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GRÜNERITE FROM ROCKPORT, MASSACHUSETTS, AND A SERIES OF SYNTHETIC FLUOR-AMPHIBOLES

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GRÜNERITE

In our thermal studies of iron silicates we have found the fayalite of Rockport, Mass., a very useful natural material, on account of its unusually close approach to the theoretical composition, Fe_2SiO_4 . The best fayalite from that source always has inclusions of grünerite, which we identified in an earlier paper. The refractive index $\gamma = 1.73$, then measured, is higher than that of any grünerite hitherto recorded and suggests that, like the fayalite, it is very close to the pure ferrous end-member of its series.¹ We have accordingly investigated it further and find that this suggestion is fully borne out by the facts.

Our first Rockport fayalite contained only a very small amount of disseminated grünerite, but upon examining other specimens in the collections of the U. S. National Museum we found that the fayalite was, in some examples, surrounded by a zone consisting almost entirely of grünerite. The specimens available do not show the relations of these minerals to the other minerals of the pegmatitic mass from which they were obtained, but an "anthophyllite" from this locality was described by Warren in 1903 in a brief preliminary note as follows: "Where the fayalite comes in contact with the quartz of the pegmatite, a reaction rim is developed consisting of radial fibrous aggregates. . . . The fibres are translucent, white to light brown in color, and at once suggest anthophyllite by their appearance." Warren then gives optical relations which indicate that it was an amphibole, apparently of orthorhombic symmetry.² Qualitative chemical tests showed it to be nearly pure iron

¹ Bowen, N. L., and Schairer, J. F., *Am. J. Sci.*, vol. **24**, p. 201, 1932.

² Warren, C. H., *Am. J. Sci.*, vol. **16**, pp. 339-342, 1903.

silicate. The description applies in all particulars to the material we have investigated except that ours is always monoclinic, with extremely fine polysynthetic twinning, and, therefore, to be classed as grünerite. Possibly in his brief preliminary examination Warren overlooked the fine twinning and we may be dealing with the same material. Indeed, an anthophyllite with nearly all the Mg replaced by Fe'' has not yet been definitely identified among natural minerals.

The best grünerite from this locality was found in the Roebbling collection, now in the U. S. National Museum. It occurs as radiating, fibrous to asbestiform aggregates constituting a shell upwards of 1 cm. thick about masses of fayalite. It is pale gray to greenish-gray in color, though in places somewhat brownish from oxidation. The density, kindly determined by Dr. H. E. Merwin, is 3.597.

Under the microscope the fibres are found to be universally twinned after 100 and the twin bands are usually of hair-line width, a fact that renders the measurement of optical properties very difficult. The refractive indices, measured in immersion liquids in sodium light, are as follows: $\gamma = 1.729$, $\beta = 1.709$, $\alpha = 1.686$, all $\pm .002$. From these values the optic axial angle is calculated as $2V$ negative = 86° which is in general agreement with the direct observation of the interference figure though no great reliance is to be placed upon this on account of the fine twinning, nor, of course, is the calculated value of high accuracy because of the large possible error in refractive indices. The extinction angle $c \wedge \gamma = 10^\circ$.

CHEMICAL COMPOSITION OF ROCKPORT GRÜNERITE

A very satisfactory separation of the mineral from associated fayalite can be effected by hand-picking and when this is followed by magnetic separation of magnetite a substantially pure product is obtained. The analysis of this product is given in Table 1. It proves to be, as was expected, the nearest approach to the pure $\text{Fe}_7\text{H}_2(\text{SiO}_3)_8$ that has yet been encountered. The small amount of Fe_2O_3 is probably largely secondary, for it is impossible to avoid including some material that has been changed to a slightly brownish color. The MnO content is small and comparable with that

found in the associated fayalite. Fluorine is excessively low and the mineral may be regarded as a definite hydroxy-amphibole.

TABLE I
CHEMICAL COMPOSITION OF GRÜNERITE

	I	II
SiO ₂	47.54	48.08
Al ₂ O ₃	0.20	—
Fe ₂ O ₃	0.71	—
FeO	47.25	50.13
MnO	2.14	—
MgO	0.04	—
CaO	none	—
Na ₂ O	0.29	—
K ₂ O	0.11	—
H ₂ O	1.55	1.79
F	0.01*	—
	99.84	100.00

I. Grünerite from Rockport, Massachusetts.

II. Theoretical H₂Fe₇(SiO₃)₈ or (OH)₂Fe₇(Si₄O₁₁)₂.

* Determined by E. S. Shepherd.

