Zeophyllite.

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Summary. A new analysis gives the formula $Ca_4Si_3O_{12}F_2H_6$; the specimen was from Alter Berg, Leitmeritz, Bohemia, and also contained apophyllite. The unit cell is triclinic, but all reflections can be indexed on a geometrically monoclinic cell which is c-face centred and has a 16·2, b 9·34, c 13·2 Å., β 113°, $Z = 6$, principal cleavage (001). This cell could also be described as having a hexagonal base of side 9·34 Å., but with c tilted through 23° from the vertical in the plane of one of the sides. A dehydration curve showed a step at 300–400° C., corresponding to loss of two-thirds of the water. The remaining water is lost between 400° and 940° C., together with some fluorine, the latter probably as HF. Crystals heated at 450–600° C. retain the hexagonal-based cell, but d_{001} shrinks from 12·1 to 11·1 Å. and there is evidence of much stacking disorder of layers normal to c. Single crystals heated at 700° C. show ordered transformation, giving cuspidine twinned in three orientations as the only recognizable product. At 940° C. a mixture is obtained, mainly β-$CaSiO_3$ with some β-Ca_2SiO_4.

ZEOPHYLLITE was discovered at Leitmeritz, Bohemia, by Pelikan (1902 *a* and *b*), associated with apophyllite and zeolites in cavities in basalt. Pelikan considered the composition to be $Ca_4Si_3O_{11}H_4F_2$. The crystals were lamellar, and from etch figures he concluded that they were trigonal with cleavage (0001). Optically they were uniaxial negative with ω near 1·52, though towards the edges the crystals appeared biaxial with 2E up to $27\frac{1}{2}$° (2V up to 17°). Some goniometric observations were recorded by Pelikan, and also by Koechlin (1934), both of whom believed that the crystals were probably rhombohedral. Larsen (1921) gives data for the uniaxial form: $\omega = 1·565$, $\epsilon = 1·560$. No X-ray studies have been reported.

The present investigation was made on crystals kindly provided by the Geology Department of Aberdeen University. The specimen was labelled: Zeophyllite, Alter Berg, Leitmeritz, Bohemia; Aberdeen 6186. Crushed material consisted of elongated flakes, which were striated parallel to their length (fig. 1). They were optically negative, with low birefringence. The refractive index for light vibrating in the cleavage

plane was 1·568–1·569. They gave negative acute bisectrix figures with 2V varying between 0° and 10° from one crystal to another. Their extinction was indefinite, but γ was approximately parallel to the length of the flake and α was roughly normal to the cleavage. The tips of some crystals were opaque and had a lower refractive index; X-ray results
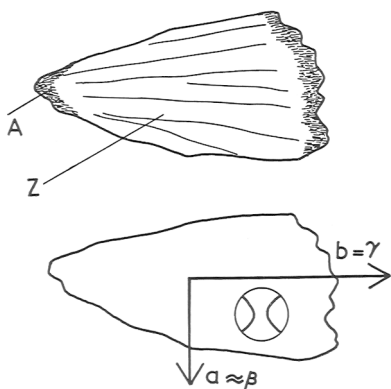

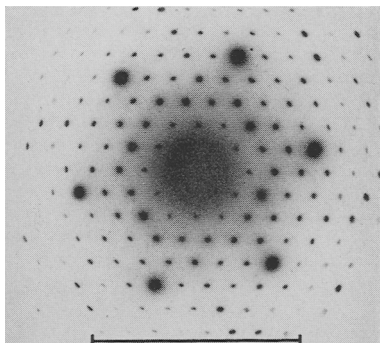Fig. 1.   Fig. 2.

FIG. 1. *Top*: sketch of typical flake. Z = Zeophyllite. A = Apophyllite. *Bottom*: optical orientation.

FIG. 2. Electron diffraction pattern from zeophyllite crystal lying with (001) normal to the beam. Horizontal line represents 1 Å.$^{-1}$.

indicated that these ends consisted partly or wholly of apophyllite. The general appearance of our specimen agreed with Pelikan's original description except for the value of ω, which is close to that given by Larsen. The identity of the material was also confirmed by the chemical analysis (discussed later; table II) and by the correlation of the X-ray results with the earlier goniometric data.

