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ART. VII.—*On the Chemical Composition of Staurolite, and the regular arrangement of its Carbonaceous Inclusions;*
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Historical.—In the early analyses of staurolite, especially those of Jacobson* and Rammelsberg,† a great variation was found in the chemical composition, especially in the amounts of silica, which varied all the way from 27 to 50 per cent. The iron oxide, moreover, was regarded by some investigators as ferric, by others as ferrous, while still others considered that it existed in both states of oxidation.

In 1865 Lechartier‡ observed that pulverized staurolite from Brittany and Bolivia, when examined with the microscope, showed both brown and colorless grains. On treatment with hydrofluoric acid, it was found that the colorless ones dissolved, while the staurolite was very slightly attacked. Furthermore, material purified by this treatment was found to be nearly uniform in specific gravity and gave amounts of SiO_2 varying from 28–29 per cent, agreeing with the purest staurolite from St. Gothard. He also proved that water was an essential constituent of the mineral.

In 1872, von Lasaulx§ showed, from a microscopic examination of staurolite from various localities, that all crystals are more or less impure from mechanical admixtures, especially of

* Pogg. Ann., lxii, p. 419, 1844 and lxviii, p. 414, 1846.

† Pogg. Ann., cxiii, p. 599, 1861.

‡ Bull. Soc. Chimique, iii, p. 378.

§ Min. Mittheilung, 1872, p. 173.

quartz, while garnet, cyanite, magnetite and mica were also observed. These inclusions of quartz, amounting sometimes to 30–40 per cent of the total weight of the crystal, account for the great variation of the silica percentages in the older analyses.

In 1873 Rammelsberg* reëxamined the exceptionally pure staurolite from St. Gothard and also the impure material from Pitkäranta and Brittany, in which he had previously found over 50 per cent of silica. After purifying these latter by treatment with hydrofluoric acid, only from 29 to 30 per cent of silica was found and the analyses agreed with that of the St. Gothard mineral. From these analyses he deduced the formula $H_2Fe_3Al_{12}Si_6O_{34}$, the iron being regarded as ferrous and replaced in part by magnesia.

In 1885 Friedl† investigated carefully selected material from St. Gothard and Tramnitzberg in Mähren, which by examination with the microscope had been found to be free from foreign inclusions. From the results of his analyses he deduced the formula $H_4Fe_6Al_{24}Si_{11}O_{66}$. In the same year Coloranio‡ analyzed the St. Gothard staurolite, which had been carefully selected and digested with hydrofluoric acid, the formula deduced by him being $H_2Fe_2Al_{12}Si_5O_{31}$.

It is interesting to note the variations in the proposed formulæ, each investigator in turn finding a smaller amount of silica as shown below, where the formulæ of Rammelsberg and Coloranio have been doubled for more ready comparison.

Rammelsberg	$H_4Fe_6Al_{24}Si_{12}O_{68}$
Friedl	$H_4Fe_6Al_{24}Si_{11}O_{66}$
Coloranio	$H_4Fe_4Al_{24}Si_{10}O_{62}$

From a consideration of the analyses of Friedl and Coloranio Groth§ concludes that staurolite has a still simple formula and suggests a basic orthosilicate $(AlO)_4(AlOH)Fe(SiO_2)_2$.

Selection and preparation of material for analysis.—In the present investigation, material of exceptional purity was selected from the four following localities: St. Gothard, Switzerland; Windham, Maine; Lisbon, New Hampshire and near Burnsville, North Carolina. The material from the first of these is too well known to need special description. Some crystals from the Brush collection were available. At Windham, Maine, it occurs in crystals measuring up to 25^{mm} in diameter, imbedded in mica schist, as represented by an excellent suite of specimens in the Brush collection. This has

* Zeitschr. Deutsch. Geol. Gesell., xxv, p. 53.

† Zeitschr. Kryst., x, p. 366.

‡ Bull. Soc. Chimique, xlv, p. 427.

§ Tabellarische Uebersicht der Mineralien, 1889, p. 104.

never been previously analyzed. The material from Sugar Hill in Lisbon, N. H., was collected in the summer of 1893 by Prof. G. J. Brush. As observed by him extensive ledges of gray, staurolitic mica schist occur, extending several miles north from Pearl Lake, better known as Mink Pond, and including the ledges on Garnet Hill and Cowen Hill. In the ledges on Cowen Hill unusually large and fresh crystals are found, measuring up to 115^{mm} long by 40^{mm} broad. Thin sections of these crystals revealed the fact that they are remarkably free from inclusions of quartz and garnet, which are so common in staurolite, but they contain carbonaceous material arranged in certain definite planes, as described later. The staurolite from near Burnsville was collected by the writers in the summer of 1892, while engaged in work for the North Carolina Geological Survey. It was found at and near a prospect pit on the property of Mr. D. M. Hampton, which had been dug in exploiting for iron ore. The associated minerals are magnetite, menaccanite and corundum. The staurolite occurs in crystalline aggregates, often intimately associated with the iron ores.

