)	Be_1	(.917, .239)	P_1	(.921, .238)
	Na_2	(.747, .084)	Be_2	(.103, .082)	P_2	(.106, .081)
	Na_3	(.763, .069)	Be_3	(.431, .090)	P_3	(.432, .092)

hkl	Na_1	Na_2	Na_3	Be_1	Be_2	Be_3	P_1	P_2	P_3
002	−2.000	.986	1.294	−1.980	1.028	.852	−1.978	1.050	.806
004	1.998	−1.028	−.326	1.924	−.942	−1.274	1.910	−.896	−1.350
*006	−1.994	−2.000	−1.716	−1.830	−1.998	−1.938	−1.798	−1.992	−1.894
008	1.990	−.942	−1.894	1.702	−1.114	−.374	1.648	−1.196	−.176
0010	−1.984	1.072	−.736	−1.542	.852	1.618	−1.458	.736	1.752
*0012	1.978	1.998	.942	1.350	1.990	1.752	1.236	1.970	1.588
101	−1.000	.487	.572	.557	1.091	−1.758	.580	1.072	−1.751
103	.999	1.000	.982	−.844	−.583	−.190	−.858	−.570	−.111
105	−.997	.498	.778	1.056	−1.670	1.655	1.090	−1.648	1.660
107	.995	−.509	.025	−1.247	−1.156	1.788	−1.297	−1.164	1.770
*303	−.997	−.999	−1.065	−.980	−.941	−.923	−.990	−.927	−.893
*$30\bar{3}$	1.000	.998	.805	.977	.923	.990	.953	.891	.992
*309	.989	1.000	1.020	.816	.957	.700	.729	1.012	.578
*$30\bar{9}$	−.997	−.999	−.317	−.809	−.902	−1.092	−.823	−.793	−1.114
200	−2.000	−1.998	−1.974	1.008	.546	1.294	1.092	.474	1.314
400	1.998	1.994	−1.894	.986	−1.702	.326	.806	−1.776	.276
*600	−1.994	−1.988	−1.764	−2.000	−1.476	−1.716	−1.974	−1.314	−1.676
800	1.990	1.978	−1.588	1.028	.896	1.894	1.350	1.156	1.924
10.00	−1.984	−1.964	−1.370	.964	1.964	−.736	.498	1.860	−.852
12.00	1.978	1.950	−1.114	−2.000	.176	−.942	−1.894	−.276	−.806

* Systematically strong reflections (Fig. 2).

in the Na_2 sites of beryllonite. Alternate subcells are of different composition. The pseudo-hexagonal array of Pb-Ca-(Ca, Pb) is outlined.

We surmise from this structural model that a variety of ratios of Ca to Pb is permissible. However, at the 2 to 1 ratio the need for a superstructure may be eliminated, since all subcells will have identical compositions and cation distributions. This is conjectural: there may be a geometric reason for slight coordinate shifts, as in anorthite (Megaw *et al.*, 1962); or there may be a structure at the 2:1 composition analogous to trimerite, $CaMn_2(BeSiO_4)_3$, which in turn is comparable in some respects to the intermediate plagioclases with "split-'b' " or 'e'-type reflections (Megaw, 1960). A study of the type material whose Ca to Pb ratio is 2.35 to 1 would be most informative in this respect.

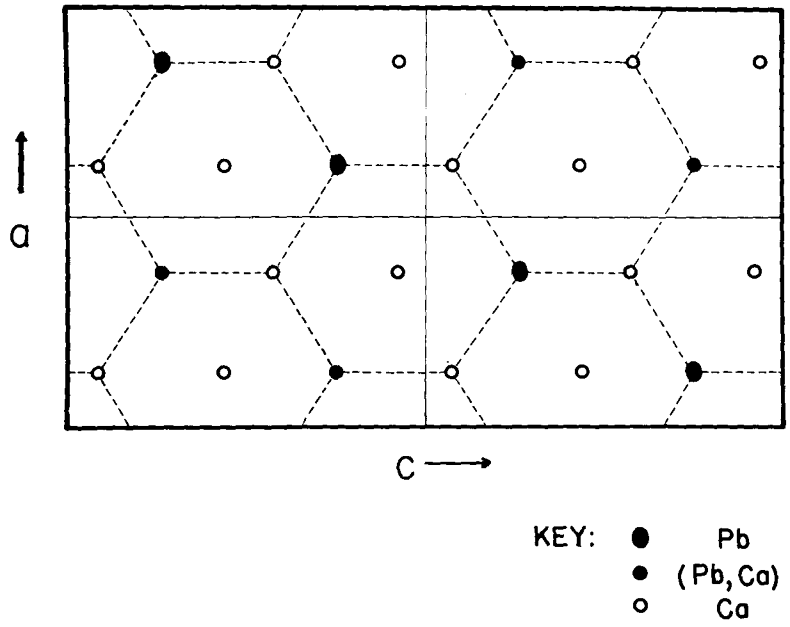

FIG. 4. Schematic *b*-axis projection of esperite, showing a possible ordered distribution of Pb, (Ca,Pb), and Ca atoms in four beryllonite-like subcells.

