COMMUNICATIONS FROM THE OXFORD MINERALOGICAL LABORATORY, No. XXVIII.

An occurrence of grunerite at Pierrefitte, Hautes-Pyrénées, France.

By HARRY V. WARREN, B.Sc., D.Phil.,
Queen's College, Oxford.

[Read January 13, 1931; communicated by Prof. H. L. BOWMAN.]

AS grunerite is a somewhat uncommon mineral, and as its occurrence at Pierrefitte in association with lead and zinc ore is unusual, if not unique, it may be worth while to put on record the following notes on some material which I collected during an examination of the Pierrefitte deposits.

The name 'grunerite'[1] was originally given to a fibrous mineral approximating in composition to $FeSiO_3$ and occurring with magnetite and garnet at Collobrières in the dept. of Var, in the south of France, which was described by Gruner in 1847. It was originally supposed to be a pyroxene, but was later shown by Des Cloizeaux and Lacroix to belong to the amphibole group. A similar mineral occurs in the iron deposits of the Lake Superior district,[2] and elsewhere; but it has not been recorded from the Pyrenees.

Mode of occurrence.

The mineral occurs at the Pierrefitte mine, near the village of Pierrefitte-Nestales, 10 miles south of Lourdes, in two forms, which are quite distinct: (i) as nearly the sole constituent of a grunerite-

[1] The name of the mineral is often erroneously spelt grünerite. The name grunerite (Grunerit) was given to it by A. Kenngott (Das Mohs'sche Mineralsystem, 1853, p. 69) in honour of E. L. Gruner, who first described it in 1847 (Compt. Rend. Acad. Sci. Paris, 1847, vol. 24, p. 794; Annales des Mines, Paris, 1848, ser. 4, vol. 14, pp. 284–301). Emmanuel Louis Gruner (1809–1883) was at that time professor at the École des Mineurs, St. Étienne, and afterwards Inspecteur Général des Mines, and professor at the École des Mines in Paris.

[2] A. C. Lane and F. F. Sharpless, Amer. Journ. Sci., 1891, ser. 3, vol. 42, p. 505. S. Richarz, Amer. Journ. Sci., 1927, ser. 5, vol. 14, p. 150. [Min. Abstr., vol. 3, p. 375.]

schist which overlies the ore-bodies; (ii) as distinct needles, either isolated or forming a network, in the ore.

Under the microscope the grunerite-schist resembles a normal amphibole-schist, but the rock itself is harder, tougher, and more massive, and, indeed, the term schist is hardly applicable, as the grunerite needles are matted together irregularly and there is little tendency to splitting. It is commonly associated with a carbonaceous schist, and the ore in its neighbourhood usually contains magnetite.

Where found in the ore, the grunerite is usually associated with galena, blende, chalcopyrite, magnetite, and pyrrhotine. However, it is in galena that the needle-like crystals are most in evidence.

Mineralogical properties.

Under the microscope the Pierrefitte grunerite is clear and colourless if free from other minerals, but in the mass it is frequently dirty white or grey. In polished specimens of the ore the grunerite sometimes shows a decided yellow tinge when viewed by reflected light. The individual needles are rarely a tenth of an inch in length and are usually much smaller.

The grunerite needles in the schist frequently show a core of an undetermined bluish-green mineral which possesses weak pleochroism, and appears to resemble a similarly related mineral in some of the Lake Superior grunerite.

The grunerite possesses perfect prismatic cleavage, and although most of the fragments were too small to measure, a few were large enough. The cleavage-angles on some of the larger fragments were measured. The fragments were then broken up and examined optically to see if their properties differed visibly from those of the finer material, but no differences could be discovered. The goniometer readings were not entirely satisfactory owing to imperfections on many faces. The measured cleavage angles varied from 53° 55′ to 54° 55′, the mean being about 54° 20′. The readings from the best fragment, which agreed well together, gave a somewhat larger mean angle, 54° 48′. Even this angle is considerably less than that of most varieties of amphibole.

The refractive indices were determined by the immersion method. Three mixtures of α-monobromnaphthalene and methylene iodide were made, to agree with α, β, and γ, respectively, and Miss M. W. Porter very kindly determined for me the indices of these mixtures by means of an Abbe-Pulfrich refractometer. Care was taken to maintain a constant temperature during the final determinations. The results, with Na-light, are $\alpha = 1{\cdot}676$, $\beta = 1{\cdot}693$, $\gamma = 1{\cdot}707$, $\gamma - \alpha = 0{\cdot}031$. Using the approximate formula $\cos V_\alpha = \sqrt{(\beta-\alpha)/(\gamma-\alpha)}$, we find that $2V_\alpha = 84^\circ\ 26'$. The plane of the optic axes is parallel to (010), and the acute bisectrix (α) emerges through (100). A direct determination of the optic axial angle was made with a grunerite needle mounted on a stage goniometer and immersed in a liquid mixture whose index coincided with β. This gave $2V = 84^\circ\ 15'$. The close agreement between the observed and the calculated optic axial angle is doubtless accidental, but, nevertheless, it probably indicates that the indices of refraction are approximately correct.

In the same way the maximum extinction-angle ($c : \gamma$) in the prism-zone was found to be $13^\circ\ 22'$. Dispersion of the optic axes was not noticeable.

Chemical composition.

It was extremely difficult to separate the grunerite when occurring in the ore, and the separation was eventually only accomplished by boiling the crushed fragments of ore in aqua regia for several hours. This drastic treatment had no visible effect on the optical properties of the mineral, though it may possibly have affected slightly the chemical composition.

