Stability of Al_2SiO_5 *solid solutions*

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Summary. An ideal solution model has been used to calculate the effect of the substitutions $\mathrm{Fe} \overset{3+}{\rightleftharpoons} \mathrm{Al}$ and $(\mathrm{Fe, Mn}) \overset{3+}{\rightleftharpoons} \mathrm{Al}$ on the stability fields of the Al_2SiO_5 minerals. The results show that divariant assemblages of andalusite+sillimanite and sillimanite+kyanite solid solutions can coexist over ranges of 0·1 to 0·4 kbar at 527° C, but that kyanite+andalusite would be stable over a much narrower range. On adding $(\mathrm{Fe, Mn})^{3+}$ to the system, the andalusite/sillimanite curve can be considered to rotate about the invariant point, first eliminating the sillimanite field, and then penetrating the kyanite field. Wide zones of viridine+sillimanite and viridine+kyanite are thus formed.

In view of the ease with which epitaxial nucleation occurs in the Al_2SiO_5 system, it is considered that extensive metastable growth of andalusite, sillimanite, and kyanite is improbable in nature. Metastable persistence is likely to occur in dry systems, or in the presence of an 'armour' of the stable phase, but reaction of millimetre-sized crystals should be completed in geologically short times when aqueous or silicate liquids are present. The combination of the effects of metastable persistence and solid solution seems adequate to account for essentially all the examples of kyanite+sillimanite and kyanite+andalusite, and for many sillimanite +andalusite assemblages. In addition, if small supersaturations develop during metamorphism, simultaneous growth of andalusite+sillimanite could occur over a restricted temperature range.

The relationships of the three Al_2SiO_5 polymorphs, andalusite, sillimanite, and kyanite, continue to pose a number of problems of petrological importance, including the accurate definition of the P–T stability fields in the pure Al_2SiO_5 system, the possibility of metastable growth and persistence of these minerals, and the stability or instability of the common polyphase assemblages andalusite+sillimanite and sillimanite+kyanite. The last of these problems is linked with the effect on the stability fields of replacing $(\mathrm{Al})^{\mathrm{vi}}$ by Fe^{3+} and Mn^{3+}, which forms the main subject of this paper; but before considering these second-order effects, the general form of the P–T diagram for the pure Al_2SiO_5 system must be defined.

P–T stability fields in the pure Al_2SiO_5 *system.* Accurate volume and entropy data are now available (Skinner *et al.*, 1961; Pankratz and Kelley, 1964; see also Fyfe, 1967) for all the Al_2SiO_5 minerals, allowing

the reaction slopes to be calculated with reasonable precision: the andalusite, sillimanite, and kyanite fields can thus be defined if either the invariant point or the *P–T* co-ordinates of a single point on at least two (and preferably all three) univariant reaction curves can be precisely located. Experimental determinations of the stability fields of the Al_2SiO_5 minerals have utilized methods that vary considerably in directness and reliability, and it is not particularly surprising that many of the results are contradictory, or that some are in conflict with geological observations. A critical examination of the reliability of each method is certainly essential before the experimental data are used as evidence for large tectonic overpressures, or for very high load pressures in regional metamorphism. Such an examination has been undertaken by Fyfe (1967), who places the invariant point at $\sim$ 450° C and $\sim$ 2·5 kb, mainly on the basis of hydrothermal work by Newton (1966*a*, *b*) and solution studies by Weill (1966). Taking later experimental work (Matsushima *et al.*, 1967; Richardson *et al.*, 1967) into account, and adopting a more cautious attitude to the accuracy of the Temkin model of melt structure used by Weill, the present writer estimates the values of $500 \pm 100°$ C and $3{\cdot}7 \pm 2$ kb adopted in this paper.

