Experimental study of subsolidus phase relations and mixing properties of clinopyroxene in the silica-saturated system CaO-MgO-Al₂O₃-SiO₂

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ABSTRACT

In the system CaO-MgO-Al₂O₃-SiO₂ (CMAS), the equilibrium compositions of the clinopyroxene coexisting with anorthite and quartz were experimentally determined at 20 different P-T conditions (1200–1400°C, 14.0–30.4 kbar), and those of the clinopyroxene coexisting only with anorthite were determined in 15 experiments, using PbO as flux. The data were fitted to the Redlich-Kister equation for a ternary solution, providing the following mixing properties of the CaMgSi₂O₆-CaAl₂Si₂O₆-Ca₅Al₂Si₃O₁₂ (Di-CaTs-CaEs) pyroxene (units: joules, kelvins, bars):

\[
G^\text{mix}_{\text{P-x}} = X_{\text{CaTs}}X_{\text{Di}}[10000 - 10T - 0.07P - (50000 - 31.19T + 0.04P)(X_{\text{CaTs}} - X_{\text{Di}}) - 7000(X_{\text{CaTs}} - X_{\text{Di}})^2] + X_{\text{CaTs}}X_{\text{CaEs}}[-20160 + 14760(X_{\text{CaTs}} - X_{\text{CaEs}})] + X_{\text{Di}}X_{\text{CaEs}}[-5950].
\]

This solution model is consistent with the properties of the Di-CaTs binary determined previously, but does not give the correct CaTs-CaEs properties because of inferred anomalous mixing behavior of the ternary pyroxenes with low Di content.

The assemblages pyroxene + anorthite + quartz at lower pressures and pyroxene + garnet + kyanite + quartz at higher pressures are potentially useful as thermobarometers, applicable to quartz-bearing granulites and grospydites with low MgO and Na₂O contents.

INTRODUCTION

Clinopyroxenes in the system CaO-MgO-Al₂O₃-SiO₂ can have up to four components in solution: diopside (Di—CaMgSi₂O₆), Ca-Tschermak pyroxene (CaTs—CaAl₂Si₂O₆), Ca-Eskola pyroxene (CaEs—Ca₅Al₂Si₃O₁₂), and enstatite (En—Mg₅Si₃O₁₂). Diopside and Ca-Tschermak pyroxene are the only endmembers that are stable and can form a complete solid solution. The present study focuses on the silica-saturated CMAS system in which the clinopyroxene in equilibrium with anorthite (An), kyanite (Ky), or a silica polymorph incorporates variable amounts of the Ca-Eskola component. The En component, significant in the clinopyroxene coexisting with orthopyroxene and other MgO-rich phases, turned out to be negligible in the equilibria considered here.

Before the extent of solubility of the CaEs component in clinopyroxene was known, the silica-saturated CMAS system had appeared to provide an ideal opportunity for an experimental determination of mixing properties of the Di-CaTs solid solution. Such a study was carried out by Wood (1979), who investigated equilibria in the assemblage pyroxene (Px) + anorthite + quartz (Q). The major conclusion of Wood’s study was that at 1 bar and 1200–1300°C, the activity of the CaTs component in solution with diopside approximately corresponded to its mole fraction. However, the pyroxene in equilibrium with anorthite and quartz contains, especially at higher pressures, significant amounts of the CaEs component (Wood and Henderson, 1978). Thus, the activities of the CaTs component determined by Wood (1979) do not apply to the Di-CaTs binary solution; instead, they are modified by the CaEs component. In the present study, which uses the same experimental approach as Wood (1979), the ternary pyroxene properties were extrapolated to the Di-CaTs binary using a ternary-solution model. New experimental data were obtained for the following reasons:

1. The small size of pyroxene crystals in Wood’s experimental products prevented the use of an electron microscope, which can provide analyses of higher quality than the electron microscope microanalyzer used by Wood. In the present study, microprobe analyses were made possible by seeding starting materials with large pyroxene crystals.

2. Most of Wood’s experiments were conducted at and below 20 kbar. Under these pressures, the pyroxene composition is quite insensitive to changes in P-T conditions, and only a limited range of the Di-rich compositions can be covered in experiments. In the present study, most of the experiments were conducted at higher pressures to cover a wider range of pyroxene compositions.

