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Abstract

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THE CRYSTAL STRUCTURE OF RINKITE

$$Na(Na,Ca)_2(Ca,Ce)_4(Ti,Nb)[Si_2O_7]_2(O,F)_2F_2$$

In the literature on rinkite there is no agreement concerning the symmetry of this mineral. Gossner and Kraus ([1]) considered it monoclinic, which is repeated by Betekhtin ([2]), but in Strunz' s well-known handbook ([3]) we find an indication of the pseudorhombicity of this silicate. In Sahama and Hytönen ([4]) the symmetry of rinkite is lowered to triclinic. Within the framework of this symmetry, in the laboratory of Kh. S. Mamedov a structure of the seidozerite type ([6]) was proposed for rinkite ([5]), with the sole difference being the doubled orientation of those double ribbons which, in the seidozerite motif, link the parallel infinite walls.*

One of the reasons for the discrepancy may have been the use in the analysis of representatives, in fact different, of a closely related series of minerals. The broad limits of isomorphism characteristic of all minerals of the seidozerite–rinkite group complicate the structural analysis of these silicates. The task, undertaken at the Institute of Crystallography, of a systematic structural investigation of the entire götzenite–lavenite ([7,8]) and seidozerite–rinkite ([6,9]) group was a prerequisite for a refined complete structural determination of rinkite, which should bring maximum clarity to the question of the symmetry and crystal chemistry of this mineral.

Yellow-brown crystals of a standard Greenland rinkite were kindly provided to us by M. D. Dorfman. The question of the symmetry of the mineral was analyzed specially. From a spherical specimen of diameter ~ 0.5 mm, in an integrating X-ray goniometer (Mo radiation), developments of eight layer lines were obtained: $h0l$ $-h3l$, $hk0$ $-hk2$, and $0kl$. The intensities of the reflections of zero layer lines were measured on an MF-4 microphotometer. Weak reflections of equatorial and all reflections of nonzero layer lines were estimated visually on a blackening scale with a step of $\sqrt[4]{2}$. The true symmetry of rinkite is monoclinic, but it has a peculiar pseudorhombic character. Calculation of an analogue of the R-factor

$$R_{h0l} = \sum |I_{h0l} - I_{h0l}| \,/\, \sum I_{h0l}$$

separately for reflections with even and odd l leads to the values $R_{l=2n+1} = 27.4\%$ and $R_{l=2n} = 5.8\%$. If the second of these quantities is regarded as an indicator of random measurement errors, then the first characterizes the real deviation of the symmetry of rinkite from rhombic. Similar calculations for the reflections $hk0$ gave, as could be expected for the side development of a monoclinic crystal, close values $(R_{hk0})_{h=2n+1} = 8.0\%$ and $(R_{hk0})_{h=2n} = 6.9\%$.

From rotation radiographs the parameters of the unit cell are
$a = 18.28 \pm 0.10$ Å, $b = 5.59 \pm 0.06$ Å, $c = 7.38 \pm 0.09$ Å; $\beta \approx 90°$.

The results of the structural determination presented below were obtained from experimental data for two zero layer lines: $h0l$ (270 un-

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* In comparing the experimental material it was possible to establish that in work ([5]) an error had been made in indexing the X-ray photographs.

dependent and nonzero reflections; $\max \sin \vartheta/\lambda = 1.23$ Å^{-1}) and $hk0$ (130 reflections; $\max \sin \vartheta/\lambda = 1.05$ Å^{-1}). Refinement of the structural parameters of rinkite from the partial three-dimensional set of reflections is continuing.

