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Grenmarite, a new member of the götzenite-seidozerite-rosenbuschite group from the Langesundsfjord district, Norway: definition and crystal structure

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Abstract: Grenmarite, a new mineral of the götzenite-seidozerite-rosenbuschite group, was found in a syenite pegmatite at the eastern side of the island Vesle Arøya in the Langesundsfjord district, Norway. Grenmarite, ideally $(Zr,Mn)_2(Zr,Ti)(Mn,Na)(Na,Ca)_4(Si_2O_7)_2(O,F)_4$, is the Zr-analogue of seidozerite. It is monoclinic with space group $P2/c$, $Z = 2$, $a = 5.608(1)$, $b = 7.139(1)$, $c = 18.575(5)$ Å, $\beta = 102.60(2)°$ and $V = 725.72(3)$ Å^3. It occurs as yellowish brown, semi-parallel aggregates of elongated, flattened crystals up to 1 cm in length. The mineral is translucent, with vitreous lustre, good {001} cleavage and uneven fracture. Mohs' hardness is $4^1/_2$; the measured density is 3.49(1) g/cm^3. The strongest five X-ray diffraction lines of the powder pattern [d in Å (I)] are: 2.898(100), 3.027(68), 2.613(26), 2.459(24), 1.853(24). An average of fifteen electron microprobe analyses of grenmarite gave SiO_2 29.85, TiO_2 4.51, CaO 1.84, MnO 8.25, FeO 2.01, Na_2O 15.43, Y_2O_3 0.22, Ce_2O_3 0.01, ZrO_2 31.63, Nb_2O_5 0.06, F 5.24, O ≡ F 2.21, total 96.84 wt.%. The empirical formula, based on 4 Si atoms, is $(Zr_{1.52}Mn_{0.46}Y_{0.02})_{\Sigma 2.00}(Zr_{0.55}Ti_{0.45})_{\Sigma 1.00}(Mn_{0.48}Na_{0.29}Fe_{0.23})_{\Sigma 1.00}(Na_{3.72}Ca_{0.26})_{\Sigma 3.98}\ Si_4O_{15.40}F_{2.22}$.

Grenmarite is isostructural with seidozerite: its structure can be described as built up with three distinct modules connected through corner-sharing: an "octahedral" layer, an "octahedral" ribbon, and disilicate groups. The crystal structure has been refined to a final R of 0.043. The crystal chemical formula resulting from the structural refinement is: $(Zr_{1.76}Mn_{0.24})_{\Sigma 2.00}(Zr_{0.54}Ti_{0.46})_{\Sigma 1.00}(Mn_{0.76}Na_{0.24})_{\Sigma 1.00}(Na_{3.32}Ca_{0.38}Mn_{0.30})_{\Sigma 4.00}(Si_2O_7)_2O_{1.96}F_{2.04}$.

Key-words: grenmarite, götzenite-seidozerite-rosenbuschite group, new mineral, crystal structure.

Introduction

The syenite pegmatites in the Larvik plutonic complex, Oslo Region, Norway, became famous from the classic monograph by Brøgger (1890). A brief description of the minerals was published by Andersen *et al.* (1996). The pegmatites are characterized by the abundance of beryllium minerals and zirconosilicates; the pegmatites at the Langesundsfjord district are specially rich in zirconosilicates. The type localities for wöhlerite, låvenite, rosenbuschite, hiortdahlite and catapleiite are all to be found within this area. Minerals of the eudialyte group are also abundant, an indicator of the agpaicity of the pegmatites.

In the 1989 the private collector T. Engvoldsen found a mineral which gave a diffraction pattern unmatching any known species. Preliminary investigations showed that the mineral was a manganese rich zirconosilicate, later called UK-9 by Andersen *et al.* (1996).

Our investigation showed that the mineral is a new member of the götzenite-seidozerite-rosenbuschite group, and has been named grenmarite after Grenmar, the Norse name of the Langesundsfjord.

The minerals of the götzenite-seidozerite-rosenbuschite group have triclinic or monoclinic symmetry and a general crystal chemical formula of the type $M_{16}(Si_2O_7)_4(O,OH,F)_8$, where M denotes cations with various possible charges and radii ranging from relatively large (Na, Ca) to medium (Ti, Zr, Mn, Fe). They are characterized by six-fold to eight-fold coordination (Table 1).

The new mineral species and its name have been approved by the Commission on New Minerals and Mineral Names, International Mineralogical Association (CNMMN no. 2003-024). The holotype material of grenmarite is stored in the Museo di Storia Naturale, Università di Pisa (Italy) under catalogue no. 18550, and in the Geological Museum, University of Oslo (Norway) under catalogue no. 33974.

