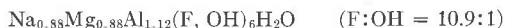


RALSTONITE FROM IVIGTUT, SOUTH GREENLAND

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ABSTRACT

Ralstonite of the following composition

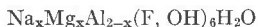


has been found in the cryolite deposit in Ivigtut, South Greenland. Various cubic minerals of ralstonite type have been registered from this deposit. These and ralstonite from other localities as well as from Ivigtut can be arranged in a series where the new compound represents a member close to one end of the series, $\text{NaMgAl}(\text{F}, \text{OH})_6\text{H}_2\text{O}$. The other members of the series show decreasing amounts of Na and Mg. Among Ivigtut samples a formula content of 0.34 Na and Mg represents the lowest value; a specimen from Kazakhstan is registered in literature with a content of Na and Mg in the formula at 0.29. Basic aluminium fluoride $\text{Al}_2(\text{F}, \text{OH}) \cdot \text{H}_2\text{O}$ may be regarded as the other end member, as its structural data correspond closely to those of the ralstonite series.

Examination of optical data, x-ray data and specific gravity for a number of samples together with corresponding data from literature indicates certain regularities in the series of ralstonite with the mentioned compositional variation. Low refractive index occurs together with high specific gravity, $d \sim 2.6$, $n \sim 1.37$, and a large unit cell, a about 10.02 Å. Samples with high refractive index, $n \sim 1.43$, have low specific gravity, $d \sim 2.4$, and cell dimension about 9.90. The first group has a high content of Na and Mg, whereas the last group has a low amount of these elements.

RALSTONITE AND CUBIC MINERALS, OLD AND NEW MATERIAL

Brush investigated material from Ivigtut and published the first description of ralstonite, Brush (1871). In spite of the several analyses carried out in the following years it seemed hard to establish a satisfactory formula for the mineral. It was not until Pabst (1939) published his paper "Formula and Structure of Ralstonite," that a convincing formula was given. Ralstonite is, according to Pabst, a fluoride of pyrochlore structure of the following composition:



In the various analyses the amounts of water seem to correspond to a little less than one molecule. According to Penfield's and Harper's analysis chosen by Pabst as a basis for his calculations, the value of x is about 3/8.

In the course of years ralstonite has been mentioned from several localities outside Ivigtut: Cross and Hillebrand (1883) think they have found it in Pikes Peak, St. Peter's Dome, Colorado.

From fumarole deposits at Vesuvius, Italy, Carobbi and Cipriani (1951) mention ralstonite, and from corresponding formations in Kamtchatka and from occurrences in the Ilmen Mountains and Kazakhstan Stepanov and Moleva (1962) describe the mineral.

In a note on weberite from Pikes Peak, the present author, Pauly (1954), mentioned the observation of what was termed "cubic minerals" in material from Pikes Peak.

The use of the term "cubic mineral" has been adopted from Bøggild who in this way tried to maintain a distinction between the cubic mineral ralstonite with octahedral habit and the various "cubic minerals" mainly of hexahedral habit. This is quite clear in Bøggild (1913) in which he argues against Cross and Hillebrand's ralstonite. They have described the mineral as being cubes with small octahedral faces, and such a shape rather points to the mineral being of the kind Bøggild provisionally termed "first cubic mineral." The lack of refractive indices and specific gravity determinations, however, prevents further discussion.

According to Bøggild (1953) ralstonite occurs as octahedra, less commonly modified by small faces of the cube. He gives the refractive index at 1.4267 and states that he has found most ralstonites to have values above 1.41, but it might go as low as 1.399 as Gordon gives it, Bøggild comments, (Gordon 1939). The specific gravity of ralstonite is found to be 2.614. Optically ralstonite is anomalous in that it shows a distinct birefringence. Based on this, Bøggild describes ralstonite as consisting of eight pyramidal sectors with their apex in the center of the crystal and the bases in the octahedral faces. There is, as he says, a number of exceptions from this rule when it comes to details.

Apart from the different values of specific gravity and refractive indices, the first and second regular (=cubic) minerals deviate from ralstonite in their microscopic structure revealed by their anomalous optical anisotropy. On the whole Bøggild keeps them as separate minerals, distinct from ralstonite also in his last edition of *Mineralogia*: "The Mineralogy of Greenland," Bøggild (1953).