The cell of the indicated dimensions contains two units of

$$Ca_{3.35}Na_{2.11}K_{0.06}Ce_{1.05}Th_{0.04}Nb_{0.33}Zr_{0.07}Ti_{0.52}Fe_{0.09}Mg_{0.08}Al_{0.09}[Si_2O_7]_2OF_3^*.$$

The only systematic extinction of reflections within monoclinic symmetry determines for rinkite two possible Fedorov groups

Table 1

Coordinates of the basic atoms of rinkite

Atoms	x/a	y/b	z/c	Atoms	x/a	y/b	z/c
$(Ca, Ce)_1$	0,059	0,157	0,125	O_4	0,064	0,896	0,879
$(Ca, Ce)_2$	0,442	0,843	0,125	O_5	0,062	0,424	0,373
$(Ca, Ce)_3$	0,059	0,157	0,625	O_6	0,063	0,424	0,918
$(Ca, Ce)_4$	0,441	0,843	0,625	O_7	0,132	0,638	0,625
(Ti, Nb)	0,250	0,500	0,125	O_8	0,368	0,357	0,630
$(Na, Ca)_1$	0,250	0,500	0,626	O_9	0,308	0,353	0,934
$(Na, Ca)_2$	0,250	0,000	0,376	O_{10}	0,308	0,353	0,316
Na	0,250	0,000	0,874	O_{11}	0,428	0,104	0,871
Si_1	0,110	0,655	0,410	O_{12}	0,439	0,576	0,913
Si_2	0,110	0,655	0,840	O_{13}	0,438	0,104	0,371
Si_3	0,390	0,345	0,839	O_{14}	0,438	0,576	0,371
Si_4	0,390	0,345	0,409	$(O, F)_1$	0,187	0,175	0,124
O_1	0,192	0,634	0,314	$(O, F)_2$	0,313	0,825	0,124

Atoms	x/a	y/b	z/c	Atoms	x/a	y/b	z/c
O_2	0,184	0,634	0,946	F_1	0,187	0,175	0,626
O_3	0,076	0,896	0,369	F_2	0,313	0,825	0,626

$P2_1$ and $P2_1/m$. However, in addition to the reflections $0k0$ with $k = 2n + 1$, the radiographs lack reflections $h00$ with $h = 2n + 1$ and $00l$ with $l = 2n + 1$. If one neglects the approximately 30% "monoclinic" difference in the intensities of hkl and $\bar{h}kl$, then the symmetry of the mineral becomes, in a first approximation, rhombic, and its Fedorov pseudosymmetry group $P2_12_12_1$ is determined uniquely. Upon lowering the symmetry to monoclinic it is easy to understand the disappearance of two screw axes out of three, but it is difficult to allow for the appearance of a mirror plane and a center of symmetry. On this basis, the group $P2_1$ was proposed for rinkite, and this was confirmed later. The structure was solved by the superposition method with effective use of pseudosymmetry at the first stage ([10]). The Patterson projection $p(x, y)$ was analyzed on the assumption of pseudosymmetry pgg for any coordinate projection of the electron density (with three-dimensional pseudosymmetry $P2_12_12_1$). We do not dwell on the now-standard details of the use of pseudosymmetry (for example ([8,9])). The two vectors fixed on $p(x, y)$, corresponding to atoms related by a pseudocenter of symmetry, made it possible to construct two minimization functions, the rank of which was increased to four by means of glide-reflection lines. Superposition and minimization of two $M_4(x, y)$ led to the function $M_8(x, y)$, on the basis of which a planar model of the structure was constructed. The process of solving the second Patterson projection $p(x, z)$ was analogous, but knowledge of the x-coordinates made the choice of vectors for the superposition of $p(x, z)$ more reliable. The structure was refined by the usual procedure of alternating calculations of F_{calc} and electron-density projections. The final values of the discrepancy factors for all

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* A new chemical analysis of Greenland rinkite was kindly communicated to us by E. I. Semenov, to whom the authors are very grateful.

for the nonzero reflections were: $R_{hk0} = 16.1\%$ (with an averaged isotropic temperature factor $B = 0.60$ Å^2) and $R_{h0l} = 18.6\%$ ($B = 0.64$ Å^2). Introduction of an absorption correction reduced the R-factors respectively to 14.5% ($B = 0.70$ Å^2) and 18.1% ($B = 0.72$ Å^2). The higher value of the discrepancy factor for the $h0l$ reflections, as well as its lower sensitivity to allowance for absorption, reflects a certain inaccuracy in the z-coordinates, which is difficult to exclude when using reflections from a single equatorial layer line. The coordinates of the basis atoms of rinkite are given in Table 1.