  X-ray and electron diffraction investigation. X-ray single-crystal photographs showed that the crystals were triclinic, although all reflections could be indexed on a *c*-face centred, geometrically monoclinic cell. Referred to the monoclinic axes, the photographs taken were oscillations about *b*, rotations about *b* and *c*, and *h0l*, *h1l*, *h2l*, *h3l*, *h4l*, and *hk0* Weissenbergs. Electron diffraction patterns of flakes lying with their cleavages perpendicular to the beam were obtained using a Metropolitan Vickers type EM3 electron microscope.

  The monoclinic cell has $a = 16·2$, $b = 9·34$, $c = 13·2$ Å., $\beta = 113°$, elongation *b*, cleavage (001). β was found less accurately than the 100 and 001 spacings; d_{100} was $14·80 \pm 0·05$ and d_{001} was $12·13 \pm 0·10$ Å. The

b-oscillations showed that the crystals were only geometrically mono-
clinic. A triclinic cell can be chosen with $a = b = 9\cdot34\pm0\cdot05$, $c = 13\cdot2\pm$
$0\cdot1$ Å., $\alpha = 90\cdot0°\pm0\cdot1°$, $\beta = 110°\pm2°$, $\gamma = 120°\pm0\cdot1°$. This cell can be
described as hexagonal with $a = 9\cdot34$ Å., and a tilted c-axis. The pseudo-
hexagonal character is shown by the electron diffraction patterns (figs.
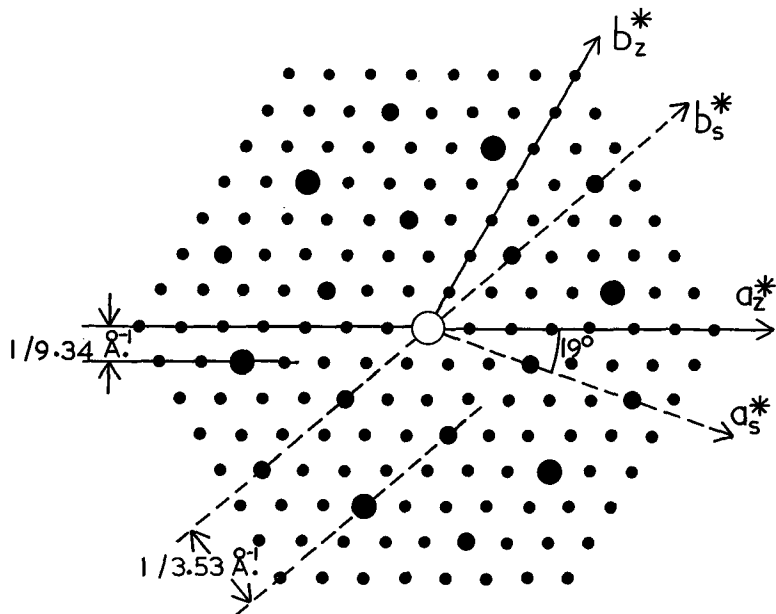2 and 3) which represent a projection of the $hk0$ section of the reciprocal

FIG. 3. Drawing from fig. 2, showing the relation of the sub-lattice formed by the
strong reflections to the reciprocal lattice of zeophyllite. a_z^*, b_z^*, projections on
(001) of triclinic reciprocal axes of zeophyllite. a_s^*, b_s^*, projections on (001) of
reciprocal axes of the sub-lattice.

lattice on (001). The strong reflections form a sub-lattice with pseudo-
hexagonal $a = 3\cdot53$ Å., which is similar to the a-axis of calcium
hydroxide (3·59 Å.).

X-ray powder data were obtained (table I) using 6 cm. and 11·46
cm. diameter cameras with Cu-$K\alpha$ radiation. It was found impossible
to select specimens entirely free from apophyllite. The apophyllite lines
were detected by comparison with standard photographs; also, in speci-
mens not too finely ground they were more spotty than the zeophyllite
lines. Removal of the opaque portions of the flakes before crushing
diminished the intensity of these lines but did not entirely eliminate

them. Lines due wholly or partly to apophyllite are asterisked in table I. An attempt was made to index the data, but to do so was impracticable for all but the longest spacings because of the large number of reflections

TABLE I. X-ray powder data.

d, Å.	I	d, Å.	I	d, Å.	I
12·03	vvs	2·832	mw	1·953	vvw
7·97	vw*	2·702	w	1·913	vw
6·09	s	2·648	ms	1·858	ms
4·66	vvw*	2·547	ms	1·832	w
4·36	w*	2·431	vw	1·771	s* (d)
4·05	mw	2·344	w	1·756	w
3·96	w*	2·305	vw	1·735	vvw
3·71	ms	2·248	mw	1·704	mw
3·31	vw	2·196	mw	1·625	m
3·20	m	2·159	vw	1·601	vvw
3·07	m	2·070	m	1·554	vw
3·03	vs	2·025	m	1·535	w
2·946	s	1·986	w*	1·517	vw

* Indicates lines due wholly or partly to apophyllite.

contributing to nearly all the lines; it was therefore not possible to refine the cell parameters by using the powder data.

