

CRYSTAL STRUCTURE OF GÖTZENITE*

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Published in *Kristallografiya*, Vol. 16, No. 6,
pp. 1167-1173, November-December, 1971
Original article submitted April 20, 1971

Götzenite is a silicate of Ti, Ca, and Na; its unit cell parameters are: $a = 9.667 \text{ \AA}$, $b = 5.731 \text{ \AA}$, $c = 7.334 \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 101.05^\circ$, $\gamma = 101.31^\circ$, space group $P\bar{1}$. The x-ray structure analysis has been carried out on a twinned crystal. The crystal structure of götzenite is similar to that of rosenbuschite and seidozerite. The relations among these silicates are discussed and the structural interpretation of twinning is given.

INTRODUCTION

Götzenite is a silicate of Ca, Na, and Ti which was first described by Sahama and Hytönen [1] in an unusual volcanic rock from Mount Shaheru (Republic of Congo). Neumann [2] and Sahama et al. [3] stated the unit cell parameters, the chemical formula and the close structural relations of götzenite with rosenbuschite.

The following data are quoted from [3]: cell parameters: $a = 9.667 \text{ \AA}$, $b = 5.731 \text{ \AA}$, $c = 7.334 \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 101.05^\circ$, $\gamma = 101.31^\circ$, space group: $P\bar{1}$, chemical formula: $(\text{Ca}, \text{Na})_3\text{Ti}(\text{Si}_2\text{O}_7)(\text{F}, \text{OH})_2$; $Z = 2$.

The crystal structure of rosenbuschite has been investigated [4] by Shibaeva et al. The following data are quoted from [3]: cell parameters: $a = 10.14 \text{ \AA}$, $b = 11.41 \text{ \AA}$, $c = 7.28 \text{ \AA}$, $\alpha = 91^\circ 21'$, $\beta = 99^\circ 38.5'$, $\gamma = 111^\circ 54.5'$, space group: $P\bar{1}$, chemical formula: $\text{Ca}_{3.5}\text{Na}_{2.5}(\text{Ti}, \text{Mn})\text{Zr}(\text{Si}_2\text{O}_7)_2(\text{O}, \text{OH}, \text{F})_4$; $Z = 2$.

A careful examination of the unit cell parameters of götzenite and rosenbuschite reveals that they correspond to different choices of axes: b and c are taken in the same directions while a of rosenbuschite corresponds to the short diagonal of the ab face of the götzenite unit cell. If the cell parameters of rosenbuschite are redefined in the orientation of götzenite, they are nearly identical to those of götzenite (taking into account that b of the latter is halved). This fact is a further support to the hypothesis that the minerals are isostructural.

The unit cell of götzenite is also related to that of seidozerite [5]: cell parameters: $a = 5.53 \text{ \AA}$, $b = 7.10 \text{ \AA}$, $c = 18.30 \text{ \AA}$, $\beta = 102^\circ 43'$, chemical formula: $\text{Na}_4\text{Zr}_2\text{TiMnO}_2(\text{Si}_2\text{O}_7)_2$; $Z = 2$, space group: $P2/c$.

The aim of this work is to define the crystallochemical relations of götzenite with rosenbuschite and seidozerite, by means of crystal structure analysis.

During the investigation the götzenite reduced cell of Sahama et al. [3] has been adopted. The cell of rosenbuschite can be transformed into that of götzenite through the matrix:

$$\begin{pmatrix} \bar{1} & \bar{1}/2 & 0 \\ 0 & 1/2 & 0 \\ 0 & 0 & \bar{1} \end{pmatrix}$$

EXPERIMENTAL

Sahama and Hytönen [1] observed that: "Almost every crystal shows lamellar twinning, with twin axis $c \dots$ ". Since it was impossible to find a crystal fragment of götzenite from Mount Shaheru not affected by twinning, it has been decided to try the determination of the crystal structure using a twinned crystal.

A very tiny crystal fragment from a sample kindly provided by Prof. Sahama was used to col-

*The publisher thanks the authors for supplying the original English manuscript.

lect the x-ray diffraction data. Integrated Weissenberg pictures of seven reciprocal lattice layers (l from 0 to 6) were taken using the multiple films technique and nickel filtered copper radiation. The intensities were measured photometrically and corrected for the Lorentz-polarization factor and for the incomplete α_1 - α_2 spot doubling. Owing to the very small dimensions of the crystal (about two tenths of a millimeter in length and a few hundredths of a millimeter in cross section) no absorption correction was applied.

