FORMULA AND STRUCTURE OF RALSTONITE

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The rare fluoride, ralstonite, is found in small, clear, colorless octahedrons with cryolite and thomsenolite at Ivigtut, Greenland. It has also been reported from Colorado and Japan, but only the Greenland material has been analyzed. The best analyses of ralstonite are those of Brandl[1] and of Penfield and Harper.[2] From these analyses Penfield and Harper calculated the formula, $(Mg,Na_2)Al_3(F\text{-}OH)_{11}\cdot 2H_2O$.

Table 1 shows these two analyses together with recalculations considering part of the water to represent (OH) in order to satisfy valence requirements. The figures of the first column give Brandl's analysis as corrected by Penfield and Harper for thomsenolite impurity. The figures in the last column differ slightly from those calculated by Penfield and Harper, partly because they apparently used different atomic weights and partly because their calculation does not exactly fulfill valence requirements.

TABLE 1. ANALYSES OF RALSTONITE

	1	2	1*a*	2*a*
Na	5.05	4.27	5.05	4.27
Mg	3.90	4.39	3.90	4.39
Al	23.06	24.25	23.06	24.25
F	57.68	39.91	57.68	39.91
OH			1.19	19.46
H_2O	10.17	18.73	9.56	8.43
	99.85	91.55	100.43	100.71

1. Analysis by Brandl, as corrected by Penfield and Harper.
2. Analysis by Penfield and Harper.

1*a* and 2*a*. Analyses 1 and 2 recalculated to account for the presence of OH.

CELL CONTENTS

Thanks to the kindness of Mr. Dore of the Division of Plant Nutrition, University of California, the writer obtained powder, Laue and rotation *x*-ray diffraction photographs of ralstonite from Greenland. The material used was from the collections of the Department of Geological Sciences, University of California.

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[1] Brandl, J., Ueber die chemische Zusammensetzung der Mineralien der Kryolithgruppe: *Liebig's Annalen der Chemie,* **213,** 1–15 (1882).

[2] Penfield, S. L., and Harper, D. N., On the chemical composition of ralstonite: *Am. Jour. Sci.,* (3) **32,** 380–386 (1886).

Table 2 gives the data for a powder photograph made with Mo radiation, using a zirconium filter and a cassette of 8 inch radius, calibrated by a comparison pattern with halite. This leads to a lattice constant of 9.87Å and to a cell volume of 961.5Å.^{3} A cell of these dimensions does not contain an integral number of formular units, if the hitherto accepted formula is used. Instead Table 3 shows the census of the cell contents for both analyses assuming a density of 2.61. In the case of Penfield and Harper's analysis the results are shown also for an assumed density of 2.56, the figure they reported for their best material. It is probable that the density of ralstonite is variable and that the material

TABLE 2. POWDER PHOTOGRAPH OF RALSTONITE FROM GREENLAND. MO-RADIATION. CASSETTE RADIUS 8 INCHES

Estimated intensity	$\sin^2\theta$	$(h^2+k^2+l^2)\times q$	*hkl*
10	0.00388	3×0.001294	111
8	0.01422	11×0.001293	311
7	0.01554	12×0.001295	222
1			400
2	0.02452	19×0.001291	331
4	0.03106	24×0.001293	422
6	0.03549	27×0.001299	333, 511
7	0.04137	32×0.001292	440
1	0.04524	35×0.001293	531
1	0.05194	40×0.001298	620
4 (broad)	0.05682	43	533
		44×0.001292	622
1	0.06206	48×0.001293	444
3	0.06591	51×0.001293	711, 551
3	0.07625	59×0.001293	731, 553
1	0.08306	64×0.001298	800
2	0.09340	72×0.001298	822, 660
1	0.09859	76×0.001298	662
1	0.10321	80×0.001292	840

