Chromian mica from Sierra Nevada, Spain

J. D. MARTÍN-RAMOS AND M. RODRÍGUEZ-GALLEGO

Department of Crystallography and Mineralogy, University of Granada, Spain

SYNOPSIS

EMERALD green chromian $2M_1$ mica occurs in metamorphosed and metasomatized limestones, related to serpentinic rocks from Sierra Nevada, Spain. Chemical analysis gave: SiO_2 44.51, Al_2O_3 27.60, TiO_2 0.17, Cr_2O_3 3.35, Fe_2O_3 1.76, FeO 0.07, MnO 0.00, MgO 8.59, Li_2O 0.03, Rb_2O 0.01, BaO 0.01, CaO 1.71, Na_2O 0.40, K_2O 7.86, H_2O 4.21 = 100.28. Optic properties are: pleochroism X blue, Y green, Z bluish green; refractive indices: $\alpha = 1.562$, $\beta = 1.611$, $\gamma = 1.616$ (yellow light); inclined dispersion, r > v. Orientation: second order mica. Refined parameters are $a = 5.2116(6)$, $b = 9.045(2)$, $c = 19.97(2)$ Å, $\beta = 95.7(3)°$. The structure is discussed and an order in the octahedral $M(1)$ sites is observed, but no ordering in the tetrahedral $T(1)$ and $T(2)$ cations is detected. The mica described is a mariposite with anomalously high contents of Ca and Mg.

Chromian mica from Sierra Nevada, Spain

J. D. Martín-Ramos   and M. Rodríguez Gallego

Department of Crystallography and Mineralogy, University of Granada, Spain.

Many chromian micas with fuchsite and mariposite optical characteristics have been described in the Sierra Nevada area of the Betic Cordillera (Puga, 1971, Pérez del Villar, 1972). Detailed study has been difficult because these minerals are usually found in small amounts in limited outcrops.

The chromian mica analysed in this study occurs together with actinolite crystals on some fracture surfaces in limestones. These outcrops are of a small size (15 - 20 m long and 1 m thick) and the limestones are included as xenoliths in a peridotite mass metasomaticed to serpentinites, close to the contact with the enclosing mica-schists of the Mulhacen nappe (Martín-Ramos et al., 1979) in the inner areas of the Betic Cordillera (Puga et al., 1974).

The optical characteristics of this chromian mica and other chromian micas found in Sierra Nevada are similar to those of a normal fuchsite, but X-ray diffraction has shown certain differences in the lattice parameters (Martín-Ramos, 1976). The chemical composition of this mica, with anomalously high contents of Ca and Mg, also suggests the possibility of an unusual intermediate composition. Similar minerals have been described in the literature by Chang Pao Kwei and Lin Kuo Cheng (1974) and by Chaterjee (1968). Nevertheless they are significantly different from the mica studied in this paper.

Chemical analysis.- This has been carried out by the hydrofluoric acid decomposition technique (Langmyhr and Paus, 1968) and with an atomic absorption spectrophotometer "Unicam SP 1900". A complete analysis by means of Linares and Huertas method (1973)has also been carried out. The agreement between both methods is excellent. The results are shown in Table I. The formula obtained on the basis of 20 oxygens is:

$$[Si_{6.18}Al_{1.82}]O_{20}[Al_{2.65}Cr_{0.36}Fe^{3}_{0.15}Fe^{2}_{0.04}Mg_{1.18}][Ca_{0.25}Na_{0.11}K_{1.38}](OH)_{3.78}$$
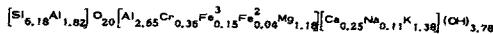
Table I.- Chemical analyses on the basis of 20 oxygens.

	%	Number of cations	Charge/Layer	
K_2O	7.86	1.38		
Na_2O	0.40	0.11		
CaO	1.71	0.25	Interlayered	2.00
BaO	0.01	0.01		
Rb_2O	0.01	0.01		
MgO	8.59	1.18		
Fe_2O_3	1.76	0.15		
FeO	0.07	0.06		
MnO	0.00	0.00		
Li_2O	0.03	0.01	Octahedral	11.97
Cr_2O_3	3.35	0.36		
TiO_2	0.17	0.02		
SrO	0.00	0.00		
			2.65 (Al^{VI})	
Al_2O_3	27.60			
			1.82(Al^{IV})	
SiO_2	44.51	6.18	Tetrahedral	30.18
H_2O	4.21	3.87	H	3.87
Total	100.62		Total	46.02

In the chemical analysis special care has been taken to eliminate the calcium and magnesium carbonates which could have remained as a residue from the enclosing rock. The purity of the mineral analysed approaches 100 % , although small actinolite (and anatase?) inclusions could not be eliminated ; however they were never greater than 0.5 % .

