

Crystal structure of Hibbing rinkite

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The structure of rinkite from the Hibbing deposit is refined [Enraf-Nonius, Mo radiation, 2681 reflections with $I \geq 2\sigma_I$, $R = 5.02\%$ (anisotropic), AREN programs, PC-AT computer]. The cell constants are $a = 5.679(3)$, $b = 7.412(3)$, $c = 18.835(6)$ Å, $\alpha = 101.26(3)^\circ$, $V = 777.6$ Å³, space group $P2_111$, $Z = 2$, $\rho_{\text{exp}} = 3.29(3)$, $\rho_{\text{calc}} = 3.36$ g/cm³. The crystal chemical formula taking into account electron microprobe analysis is $\{\text{TiF}(\text{O},\text{F})[\text{Si}_2\text{O}_7]_2\} \{\text{Na}(\text{Na},\text{Ca})_2(\text{O},\text{F})\} \{(\text{Ca}, \text{RE})_2\}$. The round brackets separate a mixed chain of radicals and the middle and external layers of the trilayered structure. The mixed Ti, Si-nets in rinkite are transformed into the radical chain by decreasing the ratio of non-ferrous cations to Si from 1:1 in bafertisitite to 1:4.

The rinkite minerals include four varieties.^{1,2} Two of these are monoclinic, rinkite (from Greenland) and rinkolite (from Hibbing and Lovozero deposits), and differ in crystal-optical orientation (the plane of the optical axis is perpendicular or parallel to crystals lengthened along the c axis). The other two varieties are triclinic, calcium rinkite from Hibbing (also known as Zaire rinkite, described as the discrete mineral getzenite), which contains practically no rare earth (RE) and has an a axis that is one half as long as that of rinkite and the same optical orientation, and calcium rinkite (from Priazov) with the optical orientation of rinkolite. X-ray structure analysis (photographic method) was used to study Greenland rinkite³⁻⁵ and Zaire getzenite.⁶ The structures of rinkolite and calcium rinkite from Hibbing have not been solved since they are amorphous to x-rays. It seemed interesting to study their crystal structures and to find the symmetry of this mineral since a single Greenland rinkite exhibited orthorhombic,³ monoclinic,^{4, 5} and triclinic cells (powder data).⁷

According to Gottardi,⁸ the differences found in the symmetry of the pseudoorthorhombic mineral result from choosing the cells by different methods. However, solution of the rinkite structure with the monoclinic cells^{4, 5} gave the different space groups $P2_1$ and $P2_1/c$, respectively. The principal difference in the proposed models involves the distribution of Na and Ca atoms. Previous data⁴ suggests that they occupy three independent positions (two Na and one Ca) whereas Ca and RE are statistically distributed over the other four positions. In the second study, all of these positions have mixed composition, (Na, Ca) and (Ca, RE). The symmetry is reduced to $P2_1$ is due to the fact that two polyhedra related by a pseudoplane are occupied by different atoms, Ca and Ti, respectively, i.e., the difference in symmetry is related to ordering of Na, Ca and RE over the structure positions.

The goal of the present investigation was to refine the structure of a monoclinic Hibbing rinkite sample using diffractometer data (Enraf-Nonius diffractometer, Mo radi-

TABLE I. Coordinates for Si, Ti, Na, M, and z for (O, F) ($\times 10^4$); x and y for (O, F) ($\times 10^3$); and Thermal Parameters in Hibbing Rinkite

