

Stability of Orthopyroxene in pyroxene quadrilateral at 1 atm and High Temperatures

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Pyroxene is one of the most important rock-forming minerals not only for its abundant occurrence but also for various paragenesis which provide information on the thermal history of pyroxene-bearing rocks. In the system $Mg_2Si_2O_6$ (En) - $CaMgSi_2O_6$ (Di), there had been the controversy about the appearance and stability of the orthopyroxene (Opx) phase near 1400 C other than protopyroxene (Ppx) since the discovery by Foster and Lin (1975). In recent years, Ohi et al. (2008) observed the phase transition between low-temperature Opx (LT-Opx) and high-temperature Opx (HT-Opx) at 1170 C during both heating and cooling processes by high-temperature synchrotron X-ray powder diffraction experiments for the composition of $(Ca_{0.06}Mg_{1.94})Si_2O_6$. They concluded that Opx the phase near 1400 C was HT-Opx and that below 1000 C was LT-Opx. In $Mg_2Si_2O_6$ - $CaMgSi_2O_6$ - $CaFeSi_2O_6$ - $Fe_2Si_2O_6$ system, Opx contain a little amount of Ca and have the composition between $Mg_2Si_2O_6$ - $Fe_2Si_2O_6$ solid solution. However, there was no report about the stability field of HT-Opx in pyroxene quadrilateral system. Purpose in present study is to reveal the stability field of LT- and HT-Opx in pyroxene quadrilateral system by synthesis experiments.

About 20 samples were synthesized from gels with 6 kinds of composition in the range of Ca : Mg : Fe = 0.03-0.15 : 0.92-0.65 : 0.05-0.20 at 1180, 1280, 1345 and 1375 C. Run durations were about 3-14 days. All samples were synthesized dry at 1 atm using a $H_2 + CO_2$ gas mixture to maintain the oxygen fugacity near that of the iron-wüstite assemblage. They were analyzed with X-ray powder diffractometer (XRD: RIGAKU, SmartLab), a scanning electron microscope (SEM: HITACHI S-3000H) + energy dispersive X-ray spectrometer (EDX: HORIBA EMAX7000) and an electron backscattered diffraction (EBSD: HKL, CHANNEL5). Peaks of clinopyroxene (Cpx: inverted from protoenstatite) and pigeonite (Pig) were not identified by XRD in present study. Therefore, these phases were described as Ca-poor Cpx.

At 1180 C, most crystals were smaller than 5 μm in diameter and the chemical compositions of those could not be analyzed method by SEM-EDX. All XRD patterns of crystals synthesized at 1180 C showed the presence of Ca-poor Cpx and (or) Di and there were no Opx peaks in XRD spectra. At 1280 C, most crystals were about 3-5 μm in diameter and some crystals were large enough to be analyzed by SEM-EDX. Analytical data by SEM-EDX showed the presence of Opx ($Ca_{0.06}Mg_{1.84}Fe_{0.10}Si_2O_6$). XRD patterns showed the presence of Opx in the samples with chemical compositions of $Fs/(En + Fs) > 0.1$, whereas there were no Opx in the sample $Fs/(En + Fs) < 0.1$. At 1345 and 1375 C, most crystals were about 5-10 μm in diameter. Analytical data by SEM-EDX and SEM-EBSD showed the presence of Cpx, Opx, Pig and Di.

In Fe-free En-Di system at 1 atm, the stability field of LT-Opx is below 1005 C and that of HT-Opx is above 1370 C. In present study, there were Opx in some samples synthesized above 1280 C whereas there were no Opx in samples synthesized at 1180 C. It suggested that all Opx in present study were HT-Opx and the stability field of HT-Opx was spread to lower temperature with increasing Fe-content in HT-Opx. This trend was same as the stability field of Pig.

Keywords: orthopyroxene, high temperature, enstatite-diopside-hedenbergite-ferrosilite system, phase transition