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CHARACTERISTICS OF THE CRYSTAL STRUCTURE OF RINKITE

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The structure of rinkite $Na_2Ca(Ca, Ce)_4(Ti, Nb)[Si_2O_7]_2(O, F)_2F_2$ is refined by reference to a partial three-dimensional set of experimental structure amplitudes. Isomorphic substitutions in rinkite are discussed together with the place of this substance among minerals of the cuspidine-lovenite and seidozerite-rosenbuschite groups.

The solution of the structure of rinkite given in [1] compels us to look very carefully at the mineralogically related group of rinkite-seidozerite minerals, which according to the handbooks is headed by the rinkite-rinkolite type [2, 3]. Analysis of seidozerite [4, 5], rosenbuschite [6], and lamprophyllite [7] shows that the motifs of the first two silicates are identical but gives an unexpected result in respect to the third. Lampropyllite is apparently closer to bathertisite [8] than to the minerals of its "own" group. The high content of Ce in rinkite is responsible for its structural differences from both lamprophyllite and seidozerite–rosenbuschite. In order to fit these minerals into a single scheme we must not only establish their structural motifs but also analyze the complex picture of isomorphic substitutions.

The coordinates of the basic atoms of rinkite were established in [1] by reference to two projections of electron density. The pseudorhombic character of the structure, with a sharply-expressed pseudoperiod $c' = c/2$, caused overlapping of the atoms on the projections, which made it difficult to obtain exact values of the coordinates of the atoms and the quantitative characteristics of the ismorphic intrusions. In order to refine the structure, use was made of the visually-estimated nonzero reflections of six x-ray goniometrical scannings ($h0l-h2l$ and $hk0-hk2$) taken in an integrating Weissenberg goniometer in Mo radiation from a rinkite sample rounded into a sphere ~0.5 mm in diameter. In all, 1291 independent structure amplitudes were obtained; these were calculated from the intensities without correcting for absorption.

The description of the rinkite structure in [1] was based on a pseudorhombic cell with an angle of $\beta = 90°$. An attempt to refine the structure on this basis gave unsatisfactory results. Careful inspection of the x-ray photographs compelled us to double (split) the a axis, which led to a pseudorhombic Bravais lattice centered on the B face. Passing back to the monoclinic aspect gives a primitive cell with parameters $a = 18.60$, $b = 7.421$, $c = 5.636$ Å, $\beta = 101°25'$.[1]

The refinement of the structure was carried out by the method of least squares in accordance with the programs given in [9], which were incapable of refining the coordinate parameters of all the basic atoms simultaneously. Stages of improving the cations (the behavior atoms) and anions were taken in turn, the reduction factor for converting to the absolute scale and the general isotropic temperature constant B being refined at every stage. It was necessary to forgo the "least-squares" refinement of the absolute-scale reduction factors of the reflections from different layer lines (taken by rotating the crystal around the c axis), since any such reduction in the functional (and R factor) involved a systematic reduction in the coefficient k_1 and the actual exclusion of reflections containing information relating to the deviation of the structure from the $c' = c/2$ pseudoperiod. The temperature factor B was always close to zero, which was doubtless due to the neglect of absorption (the linear absorption coefficient for rinkite at $\lambda = 0.71$ Å is

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[1] The authors take this opportunity of thanking L. V. Gorbatyi for measuring the parameters of the unit cell of rinkite on the diffractometer.

