

THE
AMERICAN
JOURNAL OF SCIENCE.

EDITOR: EDWARD S. DANA.

ASSOCIATE EDITORS

PROFESSORS GEO. L. GOODALE, JOHN TROWBRIDGE,
W. G. FARLOW AND WM. M. DAVIS, OF CAMBRIDGE,

PROFESSORS A. E. VERRILL, HENRY S. WILLIAMS, AND
L. V. PIRSSON, OF NEW HAVEN,

PROFESSOR GEORGE F. BARKER, OF PHILADELPHIA,
PROFESSOR H. A. ROWLAND, OF BALTIMORE,
MR. J. S. DILLER, OF WASHINGTON.

FOURTH SERIES.

VOL. IX—[WHOLE NUMBER, CLIX.]

WITH FIVE PLATES.

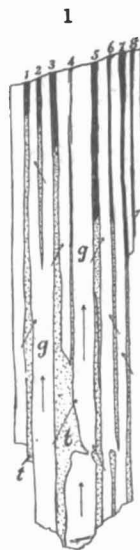
NEW HAVEN, CONNECTICUT.

1900.

ART. IV.—*On Graftonite, a new Mineral from Grafton, New Hampshire, and its Intergrowth with Triphylite; by S. L. PENFIELD.*

MATERIAL for this investigation was sent to the author for identification by Mr. George L. English of New York, who, on being informed that it was probably a new mineral, took special pains to secure a supply of it, and has given the following information concerning its occurrence: The mineral was found on the south side of Melvin Mountain, about five miles west of the village of Grafton. It was irregularly disseminated through a coarse crystalline mass of quartz and feldspar, probably a pegmatite vein, the feldspar individuals being at times fully four feet long. Associated with the new mineral in the vein were found beryl, black tourmaline, almandine garnet, muscovite and biotite, all crystallized on a rather large scale, especially the beryl. All of the new mineral that could be found was taken from the vein, and the total output consisted of a few crystals and a considerable quantity of irregular fragments. The crystals and also the fragments present a rough, weathered appearance, and, what is unusual and at once very striking, they consist of alternating layers or lamellæ of dark and light material, the lamellæ being less than 0.5^{mm} in diameter and often exceedingly thin. Both the light and the dark material gave reactions for a phosphate containing iron and manganese as bases. The light material, however, contained only ferrous iron, while the dark reacted chiefly for ferric. The light and dark portions were so nearly alike in specific gravity that they could not be satisfactorily separated by means of the silver-thallium nitrate fusion. The dark portion was found to have a somewhat lower specific gravity than the light, and a product was separated which represented a partial separation of the two minerals and consisted chiefly of the light-colored material. This was analyzed by Mr. W. E. Ford of the Sheffield Laboratory with results which are given beyond. The iron was found by Ford to be both ferrous and ferric, and, since a little of the carefully selected light-colored material gave only the reactions for ferrous iron, it was inferred that the original mineral was undoubtedly a ferrous compound, and that the dark portions were the result of partial decomposition, attended by the oxidation of the iron and manganese. Although the analysis indicated that the mineral was undoubtedly new, the results, owing to the character of the material, were not wholly satisfactory and conclusive, and there was some doubt as to the propriety of giving a new name to the species.

