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TRANSITION-METAL CONTENTS OF Al_2SiO_5 POLYMORPHS

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ABSTRACT. Electron-probe measurements of minor elements in the range Na-Fe of natural andalusite, kyanite, and sillimanite indicate that (viridine excepted) the only elements occurring in amounts greater than 0.01 percent are Ti, V, Cr, Fe; of these the only metal occurring regularly in amounts greater than 0.2 percent is Fe, although Cr in eclogite and glaucophane-schist kyanites may exceed this value. Fe contents are generally higher in Al_2SiO_5 minerals whose paragenesis suggests higher PO_2 of formation, the highest recorded in this study, 1.6 percent, being of a kyanite from a hematite-bearing schist. In Glen Clova, the Fe content of kyanite increases steadily with increasing Fe^{3+}/Fe^{2+} ratio in the host rock.

Abrupt spatial variation of Fe content across aluminum silicates indicates lack of equilibrium, probably caused by diffusion control of chemical supply during growth. Nonetheless a detailed study of the Fe contents shows generally consistent distribution patterns between coexisting polymorphs which may represent an approach to equilibrium. For coexisting andalusite-kyanite and kyanite-sillimanite pairs, ranges of Fe content generally overlap, the median values being higher for andalusite than for coexisting kyanite, and lower for kyanite than for coexisting sillimanite. It is argued that in regional environments any influence of Fe^{3+} on the occurrence of an aluminum silicate in the stability field of another is probably overshadowed by other effects—in particular the metastable persistence of one polymorph after a change in pressure-temperature conditions.

INTRODUCTION

Despite the obstacles and pitfalls which have beset experimental determination of the stability fields of kyanite, andalusite, and sillimanite, the aluminum silicate system remains as one of great potential value in the geothermometry and geopiezometry of metamorphic rocks; with the recently renewed activity and interest in this system, it seems likely that in the not too distant future an equilibrium phase diagram will be available (Fyfe, 1967). The applicability of such a diagram to the interpretation of natural aluminum silicate occurrences will, however, be dependent *inter alia* on the extent to which natural polymorphs depart from the ideal Al_2SiO_5 composition. As yet, little reliable information on this dependence has been published. Gravimetric and spectrographic analyses are indeed available in the literature; many of these must, however, be suspect, for unseparated inclusions in an Al_2SiO_5 mineral concentrate may completely mask the minor elements present. Thus Jakob's (1937) premature suggestion that alkalis are an essential constituent of kyanite was based on chemical analyses of kyanites now thought to have been contaminated by sericitic alteration products. Henriques (1957) was able to show with spectrochemical analyses that the alkali content of kyanites is less than 0.06 percent, but the separation procedure was very tedious and unsuited to routine study.

The advent of electron-probe X-ray emission analysis permits rapid and accurate analyses of minor elements in selected small volumes. Minor element contents of kyanite, andalusite, and sillimanite were reported in abstract by Corlett and Smith (1964), and this paper extends the study

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to coexisting aluminum silicate pairs from a variety of petrological environments.

ANALYTICAL METHODS

Individual grains were mounted in epoxy cement contained in cylindrical holes of brass discs. A paste of ¼-micron diamond powder was used for the final polish.

Thin sections were prepared either by the procedure described by Smith (1965) in which the section was thinned after one surface had been polished or by polishing of a normal thin section after removal of the cover slip. The former procedure yields flatter surfaces with less "plucking" of weakly-held inclusions, but the latter procedure was satisfactory for this study since the K spectra of the transition metals are absorbed only slightly before escaping from the specimens. Indeed, test measurements of an *unpolished* surface from a normal thin section showed errors of only a few percent in spite of the rough surface remaining from the coarse carborundum powder used in the final grinding.

Analyses were made on an Applied Research Laboratory microprobe using a 2 to 10 micron beam spot. Initial search for minor constituents of the mineral grains was made using 25KV and 0.4 to 1.0 microamps of specimen current. A wavelength scan from 3.8 to 1.4A with a LiF detecting monochromator using a potentiometric recorder permitted detection of elements from K to Ni at the 0.01 wt percent level. Counting at selected wavelengths permitted detection of lower concentrations in the range 10 to 100 ppm but was rarely used. Elements found in the initial scan usually were measured quantitatively by counting at selected wavelengths if at concentrations over 0.1 percent, or from area on the potentiometric scan if at concentrations below 0.1 percent. Since the early work on the specimens from the mineral collection showed significant concentrations of elements in the range Ni-K only for Fe, Cr, and Ti, analyses of specimens from the thin sections were confined to these three elements. Such analyses were made by counting at peak wavelengths followed by careful measurement of the X-ray background. An olivine with 5.6 wt percent Fe was used as a reference standard for Fe (Smith, 1966; Turkevich specimen): a trivial efficiency-of-generation correction was applied according to the method of Smith (1965). For Cr and Ti, metal Cr and rutile were used as standards, and corrections (Smith, 1965) applied for efficiency-of-generation.

Elements lower in the Periodic Table, namely Na-Ar, were checked in detail only for the specimens from the mineral collection. Na and Mg were obtained by counting at appropriate wavelengths using a KAP monochromator crystal and a sealed Ar counter. Other elements were checked by scanning using an ADP crystal. In addition to the major elements of Al and Si, small concentrations of P (calibrated against apatite) were indicated in some specimens.

Measurement of the aluminum silicates in the thin sections met with many difficulties. Not only are many aluminum silicates altered, either

completely or partially, to mica and other minerals, but the formation of fluorescent X-rays from *outside* the region of primary excitation of X-rays results in a contribution from neighboring minerals to the total X-ray output. Alteration in the aluminum silicates was detected in three ways (a) in the original optical examination, (b) by examination of the cathodoluminescence, (c) by routine monitoring of the X-ray signals for Al and K. Sillimanite was often extensively altered to a mica with Fe content ranging from 0 to 10 wt percent. Most of the alteration product is muscovite, but that with higher Fe contents may be biotite or even muscovite-chlorite aggregates. In some specimens, the least altered areas were selected by examining the cathodoluminescence which was usually a dull blue for the sillimanite and absent for the mica. In these areas the mica-free regions were selected by absence of an X-ray signal for K. In a few specimens, no unaltered areas were found, but some areas were almost K-free. For these areas, graphs were prepared of the K versus Fe content, and the Fe content of the sillimanite estimated by extrapolating to K = 0. Of course, these measurements are of lower accuracy. No measurements of *any* aluminum silicate were made unless the X-ray signal for Al was consistent with Al_2SiO_5. Such caution is valuable for fine grained specimens in which corundum showing red cathodoluminescence may be mistaken for kyanite.

