

An X-ray examination of substituted edingtonites.

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I. *Introduction. The Edingtonite Structure.*

THE rare barium zeolite edingtonite has been examined in the course of the systematic investigation of the zeolites now being made at the British Museum,¹ and several substitution derivatives have been prepared. The structure of natural edingtonite has also been completely determined by X-ray methods,² and in the present paper an account is given of an attempt to discover the exact positions occupied in the substituted edingtonites by the potassium and thallium ions which replace the barium ions of ordinary edingtonite.

Base-exchange products obtained from some other zeolites have already been examined in detail by X-ray methods. In silver-analcime³ and silver-natrolite⁴ the intensities of X-ray reflections are explained satisfactorily on the assumption that each silver ion occupies the exact position previously occupied by the sodium ion which it replaces. In these crystals a monovalent ion in the natural compound is replaced by another monovalent ion in the substitution product. The peculiar interest of base-exchange in edingtonite arises from the fact that each divalent (barium) ion in the natural compound may be replaced by *two* monovalent ions in the substitution product, and the aim of the work to be described is to show how the extra cation is accommodated without any breakdown of the crystal-structure.

¹ M. H. Hey and F. A. Bannister, Studies on the zeolites. Part VI. Edingtonite. *Min. Mag.*, 1934, vol. 23, p. 483.

² W. H. Taylor and R. Jackson, The structure of edingtonite. *Zeits. Krist.*, 1933, vol. 86, p. 53. [M.A. 5-354.]

³ W. H. Taylor, The structure of analcite . . . *Zeits. Krist.*, 1930, vol. 74, p. 1. [M.A. 4-369.]

⁴ W. H. Taylor, C. A. Meek, and W. W. Jackson, The structures of the fibrous zeolites. *Zeits. Krist.*, 1933, vol. 84, p. 373. [M.A. 5-354.]

Natural edingtonite is a simple example of an aluminosilicate framework structure, of which a large number have been examined.¹ It is closely related to the zeolites thomsonite and natrolite (with scolecite and mesolite), all being fibrous parallel to the c -axis, with right-angled cleavages in the $[hk0]$ zone, and a c -axis of length 6.6 Å.

The orthorhombic unit cell of edingtonite with a 9.6, b 9.7, c 6.6 Å., is dimensionally pseudo-tetragonal, and the intensities of reflection correspond to tetragonal symmetry, the space-group being D_{2d}^3 (tetragonal) or V^3 (orthorhombic). The unit cell of fully hydrated material contains $\text{Ba}_2\text{Al}_4\text{Si}_6\text{O}_{20}\cdot 8\text{H}_2\text{O}$, and the structure is essentially tetragonal, the slight *dimensional* departure from tetragonal symmetry probably being a consequence of the small difference in the sizes of (SiO_4) and (AlO_4) groups.

Fig. 1 represents a chain of linked tetrahedral (SiO_4) and (AlO_4) groups such as is found in edingtonite, thomsonite, and natrolite. The chain is a rigid structural unit of length 6.6 Å., and in all these crystals the tetrahedron chains lie side by side with their lengths parallel to the crystallographic c -axis. The chains are linked together laterally by sharing oxygen atoms and so form a continuous three-dimensional framework of linked (SiO_4) and (AlO_4) groups. The linkage of the chains is different in the three crystals; in edingtonite every oxygen atom common to two chains lies on a reflection plane as shown in fig. 2, which represents the complete atomic arrangement in the unit cell. The relation between the crystal-structure and physical properties of edingtonite has been discussed in detail elsewhere.

The line of intersection of two reflection planes (fig. 2) marks the centre of a channel parallel to the c -axis of the crystal and bounded

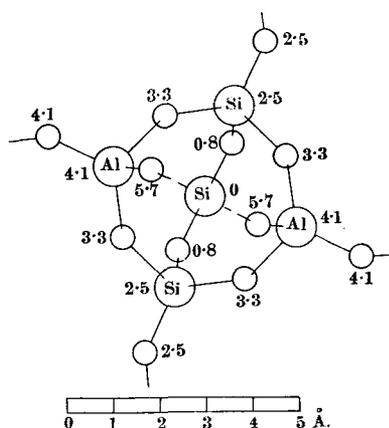


FIG. 1. The tetrahedron chain of edingtonite viewed along its length. Large circles represent silicon or aluminium atoms, small circles represent oxygen atoms. The heights of the atoms are given in Å.

