

THE DETERMINATION OF THE STRUCTURE OF SEIDOZERITE

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The crystal structure of the Zr-Ti silicate seidozerite has been elucidated by superposition on the (x, z) Patterson projection and by statistical determination of the signs of the F_{0kl} reflections. From the structure the expanded chemical formula of seidozerite is given as $\text{Na}_4\text{MnTi}(\text{Zr}_{1.5}\text{Ti}_{0.5})\text{O}_2(\text{F}, \text{OH})_2[\text{Si}_2\text{O}_7]_2$ and its diorthosilicate nature (containing the group Si_2O_7) is revealed, despite the orthosilicate stoichiometric formula.

I. The new zirconium-titanium silicate seidozerite was discovered by E. I. Semenov in the Lovozerskii massif (Kol'skii P-ov) and was named after the place where it was first discovered, the Seidozero region [1]. In accordance with an analysis carried out by M. E. Kazakova, E. I. Semenov wrote the chemical formula of seidozerite in the form $\text{Na}_2(\text{Mn}_{0.5}\text{Ti}_{0.75}\text{Zr}_{0.75})\text{Si}_2\text{O}_8(\text{F}, \text{OH})$. The monoclinic symmetry of the mineral, which was fairly obvious from optical goniometry [1], was confirmed, first from Laue photographs and later from an analysis of x ray rotation photographs and moving films of the zero, first and second layer lines (Mo radiation) about the axes [100] and [010]. The systematic absences among the $h0l$ reflections, with $l = 2n + 1$, observed in the films, are of the Laue class $C_{2h} = 2/m$ (the unique axis being \underline{b} and the primitive ac parallelogram in the unique plane) and lead to the x ray group $2/mP\text{---}/c$ with a \underline{c} glide plane, i.e., to two possible space groups $C_3^2 = Pc$ and $C_{2h}^4 = P2/c$.

The parameters of the unit cell of seidozerite are: $a = 5.53 \pm 0.2$ A, $b = 7.10 \pm 0.03$ A, $c = 18.30 \pm 0.10$ A and $\beta = 102^\circ 43' \pm 1'$. The angle β was measured on an optical goniometer. This setting corresponds to the three pinacoids characteristically appearing in the habit of the crystals [1]. If we select as axes the two shortest translations in the plane of symmetry, we arrive at the setting $2/mP\text{---}/\bar{n}$ with the parameters: $a_1 = 5.53$, $b_1 = 7.10$, $c_1 = 17.90$ A and $\beta_1 = 85^\circ 19'$. The new axes are related to the old by the simple relationship
$$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 1 & 0 & 1 \end{pmatrix}$$

In the subsequent work we used the first setting which proved to be the most natural one in the analysis.

The conclusion that seidozerite was probably centrosymmetric, based on the crystal habit [1] and on the absence of a piezo effect (the experiments were kindly carried out by V. A. Koptsik), was confirmed by a statistical analysis of the intensities I_{h0l} by the method described in [2]. Another indication of centrosymmetry in seidozerite was obtained from the appearance in the Patterson projections of the characteristic trios of peaks described in [3]. We were therefore able to assign seidozerite, with reasonable certainty, to the holohedral group $P2/c = C_{2h}^4$.

From the density of seidozerite $d = 3.47$ (according to Semenov [1]) and from the volume of the unit cell, it appears that the latter contains 4 (3.87) formula units of $\text{Na}_2(\text{Mn}_{0.5}\text{Ti}_{0.75}\text{Zr}_{0.75})\text{Si}_2\text{O}_8(\text{F}, \text{OH})$.

Thus, in the unit cell of seidozerite, there are sited 3 Ti atoms and 3 Zr atoms in the space group $P2/c$, which contains only two-fold and four-fold positions (in the group Pc only two-fold), which leads to the interesting necessity, from a crystal- and geochemical standpoint, of filling certain crystallographically equivalent positions