Optical properties.- Pleocroism : X= blue , Y= green , Z= bluish green . Refractive indices : α= 1.562 , β= 1.611 , γ= 1.616 . Birefringency = 0.054 (yellow light) . $2V_z$ = 33.6(4) (white light) , 32.4(3) (blue light) , 36.2(3) (red light) . Inclined dispersion , r>v. The plane of the optical axes is parallel to (010) and the Y axis of the indicatrix coincides with the b parameter . This means the present mineral is a second order mica.

X-ray data. - The unit-cell parameters have been obtained with one of the standard programmes (LAT) from Philips PW 1100 single crystal diffractometer . With this programme , the rows 200, 020, 111, 1$\bar{1}$1, 002, $\bar{2}$02, 110, $\bar{3}$31, $\bar{1}$31, 131, 331, 201, $\bar{1}$33 and $\bar{1}\bar{1}$4 have been measured . By using the circle with highest precision ω, with coupled 2θ , each row was scanned in the positive and in the negative regions . The d_{hkl}-spacings of the fourteen measured rows were then used to obtain a, b, c and β parameters by a least-square programme . The results are : a = 5.2116(6) , b = 9.045(2) , c = 19.97(2) Å and β= 95.7(3) $^{\circ}$: Determination of the space group carried out from the long exposure Weissenberg photographs , was C 2/c . Extra-weak reflections with (h + k) = (2n - 1) were observed., X - ray diffraction intensity data were collected with the above mentioned single crystal diffractometer using Mo K_α radiation monochromatized by a flat graphite crystal. The intensities of the 2761 reflections for 2°< θ < 30° were measured with the ω/2θ scan mode . The equivalent reflections were scanned and 1383 were independent . Three standard reflections were monitored at four hour intervals. No variations greater than 3 % were observed. The intensities were aproximately corrected for absorption following the method of North et al. (1968) and the values of the equivalent pairs were averaged. The resulting absorption discrepancy factor was always 0.07, which is an excessively high value, but it was very difficult to improve due to the extreme thinness and lath-like shape of the available crystals. The X-ray data were processed with a modified version of a programme specifically written for the PW 1100 single crystal diffractometer by Hornstra and Stubbe (1972). The least-squares structure refinements were carried out using a rewritten version of the ORFLS programme (Busing et al., 1962). Seven isotropic least-squares cycles were carried out. Anisotropic treatment for the atoms does not improve the results. Last R before isotropic convergence was 0.117. The scattering curves for neutral atoms given by the International Tables for X-ray Crystallography (1974) were used. The initial atomic parameters were those from phengite (Güven, 1971). Only the reflections with I > 3σ were processed with equal weight in the refinements. The atomic scattering factors of Si and Al for T(1) and T(2) tetrahedrals, Al (Al, Mg) and Fe(Fe, Cr) for octahedral M(1) sites and K and Na (Na, Ca) for interlayered cations were used. Difference Fourier synthesis was computed following the isotropic cicles.

Results. - Table II shows the positional parameters and temperature factors for the refined chromian mica structure. Selected interatomic distances and angles are listed in Tables III and IV, and also drawn in figs. 1 and 2.

Table II. Atomic coordinates and temperature factors .

Atoms	Equipoint	X	Y	Z	$B(Å^2)$
K(K, Na, Ca)	4e	0.0000	0.0967	0.2500	1.94
M(I)(Al, Cr, Mg, Fe)	8f	0.2489	0.8260	0.0001	0.64
O(1)	8f	0.9558	0.4386	0.0546	1.09
O(2)	8f	0.3935	0.2529	0.0546	1.00
O(3)	8f	0.4390	0.0934	0.1692	1.29
O(4)	8f	0.7385	0.3234	0.1603	1.47
O(5)	8f	0.2384	0.3611	0.1694	1.13
OH	8f	0.9547	0.0654	0.0515	1.15
T(1)(Al, Si)	8f	0.9635	0.4296	0.1353	0.56
T(2)(Al, Si)	8f	0.4517	0.1589	0.1355	0.63

Table III . Interatomic distances in angstroms.