TABLE 3. CONTENTS OF UNIT CELL OF RALSTONITE

	1		2			
	Sp. Gr. 2.61		Sp. Gr. 2.61		Sp. Gr. 2.56	
Na	3.25		2.82		2.76	
Mg	2.45	15.45	2.75	16.45	2.70	16.13
Al	13.00		13.70		13.43	
F	46.30	47.37	32.00	49.42	31.35	48.44
OH	1.07		17.42		17.09	
H_2O	8.08		7.14		7.00	

of the second analysis, having more fluorine replaced by hydroxyl and having, as will be shown, some vacancies in its water positions, is actually of lower density. The table shows that the number of Al plus Mg in the cell is nearly 16, and the number of F plus OH is nearly 48. The sum of Na and Mg, on the other hand is between 5 and 6, and does not correspond to any number of equivalent points possible in a cubic cell.

SPACE GROUP

The Laue symmetry of ralstonite is O_h. Both powder and rotation patterns show only lines compatible with a face centered lattice. Space groups requiring the extinction of *hhl* when *h* is odd are excluded by the appearance of 113, 115 and other similar lines. This leaves five possible space groups, T_d^2, O^3, O^4, O_h^5 and O_h^7. The lines *hk*0 are found only with $h+k=4n$ (Table 6). Of the possible space groups only the last mentioned requires this restriction. It may be concluded that O_h^7-Fd3m is most probably the space group of ralstonite.

STRUCTURE

Proceeding from the figures of column 3 of Table 3, it is necessary to accommodate 48 (F, OH), 16 (Al, Mg), 2.8 Na and 7 H_2O in the unit cell. In the space group O_h^7 there is but one 48-fold position, $x00$. This will serve for (F, OH). There are two 16-fold positions, (*c*) $\frac{1}{8},\frac{1}{8},\frac{1}{8}$ and (*d*) $\frac{5}{8},\frac{5}{8},\frac{5}{8}$, but they are similar and the choice of one or the other for (Al, Mg) is equivalent to a choice of origin, so that 16 (*c*) may be taken arbitrarily for Al and Mg. A preliminary choice of the parameter for (F, OH) may now be made from the known radii of Al and F. If this is done it is found that neither Na nor H_2O can be fitted into the position 8: (*a*) 000. This leads to the following possible arrangement:—

48	(F, OH)	in 48: (*f*) $x, 0, 0$;
16	(Al, Mg)	in 16: (*c*) $\frac{1}{8}, \frac{1}{8}, \frac{1}{8}$;
2.8	Na	in 16: (*d*) $\frac{5}{8}, \frac{5}{8}, \frac{5}{8}$;
7	H_2O	in 8: (*b*) $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$;

both the last two positions being only partly occupied. This arrangement is the type $E8_1$ (*Strukturbericht*, **II**, 1928–1932), the structure type of pyrochlore and related minerals.

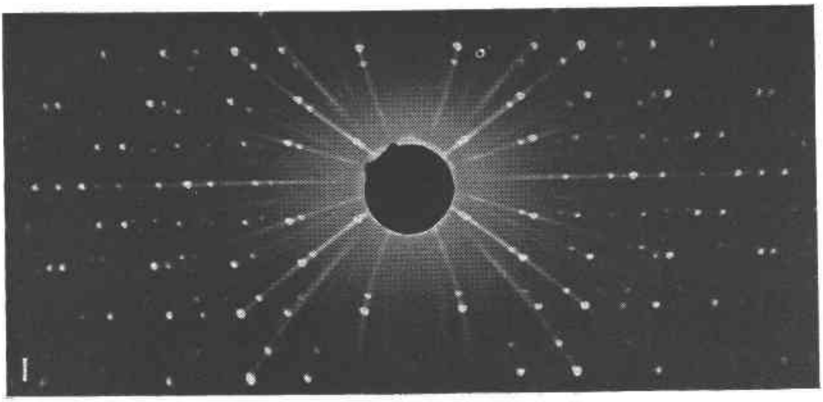
Table 4 shows the comparison of calculated and observed intensities of the first 22 possible lines in a powder pattern of ralstonite. From this it may be seen that the parameter of the (F, OH) is 0.19, the agreement of calculated and observed intensities being excellent for this value.