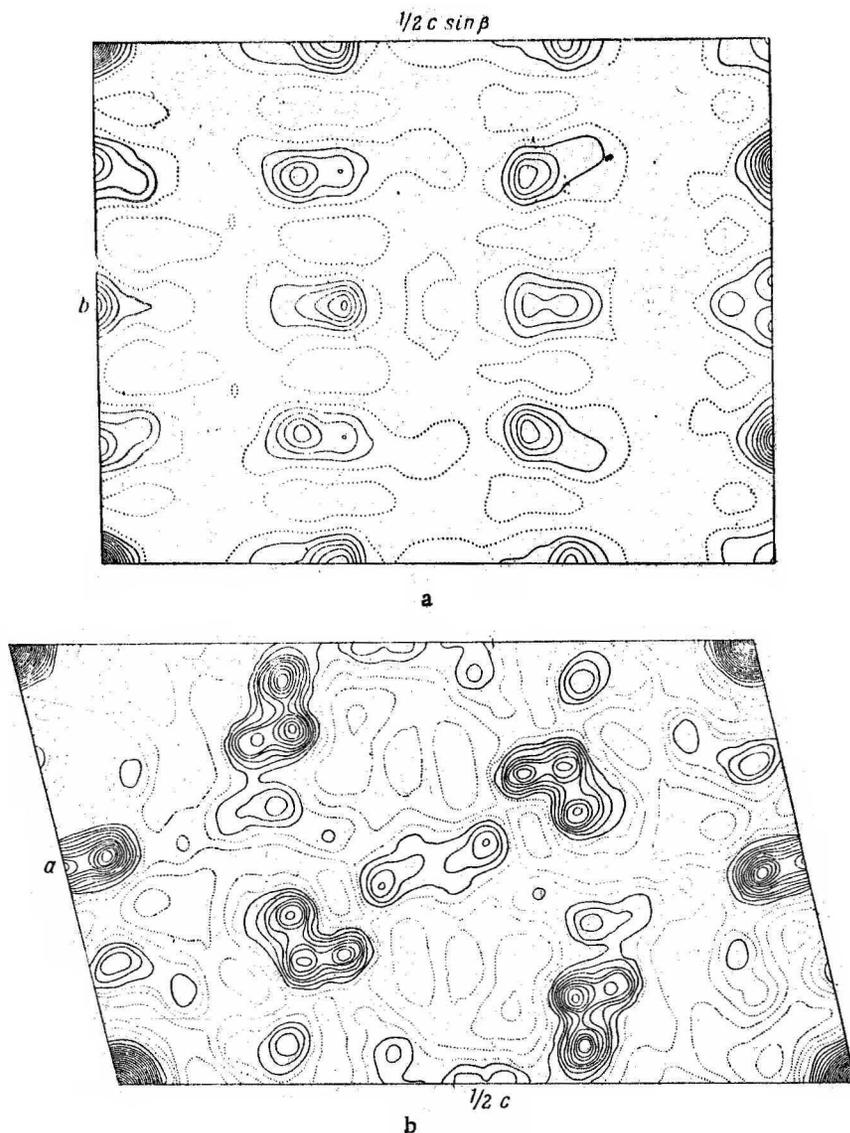


Fig. 1. Patterson projections for seidozerite: a) $p(y, z)$; b) $p(x, z)$.

by both Zr and Ti whose atomic radii differ by $\sim 30\%$ ($r_{\text{Ti}^{+4}} = 0.64$, $r_{\text{Zr}^{+4}} = 0.82$ Å). * Ti does not appear in the Fersman "star" of isomorphs for Zr [4], but it does occur persistently as such in all works on the Lovozerskii massif. Thus, the richest Zr lovenites may contain up to 30% of ZrO_2 , and a significant part of this, as much as half, is commonly replaced by TiO_2 [5].

E. I. Semenov attributed seidozerite to the velerite group which contains the following silicates of fairly complex structure [6]: velerite $(\text{Ca}, \text{Na})_3(\text{Zr}, \text{Nb})[\text{SiO}_4]_2\text{F}$, rosenbushite $(\text{Na}, \text{Ca})_3(\text{Fe}, \text{Ti}, \text{Zr})[\text{SiO}_4]_2\text{F}$, guarinite $\text{Ca}_2\text{NaZr}[\text{SiO}_4]_2\text{F}$ and lovenite $(\text{Na}, \text{Ca}, \text{Mn}^{++})_3\text{Zr}[\text{SiO}_4]_2\text{F}$. No crystal structure has as yet been found for any of the minerals listed. This fact, together with the large number of minerals of such elements as Zr, Ti and Nb made the structure analysis interesting, not only from the geo-(crystal-)chemical point of view, but also from a practical standpoint.

In the analysis of the structure of seidozerite, 378 nonzero $h0l$ and 331 $0kl$ reflections were used. The intensities were assessed visually and converted to $|F_{hkl}|$ in the usual way. Owing to the large size of the c

*For $r_{\text{Zr}^{+4}}$ we took the figure of Bokii and Belov of 0.82 Å. If the Goldschmidt value of $r_{\text{Zr}^{+4}} = 0.87$ is taken then the difference is as large as 36%.

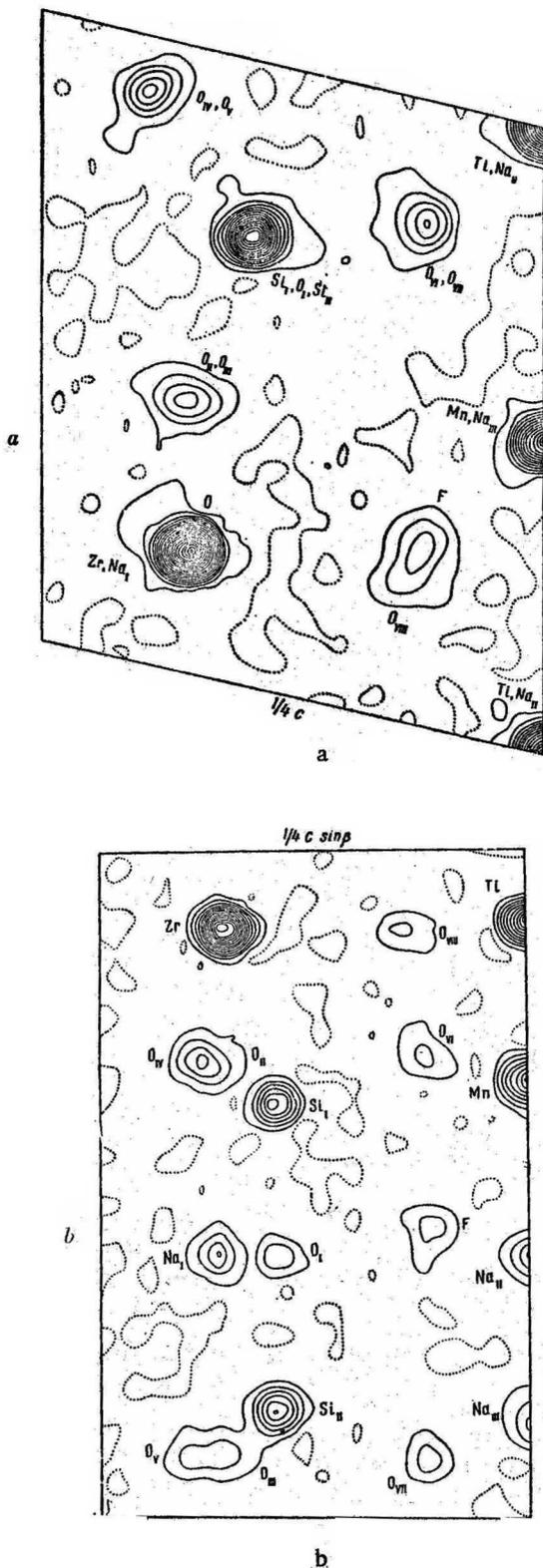


Fig. 2. Final electron density projections for seidozerite. a) $\rho(x, z)$; b) $\rho(y, z)$.