The importance of fluorescence error in the analysis of minor elements has been discussed by Smith (1965) on the basis of work by S. J. B. Reed, J. V. P. Long, and others. Since Fe was the principal minor element measured in the thin sections, analyses were made deliberately as far away as possible from Fe-rich impurities, principally hematite and mica. This was especially difficult for the kyanites from Glen Clova, which contain large inclusions of hematite, and for the sillimanites altered to mica. Not only may there be a sampling bias if the true composition of the aluminum silicate depends on proximity to an Fe-rich impurity, but there will be a systematic error causing indicated compositions to be too high. Crude estimates suggest that even in the Glen Clova kyanites, the systematic error is not greater than 0.1 wt percent Fe and is usually less than 0.02 wt percent; this is not sufficient to affect any of the conclusions of this paper. For many specimens the error is not greater than 0.02 wt percent Fe. The accelerating voltage was reduced to 15KV for the analyses of thin sections.

An estimate of the amount of fluorescence was obtained from the Cu and Ni analyses of the mineral grains (Smith, 1965, p. 862). Although there is little or no Cu and Ni in aluminum silicates, weak X-ray signals corresponding to 0.00 to 0.05 wt percent were obtained by X-ray fluorescence from the brass holders typically 100 microns away from the place of electron impact. Since the fluorescent yield for Fe is less than for Cu and Ni, these measurements provide a maximum value; of course, a correction must be made for distance, solid angle, and Fe content of the fluorescing impurity.

The cathodoluminescence was quite variable in color and in intensity from one polymorph to another, from one rock specimen to another, and sometimes from place to place in a single grain. Undoubtedly valuable petrogenetic conclusions could be derived from a detailed study analogous to the studies made by Long and Agrell (1965) and Smith and Stenstrom (1965) for other minerals. Only qualitative measurements were made in the present work; colors were estimated by eye.

METAL CONTENTS OF INDIVIDUAL POLYMORPHS

Since the magnitude of the effect of foreign metals on the stability fields of kyanite, andalusite, and sillimanite will depend on the distribution ratio of such metals between the polymorphs, attention was directed mainly to rocks in which two polymorphs coexisted. Measurements on individual polymorphs were, however, undertaken to give an idea of the significant substituents, and are tabulated in tables 1 and 2.

Table 1 shows all minor elements detected in the range Na-Fe for specimens selected from mineral collections (Corlett and Smith, 1964) plus further measurements by C. R. Knowles and measurements on mullites studied by Agrell and Smith (1960). This does not provide a precise estimate of the typical ranges of the minor elements: the number of specimens examined is too small, and, furthermore, specimens in mineral collections tend to be biased toward large size and special provenance. Indicated elements are Na, P, K, Ca, Ti, V, Cr, Mn, and Fe. The concentrations of Na and K are spatially variable, and even when a discrete impurity is not visible, submicroscopic inclusions may be suspected. The concentrations of Ca and P vary simultaneously as would be expected for inclusions of apatite.

In all specimens but the mullites for which Na, K, Ca, or P were located, there were areas in which these constituents were absent at the 0.01 wt percent level: consequently it is claimed that these elements do not occur in the structure of aluminum silicates, at least at the detection level. In the mullites Rβ 58480 and 70718, small amounts of calcium were detected in regions apparently free of apatite inclusions. We could not decide whether the calcium is in the crystal structure, or whether it is spurious, arising merely from secondary fluorescence.

White and White (1967) as part of a study of the color of kyanite detected the following concentrations in 7 specimens using microprobe methods: Ti = 0.002-0.12; V = 0.006-0.01; Cr = 0.003-0.015; Fe = 0.09-0.70; Mn = 0.01 for the only specimen measured. No attempt was made in this study to detect concentrations below 0.01 wt percent.

Crystal-chemical speculations based on the known structures of the aluminum silicates are not sufficient to lead to definitive assignments of all the minor elements to specific sites. While much of the transition metal content should substitute for Al in octahedral coordination, some of the Ti might substitute for Si, and some of the Fe might substitute for tetrahedral Al in sillimanite and trigonal pyramidal Al in andalusite. Techniques utilizing electron paramagnetic resonance, Mossbauer gam-

TABLE 1

Microprobe analyses (weight percent metal) of mineral specimens

	Locality	Color	Ca	Ti	V	Cr	Fe
			Kyanites				
M6047	Litchfield, Conn.	blue/green	...	0.05	...	0.01	1.0
M6047	Litchfield, Conn.	green	...	...	...	0.01	1.1
M7151	Sugar Loaf Mtn., N. C.	blue	...	...	0.01	...	0.07-0.13
M7976	Yuma Co., Ariz.	turquoise	...	...	...	...	0.5-0.7
M9128	Yancy Co., N. C.	green	...	...	...	0.01	0.7-0.9
M14279	Wyndham, Maine	blue	...	...	0.01	0.01	0.1-0.3
M16554	Tyrol, Austria	clear	...	...	0.02	...	...
M16561	Tyrol, Austria	yellow	...	...	0.01	...	...
M17724	Nev.	green	...	...	...	...	0.3-0.6
M18457	Lapsa Bura, India	white	...	...	0.01	0.02	0.01-0.04
			Sillimanites				
M2240	Custer, S. Dak.	gray	...	...	0.01	0-0.02	1.0
M1104	Norwich, Conn.	brown	...	...	0.02	...	0.7
79818	Siebengebirge, Germany	white	...	...	0.03	0.01	0.13
3076	Connecticut	white	...	...	0.02	0.02	0.6
M627	Lisenz, Austria	white	...	...	...	...	0.1
41483	Williamstown, South Australia	white	...	...	...	...	0.26
			Andalusites				
M9122	Orville, S. Dak.	gray-pink	...	...	...	...	0.16
M15228	Mocalro, Calif.	white	...	...	0.02	...	0.45
M618	Brainsdorf, Saxony	gray	...	...	...	...	0.04-0.12
			Mullites				
70718	Argyll, Scotland	...	0.02	0.5	...	0.02	1.9-2.1
Rβec	Electrocast brick	...	...	0.6	...	...	0.01
Forster	Synthetic	...	...	...	...	...	...
58480	Arc fusion	...	0.03	0.8-2.4	...	0.01	0.02-0.05
Rβ	Synthetic	...	0.05	0.02	...	...	...
76402	Mull, Scotland	...	n.d.	n.d.	n.d.	n.d.	0.28

