ART. XXX.-Communications from the U. S. Geological Survey, *Rocky Mountain division.* IV. On minerals of the Cryolite *group recently found in Colorado;* by 'WHITMAN CROSS and W. F. HILLEBRAND.

In this Journal. for October, 1882,\* we announced, in connection with the description of zircon and other minerals from the neighborhood of Pike's Peak, that cryolite and several allied fluorides had been identified from the same region and would form the subject of a paper at an early day. Shortly after the above date there appeared in the "Zeitschrift fur Krystallographie," etc., an interesting and valuable paper by Professor P. Groth+ containing the results of a searching investigation into the crystallographical and chemical properties, not only of cryolite and its alteration products, but also of the few

\* Third series, vol. xxiv, p. 281.

+ P. Groth, "Beiträge zur Kenntniss der natürlichen Fluorverbindungen," Zeitschrift für Krystallographie, vii, pp. 375-388 and 457-493.

allied minerals occurring independently. The chemical anal· yses of the above article, which had been previously published apart, were made by J. Brandl\* upon material selected and crystallographically examined by Professor Groth. By a crit· ical review of the existing literature, and by renewed investi: gations in doubtful cases, it was hoped to clear away the uncertainty which had hung about some of the members of the group, and as the available material was, for the most part, far better than had been examined before, it was possible to obtain very satisfactory results.

In the present paper, frequent reference will necessarily be made to the results of Messrs. Groth and Brandl. Owing to better material, we are in some cases able to give new or supplementary data, and only in one instance, namely, in regard to the composition of pachnolite, is there any discrepancy between our results and those contained in the articles above cited.

*Locality and occurrence.*-The point at which these minerals occur may be described as at the northeast base of St. Peter's Dome, a small conical peak, due west of Cheyenne Mountain, and near the Pike's Peak toll-road, which is now completed from Colorado Springs to the Seven Lakes, at the base of Pike's Peak. Although several miles in a straight line from the mountain proper, the locality may be considered as within the" Pike's Peak region."

The country rock of this whole district is a coarse, reddish, biotite granite, of a general type which is common in the Colorado Range of the Rocky Mountains, and is, in all probability, a part of the Archean formation. A specimen collected near St. Peter's Dome shows largely predominant reddish feldspar, brilliant, black biotite, and q unrtz, the latter rather su bordinate, in small grains between the other minerals. The feldspar consists largely of an intergrowth of orthoclase and' albite, some· what after the manner of perthite. The rock disintegrates very readily (1. c., p. 281), and the study of the geognostic relations in the region is much hindered by the gravelly debris which covers many slopes almost entirely.

The cryolite locality lies on the southeast border of the extensive district within which Amazon stone and its associated minerals are so abundantly found in cavities in the granite. In the immediate vicinity astrophyllite and associated zircon occur in granitic veins, and also, as does the arfvedsonite, in veins of white quartz.

The minerals to be described occur in two veins of massive white quartz, and in each case they were discovered by prospectors. The two veins are scarcely more than one-third of a

\* J. Brandl, Sitzungsbericht der konigl. bayr. Akademie der Wissenschaften zu Miinchen, 1882, p. 118, and Annalen der Ohemie, ccxiii, p. 1.

mile apart, and their continuation is so concealed by soil and debris that it cannot be seen what their relation to each other and to the other veins may be. They differ, however, so greatly in the minerals they contain and in the manner of occurrence of the latter, as to make it improbable that they are united.

In the vein which we will designate vein A, cryolite, pachnolite, thomsenolite, gearksutite, prosopite and probably ralstonite appear, with but rare associated minerals. In vein B, on the other hand, prosopite, fluorite and mixed fluorides occur intimately associated with zircon, kaolinite and a greenish yellow mica. As the minerals of the two veins are so distinct, we can best consider them in the groups afforded by the veins themselves.

# YEIN A.

At this place a very steep incline was sunk on an outcrop of white quartz. At about ten feet from the surface a small, solid mass of fluorides, some two feet in thickness, was struck, and below it carne massive quartz again. The boundaries of this mass are quite irregular, and its lnteral extent is still unknown.

This small body of mineral, which was no doubt wholly cryolite originally, is now composed of the same alteration products which are known in conneetion with the Greenland cryolite, some of them in better development than is known in this latter locality. The only associated minerals observed to penetrate the cryolite mass are astrophyllite and columbite, the former being almost wholly altered to a dull green substance which is not homogeneous and whose composition is unknown. The astrophyllite springs from the granitic wall of the vein in the form of blades several inches long, and zircon was noticed with it in the mass at the base of the blades, while never seen imbedded directly in the cryolite. The columbite is in small, rhombic prisms of the type found with the Amazon stone, and occurs quite rarely in isolated crystals. The cryolite decomposition products adjacent to the astrophyllite will be described later (page 289).

Adjoining the quartz, the cryolite is always decomposed, and is generally replaced by a massive mixture of pachnolite and thomsenolite, but not infrequently the alteration has gone still farther and a white powder of extreme fineness, like purest kaolin, fills the space between quartz and more solid pachnolite. This is the geark sutite which, when wet, as it usually is here, makes a thick paste or mud. The description of the minerals will begin with cryolite and proceed through the different stages of alteration here exhibited.

# CRYOLITE.

Within the mass of fluorides in vein  $A$  there is a surprisingly large amount of fresh cryolite. It can be obtained in solid pieces several inches in diameter, and the process of alteration can be readily followed from the perfectly fresh material. It occurs in massive aggregates of crystalline individuals which, as shown by the continuous cleavage surfaces, are often two to three inches in diameter, and are never very small. The fresh· est substance has usually a delicate pink or even decidedly rose color; less frequently a faint greenish tinge, and none so far obtained has the snowy whiteness or the clearness of the Greenland cryolite. The color disappears on heating, leaving the cryolite pure white. Cleavage, in three directions, very nearly at right angles to each other, is quite distinct, but although as plainly marked as in the Greenland mineral, actual separation parallel to the cleavage. planes is not so easily effected as is normal. The cause of this lies, undoubtedly, in the complicated polysynthetic twin structure revealed by the microscope.