Fortunately for the solution of the problem in hand, among several pounds of material sent by Mr. English, a single fragment, about as large as the end of one's finger, was found, which showed only a very little of the dark, decomposed material. It was undoubtedly the central portion or core of a crystal, the outer portion of which had been oxidized, leaving within a core of fresh unaltered material. Upon careful examination this fresh portion was found to consist of two minerals in alternating layers, and fig. 1, which represents the appearance of a thin section prepared at approximately right angles to the lamination, will give an idea of the arrangement and relative proportions of the two minerals. The white portions, *g*, represent the new mineral, graftonite, which constitutes about two-thirds to three-quarters of the total material. This in the fragment possessed a delicate salmon color, but appeared almost colorless in thin section. The other mineral *t*, which in the figure is represented by the stippled portions, was found to be triphylite. The latter possessed a pale green color as seen in the fragment, but appeared almost colorless in thin section. The exterior of this fragment of fresh material showed in places a darkening, due to the oxidation of the iron and manganese, and the thin section showed, as represented by fig. 1, that the oxidation is confined wholly to the triphylite lamellæ, the new mineral being evidently a more stable material. On breaking up the fragment it was found that the lamellæ separated quite readily, and it was possible to obtain the two minerals practically pure, by careful working, splitting off lamellæ at times almost as thin as a sheet of paper, and examining each particle with a lens. Thus, discarding everything which seemed at all questionable and using all of the available material, 0.546 grams of the new mineral and 0.166 grams of the triphylite were secured. The specific gravity of the graftonite was found to be 3.672. The hardness is 5 and the luster is vitreous to resinous. In appearance it resembles very closely the salmon-colored varieties of lithiophilite. The associated triphylite was found to have a specific gravity of 3.58.



Making complete analyses of the two minerals on the small quantities of available material proved to be a somewhat interesting problem in analytical chemistry, and a brief outline of the method employed is as follows: It was first proved by qualitative tests that the iron was wholly ferrous. All of the

material of each substance being employed, water was first estimated by ignition in a closed tube, as described by the author.* The contents of the tube were then dissolved in hydrochloric acid, the solution evaporated to dryness and the residue was taken up in water and a very little acid. To this solution, heated to boiling, barium hydroxide was added, which precipitated barium phosphate, along with the iron, manganese, magnesium and the bulk of the calcium, leaving the alkalis in solution. After filtering, the barium was separated from the filtrate by means of ammonia and ammonium carbonate, and the alkalis were finally obtained in the form of chlorides. From the very hygroscopic character of the chlorides it was evident that lithium was the prevailing alkali, and, since the quantities were small, it was considered best to weigh the alkalis as sulphates, and subsequently determine the SO_4 , thus obtaining data for estimating both the per cent of the alkali oxides, R_2O , and their joint molecular weight. The precipitate produced by barium hydroxide, containing the phosphoric acid and bases, was dissolved in hydrochloric acid, and barium was precipitated by means of sulphuric acid. The barium precipitates, obtained at this stage of the analysis and from the alkali separations, were carefully examined for traces of P_2O_5 and bases. The filtrate from the barium sulphate, containing P_2O_5 and bases, after evaporating to dryness and taking up in a very little acid, was diluted, heated to boiling, precipitated by an excess of sodium carbonate and filtered. The filtrate contained the bulk of the P_2O_5 , which was precipitated by magnesia mixture. The precipitate consisted of basic phosphates and carbonates of iron, manganese, magnesium and calcium. The latter was dissolved in a little hydrochloric acid, and the iron in combination with the P_2O_5 was separated by a basic acetate precipitation. After filtering, the precipitate was dissolved in acid, the iron together with the P_2O_5 was precipitated with ammonia, weighed and subsequently the P_2O_5 was separated by means of ammonium molybdate. In the filtrate from the basic acetate precipitate the manganese, magnesium and calcium were estimated by well known methods.

The results of the analyses are given below, together with the analysis made by Mr. Ford on partially purified material.

The analysis of the triphylite, though showing a slight deficiency, compares favorably with the analyses of triphylite from Bodenmais, Bavaria and Norwich, Mass., made by the author† and quoted in Dana's Mineralogy, page 757. The alkali oxide was found to have a molecular weight of almost exactly 30, which is the molecular weight of Li_2O , thus indicating the purity of the oxide.

* This Journal, III, xlviii, p. 31, 1894.

† Ibid., III, xvii, p. 226, 1879.

