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KYANITE-SILLIMANITE TRANSITION WITH EXCESS QUARTZ AND CORUNDUM

by

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(with 3 Tables and 3 Text-figures)

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Abstract

The kyanite-sillimanite transition have been studied by using starting materials with various composition. The univariant line of this transition with excess quartz and excess corundum passes through the points of slightly higher pressure than that of ideal composition, Al_2SiO_5. Since natural Al_2SiO_5 polymorphs are sometimes associated with quartz or corundum, this conclusion obtained by experiment may be applied to estimate the pressure-temperature condition of the natural occurrence of sillimanite or kyanite with quartz or corundum.

Introduction

Three polymorphs of Al_2SiO_5 are considered as the most important minerals in metamorphic rocks of pelitic composition. Precise knowledge of the stability field of sillimanite, kyanite, and andalusite will, therefore, contribute to unravelling the metamorphic history of these rocks. Since these minerals coexist with a number of other minerals in metamorphic rocks, their parameters may yield even better information concerning the pressure and temperature condition during metamorphism.

The pressure-temperature field of the polymorphs in the system Al_2O_3-SiO_2 have been experimentally studied by many investigators. Unfortunately the results reported have been in serious disagreement. Some reasons for this discrepancy may be adduced. First, incorrect calibration of the pressure apparatus, and existence of pressure inhomogenity in the reaction chamber should be considered. Different polymorphs may form simultaneously in the same chamber, if pressure gradients exist in the reaction chamber. Second, some of the synthetic Al_2SiO_5 phases may not belong to the unary system and contain the component H_2O because many experiments were made in the presence of water. Richardson et al. (1968) reported that the results from their

dry runs did not agree with those from their wet runs, although H_2O content was insignificant in the run products. Newton (1966) also discussed this problem and concluded that water can not be a major culprit. Third, in the experimental studies of the stability relations, different starting materials have been used, i.e., the natural samples from different localities, and the artificial materials are generally not pure but contain small amounts of other trivalent cations that are proxy partly for aluminum. Most important among these cations are iron, manganese, and chromium which may have a great influence on the stability field of Al_2SiO_5 polymorphs.

Deviation from ideal Al_2SiO_5 as shown by many chemical analyses may effect the relative stabilities of the polymorphs. Al-Si disorder in sillimanite may also have a great influence. Therefore it is tempting to ascribe the observed differences to chemical composition.

Al_2SiO_5 minerals occur under various metamorphic condition, such as, for example, corundum-bearing (Al_2O_3-buffered), quartz-bearing (SiO_2-buffered), and corundum- and quartz-free assemblage. In some previous experiments on the kyanite-sillimanite transition, quartz was present as a free SiO_2 phase. The uncertainty of the compositions of the run products can be partly eliminated by adding buffering phases, such as quartz or corundum. If there are compositional variations in the Al_2SiO_5 polymorphs, the stable field of two-phase assemblage, for example, a field of stoichiometric kyanite + nonstoichiometric sillimanite may appear on the pressure-temperature projection.

This paper presents our result on the stability relations of kyanite and sillimanite at 7 to 26.5 kilobars in the temperature range from 1000° to 1500°C, using following starting materials: $2Al_2O_3 + SiO_2$ composition, $Al_2O_3 + SiO_2$ composition, and $Al_2O_3 + 2SiO_2$ composition.

Experimental equipment and techniques

The present experiments were carried out with piston-cylinder apparatus of 1.25cm in diameter and 5.00cm in length. The pressure transmitting medium was molten pyrex glass, and the pressure cell was similar to that designed by Hariya and Kennedy (1967). Temperature was measured with Pt-Pt13Rh thermocouple which was in contacted with the Pt sample capsule. No correction was made for the effect of pressure on the e.m.f. of the thermocouple. Temperature fluctuation were as much as ±14°C in overnight runs and ±7°C in shorter runs.