No crystals of cryolite have been found, and a thoroughly satisfactory study of the laws of twinning which appear in this massive material would require much more time than we have been able to devote to it. In some of the thin sections which have been prepared the relations are simple and admit of perfectly satisfactory explanation. Thus, in some sections par· allel to the plane of most perfect cleavage, a lamellar polysyn. thetic twin structure like that of common plagioclase is visible. These lamellæ lie parallel to one of the two visible systems of cleavage lines, are continuous, approximately of equal width, appear most distinctly when parallel to the principal section of one of the crossed Nicols, and extinction takes place simultaneously, so far as can be determined by the weak polarization of the mineral, at an angle of about  $45^{\circ}$  from the twinning line and parallel to the diagonals of the prism as indicated by the cleavage fissures. This structure evidently indicates ·the law of twinning freq uently noticed in the Greenland cryolite. namely, that parallel to  $I(110)$ . The same twinning law is seen in many sections parallel to one of the less perfect or prismatic cleavage surfaces. A similar laminated structure appears, and extinction takes place at 30° to 33° from the twinning line, in opposed directions in alternate lamine,  $31^{\circ}$  $15'$  being the angle of extinction with the edge of  $I$ , theoretically required in sections parallel to a prism face (Groth). Such a section usually shows two systems of lamine situated nearly at right angles to each other but seldom, if ever, cross· ing. The second system seems probably to represent a twin· ning parallel to the base. Associated with these two systems

is frequently a third crossing the other two at nearly 45°, as seen in a section parallel to  $\tilde{I}$ . This may be caused by twinning parallel to a hemiorthodome, but, as stated above, the laws here represented have not as yet been fully investigated.

*Ohemical investigation.-For* all analyses of this and the following minerals the greatest care was taken to have the purest of reagents. The fluorine was in all cases determined by the Wohler-Fresenius method, with the slight modifications introduced by Brandl,\* except that the iron plate, instead of the oil bath, was used for heating. The sulphuric acid was obtained of the highest degree of concentration and purity by distillation from a platinum retort. The water was determined by absorption in a chloride of calcium tube, the mineral having been heated in a tube with either oxide of lead or carbonate of sodium, the results being the same whether one or the other was used.

The cryolite, of which the analysis is here given, possessed the specific gravity 2'972 at 24° C., was faintly pink in color, and contained as a visible impurity the oxide of iron represented in the analysis:



The presence of a slight amount of water indicates incipient alteration. Purer material was subsequently obtained but a second analysis seemed unnecessary.

*Alteration of cryolite.*—The alteration of the cryolite proceeds in two ways, producing the same minerals in the end. By one process the principal cleavage fissures are utilized by the solutions which effect the change, and thin walls are formed of a white crystalline substance. The next step seems to be the bodily removal of the cryolite matter between these walls, leaving a network of partitions in the three directions of the chief cleavages of the original cryolite. These partitions or walls are lined by minute crystals. The second mode of alteration proceeds from the neighboring quartz, and from the boundaries of the different crystalline individuals of the cryolite, the result being a compact crystalline mass of a faint bluish tinge. The material at hand illustrates the two processes and their products about equally well, and they are often naturally combined.

\* A.nnalen der Chemie, ccxiii, p. 1.

t As the mean of 53'35, 53'46.53'55 and 53'85.

## PACHNOLITE.

*a. From the thin walls.-The* microscopical examination of the walls and membranes produced by the first mode of alteration of the cryolite shows them to be coated by many minute but perfect, colorless and transparent, prismatic crystals which are usually placed at right angles to the central plane of the wall, though sometimes in irregular manner. They reach a maximum length of  $2^{mm}$  by a thickness of 0.2 to 0.4mm. The crystals are occasionally yellow in color, while retaining their transparency, the color being doubtless owing to some matter produced by the alteration of the astrophyllite which pene· trates all such specimens. The crystallographical identification of these crystals with pachnolite is quite certain, for upon placing them in vertical position under the microscope the prism angles can readily be measured and correspond closely to  $81^{\circ}$  24' and 98° 36', the theoretical angles of pachnolite (see Groth, l. c. p. 463). The prism  $I(110)$  and base  $O(001)$  are in all cases the chiet faces, accompanied frequently by a hemiorthodome, and very rarely by a clinodome, both very slightly developed. The former is considered to be  $-\overline{i} (101)$  from data given below. Pyramid faces have not been seen upon crystals of this growth. Although all detached crystals show when examined in polarized light as lying upon a prism face, an oblique twinning plane in the prismatic zone,\* still a projecting angle upon the base can but rarely be seen. The reflecting surfaces of the thinnest walls are composed of innumerable small facets of rhombic outline-the basal planes of the very low prisms. In fragments from some of the thinnest walls, placed horizontally under the microscope and observed in polarized light, twinning parallel to the shorter (ortho-) diagonal could easily be seen. The crystals are usually quite equally bisected by the twinning line. The central portion of these walls is rather dull white and probably represents the alteration product on cleavage planes of the original cryolite, while the crystals themselves were formed during or after the removal of the intermediate cryolite substance.

Tbomsenolite is but rarely present with pachnolite on these walls. The few crystals found correspond to the pachnolite in size and possess a prism angle of nearly 90°, and a very perfect cleavage parallel to the base.

Material from a network of thin walls covered by pachnolite crystals was subjected to chemical analysis, yielding the result under II. p. 281.

