

The Triple Point Andalusite — Sillimanite — Kyanite

An Experimental and Petrologic Study

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Abstract. The triple point in the Al_2SiO_5 polymorphic system has been determined experimentally; it lies at 6.5 ± 0.5 kb and $595 \pm 10^\circ\text{C}$. This result differs strongly from the data of other experimental investigations on this system; the reasons for this are discussed. The new data given here for the phase boundaries kyanite/sillimanite and andalusite/sillimanite as well as the resulting position of the triple point agree with petrologic considerations based upon both experimental work in related systems and petrographic observations.

1. Introduction

The system of the Al_2SiO_5 minerals has been of primary interest to petrographic and experimental investigations for a long time. However, despite considerable experimental work, our knowledge on this system has remained rather meagre. Nearly a dozen experimentators have tried to solve this problem, each of them obtaining results strongly differing from those of others, so much so, that the whole p - t -field of metamorphism is now practically covered with the various "equilibrium curves" and "triple points" (see Fig. 1). Only very few previous experimental results are in accord with petrologic considerations based upon fairly well established experimental data in other systems, which are more easily amenable to experimental exploration than the Al_2SiO_5 system. This very fact shows that the experimental work hitherto done on this system must be at least in part erroneous. The present study was not undertaken in order to increase the number of investigations, but to bring into accord the experiments on the Al_2SiO_5 system with petrographic observations as well as with experimental data from other, related systems. As will be shown below, this goal seems to have been reached, because no reliable experimental data nor petrographic observations are irreconcilable with the present results. Slight, insignificant deviations from true equilibrium values may of course occur, caused by very slow reaction rates in this system preventing approach of equilibrium conditions as closely as in other experiments.

2. Previous Work

The question, whether all the Al_2SiO_5 polymorphs have true fields of stability in the p - t -diagram and whether a triple point exists where all the three polymorphs coexist stably, has been the subject of many discussions. HARKER (1950, p. 151) suggests that andalusite and kyanite are only metastable phases with respect to sillimanite. WELL and FYFE (1961) concluded from solubility measurements and thermodynamic considerations, that andalusite might have no true field of stability under the temperature and pressure conditions of metamorphism; however, in later papers (WELL, 1966; FYFE and TURNER, 1966) a small stability

field is conceded to andalusite. ROY and OSBORN (1954) and ARAMAKI and ROY (1963) did not succeed in synthesizing any of the normal Al_2SiO_5 -polymorphs. The latter authors very frequently obtained the association quartz + corundum wherefrom they concluded, that perhaps neither of the polymorphs was stable under the conditions applied. But many other authors are of the opinion that each of the polymorphs has a true stability field, and that a triple point exists where all

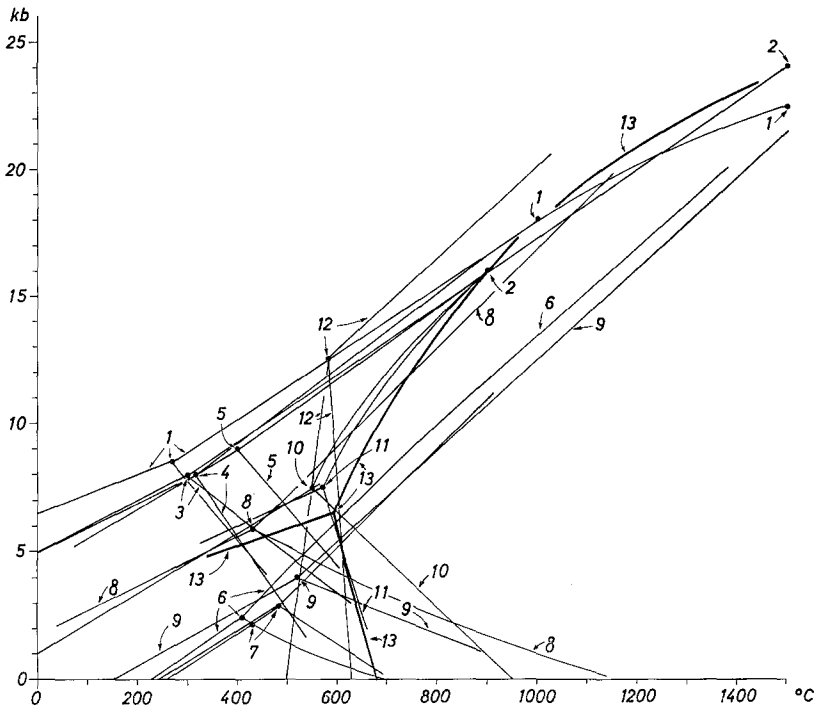


Fig. 1. Phase boundaries in the system Al_2SiO_5 , given by various authors. 1: CLARK et al. (1957). 2: CLARK (1961). 3: BELL (1963). 4: MIYASHIRO (1961). 5: KHITAROV et al. (1963). 6: WELL (1966). 7: FYFE and TURNER (1966). 8: HOLM and KLEPPA (1966). 9: NEWTON (1966). 10: SCHULING (1962). 11: WINKLER (1965). 12: KENNEDY (in BUERGER, 1961). 13: present study

three polymorphs are stable. CLARK et al. (1957) tentatively suggested a triple point at about $260^\circ\text{C}/8\text{ kb}$; tentatively, because they did not have any synthesis data on andalusite.

