

## Crystal structure of a Cr<sup>2+</sup>-bearing pyroxene

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### ABSTRACT

The structure of a pyroxene of composition  $\text{Mg}_{1.425}\text{Cr}_{0.611}\text{Si}_{1.964}\text{O}_6$  has been determined by refinement of X-ray diffraction data. This pyroxene is monoclinic with unit-cell parameters  $a = 9.713(2) \text{ \AA}$ ,  $b = 8.910(2) \text{ \AA}$ ,  $c = 5.238(2) \text{ \AA}$ ,  $\beta = 109.41(2)^\circ$ , and  $V_{\text{cell}} = 427.6(2) \text{ \AA}^3$ . The space group is  $P2_1/c$ , and the structure is very similar to that of low clinoenstatite. Most of the Cr is accommodated on the M2 site of the structure, which is consequently much more distorted than that found in the structure of end-member  $\text{MgSiO}_3$ . Refined site occupancies are

$$\text{M1} = 0.946(6)\text{Mg} + 0.054(6)\text{Cr}$$

$$\text{M2} = 0.479(6)\text{Mg} + 0.521(6)\text{Cr}$$

$$\text{TA} = 0.983(7)\text{Si} + 0.017(7)\text{Cr}$$

$$\text{TB} = 0.981(7)\text{Si} + 0.019(7)\text{Cr}$$

The substitution of Cr for Mg in the M2 site is associated with an increase in the mean M2–O bond distance (2.209 Å) over that found in  $\text{MgSiO}_3$ , whereas the M1–O distance is 2.093 Å, similar to  $\text{MgSiO}_3$ . These results are also consistent with the majority of the Cr in this pyroxene being in the divalent state, in agreement with spectroscopic observations. Mean T–O distances are TA–O = 1.631 Å and TB–O = 1.636 Å, and the O3–O3–O3 chain extension angles are  $199.5(4)^\circ$  for the A chain, and  $147.1(4)^\circ$  for the B chain.

### INTRODUCTION

The presence of Cr in minerals in the 2+ rather than 3+ oxidation state would be a clear indicator of very low oxygen fugacities at the time of mineral formation. Not surprisingly then, the first deduction of the presence of Cr<sup>2+</sup> in pyroxenes was made in lunar samples by Boyd and Smith (1971). The parallel claims for Cr<sup>2+</sup> in lunar olivines (e.g., Haggerty et al., 1971) are based upon optical absorption spectra, the interpretation of which were somewhat controversial (Burns et al., 1973). More recently (Rossman, 1988, personal communication), it has been demonstrated that synthetic olivines containing Cr<sup>2+</sup> display a characteristic absorption band in the near infrared. In contrast, the question of Cr<sup>2+</sup> in pyroxenes has remained largely dormant. The little spectroscopic work that has been done on Cr in pyroxenes has been restricted to synthetic blue diopside in which it appears to be in some higher valence state, probably 3+ (Ikeda and Yagi,

1977) or 4+ (Schreiber, 1977), rather than Cr<sup>2+</sup> as originally proposed by Mao et al. (1972).

Gasparik (1981) undertook a series of experiments to investigate the phase relations of the system  $\text{MgO}-\text{Cr}^0-\text{Cr}_2\text{O}_3-\text{SiO}_2$  under very low oxygen fugacities and was successful in synthesizing a number of phases containing Cr<sup>2+</sup>. The Cr analogue of gillespite was described by Belsky et al. (1984), and Belsky (1982) presented some preliminary observations on the clinopyroxenes synthesized by Gasparik (1981). In this paper we describe the refinement of the structure of a Cr<sup>2+</sup>-bearing clinoenstatite from single-crystal X-ray diffraction data. This analysis, like that of the Cr analogue of gillespite (Belsky et al., 1984), demonstrates that Cr<sup>2+</sup> can be accommodated within silicate minerals under suitably reducing conditions.