The three kinds of mixture with following compositions were prepared as starting materials, $Al_2O_3 + SiO_2$ (1:1, a stoichiometric composition), $Al_2O_3 + 2SiO_2$ (1:2, 1 mole excess quartz), and $2Al_2O_3 + SiO_2$ (2:1, 1 mole excess corundum), by heating mixtures of corundum and cristobalite at 1500°C 1 atom for 6 hours.

Due to the extreme fine grain size of the run products, it was not possible to determine their composition by an electron microprobe. The phases obtained in the experiments were identified by x-ray powder diffraction patterns. The x-ray diffraction patterns were recorded by using CuKα radiation with LiF monochrometer and a scanning speed of 0.25 2θ/min. The unit-cell parameters were determined by using following reflection lines: (122), (230), (320), (400), (312), (332), (042), (240), and (400) for silimanite; (200), ($\bar{2}$20), ($\bar{1}$21), (021), (2$\bar{1}$1), ($\bar{2}$02), (1$\bar{3}$1), ($\bar{1}$22), (300), (1$\bar{1}$3), ($\bar{1}$40), (311), (500), and ($\bar{1}$43) for kyanite. The unit-cell parameters were calculated by using a RSLC-3 computer program written by Sakurai (1967) at the FACOM 230-60 computer system of the Hokkaido University Computing Center.

Results

Since the reaction rate is very low, the direct determination of the kyanite-sillimanite transition boundary at lower temperatures was difficult. In this study, all of the experiments were undertaken at temperature range from 1000° to 1500°C. Our experimental results are shown in table 1 and figure 1.

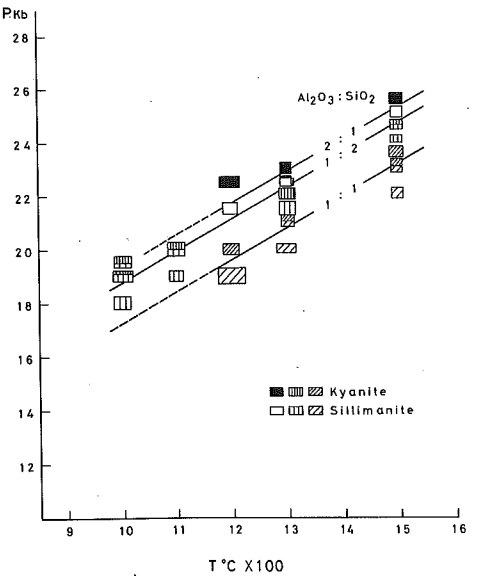

Fig. 1 Experimental data for the sillimanite-kyanite transition with excess quartz and corundum, and ideal composition.

Table 1. Experimental results

	Pressure (Kb)	Temperature (°C)	Time (hours)	Result
Al_2O_3:SiO_2 1:1	10.0	1500	6	Sill only
	22.0	1500	6	Sill, trace Qtz
	7.0	1500	6	Sill only
	20.0	1500	6	Sill, trace Qtz
	23.0	1500	6	Sill + Ky
	15.0	1500	6	Sill, trace Qtz
	23.5	1500	6	Ky only
	25.0	1500	6	Ky only
	21.0	1300	10	Sill + Ky
	22.0	1300	20	Ky, trace Mull
	20.0	1300	15-1/2	Sill, trace Qtz
	19.0	1200	116-1/2	Sill, trace Qtz
	20.0	1200	106-2/3	Ky, trace Cor
	18.0	1200	143-1/3	Sill, trace Qtz
Al_2O_3:SiO_2 1:2	10.0	1500	6	Sill + Qtz
	7.0	1500	6	Sill + Qtz
	23.0	1500	6	Sill + Qtz
	24.0	1500	6	Sill + Qtz
	24.5	1500	6	Sill + Ky + Qtz
	23.5	1500	6	Sill + Qtz
	25.0	1500	6	Ky + Qtz
	7.0	1300	9-1/6	Sill + Qtz
	10.0	1300	10	Sill + Qtz
	21.0	1300	10	Sill + Qtz
Al_2O_3:SiO_2 1:2	21.5	1300	10-1/4	Sill + Qtz
	22.0	1300	8	Ky + Qtz, trace Sill
	22.5	1300	8	Ky + Qtz
	23.5	1300	8	Ky + Qtz
	19.0	1100	24	Sill + Qtz
	20.0	1100	31-1/3	Sill + Ky + Qtz
	18.0	1000	51-1/3	Sill + Qtz
	19.0	1000	70	Sill + Qtz, trace Ky
	19.5	1000	49-5/6	Sill + Ky + Qtz
$Al_2O_3SiO_2$ 2:1	23.0	1500	6	Sill + Cor
	24.0	1500	6	Sill + Cor
	26.0	1500	6	Ky + Cor
	25.0	1500	6	Sill + Cor
	25.5	1500	6	Ky + Cor
	26.5	1500	6	Ky + Cor
	21.5	1300	8	Sill + Cor
	22.0	1300	19	Sill + Cor
	22.5	1300	30	Sill + Cor, trace Ky
	23.0	1300	46	Ky + Cor
	24.0	1300	12-1/2	Ky + Cor
	24.5	1300	13	Ky + Cor, trace Mull
	20.0	1200	116	Sill + Cor
	21.5	1200	120	Sill + Cor
	22.5	1200	118	Ky + Cor, Mull

