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Fe-Mg M1 site distribution in some clinopyroxenes from Santa Olalla (Huelva, Spain)

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SUMMARY

The crystal structures of two clinopyroxenes related to the skarns from Santa Olalla (Huelva, Spain) have been refined. From these refinements it is shown that pyroxene SO-1 of metamorphic origin is almost pure diopside, whereas for pyroxene SO-2 of metasomatic origin the following formula $CaMg_{0.64}Fe^{2+}_{0.34}Si_2O_6$ was found. These clinopyroxenes show cation ordering.

INTRODUCCIÓN

A previous X-ray and Mössbauer study (Amigo et al., 1980) showed the existence of different oxidation states in clinopyroxenes related to the skarns from Santa Olalla (Velasco and Amigo, 1979) as a consequence of replacement reactions under the influence of hydrothermal solutions that transform carbonates into calc-silicates.

Fe^{2+}–Mg M1 site distribution has been carried out by structural refinement of X-ray diffraction data of these clinopyroxenes. Two types of pyroxenes have been studied: pyroxene SO-1 of metamorphic origin, and pyroxene SO-2 of metasomatic origin.

According to X-ray study and to previous work (Amigo, et al., 1980) carried out with these pyroxenes, it is confirmed that these two clinopyroxenes show cation ordering.

EXPERIMENTAL

Two samples (SO-1 and SO-2) were prepared as spheres. Information on the material used is compiled in Table I. X-ray intensities were collected on a Phillips PW1100 diffractometer ($MoK\alpha_1$ radiation, graphite monochromator, $\theta_{max} = 40°$, $\omega 2\theta$ scan). Intensities with $I \geq 2.5\delta(I)$ were considered to be observed (1429 for sample SO-1, 1402 for sample SO-2). The relative intensities were corrected for the usual Lorentz and polarization factors. No corrections were made for absorption.

Refinement was begun with the coordinates of other known pyroxenes (Warren and Bragg, 1928) and carried out by the programme SHELX76 (Sheldrick, 1976) with anisotropic thermal parameters to a final R value of 0.0287 ($R\omega = 0.0403$) and 0.0262 ($R\omega = 0.0319$) for pyroxenes SO-1 and SO-2, respectively.

The final parameters are shown in Table II. Our results for these clinopyroxenes closely agree with those of Clark et al. (1969).

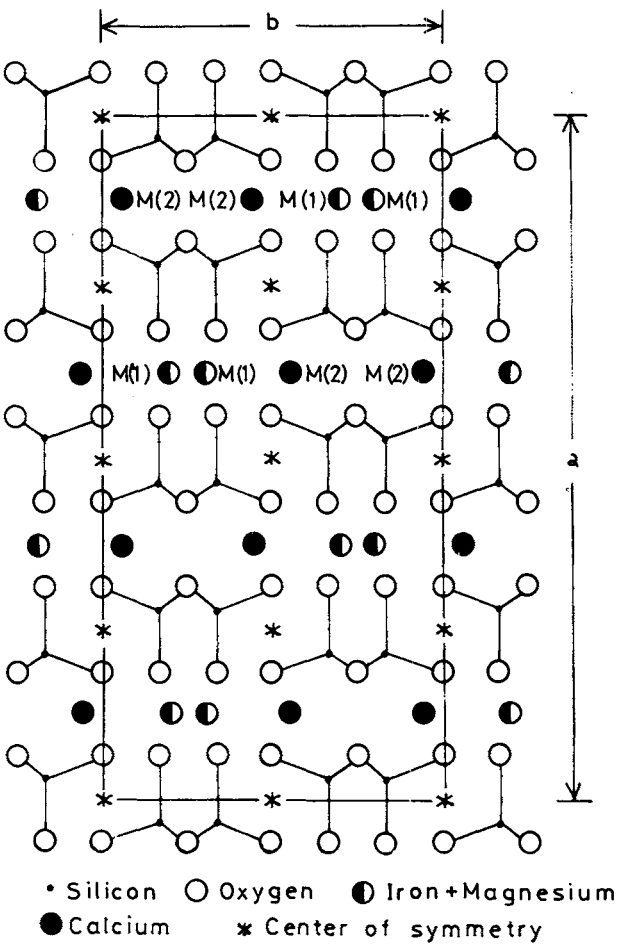

Fig. 1. Projection along z-axis of an idealized pyroxene structure, showing the pyroxene chains and two disctinct cation sites M (1) and M (2). The latter are in oxygen polyhedra which also form chains or bands parallel to z.

RESULTS

Tables III and IV show the interatomic distances and angles in these clinopyroxenes. All values perfectly agree with those shown in the bibliography for ordered clinopyroxenes.