the minimalization. The results of the minimalization from all three vectors were used in the construction of the

axis, 15 reflections of low $\sin \theta / \lambda$ were obscured on the $h0l$ and $0kl$ moving films which were taken with Mo radiation, and their intensities were assessed from x ray photographs taken with Cu radiation. The linear absorption coefficient $\mu = V^{-1} \sum n_i \mu_i^a (\mu_i^a$ is the atomic absorption coefficient for $\lambda = 0.71 \text{ \AA}$ [7]), calculated for seidozerite, is 35 cm^{-1} . The $h0l$ zero layer line moving film was taken from a crystal with a roughly rectangular cross section $0.15 \times 0.20 \text{ mm}$. The $0kl$ reflections were measured from scattering from a crystal with cross section $0.3 \times 0.5 \text{ mm}$. No correction for absorption was applied in the structure determination. This introduces an error of up to 10% in the $|F_{h0l}|_{\text{obs}}$ and up to 17% in $|F_{0kl}|_{\text{obs}}$.

II. The Patterson projections $P(y, z)$ and $P(x, z)$ for seidozerite are shown in Fig. 1. It was hoped, owing to the presence of the heavy Zr ($Z = 40$), to find the Zr-Zr peaks and to carry out superpositions from them [8-13]. It was natural to begin with the Patterson projection down the shortest translation $p(y, z)$. The peaks on it are arranged at the points of an almost regular rectangular net $b/4 \times c/6$, and differ in height by a factor of not more than two. Because of this regularity, minimalization from any peak preserved, with changed heights, all the peaks in $p(y, z)$ and it was impossible to draw convincing conclusions as to the structure from $M(y, z)$.

Important results were obtained from the projection $p(x, z)$ where, because of the \underline{c} glide, the period along \underline{z} is halved. An analysis of the peak distribution in $p(x, z)$ made it possible to separate all the peaks into two types. Each peak of the first kind, with coordinates (x, z) corresponds to a peak at $(x + \frac{1}{2}, z)$, their heights differing by 10-15%. The peaks of the second kind, displaced by $(\frac{1}{2}, 0)$, have no mates. Such a peculiarity in the arrangement of the peaks, together with the fact that, there is a strong peak at the point of symmetry $(\frac{1}{2}, 0)$ in the projection, $p(x, z)$, (Fig. 1b), indicates the special position in the structure of seidozerite of two atoms with atomic numbers Z , differing by 10-15%. The only special positions are the translationally nonidentical points of symmetry (projections of centers of symmetry or of two-fold axes) separated by $a/2$. We met with an analogous regularity in the analysis of the structure of amblygonite [13] (and earlier still in the structure of epidote [17]).

The regularity in the Patterson functions of centrosymmetric crystals mentioned above [3] enabled us to find, in $p(x, z)$ two maxima with coordinates $(1.62, 0.36)$ and $(0.55, 0.29)$ corresponding to distances between the atoms related by a point of symmetry.

Besides these two vectors, a third $(\frac{1}{2}, 0)$ was used for

TABLE 1

Coordinates of the Atoms in the Asymmetric Unit of Seidozerite (in fractions of the axes a, b, c)

Atom	x	y	z	Atom	x	y	z
(4) Zr	0.200	0.119	0.074	(4) O _{II}	0.438	0.327	0.070
(2) Mn (Mg)	0.500	0.350	0.250	(4) O _{III}	0.438	0.907	0.071
(2) Ti	0.000	0.111	0.250	(4) O _{IV}	0.908	0.318	0.050
(4) Si _I	0.718	0.384	0.104	(4) O _V	0.915	0.912	0.056
(4) Si _{II}	0.718	0.843	0.104	(4) O _{VI}	0.804	0.314	0.191
(4) Na _I	0.195	0.611	0.069	(4) O _{VII}	0.804	0.915	0.192
(2) Na _{II}	0.000	0.613	0.250	(4) O _{VIII}	0.243	0.121	0.185
(2) Na _{III}	0.500	0.860	0.250	(4) (F,OH)	0.294	0.570	0.193
(4) O _I	0.719	0.615	0.105				

TABLE 2

Valency Balance in the Seidozerite Structure

Anion	Cation								Sum of valencies
	Si _I	Si _{II}	Zr	Ti	Mn	Na _I	Na _{II}	Na _{III}	
O _I	4/4	4/4							2
O _{II}	4/4		4/6			1/6			2 - 1/6
O _{III}		4/4	4/6			1/6			2 - 1/6
O _{IV}	4/4		4/6			2/6			2
O _V		4/4	8/6			1/6			2 + 1/2
O _{VI}	4/4			4/6	2/6		1/6		2 + 1/6
O _{VII}		4/4		4/6			1/6	1/6	2
O _{VIII}			4/6	4/6	2/6			1/6	2 - 1/6
(F,OH)					2/6	1/6	1/6	1/6	1 - 1/6

function $M6(x, z)$, which also gave the preliminary planar model of the structure. The refinement of the model was carried out by the subsequent calculation of the signs of the F_{h0l} s and the calculation of the electron density projection $\rho(x, z)$ (Fig. 2a).

One of the lines of symmetry in the (y, z) projection of the space group $P2/c$ contains a glide, which facilitates the use of a statistical testing method [14].