CUMMINGTONITE-GRÜNERITE SERIES

The establishment of the properties of the end-members of mineral groups is of especial value in systematic mineralogy. As an end-member of the cummingtonite-grünerite series it is of interest to compare the properties of the present grünerite with other members of this series. Sundius has collected the data for a number of representative amphiboles.³ Unfortunately when one attempts to correlate the properties with the composition it is necessary to make simplifying assumptions regarding the composition, certain constituents being neglected, and MnO, when present in small amount, being added to FeO. Accepting Sundius's simplified compositions but stating them with hydroxyl recognized as essential, we may present his data and ours as in Table 2.

³ Sundius, N., *Am. J. Sci.*, vol. 21, p. 330, 1931.

Winchell, Kunitz, and others have made similar correlations but Sundius has been able to include their data.

TABLE 2
OPTICAL PROPERTIES OF THE GRÜNERITE-CUMMINGTONITE SERIES

	Composition mol. per cent		α	β	γ	$\gamma-\alpha$	$2V_{\alpha}$	$c \wedge \gamma$
	(OH) ₂ (Fe,Mn) ₇₋ (Si ₄ O ₁₁) ₂	(OH) ₂ Mg ₇₋ (Si ₄ O ₁₁) ₂						
A	100	0	1.686	1.709	1.729	0.043	86°	10°
1	90.5	9.5	1.672	1.697	1.717	.045	82°	10°-11°
2	77.5	22.5	1.666	1.684	1.704	.038	90°	14°
3	60.5	39.5	1.655	1.669	1.686	.031	93°	17°
4	42.5	57.5	1.639	1.648	1.667	.028	111°	20°
5	40.0	60.0	1.640	1.647	1.665	.025	115°	20°

A. Grünerite, Rockport, Mass.

1. Grünerite, Collobrières (La Mallière) France. Sundius, *Am. J. Sci.*, vol. **21**, pp. 330-344, 1931.
2. Grünerite, Cummington, Mass. Sundius, *Am. J. Sci.*, vol. **21**, pp. 330-344, 1931.
3. Grünerite, Bijiki, Marquette, Mich. Sundius, *Am. J. Sci.*, vol. **21**, pp. 330-344, 1931.
4. Cummingtonite, Röbergsgruvan, Sweden. Sundius, *Am. J. Sci.*, vol. **21**, pp. 330-344, 1931.
5. Cummingtonite, Persberg, Sweden. Sundius, *Am. J. Sci.*, vol. **21**, pp. 330-344, 1931.

In Fig. 1 the data of Table 2 are plotted and the curves (straight lines) therefore give the variation of refractive indices with composition in the cummingtonite-grünerite series in so far as these are determined by existing data on natural minerals. The curves are drawn so as to give particular weight to our especially pure end-member. It will be noted that when this is done the value of α for the Collobrières grünerite (No. 1, Table 2 and Fig. 1) lies well below the curve. The Collobrières mineral is, however, notably divergent in chemical composition from that strictly characteristic of the series in question. Indeed, it contains so much CaO, Al₂O₃, Fe₂O₃, and alkalis that only by courtesy can it be regarded as a member of the series.⁴ Its birefringence is too high for any member of the series, being somewhat greater than that of the very pure Rockport grünerite.

The other members plotted show a fairly close approach to the theoretical composition of a member of the series and the plot as a whole may therefore be regarded as giving a rather reliable picture of the variation of properties with composition.

⁴ An analysis of this grünerite is given by Kreutz, *Z. Kryst.*, vol. **49**, p. 210, 1910.