*b. From the bluish alteration product.*-The pale bluish mass formed by the second mode of decomposition has in great part a regular crystalline structure produced by a more or less per-

\* Groth, 1. c. p. 464.

fect intergrowth of pachnolite individuals in three directions approximately at right angles to each other. Nearly simultaneous reflection over the greater part of certain irregular sur· faces makes this relation plain. By the examination of such a surface with a loupe, one can usually identify a number of rhombic facets which are nearly or quite coincident in position with striated planes, the two corresponding to  $O$  and  $I$  of different individuals. Sucb a structure is also illustrated by the crystals in the numerous small cavities occurring in the massive material.

These cavities are of wholly irregular shape and reach a maximum observed diameter of  $\tilde{S}$  to  $4^{\tilde{m}}$ . The crystals lining them are often very perfect and are occasionally  $2$  or  $3<sup>mm</sup>$  in length, with a thickness of  $1^{mm}$  or less. The study of these crystals proves that, as in the preceding case, most of them must be referred to pachnolite, although thomsenolite is sparingly present. These pachnolite crystals differ in habit from those already described in that the pyramid is usually prominent, being, however, in nearly every case truncated by the basal plane; in fact, crystals without O are very rare. The rhombic section of the prism is everywhere plain. Although every prism on being optically tested showed a twinning plane in the prismatic zone, the low projecting angle of  $179^{\circ}$  20' upon  $\overline{O}$  could seldom be distinctly seen. Many crystals are somewhat extended parallel to one pair of prism faces. A hemiorthodome of the same order as the pyramid is sometimes devel· oped and probably corresponds to that noticed upon the crystals of the foregoing type. Most of the crystals of these cavities, while very perfect and distinctly recognizable as pachnolite, are too small and their surfaces are too frequently covered by minute crystals of a later growth to be available for measurements with the goniometer.

Whether thomsenolite is mixed with pachnolite in the mas· sive portion or not is difficult to determine. It is certainly in comparatively small quantity if present, and in the cavities all the recognizable crystals are deposited upon the pachnolite and are apparently distinctly later in formation.

Two specimens of the bluish, massive material when carefully examined proved to contain pachnolite in a form allowing of more exact crystallographic, optical and chemical in vestigation.

The first of these, which we will designate specimen A, is about  $8\times5\times2^{cm}$  in size, is somewhat more coarsely granular than the variety described, and possesses in an eminent degree the regular structure there observed. While quite compact in the greater part of the specimen there are portions in which the grains are more loosely aggregated together and parts of

various individuals have perfectly developed crystal faces. In some minute cavities a few crystals with quite perfect terminations were found, and upon these some faces were sufficiently large and polished to admit of measurements with a Fuess reflection goniometer. These crystals are about  $1^{mm}$  long and nearly the same in thickness. They show  $I(110)$ ,  $O(001)$ , with subordinate  $-1$  (111) and a negative pyramid determined as  $-3.3$  (311). They are all twinned parallel to  $i\text{-}i(100)$  and the low projecting angle upon  $O$  is sometimes distinctly visible.

The angles given in the following table are all means of numerous closely agreeing measurements, and demonstrate the crystallographical identity of the mineral under discussion with pach notite:



The face  $-3.3$  was observed on a number of distinct twin crystals with projecting angle on 0, and in several cases on both of the negative angles.

Upon one side of specimen  $A$  are a few thomsenolite crystals, distinguishable by their prism angle of nearly 90°. They lie irregularly and seem to be later in formation than the pachnolite. Upon them are deposited minute prosopite crystals and indistinct alteration products. In the mass of this specimen no thomsenolite can be detected, while all individuals with partially free development are plainly pachnolite. Analysis III of table (page 281), was made on material obtained from the clear, loosely granular portions of specimen A, and although it was necessary to include many transparent grains of irregular shape in order to obtain a desirable amount of substance, there is no doubt in our own minds but that thomsenolite was wholly absent from the material analyzed.

The second specimen (B), from which especially good material was obtained, had a seam  $2<sup>cm</sup>$  thick of coarse granular structure running through it, and upon splitting it open along this seam two surfaces of water-clear, loosely adhering crystalline grains of pachnolite were exposed, with the regular arrangement described. Actual development of crystal faces other than the prism is rarer than in specimen A, but the size of the grains, reaching  $5^{mm}$  in length by  $1-3^{mm}$  in thickness, is such as to admit of the preparation of thin sections for optical examination, and also gave absolutely pure material for chemical analysis. None of the crystals upon which the faces were well formed were superior to those from specimen A, and only measurements of the prism angles were made. The face  $-3\overline{3}$ was not observed at all.

The optical properties of these pachnolite crystals are such as to leave no room for doubt concerning their crystallographical identity with the mineral described by Professor Groth as pachnolite. Several sections were prepared as nearly parallel to the clinopinacoid as possible. These exhibit in all cases a twin structure, and this is frequently polysynthetic. The twinning lines are straight and lie parallel to the vertical axis. Extinction takes place at  $21^{\circ}$   $30'$  -  $22^{\circ}$  or  $68^{\circ}$  -  $68^{\circ}$  30' from the twinning line, in opposed directions in alternate laming. According to Professor Groth the bisectrix is in the plane of symmetry and inclined  $68^{\circ}5'$  forward from the vertical axis. Sections parallel to the base show the twinning structure also, the line lying parallel to the orthodiagonal.

A large part of the purest crystals and pyramids from this specimen were used for chemical analysis and repeated water determinations, the results of which are given below (IV, page 281).

*Ohemical investigation.* - Previous to the analysis by **J**. Brandl' of pachnolite carefully selected by Professor Groth, pachnolite and thomsenolite were considered to possess the same chemical composition. The results of all earlier analyses, excluding such as referred to manifestly very impure material, while frequently deviating materially from the figures required by theory for the formula NaF, CaF<sub>2</sub>, AlF<sub>3</sub>, H<sub>2</sub>O, still agree on the whole very well, as shown in the accompanying table, and fully justified the belief in the chemical identity of the two species:



<sup>1</sup> Ann. d. Chem., ccxiii, p. 6.<br><sup>2</sup> Neues Jahrbuch für Min., etc., 1876, p. 851.<br><sup>3</sup> Proceedings Acad. Sci. of Philad., 1876, p. 42.