At the Mineralogical Department of Kryolitselskabet Øresund A/S examinations of many samples of ralstonite and "cubic minerals" have shown that there exist a number of minerals which according to their refractive indices can be arranged into a series ranging from n about 1.36 to n about 1.43.

Crystals from within a single sample show, however, variations in their refractive indices, and even within the same crystal such variations can be found, but it seems that the values found in material from a single specimen mostly lie around one value.

Some of these crystals are cubes; some have the cubes modified by octahedral faces (Fig. 1); others are octahedral which may be modified by cube faces. The modifying faces may vary in size also among the crystals of a single sample. However, it seems that the crystals of a single sample are mainly of the same shape. One might easily collect a series of

crystals ranging from cubes to octahedra; hence the cubic minerals, including ralstonite, seem to constitute a series with respect to both refractive index and shape.

Pointing out ralstonite among the mentioned minerals may be rather difficult, and it is no wonder that some confusion as to what ralstonite is can be noted in the literature.

Pabst (1950) in his paper "A structural classification of fluoaluminates," is aware of the problem constituted by the cubic minerals. He



Fig. 1. Ralstonite crystals from Ivigtut; cubes truncated by the octahedron, 100/111. Sample no. 9, magnification 4X. Chr. Halkier phot.

says, "It may be that some of the unnamed and unanalysed cubic minerals from Ivigtut having but slightly different refractive indices and densities are but variants of ralstonite."

Stepanov (1963) simply registers one of the cubic minerals from Ivigtut (an analysis of which was given in the paper on "Weberite from Pikes Peak" Pauly, 1954) as ralstonite, as was also done in the paper on ralstonite from the Ilmen Mountains, Kazakhstan and Kamtchatka by Stepanov and Moleva (1962).

Being familiar with the common occurrence and the appearance of the various cubic minerals in the Ivigtut cryolite deposit, the author found it quite natural to look at these as belonging to one closely related group, but establishing them into a series or otherwise clarifying the relations between the different members of the group demanded chemical analyses. Material for such analyses was not easily obtained. Picking out crystals

from a sample with many different indices of refraction was not encouraging. Likewise making an analysis on a single crystal did not look promising either, because even there single parts showed variations in properties.

During work in the cryolite mine in 1961 a powdery or sandlike material was found in cavities lined by thomsenolite and other secondary minerals. The primary material was cryolite with much quartz and siderite. As the cavities were opened by breaking the rock, the presence of the powdery material seemingly as original deposits aroused suspicion. In the microscope it was found that the finer grain sizes, less than 100 μ in diameter, for a greater part, consisted of crystallites in the shape of cubes. It was quite obvious that the material represented one of the cubic minerals. The remaining material consisted mainly of thomsenolite, and a separation in ethylene tetrabromide was carried out with good results, as we obtained 10–15 grams of material with only a few per cent impurities (dominated by "ivigtite"-K-mica).

The specific gravity was determined by means of a mixture of the mentioned heavy liquid and benzene, and found to be close to 2.67. The refractive index of most of the cubes was found to be close to 1.37, but some having larger values up to 1.39. Optically anomalous anisotropy characterizes this material as well as all the other cubic minerals of Ivigtut. It should be pointed out here that the first cubic mineral of Bøggild was reported with refractive index and specific gravity values similar to those of the present material, 1.3852 and 2.676 respectively.

The chemical analysis was carried out by Mrs. E.-L. Mortensen, M.Sc., of the Chemical Laboratory of Kryolitselskabet Øresund A/S. It is given in Table I.

The formula according to Pabst from this analysis is:



The last two columns of Table I give the composition according to the formula and the original analysis recalculated to hundred per cent omitting insoluble (mica). The agreement seems to be fairly good.

The results of the chemical analysis were rather encouraging, especially since the material seems to represent a member in the series indicated by Pabst's ralstonite formula close to an end-member.

