

## The Crystal Structure of Zeophyllite

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Zeophyllite is rhombohedral, space group  $R\bar{3}$ , with a triple hexagonal cell having  $a=9.36$ ,  $c=36.48$  Å. The structure was solved by means of the symbolic addition method and refined by the least-squares method to a final  $R$  value of 0.096. The crystal structure is made up of layers consisting of a central sheet of calcium polyhedra sandwiched between two centrosymmetrically equivalent sheets of silicon tetrahedra and calcium polyhedra. These sheets are characterized by rings of twelve tetrahedra, and the centre of each ring is occupied by a group of three calcium polyhedra around a threefold axis. The three-sheet structural layers succeed each other in the  $c$  direction and are connected only by hydrogen bonds. The formula obtained for the specimen studied is  $(\text{Ca}_{12.1}\text{Al}_{0.7}\text{Mg}_{0.1}\text{Na}_{0.1})\text{Si}_{10}\text{O}_{28}\text{F}_{7.4}\text{O}_{0.6}(\text{OH})_{2.0} \cdot 6\text{H}_2\text{O}$ .

### Introduction

Zeophyllite is a calcium silicate discovered by Pelikan (1902*a, b*), associated with apophyllite and zeolites at Leitmeritz, Bohemia. The crystals have a micaceous appearance and Pelikan indicated they are trigonal with a cleavage (0001). By means of morphological studies, both Pelikan and Koechlin (1934) concluded that zeophyllite crystals are probably rhombohedral.

A comprehensive study of zeophyllite was made by Chalmers, Dent & Taylor (1956) on a sample from Alter Berg, Leitmeritz, Bohemia. They obtained unit-cell data by means of X-ray and electron diffraction, presented a new chemical analysis and a dehydration curve and studied, by X-ray diffraction methods, crystals heated at various temperatures from 450°C to 1000°C; they finally suggested a formula and a structural hypothesis for zeophyllite. They indicated a triclinic unit cell with  $a_t=b_t=9.34$ ,  $c_t=13.2$  Å,  $\alpha_t=90^\circ$ ,  $\beta_t=110^\circ$ ,  $\gamma_t=120^\circ$ , but observed that it could be described as hexagonal with  $a=9.34$  Å and a tilted axis, and remarked that the pseudo-hexagonal character was shown by the electron diffraction pattern from a crystal lying with the cleavage plane normal to the beam.

As regards the chemical composition, Pelikan (1902*b*) gave the formula  $\text{Ca}_4\text{Si}_3\text{O}_{11}\text{H}_4\text{F}_2$ . Chalmers *et al.* (1956), on the basis of the new chemical analysis and of the dehydration curve which showed a step at 300–400°C corresponding to the loss of two thirds of the water, proposed  $\text{Ca}_{12}\text{Si}_9\text{O}_{24}(\text{OH})_6\text{F}_6 \cdot 6\text{H}_2\text{O}$  as the cell content of zeophyllite.

### X-ray crystallography

For the present crystal structure determination a sample from Radzein, Bohemia was used. From X-ray

Weissenberg and precession photographs a trigonal symmetry was found and a rhombohedral cell was determined. The unit-cell data, referred to hexagonal axes, are:

$$a_{\text{hex}}=9.36, \quad c_{\text{hex}}=36.48 \text{ \AA}, \quad U_{\text{hex}}=2767.8 \text{ \AA}^3.$$

Space group:  $R\bar{3}$  or  $R3$ .

The corresponding rhombohedral single cell has parameters:

$$a_{\text{rh}}=13.31 \text{ \AA} \quad \alpha_{\text{rh}}=41^\circ 11' \quad U_{\text{rh}}=922.6 \text{ \AA}^3.$$

The hexagonal and rhombohedral cells are simply related to the triclinic cell assumed by Chalmers, Dent & Taylor\* (1956):  $a_t$  and  $b_t$  axes correspond to the  $a_{\text{hex}}$  and  $b_{\text{hex}}$  axes of the hexagonal cell and  $c_t$  axis corresponds to  $c_{\text{rh}}$  axis of the rhombohedral cell. It should be noted that the 'reverse' setting was adopted for the rhombohedral cell: thus the triple hexagonal cell has equivalent lattice points at  $\frac{1}{3}\frac{2}{3}\frac{1}{3}$  and  $\frac{2}{3}\frac{1}{3}\frac{2}{3}$ , and reflexions are present only for  $h-k+l=3n$ .

The transformation matrices from the triclinic to the rhombohedral and hexagonal unit cells are respectively [101/111/001] and [100/010/213].

### Data collection and reduction

For the intensity data collection, a cleavage fragment was cut to a nearly rectangular plate with dimensions  $0.77 \times 0.43 \times 0.0029$  cm. The data were collected by means of integrated Weissenberg photographs and the multiple-film technique. The crystal was rotated about

\* Professor Taylor has informed me that he and Dr Dent-Glasser have looked again at their original X-ray photographs and they agree that their specimen also is rhombohedral.

the  $b_{\text{hex}}$  axis; eight layers ( $k=0$  to 7) were taken using Cu  $K\alpha$  radiation ( $\lambda=1.5418 \text{ \AA}$ ) and 996 independent reflexions were observed. The intensities, measured on a Nonius microdensitometer, have been corrected for Lorentz and polarization factors; the absorption correction ( $\mu=88.6 \text{ cm}^{-1}$  for Cu  $K\alpha$  radiation) was made by computing the transmission factors by means of a program (Alberti, 1968) based on the Monte Carlo method proposed by Alberti & Gottardi (1966).

