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Kyanite-Andalusite Equilibrium from 700° to 800°C

Abstract. *The metastable kyanite-andalusite equilibrium in the* Al_2SiO_5 *system has been reversed at 700°, 750°, and 800°C at elevated water pressures, with a variety of natural and synthetic kyanites and andalusites as starting materials. Sillimanite, the stable form of* Al_2SiO_5 *under these conditions, did not appear. The value of the transition pressure at 750°C is 6.6 ± 0.4 kilobars, several kilobars below pressures given by several convergent previous determinations. The* Al_2SiO_5 *pressure-temperature triple point now indicated lies far from the points found by others. The revised aluminum silicate phase diagram indicates that many rocks crystallized at lower pressures than formerly thought possible.*

The problem of the stability of andalusite, orthorhombic Al_2SiO_5, has been outstanding in petrology for many years. The least dense of the three aluminum silicate polymorphs (3.14 g/cm^3), andalusite is considered to be a product of relatively shallow-level rock metamorphism.

The suggestion that andalusite may have no pressure-temperature (*P-T*) stability field relative to the kyanite (3.66 g/cm^3) and sillimanite (3.24 g/cm^3) polymorphs has been made several times. This concept has its origin in the often weakly recrystallized character of andalusite-bearing rocks, in the notorious slowness of reactions among aluminum silicates in laboratory tests, and in the results of certain early thermochemical studies (*1*).

Khitarov *et al.* (*2*) produced a synthesis diagram for the aluminum silicate system which showed a large andalusite field and a triple point among the three polymorphs at 9.0 kb and 380°C. They used the Bridgman anvil device with external heater and alumina-silica gels as starting material. They did not reverse the boundaries. Bell (*3*) found a diagram very similar to that of Khitarov *et al.* He used an oscillating-piston "simple squeezer" and obtained reversals of the reaction at temperatures as low as 250°C in runs of a few hours duration, by virtue of the enormous acceleration effect of shear on the rate of reaction. He demonstrated that andalusite could be created from natural kyanite and sillimanite under conditions of high shear, in spite of its reputation as an "antistress" mineral (*4*) and, in so doing, showed that andalusite must have a large *P-T* field of stability. Other workers (*5*) using simple squeezer device and gel starting material found kyanite-sillimanite boundaries in agreement with Bell (*2*) and Khitarov *et al.* (*3*) in the range 300° to 800°C.

Precision of location of the Al_2SiO_5 phase boundaries has been limited by the large uncertainty of the pressure conditions between the Bridgman anvils. Many cases are known of phase transitions in which the transition pressure was grossly overestimated on the basis of first determinations with a simple squeezer. Some examples are Cs (II) to Cs (III) (*6*), Ba (II) to Ba (III) (*6*), and the grossularite-quartz reaction (*7*). Newton (*8*) found that the kyanite-sillimanite transition at 750°C was 5 to 6 kb below the simple squeezer determinations. His work was done hydrothermally in the solid pressure piston-cylinder apparatus, with natural minerals for starting material.

All previous experiments indicate that the kyanite-andalusite equilibrium is metastable in the range 700° to 800°C. Nevertheless, since seeding strongly controls aluminum silicate reactions, the kyanite-andalusite reaction is univariant in this region and proved to be reversible in the absence of sillimanite seeds.

The runs were made in the piston-cylinder apparatus with 1-inch (2.54-cm) diameter chamber (*8*). Starting material consisted of two specimens of natural andalusite, two specimens of natural kyanite, and synthetic kyanite and andalusite. The natural minerals were analyzed with the electron microprobe.

One starting mixture consisted of

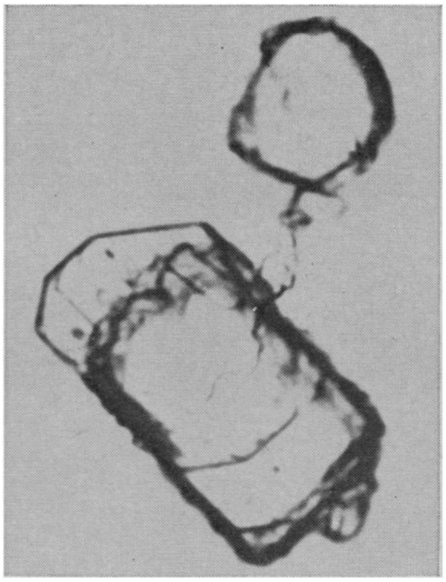

Fig. 1. Photomicrograph showing clear, geometrical end growth on kyanite seed crystal. Kyanite crystal is 20 μ wide. Other grain is quartz. Run No. 11, Table 1.