Table I. Data on the material used for X-ray intensity collection

	SO-1	*SO-2*
Colour	yellowish-green	dark-green
Formula*	$CaMg_{0.97}Fe^{2+}_{0.03}Si_2O_6$	$CaMg_{0.65}Mn_{0.02}Fe^{2+}_{0.15}Si_2O_6$
a (Å)	9.768 (1)	9.796
b (Å)	8.944	8.970 (1)
c (Å)	5.266 (2)	5.261 (5)
β (°)	105.84 (1)	105.65
Space group	C2/c	C2/c
Z	4	4
D_x (g cm^{-3})	3.25	3.39
μ (Mo (cm^{-1})	20.4	30.2
Diameter of sphere (mm)	0.31	0.40

* From electron microprobe analysis (Amigo et al., 1980).

CONCLUSIONS

The unit formula of these clinopyroxenes calculated from the electron microprobe analysis (Amigo et al., 1980) and the one obtained from X-ray single crystal data are in mutual agreement. From the X-ray and chemical studies it is deducted that pyroxene SO-1 is an almost pure diopside, whereas in pyroxene SO-2 there is substitution of Mg^{2+} ion by Fe^{2+} ion in the M1 site in the ratio Mg (0.64): Fe^{2+} (0.34). This is in agreement with the data obtained by Mössbauer spectroscopy (Bancroft et al., 1971; Matsui et al., 1971; Virgo, 1973; Marfunin, 1979; Amigo et al., 1980).

Table II. Atomic coordinates (x10^4), occupation factors and anisotropic temperature factors (x10^4)

Pyroxene SO-1

Atom	*x*	*y*	*z*	*K*	*U11*	*U22*	*U33*	*U12*	*U13*	*U23*
SiA1	2861	932	2292 (1)	1.00	42 (2)	44 (2)	39 (2)	-2 (1)	17 (1)	-3 (1)
O1A1	1160 (1)	873 (1)	1426 (2)	1.00	40 (3)	67 (4)	56 (4)	3 (2)	17 (3)	-2 (3)
O2A1	3611 (1)	2503 (1)	3185 (2)	1.00	91 (4)	52 (3)	73 (4)	-21 (3)	20 (3)	-2 (3)
O3A1	3506 (1)	177 (1)	-47 (2)	1.00	65 (3)	80 (4)	55 (4)	-1 (2)	29 (3)	-24 (3)
CaM2	0	3016	2500	0,50	94 (2)	58 (2)	58 (2)	0	5 (1)	0
MgM1	0	9082 (1)	2500	0.50	49 (3)	40 (3)	31 (3)	0	12 (2)	0

Pyroxene SO-2

SiA1	2869	928	2309 (1)	1.00	54 (2)	50 (2)	47 (2)	-2 (1)	13 (1)	-3 (1)
O1A1	1164 (1)	878 (1)	1445 (2)	1.00	52 (4)	87 (4)	75 (4)	1 (3)	8 (3)	-1 (3)
O2A1	3619 (1)	2489 (1)	3207 (2)	1.00	110 (4)	62 (4)	87 (4)	-25 (3)	18 (3)	-8 (3)
O3A1	3505 (1)	178 (1)	-46 (2)	1.00	71 (4)	93 (4)	58 (4)	-1 (3)	15 (3)	-26 (3)
CaM2	0	3008	2500	0.50	113 (2)	80 (2)	70 (2)	0	1 (1)	0
MgM1	0	9073 (1)	2500	0.332 (2)	88 (25)	39 (34)	76 (25)	0	47 (18)	0
FeM1	0	9073 (1)	2500	0.168 (2)	51 (16)	68 (26)	36 (16)	0	-15 (12)	0

Table III. Bond distances in a Å, standard deviation in parentheses.

		SO-1	*SO-2*
Si	- 01	1.599 (1)	1.608 (1)
Si	- 02	1.595 (1)	1.592 (1)
Si	- 03	1.672 (1)	1.671 (1)
CaM2	- 01A1	2.372 (1)	2.367 (1)
MeM1	- 01A1	2.126 (1)	2.138 (1)
MeM1	- CaM2	3.519 (1)	3.503 (1)
MeM1	- MeM1	3.103 (1)	3.112 (1)

Tabla IV. Bond angles (in degree), standard deviation in parentheses.

			SO-1	*SO-2*
01	- Si	- 02	118.1 (1)	118.0 (1)
01	- S1	- 03A1	110.3 (1)	110.2 (1)
02	- Si	- 03A1	109.8 (1)	109.8 (1)
CaM2	- 01A1	- Si	115.6 (1)	116.1 (1)
MeM1	- 01A1	- Si	122.5 (1)	122.2 (1)
MeM1	- 01	- CaM2	102.8	103.1 (1)
01A1	- CaM2	- 01B1	72.2	72.3 (1)
01A1	- MeM1	- 01B1	82.2	81.6 (1)
MeM1	- CaM2	- 01	36.1	36.2
CaM2	- MeM1	- 01	41.1	40.8

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