By means of the *DATFIX* program, incorporated in the *Crystal Structures Calculations System X-RAY 63* (Stewart, 1964), an overall isotropic temperature factor, the scale factors for the intensity data and the normalized structure factor magnitudes  $E$  were calculated. The method of calculation of the estimated parameters is based upon the normal statistics of the  $E$  magnitudes. The statistical averages and distribution of  $E$  are given in Table 1, in which they are compared with the theoretical values for both a centrosymmetric and a non-centrosymmetric distribution of atoms in the unit cell. The unobserved reflexions were given an intensity of one half the minimum observed intensity. The experimental values in Table 1 correspond to a crystal with a centre of symmetry; thus the space group  $R\bar{3}$  was assumed for zeophyllite and the choice was subsequently confirmed by structure analysis.

Table 1. *Statistical averages and distribution of E for zeophyllite*

	Experi- mental	Centro- symmetric	Non-centro- symmetric
$\langle  E  \rangle$	0.752	0.798	0.886
$\langle  E^2 - 1  \rangle$	1.098	0.968	0.736
$\langle  E^2  \rangle$	1.000	1.000	1.000
$ E  > 3$	0.6%	0.3%	0.01%
$ E  > 2$	5.6	5.0	1.8
$ E  > 1$	29.2	32.0	36.8

#### Determination and refinement of the structure

It was observed by Chalmers *et al.* (1956) that the strong  $hk.0$  reflexions form a sub-lattice with hexagonal  $a=3.53 \text{ \AA}$ , which is similar to the  $a$  axis ( $3.59 \text{ \AA}$ ) of  $\text{Ca}(\text{OH})_2$  (portlandite): the basal area of the zeophyllite cell is seven times that of portlandite. Thus, following their suggestion, some trials were made to solve the structure assuming two calcium ions sheets (six sheets in the triple hexagonal cell) variously stacked. The trials were, however, inconclusive and the reason, as will be seen from the following, lies in the fact that there is only one such sheet of seven calcium ions; moreover these seven ions are not exactly at the same level as there are differences in level of up to  $0.95 \text{ \AA}$ .

Direct methods were successfully applied to the

solution of the structures, using a program written by Hall (1966) and modified by Ahmed (1969). As the origin is specified in the space group  $R\bar{3}$  by assigning the phase to only one reflexion with  $l$  odd, a positive sign was given to the reflexion  $70\bar{7}$  ( $E=3.28$ ). The program then conveniently assigns symbols to other reflexions. The symbolic addition procedure was applied to the reflexions with  $E \geq 2.0$  and then extended to those with  $E \geq 1.5$ . At the end of the process, signs were obtained for 90% of the reflexions with  $E \geq 1.5$  in terms of only one symbol. Of the two three-dimensional  $E$  maps computed on the basis of the set of phases corresponding to the two possible choices of the sign of the unknown symbol, one was not interpretable. The other showed the required number of distinct maxima corresponding to the cations in the structure, as well as a number of lower peaks hardly distinguishable from the background.

From the positions of the distinct maxima, which on the basis of their heights were attributed to calcium or silicon atoms, and by making use of crystal chemical considerations, the positions of the oxygen and fluorine atoms were selected among the lowest peaks appearing in the  $E$  map.

A sound structure was thus obtained and three cycles of full-matrix least-squares refinement of the resulting set of parameters were computed by means of the *ORFLS* program (Busing, Martin & Levy, 1962) adapted to the *X-RAY 63* System (Stewart, 1964). The scale factors and individual isotropic temperature factors were included in the refined parameters. The  $R$  value for the observed reflexions was reduced to 0.12 ( $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ ).

Up to this point no distinction was made between the oxygen and fluorine atoms. At this stage, however, two temperature factors resulted negative and one more was positive but anomalously low: they corresponded to three supposed oxygen atoms, one in a general position and two in special positions along a threefold axis. This observation suggested a distribution of fluorine among these sites and the resulting distribution was very satisfactory from a crystal chemical point of view.

Two more refinement cycles were calculated and the following weighting scheme, based on the plot of  $\Delta F$  vs.  $F_o$ , was applied to all the observed reflexions:

$$|w| = (0.63|F_o| + 1.0)^{-1}.$$

The final  $R$  value was 0.096. The shifts in all parameters in the last cycle were well within the standard deviations, with an average  $\Delta/\sigma=0.04$ , where  $\Delta$  is defined as the change in a parameter in the last least-squares cycle and  $\sigma$  as the e.s.d. of the parameter in that cycle.

The atomic scattering factors for Ca, Si, O and F were taken from *International Tables for X-ray Crystallography* (1962).

The observed and calculated factors are compared in Table 2. Table 3 gives the final positional and thermal parameters with their standard deviations.

