Roggianite: revised chemical formula and zeolitic properties

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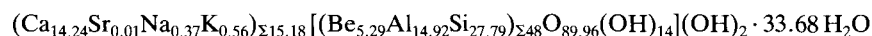
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Abstract

The holotype roggianite from Alpe Rosso (Novara, Italy) has been chemically re-analysed using modern analytical procedures (microprobe, atomic absorption spectrophotometer, TG analyses) and tested for its zeolitic behaviour. When compared with that given in the original description, the new chemical composition shows an appreciable amount of Be and a different Si/Al ratio. On the basis of its structural data, the chemical formula here proposed for roggianite is:

$$(Ca_{14.24}Sr_{0.01}Na_{0.37}K_{0.56})_{\Sigma 15.18} [(Be_{5.29}Al_{14.92}Si_{27.79})_{\Sigma 48}O_{89.96}(OH)_{14}](OH)_2 \cdot 33.68\,H_2O$$

An accurate powder pattern, index taking into account the structural factors, is also given. Since the mineral showed an almost complete rehydration after heating to 750 °C and an appreciable ion exchange capacity, it must be considered as belonging to the zeolitic group of minerals, and, in this frame, it represents the first and up to now the only zeolite with Be as fundamental constituent and, like partheite, with OH groups in the framework.

KEYWORDS: roggianite, zeolitic properties, Alpe Rosso, Italy

Introduction

ROGGIANITE is a natural hydrated calcium alumino silicate to date described from only two localities, both in Val Vigezzo (Novara, Italy)—the first (Passaglia, 1969) at Alpe Rosso, the second (Vezzalini and Mattioli, 1979) at Pizzo Marcio. The chemical composition of the holotype material (Passaglia, 1969) was obtained on material containing small quantities of an unknown organic contaminant using analytical procedures available at that time—gravimetric, emission spectrophotometric, volumetric complessometric and colorimetric methods. The chemical composition of a sample from Pizzo Marcio (Vezzalini and Mattioli, 1979) was obtained with an electron microprobe, the water content being given as a difference to 100%. The two analyses, so obtained, show the same most abundant cations (Si, Al, Ca, H_2O), but in significantly different ratios.

Galli (1980), using a single crystal of the sample from Pizzo Marcio (the holotype sample from Alpe Rosso occurs only as fibrous aggregates) solved the structure that resulted in an interrupted (Si, Al) framework with some OH vertices unshared by two tetrahedra; Ca cations and water molecules lie in cavities where the framework is interrupted and in the largest channels, respectively. Such a structure led Galli to classify roggianite as a zeolite-like silicate and it was considered in the same way by Gottardi and Galli (1985), although properties peculiar to zeolites (rehydration, cation exchange capacity) have not yet been proved for it.

Recently, the Commission on New Minerals and Mineral Names of IMA, urged us to test the holotype roggianite for Be content, not determined in the original description. Since this resulted in a determination of 3.19% BeO, the mineral was completely re-examined in order to determine its complete and accurate chemical and crystallographic features by using modern analytical procedures (electron microprobe, atomic absorption spectrometer, TG analyser, X-ray diffractometer) and to test its zeolitic behaviour.

X-ray powder diffraction

The X-ray powder data of roggianite given in the original description were obtained by using a Debye-Scherrer camera (114.9 mm in diameter). In this work, a more accurate and complete X-ray powder pattern was measured on a Philips diffractometer with Ni-filtered Cu–$K\alpha$ radiation (λ = 1.54051 Å) and Pb(NO$_3$)$_2$ as an internal standard. As some peaks of the internal standard overlap some peaks of roggianite, a powder pattern without the internal standard was also obtained. The data reported in Table 1 are therefore the combination of the two powder patterns. The reflections are indexed according to the structure factors given by Galli (1980). Compared with the pattern given in the original description, this one shows several weak reflections not previously observed and the splitting of some lines with medium intensity.

Cell dimensions from the powder pattern were determined by a least-squares refinement program using an indexing method (Alberti, 1976) which takes into account the structure factors. The reflections too far from, or overlapping with the standard lines were discarded; therefore only the spacings marked with a star in Table 1 were used in this calculation.

The unit cell dimensions so calculated are: a 18.370(4); c 9.187(4) Å. These values differ from those reported both in the original description (Passaglia, 1969) and by Gard (1969) within the experimental errors, but they are decidedly more accurate. The values given by Galli (1980) for roggianite from Pizzo Marcio are very similar to those here measured.