No Na, Mg, P, K, Sc, or Mn was detected in any of the above specimens at the 0.01 percent level.

Three dots indicate not observed at 0.01 percent level; n.d., not determined.

Most crystals are inhomogeneous, and the ranges of composition may be too narrow.

Specimens prefixed M are from University of Chicago Mineral Collection; the others are from the Harker Collection, Department of Mineralogy and Petrology, Cambridge University.

ma-ray resonance of Fe^{57}, and optical absorption are needed to resolve the uncertainty. Even these techniques will be difficult to apply as may be seen from the paramagnetic resonance study of Hutton and Troup (1964) of Cr^{3+} in kyanite. Although three types of sites were found to be occupied, assignment to specific positions out of the six possible sites was not made. White and White (1967) claimed to rule out occupancy of Si sites by Ti^{4+} in kyanite on the basis of crystal chemical considerations and from the frequency of the absorption band; furthermore they supposed that the Ti ions were clustered in order that they could show a collective electron behavior. In future years, much work can be expected on assignment of minor elements in aluminum silicates; until this has been completed, it seems wise to be cautious in discussing the crystal-chemical basis of minor element distribution in the aluminum silicates.

Table 2 lists all analyses of aluminum silicates from rock thin sections in which Mn, Cr, and Ti were recorded in amounts greater than 0.01 percent. Mn is generally less than 0.01 percent, Cr is generally present in amounts less than 0.1 percent, and Ti in amounts barely exceeding the lower limit. It is clear that iron is the only significant substituent, and that Mn, Cr, and Ti may be ignored as significant factors in modifying stability fields. Before discussing the role of iron however, some features may be observed:

Andalusite.—The low transition-metal contents of andalusites in tables 1 and 2 may seem surprising in view of many published analyses showing high iron contents (2.04 percent Fe; MacDonald and Merriam, 1938) or high Mn and Fe contents (up to 7.66 percent Mn^{3+} and 6.71 percent Fe^{3+} in viridines; Deer, Howie, and Zussman, 1962). High Mn contents of andalusite rather than of kyanite or sillimanite have been attributed by Strens (1965) to the existence in andalusite of tetragonally distorted AlO_6 sites which stabilize the Mn^{3+} ion. Such high contents do, however, appear to be correlatable with rather unusual conditions of formation. Ferriferous andalusites occur in pegmatites, and the viridines are usually associated with oxides of manganese and iron of high oxidation state, suggesting a high P_{O_2} of formation. Under the physical conditions accompanying the formation of most crystalline schists the transition-metal content of andalusites is clearly low.

Many andalusites show an abrupt spatial variation in cathodoluminescence from light to dark blue. The variation could not be correlated with other phenomena such as variation in pleochroism or arrangement of inclusions, and its origin is unknown. The more spectacular variation in pleochroism seen in so many andalusites was, however, readily correlated with Fe and Ti content. Thus andalusites from the gneiss of the Buck of the Cabrach, Aberdeenshire, zoned irregularly with a strongly pleochroic core and a colorless rim, gave the figures (table 2):

	Fe	Ti
Pleochroic core:	0.26	0.035
Colorless rim:	0.17	0.010

The more strongly pleochroic areas display a slightly lower birefringence.[1]

Kyanite.—Although kyanite has not shown the high transition-metal substitution achieved by the pegmatitic and viridine andalusites, rock-forming kyanites and andalusites generally have similar composition ranges, the Ti content of kyanite being somewhat lower. Individual kyanites frequently show considerable areal irregularity of Fe and Cr; this irregularity is only rarely a concentric zoning and may reflect the

[1] Hollister and Bence (1967), after supporting these conclusions, proceeded to presume that the variation in composition results from differential growth rates along, and normal to, the c axis. These variations are, however, frequently too irregular for such a hypothesis to be applicable universally, and in some localities (for example, the Ardara Aureole, Akaad, 1956, fig. 2) the andalusites are clearly the product of two stages of growth. We do not imply that their hypothesis is untenable for the *specific* specimens studied by them.

TABLE 2

Ti, Cr, and Fe contents (weight percent metal) of Al_2SiO_5 polymorphs from metamorphic rocks

