

CONTRIBUTIONS TO THE MINERALOGY OF NORWAY

No. 13. Rosenbuschite and its relation to Götzenite.

By

HENRICH NEUMANN

Rosenbuschite

Rosenbuschite was first described by W. C. BRØGGER (1887 and 1890) from a nepheline syenite pegmatite on the tiny island Skudesundskjær in Langesundfjord in Southern Norway. Langesundfjord remained the only locality for rosenbuschite until it was reported by A. E. TÖRNEBOHM (1906) as an accessory mineral in the nepheline syenite at Norra Kärr in Sweden, and it has later been found also in a few other places, always in nepheline syenitic rocks.

As far as the author knows, there exist only three chemical analyses of rosenbuschite (BRØGGER, 1890), see table 1: The first gives mean values of duplicate analyses by P. T. Cleve reporting a low loss on ignition (0.20%), no fluorine, and a fairly high content of rare earths (2.38%); the second gives a high content of fluorine (5.83%, determined by H. Bäckström), while the remainder of the analysis completed by Cleve gives a very low and query-marked content of rare earths (0.33%) and no loss on ignition. The third analysis is a compilation of what Cleve believed to be the most probable figures after having critically examined and discussed the data of the first and second analysis. This somewhat unsatisfactory state of affairs seemed to warrant a reinvestigation of the chemical composition of rosenbuschite.

A sample of rosenbuschite from the type locality was very carefully freed from impurities by repeated separations with heavy liquids as well as with numerous runs through a Frantz isodynamic separator. The material which was analyzed seemed to consist entirely of rosenbuschite without any recognizable traces of other minerals. The analysis is given in table 2, column 1, and is in fairly close agreement with the analyses published previously (see table 1).

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Table 1.

Previously published analyses of rosenbuschite, Skudesundskjær,
Langesundfjord (BRØGGER, 1890, pp. 382–383.).

	1	2	3
SiO ₂	31,53	31,36	31,44
ZrOF ₂			22,09
ZrO ₂	18,69	20,10	0,67
TiO ₂	7,59	6,85	7,22
Fe ₂ O ₃ ¹	1,15	1,00	1,07
Rare Earths	2,38 ²	0,33 ³	0,33 ³
MnO	1,85	1,39	1,62
CaO	25,38	24,87	25,12
Na ₂ O	10,15	9,93	10,04
Loss on ignition	0,20		
F		5,83	
— O for F		2,45	
	98,92	99,21	99,60

1. Analyst P. T. Cleve. 2. Analysts P. T. Cleve and H. Bäckström. 3. Best values from 1. and 2., selected by Cleve.

¹ State of oxidation not determined.

² Reported as "La₂O₃ (mit Spuren von Ce₂O₃ und Di₂O₃)".

³ Reported as "Ceritoxide (?)".

The structural data given by M. A. Peacock (1937) are used for calculation of atomic content of the unit cell together with the measured density of the analyzed material, = 3.35, and results are given in table 3. If the large ions are grouped together as X = Ca + Na + K + R.E. + Th + Mn, and the smaller ions as Y = Zr + Ti + Al + Fe the calculated unit cell content is X_{12.11}Y_{4.02}Si_{7.99}O_{31.09}(F + OH)_{5.42}. To account for the low figure for oxygen it seems most reasonable to assume that a minor part of the oxygen sites are occupied by OH (or F), which is a most common phenomenon in silicates, giving a model cell formula¹ X₁₂Y₄Si₈O₃₂(F, OH)₄, where X is mainly

¹ There is still a very minor surplus of fluorine and X-ions over the model formula. This might be explained by an admixture of very little fluorspar to the analyzed material, although this mineral could not be detected with the microscope.

Table 2.

Analysis of rosenbuschite, Skudesundskjær, Langesundfjord.