The sign relationships of a basic group of reflections were found as the first stage of testing in the determination of the signs of the $0kl$ reflections of seidozerite, and the Zachariasen equation was systematically applied to find the signs of all the F_{0kl} as the second stage.

As is usual, the sign relationships arising from the structure factor formulae were used as a basis for the comparison of the amplitudes. For the $0kl$ zone of $P2/c$ these relationships are as follows: 1) $l = 2n - F_{0kl} = F_{0k\bar{l}} = F_{0k\bar{l}}$; 2) $l = 2n + 1 - F_{0kl} = -F_{0k\bar{l}} = -F_{0k\bar{l}} = F_{0k\bar{l}}$.

The 70 strongest unitary structure amplitudes were included out of the 331 nonzero $0kl$ in the basic group. A sign was considered as found if, in the general number of pairs being determined $n > 3$ the ratio of the number of pairs indicating the given sign to n was $w \geq 0.75$ (for $n = 3$ it was necessary to take $w = 1.0$). Under these conditions the signs of 264 of the 331 nonzero $0kl$ were determined.

The electron density projection $\rho(y, z)$ was constructed from the F_{0kl} with these "statistical" signs. In analyzing it we relied on the previously constructed $\rho(x, z)$ the reliability of which was attested by the good agreement between the observed and calculated F_{h0l} .

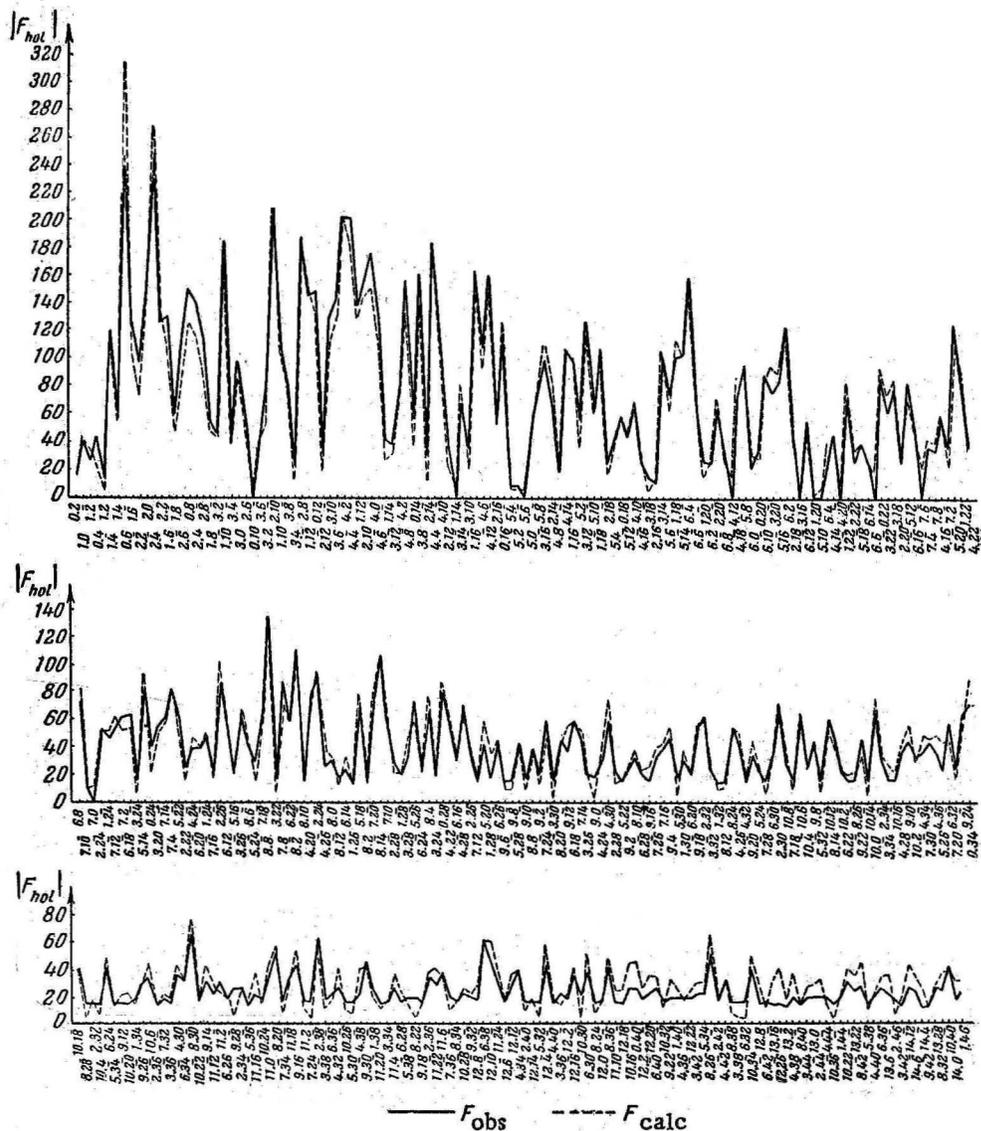


Fig. 3b. Graphical representation of the agreement between F_{obs} and F_{calc} for the $h0l$ zone.

subgroup of reflections. Consequently the basic group must be such that it contains reflections whose contribution to the intensity from a given atom in the structure is important.

The y coordinates of the cations were determined from $\rho(y, z)$ with the help of the known z coordinates from $\rho(x, z)$ and the positions of the lighter anions were indicated so that it was possible to refine the projection by means of successive calculations of the signs of the F_{0kl} and of synthesis $\rho(y, z)$.

The final electron density projections for seidozerite are shown in Fig. 2.

