Two-pyroxene thermobarometry with new experimental data in the system CaO—MgO—Al₂O₃—SiO₂

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Abstract. In the system CaO—MgO—Al₂O₃—SiO₂ (CMAS), equilibrium alumina contents of orthopyroxene and clinopyroxene, both coexisting with spinel + forsterite or spinel + anorthite, have been reversed in 16 runs at 1,300–1,400°C and 10.2–20.8 kbar, using PbO flux. The present data and the data of Perkins and Newton (1980) have been modeled using the Redlich-Kister equation. The resulting model satisfies most of the reversed data in the CMAS system, agrees very well with thermochemical measurements, and is consistent with the model for the enstatite-diopside join of Lindsley et al. (1981) and with the system MgO—Al₂O₃—SiO₂ of Gasparik and Newton (1984). The present data, however, do not confirm the negative slopes of Al-isopleths in the spinel lherzolite field suggested by Dixon and Presnall (1980). The new model has been used to calculate a graphical two-pyroxene thermobarometer applicable to natural two-pyroxene assemblages closely approaching in composition the CMAS system.

Introduction

Natural mineral assemblages containing orthopyroxene (Opx) and clinopyroxene (Cpx) have great potential for providing the pressures and the temperatures of equilibration due to the fact that the pyroxene compositions are very sensitive to variations in \( P-T \) conditions. Because of the widespread occurrence of such assemblages and, hence, many opportunities for application, a great deal of experimental effort has been focused on calibrating the two-pyroxene thermobarometer.

The simplest system containing coexisting orthopyroxene and clinopyroxene is the enstatite (\( \text{En} - \text{Mg}_2 \text{Si}_2 \text{O}_6 \))—diopside (\( \text{Di} - \text{CaMgSi}_2 \text{O}_6 \)) join in the system CaO—MgO—SiO₂ (CMS). The vast number of experimental studies investigating compositions of coexisting orthopyroxene and clinopyroxene in the CMS system have recently been summarized and modeled by Lindsley et al. (1981). Clinopyroxene composition represents an excellent geothermometer, because the Ca/(Ca+Mg) ratio of clinopyroxene is only slightly pressure dependent.

The next step in approaching multicomponent natural systems is either addition of FeO or Al₂O₃ to the CMS system. Addition of FeO produces pyroxenes in the enstatite-diopside-hedenbergite-ferrosilite quadrilateral. Experimental work in the pyroxene quadrilateral has been summarized in a graphical two-pyroxene thermometer by Lindsley (1983). Application is limited to low-pressure assemblages, where the Al-content of pyroxenes is very small.

Solubility of Al₂O₃ in pyroxenes increases substantially at higher pressures, while the FeO content in natural samples of deepseated origin is less important; upper mantle pyroxenes generally contain less than 20 mol percent of the hedenbergite-ferrosilite component. Thus, for the high-pressure natural assemblages, the CMAS system, which is the focus of the present study, can be used as a first approximation. In the silica undersaturated CMAS system, pyroxenes are ternary solid solutions. In addition to enstatite and diopside, clinopyroxene has the Ca-Tschermak component (\( \text{CaTs} - \text{CaAl}_2 \text{SiO}_6 \)), and orthopyroxene has the Mg-Tschermak component (\( \text{MgTs} - \text{MgAl}_2 \text{SiO}_6 \)). Experimental study of two-pyroxene equilibria in the CMAS system is complicated by a high degree of compositional freedom which decreases the quality of equilibration in relatively short-term laboratory experiments; this is reflected in larger compositional ranges observed in single experiments in the CMAS system than in systems with lower degrees of compositional freedom at similar conditions. Thus, it is preferable to obtain as much information as possible from simpler systems.

Solubility of Al₂O₃ in orthopyroxene can be investigated in the system MgO—Al₂O₃—SiO₂ (MAS), where orthopyroxene is a binary \( \text{En} - \text{MgTs} \) solid solution. The MAS system has recently been modeled by Gasparik and Newton (1984). Their calculated \( P-T \) phase relations are shown in Fig. 1. The system has two divariant fields: a spinel peridotite field with the assemblage orthopyroxene + spinel (Sp) + forsterite (Fo), and a garnet peridotite field with the assemblage orthopyroxene + pyrope (Py). Addition of calcium to the system will add clinopyroxene to the assemblages, but the phase relations should not change significantly because the amount of calcium in orthopyroxene is very small.

Two-pyroxene phase relations in the CMAS system can be viewed as combination of phase relations of two simpler systems, CMS and MAS. Experimental investigation of the CMAS system is necessary in order to establish how the phase relations of the two simple systems are modified when extrapolated to the CMAS system.

Previous experimental work in the CMAS system

Experimental difficulties inherent to the CMAS system are reflected in many inconsistencies among previous studies.
Most of the studies produced synthesis experiments which yielded pyroxenes higher in $\text{Al}_2\text{O}_3$ than the equilibrium compositions. Very few studies report compositions of both ortho- and clinopyroxene.

In the garnet lherzolite field, the present study makes use of 13 reversals of Perkins and Newton (1980) at 900–1,100°C and 15–40 kbar. Their data indicate Al-contents of pyroxenes significantly lower than the largely the synthesis experiments of Akella (1976), but agree reasonably well with the data of O'Hara and Howells (1978).