Chemical analyses of grunerite from the schist and from the ore were kindly made for me by Mr. E. G. Radley, of the Museum of Practical Geology, London. Owing to the presence of carbon, the analyses were complicated, and I am very grateful to Mr. Radley for the trouble which he took on my behalf. The results are given in columns I and II of the following table (p. 480), which shows also the analyses of grunerite from other localities.

The higher percentage of silica in the grunerite from the ore is probably due to a small amount of quartz which occurs in the ore. Some of the iron and some of the carbon may have been oxidized, and possibly a little of the former has gone into solution, as a result of the treatment with aqua regia. In the discussion and table dealing with the relation existing between the chemical composition and the optical properties the analysis of the grunerite from the schist will be used, as this was only treated with aqua regia for a short time.

The carbon can be seen as minute specks in nearly all the grunerite, and is partly responsible for the dirty colour. It remains as a black flocculent residue on solution of the grunerite in hydrofluoric acid.

Analyses of grunerite.

	I.	II.	III.	IV.	V.
SiO_2	46·42	49·11	48·53	47·17	43·9
TiO_2	0·15	0·12	—	—	—
Al_2O_3	0·25	1·81	1·02	1·00	1·9
Fe_2O_3	0·09	2·03	1·14	1·12	—
FeO	42·60	38·98	39·20	43·40	52·2
MnO	2·23	0·79	0·66	0·08	—
MgO	3·12	2·97	4·06	2·61	1·1
CaO	1·51	0·75	1·31	1·90	—
Na_2O	0·70	0·94	1·06	0·47	—
K_2O	0·43	0·64	0·19	0·07	—
H_2O	0·14 *a* / 1·78 *b*	0·10 *a* / 1·39 *b*	1·71 *c*	2·22	0·5
C	0·65	0·31	—	—	—
F	—	—	—	0·07	—
	100·07	99·94	98·88	100·11	99·6
Sp. gr.	—	—	3·44	3·518	3·713

a Below 105° C.; *b* above 105° C.; *c* above 110° C.

I. Pierrefitte, Hautes-Pyrénées, France (from schist). (Analyst, E. G. Radley.)
II. Pierrefitte, Hautes-Pyrénées, France (from ore). (Analyst, E. G. Radley.)
III. Mt. Humboldt, Lake Superior, Michigan, U.S.A. S. Richarz, loc. cit., 1927, p. 151.
IV. La Mallière, near Collobrières, Var, France. S. Kreutz, Sitzungsber. Akad. Wiss. Wien, Math. naturwiss. Kl., Abt. I, 1908, vol. 117, p. 910.
V. Collobrières, Var, France. E. L. Gruner, Ann. des Mines, Paris, 1848, ser. 4, vol. 14, p. 301.

Relation between chemical composition and optical properties.

These results agree, on the whole, with those of previous work,[1] namely, that the indices of refraction and the birefringence increase with an increase in the percentage of FeO and MnO. The birefringence and the index α of the Pierrefitte grunerite are not in complete accord with the above conclusion, but the discrepancies are small and there is clearly a general agreement.

The following table (p. 481) summarizes the data which are known at present. Neglecting other constituents, I have calculated the molecular percentages of $FeSiO_3$, $MnSiO_3$, $MgSiO_3$, and $CaSiO_3$.

It will be noticed that the Pierrefitte grunerite is high in $MnSiO_3$ and low in $MgSiO_3$ when compared with the grunerite from Mt. Humboldt. This may account for the slight discrepancy in birefringences. Both also contain considerably more $MnSiO_3$ than the

[1] S. Richarz, loc. cit., p. 153.

	Collobrières.[1]	La Mallière.[2]	Pierrefitte.	Mt. Humboldt.[3]
$FeSiO_3$	96·4	85·8	81·4	80·4
$MnSiO_3$	0·0	0·2	4·3	1·4
$MgSiO_3$	3·6	9·2	10·6	14·8
$CaSiO_3$	0·0	4·8	3·7	3·4
α	—	1·672	1·676	1·666
β	1·73*	1·697	1·693	1·684
γ	—	1·717	1·707	1·700
$\gamma-\alpha$	0·056	0·045	0·031	0·034
2V	50°	80–84°	84° 15′	85°
$c:\gamma$	11–15°	10–11°	13° 22′	14–15°

* Strictly $(\alpha+\beta+\gamma)/3$.

other grunerite and this may be due to the presence of the undetermined green mineral.

Origin of the grunerite.

Grunerite is supposed to have resulted from the metamorphism of ferrous carbonate in depth,[4] but there appears to be no evidence for such an origin in this area. It is possible that the carbon, which is present in the grunerite itself and in the neighbouring carbonaceous schist, has exerted a reducing action which has some bearing on the formation of the grunerite. The grunerite of the Krivoy Rog[5] in South Russia is also stated to be associated with carbonaceous schists. Quartz, which is rare at Pierrefitte, may have combined with the magnetite, in the presence of carbon, to form grunerite according to the equation :

$$C + 2Fe_3O_4 + 6SiO_2 = 6FeSiO_3 + CO_2.$$

This appears to be a possible explanation of the presence of grunerite at Pierrefitte. But it is probable that in different occurrences the mode of formation may not always have been the same.

[1] E. L. Gruner, loc. cit.; A. Lacroix, Bull. Soc. Franç. Min., 1886, vol. 9, p. 40.

[2] S. Kreutz, loc. cit.

[3] S. Richarz, loc. cit.

[4] C. R. Van Hise, A treatise on metamorphism. Monogr. U.S. Geol. Survey, 1904, no. 47, pp. 244, 834.

[5] F. Beyschlag, J. H. L. Vogt, and P. Krusch, The deposits of the useful minerals and rocks. Translated by S. J. Truscott, 1914–16, p. 1059.