Atom	x/a	y/b	z/c	B_{eq}
Si ₁	3502(8)	934(2)	3879(1)	0.99(4)
Si ₂	3490(9)	5271(4)	3891(1)	2.43(6)
Si ₃	6584(6)	9528(2)	1102(7)	0.73(3)
Si ₄	6580(8)	3856(3)	1126(1)	1.94(5)
Ti	5083(7)	7480(3)	2512(1)	2.32(3)
Na	5069(13)	2642(7)	2519(3)	1.67(5)
M ₁	83(9)	5044(6)	2505(2)	1.80(5)
M ₂	62(10)	9977(7)	2516(2)	2.09(6)
M ₃	8424(1)	8468(1)	4421(1)	1.24(2)
M ₄	1652(1)	6514(1)	581(1)	1.41(2)
M ₅	8395(3)	3456(1)	4410(1)	1.72(3)
M ₆	1674(3)	1580(1)	598(1)	1.76(2)
O ₁	566(1)	859(8)	4403(3)	1.8(2)
O ₂	897(1)	4146(7)	684(3)	1.5(2)
O ₃	108(2)	590(1)	4319(4)	3.1(2)
O ₄	571(1)	603(1)	4421(2)	1.0(1)
O ₅	353(2)	578(1)	3109(3)	2.0(1)
O ₆	898(1)	905(1)	648(3)	1.4(2)
O ₇	648(2)	893(1)	1897(3)	2.1(1)
O ₈	436(2)	889(1)	606(6)	4.2(1)
O ₉	368(2)	961(1)	3078(3)	2.4(2)
O ₁₀	654(2)	512(1)	1918(3)	1.9(1)
O ₁₁	386(2)	300(1)	3684(4)	3.1(2)
O ₁₂	646(2)	177(1)	1298(4)	2.4(1)
O ₁₃	433(2)	413(1)	594(4)	2.7(2)
F ₁	88(2)	85(1)	4238(5)	4.0(3)
(O, F) ₂	793(1)	776(1)	3112(2)	2.2(2)
(O, F) ₃	158(1)	215(1)	1889(3)	3.0(2)
F ₂	197(1)	717(1)	1901(3)	3.4(2)
F ₃	848(2)	278(1)	3132(3)	3.5(2)

Note: $M_1 = M_2 = \text{Ca}_{0.3}\text{Na}_{0.7}$, $M_3 = M_5 = M_6 = \text{Ca}_{0.8}\text{RE}_{0.2}$, $M_4 = \text{Ca}_{0.7}\text{RE}_{0.3}$.

TABLE II. Principal Interatomic Distances in Hibbing Rinkite

Tetrahedral					
Si ₁ -O ₁	1,580(7)	Si ₂ -O ₅	1,590(8)	Si ₃ -O ₈	1,590(11)
-O ₁₄	1,588(11)	-O ₃	1,623(9)	-O ₆	1,611(6)
-O ₉	1,636(7)	-O ₄	1,638(6)	-O ₁₂	1,634(5)
-O ₁₅	1,647(7)	-O ₁₁	1,654(7)	-O ₇	1,644(7)
	(1,612)		(1,626)		(1,620)
Si ₄ -O ₁₆	1,600(6)			-O ₂	1,628(7)
				-O ₁₃	1,639(6)
				-O ₁₃	1,661(9)
					(1,631)

Octahedral					
Ti-O ₉	1,896(7)	M ₁ -O ₅	2,274(9)	M ₂ -(O, F) ₂	2,339(9)
-O ₇	1,900(8)	-O ₁₀	2,305(10)	-F ₄	2,353(8)
-F ₁	1,961(7)	-(O, F) ₃	2,374(9)	-O ₉	2,354(10)
-O ₅	2,047(8)	-(O, F) ₂	2,388(8)	-O ₇	2,398(10)
-O ₁₀	2,056(6)	-F ₄	2,407(9)	-(O, F) ₃	2,427(8)
-(O, F) ₂	2,098(8)	-F ₁	2,442(7)	-F ₁	2,476(8)
	(1,993)		(2,385)		(2,391)

7-Coordinate					
M ₃ -O ₃	2,358(8)	M ₄ -O ₉	2,329(11)		
-O ₁₁	2,382(10)	-O ₁₃	2,335(8)		
-O ₁	2,373(6)	-O ₂	2,362(5)		
-O ₂	2,375(5)	-O ₄	2,404(5)		
-F ₁	2,434(5)	-(O, F) ₃	2,445(6)		
-O ₁	2,518(8)	-O ₁₁	2,541(6)		
-O ₁₄	2,839(10)	-O ₂	2,682(5)		
	(2,465)		(2,442)		