¹ See, for example, W. H. Taylor, Proc. Roy. Soc. London, Ser. A, 1934, vol. 145, p. 80. [M.A. 6-59.]

by four tetrahedron chains. Water molecules of type Aq_1 form, with oxygen atoms O_A , double columns which bound the 'channels' and include a series of identical cavities with centres at intervals of 3.3 Å.

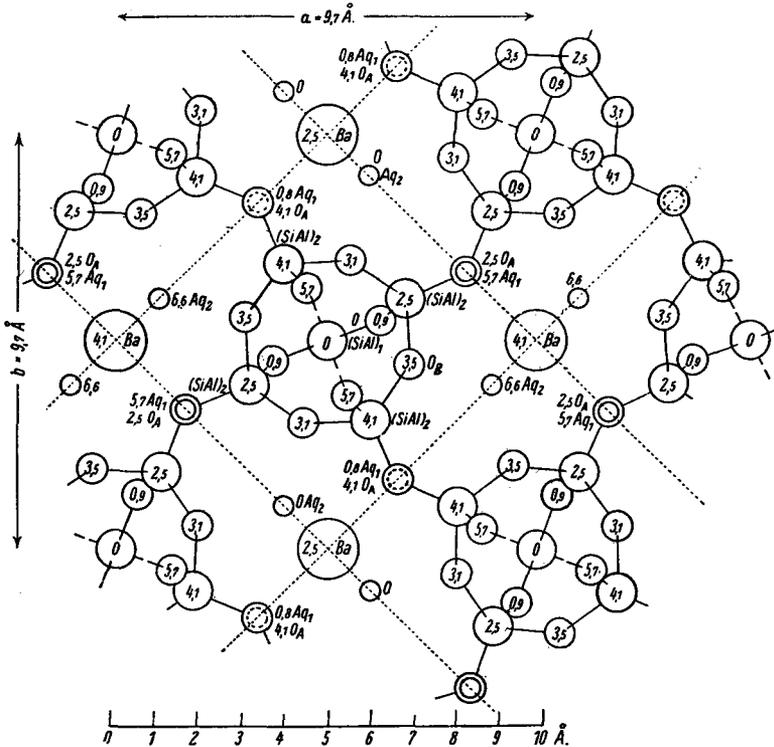


FIG. 2. The unit cell of edingtonite viewed along the c -axis. The heights of the atoms above the base of the unit cell are given in Å., and the reflection planes (110) and $(1\bar{1}0)$ are indicated by dotted lines. Full lines represent bonds between oxygen and silicon or aluminium.

along the centre line of the channel. At the right-hand side of fig. 2 a barium ion with its centre at height 4.1 Å. above the base of the unit cell occupies one such cavity; cavities at heights 0.8 Å. and 7.4 Å. are unoccupied, only *alternate* cavities at intervals of 6.6 Å. being occupied by barium ions in ordinary edingtonite. The water molecules of type Aq_2 also lie within the channels parallel to the c -axis.

Similar channels are found in other zeolite structures, and since

the channels are large enough to permit the movement of ions and water molecules without breaking the strong tetrahedron framework,

