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Giovanna Vezzalini, Roberta Oberti

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Abstract

Gismondine samples from 17 localities have been analyzed by electron microprobe and TG analysis and their unit cell dimensions have been determined. The chemical composition varies within narrow limits from the stoichiometric formula $Ca_4Al_8Si_8O_{32}. 18H_2O$. The Si/(Al+Si) ratio varies from 0.514 to 0.542, Ba, Fe and Mg are always absent and K, Na and Sr are low or absent. The chemical and X-ray data demonstrate the non-existence of K-rich gismondines. The K-rich analyses from the literature are explained by the frequent phillipsite-gismondine intergrowths. Unit-cell dimensions turned out to be rather constant, and no correlation with chemical composition has been found. The largest correlation is between two chemical parameters : Si/(Al+Si) and (Na+K)/(Na+K+Ca). The narrow field of chemical variability of this zeolite is attributed to the (Si,Al) ordered distribution.

Résumé

Des échantillons de gismondine de 17 localités différentes ont été examinés à la microsonde électronique et par thermogravimétrie ; les paramètres de la maille ont été déterminés. La composition chimique, à peu près constante, est proche de la composition théorique $Ca_4Al_8Si_8O_{32}. 18H_2O$. Le rapport Si/(Si+Al) oscille entre 0,514 et 0,542 ; Ba, Fe et Mg sont toujours absents, la teneur en K, Na et Sr est faible, ou ces éléments sont absents. Les données chimiques et les diagrammes de poudre montrent l'inexistence des gismondines riches en K. Les gismondines riches en K de la littérature, sont imputées à des intercroissances fréquentes phillipsite-gismondine. Les paramètres de la maille et la composition chimique ne peuvent pas être corrélés : seul, le rapport Si/(Si+Al) peut être relié au rapport (Na+K)/(Na+K+Ca). Dans le groupe des zéolites, la gismondine montre une composition chimique très constante avec une distribution ordonnée (Si, Al).

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The crystal chemistry of gismondines : the non-existence of K-rich gismondines

by GIOVANNA VEZZALINI* and ROBERTA OBERTI**

* Istituto di Mineralogia e Petrologia dell'Università, Largo S. Eufemia 19, 41100 Modena, Italy.

** Dipartimento di Scienze della Terra, via Bassi 4, 27100 Pavia, Italy.

Abstract. — Gismondine samples from 17 localities have been analyzed by electron microprobe and TG analysis and their unit cell dimensions have been determined. The chemical composition varies within narrow limits from the stoichiometric formula $Ca_4Al_8Si_8O_{32}.18H_2O$. The Si/(Al+Si) ratio varies from 0.514 to 0.542, Ba, Fe and Mg are always absent and K, Na and Sr are low or absent. The chemical and X-ray data demonstrate the non-existence of K-rich gismondines. The K-rich analyses from the literature are explained by the frequent phillipsite-gismondine intergrowths. Unit-cell dimensions turned out to be rather constant, and no correlation with chemical composition has been found. The largest correlation is between two chemical parameters : Si/(Al+Si) and (Na+K)/(Na+K+Ca). The narrow field of chemical variability of this zeolite is attributed to the (Si,Al) ordered distribution.

Key words : zeolite, gismondine, electron-probe data, thermogravimetric analysis, unit cell, X-ray powder diffraction.

Cristallochimie des gismondines : inexistence des gismondines, riches en K.

Résumé. — Des échantillons de gismondine de 17 localités différentes ont été examinés à la microsonde électronique et par thermogravimétrie ; les paramètres de la maille ont été déterminés. La composition chimique, à peu près constante, est proche de la composition théorique $Ca_4Al_8Si_8O_{32}.18H_2O$. Le rapport Si/(Si+Al) oscille entre 0,514 et 0,542 ; Ba, Fe et Mg sont toujours absents, la teneur en K, Na et Sr est faible, ou ces éléments sont absents. Les données chimiques et les diagrammes de poudre montrent l'inexistence des gismondines riches en K. Les gismondines riches en K de la littérature, sont imputées à des intercroissances fréquentes phillipsite-gismondine. Les paramètres de la maille et la composition chimique ne peuvent pas être corrélés : seul, le rapport Si/(Si+Al) peut être relié au rapport (Na+K)/(Na+K+Ca). Dans le groupe des zéolites, la gismondine montre une composition chimique très constante avec une distribution ordonnée (Si,Al).

