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THE STABILITY RELATIONS OF THE POLYMORPHS OF ALUMINUM SILICATE: A SURVEY AND SOME COMMENTS*

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ABSTRACT. Existing determinations of the pressure-temperature relations of sillimanite, kyanite, and andalusite show large discrepancies in the locations both of the univariant lines and of the invariant point. The discrepancies probably resulted partly from determination of synthesis rather than stability fields and partly from experimental difficulties in pressure determinations. However, these explanations probably do not account for all the observed spread, and possible effects of compositional variations cannot be excluded. The rapidly grown, fine-grained sillimanites have never been verified as to their stoichiometry and the crystal-chemical ordering of the cations; few of the reports even include adequate characterizing X-ray data. Lack of such compositional and/or structural perfection in the synthetic crystals as has been ascertained for coarse natural samples could profoundly affect the location of the stability fields of these aluminum silicate polymorphs.

INTRODUCTION

The stability relations of the naturally occurring aluminum silicates, sillimanite, kyanite, andalusite, and mullite, have been subjected to repeated investigations, both by direct experimental determination of the pressure and temperature boundaries of their regions of stability and by calculations based on available thermochemical data. The early experimental works of Griggs and Kennedy (1956; see Matsushima and others, 1967) and of Clark, Robertson, and Birch, (1957), followed by the supplementary work of Clark (1961), Khitarov and others (1963), and Bell (1963) were in fair mutual agreement; the results of Bell and of Khitarov and others suggest a triple point for andalusite–kyanite–sillimanite near 8 kb and 300° to 400°C (fig. 1). Although most of these early experiments were performed in apparatus in which nonhydrostatic pressure was applied, in at least one series of experiments (Clark, Robertson, and Birch, 1957) hydrostatic pressure was probably closely approached (see table 1).

In the past few years, additional experimental work has resulted in a large spread of location of the p-T univariant curve between various pairs of polymorphs and for the triple point, which has been revised by and large toward lower pressures. The conclusions drawn from the work of Newton (1966a, b), like the earlier conclusions of Bell, were based on the reversible transition of kyanite and sillimanite; the considerably lower pressure of the triple point reported by Newton (1966b) was therefore somewhat surprising. More recently, additional work has been done by Althaus (1967), by Richardson, Bell, and Gilbert (1967; 1968a, b), by Richardson, Gilbert, and Bell (1967), by Matsushima and others (1967), and by Pugin and Khitarov (1968). However, the discrepancies among the various studies remain large and, what is more disturbing, not satisfactorily explained; the recent reviews on the subject, by Boyd (1967),

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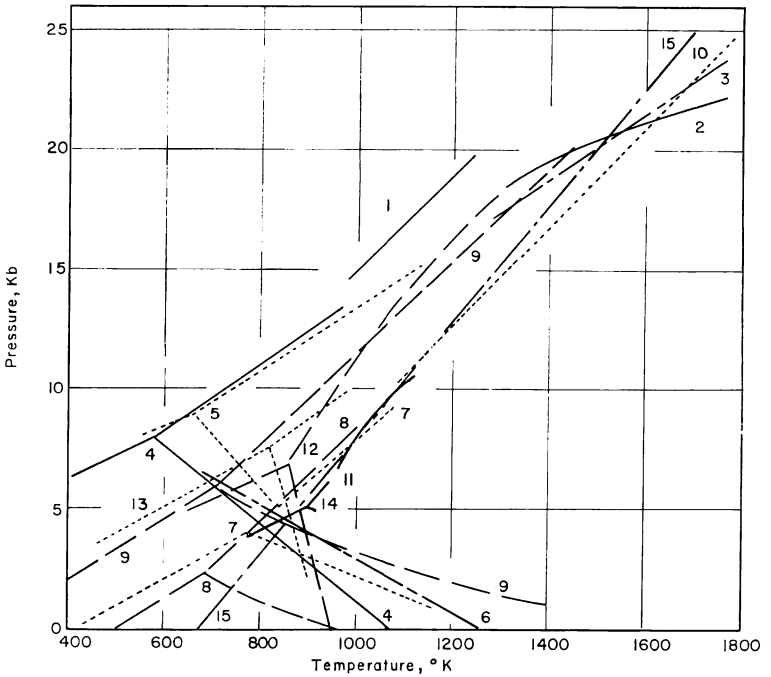