Occurrence

Grenmarite was found in a small nepheline syenite pegmatite dyke in larvikite at the eastern side of the island Vesle Arøya in the Langesundsfjord district, Vestfold,

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Table 1. Crystal chemical formulas and space groups for the members of the götzenite-seidozerite-rosenbuschite group.

Ref.	Mineral	Formula	Space group
a	Götzenite	$Ca_4(Ca,Na)_4Ca_4Na_2Ti_2(Si_2O_7)_4F_8$	$P\bar{1}$
a	Rosenbuschite	$Zr_2Ca_2(Na,Ca)_4Ca_4Na_2ZrTi(Si_2O_7)_4F_4O_4$	$P\bar{1}$
a	Hainite	$(Ca,Zr,Y)_4(Na,Ca)_4Ca_4Na_2Ti_2(Si_2O_7)_4F_8$	$P\bar{1}$
b	Kochite	$Zr_2(Mn,Zr)_2(Na,Ca)_4Ca_4Na_2Ti_2(Si_2O_7)_4F_4O_4$	$P\bar{1}$
a	Seidozerite	$Zr_4Ti_2Mn_2Na_8(Si_2O_7)_4F_4O_4$	$P2/c$
c	Grenmarite	$(Zr,Mn)_4(Zr,Ti)_2(Mn,Na)_2(Na,Ca)_8(Si_2O_7)_4(F,O)_8$	$P2/c$

References: a) Christiansen *et al.*, 2003b; b) Christiansen *et al.*, 2003a; c) this work.

Norway [32VNL457415 (WGS84)]. This is the type locality also for cappelenite-(Y), described by Brøgger (1884; 1890). The dyke was extensively blasted already during the 1880's. Only remnants of the pegmatite are still present. Thus, grenmarite must be considered a very rare mineral, as there are only very few samples known to exist. Grenmarite occurs embedded in microcline and fine-grained albite. Associated minerals include (in order of decreasing abundance) microcline, aegirine, biotite, nepheline, albite, astrophyllite, låvenite, catapleiite, leucophanite, pyrochlore and fluorite. Minor amounts of molybdenite, sphalerite, galena and löllingite are also present. From observations of the paragenesis it can be concluded that grenmarite is among the first crystallized minerals in the pegmatite.

Physical and chemical data

Grenmarite occurs as semi-parallel aggregates of elongated, flattened crystals, up to 1 cm in length, striated parallel to [010] and often slightly curved. The crystals are dominated by the pinacoids {201} and $\{20\bar{3}\}$. Crystals of grenmarite are translucent, yellowish brown, dark brown when altered, with vitreous lustre. The streak is very pale yellowish brown. The mineral is brittle with a good {001} cleavage and uneven fracture. Mohs' hardness is $4^{1}/_{2}$. The density, measured with sink/float method using Clerici's liquid, is 3.49(1) g/cm^3; the density calculated using the empirical formula based on 4 Si atoms is 3.568 g/cm^3.

Optically, grenmarite is biaxial positive; optical orientation is X = *b*, Z ^ *a* = 42° with refractive indices (measured with λ = 589 nm) n_α = 1.694, $n_{\gamma I}$ = 1.735. The mineral is pleochroic being X colourless and Z_I light brown. Gladstone-Dale calculations (Mandarino, 1981) give compatibility indices of 0.022 (using the calculated density, and the mean of α and γ_I as refractive index), which is excellent, and 0.000 (using the measured density), which is superior.

Grenmarite was ground and pressed into a KBr pellet, and the infrared spectrum was recorded over the region 400 - 4000 cm^{-1} using a Perkin Elmer S-2000 FT-IR spectrometer (Fig. 1). The spectrum shows a minor, broad absorption band at 3460 cm^{-1} (O-H stretching) and a small, but sharp band at 1621 cm^{-1} (H-O-H bending). Absorption bands due to Si-O stretching and bending vibrations appear at (cm^{-1}, w - weak, m – medium, s - strong): 1082 w, 987 w, 938 s, 855 w, 730 w, 605 w, 535 w, 493 w, 440 s.

Fifteen chemical analyses [three analytical points (core, middle, rim) in five crystals] were carried out in wavelength-dispersive (WD) mode on a ARL-SEMQ electron microprobe. Data reduction was done with ϕρZ routine.