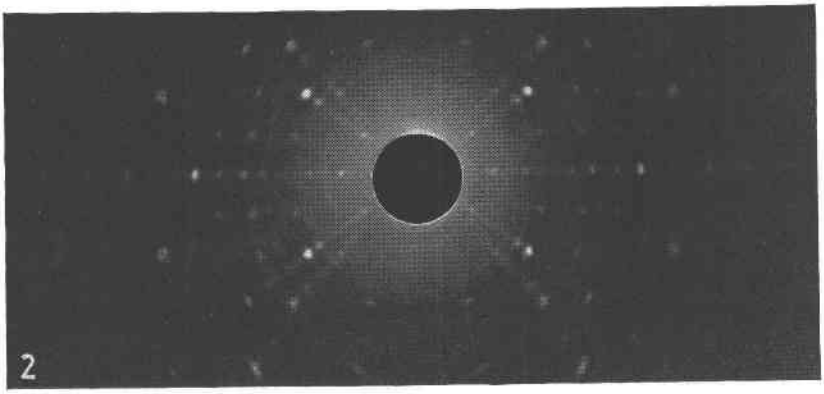
TABLE 4. OBSERVED AND CALCULATED INTENSITIES OF LINES IN POWDER PHOTOGRAPH OF RALSTONITE

	Observed	Calculated			
		Mg with Al in 8 (*c*)			Mg with Na in 8 (*d*)
hkl	x	.20	.19	.18	.19
111	10	2.08	2.52	3.22	1.57
220	—	.07	.03	.01	.03
311	8	1.40	1.42	1.26	.80
222	7	1.10	1.10	1.10	1.10
400	1	.25	.15	.07	.15
331	2	.27	.32	.34	.13
422	4	.45	.53	.62	.53
511 333	6		1.11 { .04 1.07	.03 1.11	
440	7		1.46	1.04	
531	1		.22	.16	
620	1		.27	.44	
533 622	4		.98 { .36 .62	.48 .62	
444	1		.12	.19	
711 551	3		.62 { .06 .56	.11 .38	
642	—		.02	.03	
731 553	3		.53 { .52 .01	.33 .03	
800	1		.18	.19	
733	—		.06	.03	
822 660	2		.37 { .20 .17	.14 .21	
751 555	—		.03 { .02 .01	.00 .01	
662	1		.21	.20	
840	1		.24	.19	

TABLE 5. INTERATOMIC DISTANCES IN RALSTONITE

	Distances calculated from structure	Sum of radii	
F–F (0, .19, 0)–(0, 0, .19)	2.65Å		2.66
F–F (.25, .06, .25)–(0, 0, .19)	2.60		2.66
F–(Al, Mg)	1.86	F–Al	1.90
		F–Mg	2.11
F–Na	2.54		2.31
F–H_2O	3.06		2.65
Na–H_2O	2.14		2.30
F–(0, 0, 0)	1.88		
F–(x, x, x) $x=\frac{7}{8}$	1.86		





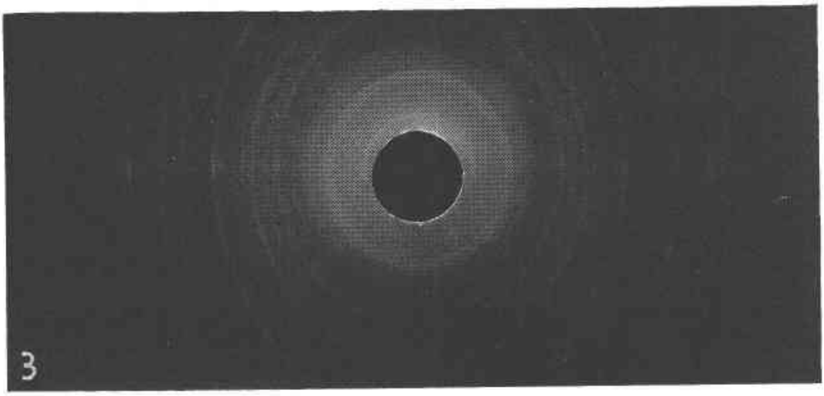


FIG. 1. Fresh ralstonite.