Quantity,	Triphylite. 0.1668 gr.	Graftonite. 0.5462 gr.	Ratio.		Analysis by Ford.	
P ₂ O ₅	42.3	41.20		} .290	P ₂ O ₅	40.80
FeO	33.4	30.65	.426		Fe ₂ O ₃	10.16
MnO	9.9	17.62	.248	} .857	FeO	24.28
MgO	1.3	0.40	.010		MnO	15.38
CaO	0.2	9.23	.165		CaO	7.25
Li ₂ O	9.2	0.33*	.008		Na ₂ O	1.15
H ₂ O	1.7	0.75			K ₂ O14
	<hr/>	<hr/>			H ₂ O	1.17
	98.0	100.18			<hr/>	100.33

As shown by the analysis of the graftonite, alkalis are practically wanting in the new mineral. The 0.33 per cent recorded as Li₂O was found to have a molecular weight of 44, indicating that the alkali was chiefly lithia, and it is probable that it was derived, for the most part at least, from a slight admixture of triphylite. Since triphylite, however, is a normal phosphate, its presence in very small quantity would have no appreciable effect upon the ratio of P₂O₅ to the total metallic oxides, and hence an amount of triphylite corresponding to 0.33 per cent of alkali oxide has not been deducted from the analysis. The ratio of P₂O₅ : RO, as indicated by the analysis, is .290 : .857 = 1 : 2.95, or, approximately, 1 : 3. The formula of graftonite is, therefore, R₂P₂O₆, R standing for the bivalent metals, iron, manganese and calcium, which evidently are isomorphous with one another and not present in fixed or definite proportions. In Ford's analysis the considerable amount of Fe₂O₃, which is recorded, indicates that the original mineral has suffered some alteration, attended by oxidation, the amount of oxygen in the 10.16 per cent of Fe₂O₃ in excess of FeO being 1.02 per cent. This oxidation, in all probability, belongs as much to the manganese as to the iron, if not more. If the oxidation is neglected, and the iron considered wholly as FeO, the ratio of P₂O₅ : RO in Ford's analysis becomes 1 : 2.90, or, practically, 1 : 3, as required by a normal phosphate. Moreover, the oxidation has not been attended by any considerable amount of hydration, the amount of water, 1.17 per cent, being small.

From a chemical standpoint graftonite is interesting as being one of the very few anhydrous, normal phosphates thus far observed. Thus, we have xenotime and monazite, normal phosphates of the yttrium and cerium metals, and the minerals of the triphylite group, characterized by containing an alkali metal, as follows: triphylite, LiFePO₄; lithiophilite, LiMnPO₄; natrophilite, NaMnPO₄, and beryllonite, NaBePO₄,

* Molecular weight 44, hence containing some Na₂O.

while all other mineral phosphates contain either fluorine or hydroxyl radicals, or water of crystallization.

Before the blowpipe graftonite darkens and fuses at about 2 to a globule which is slightly magnetic. The globule becomes decidedly magnetic after continued heating on charcoal. During fusion in the forceps the mineral imparts to the flame the pale bluish-green color characteristic of a phosphate. Fused in a sodium carbonate bead in the oxidizing flame, the green color characteristic of manganese is obtained. The mineral is readily soluble in hydrochloric acid, and if a little of the concentrated solution on a watch glass is brought in contact with a drop of dilute sulphuric acid a precipitate of calcium sulphate is formed. In the closed tube only a trace of water is given off, and at a full red heat the material shows signs of fusion.

The crystallization of graftonite is monoclinic, although no material for obtaining exact and reliable data has thus far been found. The crystals are without exception dark from the presence of oxidized triphylite, while the outer surfaces of the graftonite itself have undoubtedly suffered more or less oxidation. In some cases oxidation and decomposition have gone on to such an extent that only a rude suggestion of the crystal form remains. The crystals, moreover, are either fragmentary, or they are attached so that only a portion of their faces are developed. The crystals averaged over 4^{cm} in greatest diameter, and admitted only of approximate measurement by means of the contact goniometer.