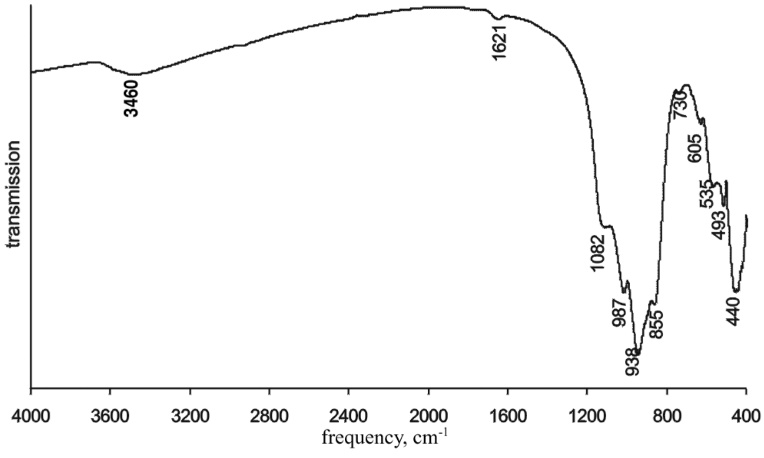

Fig. 1. Infra-red spectrum of grenmarite.

The operating voltage was 15 kV, the beam current was 20 nA and the beam diameter was 20 µm. Standards used were albite (Si*K*α, Na*K*α), ilmenite (Ti*K*α, Fe*K*α), anorthite (Ca*K*α), spessartine (Mn*K*α), synthetic Y_2O_3 (Y*L*α), synthetic $LaPO_4$ (La*L*α), synthetic $CePO_4$ (Ce*L*α), Zr metal (Zr*L*α), Nb metal (Nb*L*α), fluorite (F*K*α). The mean chemical composition and ranges are reported in Table 2. A very minor amount of water was detected in the IR spectrum, but not quantified. The presence of OH groups can be excluded on the basis of some structural considerations (see "Crystal structure determination and refinement"). Therefore it should be due to very minor adsorbed water. The relatively low total of the EPM analyses had been tentatively attributed to the possible presence of some components not analysed for, such as Al_2O_3, MgO, SrO and HfO_2. However, the same and even heavier deficits have been observed in all the samples (apart from the sample of götzenite, with a total of 98.43 %) examined by Christiansen *et al.* (2003b), namely kochite (total 95.95 %), hainite (total 97.08 %), rosenbuschite (two samples with totals 95.84 % and 96.74 %), seidozerite (total 95.58 %), notwithstanding Al_2O_3, MgO, SrO and HfO_2 were included among the analysed components. We have no clear and convincing explanation for this, actually limited, deficit, which seems recurrent in EPM analyses of minerals in this group.

The empirical formula, recalculated on the basis of 4 Si atoms is: $(Zr_{1.52}Mn_{0.46}Y_{0.02})_{\Sigma 2.00}(Zr_{0.55}Ti_{0.45})_{\Sigma 1.00}(Mn_{0.48}Na_{0.29}Fe_{0.23})_{\Sigma 1.00}(Na_{3.72}Ca_{0.26})_{\Sigma 3.98}\ Si_4O_{15.40}F_{2.22}$, which may be written in simplified form as $(Zr,Mn)_2(Zr,Ti)(Mn,Na)(Na,Ca)_4(Si_2O_7)_2(O,F)_4$.

Table 2. Chemical composition (in wt.%) of grenmarite.

	mean, n = 15	range
SiO_2	29.85	29.26 - 30.53
TiO_2	4.51	3.52 - 5.24
CaO	1.84	1.31 - 2.61
MnO	8.25	7.59 - 9.28
FeO	2.01	1.65 - 2.54
Na_2O	15.43	15.14 - 15.72
Y_2O_3	0.22	0.10 - 0.42
La_2O_3	0.00	0.00 - 0.02
Ce_2O_3	0.01	0.00 - 0.05
ZrO_2	31.63	29.45 - 34.86
Nb_2O_5	0.06	0.00 - 0.29
F	5.24	3.12 - 6.38
Sum	99.05	
O=F	-2.21	
Total	96.84	

X-ray crystallography

Single-crystal rotation and Weissenberg photographs of grenmarite show that it is monoclinic, space group *P*2/*c*, with cell parameters very close to those of seidozerite. X-ray powder diffraction data were obtained using a Philips X'pert diffractometer with Cu-target source, automatic divergence slits, and a secondary graphite monochromator

Table 3. X-ray powder diffraction data for grenmarite.

