Crystal structure of a Cr$^{2+}$-bearing pyroxene

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ABSTRACT

The structure of a pyroxene of composition Mg$_{0.425}$Cr$_{0.575}$Si$_{1.964}$O$_6$ has been determined by refinement of X-ray diffraction data. This pyroxene is monoclinic with unit-cell parameters $a = 9.713(2)$ Å, $b = 8.910(2)$ Å, $c = 5.238(2)$ Å, $\beta = 109.41(2)^\circ$, and $V_{cell} = 427.6(2)$ Å$^3$. 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 MgSiO$_3$. Refined site occupancies are

- M1: 0.946(6[Mg] + 0.054(6)Cr
- M2: 0.479(6)Me + 0.521(6)Cr
- TA: 0.983(7)Si + 0.017(7)Cr
- TB: 0.981(7)Si + 0.019(7)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 MgSiO$_3$, whereas the M1-O distance is 2.093 Å, similar to 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 chain extension angles are 199.5(4) for the A chain, and 147.1(4) 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$^{2+}$ in pyroxenes was made in lunar samples by Boyd and Smith (1971). The parallel claims for Cr$^{2+}$ 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$^{2+}$ display a characteristic absorption band in the near infrared. In contrast, the question of Cr$^{2+}$ 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$^{2+}$ as originally proposed by Mao et al. (1972).

Gasparik (1981) undertook a series of experiments to investigate the phase relations of the system MgO-Cr$_2$O$_3$-SiO$_2$ under very low oxygen fugacities and was successful in synthesizing a number of phases containing Cr$^{2+}$. The Cr analogue of gillespite was described by Belsky et al. (1984), and Belsky (1982) presented some preliminary observations on the clino-pyroxenes synthesized by Gasparik (1981). In this paper we describe the refinement of the structure of a Cr$^{2+}$-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$^{2+}$ 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% SiO$_2$, 36 mol% MgO, 5 mol% Cr$_2$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...
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$^{2+}$-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$_{100}$-Pt$_{13}$Rh$_{10}$ thermocouple; the reported temperature is probably correct to within ±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$_3$ and 29 mol% CrSiO$_3$ (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$^{2+}$ in the near-infrared spectra from this pyroxene (Rossman, 1988, personal communication).

A single untwinned crystal of the Cr-bearing enstatite with approximate dimensions $70 \times 40 \times 15$ μm 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 MoKα 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 $35^\circ < 2\theta < 55^\circ$ 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 $h0l$ and $k$ odd in $0k0$. The space group was thus uniquely determined to be that of low clinoenstatite, $P2_1/c$. 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 $R_{int} = 5.6%$ (2.9% for observed reflections) to give 1141 symmetry-independent reflections, of which 504 with $I > 3\sigma(I)$, were treated as observed and were included in the refinements.

Refinements were carried out with RFIN4, a development version of RFIN4 (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 $\Sigma w(F_o) - |F_o|^2$. 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$^{2+}$ and the trace of Cr$^{3+}$ 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, 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

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1 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 $5.00 in advance for the microfiche.
details to Cameron and Papine (1980). It is clear from
the results of this structure refinement of Cr-bearing en-
statite that Cr$^{2+}$ is accommodated by solid solution
within the clinopyroxene structure in much the same way
as other transition-metal cations, e.g., Mn$^{2+}$ and Fe$^{2+}$.
For these cations, as well as for Ca$^{2+}$ (Ohashi and Finger,
1976), the substitution of a larger cation for Mg within
the $P_2_1/c$ structure results in the expansion of the unit-
cell edges. One unusual feature, however, of this Cr-bear-
ing enstatite is the large increase in the $\beta$ cell angle
(109.41$^\circ$) over that in MgSiO$_3$, whereas for most other
substitutions, this angle is reduced from the value of
108.35$^\circ$ in MgSiO$_3$ (Ohashi, 1984). The only other re-
ported examples of clinopyroxenes with larger $\beta$ angles are
one with a composition of Mn$_{0.9}$Mg$_{0.1}$SiO$_3$ (Ghose et
al., 1975) and $\beta = 108.51^\circ$ and a number of pyroxenes
with Li on the M1 site (see Cameron and Papine, 1980).

The results of this structure refinement place the ma-
jority of the Cr in the M2 site, which, being more dis-
torted 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 dif-
fferences between this Cr-bearing enstatite and that of
the end-member MgSiO$_3$. The M1 site in Cr-bearing enstatite
(with 0.05 Cr) is marginally larger and marginally more
distorted than that of MgSiO$_3$, 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$^{2+}$ and
Cr$^{2+}$ 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$_3$ (1.043). The same distortion pattern
with respect to MgSiO$_3$ is observed in FeSiO$_3$ (Burnham,
1966b) and the high-pressure low-spin Mn$^{2+}$ phase
MnSiO$_3$ (Tokonami et al., 1979) and is presumably re-