The forms observed, which are represented in the accompanying figures, are as follows :

<i>a</i> , 100	<i>m</i> , 110	<i>n</i> , 130	<i>e</i> , 021
<i>b</i> , 010	<i>l</i> , 120	<i>d</i> , 011	<i>p</i> , 111

In establishing the axial ratio the value of β was derived from a direct measurement of the angle made by the edge between *b* and *e*, fig. 2, with the vertical edge between *b* and *n*. Other fundamental measurements were, $b \wedge m = 51^\circ$ and $b \wedge d = 62^\circ$. The axial ratio obtained from these values is as follows :

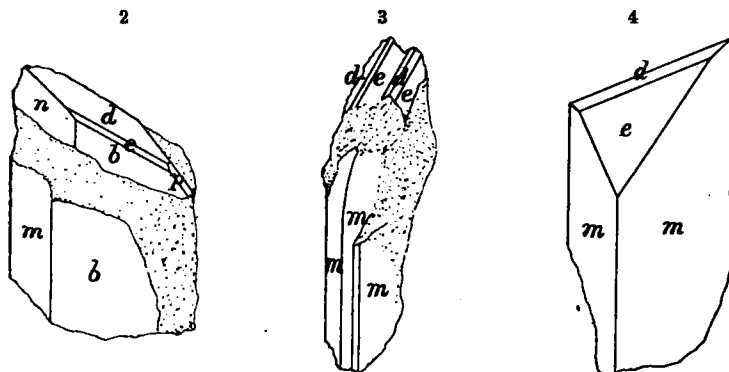
$$a : b : c = 0.886 : 1 : 0.582 ; \beta = 66^\circ$$

It must be borne in mind, however, that the fundamental measurements are not very reliable, and that the axial ratio therefore can only be approximately correct.

A few of the more important measured and calculated angles are as follows :

	Measured.	Calculated.
$m \wedge m, 110 \wedge 1\bar{1}0 =$	-----	78° 00'
$l \wedge l, 120 \wedge 1\bar{2}0 =$	115°	116 36, fig. 6
$b \wedge n, 010 \wedge 1\bar{3}0 =$	22 30'	22 22, fig. 2
$e \wedge e, 021 \wedge 0\bar{2}1 =$	-----	93 31
$p \wedge p, 111 \wedge 1\bar{1}1 =$	-----	41 32

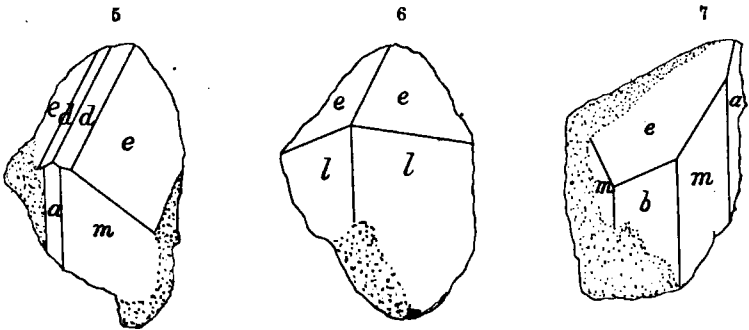
Figures 2 to 7 represent the crystals which were available for study. Fig. 2, drawn with $b, 010$, in front, shows a portion of a crystal, about 5^{mm} wide, which is attached to a rather large, irregular mass of graftonite associated with biotite. In this and in other figures no attempt has been made to represent by means of an artistic effect the irregular, broken surfaces of the graftonite and associated minerals. The stippled portions of the figures are intended to represent the irregular surfaces, and, if carried out in the proper proportion in fig. 2, the stippling



should continue for a considerable distance above and to the right, beyond the limits of the figure. Fig. 3 represents two crystals, about 7^{mm} long, which have grown together in parallel position and have suffered deformation, the vertical edges and faces of the prism being decidedly curved, although the monosymmetric character of the crystal seems not to have been disturbed. No cracks, resulting from cleavage or fracture, are visible in this specimen, and no other specimen was observed which showed similar deformation. Figs. 4, 5, 6 and 7 represent fragments and corners of much decomposed crystals with rough faces. The material as a whole was very unfavorable for crystallographic study, and it is possible that the conclusions reached concerning the orientation of some of the crystals and the identification of the forms are erroneous, although, as far as could be told with the contact goniometer, the measure-

ments indicated the simple forms which have been recorded in the foregoing list.