I	d_{meas}	d_{calc}	*hkl*	I	d_{meas}	d_{calc}	*hkl*
12	7.142	7.139	0 1 0	5	2.148	2.148	2 0 4
12	6.645	6.645	0 1 1	3	2.117	2.116	2 2 1
2	5.601	5.612	0 1 2	3	2.083	2.082	-1 2 7
5	5.484	5.484	1 0 0	1	2.027	2.027	-2 2 5
1	5.231	5.227	-1 0 2	3	1.971	1.973	-2 0 8
2	4.544	4.538	0 0 4	3	1.942	1.942	2 2 3
3	4.404	4.406	-1 1 1	24	1.853	1.853	1 2 7
9	4.348	4.349	1 1 0	2	1.828	1.827	-2 2 7
3	4.220	4.218	-1 1 2			1.824	3 0 0
12	4.071	4.073	1 1 1	3	1.812	1.812	-2 3 1
15	3.949	3.946	-1 0 4	14	1.786	1.785	0 4 0
9	3.683	3.681	1 1 2	3	1.772	1.773	-1 2 9
10	3.453	3.454	-1 1 4	5	1.738	1.737	2 2 5
3	3.320	3.322	0 2 2	3	1.718	1.717	3 0 2
7	3.235	3.236	0 1 5	5	1.695	1.694	-2 0 10
2	3.161	3.172	1 0 4	14	1.650	1.651	-3 2 3
5	3.056	3.061	-1 1 5	7	1.626	1.626	-1 4 4
68	3.027	3.025	0 0 6	3	1.605	1.606	0 1 11
4	2.988	2.992	1 2 0			1.603	-3 2 5
2	2.933	2.934	-1 0 6	6	1.586	1.586	2 0 8
100	2.898	2.897	1 2 1	10	1.539	1.538	2 2 7
5	2.797	2.800	-2 0 2			1.536	0 4 6
7	2.740	2.742	-2 0 0	9	1.524	1.524	-1 2 11
3	2.708	2.714	-1 1 6	7	1.513	1.515	-3 2 7
26	2.613	2.614	-2 0 4	6	1.498	1.497	3 2 3
6	2.564	2.563	1 2 3	5	1.474	1.474	-2 4 4
4	2.478	2.479	2 0 2	4	1.448	1.449	2 4 2
24	2.459	2.457	-1 2 5	3	1.441	1.438	1 4 6
5	2.434	2.433	1 0 6	4	1.400	1.399	-4 0 2
2	2.339	2.342	2 1 2	4	1.382	1.381	1 0 12
2	2.297	2.297	-2 0 6	3	1.367	1.368	-4 0 0
6	2.269	2.269	0 0 8	3	1.291	1.290	3 0 8
8	2.205	2.205	-2 2 1	3	1.284	1.283	-1 4 10
3	2.185	2.184	1 2 5	2	1.239	1.237	4 0 4
11	2.171	2.170	-2 2 3	3	1.228	1.229	-2 4 10

Table 4. Crystal data and refinement details for grenmarite.

Space group	$P2/c$
a	5.608(1)Å
b	7.139(1)Å
c	18.575(5)Å
β	102.60(2)°
Density (meas. and calc.)	3.49 g/cm^3 and 3.568 g/cm^3
Cell volume	725.72(3)Å^3
Z	2
Radiation type (wavelength)	Mo$K\alpha$ (0.71073 Å)
Crystal size	0.28 x 0.14 x 0.08 mm^3
Scan mode	θ-2θ
Scan width	± 0.57 ° (in θ)
Scan speed	2 °/min
θ range for data collection	4 - 59.99° (in 2θ)
Reflection ranges	$-1 \leq h \leq 7$
	$-1 \leq k \leq 10$
	$-25 \leq l \leq 25$
Reflections collected / unique	2125 / 1455
Reflections observed	1427 with $F_0 > 4\sigma F_0$
Absorption correction	Ψ-scan on 3 reflections
Absorption coefficient	3.639 mm^{-1}
Data / restraints / parameters	1427 / 0 / 150
Goodness of fit[(a)]	1.069
Final $R^{(b)}$ indices [I>2σ(I)]	$R_1 = 0.043$
	$wR_2 = 0.114$
Largest diff. peak and hole	3.11 and -1.55 e/Å^3

(a): Goodness-of-fit = $[\Sigma[w(F_o^2 - Fc^2)^2]/(N-P)]^{1/2}$, where N, P are the numbers of data and parameters.

(b): $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$; $w = 1/[\sigma^2(F_o^2)+(0.0853Q)^2+0.00Q]$ where Q = [Max (F_o^2,0)+2F_c^2)/3

(Cu$K\alpha$ radiation). Single crystal Si zero background plate was used. Data were collected from 5° to 80° 2θ with steps of 0.02° 2θ and 10 s counting time per step. Si (NBS 640a) was used for calibration of the diffractometer. The X-ray powder diffraction pattern of grenmarite shown in Table 3 is obtained after computerised $K\alpha_2$ stripping. Indexing was made taking into account the intensity data collection. Indexing and least squares refinement were done by the program CELREF (Laugier & Bochu, 1999). The refined unit cell dimensions found are a = 5.620(1) Å, b = 7.140(1) Å, c = 18.602(5) Å, β = 102.64(2)°, and V = 728.45 Å^3.