X-ray powder patterns were also recorded by a Gandolfi camera on roggianite previously heated to various temperatures. Heating up to 850 °C, the spectrum is substantially identical to that of the unheated sample, whereas after heating to 900 °C the powder pattern is that of a feldspar. The roggianite framework breaks down only at temperatures higher than 850 °C and it reconstructs immediately in a feldspar framework.

Chemical composition

The chemical composition was obtained by combination of data from atomic absorption spectrometer (Be), thermal gravimetric (H$_2$O) and electron microprobe (all other elements) analyses.

Electron microprobe analysis was carried out in the wavelength dispersive mode on an ARL-SEMQ instrument operated at 15 kV and 15 nA beam current and with a defocused beam (spot size 18 µm). On-line data reduction was based on the Ziebold and Ogilvie (1964) method by use of the Albee and Ray (1970) correction factors. Natural albite, microcline and synthetic plagioclase glasses were used as standards for Si, Al, Na, K and Ca, synthetic anorthite for Sr. Fe, Ba and Mg were tested for but found to be absent. The chemical composition was obtained by averaging five point-analyses on pure fibrous aggregates (Table 2, col. 1a). The microprobe data were normalized to 100% taking into account the water content derived by TG analysis and BeO content resulting from atomic absorption spectrophotometry. The normalization was made to correct for the undetermined loss of zeolitic water under electron bombardment in the vacuum chamber of the microprobe (Table 2, col. 1b).

The TG analysis was made on 2.32 mg of powdered pure material using a Du Pont thermal analyser operated in air with a heating rate of 10 °C/min. TG and DTG curves (Fig. 1) indicate a faster weight loss (7%) between 30 °C and 200 °C followed by a slow and continuous one (7.5%) up to 850 °C; between this temperature and 950 °C a faster reaction (3.6% weight loss) occurs. From 950 °C to the final temperature of the experiment (1050 °C) no appreciable weight loss is observed. These curves are very similar to the DT curve of the original description (Passaglia, 1969) where two sharp endothermic peaks at 113 °C and 874 °C are present.

In Table 2 the new chemical analysis is compared with that reported in the original description and that given for roggianite from Pizzo Marcio (Vezzalini and Mattioli, 1979). The new data are quite different from those of the original description, but are very similar to those obtained for the sample from Pizzo Marcio. In this last case, the differences decrease if we consider, also in the sample from Pizzo Marcio, a Be content similar to that found here for the sample from Alpe Rosso. A test for this purpose was impossible due to the scarcity of the available material, but the closeness of Alpe Rosso and Pizzo Marcio (about 1 km apart) and the presence of crysoberyl in the paragenesis at Pizzo Marcio favours this hypothesis.

In the calculation of the chemical formula, the results of both structural refinement (Galli, 1980) and TG tracing were taken into account.

Galli (1980) found three independent tetrahedral sites fully occupied (multiplicity 16 × 3 = 48) and five framework anion sites; out of these five sites, four, coded O(1), O(2), O(3), and O(4), have bond strengths near to 2 and hence are occupied by oxygens, and the remaining one, coded OH(1), has a bond strength of 1.51 and hence may be occupied by oxygen or hydroxyl; Galli's

Table 1. X-ray powder diffraction data for Roggianite, CuKα radiation ($\lambda=1.54051$), $a=b=18.370(4)$ Å, $c=9.187(4)$ Å.