Extent of solid solution in the Al_2SiO_5 *system.* Recent work on Al_2SiO_5 minerals from metamorphic rocks (Chinner, Knowles, and Smith, 1968) has shown that the impurities are major Fe^{3+} and minor Cr^{3+} and Ti^{4+}, all of which are presumed to replace octahedrally co-ordinated aluminium. In most modern analyses of Al_2SiO_5 minerals the iron contents range up to 0·9 % Fe_2O_3 in sillimanite, and about 2 % in kyanite and andalusite (Deer, Howie, and Zussman, 1962; Hertz and Dutra, 1964), although some older analyses suggested Fe_2O_3 contents as high as 4 to 6 %, and possibly 10 %, in andalusite, with up to 4 % in kyanite and 2·5 % in sillimanite.

Contents of $(Fe,Mn)_2O_3$ probably reach 15 % in the Timptomsk viridines (Shabynin, 1948), and the presence of large amounts of Mn^{3+} apparently facilitates the entry of Fe^{3+} (fig. 1). The peculiar stereochemical requirements of the high-spin Mn^{3+} ion are satisfied in andalusite (Strens, 1965, 1966*a*, *b*; Burns and Strens, 1967), but not in sillimanite or kyanite, in which the presence of significant amounts of Mn^{3+} has not been reported.

Electron spin resonance work on kyanite (Troup and Hutton, 1964) has shown that Fe^{3+} is partitioned between the four nonequivalent octahedral sites in the ratio 4:1:1:0·1, and similar work on andalusite (Holuj *et al.*, 1966) indicates that most of the Fe^{3+} occupies the octahedral Al_I site, with a small but not negligible proportion in the five co-ordinated Al_{II} position. Absorption spectra of viridines (Strens, unpublished) confirm that Mn^{3+} is confined to the octahedral site.

The observation that the Fe_2O_3 contents of andalusite and kyanite formed under similar conditions are approximately equal implies that

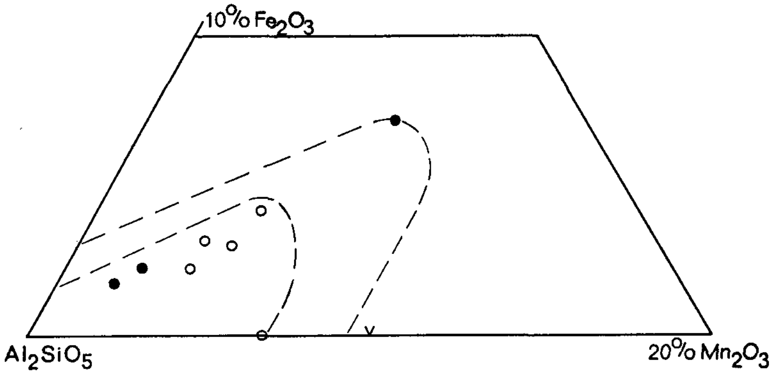

FIG. 1. Compositions of some minerals in the Al–Fe–Mn andalusite system: ○ analysed viridines; ● viridine compositions determined optically using the relation $n \parallel b = 1{\cdot}624 + 0{\cdot}33(Fe,Mn)^{3+}$, and plotted at Fe:Mn = 1:1. Calculated 500° and 630° C envelopes are shown.

solid-solution effects on the andalusite–kyanite reaction will be small, but the low Fe_2O_3 content of sillimanite means that kyanite and andalusite will be stabilized into the sillimanite field, creating zones of andalusite+sillimanite and kyanite+sillimanite. In the case of viridine, containing up to 15 % $(Fe, Mn)_2O_3$, wide zones of viridine+kyanite should form.

Experimental determination of these relationships would pose formidable problems in view of the high precision required in (P, T) measurements, the very slow reaction rates, and the necessity for buffering. Even crude calculations of the effect of impurities on the stability fields are therefore useful, and these calculations must be referred to the univariant lines if they are to remain valid in any future revision of the phase diagram.