Preliminary results of this study were reported by Gasparik and Lindsley (1980) and Gasparik (1981). Since
then, the mixing properties of the Di-CaTs solution were
determined by Gasparik (1984a) using equilibria in the
assemblage pyroxene + garnet (Ga) + corundum (Cor).
The latter approach avoided ambiguities caused by a mod-
el-dependent extrapolation of the ternary-pyroxene prop-
ties to the Di-CaTs binary, because the pyroxene in
equilibrium with garnet and corundum contains, in addi-
tion to Di and CaTs, only minor amounts of the En
component. The disadvantages of the latter approach are
that the Di-rich pyroxene compositions cannot coexist
with garnet and corundum and that the garnet is also a
solid solution. Because neither of the two approaches for
determining the properties of the Di-CaTs solution is per-
fect, the data from both studies were used to derive a set of
mixing parameters for the Di-CaTs solution that sat-
sified all experimental observations.

**Experimental techniques**

**General procedures**

Experiments were carried out using a conventional piston-cyl-
der apparatus with a 0.5-in.-diameter assembly made of talc
and boron nitride. Samples were encased in platinum capsules.
The description of the assembly, its pressure calibration, and
experimental procedures are in Gasparik (1985). For this assem-
bly, the temperature-dependent pressure correction is $-(19
- 0.017)$ percent, when $T$ is in degrees Celsius.

The nominal pressures were maintained within ±200 bars of
the desired value. Temperature was measured by W-3 Re vs.
W-25 Re thermocouples and controlled automatically. No cor-
rection for the effect of pressure on emf was applied. Uncertainty
in the temperature is less than ±5°C.

**Starting materials**

Starting materials were mechanical mixes made of ultrapure
oxides, CaSiO$_3$, and CaAl$_2$O$_3$ (Table 1). PbO was used in the
starting materials as flux to promote equilibration of charges.
Large crystals (20–50 μm) of synthetic diopside and Ca-Tscherm-
iski pyroxene were added to the starting materials in the amounts
of approximately 3 wt% each. The crystals reacted with the co-
existing phases, approaching an equilibrium pyroxene com-
position from two different directions. Thus, the equilibrium com-
positions were reversed with respect to Di and CaTs, but not
CaEs.

The original seed crystals change their composition by two
processes: reconstruction and equilibration. In the first process,
a new pyroxene of a presumably equilibrium composition nu-
cleates on the surface of the original seed and replaces it by
growing from the surface to the center of the crystal. At the same
time, the center of the original seed changes its composition by
equilibration. The process of reconstruction is more efficient than
equilibration when the change of composition requires a coupled
substitution. In such a case, the new pyroxene forms an irregular
rim around the original seed, with the core having a composition
that is much closer to the original composition than the rim, or
unchanged at all. However, if the original seed composition is
very different from the equilibrium composition, the equilibra-
tion process is much more efficient, and the result is a crystal
with gradual zonation. It must be stressed that the rims do not
form by synthesis from oxides used in the starting materials. The
oxides fully react in the press by the time the initial pressure and
temperature are reached. If quenched immediately, the experi-
mental product is crystalline, with all phases already present.
The crystalline matrix is very fine and unsuitable for microprobe
analysis. Any rims around the seed crystals formed by synthesis
from oxides are equally too fine to be detected by an electron
microprobe.

**Analytical procedures**

Experiments produced hard pellets composed of crystals sur-
rounded by a PbO-rich glass. Approximately one half of a pellet
was ground and used for phase identification by X-ray diffraction.
The other half of the charge was mounted for microprobe anal-
ysis.

Wavelength-dispersive analyses were obtained with an auto-
mated ARL-EMX electron microprobe. All analyses were taken at
15-kV accelerating potential and 0.015-μA sample current on
brass, using the minimum spot size (∼1 μm). Standards were
natural diopside for Ca, Mg, and Si, and natural anorthite for
Al. The data were reduced using the correction procedures of
Bence and Albee (1968). Analyses were obtained from the re-
action rims developed around the seed crystals. The original
compositions were preserved in the cores of the seeds; thus, it
was always possible to infer the direction of the approach to
equilibrium. Typically, 20–50 analyses were taken from several
gains of each kind of seed. Only those pyroxene analyses were
accepted that gave the sum of cations in the M 1 and the T sites
in the range 2.99–3.01. The concentrations of PbO in all crys-
talline phases were below the detection limit.