Mots-clés : zéolite, gismondine, données microsonde électronique, analyse thermogravimétrique, maille élémentaire, diagramme de poudre.

INTRODUCTION

Gismondine, first described in 1817 by Gismondi, is a rather rare monoclinic zeolite whose unit cell content can be schematized as : $Ca_4Al_8Si_8O_{32}.18H_2O$. All the gismondine analyses reported in literature before 1962 (Zambonini, 1902 ; Doelter, 1921 ; Caglioti, 1927) and that reported by Van Reeuwijk (1971) show a considerable amount of Na and K (up to 0.92 and 0.87 atoms in the formula of Na and K respectively). In 1962 Walker identified gismondine in basalts from Ireland and Iceland and, owing to their negligible potassium content in respect to those from the literature, called them "low potash" gismondines. Afterwards complete crystal chemical data for K-poor gismondines were given for samples from "Gruppo di Voltri" (Genova, Italy) (Cortesogno *et al.*, 1975) and from Montalto di Castro (Viterbo, Italy) (Passaglia and Turconi, 1982).

The gismondine structure was solved by Fisher (1963) and subsequently refined by Fisher and Schramm (1970), who found an ordered (Si,Al) distribution. As observed by Alberti *et al.* (1982 and related literature) zeolites with an ordered (Si,Al) distribution usually have a very narrow compositional field ; whereas gismondines from the literature have Ca as a prevalent extraframework cation, but show a considerable amount of Na and K. As leucitite from the Rome area displays a paragenesis with K-rich chabazite (Passaglia, 1970) and K-rich phillipsite (Galli and Loschi Ghittoni, 1972), with a chemical composition very close to one another, it is possible that either gismondine from this zone is really K-rich or an intergrowth between gismondine and phillipsite or chabazite is present ; if that is the case, some analyses in the literature could be incorrect because of impurity of these last zeolites.

The aim of this work is to define the compositional field of gismondine, to determine the unit-cell dimensions and to establish the relationships, if any, between composition and cell parameters.

SAMPLES STUDIED

In this work a total of 17 samples, for which the experimental data were obtained by the authors, are taken into account. Chemical data for sample No. 8 were obtained from Rinaldi and Vezzalini (in preparation). The sample locations and references to literature are : No. 1 Capo di Bove, Rome, Italy (Caglioti, 1927) ; No. 2 Casal Brunori, Rome, Italy ; No. 3 Appia Antica, Rome, Italy ; No. 4 Vallerano, Rome, Italy (Zambonini, 1902) ; No. 5 Osa quarry, Rome, Italy ; No. 6 Acquacetosa, Rome, Italy ; No. 7 Ariccia, Rome, Italy ; No. 8 Montalto di Castro, Viterbo, Italy (Passaglia and Turconi, 1982) ; No. 9 Rio Pan del Foco, Genova, Italy (Cortesogno *et al.*, 1975) ; No. 10 Aci Reale, Sicily, Italy* ; No. 11 Chabane, Saint-Agrève, Ardèche, France (Hintze, 1897) ; No. 12 Ile aux Serpents, Sénégal ; No. 13 Wingendorf near Luban, Poland ; No. 14 Zalezly (=Salesl) near Usti nad Labem, Bohemia, Czechoslovakia (Doelter, 1921) ; No. 15 Schieferberg near Zalezly, Bohemia, Czechoslovakia ; No. 16 Brusleequarry, Ballyclare, Co. Antrim, Ireland (Walker, 1962) ; No. 17 Cat Carn, Legoniel, Upper Belfast, Co. Antrim, Ireland (Walker, 1962).

Samples No. 16 (BM 1959-609) and No. 17 (part Ashcroft Irish Colln. no. 787) correspond to G1 and G16 of Walker (1962) respectively.

Usually gismondine appears as pseudotetragonal transparent bipyramid, but in samples No. 16 and No. 17 it appears as a chalky white crust, lining cavities containing chabazite. The samples from Rome area are from a leucitite rock, sample No. 8 is from a phonolite whereas all the others are from basaltic rocks. In sample No. 8 gismondine is associated to vertumnite and tobermorite, in the other samples to phillipsite or phillipsite and chabazite.

