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THE CRYSTAL STRUCTURE OF DELHAYELITE

RIASSUNTO. — La delhayelite è un silicato per il quale sono state proposte dagli autori dei due ritrovamenti le seguenti due formule: $(\text{Na}, \text{K})_4 \text{Ca}_6 \text{Al}_6 \text{Si}_{26} \text{O}_{60} \cdot 18 \text{H}_2\text{O} \cdot 3(\text{Na}_2, \text{K}_2)(\text{Cl}_2, \text{F}_2, \text{SO}_4)$ (Sahama e Hytönen); $(\text{Na}, \text{K})_6 \text{Ca}_4 \text{Al}_2 \text{Si}_{12}(\text{O}, \text{OH}, \text{F}, \text{Cl})_{26}$ (Dorfman, Belova, Neronova).

La delhayelite appartiene al gruppo spaziale Pmmn; le costanti reticolari sono le seguenti: $a = 24.86$, $b = 7.07$, $c = 6.53 \text{ \AA}$.

La struttura è stata determinata attraverso l'esame della sintesi di Patterson tridimensionale e l'assunzione di una analogia fra la struttura della delhayelite e quella della maedonaldite, recentemente studiata dagli autori di questo lavoro. I rapporti fra le costanti reticolari della maedonaldite ($c = 23.56$, $a = 14.08$, $b = 13.11 \text{ \AA}$) e quelle della delhayelite sono evidenti. Invece la formula chimica della maedonaldite, $\text{BaCa}_7 \text{H}_2 \text{Si}_{16} \text{O}_{36} \cdot 10.4 \text{ H}_2\text{O}$, non sembra, a prima vista, aver molto a che fare con quelle scritte sopra per la delhayelite. Bisogna però ricordare che nella struttura della maedonaldite, fatta salva l'impalcatura costituita dai tetraedri del Si e dagli ottaedri del Ca, c'è ampio spazio per sostituzioni e aggiunte di altri cationi.

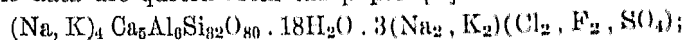
L'ipotesi assunta è stata confermata dall'esame di sintesi di Fourier tridimensionali e i parametri sono stati raffinati fino a un fattore di discordanza del 1,8%, attribuendo via via una appropriata natura chimica ai diversi massimi di densità elettronica, sulla base delle loro intensità e delle distanze formate con quelli adiacenti.

La formula chimica della delhayelite viene così modificata dai risultati dell'analisi strutturale: $\text{Ca}_7(\text{Na}_6\text{Ca})\text{K}_7(\text{Si}_{14}\text{Al}_2)\text{O}_{66}\text{Cl}_2\text{F}_1$. La composizione percentuale in ossidi, ricalcolata da questa formula è molto vicina a quella pubblicata da Dorfman e coll., mentre quella di Sahama e Hytönen, che trovano molto più silicio e molti mono alcali, è probabilmente vizziata dall'attacco acido, reso necessario per purificare il loro campione.

Come ipotizzato, l'impalcatura della maedonaldite si mantiene nella delhayelite. La sostituzione del Si con Al avviene ordinatamente in una delle tre posizioni indipendenti occupate dai cationi tetraedrici. Le catene di ottaedri del Ca, collegate fra loro da legami d'idrogeno nella maedonaldite, qui sono collegate da catene di prismi del Na. L'impalcatura della maedonaldite è attraversata da un doppio sistema di canali, in cui trovano posto gli atomi di bario e le molecole d'acqua non legate ai cationi. Nella delhayelite in questi spazi vuoti trovano posto atomi di K e di Cl, che occupano in parte posizioni nuove o in parte posizioni già occupate nella maedonaldite dal bario o dall'acqua.

Introduction.

Delhayelite is a silicate found by Sahama and Hytönen [1] in a complex kalsilite-bearing melilite-nephelinite lava from M. Saheru, Nyiragongo Area, North Kivu (Congo). These chemical and crystallographic data are quoted from the paper [1]: chemical formula:



unit cell parameters:

$$a = 6.53 \pm 0.03 \text{ \AA}$$

$$b = 24.65 \pm 0.2 \text{ \AA}$$

$$c = 7.04 \pm 0.03 \text{ \AA}.$$

The a side should be doubled owing to « extremely weak layer-lines » showed by the a -axis rotation photographs. The unit cell with the doubled a -axis contains one formula unit. The possible space groups are $\text{Pmn}2_1$ and Pmmn . Sahama and Hytönen write that the chemical formula (derived from chemical analyses carried out by Pennti Ojanperä of the Geological Survey of Finland) is only a provisional approximation because of the low purity of the analysed material.

