Studies on the zeolites.   Part VI.   Edingtonite.[1]

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THE very rare barium zeolite edingtonite was described by W. Haidinger (1825), and named in honour of Mr. Edington. Haidinger's material consisted of small crystals on thomsonite from Dumbartonshire. An analysis by E. Turner indicated a calcium aluminosilicate, but there was a loss of 11·22 %. The crystals (sp. gr. 2·71) were morphologically tetragonal, with the prism $m(110)$ and sphenoids $p(111)$ and $n(1\bar{1}2)$, and an axial ratio $c/a = 0·6725$. A. Breithaupt (1832) gave the name ' Antiëdrit ' on account of this symmetry.

M. F. Heddle (1855) examined material from Old Kilpatrick, and showed it was a barium zeolite. His analysis was not very good; it suggested the formula $BaAl_2Si_3O_{10}.3H_2O$, which has been generally adopted, but is not quite correct. The only other analysis in the literature is one by G. Lindström (1896) of material from Böhlet, Westergotland, Sweden. This agrees with the Old Kilpatrick material in composition, but there have been doubts about their identity, for O. Nordenskjöld (1895) showed that the Böhlet material is orthorhombic and optically biaxial, whereas A. Des Cloizeaux

[1] Part V. Mesolite. Min. Mag., 1933, vol. 23, p. 421.

M m

(1862) had described Old Kilpatrick edingtonite as uniaxial negative. Although A. Lacroix (1896) and H. Sjögren (1906) showed that the Old Kilpatrick crystals are really biaxial, and explained their pseudo-uniaxial behaviour as due to complex twinning on m (110), these doubts have persisted to some extent.

In order to make quite certain that the Böhlet material really is true edingtonite, Mr. F. A. Bannister has taken X-ray rotation photo-graphs of cleavage fragments from a Böhlet specimen (B.M. 81049) and an Old Kilpatrick specimen (B.M. 26607). The photographs were identical except as regards the axial ratio. While the Böhlet material is distinctly orthorhombic, having cell sides a 9·56, b 9·68, c 6·53 Å. (all $\pm$ 0·02 Å.), no departure of the Old Kilpatrick material from tetragonal symmetry could be detected by Lauegrams or rota-tion photographs. The cell size of the Old Kilpatrick material is a 9·585, b 9·585, c 6·53 Å. (all $\pm$ 0·02 Å.). Since optical study shows that the Old Kilpatrick material is also biaxial, and the X-ray photo-graphs are identical save for the difference of axial ratio, we conclude that the Böhlet material is indeed true edingtonite. The difference is probably due to the higher calcium content of the Old Kilpatrick crystals.

None of the material available was suitable for goniometric study. The Old Kilpatrick material was studied by W. Haidinger (1825) who found it to be tetragonal with $c/a = 0.6725$, while H. Sjögren (1906) found $c/a = 0.6793$, in better agreement with the X-ray value, 0·681. The Böhlet material was studied by O. Nordenskjöld (1895), who found $a : b : c = 0.9872 : 1 : 0.6733$, and by H. Sjögren (1906), who found $a : b : c = 0.9867 : 1 : 0.6743$; the X-ray value is $0.988 : 1 : 0.675$.

W. H. Taylor and R. Jackson (1933) have made a complete crystal-structure analysis of edingtonite. Assuming the mineral is orthorhombic, they find the space-group D_2^3, a result which Mr. Ban-nister's photographs confirm. Mr. Bannister has also found that with Böhlet material, the intensity of ($hk0$) diffractions is less than that of ($kh0$) diffractions; but (hkl) and (khl) diffractions are of equal intensity, except for high orders, for which those for (hkl) are the more intense. Mr. Bannister has also confirmed the relative intensities tabulated by Taylor and Jackson. The structure is based on $(Al_2Si_3O_{10})''$ strings similar to those present in thomsonite and natrolite, but linked together differently. It may be of interest to note that while in natrolite, mesolite, and scolecite, the strings (which are polar) are probably all arranged with their similar ends pointing

in the same direction, the presence of two-fold screw-axes parallel to a and b in the edingtonite space-group requires either that half the chains point in the opposite direction to the other half, as they probably do in thomsonite, or that the chains of edingtonite are not polar, or that the crystal is not truly orthorhombic, but really monoclinic. The last possibility is supported by the optical anomalies observed by H. Sjögren (1906) and O. Nordenskjöld (1895). Dr. W. A. Wooster, of Cambridge, has kindly examined edingtonite for pyroelectricity, and found a distinct effect, indicating the absence of a centre of symmetry.