### EXPERIMENTAL DETAILS

The single crystals of Cr-bearing enstatite were synthesized from a starting material of composition 52 mol%  $\text{SiO}_2$ , 36 mol%  $\text{MgO}$ , 5 mol%  $\text{Cr}_2\text{O}_3$ , and 7 mol% Cr metal. This mixture was packed into a silica tube that was evacuated at 800 °C for 30 min, sealed, and then

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TABLE 1. Crystal data for Cr-enstatite

Composition on the basis of six oxygens*		
Cr <sup>2+</sup>	0.540(5)	
Cr <sup>3+</sup>	0.071	
Si <sup>4+</sup>	1.964(5)	
Mg <sup>2+</sup>	1.425(5)	
Total	4.000	
<i>a</i> (Å)	9.713(2)	Space group <i>P</i> 2 <sub>1</sub> / <i>c</i>
<i>b</i> (Å)	8.910(2)	<i>Z</i> = 4
<i>c</i> (Å)	5.238(2)	$\rho_{\text{calc}} = 3.38$
$\beta$ (°)	109.41(2)	
<i>V</i> (Å <sup>3</sup> )	427.6(2)	
<i>R</i> (obs. reflns.)	3.2	
<i>R</i> <sub>w</sub>	3.0	$\lambda = 0.7093$ Å
<i>G</i> <sub>int</sub>	0.90	$2\theta_{\text{max}} = 60^\circ$
<i>N</i> <sub>par</sub>	94	$\mu = 23.84$ cm <sup>-1</sup>
<i>N</i> <sub>obs</sub> <i>I</i> > 3 $\sigma$ <sub><i>I</i></sub>	504	

Note: Numbers in parentheses are the estimated standard deviation (1 $\sigma$ ) in the last decimal place quoted. This convention applies to all subsequent tables.

\* Average of nine microprobe analyses. Numbers in parentheses indicate the range of observed variations in composition.

inserted into a second silica tube that was evacuated in turn for 15 min and then sealed. This assembly, placed in a Pt bucket, was suspended in a vertical furnace and heated at 1350 °C for 13.5 h. The experimental product consisted of Cr-bearing enstatite, cristobalite, Cr metal, and quenched glass. An excess of silica in the starting material minimized reaction with the container. The presence of Cr metal assured the low oxygen fugacity necessary to produce Cr<sup>2+</sup>-bearing phases. The silica tubes softened and collapsed during heating, which indicated that the internal pressure was below 1 atm. The temperature was measured with a Pt<sub>100</sub>-Pt<sub>90</sub>Rh<sub>10</sub> thermocouple; the reported temperature is probably correct to within  $\pm 5$  °C.

The Cr-bearing enstatite crystals showed weak pleochroism, colorless to pale green, and displayed pervasive polysynthetic twinning. Electron-microprobe analyses indicated that the Cr-bearing enstatite was homogeneous, with a composition of approximately 71 mol% MgSiO<sub>3</sub> and 29 mol% CrSiO<sub>3</sub> (Table 1) if cation stoichiometry is assumed. This composition requires most of the Cr to be in the divalent state, a result supported by the observation of a strong absorption band typical of Cr<sup>2+</sup> in the near-infrared spectra from this pyroxene (Rossman, 1988, personal communication).

A single untwinned crystal of the Cr-bearing enstatite with approximate dimensions 70 × 40 × 15  $\mu$ m was selected for X-ray diffraction experiments that were carried out with a Rigaku AFC-5 goniometer equipped with a rotating-anode generator operated at 50 kV and 180 mA. Graphite-monochromatized MoK $\alpha$  radiation ( $\lambda = 0.7093$  Å) was used. Scans of all diffraction peaks were sharp and lacked any of the diffuse background structure so typical of pyroxene diffraction patterns. Unit-cell parameters (Table 1) were determined from the positions of 21 centered reflections in the range 35° < 2 $\theta$  < 55° and are consistent with those reported on the basis of

powder-diffraction data by Gasparik (1981) for similar compositions.

All reflections in one hemisphere of reciprocal space were collected to  $\sin \theta/\lambda = 0.71$ , with  $-13 < h < 13$ ,  $0 < k < 12$ ,  $-7 < l < 7$  (two asymmetric units) with continuous  $\omega$  scans in a constant-precision mode. Three reflections were monitored as intensity and orientation standards every 150 reflections during the data collection, and these showed no systematic variation with time. The systematic absences in the diffraction pattern were those reflections with *l* odd in *h*0*l* and *k* odd in 0*k*0. The space group was thus uniquely determined to be that of low clinoenstatite, *P*2<sub>1</sub>/*c*. The 2553 symmetry-allowed reflections that were measured were corrected for Lp effects and absorption (transmission coefficients ranged from 90 to 95%) and were reduced to structure factors with the program of Burnham (1966a). These were then averaged in Laue group 2/*m* with *R*<sub>int</sub> = 5.6% (2.9% for observed reflections) to give 1141 symmetry-independent reflections, of which 504 with *I* > 3 $\sigma$ <sub>*I*</sub> were treated as observed and were included in the refinements.

