Fig. 2. Conditions under which the reaction was reversed. Solid squares represent sillimanite formed from kyanite, solid circles represent kyanite formed from sillimanite, and open squares represent unaffected kyanite.

The curves in figure 3 have been extrapolated to low temperatures without regard for other reactions that complicate the stable phase diagram. Natural occurrences suggest the existence of a triple point between andalusite, kyanite, and sillimanite at moderate temperatures and pressures. It has also been suggested, although not demonstrated, that quartz plus corundum have a field of stability (Aramaki and Roy, 1958). This suggestion does not agree well with natural evidence; in the rare cases in which they both occur in the same rock, quartz and corundum are usually separated from each other by an aluminous silicate. One of the commonest occurrences of margarite is as a coating surrounding corundum crystals in quartzose rocks (Pratt and Lewis, 1905).

The slope of the phase boundary determined in the present study is 13.2 bars/degree. This is slightly larger than the value found previously (about 10 bars/degree), but it is decidedly smaller than the slope calculated from room-temperature thermochemical data. Todd (1950) found that the change in entropy of the reaction at room temperature was 123 ± 6 decijoules/mol°C, and an extensive study of the lattice parameters of kyanite and sillimanite (Skinner, Clark, and Appleman, 1961) shows that the change in volume is 5.80 ± 0.03 cm³/mol. According to these figures, the slope of the phase boundary is 21.2 ± 1.1 bars/degree.

High-temperature X-ray studies at atmospheric pressure (Skinner, Clark, and Appleman, 1961) show that kyanite has a larger thermal expansion than sillimanite at moderate temperatures. $(\partial \Delta V/\partial T)_{P=0}$ is about 0.4×10^{-3} cm³/mole °C at 200°C and decreases at higher temperatures. The net decrease in ΔV between 0° and 1000°C is about $3\frac{1}{2}$ percent. It is unlikely that this result will be greatly altered at the pressures of the equilibrium curve. The effect of pressure on ΔV is likely to be no larger than the effect of temperature
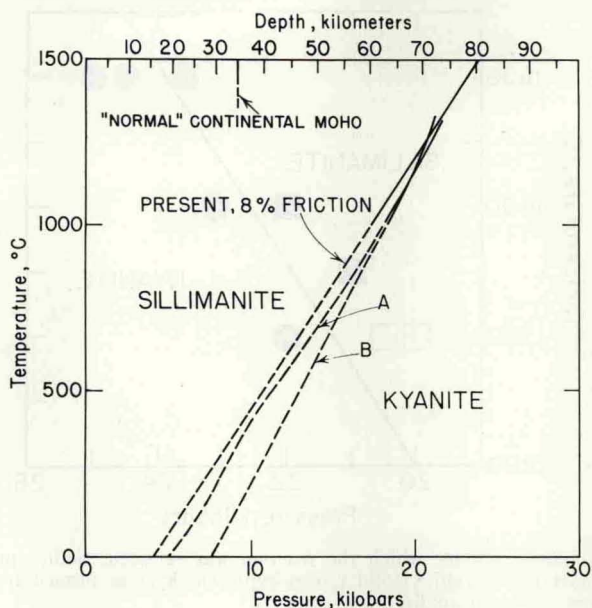
Fig. 3. Comparison with previous work. Curves A and B are the curves given by Clark, Robertson, and Birch (1957, fig. 2).

according to the argument given previously (Clark, Robertson, and Birch, 1957).

The effect of pressure on ΔS, the entropy change of the reaction, is given by the Maxwell relation $(\partial \Delta S/\partial P)_T = -(\partial \Delta V/\partial T)_P$. At high temperatures the pressure effect is small because $(\partial \Delta V/\partial T)_P$ is small, and at low temperatures it is small because the pressures of the equilibrium curve are low. The increase in ΔS is unlikely to exceed 3 percent under any conditions. The effect of allowing for the derivatives of volume and entropy discussed so far is to increase the slope of the phase boundary, in conflict with the experimental results. But the predicted increase is much less than the reduction in slope of about 50 percent that is required to secure agreement between the high-temperature, high-pressure experimental results and the room-temperature thermochemical data.

Measurements of heat capacity at high temperatures (Kelley, 1949) indicate that a change in ΔS with temperature may alter the slope of the phase boundary by roughly the amount required to bring the two sets of data into agreement. The change in slope may be uncertain by as much as 50 percent, however, and no account was taken of the correction in drawing the phase boundary in figure 3 for this reason. Because heat capacities of solids usually depart most widely from their classical values at low temperatures, most of the curvature probably takes place below 500°C. Hence the position of the phase boundary will not be greatly affected by this correction.