The amount of Old Kilpatrick material available for study was insufficient for chemical analysis, and little could be done beyond the X-ray work. Optical examination of several fragments showed that the crystals are biaxial negative, with a small optic axial angle, 2E varying from 15 to 20° in different fragments. Twinning on $m(110)$ was observed in one fragment. The refractive indices, a 1·542, β and γ 1·550 ($\pm$ 0·002) are distinctly different from those of the Böhlet material, the birefringence being less. Differences in composition appeared the most likely explanation of the optical and dimensional differences between the Böhlet and Old Kilpatrick edingtonites, though the complete analyses reveal no such differences. But Heddle's analysis (1855) of Old Kilpatrick material showed a loss of over 1 %; and he mentions another partial analysis which showed 6·22 % CaO. The specimen studied optically and by X-rays (B.M. 26607) was therefore examined micro-chemically for calcium, which was found to be present in appreciable amount. As calcium is only present in very small amounts in the Böhlet material, it seems reasonable to attribute the optical and dimensional differences to its presence.

The Böhlet edingtonite was employed for the remainder of the present work. A chemical analysis was made (table Ia) and is compared with Heddle's and Lindström's analyses in table Ib. The number of oxygen atoms per unit cell was calculated from the cell-size, analytical and density figures as usual, and shown to be 20. Calculating the analyses on this basis, it is clear that the commonly accepted formula is correct except for the water. The vapour-pressure study shows that the air-dry material has a water-vapour pressure equal to the partial pressure of the water-vapour in the air, and on exposure to higher water-vapour pressures, more water is taken up; saturation of the zeolite is, however, reached before the

saturation pressure for liquid water. The unit cell formula of fully-hydrated edingtonite is $Ba_2Al_4Si_6O_{20}.8H_2O$.

TABLE I a. New chemical data on air-dry edingtonite from Böhlet, Sweden (B.M. 81049). Material used for main analysis 0·4422 gram, for alkalis 0·2227 gram.

SiO_2.	Al_2O_3.	BaO.	CaO.	Na_2O.	K_2O.	H_2O.	Total.	Oxygen.
35·35	19·98	30·83	0·10	0·04	0·65	13·11	100·06	31·59 %

TABLE I b. New and old analyses of edingtonite, calculated to unit-cell contents (atomic ratios on an assumed basis of 20 oxygen atoms). Also the oxygen atoms per unit cell, calculated from the analyses and specific gravities and the unit-cell dimensions.

	1.	2.	3.
Si	5·94	6·01	5·96
Al	4·29	3·94	3·97
Ba	1·67	1·96	2·03
Ca	trace	0·03	0·02
Na	} trace {	0·08	0·01
K		0·07	0·14
H_2O	6·68	7·23	7·37
Si+Al	10·23	9·95	9·93
Kations	1·67	2·14	2·20
Class of analysis *	C.	A.	B.
Sp. gr.	2·694	2·782	2·777
Oxygen, atoms per unit cell	20·8†	20·33	20·08

1. M. F. Heddle, 1855. Old Kilpatrick, Dumbartonshire.
2. G. Lindström, 1896. Böhlet, Sweden.
3. B.M. 81049, Böhlet.

* See Part II of this series for the method of classification used.

† The cell size determined for the Böhlet material was used for all three analyses, since Heddle's shows only traces of lime. If the cell size determined for the calciferous Old Kilpatrick specimen is used for Heddle's analysis, the oxygen content comes to 20·7 atoms per unit cell.