Pelikan (1902b) observed faces inclined at 78° to (001) which he considered to be rhombohedral faces. Koechlin (1934) confirmed this and also found faces inclined at 90° and at about 63° to (001). The 78°, 90°, and 63° faces can be indexed respectively as (20$\bar{1}$), (010), and (100) on the pseudo-monoclinic axes. The calculated angles are 77°, 90°, and 67°.

Chemical analysis and cell contents. The results of a chemical analysis are given in table II, col. 2. They agree substantially with Pelikan's (col. 1) but suggest a higher water content. An X-ray powder diagram of the material analysed showed slight contamination with apophyllite, but the contamination was thought to be less than 5 % ; in view of the relatively similar compositions of the two minerals, the errors caused would not be large. The analysis was conducted on 2–25 mg. samples withdrawn from a total sample of about 100 mg. Silica was determined by the quinoline silicomolybdate method (Miller and Chalmers, 1953a); alumina was determined once gravimetrically with oxine (Miller and Chalmers, 1953b) and once colorimetrically by the calcium alizarin-red method (Parker and Goddard, 1950). The alkali metals were determined by flame photometry and lime and magnesia by titration with EDTA.[1] The experimental error in the lime determination precluded the accurate determination of the small amount of magnesia which was estimated to be not more than 0·5 %. Iron was tested for qualitatively and found to

[1] i.e. ethylene-diamine-tetra-acetic acid.

TABLE II. Chemical analyses and unit cell contents

|	1.	2		3.	4.	5.
SiO₂	38·84	36·0	Si	9·9	9·0	9
Al₂O₃	1·73	1·5	Al	0·5	0·4	—
Fe₂O₃	0·10	nil	Fe	0·1	nil	—
MgO	0·17	<0·5	Mg	0·1	<0·2	—
CaO	44·32	46·3	Ca	12·2	12·5	12
Na₂O	0·38	0·48	Na	0·2	0·2	—
K₂O	0·24	0·09	K	0·1	<0·1	—
H₂O	8·98	11·0	H₂O	7·7	9·2	9
F	8·23	7·49	F	6·7	6·0	6
			O (not as H₂O)	29·7	28·4	27
	102·99	102·9				
Less O for F	3·47	3·2				
	99·52	99·7				
Sp. gr.	2·763	2·747				

1. Pelikan (1902b). Analyst, E. Zdarek.
2. This investigation. Analyst, R. A. Chalmers.
3. Atomic cell contents calculated from analysis 1.
4. Atomic cell contents calculated from analysis 2.
5. Theoretical atomic cell contents for 3[Ca₄Si₃O₉F₂.3H₂O].

be absent. Fluorine was determined by a modified Willard and Winter distillation and spectrophotometric titration with thorium nitrate solution (Hollingworth, 1957). Total water was measured as the loss in weight of a sample fused with dry sodium tungstate, which was used as a flux and as a retainer for fluorine. Tests on opal glass (F = 5·7 %) indicated that sodium tungstate did act as a fluorine-retaining flux. A Penfield determination of water on a separate sample, using bismuth oxide as retainer for fluorine, gave a slightly higher result for the water content, but the sample used was found to have contained some apophyllite, which would account for the difference.

The specific gravity was determined by suspension in bromoform-benzene mixtures. The atomic contents of the triclinic cell, calculated using the present X-ray data, are approximately $Ca_{12}Si_9O_{27}F_6.9H_2O$ (table II, cols. 3-5).

