

### Minerals of the Varuträsk Pegmatite.

#### XXIX. An X-ray study of stanniferous columbite from Varuträsk and of the related Finnish minerals ainalite and ixiolite.

By

KARIN ÅMARK.

Three Finnish minerals of specific character, related in different ways to the niobate-tantalate group, were described by A. E. Norden-skiöld (1) in the middle of last century. One was named ainalite and described as cassiterite with an isomorphous intermixture of  $(\text{Nb}, \text{Ta})_2\text{O}_5$ ; the second, ixiolite, was defined as an orthorhombic tantalite with high contents of  $\text{SnO}_2$ . The third species was of a more definite mineralogical character. It was named tapiolite and defined as a tetragonal modification of tantalite. The last species has later been found and described from different localities and its validity as a definite mineral species has long been manifest. This can not be said of the two other species. Ainalite has not been described from any other locality, and the few descriptions of ixiolite of later years are dubious.

From a more theoretical view point the minerals have been discussed at some length with reference to the isomorphy of their components. Schaller (2), for instance, has advanced a theory that different compounds of Sn and Ta enter as isomorphous mixtures in the minerals of his rutile group.

In recent years X-ray studies of the crystal structure of synthetic tantalates have been published (3). Whereas cassiterite is of the tetragonal monorutile type, most synthetic tantalates are of the trirutile type. Their c-axes are three times that of the monorutile cell. On the other hand most synthetic niobates are orthorhombic, of the columbite type, according to experimental studies of the author (not yet published).

In the light of these investigations the older theories of isomorphous miscibility of  $\text{SnO}_2$  and  $(\text{Nb}, \text{Ta})_2\text{O}_5$  seemed in many respects inconsistent with the experimental results.

The study of the tin-bearing minerals of Varuträsk made this question of current interest. Two analyses of cassiterite from this locality

represented a composition with a small amount — less than 1 % — of  $(\text{Nb}, \text{Ta})_2\text{O}_5$ . Two other specimens were found to represent a columbite with about 33 %  $\text{SnO}_2$ . An X-ray examination of these minerals, as well as a revision of the minerals ainalite and ixiolite, the only species on record related in composition, was therefore planned. Professor Quensel entrusted me with this work.

Thanks to the courtesy of Professor Eskola in Helsingfors a series of specimens of ainalite, ixiolite and tapiolite were put at our disposal. Though uncertain if the specimens actually represent the original material of A. E. Nordenskiöld, Eskola communicates that all the specimens are of old date and in all probability refer to the original finds of the minerals.

Of the Finnish material three specimens were labelled ainalite, two from Sukkula and one from Pennikoja, two ixiolite from Skogsböle and two tapiolite, one from Skogsböle and one from Sukkula.

Powder photographs were taken of these seven specimens, as well as of the two from Varuträsk. In all cases every line could be interpreted as belonging either to a monorutile or a trirutile phase or to a columbite phase. The results are given in table I.

Table I. Summary of the experimental results.

Description of the Mineral Localities	Structure type	Crystal form	Unit cell edges (in Å)			Cell vol (in Å <sup>3</sup> )
			a	b	c	
Tapiolite (Nr 1015), Skogsböle, Kimito	Trirutile	tetragonal	4.75		9.29	207
Tapiolite (Nr 1072), Sukkula, Tammela	Trirutile	tetragonal	4.74		9.24	208
Ainalite (Nr 443), Sukkula, Tammela	Trirutile	tetragonal	4.75		9.24	208
Ainalite (Nr 444), Sukkula, Tammela	Cassiterite	tetragonal	4.72		3.17	71
Ainalite (Nr 4561), Pennikoja, Tammela	<i>Cassiterite</i> + Columbite	tetragonal + orthorhombic	4.73		3.18	71
			5.14	14.2	5.74	418
Tapiolite (Nr 1014) (tantalite), Skogsböle, Kimito	<i>Cassiterite</i> + Columbite	tetragonal + orthorhombic	4.72		3.18	71
			5.14	14.1	5.76	417
Tapiolite (Nr 1035) (ixiolite), Skogsböle, Kimito	Trirutile + Columbite	tetragonal + orthorhombic	4.74		9.24	208
			5.16	14.2	5.74	420
Varuträsk (Nr 7039) and Varuträsk, (Nr 7003), Sweden	<i>Cassiterite</i> + Columbite	tetragonal + orthorhombic	4.72		3.17	71
			5.12	14.3	5.74	418

(italic component marks the chief part of the specimen)

The two Varuträsk specimens gave the same powder photographs. Their average composition is:

SnO <sub>2</sub> . . . . .	33 %
Ta <sub>2</sub> O <sub>5</sub> . . . . .	20 »
Nb <sub>2</sub> O <sub>5</sub> . . . . .	34 »
MnO . . . . .	12 »
and traces of Ti, Na, Fe and Mg.	

It is clear that the specimens labelled ainalite and ixiolite are only mixtures of cassiterite and orthorhombic columbite, or a mixture of tapiolite (trirutile) and columbite, or else are only pure tapiolite or pure cassiterite. According to the experimental results given above, the minerals in question must therefore be considered as mechanical mixtures of the three components: cassiterite (tetragonal monorutile type), tapiolite (tetragonal trirutile type) and columbite (orthorhombic). The exact chemical composition of the Finnish mineral specimens was not definitely known, and therefore it was not possible to decide whether the minerals of rutile type show any appreciable isodimorphous solubility.