**Experimental results**

Equilibrium compositions of the clinopyroxene coex-
isting with anorthite and quartz were obtained at 20 differ-
ent $P$-$T$ conditions, and those of the clinopyroxene coex-
isting only with anorthite were determined in 15 experi-
ments. For each experiment, average compositions of
equilibrated rims on each kind of seed were calculated
separately. The resulting averages obtained from the diop-
side and the CaTs seeds were then averaged to calculate
the compositions used in the least-squares solution mod-

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**Table 1. Compositions of starting materials (in moles)**

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<tr>
<th>(\text{Mix})</th>
<th>(\text{CaAl}_2\text{O}_4)</th>
<th>(\text{CaSiO}_3)</th>
<th>(\text{MgO})</th>
<th>(\text{SiO}_2)</th>
<th>(\text{PbO})</th>
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Fig. 1. Results of equilibration experiments containing the assemblages Px + An + Q and Px + An, shown in the compositional plane Di-CaTs-CaEs. Labeled: temperature (°C)/nominal pressure (kbar). (a) Pyroxene compositions from selected experiments. Shown are the typical compositional ranges observed in single experiments, and the variable degree of the approach to equilibrium. Envelopes enclose all accepted microprobe analyses. Average compositions calculated for each kind of seed (open circles) were averaged to produce the compositions used in the modeling (solid dots). (b) A complete set of the determined compositions of the pyroxene in equilibrium with anorthite and quartz (solid dots) and with anorthite only (open circles).

Fig. 2. Subsolidus P-T phase relations in the silica-saturated CMAS system. The heavy line is the univariant curve for Reaction 4. Thin lines are the pyroxene and garnet isopleths in mole percent; solid line = Di; dashed line = CaTs; dash-dot line = CaEs; and dotted line = Py. Solid dots represent the P-T locations of the present experiments with the assemblage Px + An + Q, in some cases metastably in the garnet field. Omitted from the diagram are α-Q = β-Q and Q = Cs transitions.
Table 2. Conditions of equilibration experiments and average compositions of clinopyroxene in equilibrium with phases in the given assemblage and PbO-rich liquid

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</table>

Thermodynamic evaluation of results

Equilibrium in the assemblage Px + An + Q can be described by the reactions:

\[ \text{An = CaTs + Q} \]  \hspace{1cm} (1)
\[ \text{An + 2Q = 2CaEs} \]  \hspace{1cm} (2)

Because anorthite and quartz are stoichiometric, the equilibrium conditions corresponding to these reactions may be written as RT ln \( a_{\text{CaTs}} \) + \( \Delta G_1 \) = 0, and 2RT ln \( a_{\text{CaEs}} \) + \( \Delta G_2 \) = 0, where \( a_{\text{CaTs}} \) = \( X_{\text{CaTs}} \), \( a_{\text{CaEs}} \) = \( X_{\text{CaEs}} \). Equilibrium in the assemblage Px + An can be described by the reaction

\[ 3\text{An = 2CaTs + 2CaEs} \]  \hspace{1cm} (3)

At equilibrium, \( 2RT \ln (a_{\text{CaTs}} \cdot a_{\text{CaEs}}) + \Delta G_3 \) = 0, where \( \Delta G_3 = 2\Delta G_1 + \Delta G_2 \). The free-energy change of a reaction was evaluated at a reference temperature of 1573 K, which is in the middle of the temperature range covered by the present experiments: \( \Delta G_{\text{f,p}} = \Delta H_{1573 \text{ K}} - T \Delta S_{1573 \text{ K}} + \Delta V_{1573 \text{ K}} - 0.5 \Delta P_{V} \Delta V \). Volume differences for all reactions were calculated using the unit-cell volumes and the coefficients of thermal expansion (\( \alpha \)) and compressibility (\( \beta \)) listed by Gasparik (1984a, 1984b). For the CaEs endmember, the unit-cell volume of jadeite, 6.040 \( \mu \text{bar} \), given by Holland (1980), was used as an approximation. This volume is consistent with a linear extrapolation.
Table 3. Unit-cell constants of synthetic Di-CaTs clinopyroxenes