The optical properties of the graftonite, as far as they were studied, indicate monoclinic symmetry. The lamination, as will be explained more in detail later, is parallel to the pinacoid $b, 010$, of the graftonite, and hence a section like that represented by fig. 1, cut at right angles to the lamination, is at



right angles to the symmetry plane. Two sections were thus prepared from the small fragment of fresh material, and, except that they were at right angles to the symmetry plane, nothing is known concerning their orientation. In these sections, when examined in polarized light, the graftonite was found to have an extinction parallel to the lamination, as indicated by the arrows, fig. 1. In one of the sections, when examined in convergent polarized light, a portion of a biaxial interference figure was observed toward the limit of the field, and the position of the figure indicated distinctly that the plane of the optical axes is at right angles to the symmetry plane, the acute bisectrix being in the symmetry plane. By mounting a small fragment of the thin section on the little axial angle apparatus devised by Professor Klein,* filling the vessel with a liquid of high index of refraction, and turning until the bisectrix came to the center of the field of the polariscope, the horizontal character of the dispersion could be distinctly seen, and it was estimated that the divergence of the optical axes, $2V$, was about 50° to 60° . The birefringence is not very strong and its character is positive.

The interlamination of two minerals such as graftonite and triphylite, differing in chemical composition and crystallizing in different systems, is an interesting and unusual phenomenon which seemed worthy of some study. Before discussing the

* Groth's *Physikalische Krystallographie*, 1895, fig. 690, p. 750.

problem presented by this particular intergrowth, however, it may be well to cite a few illustrations of a somewhat similar nature. The best and undoubtedly the most familiar illustration of the lamellar intergrowth of two minerals is that of albite (triclinic) and orthoclase (monoclinic), a phenomenon commonly observed in studying thin sections of rocks, and familiarly known to petrographers as the perthitic or micro-perthitic structure. In the case of the feldspars the two minerals are closely related both in chemical composition and crystalline form, they are united by their pinacoid faces $b, 010$, having their vertical axes parallel, and thus the cleavage directions and the interfacial angles of the two minerals conform very closely to one another. Other familiar instances of parallel, though not of lamellar intergrowth are of staurolite (orthorhombic) on cyanite (triclinic), rutile (tetragonal) on hematite (hexagonal-rhombohedral), and chalcopyrite (tetragonal) on both tetrahedrite and sphalerite (isometric). In each of these cases it is probable that the two minerals have certain molecular or crystallographic features so nearly alike that the two substances can grow together in certain definite positions, somewhat analogous to the growth of two crystals of the same material in parallel or in twin position.

Evidently the most important thing to be determined in connection with the study of the interlamination of the monoclinic graftonite and the orthorhombic triphylite is the manner in which the two minerals are intergrown. Undoubtedly the graftonite, which makes up from two-thirds to three-quarters of the total mass of the crystals, has exerted the controlling influence upon the crystalline form, for the external shape of the crystals is monoclinic and not orthorhombic. In all of the specimens the lamination is very pronounced and parallel to the clinopinacoid $b, 010$, of the graftonite; however, the surfaces by which the two minerals are united are not plane and even, like cleavage or crystal faces, but undulatory, somewhat resembling in miniature a surface presented by a slab of sedimentary rock exhibiting ripple marks. An idea of the uneven character of the surfaces may be gained by noting the irregular, wavy lines of juncture between the two minerals as seen in cross section, fig. 1. In the specimen represented by fig. 2 there was a limited area where the lamination was apparently parallel to the prism m of the graftonite, but in other parts of the specimen and in all other crystals the lamination was throughout parallel to the clinopinacoid b .