The interesting problem, from the point of view of crystal chemistry and mineralogy, of the isomorphous replacement in seidozerite had to be answered before the final variant of the structure could be selected. A comparison of the precise chemical analyses [1] with the heights of the maxima in the two electron density projections, and with the interatomic distances, led to the following picture of the isomorphous substitutions in seidozerite: $-2Zr(1.44 Zr + 0.50 Ti)$; $Mn(0.46 Mn + 0.34 Mg + 0.10 Fe^{2+})$; $Ti(0.76 Ti + 0.04 Nb + 0.10 Al + 0.09 Fe^{3+})$; $4 Na(3.58 Na + 0.38 Ca)$. The values shown in brackets to two significant figures are based primarily on the chemical analysis by Kasakova [1] and not on the heights of the electron density peaks.

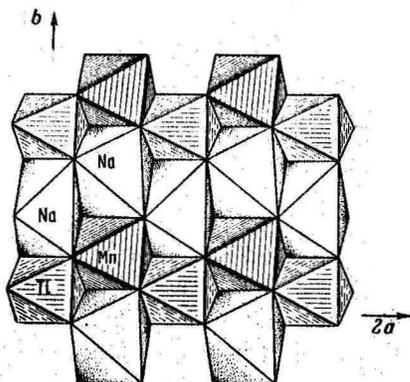


Fig. 4. Scheme showing the alternation of octahedra of different cations (Ti, Na II, Mn, Na III) in the continuous wall of seidozerite.

may not correspond to reality, but the symmetrical form of the peaks argues in favor of the reasonable closeness of the coordinates of the overlapping atoms. As the a axis is the shortest in seidozerite, an error in the relative x coordinate has less influence on the accuracy of the interatomic distances than one in the y or z coordinates.

F_{h0l} and F_{0kl} were calculated from the coordinates in Table 1 and f_{eff} , and a comparison of their absolute magnitudes with F_{Obs} is shown in Figs. 3a and 3b. The discrepancies for the structure are, including all reflections $h0l$ and $0kl$, ($F_{\text{Obs}} \neq 0$ to $\sin \theta / \lambda \leq 1.30$ and $F_{\text{Obs}} = 0$ out to $\sin \theta / \lambda \leq 0.66$), are 17.2 and 22.5% respectively. Excluding the reflections with $F_{\text{Obs}} = 0$ these values are 16.6 and 20.7%. The difference in the indexes for the two zones may be explained by the different effect of neglecting absorption on the $h0l$ and $0kl$ reflections.

The valency balance, according to Pauling's Second Rule (for ionic crystals) is given in Table 2. The greatest divergence in the sum of the valency strengths from the norm is observed for O_V . Formally, the excess of positive valencies is equal to 25% (a value which we may assume is the maximum possible) but in fact it is less because of the noticeably enlarged interatomic distance $Zr-O_V^*$ (Table 3).

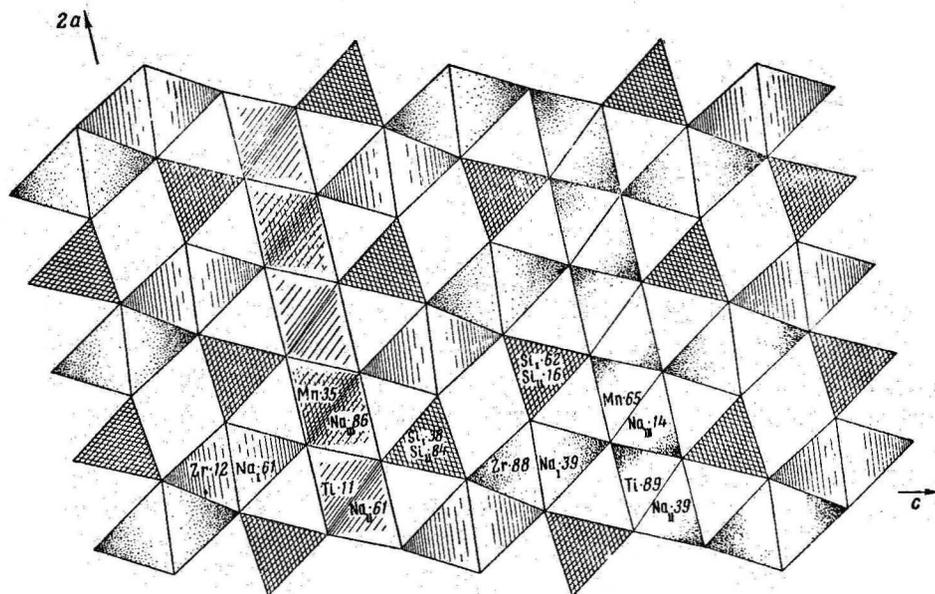


Fig. 5. Plan of the structure of seidozerite in coordination polyhedra. The (x, z) projection is perpendicular to the long axis of the crystal, the y coordinates of the cations are given in hundredths of the b axis.

The effective atomic scattering functions were calculated, as general averages from the corresponding individual atom factors, for each of the crystallographically occupied positions. The F_{h0l} and F_{0kl} whose signs were used in the calculation of $\rho(x, z)$ and $\rho(y, z)$ where, in the first projection, the cell edges were divided into 60 parts along a and 120 along c , and in the second both b and c were divided into 100 parts, were calculated using these f_{eff} .

The coordinates of the 17 atoms in the asymmetric unit of seidozerite (43 parameters), obtained by graphical interpolation, are given in Table 1.

