

# LUDLAMITE FROM THE PALERMO MINE, NORTH GROTON, NEW HAMPSHIRE

C. W. WOLFE,

*Boston University, Boston, Mass.*

## ABSTRACT

Ludlamite, hydrous iron phosphate, has been found in crystals in small veins and in large masses in triphylite at the Palermo mine, North Groton, New Hampshire.

Powder pictures of the Palermo material are identical with those of the type Cornwall material and of the Hagendorf, Bavaria lechnerite. Rotation and Weissenberg pictures about [010] and [001] give: Space group  $P2_1/a$ ;  $a_0$   $10.48 \pm 0.06$ ,  $b_0$   $4.63 \pm 0.05$ ,  $c_0$   $9.16 \pm 0.06$ ,  $\beta = 100^\circ 36'$ ;  $a_0:b_0:c_0 = 2.26:1:1.98$ . Cell volume and G. 3.14 measured on 10 crystals give  $M_0$  833.1. An analysis by Gonyer of Palermo ludlamite gives  $\text{Fe}_6(\text{PO}_4)_8 \cdot 8\text{H}_2\text{O}$  in the unit cell with molecular weight of 859.3.

Opt.: Biaxial (+);  $2V$   $80^\circ$ ;  $\alpha = 1.650$ ;  $\beta = 1.667$ ;  $\gamma = 1.688$ .  $r > v$  slight.

The little known iron phosphate, ludlamite, has recently been discovered amongst the interesting phosphate pocket minerals in the Palermo Mine of North Groton, New Hampshire. The original find was made by Mrs. Leland Wyman and was transmitted to the author by Dr. Wyman for study. Although the first material was very limited in quantity, the Wymans kindly offered all of it for study.

## OCCURRENCES

The first find of ludlamite at Palermo was as crystals in narrow veinlets in the triphylite, which is the primary phosphate of the pegmatite. The largest diameter of the crystals was about 2 mm. In small cavities within the veinlets additional phosphates are found coating the ludlamite. The first of these is *fairfieldite* which occurs as white sheaf-like aggregates. *Vivianite* occurs on the fairfieldite as separate crystals, flattened on  $b$  and elongated parallel to  $c$ . One of the vivianite crystals was 4 mm. long. Coating the vivianite was a *white fibrous mineral* with high birefringence, the indices ranging between 1.615 and 1.71 approximately.  $2V$  is about  $80^\circ$  and the optical sign is positive (+). It may well be a new mineral, but there was insufficient material available for further study. *Reddingite* occurs in very small crystals on the ludlamite. Some yellowish orange bladed crystals with three triclinic pinacoids were implanted on the reddingite and were measured, but because of lack of material they were not subject to adequate study. They may well represent the incompletely described mineral *stewartite*.

In a trip made by the author to the Palermo quarry this past summer in company with Dr. Frondel, a large newly exposed altered triphylite pocket was discovered in which large quantities of massive ludlamite

were found capping and penetrating the triphyllite. The sequence of mineralization in the massive material was essentially the same as that described in the veins. The *triphyllite* is altered to *ludlamite*, frequently forming crystals 5 mm. in greatest dimensions. The best ludlamite crystals usually occur in a matrix of powdery white *fairfieldite* which is later than the ludlamite. *Siderite* is the next alteration product; it occurs in crystallized rhombs and in a very light brown massive form. The triphyllite, in many sections several inches across, is completely replaced by siderite. Dark blue massive *vivianite*, which is probably later than the siderite, is sparsely distributed through the altered portions of the triphyllite. The end stage of alteration of the triphyllite is *wad*. Pyrite and arsenopyrite are frequently present in small amounts.

#### CRYSTALLOGRAPHY

Five well formed crystals were measured, yielding data which are so similar to those of the original description of Maskelyne and Field (1877) that nothing further need be added here. The best crystals are complete counterparts of that figured in Dana (1892).

#### UNIT CELL

Powder pictures were taken of the type ludlamite from Cornwall, of the Palermo ludlamite, and of the lehnerite from Hagendorf, Bavaria. They proved identical. Berman (1925) concluded that lehnerite and ludlamite are identical on optical and physical grounds, and the identification is herewith confirmed.

Rotation and Weisenberg pictures were taken about the [010] and [001] axes, with the following results: Space group  $P2_1/a$ ;  $a_0$   $10.48 \pm 0.06$ ,  $b_0$   $4.63 \pm 0.05$ ,  $c_0$   $9.16 \pm 0.06$ ;  $\beta = 100^\circ 36'$ ;  $a_0:b_0:c_0 = 2.26:1:1.98$ . The elements of Maskelyne and Field (1877) were  $a:b:c = 2.2520:1:1.9819$ ;  $\beta = 100^\circ 33'$ .

#### CHEMISTRY

The precise chemical formula of ludlamite has been in doubt since the first analysis by Flight in Maskelyne and Field (1877), which indicated that the mineral was a basic hydrated iron phosphate. The analysis of Mullbauer (1925) indicated once more the basic hydrated character of the mineral, but there was less water and also a substitution of manganese and magnesium for iron in comparison with the earlier analysis. The x-ray examination of the mineral indicated that the unit cell could not possibly house the complicated formulae listed for ludlamite and lehnerite, and a simple hydrate of iron phosphate with isomorphous replacement of manganese and magnesium for iron was predicted.