MIYASHIRO (1961) and SCHULING (1957) gave triple points based on field evidence and early experimental investigations as well as on thermodynamic considerations at $320^\circ\text{C}/8\text{ kb}$ and $540^\circ\text{C}/3.5\text{ kb}$, respectively. Later on, SCHULING (1962) shifted his triple point to $560^\circ\text{C}/7.5\text{ kb}$, because meanwhile new experimental and petrographic data had become available. BUERGER (1961) gives a triple point derived from experimental results of G. KENNEDY at about $580^\circ\text{C}/12.5\text{ kb}$. The first attempts to determine the position of the triple point directly were undertaken in 1963 by BELL and by KHITAROV et al., both using the opposed anvil technique. Their results are in relatively close agreement with each other and

with the points suggested by MIYASHIRO and CLARK et al.: BELL 300°C/8 kb; KHITAROV et al. 400°C/9 kb. But they disagree strongly with other experimental works and petrographic observations, as was shown by WINKLER (1965).

WINKLER concluded from petrographic evidence, reliable experimental data on related systems and some preliminary, then unpublished experiments of the present author, that the triple point must lie at 570°C/7.5 kb, i.e. very close to the anticipated values of SCHUILING (1962). As will be shown later, this assumption needs only be slightly corrected.

The triple point of WEILL (1966) at 410°C/2.4 kb was calculated from ΔG of solution measurements in cryolite melts at 1 atmosphere and from thermochemical data of PANKRATZ and KELLEY (1964) and SKINNER et al. (1961). FYFE and TURNER (1966) have calculated a triple point near the one of WEILL, between 430°C/2.1 kb and 480°C/2.8 kb; presumably it has been computed from the same thermodynamic data. However, as will be shown below, thermodynamic calculations are unfortunately not yet very reliable in this system.

The most recent experimental study upon the triple point, which was published prior to that of the present author, is that of NEWTON (1966b). The area in which he located the triple point is a slender rhombus extending from 400°C/2.5 kb to 630°C/5.7 kb, the centre being at 510°C/4 kb. In the paper of HOLM and KLEPPA (1966) a triple point is given at 430°C/5.9 kb.

The results of all these experimental and theoretical works on the triple point and phase boundaries in this system are exhibited in Fig. 1. Besides these studies directly concerning the triple point, a number of other papers have appeared, dealing with individual phase boundaries between the polymorphs, of which only the most important and the most recent ones are mentioned here. These are the papers of CLARK et al. (1957) and CLARK (1961) on the kyanite \rightleftharpoons sillimanite boundary at pressures above 16 kb, those of CARR and FYFE (1960), CARR (1963) and — to some extent — ARAMAKI and ROY (1963) on the formation of pyrophyllite from kaolinite and of X-andalusite from pyrophyllite, those of NEWTON (1966a, b) on the reactions kyanite \rightleftharpoons sillimanite and kyanite \rightleftharpoons andalusite, respectively and, finally, three short notes of the present author (ALTHAUS, 1966a, b and 1967). The p - t -coordinates given by various authors for these phase boundaries differ considerably. Sporadic data of a few other investigators bearing on the problems involved will be discussed below.

3a. Experimental procedures

In contradistinction to all previous investigations on the triple point, the experiments of the present author were performed with standard hydrothermal equipments. The pressure vessels — made of the alloys Nimonic 105 and René 41 respectively — were capable of sustaining pressures up to 12 kb at temperatures up to at least 750°C for a few weeks. Pressure was generated with an SC Air Operated Pump and Harwood intensifiers of various types. Pressure medium was water in the setup ranging to 7 kb, and water-ethylene glycol mixture (50:50 by volume) in the 7–12 kb apparatus. Pressures up to 8 kb are measured directly with a 10 kb bourdon type gauge (of Dreyer, Rosenkranz und Droop, Hannover) and up to 7 kb with a 100.000 psi Aminco straight type gauge, respectively. The two manometers agreed mutually to 100 bars. For higher pressures, a bourdon

gauge on the low-pressure side of the intensifier was calibrated against the 10 kb gauge on the high pressure side up to 8 kb. From 3.5 to 8 kb, the relation proved to be linear; extrapolation from 8 to 12 kb should therefore be correct. Deviations are probably not greater than ± 0.1 kb in the 2–8 kb range, and ± 0.2 – 0.3 kb above 8 kb.

