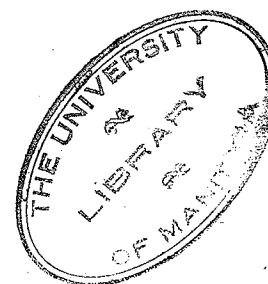


AN INVESTIGATION OF THE CRYSTAL STRUCTURE
OF THOMSENOLITE $\text{NaCaAlF}_6 \cdot \text{H}_2\text{O}$

A Thesis
Presented to
the Faculty of Graduate Studies and Research
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CHAPTER I

THE ALUMINOFLUORIDE MINERALS

The natural aluminofluorides comprise twelve rare minerals, the commonest of which is cryolite, Na_3AlF_6 . Except for fluellite with composition $\text{AlF}_3 \cdot \text{H}_2\text{O}$, these minerals are aluminofluorides of Na, Ca, Li, and Sr, sometimes with Mg and OH substituting for Al and F respectively; several members contain H_2O . The twelve aluminofluoride minerals are set forth in Table I, p. 3. In addition to these natural aluminofluorides, some that do not occur in nature are also known.

Structural Classification. The crystal structures of about half a dozen natural and an equal number of synthetic aluminofluorides have been determined. In all of them there has been found a common structural unit, the AlF_6 octahedron--six F ions arranged in octahedral coordination around one Al. These octahedra pervade each structure, and Brosset (1942) has suggested that they apparently play the same role in the aluminofluorides as do the SiO_4 tetrahedra in the silicates. Thus, the AlF_6 octahedra may exist in a given structure as separate units, chains, sheets, or 3-dimensional frameworks, and the Al:F ratio in the chemical formula varies accordingly. Since no one had previously suggested a classification of the aluminofluorides based on the AlF_6 structural unit, R. B. Ferguson did so in April, 1948 in a private communication to Dr. Clifford Frondel of Harvard University. This was

sent to Dr. Frondel as a possible aid in his compilation of Volume II of the Seventh Edition of Dana's System of Mineralogy; this volume is to include the aluminofluorides. This communication came into the hands of Dr. Adolph Pabst of the University of California (Berkeley), at that time a guest in Dr. Frondel's laboratory, and Dr. Pabst used it as the basis for a complete summary, including the structural classification, of the aluminofluoride minerals (Pabst, 1950). Table I lists the aluminofluoride minerals as classified originally by Ferguson and including some of Pabst's modifications.

Occurrence. All the aluminofluoride minerals are rare and occur in only a few isolated deposits throughout the world. The most important locality is Ivigtut, Greenland, where cryolite is abundant and most of the other aluminofluorides including thomsenolite occur in small amount. Thomsenolite has also been described from Pike's Peak, Colorado; Yellowstone Park, Wyoming; Aragon, Spain; and the Ilmen Mountains in Russia. The thomsenolite crystals used for the present investigation are from Ivigtut.

Physical Description of Thomsenolite. For reasons which are given later, the aluminofluoride chosen for the present structural study was thomsenolite, one of the dimorphs of $\text{NaCaAlF}_6 \cdot \text{H}_2\text{O}$; the other is pachnolite. Thomsenolite occurs as an alteration product of cryolite as well-developed, colorless, white, or light amber crystals of monoclinic symmetry in vugs in the cryolite, and as massive white, gray,

TABLE I

THE ALUMINOFLUORIDE MINERALS AND THEIR STRUCTURAL CLASSIFICATION

Mineral	Composition	Formula Type	Structure Type
Cryolite	Na_3AlF_6		
Cryolithionite	$\text{Na}_3\text{Li}_3\text{Al}_2\text{F}_{12}$		
Elpasolite	K_2NaAlF_6	$(\text{AlF}_6)^{3-}$	Separate octahedra
Thomsenolite [*]	$\text{NaCaAlF}_6 \cdot \text{H}_2\text{O}$		
Pachnolite [*]	$\text{NaCaAlF}_6 \cdot \text{H}_2\text{O}$		
Gearsutite [*]	$\text{CaAl}(\text{F},\text{OH})_5 \cdot \text{H}_2\text{O}$	$(\text{AlF}_5)^{2-}$	Chains
Chiolite	$\text{Na}_5\text{Al}_3\text{F}_{14}$	$(\text{Al}_3\text{F}_{14})^{5-}$	Interrupted sheets
Prosopite [*]	$\text{CaAl}_2(\text{F},\text{OH})_8$	$(\text{AlF}_4)^-$	Sheets
Weberite	$\text{Na}_2\text{MgAlF}_7$	$(\text{MgAlF}_7)^{2-}$	Interrupted framework
Ralstonite	$\text{Na}_x(\text{Mg}_x\text{Al}_{2-x})(\text{F},\text{OH})_6 \cdot \text{H}_2\text{O}$	$(\text{MgAlF}_6)^- \dagger$	Pyrochlore framework
Fluellite [*]	$\text{AlF}_3 \cdot \text{H}_2\text{O}$	AlF_3	Complete frameworks
Jarlite	Disproven as $\text{NaSr}_3\text{Al}_3\text{F}_{16}$; still unknown	Unknown	