Refinements were carried out with *REFINE88*, a development version of *REFINE4* (Finger and Prince, 1975). A weight of  $w = \sigma^{-2}(F_o)$  was assigned to each observed reflection, where  $\sigma(F_o)$  is the error derived from counting statistics, and the function minimized was  $\Sigma w(|F_o| - |F_c|)^2$ . The atomic coordinates of low clinoenstatite (Ohashi, 1984) were used as a starting model, and complex scattering factors for neutral atoms were taken from *International Tables for X-ray Crystallography* (1974). Refinements were carried out with the chemistry constrained to the composition indicated by the microprobe analyses (Table 1), which has been calculated with the assumption that all of the cation sites are fully occupied. With the analysis as given, this requires the allocation of 0.036 atoms of Cr to the tetrahedral sites, but we are unable to determine the distribution of Cr<sup>2+</sup> and the trace of Cr<sup>3+</sup> between the various sites on the basis of X-ray diffraction data. With the addition of a correction for isotropic type I extinction using the Becker and Coppens (1974) formalism, refinement converged smoothly to the final agreement indices reported in Table 1. Atomic coordinates and temperature factors are listed in Table 2, observed and calculated structure factors in Table 3,<sup>1</sup> and bond lengths and angles in Table 4. Duplicate refinements using form factors appropriate for fully charged atoms converged to the same structural parameters and site occupancies, but with slightly modified thermal parameters.

## DISCUSSION

The general features and trends of pyroxene crystal chemistry are well known, and the reader is referred for

<sup>1</sup> A copy of Table 3 may be ordered as Document AM-89-406 from the Business Office, Mineralogical Society of America, 1625 I Street, N.W., Suite 414, Washington, D.C. 20006, U.S.A. Please remit \$5.00 in advance for the microfiche.

TABLE 2. Positional and thermal parameters from refinement of Cr-bearing enstatite

Site	<i>x</i>	<i>y</i>	<i>z</i>	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$	$B_{eq}$
M1	0.2506(3)	0.6537(2)	0.2253(4)	0.0019(2)	0.0021(3)	0.0034(8)	0.0001(4)	0.0004(3)	0.0008(6)	0.58
M2	0.2528(2)	0.0162(2)	0.2209(3)	0.0019(2)	0.0019(2)	0.0044(6)	0.0005(2)	0.0003(3)	0.0002(3)	0.58
TA	0.0456(2)	0.3387(3)	0.2891(3)	0.0020(3)	0.0020(3)	0.0040(7)	-0.0003(3)	0.0011(3)	0.0001(4)	0.55
TB	0.5493(2)	0.8381(3)	0.2437(3)	0.0012(2)	0.0017(3)	0.0043(7)	0.0002(3)	0.0002(3)	0.0002(4)	0.47
O1A	0.8694(6)	0.3347(7)	0.1748(9)	0.0020(6)	0.0030(7)	0.005(2)	0.0008(7)	0.0004(8)	0.001(1)	0.73
O2A	0.1226(6)	0.4984(6)	0.3269(9)	0.0024(7)	0.0011(7)	0.006(2)	-0.0007(6)	0.0016(9)	-0.001(1)	0.55
O3A	0.1092(5)	0.2753(5)	0.6055(9)	0.0021(6)	0.0020(6)	0.002(2)	-0.0007(5)	-0.0002(8)	0.0012(9)	0.57
O1B	0.3726(6)	0.6399(6)	0.1336(9)	0.0009(6)	0.0023(7)	0.003(2)	-0.0006(7)	-0.0000(7)	0.000(1)	0.48
O2B	0.6321(6)	0.9871(6)	0.3820(9)	0.0034(7)	0.0017(7)	0.008(2)	-0.0010(6)	0.0034(9)	-0.001(1)	0.72
O3B	0.6021(5)	0.7066(5)	0.4834(8)	0.0013(6)	0.0025(6)	0.003(2)	-0.0000(5)	-0.0015(8)	0.0013(8)	0.61

## Refined site occupancies

M1 = 0.946(6)Mg + 0.054(6)Cr

M2 = 0.479(6)Mg + 0.521(6)Cr

TA = 0.983(7)Si + 0.017(7)Cr

TB = 0.981(7)Si + 0.019(7)Cr

Note: Extinction parameter (isotropic),  $g = 0.5(1) \times 10^{-4}$ .