Crystal structure determination and refinement

A crystal with dimensions of 0.28 x 0.14 x 0.08 mm^3 was chosen for X-ray single-crystal data collection. The intensity data were collected with an Ital Structure automatic four-circles diffractometer using Mo$K\alpha$ radiation. The measured reflections were corrected for Lorentz, polarization and absorption factors. This last correction was made according to the method of North *et al.* (1968). The unit-cell parameters were determined by the least squares method based on the angular parameters of 30 reflections in the range $18° \leq 2\theta \leq 30°$. The structure was refined in the space group $P2/c$ starting from the atomic coordinates reported by Puschcharovskii *et al.* (2002) for seidozerite. Details of the data collection and structure refinement are given in Table 4.

The refinement of the structure was carried out using the SHELXL97 program package (Sheldrick, 1997). Initially, the structure was refined isotropically to R = 0.085, thus validating the initial structural model. The distribution of the cations over the six non-equivalent "octahedral" sites (called M-sites) was established taking into account the corresponding electron densities, bond valence balance, agreement between the average interatomic distances and the sum of the ionic radii in the various polyhedra; in assessing the cationic distribution in the polyhedral sites, Mn represents also Fe, due to the very similar scattering power. The occupancies were subsequently refined and after introduction of the anisotropic thermal parameters the final residual was R = 0.043 for 1427 reflections with $F_o > 4\sigma(F_o)$. Positive residual densities have been observed near some cationic sites [0.81-0.83 Å from M(1) and M(2)]. They are probably due to incomplete account for absorption; in fact an additional absorption correction with the XABS2 program (Parkin *et al.*, 1995) completely eliminates the Δρ positive maxima (and gives a better final R index); however we did prefer to keep the reflection data set without this "theoretical" correction. Table 5 reports the occupancies of the six independent "octahedral" structural sites present in the structure of grenmarite, together with those of the structure of seidozerite as given by Simonov & Belov (1960) and Pushcharovskii *et al.* (2002). As it can be seen, with respect to seidozerite, zirconium is the major cation in both M(1) and M(2) structural sites of grenmarite.

Table 5. Wyckoff multiplicity and occupancy for the M-sites in grenmarite and seidozerite.

Position	Wyckoff multiplicity	Occupancies		
		Grenmarite (present study)	Seidozerite (Simonov & Belov, 1960)	Seidozerite (Pushcharovskii *et al.*, 2002)
M(1)	4	$Zr_{0.88}$ $Mn_{0.12}$	$Zr_{0.75}$ $Ti_{0.25}$	$Zr_{0.8}$ $Ti_{0.2}$
M(2)	2	$Zr_{0.54}$ $Ti_{0.46}$	Ti	$Ti_{0.70}$ $Zr_{0.25}$
M(3)	2	$Mn_{0.76}$ $Na_{0.24}$	Mn (Mg)	$Mn_{0.58}$ $Na_{0.25}$ $Ti_{0.05}$
M(4)	4	$Na_{0.85}$ $Mn_{0.15}$	Na	$Na_{0.965}$ $Ca_{0.035}$
M(5)	2	$Na_{0.86}$ $Ca_{0.14}$	Na	$Na_{0.86}$ $Ca_{0.14}$
M(6)	2	$Na_{0.76}$ $Ca_{0.24}$	Na	$Ca_{0.34}$ $Mn_{0.27}$ $Na_{0.16}$

The estimated standard deviations for occupancies in grenmarite are ~ 0.01.

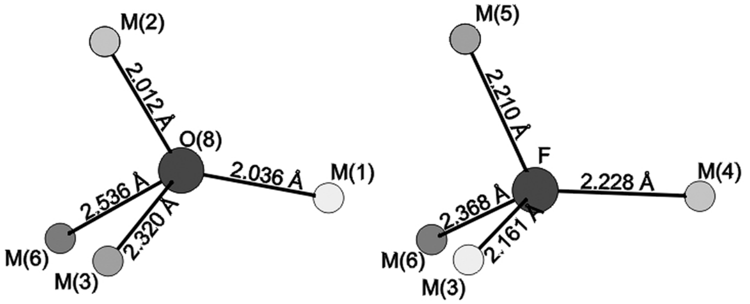

Fig. 2. Coordination polyhedra for the O(8) and F anion sites.

Table 6. Atomic coordinates and thermal parameters for the basis atoms in grenmarite.