In the preparation of material for analysis the carefully selected crystals were pulverized and sifted to a uniform grain. In the case of the North Carolina mineral the magnetite and menaccanite were removed by means of an electro-magnet. In order to separate a powder of uniform specific gravity the use of fused silver nitrate, which can be diluted with potassium nitrate was resorted to, as recommended by J. W. Retgers.* It was found convenient to use a double walled, cylindrical, copper air bath, shown in section in the accompanying figure. The outer cylinder *a* stands on legs which are not represented. The inner bath is supported by brackets, *b*, and is provided with several perforated discs near the bottom, which serve to disseminate the heat of the lamp. The well *A* holds a test tube containing the silver nitrate, which can readily be kept in a state of fusion and at a constant temperature for any desired length of time; this latter condition being very essential in order to avoid circulating currents. The fusing point of silver nitrate is 198° C. but the temperature which was found most convenient for work was about 250° C. The specific gravity of fused AgNO₃,

* Jahrb. f. Min., 1889, ii, p. 190.

is about 4.1 which can be lowered by addition of KNO_3 . The fused salt is a clear mobile liquid, through which the particles of mineral move freely, and separations can be made in this as accurately as in any of the heavy solutions. On cooling, the fusion solidifies to a cake with the heavier and lighter portions at the bottom and top respectively. The test tube readily breaks away from the fused mass, the cake can be cut in two and the minerals separated by dissolving the nitrates in water. The latter can be reclaimed by evaporating the solutions to dryness on a water bath and finally fusing. By eliminating the heavier and lighter portions and repeating the separation remarkably pure products were obtained, of nearly uniform specific gravity. The manipulations are very simple and the results extremely satisfactory. A preliminary experiment that was made showed that staurolite does not suffer any decomposition or loss in weight when exposed to a temperature of 250°C . The separated material, when examined with the microscope, was found to be homogeneous and very free from visible inclusions.

Method of analysis.—The silica and bases were determined by well known methods. The evaporations were carried on in platinum, the purity of the silica tested by evaporation with hydrofluoric acid and account taken of the small quantity of silica carried along and weighed with the sesquioxides. Especial pains was taken in the determination of ferrous and ferric iron. The very finely pulverized mineral was treated in a small platinum bottle with a mixture of strong hydrofluoric and sulphuric acids and boiled vigorously for about twenty minutes, the neck of the bottle being covered by a cone of platinum foil. The contents of the bottle were then diluted with cold, boiled water, washed into a casserole and titrated with potassium permanganate. Preliminary experiments were made by treating known weights of ferrous sulphate in the same manner and it was found that no appreciable oxidation from the air took place. As the staurolite is very slowly attacked by hydrofluoric acid only a portion in each experiment went into solution. After titration, the insoluble portion was filtered off and the filtrate evaporated in a platinum dish till all the hydrofluoric acid was expelled. After diluting, the iron was reduced by hydrogen sulphide, the excess of the latter removed by boiling and the total iron determined by means of potassium permanganate. The determinations give the ratio of ferrous to ferric iron in that portion which had been dissolved by the hydrofluoric acid, and the total iron in the mineral having been previously found in that portion used for silica and bases, the percentages of ferrous and ferric iron are readily calculated. Direct determinations of water were

made in all cases, as loss by ignition would naturally give too low results, owing to the oxidation of the ferrous iron.

Analytical results.—The results of the analyses are given below, together with the specific gravity determinations which were made very carefully by means of the pycnometer.

St. Gothard, Switzerland.

Specific gravity = 3.748.

	I.	II.	Average.
SiO ₂	27.80	27.65	27.73
Al ₂ O ₃	53.23	53.35	53.29
Fe ₂ O ₃	2.83	2.83	2.83
FeO	11.21	11.20	11.21
MnO	.63	.44	.53
MgO	1.77	1.85	1.81
H ₂ O	2.19	----	2.19
			<hr/>
			99.59

Windham, Maine.

Specific gravity = 3.728.

	I.	II.	III.	Average.
SiO ₂	27.81	27.88	----	27.84
Al ₂ O ₃	54.44	54.51	54.36	54.46
Fe ₂ O ₃	2.81	2.90	2.86	2.83
FeO	10.52	10.85	10.44	10.60
MnO	.59	.62	.56	.59
MgO	1.83	1.87	----	1.85
H ₂ O	2.24	----	----	2.24
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				100.41

Lisbon, New Hampshire.