Optical study of the Böhlet edingtonite gave results in good agreement with those of O. Nordenskjöld (1895) and H. Sjögren (1906). The negative Bx_a is perpendicular to c (001), and the axial plane parallel to b (010). The refractive indices, optic axial angle (2V), and birefringence ($\gamma - \beta$) were determined for a series of wave-lengths; the results are given in tables II and III and shown graphically in fig. 1. The accuracy of the optical measurements was checked by comparing the measured values in the same manner as was done for natrolite.[1] These figures are all for air-dry material, with 7·4 mol.

[1] Part III of this series, Min. Mag., 1932, vol. 23, p. 243.

H_2O per unit cell. For fully hydrated edingtonite, the refractive indices would probably all be appreciably higher.
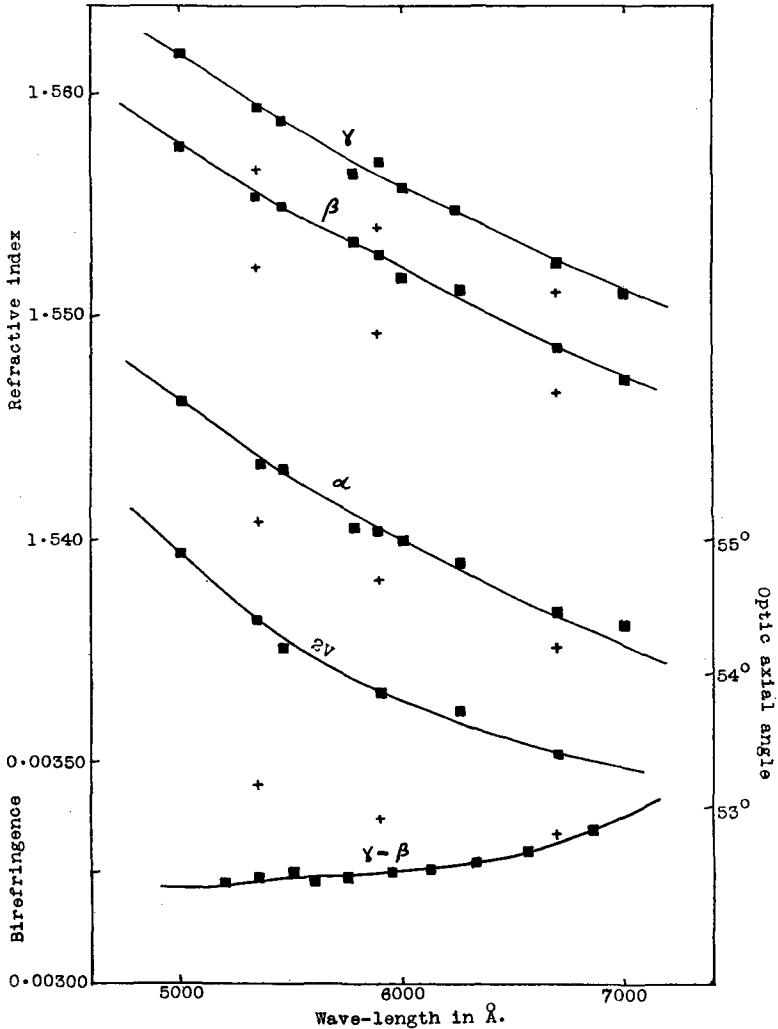

FIG. 1. The variation of the refractive indices, optic axial angle, and bire-fringence of edingtonite from Böhlet (B.M. 81050) with the wave-length of the light. The small crosses show the results of O. Nordenskjöld (1895) for α, β, γ, and 2V.

The only published dehydration data on edingtonite appear to be determinations of the water loss at 100° C. and 230° C. by G. Lind-

ström (1896) ; at the former temperature, 5·12 mols. water per unit cell are left, and at the latter 2·87 mols.[1] The lost water is wholly recovered in moist air.

TABLE II. Refractive indices and optic axial angles of air-dry (7·37 mol. H_2O per unit cell) Böhlet edingtonite (B.M. 81050), for light of various wave-lengths. Maximum probable error in the refractive indices ±0·0010, mean probable error ±0·0005; 2V ±10′. The column $\gamma-\alpha$ is calculated from the measured values of β, $\gamma-\beta$, and 2V.