Atom	*x*/*a*	*y*/*b*	*z*/*c*	U_{eq}
M(1)	0.2004(1)	0.1197(1)	0.0733(1)	0.012(1)
M(2)	0	0.1143(1)	1/4	0.012(1)
M(3)	1/2	0.3533(2)	1/4	0.016(1)
M(4)	0.2051(4)	0.6151(3)	0.0695(1)	0.023(1)
M(5)	0	0.6152(4)	1/4	0.023(1)
M(6)	1/2	0.8589(4)	1/4	0.028(1)
Si(1)	0.7237(3)	0.3884(2)	0.1034(1)	0.012(1)
Si(2)	0.7203(3)	0.8413(2)	0.1041(1)	0.012(1)
O(1)	0.7355(9)	0.6144(5)	0.1071(3)	0.029(1)
O(2)	0.4473(7)	0.3259(6)	0.0661(2)	0.022(1)
O(3)	0.4398(7)	0.9015(5)	0.0755(2)	0.020(1)
O(4)	0.9256(7)	0.3239(6)	0.0587(2)	0.020(1)
O(5)	0.9035(7)	0.9074(5)	0.0515(2)	0.019(1)
O(6)	0.7911(7)	0.3185(6)	0.1891(2)	0.019(1)
O(7)	0.8161(7)	0.9100(5)	0.1881(2)	0.019(1)
O(8)	0.2439(8)	0.1266(5)	0.1851(2)	0.019(1)
F	0.3025(8)	0.5879(6)	0.1919(2)	0.034(1)

Concerning the question if OH groups are present, from a structural point of view the presence of hydroxyls can be excluded: only two anions are not linked to Si, namely O(8) and F; both are tetrahedrally coordinated by M-cations as it is shown in Fig. 2, so the presence of OH can be excluded even in these sites, whereas a substitution of oxygen with fluorine may be possible.

Final positional coordinates of the atoms and their equivalent isotropic displacement parameters are given in Table 6.

Description of the structure

Grenmarite is a member of the götzenite-seidozerite-rosenbuschite group, together with götzenite (Cannillo *et al.*, 1972), rosenbuschite (Shibaeva *et al.*, 1964), hainite (Atencio *et al.*, 1999), kochite (Christiansen *et al.*, 2003a) and seidozerite (Simonov & Belov, 1960; Pushcharovskii *et al.*, 2002). Grenmarite is isostructural with seidozerite, with zirconium dominating in both the M(1) and M(2) sites, occupied by high-charge cations.

The crystal structure of grenmarite, drawn by the program ATOMS (Dowty, 1995), is represented in Fig. 3 in terms of octahedra and tetrahedra: M(4) and M(5) sites are actually eight-fold coordinated, but they were drawn as octahedra to obtain a clearer view of the structure.

In accordance with the other minerals of the group, grenmarite can be described as built up by three

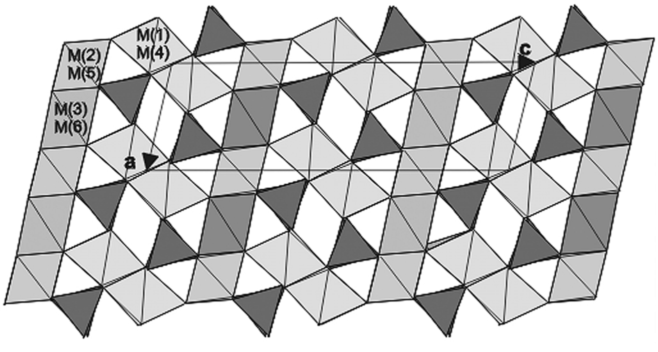

Fig. 3. Crystal structure of grenmarite, as seen along [010]. The occupancies of the six independent M-sites are:

M(1): $Zr_{0.88}Mn_{0.12}$ M(4): $Na_{0.85}Mn_{0.15}$
M(2): $Zr_{0.54}Ti_{0.46}$ M(5): $Na_{0.86}Ca_{0.14}$
M(3): $Mn_{0.76}Na_{0.24}$ M(6): $Na_{0.76}Ca_{0.24}$

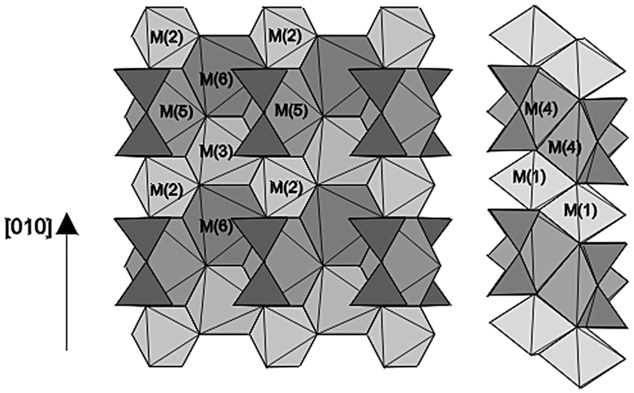

Fig. 4. Regular alternation of structural sites along [010] in the octahedral layer (a) and in the ribbon (b) of grenmarite.