Table 2. Observed and calculated structure factors ( $\times 10^2$ )

h.k.l	Obs.	Calc.	h.k.l	Obs.	Calc.
2 310 -114	14 422	-1414	30 1710 -4430	2 002 933	3 211
4 242 -131	17 1542	-1522	30 1710 -4430	2 002 933	3 211
6 370 -196	21 2210	-2100	30 1710 -4430	2 002 933	3 211
8 500 -261	25 2878	-2868	30 1710 -4430	2 002 933	3 211
10 630 -326	29 3546	-3536	30 1710 -4430	2 002 933	3 211
12 760 -391	33 4214	-4204	30 1710 -4430	2 002 933	3 211
14 890 -456	37 4882	-4872	30 1710 -4430	2 002 933	3 211
16 1020 -521	41 5550	-5540	30 1710 -4430	2 002 933	3 211
18 1150 -586	45 6218	-6208	30 1710 -4430	2 002 933	3 211
20 1280 -651	49 6886	-6876	30 1710 -4430	2 002 933	3 211
22 1410 -716	53 7554	-7544	30 1710 -4430	2 002 933	3 211
24 1540 -781	57 8222	-8212	30 1710 -4430	2 002 933	3 211
26 1670 -846	61 8890	-8882	30 1710 -4430	2 002 933	3 211
28 1800 -911	65 9558	-9572	30 1710 -4430	2 002 933	3 211
30 1930 -976	69 1026	-1016	30 1710 -4430	2 002 933	3 211
32 2060 -1041	73 1094	-1084	30 1710 -4430	2 002 933	3 211
34 2190 -1106	77 1162	-1152	30 1710 -4430	2 002 933	3 211
36 2320 -1171	81 1230	-1220	30 1710 -4430	2 002 933	3 211
38 2450 -1236	85 1298	-1288	30 1710 -4430	2 002 933	3 211
40 2580 -1301	89 1366	-1356	30 1710 -4430	2 002 933	3 211
42 2710 -1366	93 1434	-1424	30 1710 -4430	2 002 933	3 211
44 2840 -1431	97 1502	-1492	30 1710 -4430	2 002 933	3 211
46 2970 -1496	101 1570	-1560	30 1710 -4430	2 002 933	3 211
48 3100 -1561	105 1638	-1628	30 1710 -4430	2 002 933	3 211
50 3230 -1626	109 1706	-1696	30 1710 -4430	2 002 933	3 211
52 3360 -1691	113 1774	-1764	30 1710 -4430	2 002 933	3 211
54 3490 -1756	117 1842	-1832	30 1710 -4430	2 002 933	3 211
56 3620 -1821	121 1910	-1900	30 1710 -4430	2 002 933	3 211
58 3750 -1886	125 1978	-1968	30 1710 -4430	2 002 933	3 211
60 3880 -1951	129 2046	-2036	30 1710 -4430	2 002 933	3 211
62 4010 -2016	133 2114	-2104	30 1710 -4430	2 002 933	3 211
64 4140 -2081	137 2182	-2172	30 1710 -4430	2 002 933	3 211
66 4270 -2146	141 2250	-2240	30 1710 -4430	2 002 933	3 211
68 4400 -2211	145 2318	-2308	30 1710 -4430	2 002 933	3 211
70 4530 -2276	149 2386	-2376	30 1710 -4430	2 002 933	3 211
72 4660 -2341	153 2454	-2444	30 1710 -4430	2 002 933	3 211
74 4790 -2406	157 2522	-2512	30 1710 -4430	2 002 933	3 211
76 4920 -2471	161 2590	-2580	30 1710 -4430	2 002 933	3 211
78 5050 -2536	165 2658	-2648	30 1710 -4430	2 002 933	3 211
80 5180 -2601	169 2726	-2716	30 1710 -4430	2 002 933	3 211
82 5310 -2666	173 2794	-2784	30 1710 -4430	2 002 933	3 211
84 5440 -2731	177 2862	-2852	30 1710 -4430	2 002 933	3 211
86 5570 -2796	181 2930	-2920	30 1710 -4430	2 002 933	3 211
88 5700 -2861	185 2998	-2988	30 1710 -4430	2 002 933	3 211
90 5830 -2926	189 3066	-3056	30 1710 -4430	2 002 933	3 211
92 5960 -2991	193 3134	-3124	30 1710 -4430	2 002 933	3 211
94 6090 -3056	197 3202	-3192	30 1710 -4430	2 002 933	3 211
96 6220 -3121	201 3270	-3260	30 1710 -4430	2 002 933	3 211
98 6350 -3186	205 3338	-3328	30 1710 -4430	2 002 933	3 211
100 6480 -3251	209 3406	-3396	30 1710 -4430	2 002 933	3 211
102 6610 -3316	213 3474	-3464	30 1710 -4430	2 002 933	3 211
104 6740 -3381	217 3542	-3532	30 1710 -4430	2 002 933	3 211
106 6870 -3446	221 3610	-3600	30 1710 -4430	2 002 933	3 211
108 7000 -3511	225 3678	-3668	30 1710 -4430	2 002 933	3 211
110 7130 -3576	229 3746	-3736	30 1710 -4430	2 002 933	3 211
112 7260 -3641	233 3814	-3804	30 1710 -4430	2 002 933	3 211
114 7390 -3706	237 3882	-3872	30 1710 -4430	2 002 933	3 211
116 7520 -3771	241 3950	-3940	30 1710 -4430	2 002 933	3 211
118 7650 -3836	245 4018	-4008	30 1710 -4430	2 002 933	3 211
120 7780 -3901	249 4086	-4076	30 1710 -4430	2 002 933	3 211
122 7910 -3966	253 4154	-4144	30 1710 -4430	2 002 933	3 211
124 8040 -4031	257 4222	-4212	30 1710 -4430	2 002 933	3 211
126 8170 -4096	261 4290	-4280	30 1710 -4430	2 002 933	3 211
128 8300 -4161	265 4358	-4348	30 1710 -4430	2 002 933	3 211
130 8430 -4226	269 4426	-4416	30 1710 -4430	2 002 933	3 211