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<tr>
<th>Composition (mol %)</th>
<th>a(Å)</th>
<th>b(Å)</th>
<th>c(Å)</th>
<th>β (Deg.)</th>
<th>V (Å³)</th>
<th># of obs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Di₁₀₀CaTs₀</td>
<td>9.7475(12)</td>
<td>8.9232(10)</td>
<td>5.2496(7)</td>
<td>105.853(8)</td>
<td>439.233(124)</td>
<td>30</td>
</tr>
<tr>
<td>Di₉₀CaTs₁₀</td>
<td>9.7293(10)</td>
<td>8.8976(8)</td>
<td>5.2559(6)</td>
<td>105.969(6)</td>
<td>437.434(109)</td>
<td>38</td>
</tr>
<tr>
<td>Di₈₀CaTs₂₀</td>
<td>9.7082(8)</td>
<td>8.8647(7)</td>
<td>5.2647(5)</td>
<td>106.063(5)</td>
<td>435.386(86)</td>
<td>36</td>
</tr>
<tr>
<td>Di₇₀CaTs₃₀</td>
<td>9.6905(8)</td>
<td>8.8341(7)</td>
<td>5.2713(5)</td>
<td>106.172(7)</td>
<td>433.500(88)</td>
<td>34</td>
</tr>
<tr>
<td>Di₆₀CaTs₄₀</td>
<td>9.6732(8)</td>
<td>8.8033(7)</td>
<td>5.2761(5)</td>
<td>106.161(5)</td>
<td>431.533(91)</td>
<td>35</td>
</tr>
<tr>
<td>Di₅₀CaTs₅₀</td>
<td>9.6576(9)</td>
<td>8.7716(7)</td>
<td>5.2790(6)</td>
<td>106.188(6)</td>
<td>429.467(100)</td>
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<tr>
<td>Di₄₀CaTs₆₀</td>
<td>9.6447(8)</td>
<td>8.7392(7)</td>
<td>5.2822(5)</td>
<td>106.166(6)</td>
<td>427.614(92)</td>
<td>31</td>
</tr>
<tr>
<td>Di₃₀CaTs₇₀</td>
<td>9.6356(9)</td>
<td>8.7216(7)</td>
<td>5.2811(6)</td>
<td>106.164(7)</td>
<td>426.265(103)</td>
<td>31</td>
</tr>
<tr>
<td>Di₂₀CaTs₈₀</td>
<td>9.6272(9)</td>
<td>8.7000(9)</td>
<td>5.2805(6)</td>
<td>106.149(7)</td>
<td>424.822(101)</td>
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<tr>
<td>Di₁₀CaTs₉₀</td>
<td>9.6163(8)</td>
<td>8.6801(7)</td>
<td>5.2794(5)</td>
<td>106.111(6)</td>
<td>423.634(91)</td>
<td>33</td>
</tr>
<tr>
<td>(Di₂₀CaTs₈₀)₁₀₀⁻CaEs₁₅</td>
<td>9.5912(12)</td>
<td>8.6943(14)</td>
<td>5.2671(8)</td>
<td>106.321(8)</td>
<td>421.517(146)</td>
<td>24</td>
</tr>
</tbody>
</table>

Note: The uncertainty in the last digit is given in parentheses.
*1 mol% PbO added as flux.

The Di-CaTs binary exhibits a nonideal mixing with respect to volume, as indicated by the unit-cell volume measurements of Newton et al. (1977). Because the CaTs-rich compositions were not sufficiently covered in that study, the measurements were repeated using an automated powder diffractometer system developed by Wechsler (1981) and a CaF₂ standard. Eleven compositions of the Di-CaTs pyroxenes were synthesized at 1350°C and 19 kbar for 24 h, and the results of the measurements are given in Table 3 and Figure 3. The calculation of the excess volume did not include sample Di₁₀₀CaTs₀ (mol%), because a small amount of grossular (Gr) was present in the synthetic material. Figure 3 shows small discrepancies between the present measurements and the data of Newton et al. (1977) for the Di-rich compositions. However, the present results for the intermediate compositions agree well with the unit-cell volume measurements of Clark et al. (1962).