M(1)-O(1)	1.951	K-O(3)	2.928
M(1)-O(1)	1.983	K-O(4)	2.964
M(1)-O(2)	1.948	K-O(5)	2.925
M(1)-O(2)	1.990	K-O(3)	3.196
M(1)-OH	1.934	K-O(4)	3.199
M(1)-OH	1.939	K-O(5)	3.203
Average	1.958(23)	Average shorter	2.939(18)
Polyhedral volume	9.824 $Å^3$	Average longer	3.199(03)
T(1)-O(1)	1.612	T(2)-O(2)	1.616
T(1)-O(3)	1.640	T(2)-O(3)	1.645
T(1)-O(4)	1.632	T(2)-O(4)	1.634
T(1)-O(5)	1.644	T(2)-O(5)	1.642
Average	1.632(23)	Average	1.634(13)
Average T-O(basal)	1.639(05)	Average T-O(basal)	1.640(05)
Polyhedral volume	2.224 $Å^3$	Polyhedral volume	2.234 $Å^3$

Standard deviations are indicated in parentheses in terms of the last significant figures.
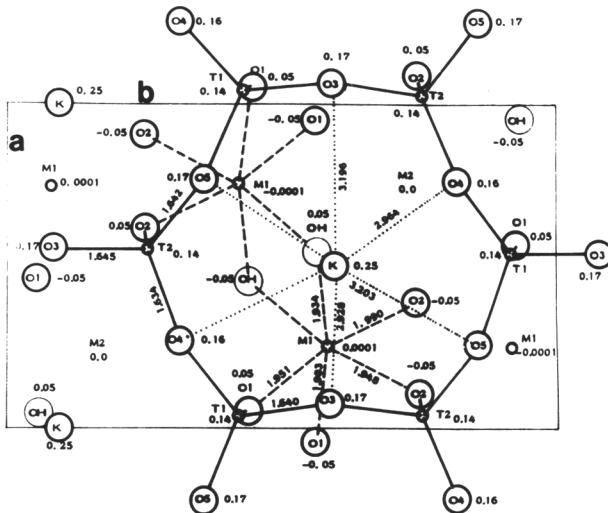
Figure 1. View of the projection of the structure along 001 in the interval ~0.05 ≤ Z ≤ 0.25 for chromian mica. The cation-anion distances are indicated in Å. Tetrahedral edges are drawn with continous lines. Potassium-tetrahedral basal oxygen bonds are drawn with dotted lines. Octahedral cations- apical oxygens and OH, are drawn with dashed lines.
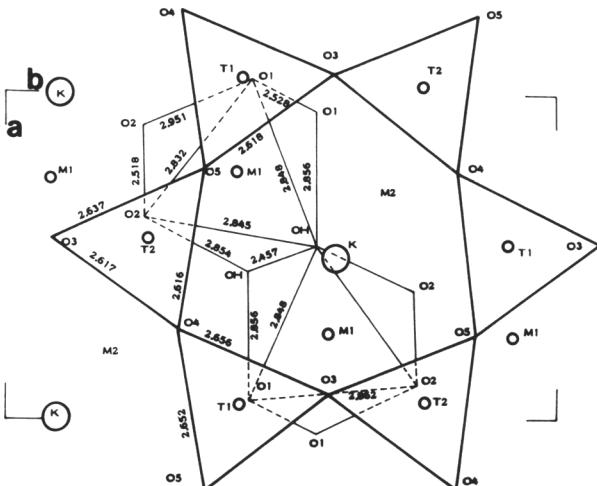
Figure 2. T(1), T(2) and M(1) coordination polyhedra are projected along 001 for chromian mica. Only the "visible" parts from each polyhedra are shown. Cation positions and edge lengths for the coordination polyhedra are included.

Discussion. – From the chemical analysis (see Table I) it can be seen that the mineral is a chromian mica with anomalously high content of Ca and Mg. From the study carried out by X-ray diffraction (single crystal method) some interesting conclusions can be reached relating to possible order-disorder cations. In relation to the tetrahedral cations, no ordering can be detected, taking into account that the values of the T(1)–O and T(2)–O distances are very alike (see Table III). It is interesting to note that the tetrahedrons are not regular in any of the cases (figs. 1 and 2, Tables II and III). The T(1)–O(1) and T(2)–O(2) distances, that is to say, those corresponding to the apical oxygens, are

significantly shorter than the rest. The average of the distances T(1)–O(basals) is 1.639(5) Å and the T(2)–O(basals) is 1.640(5) Å. Such similar measures are too close to think of any kind of ordering in the tetrahedral cations. Considering its octahedral layer, the average octahedral metal-oxygen distance (1.958 Å) approaches to a phengite more than a muscovite (1.956 and 1.932 Å respectively, Güven 1971). The octahedrals are very distorted. Table II and fig. 1 show that the OH–OH edge is shorter than the other two shared edges. On the other hand, the M(2) octahedral vacant polyhedrons are much more regular in form than the M(1). From the difference synthesis, no residual electronic density in the M(2) sites was