EXPERIMENTAL

For most of the samples accurate measurements of the lattice parameters were performed by using a four-circle Philips PW1100 diffractometer and MoKα graphite monochromatized radiation. An improved version of the Philips LAT routine, written at the "Centro di Studio per la Cristallografia Strutturale" of Pavia was employed which allows a fast and accurate determination of the *d* spacings by determining the center of gravity of the reflections in a row of the reciprocal space passing through the origin only if their intensities exceed a predetermined counting threshold. Lattice parameters are then calculated and refined. The comparison of the *d* values experimentally determined with those calculated from the refined cell parameters allow to evidentiate those which might have been unaccurately determined due to the weakness of some reflections or to their irregular diffraction profile. More accurate lattice parameters are then calculated by using only the best *d* values. During this work 32 selected rows were explored for every gismondine crystal in the range of 2-30°. For samples No. 8, No. 16 and No. 17 unit cell parameters were derived by a least-squares refinement program using the reflections measured on powder diffractograms. The reflections were indexed using a method (Alberti, 1976) which takes the structure factors into account. The indexed X-ray powder pattern for gismondine No. 16 is reported in table I. Unit cell parameters for gismondines are reported in table II. The cell parameters of the samples No. 2, No. 6, and No. 13 were not measured because no single crystal suitable for X-ray diffractometry has been found and enough material for powder pattern was not available.

Electron microprobe analyses were carried out in the wavelength dispersive mode on an ARL-SEMQ instrument operating at 15 kV, 20 nA and using a defocused beam (spot size ~ 20 μm). On-line data reduction was based on the Ziebold and Ogilvie (1964) method using Albee and Ray (1970) correction factors. Natu-

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* This occurrence of gismondine is not mentioned in the literature ; the chemical data of this sample, as reported later, are very similar to those of the samples from the Roma area.

h k l	d_{calc}	d_{obs}	I/I_o	h k l	d_{calc}	d_{obs}	I/I
1 1 0	7.286	7.290	51	2 0 $\bar{4}$*	2.244	2.241	12
1 1 $\bar{1}$	5.939	5.945	7	2 1 $\bar{4}$	2.195	2.194	10
1 1 1	5.772	5.762	14	1 2 $\bar{4}$	2.194		
2 0 0*	5.011	5.012	12	2 3 $\bar{3}$	2.193		
0 0 2*	4.916	4.921	68	3 3 2	2.152	2.150	8
0 2 1*	4.669	4.669	18	4 1 2	2.150		
0 1 2*	4.460	4.463	11	2 4 $\bar{2}$*	2.132	2.134	9
1 2 $\bar{1}$*	4.264	4.267	100	3 2 3	2.105	2.101	9
1 2 1*	4.201	4.203	46	2 4 2*	2.100		
2 1 $\bar{1}$*	4.175	4.197	20	3 4 0	2.077	2.078	9
2 1 1*	4.058	4.061	10	1 5 0*	2.076		
2 2 0*	3.643	3.645	5	4 3 0	2.044	2.043	10
0 2 2*	3.606	3.607	5	3 4 $\bar{1}$*	2.043		
1 2 $\bar{2}$*	3.426	3.427	13	1 4 $\bar{3}$*	2.030	2.029	11
2 2 1*	3.383	3.379	8	4 2 2	2.029		
1 2 2	3.361			1 5 1	2.028		
3 0 0	3.341	3.332	47	4 3 $\bar{1}$	2.015	2.012	10
0 3 1*	3.328			2 2 4	2.010		
3 1 0*	3.186	3.187	99	1 4 3	2.009		
0 1 3*	3.131	3.132	73	2 2 4	2.010	2.008	10
1 1 $\bar{3}$*	3.023	3.020	7	1 4 3	2.009		
3 1 1*	2.997	2.997	12	5 0 0	2.004		
0 3 2*	2.871	2.871	4	0 1 5*	1.933	1.934	9
3 0 $\bar{2}$*	2.818	2.819	4	3 4 $\bar{2}$	1.931		
1 3 2	2.743	2.743	66	1 1 $\bar{5}$	1.913	1.911	8
3 2 $\bar{1}$*	2.742			2 5 1	1.911		
3 0 2	2.712	2.710	58	4 3 $\bar{2}$	1.911		
1 2 $\bar{3}$*	2.711			5 2 $\bar{1}$	1.855	1.854	8
3 2 1*	2.692	2.693	74	5 1 $\bar{2}$	1.854		
1 2 3	2.662	2.657	66	2 3 4	1.851		
0 4 0	2.653			5 1 $\bar{2}$	1.854	1.851	8
3 1 2*	2.627	2.626	21	2 3 4*	1.851		
1 4 0*	2.564	2.564	4	4 4 0*	1.821	1.821	13
0 4 1*	2.561	2.553	3	5 1 2	1.803	1.802	8
2 3 $\bar{2}$*	2.517	2.518	11	0 4 4	1.803		
3 2 $\bar{2}$*	2.488	2.489	10	1 2 5	1.801		
2 2 $\bar{3}$	2.474	2.466	9	4 4 1	1.781	1.779	8
2 3 2*	2.466			2 1 5*	1.780		
0 0 4	2.458			3 4 $\bar{3}$	1.775		
1 0 $\bar{4}$	2.410	2.406	12	3 3 $\bar{4}$*	1.754	1.755	11
0 3 3*	2.404			2 2 $\bar{5}$	1.753		
0 4 2*	2.334	2.335	15	6 0 0*	1.670	1.670	11
3 1 $\bar{3}$	2.331			2 6 0	1.668		
2 4 1*	2.271	2.270	13	3 2 $\bar{5}$	1.641	1.638	10
4 0 $\bar{2}$	2.270			0 0 6*	1.639		
1 4 2	2.264	2.264	13	1 6 2	1.638		
4 2 0*	2.266						