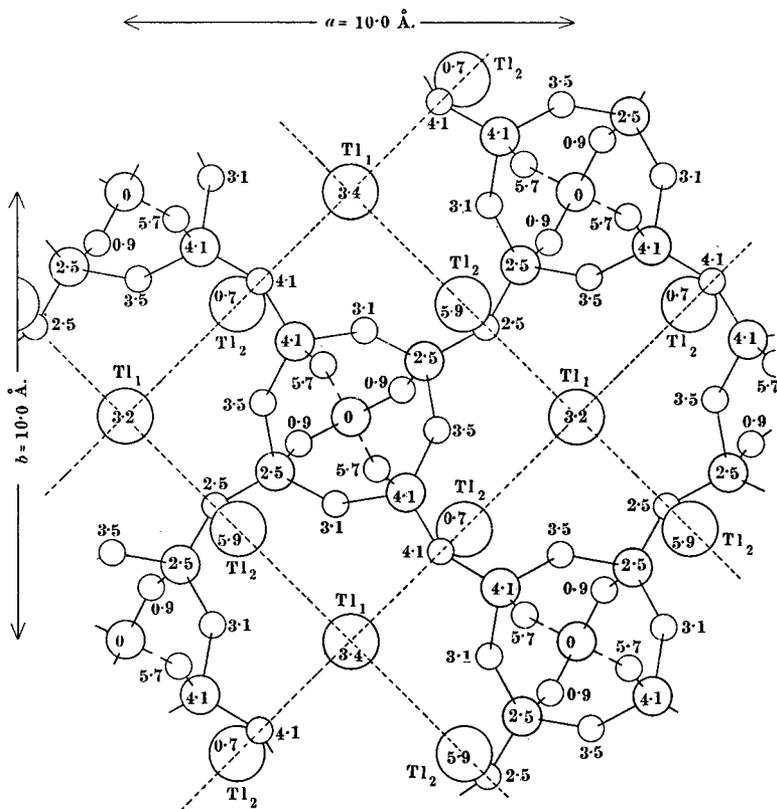


FIG. 3. The unit cell of thallium-edingtonite. This diagram should be compared with fig. 2. In thallium-edingtonite the tetrahedron chains are rotated through a small angle from their positions in ordinary edingtonite, and the atoms Tl_1 are at heights different from those of the Ba atoms which they replace. All atomic positions Tl_2 are shown, although probably only one half of these are occupied.

it is assumed that their existence explains the peculiar dehydration and base-exchange properties of zeolites.

Of the four substituted edingtonites prepared by M. H. Hey,¹ sodium pseudo-edingtonite must differ fundamentally from other edingtonites, since its c axis is not a multiple of 6.6 Å.; silver-edingtonite gives extremely weak X-ray photographs, and therefore

¹ M. H. Hey and F. A. Bannister, loc. cit.

insufficient data for a detailed investigation; the potassium and thallium derivatives give good photographs and have been used for the present work.

II. *Thallium-edingtonite*.

The unit cell of thallium-edingtonite has been measured by F. A. Bannister,¹ and the chemical composition determined by M. H. Hey.¹ The cell, with axes a 9.94, b 10.00, c 6.65 Å., is slightly larger than that of barium-edingtonite and contains 5.82 Si, 3.92 Al, 0.32 Ba, 4.37 Tl, 20 O, 4.87 H₂O, i.e. in whole numbers Tl₄Al₄Si₆O₂₀ and water. The intensities of the reflections show tetragonal symmetry and no reflections occur which are forbidden by the space-group D_{2d}^3 of barium-edingtonite; this is therefore assumed to be the space-group of the thallium derivative.

The scattering power of the water molecules is very small by comparison with that of thallium, and they may be left out of account until the main features of the structure are known. The whole investigation is based on the assumption that there is no essential change in the tetrahedron framework during base-exchange, though a small rotation of the tetrahedron-chains is indicated by the longer a - and b -axes.² It remains, therefore, to find the positions of the thallium ions; the following possible arrangements have been tested.

(i) The simplest assumption is that thallium ions occupy the cavities previously occupied by barium ions and also the similar cavities (midway between occupied cavities) which are empty in barium-edingtonite (see Section I and fig. 2).³ In this case the four thallium atoms per unit cell comprise two groups of two equivalent atoms each, with typical co-ordinates $\theta_1 = 180^\circ$, $\theta_2 = 0^\circ$, $\theta_3 = 225^\circ$, and $\theta_1 = 180^\circ$, $\theta_2 = 0^\circ$, $\theta_3 = 45^\circ$, respectively (cf. the atomic co-ordinates quoted in table II). Table I contains a comparison of observed intensities for reflections of low indices and F -values calculated for an arrangement of water molecules and tetrahedron framework identical with that in barium-edingtonite, with thallium ions in the above positions. The complete lack of agreement indicates that the real structure must be quite different from that assumed in calculating the above F -values. On account of the great scattering power of the thallium ions, omission of the water molecules or rotation of the tetrahedron chains could make no appreciable difference in this comparison.

¹ M. H. Hey and F. A. Bannister, loc. cit.

² See also W. H. Taylor, 1934, loc. cit., p. 83.

³ See also *ibid.*, p. 94.

TABLE I. Thallium-edingtonite. Comparison of observed intensities of reflection and calculated F -values.