TABLE 1. Coordinates of the Basic Atoms of Rinkite

Atoms	x/a	y/b	z/c	Atoms	x/a	y/b	z/c	Atoms	x/a	y/b	z/c
(Ca, Ce)$_1$	0.061_0	0.140	0.164	Si_3	0.386_4	0.351	0.045	O_9	0.305_0	0.361	0.084
(Ca, Ce)$_2$	0.445_6	0.835	0.355	Si_4	0.391_0	0.320	0.601	O_{10}	0.307_9	0.345	0.081
(Ca, Ce)$_3$	0.063_7	0.132	0.648	O_1	0.186_0	0.617	0.399	O_{11}	0.431_8	0.121	0.100
(Ca, Ce)$_4$	0.443_7	0.804	0.839	O_2	0.190_4	0.636	0.035	O_{12}	0.437_4	0.578	0.110
(Ti, Nb)	0.256_8	0.516	0.247	O_3	0.058_5	0.876	0.421	O_{13}	0.434_3	0.072	0.591
Ca	0.244_4	0.473	0.729	O_4	0.074_1	0.883	0.914	O_{14}	0.437_8	0.546	0.560
Na_1	0.246_1	0.000	0.509	O_5	0.058_0	0.423	0.381	(O, F)$_1$	0.190_4	0.195	0.239
Na_2	0.259_1	0.980	0.016	O_6	0.051_9	0.424	0.903	(O, F)$_2$	0.318_0	0.778	0.295
Si_1	0.108_0	0.645	0.472	O_7	0.127_6	0.594	0.691	F_1	0.187_4	0.131	0.751
Si_2	0.113_8	0.622	0.896	O_8	0.372_1	0.348	0.814	F_2	0.311_4	0.842	0.777

quite large: $\mu = 62.3$ cm^{-1}). Attempts at refining individual isotropic temperature factors u_j gave no physically justifiable results.

The complication with the pseudoperiod made it necessary to check the "least-squares" refinement with ordinary and weighted electron-density projections from hk0, h0l, h1l, and h2l reflections. Use of the hk1 and hk2 systems for constructing weighted projections was excluded because of the above-mentioned c' = c/2 pseudoperiod. In order to reveal the details of the structure responsible for disrupting this pseudoperiod, we turned to partial syntheses of electron density $\sigma'(x, z)$, constructing these from reflections with $l = 2n + 1$. The method of partial syntheses was proposed by Burger [10], and played an important part in the analysis of rosenbuschite [6].

The electron-density distribution in a structure with a pseudoperiod is made up of two parts: the distribution for which the pseudoperiod is a strict period (substructure), and the distribution not obeying the pseudoperiod (additional structure). The algebraic sum of the substructure and additional structure makes up the whole structure of the crystal. For the rinkite substructure, c' = c/2 becomes the period, and all information regarding it is concentrated in reflections with $l = 2n$. Information regarding the additional structure is partly included in the same reflections and partly in the reflections with $l = 2n + 1$, which relate only to the additional structure and contain no contribution from the substructure. Figure 1a shows a very simple one-dimensional example of a structure with a pseudoperiod $a' = a/2$. The coordinates of two atoms of this structure exactly obey the pseudoperiod, but violate the weights: The weight of the $\rho_2(x - {}^1\!/_2 - x_0)$ equals 0.8 of that of the $\rho_1(x - x_0)$.

In this case the substructure (Fig. 1b) consists of two equal atoms $0.8\rho_1(x - x_0)$ and $\rho_2(x - {}^1\!/_2 - x_0)$, and the additional structure (Fig. 1c) is represented by one atom $0.2\rho_1(x - x_0)$. Partial syntheses with respect to amplitudes with h = 2n (Fig. 1d) and h = 2n + 1 (Fig. 1e) separate the two component parts from the structure in a different way: In the first of these syntheses, two different atoms with weight $(\rho_1 + \rho_2)/2$ are revealed, and in the second, characterized by an antitranslation $a/2$, we find two atoms of weight $\pm(\rho_1 - \rho_2)/2$, equal in absolute magnitude but opposite in sign. If the pseudoperiod is violated by displacements in the coordinates of the atoms the picture becomes more complicated, but the different principles of decomposing the structure a) in the Burgers manner (substructure plus additional structure) and b) into partial syntheses remain inviolate. Although partial syntheses plotted only from odd reflections cannot give the whole picture of the additional structure, their maxima indicate the directions of the displacements and the changes in the Z_{eff} of the atoms of the structure necessary in order to convert to the true structure. The use of partial syntheses is usually complicated by the fact that reflections with $l = 2n + 1$ are extremely weak in the presence of a c/2 pseudoperiod, so that measurements involve substantial errors.