h	k	l	d_{calc}	d_{obs}	I/I_0		h	k	l	d_{calc}	d_{obs}	I/I_0
1	1	0	12.990	13.040	100		3	3	4	2.0290	2.0280	7
2	0	0	9.185	9.230	49		9	1	0	2.0286		
2	2	0	6.495	6.525	5		9	2	1	1.9472	1.9436	7
2	1	1	6.124	6.150	42		7	6	1	1.9472		
3	1	0	5.809	5.834	20		5	1	4	1.9367	1.9375	13
0	0	2	4.594	4.589	2		9	3	0*	1.9364		
4	0	0	4.593				5	3	4	1.8559	1.8546	17
3	2	1	4.456	4.472	2		7	7	0	1.8557		
1	1	2	4.331	4.339	10		8	1	3	1.8280		
3	3	0	4.330				7	4	3*	1.8280	1.8253	8
2	0	2*	4.108	4.111	9		9	4	1	1.8279		
4	2	0	4.108				6	2	4	1.8016	1.8008	7
2	2	2*	3.750	3.752	7		10	2	0	1.8013		
3	1	2*	3.603	3.605	41		9	5	0*	1.7843	1.7843	2
5	1	0	3.603				10	3	1*	1.7281	1.7284	5
4	3	1*	3.411	3.411	68		7	1	4	1.7207		
4	0	2*	3.248	3.246	12		5	5	4*	1.7207	1.7202	10
5	2	1*	3.198	3.198	34		7	7	2	1.7205		
5	3	0	3.150	3.154	43		6	4	4	1.7058		
3	3	2	3.151				0	10	2	1.7056		
6	2	0*	2.905	2.905	14		6	8	2	1.7056	1.7069	7
6	1	1	2.869	2.869	24		4	10	0	1.7056		
2	1	3	2.869				9	6	1	1.6700	1.6698	3
5	1	2*	2.835	2.833	23		7	3	4	1.6633		
3	0	3	2.739	2.740	3		9	5	2	1.6632	1.6600	3
5	4	1	2.738				1	11	0	1.6631		
4	4	2*	2.652	2.652	17		0	0	6	1.5312		
3	2	3	2.625	2.623	6		8	4	4	1.5310	1.5314	3
6	3	1	2.624				8	8	2	1.5309		
5	3	2	2.5981				1	1	6	1.5206		
7	1	0	2.5979	2.5985	10		1	9	4	1.5205		
5	5	0	2.5979				3	11	2	1.5203	1.5200	6
6	0	2*	2.5476	2.5481	21		7	9	2	1.5203		
6	4	0	2.5475				5	11	0	1.5203		
6	2	2*	2.4549	2.4544	10		3	1	6	1.4806	1.4806	6
3	4	3	2.3523	2.3530	6		3	9	4	1.4804		
0	0	4	2.2968	2.2962	13		4	0	6	1.4526		
8	0	0	2.2963				0	12	2	1.4523		
5	2	3	2.2788	2.2790	8		4	12	0	1.4523	1.4490	3
6	5	1	2.2785				2	11	3	1.4478		
1	1	4	2.2617	2.2600	5		5	10	3	1.4478		
5	5	2	2.2613				6	11	1	1.4478		
8	2	0*	2.2276	2.2281	9		3	3	6	1.4436		
2	0	4	2.2280				5	11	2	1.4433	1.4420	2
2	2	4	2.1653	2.1660	4		9	9	0	1.4433		
6	6	0	2.1649				5	1	6	1.4092		
3	1	4	2.1358	2.1348	6		9	5	4	1.4090		
7	3	2*	2.1355				1	13	0	1.4089	1.4088	2
4	0	4	2.0541				7	11	0	1.4089		
8	0	2*	2.0539	2.0535	9		4	11	3	1.3967	1.3966	1
8	4	0	2.0538				9	9	2	1.3769	1.3766	7

* reflections used for the cell parameters refinement

Table 2. Chemical analyses of Roggianite.

	1a	1b	2	3
SiO_2	41.05	40.22	36.58	44.11
Al_2O_3	18.70	18.32	22.34	18.54
BeO	n.d.	3.19	n.d.	n.d.
Fe_2O_3	-	-	0.42	0.05
MgO	-	-	0.87	-
CaO	19.64	19.24	14.73	19.97
SrO	0.02	0.02	n.d.	0.04
BaO	-	-	n.d.	0.09
Na_2O	0.29	0.28	0.94	0.01
K_2O	0.64	0.63	0.76	0.02
H_2O	n.d.	18.10	21.63	17.17
Total	80.34	100.00	98.27	100.00

1. Roggianite Alpe Rosso (this work).
a) Microprobe data.
b) Microprobe data normalized to 100% with H_2O and BeO contents.
2. Roggianite Alpe Rosso (Passaglia, 1969). The analysis includes also 0.32% of SO_3, 0.10% of F, 0.05% of Cl, 0.19% of H and 1.43% of C considered as due to impurities.
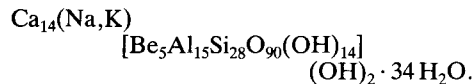3. Roggianite Pizzo Marcio (Vezzalini and Mattioli, 1979). H_2O content as difference to 100%.