Locality and environment	Ti	Cr	Fe
	Kyanites		
Slack Burn, Kincardineshire	...	...	0.5-0.6
Glen Urquhart, Inverness shire	...	0.03-0.05	0.11-0.13
New Hampshire	0.01	0.07-0.09	0.21-0.30
Barnes, Donegal, 71837A			
red luminescence	0.00-0.01	0.034-0.04	0.12-0.19
purple luminescence	0.01	0.016-0.026	0.12-0.22
Proclamation Island, Enderby Land, 33671	...	0.06-0.23	0.26-0.35
Saastal, Valais, 93648, glaucophane schist	...	0.10-0.20	0.10-0.12
Dill Township, Ontario	0.01	0.07-0.09	0.21-0.30
Williamstown, South Australia, 54446, metasomatic	...	0.05	0.09-0.18
66154, Silberbach, Bavaria, eclogite	...	0.25	0.03-0.13
	Sillimanites		
Ardveen, Donegal	...	0.02	0.24-0.42
Williamstown, South Australia, 54446, metasomatic	...	0.04-0.10	0.13-0.21
Narin, Donegal	0.01	0.14-0.40	0.18-0.31
Laughanures, Donegal	0.01	0.06-0.08	0.10-0.15
	Andalusites		
Hill of Cabrach, Aberdeenshire, 38240			
I pleochroic core	0.035	...	0.26
rim	0.010	...	0.17
II pleochroic core	0.060-0.065	...	0.32-0.57
rim	0.013-0.032	...	0.20
27979, very irregular dark blue, light blue luminescence	0.01-0.06	...	0.2-0.4
Barnes, Donegal, 71837A	0.01-0.09	0.01-0.02	0.22-0.28
Proclamation Island, Enderby Land, 33671	...	0.04-0.29	0.24-0.31
Skiddaw, Cumberland, EM 1388	0.01-0.02	0.02-0.05	0.18-0.39
Shelton Property, Gaston County, N. C., 103473	0.05	...	0.91-1.24

texture of a preexisting mineralogy. Lamellar variations of luminescence are quite common (pl. 1). Since some of the lamellae are parallel to the traces of external faces they are either growth features or the result of chemical migration along cleavage cracks. In several specimens showing bright-red luminescence, zircon inclusions are surrounded by blue-luminescing haloes, an effect presumably due to radiation damage.

The relation between chemical substitution and petrological growth environment of kyanite is more clearly marked than for andalusite. Cr contents above 0.10 percent are found only in those metamorphic facies in which kyanite can appear in rocks of basaltic composition, namely, glaucophane schists and eclogites. Fe contents show a strong correlation with the Fe^{3+}/Fe^{2+} ratio of the environment. Table 3 gives the Fe contents of kyanites from Glen Clova (Chinner, 1960) and the FeO and Fe_2O_3 contents of their host rocks; kyanite Fe is plotted against rock $Fe_2O_3 \times 100/Fe_2O_3 + FeO$ in figure 1. If the rock oxidation ratio truly reflects the oxygen partial pressure prevailing at the time of kyanite formation, one may conclude (as might be expected if the iron is present as Fe^{3+}) that substitution of Fe for Al in kyanite is controlled by the oxygen partial pressure of the environment.

Sillimanite.—Although coarse prismatic sillimanite is common enough, most sillimanites studied by us were those coexisting with andalusite or kyanite and were thus of the finely fibrolitic variety, usually intimately intergrown with biotite. An overwhelming proportion of such seeming sillimanites showed high K contents and were clearly muscovite. It would seem that much of the sillimanite recorded by petrographers is in fact a muscovite pseudomorph in which compensation by overlapping crystals has reduced the apparent birefringence; this adds support to Chinner's (1967) emphasis of the role of K equilibria in the development or suppression of Al_2SiO_5 minerals in metamorphism. Such pseudomorphism severely restricted the choice of sillimanite specimens for measurement. Some specimens with patchy alteration were salvaged as described earlier, and the values denoted by (e).

COEXISTING POLYMORPHS

Fe contents of andalusite-kyanite and kyanite-sillimanite associations are given in tables 4 to 6. Most grains show a considerable range in Fe content, and the median (that is, that value that has equal numbers of measurements greater and less than it) is given in parentheses. For most specimens, several sets of measurements are given for pairs of crystals separated by less than a few microns. Typical pairs are illustrated in figure 2.

Whether any of the associations measured represents an equilibrium assemblage is a difficult question. Some (the kyanite-sillimanite and pseudomorphous andalusite-kyanite) clearly do not. The status of the others will be discussed in the appropriate places, but it can be said here that the argument is usually that a particular pair shows no evidence of disequilibrium. The wide range of Fe, often shown by an individual crystal

PLATE 1

A.

B.

Black and white reproduction of an Ektachrome color transparency of cathodoluminscence in kyanite from specimen 67575 from Burke Quadrangle, Vt. The luminescence is red, and the variation results more from changes of intensity than changes in hue. The inclusions shown as black in the key are either feldspar or Fe-rich minerals. A lamellar variation of intensity of luminescence occurs over the entire kyanite crystal: the lamellae are particularly narrow and sharp in area (a). There are additional intensity variations outlining wider areas with either planar or curved boundaries: (b) and (c) indicate particularly pronounced boundaries. It is tentatively suggested (see text) that the lamellar structure is a growth feature, whereas the broader areas may outline preexisting mineral grains now transformed to kyanite. Horizontal dimension corresponds to 200 microns.

TABLE 3

Fe contents of kyanites from Glen Clova, Angus

Rock no.	Rock FeO	Rock Fe_2O_3	Oxidation ratio	Rock MnO	Kyanite Fe	Median
83112	3.66	12.01	74.8	0.37	0.75-1.41	(1.15)
93697	2.29	6.66	72.3	0.17	0.81-1.43*	(1.0)
83117	4.57	8.01	61.2	0.38	1.07-1.31	(1.2)
83118	5.36	8.69	59.4	0.34	0.8-1.6*	(1.2)
83094	6.05	5.47	44.8	0.25	0.72-1.03*	(0.84)
83114	5.88	5.09	43.7	0.16	0.69-0.92	(0.76)
83121	6.56	4.28	37.0	0.14	0.74-0.90	(0.77)
83082	7.55	3.62	30.1	0.14	0.68-1.02	(0.83)
93698	5.73	2.65	29.4	0.19	0.38-0.89	(0.62)
83066	6.69	3.04	29.0	0.17	0.37-0.85	(0.52)
83153	5.90	1.23	18.8	0.12	0.13-0.26	(0.20)
83007	8.15	1.44	13.7	0.15	0.14-0.19	(0.16)

*See table 6 for more detailed data.