	1	2		1	2
SiO ₂	30,96	515,48	ThO ₂	0,14	0,53
TiO ₂	6,25	78,22	Al ₂ O ₃	1,35	13,24
ZrO ₂	18,25	148,11	Fe ₂ O ₃	0,52	3,26
La ₂ O ₃	0,10	0,31	FeO	none	
Ce ₂ O ₃	0,23	0,70	MnO	0,90	12,69
Pr ₂ O ₃	0,08	0,24	MgO	0,10	2,48
Nd ₂ O ₃	0,35	1,04	CaO	24,70	440,44
Sm ₂ O ₃	0,10	0,29	Na ₂ O	9,25	149,22
Eu ₂ O ₃	?		K ₂ O	0,05	0,53
Gd ₂ O ₃	0,16	0,44	P ₂ O ₅	n.d.	
Tb ₂ O ₃	0,03	0,08	SO ₃	n.d.	
Dy ₂ O ₃	0,24	0,64	CO ₂	none	
Y ₂ O ₃	1,94	8,59	Cl	n.d.	
Ho ₂ O ₃	tr.		F	5,57	293,16
Er ₂ O ₃	0,24	0,63	H ₂ O ⁺	0,51	28,30
Tm ₂ O ₃	?		H ₂ O ⁻	0,06	
Yb ₂ O ₃	0,39	0,99	- O for F	2,34	
Lu ₂ O ₃	?			100,13	

1. Weight per cent. 2. Molecular proportions. Analyst B. Bruun. X-ray spectrographical determinations of the individual rare earths by Gjert C. Faye of Statens Råstofflaboratorium.

Table 3.

Unit cell content of rosenbuschite.

O	31,094	Th	0,008	} 0,433
OH	0,877	La	0,010	
F	4,542	Ce	0,022	
Si	7,987	Pr	0,007	
Zr	2,295	Nd	0,032	
Ti	1,212	Sm	0,009	
Al	0,410	Gd	0,014	
Fe	0,101	Tb	0,002	
Mg	0,038	Dy	0,020	
Mn	0,197	Y	0,266	
Ca	6,824	Er	0,020	
Na	4,624	Yb	0,031	
K	0,016			

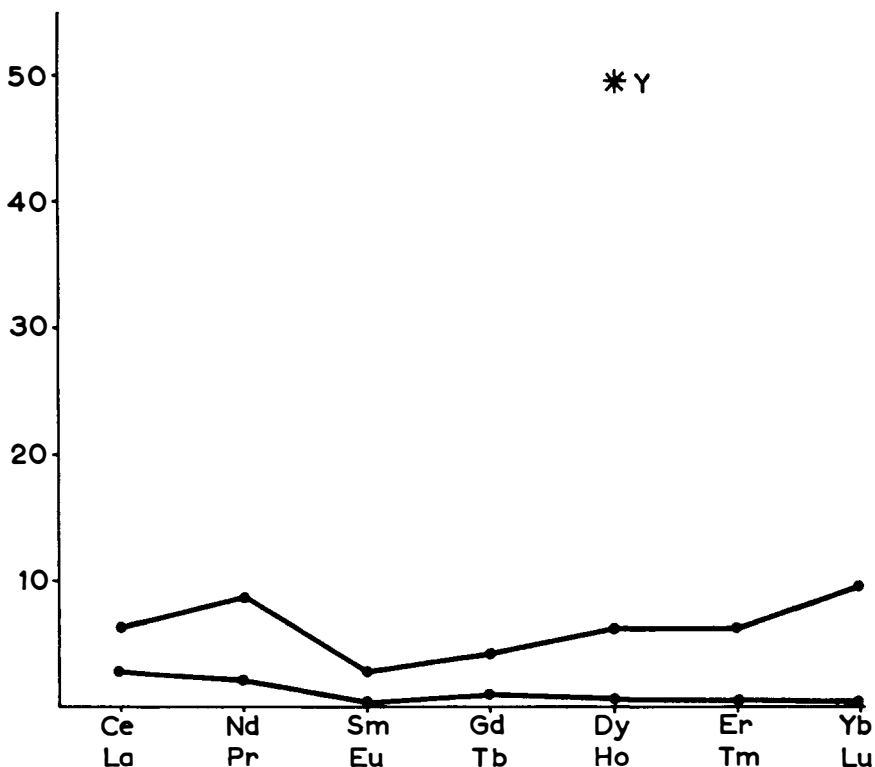


Fig. 1. Distribution of rare earths contained in rosenbuschite. (Analysed material.) Figures for individual elements in weight percent of total rare earth oxide content.