8-Coordinate					
Na-F ₁	2,249(10)	M ₅ -F ₄	2,362(7)	M ₆ -(O, F) ₂	2,387(5)
-O ₁₁	2,301(11)	-O ₁₄	2,401(9)	-O ₁₃	2,419(8)
-(O, F) ₂	2,303(9)	-O ₄	2,438(5)	-O ₂	2,427(5)
-O ₁₂	2,399(9)	-O ₃	2,449(8)	-O ₆	2,429(6)
-O ₁₀	2,483(9)	-O ₁	2,472(6)	-O ₈	2,512(11)
-O ₈	2,527(8)	-O ₄	2,531(5)	-O ₄	2,586(11)
-O ₆	2,778(10)	-O ₃	2,691(9)	-O ₆	2,648(6)
-O ₇	2,889(8)	-O ₁₁	3,007(12)	-O ₁₂	3,015(10)
	(2,491)		(2,544)		(2,553)

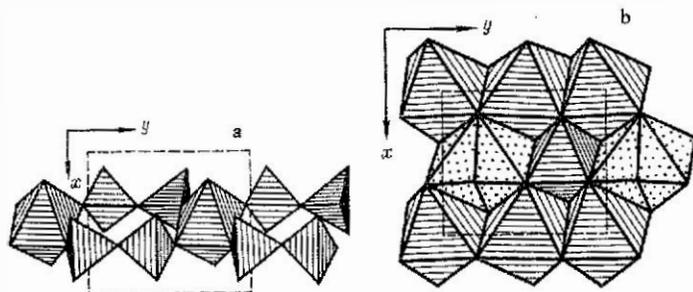


FIG. 1. Portion of the Hibbing rinkite structure projected on (001). Chains of Si₂O₇ and Ti octahedra (a), a layer of Ti octahedra (streaked), 8-coordinate Na (dotted), and (Na, Ca) octahedra M₁ and M₂ (widely spaced streaks).

tion, 2681 reflections with $l \geq 2\sigma_1$). A sample of the mineral was taken from feldspar-aegirine pegmatite in medium-grained nepheline syenites (Hibbing deposit). Single crystals were platelike brown aggregates with a green tint associated with feldspar, sodalite, aegirine, sulfides, fluorite, and lamprophyllite. The sample studied gave a good diffraction pattern and had the rinkite crystal-optical orientation. The plane of the optical axes was close to (001), $\angle Nmc = 7^\circ$, $Np = b$, $+2V = 50^\circ$.

The monoclinic cell constants refined on the diffractometer were $a = 5.679(3)$, $b = 7.412(3)$, $c = 18.835(6)$ Å, $\alpha = 101.26(3)^\circ$, $V = 777.6$ Å³. According to electron microprobe analysis (analyzed by A. I. Tsepin), the chemical formula is $(Ti_{0.92}Nb_{0.06}Zr_{0.03})(Ca_{3.7}Na_{2.4}RE_{0.8}Sr_{0.15})(Si_{3.85}O_{14})O_{1.3}F_{2.55}$, where $RE = Ce_{0.315}Nd_{0.19}La_{0.10}$.

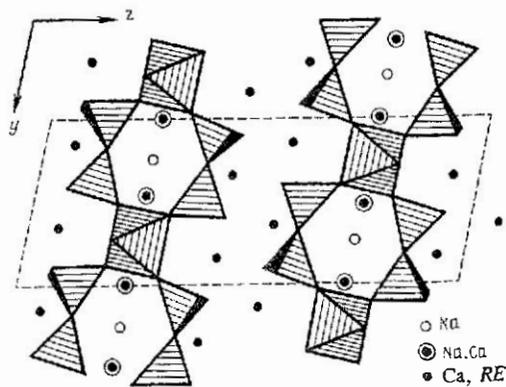


FIG. 2. Structure of Hibbing rinkite projected on (100). Mixed Si, Ti chains are highlighted.

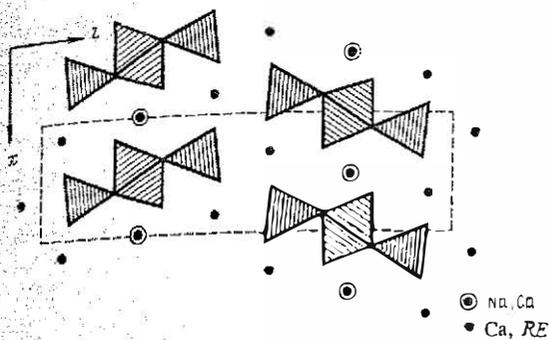


FIG. 3. Structure of Hibbing rinkite projected on (010). Ends of the Si, Ti chains and their packing in the cell.