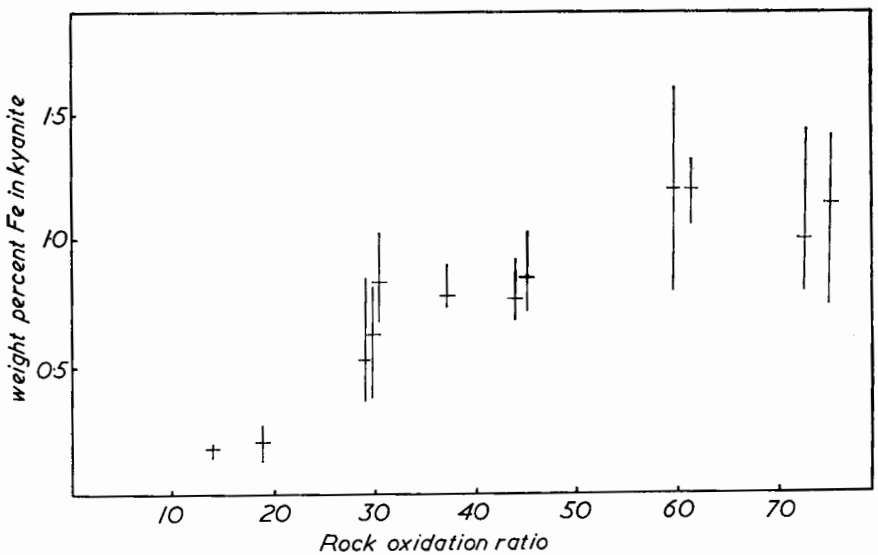

Fig. 1. Plot of Fe contents of kyanites from Glen Clova, Angus, against oxidation ratios $\left(\text{Mole}\frac{(Fe_2O_3 \times 100)}{(Fe_2O_3 + FeO)}\right)$ of host rocks. Lines show the range of measured Fe contents; horizontal dashes, the median.

in a completely irregular and unzoned manner, suggests that the distribution of Fe between two polymorphs is unlikely to provide a precise indication of attainment of equilibrium. Nonetheless, certain general patterns of Fe distribution are evident and may be discussed in terms of the individual pairs.

Andalusite-kyanite.—Occurrences of andalusite-kyanite were divided into two categories: coexisting, in which the two minerals occur together with no textural indication of disequilibrium; and pseudomorphous, in

which there is clear textural evidence that one is replacing the other. Typical examples of the two categories are illustrated in figure 2.

The coexisting andalusite-kyanite pairs (table 4) are predominantly from amphibolite facies environments: 103473, from Gaston County, N. C., in association with kyanite quartzites (Espenshade and Potter,

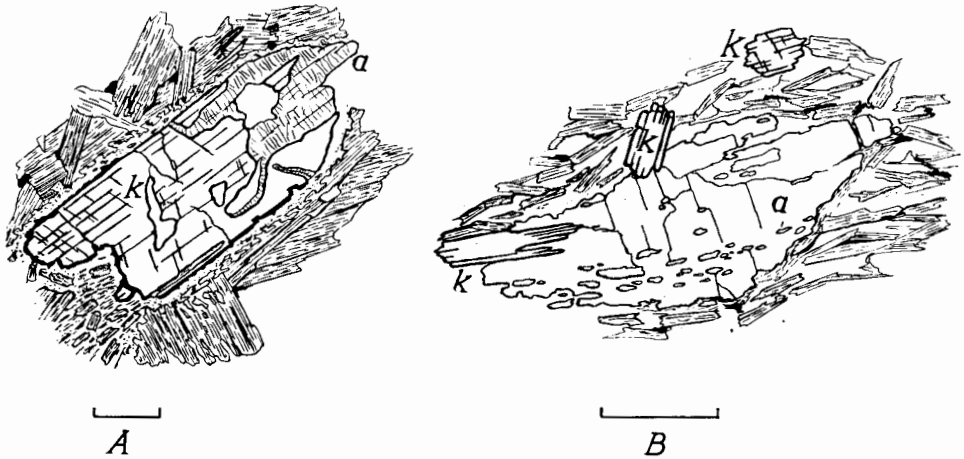

Fig. 2. Microdrawings to illustrate the usage of "coexisting" and "pseudomorphous" of this paper. A, pseudomorphous andalusite and kyanite. The kyanite (k), originally crystallized under amphibolite facies conditions, has been quenched during inversion to andalusite (a) aggregates when subjected to pyroxene hornfels facies conditions. 82937, Glen Clova, Angus. B, coexisting andalusite and kyanite. Small grains of kyanite (k) give no textural indication of instability in the presence of andalusite (A). 103473, Shelton Property, Gaston County, N. C. Scale line is 250 microns in each case.

TABLE 4

Coexisting andalusites and kyanites

Locality		Andalusite Fe	Kyanite Fe
Gaston County, N. C.			
103473*	(a)	0.91-1.24 (1.00)	0.46-0.69 (0.57)
	(b)	0.75-0.98 (0.90)	0.38-0.66 (0.61)
Barnes, Donegal			
71837*		0.22-0.28 (0.25)	0.12-0.22 (0.17)
Proclamation Island, Antarctica			
33671	(a)	0.24-0.32 (0.25)	0.26-0.34 (0.32)
	(b)	0.30, 0.32	0.33, 0.28
Boehl's Butte Quadrangle, Idaho			
103549**	(a)	0.11-0.19 (0.17)	0.09-0.14 (0.13)
	(b)	0.21-0.30 (0.25)	0.11-0.19 (0.16)

*Cr and Ti contents given in table 2.

**Cr and Ti less than 0.01 percent.

TABLE 5

Pseudomorphous andalusite and kyanite

Locality	Andalusite Fe	Kyanite Fe
Boehl's Butte Quadrangle, Idaho (ky → and)		
103544	0.18-0.23 (0.21)	0.22-0.30 (0.26)
103545 (a)	0.30-0.35 (0.32)	0.16-0.26 (0.20)
(b)	0.24-0.37 (0.30)	0.16-0.21 (0.18)
103546	0.30-0.44 (0.34)	0.20-0.30 (0.25)
103547	0.25-0.43 (0.33)	0.23-0.34 (0.28)
103548	0.25-0.38 (0.30)	0.20-0.24 (0.23)
Glen Clova, Angus (ky → and)		kyanite very irreg.
82937 (a)	0.20-0.27 (0.23)	0.08-0.26 (0.16)
(b)	0.23-0.31 (0.26)	0.12-0.20 (0.17)
(c)		0.04-0.24 (0.13)
Silvretta, Tyrolean Alps (and → ky)		
195312	0.12-0.16 (0.15)	0.05-0.40 (0.12)

Cr and Ti less than 0.01 percent.