The pressure vessels were heated by external electric furnaces. The temperature was controlled and regulated within $\pm 2.5^\circ\text{C}$. The metal masses of the vessels being much greater than in standard devices, no temperature fluctuation occurred within the samples. Temperature measurements were performed with great care. Temperatures of the samples were either measured directly during the run with mantled thermocouples adjoining the sample capsules, or pressure vessels were calibrated by comparing under pressure internal thermocouples with external ones located in a bore at the bottom of the vessel, about 2 cm apart from the centre of the sample. The temperatures at the middle of the samples are thus known to within $\pm 5^\circ\text{C}$ (this is only little worse than thermocouple accuracy). Taking into account a temperature gradient along the sample, temperatures given here are correct within $\pm 10^\circ\text{C}$, in extreme cases $\pm 15^\circ\text{C}$. All experiments were performed isochemically in sealed gold tubes of 2.8 mm internal diameter and 15 to 20 mm length. Water was present in excess, so that the pressure exerted was always hydrostatic.

Starting materials were mixtures of natural minerals listed in Table 1. They were ground in a Spex Mixer Mill with tungsten carbide grinding vessels to very fine grain sizes (until remarkable x-ray line broadening occurred) in order to facilitate dissolution of unstable and growth of stable phases. The only impurity introduced by the pulverization is tungsten carbide and very little cobalt metal, both of which are probably completely inert in this system.

Table 1. *Starting materials*

Pyrophyllite	Ro.-Mine, North Carolina	Rosettes of small prismatic crystals, almost pure ($\approx 4\%$ quartz)
Andalusite	Minas Geraes, Brazil	Rounded grains and crystal fragments, greenish to deep green, sometimes gem quality
Kyanite	Koli, Karelia, Finland	From vein in kyanite quartzite. Impurity: about 5% quartz
Sillimanite	Custer, South Dakota	Aggregates of slender prisms, no x-ray impurity
Quartz	Dörentrup, Germany	Crushed powder from very pure quartz sand; no x-ray impurity
Kaolinite	Schnaittenbach, Germany	Impurity: quartz ($\approx 4\%$) 0.75% K_2O

Mixtures of these minerals were prepared in the Mixer Mill in agate mortars under acetone. Homogeneity was examined by x-ray measurements of various powder mounts of the same mixture; no inhomogeneity being recognizable.

Of the Al_2SiO_5 polymorphs only andalusite has hitherto been observed to form spontaneously at moderate (≈ 7 kb) pressures in experiments of long durations (SCHREYER and YODER, 1964; ALTHAUS, 1966a). All attempts of various authors of synthesize kyanite and sillimanite without seeds at pressures less than about 10 kb failed, yielding either x-andalusite (CARR and FYFE, 1960; ARAMAKI and ROY, 1963; WINKLER, 1957), mullite (CARR and FYFE), sillimanite-mullite solid

solutions (KENNEDY, 1961; WINKLER, 1957), or corundum + quartz (ARAMAKI and ROY). Therefore, in the present study no attempt was made to synthesize these phases without seeds. In most runs, especially those on the andalusite \rightleftharpoons sillimanite reaction, the concentration of seeds in the starting materials was *not* just above the detection limit (which enables one to distinguish between growth and disappearance of seeds only), but high enough, so that the reaction in *either* direction could be measured by x-rays. This is necessary in order to ensure that the reaction in question has indeed taken place, and not simply that the seeds have been dissolved away by other processes.

During the very first stage of the present study it was seen that at pressures below 9–10 kb, the reaction rates in this system are very low, so that extraordinary long run times were needed to recognize the direction of reaction. However, the rate of reactions appeared to be not as slow as stated by WEILL and FYFE (1961), who, treating mixtures of all three polymorphs for “more than four weeks at 700 to 900°C and 700 to 2000 b” observed “no hint of reaction”: In the present case, runs of 6 weeks time sufficed already to recognize appreciable reaction at practically the same *p*, *t*-conditions. On the other hand, the run durations must be higher by some orders of magnitude than those applied by BELL (1963), who observed (at times even complete) reactions in runs of $1/2$ to 12 hours duration only. This cannot be understood because in the present investigation at temperatures above 400°C, i.e. even more than 100°C above BELL’s triple point, run times of $1/2$ year on the kyanite \rightleftharpoons andalusite inversion yielded hardly perceptible changes of mineral quantities in the starting mix. It is remarkable, that BELL’s experiments were performed in a completely water-free system, where diffusion in the solid state is the only mechanism that can bring about the reaction. Hence, in a dry system reactions should be much slower than in a “wet” one, and not faster (as suggested by BELL’s data).

One of the most difficult problems was to determine whether a phase has grown at all or not. Optically, it was not possible to distinguish between reaction and recrystallization. — The photograph furnished by NEWTON (1966b), for instance, showing growth of kyanite on a seed fragment and accepted by him as an evidence for kyanite formation, can be explained by recrystallization as well. Therefore, quantitative measurements of x-ray intensities was applied. This was no simple job, because the x-ray intensities of the minerals in question are strongly modified by recrystallization and the resulting increase in grain size. When the extent of reaction is not large, the direction of reaction can never correctly be recognized by comparing the x-ray patterns of the reaction products with those of the starting materials, as claimed by NEWTON (1966a). In the run times applied by the present author (21 to 182 days, see Table 3), most experiments yielded relative changes of only a few percent, so that in runs starting from mixtures of all three polymorphs the x-ray diffraction chart of the untreated samples gave an impression that all the three phases had increased in amount.