^{*}Structures not published; classified according to the structure type which seems most likely from the Al:F ratio.

[†]This formula type results if $x = 1$ and all anions are F in the ralstonite formula; in the mineral $x \sim 3/8$.

or bluish coatings on the cryolite. The crystals are frequently coated with a brownish stain of iron oxide. In size they may be up to 4 - 5 mm. in thickness and 8 - 10 mm. in length. They are typically columnar with elongated $m(110)$, prominent $p(111)$, and usually with $c(001)$. Thomsenolite has a perfect (001) cleavage with a pearly lustre, a fair (110) cleavage, and a nearly square cross section ($\alpha = 90^\circ 21\frac{1}{2}'$). Its hardness is 2 and its specific gravity 3.0.

CHAPTER II

EXPERIMENTAL WORK

X-Ray Photographs and Unit Cell Data. Since thomsenolite is monoclinic with a comparatively large unit cell, an X-ray powder photograph is not sufficiently definitive for a structure determination, and single-crystal photographs must be taken. The prismatic habit and the perfect basal cleavage of the crystals make it easy to cleave off tabular fragments suitable for single-crystal X-ray photographs. Three cleavage fragments of this kind, all about 0.25 mm. or less in cross section, were obtained from the same crystal of thomsenolite and mounted for rotation about $a[100]$, $b[010]$, and $c[001]$. Rotation, zero-, first-, and second-layer Weissenberg photographs were taken about each of the three axes using Cu radiation, unfiltered for the rotation photographs and filtered through Ni foil for the Weissenbergs.

From these twelve photographs, values of the cell dimensions in Ångström units were obtained. These differ a small amount from those published by Ferguson (1946):

	<u>a</u>	<u>b</u>	<u>c</u>	β
Ferguson (1946):	5.58	5.51	16.13 A	$96^{\circ}27'$
Ferguson and Clark (this paper):	5.59	5.56	16.15 A	$96^{\circ}27'$

The cell dimensions are believed to be accurate within $\frac{1}{2}\%$, and the angle within $15'$. The second values of the cell dimensions were used for all

calculations in this investigation. As stated in Ferguson (1946), the cell dimensions combine with the specific gravity of ~ 3.0 to give the cell content of $4[\text{NaCaAlF}_6 \cdot \text{H}_2\text{O}]$, i.e. $Z = 4$.

The systematically missing reflections from the Weissenberg photographs agreed with those of Ferguson (1946) and confirmed the unique space-group as $P2_1/c (= C_{2h}^5)$.

Intensity Measurements. In order to measure the relative intensities of the spots on the Weissenberg photographs, an intensity scale consisting of a series of spots of known relative intensities was made in the following manner. A small cleavage rhomb of Iceland Spar about $\frac{1}{4}$ mm. in cross section (the same size as the thomsenolite crystals photographed) was mounted for rotation about a cleavage edge, and then adjusted on the X-ray goniometer so as to oscillate through about 5° on either side of the angle necessary to give the strong 200 (or $20\bar{2}2$) reflection of calcite. Since $d(200)$ of calcite is 3.029 kX, the glancing angle θ is $14^\circ 42'$ for CuK_α radiation. This crystal was oscillated in the X-ray beam for variable, controlled periods, to give a row of spots of known relative intensities on one film. In this way the intensity scale was made on which are 12 spots $\frac{1}{2}$ cm. apart whose relative intensities are 1, 2, 3, 4, 6, 8, 12, 16, 20, 24, 28, 32. By superimposing this scalar film on any one of the Weissenberg photographs of thomsenolite, and translating the scale until there is substantial

visual agreement between the intensity of a spot on it and one on the Weissenberg, a good objective value for the intensity of the latter may be read off. Thus a set of relative intensity values was compiled for all spots on each of the Weissenberg photographs of thomsenolite.