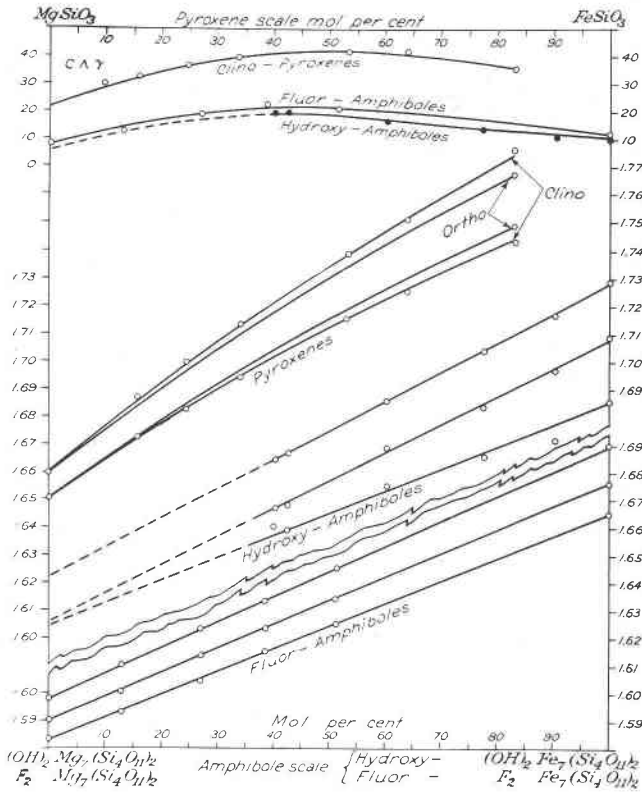


FIG. 1. Optical properties of Mg-Fe amphiboles and pyroxenes.

The curves of refractive indices have been drawn as broken lines at low-iron compositions. It may be that no such monoclinic hydroxy-amphiboles exist; certainly none has yet been found. As Sundius has emphasized, all such amphiboles now known are orthorhombic.⁵ This relation in the hydroxy-amphiboles is in strong contrast with that in fluor-amphiboles now to be described.

SYNTHETIC FLUOR-AMPHIBOLES

In our studies of the inversion of pyroxenes of the MgSiO₃-FeSiO₃ series from the orthorhombic to the monoclinic form we found certain members (bronzites) very reluctant to invert. In order to induce the change we resorted to the use of NaF as a

⁵ Sundius, N., *Min. u. pet. Mitteil.*, vol. 43, pp. 422-440, 1933.

"catalyst," a minute quantity of the fluoride being added to the pyroxene before heating it in the sealed, evacuated silica-glass tube.⁶ Success was attained by this method but in addition to the new form of pyroxene we always obtained a thin drusy coating of minute euhedral crystals having the properties of amphibole. After obtaining these crystals from bronzite thus accidentally, we then proceeded to prepare others in the same manner from pyroxenes of other compositions (in fact from pure synthetic pyroxenes). A series of amphiboles was thus prepared in the absence of oxygen and water but in the presence of fluorine and they can therefore be nothing other than members of fluorine-bearing series of Fe'', Mg amphiboles.⁷ The magnesian end-member was made from pure clino-enstatite, the ferrous end-member from a glass of composition FeSiO₃, and members having intermediate optical properties were prepared from intermediate pyroxenes. We have no means of determining the exact composition of the amphiboles because the quantities yielded are too small for analysis. Acting on the assumption that the variation of optical properties of this series is a linear function of the mol. composition, as it appears to be in the hydroxy-series, we have plotted the measured values of the refractive index, γ , of the intermediate members upon the straight line joining the values of the index, γ , of the end members. When the values of the indices β and α are then plotted at the composition thus determined by the γ value they are found to lie, within the error of measurement, on the straight lines joining the β and α values of the end members, as is shown in the resulting plot, Fig. 1, by the curves labelled "fluor-amphiboles."

The extinction angles of these synthetic amphiboles were also determined. They always show repeated twinning after 100, in the same manner as the natural grünerite, and the extinction was measured against the twinning. The members of intermediate composition always have higher extinction than do the end-members so that the extinction angle must pass through a maximum at some intermediate composition. If, again, it is assumed that the composition of the intermediate members is determined by the straight-line

⁶ Bowen and Schairer, *Am. J. Sci.*, vol. 29, p. 170, 1935.

⁷ It is possible that a little of the sodium of the NaF enters into the amphiboles but there is evidence that most of it combines with the silica glass tube. Attempts to make hydroxy-amphiboles in the same manner but with NaOH substituted for NaF gave only negative results.

relation of refractive indices discussed above, we may plot the extinction angle against composition with the result given in Fig. 1, in the upper section of the figure and in the curve labelled "fluor-amphiboles." The extinction angles of the hydroxy-amphiboles are shown in a curve that is practically parallel to this. Monoclinic hydroxy-amphiboles of this series with low iron content are, as already stated, unknown. The curve has been extended as a broken curve parallel to that for the fluor-amphiboles merely for its suggestive value.

