Stability of corundum + quartz relative to kyanite and sillimanite at high temperature and pressure

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ABSTRACT

Although natural occurrences of corundum + quartz \pm aluminosilicate are known, internally consistent thermodynamic databases suggest that they do not represent a stable assemblage. This observation has motivated two sets of experiments. In the first set, the equilibrium kyanite = corundum + quartz has been reversed (\pm 5 °C; \pm 25 MPa) at 600 °C/320 MPa and 700 °C/535 MPa (externally heated cold-seal hydrothermal autoclaves); 800 °C/775 MPa (gas apparatus; NaCl and CaF₂ furnace assemblies, non end-load piston-cylinder press); and at 900 °C/1075 MPa and 1000 °C/1325 MPa (CaF₂ furnace assembly, non end-load piston-cylinder press). These reversals imply an enthalpy of formation from the elements for kyanite of –2594.75 kJ/mol. The slope of the equilibrium curve also confirms both volume and experimental *C*_P data for kyanite. These reversals can serve as a useful calibration for the piston-cylinder press using NaCl furnace assemblies in the 700–800 °C and 500–1000 MPa range and indicate a friction correction for CaF₂ furnace assemblies of 75–100 MPa over 800–1000 °C and 1000–1500 MPa.

The second set of experiments (1200 °C and 2000 MPa) investigated the growth of kyanite along corundum-quartz grain interfaces. In experiments where no fluid was present, except adsorbed H₂O, kyanite did not nucleate and grow. In experiments with 2 wt% H₂O, kyanite formed and grew preferentially in the pores surrounding the corundum grains parallel to the corundum-quartz interface and along quartz grain boundaries. Due to a large ΔV_{R} , reaction halos around the corundum grains never become closed to fluid migration. This suggests that in nature, fluids are channeled to these reaction sites via porous reaction halos surrounding the corundum grains and indicates that, under such circumstances, formation of kyanite is self-promoting and probably goes to completion quickly. The stability of sillimanite relative to corundum + quartz is also discussed, from the standpoints of what is predicted by internally consistent mineral databases and what is observed in nature.