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 ± 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 (±5 °C; ±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 CaF$_2$ furnace assemblies, non end-load piston-cylinder press); and at 900 °C/1075 MPa and 1000 °C/1325 MPa (CaF$_2$ 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 CaF$_2$ 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 H$_2$O, kyanite did not nucleate and grow. In experiments with 2 wt% H$_2$O, 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 $\Delta V$, 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.

**INTRODUCTION**

In nature, corundum + quartz ± aluminosilicate is found to occur in relatively Al$_2$O$_3$-SiO$_2$-rich, high-grade metamorphic rocks either as an assemblage of grains isolated from each other or in direct contact (e.g., Krogh 1977; Harris 1981; Powers and Bohlen 1985; Tracy and McLellan 1985; Santosh 1987; Lal et al. 1987; Perchuk et al. 1989; Motoyoshi et al. 1990; Waters 1991; Dasgupta and Ehl 1993; Hiroi et al. 1994; Guiraud et al. 1996; Shaw and Arima 1998). In most of these occurrences, the aluminosilicate phase is sillimanite, although there are rare examples in which the assemblage consists of kyanite + corundum + quartz (e.g., Krogh 1977). However, it is uncertain whether corundum + quartz ± aluminosilicate could form a stable paragenesis. Although textures in some of these examples suggest that corundum + quartz might form a stable assemblage (e.g., Guiraud et al. 1996; Shaw and Arima 1998), this observation contradicts current thermodynamic databases (e.g., Berman 1988; Gottschalk 1997; Holland and Powell 1998). All three databases agree that corundum + quartz should not coexist together as a stable assemblage over the $P$-$T$ range represented by crustal and upper mantle rocks but should react to the relevant stable aluminosilicate phase until either the quartz or corundum have been consumed.

Experimental studies that involve reversal of the equilibrium kyanite = corundum + quartz have been performed over a wide range of temperatures and pressures. These include high $P$-$T$ (12000–20000 MPa; 800–2000 °C) reversed experiments involving breakdown of kyanite to stishovite + corundum in a multi-anvil press (Schmidt et al. 1997). They also include experiments at pressures and temperatures more typical of the lower crust (e.g., Harlov and Newton 1993). In that study, the breakdown of kyanite to corundum + quartz (700 and 800 °C), as well as the breakdown of andalusite to corundum + quartz (700 °C), were reversed metastably at pressures ranging from 600–900 MPa in an end-load, piston-cylinder press using a NaCl furnace assembly.

In the first part of the present study, the $P$-$T$ range involving the reversed breakdown of kyanite to corundum + quartz (Harlov and Newton 1993) is expanded to include the interval 600 to 1000 °C and 200 to 1500 MPa utilizing both the hydrothermal and gas apparatus as well as a non end-load, piston-cylinder press (NaCl and CaF$_2$ furnace assemblies). This has been done to confirm the slope of the equilibrium, as initially