Ni-filtered CuKα_1 radiation, angular speed 1/2° per minute, $Pb(NO_3)_2$ internal standard. Only the reflections marked with a * have been used for the refinement.

TABLE I. — *X-ray powder diffraction data for gismondine No. 16.*
Diffractogramme de poudre de la gismondine N° 16.

ral albite, microcline and synthetic plagioclase glasses were used as standards of Si, Al, Na, K and Ca ; synthetic anorthite for Sr, natural paracelsian for Ba, synthetic pyroxene for Mg and synthetic olivine for Fe. For each sample an average of 10 randomly chosen points were analyzed to test the homogenity of the mineral.

For sample No. 5 K and Ca distribution maps made on a Philips SEM 500 equipped with a EDS/EDAX (9100) analyzer, where used to determine the possible presence of phillipsite zones close to gismondine zones.

Water loss was determined, on approximately 10 mg of powdered sample, by TG analysis using a Dupont 951 instrument, working in air with a temperature rate of 10 °C/min.

Because of the impossibility in obtaining a sufficiently pure gismondine for many samples and because of the scarcity of other ones, the H_2O contents were experimentally determined only in samples No. 4, 7, 8, 9, 12, 14, 15, 16 and 17. Taking into account the small variations shown by the determined values, a medium value of 22.56 % was ascribed to all the other samples.

Sample	a(Å)	b(Å)	c(Å)	β(°)	V(Å^3)
No.1	10.016(1)	10.626(1)	9.824(1)	92.44(1)	1045
No.3	10.012(1)	10.632(1)	9.826(1)	92.41(1)	1045
No.4	10.012(1)	10.628(1)	9.826(1)	92.39(1)	1045
No.5	10.013(1)	10.617(1)	9.821(1)	92.30(1)	1043
No.7	10.018(1)	10.636(1)	9.824(1)	92.41(1)	1046
No.8*	10.021(1)	10.637(1)	9.836(1)	92.45(1)	1048
No.9	10.023(1)	10.617(1)	9.828(1)	92.47(1)	1045
No.10	10.013(1)	10.626(1)	9.843(3)	92.50(1)	1046
No.11	10.015(2)	10.630(2)	9.840(3)	92.47(4)	1047
No.12	10.016(3)	10.621(6)	9.829(1)	92.44(5)	1045
No.14	10.027(1)	10.622(1)	9.829(1)	92.47(1)	1046
No.15	10.016(1)	10.632(1)	9.833(1)	92.56(1)	1046
No.16*	10.030(3)	10.610(3)	9.840(3)	92.36(1)	1046
No.17*	10.038(4)	10.605(4)	9.842(4)	92.23(1)	1047

* Unit cell dimensions from powder pattern.

TABLE II. — *Unit cell dimensions for gismondines. Errors in brackets.*
Paramètres de la maille des gismondines.

The analyses have been normalized to 100, without changing the H_2O value, in order to correct for the undetermined loss of zeolitic water under electron bombardment in the vacuum chamber of the microprobe. The atomic ratios are reported in table III. The correlation tests were sought through the use of the BMD 02R stepwise multiple regression program.