132 8560 -4291	273 4494	-4484	30 1710 -4430	2 002 933	3 211
134 8690 -4356	277 4562	-4552	30 1710 -4430	2 002 933	3 211
136 8820 -4421	281 4630	-4620	30 1710 -4430	2 002 933	3 211
138 8950 -4486	285 4698	-4688	30 1710 -4430	2 002 933	3 211
140 9080 -4551	289 4766	-4756	30 1710 -4430	2 002 933	3 211
142 9210 -4616	293 4834	-4824	30 1710 -4430	2 002 933	3 211
144 9340 -4681	297 4902	-4892	30 1710 -4430	2 002 933	3 211
146 9470 -4746	301 4970	-4960	30 1710 -4430	2 002 933	3 211
148 9600 -4811	305 5038	-5028	30 1710 -4430	2 002 933	3 211
150 9730 -4876	309 5106	-5096	30 1710 -4430	2 002 933	3 211
152 9860 -4941	313 5174	-5164	30 1710 -4430	2 002 933	3 211
154 9990 -5006	317 5242	-5232	30 1710 -4430	2 002 933	3 211
156 10120 -5071	321 5310	-5300	30 1710 -4430	2 002 933	3 211
158 10250 -5136	325 5378	-5368	30 1710 -4430	2 002 933	3 211
160 10380 -5201	329 5446	-5436	30 1710 -4430	2 002 933	3 211
162 10510 -5266	333 5514	-5504	30 1710 -4430	2 002 933	3 211
164 10640 -5331	337 5582	-5572	30 1710 -4430	2 002 933	3 211
166 10770 -5396	341 5650	-5640	30 1710 -4430	2 002 933	3 211
168 10900 -5461	345 5718	-5708	30 1710 -4430	2 002 933	3 211
170 11030 -5526	349 5786	-5776	30 1710 -4430	2 002 933	3 211
172 11160 -5591	353 5854	-5844	30 1710 -4430	2 002 933	3 211
174 11290 -5656	357 5922	-5912	30 1710 -4430	2 002 933	3 211
176 11420 -5721	361 5990	-5980	30 1710 -4430	2 002 933	3 211
178 11550 -5786	365 6058	-6048	30 1710 -4430	2 002 933	3 211
180 11680 -5851	369 6126	-6116	30 1710 -4430	2 002 933	3 211
182 11810 -5916	373 6194	-6184	30 1710 -4430	2 002 933	3 211
184 11940 -5981	377 6262	-6252	30 1710 -4430	2 002 933	3 211
186 12070 -6046	381 6330	-6320	30 1710 -4430	2 002 933	3 211
188 12200 -6111	385 6398	-6388	30 1710 -4430	2 002 933	3 211
190 12330 -6176	389 6466	-6456	30 1710 -4430	2 002 933	3 211
192 12460 -6241	393 6534	-6524	30 1710 -4430	2 002 933	3 211
194 12590 -6306	397 6602	-6592	30 1710 -4430	2 002 933	3 211
196 12720 -6371	401 6670	-6660	30 1710 -4430	2 002 933	3 211
198 12850 -6436	405 6738	-6728	30 1710 -4430	2 002 933	3 211
200 12980 -6501	409 6806	-6796	30 1710 -4430	2 002 933	3 211
202 13110 -6566	413 6874	-6864	30 1710 -4430	2 002 933	3 211
204 13240 -6631	417 6942	-6932	30 1710 -4430	2 002 933	3 211
206 13370 -6696	421 7010	-7000	30 1710 -4430	2 002 933	3 211
208 13500 -6761	425 7078	-7068	30 1710 -4430	2 002 933	3 211
210 13630 -6826	429 7146	-7136	30 1710 -4430	2 002 933	3 211
212 13760 -6891	433 7214	-7204	30 1710 -4430	2 002 933	3 211
214 13890 -6956	437 7282	-7272	30 1710 -4430	2 002 933	3 211
216 14020 -7021	441 7350	-7340	30 1710 -4430	2 002 933	3 211
218 14150 -7086	445 7418	-7408	30 1710 -4430	2 002 933	3 211
220 14280 -7151	449 7486	-7476	30 1710 -4430	2 002 933	3 211
222 14410 -7216	453 7554	-7544	30 1710 -4430	2 002 933	3 211
224 14540 -7281	457 7622	-7612	30 1710 -4430	2 002 933	3 211
226 14670 -7346	461 7690	-7680	30 1710 -4430	2 002 933	3 211
228 14800 -7411	465 7758	-7748	30 1710 -4430	2 002 933	3 211
230 14930 -7476	469 7826	-7816	30 1710 -4430	2 002 933	3 211
232 15060 -7541	473 7894	-7884	30 1710 -4430	2 002 933	3 211
234 15190 -7606	477 7962	-7952	30 1710 -4430	2 002 933	3 211
236 15320 -7671	481 8030	-8020	30 1710 -4430	2 002 933	3 211
238 15450 -7736	485 8098	-8088	30 1710 -4430	2 002 933	3 211
240 15580 -7801	489 8166	-8156	30 1710 -4430	2 002 933	3 211
242 15710 -7866	493 8234	-8224	30 1710 -4430	2 002 933	3 211
244 15840 -7931	497 8302	-8292	30 1710 -4430	2 002 933	3 211
246 15970 -7996	501 8370	-8360	30 1710 -4430	2 002 933	3 211
248 16100 -8061	505 8438	-8428	30 1710 -4430	2 002 933	3 211
250 16230 -8126	509 8506	-8496	30 1710 -4430	2 002 933	3 211
252 16360 -8191	513 8574	-8564	30 1710 -4430	2 002 933	3 211
254 16490 -8256	517 8642	-8632	30 1710 -4430	2 002 933	3 211
256 16620 -8321	521 8710	-8700	30 1710 -4430	2 002 933	3 211
258 16750 -8386	525 8778	-8768	30 1710 -4430	2 002 933	3 211