$Y_{0.09}Pr_{0.05}Sm_{0.05}$. The experimental density $\rho_{exp} = 3.29(3)$ ($\rho_{calc} = 3.36 \text{ g/cm}^3$) corresponds to two formula units per cell.

In spite of the fact that the composition of the sample is close to both of those studied earlier,^{4,5} we did not use the previous result in order to avoid preconceptions. The structure was determined independently by direct methods in the acentric space group $P2_1$, in agreement with the systematically absent reflections. The model search, automatic refinement of phases of structure factors, and all other calculations were performed using the AREN programs⁹ on a PC-AT computer. The mixed scattering curves were composed taking into account the elemental analysis based on population factors obtained for each M -position. The crystal chemical properties were also considered in choosing the type of atoms. Refinement of the model with absorption corrections (the sample had irregular shape) reduced R to 6.2% (isotropic) and 5.02% (anisotropic).

The atomic coordinates with thermal factors B_{eq} are given in Table I. The principal interatomic distances are in Table II.

The atomic distribution found agrees in general with the models proposed in previous works. However, differences from one model or another do exist.

Our data confirm the acentric space group $P2_1$ since positions related by the pseudoplane c are occupied by Ti and Na, respectively (Fig. 1b). In this structure, Ca does not occupy an independent position but four polyhedra (M_{3-5} and M_6) together with RE and two others (M_1 and M_2) together with Na. The positions M_4 and M_6 related by the pseudoplane c are populated by Ca and RE in different proportions. In the M_6 polyhedra, Ca comprises 80%; in M_4 , 70%. This also lowers the crystal symmetry. The polyhedra M_3 and M_4 are face-centered trigonal prisms. The second pair of (Ca, RE) polyhedra are highly distorted tetragonal prisms. The 8-coordinate voids between diorthosilicates are occupied by Na^+ . The Na^+ cation attracts the bridging vertices forming the shortest contacts with them (2.3-2.4 Å). Thus, the diorthosilicates are extended along the edge of a large polyhedron. Another pair of Si tetrahedra adjoin the edge of the large 8-coordinate polyhedra M_5 and M_6 , filled primarily with Ca. The rare earths, comprising less than one atom, isomorphously replace Ca in the M_{3-6} polyhedra along with Sr.

Inclusion of rinkite in the Ti-Si micas¹⁰ may cause skepticism since chemically and structurally, as emphasized by Belov,⁴ rinkite is distinct from members of this family.

Although generally similar in geometry, the trilayered structure of rinkite differs in composition and structure from Ti-Si silicates. The ratio of nonferrous cations to Si M :Si in Ti-Si micas and their analogs varies from 6:4 to 4:4 whereas in rinkite it decreases to 1:4. This causes only one (in the middle layer) of the four octahedral M positions ($M = Ti, Fe, Mn, Zr,$ and Nb) in rinkite to be occupied by Ti. The large cations Na and Ca with RE impurities are distributed over the remaining positions. A single Ti octahedron in the middle of the structure joins four diorthosilicates into a mixed chain running along $[010]$ (Fig. 1a). The transformation of the Ti-Si layer into a chain (Figs. 2 and 3) in the complete absence of an interchain space leads to a more isometric and sometimes needlelike habit for the rinkite crystals.

Calculation of the local charge balance demonstrated¹¹ that a substantial deficit exists at those vertices of Ti, Na, and M_{1-6} polyhedra that are not shared with Si_{1-4} tetrahedra. In agreement with the elemental analysis, these anions are F or (O, F). Thus, the crystal chemical formula of rinkite can be written as $\{TiF(O, F)[Si_2O_7]_2\}\{Na(Na, Ca)_2F(O, F)\}\{(Ca, RE)_4\}$, where the round brackets separate the mixed radical chain, the middle layer, and the external layers of the structure. Thus, the crystal chemical analysis indicates (in full agreement with the proposal of Belov) that rinkite together with rosenbuschite and gotzenite form a mineralogical group that can be viewed as transitional from the Ca diorthosilicate cuspidine to Ti-Si micas. Seidozerite, which is more similar to micas than the remaining members of the group, can also be included. Its structure has mixed layers of tetrahedra and octahedra with Ti replaced by Zr in octahedral positions.

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Translated by D. W. Wester