λ(Å.).		α.	β.	γ.	2V.	$\gamma-\alpha$ calc.
7000	...	1·5362	1·5471	1·5510	—	—
6708	...	1·5368	1·5487	1·5525	53° 24′	0·0165
6250	...	1·5390	1·5513	1·5548	53 44	0·0161
6000	...	1·5401	1·5517	1·5559	—	—
5893	...	1·5405	1·5528	1·5569	53 52	0·0158
5780	...	1·5405	1·5534	1·5565	—	—
5461	...	1·5433	1·5549	1·5589	54 12	0·0155
5350	...	1·5435	1·5553	1·5594	54 24	0·0154
5000	...	1·5461	1·5576	1·5618	54 54	0·0152

TABLE III. Birefringence ($\gamma-\beta$) of air-dry (7·37 mol. H_2O per unit cell) Böhlet edingtonite (B.M. 81050), for light of various wave-lengths. Determined as extinctions in several orders, on a plate of thickness 6·76 mm., $\perp c(001)$. Maximum probable error, ±0·00002.

Order.	λ(Å.).	$\gamma-\beta$.	Order.	λ(Å.).	$\gamma-\beta$.
33rd	6860	0·00335	38th	5770	0·00325
34th	6570	0·00330	39th	5600	0·00323
35th	6330	0·00328	40th	5500	0·00325
36th	6120	0·00326	41st	5350	0·00324
37th	5950	0·00326	42nd	5200	0·00323

TABLE IV. The constants of the vapour-pressure surface of edingtonite from Böhlet (B.M. 81049). Heat of hydration, Q, in calories, and integration constant, A, of the equation $\log_{10}p = A - Q/(RT\log_e 10)$, for various water contents per unit cell, c.

c.	Q.	A.	c.	Q.	A.
8·0	$1·08 \times 10^4$	9·00	5·4	$1·73 \times 10^4$	10·30
7·7	1·14	9·25	4·7	1·91	10·38
7·4	1·28	9·62	4·15	2·10	10·42
7·15	1·36	9·84	3·5	2·26	10·47
6·8	1·44	10·00	2·8	2·48	10·50
6·4	1·55	10·08	2·4	2·59	10·52

Measurements of the vapour-pressure surface of edingtonite have been made and interpreted by the methods described in previous

[1] These figures are in good agreement with the author's vapour-pressure work. At 100° C. and about 1 mm. Hg water-vapour pressure, about 5·0 mols. water per unit cell should be left, while at 230° C. and 1 mm. Hg, the residual water should be about 2·8 mols.

papers in this series. The experimental values of Q and A, the vapour-pressure constants, are given in table IV and fig. 2, while the isohydric curves are shown in fig. 3. At 15° C. the water-vapour pressure of fully hydrated edingtonite is 7 mm. Hg, so that edingtonite
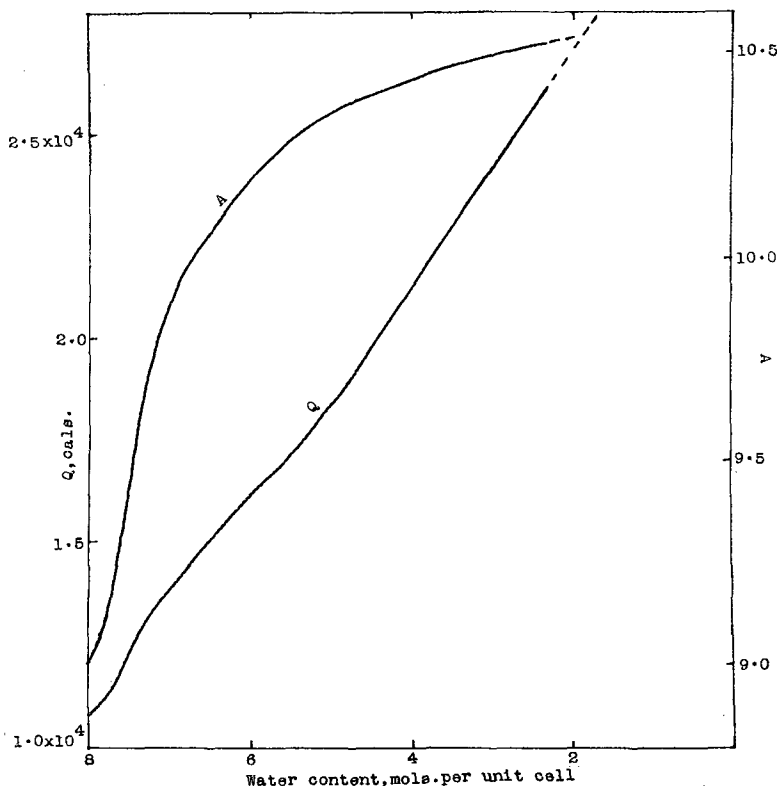