1960); 71837, from the contact aureole of the main Donegal granite (Pitcher and Read, 1960); and 103549, from the anorthosite-schist complex in the neighborhood of the Idaho batholith (Hietanen, 1956, p. 12).[2] In these, some overlap of Fe contents is evident, but both the upper limits of precision (compare p. 98), but their reality is suggested by their sponding values for kyanite. The differences are, of course, close to the limits of precision (compare p. 000), but their reality is suggested by their general consistency. The exception is found in the only example for which one can be certain that the two polymorphs formed simultaneously: 33671, the pseudomorphed cordierites from Proclamation Island, Enderby Land, described by Tilley (1937). In this case, however, the ranges are so similar that the Fe contents for the two polymorphs must be regarded as essentially the same.

The pseudomorphous andalusite-kyanite pairs (table 5) are from three regions of polymetamorphism: Goat Mountain, Boehl's Butte Quandrangle (kyanite replaced by andalusite, Hietanen, 1956), Glen Clova, Angus (kyanite replaced by andalusite, Chinner, 1962), and the Silvrettagruppe in the Tyrol (andalusite replaced by kyanite, Spaenhauer, 1933). One would expect in polymorphous inversion that the minor-element composition of the original crystal would be equal to, or greater than, that of the replacing polymorph. Thus the higher Fe contents of the replacing andalusite in the Idaho and Angus examples indicate an accession of iron from the surrounding rock. With the exception of

[2] Many andalusites from this area pseudomorph kyanite (table 4). However, in this specimen from the north fork of the Clearwater River, there is no pseudomorphous relationship.

103544 and 195312, the values are comparable to those of the coexisting polymorphs of table 4, and it seems probable that during the pseudomorphing process some approach to local equilibrium between replacing and replaced polymorphs was achieved.

TABLE 6

Coexisting kyanites and sillimanites

Locality	Kyanite Fe	Sillimanite Fe
Glen Clova, Angus		
83094	0.72-1.03 (0.85)	0.1-0.3 (e)
83118 (a)	0.8-1.6 (1.2)	0.5-0.74 (0.59)
(b)	0.81-1.65 (1.1)	0.36-0.41 (0.38)
93697	0.81-1.43 (1.0)	0.5-0.7 (e)
Glen Esk, Kincardine		
94607 (a)	0.26-0.40 (0.32)	0.27-0.38 (0.35)
(b)	0.20-0.39 (0.29)	0.30-0.33 (0.32)
96367*	0.09-0.19 (0.14)	0.23-0.33 (0.30)
96435	0.3-0.5	0.38-0.5 (e)
96366	0.20-0.30 (0.22)	0.3 (e)
96644	0.11-0.34 (0.16)	0.19-0.29 (0.21)
Williamstown, South Australia		
54446* (a)	0.09-0.18 (0.11)	0.17-0.21 (0.19)
(b)	0.08-0.21 (0.11)	0.09-0.23 (0.18)
(c)	0.09-0.18 (0.11)	0.13-0.21 (0.17)
Burke Quadrangle, Vt.		
67575	0.10-0.16 (0.13)	0.15-0.27 (e)
67580 (a)	0.11-0.13 (0.12)	0.12-0.23 (0.18)
(b)	0.15-0.21 (0.18)	0.11-0.21 (0.16)
Boehl's Butte Quadrangle, Idaho		
103544 (a)	0.19-0.30 (0.24)	0.24-0.34 (0.27)
(b)	0.22-0.30 (0.26)	0.24-0.32 (0.27)
(c)	0.22-0.30 (0.25)	0.19-0.26 (0.22)

*Cr and Ti contents given in table 2. The remainder have Cr and Ti less than 0.01 percent.

Kyanite-sillimanite.—Fe contents of kyanite-sillimanite pairs are given in table 6. The occurrence of all kyanite Al in octahedral sites might lead one to predict from naive crystal chemical considerations that the Fe content of kyanite would be greater than that of coexisting sillimanites, but only in the Glen Clova pairs is this the case. Pairs from Glen Esk in the same amphibolite facies environment as and only 15 miles northeast of the Glen Clova gneisses (Chinner, 1960; Harte and Henley, 1966) show very similar ranges; medians for sillimanite are if anything higher than those for kyanite. Textural evidence (Chinner, 1961) strongly suggests that sillimanite formation postdated that of kyanite; composition of kyanites and sillimanites may thus reflect the partial oxygen pressures prevailing during the two episodes. Fe contents of kyanites from Glen Clova are greater than those of kyanites from Glen

Esk: this reflects the occurrence of the former in hematite-bearing rocks and the latter in hematite-free rocks. Fe contents of sillimanites from the two areas, however, are more nearly equal, suggesting that during the subsequent sillimanite-forming episode, oxygen partial pressures were more spatially equalized and less dependent on local assemblages buffered by high hematite contents.

The remaining pairs from Burke County, Vt., and Boehl's Butte, Idaho (from polymetamorphic environments, Woodland, 1963; Hietanen, 1956), and Williamstown, South Australia (a metasomatic aluminous deposit, Alderman, 1942), show similar features. The ranges in Fe content of kyanite and neighboring sillimanite overlap considerably, with the upper limit and median of the sillimanite generally somewhat higher. Although there is no certainty that any of these associations represent equilibrium, and one is close to the limits of precision, the general constancy of pattern of Fe distribution in the last three pairs suggests that they represent an approach to an equilibrium distribution under moderate pressures of oxygen.

