18. The chemical composition of Tourmaline from Utö.

By

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In the same paper in which A. ARFWEDSON in 1818 relates his discovery of the new alkali lithia,[1] which he had found in the petalite of Utö, he also published an analysis of »crystallised Lepidolite» from the same locality. In an appendix to the paper BERZELIUS points out that the so-called Rubellite from Moravia and from the Ural, analysed by KLAPROTH and VAUQUELIN, contains boric acid and lithia just like the mineral analysed by ARFWEDSON and thus concludes that the minerals are probably identical. It is surprising that the defective analysis made by ARFWEDSON' nearly one hundred years ago of the green tourmaline from Utö should still remain the only published analysis of tourmaline from this interesting mineral deposit, the only one of its kind in F.

The first to mention the tourmaline from Utö in mineralogical literature seems to be D'ANDRADA in the year 1800[2], and he proposed the name *indigolith* for the bluegreen variety, which he considered a new species. The pink variety, »rothe Schörl» from the Ural, was already in 1794 by KIRWAN named *rubellite*[3] and later by HAUY »*Tourmaline apyre*»;[4] still later HAUSMANN proposed the name *apyrite* for the precious, light-coloured, hardly fusible tourmalines.[5]

Sufficient proof of the incomplete knowledge of the nature of tourmaline, possessed at that time, is shown by its description as »crystallised

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[1] »Undersökning af några vid Utö jernmalmsbrott förekommande fossilier och af ett deri funnet eldfast alkali» in Afhandl. i Fysik, Kemi och Mineralogi, Vol. 6, p. 145, 1818. Also published in the SCHWEIGER'S Journal, Vol. 22, p. 111, 1818 under the head: »Untersuchung einiger bei der Eisengrube von Utö vorkommenden Fossilien und von einem darin gefundenen neuen feuerfesten Alkali.»

[2] Journal de Physique, T. 51, p. 243, 1800, and SCHEERER'S Allgemeine Journal der Chemie, Vol. 4, p. 19, 1800.

[3] KIRWAN: Elements of Mineralogy, Vol. I, p. 288, 1794.

[4] HAUY: Traité de Mineralogie, T. 4, p. 401, 1801.

[5] HAUSMANN: Handbuch d. Mineralogie, p. 638, 1813.

Lepidolite» by contemporary mineralogical authors,[1] their reason being that at Rozena in Moravia, one of the earliest known deposits, the tourmaline occurs in the lepidolite. Even ARFWEDSON in his paper employs the description »so-called crystallised Lepidolite», without identifying the mineral with tourmaline. This was first done by BERZELIUS in the appendix to his paper. Imperfect as it was, ARFWEDSON's analysis was the first to show in tourmaline, besides lithium, the presence of boron oxide.[2]

The tourmaline in the lithia-pegmatite dykes at Utö occurs in at least three different varieties, and since ARFWEDSON's analysis of green tourmaline, carried out a hundred years ago, must be regarded as worthless, I have deemed it of interest to allow analyses of different varieties to be made with the help of more up-to-date methods. These analyses were entrusted to Dr. Naima SAHLBOHM, who carried them out partly in the laboratory of the University of Heidelberg under Prof. JANNASCH and partly in Prof. DITTRICH'S laboratory, likewise in Heidelberg, whereby she gained the advantage of the advice and support of these two eminent mineral chemists.

Four analyses were made, viz:

I The pink variety, Rubellite.
II The light green variety, Indigolite.
III A nearly colourless grayish white variety.
IV The blue black Tourmaline.

The Occurrence and Paragenesis of the Tourmaline of the Lithia-pegmatites at Utö.

The lithia-pegmatites within Fennoskandia are, so far as we know, represented almost exclusively by the Utö dykes, which represent differentiation facies of the usual potash pegmatites in which is shown every grade of transition. The felspar in the Utö dykes has been investigated by DES CLOIZEAUX[3] and G. FLINK,[4] who found that it consists, almost exclusively, of microcline perthite, Plagioclase being present only in insignificant quantities. Spodumene and particularly petalite are present in the Utö dykes in such great quantity, that they can no longer be described as accessory constituents since to a certain extent they replace

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[1] ESTNER: Versuch einer Mineralogie, Vol. II, part 1, p. 216, and REUSS: Lehrburch der Mineralogie, Vol. II, part 1, p. 113, 1802.