Calculation of solid-solution effects. Consider a point on the univariant line separating the fields of andalusite and sillimanite, for which $\Delta G_{A \to S}$ is zero; on adding hematite and quartz to the system, equilibria of the following type are set up:

$$Al_2SiO_5(A) + Fe_2O_3 + SiO_2 \rightleftharpoons (Al_{1-x}Fe_x)AlSiO_5(A).$$

If solid solution is ideal (and this is usually a reasonable assumption for dilute solutions), the Gibbs free energy (G) of the andalusite has been *lowered* by $T\Delta S_c$, where ΔS_c is the configurational entropy of mixing of the Fe and Al, and has been *raised* by $\Delta H.x$ where x is the mole fraction of $FeAlSiO_5(A)$, and ΔH its enthalpy of formation by the above reaction. Making the minor assumptions that the volume and non-configurational entropy changes are not affected significantly by small iron contents, and that the configurational entropy is given by: $\Delta S_c = R\sum_i(x_i \ln x_i)$, the free energy change of the reaction, i.e. the stabilization of an andalusite solid solution relative to pure andalusite or sillimanite is: $\Delta G = \Delta H.x - T\Delta S_c$. When the andalusite is saturated with $FeAlSiO_5$, i.e. in the presence of excess hematite and quartz,

TABLE I. *T–x* parameters used and results of calculations

Andalusite	0·035Fe^{3+} @ 773° K	ΔH = 6·7 kcal/mole $FeAlSiO_5$
Sillimanite	0·015	8·0
Kyanite	0·04	6·5
1:1 viridine	0·20$(Fe,Mn)^{3+}$	4·9
Mn-viridine	0·15Mn^{3+}	4·3

Limiting (L(2)) and most stable (M) compositions

		327° C	427°	527°	627°	727°	827°
Kyanite	L(2)	0·013	0·026	0·045	0·070	0·100	0·130
	M	—	0·010	0·019	0·029	0·039	0·050
	$-\Delta G_M$	2	13	27	47	75	111
Sillimanite	L(2)	—	—	0·018	0·031	0·047	0·069
	M	—	—	0·007	0·012	0·019	0·026
	$-\Delta G_M$	1	3	9	20	35	56
Andalusite	L(2)	0·016	0·028	0·046	0·068	0·094	0·135
	M	0·005	0·010	0·016	0·023	0·034	0·045
	$-\Delta G_M$	2	11	23	43	68	101
1:1 viridine	L(2)	0·09	0·15	0·22	0·30	0·37	0·44
	M	0·03	0·06	0·09	0·13	0·15	0·18
	$-\Delta G_M$	35	80	140	215	310	410
Mn-viridine	L(2)	0·076	0·116	0·162	0·213	0·260	0·314
	M	0·035	0·048	0·064	0·080	0·100	0·120
	$-\Delta G_M$	26	60	103	152	213	280

Calculated maximum widths of divariant zones (in kilobars)

	327° C	427°	527°	627°	727°	827°
$A+K$	0·00	0·01	(0·02)	(0·03)	(0·04)	(0·06)
$A+S$	(0·05)	(0·23)	0·36	0·59	0·85	1·15
$S+K$	(0·01)	(0·08)	0·13	0·19	0·29	0·40
$K+V(1:1)$	0·19	0·38				
$S+V(1:1)$	(0·85)	(1·92)	3·3*	5·0*	7·3*	9·3*
$K+V(1:1)$	—	—	0·55	0·35	0·25	0·15

* exceeds width of sillimanite field; ( ) metastable reaction

ΔG is zero, and: $\Delta H.x = T\Delta S_c$. Knowing x for one T, ΔH can be calculated, and once this is known $\Delta H.x$, ΔS_c and hence ΔG for the above reaction can be calculated for all (T, x). Similarly, the stabilization of sillimanite and kyanite solid solutions relative to $Al_2SiO_5(S, K)$ can be calculated, and the stabilizations of (A, S, K) solid solutions relative to each other can then be found by subtraction.