The accuracy in the localization of the atoms from the projection was assessed, after Vainshtein [15], as: $Zr \pm 0.001 \text{ \AA}$, $Mn \pm 0.002 \text{ \AA}$, $Ti \pm 0.003 \text{ \AA}$, $Si \pm 0.004 \text{ \AA}$, $Na \pm 0.005 \text{ \AA}$, $O \pm 0.009 \text{ \AA}$. It must be mentioned that all the x coordinates were taken from $\rho(x, z)$ in which there are no single peaks. The pair similarity of the x coordinates for some of the overlapping atoms (Table 1)

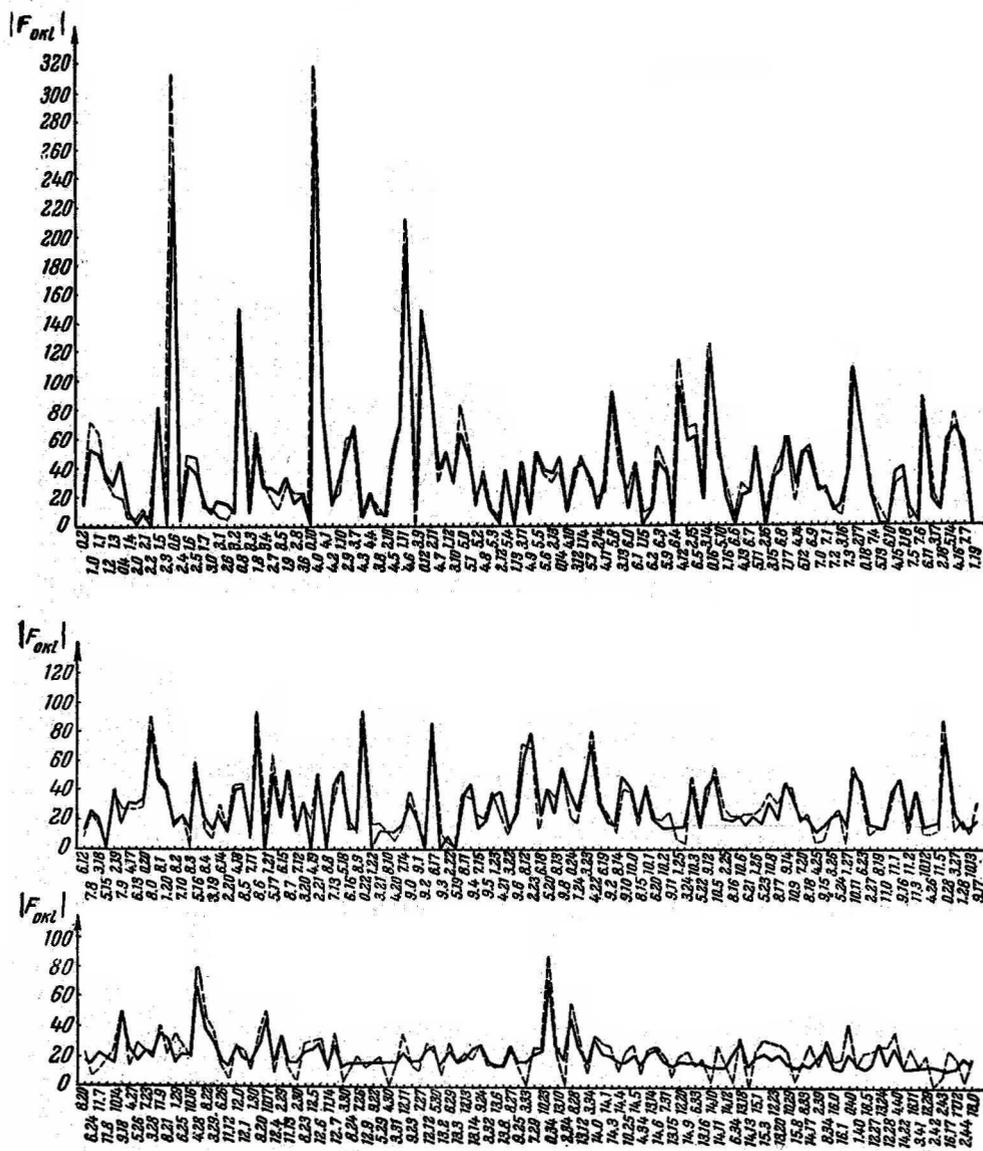


Fig. 3a. Graphical representation of the agreement between F_{Obs} and F_{Calc} for the $0kl$ zone.

The $\rho(y, z)$ synthesis showed a detrimental influence on the statistics of the geometrical regularity in the arrangement of the atoms in the (y, z) projection of seidozerite of which we spoke in the analysis of $p(y, z)$. This regularity defeated the superpositions on $p(y, z)$ and accounts for the fact that the statistics gave a large number ($\sim 25\%$) of wrong signs.

The presence in (y, z) of atoms lying at the points of an almost regular rectangular net $b/4 \times c/6$, which appeared so clearly in $p(y, z)$, is also visible in $\rho(y, z)$ (according to the statistical signs) with a strong heightening of the maxima on the two-fold axes.

Clearly, the most powerful $0kl$ reflections will be those for which the radiation scattered from the atoms lying at the points of the net $b/4 \times c/6$, is in phase. It is just those reflections which were used in the basic group used in determining the signs of all the F_{0kl} . This is the reason why, in $\rho(y, z)$ (calculated with the signs determined by the statistical method) maxima are lacking for the atoms which are not contained in the $b/4 \times c/6$ net. The inclusion in the basic group only of reflections of strong unitary structure amplitude, representing a certain condensed subgroup of reflections, materially shortens the labor involved in using the testing method, but it leads to signs from which the electron density map shows only those atoms which give rise to the indicated

