

## PYROXENES IN THE SYSTEM $Mg_2Si_2O_6$ - $CaMgSi_2O_6$ AT HIGH PRESSURE

TAKESHI MORI and DAVID H. GREEN

*Research School of Earth Sciences, Australian National University, Canberra, A.C.T. (Australia)*

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The enstatite-diopside solvus in the system  $Mg_2Si_2O_6$ - $CaMgSi_2O_6$  has been experimentally determined within the pressure range 5-40 kbars and the temperature range 900-1500°C. Experiments involving reversal of the phase boundaries by unmixing from glass starting material and by reaction of pure clinoenstatite and diopside showed difficulty in achieving equilibration due to persistence of metastable, subcalcic clinopyroxene and to the sluggishness of reaction rate. The experimental data showed that the temperature dependence of the diopside limb is less than previously accepted. At 1500°C and 30 kbars subcalcic diopside found by Davis and Boyd (1966) is shown to be metastable with respect to enstatite and more calcic diopside of composition  $En_{42.3}Di_{57.7}$ . The solvus widens with increasing pressure between 5 and 40 kbars at 1200°C, but at 900°C the pressure effect on the solvus is very small. The stability relationships of the four pyroxenes, protoenstatite, enstatite, iron-free pigeonite and diopside are summarized, based on data from the literature and the present study.

### 1. Introduction

Previous studies [1-7] have shown that the solvus between enstatite and diopside in the system  $Mg_2Si_2O_6$ - $CaMgSi_2O_6$  narrows with increasing temperature and suggest that the pressure effect on the solvus is small and may be opposite to that of temperature. However, because of the possible uncertainty of measurement and some scattering of the experimental data, the pressure effect on the solvus remains uncertain. A further problem at high pressure and temperature is the strong curvature of the diopside limb above 1400°C at 30 kbars [4] with diopside becoming subcalcic ( $En_{70}Di_{30}$  in mole %, at 1500°C and 30 kbars). Kushiro [3] suggested that these subcalcic clinopyroxenes might be pigeonitic.

In the present investigation we have concentrated our experiments on accurate determination of the pressure effect on the solvus from 5 to 40 kbars at 1200°C and on delineation of the temperature dependence of the solvus at 30 kbars. The practicability of the project was also dependent on the high accuracy and reproducibility of analysis on small grains, com-

bined with excellent optics and contemporaneous analysis for all elements attainable with TPD electron probe and energy dispersive analytical system [8].

### 2. Preparation of starting materials

Several kinds of starting materials were prepared.

#### 2.1. $En_{50}Di_{50}$ glass

Three separate glasses of the same composition,  $En_{50}Di_{50}$  (mole %), were prepared from A.R. grade chemicals of  $SiO_2$ ,  $MgO$ , and  $CaCO_3$ . Weighed mixtures of the reagents were melted on an iridium-strip heater and were stirred by a platinum rod to homogenize, then quenched by cutting off the power and simultaneously cooling by compressed air. The glasses were ground to average 25- $\mu$ m grain size. One piece of glass from each batch was polished and examined by microscope, microprobe and, in some cases, X-ray powder photography. Two batches among the three

contained a trace amount (<1%) of quench clinopyroxene and olivine. Compositions of quenched clinopyroxene were similar to those of the host glasses. The third glass was free from any crystals. Composition of the three glasses varied from  $En_{48.4}Di_{51.6}$  to  $En_{49.6}Di_{50.4}$  with an inhomogeneity of  $\pm 0.2$  to  $\pm 0.5$  mole % end member.

### 2.2. $En_{80}Di_{20}$ glass

A glass with the composition of  $En_{80}Di_{20}$  was made in the same way as above. A trace amount of crystals ( $\ll 1\%$ ) was found in the glass, but they were not identified because of their scarcity and tiny sizes. Analyzed composition of the glass was  $En_{81.6}Di_{18.4}$ .

### 2.3. Synthetic pyroxenes

In some homogenization runs, synthetic diopside ( $CaMgSi_2O_6$ ) and clinoenstatite ( $Mg_2Si_2O_6$ ) of Tem-Pres Research Co. were used. Microprobe analysis showed the presence of trace amount of CaO (<0.05 wt.%) in the clinoenstatite.

## 3. Synthesis and chemical analysis of pyroxenes

The high-pressure apparatus used was a Boyd and England [9] design piston-cylinder device and a pressure correction of -10% of nominal load pressure, using piston-in technique, was applied. This method of correction is based on calibrations on quartz-coesite at 1100°C [10] and albite = jadeite + quartz at 600°C (G. Brey and D.H. Green, unpublished data). Temperature measurement was by Pt/Pt<sub>90</sub>Rh<sub>10</sub> thermocouple with no correction applied for pressure effect on thermocouple emf. Samples were encased in sealed Pt capsules or in Pt capsules with a crimped end in those cases where the catalytic effect of low water-vapour pressures was desired.

Chemical analyses were by means of the TPD-electron probe, with an analysis area of about 3  $\mu$ m diameter as judged by fluorescence on periclase. The visible fluorescence of the pyroxenes made positioning for analysis easier and more reliable. All relevant elements were measured simultaneously and at least ten analyses were made on each pyroxene phase in every run. Some analyses with structural formulae

deviating from stoichiometry were discarded. These were less than 10% of all the analyses.

In some of the homogenization experiments the capsule was loaded with a layer of clinoenstatite in contact with a layer of diopside. A polished thin section across this contact was prepared after the run and the contact between the two pyroxene types was examined optically and with the electron probe.

## 4. Experimental results

The run procedures, products and pyroxene compositions are summarized (Table 1 and brief comments in the Appendix). Pyroxene analyses\* are shown (Fig. 1) except for the runs 2, 3 and 7 which are of shorter reaction time.

The spread of data in some of the unmixing and homogenization experiments is related to mechanisms and sluggishness of chemical reactions. As shown in run 2, the  $En_{50}Di_{50}$  glass crystallized both orthopyroxene and clinopyroxene within only 6 minutes at 30 kbars and 1200°C. The glasses found in other experiments with longer run duration are, therefore, not unreacted starting glasses but melts generated by presence of water and equilibrated with pyroxenes. The water-saturated melting point of  $En_{50}Di_{50}$  is about 1050°C at 30 kbars [7], and water added to or allowed to enter the capsules naturally causes melting at higher temperature. The run duration of 45 minutes at 30 kbars and 1200°C (run 3, Table 1) crystallized orthopyroxene and clinopyroxene of compositions lying between the original bulk composition and the equilibrium compositions. The 4-hour experiment (run 4) gave pyroxenes with a wider composition gap and appears to have reached the equilibrium compositions (see later discussion). Comparison of runs 7 and 8 shows a similar time dependent relationship for pyroxenes crystallizing from glass starting material. Although from these experiments we have no information on the initial steps of crystallization from glass, since even after 6 minutes we have two pyroxenes present, we have obtained further information in Fe-bearing experiments with varying run duration. The crystallization sequence in these runs was firstly

\* A list of pyroxene analyses is obtainable by writing to the authors.