TABLE 7

Coexisting andalusite and sillimanite

Locality	Andalusite Fe	Sillimanite Fe
Boehl's Butte Quadrangle, Idaho		
103544	0.18-0.28 (0.21)	0.24-0.32 (0.27)
Ross of Mull, Invernesshire		
43042 (a)	0.17-0.31 (0.23)	0.15-0.32 (0.24)
(b)	0.16-0.25 (0.23)	0.15-0.23 (0.18)

Cr and Ti less than 0.01 percent.

Andalusite-sillimanite.—Choice of specimens for the andalusite-sillimanite pair was limited by the ubiquitous alteration of fibrolitic sillimanite, but results were obtained (table 7) from two localities (Smith Ridge, Boehl's Butte Quadrangle, Hietanen, 1956; and the Ross of Mull, Invernesshire, Harker, 1939, p. 328). The Smith Ridge polymorphs may not have been strictly contemporaneous (compare discussion in Hietanen, 1956) but the Ross of Mull examples, with coarse sillimanite in oriented intergrowth with andalusite (Harker, 1939, fig. 172B), certainly were. As in the previously discussed pairs, spatial distribution of iron within individual crystals was irregular. The ranges for the two polymorphs overlap, and no significant partition of iron could be detected.

DISCUSSION

Compositional variation.—The abrupt and irregular variation of minor element concentration within individual polymorphs may have originated in several different ways.

In some andalusites, and in one example of kyanite, the variation is zonal and presumably arises from depletion in concentration of the particular element in the vicinity of the growing crystal, but in most examples the variation is too irregular for this mechanism to be tenable. Differential growth rates along different crystallographic directions has been suggested by Hollister and Bence (1967) to explain sectorial compositional variations in staurolite; none of the specimens examined in this study showed signs of the operation of such a mechanism.

The possibility was considered that compositional variation might be inherited from a preexisting mineralogy. However, from the pseudomorphous kyanites and andalusites it might seem that Fe ions can move rather rapidly through the Al_2SiO_5 structures—rapidly enough to allow near-equilibrium during the pseudomorphing process. It therefore seems unlikely that differences in Fe would persist through the longer period available for recrystallization during a regional metamorphic episode. Variation in iron content is thus likely to be a late stage effect, presumably arising from incomplete adjustment to changing activities of the relevant ions in the pore fluid, subsequent to the formation of the crystal.

Other possible cases of palimpsest mineralogies are provided by those specimens in which cathodoluminescence varies in a manner suggestive of ghostly relicts of an earlier fabric (pl. 1). Knowing the tendency of human beings to see that which is being sought, it seems wiser at present to make no claim that an earlier fabric can be revealed by variation in chemical composition and cathodoluminescence. Nevertheless, routine examination of suitable metamorphic minerals for cathodoluminescence may well produce clear-cut examples of earlier fabric relicts similar to those recorded by Smith and Strenstrom (1965) in carbonates.

Effect of foreign ions on the pressure-temperature fields of the aluminum silicates.—The disparity between the Fe and Mn contents of coexisting viridines and kyanites suggests widely divariant zones in which the two are stable. This does not pose a serious petrologic problem, however, for viridines require for their formation the rather rare combination of high proportion of Al_2O_3 to other rock constituents, high Mn:Fe, and a high P_{O_2}; furthermore, they are readily recognizable in hand specimen and thin section.

A more common petrologic situation is one in which two aluminum silicates have crystallized in pelites of low Mn:Fe under high oxygen partial pressures. Differences in Fe content between the two polymorphs may then be substantial (for example, Glen Clova, table 6), and some divariant coexistence may perhaps be expected, but such possible situations will always be betrayed by the presence of hematite.[3]

[3] Strens (1968), making assumptions on the limiting Fe contents of the three polymorphs in equilibrium with hematite and quartz, at an estimated 500°C, has calculated the effect on the Al_2SiO_5 phase diagram of saturating the phases in Fe^{3+} Al SiO_5. The divariant band of kyanite-andalusite coexistence is negligible, but (accepting Newton's (1966) phase diagram) andalusite-sillimanite and kyanite-sillimanite can coexist over greater ranges—at 700°C, 0.8 and 0.2 kb respectively.

It is clear, however, that for aluminum silicates crystallized under the relatively low oxygen partial pressures characterized by graphite and magnetite equilibria, partition of iron between two polymorphs is small, and divariant bands of coexistence negligible.

The possibility remains that Al_2SiO_5 structures may be stabilized—or at least that metastable nucleation may be enhanced—by the presence of small amounts of foreign ions (compare, Buerger, 1936). Pitcher (1965) cites several natural examples that might be used in support of such an argument. From the King's Mountain (Gaston County), N. C., Espenshade and Potter (1960) describe the occurrence of andalusite in pelitic schists and its absence from adjacent kyanite quartzites. In the aureole of the Main Donegal Granite, andalusite-bearing schists contain higher amounts of Fe and Mg relative to K and Al than do kyanite-bearing schists. More data on these occurrences are clearly required, although it does seem more likely that foreign-ion stabilization would lead to the coexistence of two or more polymorphs rather than the promotion of one at the expense of the other.

Establishment of foreign-ion stabilization as a significant petrogenetic factor would, of course, require very careful study of trace-element contents near the limits of detection and correlations of considerable complexity. At the present time disequilibrium seems to be a more likely interpretation of those cases where two polymorphs coexist in the localized environments of contact aureoles, veins, and pegmatites unrelated to, or in contradiction of, regional patterns of aluminum silicate distribution. The physical characteristics of such environments, involving steep thermal gradients in both space and time, and (in the case of many veins) direct deposition from solution, might be expected to favor metastable growth and not to deter metastable persistence; application of an Al_2SiO_5 phase diagram in such cases may be hazardous indeed.

In regional environments, however, confidence in the application of an Al_2SiO_5 phase diagram must depend on a regional distribution of aluminum silicate polymorphs consistent with Goldschmidt's mineralogical phase rule. This indeed appears to be the case in many regions: any two-phase bands intervening between one-phase divariant areas are of less extent than the precision to which they can be mapped.