FIG. 2. Ralstonite heated to 365°. 27% loss.

FIG. 3. Ralstonite heated to 615°.

All rotation photographs on [001] with Cu radiation. Prepared in the Mineralogisches Institut, Tübingen.

The structure may be checked by reference to Table 5 which shows the interatomic distances compared with the distances corresponding to Goldschmidt's radii. Incidentally the distances to certain vacancies are also included to show that these are not suitable positions for H_2O or Na. The similarity of the two F—F distances shows that the coordination of F or of F and OH about Al or Mg is almost ideally octahedral. All values agree well with requirements except that Mg has rather a tight fit in the Al positions. The last column of Table 4 shows the calculated intensities considering that Mg and Na share a set of positions and that part of the set of positions occupied by Al is vacant. The intensity relations of the first few lines show unequivocally that Mg is not placed in the structure in this fashion.

Column 1 of Table 6 shows the summary of observations on a rotation pattern of ralstonite (Fig. 1). The indices and intensities of all spots are in agreement with the structure outlined above, except for the spot 442, which has intensity 2, whereas 424 is not observable. This spot should be absent due to extinctions required by the special positions occupied in this structure, though it is permitted by the space group. Other spots of this character, such as 644, 842 or 882 are not found on any of the films. A search on films of the related minerals, koppite, romeite and pyrrhite failed to reveal 442 or similar spots. A rotation pattern of ralstonite with Fe radiation also showed the spot 442, but not 424. In short, the presence of this disturbing spot was not to be denied in spite of its absence, as required, on the films of other materials of supposely analogous structure.

TABLE 6. INDEXING OF ROTATION PATTERNS OF FRESH (1) AND OF HEATED (2) RALSTONITE

*hk*0	1	2	*hk*2	1	2	*hk*4	1	2
200		5*	202		5	204		3*
220		4	222	10	10	224	7	2
400	4	3	402		4*	404	9	8
420		5*	422	8	3	424		2*
440	10	10	442	2†		444	6	3
600		3*	602	5				
620	5		622	9	5	624	1	
640		5*	642	1		644		1*
800	6	4				804	4	1
			822	7				
660	4	1	662	6	3	664	3	
840	5	3				844	5	1
			10·0·2, 862	2	1			
10·2·0	3	1	10·2·2	5				
880	3	1	882		1?*			
10·6·0	4		10·6·2	5				
			12·2·2					
*hk*1			*hk*3					
111	9	5	113	10	4			
311	10	5	313	8	7			
331	7	5	333	10	7			
511	2	5	513	4	1			
531	4	2	533	8	2			
711, 551	6		713, 553	5				
731	6		733	3	1			
751	1		753	2				
911	3		913	4				
931	4		933	1				
771	1?		773	4				
951	2		953	2				
			11·1·3	3				
11·3·1	4		11·3·3	5				
11·5·1	6							

* Spots not compatible with ralstonite structure, see text.

† Spot due to indirect diffraction, see text.

Several modifications of the structure which might yield an explanation of this spot were tried but failed to give satisfactory results. Finally it seemed that the spot must be due to indirect diffraction, "Umweganregung."[3]

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[3] Renninger, M., "Umweganregung," eine bisher unbeachtete Wechselwirkungserscheinung bei Raumgitterinterferenzen: *Zeits. Physik*, **106**, 141–176 (1937) and Brandenberger, E., Umweganregungen und Auslöschungsgesetze: *Zeits. Krist*, **97**, 476–484 (1937).