<sup>4</sup> Annalen der Chemie und Pharmacie, cxxvii, p. 61.

 $^5$  Sitzungsberioht d. niederrhein Ges. für Natur- und Heilkunde, 1860, xx, p. 141.  $^6$  This Journal, 1866, II, xli, p. 119.  $^7$  Also 10°80 and 10°81.

Wöhler's analysis was entirely confirmed some years subsequently by Jannasch\* in Gottingen, who subjected to analysis pure thomsenolite selected by Professor Klein.

In view of the above, the analysis of pachnolite by Brandl, showing results agreeing well with those required by the formula NaF, CaF<sub>2</sub>, AlF<sub>3</sub> was calculated to cause no little surprise. Professor Groth accepts without question the anhydrous nature of pachnolite and endeavors to explain away the opposing evidence shown in the foregoing table by assuming that the supposed homogeneous material analyzed was contaminated largely with thomsenolite. As in no published analysis does the percentage of water fall below 7 per cent, this assumption necessitates a most improbable admixture of thomsenolite. In those cases where the percentage of water equals or exceeds that required for thomsenolite, the presence of gearksutite is suggested by Professor Groth as a possible explanation. Even on this supposition the percentage of foreign admixture could not fall below 50 per cent, in which extreme case the whole of the impurity must be gearksutite, an amount which it is difficult to conceive should have escaped the notice of such observers as König, vom Rath and Knop, the latter of whom expressly says his analysis was made upon material identified as pachnolite.<sup>†</sup> Notwithstanding the difficulty of explaining the agreement between the previous analyses of pachnolite and thomsenolite on the assumption of the anhydrous nature of the former, the correctness of Brandl's analysis was not at first questioned by us.

In the course of the present investigations, the compact bluish material (see p. 276) having the specific gravity 2'980 at  $22\frac{1}{2}$ °C. was first analyzed, the crystallized pachnolite not having yet been observed. The results of analysis as given under I below, agreed in the main so well with the fignres required for the formula NaF,  $CaF_{\gamma}$ ,  $AlF_{\gamma}$ ,  $H_{\gamma}O$ , that no hesitation was felt in considering the mineral to be thomsenolite, probably slightly contaminated with fluorite. ' Later, the crystalline coatingion the thin walls produced by the first mode of alteration of the cryolite, the crystals forming which had not yet been identified crystallographically as pachnolite, were su bjected to analysis with the results given under II. Here again the identity with thomsenolite seemed clear. It was not until the analysis of perfectly transparent fresh crystals, and crystal fragments, all taken from specimen A above described gave the results shown under III, that the possibility of the first analyses having been also made upon pachnolite, was suggested. That this was, however, so in the case of No. II sub·

\* Neues Jahrbuch für Min., etc., 1877, p. 808.

 $\dagger$  Neues Yahrbuch für Min., etc., 1876, p. 850.

sequent careful examination fully revealed, though the crystals analyzed were not entirely free from foreign admixture. It seems certain also that the compact bluish portions (I) consist almost entirely of pachnolite, although it cannot be positively asserted that some thomsenolite may not be intergrown with it. That no possible doubt might exist in the mind of any one as to the homogeneity of the material used for analysis III, a further analysis was made upon crystals from specimen B above described, particular care being taken to identify each as pachnolite by the rhombic section. The results of this analysis appear under IV.



Further determinations of water on material from specimen B gave  $7.95: 7.99; 8.14$ , and  $8.15$  per cent. Still other determinations, some on material every fragment of which showed the rhombic section, others on material taken at random from the crystalline mass gave results between 7'90 and 8'20 per cent. The spec. grav., at 17° O. of the perfectly pure material, as the mean of four determinations varying between 2'963 and  $2.968$ , was  $2.965$ . A single determination on another portion equally pure at 22° C. gave 2.962. The transparent crystals, as well as all the other portions analyzed, decrepitated violently on heating in a test tube, the walls became lined with the white deposit so characteristic of thomsenolite and pachnolite, and much water was given off. Hence, it appears that the pachnolite from Pike's Peak and thomsenolite are identical in chemical composition, unless the fact of ail analyses of thomsenolite showing slightly more water than required for the formula NaF,  $\widehat{CaF_2}$ ,  $\widehat{AlF_3}$ ,  $H_2O$  may indicate, as suggested by Professor Groth, a partial replacement of fluorine by hydroxyl in tbat mineral. Should this prove to be the case, a plausible explanation of the difference in crystallization of the two minerals is offered without recourse to the theory of dimorphism.

A satisfactory explanation of Brandl's results so opposed to those presented by all earlier analyses and the ones above

\* By difference.  $\uparrow$  Ann. d. Chem. ccxiii, p. 6. AM. JOUR. SCI.-THIRD SERIES, VOL. XXVI, No. 154.-OCT., 1883.

<sup>19</sup> 

given is impossible, but it may be well to call attention to the fact that Brandl was obliged to make his determinations of fluorine and the metals upon quantities of  $0.1106$  gr. and  $0.1430$ gr. weight respectively, whereas, material was not wanting for the present analyses, the determinations having been made upon weights of from 0·3 gr. to 0'75 gr. It nowhere appears that a direct test for water was made upon the material fur· nished by Professor Grotb. The latter, it is true, remarks (I. c. p. 461), "Ausserdem bildet sich bei letzterem (Thomsenolith) in den kiilteren Theilen des Rohrs ein Wasserbeschlag, welcber beim Erhitzen reinen Pachnolithes natürlich ausbleibt." The absence of water does not, however, seem to be hereby proven, but simply assumed from the close approximation to 100 of Brandl's results exclusive of water. Brandl himself says water is wanting, but does not mention if this was ascertained by direct experiment. The small amount of material at his dis· posal renders it not improbable that no direct test was made.