Table IV. Bond angle in degrees. Central atom is vertex.

Atoms (*) (a) (b) (c)	Angle	X(a)	Y(a)	Z(a)	X(c)	Y(c)	Z(c)
O(1)-M(1)-O(1)	79.99(41)	0.4558	-0.0614	0.0546	0.5442	0.0614	-0.0546
O(1)-M(1)-O(2)	93.11(38)	0.4558	-0.0614	0.0546	0.3935	0.2529	0.0546
O(1)-M(1)-O(2)	168.69(40)	0.4558	-0.0614	0.0546	0.1065	0.2471	-0.0546
O(1)-M(1)-OH	94.25(39)	0.4558	-0.0614	0.0546	-0.0453	0.0654	0.0515
O(1)-M(1)-OH	94.47(37)	0.4558	-0.0614	0.0546	0.0453	-0.0654	-0.0515
O(1)-M(1)-O(2)	95.94(38)	0.5442	0.0614	-0.0546	0.3935	0.2529	0.0546
O(1)-M(1)-O(2)	92.20(38)	0.5442	0.0614	-0.0546	0.1065	0.2471	0.0515
O(1)-M(1)-OH	169.73(41)	0.5442	0.0614	-0.0546	-0.0453	0.0654	0.0515
O(1)-M(1)-OH	93.12(39)	0.5442	0.0614	-0.0546	0.0453	-0.0654	-0.0515
O(2)-M(1)-O(2)	79.47(39)	0.3935	0.2529	0.0546	0.1065	0.2471	-0.0546
O(2)-M(1)-OH	92.84(38)	0.3935	0.2529	0.0546	-0.0453	0.0654	0.0515
O(2)-M(1)-OH	169.07(40)	0.3935	0.2529	0.0546	0.0453	-0.0654	-0.0515
O(2)-M(1)-OH	94.64(39)	0.1065	0.2471	-0.0546	-0.0453	0.0654	0.0515
O(2)-M(1)-OH	94.11(38)	0.1065	0.2471	-0.0546	0.0453	-0.0654	-0.0515
OH-M(1)-OH	78.76(42)	-0.0453	0.0654	0.0515	0.0453	-0.0654	-0.0515
O(1)-T(1)-O(3)	111.83(46)	0.9558	0.4386	0.0546	0.9390	0.5934	0.1692
O(1)-T(1)-O(4)	112.89(49)	0.9558	0.4386	0.0546	0.7385	0.3233	0.1603
O(1)-T(1)-O(5)	111.49(46)	0.9558	0.4386	0.0546	0.2384	0.3611	0.1694
O(3)-T(1)-O(4)	108.56(47)	0.9390	0.5934	0.1692	0.7385	0.3233	0.1603
O(3)-T(1)-O(5)	105.70(46)	0.9390	0.5934	0.1692	0.2384	0.3611	0.1694
O(4)-T(1)-O(5)	105.95(48)	0.7385	0.3233	0.1603	0.2384	0.3611	0.1694
O(3)-K-O(3)	116.58(27)	0.4390	0.0934	0.1692	-0.5610	0.0934	0.1692
O(3)-K-O(3)	63.41(27)	0.4390	0.0934	0.1692	0.5610	0.0934	0.1692
O(3)-K-O(3)	178.86(40)	0.4390	0.0934	0.1692	-0.4390	0.0934	0.1692
O(3)-K-O(4)	90.65(26)	0.4390	0.0934	0.1692	-0.4390	0.0934	0.1692
O(3)-K-O(4)	90.65(26)	0.4380	0.0934	0.1692	-0.2615	0.3233	0.1603
O(3)-K-O(4)	90.14(25)	0.4390	0.0934	0.1692	0.2615	0.3233	0.1603
O(3)-K-O(5)	50.71(23)	0.4390	0.0934	0.1692	0.2384	0.3611	0.1694
O(3)-K-O(5)	130.40(28)	0.4390	0.0934	0.1692	-0.2384	0.3611	0.3306
O(3)-K-O(5)	87.09(24)	0.4390	0.0934	0.1692	0.2616	-0.1389	0.3306
O(3)-K-O(3)	178.96(37)	-0.5610	0.0934	0.1692	0.5610	0.0934	0.3308
O(3)-K-O(3)	63.41(27)	-0.5610	0.0934	0.1692	-0.4390	0.0934	0.3308
O(3)-K-O(4)	130.84(28)	-0.5610	0.0934	0.1692	-0.2611	0.3233	0.1603
O(3)-K-O(5)	97.71(23)	-0.5610	0.0934	0.1692	0.2384	0.3611	0.1694
O(3)-K-O(5)	83.07(23)	-0.5610	0.0934	0.1692	-0.2384	0.3611	0.3306
O(3)-K-O(4)	50.11(24)	-0.5610	0.0934	0.1692	-0.2615	0.3233	0.1603
O(3)-K-O(4)	50.40(23)	-0.5610	0.0934	0.1692	-0.2616	-0.1389	0.1694
O(3)-K-O(5)	128.62(27)	-0.5610	0.0934	0.1692	0.2616	-0.1389	0.3306
O(4)-K-O(4)	92.44(39)	-0.2615	0.3233	0.1603	0.2615	0.3233	0.3397
O(4)-K-O(5)	50.02(26)	-0.2615	0.3233	0.1603	0.2384	0.3611	0.1694
O(4)-K-O(5)	66.99(24)	-0.2615	0.3233	0.1603	-0.2384	0.3611	0.3306
O(4)-K-O(5)	90.59(23)	-0.2615	0.3233	0.1603	-0.2616	-0.1389	0.1694
O(4)-K-O(5)	176.23(29)	-0.2615	0.3233	0.1603	0.2616	-0.1389	0.3315
O(5)-K-O(5)	83.37(33)	0.2384	0.3611	0.1694	-0.2384	0.3611	0.3306
O(5)-K-O(5)	116.75(29)	0.2384	0.3611	0.1694	-0.2616	-0.1389	-0.1694
O(5)-K-O(5)	129.65(08)	0.2384	0.3611	0.1694	0.2616	-0.1389	0.3306
O(5)-K-O(5)	86.47(36)	-0.2616	-0.1389	0.1694	0.2616	-0.1389	0.3306
O(2)-T(2)-O(3)	111.56(48)	0.3935	0.2529	0.0546	0.4390	0.0934	0.1692
O(2)-T(2)-O(4)	112.98(48)	0.3935	0.2529	0.0546	0.7385	0.3233	0.1603
O(2)-T(2)-O(5)	111.31(47)	0.3935	0.2529	0.0546	0.2384	0.3611	0.1694
O(3)-T(2)-O(4)	105.86(48)	0.4390	0.0934	0.1692	0.7385	0.3233	0.1603
O(3)-T(2)-O(5)	106.67(44)	0.4390	0.0934	0.1692	0.2384	0.3611	0.1694
O(4)-T(2)-O(5)	108.10(48)	0.7385	0.3233	0.1603	0.2384	0.3611	0.1694