Specific gravity = 3.775.

SiO ₂	27.81
Al ₂ O ₃	54.09
Fe ₂ O ₃	2.76
FeO	12.48
MgO	1.92
H ₂ O	1.70
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	100.76

Burnsville, North Carolina.

Specific gravity = 3.773.

	I.	II.	III.	IV.	Average.
SiO ₂	27.80	27.65	27.59	27.77	27.70
Al ₂ O ₃	53.09	53.30	----	53.27	53.22
Fe ₂ O ₃	4.81	4.81	4.83	4.85	4.82
FeO	9.70	9.68	9.74	9.79	9.72
MnO	.27	.38	.33	.36	.34
MgO	2.64	2.65	2.70	----	2.66
H ₂ O	1.99	1.96	----	----	1.97
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					100.43

For a better comparison of the above results the average analyses are given below, after recalculating Fe_2O_3 as Al_2O_3 , MnO and MgO as FeO and bringing the whole to one hundred per cent.

	St. Gothard, Switz.	Windham, Me.	Lisbon, N. H.	Burnsville, N. C.
SiO_2 ---	27·70	27·60	27·44	27·47
Al_2O_3 ---	55·04	55·75	55·16	55·83
FeO ---	15·07	14·43	15·72	14·74
H_2O ---	2·19	2·22	1·68	1·96
	<hr/> 100·00	<hr/> 100·00	<hr/> 100·00	<hr/> 100·00

The ratios in these analyses are as follows:

	$\text{SiO}_2 : \text{Al}_2\text{O}_3 : \text{FeO} : \text{H}_2\text{O}$
St. Gothard	·460 : ·540 : ·209 : ·121 = 2·12 : 2·50 : ·967 : ·560
Windham	·460 : ·546 : ·200 : ·122 = 2·11 : 2·50 : ·915 : ·557
Lisbon	·457 : ·540 : ·218 : ·093 = 2·11 : 2·50 : 1·01 : ·430
Burnsville	·458 : ·547 : ·205 : ·109 = 2·07 : 2·50 : ·934 : ·497

The above ratios approximate closely to 2:2·5:1:0·5 which would give the formula $\text{HAl}_5\text{FeSi}_2\text{O}_{11}$, in which the aluminium is partly replaced by ferric iron and the ferrous iron by magnesium and manganese. This is, moreover, the formula suggested by Groth, and, as previously stated, may be written as a basic ortho silicate, $(\text{AlO})_4(\text{AlOH})\text{Fe}(\text{SiO}_4)_2$ or equally well, $(\text{AlO})_4\text{Al}(\text{FeOH})(\text{SiO}_4)_2$. The percentage composition required by the formula is the following:

SiO_2	26·32
Al_2O_3	55·92
FeO	15·79
H_2O	1·97
	<hr/> 100·00

From a comparison of the ratios, or of the analyses, as reduced, with the theory, it will be observed that the silica is uniformly a trifle high, amounting to something over one per cent. This cannot be referred to an analytical error, as the distilled water and reagents were pure, and platinum vessels were used for the evaporations. It was not derived from the agate mortar in which the mineral was ground, for in the analysis of the mineral from Lisbon a steel mortar was used, the powder being afterwards purified by treatment with hydrochloric acid. From the careful selection of nearly pure mineral to start with, and the special precautions that were taken to eliminate all heavier and lighter portions by the specific gravity separation, it was not expected that the staurolite grains would still contain inclusions of quartz, nor were they

visible in the fragments, when examined with the microscope; from the results of the analyses, however, it is evident that they were not wholly eliminated. To test this point more carefully, the following experiments were made on some of the finely powdered minerals left over from the regular analyses. After digesting with cold, strong hydrofluoric acid for twelve hours and washing, silica determinations were made, which are given below, along with the determinations from the previous analyses.

	St. Gothard. Windham, Me. Lisbon, N. H.		
SiO ₂ after treatment with HF.,	27.52	27.36	27.15
" from regular analyses....	27.73	27.84	27.81

It will be observed that hydrofluoric acid has removed some silica, but still the percentages are higher than the theory. We should infer, therefore, that quartz is an impurity in the mineral and that it is present as very minute inclusions. If, for example, the inclusions are as fine or finer than the acicular crystals of rutile in quartz, they could not be removed by a specific gravity separation, nor, being enclosed in the staurolite, would they be wholly accessible to the action of hydrofluoric acid. That the formula suggested by Groth is correct is well established by our analyses and, surely, its simplicity is one of the strongest arguments that can be advanced for its acceptance.