Abbreviations; Sill: Sillimanite, Ky: Kyanite, Qtz: Quartz, Cor: Corundum, Mull: Mullite.

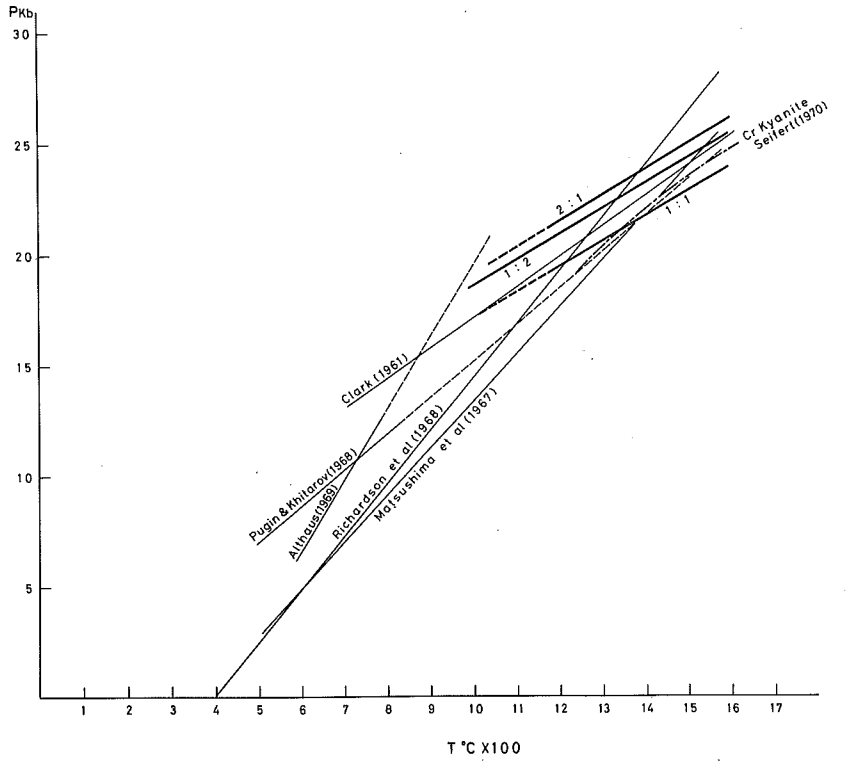

Fig. 2 Comparison of the present data with the phase boundaries of the sillimanite-kyanite, as given by various authors.

The kyanite-sillimanite transition curve of 1:1 ideal composition is slightly different from that of 2:1 composition with excess corundum and of 1:2 composition with excess quartz; i.e., they lie on the higher pressure region than that of ideal composition, the difference being 2.0 Kb and 1.5 Kb, respectively. These three curves are parallel to each other. In figure 2, our experimental results are compared with the previous determinations by many investigators. The present results agree with that of Clark (1961) closely, though the slope of the curves is slightly different from that of previous studies. The equilibrium curves of previous experiments lie on slightly higher pressure region than the present curve for ideal composition above about 1300°C.