FIG. 2. The constants of the vapour-pressure surface of edingtonite from Böhlet (B.M. 81049). Heat of hydration, Q, in calories, and integration constant, A, of the equation $\log_{10} p = A - Q/(RT \log_e 10)$, for various water contents per unit cell, c.

kept in dry air ($p_{H_2O} < 1$ mm. Hg) loses a very appreciable amount of water—up to 1 to $1\frac{1}{2}$%. There are no breaks or discontinuities in the vapour-pressure surface of edingtonite, indicative of other modifications or lower hydrates.

Owing to shortage of material, the variation of the optical properties of edingtonite during dehydration could not be studied in detail, but the material removed from the vapour-pressure apparatus

was examined by the immersion method.   The results could not be made very accurate, as the dehydrated zeolite very rapidly absorbs water-vapour from the air, the crystals (previously clear and but little shattered) decrepitating markedly in moist air.[1]   The crystals,
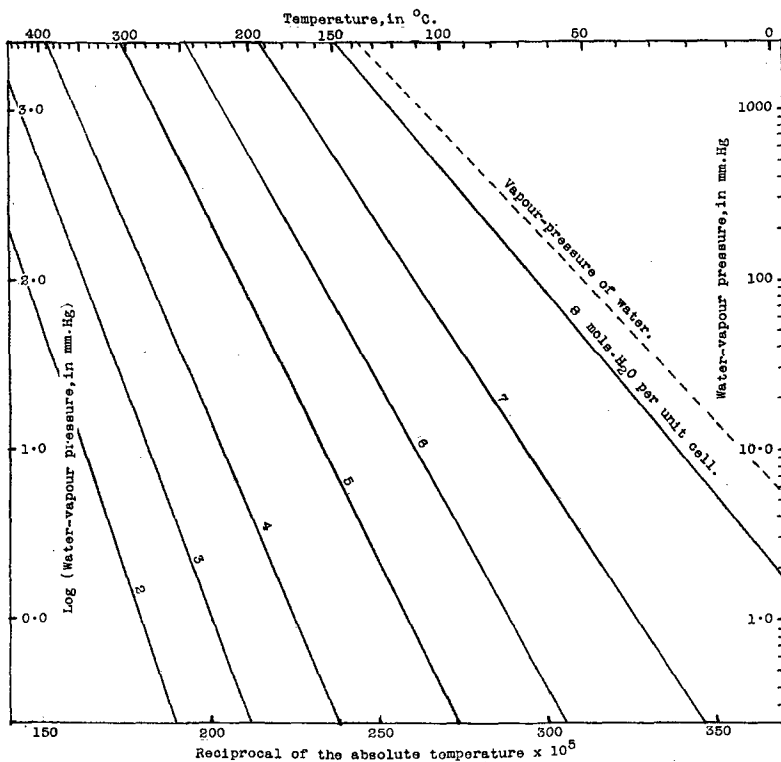

FIG. 3. Isohydric vapour-pressure curves for edingtonite
from Böhlet (B.M. 81049).

which contained 2·4 mols. H_2O per unit cell, had negative elongation ($a = c$), moderate birefringence, and a 1·544. This is higher than for edingtonite with 7·37 mol. H_2O per unit cell.   It is probable that, as with the other zeolites so far studied, the refractive indices first fall, then rise again with progressive dehydration.   Nordenskjöld's data support this conclusion, for his refractive indices are consistently lower than the author's, while Lindström's analysis shows less water.