On the regular arrangement of inclusions in staurolite crystals.—In examining orientated thin sections of crystals from Lisbon, N. H., it was observed that they all contained dark inclusions, arranged in certain definite planes, resembling the phenomena so common in andalusite. That the inclusions are carbonaceous material was proved by the fact that, on separating the pulverized mineral by specific gravity, the dark portion was found to be lighter than the clear staurolite, and on igniting it in a current of air, purified by passing over caustic potash, carbon dioxide was abundantly evolved. These inclusions can only be clearly seen in plates ground sufficiently thin to be transparent and can best be studied in basal sections.

Figures 1 to 4 represent the arrangement of the inclusions in plates cut from a simple prismatic crystal 50^{mm} in length by 11^{mm} broad from which eleven basal sections were cut. Near the ends the impurities are arranged as in fig. 1; at the middle

the appearance is that of a simple dark cross, fig. 4; while intermediate sections show the rhomb diminishing in size as the sections approach the middle of the crystal, figs. 2 and 3. A number of crystals were cut showing this same phenomena and the symmetrical arrangement of the rhomb and cross was always well marked. The central portions *a* and the outer ones *b*, up to the very edges of the section, are remarkably pure staurolite. The dark bars running parallel to the macro axis broaden as they approach the outer angle of the section and are more regular and better defined than the brachy-diagonal ones. From a series of sections, then, it is evident that each staurolite prism contains two skeleton or phantom pyramids *P*, outlined by carbonaceous material, whose bases correspond to the basal planes of the staurolite and whose apices join at the center, while from the acute and obtuse pole edges of the

pyramids the inclusions extend as films or fins *A* and *B* to the vertical edges of the prism, fig. 5, the numbers at the side of the figure indicating where sections should be cut to give the phenomena corresponding to figures 1 to 4 respectively. Regularly arranged inclusions have previously been observed in staurolite* but apparently they have never been studied from a series of sections from a single crystal.

In seeking for an explanation of these inclusions, it must be borne in mind that staurolite is a mineral occurring essentially in the crystalline schists, which were probably derived from former mud or clay deposits. The crystals were formed by metamorphic agencies, under great pressure, in rocks which

* C. T. Jackson, *Alger's Phillips Mineralogy*, 1844, p. 112; Dana's *Min.*, Sixth edition, p. 560; S. Webber, *Proc. Nat. Institution for the Promotion of Sci.*, Bull. 2, p. 197, 1842; A. Lacroix, *Min. de la France*, 1893, p. 11.

were probably quite firm and solid while the staurolite was forming. The crystals, therefore, must have exerted great force in crowding away the surrounding rock material in order to make room for their growth, and we must take into consideration their inability to exclude foreign matter under these conditions, as well as their tendency to take it up. Large crystals have surely resulted from a growth about smaller ones and the beginnings of the crystals under consideration were undoubtedly at the centers, where the apices of the pyramids P, fig. 5, join. In the development of a large crystal from a small one it is imagined that at various points on the crystal faces the growth commences. The addition of particles or of crystal molecules must then advance, forcing foreign matter to one side until the crystal surfaces are complete. The particles, however, which meet to form the edges of the crystals may come together in such a way that they cannot exclude certain foreign materials. It would, moreover, seem reasonable to expect that the more obtuse the angle at which the faces, or the crystal molecules forming the faces, meet to form an edge, the less tendency there would be to hold impurities, while the more acute the edge the greater this tendency would become. If these conclusions are correct, then inclusions would be taken up by the edges, and being largely of carbonaceous material, as in the staurolite under consideration, the result would be that, in the development of a large crystal from a smaller one, the inner prism I, fig. 6, as it enlarged to form II, III and IV, would leave a dark deposit along the paths described by its advancing edges, corresponding to the planes A, B and P of fig. 5. In examining many basal sections it has, moreover, been generally observed that the bars running parallel to the macro-axis, representing the impurities taken up at the acute edges of the prism, are the heaviest, those parallel to the brachy axis are the lightest and in some sections practically fail, while the outlines of the inner rhomb, representing the impurities taken up along the edges of 90° between prism and base, are intermediate as regards the quantity of included matter. Also the inclination of the phantom pyramid P, fig. 5, seems to be wholly dependent upon the relative development of the prism and base during the growth of the staurolite crystal and to be in no way connected with the length of the vertical axis as expressed by the axial ratio $a:b:c$.

The considerations given above seem sufficient to account for the curious arrangements of the impurities in the crystals under consideration and doubtless by a similar explanation the impurities in some andalusite crystals could be accounted for.

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