STRUCTURE DETERMINATION

A detailed analysis of the Weissenberg photographs, made on the basis of the twin law given in [1], may explain how it has been possible to use the intensities produced by the twinned crystal for the structure determination. a) The lattice shows a marked monoclinic pseudo-symmetry which can be emphasized with a multiple cell derived from the original triclinic cell through the matrix (401/010/001). b) It results, from the twin law, that each reflection corresponding to the reciprocal lattice layers with $l = 2n$ derives from the superposition of two reflections from the two individuals of the twin. More precisely, in the layer with $l = 0$ there is superposition of two equivalent reflections $hk0$ and $\bar{h}k0$; in this case the intensities are not affected by twinning; in the layers with $l = 2n$ each reflection results from the superposition of two non-equivalent reflections: $hk\bar{l}$ of one individual and $(h + l/2)k\bar{l}$ of the other (HKL and $\bar{H}\bar{K}\bar{L}$ for the monoclinic (pseudocell). c) No superposition exists in the reciprocal lattice layers with $l = 2n + 1$, but between two reflections $hk\bar{l}$ and $(h + 1)k\bar{l}$ of one individual, a reflection of indices $(h + (l + 1)/2)k\bar{l}$ of the other occurs. This feature offered the possibility to compare the intensities of some homologous reflections (the l -odd reflections are very weak) belonging to the two individuals in order to determine their relative "weight" in the crystal. The test proved that the two individuals were present in the crystal in nearly equal amounts, which is not unexpected in polysynthetic twins. For this reason the appearance of the x-ray pictures was monoclinic and so only the reflections independent for the monoclinic pseudocell were inspected: 318 reflections with $l = 2n$ and only 62 with $l = 2n + 1$ were measured; the remaining ones were too faint or did not give any blackening on the film and were considered as unobserved.

On the basis of these considerations and of the hypothesis that götzenite had the same structure

as rosenbuschite, it was decided to split the observed structure factor of each reflection with $l = 2n$ into two parts proportional to the structure factors of the two superposed reflections, computed with the atomic coordinates of rosenbuschite.

The atomic coordinates of rosenbuschite show that all the atoms but one oxygen can be grouped in pairs: the two atoms of each pair have the same x and y coordinates and z differing by about $1/2$. Thus the reflections with $l = 2n + 1$ derive mainly from the unpaired oxygen and from the difference in the scattering power of the atoms of some pairs. Since götzenite should differ from rosenbuschite mainly for the distribution of the cations Ca, Na, Ti, and Zr, two cycles of full matrix least squares were computed giving to all the cations the same scattering factor and hoping that the reflections with $l = 2n + 1$ could give the information necessary to obtain a consistent new distribution of atoms. The discrepancy factor (dropped from 0.26 to 0.10) and the examination of the cation-oxygen bond distances, as well as of the variations in the temperature factors and in the multipliers of the scattering factors, supported the adopted procedure and suggested a first distribution of the cations in götzenite. The first two cycles also showed that the calculated structure factors of the superposed reflections were almost identical. So the splitting procedure on the reflections with $l = 2n$ was stopped as practically irrelevant and the same measured value was given to both the superposed reflections.

Three cycles of least-squares were computed giving to each atom the scattering factor resulting from the analysis of the first two cycles. The discrepancy factor lowered to 0.08 for all the observed reflections (namely: 318 + 318 with $l = 2n$ and 62 with $l = 2n + 1$). At this stage the refinement was considered satisfactory taking into account the peculiar features of the experimental data obtained from a twinned crystal.

The cation distribution in götzenite resulting from the structure analysis is as follows: 1Ca, 1Ca, (0.6Ca + 0.4Na), 0.5Na, and 0.5Ti; the corresponding chemical formula is $\text{Ca}_4(\text{Ca}_{1.2}, \text{Na}_{0.8}) \cdot \text{NaTi}(\text{Si}_2\text{O}_7)_2(\text{F}, \text{OH}, \text{O})_4$, $Z = 1$. The principal difference between this formula and those obtained from the chemical analyses given by Sahama and Hytönen [3] is the presence of one Ti atom instead of two. The present formula is more consistent with the analysis of götzenite from Yukspor than with the analyses of götzenite from the Azov region and from the Congo [3].