Therefore, care must be taken that grain sizes are equal both in standard and sample x-ray mounts. This was achieved by using quartz as an internal grain size indicator: As quartz is chemically inert in this system at temperatures above the pyrophyllite stability limit, the amount of quartz is constant. Hence changes in quartz insensities must represent changes in grain size. Therefore the sample

material furnished by a run was powdered until the x-ray intensities of quartz became the same as in the standard mixtures, which were also prepared by crushing coarser mineral powders (not the very fine grained materials mentioned above, which were used for starting mixes). If the quartz intensities of sample and standard are equal, the grain size of quartz and the other minerals present is also assumed to be mutually equal, so that x-ray intensities may now be compared. The grinding time necessary to achieve this effect is between $1/2$ and $1 1/2$ hours, when an agate micro-vessel is used in the Mixer Mill.

X-ray measurements were carried out with a Philips goniometer installed at a 2 kW stabilized x-ray generator of the type "Iso-Debyeflex III A" of Rich. Seifert, Hamburg. The x-ray tube (copper) was operated at 60 kV, 32 mA. Radiation receiver was a proportional counter, combined with an impulse height analyser to improve the peak to background ratio. Goniometer speed was generally $1^\circ/8$ min, chart speed 400 mm/h. The sample powder was pressed gently into flat round cavities of 12 mm diameter and 0.5 mm depth in brass sample holders and the rims of the same cleaned carefully. To rule out surface inhomogeneities, the sample holders were rotated with 100 cycles per minute in their surface plane. Intensities were measured by graphical integration of the *areas* of the registered peaks with a planimeter. Peak heights are in these systems no reliable measures for the intensities and the mineral concentrations derived from them. Table 2 shows the peaks used for the measurement of the different phases.

Table 2

Mineral	(hkl) and 2θ ($\text{CuK}\alpha$) values of peaks used for quantitative x-ray measurements
Quartz	(20.1) at 45.8° , sometimes (10.0) at 20.9°
Andalusite	(110) at 15.98° ; (101) at 19.56° ; (220) at 32.26° ; sometimes (320) at 41.5°
Sillimanite	(110) at 16.6° ; (121) at 30.9° ; sometimes (122) at 41.0° ; with initial concentrations $<10\%$: (120) at 26.1°
Kyanite	(131+202+302+331) at 47.0° ; if little sillimanite present: (140+330) at 46.3° ; with initial concentrations $<10\%$: (021+111) at 28.0°

Reproducibility of x-ray measurements was tested and found to be very good, so that only one preparation of each sample had to be measured. By this procedure it was possible to detect changes in mineral concentrations as small as about 10% of the amount present, the standard deviation being 5% of the amount. When the mineral concentration in the starting mixes were less than 10%, the values were 20% and 10%, respectively. But all changes detected were assumed to be true only when growth of the mineral in question corresponded to the decreases of the other ones within the limits of reproducibility. In those samples where only a few percent of one mineral was present along with a large amount of another, parallel samples with the inverse ratio were run under the same conditions and reaction accepted to have taken place only when the changes of mineral concentrations in both samples corresponded to each other (at least in direction).

3b. Experimental Results

The Table 3 presents only that part of the experimental results that is necessary for the construction of the andalusite \rightleftharpoons sillimanite and kyanite \rightleftharpoons sillimanite equilibrium curves of Fig. 2. Only the data bearing on points close to the phase boundaries are reproduced, the rest being reserved for a later comprehensive discussion of the whole system Al_2O_3 — SiO_2 — H_2O . The boundary andalusite \rightleftharpoons sillimanite lies at low pressures at somewhat higher temperatures than previously stated (ALTHAUS, 1966 b), this shift being in accord with the assumption mentioned

in that paper. The new phase boundary fits quite well the data of WEILL (1966) at 1 atm and of EVANS (1965) at 3 kb.

The kyanite \rightleftharpoons sillimanite boundary had never before been investigated in this p, t region in a hydrothermal apparatus, where pressures are true hydrostatic pressures and well known. The data correspond quite well to a slightly curved extrapolation of the data of CLARK et al. (1957) and CLARK (1961). The point of EVANS (1965) on this curve does not agree as closely to the present results as that one on the andalusite \rightleftharpoons sillimanite curve.

As can be seen from Table 3, reactions had been reversed within narrow limits, proving establishment of equilibrium.