It has been shown that the diffraction $h_1k_1l_1$ may be simulated under certain conditions if an *x*-ray beam which has been diffracted by $h_3k_3l_3$ suffers a second diffraction by $h_2k_2l_2$ within the crystal. In order that this should occur it is necessary that:—

1. $h_1=h_2+h_3$, $k_1=k_2+k_3$, $l_1=l_2+l_3$; where $h_2k_2l_2$ and $h_3k_3l_3$ are permitted lines for the structure;
2. $h_1k_1l_1$ and $h_3k_3l_3$ must reach the diffraction position with the incident beam simultaneously;
3. finally $h_2k_2l_2$ and $h_3k_3l_3$ must themselves yield strong diffractions and the crystal must be sufficiently large and perfect in order that a measurable intensity of $h_1k_1l_1$ shall result.

In the present case all of these conditions are fulfilled. It was first found graphically with the aid of a reciprocal lattice projection and then checked by calculation that both for Fe and for Cu radiation 333 reaches the diffraction position simultaneously with 442 upon rotation on [001]. The diffraction spot 442 on the films then arises from the secondary beam 333 which has suffered a further diffraction on $11\bar{1}$. It reaches a notable intensity because of the perfection of the crystal and because 333 and $11\bar{1}$ are among the strongest diffractions. This explanation of 442 is in harmony with the absence of 424. If 442 were a normal diffraction 424 should appear with about double its intensity. If 442 is merely an indirect diffraction via 333 and $11\bar{1}$, 424 should be absent as it does not reach the diffraction position simultaneously with 442 and 333, *i.e.*, condition 2 is not fulfilled.

DEHYDRATION AND DECOMPOSITION

In view of the variable water content an attempt was made to trace the effect of dehydration on the structure of ralstonite. Because of the small amount of material available and the difficulty of separating it from the accompanying minerals the number of dehydration experiments was somewhat limited. A 14 mg. portion of ralstonite showed little loss at 245°C. After brief heating at 445° a loss of 19% was recorded. Since this is about the maximum amount of water found in ralstonite, the heating experiment was broken off at this point. The crystals, though rather cloudy, had lost entirely the anomalous double refraction invariably found in fresh ralstonite. The index of refraction had dropped from 1.43 to about 1.39 and the density from 2.6 to 2.3. A rotation pattern showed that the structure remained intact and that the lattice constant was but little changed. This is most surprising, for the loss of 19% indicates that not only the water of crystallization was driven off but also hydroxyl water. In order that this should occur one might suppose that certain of the 48 (f) positions are now vacated and others, formerly occupied by OH^{-1} are now occupied by O^{-2}.

Unfortunately the material used for this dehydration experiment was used up in tests for lattice constant, density and index of refraction. A new portion of 20 mg. was used for a repetition of the experiment. Again no notable loss was observed at 245°. This time the heating was carried on by more stages with the result that the crystals after 3 hours at 365° showed a loss of 27% and finally after further 4 hours at 450° reached constant weight with a total loss of about 30%. Initially clear, colorless crystals which have suffered this great loss are merely whitened and assume a porcelaneous appearance. The faces remain perfect reflecting surfaces as shown by repeated examination on the two-circle goniometer. Again a rotation photograph shows that the structure is largely maintained, as may be seen from a comparison of Figs. 1 and 2. The appearance of rings in connection with some of the spots and the "fuzziness" of the second photograph suggest the beginning of transformation to the unoriented aggregate which is obtained at still higher temperatures.

Table 6 shows the intensities and indices of spots observed on a rotation photograph of ralstonite which had been heated to 365° with a loss of weight of 27%, in parallel columns with like data for fresh ralstonite. The main features of the two patterns are similar but there are some notable changes in intensities and 8 or 9 new spots appear that are incompatible with the structure of ralstonite and with the space group O_h^7. Even though the dimensions are unchanged and the lattice remains face centered it may be concluded that there is extensive rearrangement of the remaining constituents when the volatiles are driven off from ralstonite.