Table 4. Bond lengths and angles with their standard deviations

## Silicon tetrahedra

Length			Angle		
Si(1)-O(1)	1.598	0.016 Å	O(1)-Si(1)-O(2)	111.8 [×3]	0.3°
Si(1)-O(2)	1.663 [×3]	0.007	O(2)-Si(1)-O(2 <sup>v</sup> )	107.1 [×3]	0.4
Si(2)-O(2)	1.646	0.010	O(2)-Si(2)-O(3)	98.0	0.4
Si(2)-O(3)	1.654	0.007	O(2)-Si(2)-O(5)	111.8	0.5
Si(2)-O(5)	1.616	0.008	O(2)-Si(2)-O(4 <sup>v</sup> )	114.4	0.4
Si(2)-O(4 <sup>v</sup> )	1.595	0.010	O(3)-Si(2)-O(5)	110.9	0.4
Si(3)-O(6)	1.608	0.014	O(3)-Si(2)-O(4 <sup>v</sup> )	113.2	0.4
Si(3)-O(3)	1.629 [×3]	0.008	O(5)-Si(2)-O(4 <sup>v</sup> )	108.3	0.5
			O(3)-Si(3)-O(6)	111.1 [×3]	0.3
			O(3)-Si(3)-O(3)	107.8 [×3]	0.4

## Calcium polyhedra

Length			Length		
Ca(1)-O(5)	2.359 [×6]	0.008 Å	Ca(3)-O(2)	2.690	0.008 Å
Ca(2)-O(4)	2.626	0.008	Ca(3)-O(3)	2.717	0.011
Ca(2)-F(1)	2.324	0.008	Ca(3)-O(4)	2.375	0.010
Ca(2)-F(2)	2.501	0.006	Ca(3)-O(7)	2.401	0.012
Ca(2)-O(6 <sup>III</sup> )	2.365	0.007	Ca(3)-F(1)	2.401	0.006
Ca(2)-F(1 <sup>IV</sup> )	2.350	0.007	Ca(3)-F(2)	2.521	0.006
Ca(2)-O(5 <sup>VI</sup> )	2.411	0.008	Ca(3)-F(3)	2.343	0.007
Ca(2)-F(1 <sup>VI</sup> )	2.301	0.005	Ca(3)-O(4 <sup>VII</sup> )	2.391	0.006
Ca(2)-O(5 <sup>VIII</sup> )	2.389	0.005			

## Hydrogen bonds

Length		
O(7)···O(1 <sup>I</sup> )	2.71 [×3]	0.02 Å
F(3)···F(3 <sup>II</sup> )	2.94	0.02