Ca and Na, and Y mainly Zr. In the rosenbuschite from Skudesundskjær the proportions of Ca:Na is close to 3:2². The simplified mineral formula may best be written $\text{Ca}_2\text{Na Zr Si}_2\text{O}_8\text{F}$, neglecting the fairly

² If the mechanism for R.E. replacing Ca is $\text{R.E.} + \text{Na} \rightleftharpoons 2 \text{Ca}$, rosenbuschite without rare earths will have $\text{Ca/Na} = 1.9$, (= rather close to 2). Possibly, this is not accidental, and may indicate two sets of structurally different sites of the X-positions in the model cell formula above, one set of 8 being occupied mainly by Ca, and another set of 4 mainly by Na. The two peaks of the distribution curve of the lanthanons (see fig. 1) are easily understood if there are two differently sized sets of sites for the X-ions, while that assumption is not confirmed by the chemical composition of götzenite (see later). — With the present scanty knowledge of the structure of rosenbuschite these remarks are by necessity purely speculative.

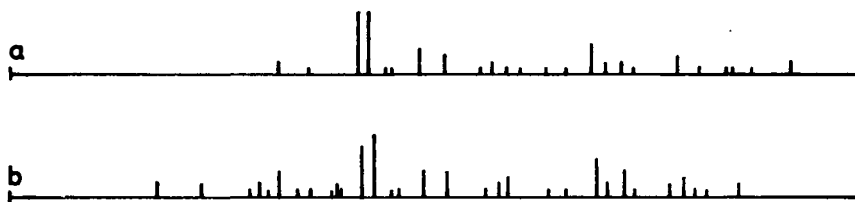


Fig. 2. X-ray powder patterns of a. götzenite, and b. rosenbuschite. Diagrams are "pictures" of X-ray films taken with filtered iron radiation in 9 cm cameras.

low content of rare earths replacing Ca + Na, and titanium replacing zirconium. The formula would indicate that rosenbuschite is a nesosilicate.

The above conclusions are in complete agreement with those of M. A. PEACOCK in his paper from 1937 "On Rosenbuschite".

The rare earths' distribution as illustrated in fig. 1 shows a pronounced preponderance of yttrium and a complete assemblage of the lanthanons with peaks for the small ytterbium and the large neodymium. The low Ce/Nd ratio is worthy of notice as seen in relation to the Nd/Pr and La/Pr ratios. It may indicate a high oxidation state with a high Ce^{IV}/Ce^{III} ratio in the chemical system concerned, a possibility which will be discussed in another context.

X-ray powder data for the analyzed rosenbuschite is presented in table 4 and fig. 2.

The relationship between rosenbuschite and götzenite

Götzenite was described in 1957 by Th. G. SAHAMA and KAI HYTÖNEN from a nephelinite from the extinct volcano Mt. Shaheru, North Kivu in Kongo. In the same year a sample was generously placed at my disposal while studying the powder patterns of silicates for publication in the X-ray atlas (NEUMANN et al. 1957). It appeared then that there is a striking resemblance between the powder patterns of rosenbuschite and götzenite as shown in fig. 2 and table 4 of this paper. Other physical constants are listed in table 5: Optically the two minerals are as closely related as most pairs of members of an isomorphous series. The difference in densities is normal for two structurally related minerals of which one is a zirconium-mineral and the other a titanium-mineral. Angles of the unit cells are the same

Table 4.
X-ray powder data for rosenbuschite and
götzenite.