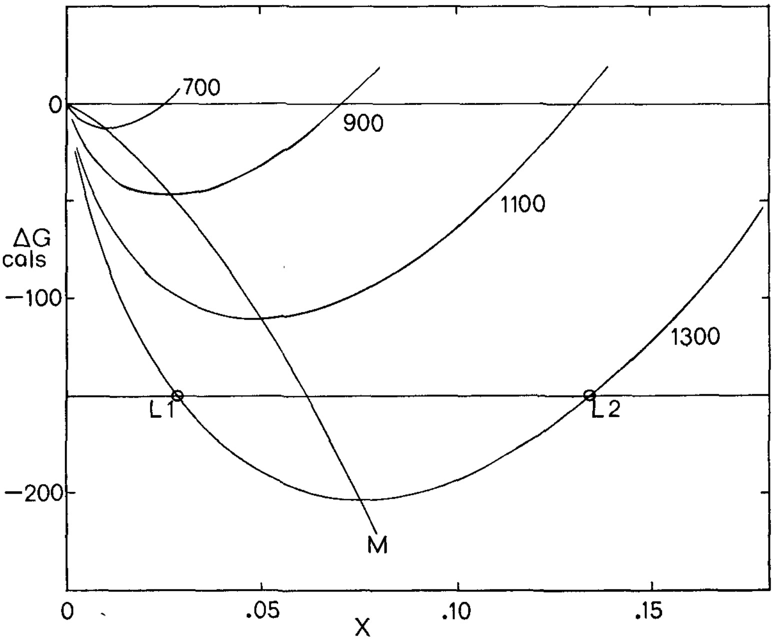

FIG. 2. Variation of ΔG for the reaction $Al_2SiO_5(A)+Fe_2O_3+SiO_2 \rightleftharpoons (Al,Fe)AlSiO_5(A)$ with temperature and composition on the join kyanite to hematite plus quartz, showing the trend of compositions of maximum stability (M), and also the upper (L(2)) and lower (L(1)) limiting compositions at 1300° K and a pressure in the sillimanite field such that (pure) kyanite is destabilized relative to (pure) sillimanite by 150 cal/mole. The stable assemblages are: $x <$ L(1), kyanite+sillimanite; L(1) $< x <$ L(2), kyanite; L(2) $< x$, kyanite+hematite+quartz.

Values of T and x were estimated from analyses of minerals for which paragenetic data were available (table I). The justification for this procedure is that only a relatively narrow range of values of T and x give results that are consistent within themselves and also compatible with petrological observation.

Stabilizations were calculated by computer at intervals of 0·01 to 0·05 x and 50° in T, and plotted (fig. 2). From these plots, it was