In the spinel lherzolite field, the first data were obtained by Fujii (1977) from synthesis experiments at different $P-T$ conditions. Herzberg (1978) conducted an extensive study of the CMAS system with most of the data pertaining to the spinel lherzolite field. The data were obtained from synthesis experiments. Only the clinopyroxene compositions were determined using an X-ray diffraction method. However, a subsequent X-ray calibration of Benna et al. (1981) produced a grid significantly different from the grid used by Herzberg. The new grid gives clinopyroxene positions higher in $\text{En}$-content and lower in $\text{CaTs}$-content than the compositions reported by Herzberg.

Most recently, the compositions of orthopyroxene and clinopyroxene coexisting with spinel and forsterite have been determined experimentally by Dixon and Presnall (1980) at 17 different $P-T$ conditions (1,100–1,405°C/10–18 kbar). The authors indicated substantial differences between the CMAS and the MAS system: slopes of the Al-isopleths for orthopyroxene in the CMAS system were such profound change in the slope of the Al-isopleths, one how a small amount of calcium in orthopyroxene can cause such dramatic difference between the two systems in real.

### Experimental techniques

#### General procedures

Experiments were carried out using a conventional piston-cylinder apparatus with a 1/2" diameter assembly made of tale and soft glass. Samples were encased in platinum capsules. Description of the assembly and experimental procedures are given by Gasparik and Newton (1984). For this assembly, the authors found a temperature dependent pressure correction of $-\frac{2.5-0.0157\text{(°C)}}{\%}$, based on calibration against the spinel peridotite-garnet peridotite boundary. The nominal pressure was kept within ±200 bars of the run value. Temperature was measured by W-3%Re vs. W-25%Re thermocouples and controlled automatically. No correction 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 and $\text{CaAl}_2\text{O}_4$ (Table 1). $\text{CaAl}_2\text{O}_4$ was prepared by sintering a mix of $\text{CaCO}_3$ and $\text{Al}_2\text{O}_3$ first at 700°C for 24 h, and then at 1,300°C for 24 h. PbO was used in the starting materials as flux to promote equilibration of charges. Large crystals of synthetic diopside, Ca-Tschermak pyroxene, enstatite, and orthopyroxene of composition $\text{En}_{72}\text{MgTs}_{28}$ were added to the starting materials in amounts of approximately 3 wt.% each.

Equilibration experiments produced two kinds of assemblages: $\text{Sp} + \text{Fo} + \text{Opx} + \text{Cpx} + \text{PbO}$-bearing liquid or $\text{Sp} + \text{An} + \text{Opx} + \text{Cpx} + \text{PbO}$-bearing liquid, depending on the bulk composition used. The large pyroxene crystals equilibrated with coexisting phases approaching equilibrium compositions from the low-alumina and the high-alumina sides. This method reversed the Al-content in both pyroxenes but not the Ca/(Ca + Mg) ratio.

#### Analytical procedures

Experiments produced hard pellets composed of crystals surrounded by PbO-rich glass. Approximately half of a pellet was ground and used for verifying the presence of the assemblage $\text{Sp} + \text{Fo} + \text{Opx} + \text{Cpx}$ or $\text{Sp} + \text{An} + \text{Opx} + \text{Cpx}$ by X-ray diffraction. The other half of the charge was mounted for microprobe analysis. The polished surface of the charge was etched for 1–2 min in a drop of 48% fluoboric acid. Etching increased contrast between the crystals and the surrounding glass. This helped to find the crystals in the probe microscope. After etching, the surface of the mount was lightly repolished to remove the residue.

Energy dispersive microprobe analyses were obtained with an ARL-EMX electron microprobe. All analyses were made at 15 kV with a minimum spot size (≥1 μ). Standards used were enstatite glass containing 10 wt.% of $\text{Al}_2\text{O}_3$ and diopside glass. Analyses were obtained from reaction rims developed around the seed crystals. Original compositions were preserved in the cores of seeds; thus it was always possible to infer the direction of the approach to equilibrium. Typically about 20 analyses were taken from several grains on each kind of seed. In most experiments, compositional fields obtained from both kinds of orthopyroxene and clinopyroxene seeds completely overlapped indicating that equilibrium was closely approached.

#### Experimental results

Equilibrium alumina contents of clinopyroxene and orthopyroxene coexisting with spinel and forsterite were reversed at 9 different $P-T$ conditions, and the Al-contents of both pyroxenes coexisting with spinel and anorthite were reversed at 7 different $P-T$ conditions. For each run, an average composition for equilibrated rims on each kind of seed was calculated separately. Equilibrium compositions used in the least squares solution modeling were obtained by averaging the average compositions obtained from two corresponding seeds: diopside and Ca-Tschermak pyroxene for clinopyroxene, enstatite and pyroxene of composition $\text{En}_{72}\text{MgTs}_{28}$ for orthopyroxene. Mol fractions of clinopy-

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Table 1. Compositions of starting materials (in moles)

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<th>$\text{CaAl}_2\text{O}_4$</th>
<th>MgO</th>
<th>$\text{Al}_2\text{O}_3$</th>
<th>SiO$_2$</th>
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