In a paper on the crystal structure of macdonaldite $\text{BaCa}_4\text{H}_2\text{Si}_{16}\text{O}_{38} \cdot 10.4\text{H}_2\text{O}$ [2], the possibility of a close structural relationship of that silicate with delhayelite and the related mineral rhodesite was discussed on the basis of the similarity of the crystallographic, physical and (at least for rhodesite) chemical properties. Also the observed structural connection between macdonaldite and the fibrous zeolites as well as the resemblance of these ones with delhayelite and rhodesite [1], [3] supported the hypothesis that the three mentioned silicates could belong to the same structural family.

The aim of this work is the determination of the crystal structure of delhayelite in order to verify that hypothesis.

Experimental.

Prof. Th. G. Sahama kindly supplied a sample of delhayelite consisting of very small crystal fragments. One of those having a roughly prismatic shape (about two tenths of millimeter long with a cross section of few hundredths of millimeter) was chosen for the collection of the X-rays experimental data.

From rotation and Weissenberg photographs the cell parameters were remeasured:

$$\begin{aligned} a &= 24.86 \pm 0.01 \text{ \AA} \\ b &= 7.07 \pm 0.02 \text{ \AA} \\ c &= 6.53 \pm 0.01 \text{ \AA} \end{aligned}$$

The possible space groups are those given by Sahama and Ilytönen: $Pmn2_1$ and $Pmnm$. The orientation of the cell axes was changed with respect to that used by the cited Authors in order to get the standard

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Rendiconti.

ERRATA CORRIGE

La formula riportata nel rigo 11 di pag. 71 del vol. XXV Fase. 1 dei Rendiconti, deve leggersi nel modo seguente:

$$I \text{ (forza ionica)} = \frac{1}{2} \sum C_i Z_i^2$$

Crystal Structure Analysis.

The starting point of the structure analysis was the hypothesis of the close relationship of delhayelite and maedonaldite. The three-dimensional Patterson synthesis of delhayelite did not discard this supposition at least for what was concerned with the chains of Ca-octahedra and the double layers of Si-tetrahedra which are the characteristic feature of maedonaldite. So a structure factors calculation, in the centric space group $Pmnm$, was carried out by giving to one calcium (in a fourfold equipoint), to three Si atoms (one in a general position and two in fourfold equipoints) and to the oxygens bonded to silicon, the same atomic coordinates of maedonaldite, taking into account that in this one the b and c cell parameters are doubled.

A three-dimensional Fo's Fourier synthesis was computed on the basis of the calculated structure factors. The Fourier maps showed well resolved peaks corresponding to the atoms employed in computing the structure factors and some more maxima that were uninterpretable on the basis of the chemical analysis given by Sahama and Hytönen. In fact a chemical formula computed from the cited analysis, on the basis of a $\text{Si}_{10}\text{O}_{38}$ tetrahedral group, shows a strong deficiency of Ca, Na and K with respect to the number of maxima in the Fourier synthesis. No new chemical analysis was possible because of the scarcity and impurity of the available material. So the attribution of a 'name' to the maxima was made, step by step taking into account

TABLE I.

	1	2	3	4
SiO_2	46.34	46.53	48.19	52.80
TiO_2	traces	0.07		0.09
RE_2O_3	0.11	0.13		
Al_2O_3	6.43	6.59	5.84	9.22
Fe_2O_3	0.54	0.73		2.72
MnO	0.08	0.12		0.07
BeO	0.02	0.17		
CaO	14.39	14.55	16.07	7.99
CrO	0.12	0.17		
MgO	0.14	0.17		1.03
Na_2O	6.42	6.88	5.33	3.20
K_2O	17.92	18.37	18.90	9.27
F	2.80	2.91	4.36	0.33
Cl	3.35	3.47	4.06	3.91
S	0.06	0.27		1.31 SO_3
H_2O^+	1.23	1.48		5.93
H_2O^-	0.43	0.06		3.35
$\text{O} \equiv (\text{F}, \text{Cl})$			-2.75	-1.01
Total			100.00	100.01

1, 2 - Analyses of Dorfman et al. [4]. These authors write the chemical formula as follows: $(\text{K}, \text{Na})_6\text{Ca}_7\text{Al}_2\text{Si}_{12}(\text{O}, \text{OH}, \text{F}, \text{Cl})_{38}$.