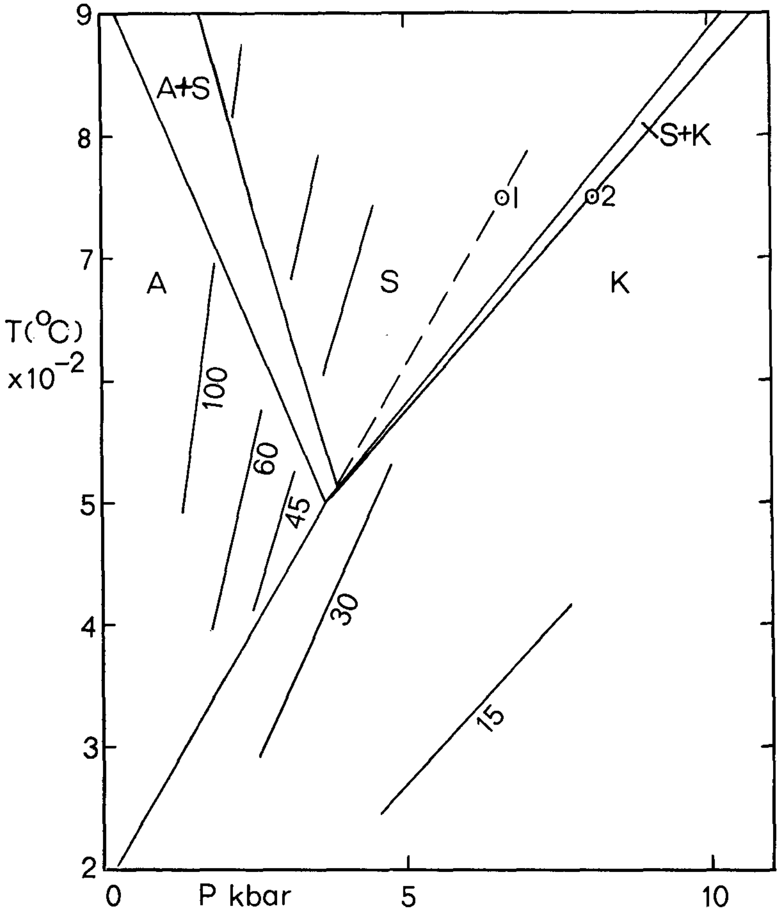

FIG. 3. Suggested form of P–T diagram showing the effect of Fe^{3+} on the stability fields of andalusite, sillimanite, and kyanite in the presence of excess quartz and at an oxygen partial pressure within the hematite field. Geothermal gradients less than about 40°/km do not intersect and andalusite field. The field of andalusite+kyanite is too narrow to be shown. 1 and 2 are Newton's (1966*a*, *b*) points. *A*—andalusite, *S*—sillimanite, *K*—kyanite.

possible to locate the lower (L(1)) and upper (L(2)) limiting compositions and the composition of maximum stability (M) at any given temperature and pressure (fig. 3). The width of the divariant zones was then found from: $\Delta P = \Delta G/24\Delta V$, where the factor of 24 converts from cm^3 kilobars to calories. To simplify the calculation, all iron was assumed to occupy one position. The errors thus introduced into the calculation of ΔS_c and ΔH for kyanite and andalusite cancel to a first approximation.

The viridine system. Three factors contribute to the extensive range of solid solution in the viridines: first, the configurational entropy is larger for a three-component than for a two-component mixture; second, Mn^{3+} is stabilized in the tetragonally distorted octahedral site in andalusite thus reducing ΔH, and third, the presence of the large Mn^{3+} ion apparently facilitates the entry of Fe^{3+} (fig. 1). For the purposes of calculation it will be assumed that 20 % of octahedral aluminium can be replaced by a 1:1 mixture of Fe^{3+} and Mn^{3+} at 500° C, whilst Fe^{3+} alone enters sillimanite and kyanite. The results are shown in fig. 4.

The calculated stabilizations are maximum values, for there is some mixing of Fe^{3+} and Mn^{3+} in the oxide bixbyite $(Fe,Mn)_2O_3$, and there are also indications of clustering, i.e. partial ordering into (Fe,Mn) and (Al) rich domains, which would reduce the configurational entropy. At large $(Fe,Mn)^{3+}$ contents the assumptions of ideality, and of negligible effect of solid solution on volume and non-configurational entropy changes will also start to break down. Nonetheless, the calculated phase diagram appears to be in reasonable agreement with petrographic observations (cf. Heinrich and Corey, 1959).

Metastable growth. Although some details of the phase diagram remain to be determined, it is now clear that all the polymorphs possess true stability fields, and that earlier suggestions that andalusite formed metastably (Weill and Fyfe, 1961) were incorrect.

In the presumed absence of extreme differences between the rates of growth of the stable and metastable phases, the most important condition to be satisfied if a mineral is to grow metastably over a wide P–T range (as opposed to persisting metastably after formation) is that nucleation of the stable phase should be suppressed, whilst nucleation of the metastable phase simultaneously occurs, and that this state should persist over the time available for reaction, which might be of the order of 10^7 years in regional metamorphism.