The analysis of one of the cubic minerals from Ivigtut, published in Pauly (1954), was therefore taken up again for new inspection. This material was established by the late chief geologist R. Bøggvad of the Kryolitselskabet Øresund A/S in 1935. It was found in a fine-grained aggregate closely resembling fine-grained, stratified sandstone or incrustations. Besides the cubic mineral, termed first cubic mineral, by

R. Bøgvad (!), the aggregate consisted mainly of prosopite together with some quartz and traces of sulfides and limonite (giving it a yellow color). The two main components were separated by boiling in diluted HCl, and as microscopical examination afterwards did not indicate any influence on the cubic mineral in the form of etchings and furthermore chemical tests did not indicate any chlorine in the boiled and washed material, it was judged to be unharmed by this otherwise drastic treatment. Further purification of the material (removal of quartz) was obtained through heavy liquid separation. R. Bøgvad in his notes in the

TABLE I. COMPOSITION OF THE NEW CUBIC MINERAL FROM IVIGTUT

	wt. %	Equiv.	Mol. equiv.	¹	Theor. wt. %	Found wt. %
Al	13.88	1.5422	0.5141	1.12	14.91	14.67
Mg	9.73	0.8002	0.4001	0.88	10.44	10.28
Ca	0.91	0.0455	0.0228		—	0.95
Na	9.34	0.4061	0.4061	0.88	9.88	9.86
F	48.63	2.5595	2.5595	5.5	51.28	51.36
OH ²			0.2347	0.5	4.66	4.22
H ₂ O ⁺	10.30		0.4550	0.99	8.83	8.65
insol.	3.50					
Total	96.29				100.00	100.00

Anal.: E.-L. Mortensen.

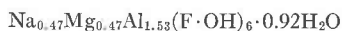
¹ Numbers of atoms found after correcting for CaF₂ admixture, although fluorite was not observed microscopically.

² Calculated as valency balance.

archive of the Mineralogical Department of the Kryolitselskabet Øresund A/S, gives the refractive index as 1.406 and the specific gravity as 2.64. The analysis, carried out by H. Buchwald, chief chemist at Kryolitselskabet Øresund A/S, is given in Table II.

The analysis is recalculated to hundred per cent after deduction of 8.11% insoluble, mainly quartz.

Stepanov (1963) has pointed out that the material of this analysis which he cites seems to contain cryolite as impurity amounting to 6.67%. Deducting this amount from the analysis, as Stepanov has done it, the following formula is obtained:



As pointed out by Stepanov and Sokalova (1963) this analysis gives a ratio F to OH as 3.28:1, whereas a ralstonite from Ivigtut, treated in Stepanov and Moleva (1962) gives 1.96:1. Their material was obtained

through the Mineralogical Museum, Copenhagen, and was termed ralstonite because the crystals, nicely depicted in Stepanov and Moleva (1962, Fig. 5), are octahedra with only minute cube faces. In the paper mentioned ralstonites from Kazakhstan are found to have F/OH ratios 2.04:1 and 2.05:1 respectively. (These data together with other relevant data are compiled in Table VI.) The ratio between F and OH in the described analysis on the new material from Ivigtut is near 11:1 (more exactly 10.7:1) (Table I).

Another problem concerns the composition of the discussed minerals. The cryolite regarded as impurity in the analysis by Buchwald was not

TABLE II. COMPOSITION OF THE CUBIC MINERAL FROM IVIGTUT

	wt. %	Mol. equiv.	Admixed cryolite ¹	Mol. equiv. minus cryolite
Al	21.03	0.7798	0.0318	0.7480
Mg	5.55	0.2282	—	0.2282
Na	7.44	0.3235	0.0953	0.2282
F	46.26	2.4347	0.1906	2.2441
OH		0.6845		0.6845
H ₂ O ⁺	14.26	0.4493		0.4493
Total	94.54			

Anal.: H. Buchwald.

¹ Calculated from Na-surplus as compared with Mg-content.

present as grains visible under the microscope. This was ascertained through reexamination of what was left of the material for analysis.

With the existing analyses of material from Ivigtut and the Russian localities, we now have representatives of several of the members of the ralstonite series as indicated by Pabst's formula proposal.

SYNTHETIC MATERIAL

At the time when the author obtained the analysis of the powdery material, which came out as a ralstonite with high proportions of Mg and Na, he happened to read the paper by Cowley and Scott (1948) in which they describe "Basic fluorides of aluminum." They describe the preparation of compounds in the range $\text{AlF}(\text{OH})_2\text{-AlF}_2(\text{OH})$ (both containing H₂O), and these compounds were found to be cubic with space group $O_h^7\text{-Fd}3m$. The lattice constant decreases with increasing fluorine content from 9.85 to 9.77 Å. The unit cell contains sixteen formula-groups plus

six molecules of water. The structure is, as stated by the authors, clearly a pyrochlore structure.