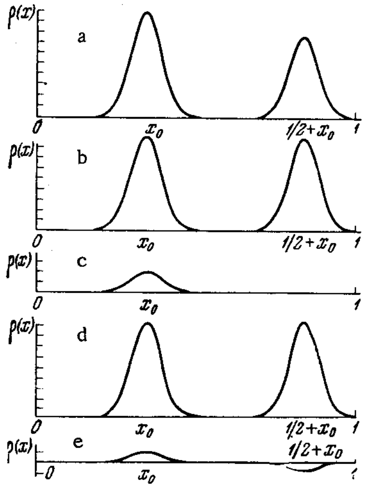

Fig. 1. One-dimensional structure with a pseudoperiod. a) Structure; b) substructure; c) additional structure; d) partial synthesis from amplitudes with h = 2n; e) partial synthesis from amplitudes with h = 2n + 1.

The results of a refinement of the coordinates of the basic atoms of rinkite are presented in Table 1 (for comparison with the coordinates of [1] due allowance must be made for the change in presentation). The final value of the R factor obtained from the 1291 independent reflections equals 14.9%.

In parallel with refining the coordinates of the basic atoms, we verified the arrangement by reference to the independent crystallographic positions of a fairly complex set of rinkite cations. We found in particular that one heavy Ce atom ($Z = 58$) belonging to an independent part of the cell did not occupy an independent crystallographic position in rinkite but was distributed in roughly equal proportions over four independent positions, which were occupied for the remaining 75% by Ca. The Ti and Nb atoms, uniting, occupy one basic octahedron of the structure. After refining the distribution of cations obtained in [1] by plotting projections, we are inclined to think that the Na in the structure occupies two crystallographically-independent positions, while the calcium left over from cooperative siting with the Ce atoms (see above) units with the K and excess Na to occupy (perhaps statistically rather than 100%) one crystallographic position in the large cavity between the two diortho-groups.

The solution of the structure showed that the expanded formula of rinkite should be $Na_2Ca(Ca, Ce)_4(Ti, Nb)[Si_2O_7]_2(O, F)_2F_2$. It is also extremely likely that small quantities of Th and Zr enter into the (Ca, Ce) polyhedra, while the (Ti, Nb) octahedra absorb the cations of tervalent Fe, Mg, and possibly Al present in rinkite.

The presence of the large quantity of Ce gives an individual character to the structural motif of rinkite; however, the two-dimensionally-infinite wall of octahedra, the main architectural feature of seidozerite, rosenbuschite, bathertisite, and lamprophyllite, is retained in rinkite also. In this the walls are constructed of two types of columns drawn out along the c axis (the projections of the walls along the c axis may be seen in Fig. 2a). In the columns of one type two independent Na octahedra alternate; in the columns of the other type there is a compact (Ti, Nb) octahedron uniting two translationally-identical diortho-groups $[Si_2O_7]$ and a (Ca, Na, K) polyhedron attached to the same diortho-group, which attracts the bridge oxygens of the two diortho-groups to itself and transforms from an octahedron into an eight-vertex figure. An analogous "adjustment" of the coordination number of the large cation was noted in Ca-seidozerite [5]. Figure 2 gives a schematic picture of fragments of the structures of rinkite, bathertisite, and seidozerite (rosenbuschite). Whereas in seidozerite and bathertisite the neighboring walls are made up of octahedra in the parallel position, in rinkite the corresponding octahedra (projections) are antiparallel, and the walls transform into each other by a 2_1 axis passing along b (in Fig. 2a the vertical line of the gliding reflection). The main difference in the structural motifs of the minerals compared in Fig. 2 lies in the coordination of the cations and the filling of the space between the walls with the corresponding polyhedra.

As already remarked, comparatively large quantities of Ce in rinkite isomorphically replace Ca in four crystallographically-independent positions. The four cations of composition $(Ca_{0.75}Ce_{0.25})$ belonging to the two $[SiO_7]$ groups are arranged in identical seven-vertex figures, which may be described as trigonal prisms with hemioctahedra on one of the side faces. Polyhedra of this type are well known in the crystal chemistry of Ca and TR [11, 12]. The $(Ca_{0.75}Ce_{0.25})$ seven-vertex figures in the rinkite structure create independent continuous walls, infinite in two dimensions, which are parallel to the basic structures described above and alternate with them. The combination of the parallel walls into an architectural whole is effected by the diortho-groups $[Si_2O_7]$ and the tips of the hemioctahedra projecting on different sides from the $(Ca_{0.75}Ce_{0.25})$ walls (Fig. 2a). In seidozerite, between the principal walls we find (on referring to two $[Si_2O_7]$ groups) two centrosymmetric pairs of $(Zr_{0.75}, Ti_{0.25})$ and Na octahedra. These octahedra form a double strip in each of the two columns of which compact $(Zr_{0.75}, Ti_{0.25})$ and severely extended