Classical nucleation theory (Fyfe, Turner, and Verhoogen, 1958; McLean, 1965), which provides a reasonable model for the nucleation of perfect crystals from solution, suggests that such a situation could easily arise. However, nucleation from solution is unlikely to be the predominant mechanism in metamorphic rocks, and both the nuclei and the reacting crystals of metamorphic minerals are imperfect, containing dislocations of thermal and mechanical origin. Under these conditions, rapid non-classical nucleation occurs through the mechanism of annealing recrystallization (McLean, 1965).

An approach to classical conditions is suggested by the occurrence in some mineral veins of a small number of large crystals, apparently

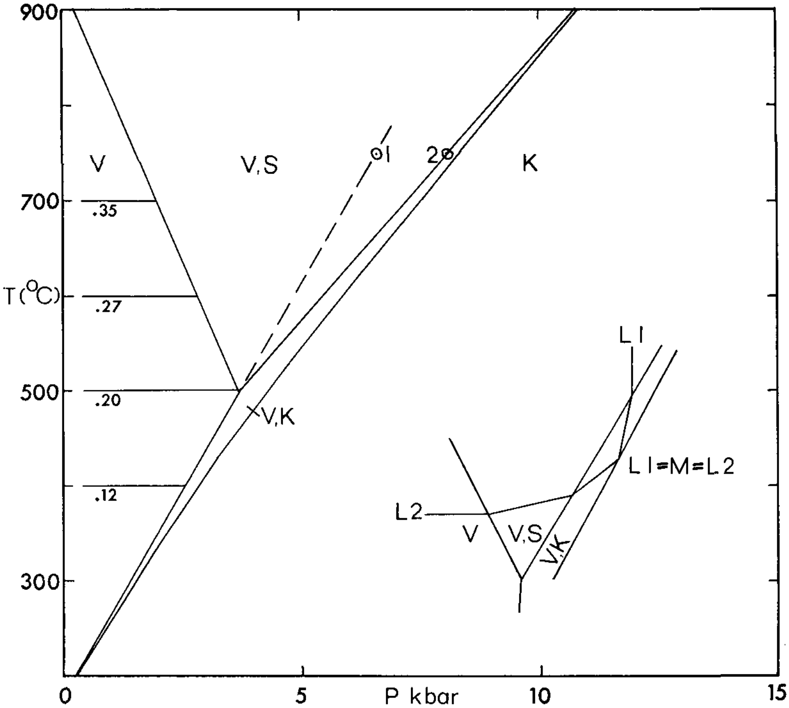

FIG. 4. Suggested form of P–T diagram showing the effect of (Fe,Mn)$^{3+}$ in 1:1 ratio on the stability fields of the Al_2SiO_5 minerals, in the presence of excess quartz and at an oxygen partial pressure within the Mn_2O_3 field. *V*—viridine. *Inset.* The line L(1)–L(2) is one of constant (Fe,Mn)$^{3+}$ content, originating in the andalusite field as the locus of (P, T) points for which x = L(2), it is 'refracted' by the A/S and S/K reactions, ultimately reaching the boundary of the viridine field at the point at which x = L(1) = M = L(2), when it is 'reflected' as a line on which fall all (P, T) points for which x = L(1).

formed over a long period of time by deposition from solution: such examples imply a very low rate of nucleation. By contrast, conditions in the shearing squeezer, in which reaction rates are very high (Bell, 1963) should be ideal for rapid non-classical nucleation and for rapid growth by grain-boundary diffusion.

Conditions in metamorphic rocks should lie between these extremes, but the relative ease of nucleation is attested by the occurrence of abundant crystals of phases that are known to nucleate only with great difficulty in unseeded hydrothermal runs, e.g. epidote, anthophyllite, and 14 Å chlorite. In the case of the Al_2SiO_5 minerals, marked structural similarities lead to easy epitaxial nucleation, and oriented overgrowths and intergrowths of these minerals are very common. In addition, the Al_2SiO_5 minerals may nucleate on other phases such as staurolite and biotite (Chinner, 1961), or on their own detrital grains, which are common in sedimentary rocks.