Since no attempt had been made, however, to standardize the photographic conditions, including exposure, of the different Weissenberg photographs, intensity relationships had to be established between these different photographs in order that all intensities could be reduced to the same standard. Because certain reflections appear on two or more Weissenbergs, such reflections can be used to work out an intensity factor which relates all spots on both films. Thus, the 001 reflections appear on both the zero layer-line Weissenberg about a and that about b, and the intensities of these reflections from both films will relate the intensities of all spots on both. By working out such factors between pairs of photographs with some reflections in common, a large set of intensities all related to the same standard was obtained. These intensities appear in Table II with the spacings calculated from the adopted cell dimensions.

$$a = 5.59, \quad b = 5.56, \quad c = 16.15 \text{ \AA}, \quad \beta = 96^{\circ}27'$$

using the formula

$$\frac{1}{d^2} = \frac{h^2}{a^2 \sin^2 \beta} + \frac{k^2}{b^2} + \frac{l^2}{c^2 \sin^2 \beta} - \frac{2hl \cos \beta}{ac \sin^2 \beta}$$

which relates the spacing d to the monoclinic cell dimensions.

TABLE II
 THOMSENOLITE: RELATIVE INTENSITIES FROM WEISSENBERG PHOTOGRAPHS AND
 CALCULATED SPACINGS

hkl	I	d(A)	hkl	I	d(A)	hkl	I	d(A)
002	2	8.024	0.2.10	0	1.390	$\bar{2}04$	4	2.414
004	16	4.012	0.2.11	$\frac{1}{2}$	1.292	$\bar{2}06$	3	2.045
006	0	2.675	0.2.12	$\frac{1}{2}$	1.205	$\bar{2}08$	$7\frac{1}{2}$	1.721
008	42	2.006	0.2.13	1	1.128	$\bar{3}02$	3	1.850
0.0.10	3	1.605	0.2.14	$<\frac{1}{2}$	1.060	$\bar{3}04$	$2\frac{1}{2}$	1.758
0.0.12	1	1.337	031	1	1.841	$\bar{3}06$	1	1.609
0.0.14	$<\frac{1}{2}$	1.146	032	0	1.806	$\bar{4}02$	$3\frac{1}{2}$	1.395
0.0.16	0	1.003	033	0	1.751	404	0	1.361
0.0.18	$<\frac{1}{2}$	0.892	034	$<\frac{1}{2}$	1.682	406	1	1.293
0.0.20	$<\frac{1}{2}$	0.802	035	1	1.605	111	2	3.749
020	$4\frac{1}{2}$	2.780	036	0	1.523	112	5	3.423
040	$1\frac{1}{2}$	1.390	037	$<\frac{1}{2}$	1.441	113	$3\frac{1}{2}$	3.053
060	$2\frac{1}{2}$	0.927	038	$<\frac{1}{2}$	1.361	114	5	2.702
100	0	5.555	039	$\frac{1}{2}$	1.285	115	$<\frac{1}{2}$	2.394
200	21	2.777	041	$3\frac{1}{2}$	1.385	116	$2\frac{1}{2}$	2.134
300	$\frac{1}{2}$	1.852	042	0	1.370	121	$3\frac{1}{2}$	2.438
400	3	1.389	043	1	1.345	122	$<\frac{1}{2}$	2.342
110	16	3.930	044	$<\frac{1}{2}$	1.313	123	$\frac{1}{2}$	2.212

TABLE II (Continued)