[2] RAMMELSBERG in his Mineralchemie (1875, p. 538) as well as HINTZE in his Handbuch (Vol. 1, p. 329, 1897) state that the presence of Boric acid in Tourmaline was first shown by LAMPADIUS and VOGEL in SCHWEIGER's Journal (Vol. 22, p. 182). However, since their work is published in the second portion of the number, of the first part which contains ARFWEDSON's paper on the subject, it seems that the credit of being the first to discover Boric acid in Tourmaline should go to ARFWEDSON In his appendix to ARFWEDSON's paper, BERZELIUS also shows that Boric acid occurs in »Siberian Rubellite».

[3] Ann. de Chimie et de Phys., T. 9, pp. 437, 448, 1876.

[4] Bidrag till Sveriges Mineralogie, part 3; Ark. för kemi etc. utg. af Vetenskapsakad. Vol. 5, part. 10, 1914.

the chief constituents, especially quartz. The texture, even for a pegmatite, is particularly coarse, individuals of felspar and petalite, having a size of several decimeters, being enclosed in a less coarse matrix of the same minerals.

Although these dykes do not show that symmetry of structure which is so characteristic of many pegmatites, yet there seems to be a certain regularity in the distribution of the mineral constituents, shown by the fact that the petalite and light tourmaline occur together with the quartz and not with the felspar.

Since in the pegmatites in general the quartz crystallises out later and at a lower temperature than the felspar, the same must apply to the petalite and tourmaline. Associated with quartz are also lepidolite and the blue-black tourmaline.

As a general rule, the light tourmalines, rubellite and indigolite, appear in quartz and petalite, while the blue black tourmaline occurs in lepidolite. The light tourmaline crystals are striated in the direction of the prism but show no developed faces, not even in the prism zone. The prisms are more idiomorphic against the quartz than against the petalite. From this one might draw the conclusion that they crystallised out simultaneously with the surrounding minerals. This is supported by the circumstance that the prisms are often bent but not cracked. Often the indigolite and rubellite occur together in the same crystal, in such a way that the indigolite forms the centre while the rubellite forms the outer shell or top of the crystal. The occurrence of the blue-black tourmaline is different. It appears only in finely laminated brownish-gray lepidolite as unoriented included prisms, some 2—4 mm in diameter. These prisms are never distorted and give a regular hexagonal section.

Methods of Analysis.

The analysis of tourmaline offers considerable difficulty, first because of its resistance towards solvents and secondly through the uncertainty of the method of determining the boric acid content. DOELTER considers the analysis of the silicates of boron to be one of the most difficult tasks offered by analytical chemistry.[1]

For two of the analyses (No. I and III) JANNASCH's method was used: the mineral being fused with $B_2 O_3$. This proved to be particularly advantageous for the light varieties of tourmaline, which are only with difficulty decomposed by soda. In the two other analyses (No. II and IV) decomposition is effected by fusing with soda.

After the fusion with $B_2 O_3$ the latter is expelled by means of methyl alcohol and HCl. After the separation of the SiO_2 the Fe and Al are precipitated with NH_3 in the presense of hydroxylamine in order to hold the Mn in solution, after which Ca is precipitated in acetic acid solution. After the ammonia salts have been volatilised off, the filtrate is dried and

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[1] C. DOELTER: Handbuch d. Mineralchemie, Vol. 2, p. 749.

the Mn and Mg separated from the alkali metals. The Mn is brought down by adding H_2O_2 in ammoniacal solution, while the Mg is separated with Na_2HPO_4. The lithium is separated from K and Na by means of ether alcohol; K is thrown down by the addition of $PtCl_4$; out of the filtrate Pt is precipitated by hydrozinc-chloride, while Na remains as chloride.

In the analyses II and IV, when solution is effected by melting with soda, there was obtained on dissolving the melt in water, a residue which was added to the SiO_2 and Al_2O_3, precipitated from the aqueous solution by ammonium carbonate. After treatment with HCl the silica is separated in the usual way and then the filtrate is treated by the »acetate method» and the Mn separated. In the filtrate NH_3 is added in order to throw down Fe + Mn (+ P_2O_5 + TiO_2). The whole is weighed and fused with $KHSO_4$, dissolved in water, reduced and titrated with permanganate. Ca is precipitated as oxalate and Mg as $Mg_2P_2O_7$. The alkali contents in both these analyses is determined by the Lawrence SMITH method. After the removal by volatilisation of the ammonium salts, amyl alcohol is added to expel all traces of B_2O_3. After weighing the chlorides first the K is thrown down with $PtCl_4$, then Li and Na are separated by the use of amyl alcohol.