Mixing properties of the Di-CaTs-CaEs solid solution were obtained by solution modeling of the present data, using the Redlich-Kister equation for a ternary solution (Redlich and Kister, 1948; Gasparik, 1984a). The solution-modeling procedure is similar to the procedure described by Lindsley et al. (1981, p. 165-166). The input phase compositions are manually adjusted within reasonable limits allowed by the data until the residuals are reduced to insignificantly small values. After a number of cycles, a set of parameters is found that satisfies all data. This procedure, however, does not provide a statistical information on the quality of the fit. The results of the modeling follow (units: joules, kelvins, bars):

\[
\Delta G_1 = 25250 + 14.7T - [1.29 + (20 \times 10^{-3})]P, \\
\Delta G_2 = 32010 + 57.0T - [2.48 - (27 \times 10^{-3})]P, \\
RT \ln \gamma_C = (10000 - 10T - 0.07P)(X_D + X_O X_E) \\
- (5000 - 31.19T + 0.04P)(3X_D^2 - 4X_D + 2X_D X_E - 6X_D X_O - 2X_D X_O^2) \\
+ 7000(12X_D - 16X_D^2 + 5X_D^3) \\
+ 20160(X_D X_O - X_D X_O^2) \\
+ 14760(3X_D^2 - 4X_D + 2X_D X_E - 6X_D X_O - 5950(-X_D X_O^2),
\]

\[
RT \ln \gamma_E = (10000 - 10T - 0.07P)(-X_D X_O) \\
+ (5000 - 31.19T + 0.04P)(2X_D X_O - 2X_D X_O^2) \\
- 7000(6X_D X_O - 3X_D X_O - 3X_D X_O^2) \\
- 20160(X_D X_O - X_D X_O^2) \\
+ 14760(4X_D^2 - 3X_D - 2X_D X_E + 6X_D X_O + 2X_D X_O^2) \\
- 5950(X_D + X_D X_O),
\]

\(X_C, X_D, X_O\) are mole fractions of CaTs, Di, and CaEs, respectively, in clinopyroxene.

**DISCUSSION**

The parameters above were used to calculate the phase relations in the silica-saturated CMAS system shown in Figures 2 and 4. Isopleths, isotherms, and isobars were calculated by simultaneously minimizing the free energy of the corresponding equilibria. This was achieved, for example, at any specified pressure and temperature by varying two compositional variables until the equilibrium conditions for Reactions 1 and 2 were satisfied.

Figure 2 shows two divariant fields representing the stability of the assemblage Px + An + Q at lower pressures and Px + Ga + Ky + Q at higher pressures. The two stability fields are separated by a univariant boundary through a single unit-cell volume measurement of pyroxene with the composition containing 15 mol% of CaEs, given in Table 3. McCormick et al. (1984) also suggested that the unit-cell volume of the CaEs endmember is similar to the volume of jadeite, based on the volume measurements of vacancy-containing omphacites from South African kimberlites.
The parameters of Reaction 6 were taken from Gasparik (1984a). The free-energy changes of Reactions 7 and 8 can be calculated from $\Delta G_1$, $\Delta G_2$, and the parameters of Reaction 5, for which Gasparik (1984b) gives (units: joules, kelvins, bars): $\Delta G_1 = -42,100 + 138.07 - (6.31 - (14 \times 10^{-7})P)P$. Thus, for Reactions 7 and 8, $\Delta G_1 = \Delta G_2 - 3\Delta G_1$, and $\Delta G_2 = \Delta G_3 - 3\Delta G_2$. The pyroxene coexisting with Ga + Ky + Q was treated as a ternary Di-CaTs-CaEs solution, although small amounts of En (up to 3 mol%) are also present. Thus, small errors in the position of the calculated isopleths can be expected at higher Py contents owing to this simplification.

In the stability field of the assemblage Px + Ga + Ky + Q, the pyroxene isopleths are significantly more temperature dependent than in the other divariant field (see Fig. 2). The CaEs content changes very slowly with temperature. The garnet composition, however, is mainly pressure dependent. Thus, the best indicators of the equilibrium pressures and temperatures are the combined compositions of the two phases pyroxene and garnet.