Since the conclusion of the above investigations we have, through the kindness of Mr. Albert F. Damon, President of the Pennsylvania Salt Manufacturing Company, obtained speci. mens of Greenland cryolite and its alteration products. From one of these specimens was removed a large number of small, needle·like, pyramidally-terminated, twinned crystals with a rhombic prismatic section, showing in fact, precisely the common occurrence\* and ordinary habitt of pachnolite as described by Professor Groth. These crystals, slightly yellowish in color but quite transparent, were individually examined under the microscope, all such as did not show beyond a doubt the above described habit being excluded. They were then tested in a small glass tube for water. Decrepitation ensued on heating and the walls of the tube became lined with a white powder, and also with a deposit of water in such quantity as to preclude the possibility of its having been derived from but a small portion of the material experimented upon.

*Other forms of pachnolite.*-In some very cellular specimens whose walls run irregularly and seemingly without reference to the cleavage of the original cryolite, are crystals of pachnolite of different habit.

One or two of these cavities show crystals corresponding in size to those upon the thin walls, but exhibiting, each and every one, a reëntering angle on the free termination. In such little crystals the basal planes are prominent, and they are bounded on the inside by a pyramid and dome, doubtless  $-1$  (111) and  $-1-\bar{i}$  (101). Outward there sometimes appears another pyramid (1 ?) though the prismatic faces themselves usually form a sharp edge with O. All these crystals are too small for measure-

\* P. Groth, l. c., p. 461.  $+$  Ibid, p. 462.

ment, but as the appearance described is such as would be normal for the termination by which the twin crystals are com· monly attached, it seems admissible to consider the faces as  $Q$ ,  $-1$ ,  $-1$ - $\bar{i}$  and probably 1. On many twins of this kind, the outer or positive angles between  $I$  and  $O$  are replaced by two faces greatly resembling those of  $-3\overline{3}$  (311) and although entirely too minute for measurement, it is probable that the form  $3\overline{3}$  ( $\overline{3}11$ ) is here represented. The crystals of Greenland pachnolite are always attached by the end with the reentering angle according to Groth.

*Secondary formations in cavities.*—In many cavities arising from both modes of decomposition of the cryolite, a second series of minerals has been deposited, chiefly as a whitish, easily crumbling aggregate of minute crystalline grains, which are recognizable under the microscope as thomsenolite, pachnolite and a mineral of the isometric system. The little thomsenolite crystals are frequently doubiy terminated, and show the monoclinic symmetry plainly through the more prominent development of the negative pyramid. The pachnolite crystals are short and stout, showing in most cases only  $I(110)$ ,  $O(001)$ and  $-1-\bar{i}$  (101). A number of large pachnolite crystals were observed which, by low powers of the microscope, seemed coated with a crystalline dust, whose particles are resolved by a power of 700-800 diameters into most perfect cubic crystals, modified by the octahedron. This is also the form of the regular crystals in the granular mass above mentioned, and were it not for a fact to be considered shortly. we should not hesitate to advocate the probable identity of these crystals with ral-stonite, described by Brush \* as occurring in a very similar manner upon thomsenolite from Greenland. The largest of the crystals occurring as described, is less than  $1^{mm}$  in diameter, and no pure material even for qualitative tests can be obtained.

*A new fluoride.*-Just at the close of our investigations, a mineral was found, occurring sparingly in a few specimens, which seems to be very different from any known species. It was found in small cavities in the massive pachnolite, as a compact irregular mass, colorless, but not perfectly clear and exhibiting but seldom traces of crystalline form. In one specimen, however, the mass of the mineral was covered by small, rounded, crystal-like projections, which seemed like crystals of the regular system. An examination with a loupe showed the absence of recognizable faces, but such particles when broken off and tested under the microscope, proved to be fully isotropic. A few faces found on one crystal seem to belong to

\* G. J. Brush, this Journal, III, ii, p. 30, 1871: also P. Groth, I. c., p. 471.

cube and octahedron, and particles detached from the same are isotropic in action in polarized light. Supposing that this substance must be ra1stonite in exceptional development, enough material for the following partial chemical analysis was selected, being carefully freed from attached particles of pachnolite and other anisotropic minerals, by microscopical examination\_ The AI, Ca and Mg were accurately determined, the Ka and Na, owing to an unfortunate mishap, only approximately. No water could be detected by direct test upon a small portion. Fluorine was present in quantity, and the percentage given below is calculated on the assumption that the metals are fully combined with it.



From the above data may be derived a formula analogous to that of cryolite, in which about two-thirds of the sodium is replaced hy potassium. Further investigation will be made upon this most interesting mineral as soon as better material can be obtained. The presence of this regular mineral. naturally renders it impossible to refer the tiny crystals observed upon pachnolite to ralstonite with any degree of certainty, but, we are inclined to believe that the two minerals are not identical.

#### GEARKSUTITE.

This mineral, first observed by Hagemann<sup>\*</sup> on compact thomsenolite, and described as earthy and kaolin-like in aspect, dull, white, opaque and of hardness 2, seems to be so rare in connection with the Greenland fluorides, that no one has had material for further examination. Groth | found it in very small quantity among the minerals at his disposal, but could not obtain enough for analysis. He, however, found that it consisted of very minute microscopic needles, with oblique extinction, and considers it as undoubtedly a definite species.

Among the minerals from St, Peter's Dome, gearksutite is quite abundant. It is not formed from other minerals by molecular replacement, but is deposited from solution, in the cavities upon fresh crystals of pachnolite, etc. Smaller cavities are sometimes filled by it, and on the contact with the quartz it is specially developed.

In appearance, it corresponds closely to the description of the Greenland mineral, as given by Dann, the resemblance to the

\* Dana, System of Mineralogy, 5th Ed., p. 130.  $+$  Groth, l. c., pp. 460 and 481.

purest, finest kaolin being especially remarkable. Examined microscopically, gearksutite is seen to consist, as stated by Prof. Groth, of exceedingly minute colorless needles, the average length of which is less than  $0.02^{mm}$ , and the thickness less than O'002mm, and apparently possessing oblique extinction.