3 - Analysis computed from the chemical formula resulting from this work.

4 - Analysis of Sahama and Hytönen [1].

the elements detected in the chemical analysis, the height of the peaks, their relative distances and their distances from the oxygens of the tetrahedra. At the end of this procedure a self-consistent arrangement of atoms was obtained and submitted to the least-squares refinement. The hypothetical cell content at this stage was: $\text{Ca}_4\text{Na}_4\text{K}_8\text{Si}_{16}\text{O}_{38}\text{Cl}_2\text{F}_4$; this stoichiometric unit does not get balanced its electrostatic charges. During the refinement the multiplier of several doubtful atoms was allowed to vary in order to obtain some supplementary informations: the positions of potassium appeared incompletely occupied, the position of the supposed sodium seemed to be occupied by a heavier cation. These informations together with those obtained from the more precise values of the bond distances led to this hypothetical cell content: $\text{Ca}_4(\text{Na}_3\text{Ca})\text{K}_7(\text{Si}_{14}\text{Al}_2)\text{O}_{38}\text{Cl}_2\text{F}_4$; it gives the best R factor: 0.088 for the observed reflexions.

TABLE II.

Final atomic parameters and their standard deviations (in parentheses).

W is the Wyckoff notation of the equipoint; N is the number of atoms per unit cell. The standard deviation of the multipliers N allowed to vary in the least-squares refinement affects the second decimal figure.

Atom	W	N	x/a	y/b	z/c	B
Na, Ca	e	4	0	0	0	1.07(15)
Ca	f	4	0.0067(1)	0.7500	0.5034 (7)	0.81 (9)
Si(1)	g	8	0.1125(1)	0.4656 (8)	0.2818 (4)	0.51 (6)
Si(2)	f	4	0.1828(2)	0.7500	0.5342 (8)	0.59 (9)
Si(3)	f	4	0.1065(2)	0.7500	0.9188 (7)	0.70 (9)
O(1)	g	8	0.0550(4)	0.4818(20)	0.3845(18)	3.76(25)
O(2)	g	8	0.1618(4)	0.5510(21)	0.4135(17)	4.01(26)
O(3)	g	8	0.1124(4)	0.5675(19)	0.0601(15)	3.28(23)
O(4)	f	4	0.0491(5)	0.7500	0.8164(20)	1.64(27)
O(5)	f	4	0.1580(6)	0.7500	0.7738(24)	2.73(31)
O(6)	f	4	0.1295(6)	0.2500	0.2433(25)	2.96(36)
O(7)	b	2	0.2500	0.7500	0.5392(32)	2.32(42)
F	f	4	0.0297(4)	0.2500	0.8146(17)	2.02(23)
Cl	a	1.8	0.2500	0.2500	0.8793(17)	3.83(32)
K(1)	f	3.7	0.1322(2)	0.2500	0.7804 (8)	1.95(14)
K(2)	a	1.8	0.2500	0.2500	0.3721(14)	2.76(25)
K(3)	b	1.7	0.2500	0.7500	0.0195(16)	4.45(31)

During the last stage of the refinement the authors of this work had the opportunity to read the summary of a paper of Dorfman *et al.* [4] about the discovery of delhayelite in the Soviet Union. This summary reported two chemical analyses which were an unexpected support to the hypothetical formula written above. In Table I the analyses of the Russian Authors are compared with that of Sahama and Hytönen and with that computed from the chemical formula resulting from this structure analysis. Of course only a microprobe analysis of congolese delhayelite could give a detailed picture of its chemical formula. In any way the formula resulting from the structural determination would not be far from the true one.

Final atomic coordinates and thermal parameters are given in Table II. The rather high values of the temperature factors of the oxygen atoms as well as the fairly high values of the standard deviations could depend from the doubling of the *c* axis observed by Sahama and Hytönen. The atomic coordinates listed in Table II should be only average values of the 'true' coordinates in the cell with the *c* axis of 13.06 Å. As it has been said in a preceding section of this paper, no extra reflexions, corresponding to the doubling of the cited cell parameter, has been observed even with the long exposure times used in taking the X-rays pictures. This fact, however, does not contradict the observation of Sahama and Hytönen because, owing to the extreme smallness of the specimen, those very long exposure times allowed the measurement of only one half of the possible reflexions. So, it is possible that, with suitable exposure times, the cell side doubling could be seen also with the crystal fragment used for this work.