hkl	I	d(A)	hkl	I	d(A)	hkl	I	d(A)
120	3	2.486	045	$< \frac{1}{2}$	1.276	124	$3\frac{1}{2}$	2.067
130	2	1.758	046	0	1.233	125	$< \frac{1}{2}$	1.919
140	$1\frac{1}{2}$	1.348	047	1	1.189	221	6	1.932
150	$< \frac{1}{2}$	1.090	048	0	1.143	222	$1\frac{1}{2}$	1.874
210	1	2.485	049	1	1.096	223	$2\frac{1}{2}$	1.799
220	17	1.965	102	2	4.452	224	$\frac{1}{2}$	1.712
230	$< \frac{1}{2}$	1.542	104	3	3.092	225	$\frac{1}{2}$	1.619
240	1	1.243	106	5	2.311	226	$\frac{1}{2}$	1.527
310	$1\frac{1}{2}$	1.757	108	5	1.822	$\bar{1}11$	4	3.889
320	$< \frac{1}{2}$	1.541	202	3	2.538	$\bar{1}12$	1	3.645
011	1	5.254	204	16	2.226	$\bar{1}13$	5	3.294
012	$< \frac{1}{2}$	4.570	206	6	1.827	$\bar{1}14$	17	2.926
013	1	3.855	302	$1\frac{1}{2}$	1.761	$\bar{1}15$	1	2.589
014	3	3.252	304	$\frac{1}{2}$	1.614	$\bar{1}16$	$< \frac{1}{2}$	2.298
015	1	2.780	306	0	1.448	$\bar{1}21$	$1\frac{1}{2}$	2.476
016	0	2.410	308	$\frac{1}{2}$	1.290	$\bar{1}22$	1	2.409
017	1	2.119	3.0.10	6	1.150	$\bar{1}23$	10	2.299
018	7	1.887	402	$2\frac{1}{2}$	1.343	$\bar{1}24$	3	2.162
019	1	1.698	404	0	1.269	$\bar{1}25$	12	2.015
0.1.10	1	1.542	406	$\frac{1}{2}$	1.179	$\bar{1}26$	$< \frac{1}{2}$	1.868

TABLE II (Continued)

hkl	I	d(A)	hkl	I	d(A)	hkl	I	d(A)
0.1.11	1	1.411	502	$1\frac{1}{2}$	1.084	$\bar{2}11$	4	2.494
0.1.12	2	1.300	602	1	0.908	$\bar{2}12$	3	2.444
021	$5\frac{1}{2}$	2.739	$\bar{1}02$	0	4.828	$\bar{2}13$	$1\frac{1}{2}$	2.345
022	0	2.627	$\bar{1}04$	3	3.441	$\bar{2}14$	1	2.214
023	$<\frac{1}{2}$	2.467	$\bar{1}06$	0	2.523	$\bar{2}15$	1	2.068
024	$4\frac{1}{2}$	2.285	$\bar{1}08$	21	1.958	$\bar{2}16$	4	1.919
025	10	2.101	$\bar{1}0.10$	0	1.590	$\bar{2}21$	20	1.969
026	2	1.927	$\bar{1}0.12$	7	1.335	$\bar{2}22$	4	1.944
027	3	1.769	$\bar{1}0.14$	0	1.148	$\bar{2}23$	$<\frac{1}{2}$	1.894
028	$<\frac{1}{2}$	1.626	$\bar{1}0.16$	6	1.007	$\bar{2}24$	2	1.823
029	1	1.501	$\bar{2}02$	0	2.721	$\bar{2}25$	$1\frac{1}{2}$	1.738

Intensity Calculations. Once a reasonable structure of the crystal has been postulated, a set of intensities must be calculated from the proposed parameters (which define the atomic positions) and compared with the observed intensities. It is only when there is substantial agreement between the relative intensities calculated for a proposed structure and those observed for a large number of reflections that the proposed structure may be considered the correct one.

Each spot on a single-crystal X-ray diffraction photograph may be regarded as the "reflection" of the X-ray beam by one set of parallel lattice planes. The intensity of each reflection is determined by several factors: the diffracting powers of the atoms, the relative positions of the atoms in space (the "structure factor"), the Bragg or glancing angle at which reflection occurs, the number of crystallographically equivalent planes contributing towards the total intensity of the spot (the "multiplicity"), the amplitude of thermal vibration of each atom (allowed for by a temperature factor), and the absorption of the X-rays by the specimen. For zero-layer Weissenberg reflections the above mentioned factors are so related that the following equation holds:

$$I \propto F^2 p \left(\frac{1 + \cos^2 2\theta}{\sin 2\theta} \right) T A$$

where I = intensity of reflection,

F = the structure factor,

p = the multiplicity,

θ = the glancing angle,

T = the temperature factor, and

A = the absorption factor.

The multiplicity p is the number of equivalent lattice planes contributing to any one reflection and it usually differs for different types of planes in powder and rotation photographs. The nature of Weissenberg photographs, however, is such that any spot on the film results from the reflection from one set of lattice planes only. Thus the multiplicity need not be considered (or it is always unity) when Weissenberg photographs are used.

The expression $\frac{1 + \cos^2 2\theta}{\sin 2\theta}$, known as the angle factor, takes account of i) the increasing polarization of the X-rays with increasing glancing angle, the intensity of any reflection being reduced by this effect to the fraction $\frac{1 + \cos^2 2\theta}{2}$; and ii) the relative time any crystal plane spends within the narrow angular range over which reflection occurs. This latter angle factor, known as the Lorentz factor, is proportional to $\frac{1}{\sin 2\theta}$. In the ITDCS (1935), p. 567, is a table giving values of the above angular expression for different values of θ .