*Ohemical investigation.*—Gearksutite was found by Hagemann {l. c,}, to possess the following composition:



An examination of the above results shows that the atomic ratio of  $Al: Ca + Na<sub>a</sub>: Fl$  is  $1:1:4$ , instead of  $1:1:5$  which would represent complete saturation and require about 12 per cent more fluorine than was found, On the assumption that the missing fluorine is replaced in the mineral by oxygen or hydroxyl, there should appear a much greater loss than the analysis indicates. An error is therefore evident, probably in connection with the determination of the fluorine, or water, or both, in consequence of which the construction of a satisfactory formula has heretofore been impossible.

The material for the following analyses was first partially crushed, then freed from admixed heavier particles of foreign matter by triturating in a beaker with water, the impurities falling to the bottom of the vessel, while the light gearksutite remained suspended in the liquid and was removed by decantation, By repeating this operation a great many times, a product was finally obtained entirely free from all foreign admixture. It was allowed to settle completely, the supernatant liquid poured off and the residue dried first on the water bath, then at  $100^{\circ}$  C. Thorough pulverization of this residue is a difficult matter, as it flattens out under the pestle, forming flakes which strongly resist the pulverizing action. This is of little moment, however, since the flakes are so spongy as to offer no hindrance to attaek by sulphuric acid. Two analyses were made from the same sample, with the results tabulated below. In  $b$ , sodium and potassium were not determined.



Taking the figures in the third column and combining the fluorine with the calcium, sodium, potassium, and, as far as possible with the aluminium, there remains of the latter 5.32 per cent, requiring 4'66 per cent of the oxygen, an amount agreeing very closely with that obtained above by difference and making the sum total almost exactly 100.



The agreement of the above analysis with that of Hagemann, after substituting in the latter for the sodium its equivalent in calcium, is very close, with the single exception of the water. As his analysis was manifestly erroneous in some particular. the assumption of the identity of gearksutite with the mineral here discussed is fully justified, supported as it is by the similarity in occurrence, appearance and physical characteristics. His error would then consist in having obtained from four to five per cent too much water, a result not difficult of explanation, in the case of a hydrated fluoride, if no precaution was taken to prevent the escape of fluorine,

Su bstituting in the mean of analyses *a* and b for sodium and potassium their equivalent of calcium, and dividing the percentages by the atomic weights, the atomic ratio is found to be as given below:



The ratio of  $A1: Ca: F$  is here nearly as  $1:1:4$ , the same as found by Hagemann. Subtracting from the atomic value for water, an amount 0'291 equal to that for oxygen, in order to form with the latter hydroxyl, the result is as given under I, while under II appears the ratio referred to calcium as unity.



It will be seen that by combining hydroxyl and fluorine the ratio  $AI: Ca: H<sub>2</sub>O: (F, OH)$  is  $1:1:1:5$  and the formula for the mineral becomes  $CaF_s$ ,  $Al(F, OH_s, H_sO,$  in which the fluorine and hydroxyl combined with the aluminium stand nearly in the proportion  $2: 1$ . Were the latter proportion exactly fulfilled, the formula might be written  $3CaF_{2}$ ,  $2AIF_{3}$ ,  $A(OH)$ ,  $3H<sub>2</sub>O$  requiring the percentages:

# Al  $15'36$ , Ca  $22'42$ , F  $42'60$ , O  $4'49$ , H<sub>2</sub>O  $15'13=100'00$

Of the  $15.46$  per cent of water found by analysis,  $5.24$  per cent has heen considered in the foregoing as basic. While this amount may, on theoretical grounds alone, enter into the inner constitution of the mineral as basic water, the remainder cannot, but must be water of crystallization. That a portion of the water is basic, is rendered more than probable by the fact that at  $300^{\circ}$  C. some is still retained. In this connection, the following experiments were made. 0'5677 gr. of the mineral, not however from the same sample as that used for analysis, dried first at  $100^{\circ}$  C. and contained in a platinum crucible, was exposed in an air bath during 145 hours to temperatures ranging from  $100^{\circ}$  C. to  $300^{\circ}$  C., the weight being taken at intervals averaging ten hours each. The results in brief showed that at  $145^{\circ}$  C., the loss was but 0.35 per cent, at  $230^{\circ}$  C. only 0.92 per cent, at 250° C. 7.02 per cent, after prolonged heating at  $265-270$ ° C. 9.49 per cent, and at  $295$ ° C. 13.92 per cent. As no further loss occurred after six hours' heating at  $295-300^{\circ}$  C., a portion of the residue, which still retained its original appearance, was subjected to a quantitative test for water, of which 1'76 per cent was found. This added to the 13'92 per cent driven off below  $300^{\circ}$  C. made the total  $15.68$  per cent. Since this is slightly higher than the mean of the previous results, it seemed possible that some fluorine might have escaped. The remainder of the residue was therefore tested quantitatively for fluorine, of which was found 40'60 per cent, thus proving the correctness of the surmise. A similar experiment with the same general results was made upon a smaller portion of another sample. A comparison of the full results of both experiments showed that by sufficiently prolonged heating at approximately  $270^{\circ}$  C, all the water of crystallization could be driven off, also that by still further beating at little, if any, higher temperature, the basic water began to escape, but was not entirely expelled, even after many hours' exposure to a temperature of  $295-300^{\circ}$  C.

In the Journal of the Chemical Society for 1883, page 140, Walter Flight describes a mineral obtained from the cryolite bed of Greenland. "It is made up of a congeries of minute white transparent crystals, mostly broken up and lying entangled among each other in every sort of direction, which gives the mass an appearance of opacity much resembling that of kaolin or chalk,"

Chemical analysis showed it to consist of



The fluorine seems to have been calculated for the metals, and the water was found by difference.