Rosenbuschite		Götzenite	
d in Å	I	d in Å	I
7,20	20		
5,58	20		
4,44	10		
4,30	20		
4,14	10		
3,96	40	3,994	15
3,71	10		
3,55	10	3,601	5
3,31	10		
3,27	20		
3,24	10		
3,06	80	3,100	100
2,94	100	2,986	100
2,83	10	2,859	10
2,78	10	2,822	7
2,63	40	2,648	40
2,48	40	2,511	25
2,30	10	2,323	10
2,23	20	2,261	15
2,20	30	2,214	7
		2,152	5
2,04	10	2,059	5
1,98	10	1,989	7
1,89	60	1,911	50
1,86	20	1,876	15
1,82	40	1,833 ¹	15
1,70	20		
1,67	30		
1,57	20		

For rosenbuschite filtered iron radiation, 9 cm camera. For götzenite filtered copper radiation, data from SAHAMA and HYTÖNEN (1957).

¹ For lower d-values see SAHAMA and HYTÖNEN (1957).

within a few percent, and so are the lengths of the axes with these two modifications: 1) one axis in the unit cell of rosenbuschite is twice as long as in götzenite, and 2) c_0 of rosenbuschite equals b_0 of götzenite while b_0 of rosenbuschite equals c_0 of götzenite. The reason for this

Table 5.

Physical constants of rosenbuschite and götzenite.

Rosenbuschite	Götzenite
$a_0 = 10,12 \text{ \AA}$	$a_0 = 10,93 \text{ \AA}$
$b_0 = 11,39 \text{ \AA} = 2 \cdot 5,70 \text{ \AA}$	$b_0 = 7,32 \text{ \AA}$
$c_0 = 7,27 \text{ \AA}$	$c_0 = 5,74 \text{ \AA}$
$\alpha = 91^\circ 21'$	$\alpha = 90^\circ$
$\beta = 99^\circ 38'$	$\beta = 100^\circ$
$\gamma = 111^\circ 54'$	$\gamma = 120^\circ$
$X = 1,678$	$X = 1,660$
$Y = 1,687$	$Y = 1,662$
$Z = 1,705$	$Z = 1,670$
$Z - X = 0,027$	$Z - X = 0,010$
$2V + = 78^\circ$	$2V + = 52^\circ$
Sp.G. = 3,35	Sp.G. = 3,138

discrepancy is hardly a different choice of axes, as the angles β and γ are nearly identical. It would seem hard to find a reasonable explanation, and it is tempting to suggest that the values for b_0 and c_0 may have been interchanged at some stage of the process leading from the Weissenberg camera to the ready printed paper.

The unit cell content of götzenite as calculated by Sahama and Hytönen is $X_{6.66} Y_{1.66} Si_{3.98} O_{15.11} (F, OH, Co)_{3.47}$ where $X = Ca + Na + K$, and $Y = Ti + Al + Fe + Mn + Mg$. In comparison with the unit cell content of rosenbuschite, götzenite contains more Ca and F, which may be caused by a few per cent fluorite in the analyzed material which, if finely grained, could easily escape recognition by optical as well as X-ray methods. If a content of 3.4 per cent fluorite is postulated the unit cell content of götzenite can be recalculated³ to $X_{6.37} Y_{1.66} Si_{4.00} O_{15.19} (F, OH)_{2.81}$. On the assumptions, firstly, that some F replaces O, and, secondly, that about 5 per cent of the large ions (mainly Ca) enter the Y sites in the lattice this formula becomes $X_{6.03} Y_{2.00} Si_{4.00} O_{16.00} (F, OH)_{2.00}$ remarkably close to a model cell formula $X_6 Y_2 Si_4 O_{16} (F, OH)_2$, half of that given above for rosenbuschite. (It is recalled that one of the axes of the unit cell is twice as long in rosenbuschite as in götzenite.)

³ The very minor amounts of P_2O_5 , Cl, SO_3 , and H_2O^- have been neglected.

It is concluded that rosenbuschite and götzenite are isomorphous species. Rosenbuschite is near the zirconium end member, and götzenite is the (aluminiferous) titanium end member of a series which may or may not form mixed crystals.

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