Boric acid Determination. A trial was first made of GOOCH's method upon pure borax but the results were constantly too low. Thereupon the older method of MARIGNAC-BODEWIG modified by JANNASCH was made use of. The Mg-borate was ignited, weighed and treated with methyl alcohol and HCl until all B_2O_3 was expelled, the residue was dissolved in HCl and the undissolved SiO_2 and Pt were filtered off. The magnesia was thrown down by the addition of Na_2HPO_4 and the MgO was calculated as pure pyrophosphate.

The F-content was determined after the well-known method of BERZELIUS.

For the analyses extremely finely powdered material was used, which had been dried over sand; the percentage of water was determined by the method of SIPÖCS. That water which escaped at a temperature lower than 105° C was not calculated into the formula for the mineral.

The analyses are incomplete so far as concerns the degree of oxidization of the iron, this not having been determined but assumed to be ferrous. In the analyses I, II and III made upon the light tourmalines, whose iron content is low, this assumption seems to be justified; into the composition of the blue-black tourmaline (analysis No. IV), it is probable that a part of the iron enters as ferric oxide.

The common varieties of tourmaline may generally be divided into the following classes:

(a) *Magnesia-tourmalines* with high Mg percentage and low Fe-percentage.
(b) *Iron-tourmalines* with a high ferrous iron content but relatively low percentage of magnesia.
(c) *Alkali tourmalines* which are poor in both ferrous iron and magnesia but instead contain more alumina.

To thuse must be added, as more uncommon types, manganese and chrome tourmalines, as well as such as contain a considerable amount of iron oxide. To the magnesia-tourmalines belong the majority of the brown, dark brown, or brownish-black kinds, to the iron tourmalines the dark green and greenish black types, whereas the alkali tourmalines passess light colours, being red, green or nearly colourless.

Even their appearance and mode of occurrence show the light tourmaline from Utö to belong to the alkali tourmalines and this is confirmed by the analyses I, II and III which show a low content of bivalent metals together with a high content (40—43 %) of alumina. These tourmalines have their parallel among the tourmalines from many Na and Li pegmatites, e. g. from San Diego in Lower California, Urulga and Schaitansk in the Ural, Auburn and Chesterfield in Maine, Elba, Brazil and many other localities.[1]

The blue-black tourmaline (analysis No. IV) is on the other hand an iron tourmaline of the same type as for instance the tourmaline from Stony Point in North Carolina or that from Paris in Maine, analysed by R. B. RIGGS, or from S. Piero, Elba, analysed by RAMMELSBERG.[2]

The formula and chemical constitution are, as is well known, ill established and many opinions have been uttered upon the subject. Besides RAMMELSBERG's full discussion of the formula of tourmaline the subject has been dealt with, among others, by S. L. PENFIELD, E. A. WÜLFING, R. SCHARIZER, P. P. JANNASCH and D. CALB, H. REINECKE and latterly by P. REINER, W. T. SCHALLER, W. VERNADSKY etc.[3] It is not intended to discuss here the formula of tourmaline and which of the explanations of its composition referred to is most likely to be true. I have confined myself to the question of whether the above analyses of the Utö tourmaline published here confirm PENFIELD's view, which is accepted by several of the newer investigators; according to it all tourmalines may be derived from the borosilicic acid

$$H_{20}B_2Si_4O_{21}.$$

If the tourmalines are constituted according to this formula then the greater part of the atoms are replaced by different metals, such as the univalent atoms of K, Na and Li, as well as those of the bivalent Mg, Ca and Fe and those of the trivalent, especially Al. According to the above formula, the proportion between the number of B- and Si atoms in the aluminium

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[1] Vide analyses No. 74—80 in DOELTER's compilation of tourmaline analyses in his Handbuch der Mineralchemie, Vol. II, p. 759, 760 (1916).

[2] Vide analyses No. 52, 55 and 56 of tourmalines in DOELTER's Handbuch d. Mineralchemie, Vol. II, p. 794—778.

[3] For the various opinions expounded by these authors the reader must consult the exposition given in Handbuch d. Mineralchemie, Vol. II, p. 764—778.

Analysis Table.