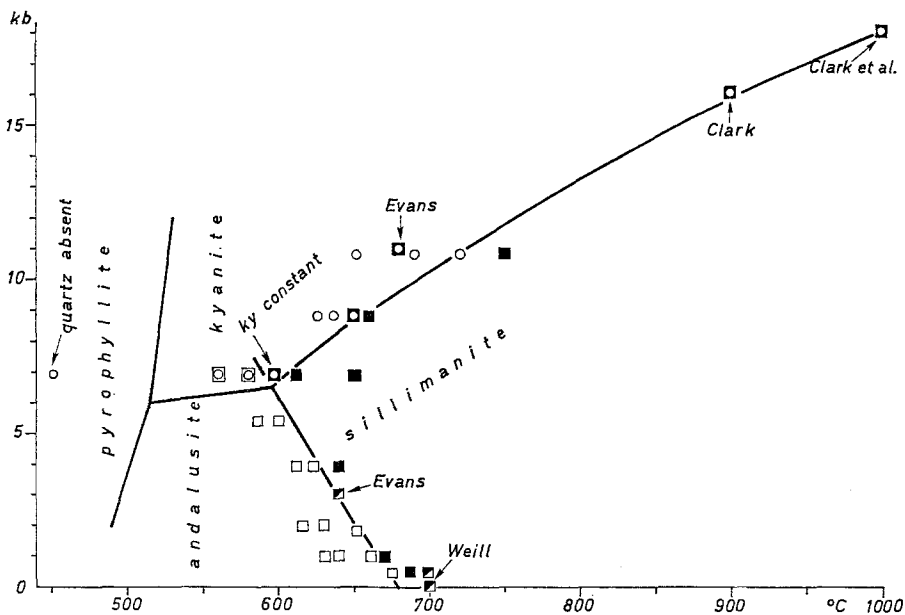


Fig. 2. Determination of the phase boundaries and the triple point. Open squares: Formation of andalusite. Filled squares: Formation of sillimanite. Open circles: Formation of kyanite. Mixed signs: Either equilibrium established or no perceptible reaction

The intersection of these two equilibrium curves at 6.5 ± 0.5 kb and $595 \pm 10^\circ\text{C}$ is the triple point in the Al_2SiO_5 system. Experiments on the third phase boundary radiating from this point, andalusite \rightleftharpoons kyanite, are despite very long run times rather inconclusive (Table 3)¹. Therefore, this curve had been constructed by connecting the point of intersection of the andalusite \rightleftharpoons sillimanite and kyanite \rightleftharpoons sillimanite curves with the one of the pyrophyllite \rightleftharpoons andalusite + quartz + water and pyrophyllite \rightleftharpoons kyanite + quartz + water curves. The values for the latter curves are taken from ALTHAUS (1966a and 1967). The diagram presented in Fig. 2 is almost identical with the one given by ALTHAUS (1967).

¹ Note: In some runs diasporite has been observed, at temperatures as high as 450°C at about 6 and 7 kb. This need not contradict the findings of NEUHAUS and HEIDE (1965), because the formation of diasporite and others from kaolinite is very probably a metastable one.

Table 3

Starting materials		temp. °C	press. kb	dura- tion days	results				others	
					absolute changes		relative changes			
qtz. %	ky. %	and. %	sill. %	others	ky. %	and. %	sill. %	ky. %	and. %	sill. %
40	17	20	654							
40	17	20	612	63	-6	0	+7	-34	0	+35
40	17	20	597	60	-2	-1	+3	-11	-5	+15
40	17	20	580	63	0	-1	+2	0	-5	+10
40	17	20	563	54	+2	+3	-4	+11	+15	-20
40	17	20	600	21	+1	+2	-2	+5	+10	-10
40	17	20	585	70	-3	+5	-1	-17	+25	-5
40	17	20	623	45	-5	+4	-2	-39	+20	-10
40	17	20	612	49	-14	+19	-6	-80	+95	-30
40	17	20	630	77	-10	+15	-3	-57	+75	-15
40	17	20	670	49	-17	+13	-5	-100	+65	-25
40	17	20	615	133	-17	+22	-4	-100	+110	-20
40	17	20	641	77	-17	+8	+7*	-100	+40	+35
40	17	20	687	133	-13	+12	-2	-75	+60	-10
40	55	5	660	13	-17	+3	+8*	-100	+15	+40
40	55	5	660	13	-0.7		+0.8	-14		+16
40	55	5	650	14	0		0	0		0
40	55	5	637	13	+0.6		-0.6	+12		-12
40	55	5	626	13	+0.8		-0.8	+12		-16
40	55	5	750	14	-2		+4.5	-40		+90
40	55	5	722	5	+1.3		-3.0	+26		-60
40	55	5	690	6			-5.0			-100

+ unidentified phase
* very broad lines;
amount may be
greater

of the phase rule is only a necessary but not sufficient condition, inasmuch as it is valid for metastable equilibria as well as for stable ones, other means must be searched for in order to demonstrate that one or the other particular set of data is correct and therefore agrees better with natural mineral assemblages. One such approach seems to be thermodynamic calculations based on thermochemical data, which proved to be very useful in other systems (e.g. METZ, 1966). Unfortunately, the thermodynamic data on the Al_2SiO_5 system are not yet reliable.