Since the loss is more than the maximum amount of water known to occur in ralstonite it seemed certain that some other constituent must have been driven off by prolonged heating at 365 to 450°. To test this about 5 mg. of fresh ralstonite were sealed in a small evacuated glass tube and heated to 375° for about 2 hours. This resulted in the etching of the glass tube and the formation of a fine white powdery deposit, thought to be H_2SiF_6. This was confirmed by dissolving the white powder in water and obtaining a positive test for F ion.

One is now forced to the conclusion that HF may be driven off from ralstonite at moderate temperature without destruction of the crystal lattice. If, in the case of ralstonite having the composition shown in column 2*a* of Table 1 all the water is driven off and the H of OH goes off with F as HF, a total loss of 31.3% would result. Some such change has occurred in the ralstonite whose diffraction pattern is shown in Fig. 2.

Further heating of ralstonite for 3 hours at 615° causes no further loss in weight. The material remains cloudy and isotropic and assumes a refractive index of about 1.57. The density varies slightly from fragment to fragment, but is near 2.4. The crystals remain outwardly perfect and the faces still yield such good reflections that the [001] axis may be accurately adjusted as rotation axis. Figure 3 shows the rotation photograph of such a "crystal." The smoothness of the rings corresponds to the appearance of a powder photograph, but slight intensification of a few of the lines where they cross the former position of layer lines suggests the last traces of common orientation. It appears at first glance that some of the lines may be indexed to correspond to the single crystal photographs, but this is not the case. Half of the lines do not correspond to any spots in the other patterns and the two strongest spots, 222 and 440 of Fig. 2 are not found in the powder pattern. It must be concluded that one or more new phases have been formed.

RELATIONS TO SIMILAR STRUCTURES

In Table 7 are summarized the data on the occupation of the several lattice positions in minerals and compounds of the structure type $E8_1$. The parameter x has in some cases been changed for $\frac{1}{2}$-x and the positions 16 (*c*) and 16 (*d*) as well as 8 (*a*) and 8 (*b*) interchanged to agree with the choice of origin adopted for pyrochlore by von Gaertner and used in this paper for ralstonite.

No numerical values are given for the disposition of metals in the structures of minerals quoted from other authors because the determinations were in part on material that had been metamict or for which reliable detailed analyses were lacking.

Both Machatschki and Reuning observe that the materials they examined show a deficiency of positive ions for full occupation of the lattice points so that vacancies may occur, say in the 16 (*c*) positions, but the variable valence of some of the metals in this group introduces a measure of uncertainty. In Sb_3O_6OH, $BiTaO_6F$ and in ralstonite partly vacant sets of positions are definitely established.

The formula $X_2Y_2(O, OH, F)_7$ has been used for minerals with pyrochlore structure, there being eight such units in the cell. Rosen and Westgren[4] object to this formula on the ground that $Ca_2Ta_2O_7$ is not isomorphous with this group. They prefer the formula $X_2Y_2O_6(OH, F)$ with no oxygen in the eight-fold position. von Gaertner originally placed (O, F) in 48 (*f*) and (F, O) in 8 (*b*). Unfortunately no consideration of intensities can establish the distribution of O, OH, F and H_2O over these two positions.

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[4] Rosen, O., and Westgren, A., Minerals of the Varuträsk pegmatite XII. On the structure and composition of minerals belonging to the pyrochlore-atopite group and an x-ray analysis of disintegrated stibio-microlite: *Geol. Fören. Förhandl.*, **60**, 216–235 (1938).