It seemed obvious that the description had a clear bearing on the ralstonite problem, and a similar thought must have occurred to Stepanov (1963), as he in the chapter on ralstonite in "Mineral" mentions the cited paper and regards the basic aluminum fluorides as synthetic ralstonite.

From the paper by Cowley and Scott (1948) two points appear which may involve an explanation of the two complicating analytical relations mentioned above.

In the preparation of the compounds they added ammonia to solutions of aluminum sulfate containing varied proportions of aluminum fluoride. The precipitate formed through boiling was washed until negative sulfate reaction was obtained. The products were analyzed and found to contain ammonium hexafluoroaluminate in amounts varying from 2.3 to 7.3 per cent. This impurity could not be removed by washing, a fact they stressed. It was not registered on the x-ray powder photographs, but "the ignition behavior of the contaminated oxyfluorides, with respect to their ammonia contents, was so closely parallel to that of ammonium hexafluoroaluminate that no doubt is felt as to the presence of the latter compound," as Cowley and Scott (1948) state in their paper (p. 106).

If it is permissible to conclude anything from these artificial products, the conclusion seems to be that cryolite, like ammoniumcryolite in the artificial product, may be submicroscopically admixed x-ray "amorphous" in these compounds. The x-ray powder photogram of the cubic mineral in the analysis of which Stepanov found 6.67% "admixed" cryolite did not show any lines which could indicate the presence of cryolite. The amount of stoichiometrically deducted cryolite was of the same order of magnitude as in Cowley and Scott's material.

In the same manner parallelization of the ralstonite and the artificial products seems to allow for variations in the F/OH-ratio. But here we must admit that Cowley and Scott found variations from 0.5 to 2.0; lower and higher values were regarded as being due to admixed $\text{Al}(\text{OH})_3$ and AlF_3 ; they furthermore stress that the range of hydroxyfluoride compositions must be confined to that range, because it seems improbable that cations containing more fluorine than AlF_2^+ or less than AlF^{2+} exist in solution to any important extent.

The analyses of the two cubic minerals from Ivigtut by Buchwald, Table II, and Mortensen, Table I, however, indicate beyond any doubt that the fluorine content in these compounds formed in an extremely F-rich milieu, in solid cryolite cavities, can pass the limits certainly valid for solutions in the laboratory. So far we can only interpret this as indi-

cating processes working in the formation of the minerals in the Ivigtut milieu, fundamentally different from those used in Cowley and Scott. On the other hand we may as well regard the processes Cowley and Scott used, or rather analogies, as a picture of some of the ralstonite-forming processes in nature.

X-RAY EXAMINATION

In several cases cubic minerals having refractive indices not hitherto observed, have been examined by means of α -ray powder diagrams, but

TABLE III. REFRACTIVE INDICES AND CELL DIMENSIONS FOR RALSTONITES FROM IVIGTUT

Sample	Crystal habit	Refractive index	Cell dimension ² in Å	Formula number of Na and Mg X
1	111/100	1.41-1.43	9.918	0.34
12		1.406	9.93	
5	100/111	~1.405	9.941	
6	100/111	~1.41	9.948	
7	100/111 ¹	1.38-1.39	10.00	
8	100/111 ¹	1.37-1.39	10.02	
9	100/111 ¹	1.37-1.39	10.01	0.88
11	100	~1.37	10.012	

¹ 111 mostly as minor faces.

² The lattice constant has been determined using a Guinier camera with monochromatized Cu-radiation.

always with the result that they were not to be distinguished from ralstonite. The ralstonite character of the cubic minerals in general was therefore what was expected by us, but in connection with the samples thoroughly chemically analyzed, it was of course essential to continue such examinations. In an attempt to get an adequate basis for these examinations a series of different cubic minerals was established according to the crystal habit. Hand pieces containing crystals of definitely octahedral habit, such containing crystals with cubic habit, and variations between these two types were chosen. The refractive indices were determined within the limits of accuracy which the nature of the material allowed.