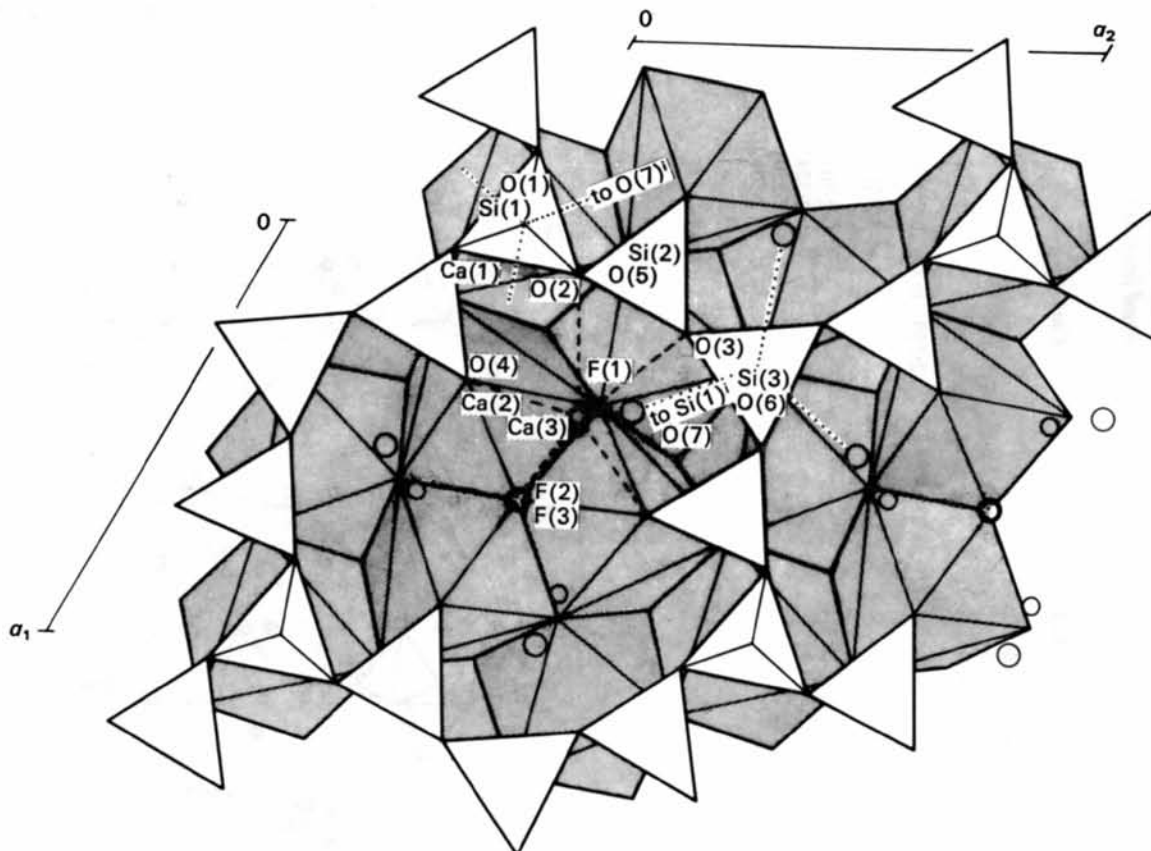
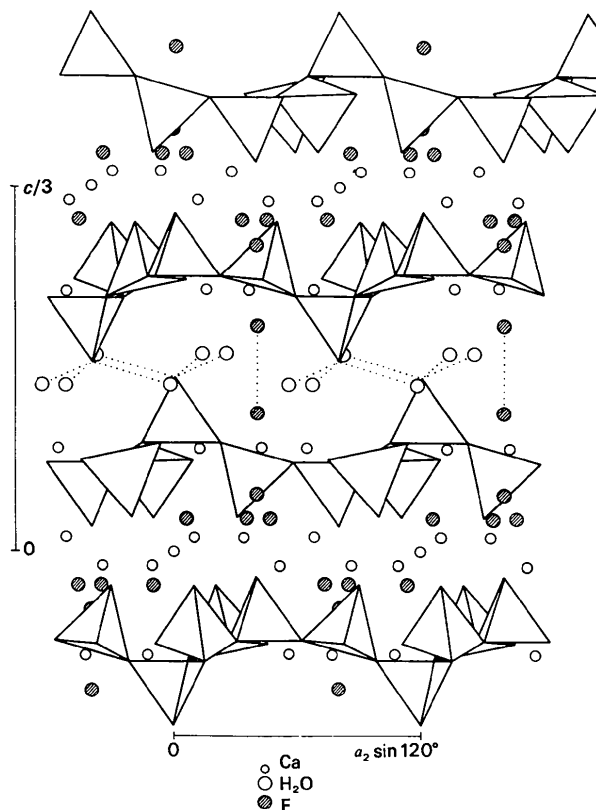
Fig. 1. (0001) Projection of the crystal structure of zeophyllite included in a slab between  $c=0$  and  $c=\frac{1}{2}$ . Bonds between Ca(3) and the coordinated atoms are indicated by dashed lines. Dotted lines indicate hydrogen bonds.

Table 5. Bond lengths (Å) and estimated bond valences in zeophyllite

Anions	Si(1)	Si(2)	Si(3)	Ca(1)	Ca(2)	Ca(3)	$\Sigma^{ev}$	Anion chemistry	$\Sigma^{ev}$ corrected for hydrogen bonds
O(1)	1.598	1.11					1.11	O <sup>2-</sup>	1.73 (1.86)
O(2)	1.663	0.97				0.18	2.690	O <sup>2-</sup>	2.11
O(3)		1.646	1.629	0.99		0.17	2.717	O <sup>2-</sup>	2.11
O(4)		1.654	1.07		2.626	0.29	2.375	O <sup>2-</sup>	1.82
O(5)		1.595	1.02	2.359	0.33	0.28	2.391	O <sup>2-</sup>	1.85
O(6)		1.616	1.04		{ 2.389	0.26	2.401	O <sup>2-</sup>	1.82
O(7)			1.608		{ 2.411	0.25		H <sub>2</sub> O	0.08 (0.03)
F(1)					{ 2.365 [×3]	0.26 [×3]	2.401	F <sub>0.85</sub> (OH) <sub>0.15</sub>	1.12
F(2)					{ 2.301	0.29	2.401	F <sub>0.7</sub> O <sub>0.3</sub>	1.38
F(3)					{ 2.324	0.28	2.521 [×3]	F <sub>0.5</sub> (OH) <sub>0.5</sub>	0.90
					{ 2.350	0.27	2.343 [×3]		
					{ 2.501 [×3]	0.22 [×3]			