Table 1. Experimental data on the andalusite-kyanite reversible reaction. The cell constants for andalusite (Orville) are *a*, 7.802 Å; *b*, 7.887 Å; and *c*, 5.566 Å For kyanite (Tyrol) they are *a*, 7.120 Å; *b*, 7.848 Å; *c*, 5.574 Å; α, 89.98°; β, 101.18°; and γ, 105.98°. For synthetic andalusite they are *a*, 7.794 Å; *b*, 7,901 Å; and *c*, 5.561 Å. A, andalusite; K, kyanite; G, glass.

Run No.	T (°C)	P (bar)	Time (hr)	Products
Andalusite (Orville) + kyanite (Tyrol) + quartz; A = K				
1	700	5600	72	A > K; Q
2	700	6100	60	A > K; Q
3	700	6500	60	K > A; Q
4	750	6100	48	A > K; Q
5	750	6500	48	A = K; Q
6	750	7000	48	K > A; Q
7	750	7400	48	K > A; Q
8	800	6500	24	A ≫ K; Q
9	800	7000	32	A > K; Q
10	800	7400	24	K > A; Q
11	800	8100	21	K + Q
12	850	7400	5	G; A = K; Q
Andalusite (unknown) + kyanite (Litchfield) + quartz; A = K				
13	750	5600	72	A ≫ K; Q
14	750	6100	51	A > K; Q
15	750	6500	96	A = K; Q
16	750	7000	56	K > A; Q
17	750	8700	96	K + Q
18	850	7200	9	G + Q
Kyanite (synthetic, 8 + trace andalusite (Orville) + quartz				
19	750	5600	96	A + Q
Andalusite (synthetic) + trace kyanite (Tyrol) + quartz				
20	750	7400	56	A = K; Q

equal amounts of andalusite from Orville, South Dakota, and kyanite from a locality in the Tyrol. The andalusite had an Fe_2O_3 content of less than 0.20 percent (by weight) and the kyanite had less than 0.10 percent Fe_2O_3 as the major impurity. These are the purest natural aluminum silicates available. To test the effect of Fe_2O_3 on the reaction, kyanite (Litchfield, Connecticut) with 0.93 percent Fe_2O_3 was used in a starting mix with andalusite from an unknown locality with 0.3 percent Fe_2O_3. All runs were made with excess quartz. Unit-cell data of the starting materials are given in Table 1.

Only runs in which water oozed out when the capsule was cut open were considered successful. Direction of the reaction was determined by comparing the relative spectral peak heights of the phases in a vaseline-mount x-ray diffractogram. In most cases the reaction was sufficiently strong that the direction of the reaction could be told by a glance at the diffractogram. Some of the runs showed complete reaction (Table 1).

Melting occurred in the runs at 850°C, as shown by hard sintering of the charge and the presence of brownish bubbly glass (index of refraction about 1.50), detectable microscopically. A field of liquid plus quartz is probably the one encountered. Reactions at 700°C in 3 days were not strong, though definite. Runs of much longer duration at 650°C would be necessary to produce observable reaction.

A value of the transition pressure at 750°C of 6.6 ± 0.4 kb was obtained by plotting the ratio of kyanite and andalusite x-ray peak heights against pressure for runs of equal duration (*8*).

The reaction was reversed at 750°C with synthetic materials. Synthetic kyanite prepared hydrothermally at 750°C and 15.7 kb (*8*) was seeded with a small amount of Orville andalusite and held at 750°C and 5.6 kb for 48 hours. The charge inverted entirely to andalusite. The x-ray properties were those of normal andalusite; no problems arose with metastable andalusite-like phases similar to those reported in hydrothermal work at lower pressures (*9*).

The only crystalline phase beside Al_2SiO_5 and quartz in the quenched charges was a pyrophyllite-like quench product with a basal spacing of 9.36 Å. Four basal reflections showed strongly in acetone-slurry x-ray diffraction patterns but nearly vanished in the vaseline-mount patterns, which have greatly reduced preferred orientation effects. The synthetic pyrophyllite of Roy and Osborn (*10*) shows a basal spacing much larger than that of natural pyrophyllite, which is variable, but not as large as that of the present quench product. Pyrophyllite is the mystery phase found in quenched charges by Newton (*8*). Pyrophyllite is not a stable phase in the present system even at the lowest temperatures, as shown by a run at 7000 bars and 700°C for 21 hours with natural pyrophyllite (Staley, N.C.), kyanite (Litchfield), and quartz, in which the pyrophyllite was completely converted to kyanite and quartz.