Fig. 1. Projection of the rinkite structure in polyhedra onto the (x, y) plane

In the independent part of the monoclinic cell of rinkite there are 30 basis

Fig. 1. Projection of the rinkite structure in polyhedra onto the (x, y) plane. Legend: $[Si_2O_7]$, (Ti, Nb), Na, (Ca, Ce).

Figure 1: Fig. 1. Projection of the rinkite structure in polyhedra onto the (x, y) plane. Legend: $[Si_2O_7]$, (Ti, Nb), Na, (Ca, Ce).

atoms. Although the amount of cerium is sufficient to ensure a distinct position both in the formula and in the structure, nevertheless Ce is distributed in approximately equal proportions over four independent positions, which for the remaining 75% are occupied by Ca atoms. These latter, "reinforced" by equally large but more highly charged Ce^{3+} atoms, determine by their rigidity certain features of the rinkite structure that make it different from the structures of other minerals of the rinkite group (cf. ([11])). As in the previously solved members of this group (seidozerite ([6]), rosenbuschite ([9])), the principal architectural feature of rinkite may be considered to be walls infinite in two dimensions, in which (at two levels along the b axis) there alternate octahedral columns usual for the rinkite and cuspidine–wöhlerite groups; in some, Na octahedra are overlain by (Na, Ca)-octahedra, in others by small Ti-octahedra and very elongated (Na, Ca)-octahedra. The Ti-octahedra have nothing in common with Ce (contrary to the usual association of Ti and Ce in formulas); the latter, together with the Ca atoms replacing them, take part in a second detail of the motif. Namely, between the principal walls described above there are located transverse ribbons composed, as in seidozerite–rosenbuschite, of two columns of (Ca, Ce)-octahedra. The rigidity of these large cations contracts their octahedra (with the use of adjacent O) to seven-vertex polyhedra, in each of which one semioctahedron is retained, while the other is transformed into a trigonal prism. The latter are drawn out into an infinite wall parallel to the principal ones and passing midway between them. The mutual connection is effected by the semioctahedra of the middle wall, facing alternately in different directions (Fig. 1); this motif of prismatic halves of seven-vertex polyhedra resembles the principal motif of cuspidine. As a result of the swelling of the (Ca, Ce)-polyhedra in projection along the c axis (the axis of the columns), the motif of solid triangles usual for the cuspidine–wöhlerite–seidozerite groups is replaced by a motif of triangles and rectangles (Fig. 1). Through the rectangles, parallel to the c axis, passes a glide line (a pseudo-axis 2_1 in three dimensions), and therefore the octahedra in the principal walls are not parallel to one another, as in seidozerite–rosenbuschite, but face in different directions. Thus, in rinkite too the period a proves to be twice the distance between the walls.

The silico-oxygen radical, as in all members of the combined cuspidine, wöhlerite, seidozerite group, is the diorthogroup $[Si_2O_7]$. The obligatory Si—O—Si angle of 150° is achieved by the fact that two vertices of the prism

with Si_2O_7 are drawn together by the (Ca, Ce) seven-vertex polyhedra to distances of $\sim$ 3.9 Å, while the third vertices of the prisms are "stretched" to $\sim$ 4.6 Å by the elongated edge of the (Na, Ca) octahedron, alternating with the

Fig. 2. Side projection of the rinkite structure onto the (x, z) plane

Figure 2: Fig. 2. Side projection of the rinkite structure onto the (x, z) plane

small Ti octahedron, as a result of which the bridging O atoms from the $[Si_2O_7]$ group come close to the vertical edges of the large (Na, Ca) octahedron and almost center them, bringing the coordination of this cation up to 8. A similar increase of the coordination of Na to $6 + 2$ also occurs in the refined structure of Ca-seidozerite (12).

Fig. 2. Side projection of the rinkite structure onto the (x, z) plane

The large Ca and Ce cations, situated midway between the main "packages" of octahedra, make rinkite mica-like (cf. bafertisite and astrophyllite), which is in good agreement with the perfect cleavage along (100). Figures 1 and 2 give the xy and xz projections of the rinkite structure in polyhedra; for greater clarity of the drawing, the aforementioned 8-vertex polyhedra are shown as octahedra.

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Note: Figure translations are in progress. See original paper for figures.