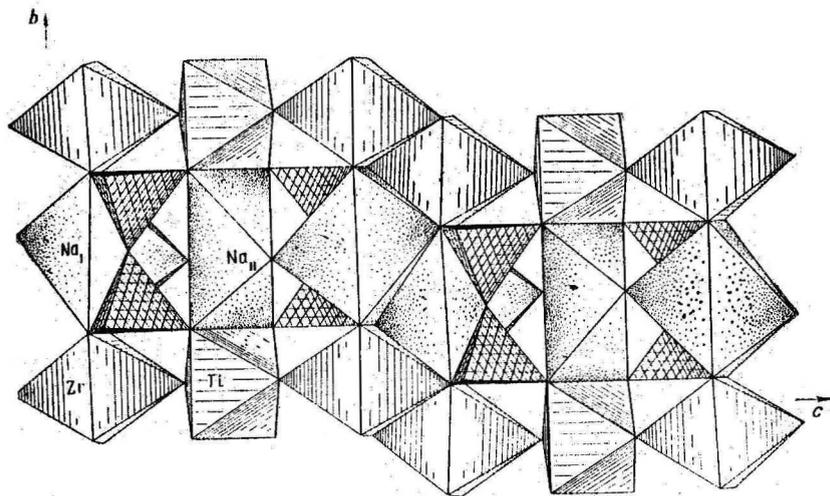


Fig. 6. The structure of seidozerite in coordination polyhedra. The (y, z) projection, omitting the columns of Mn^{II} , Na^{III} , Mn^{II} , Na^{III} octahedra which lie behind (in front of) the corresponding columns of Ti^{II} , Na^{II} , Ti^{II} , Na^{II} octahedra and are displaced relative to the latter by $b/4$ (Fig. 4).

III. Both the minerals from the Institute of Crystallography, ilvaite ($CaFe_2^{II}Fe^{III}O_7[Si_2O_7]OH$) [16], epidote ($Ca_2Al_2FeO[Si_2O_7][SiO_4]OH$) and zorsite ($Ca_2Al_3O[Si_2O_7][SiO_4]OH$) [17, 18], and seidozerite, are, despite their orthosilicate stoichiometric formulae, diorthosilicates with $[Si_2O_7]$ groups and not $[SiO_4]$ groups. The eighth oxygen atom figuring in the chemical formula does not enter into the silicate radical.

In accordance with the structure found, the expanded formula of seidozerite must be written (doubling the stoichiometric formula) as $Na_4MnTi(Zr_{1.5}Ti_{0.5})O_2(F, OH)_2 [Si_2O_7]_2$, there being two such units in the cell.

The most characteristic feature of the architecture of seidozerite is the infinite compact walls of octahedra arranged along the two-fold axes. Cations of Mn (Mg), Ti and Na alternate in the octahedra according to the motif in Fig. 4. The parallel xOy planes of the wall are at a distance $c/2$ from one another and are connected to each other by infinite double ribbons extended along y and consisting of alternating Zr and Na octahedra. These architectural details are clearly visible in Fig. 5, which shows a plan of the structure in projection parallel to the long axis of the crystal. Two isolated diortho groups are each situated between the walls and the ribbons. Their axes are parallel to the y axis and the angle $Si_I-O_1-Si_{II}$ is 180° within the limits of accuracy of our measurements. The three intercepts uniting the corresponding O atoms of the upper and lower bases of the $[Si_2O_7]$ group are the edges of the three Na octahedra (Fig. 6), i.e., the diortho groups are situated not only between the walls and the ribbons, but between the Na octahedra.

In cuspidine $Ca_4[Si_2O_7]F_2^*$ and tillevite $Ca_5[Si_2O_7](CO_3)_2$ [19] the diortho groups are linked in the same way with the Ca octahedra.

A further comparison of seidozerite with these Ca diorthosilicates is interesting. Tilleyite is made up of Ca octahedra in double (in width) infinite ribbons in two orientations. In cuspidine the analogously oriented ribbons of Ca octahedra are fourfold, and in seidozerite half the ribbons of one of the cuspidine orientations become infinite walls reinforced by tilleyite ribbons of the other orientation. The walls and ribbons are composed of columns in which the octahedra lie one on top of the other on edge, and in which, as is characteristic of a large number of Ca silicates [19], there are two octahedra in the 7.10 \AA b spacing. In tilleyite and cuspidine all the octahedra are occupied by Ca and in the ribbons and walls of seidozerite three kinds of Na octahedra alternate with Zr, Ti and Mn octahedra, and each time the Na_I , Na_{II} and Na_{III} octahedron, corresponding to the less tightly bound cations, is distorted, lengthening and shortening its edges so as most easily to enter the ribbon of octahedra round the more tightly bound atoms.

As was shown above, E. I. Semenov assigned seidozerite to the velerite group. According to the data given in the well known Mineralogical Tables of Strunz [20], these minerals are characterized by unit cell parameters which are similar to the parameters of cuspidine ($P2_1/c$, $a = 7.53$, $b = 10.41$, $c = 10.83 \text{ \AA}$) [21]. The 7.19-7.33 \AA

*As in Original — Publisher's note.