The atomic parameters are listed in Table 1; bond distances and angles are given in Table 2. The

TABLE 1. Final Atomic Parameters and Their Standard Deviations (in parentheses)

Atom	x/a	y/b	z/c	B
Ca (1)	0.6389(7)	0.2115(11)	0.9097(8)	0.07(14)
Ca (2)	0.9859 (8)	0.4955(15)	0.2418(12)	0.57(13)
Ca (3)	0.6305(7)	0.2268(11)	0.4075(9)	0.17(15)
Na	0.0	0.0	0.5	1.21(47)
Ti	0.0	0.0	0.0	0.93(27)
Si (1)	0.7197(6)	0.7475(11)	0.6460(14)	0.74(14)
Si (2)	0.7210(6)	0.7471(10)	0.2100(12)	0.27(12)
O (1)	0.762(2)	0.784(4)	0.443(3)	2.33(35)
O (2)	0.619(2)	0.927(3)	0.673(3)	0.02(28)
O (3)	0.614(2)	0.925(4)	0.127(3)	1.45(43)
O (4)	0.636(2)	0.472(4)	0.665(3)	2.09(41)
O (5)	0.676(2)	0.465(3)	0.162(3)	1.09(32)
O (6)	0.879(2)	0.819(3)	0.778(3)	1.72(30)
O (7)	0.881(2)	0.830(3)	0.171(3)	1.47(28)
O (8)	0.884(2)	0.256(3)	0.969(3)	0.28(29)
O (9) = F	0.890(2)	0.313(3)	0.475(3)	0.53(32)

list of the observed and calculated structure factors is available from the authors on request.

The balance of the electrostatic valences is given in Table 3. The sum of the valence forces of the anions could be considered fairly good, never deviating by as much as 15%. The atom O(9) is likely to be fluorine, whereas in the position of O(8) both fluorine (or hydroxyl) and oxygen should occur.

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The main feature of the crystal structure of götzenite is the presence of "walls" of octahedra

and eight-cornered polyhedra parallel to (100) which are connected by "ribbons" of octahedra parallel to [001] and by Si_2O_7 groups. This description corresponds also to that of the structure of rosenbuschite and seidozerite. A more detailed analysis of this type of structure is given by Shibaeva et al. [4] and by Simonov and Belov [5].

The coordination polyhedra of Ti and Ca are octahedra; that of Na is an eight-cornered polyhedron which can be described as a hexagonal bipyramid. The oxygen O(1), which is shared by two silicon atoms, is involved in this coordination polyhedron. The hexagonal bipyramid around Ca or Na is also present in rosenbuschite and seidozerite.

TABLE 2. Interatomic Distances and Tetrahedral Angles in Götzenite

Ca(1) — O(5)	2.28 Å	Si(1) — O(2)	1.58 Å
Ca(1) — O(8)	2.29	Si(1) — O(1)	1.62
Ca(1) — O(3)	2.30	Si(1) — O(6)	1.63
Ca(1) — O(2)	2.33	Si(1) — O(4)	1.65
Ca(1) — O(4)	2.33	Si(2) — O(7)	1.60
Ca(1) — O(3)'	2.38	Si(2) — O(5)	1.61
Ca(2) — O(9)	2.26	Si(2) — O(3)	1.63
Ca(2) — O(9)'	2.34	Si(2) — O(1)	1.68
Ca(2) — O(7)	2.36		
Ca(2) — O(8)	2.36		
Ca(2) — O(6)	2.45	O(1) — Si(1) — O(6)	100°
Ca(2) — O(8)'	2.46	O(1) — Si(1) — O(2)	109
		O(2) — Si(1) — O(4)	110
Ca(3) — O(5)	2.31	O(1) — Si(1) — O(4)	111
Ca(3) — O(4)	2.34	O(2) — Si(1) — O(6)	112
Ca(3) — O(2)	2.36	O(4) — Si(1) — O(6)	114
Ca(3) — O(9)	2.41		
Ca(3) — O(2)'	2.60	O(1) — Si(2) — O(7)	98
Ca(3) — O(3)	2.65	O(1) — Si(2) — O(5)	107
		O(5) — Si(2) — O(7)	107
Na — O(9)	2.25 *	O(1) — Si(2) — O(3)	109
Na — O(1)	2.35 *	O(3) — Si(2) — O(7)	113
Na — O(7)	2.57 *	O(3) — Si(2) — O(5)	121
Na — O(6)	2.66 *	Si(1) — O(1) — Si(2)	151
Ti — O(6)	1.97 *		
Ti — O(7)	1.99 *		
Ti — O(8)	2.00 *		

