



Ca-Esk component content in pyroxene at high PT: experimental studies

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Pyroxenes (Px) from ultrahigh pressure metamorphic terranes often contain SiO₂ lamellae which are interpreted as a product of exsolution during decompression. Day & Milchahy (2007) showed that 3 types of reactions are responsible for releasing free SiO₂ from Px: (1) vacancy consumption in non-stoichiometric Px; (2) dissolution of Ti-phases in Px and Grt; (3) reactions between accessory minerals and Px and/or Grt. Vacancy consumption links to cation deficiency, which is also expressed as CaEsk component, or "excess silica". Irifune et al. (1986) showed that Px synthesized at 4 - 8 GPa, T = 1200°C contains CaEsk = 0.11 - 0.18, which decreases up to 0.05 with increasing pressure from 10 to 15 GPa. Konzett et al. (2008) have synthesized Px with CaEsk = 0.18 at 6 GPa and 1350°C, and concluded that no significant increases of CaEsk component is observed at higher pressures.

To clarify these data we have conducted a series of "dry" experiments in a Walker-style multianvil apparatus at P = 6, 8, 10, 12 GPa, and T = 900, 1000, 1100 and 1200°C using powdered glass of the composition (wt%): SiO₂ = 58.29, Al₂O₃ = 24.12, MgO = 5.44, CaO = 11.37, Na₂O = 0.78. The glass is prepared from a mixture of chemical compounds, molten at 1500°C in a Deltech furnace followed by cooling at room temperature. The materials, assembly and apparatus calibration procedure are described in detail elsewhere (Dobrzhinetskaya and Green, 2007). Run products were studied with EDAX spectrometer coupled with a Philips XL30 SEM equipped with FEG and operated at 15 kV.

Analytical data show that at given bulk chemistry of the starting material the CaEsk component in synthetic Px falls in range 0.32 - 0.38 at 6 GPa and 0.30 - 0.36 at 8 GPa and T = 900 - 1200°C. From 10 to 12 GPa the CaEsk component in synthetic Px decreases from 0.27 to 0.16 at T = 900 - 1200°C. Contrary, the Jd component in Px increases with increasing pressures within all experimental temperature ranges. There is also well-expressed negative correlation between CaEsk component and sum of cations/6oxygens. Sum of cations/6oxygens shows a positive correlation with increasing pressure in all temperature ranges; similar, but less-pronounced tendency is observed for increasing temperature at all pressure ranges. Our experiments demonstrate that at given bulk chemistry the Px with the largest CaEsk value is crystallized at P = 6 to 8 GPa at all temperature ranges; with increasing P up to 12 GPa and T up to 1200°C the CaEsk component tends to decrease. Our data are in a good agreement with experiments by Irifune et al. (1986) because CaEsk component exhibits similar tendency, though the values of the CaEsk components are significantly different due to differences in the bulk chemistry chosen as starting materials. For example, Px synthesized from the starting material A toleite at 10 GPa, 1200°C contains CaEsk = 0.10 (Irifune et al. 1986), whereas at similar conditions we have synthesized Px with CaEsk = 0.19. We conclude that CaEsk component can be responsible for SiO₂ lamellae exsolution formation in Pxs uplifted from depth not more than about 180 km, and therefore decompressed from P = 6 - 8 GPa to ambient pressures.