Six samples thus established together with material from the two analyzed samples from Ivigtut were examined by Mrs. M. Danø of the Mineralogical Museum of Copenhagen using a Guinier camera.

In Table III are given the typical crystal form, the refractive index, the

TABLE IVa. X-RAY POWDER DIFFRACTION DATA FOR RALSTONITES AND BASIC AL-FLUORIDES

hkl	I Ivigtut		II Ivigtut		III Ivigtut		IV Ivigtut		V Kazakhstan		VI Kamtchatka		VII Basic Al-fluoride	
	Anal.: ELM		S & M ¹		Pabst		Ferguson (cubic)		S & M		S & M		C & S	
	d _{hkl}	I	d _{hkl}	I	d _{hkl}	I	d _{hkl}	I	d _{hkl}	I	d _{hkl}	I	d _{hkl}	I
111	5.74	212	5.68	10	5.68	10	5.70	10	5.71	10	5.68	9	5.70	460
200	4.98	29	—	—	—	—	—	—	—	—	—	—	—	—
311	3.01	113	2.97	10	2.97	8	2.99	9	2.97	10	3.00	9	2.979	220
222	2.88	160	2.85	10	2.84	7	2.86	8	2.86	10	2.86	8	2.841	100
400	2.49	29	2.46	3	—	1	2.47	1	2.48	4	2.45	1	2.460	26
331	2.29	68	2.27	5	2.26	2	2.27	3	2.27	5	2.27	4	2.258	21
422	2.04	58	2.01	7	2.01	4	2.03	4	2.02	8	2.01	4	2.009	44
511	1.923	81	1.897	9	1.897	6	1.909	7	1.905	10	1.897	7b	1.893	92
333														
440	1.765	183	1.745	10	1.740	7	1.750	8	1.750	10	1.745	10	1.737	110
531	1.689	20	1.677	4	1.664	1	1.679	2	1.677	4	1.677	2	1.661	33
620	1.581	32	1.564	4	1.553	1	1.568	2	1.567	6	1.572	2	1.553	26
533	1.525	34	1.512	5	1.485	b4	1.512	2	1.514	8	—	—	1.498	40
622	1.508	84	1.494	7			1.497	5	1.495	8	1.498	5b	1.480	42
444	1.443	12	1.426	3	1.421	1	1.435	1	1.431	3	1.433	1	1.417	9
711	1.400	49	1.387	8	1.379	3	1.391	4	1.388	9	1.387	4	1.375	51
551														
731	1.302	29	1.287	9	1.282	3	1.292	3	1.290	9	1.290	5	1.277	45
553														
800	1.250	43	1.240	5	1.228	1	1.240	1	1.241	5	1.241	1	1.227	13
733	—	—	1.212	1	—	—	—	—	1.213	1	—	—	1.201	2
822	1.179	34	1.168	9	1.158	2	1.171	3	1.168	9	1.170	4	1.158	31
660														
662	1.146	30	1.137	7	1.127	1	1.140	2	1.138	7	1.138	3	1.127	17
840	1.119	21	1.108	7	1.102	1	1.111	1	1.108	7	1.109	2	1.099	14
911	—	—	1.088	3	—	—	1.090	½	1.088	3	1.083	1	1.079	10
753														
664	—	—	1.057	4	—	—	1.058	½	1.058	4	1.057	2	1.047	9
931	—	—	1.038	9b	—	—	1.042	1	1.042	3	1.041	2	1.031	20

¹ Stepanov & Moleva.

b = broad.

lattice constant a , and for the two analysed samples also the value X , indicating the number of Mg and Na atoms in the formula.

It was verified that the mentioned cubic minerals have identical crystal structures, as their powder diagrams are all of the pyrochlore type with small variations in the a -values and the intensity distribution.

A diffractometer recording has been made of sample 11 using Cu K_{α} radiation. In Table IVa the intensities of the powder lines are compared with corresponding values given by Stepanov and Moleva, Ferguson, Pabst, and Cowley and Scott. The intensities are scaled together by giving the strongest reflection (111) the intensity 100 for all samples in Table IVb.