Fig. 1. Summary of experimental data on kyanite–andalusite–sillimanite equilibria and location of the triple point. Each set of curves extends as far as shown in the original report cited. 1, Griggs and Kennedy, 1956; 2, Clark, Robertson, and Birch, 1957; 3, Clark, 1961; 4, Bell, 1963; 5, Khitarov and others, 1963; 6, Evans, 1965; 7, Newton, 1966a, b; 8, Weill, 1966; 9, Holm and Kleppa, 1966; 10, Matsushima and others, 1967; 11, Richardson, Bell, and Gilbert, 1967, and Richardson, Gilbert, and Bell, 1967; 12, Althaus, 1967; 13, Pugin and Khitarov, 1968; 14, Richardson, Bell, and Gilbert, 1968a; 15, Richardson, Bell, and Gilbert 1968b. Different line patterns are used for clarity.

Althaus (1967), Newton (1966b), Richardson, Bell, and Gilbert (1968b), and Pugin and Khitarov (1968) summarize the data, point out and examine some of the experimental problems, and offer some possible explanations for the data spread.

Among recent attempts to define the p-T stability fields of the Al_2SiO_5 polymorphs by thermodynamic calculations may be cited the works of Weill (1966) and Holm and Kleppa (1966). The results of Weill, using a refreshing combination of experimental and thermodynamic tools, led to a triple point at considerably lower pressure than any other published determination. Weill's work has been discussed and criticized by Holm and Kleppa (1966, p. 1620) and by Althaus (1967, p. 39). Holm and Kleppa made fresh measurements of the enthalpy of formation of all four aluminum silicate phases and predicted a triple point for kyanite–andalusite–sillimanite that is intermediate in location (fig. 1).

POSSIBLE SOURCES OF DISCREPANCY OF RESULTS

The discrepancies among the various experimental results for the kyanite–sillimanite–andalusite polymorphic transitions are disturbingly

large, and many attempts have been made to explain the data. These can be broadly grouped into categories:

1. The data refer to synthesis fields rather than equilibrium fields. Some of the experiments failed to demonstrate the reversibility of the polymorphic transition and report, in fact, the syntheses of phases from other phases not actually involved in the equilibrium. For instance, Clark, Robertson, and Birch (1957) actually reported, with minor exception, the synthesis of sillimanite or kyanite from gels, kaolinite, or andalusite; the same may be said of the early work of Griggs and Kennedy (Matsushima and others, 1967, p. 30). The univariant line between andalusite and sillimanite reported by Evans (1965, p. 660) likewise is a synthesis boundary. In table 1, those studies in which reversibility of the equilibrium has been achieved or claimed are individually noted.

2. Incorrect calibration of the pressure apparatus, owing to failure fully to take into account the effects of strength of material, friction, et cetera, in converting the nominal gauge pressure to actual pressure on the sample. Clark (1961), for example, discussed this possibility and made corrections on his later data, obtained by using a Boyd and England type single-stage apparatus, to bring the results into reasonable agreement with the results of Clark, Robertson, and Birch (1957), obtained by using a hydrostatic gas apparatus. Richardson, Bell, and Gilbert (1968b) exhaustively reviewed this topic and modified Clark's corrections.

Another possible source of error is the existence of pressure inhomogeneities in the reaction chamber. Several of the experiments have been conducted using the opposed anvil device (see table 1), so it is conceivable that pressure gradients existed in the reaction chamber (P. M. Bell, oral commun., 1967), perhaps caused in part by the hardness of the reacting phases. Thus different polymorphs could have grown under pressures significantly different from those computed for the chamber as a whole. This problem has been ably reviewed by Kitahara and Kennedy (1964). The possibility of pressure inhomogeneity is a very reasonable explanation for some of the anomalous results; however, an analysis of the situation for an admittedly simplified hypothetical series of experiments (table 2; fig. 2) shows that if seeds are used and if the various possibilities of anomalous pressures could be systematically explored, then the conclusions arrived at should not be qualitatively different from the correct conclusions, except that the uncertainties would be greater. Problems of pressure correction have been discussed by Matsushima and others (1967), Boyd (1967), and Richardson, Bell, and Gilbert (1968b).

3. Some of the synthetic andalusite–sillimanite–kyanite phases might not be truly unary but contain the component H_2O because many experiments were made in the presence of H_2O. Richardson, Bell, and Gilbert (1968b) reported that whereas the results from their dry runs did not agree with those from their wet runs, nevertheless structural H_2O is insignificant in the run products. Newton (1966b, p. 173) also discussed this problem and concluded that H_2O cannot be the major culprit.