In figure 3, the cell volume with cell edge a of various synthetic sillimanite are plotted, together with the data of natural sillimanites by Hariya et al. (1969) and Richardson et al. (1968). It is noticed from figure 3 that there is a nearly continuous variation in the cell volume with the cell edge a both of which change systematically with change in temperature and pressure. These data give a support for the conclusion of Hariya et al. (1969) that there is a continuous change of cell edge a with cell volume from sillimanite to mullite

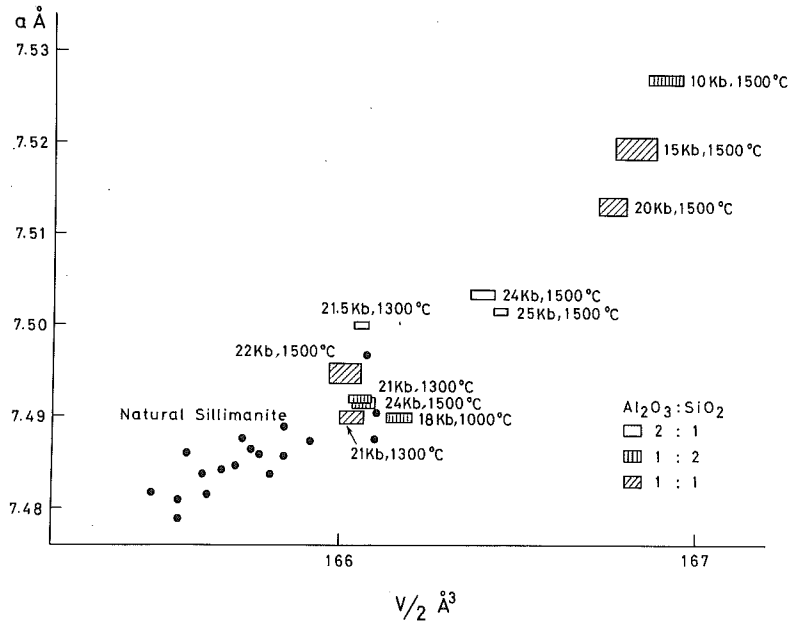

Fig. 3 Variation of cell volume with cell edge a of natural sillimanites and synthetic sillimanites formed at various conditions, temperatures and pressures of which are indicated.

and that this may suggest the presence of solid solutions between the both minerals. However, Chatterjee et al. (1972) mentioned that the natural sillimanite treated at various temperatures and pressures do not exhibit any appreciable change in cell parameters, indicating the absence of miscibility between sillimanite and mullite, and that they are progressively Al-Si disordered at higher temperatures and pressures. Sillimanite, however, is extremely stable phase and the reaction even at higher temperature is very sluggish.

As shown in figure 3, the cell volume and the cell edge a of synthetic sillimanites obtained at the temperature-pressure conditions near the kyanite-sillimanite transition curves are plotted within the region of those of natural sillimanites. It is noted that the sillimanite synthesized from 2:1 starting material has a larger cell edge a and that synthesized from 1:2 starting material has a slightly larger cell edge a than that synthesized from 1:1 starting material, whereas the cell edges b and c show no significant change. If sillimanite is disordered, it would be expected that its cell dimension increases slightly. Beger et al. (1970) showed that sillimanites treated at 1500°C between 1 bar and 24 kilobars did not change their composition but showed an increase in the unit-cell volume. They explained that this increase was caused by Al-Si