It seems reasonable to conclude that extensive metastable growth of metamorphic minerals in general, and of the Al_2SiO_5 minerals in particular, is improbable. This is not necessarily true of thermal metamorphism, in which heating is faster and of shorter duration, and mechanical generation of dislocations is probably less important. However, the small entropy difference between andalusite and sillimanite implies that their free energy curves lie within 1 calorie of each other over a temperature interval of about 5° C, and they will therefore grow simultaneously over a significant temperature range if even small supersaturations develop during metamorphism.

Metastable persistence of Al_2SiO_5 *minerals.* In considering the extent to which metastable persistence is likely to occur in this system, a sharp distinction must be drawn between two possible reaction mechanisms, one involving solution of the unstable phase and deposition of the stable phase from aqueous solution or silicate melt, and the other the solid-state reaction involving the diffusion of silicon and aluminium ions through the structure.

For the first type of reaction, Newton (1966*a*, *b*) observed growth rates of 5 to 10μ in 48 h at 750° C and 15 kb, in hydrothermal experiments on kyanite. Although growth and dissolution will be slower at the lower pressures and temperatures of regional metamorphism, and diffusion will be slower in a compact rock than in a loosely packed experimental charge, such rates seem adequate to produce reaction of millimetre-sized crystals of Al_2SiO_5 minerals in geologically very short times. Activation energies for this type of process are typically of the order of 20 kcal/mole; for example, Kusnetsov (1965) found ΔH_{act} of 17·5 and 32·0 kcal/mole for deposition on the $\{11\bar{2}0\}$ and $\{10\bar{1}1\}$ faces of corundum, and Weill and Fyfe (1964) found 16·5 and 14·5 kcal/mol respectively for solution and deposition on the $\{0001\}$ face of quartz.

A second possibility arises when the unstable phase becomes armoured by a layer of the stable phase, and also in dry systems. Reaction then requires migration of Al^{3+} and Si^{4+} ions through the structure, with an activation energy of the order of the Si–O or Al–O bond energies, e.g. McKie and McConnell (1963) found an activation energy of 74 kcal for Al–Si ordering in albite. It seems reasonable to conclude that long-term metastable persistence of Al_2SiO_5 minerals will be very common in dry rocks, but relatively rare in wet systems in the absence of armouring.

Discussion

An accurate experimental determination of the stability fields of the Al_2SiO_5 minerals by a direct method, although highly desirable, may be difficult to achieve, especially at low temperatures and pressures. However, the reactions seem well suited to study by a weight-change method (Weill, 1963). Direct determination of solid-solution effects is still more difficult, and unlikely to be undertaken experimentally, although the present calculations could be refined considerably if data were available on the iron contents of andalusite, sillimanite, and kyanite grown in equilibrium with hematite and quartz at known temperatures and pressures. This would remove much of the uncertainty in the assumed T–x values, and would also test the assumptions regarding ideality and the effect of solid solution on the volume and non-configurational entropy changes of the reactions, besides providing a possible geological thermometer.

Although the present calculations are approximate, and the results must be applied cautiously, they do indicate that quite wide bands of andalusite+sillimanite and sillimanite+kyanite can be produced in natural systems containing small amounts of Fe_2O_3. Another possible effect is the growth of sillimanite in iron-poor bands and kyanite or andalusite in iron-rich bands in the same rock mass.

In view of the confused state of the literature on this subject, it is worth emphasizing first, that metastable growth and metastable persistence of a mineral that grew stably are two very different phenomena, and second, that a knowledge of the reaction and nucleation mechanisms is essential if valid conclusions are to be drawn about the relative importance of metastable persistence and metastable growth. If the present arguments are correct, extensive metastable growth of Al_2SiO_5 minerals is improbable, and most of the polyphase assemblages are accounted for by a combination of metastable persistence and solid solution effects, with simultaneous growth of sillimanite and andalusite over a restricted (P, T) range as an additional possibility if slight supersaturation occurs.

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