Stability field of the high-temperature orthorhombic phase in the enstatite-diopside system

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ABSTRACT

This research investigated the phase transition between low- and high-temperature orthopyroxenes with composition $(Ca_{0.06}Mg_{1.94})Si_2O_6$ using differential scanning calorimetry experiments and in situ high-temperature X-ray diffraction. The transition enthalpy, temperature, volume change, and slope were estimated to be 6.2 kJ/mol, 1170 °C, 10.25 Å³/unit cell, and 0.0056 GPa/°C, respectively. The phase boundary between low- and high-temperature orthopyroxene was defined as P(GPa) = 0.0056T $(^{\circ}C) - 6.55$. This relationship shows that the invariant point for four-phase equilibria (protoenstatite + high-temperature orthopyroxene + pigeonite + diopside) is approximately 1240-1280 °C and 0.1-0.2GPa, rather than the equivalent system involving low-temperature orthopyroxene as described in previous studies. We developed phase diagrams for Mg₂Si₂O₆ and the Mg₂Si₂O₆-CaMgSi₂O₆ system taking into account the results of previous synthetic experiments and the phase boundary that we determined between low- and high-temperature orthopyroxene. The developed phase diagrams for Mg₂Si₂O₆ showed that high-temperature orthoenstatite is more stable than protoenstatite at pressure above ~ 0.8 GPa, and that the boundary between high-temperature orthoenstatite and protoenstatite has a gentle negative slope. As pressure is increased from 1 atm to about 0.2 GPa, the lower temperature limit of stability of high-temperature orthopyroxene decreases from ~1370 to ~1200 °C. Above 0.9 GPa, the stability field of protoenstatite disappears and high-temperature Ca-free orthopyroxene is stable. On the basis of these results, it is suggested that further high-resolution analyses of the thermodynamics of the enstatite-diopside system at high temperatures and high pressures are required.

Keywords: High-temperature, orthopyroxene, differential scanning calorimetry, X-ray powder diffraction, isosymmetric phase transition, phase diagram, enstatite-diopside system