To find if a trirutile compound could to a certain extent dissolve in a monorutile compound the following experiment was carried out. A compound of monorutile type and one of trirutile type were mixed in the molecular proportions 1:3, 1:1, and 3:1. For experimental reasons zincantimonate, ZnSb<sub>2</sub>O<sub>6</sub>, was chosen as a trirutile compound. According to the investigations of Byström and his co-workers, (4) ZnSb<sub>2</sub>O<sub>6</sub> is of trirutile type, gives good powder photographs and does not alter by heating. SnO<sub>2</sub>, ZnO and Sb<sub>2</sub>O<sub>3</sub> were then weighed up in the given proportions and the mixtures were ignited two days at 650°, two days at 900°, and five days at 1100° C.

Table II. Examination of the solubility of trirutile in monorutile phase.

Composition	Phases	Unit Cell a	Edges (in Å) c	Cell volume (in Å <sup>3</sup> )
SnO <sub>2</sub> . . . . .	Cassiterite	4.72	3.18	71
3 SnO <sub>2</sub> + ZnSb <sub>2</sub> O <sub>6</sub> . . .	Cassiterite	4.70	3.15	70
SnO <sub>2</sub> + ZnSb <sub>2</sub> O <sub>6</sub> . . .	Cassiterite +	4.70	3.14	69
	Zincantimonate	4.66	9.24	201
SnO <sub>2</sub> ÷ 3 ZnSb <sub>2</sub> O <sub>6</sub> . . .	Cassiterite +	4.70	3.14	69
	Zincantimonate	4.66	9.24	201
ZnSb <sub>2</sub> O <sub>6</sub> . . . . .	Zincantimonate	4.66	9.24	201

Clearly the X-ray examination of synthetic material indicates that a trirutile phase can to a certain extent, (about 25 molecular %) dissolve in the monorutile phase. From a mineralogical point of view this would mean that up to c:a 25 % of tapiolite may isomorphically enter the cassiterite structure. The dimensions of the cassiterite cell are thereby diminished. On the other hand the monorutile phase is unable to dissolve in a quantitatively predominating trirutile phase.

According to Nordenskiöld's analyses of ainalite, the mineral contains about 90 %  $\text{SnO}_2$  and 10 %  $\text{Ta}_2\text{O}_5$ . From the examination above we have seen that this quantity of  $\text{Ta}_2\text{O}_5$  in a trirutile phase, i. e. as the mineral tapiolite, may well dissolve in the cassiterite phase. This may be the case with Ainalite Nr 444. On the other hand the specimen, Ainalite Nr 4561, is only a mechanical mixture of cassiterite and columbite, and ainalite Nr 443 is pure tapiolite. The two last specimens must have a quite different composition than the ainalite Nordenskiöld once analysed.

Experiments have also been made to see if the orthorhombic columbite-tantalite phase can form a homogeneous mixture with the trirutile phase. Synthetic ferrotantalate of trirutile type and ferro-niobate of orthorhombic columbite type were mixed in the same proportions as in the investigation of the solubility of trirutile in monorutile phase above, and ignited. At a composition of 25 molecular per cent  $\text{FeNb}_2\text{O}_6$  and 75 %  $\text{FeTa}_2\text{O}_6$ , the columbite lines in the powder photographs were hardly visible, but at 75 %  $\text{FeNb}_2\text{O}_6$  and 25 %  $\text{FeTa}_2\text{O}_6$  both phases were present. As the ionic radii of niobium and tantalum are nearly alike, no perceptible alterations of the cell dimensions could be observed in this case.

According to these results we may conclude that from a mineralogical point of view columbite may dissolve in a mineral of trirutile type, for example tapiolite, if the orthorhombic phase is present in less than 25 mol. per cent. A higher content of columbite will only give a mixture of columbite and tapiolite. Probably this applies to tapiolite Nr 1035, labelled ixiolite.

Finally a similar experiment was made to investigate the miscibility between a monorutile phase and an orthorhombic phase. 25 mol.%, 50 mol.% and 75 mol.% of  $\text{SnO}_2$  were mixed with  $\text{FeNb}_2\text{O}_6$  (of orthorhombic columbite type) and ignited as before. All powder-photographs taken showed, however, only mixtures of the two phases. This would indicate that cassiterite and a columbite phase are not dissolvable in each other in the proportions as given above.

Of course here as well as in the examinations above, the capacity of solution varies with the composition of the mineral. Therefore the

figures above are only meant to give a very rough mean value of the solubility.

Concerning the minerals dealt with in this paper we may therefore conclude that if Nb is present in greater quantity than about 25 molecular % in a columbite-tantalite mineral, containing  $\text{SnO}_2$ , the orthorhombic phase will be developed and the mineral will only represent a mechanical mixture of cassiterite and columbite-tantalite. These conclusions I have made with aid of synthetic mixtures and therefore I must make a reservation as to the right of direct application to minerals. It is of interest to note that in Schaller's survey over isomorphous minerals of his rutile group, the analyses of cited tetragonal iron and manganese niobates and tantalates throughout show low contents of  $\text{Nb}_2\text{O}_5$  (generally about 20 %).

To what extent the discussion above also may refer to the miscibility of  $\text{TiO}_2$  and the niobate-tantalate phases, as for example in the mineral ilmenorutile, has not been definitely proved by the photographs taken in this connection. This question I must for the present leave open.

I wish to express my thanks to the Professors Quensel and Westgren for their continued interest during this investigation.

#### L i t e r a t u r e.

- 1) A. E. Nordenskiöld, *Beskrifning öfver de i Finland funna mineralier*. Helsingfors 1863.
  - 2) W. T. Schaller, U. S. G. S., Bull. 509.
  - 3) V. M. Goldschmidt, *Geochemische Verteilungsgesetze* VI. skr. Norske Vidensk. Akad. M. N. kl. 1926 N:o 1.
  - 4) A. Byström, B. Hök and B. Mason, K. Vetenskapsak. Arkiv för Kemi och Mineralogi. Bd 15 1941.
-