details to Cameron and Papike (1980). It is clear from the results of this structure refinement of Cr-bearing enstatite that Cr<sup>2+</sup> is accommodated by solid solution within the low clinoenstatite structure in much the same way as other transition-metal cations, e.g., Mn<sup>2+</sup> and Fe<sup>2+</sup>. For these cations, as well as for Ca<sup>2+</sup> (Ohashi and Finger, 1976), the substitution of a larger cation for Mg within the *P2<sub>1</sub>/c* structure results in the expansion of the unit-cell edges. One unusual feature, however, of this Cr-bearing enstatite is the large increase in the  $\beta$  cell angle (109.41°) over that in MgSiO<sub>3</sub>, whereas for most other substitutions, this angle is reduced from the value of 108.35° in MgSiO<sub>3</sub> (Ohashi, 1984). The only other reported examples of clinopyroxenes with larger  $\beta$  angles are one with a composition of Mn<sub>0.9</sub>Mg<sub>1.1</sub>Si<sub>2</sub>O<sub>6</sub> (Ghose et al., 1975) and  $\beta = 108.51^\circ$  and a number of pyroxenes with Li on the M1 site (see Cameron and Papike, 1980).

The results of this structure refinement place the majority of the Cr in the M2 site, which, being more distorted than M1 in pyroxene structures, tends to accept transition-metal cations (Burns, 1970; Ghose et al., 1975). This distribution is reflected in the detailed structural differences between this Cr-bearing enstatite and that of the end-member MgSiO<sub>3</sub>. The M1 site in Cr-bearing enstatite (with 0.05 Cr) is marginally larger and marginally more distorted than that of MgSiO<sub>3</sub>, the mean M1–O bond distance being increased from 2.079 Å to 2.093 Å. The much larger expansion of the average M2–O distance, from 2.144 Å (Ohashi, 1984) to 2.209 Å, is due to the higher Cr content of this site, the ionic radii of Mg<sup>2+</sup> and Cr<sup>2+</sup> being 0.72 Å, and 0.80 Å, respectively (Shannon, 1976). The majority of this expansion is taken up in two M2–O bonds that are opposite to each other, M2–O1A and M2–O3B, and is reflected in the larger value of the quadratic elongation of this site (Table 4) than that of the M2 site in MgSiO<sub>3</sub> (1.043). The same distortion pattern with respect to MgSiO<sub>3</sub> is observed in FeSiO<sub>3</sub> (Burnham, 1966b) and the high-pressure low-spin Mn<sup>2+</sup> phase MnSiO<sub>3</sub> (Tokonami et al., 1979) and is presumably re-

lated to the crystal-field stabilization of these transition-metal ions. However, one feature of clinoenstatite structures noted by Ohashi and Finger (1976) is not evident in this structure refinement. They found that the equiv-

TABLE 4. Bond lengths and angles in Cr-bearing enstatite

M1–O1A	2.155(6)	M2–O1A	2.182(6)
M1–O1A	2.035(5)	M2–O2A	2.035(5)
M1–O2A	2.046(6)	M2–O3A	2.282(5)
M1–O1B	2.184(6)	M2–O1B	2.095(5)
M1–O1B	2.073(5)	M2–O2B	2.009(6)
M1–O2B	2.062(6)	M2–O3B	2.649(5)
Avg.	2.093	Avg.	2.209
Q.E.*	1.009	Q.E.*	1.063
TA–O1A	1.616(6)	TB–O1B	1.621(5)
TA–O2A	1.591(5)	TB–O2B	1.597(6)
TA–O3A	1.653(5)	TB–O3B	1.657(5)
TA–O3A	1.664(5)	TB–O3B	1.669(5)
Avg.	1.631	Avg.	1.636
Q.E.*	1.008	Q.E.*	1.005
<b>M1 octahedron</b>		<b>M2 octahedron</b>	
O1A–O1A	92.3(2)	O1A–O2A	90.0(2)
O1A–O2A	91.1(2)	O1A–O3A	109.5(2)
O1A–O1B	82.0(2)	O1A–O1B	83.5(2)
O1A–O1B	84.2(2)	O1A–O2B	83.8(2)
O1A–O2B	177.4(2)	O1A–O3B	169.6(2)
O1A–O2A	96.4(2)	O2A–O3A	70.4(2)
O1A–O1B	84.4(2)	O2A–O1B	86.2(2)
O1A–O1B	175.5(2)	O2A–O2B	173.8(2)
O1A–O2B	86.3(2)	O2A–O3B	82.3(2)
O2A–O1B	173.1(2)	O3A–O1B	152.7(2)
O2A–O1B	86.5(2)	O3A–O2B	111.6(2)
O2A–O2B	91.3(2)	O3A–O3B	74.5(2)
O1B–O1B	92.3(2)	O1B–O2B	93.2(2)
O1B–O2B	95.6(2)	O1B–O3B	89.1(2)
O1B–O2B	97.0(2)	O2B–O3B	103.9(2)
<b>TA tetrahedron</b>		<b>TB tetrahedron</b>	
O1A–O2A	117.6(3)	O1B–O2B	117.9(3)
O1A–O3A	109.1(3)	O1B–O3B	106.9(2)
O1A–O3A	111.1(2)	O1B–O3B	107.4(3)
O2A–O3A	111.8(3)	O2B–O3B	109.0(3)
O2A–O3A	100.1(3)	O2B–O3B	105.1(3)
O3A–O3A	106.5(2)	O3B–O3B	110.4(2)
TA–O3A–TA	134.5(3)	TB–O3B–TB	133.3(3)
O3A–O3A–O3A	199.5(4)	O3B–O3B–O3B	147.1(4)