$\sin \theta$.	hkl .	$F(\text{calculated})$.	$I(\text{observed})$.	$\sin \theta$.	hkl .	$F(\text{calculated})$.	$I(\text{observed})$.
0.051	110	225	1-2	0.066	101	15	nil
0.072	200	305	2-3	0.075	111	50	5-6
0.081	120	40	nil	0.098	121	35	nil
0.103	220	270	10	0.115	102	250	nil
				0.116	221	90	4
				0.120	112	80	8
				0.136	122	280	nil

In the above table θ is the glancing angle corresponding to Mo-K $_{\alpha}$ radiation with wave-length 0.71 Å., the observed intensities are arranged on an arbitrary scale in which 1 is very weak and 10 very strong, and the F -values are calculated for the following structure (Case (i), Section II of the text):—

- { Water molecules and tetrahedron framework as in ordinary edingtonite.
- { 2Tl $_1$ with co-ordinates $\theta_1 = 180^\circ, \theta_2 = 0^\circ, \theta_3 = 225^\circ$.
- { 2Tl $_2$ $\theta_1 = 180^\circ, \theta_2 = 0^\circ, \theta_3 = 45^\circ$.

(ii) If no departure from the symmetry of D_{2d}^3 is permitted the only alternative arrangement of the thallium atoms is that they form one group of *four* equivalent atoms lying on the reflection planes. On comparing observed intensities of reflections ($hk0$) with F -values calculated for all possible parameters of the thallium atoms, we have failed to find any agreement.

(iii) The individual unit cell cannot therefore conform to the symmetry of D_{2d}^3 , which is the symmetry of the macroscopic crystal. We have therefore used the 'average' method which was applied successfully to analcime (loc. cit., 1930). In that crystal sixteen sodium ions were assumed to occupy uniformly on the average twenty-four equivalent positions of the cubic space-group; the physical interpretation (loc. cit., 1934) is that at a given time the individual unit cell does not possess cubic symmetry, but on the average it is equally probable that any sixteen of the twenty-four available (similar) positions are occupied.

To apply the 'average' method to edingtonite is more difficult, and the number of possible structures is large. Assuming, in the first place, that some thallium ions probably take up positions near those formerly occupied by barium ions, we have attempted to proceed systematically, as far as possible, in locating the remaining thallium ions. We have found one arrangement which explains fairly satisfactorily the observed relative intensities of reflection, and while we do not claim that the structure is uniquely determined, we believe that this must be a close approximation to the true *average*

structure. Table II contains the atomic co-ordinates, and table III a list of observed relative intensities of reflection with corresponding calculated F -values. Fig. 3 represents the structure, and fig. 4 reproduces in convenient form the data contained in table III.

TABLE II. Atomic co-ordinates in substituted edingtonites.

Atom.	Number in cell.	θ_1 .	θ_2 .	θ_3 .	x .	y .	z .
O _A	4	108°	72°	135°	3.0 Å.	2.0 Å.	2.5 Å.
O _B	8	10	70	170	0.3	1.95	3.1
O _C	8	40	22	50	1.1	0.6	0.9
(SiAl) ₁	2	0	0	0	0	0	0
(SiAl) ₂	8	60	45	135	1.65	1.25	2.5
Tl ₁ or K ₁	(2)	180	0	175	5.0	0	3.2
Tl ₂ or K ₂	(4)	90	90	322	2.5	2.5	5.9

The co-ordinates refer to a tetragonal unit cell with $a = b$ 10.0, c 6.6 Å., and the origin of co-ordinates is a point on a fourfold alternating axis of the space-group D_{2d}^5 . θ_1 θ_2 θ_3 are the usual angular co-ordinates ($\theta_1 = 360^\circ \times \frac{x}{a}$, &c.). The group 2(SiAl)₁ probably contains only silicon atoms; the group 8(SiAl)₂ probably contains 4 silicon and 4 aluminium atoms. The four thallium (or potassium) ions per unit cell are distributed over the positions 2Tl₁ (or 2K₁) and 4Tl₂ (or 4K₂) as described in the text. Water molecules are not included in the above table.

In the structure of fig. 3 and table II the tetrahedron chains are identical with those of ordinary edingtonite, but are rotated through a small angle to correspond with the larger cell which is assumed tetragonal with $a = b = 10.0$ Å. (cf. actual axial lengths a 9.94, b 10.00 Å.).

The water molecules cannot be located directly, on account of their small scattering power; they are probably closely associated with the thallium ions.

