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THE ROLE OF MINOR ELEMENT SOLID SOLUTION ON THE ANDALUSITE-SILLIMANITE EQUILIBRIUM IN METAPELITES AND PERALUMINOUS GRANITOIDS

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ABSTRACT. Electron probe analyses of andalusite and sillimanite in metapelites provide information on the effect of minor element partitioning on the andalusite-sillimanite equilibrium. In the field, partitioning results in a zone of coexisting andalusite + sillimanite. In general, the width of this zone is proportional to the minor element concentration of the "reactant" andalusite that preceded the andalusite-sillimanite pair. The Ardara aureole (Ireland) and the Waterville-Vassalboro area (Maine), which have andalusite and sillimanite with low impurity levels, are characterized by very sharp sillimanite isograds with little or no zone of coexisting andalusite + sillimanite. The low minor element concentrations of andalusite-sillimanite pairs in samples from Mt. Moosilauke (New Hampshire) confirm Rumble's (1973) contention that minor element partitioning has an unimportant effect on the Al_2SiO_5 phase equilibria for this area, thereby strengthening Hodges and Spear's (1982) thermobarometric analysis of this area. The central Ryoke belt of Japan, however, has a 3 km-wide zone of andalusite + sillimanite in spite of the relatively low Fe contents of these phases. The broad zone of coexisting andalusite + sillimanite is considered to reflect a progressive upgrade increase in the Fe content of the "reactant" andalusite. Prograde changes in the minor element concentrations of andalusite + sillimanite suggest evolution along a partitioning "loop" on a $T\text{-}X_{FeAlSiO_5}$ diagram. The Kiglapait aureole (Labrador) is characterized by a 300 m-wide zone of coexisting andalusite + sillimanite. As in the Ryoke area, prograde changes in the minor element concentrations of andalusite + sillimanite across this zone suggest evolution along a $T\text{-}X_{MAlSiO_5}$ partitioning loop (M = minor element). In the Kiglapait aureole, graphite-sulfide metasiltstones contain andalusite and sillimanite with significantly lower impurity concentrations compared to these phases in graphite-free metaquartzites. Such contrasts illustrate the correlation between f_{O_2} and minor element concentrations of the aluminum silicates. The composition of andalusite and the partitioning of minor elements in andalusite + sillimanite and andalusite + fibrolite in selected samples of peraluminous granitoids suggest that the observed solid solution has little effect on the andalusite-sillimanite equilibrium in these samples. With Holdaway's (1971) andalusite-sillimanite equilibrium, the equilibrium coexistence of andalusite + melt (as suggested by textural evidence) is rationalized by considering the expansion of the P-T field of melt due to B, F, and excess Al.

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INTRODUCTION

The andalusite-sillimanite equilibrium continues to be a primary thermobarometer for low-pressure metapelites (Carmichael, 1978: Ferry, 1980; Hodges and Spear, 1982). Because calibration of this equilibrium is based on combined experimental and thermodynamic data (Holdaway, 1971: Robie and Hemingway, 1984), it is important to continue to evaluate any potential complications in the *direct* application of these data to rocks. Relevant variables that can affect this application include order/disorder, solid solution, surface free energy, and strain energy arising from lattice defects. The present communication addresses the role of minor element crystalline solution on the andalusite-sillimanite equilibrium in aluminous lithologies.

Several earlier studies on natural assemblages concluded that crystalline solution had an insignificant effect on the stability relations of the Al_2SiO_5 polymorphs in metapelites (Albee and Chodos, 1969; Okrusch and Evans, 1970; Holdaway, 1971; Rumble, 1973). However, Grambling and Williams (1985) concluded that crystalline solution had a significant effect on the andalusite-sillimanite equilibrium in metapelites of the Rio Mora uplift and Truchas Range in New Mexico. Their contribution stressed the correlation between oxygen fugacity (as evidenced by the iron oxides and the presence or absence of graphite) and minor element concentration (especially Fe^{3+} and Mn^{3+}) of the aluminum silicates. The fractionation of Fe^{3+} and Mn^{3+} into the andalusite structure is such that the andalusite stability field is enlarged with increasing f_{O_2}. Grambling and Williams (1985) investigated both Mn-rich and Mn-poor assemblages. In the Rio Mora uplift their analysis of minor element solid solution was confined to a manganiferous horizon. Several samples from the Truchas Peaks uplift and the Picuras Range were analyzed for the effect of minor element partitioning on the kyanite = andalusite equilibrium; however, minor element partitioning between andalusite and sillimanite was determined in only one sample. Accordingly, they have limited data with which to evaluate the effect of minor element partitioning on the andalusite-sillimanite equilibrium.

As manganiferous metapelites are rare in comparison to Mn-poor parageneses, the present contribution is confined to an evaluation of the role of crystalline solution on the andalusite-sillimanite equilibrium in the common Mn-poor assemblages.

