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A REDETERMINATION OF EQUILIBRIUM RELATIONS BETWEEN KYANITE AND SILLIMANITE

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ABSTRACT. The equilibrium curve between kyanite and sillimanite has been established by quenching experiments at temperatures between 1000°C and 1500°C and pressures between 17 and 24 kilobars. The curve is given by the expression $P = 4.1 + 13.2 \times 10^{-3} T$, where the pressure, P, is in kilobars and the temperature, T, is in degrees Centigrade. There is some evidence that the phase boundary may depart from linearity at low temperatures, but no quantitative estimate of the amount of curvature can be obtained from present data.

If kyanite forms stably in nature, pressures of nearly 10 kilobars are required. This is equivalent to the weight of about 30 kilometers of overburden. Such great depths of burial are not required if pressure is contained by the strength as well as by the weight of the overlying rock. It is suggested that "tectonic overpressures" of a kilobar or more may exist in rocks which are undergoing deformation.

The inversion of kyanite to sillimanite is the simplest of the classical metamorphic isograds to characterize chemically. Both minerals are close to Al_2SiO_5 in composition, with other elements usually present in very small amounts. Hence they may be regarded as pure phases of the same composition, and their equilibrium relations are therefore unaffected by complicating factors such as the bulk composition of the rock in which they occur or partial pressures of volatile components. The determination of their fields of stability in the laboratory carries direct implications about the conditions under which they were formed in rocks, subject only to the assumption that chemical equilibrium is closely approached in nature.

The chemical simplicity of these phases does not imply that reactions involving them are easy to produce in the laboratory. Both are extremely refractory and react with great reluctance at temperatures below 1000°C. In earlier work on this system (Clark, Robertson, and Birch, 1957), the temperatures required for reaction to take place in a reasonable time were uncomfortably close to the maximum attainable. The number of successful runs at high temperatures was limited by failure of the apparatus, and the reversibility of the reaction was perhaps not demonstrated as convincingly as one might desire. A phase boundary, based largely but not entirely on syntheses of kyanite or sillimanite, was established between 1000°C and 1300°C, despite these difficulties.

It is comparatively easy to maintain high temperatures and pressures for extended periods of time in apparatus in which pressure is transmitted by a plastic solid and the charge is heated by a tubular graphite heating element. Such apparatus has the disadvantage that the pressure must be calculated from the force applied to the piston which produces it, and corrections for friction and the finite strength of the pressure-transmitting medium must be made. In

the previous work the pressure was measured directly and precisely by the change in resistance of a coil of manganin wire.

The present results, obtained with a solid pressure-transmitting medium, prove to be in good agreement with the previous experiments. Since the equipment used in the two studies is basically different, this agreement suggests strongly that both sets of data are essentially correct. It appears that the calculation of pressure in the present work is as accurate as could be expected, and it also appears that the phase boundary established previously is very close to the true equilibrium curve.

EXPERIMENTAL PROCEDURE AND RESULTS

The present work was done in apparatus that differs only in minor respects from that described by Boyd and England (1960). Calibration against the Bi I-Bi II transition, which takes place at 25.2 kilobars at 25°C, indicates that the pressure calculated from the load on the piston is greater than that experienced by the sample by about 13 percent at room temperature. This figure is reproducible to within a few tenths of one percent. Part of this loss of pressure is attributable to the strength of the talc sleeve which transmits the pressure. This will be lower at high temperatures, implying that a correction of less than 13 percent should be made. The pressures given below have been determined by reducing the value calculated from the load on the piston by 8 percent of the corrected pressure, in agreement with the practice of Boyd and England. The pressure calculated in this way is believed to be accurate to within 5 percent for the range of pressures through which the reaction could be followed in the present study.

Temperatures of the charges were measured with Pt-Pt 10 percent Rh thermocouples pressed against one end of the Pt capsule in which the charge was held. The thermal gradient in the furnace rarely exceeded 15°C in the length of the charge and never exceeded 20°C. No correction was made for the effect of pressure on the e.m.f. of the thermocouple.

Four materials were used as reactants in this study. Kyanite and sillimanite were synthesized from andalusite from Hill City, South Dakota and from metakaolinite prepared by firing Georgia kaolinite overnight at 600°C. The kaolinite, kindly supplied by G. C. Kennedy, contained as principal impurities 0.15 percent Na_2O and 0.30 percent TiO_2 (analysis by C. G. Engel). No analysis of the andalusite is available. Kyanite from Burnsville, North Carolina and sillimanite from Brandywine Springs, Delaware were also used in the experiments. An analysis of the kyanite has been given by Todd (1950). The sillimanite is probably very pure, judging by its lack of color and the relatively small values of its lattice parameters (Skinner, Appleman, and Clark, 1961). Fine-grained samples of the aluminosilicates were prepared by elutriating in water for 6 minutes.

Experimental results are given in table 1 and are shown in figures 1 and 2. Products were identified by their X-ray diffraction patterns. The phase boundary in figure 2 is the same as that determined by the syntheses shown in figure 1. This boundary is reversible to within a kilobar, and the results of the experiments are insensitive to the particular reactant used. This conclusion was