TABLE 3

Interatomic Distances in the Seidozerite Structure in A

Si _I - tetrahedron	Si _{II} - tetrahedron	Ti - octahedron
Si _I - O _I 1.64	Si _{II} - O _I 1.62	Ti - O _{VI} 1.98
Si _I - O _{VI} 1.63	Si _{II} - O _{VII} 1.66	Ti - O _{VII} 1.93
Si _I - O _{II} 1.62	Si _{II} - O _{III} 1.60	Ti - O _{VIII} 1.98
Si _I - O _{IV} 1.66	Si _{II} - O _V 1.62	O _{VI} - O _{VIII} 2.71 (Mn)
O _I - O _{II} 2.56	O _{III} - O _V 2.71	O _{VI} - O _{VI} 2.71 (Na _{II})
O _{VI} - O _{II} 2.65	O _I - O _{VII} 2.64	O _{VII} - O _{VII} 2.68 (Na _{II}) ^λ
O _I - O _{IV} 2.58	O _I - O _{III} 2.58	O _{VIII} - O _{VII} 3.06 (Na _{III})
O _{VI} - O _{IV} 2.52	O _I - O _V 2.63	O _{VI} - O _{VII} 2.84
O _I - O _{VI} 2.63	O _{III} - O _{VII} 2.65	O _{VIII} - O _{VI} 2.82
O _{IV} - O _{II} 2.70	O _V - O _{VII} 2.69	O _{VIII} - O _{VII} 2.86
Mn - octahedron	Na _{II} - octahedron	Na _{III} - octahedron
Mn - O _{VI} 2.21	Na _{II} - (F,OH) 2.14	Na _{III} - (F,OH) 2.48
Mn - O _{VIII} 2.31	Na _{II} - O _{VI} 2.52	Na _{III} - O _{VII} 2.21
Mn - (F,OH) 2.08	Na _{II} - O _{VII} 2.51	Na _{III} - O _{VIII} 2.47
O _{VIII} - O _{VIII} 3.28 (Na _{III})	O _{VI} - (F,OH)* 2.95 (Mn)	O _{VII} - O _{VIII} 3.28 (Mn)
(F,OH) - (F,OH)* 2.73 (Na _{II})	O _{VI} - O _{VI} 2.71 (Ti)	(F,OH) - (F,OH)* 2.73 (Mn)
O _{VIII} - (F,OH) 3.22	O _{VII} - O _{VII} 2.68 (Ti)	O _{VIII} - O _{VII} 3.06 (Ti)
O _{VI} - O _{VIII} 3.37	O _{VII} - (F,OH)* 3.34 (Na _{III})	O _{VII} - (F,OH)* 3.34 (Na _{II})
O _{VI} - O _{VII} 2.71 (Ti)	O _{VI} - O _{VII} 4.26	O _{VIII} - (F,OH) 3.92
O _{VI} - (F,OH) 3.36	O _{VI} - (F,OH) 3.26	O _{VII} - (F,OH) 3.74
O _{VI} - (F,OH)* 2.95 (Na _{II})	O _{VII} - (F,OH) 3.65	O _{VII} - O _{VIII} 3.41

distances in the $[\text{Si}_2\text{O}_7]$ group in, for example, cuspidine [21]. The Si-O distances in seidozerite and cuspidine lie within the limits 1.60-1.66 Å and 1.56-1.64 Å respectively. The edges of the tetrahedra range from 2.52-2.71 Å in seidozerite, and from 2.50-2.70 Å in cuspidine.

Leaving aside the "anomalies" mentioned (and explained), then the cation-anion distances in the Zr, Ti, Mn and Na octahedra are close to the sum of the corresponding ionic radii. Ti-O are in the limits 1.93-1.98 Å with the sum of the radii being $0.64 + 1.35 = 1.99$ Å. Analogously for Mn-O they are 2.21-2.31 Å with the sum $0.91 + 1.35 = 2.26$ Å, for Na-O, 2.18-2.62 Å with $0.98 + 1.35 = 2.33$ Å (the shortest distance Na-(F, OH) = 2.14 Å). The sum of the ionic radii of Zr^{+4} and O^{2-} , $0.82 + 1.35 = 2.17$ Å, and five of the six Zr-O distances lie in the range 1.98-2.13 Å. The reduction in the effective value of these distances may be attributed to the displacement of about a fourth part of the atoms of Zr by Ti. The lengths of the edges of all the octahedra correspond to similar ones for the given cations found in other structures.

Let us say a word about the geometric properties of the seidozerite structure which led to the peculiarities found in the beginning with the F and F² syntheses and which simplified the analysis. The fairly heavy concentrations of electrons which occupied the symmetry points separated by $a/2$ were not separate atoms but pairs of atoms, namely Ti + Na_{II} and Mn(Mg) + Na_{III}; both these and others lie on the two-fold axes (Fig. 5). The ratio of the effective Z, is $(22 + 12) : (18 + 12)$, = 1.1 and is equal to the difference in peak heights of 10-15% mentioned above. The $b/4 \times c/6$ net (Fig. 6) is made up of cations of (Ti, Na_{II}, Mn, Na_{III})-(Zr, Na_I)-(Zr, Na_I)-(Ti, Na_{II}, Mn, Na_{III})-(Zr-Na_I)-(Zr-Na_I), arranged along the c axis at every $1/6$ th. The arrangement of the atoms at four levels perpendicular to b is shown in Fig. 2b.

The exact overlapping (in the xz projection) of the atoms Si_I, O_I, Si_{II}, and the triplet of O in the two bases of the Si tetrahedra, is the result of the strict coincidence of the axis of the diortho group with the edges of the three Na octahedra. By the same token, the $[\text{Si}_2\text{O}_7]$ group registers a true trigonal prism.

E. I. Semenov found perfect cleavage along (001) in seidozerite. This plane is parallel to the continuous walls of octahedra (Figs. 5, 6) along which passes the cleavage in various silicates. This same cleavage may be caused by the breaking of bonds along the (001) plane which cuts the c axis in half (Fig. 5). In this case only the longer $\text{Zr-O}^*_{\text{V}} = 2.34$ Å bonds and the generally weaker Na-O bonds will be broken.

Seidozerite is an optically biaxial mineral and is positive. $2V = +68^\circ$. $n_g = 1.830$, $n_m = 1.758$, $n_p = 1.725$ (according to E. I. Semenov). The major axis of the optic indicatrix coincides with a , and the minor with b , and the explanation of this may be seen in the fact that the most optically active cations, the Mn, join, in their octahedra along a , with the "strong" (+4) Ti in zigzag chains, whilst along b the Mn octahedra alternate with the extended octahedra around the weak (loosely bound, with a charge of +1) Na cation (Fig. 4).

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