(*) Atom b coordinates are given in table 2.

Table V. Deviation(2 α) of interatomic angles from ideal 120°.in degrees.

Basal oxygens	Angle	2α	Apical oxygens	Angle	2α
O(3)-O(4)-O(5)	103.32(21)	16.68	O(2)-O(1)-O(2)	115.05(38)	4.95
O(4)-O(3)-O(5)	105.62(28)	14.38	O(1)-O(2)-O(1)	195.96(38)	5.96
O(3)-O(5)-O(4)	105.58(29)	14.42	O(2)-O(1)-O(2)	116.50(37)	3.50
O(3)-O(4)-O(5)	135.42(29)	15.42	O(1)-O(2)-O(1)	116.08(37)	3.92
O(4)-O(3)-O(5)	135.83(29)	15.83	O(2)-O(1)-O(2)	124.01(38)	4.01
O(3)-O(5)-O(4)	134.64(28)	14.64	O(1)-O(2)-O(1)	115.11(38)	4.89
Average.....................		15.22(84)	Average		4.54(82)

Tetrahedral cations			Octahedral cations		
T(2)-T(1)-T(2)	119.60(16)	0.40	M(1)-M(1)-M(1)	119.00(21)	1.00(21)
T(1)-T(2)-T(1)	119.51(16)	0.49			
T(2)-T(1)-T(2)	121.40(16)	1.40			
T(1)-T(2)-T(1)	120.69(16)	0.69			
Average..................	0.75(39)				

checked. This shows a strict ordering in the octahedral voids. A local short range order in the distribution of the octahedral M(1) cations in domains of the crystal, can involve the local disappearance of the C character from the unit-cell and it leads to the presence of extra-group-spacial observed reflections, as shown by Bailey (1975).