The garnet composition is very uniform along the univariant Reaction 4. It varies from $93\text{Py}$ (mol%) at 1000°C to $97\text{Py}$, at 1400°C. Similar uniformity of the garnet composition is observed along the spinel lherzolite to garnet lherzolite boundary in the CMAS system, where the experimental evidence indicates a garnet of a constant composition $93\text{Py}$ (Jenkins and Newton, 1979; Perkins and Newton, 1980).

The phase relations in Figure 2 were calculated for the assemblage Px + Ga + Ky + Q containing a Gr-rich garnet. Similar phase relations could be calculated for the same assemblage containing a Py-rich garnet. However, the coexisting pyroxene would contain a significant amount of the En component and would have to be treated as a quaternary solution. The two stability fields of the assemblagePx + Ga + Ky + Q (or coesite, Cs) converge at high pressures in a univariant equilibrium described by the reaction

$$\text{Px} + \text{An} = \text{Ga} + \text{Ky} + \text{Q}. \quad (4)$$

The reaction was located at pressures only 300 bars lower than the anorthite-breakdown reaction in the CAS system:

$$3\text{An} = \text{Gr} + 2\text{Ky} + \text{Q}. \quad (5)$$

In the stability field of the assemblage Px + An + Q, the pyroxene isopleths intersect at relatively large angles (see Fig. 2); therefore, they are potentially suitable as indicators of both the pressure and the temperature of equilibration. However, the pyroxene composition is mainly pressure dependent, which indicates that the assemblage is a better geobarometer than geothermometer.

The phase relations of the assemblage Px + Ga + Ky + Q have not been studied experimentally, but can be calculated. Equilibrium in the assemblage is described by the following reactions:

$$3\text{CaTs} + 3\text{Di} = 2\text{Gr} + \text{Py}, \quad (6)$$

$$3\text{CaTs} + 2\text{Q} = \text{Gr} + 2\text{Ky}, \quad (7)$$

$$6\text{CaEs} = \text{Gr} + 2\text{Ky} + 7\text{Q}. \quad (8)$$

The mixing properties of the Gr-Py (pyrope) garnet and

The mixing properties of the Gr-Py (pyrope) garnet and

![Graph](image-url)
Fig. 4. Phase relations of the assemblage Px + An + Q, with isotherms and isobars (thin lines) projected on the compositional plane Di-CaTs-CaEs. The heavy line is the maximum solubility limit of the CaEs component in pyroxene in the CMAS system, representing pyroxene compositions along the univariant Reaction 4.

location of the univariant reaction

\[
\text{An} = \text{Px} + Q \quad (10)
\]

at 1500°C and 32 kbar. However, Figure 4 indicates almost 12 mol% of the Di component in pyroxene at those conditions. Such a relatively high Di content is directly confirmed by the experiment no. 122, which indicates 17 mol% of Di in pyroxene at the P-T conditions essentially corresponding to the univariant Reaction 10, 1350°C and 30.2 kbar. At similar conditions (1500°C and 32 kbar nominal), Wood (1979) obtained 24 mol% of Di in the pyroxene coexisting with anorthite and quartz. The observed Di contents, at conditions where Di should not be present, are outside the range of experimental or analytical uncertainties and apparently indicate some anomalous mixing behavior of the Di-CaTs-CaEs pyroxene with the low Di content. Thus, the addition of MgO to the CAS system does not increase the stability of the pyroxene in equilibrium with anorthite and quartz until the Di content of the pyroxene reaches a certain value, e.g., 12 mol% at 1500°C. For this reason, it was not possible to use the parameters for Reaction 1 from the CAS system (Gasparik, 1984b) in the present solution model, which is not capable of reproducing such anomalous behavior. Instead, a different \( \Delta H_f^{\pm} \) was obtained by solution modeling of the present data, which placed the endmember Reaction 1 at pressures 2.5 kbar higher than indicated by the phase relations in the CAS system. A possible explanation for the inferred deviation from the smooth mixing properties of the ternary pyroxene is ordering, or tendency for the formation of intermediate compounds at various ternary compositions, which is highly probable in the vacancy-containing pyroxenes.

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