The obvious and abundant crystal overgrowths seen microscopically in all of the quenched charges show that the observed x-ray effects are due to crystal growth and are not spurious. The clear geometrical terminations on kyanite crystals quenched from runs in its field (Fig. 1) are in sharp contrast to the splintery terminations of grains of the ground kyanite starting material.

Figure 2 shows the most definitive runs of this investigation and the possible uncertainty in location of the Al_2SiO_5 triple point when the data of Newton (*8*) and the high-temperature Al_2SiO_5 entropies of Pankratz and Kelley (*11*) are taken into account. Uncertainty from errors in the heat-capacity measurements are not considered; it cannot be a large effect. The major uncertainty arises from the obliquity of intersection. The principal feature shown by Fig. 2 is that the kyanite-andalusite boundary lies a measurable distance below the kyanite-sillimanite boundary, and this fact determines a large field of stability for

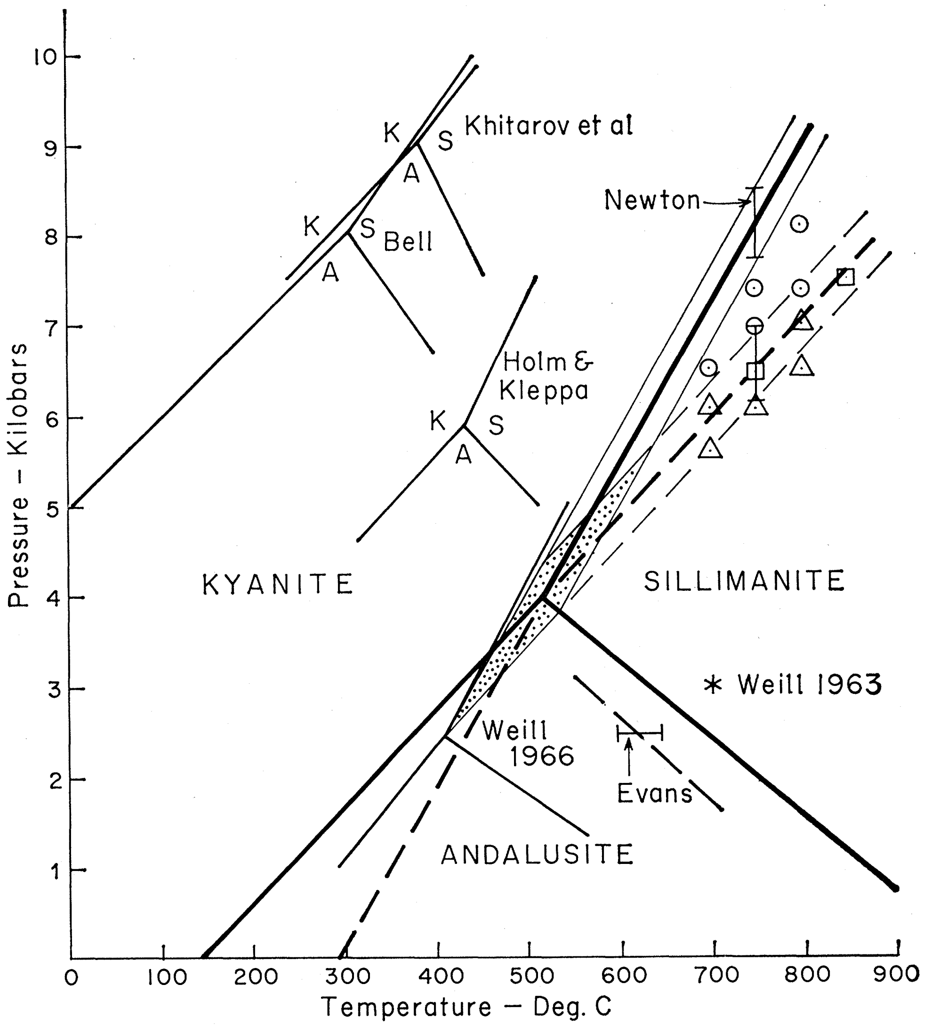

Fig. 2. Revised Al_2SiO_5 phase diagram. Runs from Table 1 are plotted. The best values of the present work at 750°C and the work of Newton (*8*) at 750°C determine the heavy lines. The stippled area covers the limits of uncertainty in location of the triple point. Also shown are experimentally determined phase boundaries of others, and a point in the sillimanite field (Weill, *14*).

andalusite, in agreement with the results of other workers.