An analysis of the Palermo ludlamite by Mr. Forrest Gonyer indicates that the early analyses can be regarded with considerable suspicion. Hydrated phosphates frequently yield analyses showing considerable variation, particularly in the phosphorus pentoxide and water content, from the theoretical formula. That this is true may be seen in Table 1 where the analysis by Gonyer is given in column 1. Ten determinations of the *specific gravity* of the Palermo material gave a rather consistent value of 3.14. This density, coupled with the cell volume obtained from *x*-ray analysis, gives a cell weight of 833.08, and the composition of the unit cell may be calculated as in column 6. Column 5 gives the composition for the theoretical composition of  $\text{Fe}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$  which is in satisfactory agreement with the analysis by Gonyer.

TABLE 1. ANALYSES AND CHEMICAL COMPOSITION OF LUDLAMITE

	1.	2.	3.	4.	5.	6.	7.	8.	9.
FeO	49.22	49.59	45.91	52.76	50.17	5.75	5.41	6.09	6
MnO	—	—	3.10	—	—	—	5.95	.37	6.25
MgO	0.96	0.97	2.21	—	—	0.20	.47	—	—
P <sub>2</sub> O <sub>5</sub>	32.95	33.20	33.87	30.11	33.06	1.95	2.02	1.76	2
H <sub>2</sub> O	16.12	16.24	14.91	16.98	16.77	7.51	7.00	7.82	8
Insol.	.57	—	—	—	—	—	—	—	—
Total	99.85	100.00	100.00	99.85	100.00	—	—	—	—

1. Weight percentages—Palermo ludlamite—analyst Gonyer.
2. Weight percentages of "1" recalculated to =100%.
3. Weight percentages Hagendorf "lehnerite"—analyst Mullbauer.
4. Weight percentages Cornwall ludlamite—analyst Flight.
5. Weight percentages theoretical formula  $\text{Fe}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ .
6. No. of molecules in unit cell of "2";  $M_0=833.08$ , S.G.=3.14 (meas.).
7. No. of molecules in unit cell of "3";  $M_0=846.34$ , S.G.=3.19 (meas.).
8. No. of molecules in unit cell of "4";  $M_0=827.77$ , S.G.=3.12 (meas.).
9. No. of molecules in unit cell of "5";  $M_0=859.25$ , S.G.=3.24 (calc.).

If the cell contains two molecules of this composition, the cell molecular weight would be 859.25, which is substantially higher than the value of 833.08 calculated for the Palermo material. The calculated specific gravity for the theoretical formula based on the cell volume and a cell weight of 859.25 is 3.24 which is about 3% higher than the measured 3.14. This discrepancy is higher than the usual experimental error and must be ascribed to physical factors, such as the excellent basal cleavage; or to chemical factors such as partial leaching of phosphoric acid or incomplete hydration of the mineral with definite omission of some of the water molecules in the structure.

There seems to be little doubt that the composition is  $\text{Fe}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ . Ludlamite, therefore, must be grouped with hopeite, parahopeite, anapaite, and phosphophyllite. A comparison of phosphophyllite (Wolfe, 1940) and ludlamite indicates the similarity in crystallographic properties.

<i>Ludlamite</i>	<i>Phosphophyllite</i> (Wolfe, 1940)
$a_0$ 10.48	$c$ 10.49
$b_0$ 4.63	$b$ 5.08
$c_0$ 9.16	$a$ 10.23
$\beta$ $100^\circ 36'$	$\beta$ $120^\circ 15'$
Cell volume 437.7	470.92
Space Group $P2_1/a$	$P2_1/a$ in ludlamite orientation
Cleavage {001} perfect	{100} perfect = {001} in ludlamite orientation
Cell contents: $\text{Fe}_6(\text{PO}_4)_4 \cdot 8\text{H}_2\text{O}$	Cell contents: $\text{Zn}_4(\text{Fe}, \text{Mn})_2(\text{PO}_4)_4 \cdot 8\text{H}_2\text{O}$

The habit of both species is entirely comparable; although twinning which is so common in phosphophyllite is lacking in ludlamite. The larger cell of phosphophyllite can be ascribed to the greater ionic radius of the zinc which forms two thirds of the cation content.

The thermal analysis curve for ludlamite shows one sharp endothermic reaction at a temperature of  $335^\circ \text{C}$ ., a much smaller similar reaction at  $545^\circ \text{C}$ ., a small exothermic reaction at  $625^\circ \text{C}$ ., and a very small endothermic reaction at  $935^\circ \text{C}$ . The  $335^\circ \text{C}$ ., endothermic reaction undoubtedly is the result of the loss of water. The other minor breaks have not been explained, but it is doubtful whether either of the two other small endothermic breaks can represent a loss of hydroxyl, which was required by the earlier analyses.

#### OPTICS

$n$	Biaxial positive (+)
$\alpha = 1.650$	$r > v$ slight
$\beta = 1.667$	
$\gamma = 1.688$	

*Acknowledgment.* The facilities of the Berman laboratory in the Department of Mineralogy at Harvard were made available to the author during the course of this investigation for which he is highly grateful. The excellent analysis by Mr. Forrest Gonyer and the thermal analysis by Dr. Clifford Frondel are much appreciated.

#### REFERENCES

- BERMAN, HARRY (1925), *Am. Mineral.*, **10**, 428.  
 MASKELYNE AND FIELD (1877), *Phil. Mag.*, **3**, 52, 135, 525.  
 MULLBAUER, F. (1925), *Zeit. Kryst.*, **61**, 331.  
 WOLFE, C. W. (1940), *Am. Mineral.*, **25**, 789.