The thallium ions comprise two groups. The ions of group (2Tl₁) lie on the line of intersection of two reflection planes as do the barium ions in ordinary edingtonite, but at a height which differs by 0.9 Å. (cf. figs. 2 and 3). The ions of group (4Tl₂) lie on the reflection planes in such positions that they are as far as possible from other positive ions—thallium, silicon, and aluminium. The best agreement between observed intensities and calculated F -values is obtained by assuming that the four thallium ions per unit cell are distributed *uniformly* among the six positions 2Tl₁ + 4Tl₂. This distribution is discussed in Section IV.

TABLE III. Comparison of observed and calculated intensities for thallium-edingtonite.

$\sin \theta$.	hkl .	F .	I .	$\sin \theta$.	hkl .	F .	I .
0-051	110	15	1-2	0-066	101	25	nil
0-072	200	90	2-3	0-075	111	125	5-6
0-081	120	25	nil	0-091	201	190	8-9
0-103	220	290	10	0-098	121	15	nil
0-115	130	125	6	0-115	102	20	nil
0-131	230	25	nil	0-116	221	125	4
0-145	400	235	8	0-120	112	245	8
0-150	140	5	nil	0-122	301	15	nil
0-154	330	70	1-2	0-127	131	200	8
0-163	240	75	3-4	0-131	202	65	4-5
0-182	340	40	nil	0-136	122	15	nil
0-185	150	70	3	0-142	231	35	nil
0-196	250	20	nil	0-150	222	125	3-4
0-206	440	290	8	0-154	302	25	nil
0-212	350	35	<1	0-156	401	75	1
0-218	600	25	<1	0-159	141	20	1-2
0-221	160	15	nil	0-159	132	190	7
0-230	260	230	6-7	0-163	331	135	3-4
				0-170	232	30	nil
				0-171	241	210	6
0-054	001	25	nil	0-182	402	160	4
0-108	002	200	8	0-185	142	35	nil
0-161	003	135	5	0-189	341	20	nil
0-215	004	130	3	0-190	332	160	5-6
0-269	005	160	2-3	0-192	242	70	2

In the above table θ is the glancing angle corresponding to Mo-K α radiation with wave-length 0.71 Å., calculated for the unit cell of ordinary edingtonite. I is the observed intensity, and the F -values are calculated for the atomic coordinates listed in table II. The observed intensities are arranged on an arbitrary scale in which 1 is very weak and 8 is very strong.

III. Potassium-edingtonite.

The true unit cell of potassium-edingtonite, determined by F. A. Bannister (loc. cit., 1934), is approximately eight times as large as the unit cell of barium-edingtonite, but there is a well-defined pseudo-cell with axes a 9.73, b 10.02, c 6.68 Å., the true axes being twice as long. Only a few weak reflections indicate the size of the true unit cell. The pseudo-cell contains, according to the analysis of M. H. Hey, 5.76 Si, 4.17 Al, 0.43 Ba, 3.59 K, 20 O, 3.60 H $_2$ O, i.e. in whole numbers K $_4$ Al $_4$ Si $_6$ O $_{20}$ and water. All indices quoted in this paper refer to the pseudo-cell and so are comparable with indices of ordinary edingtonite. The intensities of reflections correspond to tetragonal

symmetry and the space-group (of the pseudo-cell, assumed tetragonal) is D_{2d}^3 .

The investigation of potassium-edingtonite is much more difficult than that of the thallium compound, for the following reasons:

(i) All calculations are based on the pseudo-cell, which can only give an approximation to the true structure.