Dehydration. A weight-loss curve (fig. 4) was obtained on a 50 mg. sample using a semi-micro balance. The partial pressure of water vapour in the furnace was 6 mm. Except for the range 595-805° C. inclusive, constant weight was normally reached at each temperature. This was impracticable between 595° and 805° C. because the specimen lost weight steadily at each temperature at the rate of 50–60 μg. per day. The total loss at 1000° C. exceeded that found using a fluorine retainer, and the difference was attributed to loss of fluorine, as HF or as SiF_4. If no fluorine is lost below 400° C., the initial sharp rise in the curve

corresponds to the loss of two-thirds of the water, the remaining water being lost, together with some of the fluorine, above this temperature. If these losses correspond to water present in the structure as H_2O and as OH respectively, the cell contents can be rewritten as

$$Ca_{12}(Si_9O_{24})(OH)_6F_6.6H_2O.$$
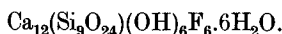
X-ray photographs were taken of samples withdrawn from the dehydration apparatus at 450°, 600°, 710°, 940°, and 1000° C. Powder photographs of the material heated to 450° or 600° C. showed diffuse patterns with a distribution of intensity generally resembling that of the original material. Oscillation, rotation, and $h0l$ Weissenberg photographs of the 450° C. product showed that traces of unaltered material were left, but that the main constituent was a partly disordered phase with d_{001} reduced from 12·13 to 11·1 Å. Non-basal reflections were almost continuous streaks parallel to c^*, indicating stacking disorder of layers parallel to (001). The electron diffraction patterns were identical with those of the original material except for some changes in intensity, and showed that triclinic a and b were unchanged. The X-ray photographs confirmed this. The cell may therefore be treated as hexagonal with a 9·34, c 11·1 Å.

The 600° C. product was similar but still more disordered. The a-axis was still unchanged, but c had shrunk to about 10·3 Å. Traces of the 450° C. product with c 11·1 Å. remained. Certain changes in the relative intensities of the (hk) reflections were noticed both in the 450° and 600° C. products.

The specimen heated at 710° C. gave X-ray patterns of cuspidine $(Ca_4Si_2O_7F_2)$; no other product could be detected. The change was ordered, the plane of the flake becoming cuspidine (012) or (01$\bar{2}$). The cuspidine was twinned in three orientations with a-axes coinciding with the three hexagonal axes of the strong sub-lattice of zeophyllite (figs. 2 and 3).

Powder specimens heated at 940° and 1000° C. gave X-ray patterns of β-$CaSiO_3$, with the strongest line of larnite.

Discussion. The present results confirm the earlier data for zeophyllite, except for the crystal system and the water content; the formula is shown to be $Ca_4Si_3O_8F_2(OH)_2.2H_2O$. A layer structure is indicated by the good basal cleavage, and especially by the behaviour on dehydration at 450° or 600° C., which can hardly be explained except on the assumption of distinct layers. Since the a- and b-axes remain unchanged at 450° and at 600° C., much of the structure in this plane must be preserved. It follows that the atoms are most probably arranged in layers from

which the elements of water can be lost without breakdown of the layers. Possibly the initial shrinkage of d_{001} to $11 \cdot 1$ Å. is connected with the loss of water molecules, and the second shrinkage to $10 \cdot 3$ Å. with the loss of hydroxyl groups. In both cases there is a successively closer
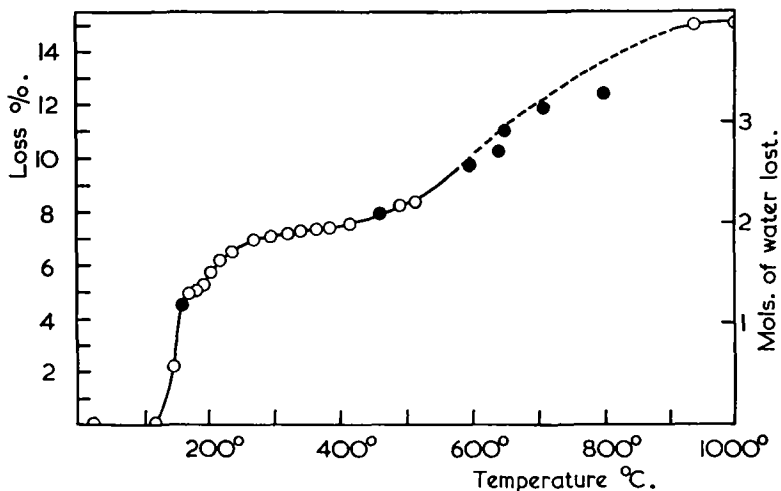

FIG. 4. Weight-loss curve for zeophyllite; partial pressure of water vapour, 6 mm. Open circles: equilibrium points. Solid circles: non-equilibrium points.

packing of the layers; at the same time there is loss of order in the stacking, which leads to the non-basal reflections becoming streaks parallel to c^*.