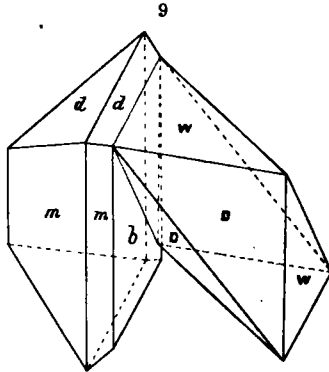
When a section like fig. 1 is examined in polarized light, the graftonite, as already stated, shows parallel extinction; the extinction of the triphylite, however, in the particular section under consideration, is inclined about 27° to the direction of

lamination, and differently in different lamellæ, as indicated by the arrows, fig. 1. In lamellæ 1, 3 and the upper part of 5 the extinction is to the right, while in 2, 6, 7 and the lower part of 5 it is to the left. Thus evidently the orthorhombic triphylite and the monoclinic graftonite have not intergrown with pinacoid faces in common, for in that case both minerals would have shown parallel extinction. The inclined extinction of the triphylite naturally suggested the idea that one of its prism or dome faces might be parallel to the clinopinacoid of the graftonite, and, on looking for some similarity between the forms and angles of the two minerals, it was observed that the angle of the macrodome 102 of triphylite ($102 \wedge \bar{1}02 = 62^\circ 23'$) was practically the same as the angle between the clino-dome d , 011, and the clino-pinacoid b , 010, of graftonite ($011 \wedge 010 = 62^\circ$). If therefore a triphylite crystal is orientated so that its macro-axis is parallel to the clino-axis of graftonite, and is then tipped 31° so that a dome face 102 comes in contact with the clinopinacoid b of graftonite, then the clinodome d of the graftonite and the macrodome of the triphylite fall practically in one plane. In trying to find other points of similarity which the two minerals might possess, recourse was had to the spherical projection. Fig. 8 represents in its full lines the spherical projection of graftonite, the location of the forms recorded on p. 24 being indicated by italic letters, while the location of four forms, 001, 031, 301 and $\bar{2}21$, which were not observed as crystal faces, are indicated by indices in small figures. The projection of the triphylite is given in dotted lines, the known forms being indicated by heavy, full-faced letters, while the indices of a few possible forms are also given in heavy figures. The lettered forms of the triphylite are as follows:

B, 010	M, 110	W, 102	V, 302
C, 001	L, 120	E, 101	D, 021

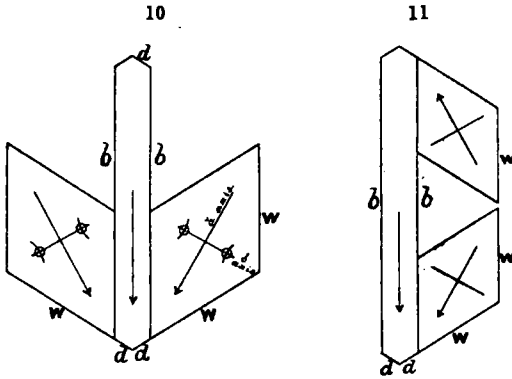
As a starting point in constructing the projection of the triphylite, the zone in which 100 and C, 001, are located was made to coincide with the zone b , d , \bar{d} , of the graftonite, and the location of two faces of the macrodome W of the triphylite to coincide, one with the clinodome d , the other with the clinopinacoid b of the graftonite. Thus, as shown by the figure, the forms C, V and 100 of triphylite correspond closely to 031, 001 and \bar{d} , 011 of graftonite respectively. A zone W, 122, M, W of triphylite is almost coincident with that joining b and p of graftonite, though the forms M and 122 of the former are located several degrees distant from the pyramid p of the latter. Finally the faces of the dome D, 021 and 021, of triphylite fall one within about 3° of the prism

is almost parallel to the prismatic face m , 110, of the graftonite, as shown by the fact that the edges between m and d and W and D , fig. 9, form almost a continuous line, or from fig. 8, that the angle between d and m ($011 \wedge 110 = 54^\circ 56'$) is almost the same as that between W and D ($102 \wedge 021 = 53^\circ 54'$)