TABLE IVb. COMPARISON OF INTENSITIES OF SPACINGS GIVEN
IN TABLE IVa, — (111) = 100

<i>hkl</i>	I	II	III	IV	V	VI	VII
	Iviglut				Kazakhstan	Kamtchatka	Basic Al-fluoride
111	100	100	100	100	100	100	100
200	14	—	—	—	—	—	—
311	53	100	80	90	100	100	48
222	75	100	70	80	100	89	22
400	14	30	10	10	40	11	6
331	32	50	20	30	50	44	5
422	27	70	40	40	80	44	10
511	} 38	90	60	70	100	78 <i>b</i>	20
333							
440	86	100	70	80	100	111	24
531	9	40	10	20	40	22	7
620	15	40	10	20	60	22	6
533	16	50	} <i>b</i> 40	20	80	—	9
622	40	70		50	80	56 <i>b</i>	9
444	6	30	10	10	30	11	2
711	} 23	80	30	40	90	44	11
551							
731	} 14	90	30	30	90	56	10
553							
800	20	50	10	10	50	11	3
733	—	10	—	—	10	—	$\frac{1}{2}$
822	} 16	90	20	30	90	44	7
660							
662	14	70	10	20	70	33	4
840	10	70	10	10	70	22	3
911	} —	30	—	5	30	11	2
753							
664	—	40	—	5	40	22	2
931	—	90 <i>b</i>	—	10	30	22	4

b = broad.

The first and the last column show that some of the lines have intensities very sensitive to changes in composition—provided the basic Al-fluoride is of the ralstonite type. To confirm this, the intensities for ralstonite with $X=0.34$ and $X=0.88$ were calculated using the structure proposed by Pabst, with all water positions occupied (Table V).

In the first part of Table V are given the calculated intensities for the two ralstonites together with the measured intensities for sample 11 and the basic fluoride; no scaling has been done in order not to lose accuracy. It is seen that the reflection 111 changes very much with composition and

TABLE V. CALCULATED AND OBSERVED INTENSITIES FOR RALSTONITES AND BASIC AL-FLUORIDE

hkl	Intensities							
					Recalculated to 422=100			
	Calculated		Observed		Calculated		Observed	
	0.34 ¹	0.88 ²	ELM	C&S	0.34	0.88	ELM	C&S
111	1733	1219	212	460	722	508	365	1046
200	—	—	29	—	—	—	50	—
220	0	0	0	0	0	0	0	0
311	871	593	113	220	363	247	195	500
222	630	919	160	100	263	383	276	227
400	103	43	29	26	43	18	50	59
331	179	296	68	21	75	123	117	48
422	240	240	58	44	100	100	100	100
511	34	71	81	92	14	30	140	209
333	604	523			252	218		
440	829	1002	183	110	345	418	315	250
531	118	50	20	33	49	21	34	75
620	147	147	32	26	61	61	55	59
533	203	157	34	40	85	65	59	91
622	245	346	84	42	102	144	145	95
444	34	54	12	9	14	23	21	20
711	20	9	49	51	8	4	84	116
551	210	181			88	75		
642	15	15	0	—	6	6	0	—
731	212	166	29	45	88	69	50	102
553	4	0			2	0		
800	90	110	43	13	38	46	74	30
733	35	35	0	2	15	15	0	5
822	103	103	34	31	43	43	59	70
660	87	87			36	36		
751	10	3	0	—	4	1	0	—
555	48	44			20	18		
662	94	132	30	17	40	55	52	39
840	52	77	21	14	22	32	36	32

¹ Ralstonite with Na_{0.34}

² Ralstonite with Na_{0.83}

therefore we have put (422) instead of (111) equal to 100. ((422) is the strongest reflection which does not change with composition.) The second part of the table shows the results of this scaling process.

The agreement between the measured and the calculated intensities is as good as could be expected using as a basis for the calculation the approximate structure which was the best estimate that could be made with data then available to Pabst. The measured intensities of the basic aluminum fluorides fits into the pattern as was expected.

In Table V the (200) reflection which is forbidden in the space group $Fd3m$ is given with a not negligible intensity. Pabst mentions the appearance of this and other forbidden reflections in *heated* samples of ralstonite. We have not been able to see other of the mentioned reflections on the diffractometer recording, except perhaps (600).