TABLE 1

Compilation of published experimental data on univariant and invariant equilibria involving the polymorphs andalusite, kyanite, and sillimanite

Author	Starting material	Reversed?	H_2O	Identification method	Pressure by	Remarks
Griggs and Kennedy, 1956	Kaolinite	no	?	?	Piston and anvil	See Matsushima and others, 1967, for more details; synthesis runs
Clark, Robertson, and Birch, 1957	Kaolinite, gibbsite, natural andalusite, sillimanite, and kyanite	no (see remarks)	may be some	Optical and X-ray	Hydrostatic gas apparatus	Both sillimanite to kyanite and kyanite to sillimanite achieved, but not at the same p, T; other runs are synthesis runs; show comparison of X-ray powder patterns
Clark, 1961	Kaolinite, natural sillimanite and kyanite	yes	no	X-ray	Boyd and England type piston and cylinder	No identification details
Aramaki and Roy, 1963	Gel, natural sillimanite and kyanite	no	yes	X-ray slow scan	Hydrothermal with flux, and opposed anvil	No details; synthesis runs
Bell, 1963	Gel and natural seeds	yes	possible	X-ray	Bridgman-type piston and anvil, with shearing	No details on X-ray method or cell data
Khitarov and others, 1963	Gel	no	yes	Optical and auxiliary X-ray	Bridgman-type anvil device, pyrophyllite pressure medium	No X-ray data; synthesis runs
Evans, 1965	Natural andalusite, sillimanite	no	yes	——	——	Weight-change method; synthesis runs
Newton, 1966a, b	Synthetic and natural kyanite, andalusite, sillimanite	yes	yes	X-ray pattern and optical data	Single stage piston and cylinder; talc pressure medium	Cell size noted

TABLE 1 (continued)

Author	Starting material	Reversed?	H_2O	Identification method	Pressure by	Remarks
Weill, 1966	No direct determination	—	—	——	———	———
Matsushima and others, 1967	Gel, kaolinite, and seeds of both kyanite and sillimanite	no	yes	Not specified	Boyd and England type piston and cylinder	Results of Griggs and Kennedy reported here
Richardson, Bell, and Gilbert, 1967; Richardson, Gilbert, and Bell, 1967	Sillimanite and kyanite	yes	yes	X-ray	Similar to Newton's equipment, but use gas pressure	Source of material not specified
Althaus, 1967	Natural sillimanite and kyanite	yes	no	X-ray on integrated peak intensity of selected lines	Cold-seal hydrothermal apparatus, gold capsule, water-ethylene glycol pressure medium	———
Pugin and Khitarov, 1968	Natural sillimanite, kyanite, andalusite	yes	yes	Optical, relative amounts of original mixtures	Piston-cylinder apparatus	Source of material not specified; no X-ray data; quartz in excess in some runs
Richardson, Bell, and Gilbert, 1968a	Natural kyanite, andalusite	yes	?	Not specified	Gas-pressure apparatus	Excess quartz; products analyzed by electron probe
Richardson, Bell, and Gilbert, 1968b	Natural sillimanite, kyanite	yes	Excess for some, trace for some, dry for others	X-ray by relative peak intensity	Gas-pressure and piston-and-cylinder apparatus	Instroke-outstroke data on piston-and-cylinder runs, effect of H_2O and of friction assessed. Systematic difference exists between data for the two types of apparatus. Cell parameters of product phases given and compared with those of starting material. Some run products microprobe analyzed for Al/Si ratio.

It therefore seems probable that the above factors, taken together or individually, are unlikely to be adequate to explain the spread of experimental data. Boyd (1967, p. 595) pointed out that the triple points deduced by Bell (1963) and by Khitarov and others (1963) differ considerably in temperature, and temperature measurements are not subject to the same sort of experimental difficulties. However, this temperature discrepancy may be more apparent than real, because the triple point temperature is determined by intersection of univariant lines.

TABLE 2

Hypothetical experiments in a reaction chamber having nonhomogeneous pressure distribution

It is assumed that just one annular ring of high pressure surrounds a core of low pressure. The mean pressure, P_m, is the computed pressure. $P_h > P_m > P_l$. The isothermal equilibrium transition pressure is P_e.