Reliable data for the enthalpies of formation are not yet known; the older values derived from data of NEUMANN (1925), around -40 kcal/mole, are highly erroneous, as has been convincingly pointed out by FLOOD and KNAPP (1957), MIYASHIRO (1960) and COOPER et al. (1961). FLOOD and KNAPP show that the free energies of formation from the oxides must be between 0 and -10 kcal/mole, COOPER et al. suggest that they are "very nearly zero", while MIYASHIRO concludes that the values are about -3 kcal/mole. These estimates have been confirmed by the data recently found by HOLM and KLEPPA (1966); they measured and calculated values between -0.6 and -1.88 kcal/mole for ΔH_{298}^0 for the three polymorphs. The measurements have been performed at 986°K ; uncertainties in ΔS may therefore considerably affect the data for 298°K . Experimental errors are fairly large; for the andalusite/sillimanite boundary, for instance, the authors estimate the uncertainties of the equilibrium temperatures to be in the order of ± 100 to 200° , even if errors of the entropy values are neglected. From the data of HOLM and KLEPPA can therefore only be concluded, that the enthalpies of formation are indeed very small, so that the estimates of the authors mentioned before are correct and the old values of NEUMANN should be disregarded. The calculations of HOLM and KLEPPA lead to data for the triple point far away from the present results; as will be shown below, they conflict with several petrological criteria. It can be stated, however, that the enthalpies of formation for the three polymorphs are very small. The enthalpy differences for the transitions between the polymorphs must than be even smaller, in any case of the order of 1 kcal/mole.

Entropy values seem to be somewhat more reliable, since they have been derived from heat capacity measurements, which can be done with greater accuracy than the measurements of heats of solution. But even here care must be taken, because the entropy values for the three polymorphs are very similar, so that the entropy differences ΔS for the mutual equilibria are in the range of 1 cal per degree and mole. Moreover, different authors give values for the specific heats of the polymorphs differing more than 1 cal/mole·degree in the temperature range of our interest. This may be seen from the c_p data of kyanite (Fig. 3), which were determined by three independent authors (NEUMANN, 1925; PANKRATZ and KELLY, 1964; LEONIDOV et al., 1964). Even if the older values of NEUMANN are disregarded, the differences in c_p are so conspicuous, that uncertainty in $S = \int \frac{c_p}{T} dT$ is greater than the values of ΔS for the various reactions. Nothing at all is yet known about the compressibilities of the polymorphs, which are necessary for calculating the pressure dependence of entropy and molar volume. The only reliable data of interest for thermodynamic considerations are probably the molar volumes and thermal expansion coefficients measured by SKINNER et al. (1961).

While comparing them, another difficulty involving the Al_2SiO_5 system is seen, namely, the ΔV values for the transitions between the polymorphs are low, being only 1.5—2.5 cm^3 per mole for the reaction andalusite \rightleftharpoons sillimanite, about 5 cm^3 per mole for kyanite \rightleftharpoons sillimanite, and about 8 cm^3 per mole for kyanite \rightleftharpoons andalusite. Hence, the gradients $\frac{dP}{dT} = \frac{\Delta S}{\Delta V}$ are quotients of small differences of much larger numbers, so that slight errors (which need not necessarily cancel each other) may cause great deviations. Therefore, in this system thermodynamic considerations are not yet reliable criteria to decide whether experimentally determined

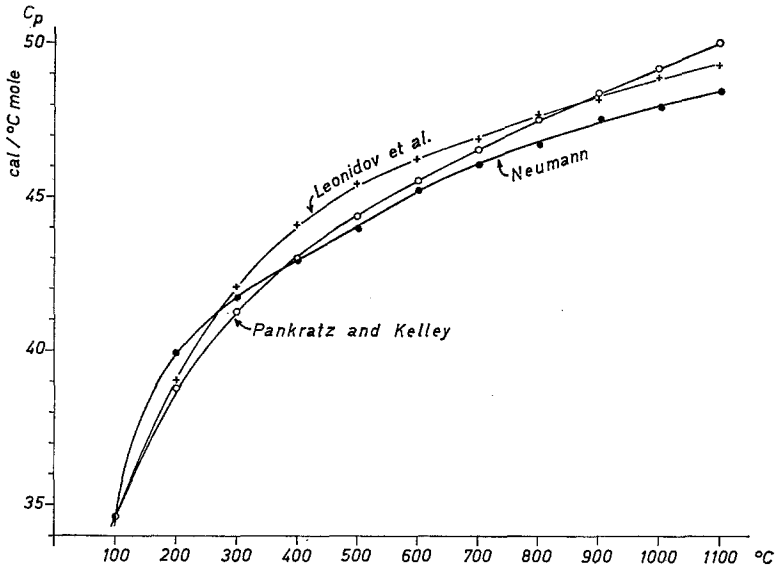


Fig. 3. Heat capacities of kyanite versus temperature

data are correct or erroneous. The calculations of WEILL (1966) and FYFE and TURNER (1966) suffer from the same uncertainties, so that their results, which differ greatly from those of the present author, should not be regarded to be more correct.

As can be seen from this discussion, thermodynamic calculation is no way to distinguish between improbable experimental values and more reliable ones. Fortunately, for a lot of other reactions equilibrium p, t -conditions are quite well known from experimental studies; these reactions, together with petrographic observations, bracket the probable region of the Al_2SiO_5 triple point. This method was used already by several authors (MIYASHIRO, 1961; SCHULING, 1957 and 1962; WINKLER, 1965). However, since then new data have become accessible, which give a more secure basis to the following considerations.