Sample	K	Na	Sr	Ca	Al	Si	H_2O	E*	R**	M/(M+D)$^+$
No.1	0.23	0.11	0.03	3.63	7.49	8.47	17.98	-2.3	0.531	0.085
No.2	0.22	0.07	0.02	3.85	7.52	8.35	18.05	-6.5	0.526	0.070
No.3	0.14	0.06	0.02	3.81	7.56	8.37	17.99	-4.0	0.525	0.050
No.4	0.31	0.16	0.03	3.44	7.32	8.65	17.37	-1.5	0.542	0.119
No.5	0.21	0.12	0.01	3.68	7.57	8.39	17.98	-2.1	0.526	0.082
No.6	0.19	0.08	0.05	3.80	7.60	8.31	18.05	-4.6	0.522	0.066
No.7	0.24	0.12	0.03	3.79	7.44	8.42	17.48	-7.3	0.531	0.086
No.8	0.00	0.00	0.00	3.91	7.77	8.22	17.57	-0.5	0.514	0.000
No.9	0.04	0.15	0.00	3.73	7.46	8.49	16.82	-2.6	0.532	0.048
No.10	0.21	0.11	0.05	3.66	7.45	8.49	17.99	-3.6	0.533	0.079
No.11	0.03	0.19	0.01	3.86	7.60	8.31	17.98	-4.4	0.522	0.054
No.12	0.01	0.10	0.06	3.94	7.69	8.20	18.40	-5.1	0.516	0.027
No.13	0.05	0.24	0.20	3.53	7.45	8.48	18.08	-4.0	0.532	0.072
No.14	0.01	0.17	0.00	3.82	7.67	8.30	18.60	-2.0	0.520	0.045
No.15	0.02	0.22	0.00	3.75	7.42	8.51	19.08	-4.0	0.534	0.060
No.16	0.03	0.22	0.00	3.77	7.53	8.41	17.76	-3.3	0.528	0.062
No.17	0.04	0.38	0.00	3.63	7.32	8.59	18.45	-4.6	0.540	0.104

*E= balance error= $\{[Al-(M+2D)]/(M+2D)\} \times 100$. **R= Si/(Al+Si). $^+$M/(M+D)=(Na+K)/(Na+K+Ca+Sr).

TABLE III. — *Atomic ratios (on the basis of 32 oxygens) of gismondines.*
Formules structurales (sur 32 oxygènes) des gismondines.

ANALYSIS OF THE RESULTS

Powder patterns performed on the samples No. 1, 2, 3, 4, 5, 6 and 7 from the Rome area, to test the possible presence of phillipsite-gismondine intergrowths, shows the strongest peaks of phillipsite and the absence of chabazite reflections.

The chemical analyses of these last samples show some interesting features : the composition of some analyzed points yields a Si/Al ratio of 8.4/7.6 atoms and 3.6 atoms of Ca in the unit cell ; the oxide weight of Na and K is always < 1 %. At other points however the Si/Al ratio is 10/6 and K reaches 2.5 atoms, whereas the Ca content decreases considerably ; some others shows Si/Al and K/Ca ratios rather variable between these two extreme values. On the basis of Si/Al ratios and of the indications of the

X-ray data, the analyses of the first type can be interpreted as gismondine with a very low amount of K, those of the second type as phillipsite and the last ones as areas with small domains of the two phases. Therefore it can be stated that in the samples from the Rome area gismondine and phillipsite are intimately associated and not morphologically distinguishable.

To confirm the hypothesis that the high K content of gismondine from the Rome area, as reported in the literature (Zambonini, 1902 ; Doelter, 1921 ; Caglioti, 1927 ; Van Reeuwijk, 1971) is probably due to analyses obtained on intergrowths of phillipsite and gismondine, distribution maps of K and Ca were performed on sample No. 5. As shown in figures 1*a* and 1*b* in the right side, where the K concentration is low, the Ca amount is high and viceversa. An EDAX semiquantitative analysis confirmed that in the right side the Si/Al ratio is that of a gismondine, whereas in the upper area this ratio is typical for a phillipsite.