The ratio F:Ca is the same in cuspidine as in zeophyllite. This suggests that little or no fluorine is lost below 710° C.; in agreement with this the loss in weight at this temperature is approximately equal to the total water content. The stoichiometry of the dehydration process can therefore be written approximately as: $Ca_4Si_3O_8F_2(OH)_2.2H_2O \xrightarrow{\ 400°\,C.\ }$

$$Ca_4Si_3O_8F_2(OH)_2 + 2H_2O\uparrow \xrightarrow{\ 700°\,C.\ } Ca_4Si_2O_7F_2 + SiO_2 + H_2O\uparrow$$
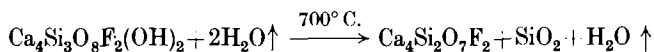
This scheme is somewhat similar to that proposed by Brindley (1952) for the dehydration of chlorites; in this case also the final product (olivine) was twinned in three orientations at 120° apart in the plane of the flake. In zeophyllite the water cannot be present in a hydrogen-bonded layer similar to that in montmorillonite, for the total shrinkage

is too small; the water, although fairly loosely bound, presumably fits into hollows in the main structural sheets.

The reaction at 700–1000° C. could be explained as:

$$Ca_4Si_2O_7F_2 + SiO_2 \longrightarrow \beta\text{-}CaSiO_3 + 1\tfrac{1}{2}\beta\text{-}Ca_2SiO_4 + \tfrac{1}{2}SiF_4\uparrow,$$

but this gives an expected total weight-loss of 22·1 %, against the observed 15·0 %. An alternative explanation is that water is re-absorbed from the air: $Ca_4Si_2O_7F_2 + SiO_2 + H_2O \longrightarrow 2\beta\text{-}CaSiO_3 +$ $\beta\text{-}Ca_2SiO_4 + 2HF\uparrow$. This is perhaps more likely, as it gives an expected weight-loss of 15·8 %, and a higher ratio of $\beta\text{-}CaSiO_3$ to $\beta\text{-}Ca_2SiO_4$ in the product, which agrees better with the X-ray result.

It seems likely that the hydroxyl present in zeophyllite is attached to calcium rather than to silicon, since it is not lost until about 600° C. (hydroxyl attached to silicon is usually lost below this temperature). If this is assumed to be so, the mineral contains silicon-oxygen sheets of empirical formula Si_3O_8. The triclinic cell contains three formula units, and consideration of its basal area suggests that there is a single Si_9O_{24} sheet in the height of the cell.

These considerations, together with the electron diffraction data, and the observed relation of orientations in the transformation to cuspidine, give some clues to the structure of zeophyllite. The sub-lattice of strong $(hk0)$ reflections (fig. 3) suggests that the heavy calcium ions may occur in a pattern similar in (001) projection to that of calcium hydroxide, and from the reasons outlined above it seems likely that the calcium ions may be present in sheets. To account for the pattern completely the orientation of such sheets relative to the Si–O sheets must be the same as that of the sub-lattice to the true lattice. The basal area of the zeophyllite cell is about seven times that of the calcium hydroxide cell, which contains a single calcium ion. The unit cell of zeophyllite with 12 calcium ions therefore probably contains two such sheets, one or both of which must in some way be defective in calcium.

The same conclusions may be reached by considering the transformation to cuspidine, the structure of which has been determined by Smirnova, Rumanova, and Belov (1955). The unit cell is monoclinic with a 7·53, b 10·41, c 10·83 kX, β 69° 56'. The Si_2O_7 groups have their long axes parallel to a, and there are bands of $Ca(O,F)_6$ octahedra parallel to (012) and (01$\bar{2}$) (fig. 5). These bands are equivalent to strips of calcium hydroxide sheets, without the hydrogen atoms and with partial replacement of oxygen by fluorine. The occurrence of three orientations in the cuspidine formed from zeophyllite confirms that the sheets in zeophyllite must have hexagonal or trigonal symmetry. Half