	I (rubellite)			II (indigolite)			III (white gray)			IV (blue-black)		
	%	$\frac{\% \times 100}{\text{mol. weight}}$	x	%	$\frac{\% \times 100}{\text{mol. weight}}$	x	%	$\frac{\% \times 100}{\text{mol. weight}}$	x	%	$\frac{\% \times 100}{\text{mol. weight}}$	x
H_2O below 105° . .	0,24	—	—	0,17	—	—	0,45	—	—	0,09	—	—
H_2O over 10° . . .	2,75	15,26	30,52	3,85	21,37	42,74	4,02	22,32	44,64	2,64	14,59	29,18
K_2O	0,49	0,52	17,78	0,86	0,91	18,82	0,50	0,53	19,58	0,60	0,64	16,22
Na_2O	3,36	5,41		2,99	4,81		3,04	4,90		3,15	5,07	
Li_2O	0,89	2,96		1,11	3,69		1,31	4,36		0,72	2,40	
FeO	1,35	1,88	7,20	3,51	4,88	13,34	1,35	1,88	10,12	9,04	12,60	34,60
MnO	0,28	0,40		0,40	0,58		0,37	0,58		0,41	0,58	
CaO	0,60	1,07		trace	—		0,95	1,69		1,08	1,92	
MgO	0,10	0,25		0,08	0.20		0,16	0,40		0,89	2,20	
Al_2O_3	42,99	42,06	252,36	40,08	39,22	235,32	40,99	40,11	240,66	34,69	33,94	203,64
B_2O_3	10,76	15,37	30,74	9,74	13,91	27,82	9,79	14,31	28,62	10,45	14,93	29,86
SiO_2	36,70	60,76	60,76	36,48	60,40	60,40	36,33	60,15	60,15	35,40	58,61	58,61
P_2O_5	0,00	—	—	0,17	—	—	0,00	—	—	0,13	—	—
F_2	0,10	0,50	—	0,40	1,05	—	0,39	1,02	—	0.29	0.76	—
Total	100,70	—	—	99,84	—	—	99,65	—	—	99,58	—	—
O deducted for F_2 .	0,08	—	—	0,17	—	—	0,17	—	—	0,12	—	—
	100,62	—	—	99,64	—	—	99,46	—	—	99,46	—	—

The column x gives the numbers of metal atoms expressed in terms of the equivalent number of H atoms and the number of Si and B atoms.

borosilicate from which the tourmalines are derived is as 1 : 2. Moreover if the metal atoms are expressed in terms of the equivalent number of H atoms as reckoned on their valencies, then their number is 5 times as great as that of the Si atoms and 10 times that of the boron. We shall test how well the analyses made upon the tourmalines at Utö satisfy these conditions.

Proportion between B and Si.

Analysis	Boron	Silicon
I	1	1,97
II	1	2,17
III	1	2,10
IV	1	1,96

As can be seen the proportions correspond pretty closely with the 1 : 2 relation demanded by the formula. Taking into consideration the difficulties met with in making a quantitative determination of the boric acid, the agreement between the results and the formula may be regarded as rather satisfactory. In the analyses II and III the determination of the boric acid apparently turned out too low to satisfy the formula completely. A comparison between the number of the metal atoms expressed in terms of the equivalent number of H atoms and the number of Si and B atoms is contained in the table given below. In this that portion of the water that escapes under 105° C has not been considered as entering into the constitution of the mineral, the F has not been included in the reckoning since the role that it plays is not known, while the insignificant quantity of P present in analyses II and IV has also been neglected.

Table.

Analysis	Number of metal atoms expressed in terms of the equivalent number of H atoms	Number of Si atoms multiplied by 5	Number of B atoms multiplied by 10
I	20	19,73	20,00
II	20	19,47	17,94
III	20	19,10	18,17
IV	20	20,66	21,05

From this it is evident that the Si content in all the analyses corresponds in an entirely satisfactory manner with the theoretical values compared with the number of metal atoms required by the formula. The values for the B content, however, in analyses II and III are somewhat too low to answer to the proper values for the corresponding metal and Si atoms. On the other hand, in analyses I and IV even the values for B show a satisfactory agreement.

On the whole, it can be said that the four analyses published here of the tourmaline from Utö support the formula $H_{20}B_2Si_4O_{21}$ suggested by PENFIELD for the boro silicic acid from which the tourmaline compound is derived.

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