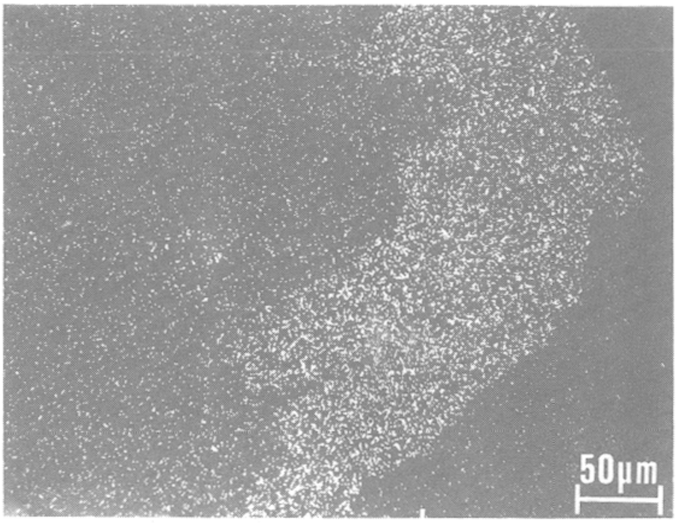

FIG. 1*a*. — *Distribution map of K in gismondine No. 5.*

Carte de distribution du potassium dans la gismondine N° 5.

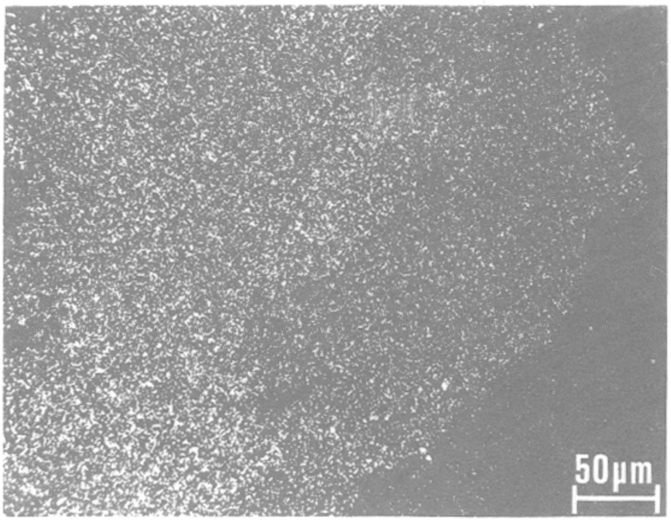

FIG. 1*b*. — *Distribution map of Ca in gismondine No. 5.*

Carte de distribution du calcium dans la gismondine N° 5.

The atomic ratios, on the basis of 32 oxygens, the balance error E, the R ratio (= Si/(Si+Al)) and M/(M+D), where M = Na+K and D = Ca+Sr are reported in table III. For the samples from Rome area averages of the only analysis points with the Si/Al ratio of gismondine are reported. As well as the elements reported in table III, also Fe, Mg and Ba were tested in all samples, but were found to be always present in negligible amounts. The chemical data can be summarized as follows : both R and M/(M+D) ratios show very narrow ranges of variability, from 0.514 to 0.542 and from 0.00 to 0.104 respectively ; this means that Si and Al show a ratio near the theoretical value of 1 and exchangeable cations are mainly represented by Ca, Na and K being always in quite low amounts.

The very narrow compositional field of gismondine is also shown by the diagram in figure 2, which is an enlarged part of the triangular mole plot $Si\text{-}D_{.25}Al_{.5}Si_{.5}\text{-}M_{.5}Al_{.5}Si_{.5}$.

The unit cell dimensions are listed in table II. The variation ranges are : *a* 10.011 ÷ 10.038, *b* 10.605 ÷ 10.637, *c* 9.821 ÷ 9.843 Å and β 92.227 ÷ 92.555°. The correlation matrix between chemical and crystallographic parameters is reported in table IV. Owing to the modest variations of both the unit cell dimensions and the chemical compositions no significant correlation has been found between them. The only significant correlation is between the chemical parameters R and M/(M+D) which proves the substitution MSi $\rightleftharpoons$ DAl ; this substitution can be explained on the basis of the gismondine structure. Fischer and Schramm (1970) found only one site (with a multiplicity of 4), occupied by extraframework cations, with nearly complete occupancy (92 %). Therefore as Al increases, in order to maintain the cation numbers $\leq$ 4, some monovalent cations must be substituted by divalent ones. The correlation between R and M/(M+D) is displayed in figure 3, where the regression straight line is dashed.