HEAT TREATMENT

Esperite decomposes between 700 and 800° C. according to the formula

$$\underset{\text{esperite}}{2\,Ca_3Pb(ZnSiO_4)_4} \rightarrow \underset{\text{hardystonite}}{3\,Ca_2ZnSi_2O_7} + \underset{\text{larsenite}}{2\,PbZnSiO_4} + \underset{\text{zincite}}{3\,ZnO}$$

After four days at 1050° C. the above assemblage further decomposes to

$$\begin{array}{ccc} 3\,\mathrm{Ca_2ZnSi_2O_7} + & 2\,\mathrm{Zn_2SiO_4} + & \underline{\mathrm{Zn} + 2\,\mathrm{Pb} + 3/2\,\mathrm{O_2}} \\ \text{hardystonite} & \text{willemite} & \text{volatiles} \end{array}$$

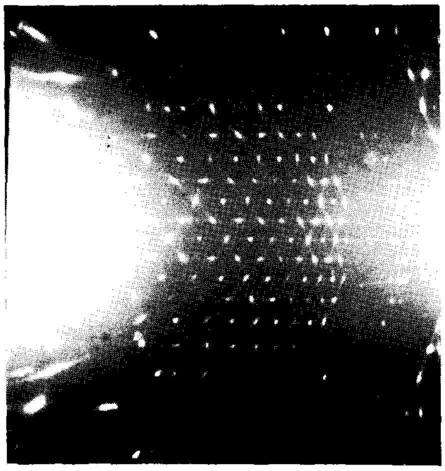

FIG. 5. Part of an *a*-axis oscillation photograph of esperite quenched from ~710° C. demonstrating the hexagonal array of structural defects. The super-lattice reflections are streaked to form a star-of-David pattern.

Hardystonite and willemite are relatively stable end-products. A composite of *x*-ray powder photographs illustrates the decomposition. The total weight loss by such a reaction and decomposition is calculated to be 27.6%. The observed weight loss of a 600-mg specimen of esperite after four days at 1050° C. was 28.5%.

The inversion of esperite from its ordered (low-temperature) form to a disordered form is currently under investigation. A thermally induced transformation of considerable crystallographic interest has been discovered in the course of this study. It involves the development of a hexagonal array of stacking faults or some other structural defect when a single crystal is quenched from ~710° C. (Fig. 5). Details of this and other crystallographic investigations, including the crystal structure determination will appear elsewhere.

FLUORESCENCE AND LUMINESCENCE

Esperite is famed for its brilliant yellow-green fluorescence (~5200 Å) in short-wave ultraviolet light. A similar fluorescence is observed in Mo, Cu and Fe *x*-rays. This mineral responds to high-energy electron bombardment by emitting a kelly-green light which is similar in color, though considerably less intense than that emitted by associated willemite,

$Zn_{1.9}Mn_{0.1}SiO_4$. When the electron beam is finely focussed and of high intensity, esperite emits a pale blue light. The wavelength shift may be caused by heat from the electron bombardment and thus may be a combination of thermo- and cathodo-luminescence effects.

CONCLUSIONS

Esperite, trimerite and beryllonite on the basis of precession studies appear to have similar crystal structures. All three minerals, disregarding superstructure, possess extinctions consistent with space group $P2_1/n$; the cell geometries are markedly pseudo-hexagonal, evidenced by h0l precession photographs. Evidence of twinning was carefully looked for and no "strange" extinctions were found. Accounting for superstructure, trimerite and esperite can be described by *B*-centered cells, with doubled *a*- and *c*-axes.

Crystal structure analysis of esperite is presently being undertaken, with the known beryllonite structure as a guide. It is hoped that through this study, explanations for the superstructure and the interesting thermally induced transformation can be offered.

ACKNOWLEDGEMENTS

We wish to thank the U. S. National Museum for the excellent single crystals of trimerite (USNM R 3531, Långban, Sweden) and larsenite (USNM C 6174, Franklin, N. J.). Single crystal material of beryllonite from Stoneham, Maine was supplied by Dr. D. Jerome Fisher and the fine "calcium-larsenite" specimen by Mr. Richard Hauck. Dr. Charles W. Burnham of the Geophysical Laboratory, Carnegie Institution of Washington, generously offered the *x*-ray facilities during the early stages of this work.

REFERENCES

AMINOFF (1926) *X*-ray studies on trimerite. *Geol. Fören. Förh.* **48,** 19.

BROWN, M. AND P. GAY (1958) The reciprocal lattice geometry of the plagioclase felspar structures. *Zeit. Krist.* **111,** 1–14.

GOLOVASTIKOV, N. I. (1961) The crystal structure of beryllonite. *Kristallografiya* **6,** 909–917.

LAYMAN, F. G. (1957) Unit cell and space group of larsenite. *Am. Mineral.* **42,** 910–911.

MEGAW, H. D. (1960) Order and disorder I, II, III. *Proc. Roy. Soc.* **A 259,** 59–78, 159–183, 184–202.

——— C. J. E. KEMPSTER AND E. W. RADOSLOVICH (1962) The structure of anorthite: II. Description and discussion. *Acta Cryst.* **15,** 1017–1035.

PALACHE, C. (1935) The minerals of Franklin and Sterling Hill, Sussex County, New Jersey. *U.S.G.S. Prof. Paper* **180,** 80–82.

——— L. H. BAUER AND H. BERMAN (1928) Larsenite, calcium-larsenite and associated minerals at Franklin, N. J. *Am. Mineral.* **13,** 334–340.

WEHRENBERG, J. P. (1954) A corrected unit cell for beryllonite. *Am. Mineral.* **39,** 397.

Manuscript received, January 28, 1965; accepted for publication, April 22, 1965.