If	The starting material is	and the product is	We would conclude that the run is
$P_e > P_h$	sillimanite, S	same	in S field
	kyanite, K	S	in S field
$P_h > P_e > P_m$	S	K in P_h area	in K field
	K	S in P_l area	in S field
$P_m > P_e > P_l$	S	K in P_h area	in K field
	K	S in P_l area	in S field
$P_l > P_e$	S	K	in K field
	K	same	in K field

One might surmise at first that at least some of the published reversed kyanite-sillimanite univariant curves are metastable, even though no parameter affecting internal homogeneous equilibrium is involved (see Althaus, 1967, p. 37). This explanation is unacceptable in its simple form, however, if each of the phases involved is, at given p and T values, constant in composition, such that the Gibbs free energy surface for each phase is single-valued in the G-p-T space. For under such conditions the intersection of the two free energy surfaces leading to the univariant line is itself unique and single-valued, and metastable displacement of the univariant line into the divariant field of one of the phase assemblages involved is impossible.

Metastable displacement of the univariant line, in the manner discussed, however, would be possible if one of the phase assemblages (in the present case, of a single phase each) participating in the equilibrium were capable of compositional and/or crystallostructural variations, such that the phase is represented by a series or a continuum of Gibbs free energy values at a given set of p and T; in this event, the univariant line on the p-T diagram would expand into a family of lines, or into a band, even though no more than one line out of the many could be stable. The possibility of compositional variation in the experimentally produced kyanite and sillimanite has not been much explored hitherto-fore, with the exception of discussions by Aramaki (1961), Aramaki and

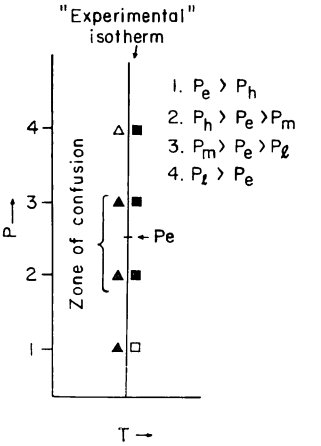

Fig. 2. An hypothetical series of experiments, showing that pressure inhomogeneity in the reaction chamber does not necessarily lead to systematic errors in location of univariant p-T curve. Squares, sillimanite as starting material; triangles, kyanite as starting material. Open symbols, no reaction; solid symbols, reaction occurred. The four pressures correspond to the four situations of table 2, from top to bottom, in order.

Roy (1963), and Richardson, Bell, and Gilbert (1968b); one purpose of this note is to suggest the need to explore some possible effects of compositional variations.

SILLIMANITE AND MULLITE

Investigators have debated as to whether sillimanite and mullite are two distinct phases, or whether under appropriate conditions they could show continuous or partial mutual solid solutions. Roy and Osborn (1954, p. 857) noted that the X-ray powder technique is not readily adopted for their unequivocal differentiation. Kennedy (1961, p. 320) stated that mutual solution exists, and that under appropriate conditions this solution is complete. On the other hand, Agrell and Smith (1960) studied several natural sillimanite and mullite samples and concluded that their samples show that (1) sillimanite is stoichiometric Al_2SiO_5; (2) mullite composition, while variable, does not extend to lower Al:Si atomic ratio than 3:1; and (3) it is possible positively to distinguish sillimanite from mullite by their cell parameters. More recently, Smith and McConnell (1966), by using electron-diffractometry, concluded that it is possible to distinguish these minerals by such a method.

Nevertheless, persistent doubts exist on the stoichiometry of sillimanite and on the possible extension of mullite composition toward lower Al:Si ratios. Aramaki (1961) attempted to show, by mechanical separation and chemical analysis of the separate, that a fine-grained sillimanite from a xenolith of Asama volcano shows excess aluminum, that is, solid solution toward mullite. Aramaki gave two separate analyses;

they show the atomic Al:Si ratio of 2.2 and 2.3 as against the ideal value of 2.0; Aramaki argued that impurities in the sample and errors of chemical analyses cannot account for the discrepancy. The same sample of sillimanite also showed unit-cell dimensions half way between those of other, established sillimanite samples and those of mullite. These interesting data, however, must be accepted with caution, because of possible unaccounted mineral impurities remaining after the difficult separation, and because of possible analytical errors on small samples, especially for two oxides that are difficult to determine. Aramaki and Roy (1963, p. 1337-1340) discussed the problem further and provided data showing that some synthetic "sillimanite" has cell volume and axial dimensions that are also intermediate between the field occupied by mullite and the small clustering of points for natural, well-crystallized sillimanite. The question must remain, then, that even though coarse, well-crystallized natural sillimanites studies by Agrell and Smith (1960) are stoichiometric and show constant cell dimensions, fine-grained crystals, particularly those synthesized in high-pressure experiments of relatively short duration and those formed at very high temperatures, may be compositionally more variable.