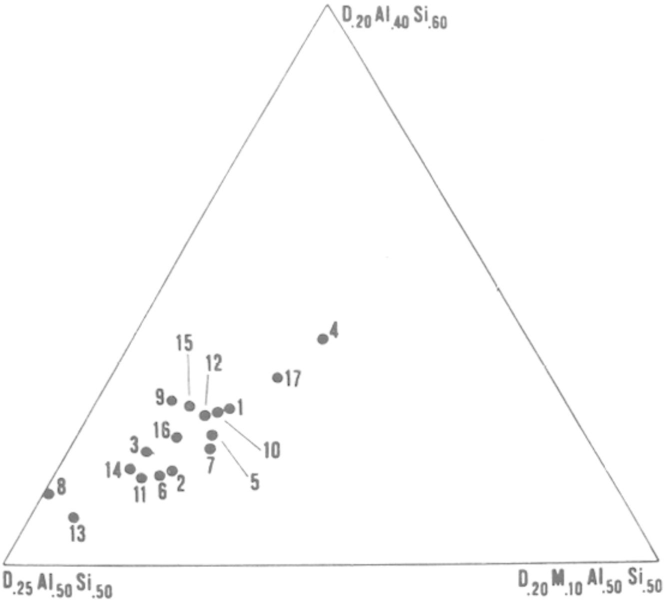

FIG. 2. — *Distribution of gismondines in the* $D_{.20}Al_{.40}Si_{.60}$-$D_{.25}Al_{.50}Si_{.50}$-$D_{.20}M_{.10}Al_{.50}Si_{.50}$ *diagram.*

Distribution des gismondines dans le diagramme $D_{0.20}Al_{0.40}Si_{0.60}$-$D_{0.25}Al_{0.50}Si_{0.50}$-$D_{0.20}M_{0.10}$ $Al_{0.50}$ $Si_{0.50}$.

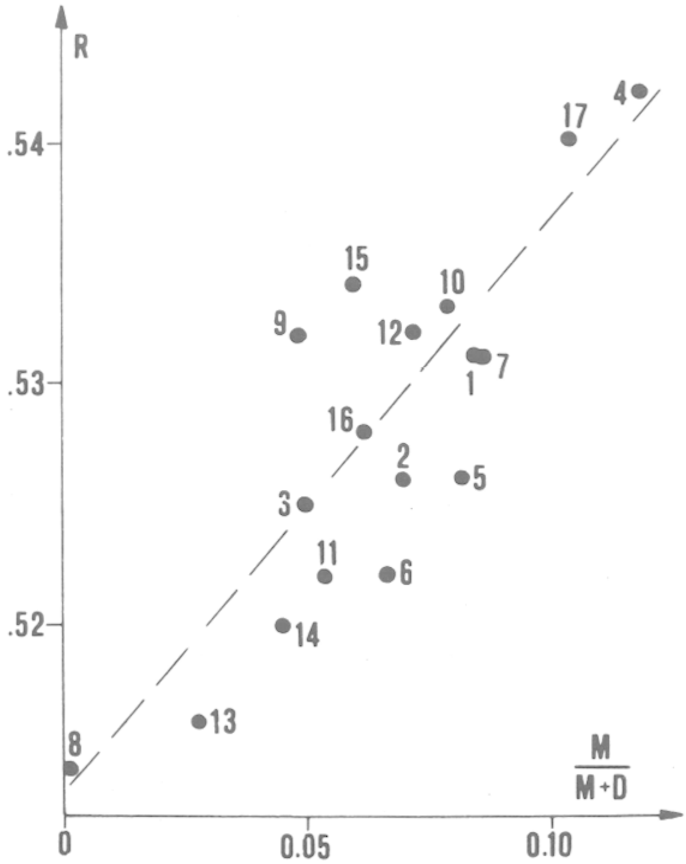

FIG. 3. — *Variation of R and M/(M+D) in gismondines.* Dashed line represents the regression straight line.

Diagramme de corrélation de R et M/(M+D) dans les gismondines. La courbe de régression est en trait discontinu.

WATER MOLECULES

TG and DTG curves of gismondines are in good agreement with those reported by Van Reeuwijk (1971). The dehydration occurs in 5 steps below 300°C and in some more steps above 300°C (see figure 4) ; however the relative intensities and the position of the peaks are rather variable in the examined samples.