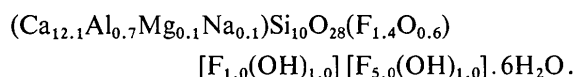
the results of crystal-structure analysis, which suggest the distribution of fluorine atoms; (b) of the chemical composition of the investigated specimen; (c) of crystal chemical considerations. Thus O(7) belongs to a water molecule. F(1), which is nearly tetrahedrally coordinated by four calcium ions, is a fluoride ion with possibly only a minor substitution by a hydroxyl ion. F(2) is trapped among six calcium cations; thus no hydrogen bonding can be invoked to modify the substantial deviation from an integer number of the valence sum (1.38) of bonds joining this anion. It was assumed that this position can be occupied by oxygen or fluorine atoms. The introduction of oxygen ions in this position requires the partial substitution of calcium by aluminum cations to maintain the balance of charges. The stoichiometry F<sub>0.7</sub>O<sub>0.3</sub> for the F(2) position was established by taking account of the valence sum of bonds joining this anion and of the chemical composition of the specimen. The F(3) position can correspond to a hydroxyl or a fluoride ion. Table 4 shows that a short approach exists between two centrosymmetrically related F(3) anions. In fact a hydrogen bond can be formed between the two F(3) anions if one is a hydroxyl and the other a fluoride ion; this implies the stoichiometry F<sub>0.5</sub>(OH)<sub>0.5</sub> for the F(3) position.

As regards O(1), Table 4 shows that it is engaged in three strong hydrogen bonds with three symmetrically

Fig. 2. The crystal structure of zeophyllite projected on a plane perpendicular to the  $a_1$  axis.

related water molecules. As it appears in the last column of Table 5, the valence sum of bonds reaching this anion, corrected for the contributions of the hydrogen bonds, is 1.73, which indicates that O(1) is an oxygen ion. The hydrogen bond valence strengths were estimated, by the procedure of Donnay & Allmann (1970), from the distances between the hydrogen bonded atoms. However, better valence sums for O(1) and O(7) are obtained if the values  $v=0.25$  for  $H \cdots O(1)$  and  $v=0.75$  for  $O(7)-H$  are assumed, according to the correlation between strength and length of hydrogen bonds given by Zachariassen (1963). These valence sum values are given, in parentheses, in the last column of the Table.

The formula which corresponds better to the chemical composition (reported in Table 6) of the specimen studied and to the results of the structural analysis is:



#### Calcium polyhedra sheet

In the central sheet of the calcium polyhedra there is a calcium ion Ca(1) in a special position on the origin and a calcium ion Ca(2) in a general position with sixfold multiplicity.

The Ca(1) ion is octahedrally coordinated by six equivalent oxygen anions with a bond length Ca(1)-O of 2.359 Å. The eightfold coordination polyhedron about Ca(2) can be described as a distorted triangular dodecahedron (Lippard & Russ, 1968). The bond lengths with their standard deviations are given in Table 4.

The Ca(1) octahedron shares six edges with Ca(2) polyhedra. Each Ca(2) polyhedron has four unshared

edges; nine edges are shared with another calcium polyhedron; four edges are shared with two calcium polyhedra and one edge with a silicon tetrahedron. These last contacts have the shortest lengths.

#### Sheet of silicon tetrahedra and calcium polyhedra

Two silicon tetrahedra, Si(1) and Si(3), are in special positions along threefold axes and share three oxygen atoms with Si(2) tetrahedra, which are in general positions and share only two oxygen atoms with Si(1) and Si(3) tetrahedra.

As can be seen from Fig. 1, the tetrahedra form infinite sheets characterized by rings of twelve tetrahedra. In the conventional classification of silicates developed by Bragg, zeophyllite should take its place among the sheet silicates, with a sharing coefficient of 1.60 according to Zoltai (1960) [or 2.40 according to a modified definition by Coda (1969)].

The centre of each ring of twelve tetrahedra is occupied by a group of three symmetry-equivalent calcium polyhedra disposed around a threefold axis. Also, this eightfold coordination polyhedron about Ca(3) can be described as a distorted triangular dodecahedron.

The bond lengths are reported in Table 4. It can be observed that the four independent non-bridging Si-O distances are shorter than the four bridging Si-O distances: their mean values are 1.602 and 1.648 Å respectively, with a highly significant difference.