With the exception of Newton (1966a, b), Althaus (1967), and Richardson, Bell, and Gilbert (1968b), the reports on experimental syntheses of kyanite and sillimanite do not include data on the cell parameters of the products and only casually state the method of identification of the phases (see table 1). Clark, Robertson, and Birch (1957, p. 631) presented X-ray powder patterns of natural and their synthetic sillimanite and kyanite for comparison; this is an exceptional step, but the authors gave no further details and did not remark on some obvious differences in the patterns. These same authors also noted (p. 632) the refractive indices of the synthetic sillimanite, but the data are not diagnostic of possible compositional departures from the ideal formula. For most studies reported in the literature, however, the identifications of the product phases were made apparently by simple comparison of powder patterns of the products with standard patterns, without mention of specific measurements of the cell parameters or of the nature of the diffraction pattern as a whole. Presumably, most of the synthetic grains are far too small for detailed crystallographic work, but the ambiguities intrinsic to such identification procedures seem clear. The uncertainty of compositions of the products can be partly removed by adding buffering phases, such as quartz and corundum, to the runs; however, even this expedient by no means ensures the compositional constancy of the phases.

One interesting consequence of possible compositional variations in the aluminum silicate phases is that a p-T projection of the stable phase diagram should contain 2-phase fields, for example, a field of stoichiometric kyanite and a nonstoichiometric sillimanite. Univariant equilibria will then refer to three phases, which might be these two plus quartz. The existence of such two phase fields, however, could not be revealed

by the experimental methods used in the available investigations. Thus, the technique of determination of synthesis fields certainly cannot elucidate this point. Moreover, even the reversed equilibrium studies throw no light here, because these studies (see, for instance, Newton, 1966a, b; Althaus, 1967; Richardson, Bell, and Gilbert, 1968b; Pugin and Khitarov, 1968) determined stability fields primarily by the relative increase and decrease of X-ray intensities of chosen diffraction peaks; review of the published data show remarkably few data points that cannot be equally well interpreted by assuming reactions in two-phase fields as by assuming incomplete reaction.

ORDER-DISORDER IN SILLIMANITE

Sillimanite, whether natural or synthetic, has been customarily considered to be stoichiometric in gross composition. Moreover, the aluminum and silicon atoms have been considered as fixed in their crystallographic positions, showing no mixing.

Burnham (1963a, 1964a) studied the detailed crystal structure of a sillimanite from LaBelle County, Quebec, and of a 3.84:1 mullite. He concluded that the sillimanite is ordered, in that the aluminum and the silicon tetrahedra occupy distinct structural positions and show no evidence of mixing. On the other hand, the mullite contains two sets of aluminum tetrahedra: one set corresponds to the aluminum tetrahedra in sillimanite, to which the phase is closely related structurally, whereas the other set ("excess aluminum") is distributed among the silicon tetrahedral positions of sillimanite. Oxygen deficiency in the structure compensates for the substitution of Al for Si in the structure. Burnham concluded (1964b, p. 228) that there is no *a priori* structural reason for the absence of solid solution for the entire range between the Al_2SiO_5 composition and the Al_2O_3 composition, but the requisite details do not yet exist on possible ordering of the location of oxygen vacancies and of the excess aluminum. Holm and Kleppa (1966, p. 1615) studied the entropy of formation of a 3:1 mullite and concluded that their data are best explained by assuming the total disorder between the silicon and the "excess" tetrahedral aluminum. Whereas Holm and Kleppa found no thermochemical evidence that the other set of the 4-fold aluminum is also involved in the order-disorder process, their method is not sensitive enough to rule out the possibility.