The triple points resulting from the squeezer determinations lie well outside the present limits of error. A determination calculated from heat of solution measurements in a fused-salt calorimeter by Holm and Kleppa (*12*) lies somewhat closer to my result. The triple point calculated by Weill (*13*) from measurements of the solubilities of the aluminum silicates in fused cryolite at 1 atm borders on the present limits of error. The water-solubility data (*14*) bearing on the relative stability of the polymorphs at 700°C and 3 kb is also consistent. The point on the andalusite-sillimanite boundary deduced by Evans (*15*) from the apparent positions of the reactions of muscovite and quartz to yield potash feldspar and sillimanite or andalusite lies between 600° and 640°C at about 2½ kb.

The discrepancy between the present results and the squeezer determinations cannot be accounted for by pressure uncertainty in the present runs, presence of Fe_2O_3 in the system, formation of alternative phases, or strain or orientation effects on the peak height of the x-ray signal. If water preferentially entering the kyanite structure causes the discrepancy, then my experiments establish that availability of water produces the same variation of *P-T* stability in nature, for the kyanite formed from well-crystallized natural andalusite and vice-versa over a small pressure interval of uncertainty. That the possibility of the formation of water-bearing kyanite is small is indicated by the normal *d*-spacings of overgrowths from runs showing complete reaction, the small interval of uncertainty adjacent to the kyanite-andalusite boundary, and the fact that normal, water-free kyanite is often found as hydrothermal vein deposits in metamorphic rocks.

The heats of formation of the Al_2SiO_5 polymorphs calculated by Waldbaum (*16*) were based on the triple-point locations of Khitarov *et al.* (*2*) and Bell (*3*), and hence may require some revision.

Figure 2 implies that andalusite-bearing rocks form at depths no greater than 12 to 15 km. The corresponding temperatures can be progressively higher as depth of origin is decreased. Kyanite is known to have inverted to andalusite in the thermal aureoles around some granite bodies (*17*), and to sillimanite in others (*18*). If this represents equilibrium inversion, the granite was emplaced at a depth less than 15 km in the former case and at greater depth in the latter. The conditions for the classical sillimanite "isograd" are 4 to 6 kb and 500° to 600°C, according to Fig. 2.

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Thermal Conductivity Effect of Carrier Gases on Flame-Ionization Detector Sensitivity

Abstract. *Data for six carrier gases of different thermal conductivities show a linear correlation between the logarithm of thermal conductivity and detector response. Carbon dioxide with a lower thermal conductivity than helium gives a ninefold increase in detector response.*

When other variables are held constant, the sensitivity of a flame-ionization detector is a direct function of flame temperature (*1*). Optimum ion yield results from flames of highest possible temperature that give maximum detector response (*2*). Ionization efficiency and flame-ionization detector response are greatly reduced with carrier gases of high thermal conductivity because these tend to decrease flame temperature.

Figure 1 relates sensitivity of the flame-ionization detector, as measured by peak height, to isothermal column temperature for six carrier gases of different thermal conductivities. Peak height is maximum when temperatures of the column are highest; however, triangulated peak areas are kept constant by sample injections of equal size. All operating parameters were held constant. In a comparison of the usual carrier gas, He, with CO_2, it is clearly evident that CO_2 offers greatest flame-ionization-detector sensitivity over the experimental temperature ranges used. At a column temperature of 100°C, peak heights with CO_2 were about nine times greater than those recorded with He as the carrier gas. Other carriers exhibited peak heights in agreement with their thermal conductivities and with those observed for CO_2 and He. Figure 2 shows that flame-ionization detector response depends logarithmically upon the thermal conductivities of the carrier gas and illustrates the advantages of carriers of low thermal conductivity.

When maximum sensitivity of the flame ionization detector is desired, a carrier gas with the lowest possible thermal conductivity, in keeping with good column efficiency, should be chosen. Maximum column efficiency in gas-solid chromatography may not always be provided by carriers of low thermal conductivity because of the competition between carrier and sample for active sites on the adsorbent (*3*). In gas-liquid chromatography, column efficiency is not so powerfully influenced by the carrier gas employed.

For the operator's convenience, many chromatographic instruments equipped with both flame-ionization and thermal conductivity detectors are often plumbed to use only He because it is required by the thermal-conductivity detector for maximum sensitivity. Although hydrogen gives slightly greater sensitivity for thermal-conductivity detection, its explosive properties make it an infrequent choice. Furthermore, little advantage can be gained in sensitivity through use of H_2 as a carrier gas since its thermal conductivity is 41.6×10^5 cal cm^{-1} sec^{-1} $(°C)^{-1}$, compared with 34.8×10^5 for He—a unit increase of only 9 percent. Installation of a manifold for operation of the column with either N_2, or CO_2 when feasible, for the flame-ionization