Table 2. Unit-cell parameters of synthetic sillimanites

	a (Å)	b (Å)	c (Å)	V/2 (Å^3)
Al_2O_3:SiO_2 1:1				
1500°C at 22 Kb	7.4948	7.6792	5.7692	166.02
	±0.005	±0.006	±0.001	±0.24
1500°C at 20 Kb	7.5128	7.6916	5.7716	166.76
	±0.004	±0.004	±0.002	±0.15
1500°C at 15 Kb	7.5196	7.6907	5.7696	166.83
	±0.005	±0.004	±0.001	±0.16
1300°C at 21 Kb	7.4900	7.6820	5.7714	166.04
	±0.002	±0.004	±0.001	±0.11
Al_2O_3:SiO_2 1:2				
1500°C at 24 Kb	7.4922	7.6821	5.7708	166.06
	±0.002	±0.002	±0.001	±0.08
1500°C at 10 Kb	7.5276	7.6905	5.7664	166.91
	±0.002	±0.003	±0.001	±0.11
1300°C at 21 Kb	7.4939	7.6816	5.7694	166.06
	±0.005	±0.005	±0.001	±0.17
1100°C at 19 Kb	7.4909	7.6814	5.7722	166.07
	±0.001	±0.002	±0.001	±0.04
1000°C at 18 Kb	7.4901	7.6819	5.7758	166.17
	±0.002	±0.002	±0.001	±0.08
Al_2O_3:SiO_2 2:1				
1500°C at 24 Kb	7.5037	7.6883	5.7686	166.40
	±0.001	±0.002	±0.001	±0.05
1500°C at 25 Kb	7.5017	7.6914	5.7696	166.45
	±0.001	±0.001	±0.001	±0.02
1300°C at 21.5 Kb	7.5001	7.6779	5.7680	166.07
	±0.001	±0.001	±0.001	±0.01

disorder. Difference of sillimanite-kyanite transition boundaries in the present results may be related to the order-disorder phenomena of Al_2SiO_5 polymorphs.

Holdway (1971) suggested that Al-Si disorder in sillimanite will increase with increasing temperatures. From figure 1, it seems more likely, however, that slight increase of the transition pressure of sillimanite-kyanite may be explained by Al-Si disorder, if these sillimanites are Al-Si disordered at all.

Unit-cell parameters of synthetic kyanites are given in table 3. According to Skinner et al. (1961), the increase in parameter c may be due to Al substitution for Si in the chains which are parallel to the c axis in the kyanite structure. The cell parameters of our synthetic kyanites including a, b, c, α, β, and γ agree well with the single crystel data by Burnham (1963). Present synthetic kyanites may be expect to have an ideal composition.

Table 3. Unit-cell parameters of synthetic kyanites

	a (Å)	b (Å)	c (Å)	α (deg.)	β (deg.)	γ (deg.)	V (Å³)
Al_2O_3:SiO_2 = 1:2	7.126	7.853	5.577	89.71	101.03	106.24	293.76
1300°C at 23.5 Kb	±0.006	±0.009	±0.008	±0.07	±0.11	±0.13	±0.56
Al_2O_3:SiO_2 = 1:1	7.119	7.860	5.576	89.81	101.09	105.89	294.11
1500°C at 25 Kb	±0.004	±0.006	±0.001	±0.04	±0.05	±0.10	±0.25
Al_2O_3:SiO_2 = 2:1	7.117	7.841	5.568	90.08	101.17	105.91	292.69
1500°C at 26 Kb	±0.004	±0.007	±0.003	±0.09	±0.11	±0.08	±0.35
Celo mines, Burnsville, N. C. Burnham (1963)	7.1192	7.8475	5.5724	89.98	101.21	106.01	

Conclusion

Most of the Al_2SiO_5 polymorphs occur in the low as well as high grade metamorphic rocks of pelitic and argillaceous composition and are associated with other minerals such as quartz or corundum. The triple point and the univariant lines in the system Al_2O_3-SiO_2 may change with associated minerals. The present study shows that the kyanite-sillimanite transition curve with excess quartz or corundum lies slightly higher pressure region than that of ideal composition. Owning to the low reaction rate in this system, the experimental determination of the phase quilibrium of Al_2SiO_5 polymorphs in relation to their compositional variation is very difficult at lower temperature. From this point of view, the direct application of the present results to the natural occurrence should be made with much caution. Further experiments at lower temperature are expected to throw light for this problem.

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