extra-framework site OH(2), with bond strength 0.60, could be occupied by hydroxyl or water. On the basis of available chemical data (Vezzalini and Mattioli, 1979), Galli assigned hydroxyls to both OH(1) and OH(2) sites, in the form of the following chemical formula:

$$Ca_{16}[Al_{16}Si_{32}O_{88}(OH)_{16}](OH)_{16} \cdot c. \; 26 \, H_2O.$$
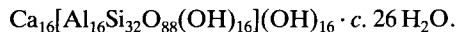
Due to the uncertainty in the assignment of some anion sites, the chemical formula from the data of Table 2 has been calculated on the basis of 48 tetrahedral cations (Si + Al + Be), so obtaining for unit cell:

$$(Ca_{14.24}Sr_{0.01}Na_{0.37}K_{0.56})_{\Sigma 15.18}$$
$$[(Be_{5.29}Al_{14.92}Si_{27.79})_{\Sigma 48}O_{89.96}(OH)_{14}]$$
$$(OH)_2 \cdot 33.68 \, H_2O$$

or schematically:

$$Ca_{14}(Na,K)$$
$$[Be_5Al_{15}Si_{28}O_{90}(OH)_{14}]$$
$$(OH)_2 \cdot 34 \, H_2O.$$
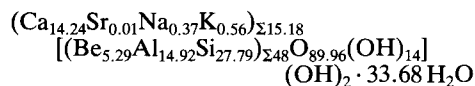
With respect to the original schematical formula $Na_2Ca_{12}Al_{18}Si_{26}O_{92} \cdot 40 \, H_2O$ (Passaglia, 1969), the above formula shows lower Na and higher Ca contents, while, among the framework cations, the relevant presence of Be is accompanied by lower Al and higher Si contents. Besides the different analytical procedures, these differences may also be ascribed to the impurity of the

material analysed in the original description, as suggested by the relevant Na content, very likely due to the contaminant presence of sodium feldspar on which the fibrous aggregates of roggianite rest. When compared with the structural formula (Galli, 1980) of the sample from Pizzo Marcio (Vezzalini and Mattioli, 1979), our new formula shows almost the same extra-framework cation content, but it is significantly different for framework cation, anion and water molecule contents. In fact, apart from the presence of Be (absent in Galli's formula), the framework contains almost the same number of Al atoms (15 against 16), but it is decidedly Si-poorer (28 against 32 atoms). According to Galli (1980), the 32 Si and 16 Al atoms of his formula are distributed, in an ordered way, in three independent tetrahedral sites (multiplicity 16), coded Si(1), Si(2), and Al respectively. Since the average interatomic distances, Si(1)–O = 1.62 Å, Si(2)–O = 1.63 Å, and Al–O = 1.715 Å, differ from the values of 1.603 and 1.761 Å quoted by Jones (1968) for a tetrahedron centered by Si or Al respectively, Galli suggested some substitution of Si atoms by Al, and vice versa, in the tetrahedral sites. By assuming the same chemical composition here obtained for the sample studied by Galli, the framework content may be distributed as follows: the two Si sites are fully occupied by 27.79 Si and 4.21 Al atoms (86.8% of Si and 13.2% of Al), the Al site is fully occupied by 10.71 Al and 5.29 Be atoms (66.9% of Al and 33.1% of Be). The average interatomic distances calculated with such a distribution give values of 1.623 Å for Si sites and 1.724 Å for the Al site, very similar to those found by Galli (1980) in his structural refinement. By considering Be, instead of Al, in Si sites, the calculated average interatomic distances are 1.609 and 1.754 Å for Si sites and Al site respectively, values quite different from those found by Galli. The presence of Al atoms in Si sites and of Be atoms in Al site is hence very likely in roggianite, and a close chemical similarity between roggianite from Alpe Rosso, here studied, and roggianite from Pizzo Marcio, used for structural refinement, is again strongly emphasized.

As far as the anionic content is concerned, the chemical formula obtained in this work is characterized, in agreement with structural data, by the presence of hydroxyl groups. The electrostatic charge balance, computed according to Donnay and Allman (1970), gives bond strength values very similar to those obtained by Galli (1980; Table 5). Nevertheless, our chemical formula differs significantly from that proposed by Galli (1980): the OH(1) site (multiplicity 16), assigned by Galli to hydroxyls, is occupied by 2 oxygens
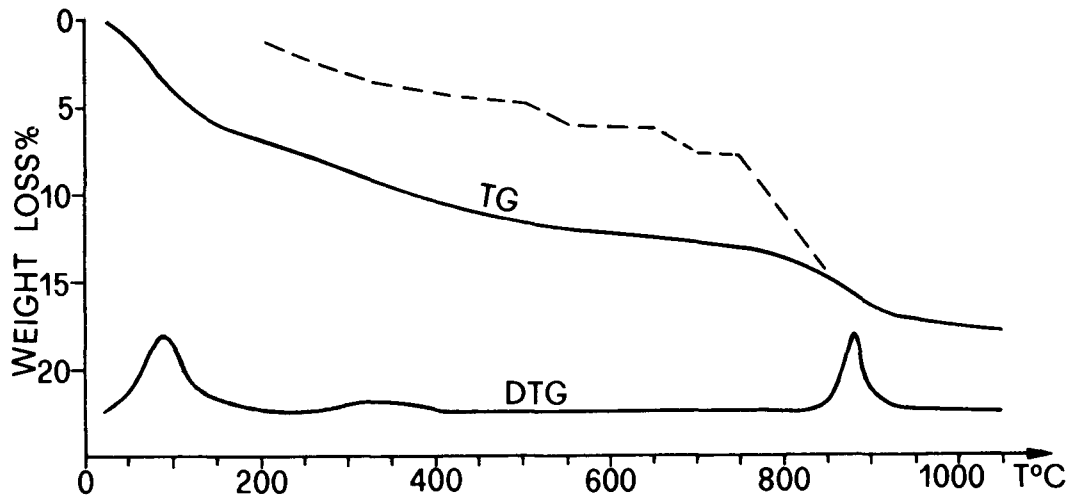
FIG. 1. TG, DTG and rehydration curves of roggianite.