of the Ca-containing bands in the cuspidine could be formed directly from the calcium sheets in the zeophyllite; both the plane of the sheets and the orientation within the plane correspond. The observed relation of orientations in the transformation further suggests that the Si_3O_8 sheets in zeophyllite may be capable of giving Si_2O_7 groups with their long axes parallel to each of the a-directions in the sub-lattice.
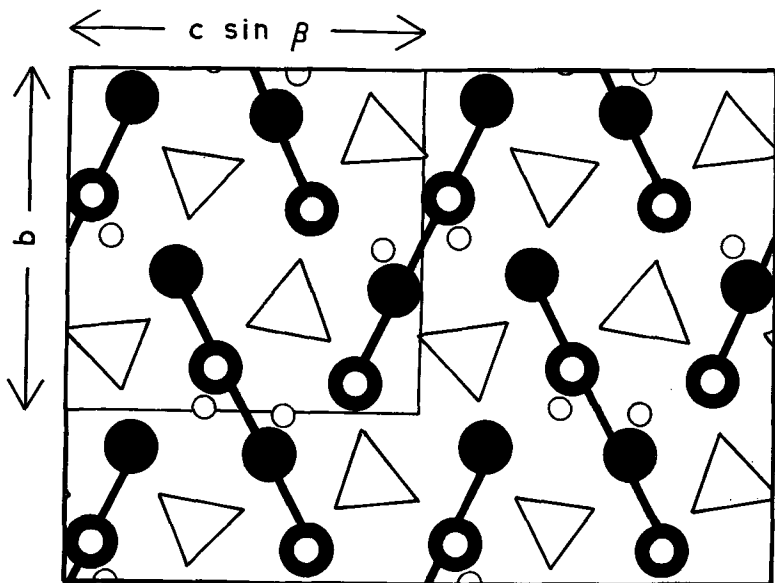

FIG. 5. Structure of cuspidine (after Smirnova, Rumanova, and Belov, 1955) projected on (100). Large full circles represent Ca ions at heights 0 and $\frac{1}{2}$; large open circles, Ca ions at heights $\frac{1}{4}$ and $\frac{3}{4}$; small circles, fluorine; triangles, Si_2O_7 groups viewed end-on; heights not indicated.

The empirical formula of the Si_3O_8 sheets could most obviously be attained by a fusion of rings of six and nine tetrahedra. Experiments with scale models suggested that the sheets might be of the form shown in fig. 6. The tetrahedra forming the six-membered rings are all at the same level, and are joined to each other by bridge tetrahedra at a different level. Points in favour of such a sheet include: the hexagonal base of the unit cell is of the right size, and bears the correct relationship to the postulated Ca–O sheets; portions of the Si–O sheets resemble the types of chain characteristic of calcium silicate minerals such as wollastonite, xonotlite, and tobermorite, with a repeat unit of three tetrahedra in a distance of 7·3 Å.; and Si_2O_7 groups in the correct orientation
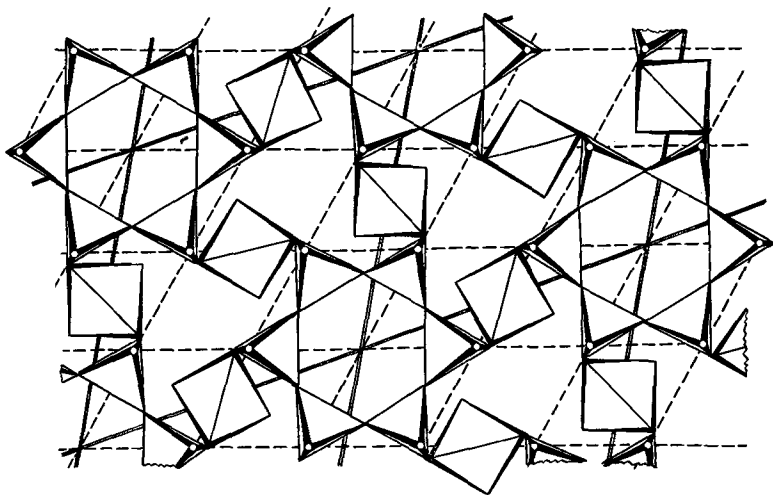
Fig. 6. Suggested arrangement of SiO_4 tetrahedra to give a sheet of empirical formula Si_3O_8. Heavy lines outline lattice of zeophyllite ($a = 9.34$ Å.); broken lines outline sub-lattice ($a = 3.53$ Å.).

for the formation of cuspidine can be selected from the six-membered rings.

It is hoped to test these hypotheses by a structural analysis.

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