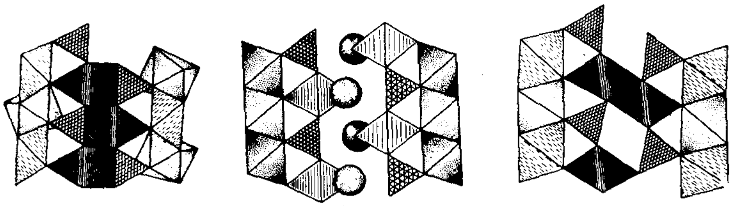

Fig. 2. Fragments of structural motifs of: a) rinkite; b) bathertisite; c) seidozerite (rosenbuschite).

Na octahedra alternate (Fig. 2c). For this solution the ($Zr_{0.75}$, $Ti_{0.25}$) and Na octahedra have common edges (parallel to the plane of Fig. 2). The original mode of packing the cations in the space between the principal walls gives the structure of bathertisite, in which two Ti and two Ba cations (sharply differing in ionic radius) belong to the two diortho-groups [Si_2O_7]. In Fig. 2b we can easily see the Ti octahedra; together with the [Si_2O_7] groups, these form a "chain-mail" lattice, which "armors" the principal walls of Fe octahedra. In the same figure, the large circles show the positions of the Ba atoms. If we construct the corresponding coordination polyhedra, we find around the Ba atoms several distorted (Archimedes) cubo-octahedra (cubic close packing). The Ba entering with equal validity into this packing is surrounded by 12 O atoms. Lamprophyllite repeats the structural motif of bathertisite, but the Ti octahedron of the latter is replaced in lamprophyllite by a tetragonal pyramid (hemioctahedron), which is formed by the removal of the anion corresponding (in Fig. 2b) to the vertex of the Ti octahedron covered by the Ba atoms. The five-fold coordination of the Ti in lamprophyllite was not unexpected, being prepared for by the already-established crystal-chemical laws regarding the departure of Ti from the center of the oxygen octahedron. Whereas in the tetragonal ferroelectric phase $BaTiO_3$ a displacement of this kind is only observed with difficulty by x-ray diffraction, in the analysis of bathertisite [13] and bathysite [14] it appears very clearly. Rinkite is not an exception in this respect, although in contrast to bathertisite and lamprophyllite its (Ti, Nb) polyhedra enter into the principal walls of octahedra. The distance to the sixth anion in the (Ti, Nb) octahedra of rinkite reaches 2.19 Å, which after allowing for the scatter in the coordinates of the basic atoms cannot be ascribed to errors. Thus rinkite may be regarded as one more "crystal-chemical" stage on the way to lamprophyllite, in which the limiting case of the complete removal of the sixth anion from the coordination polyhedra of the Ti is achieved.

Table 2 shows the principal interatomic distances in the structure of rinkite. The Si–O–Si angles of the two diortho-groups equal 153 and 159°, to the accuracy of our experiments. The corresponding deformation of the trigonal prisms described around the [Si_2O_7] is attributable to the fact that two edges of the trigonal prisms are drawn out by the (Ca, Ce) seven-vertex figures to a distance of c/2, and the third edge coincides with the elongated edges of the Ca octahedra, which alternate in columns with the small (Ti, Nb) octahedra.

TABLE 2. Principal Interatomic Distances in the Structure of Rinkite, in Å

Si_1 tetrahedron		Si_2 tetrahedron		Si_3 tetrahedron	
$Si_1 - O_1$	1.67	$Si_2 - O_2$	1.60	$Si_3 - O_9$	1.61
$Si_1 - O_3$	1.60	$Si_2 - O_4$	1.67	$Si_3 - O_{11}$	1.56
$Si_1 - O_5$	1.63	$Si_2 - O_6$	1.62	$Si_3 - O_{12}$	1.61
$Si_1 - O_7$	1.62	$Si_2 - O_7$	1.60	$Si_3 - O_8$	1.68