and by 14 hydroxyls, while the OH(2) site (multiplicity = 16), assigned by Galli to hydroxyls is occupied by 2 (OH), the remaining by water molecules. Consequently, our formula shows a minor content of both framework and extra-framework hydroxyls, and more water molecules. The amount of hydroxyl in our formula corresponds to a H_2O loss of 3.47%, a value very close to the weight loss (3.60%) observed in TG analysis between 850 °C and 1050 °C. In fact, the mineral does not regain the weight loss after heating to 850 °C (see next section) and it was found to transform into a feldspar after heating at 900 °C (see previous section).

Zeolitic behaviour

Since the reversible dehydration and the ion exchange capacity are considered peculiar and distinctive physical properties of the zeolitic minerals, roggianite, showing a zeolite-like structure, was tested for these properties.

Reversible dehydration. By using a Du Pont thermobalance, pure roggianite powder was heated to various temperatures and then cooled and maintained at room temperature for 12 hours. With a heating rate of 10 °C/min, the powder was heated between 200 °C and 900 °C at intervals of 50 °C. The rehydration curve (Fig. 1) shows that roggianite regains most of the weight loss until heated to 750 °C. At temperature higher than 750 °C, the rehydration capacity of roggianite decreases and becomes very low at 800 °C and zero at 850 °C. Since at about 850 °C a faster weight loss begins (see TG and DTG curves in Fig. 1),

this reaction very likely corresponds to the hydroxyl loss with the consequent framework breakdown.

Ion exchange capacity. 3.7 mg of pure powdered material was placed in a glass tube containing $3\,cm^3$ of a Na 1N-solution prepared with Merck 'suprapur' NaCl and deionized water. The tube was slowly oscillated in an oven at 60 °C for 10 days. The solution, carefully filtered, was then tested for Ca content by atomic absortion spectrophotometer. It was found to contain 4.20 wt.% CaO; as 19.20 is the weight percent of CaO in roggianite, this means that little more than $\frac{1}{5}$ of the Ca has been exchanged. This value is low when compared with that generally shown by most zeolites, but it may be explained taking into account the structural features of the mineral. In fact, the Ca atoms lie in the cavities where the tetrahedral framework is interrupted, and are firmly bound to the framework, as they are octahedrally coordinated by two oxygens and four hydroxyls. On the other hand, the doubling of the exchangeable cation number due to the Na → Ca substitution, requires, besides complete occupancy of the Ca sites, accommodation of some Na cations in other sites (i.e. largest channels), probably less electrically favourable.

Conclusion

The check of reversible dehydration and cation exchange capacity, allows us to classify roggianite among the zeolitic minerals, as already suggested by Galli (1980) on the basis of its structural features. New chemical data revealed a substantial

amount of Be and (OH) groups. Therefore, roggianite is the first and up to now the only zeolite with many tetrahedral sites occupied by Be atoms; in particular, the structural data (Galli, 1980) suggest that Be atoms are present only in Al tetrahedra. Among the zeolitic minerals, the interrupted framework for the (OH) groups is known in partheite (Engel and Yvon, 1984); unlike partheite, roggianite is characterized also by the presence of extra-framework (OH) groups, which is unique in this group of minerals.

Acknowledgements

Note

After submission of the manuscript, Voloshin et al. (Mineral. Zh. 8, 85–90, 1986) published a paper on a new calcium–beryllium silicate named glnzburgite. Except for a lower water content, this mineral has che-

mical formula and unit cell dimensions very close to those here reported for roggianite.

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