Because all thermodynamic and crystallographic studies so far have been made on relatively coarse, well-crystallized material, it is possible that the conclusions thereby derived do not apply to the exceedingly fine grained or rapidly grown synthetic material, especially as these synthetic crystals have not yielded other than rough powder data suitable for first identification only. If order-disorder of the tetrahedral aluminum and silicon should occur even to a limited extent, the resulting displacement of the univariant line between sillimanite and kyanite/andalusite could be drastic. For illustration, consider the extreme case where the tetrahedral aluminum and silicon mix ideally in sillimanite. As each

gram atomic formula of sillimanite contains one gram atom each of tetrahedral aluminum and silicon, the ideal entropy of mixing per gram atomic formula of sillimanite is 2R ln 2. For a temperature of 1000°K, which approximates the conditions of formation of many synthetic sillimanites, this corresponds to a free energy of mixing of −114 cc-kb. If we next assume that Δ V for the sillimanite-kyanite transition equals that for the well-crystallized material under room condition, then Δ V is about 5.8 cc/gram-atomic formula (Skinner, Clark, and Appleman, 1961), and the isothermal displacement of the univariant curve, in this particular instance, will be a nearly 20 kb expansion of the field of sillimanite stability. The above result is clearly extreme, and the assumptions that enter into its calculation probably unsupportable; however, it does demonstrate the possible importance of order-disorder processes in the position of the kyanite-sillimanite curve and point to the need for more discriminating experimental criteria. It is apparent that single-crystal studies of synthetic material are needed to settle this question unequivocally.

Andalusite and sillimanite have similar crystal structures (Burnham, 1963a; Burnham and Buerger, 1961). Tetrahedral positions for aluminum, similar to those actually existing in sillimanite, can be created in andalusite by slight rotation of the aluminum octahedra. Thus order-disorder of aluminum and silicon atoms might occur in both these phases. Such a possibility, however, does not exist in kyanite (Burnham, 1963b). If the process of order-disorder occurs only in sillimanite, then the displaced triple point should be located near the stable part of the andalusite-kyanite univariant line; if the process occurs to the same extent in andalusite and in sillimanite, then the displacement of the triple point should be along the metastable extension of the andalusite-sillimanite univariant line. The existing data do not show such systematic relations (fig. 1), even though overlap of invariant points and univariant lines does seem curiously frequent.

The structure of sillimanite involves paired tetrahedra of Al and Si which form bands along the C-axis direction. In the ordered sillimanite analyzed by Burnham (1963a, p. 146), each Al tetrahedron shares apices with three Si tetrahedra, and vice versa. Any disorder of Si and Al^{IV} would result in the contiguity of Si tetrahedra and of Al tetrahedra, leading to increased local charge unbalance, and presumably, also bond-angle strain. However, even if we assume that *all* the Si and Al^{IV} have "wrong" neighbors, that is, each band consists of a chain of Al^{IV} and a chain of Si (which is equivalent to systematic stacking error involving a-b sheets of sillimanite superimposed on one another with 180° relative rotation about the C-axis), the maximum electrostatic charge unbalance on an oxygen atom is only 0.5, not much larger than the value of 0.4 that actually exists in andalusite (Burnham and Buerger, 1961), and the total positive (or negative) charge unbalance per unit cell is exactly that in the sillimanite analyzed by Burnham (1963a). The Al^{IV}–O–Al^{IV} linkage, though unusual, does exist in nature: in $CaAl_2O_4$

(Dougill, 1957), in $KAlO_2$ (Barth, 1935), and probably in $NaAlO_2$ (Barth, 1935), and possible in mizzonite scapolite (Papike and Stephenson, 1966). It is interesting to note that $NaAlO_2$ forms solid solution with α-carnegeite, so that no simple ordered scheme involving Al-Si, as occurs in well-crystallized anorthite and certain zeolites, is possible.

SOME ADDITIONAL REMARKS

If any of the suggestions above is even partly correct, the petrologic implications would be considerable; for then the existence of an aluminum silicate pair, even when proven to be in mutual equilibrium, would not yield direct information on the temperature and pressure conditions of their recrystallization; additional parameters such as detailed composition or structural state of the crystals would be needed.

Many medium to high grade schists that contain sillimanite show this mineral to occur in two distinct size and habit groups: large prisms of sillimanite and fine mats of "fibrolite". The genesis of these two groups of sillimanite has been a matter of much debate (see, for instance, Pitcher, 1965; Chinner, 1961); if it could be shown that the "sillimanite" having such contrasting habits indeed also has different compositions or atomic site occupancies, then their apparent coexistence would have to be interpreted in an entirely different light.

The experimental studies of the stability relations have used different starting materials: the natural samples come from different localities, and the artificial materials have had different histories of preparation. It would be interesting to put into a single hydrothermal chamber samples from different places and of different history; for until it can be shown that the results of the runs do not depend on these properties, interpretation of the disparate data in terms of experimental conditions would be useless attempts.

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