Si_4 tetrahedron		(Ti, Nb) octahedron	
$Si_4 - O_{10}$	1.64	(Ti, Nb) — O_1	1.99
$Si_4 - O_{13}$	1.63	(Ti, Nb) — O_2	1.93
$Si_4 - O_{14}$	1.61	(Ti, Nb) — O_9	1.87
$Si_4 - O_8$	1.69	(Ti, Nb) — O_{10}	2.05
		(Ti, Nb) — $(O, F)_2$	1.86
		(Ti, Nb) — $(O, F)_1$	2.19

Na_1 octahedron		Na_2 octahedron	
$Na_1 - (O, F)_1$	2.34	$Na_2 - F_1$	2.31
$Na_1 - F_1$	2,40	$Na_2 - (O, F)_1$	2.59
$Na_1 - (O, F)_2$	2.60	$Na_2 - (O, F)_2$	2.43
$Na_1 - F_2$	2.30	$Na_2 - F_2$	2.32
$Na_1 - O_1$	2.49	$Na_2 - O_2$	2.35
$Na_1 - O_{10}$	2.30	$Na_2 - O_9$	2.33

$(Ca, Ce)_1$ seven-vertex figure		$(Ca, Ce)_2$ seven-vertex figure	
$(Ca, Ce)_1 - O_3$	2.43	$(Ca, Ce)_2 - O_{11}$	2.46
$(Ca, Ce)_1 - O_4$	2.41	$(Ca, Ce)_2 - O_{13}$	2.24
$(Ca, Ce)_1 - O_5$	2.28	$(Ca, Ce)_2 - O_{12}$	2.31
$(Ca, Ce)_1 - O_6$	2.49	$(Ca, Ce)_2 - O_{14}$	2.25
$(Ca, Ce)_1 - (O, F)_1$	2.40	$(Ca, Ce)_2 - (O, F)_2$	2.37
$(Ca, Ce)_1 - O_4^*$	2.84	$(Ca, Ce)_2 - O_{13}^*$	2.66
$(Ca, Ce)_1 - O_6^*$	2.41	$(Ca, Ce)_2 - O_{14}^*$	2.46

$(Ca, Ce)_3$ seven-vertex figure		$(Ca, Ce)_4$ seven-vertex figure	
$(Ca, Ce)_3 - O_5$	2.56	$(Ca, Ce)_4 - O_{12}$	2.40
$(Ca, Ce)_3 - O_6$	2.54	$(Ca, Ce)_4 - O_{14}$	2.52
$(Ca, Ce)_3 - O_3$	2.21	$(Ca, Ce)_4 - O_{11}$	2.67
$(Ca, Ce)_3 - O_4$	2.40	$(Ca, Ce)_4 - O_{13}$	2.36
$(Ca, Ce)_3 - F_1$	2.29	$(Ca, Ce)_4 - F_2$	2.44
$(Ca, Ce)_3 - O_3^*$	2.63	$(Ca, Ce)_4 - O_{11}^*$	2.51
$(Ca, Ce)_3 - O_5^*$	2.54	$(Ca, Ce)_4 - O_{12}^*$	2.67

Ca eight-vertex figure			
$Ca - O_1$	2.61	$Ca - F_1$	2.23
$Ca - O_2$	2.82	$Ca - F_2$	2.42
$Ca - O_9$	2.72	$Ca - O_7$	2.26
$Ca - O_{10}$	2.49	$Ca - O_8$	2.46

As already mentioned, the displaced central O atoms of the diortho-groups transform the Ca octahedra into eight-vertex figures. The identification of the O, (O, F), and F ions reflected in Table 2 is effected on the basis of the second Pauling rule regarding the sums of the valence forces converging at these anions.

The detailed structural analysis of a number of minerals of the rinkite-seidozerite and cuspidine-lovenite groups carried out in recent years enables us to give a detailed picture of the classification of these minerals proposed in [15]. Whereas the structural motif of cuspidine [16] was completely applicable to lovenite [17], wöhlerite [18], and niokalite [19], only rosenbuschite [6] is isostructural with seidozerite [4, 5]. Lamprophyllite [7] is linked with bathertisite [8], and the presence of a large quantity of Ce in rinkite distinguishes it with respect to structure [20].

All the calculations made in solving and refining the structure were carried out in the Computing Centers of Moscow State University and the

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