The final observed and calculated structure factors are compared in Table III. Bond distances and angles as well as their standard deviations are given in Table IV.

Discussion.

Calcium. One Ca atom is present in the asymmetric unit and is located on the mirror plane (010). It has a six-fold coordination built up by five oxygens of the tetrahedra (Ca-O from 2.30 to 2.37 Å) and one fluorine (Ca-F 2.26 Å). The coordination polyhedron could be roughly described as an octahedron. These octahedra, by sharing two opposite edges, form chains parallel to *b*.

TABLE IV.
*Interatomic distances (Å) and angles (°) and their standard deviations
 (in parentheses).*

A sign ' is used to distinguish equivalent atoms. The distances preceded by one asterisk occur twice; those preceded by two asterisks occur four times.

Atoms	Bond lengths	Atoms	Bond angles
Si(1)	—O(1)	O(1)—Si(1)—O(2)	115.7 (7)
	—O(2)	O(1)—Si(1)—O(3)	110.2 (7)
	—O(3)	O(1)—Si(1)—O(6)	112.0 (8)
	—O(6)	O(2)—Si(1)—O(3)	108.1 (6)
Si, Al	—O(2)	O(2)—Si(1)—O(6)	103.7 (8)
	—O(7)	O(3)—Si(1)—O(6)	106.5 (7)
	—O(5)	O(2)—Si(2)—O(7)	108.5 (7)
Si(3)	—O(5)	O(2)—Si(2)—O(5)	108.6 (6)
	—O(4)	O(2)—Si(2)—O(2)'	112.2(1.0)
	—O(3)	O(7)—Si(2)—O(5)	110.4 (8)
Na, Ca	—F	O(4)—Si(3)—O(3)	109.3 (7)
	—O(4)	O(4)—Si(3)—O(5)	118.4 (8)
	—O(1)	O(3)—Si(3)—O(5)	105.7 (6)
	—O(3)	O(3)—Si(3)—O(3)'	108.2(1.0)
Ca	—F	Si(1)—O(3)—Si(1)'	145 (2)
	—O(4)	Si(2)—O(7)—Si(2)'	178 (2)
	—O(1)	Si(1)—O(2)—Si(2)	142 (1)
	—O(1)'	Si(1)—O(3)—Si(3)	152 (1)
K(1)	—F	Si(2)—O(5)—Si(3)	148 (1)
	—O(3)		
	—Cl		
	—O(6)'		
	—O(2)		
	—O(6)		
	—O(5)		
	—O(1)		
K(2)	—O(2)		
	—O(6)		
	—Cl		
	—Cl'		
K(3)	—O(5)		
	—O(7)'		
	—O(7)		
	—Cl		
	—O(2)		
	—O(3)		

Sodium. The best scattering curve for this atom lying on a symmetry center, was that based on the assumption that the site would be occupied by 3/4 Na and 1/4 Ca. Sodium is bonded to two F atoms (Na—F 2.27 Å) and to six oxygens of the tetrahedra (two Na—O of 2.46 and four Na—O of 2.86 Å). The eight mentioned atoms occur at the vertices of a sort of orthorhombic prism. The prisms share two opposite edges thus forming chains parallel to those of octahedra.

Potassium. The potassium atoms have not a regular coordination owing to their occurrence in large cavities of the structure. One can remark the short distances between K(1) and F and K(1) and Cl; they are shorter than the sum of the ionic radii of the involved atoms. K(2) occupies the same position of Ba in maedonaldite; its coordination is more regular being formed by six oxygens at the vertices of a folded hexagon with one chlorine atom above and one below.

Some more words on the role of potassium and chlorine will be spent in the course of the description of the structure.

Silicon. Three silicon atoms are present in the asymmetric unit; one of them shares all the oxygens with other tetrahedra; the remaining two have one oxygen unshared. These ones have Si—O bond distances of about 1.60 Å while the Si—O bond lengths of the former range from 1.67 to 1.70 Å. For this reason it was assumed that the corresponding fourfold equipoint was occupied by 50% Si and 50% Al. As one can see in Table IV the lengths of the Si—O bonds are not much influenced by the fact that the oxygens are unshared or shared with other tetrahedra: Si(1)—O(1) 1.58 Å, Si(3)—O(4) 1.57 Å; the average Si—O distance for shared oxygens is about 1.60 Å. As suggested by Cruickshank [5] this fact is due to the presence of Al in the tetrahedral framework. It seems worthy to point out that in maedonaldite, which has the same tetrahedral framework, but is free of Al, the average bond distances of Si with the unshared oxygens were about 1.57 Å and those with the shared ones were about 1.63 Å.