TABLE 7. MINERALS AND ARTIFICIAL COMPOUNDS OF THE PYROCHLORE GROUP

Name or formula	Lattice constant	16 (*c*)	16 (*d*)	48 (*f*) $x00$	x	8 (*b*) $\frac{1}{2}\frac{1}{2}\frac{1}{2}$	Reference
Pyrochlore synthetic	10.38Å	Nb	Na, Ca	O	.20	F	v. Gaertner
Pyrochlore natural	10.34	Nb, Ti, Ta	Ca, Na, Ce, etc.	O, F	.20	F, O	v. Gaertner
Koppite	10.37	Nb, Fe	Ca, Ce, Na, K	O	.19	O, OH, F	Brandenberger
Romeite*	10.26	Sb	Ca, Na, Mn	O	.20	OH(F)	Zedlitz
Schneebergite	10.30	Sb	Ca, Na, Fe	O		OH	Zedlitz
Lewisite	10.27	Sb, Ti	Ca, Fe, Na, Mn**	O, OH		***	Machatschki
Pyrrhite	10.41	Nb, Ta, Ti	Ca, Na, Fe	O		OH, F	Machatschki
Microlite	10.38	Ta, Nb	Ca, Na, Fe	O		OH, F	Reuning
Bindheimite	10.41	Sb	Pb	O		O	Hägele
Ralstonite	9.87	13Al, 3Mg	3Na	31F, 17OH	.19	$7H_2O$	
Sb_3O_6OH†	10.28	$16Sb^{V}$	$8Sb^{III}$	48 O	.21	8 OH	Dihlström and Westgren
$BiTa_2O_6F$	10.46	16Ta	8Bi	48 O	.21	8F	Dihlström and Westgren
$NaSbO_3$††	10.20	16Sb	16Na	48 O	.21		Schrewelius
$AgSbO_3$	10.23	16Sb	16Ag	48 O	.21		Schrewelius

* Atopite and weslienite are varieties of romeite.

** There are many vacancies in the 16 (*d*) position of lewisite.

*** The 8 (*b*) position of lewisite is practically unoccupied.

† Dihlström and Westgren consider that Sb_2O_4 or $Sb_2^{III}Sb_2^{V}O_8$ described by G. Natta and M. Baccaredda, Tetrossido di antimonio e atimoniati; *Zeits. Krist.*, **85**, 271–296 (1933), is really Sb_3O_6OH.

†† There also exists a rhombohedral form of this compound, isomorphous with ilmenite.

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MACHATSCHKI, F., Die Pyrochlor-Romeit-Gruppe: *Chemie der Erde*, **7**, 56–76 (1932).

REUNING, E., Mikrolithvarietäten von Donkerhuk, Südwestafrika: *Chemie der Erde*, **8**, 186–217 (1933).

HÄGELE, G., Röntgenographische Untersuchung des Bindheimits von Waitschach bei Hüttenberg, Kärnten: *Zentralbl. Min.*, **1937A**, 45–50.

DIHLSTRÖM K., and WESTERN, A., Über den Bau des sogenannten Antimontetroxyds und der damit isomorphen Verbindung $BiTa_2O_6F$: *Zeits. anorg. u. allgem. Chem.*, **235**, 153–160 (1937).

SCHREWELIUS, N., Röntgenuntersuchung der Verbindungen $NaSb(OH)_6$, $NaSbF_6$, $NaSbO_3$ und gleichartiger Stoffe: *Zeits. anorg. u. allgem. Chem.*, **238**, 241–254 (1938).

In many of the minerals of this group the intensity of the lines is largely controlled by the heavy Sb and Nb and related ions. With ralstonite no such difficulty arises and it is possible to show that certain positions are partly vacant. In lewisite the eight-fold position is likewise largely vacant and in $AgSbO_3$ and $NaSbO_3$ it is wholly unoccupied, suggesting that the pyrochlore structure may be stable in spite of wide variation in the number and character of negative ions and water molecules. The essential feature, common to all the examples listed in Table 7, is the coordination of negative ions in $x00$ about the position $\frac{1}{8},\frac{1}{8},\frac{1}{8}$, giving a continuous network of linked octahedrons.

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