The refractive indices of the fluor-amphiboles are, it will be noted, lower than those of the hydroxy-series. It has, however, been necessary to break scale in plotting them both on one diagram, otherwise the γ -values of the fluor-series would, in part, overlap the α -values of the hydroxy-series. The curve of α for the fluor-series is sensibly parallel to the curve of α for the hydroxy-series and the actual lowering of index resulting from the substitution of fluorine for hydroxyl is about the same as that produced in topaz by an equal amount of substitution of fluorine for hydroxyl. For the index γ the lowering is not uniform throughout the series on account of the fact that in the hydroxy-amphiboles a strong increase of birefringence is brought about by increase of iron content whereas in the fluor-amphiboles a much more moderate effect of that kind occurs.

To the diagram, Fig. 1, have been added for comparison the curves of refractive indices of the pyroxenes of the $MgSiO_3$ - $FeSiO_3$ series in both orthorhombic and monoclinic forms and also the curve of extinction angles of the monoclinic series which, like the

TABLE 3
OPTICAL PROPERTIES OF SYNTHETIC FLUOR-AMPHIBOLES

Composition mol. per cent		α	β	γ	$c \wedge \gamma$	Initial pyroxene mol. % $MgSiO_3$
$F_2Mg_7(Si_4O_{11})_2$	$F_2Fe_7(Si_4O_{11})_2$					
100	0	1.583	1.590	1.598	8°	100
87*	13	1.593	1.600	1.610	13°	84
73*	27	1.604	1.613	1.623	20°	68
62*	38	1.615	1.623	1.633	23°	47
48*	52	1.625	1.634	1.645	21°	26
0	100	1.665	1.676	1.690	12°	$FeSiO_3$ glass

* Probable composition assuming linear variation (see text).

fluor-amphibole curve, passes through a maximum at an intermediate composition.⁸

In Table 3 the optical properties of the fluor-amphiboles are given together with their probable compositions and the composition of the pyroxene from which each was produced.

GENERAL CONSIDERATIONS

Fluorine-bearing amphiboles have been prepared by various investigators but apparently always from mixtures of extremely complex character and they throw little light on the nature of amphiboles except to emphasize their complexity. In the recent work of Scheumann and Lüdke such very complex amphiboles were prepared, the novel feature being that the synthesis was carried out at atmospheric pressure.⁹ Closed tubes were used in the preparation of our amphiboles but our sole object was the exclusion of air and consequent maintenance of the iron in the ferrous state. We did not measure the pressure, and while it is possible that pressures moderately exceeding the atmospheric were built up in the tube we have no reason to believe that high pressure prevailed.

Examination of Table 3 shows that the amphibole produced by this method was always much more magnesian than the pyroxene from which it was produced. Even if the composition assigned to the amphibole is in each case only approximately correct this relation will still hold. We are not sure that the amphibole formed is that which is in equilibrium with the pyroxene, but it almost certainly differs from the pyroxene in the direction approaching equilibrium. It is of interest therefore to recall that, in the pure Mg, Fe pyroxenes and olivines, the pyroxene is always more magnesian than the olivine with which it is in equilibrium, a relation whose significance we have commented upon.¹⁰ In the series olivine, pyroxene, amphibole, which is a typical discontinuous reaction series, we appear to have, then, the general relation that each phase is more magnesian than that member of the preceding phase with which it is in equilibrium. In igneous rocks there is ordinarily a change of composition of the liquid whereby it becomes less magnesian and these three phases separating successively from the

⁸ See Bowen and Schairer, *Am. J. Sci.*, vol. 29, p. 198, 1935.

⁹ Scheumann, K. H. and Lüdke, W., *Berichte der sächsischen Akad. Wiss. Leipzig*, vol. 85, pp. 273-278, 1933.

¹⁰ Bowen and Schairer, *Am. J. Sci.*, vol. 29, p. 213, 1935.

liquid reflect that fact in their composition. But in a rock formed by recrystallization during a metamorphic episode and containing all three of these phases we should expect that the amphibole would be more magnesian than the pyroxene and the pyroxene, in turn, more magnesian than the olivine.

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