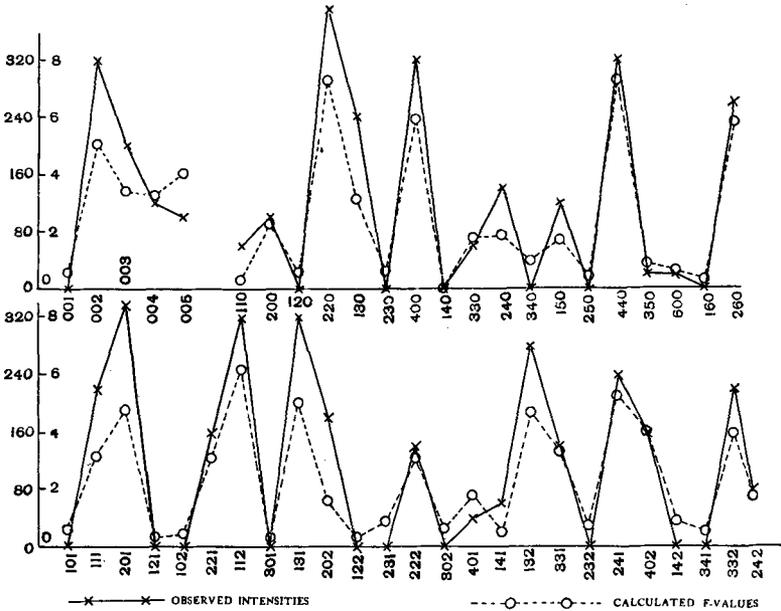


FIG. 4. Comparison of observed intensities of reflection (scale 0 to 8) with calculated F -values (scale 0 to 320) for thallium-edingtonite.

(ii) The scattering power of the potassium ion is only a little greater than that of the other ions in the crystal, and therefore the contribution to the total F made by the four potassium ions per pseudo-cell does not stand out obviously as does the corresponding thallium contribution.

(iii) The water molecules, approximately four per pseudo-cell, may add important contributions to some reflections of low indices and so complicate the search for the correct positions of the potassium ions.

(iv) A small rotation of the tetrahedron chains affects certain calculated F -values to an extent comparable with the total contribution made by potassium ions.

For these reasons we have not been able to proceed as directly as in the case of thallium-edingtonite. It can be shown, however, that simple filling of all similar cavities on the lines of intersection

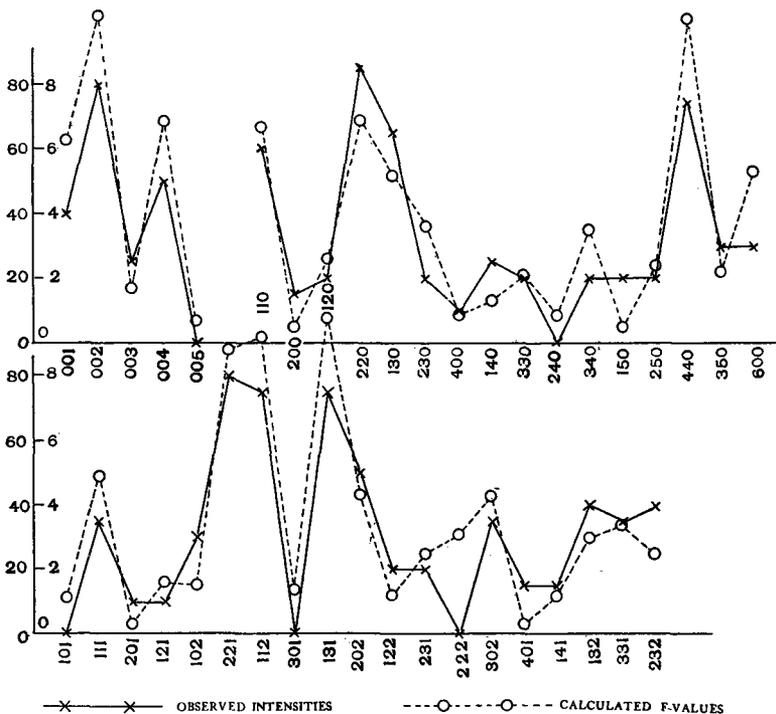


FIG. 5. Comparison of observed intensities of reflection (scale 0 to 8) with calculated F -values (scale 0 to 80) for potassium-edingtonite.

of reflection planes (Case i in Section II on thallium-edingtonite) cannot explain the observed intensities of reflection. We have also explored a number of other possibilities, but conclude finally that a structure identical with that of thallium-edingtonite best explains the observed intensities of reflection. The agreement is definitely improved if it is assumed that two potassium ions occupy positions $2K_1$ and that the other two potassium ions are distributed uniformly among the positions $4K_2$. (This distribution is discussed in Section IV.) The agreement is also slightly improved by adding to the F -value for each reflection one-half of the contribution made by the water molecules in ordinary edingtonite to that reflection. It is doubtful whether

this corresponds to reality, although the four water molecules per pseudo-cell could be accommodated since only one half of the positions $4K_2$ are occupied by potassium ions.

Table IV contains a list of observed relative intensities of reflection with calculated F -values for the structure as described above (the contribution from the water molecules being added), and fig. 5 represents these data in graphical form.

TABLE IV. Comparison of observed and calculated intensities for potassium-edingtonite.