As regards bond angles, Table 4 shows that the deviations from the ideal value of 109.5° do not exceed 2.4° for all the bond angles excepting O(2)-Si(2)-O(3), whose value is 98.0°. This low value is the result of two different concurrent causes. In fact, among the bond angles in the Si(2) tetrahedron, the lowest values (98.0°

Table 6. *Chemical analyses and unit cell contents*

	1	2	3	1a	2a	3a	
SiO <sub>2</sub>	38.82	38.84	36.0	9.87	9.92	9.15	
Al <sub>2</sub> O <sub>3</sub>	2.16	1.73	1.5	0.64	0.52	0.45	
Fe <sub>2</sub> O <sub>3</sub>	-	0.10	-		0.02		
MgO	0.26	0.17	< 0.5	0.09	0.06	< 0.19	} ~ 13
CaO	43.44	44.32	46.3	11.82	12.13	12.61	
Na <sub>2</sub> O	n.d.	0.32	0.48	(0.18)	0.18	0.24	
K <sub>2</sub> O	n.d.	0.24	0.09	(0.08)	0.08	0.03	
H <sub>2</sub> O	8.56	8.98	11.0	14.52	15.30	18.66	
F	9.48	8.23	7.49	7.62	6.65	6.02	
	<u>102.72</u>	<u>102.93</u>	<u>102.86</u>				
Less O for F	3.99	3.47	3.15				
	<u>98.73</u>	<u>99.46</u>	<u>99.71</u>				
Density	2.75*	2.764†	2.747‡				
	2.748§						

1 and 1a: Zeophyllite from Radzein, analysis by F. Cornu (Hibsch, 1917). Alkalies were not determined; in column 1a the unit-cell contents for sodium and potassium were assumed equal to those obtained for zeophyllite from Grosspriesen.

2 and 2a: Zeophyllite from Grosspriesen, analysis by E. Zdarek (Pelikan, 1902b).

3 and 3a: Zeophyllite from Leitmeritz, Alter Berg, analysis by R. A. Chalmers (Chalmers Dent & Taylor, 1956).

\* Hibsch (1917).

† Cornu (1905).

‡ Pelikan (1902b).

§ Chalmers, Dent & Taylor (1956).

and  $108.3^\circ$ ) correspond to the two opposite edges O(2) O(3) and O(5) O(4<sup>v</sup>) which Si(2) shares with the Ca(3) and Ca(2) polyhedra respectively. A similar situation exists in grossular, where the silicon tetrahedron shares two symmetry equivalent opposite edges O(1) O(2) with calcium dodecahedra, with an angle O(1)–Si–O(2) of  $102.5^\circ$  (Novak & Gibbs, 1971). However, the two shared edges in the Si(2) tetrahedron of zeophyllite are not equivalent because O(2) and O(3) are bridging oxygen atoms [Si(2)–O(2) 1.646, Si(2)–O(3) 1.654 Å], whereas O(5) and O(4<sup>v</sup>) are non-bridging [Si(2)–O(5) 1.616, Si(2)–O(4<sup>v</sup>) 1.595 Å]: the Si(2) atom is shifted toward the O(5) O(4<sup>v</sup>) edge, thus increasing the value of the O(5)–Si(2)–O(4<sup>v</sup>) angle and correspondingly reducing the value of the O(2)–Si(2)–O(3) bond angle.

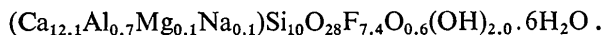
The Ca(3) polyhedron has nine unshared edges: four are shared with another calcium polyhedron, four are shared with two calcium polyhedra, and one with a silicon tetrahedron. As in the case of Ca(2) polyhedron, these last contacts present the shortest lengths.

Distances shorter than 3.0 Å between anions not bonded to the same cation indicate hydrogen bonding and are reported in Table 4.

In conclusion, as can be seen from Figs. 1 and 2, O(1), O(7) and F(3) are engaged in hydrogen bonds with O(7<sup>i</sup>), O(1<sup>i</sup>) and F(3<sup>ii</sup>) respectively, situated in a succeeding symmetry-related layer. The chemical nature of these anions has already been discussed in the section on anion chemistry.

### Crystal chemistry

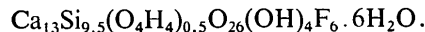
The three known chemical analyses of zeophyllite are reported in Table 6, together with the empirical unit-cell contents. It can be seen that the results of the chemical analyses of zeophyllite from Radzein, on which this structural study was undertaken, and of zeophyllite from Grosspriesen are very similar. Thus, for both specimens, the formula already given in preceding section can be assumed:



The presence of six water molecules is in agreement with the dehydration study of Chalmers *et al.* (1956).

As regards zeophyllite from Leitmeritz, which was analyzed and studied by Chalmers *et al.* (1956), its chemical composition appears to deviate measurably

from the formula given above. The deficiency in silicon and the increase in water content are the most apparent features. As the dehydration data of Chalmers indicate the presence of six water molecules in the rhombohedral unit cell, the excess water should appear as hydroxyl ions in the crystal structure. Thus a substitution of the type (O<sub>4</sub>H<sub>4</sub>) for (SiO<sub>4</sub>), as has been postulated for certain phyllosilicates, the hydrogarnets and others, can be assumed, leading to the following formula for zeophyllite from Leitmeritz:



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