The foregoing demonstrations furnish a working hypothesis for explaining how the two minerals might possibly have grown together because of similarity in certain prominent crystallographic features, and it remains to be shown to what extent the hypothesis conforms to the structural features presented by the intergrowth of the two minerals. In fig. 10 there is represented in the center an ideal cross-section of a graftonite crystal, at right angles to the clino-axis, and showing the outlines of the forms d and b . Such a section should exhibit in polarized light parallel extinction, as is the case with the graftonite in fig. 1. On either side of the graftonite in fig. 10 are represented sections of triphylite crystals at right angles to the macro-axis b and so orientated that faces of the macrodome W are parallel to and in contact with the clinopinacoid b of the graftonite; compare fig. 9. Such sections should show extinction angles of 31° to the right and to the left of the interposed graftonite, as indicated by the arrows. The structure indicated by the ideal section, fig. 10, corresponds to the optical properties of the minerals in the section represented by fig. 1, where the interlaminated triphylite (compare lamellæ 1, 2 and 3) shows inclined extinction, symmetrically disposed to the right and to the left of the plane of lamination. If a cross section of the composite crystal were at right angles to the symmetry plane of the graftonite, but not at right angles to the clino-axis, then the extinction angles of the triphylite would be less than 31° , but still remain equal on either side of

the plane of lamination. In the section represented by fig. 1 the extinction angle of the triphylite is about 27° ; hence, if the hypothesis which is proposed is the correct one, the section should be nearly though not quite at right angles to the clin-axis of the graftonite and the macro-axis of the triphylite. Furthermore, according to the investigation of Penfield and



Pratt,* it may be assumed that in triphylite having about 33 per cent. of FeO the acute bisectrix is the *b*-axis, the plane of the optical axes being 100, as indicated by fig. 10, and the divergence of the optical axes, $2V$, about 80° . Hence in a section similar to fig. 10, at right angles to the *b*-axis of the triphylite, the latter should show a bisectrix; while if slightly inclined, as may be assumed to be the case in the section represented by fig. 1, some portion of the interference figure ought to be visible. This in reality is the case when the triphylite lamellæ are examined, although, owing to the character of the material, the interference figures are not very distinct. Thus the optical properties, as far as they have been made out, confirm the hypothesis that a dome face of the triphylite is in contact with a clinopinacoid face of the graftonite. Fig. 11 represents two crystals of triphylite orientated in twin position to one another upon a clinopinacoid face of graftonite. Crystals thus orientated, provided they increased in size, would have to adapt themselves to circumstances as they grew together, and the surface of contact between them would probably be irregular and not conformable to any definite crystal plane. Such a condition may have existed when lamella 5, fig. 1, was forming, for in one portion the extinction is to the right, in another to the left, while the two portions unite along an

* This Journal, III, 1, p. 387, 1895.

irregular line which can be distinctly traced under the microscope.

The composite crystals of graftonite and interlaminated triphylite are large, and, therefore, it seems probable that a very long time would be required for their growth and development. It does not seem probable that the crystals could have been originally of one material and subsequently, without oxidation of the iron or manganese, have been changed in part to a material of different composition. The acceptance of such a theory would require that the product resulting from the alteration (in this case the rare mineral triphylite) should have developed as interspersed lamellæ having definite crystallographic orientation with reference to the original material. Again it does not seem probable that they were at one time wholly graftonite, and that later, by pressure or other agency, they were broken up into lamellæ, leaving interstices for the subsequent infiltration of triphylite as a cementing material. The crystals, with the exception perhaps of the one represented by fig. 3, show no evidence of having been crushed and cemented together, nor are there any inequalities, striations or offsets visible on their faces to lead one to suspect that the crystals have been opened out and broadened as a result of the interlaminated triphylite. It seems rather probable that the crystals must have developed in a solution or medium which contained the chemical constituents for the formation of both compounds, and that the growth was of such a nature that graftonite was deposited at one period and triphylite at another. Thus, according as the supply of material favorable for the formation of the one compound or the other was most abundantly at hand, the growth of the crystals proceeded until the large interlaminated individuals were formed.

It is to be regretted that only one small fragment of fresh unaltered material, without definite crystal faces, was found. The material as a whole was of such a nature that accurate crystallographic measurements could not be made, and orientated sections containing unaltered triphylite could not be prepared, hence the crystallographic relations of the two minerals have not been established with absolute certainty. It is hoped, however, that the time devoted to finding even a possible explanation of the remarkable intergrowth presented by the two minerals has not been spent in vain.

Laboratory of Mineralogy and Petrography,
Sheffield Scientific School of Yale University, November, 1899.