From the above data the author obtains the formula  $2CaF_z$ ,  $\text{Al}_4\text{F}_8$ ,  $2\text{H}_4\text{O}$ ,\* and considering the mineral new, names it *evigtokite.* Mr. Flight seems to have overlooked the description of gearksutite in Dana's System of Mineralogy, and Prof. Groth's remarks upon the same (l. c. pp. 481 and 493), else the very fair agreement of his analytical data for the metals with those of Hagemann, and the similarity in occurrence, appearance and physical characteristics of the two minerals must have led to at least a suspicion of their identity. There can hardly exist a doubt that Flight has analyzed gearksutite, and that the name evigtokite is therefore to be dropped.

#### PROSOPITE.

This rare species hitherto unobserved in association with the cryolite minerals, and known only in connection with the tin-bearing veins of Altenberg, in Saxony, has been identified in both veins at St. Peter's Dome. It is most abundant in vein B, and the chief description of it will come under that head, but close examination has proved its presence also among the minerals of vein A,

Both of the coarsely crystalline specimens of pachnolite, above described as A and B, have prosopite upon them. Specimen B is, in parts, in process of alteration to a dull, white, porous substance, with little cavities in which are minute crystals of prosopite. These are colorless, transparent, tabular in shape, showing  $i \cdot i$  (010) predominant,  $I(110)$ , 1 (111) and  $-2 \cdot 2$ (211), agreeing exactly in form and optical behavior with those determined as prosopite in vein B. In two other specimens of pachnolite, prosopite tablets may be seen upon certain granular surfaces when decomposition of the pachnolite has already begun. The crystals are usually attached by the prismatic edges. although free and perfect terminations are to be found. Gearksutite was noticed upon them in one specimen, and the

<sup>\*</sup> Probably a printer's error. It should read  $2CaF_2$ ,  $Al_2F_6$ ,  $H_2O$ .

position of prosopite in the series of hydrous fluorides is doubtless between thomsenolite and gearksutite. No material for chemical tests could be procured from the specimens descrihed.

The penetration of the fluoride mass by astrophyllite blades springing from the side of the vein has been mentioned (p. 273). Here the cryolite has been altered to cellular pachnolite, according to the first mode described, and this has for the greater part given way to other products or been dissolved and carried away, leaving the astrophyllite blades more or less free or imbedded in gearksutite and other soft, crumbling material. The free blades usually have a coating composed of a little purplish fluorite immediately adjacent to the blades, and over this a nearly colorless or slightly vellowish substance. At and toward the base of the astrophyllite blades the latter is present in roundish aggregates made up, as shown by the loupe, of clear tablets, in more or less radiate arrangement. The crystal form is here quite obscure, but the general appearance was so suggestive of prosopite that by sacrificing the best specimen enough material was obtained for determination of the bases and of fluorine, with the result given below- $V$ , p. 293.

#### VEIN B.

*Descriplion.-The* minerals found in this vein have been exposed by the "Eureka" tunnel which has been driven in upon it for one hundred feet or more. Unfortunately the walls are so blackened by the smoke from the blasting that the relations of the different mineral bodies encountered to each other cannot be clearly seen, and the data here given are derived from the study of the material upon the dump and from a partial examination of the tunnel walls with the aid of a hammer.

The main part of the vein is white, massive quartz with here and there immense individuals of pinkish feldspar, which proves on microscopical examination to be microcline with thin, irregular laminæ of albite intergrown nearly parallel to the macropinacoid. This microcline is sometimes wholly altered to pure white, coarsely foliate kaolin, which is impregnated with fine particles of galena.

Smaller and apparently wholly irregular parts of the vein are occupied on the one hand by quartz containing zircon in great abundance, quite equally distributed through it, and on the other by a mass of mixed fluorides. The quartz containing zircon (see this Journal, October, 1882, page 284), is always sharply defined from the massive white quartz of the main vein which is wholly without included minerals. The zircon crystals are imbedded largely in the quartz itself and to a less degree in compact, white kaolinite, a greenish yellow mica, and purple or green fluorite. These three minerals fill small irregular spaces in the quartz, and probably replace feldspar, for they are also found on fissure planes as distinct secondary deposits.

The kaolinite is usually very compact, but crystals were found in some small cavities. These are exceedingly thin, colorless, transparent, rhombic leaves, the acute angle being usually evenly truncated, producing sometimes an almost perfeet hexagon. The result of many measurements under the microscope seems to indicate that the obtuse angle of the rhomb is slightly less than 120", the best results varying from 118° 30', to 119° 30'. The thinnest leaves show distinct action on polarized light, and extinguish parallel to the diagonals of the rhomb. The thicker crystals are made up of many thin ones which are usually not perfectly coincident in position, and sometimes form more or less perfect rosettes.

The mica occurs in masses or foliated upon fissure planes, and no crystals have been found. The kaolinite possesses the composition I, and the mica II, as given below. The kaolinite contained a small amount of fluorite in almost microscopic crystals, the quantity being calculated from the Ca found.



The fluorides seem to fill the small irregular spaces left after the decomposition of the zircon-bearing quartz, the thickness of the fluoride mass varying from a thin seam to possibly two or three feet. They are always sharply defined against both pure and zircon-bearing quartz, the contact surfaces of the former being sometimes apparently huge crystals.

The greater part of the fluoride mass is now dull white and very compact, and is evidently made up of a mixture of at least two substances, neither of which has as yet been identified. Only in a single specimen is there any clue to the original mineral, but in this there is a small, solid mass of unmistakable cryolite with alteration to pachnolite (?) progressing upon its cleavage planes in the exact manner described in vein A, but passing into the compact white mixture already mentioned.