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[1] It is possible that absorption of air may also be involved, since the material had been dehydrated in vacuo.

The heat of hydration of edingtonite was determined directly, by the same method as was used for natrolite and mesolite, as a check on the vapour-pressure work. With 2·06 grams edingtonite, dehydrated to a loss of 0·204 gram water (leaving 2·4 mol. per unit cell), a temperature rise of 4·5° C. (corrected to zero time) was observed, with a water-equivalent of 16·68 grams. The heat evolution continued during 6 minutes. From these data the mean heat of hydration of edingtonite by water-vapour, over the range 2·4 to 8·0 mol. H_2O per unit cell, is 17,000 cals. per gram-mol. of water reacting. The value deduced from the vapour-pressure experiments is 18,000 cals.

A few base-exchange experiments were carried out on the material which had been used for the vapour-pressure work and for the heat of hydration. Fusions of sodium chlorate, potassium thiocyanate, silver and thallous nitrates all gave considerable reaction. The products were analysed and examined optically and by X-rays, with results given in table V (p. 492).

The thallium compound was somewhat contaminated with thallous iodide and with barium sulphate, but apart from these impurities appeared to be homogeneous. Its X-ray rotation photograph showed that the unit cell is somewhat larger than that of the parent substance, and more nearly tetragonal. There were marked changes in the intensity of many diffractions, but there can be no doubt that the material is essentially an edingtonite. The very high refractive index and density are of course due to the high thallium content.

The silver compound was brownish in colour, probably owing to free silver oxide, but appeared quite homogeneous. An X-ray photograph was very weak, despite long exposure, indicating that the structure has probably broken down to a considerable extent, but it appears to be essentially silver-edingtonite.

The action of potassium thiocyanate yielded a product contaminated with barium sulphate, but otherwise homogeneous. Its unit cell is eight times as large as that of edingtonite, each dimension having been doubled, or rather slightly more than doubled. Hence it can no longer be classed as an edingtonite, and may be called potassium pseudo-edingtonite. The odd layer lines on the rotation photograph of this compound are very weak, the unit cell is face-centred, and there is a very close resemblance to the edingtonite photograph, indicating that the anionic $(Si,Al)O_2$ framework remains unaltered.

Table V. Base-exchange data for Böhlet edingtonite. The material (B.M. 81049) was treated for 96 hours with salt fusions, thoroughly leached, and examined air-dry. The untreated material had a 1·541, β 1·553, γ 1·557 for Na-light, and cell sides a 9·56, b 9·68, c 6·53 Å.; for its composition see tables Ia and Ib.

		TlNO₃.	AgNO₃.	NaClO₃.	KCNS.
Salt used		270°.	270°.	270°.	220° C.
Temperature ...					
Percentage composition ...	SiO₂ ...	16·85	31·76	42·25	31·46
	Al₂O₃ ...	9·62	18·84	24·60	19·29
	BaO ...	2·38	10·75	16·46	5·99
	R₂O* ...	44·73	35·66	8·79	[15·35]‖
	H₂O ...	4·22	2·07	7·55	5·89
	Total ...	[100·00]†	99·74‡	100·32§	[100·00]¶
Oxygen, %**		19·85	29·64	38·23	37·28
Atoms per 20 oxygen ...	Si	5·82	5·76	5·92	5·76
	Al	3·92	4·03	4·05	4·17
	Ba	0·32	0·76	0·90	0·43
	R*	4·37	3·35	·2·38	3·59
	H₂O	4·87	1·25	3·52	3·60
Sp. gr., calc.		4·03	3·13	2·56	2·21‖‖‖
Sp. gr., found		4·2±	3·2	2·50§§	2·47
Refr. index (Na-light)	α'	1·710††	1·645††	{ 1·518	1·547
	γ'			{ 1·525	1·555
Optic orientation; elongation		positive	positive	positive	negative
Cell sides in Å.‡‡	a	9·94	9·36	19·03	19·46
	b	10·00	9·36	19·03	20·04
	c	6·65	6·5	11·90	13·17
	r^*	1·7 ?	1·5 ?	0·98	1·33
Water retained at 300° C., mols. per 20 oxygen	... ...	3·32	0·73	0·85	1·39

    * R is the portion of the salt employed in the base-exchange, and r its radius in Å. The radius of Ba·· is about 1·31 Å. (W. H. Zachariasen, 1931).