Regional coexistence of two polymorphs introduces problems that must be approached *sui generis*. In the authors' opinion disequilibrium is the most probable cause, one phase remaining as a metastable relic from an earlier stage in a sequence of plurifacial or polymetamorphic episodes; if the intersection between the pressure-temperature trace of the geothermal gradient and the Al_2SiO_5 two-phase field boundary were a shallow one (as could be the case for andalusite-kyanite or kyanite-sillimanite) the thermal perturbation involved would not necessarily be great. The further possibility that much of the fibrolite which occurs with kyanite or andalusite in regionally metamorphosed rocks represents a faulty or disordered phase distinct from sillimanite cannot yet be ruled out.

Electron-diffraction studies of such fibrolites would seem to be the logical next step in this research.

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REFERENCES

Agrell, S. O., and Smith, J. V., 1960. Cell dimensions, solid solution, polymorphism, and identification of mullite and sillimanite: Am. Ceramic Soc. Jour., v. 43, p. 2-8.

Akaad, M. K., 1956, The northern aureole of the Ardara Pluton of County Donegal: Geol. Mag., v. 93, p. 377-392.

Alderman, A. R., 1942, Sillimanite, kyanite, and clay deposits near Williamstown, South Australia: Roy. Soc. South Australia Trans., v. 66, p. 3-12.

Buerger, M. J., 1936, The general role of composition in polymorphism: Natl. Acad. Sci. Proc., v. 22, p. 685.

Chinner, G. A., 1960, Pelitic gneisses with varying ferrous/ferric ratios from Glen Clova, Angus, Scotland: Jour. Petrology, v. 1, p. 178-217.

———— 1961, The origin of sillimanite in Glen Clova, Angus: Jour. Petrology, v. 2, p. 312-323.

———— 1962, Almandine in thermal aureoles: Jour. Petrology, v. 3, p. 316-340.

———— 1966, The significance of the aluminum silicates in metamorphism: Earth Sci. Rev., v. 2, p. 111-126.

———— 1967, Chloritoid, and the isochemical character of Barrow's zones: Jour. Petrology, v. 8, p. 268-282.

Corlett, M., and Smith, J. V., 1964, Significance of minor element analysis by the microprobe X-ray emission analyser: Geol. Soc. America Spec. Paper 82, p. 32-33.

Deer, W. A., Howie, R. A., and Zussman, J., 1962, Rock-forming minerals, v. 1: Ortho and ring silicates: London, Longmans, 333 p.

Espenshade, G. H., and Potter, D. B., 1960, Kyanite, sillimanite and andalusite deposits of the southeastern states: U. S. Geol. Survey Prof. Paper 336, 121 p.

Fyfe, W. S., 1967, Stability of Al_2SiO_5 polymorphs: Chem. Geology, v. 2, p. 67-76.

Harte, B., and Henley, K. J., 1966, Occurrence of compositionally zoned almanditic garnets in regionally metamorphosed rocks: Nature, v. 210, p. 689-692.

Harker, A., 1939, Metamorphism, 2d ed.: London, Methuen, 362 p.

Henriques, A., 1957, The alkali content of kyanite: Arkiv. Mineralogi Geologi, v. 2, p. 271.

Hietanen, Anna, 1956, Kyanite, andalusite, and sillimanite in the schist in Boehl's Butte quadrangle, Idaho: Am. Mineralogist, v. 41, p. 1-27.

Hollister, L. S., and Bence, A. E., 1967, Staurolite: Sectorial compositional variations: Science, v. 158, p. 1053-1056.

Hutton, D. R., and Troup, G. J., 1964, Paramagnetic resonance of Cr^{3+} in kyanite: British Jour. Appl. Physics, v. 15, p. 275-280.

Jakob, J., 1937, Uber den Alkaligehalt der Disthene: Schweizer. min. pet. Mitt., v. 17, p. 214-219.

Long, J. V. P., and Agrell, S. O., 1965, The cathodoluminescence of minerals in thin-section: Mineralog. Mag., Tilley v., p. 318-326.

MacDonald, G. A., and Merriam, R., 1938, Andalusite from Fresno County, California: Am. Mineralogist, v. 23, p. 588-594.

Newton, R. C., 1966, Kyanite-andalusite equilibrium from 700° to 800°C: Science, v. 153, p. 170-172.

Pitcher, W. S., 1965, The aluminium silicate polymorphs, *in* Pitcher, W. S., and Flinn, G. W., eds., Controls of Metamorphism: Edinburgh, Oliver and Boyd, p. 327-341.

Pitcher, W. S., and Read, H. H., 1960, The aureole of the main Donegal granite: Geol. Soc. London Quart. Jour., v. 116, p. 1-36.

Smith, J. V., 1965, X-ray emission microanalysis of rock-forming minerals. I. Experimental techniques: Jour. Geology, v. 73, p. 830-864.

———— 1966, X-ray emission microanalysis of rock-forming minerals. II. Olivines: Jour. Geology, v. 74, p. 1-16.

Smith, J. V., and Stenstrom, R. C., 1965, Electron excited luminescence as a petrologic tool: Jour. Geology, v. 73, p. 627-635.

Spaenhauer, F., 1933. Die Andalusit-und Disthen vorkommen der Silvretta: Schweizer. min. pet. Mitt., v. 13, p. 323-346.

Strens, R. G. J., 1965. Instability of the garnet $Ca_3Mn_2Si_3O_{12}$, and the substitution $Mn \rightleftharpoons Al$: Mineralog. Mag., v. 35, p. 547-549.

———— 1968, Stability of Al_2SiO_5 solid solutions: Mineralog. Mag., v. 36, p. 839-849.

Tilley, C. E., 1937, Rocks from Enderby Land, Antarctica: British-Australian-New Zealand Antarctic Research Expedition 1929-1931, Repts., ser. A, v. 2, p. 1-16.

White, E. W., and White, W. B., 1967. Electron microprobe and optical absorption study of colored kyanites: Science, v. 158, p. 915-917.

Woodland, B. G., 1963. A petrographic study of thermally metamorphosed pelitic rocks in the Burke area, north-eastern Vermont: Am. Jour. Sci., v. 261, p. 354-375.