Adjoining the quartz is usually an irregular zone of purplish or greenish fluorite, and next to this a rather coarsely granular

\* The presence or absence of fluorine was not ascertained,

mass of a colorless mineral with two distinct cleavage planes which passes gradually into the compact white substance. This zonal arrangement is not without exceptions, for both granular and compact masses come directly in contact with the· quartz in some specimens, and fluorite is more or less abund· antly sprinkled through the other substances: in fact the relation of the minerals to each other is such as to indicate that they are but different phases of alteration from a common source. The granular mineral occurs in sufficient purity to afford material for chemical analysis, and its individuals are large enough to admit of the preparation of thin sections with definite relations to the cleavage planes. The analysis first proved the identity of this mineral with prosopite, the optical properties shown by the thin section confirmed this determination and quite recently a few minute crystals were found in one specimen which agree with the published data on the Saxon mineral. As the identification of this rare species, particularly in its present association, is a matter of considerable interest, we will describe it somewhat in detail.

## PROSOPITE.

*Orystalline form and physical properties.*-The minute crystals found in a single specimen from vein B as well as those·

observed on pachnolite, etc., in vein A (p. 288) are all of the habit shown in the accompanying figure. This is from a camera lucida drawing of a crystal measuring 0'5mm normal to the edge of the prism, and can therefore make no pretensions to crystal-



lographical accuracy. The crystals are colorless and transparent, have uniformly a tabular form through the development of  $i \cdot i$  (010) and show plainly the prism and two pyramids which may be considered as 1 (111) and  $-2\overline{2}$  (211) for extinction takes place nearly or quite parallel to the edge of  $-2\overline{2}$ , which is, according to DesCloizeaux<sup>\*</sup> and Groth,<sup>†</sup> the position of the bisectrix.

Thin sections prepared as nearly as possible perpendicular to the edge of the two cleavage faces in the irregular granular individuals, show that the angle of the cleavage planes is very nearly 135°, and that extinction takes place parallel to the direction bisecting that angle. This behavior agrees perfectly with the statements concerning prosopite, according to which the chief cleavage is parallel to  $-2\overline{2}$ , the angle of which is about 134°. The present material does not allow of a definite settlement of the question of the crystalline form of prosopite,

\* Bull. Soc. Min. de Fr., v, 317.  $+$  1. c., p. 290.

but nothing observed is in conflict with the reference to the monoclinic system.

*Chemical investigation.*-The formula deduced by Brandl\* for prosopite, from the results of his analysis as here given  $:$ 



is  $CaF<sub>s</sub>$ ,  $2Al(F, OH)<sub>s</sub>$ . The whole of the water is assumed to be basic, entering with oxygen into the constitution of the mineral as hydroxyl, the latter replacing an equivalent amount of fluorine. In support of this assumption, Brandl mentions that no loss is perceptible below  $260^{\circ}$  C.

In an earlier partial analysis, Scheerer (Pogg, Ann., ci, p. 861) found

# Al 22.77, Ca 16.41, H<sub>2</sub>O 15.50

Of the analyses tabulated below, those under I, II, III and IV were made upon material from vein B. That analyzed under I, *a* and *b*, was composed of comparatively large irregular crystalline pieces, showing no visible impurity whatever, having a sp. grav. at  $23^{\circ}$  C. of  $2.880$  and a hardness of about 4'5. As the ratio AI: Oa differed materially from that of 2 : 1 required by Brandl's formula, it appeared that some foreign matter must be present, consequently no further determinations were made, as it was hoped better material might be obtained,

Analysis II was made upon material separated from quartz, zircon, fluorite and other accompanying minerals by a solution of iodide of mercury in iodide of potassium. The result was a slight improvement upon the previous and the analysis was completed. The material for III was picked out carefully by hand with the aid of the loupe, but as the result was still not satisfactory, a further portion (IV) aggregating however only 0'1022 gr. was selected with the greatest possible care, every particle being distinctly crystalline and showing under the microscope no trace of impurity. Here a slight improvement becomes evident in the ratio, but as the amount taken for analysis was so extremely small, it cannot be asserted that the better results may not be due to unavoidable errors of analysis. The material for analysis V was derived from vein A, where the prosopite occurred on astrophyllite associated with cryolite, pachnolite, etc. This material was, however, evidently not

\* Ann. de Chem., ccxiii, p. 13.

quite pure, being opaque and very slightly colored in part by oxide of iron. The analysis was made merely to prove its. identity with the prosopite from vein B.



The mean of all the results under analyses I-IV is as follows:



After subtracting from the fluorine an equivalent for the calcium, magnesium and sodium, and combining the remainder with aluminium, there remains of the latter 14'44 per cent, requiring 12·65 per cent oxygen, instead of 13'26 per cent found by difference. The atomic values appear as follows, after substituting for magnesium and sodium, an equivalent of calcium  $\cdot$ 



The result is unsatisfactory, the ratio of  $Ca: Al$  being as 1:1.78 instead of 1:2. In none of the material analyzed was the slightest trace of kaolinization to be observed, nor any other foreign matter. It therefore becomes impossible to explain with any degree of certainty the above abnormal results.

The general agreement of all the analyses, the aluminium being found too low and the calcium too high in each case, shows pretty conclusively that an explanation cannot be sought for in analytical errors.

As fluorite occurs here always in most intimate association with prosopite, and the possibility suggested itself that some of this might be so intergrown with the latter as to escape the closest scrutiny, it became desirable to ascertain what change

would be effected in the ratio above given by subtracting enough calcium to make the ratio  $Ca: A^{\dagger}$  as  $1:2$  and an equivalent amount of fluorine. The atomic values then become:



which agree quite as well for the formula  $CaAl($ F, OH) $)$  as those obtained by Brandl.

If instead of the mean of all the analyses, the figures of II alone are taken for calculations similar to the above, the result is the same, even a little more closely approximating to the ratio 2:1:8.

The observation made by Brandl, that below  $260^{\circ}$  C. no loss in weight occurs, was found to apply here, provided the exposure to this degree of temperature is short. If continued for many hours a slight but sensible loss is observed.

Denver, Colorado, June, 1883,