Table 7. Bond distances (Å) for the diorthosilicate groups in grenmarite (standard deviations in parentheses).

Si(1) - O(4)	1.611(4)	Si(2) - O(3)	1.605(4)
- O(1)	1.615(4)	- O(7)	1.612(4)
- O(2)	1.617(4)	- O(1)	1.622(4)
- O(6)	1.631(4)	- O(5)	1.634(4)
Average value	1.619	Average value	1.618

“modules”, namely “octahedral layers” parallel to (001), “octahedral ribbons”, two columns wide and running along [010], as well as diorthosilicate groups. As represented in Fig. 4, both “layers” and “ribbons” are made up by edge-sharing polyhedra, characterized by six-fold to eight-fold coordination, interconnected through corner-sharing to form a polyhedral framework. Each diorthosilicate group shares common corners with one layer and two ribbons.

Diorthosilicate groups

The main geometrical features of the diorthosilicate groups are given in Table 7. As in seidozerite, in grenmarite all the Si-O bond lengths are similar, whereas in the other minerals of the group the bonds to the bridging oxygen O(1) are generally longer than the other Si-O bonds (Christiansen *et al.*, 2003b). The Si-O-Si angle is 173.3° which is the same value observed in seidozerite. This angle is definitely larger in grenmarite and seidozerite than in the other minerals of the group, in which it ranges from 154.1° to 163.6° (Christiansen *et al.*, 2003b).

Bond valence calculations, reported in Table 8, indicate that in grenmarite the bridging oxygen atom is overbonded by more than 0.2 valence units. A similar overbonding of the bridging oxygen atoms has also been observed in members of the cuspidine group (Mellini, 1981; Merlino *et al.*, 1990, Perchiazzi *et al.*, 2000). As stated by Mellini (1981), the systematic overbonding of the bridging oxygen atoms may be due to the use of a correlation between bond distance and bond strength which does not take into account other parameters like bond angles and mutual screening among atoms. In the case of grenmarite, the bridging oxygen atom of the diorthosilicate group is screened by the non-bridging oxygen atoms, and it is conceivable that this results in a weaker interaction with the M(4) and M(5) sites, with respect to that expected on the basis of the measured distance.

Table 8. Bond valence sums for grenmarite. $\Sigma_c v$ and $\Sigma_a v$ give the sum of charge reaching each anion and cation, respectively, together with the values calculated from the occupancies (in parentheses).

	O(1)	O(2)	O(3)	O(4)	O(5)	O(6)	O(7)	O(8)	F	$\Sigma_a v$
M(1) ($Zr_{0.88}Mn_{0.12}$)		0.71	0.71	0.63	0.45 0.39			0.74		3.63 (3.76)
M(2) ($Zr_{0.54}Ti_{0.46}$)						0.66^{x2}	0.74^{x2}	0.72^{x2}		4.24 (4.00)
M(3) ($Mn_{0.76}Na_{0.24}$)						0.28^{x2}		0.20^{x2}	0.28^{x2}	1.52 (1.76)
M(4) ($Na_{0.85}Mn_{0.15}$)	0.06 0.05	0.16	0.19	0.21 0.12	0.10				0.23	1.12 (1.15)
M(5) ($Na_{0.86}Ca_{0.14}$)	0.08^{x2}					0.14^{x2}	0.16^{x2}		0.26^{x2}	1.28 (1.14)
M(6) ($Na_{0.76}Ca_{0.24}$)							0.26^{x2}	0.16^{x2}	0.18^{x2}	1.20 (1.24)
Si(1)	1.02	1.02		1.04		0.98				4.06 (4.00)
Si(2)	1.00		1.05		0.98		1.03			4.06 (4.00)
$\Sigma_c v$	2.21	1.89	1.95	2.00	1.92	2.06	2.19	1.82	0.95	

Bond valence parameters taken from Brese & O’Keeffe (1991). Right “x2” superscript means that the corresponding bond valences have been considered twice in the horizontal sums, in keeping with the special positions of the involved atoms.