Note: A sign' is used to distinguish equivalent atoms. The distances preceded by one asterisk occur twice. The estimated standard deviations are 0.02 Å for distances and 1° for angles.

TABLE 3. Valence Balance in Götztenite

Cations	Anions								
	O(1)	O(2)	O(3)	O(4)	O(5)	O(6)	O(7)	O(8)	O(9)
Ca (1)		0.33	0.66	0.33	0.33			0.33	
Ca (2)						0.33	0.33	0.66	0.66
Ca (3)		0.66	0.33	0.33	0.33				0.33
Na	0.125					0.125	0.125		0.125
Ti						0.66	0.66	0.66	
Si (1)	1.00	1.00		1.00					
Si (2)	1.00		1.00		1.00		1.00		
Sum	2.125	1.99	1.99	1.66	1.66	2.115	2.115	1.65	1.115

In götzenite and rosenbuschite two successive "walls" are equivalent by translation while in seidozerite (monoclinic) they are related by a glide plane.

The arrangement of the cations in the "walls" and in the "ribbons" of these three minerals is shown in Fig. 1; in Table 4 the corresponding average cation-oxygen distances are listed. It is possible on this basis to make some considerations on the relations existing among götzenite, rosenbuschite and seidozerite. They are without any doubt isostructural. At this point the question arises whether they could also be isomorphous. The three minerals could be considered as terms of an isomorphous series if the minor differences in symmetry, bond distances and coordinations of the cations are neglected. In this case götzenite would be the Zr-free term, seidozerite the Zr-rich term and rosenbuschite an intermediate phase. This opinion would imply however that Zr and Ca are fully replaceable cations. One could also consider götzenite and rosenbuschite more strictly connected with each other than with seidozerite. In effect their "walls"

differ only for the ordering of Ca and Na while in seidozerite Mn is present. This atom has an average distance with oxygen of 2.19 Å; the corresponding octahedra in götzenite and rosenbuschite have mean metal-oxygen distances of about 2.37 Å. While in the "ribbons" of seidozerite two Zr atoms are present with an average Zr-O distance of 2.09 Å, only one zirconium occurs in rosenbuschite with an average Zr-O distance of 2.17 Å which is closer to a Ca-O distance. This Zr could be replaced by Ca, as in götzenite, without important changes in the structure. The presence of Mn and of a greater amount of Zr in seidozerite produces a significant contraction of the unit cell, while the cell parameters of götzenite and rosenbuschite are nearly identical (the doubling of *b* in the latter is due only to the ordering of some cations). In any event, only the crystallochemical study of other natural or synthetic examples of this type of mineral could give a conclusive answer to the question.

THE TWINNING IN GÖTZENITE

In the structure of götzenite the positions occupied by the atoms are nearly consistent with a mono-

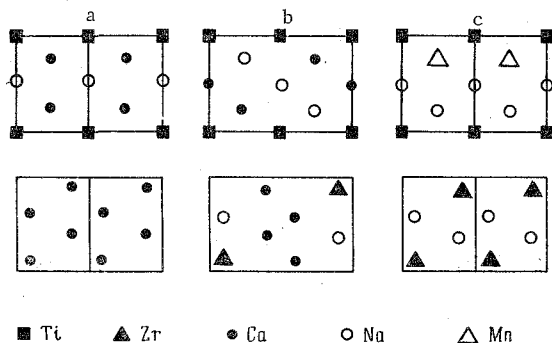


Fig. 1. Schematic view of the arrangement of the cations in the "walls" (top) and in the "ribbons" (bottom) of a) götzenite, b) rosenbuschite, and c) seidozerite. The plane of projection is normal to *a* in götzenite and to equivalent directions in rosenbuschite and seidozerite.