$\sin \theta$.	hkl .	F .	I .	$\sin \theta$.	hkl .	F .	I .
0.051	110	65	6	0.066	101	10	nil
0.072	200	5	1-2	0.075	111	50	3-4
0.081	120	25	2	0.091	201	5	1
0.103	220	70	8-9	0.098	121	15	1
0.115	130	55	6-7	0.115	102	15	3
0.131	230	35	2	0.116	221	90	8
0.145	400	10	1	0.120	112	90	7-8
0.150	140	15	2-3	0.122	301	15	nil
0.154	330	20	2	0.127	131	100	7-8
0.163	240	10	nil	0.131	202	45	5
0.182	340	35	2	0.136	122	15	2
0.185	150	5	2	0.142	231	25	2
0.196	250	25	2	0.150	222	30	nil
0.206	440	105	7-8	0.154	302	45	3-4
0.212	350	25	3	0.156	401	5	1-2
0.218	600	55	3	0.159	141	10	1-2
				0.159	132	30	4
				0.163	331	35	3-4
				0.170	232	25	4
0.054	001	65	4				
0.108	002	110	8				
0.161	003	20	2-3				
0.215	004	70	5				
0.269	005	5	nil				

In this table θ is the glancing angle corresponding to Mo- K_α radiation of wave-length 0.71 Å., calculated for the unit cell of ordinary edingtonite and therefore approximately correct for the pseudo-cell of potassium-edingtonite to which all indices (hkl) refer. The observed intensities (I) are arranged on an arbitrary scale in which 1 is very weak and 8 very strong. F is calculated from the atomic co-ordinates listed in table II, but includes *also* one half the contribution made by the water molecules to the corresponding reflections in ordinary edingtonite.

IV. Discussion.

The evidence presented in support of the suggested structures, though not absolutely conclusive, is probably satisfactory. It is rather surprising, however, that the thallium and potassium ions should be distributed differently over the six available positions. It

would be expected that all the cavities previously occupied by barium ions would again be occupied in the substituted materials, with the additional cations distributed uniformly over the additional positions and so occupying one-half of them on the average. This is the distribution chosen for the potassium derivative, but there is no doubt that in the case of thallium-edingtonite a better agreement between observation and calculation is obtained with a uniform distribution of four atoms over all six available positions—i.e. when more weight is given to the group Tl_2 . The most reasonable explanation seems to be that the distribution is really the same in both potassium and thallium derivatives when substitution is complete—probably positions $2Tl_1$ or $2K_1$ fully occupied, positions $4Tl_2$ or $4K_2$ one-half occupied—but that in the actual crystals the apparently different distributions are due to incomplete replacement of the divalent barium atoms.

In 'average' structures so complex as these, there is little point in discussing the finer details of atomic environments. It may be worth while to remark that in the structure of fig. 3 each ion Tl_1 or K_1 has as nearest neighbours two oxygen atoms at distance 2.9 \AA . with four more at 3.1 \AA ., and each ion Tl_2 or K_2 has two oxygen atoms at 2.9 \AA . with four more at 3.3 \AA . In addition, the water molecules, not included in fig. 3, will certainly be associated with the cations.

There are two reasons why the cations should be distributed among the positions Tl_1 and Tl_2 (or K_1 and K_2) instead of occupying all the cavities along the line of intersection of the reflection planes (Case i, Section II). In the first place, the observed arrangement results in a more uniform distribution of the positive ions among the oxygen ions. Secondly, there is the question of the location of the residual valency of the anionic framework, which is probably closely associated with the aluminium atoms; these atoms cannot be distinguished directly from silicon atoms, but the most reasonable hypothetical allocation of silicon and aluminium atoms among the tetrahedra results in a distribution of residual valency, which is better satisfied by the observed structure than if cations occupied all the cavities, as in Case i, Section II.

Our knowledge of the structures is not sufficiently detailed to permit any suggestion as to the reason why the true unit cell of the potassium compound is eight times as large as that of the barium and thallium compounds.

I am indebted to Mr. F. A. Bannister for the loan of his X-ray photographs of substituted edingtonites, to Mr. M. H. Hey for supplies of material from which my own photographs were obtained, and to both for helpful discussion of the problem. Most of the work was carried out in the Physical Laboratories of Manchester University, and I wish to thank Professor W. L. Bragg for his continued interest in the research. I am also indebted to the Leverhulme Trustees for the award of a Fellowship, during the tenure of which this work was completed.