Description of the structure (see Fig. 1). As previously pointed out the structural features common to maedonaldite and delhayelite are the double tetrahedral layers of the apophyllite type and the chains of Ca-octahedra. The « idealized » apophyllite layer is derived from the condensation of wollastonite chains through the xenotlite ribbon. In maedonaldite the double layers are imbedded between layers of Ca-

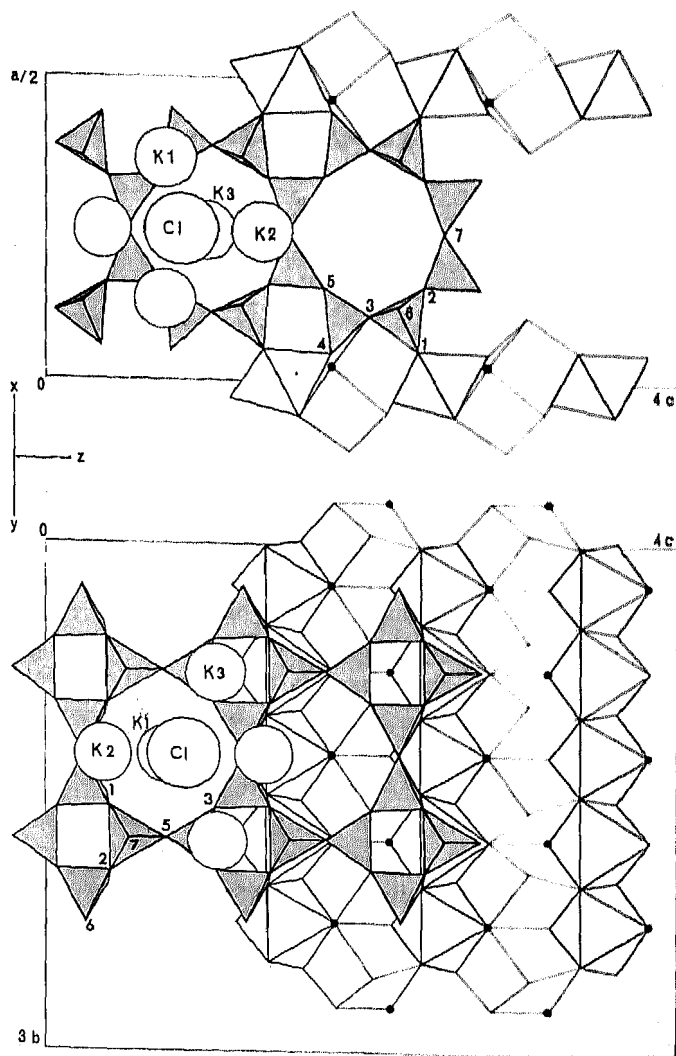


Fig. 1. — *Bottom*: schematic partial projection of the crystal structure of delhayelite along the a axis and key to the identification of the atoms (small black circles are fluorine atoms). The layers of Si-tetrahedra as well as of Ca-octahedra and Na-prisms are shown. *Top*: schematic partial projection along the b axis. A section of the channel parallel to b is shown. The other channel runs parallel to a .

octahedra. These layers are formed by chains of octahedra connected together by hydrogen bonds. In delhayelite the chains of octahedra are tied together by sodium atoms; in such a way the Ca-octahedra and the prisms of sodium form a sort of compact « wall » of polyhedra. The tetrahedral double layers occur between two of such « walls ». Taking into account the common structural features, delhayelite and maedonaldite belong without any doubt to the same structural family of Zoltai's [6] classification of silicates.

A number of structural details will be described in order to show some interesting peculiarities of delhayelite.

In maedonaldite two adjacent Ca atoms are not equivalent by symmetry: one lies on a symmetry center, the other on a mirror plane. In delhayelite both of them occur on a mirror plane. So, while in maedonaldite one octahedron is built up by six oxygens of the tetrahedra and the other by four oxygens and two water molecules, in delhayelite all the octahedra are formed by five oxygens and one fluorine. These different situations of calcium in the two minerals implies different situations of the tetrahedral layers with respect to the layers of octahedra (see Fig. 2).