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

<table>
<thead>
<tr>
<th>Site</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>$\beta_{11}$</th>
<th>$\beta_{22}$</th>
<th>$\beta_{33}$</th>
<th>$\beta_{12}$</th>
<th>$\beta_{13}$</th>
<th>$\beta_{23}$</th>
<th>$B_{eq}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>M1</td>
<td>0.2508(3)</td>
<td>0.6537(2)</td>
<td>0.2253(4)</td>
<td>0.0019(2)</td>
<td>0.0021(3)</td>
<td>0.0034(8)</td>
<td>0.0001(4)</td>
<td>0.0000(3)</td>
<td>0.0000(6)</td>
<td>0.58</td>
</tr>
<tr>
<td>M2</td>
<td>0.2528(2)</td>
<td>0.0162(2)</td>
<td>0.2209(3)</td>
<td>0.0019(2)</td>
<td>0.0019(2)</td>
<td>0.0044(6)</td>
<td>0.0005(2)</td>
<td>0.0003(3)</td>
<td>0.0002(3)</td>
<td>0.58</td>
</tr>
<tr>
<td>TA</td>
<td>0.0456(2)</td>
<td>0.3387(3)</td>
<td>0.2891(3)</td>
<td>0.0020(3)</td>
<td>0.0020(3)</td>
<td>0.0040(7)</td>
<td>0.0003(3)</td>
<td>0.0011(3)</td>
<td>0.0000(4)</td>
<td>0.55</td>
</tr>
<tr>
<td>TB</td>
<td>0.5493(2)</td>
<td>0.8381(3)</td>
<td>0.2437(3)</td>
<td>0.0012(2)</td>
<td>0.0017(3)</td>
<td>0.0043(7)</td>
<td>0.0020(3)</td>
<td>0.0002(3)</td>
<td>0.0024(7)</td>
<td>0.47</td>
</tr>
</tbody>
</table>

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

### Table 4. Bond lengths and angles in Cr-bearing enstatite

<table>
<thead>
<tr>
<th>Site</th>
<th>Bond Lengths (Å)</th>
<th>Site</th>
<th>Bond Lengths (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M1-O1A</td>
<td>2.155(6)</td>
<td>M2-O1A</td>
<td>2.182(6)</td>
</tr>
<tr>
<td>M1-O2A</td>
<td>2.035(5)</td>
<td>M2-O2A</td>
<td>2.035(5)</td>
</tr>
<tr>
<td>M1-O2B</td>
<td>2.046(6)</td>
<td>M2-O3A</td>
<td>2.282(5)</td>
</tr>
<tr>
<td>M1-O1B</td>
<td>2.184(6)</td>
<td>M2-O1B</td>
<td>2.095(5)</td>
</tr>
<tr>
<td>M1-O1B</td>
<td>2.073(5)</td>
<td>M2-O2B</td>
<td>2.006(6)</td>
</tr>
<tr>
<td>M1-O1B</td>
<td>2.062(6)</td>
<td>M2-O3B</td>
<td>2.648(5)</td>
</tr>
<tr>
<td>Avg.</td>
<td>2.093</td>
<td>Avg.</td>
<td>2.209</td>
</tr>
<tr>
<td>Q.E.*</td>
<td>1.009</td>
<td>Q.E.*</td>
<td>1.063</td>
</tr>
<tr>
<td>TA-O1A</td>
<td>1.616(6)</td>
<td>TB-O1B</td>
<td>1.621(5)</td>
</tr>
<tr>
<td>Avg.</td>
<td>1.631</td>
<td>Avg.</td>
<td>1.636</td>
</tr>
<tr>
<td>Q.E.*</td>
<td>1.008</td>
<td>Q.E.*</td>
<td>1.005</td>
</tr>
</tbody>
</table>

* 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 clinoen-
statites in which a small amount of Ca was substituted
for Mg in M2. This effect was attributed to different po-
tions 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 sub-
stitution 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 dif-
fences 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 MgSiO3)
and increased in the B chain (147.1° vs. 138.4° in Mg-
SiO3). These changes are in line with the trends noted by
Cameron and Papike (1980), who found that straighten-
ing of both chains in P21/c pyroxenes is correlated with
increasing mean cation size on the M1 and M2 sites. Con-
comitant with this chain straightening is a small reduc-
tion in the Si–O3 (i.e., bridging oxygens) bond lengths
relative to those in MgSiO3, 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 pyrox-
dene could be mostly trivalent. This may be done because
an increase in the ratio of Cr3+ to Cr2+ over that given in
Table 1 would require a corresponding reduction in the
overall cation to anion ratio and therefore the introduc-
tion of vacancies on the cation sites, a possibility directly
testable by structure refinement. A structure model cor-
responding 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 occupan-
cies did not deviate (within the much larger esd’s) from
those reported in Table 2 for the Cr2+ refinement. Fur-
thermore, 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 Cr3+ in octahedral coordination is 0.615 Å, com-
pared to a value of 0.72 Å for Mg2+. Were all of the Cr
in the 3+ oxidation state in this pyroxene, we would there-
fore expect the M2 octahedron to be significantly smaller
than that found in MgSiO3, even allowing for the expan-
sion effect of the necessary vacancies. Our results,
on the contrary, show the opposite affect and are clearly
far more consistent with the presence of Cr2+.

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