\* Q.E. is the quadratic elongation as defined by Robinson et al. (1971).

alent isotropic temperature factor of the M2 site was greatly increased over that of M1 in a series of clinoenstatites in which a small amount of Ca was substituted for Mg in M2. This effect was attributed to different positions being occupied by the Mg and Ca cations on the M2 sites within the crystal. Clearly this process, if present between Cr and Mg in this structure, is too small to be apparent in the refined thermal parameters (Table 2).

The microprobe analyses of this material (Table 1) show it to be slightly deficient in Si with respect to oxygen. We have interpreted this deficiency as being due to the substitution of a small amount of Cr on the tetrahedral sites. The amount of substitution (Table 2) is insufficient to have any effect on the structural parameters, and the differences in the tetrahedral configurations between Cr-bearing enstatite and low clinoenstatite can be attributed to the difference in M-site chemistry. Compared to low clinoenstatite (Ohashi, 1984), the chain extension angle, as measured by the O3–O3–O3 angle along the chains, is decreased in the A chain (199.5° vs. 202.7° in MgSiO<sub>3</sub>) and increased in the B chain (147.1° vs. 138.4° in MgSiO<sub>3</sub>). These changes are in line with the trends noted by Cameron and Papike (1980), who found that straightening of both chains in *P2<sub>1</sub>/c* pyroxenes is correlated with increasing mean cation size on the M1 and M2 sites. Comitant with this chain straightening is a small reduction in the Si–O3 (i.e., bridging oxygens) bond lengths relative to those in MgSiO<sub>3</sub>, but these changes are only significant in the TB tetrahedron (at the 2σ level).

Refinements were also carried out to examine whether, despite the spectroscopic evidence, the Cr in this pyroxene could be mostly trivalent. This may be done because an increase in the ratio of Cr<sup>3+</sup> to Cr<sup>2+</sup> over that given in Table 1 would require a corresponding reduction in the overall cation to anion ratio and therefore the introduction of vacancies on the cation sites, a possibility directly testable by structure refinement. A structure model corresponding to the extreme case of all of the Cr being trivalent was therefore refined to our X-ray diffraction data. The problem with such a refinement was that the presence of partially occupied cation sites added several degrees of freedom to the structure model. As a result the refinement was ill-constrained, but cation-site occupancies did not deviate (within the much larger esd's) from those reported in Table 2 for the Cr<sup>2+</sup> refinement. Furthermore, crystal-chemical considerations support the spectroscopic observations from this material (Rossman, 1988, personal communication), which suggest that the majority of the Cr is divalent. The ionic radius (Shannon, 1976) of Cr<sup>3+</sup> in octahedral coordination is 0.615 Å, compared to a value of 0.72 Å for Mg<sup>2+</sup>. Were all of the Cr in the 3+ oxidation state in this pyroxene, we would therefore expect the M2 octahedron to be significantly smaller than that found in MgSiO<sub>3</sub>, even allowing for the expansion effect of the necessary vacancies. Our results, on the contrary, show the opposite effect and are clearly far more consistent with the presence of Cr<sup>2+</sup>.

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