As pointed out already by SCHULING (1962) and WINKLER (1965), the triple point cannot lie within the stability field of the hydrous aluminium silicates kaolinite or pyrophyllite. The phase boundaries kaolinite + quartz \rightleftharpoons pyrophyllite + water and pyrophyllite \rightleftharpoons andalusite (or kyanite) + quartz + water are now well known (ALTHAUS, 1966a and 1967). They are shown in Fig. 4. The older values of CARR and FYFE (1960) and CARR (1963) for the synthesis boundaries of these phases

agree within 25°C with these data. The triple points of the Al_2SiO_5 -modifications as assumed by WEILL (1966), HOLM and KLEPPA (1966) and FYFFE and TURNER (1966) lie well within the pyrophyllite field, and a considerable part of NEWTON'S (1966b) rhombus is also cut off by the upper stability limit of pyrophyllite. If the triple point of the Al_2SiO_5 phases lay within the pyrophyllite field, then not only andalusite and kyanite, but also sillimanite ought to result through the decomposition of pyrophyllite. However, it is well known that the first Al_2SiO_5 polymorph to occur in regions of rising metamorphic grades is andalusite or kyanite,

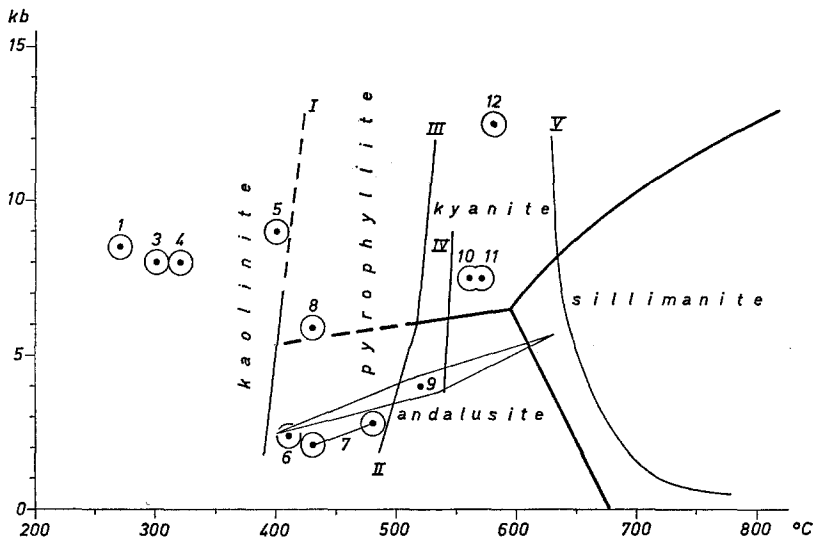


Fig. 4. Bracketing of the triple point of Al_2SiO_5 by other reactions. Arabian numbers see Fig. 1; I: kaolinite + quartz \rightleftharpoons pyrophyllite + water (ALTHAUS, 1966a). II: pyrophyllite \rightleftharpoons andalusite + quartz + water (ALTHAUS, 1966a). III: pyrophyllite \rightleftharpoons kyanite + quartz + water (ALTHAUS, 1967). IV: chloritoid + $\text{Al}_2\text{SiO}_5 \rightleftharpoons$ staurolite + quartz + water (HOSCHEK, 1967). V: minimum melting curve of granite (after TUTTLE and BOWEN, 1958)

and never sillimanite, so that the upper stability limit of pyrophyllite cannot border on to the sillimanite field (WINKLER, 1965). This is also confirmed by the experiments listed in Table 4.

These results contrast with those of KENNEDY (1961), who gives a curve for the breakdown of pyrophyllite to sillimanite + quartz + water. But sillimanite (not mullite) forms at the breakdown of pyrophyllite *only* if seeds of sillimanite alone are present. If no seeds are present, mullite will be formed instead of or along with andalusite at lower pressures (see, for instance, CARR and FYFFE, 1960). If seeds of andalusite besides sillimanite are present, then andalusite grows and sillimanite diminishes, indicating that andalusite is the more stable phase, not sillimanite (Table 4). The reason for this behavior is that, if pyrophyllite breaks down, the differences of ΔG to each of the Al_2SiO_5 phases must be much greater than the mutual differences of ΔG among the polymorphs. Hence, if sillimanite cannot be formed stably through the decomposition of pyrophyllite, all triple points that are supposed to lie within the pyrophyllite field cannot be accepted. The triple points of CLARK et al. (1957), MIYASHIRO (1961), BELL (1963) and

Table 4

Starting materials				° C	kb	days	results *
60 pyr.	10 and.	10 ky.	20 qz.	530	9.8	53	pyr. van., ky. incr., and. decr.
55 pyr.		5 ky.	40 qz.	530	7.8	17	pyr. van., ky. incr.
55 pyr.		5 ky.	40 qz.	530	11.8	10	ky. incr.
55 pyr.		5 ky.	40 qz.	512	11.8	10	ky. decr.
65 pyr.	7.5 and.	7.5 sill.	20 qz.	530	6.9	19	pyr. van., and. incr., sill. decr.
65 pyr.	7.5 and.	7.5 sill.	20 qz.	545	6.9	22	pyr. van., and. incr., sill. decr.
65 pyr.	7.5 and.	7.5 sill.	20 qz.	520	3.9	20	pyr. van., and. incr., sill. decr.
65 pyr.	7.5 and.	7.5 sill.	20 qz.	515	5.4	20	pyr. decr., and. incr., sill. decr.
65 pyr.	7.5 and.	7.5 sill.	20 qz.	487	2	25	pyr. decr., and. incr., sill. decr.
85 kaol.		15 sill.		570	6.9	60	sill., qz
85 kaol.		15 sill.		545	6.9	63	sill., and., qz
90 pyr.	10 and.			550	6.9	63	and., qz