Table 9. Bond distances (Å) for the non-tetrahedral coordination polyhedra in grenmarite (standard deviations in parentheses).

cation	anion	distance (Å)	cation	anion	distance (Å)
M(1)	- O(8)	2.037(4)	M(2)	- O(7)^{XIII}	1.999(4)
($Zr_{0.88}Mn_{0.12}$)	- O(2)	2.045(4)	($Zr_{0.54}Ti_{0.46}$)	- O(7)^{XII}	1.999(4)
	- O(3)^{XX}	2.051(4)		- O(8)	2.013(4)
	- O(4)^{IX}	2.094(4)		- O(8)^{XI}	2.013(4)
	- O(5)^{XII}	2.222(4)		- O(6)^{VII}	2.049(4)
	- O(5)^{VI}	2.273(4)		- O(6)^{IX}	2.049(4)
	Average	2.120		Average	2.020
M(3)	- F^{VII}	2.162(4)	M(4)	- F	2.229(4)
($Mn_{0.76}Na_{0.24}$)	- F	2.162(4)	($Na_{0.85}Mn_{0.15}$)	- O(4)^{VI}	2.374(4)
	- O(6)	2.194(4)		- O(3)	2.421(4)
	- O(6)^{VII}	2.194(4)		- O(2)	2.480(5)
	- O(8)	2.319(4)		- O(4)^{IX}	2.585(5)
	- O(8)^{VII}	2.319(4)		- O(5)^{IX}	2.661(5)
	Average	2.225		- O(1)^{IX}	2.868(5)
				- O(1)	2.904(5)
				Average	2.565
M(5)	- F	2.208(4)	M(6)	- O(7)	2.342(4)
($Na_{0.86}Ca_{0.14}$)	- F^{XI}	2.208(4)	($Na_{0.76}Ca_{0.24}$)	- O(7)^{VII}	2.342(4)
	- O(7)^{VII}	2.510(5)		- F	2.368(5)
	- O(7)^{IX}	2.510(5)		- F^{VII}	2.368(5)
	- O(6)^{IX}	2.561(5)		- O(8)^{VIII}	2.532(5)
	- O(6)^{VII}	2.561(5)		- O(8)^{II}	2.532(5)
	- O(1)^{VII}	2.744(5)		Average	2.414
	- O(1)^{IX}	2.744(5)			
	Average	2.506			

Operations for generating equivalent atoms are:

I. x+1,y,z
II. x,y-1,z+1
III. x+1,y+1,z
IV. -x,-y,-z
V. -x,-y+1,-z
VI. -x+1,-y+1,-z
VII. -x+1,y,-z+1/2
VIII. -x+1,y+1,-z+1/2
IX. x-1,y,z
X x,y-1,z
XI. -x, y,-z+1/2
XII. x-1,y-1,z
XIII. -x+1, y-1, -z+1/2

Large coordination polyhedra

Bond distances for the six independent cation sites present in the grenmarite structure are given in Table 9. The arrangement of the cation sites in the layers and in the ribbons is shown in Fig. 4: the M(2), M(3), M(5) and M(6) sites regularly alternate in the layers, M(1) and M(4) sites in the ribbons. M(2) site hosts zirconium and titanium, with zirconium dominant, whereas in seidozerite the M(2) site hosts only titanium (Simonov & Belov, 1960) or titanium largely dominating over zirconium and vacancies (Pushcharovskii *et al.*, 2002). As it happens in seidozerite, the incorporation of a small Mn octahedron [M(3) site] in the polyhedral layers of grenmarite results in a *b* parameter shorter than that of the other members of the götzenite-seidozerite-rosenbuschite group, in which the corresponding site is occupied by larger cations (Na, Ca).

The coordination polyhedra of the sites M(1), M(2), M(3), and M(6) are octahedra. M(4) and M(5) have eight ligands. Their coordination polyhedra are the biggest polyhedra in the structure: the diorthosilicate groups are attached to these polyhedra.

For what is concerning the bond valence balance (Table 8), no significant discrepancies are found between the sum of the valences reaching each large coordination cation and the values calculated from occupancies, whereas the low sum of the valences reaching the O(8) anion suggests a possible substitution of oxygen with fluorine.

Taking into account these latter considerations, the crystal-chemical formula which results from the structural study is $(Zr_{1.76}Mn_{0.24})_{\Sigma 2.00}(Zr_{0.54}Ti_{0.46})_{\Sigma 1.00}(Mn_{0.76}Na_{0.24})_{\Sigma 1.00}(Na_{3.32}Ca_{0.38}Mn_{0.30})_{\Sigma 4.00}(Si_2O_7)_2O_{1.96}F_{2.04}$.

Conclusions

Grenmarite is a new natural phase in the götzenite-seidozerite-rosenbuschite group. It is isostructural with seidozerite, with zirconium dominating not only in M(1) site, as it happens in seidozerite, but also in the M(2) site where it substitutes for titanium. The Zr ↔ Ti substitution results in a compositional series between grenmarite and seidozerite, in which grenmarite represents the Zr-rich end-member. Christiansen *et al.* (2003b) found a similar compositional series between kochite and rosenbuschite, in which the Zr-rich end-member is represented by kochite.

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