TABLE 4. Mean Cation-Oxygen Bond Distances in the Coordination Polyhedra of the "Walls" (a) and the "Ribbons" (b) of Götzenite, Rosenbuschite, and Seidozerite

Götzenite		Rosenbuschite		Seidozerite		
a	Ti	1.99	(Ti, Mn) (1)	2.00	Ti	1.96
	Ca(2)	2.37	(Ti, Mn) (2)	2.04		
	Na	2.45	Ca(3)	2.37	Mn	2.20
			Na(2)	2.38		
			Ca(4)	2.43	Na(II)	2.45
			Na(3)	2.44	Na(III)	2.45
b	Ca(1)	2.32	Zr	2.17	Zr	2.09
			Na(1)	2.43		
	Ca(3)	2.44	Ca(1)	2.34	Na, Ca	2.42
			Ca(2)	2.46		

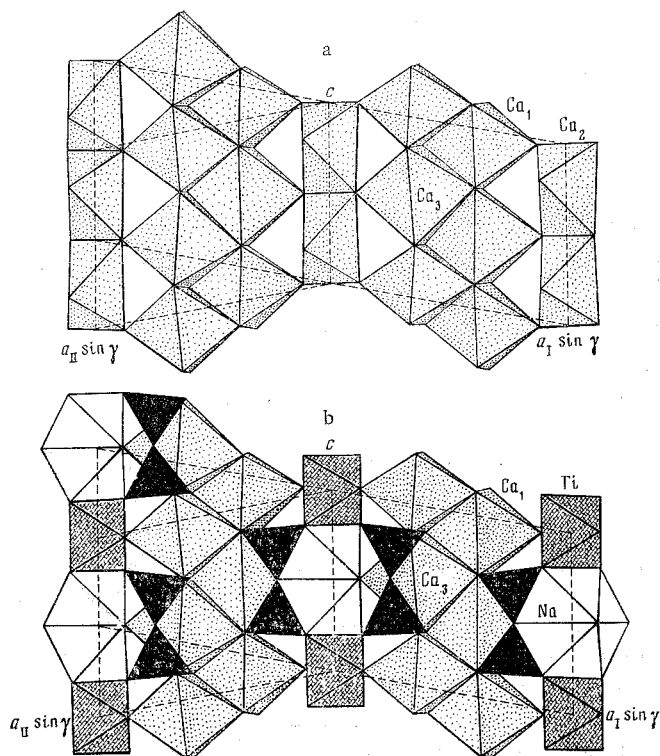


Fig. 2. The structural aspect of the twin in götzenite. a) Arrangement of Ca-polyhedra, which maintain their positions through the boundary between the individuals of the twin; b) the shift of $c/2$ of the Si_2O_7 groups and the consequent interchange between Na and Ti polyhedra caused by twinning.

clinic symmetry; however O(1), Si (1), and Si (2) occupy only one half of their respective sets of "monoclinic" positions, thus lowering the symmetry. In the twinned crystals the mentioned atoms occupy one half of their "monoclinic" positions in one individual and the other half in the second individual

of the twin. This fact appears as a shift of $1/2c$ of the Si_2O_7 groups and as an interchange of the positions of Na and Ti (Fig. 2 bottom). The remaining atoms maintained their positions through the boundary between the individuals of the twin as it is shown in Fig. 2 top by the Ca-octahedra. The features described above explain the fact that the intensities of the superposed reflections with $l = 2n$ are almost identical, as they correspond to equivalent reflections in the monoclinic pseudocell.

In rosenbuschite this type of twinning would produce a greater distortion of the structure owing to the presence of Zr. However, it has been observed in Weissenberg pictures of rosenbuschite from Langesund (Norway) that this mineral can be twinned in the same way as götzenite.

ACKNOWLEDGEMENTS

We are much indebted to Prof. Th. G. Sahama who made possible this investigation by sending a sample of götzenite from Mount Shaheru.

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