The structure factor F takes account of i) the diffracting power and ii) the position of each atom or ion. The diffracting power f is determined by the number of electrons surrounding the nucleus, i.e. by

the atomic number of the element, and it varies with the interplanar spacing in such a way that f is a function of $\frac{1}{2}d$ ($= \sin\theta/\lambda$). A table of the diffracting powers of all atoms for a range of values of $\sin\theta/\lambda$ is given in the ITDCS (1935), p. 571. It is convenient to plot graphs of f against $\sin\theta/\lambda$ for all atoms or ions present in a structure under investigation in order to be able to read off accurate values of f for any value of $\sin\theta/\lambda$. Such graphs were drawn up during this investigation for Na^+ , Ca^{2+} , Al^{3+} , F^- , and O^{2-} (in place of H_2O). These are reproduced in Figure 1, p. 14.

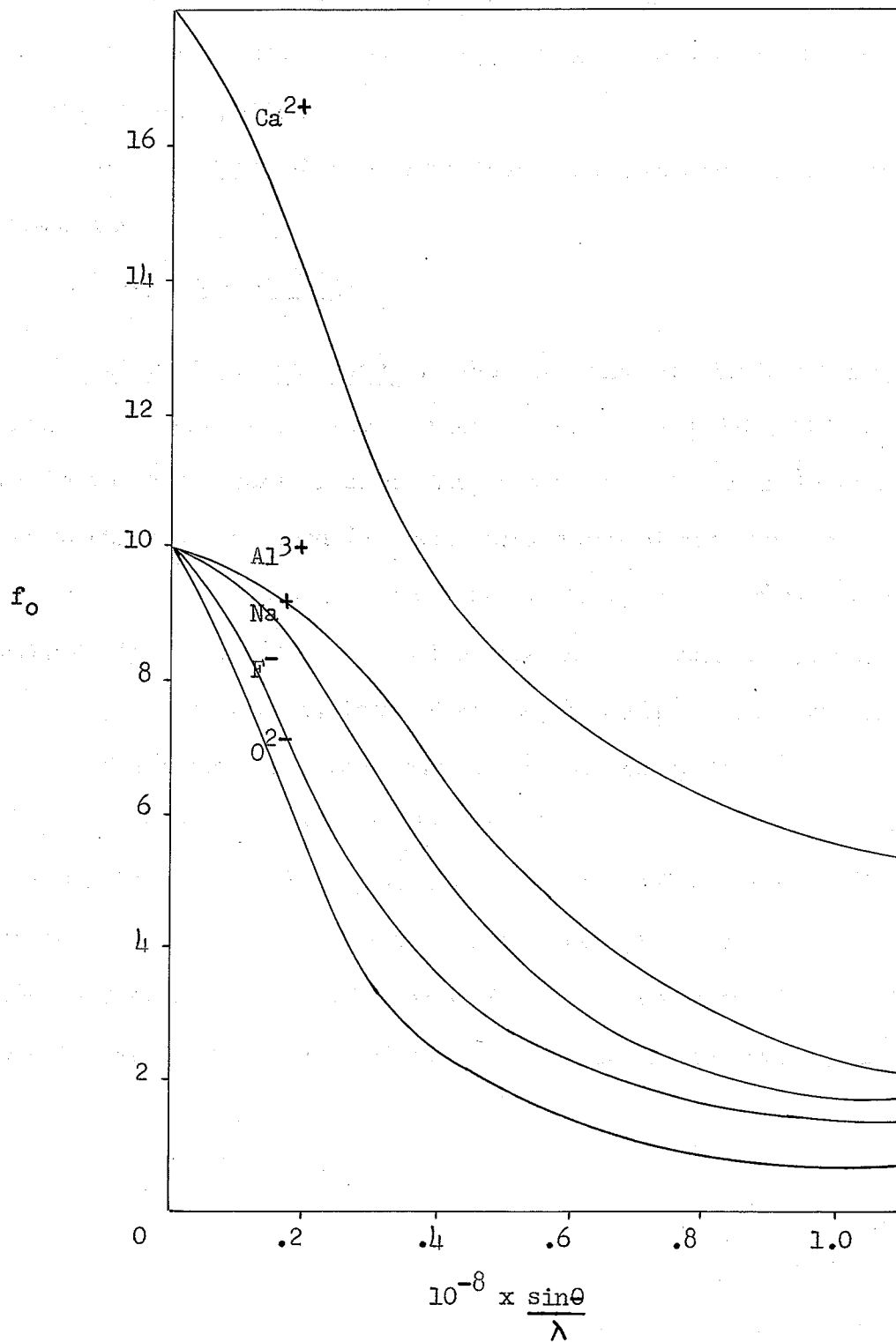
Regarding the position of each atom, the ITDCS (1935) gives the structure factor for each space group; this is an expression for the contribution to the structure amplitude of all structurally equivalent atoms in the general position. This expression includes the diffracting power f of the atom whose contribution is being calculated. In the case of the space group $\text{P2}_1/\text{c}$, the intensity contribution to the plane hkl of four structurally equivalent atoms of diffracting power f and in a general position with parameters $x y z$ is, for the origin at a symmetry centre,