    † Including 10·98 % BaSO₄ and 11·22 % TlI (by difference), impurities.

    ‡ Including 0·66 % BaSO₄, impurity.

    § Including 0·47 % BaSO₄, impurity.

    ‖ By difference.

    ¶ Including 22·02 % BaSO₄, impurity.

    ** Calculated after deduction of impurities.

    †† Birefringence very weak. Probable accuracy ±0·010.

    ‡‡ Probable accuracy, ±0·02 for Tl, ±0·04 for Na and K, ±0·04(?) for Ag derivatives.

    §§ Probable accuracy, ±0·05; hence, oxygen per unit cell, 156±3·5 atoms.

    ‖‖‖ Some of the BaSO₄ is included in the zeolite. If it were all included, the calculated sp. gr. would become 2·71. The figure of 2·21 corresponds to the zeolite free from inclusions.

By the action of sodium chlorate, a homogeneous product was obtained which gave a weak X-ray photograph. The unit cell has approximately doubled in each direction, compared to edingtonite, but unlike the potassium compound the odd layer-lines are not weak, and there is one very weak diffraction, (321), which does not correspond to a face-centred cell. Moreover, the c spacing is considerably less than twice that of edingtonite, whereas in all the base-exchange products of zeolites based on $(Al_2Si_3O_{10})''$ strings so far examined the dimension parallel to the strings is but little affected during base-exchange. The compound is provisionally classed as sodium pseudo-edingtonite, corresponding to the potassium compound; it would undoubtedly repay further study, but time did not permit of this.

All of these base-exchange products differ optically and in their X-ray photographs from the corresponding derivatives prepared from thomsonite or from any of the members of the mesotype group—natrolite, mesolite, and scolecite. Hence the structures must be different, the base-exchange work thus affording confirmation of the structural study of W. H. Taylor and R. Jackson (1933).

The synthesis of barium zeolites, supposed to be edingtonite, has twice been described. J. Lemberg (1876) treated potassium-natrolite with barium chloride, and obtained a compound of composition near that of edingtonite. But as natrolite and edingtonite differ structurally, this must have been a barium-natrolite, not an edingtonite, unless the zeolite had passed into solution and recrystallized. O. C. Magistad (1929) prepared a barium aluminosilicate by treating with barium chloride the precipitate obtained on mixing sodium silicate and sodium aluminate solutions. A 'concentrated water extract' of this barium compound was set aside, and 'several months later small crystals 1–4 mm. long were discovered, which upon analysis . . . were found to be eddingtonite' [sic]. This identification is hardly conclusive, and it would seem probable that an artificial production of edingtonite has yet to be performed.

Summary.

Edingtonites from Old Kilpatrick and from Böhlet have been shown to be essentially identical, small differences being due to an appreciable calcium content in the former. The unit-cell formula of edingtonite is $Ba_2Al_4Si_6O_{20}.8H_2O$. The cell dimensions have been determined for both Old Kilpatrick and Böhlet material which differ

appreciably.   In both cases there is good agreement between the goniometric and X-ray axial ratios.   The optical properties of both Old Kilpatrick and Böhlet material have been studied.   A new analysis of the latter gives results in agreement with the above formula.   The vapour-pressure of Böhlet edingtonite has been determined at various temperatures and degrees of hydration, and checked by a direct determination of the heat of hydration.   By base-exchange, thallous- and silver-edingtonites have been prepared, and also potassium and sodium compounds (pseudo-edingtonites), which have a unit cell approximately eight times as large as that of edingtonite.   None of these products is identical with the corresponding base-exchange products from the mesotypes or from thomsonite, in conformity with their essentially different structures.

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