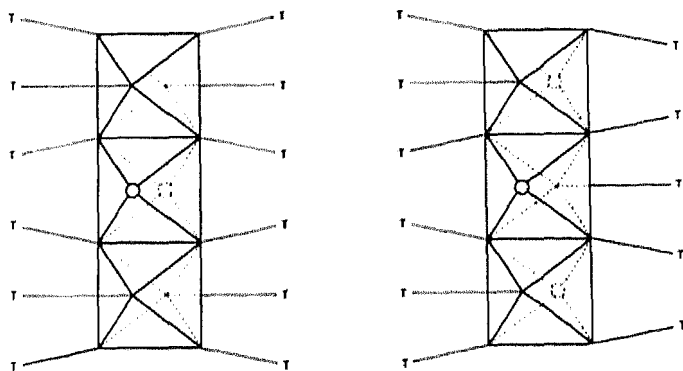


Fig. 2. — Schematic drawing showing the relationships between the chains of Ca-octahedra and the tetrahedral layers in maedonaldite (left) and in delhayelite (right). Each « T » represents a Si-tetrahedron and the segment running from one corner of the octahedron to a « T » is a Si—O bond. Small circles are water molecules in the maedonaldite chain and fluorine atoms in the delhayelite chain.

The channels that are present in maedonaldite exist also in delhayelite; they run within the tetrahedral layers parallel to b and c ; their free diameter is about 3.8 Å. In maedonaldite the channels are occupied by barium and water molecules which do not fill completely the large cavities of the structure: it is a typical feature of zeolites. In delhayelite there is no water; the channels are nearly completely filled by potassium and chlorine. In the channel parallel to c there is an infinite sequence ... K(2)—Cl—K(2)—Cl... running at the intersection of two mirror planes. It could be of some interest to point out that the c cell parameter of delhayelite (6.53 Å) is only a little longer than the cell edge of KCl (6.26 Å). Another infinite sequence ... K(3)—Cl—K(3)—Cl... occurs in the channel parallel to b .

Another interesting feature of delhayelite is a sort of finite chain or linear group F—K(1)—Cl—K(1)—F. This group is nearly parallel to a and runs between two adjacent walls of polyhedra in a cylindrical cavity which has the same free diameter of the channels. The chlorine atoms are located at the intersection of the two infinite sequences and the linear group; in such a way each chlorine is surrounded by six K atoms that form a distorted octahedron.

The a cell parameter of delhayelite is significantly longer than the corresponding cell edge of maedonaldite: 24.86 Å against 23.56 Å. This difference of 1.3 Å is caused by a rearrangement of the tetrahedral framework achieved through the increasing of some Si—O—Si angles.

TABLE V.

Mineral	Cell dimensions			Chemical formula
Maedonaldite	$a = 14.08$	$b = 13.11$	$a = 23.56 \text{ Å}$	$4[\text{BaCa}_2\text{H}_2\text{Si}_6\text{O}_{24} \cdot 10.4\text{H}_2\text{O}]$
Rhodesite	$c = 14.10$	$b = 13.08$	$a = 23.8 \text{ Å}$	$4[\text{K}_2\text{Na}_2\text{Ca}_2\text{Si}_6\text{O}_{24} \cdot 12\text{H}_2\text{O}]$
Delhayelite	$b = 7.07$	$c = 6.53$	$a = 24.86 \text{ Å}$	$\text{Ca}_1(\text{Na}_3\text{Ca})\text{K}_7(\text{Si}_{11}\text{Al}_2)\text{O}_{28}\text{Cl}_7\text{F}_2$

Conclusions. Table V shows a comparison of the crystallographic and chemical data of maedonaldite, rhodesite and delhayelite. The close structural relationship between maedonaldite and delhayelite has been fully confirmed by the crystal structure analysis in spite of the difficulties encountered with the chemical formula.

The absence of water and the presence of F and Cl in delhayelite as well as its occurrence in a volcanic rock of unusual chemical and mineralogical composition [7] give a particular character to this mineral with respect to maedonaldite and rhodesite. These ones are more strictly comparable with fibrous zeolites for their occurrence, their morphological features (rhodesite is fibrous) and their water content.

It would be very interesting to investigate the crystal structure of rhodesite also in order to know whether Na is in the channels as K and Ba or it connects together the chains of octahedra as in delhayelite. In such a way one could have a complete structural picture of this family of silicates whose members can occur in such different environments.

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