$$4f \cos 2\pi \left(hx + lz + \frac{k+1}{4} \right) \cos 2\pi \left(ky - \frac{k+1}{4} \right).$$

The total structure amplitude for any plane hkl is of course the sum of the structure amplitudes of all atoms, that is

$$F_{hkl} = \sum 4f \cos 2\pi \left(hx + lz + \frac{k+1}{4} \right) \cos 2\pi \left(ky - \frac{k+1}{4} \right).$$

FIGURE 1

GRAPH OF DIFFRACTING POWERS (f_o)

of thomsenolite, for all the simpler combinations of permissible indices in each of the three principal zones. About 15 charts were made and, because of the interchangeability of indices, these 15 charts enabled the reading off of the structure factors for about 35 different lattice planes. These valuable charts were of great assistance in evaluating the structure amplitudes of these 35 planes in thomsenolite.

Heating Experiment on the Dehydration of Thomsenolite. In his textbook Structural Inorganic Chemistry, Wells (1945, p. 364) briefly summarizes the different effects of dehydration on different hydrated compounds:

"We see therefore that there are different effects on dehydration, from the complete breakdown of the crystal in the case of a salt hydrate through the intermediate examples such as clay minerals and certain proteins, where removal of water merely brings the structural units closer together with continuous changes in one or more of the cell dimensions, to the 'framework' crystal which may be reversibly hydrated without appreciable alteration of the structure of the anhydrous crystal."

Although the authors strongly suspected that thomsenolite was simply a salt hydrate, the heating experiment was carried out to check this idea, to determine the dehydration temperature and, if possible, to identify the dehydration product(s).

Two samples of cleavage fragments of thomsenolite, one weighing about $1/3$ gm., the other about $2/3$ gm., were independently heated in a controlled electric furnace equipped with a mercury thermometer and a simple apparatus for condensing and catching any water vapour given

off. The two samples were heated in stages and were held at the final stage until the residues were of constant weight. The experiment resulted in the following observations and conclusions:

- (1) Clear crystals of thomsenolite are apparently little affected by temperatures below about 300°C.
- (2) At that temperature, 300°C, the crystals were heated to a constant weight in about 9 hours with an accompanying breakdown of the structure.
- (3) The loss in weight after 9 hours' heating at 300°C was 8.04% although the water collected constituted only 6.34% of the original sample. Part of this difference is likely due to experimental error in the water determination. The theoretical water content of thomsenolite is 8.11%. The condensate gave an acid reaction with litmus and, although it gave a negative reaction for F with CaCl_2 solution, it did etch the glass tubing indicating that some F was present in the water.
- (4) The previously clear colourless cleavage fragments became, at 300°C, milky and cryptocrystalline. Attempts to take single-crystal X-ray pictures of some of the fragments failed but a powder picture was taken and the observed data for it appear in Table III. A microscopic examination of the fragments confirmed their cryptocrystalline character, and yielded the refractive index $n \sim 1.354$.
- (5) The X-ray powder picture referred to in (4) is different from that of any known aluminofluoride mineral or combination of minerals, and the refractive index 1.354 does not agree with any known aluminofluoride.

Thus it is concluded that the disintegration product of thomsenolite heated to 300°C for 9 hours is no existing aluminofluoride. The evidence in (3) suggests that the residue may have the composition NaCaAlF_6 but this is by no means convincing. The residue was not analysed chemically.

The principal contribution of the heating experiment to the immediate problem was to prove that the water forms an essential feature of the structure, i.e. thomsenolite is a true salt hydrate and does not "hydro-structurally" resemble either the clay minerals or the zeolites.