* Figures for the changes of mineral concentrations cannot be given in these samples because of preferred orientation in the x-ray mounts.

KHITAROV et al. (1963) lie within the stability field of kaolinite and must be even more erroneous than those discussed above.

Because the reactions mentioned above involve dehydration, their equilibrium temperatures are dependent on the chemical potential of water in the system. Therefore it may be argued that, if $\mu_{\text{H}_2\text{O}}$ is very low, the upper stability limits of the hydrous aluminium silicates may be considerably lower than in the experimental systems with excess water. Through this "shrinking" of the pyrophyllite field, the triple points of WEILL and HOLM and KLEPPA could move outside the pyrophyllite field. But if this were so, then low values of $\mu_{\text{H}_2\text{O}}$ must have prevailed everywhere. This, however, is a very improbable assumption.

Further it might be objected that pyrophyllite still has been rarely recognized in regional metamorphic rocks, while the Al_2SiO_5 polymorphs are of widespread occurrence. Therefore, the above mentioned reactions of decomposition of pyrophyllite could not be responsible for the formation of Al_2SiO_5 phases², but other reactions involving, for instance, muscovite, paragonite or chlorite. However, the formation of *pyrophyllite* by such reactions has never been observed, so that they must occur on the high temperature side of the upper stability limit of pyrophyllite. Therefore the conclusions of WINKLER and of SCHULING based on the pyrophyllite stability retain their high degree of probability even if the breakdown of pyrophyllite is not responsible for the formation of the Al_2SiO_5 minerals.

This is confirmed by another observation: chloritoid is known to occur in stable paragenesis with kyanite (e.g. READ, 1932) or andalusite (for example SEKI, 1955), but not with sillimanite, whereas staurolite coexists stably with each of the Al_2SiO_5 polymorphs. The triple point must therefore lie on the high temperature side of the curve for the reaction chloritoid + $\text{Al}_2\text{SiO}_5 \rightleftharpoons$ staurolite + quartz + H_2O . Recent experimental investigations by HOSCHEK (1967) show that the boundary lies at about 545°C/4 kb and 550°C/8 kb. The positions of all the "triple points" mentioned before would postulate stable coexistence of chloritoid and sillimanite; therefore they cannot be correct. The greatest part of NEWTON'S

² The inverse reaction, formation of pyrophyllite from Al_2SiO_5 , has been observed (e.g. HERZ and DUTRA, 1964).

triple point area is also cut away by this curve and needs therefore no more being taken into account. Only a small part of NEWTON'S rhombus, the estimates of WINKLER and of SCHULING as well as the experimental determination of the present author agree with HOSCHEK'S results. NEWTON'S results agree passably with those of the present author in the p,t -region near the Al_2SiO_5 triple point, but they are in very severe disagreement at higher temperatures and pressures both with those of the present author and with those of CLARK et al. (1957) and CLARK (1960).

Like the rest of the triple point area of NEWTON, also the triple point of KENNEDY (see BUERGER, 1961) can be reconciled with the petrographic criteria enumerated above. However, the pressure of 12 kb at 570°C can only be generated by high overpressures or very small geothermal gradients, which are both highly improbable for metamorphism of the amphibolite facies (see WINKLER, 1965). However, a reaction curve giving an upper pressure limit for the p,t -data of the Al_2SiO_5 triple point is not yet known.

An upper *temperature* limit is the minimum melting curve of water-saturated granite, because andalusite is not found to exist stably in regions of anatexis, but only sillimanite and, less common, kyanite. So the curve for the reaction andalusite \rightleftharpoons sillimanite should not intersect the granitic minimum curve; this postulate is met by the present author's curve as well as by those of WEILL (1966), WINKLER (1965) and of FYFE and TURNER (1966), but not by the curves of the other investigators.

5. Conclusions

From all the above considerations it must be concluded, that the triple point experimentally determined by the present author under truly hydrostatic gas pressure, which differs only slightly from the estimates of SCHULING (1962) and WINKLER (1965), is in accord both with petrographic observations and experimental findings in related systems. Taking into account the long run times, the seeding of mixes with all relevant Al_2SiO_5 modifications, the very careful establishment of increase in amounts of more stable phases and thus of real growth (not merely recrystallization) as well as the agreement with petrographic observations it is stated that the data given here on the phase boundaries are *stable equilibrium data*.

Petrogenetic implications arising from the data presented here on the Al_2SiO_5 triple point will be treated in a later paper.

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