The interlayered cations are in twelve fold coordination with the basal oxygen atoms from the upper and lower tetrahedral layer, with and average distance of 2.939(18) Å for the six nearest oxygens and 3.199(3) Å for the outer ones, values that match phengite more than muscovite (Güven, 1971; Radoslovich, 1963).

The atomic planes in this mica are distorted in two ways: by rotation in the plane (001) and by tilting in elevations. In an ideal atomic configuration, both anions and cations form hexagonal arrays with interatomic angles of 120°. Deviations (2α) from this value give the distortion in the plane. The values of 2α for this mica are given in Table V. The tetrahedral cations show, however, smaller displacements form their ideal position. Tilting of the tetrahedrons give rise to typical differences in the coordinates of the basal oxygen atoms for dioctahedral micas. One of the basal oxygen atoms O(4) is displaced in the plane of O(3) and O(5) by 0.18(1) Å. The same phenomena was detected in phengites by Güven. In conclusion it can be established that the mica described above is a mariposite (chromian phengite) with anomalously high contents of Ca and Mg, ordered in octahedral voids, with partial ordering of the octahedral cations in located domains of the crystal and disordered in tetrahedral Si and Al.

REFERENCES

Bailey, S.W. (1975). Cation ordering and Pseudosymmetry in layer silicates. Am.Mineral, 60, 175-187.

Busing, W.R., K.O. Martin and H.A. Levy (1962). ORFLS, a Fortran crystallographic least-squares refinement program. U. S. Natl. Tech. Inf. Serv., ORNL-TM-305.

Chang-Pao-Kwei and Lin-KUo-Cheng (1974). Chrome phlogopite -a new subspecies of phlogopite (abstr.). Geochim., 1, 71-74.

Chaterjee, N.D. (1968). Chromian phengite in an ankerite marble from the Suse Valley Western Italian Alps. Neues Jahrb.Mineral Mh., 103-110.

Guven, N. (1971). The crystal structures of $2M_1$ phengite and $2M_1$ muscovite. Z.Kristallogr., 234, 196-212.

Hornstra, J. and B. Stubbe (1972). Pw-1100 data processing program. Philips Research Labs, Eindhoven, Holland.

Ibers, J.A. and W.C. Hamilton (Eds.) (1974).International Tables for X-Ray Crystallography, IV, 99-101. Kynoch Press,Birmingham.

Langmyhr,J.F. and F.E. Paus (1968). The analysis of inorganic siliceous materials by atomic absorption spectrophotometry and the hydrofluoric acid decomposition technique. Part II. The analysis of silica. Anal. Chim. Acta, 43, 506-510.

Langmyhr, J.F. and F.E. Paus (1968). The analysis of inorganic siliceous materials by atomic absorption spectrophotometry and the hydrofluoric acid decomposition technique. Part. I. The analysis of silicate rocks. Anal. Chim. Aeta, 43, 397-408.

Linares, J. y F. Huertas (1973). Normas para el análisis químico de minerales y rocas. C.S.I.C. Granada, Spain.

Martín-Ramos, J.D. (1976). Las micas de la Cordillera Bética. Geol.D. Thesis. Granada University, Spain.

_____ , M. Rodríguez Gallego y J. Burgos (1979). Sobre una mica crómica de Sierra Nevada. Soc. Esp. Mineral, 1, 93-102.

Pérez del Villar, L. (1972). Estudio geológico del área comprendida entre las ramblas del Raposo y del agua. Geol.L.Thesis.Granada University, Spain.

Puga,E., A. Díaz de Federico y J.M. Fontboté (1974). Sobre la individualización y sistematización de las unidades profundas de la zona Bética. Estudios Geol., 30, 543-548.

Radoslovich, E.W. (1962). The cell dimension and symmetry of layer lattice silicates. IV Interatomic forces. Am. Mineral., 48, 76-99.