The Guinier films of the samples 7, 8, 9 and 11 show (200) too, but the films of 1, 5, 6 and 12 do not. These two sets show another difference, namely the ratio between the intensities of (311) and (222). For the last group it is near 1, whereas it is much smaller for the first group in good agreement with the calculations as the X-values for species in the two groups are 0.88 and 0.34 respectively (Table III).

It has been shown that the atomic arrangement proposed by Pabst gives a good picture of the structure of the ralstonites, but some adjustments of the positions of the atoms in the unit cell are needed, and the symmetry imposed by the space group is not quite fulfilled. The departure from the high symmetry seems to increase as the 16-fold positions (d) are filled with Na, in other words as the X-value is increasing. This problem demands single crystal examination in order to be solved. Difficulties may, however, be encountered in such examination due to the nature of the crystals.

As pointed out by Bøggild (1953) and Stepanov and Sokalova (1963), ralstonite crystals, in spite of their well developed outer shape, can be seen to be composed of zones with differences in optical properties. This is also indicated by the spread in refractive indices observed in powder preparations made from single crystals. This might be taken as an indication of structural variability within the single crystal, but it may also indicate compositional variations.

CONCLUSION

The mineral ralstonite shows rather wide variations in most of its properties, but, in spite of this, the present examination indicates certain regularities in the variations of these properties, and moreover there appears an interesting coherence between the different properties.

Samples with high densities have low refractive indices as a common

TABLE VI. PHYSICAL PROPERTIES AND COMPOSITION OF RALSTONITES

	Habit	Specific gravity	Refractive index	Number of Na } atoms Mg }	Cell dimension	F/OH
Ralstonite No. 11 found as powder 1. cubic mineral of O. B. Bøggild	100 100/111	2.67 2.676	~1.37 1.3852	0.88 —	10.01 —	10.9 —
Ralstonite No. 8	100/111	$1 \leq 2.66$	1.37-1.39	—	10.02	—
Ralstonite No. 9	100/111	$1 \sim 2.64$	1.37-1.39	—	10.01	—
Ralstonite No. 7	100/111	$1 \sim 2.64$	1.38-1.39	—	10.00	—
Ralstonite No. 5	100/111	$1 \sim 2.60$	~1.405	—	9.94	—
Ralstonite No. 6	100/111	$1 \sim 2.59$	~1.41	—	9.95	—
Ralstonite No. 1 1. cubic mineral	111/100	$1 \sim 2.58$	1.41-1.43	—	9.92	—
of Bøgvad No. 12	—	2.64	1.406	0.47	9.93	3.28
Penfield and Harper	111/100?	2.56	—	0.35	—	1.84
Ralstonite, Ivigtut, Stepanov and Moleva	111/100	2.56	1.420	0.34	9.90	1.96
Kazakhstan, Stepanov and Moleva	111/100?	2.54	1.419	0.34	9.91	2.05
Kazakhstan, Stepanov and Moleva	111/100?	2.50	1.429	0.29	9.88	2.04
Pabst, 1939	111/?	—	1.43	—	9.87	—
2. cubic mineral of O. B. Bøggild	100/111	2.377	1.4420	—	—	—
Kamtchatka, Stepanov and Moleva	—	2.24	1.386	—	9.91	—
Basic Al-fluoride, Cowley and Scott	—	2.25	—	0	9.85-9.77	0.15-2.25

¹ These values may vary ± 0.02 , but the succession: $7 > 5 > 6 > 1$ was established by testing the samples two and two in the same heavy liquids.

feature, and their cell dimensions are large. It seems that the dominating crystal form in this group is the cube. Ralstonites with low densities have high indices of refraction and small cell dimensions and their crystal forms are dominated by the octahedron.

Data for ralstonites are compiled in Table VI, and it can be seen that the variation in chemical composition may be interpreted in accordance with the variations of the physical properties.

X-ray examinations also indicate that the material examined belongs either to a group with cell dimension close to 10.01 or to a group where $a \sim 9.93$. The space group $Fd\bar{3}m$ to which ralstonite is ascribed may not be quite in accordance with the results, as at least one reflection—(200)—forbidden in this group, definitely appears in material from the group of ralstonite having cell dimensions near 10.01. Pabst in his publication indicated the presence of this line—and others—in ralstonite that had been heated.

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