Only one site occupied by extraframework cations is present in the gismondine structure (Fischer and Schramm, 1970) and this site is at coordination distance from the six sites occupied by water molecules. $H_2O(1)$, $H_2O(2)$ and $H_2O(3)$ are always present : of the other three, if $H_2O(4)$ is present, $H_2O(5)$ and $H_2O(6)$ must be absent and viceversa, as the distances between these water molecules are too short. Therefore the cation site coordinates 4 or 5 water molecules ; owing to the complexity of this coordination and to the large number of water molecules,

	a	b	c	cosβ	V	R*	M/(M+D)**
a	1.000	-.691	.449	.410	.506	.121	.016
b		1.000	-.317	-.694	.064	-.271	-.282
c			1.000	-.046	.798	.110	-.030
cosβ				1.000	-.266	.405	.614
V					1.000	-.030	-.209
R						1.000	.878
M/(M+D)							1.000

*R=Si/(Al+Si). **M/(M+D)=(Na+K)/(Na+K+Ca+Sr).

TABLE IV. — *Correlation matrix between cell and chemical parameters for gismondines.*

Matrice de corrélation entre les paramètres de la maille et les paramètres chimiques pour les gismondines.

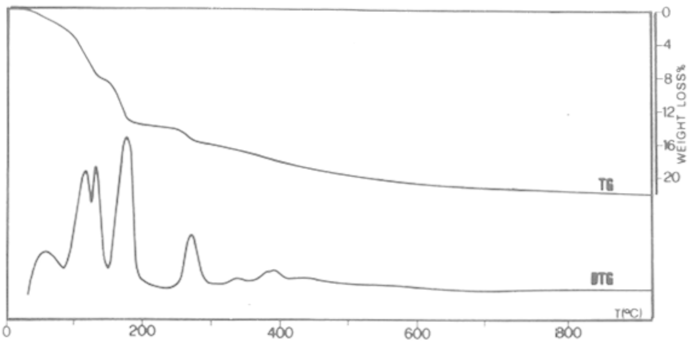

FIG. 4. — *TG and DTG curves for gismondine No. 9.*
Courbes d'analyse thermogravimétrique et courbe relative dérivée de la gismondine n— 9.

it is very difficult to give a correct interpretation of the DTG curve.

On average, the water content is 18 water molecules against 17.28 from the crystal refinement. Assuming that the water in excess could be due, as in fibrous zeolites (Alberti *et al.*, 1982), to water absorbed on the surface of the grains, TG and DTG curves were obtained, for one gismondine, on large crystals. The weight loss was, as in Alberti *et al.* (1982), 0.5 % lower than that from the powder and the number of resulting water molecules was 17.40, which is now in good agreement with the value found in the structural refinement.

CONCLUSIVE REMARKS

The results of this work indicate, for gismondine, a chemical composition quite near the stoichiometric formula $Ca_4Al_4Si_4O_{32}.18H_2O$. The largest departures from this formula, as apparent from the literature, are to be ascribed to erroneous analyses of phillipsite-gismondine intergrowths, which led to high K contents. However the samples from the Rome area resulted in being the richest in K, with a maximum of 0.31 atoms per unit cell, much less than the previous values of 0.9 (Caglioti, 1927). The presence in the same rock of K-rich chabazite (Passaglia, 1970) and K-rich phillipsite (Galli and Loschi Ghittoni, 1972) indicates that the hydrothermal solutions, from which these zeolites crystallized, were K-rich. As no particular paragenetical order among these zeolites has been observed, gismondine also grew from K-rich solutions but with a low K content : so there is some incompatibility of this zeolite for the K cation. Therefore the K content of these samples represents the upper limit of this element in the chemical composition of gismondine.

Amicite, a zeolite with the gismondine structural topology (Alberti and Vezzalini, 1979) and with a Si/Al ratio equal to 1 and Na/K equal to 1, has been found only once. It is possible that its crystallization, instead of the more common gismondine, is due to the following reason : amicite is associated to aragonite, which, being the first to crystallize, in the presence of an CO_2 excess, uses the Ca present in the solution ; in this way the monovalent cation concentration is raised thus allowing the formation of amicite.

Garronite, the other zeolite with a gismondine framework, has a disordered (Si,Al) distribution (Gottardi and Alberti, 1974) and, as all the disordered zeolites, shows a Si/Al ratio $\neq 1$ (chemical formula $NaCa_{2.5}Al_6Si_{10}O_{32}.14H_2O$) and a high chemical variability in the exchangeable cations.

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