ANALYTICAL METHODS

Electron probe analyses of andalusite and sillimanite from the Kiglapait aureole were obtained by J. A. Speer using an automated ARL-SEMQ electron probe using silicates and oxides as standards. The data were converted to oxide weight percentages by a computer program based on the alpha factor correction scheme of Ziebold and Oglivie (1964) as extended by Bence and Albee (1968) using the correction factors of Albee and Ray (1970). All other electron probe analyses reported in this paper were obtained by D. M. Kerrick with an

ETEC Autoprobe using the same data reduction procedure as that of the Kiglapait samples. Al and Si were calibrated with a kyanite standard, whereas minor elements were calibrated using standards other than the Al_2SiO_5 polymorphs. The accuracy of our minor element[1] analyses with the ETEC probe was checked by comparison with sillimanite from Benson Mines, N.Y. We obtained an Fe_2O_3 content of 1.54 wt percent, which is in good agreement with Grew's (1980) analysis of the Fe_2O_3 content of sillimanite from this locality.

The electron probe data were used to calculate the equilibrium constant for the andalusite-sillimanite equilibrium: $K_D = X^{Sill}_{Al_2SiO_5}/X^{And}_{Al_2SiO_5}$. The $X_{Al_2SiO_5}$ values were calculated from: $X_{Al_2SiO_5} = 1 - X_{MAlSiO_5}$, where M is the sum of the "impurity" cations (that is, Fe^{3+}, Ti, et cetera). Using the error propagation equation of Hodges and Spear (1982, p. 1126), a ± 2 percent relative standard error in weight percent of each of these oxides introduces a negligible error in the equilibrium constant.

THERMODYNAMIC ANALYSIS AND PHASE EQUILIBRIA

Following the thermodynamic approach of Strens (1968), Holdaway (1971) evaluated the enthalpy contribution arising from iron in crystalline solution in the Al_2SiO_5 polymorphs. As illustrated by Holdaway (1971), considerable thermodynamic mixing information could be extracted from Al_2SiO_5 + hematite + quartz assemblages. New data on the compositions of andalusite and sillimanite coexisting with hematite + quartz in parageneses with well-calibrated P-T conditions, such as those described by Grambling and Williams (1985), would permit refined evaluation of the mixing properties of these polymorphs. Information on the enthalpy of mixing would obviate the need for the simplifying assumption of ideal mixing (compare Okrusch and Evans, 1970; Grambling and Williams, 1985). In view of the potential importance of this method, we re-evaluate their approach. Holdaway (1971, p. 99) started with the equation[2]:

$$\Delta G_m = X_{FeAlSiO_5}\overline{\Delta H}_{FeAlSiO_5} + RT[X_{FeAlSiO_5} \ln X_{FeAlSiO_5} + X_{Al_2SiO_5} \ln X_{Al_2SiO_5}] \quad (1)$$

where:

ΔG_m = change (upon mixing) in the Gibbs free energy of the phase
X_i = mole fraction of component i
$\overline{\Delta H}_i$ = change (upon mixing) in the partial molar enthalpy of component i

[1] Strictly speaking, the term "minor element" is reserved for those constituents in concentrations ≤1 wt percent. However, for convenience of discussion, we refer to all impurities as minor elements. With the exception of Fe_2O_3, the individual contents of other impurities are indeed ≤1 percent. Herein we include Fe_2O_3 as a minor constituent in spite of the fact that Fe_2O_3 is present in the 1 to 2 wt percent range in some andalusites considered in this paper.

[2] The notation differs from that of Holdaway (1971).

T = temperature (Kelvin)
R = gas constant

From this expression, Holdaway (1971) derived the equation:

$$\frac{d\Delta G_m}{dX_{FeAlSiO_5}} = 0 = \Delta\overline{H}_{FeAlSiO_5} + RT \ln \left[\frac{X_{FeAlSiO_5}}{X_{Al_2SiO_5}}\right] \quad (2)$$

Holdaway (1971) equated the saturation value of $X_{FeAlSiO_5}$ with the minimum on the free energy curve on a plot of ΔG_m versus $X_{FeAlSiO_5}$ (see Holdaway, 1971, fig. 1). In so doing, he correlated this maximum $X_{FeAlSiO_5}$ value with that of andalusite and sillimanite in metapelites containing the assemblage: hematite + quartz. Analytical data on the Fe contents of andalusite and sillimanite in such assemblages, coupled with independent estimates of temperature during metamorphism, permitted evaluation of $\Delta\overline{H}_{FeAlSiO_5}$ (from eq 2) and then ΔG_m (from eq 1). We evaluate Holdaway's (1971) approach using the fundamental equation for a binary mixture of the components Al_2SiO_5 and $FeAlSiO_5$:

$$\begin{aligned}\Delta\overline{G}_m = {} & X_{Al_2SiO_5}\Delta\overline{H}_{Al_2SiO_5} + X_{FeAlSiO_5}\Delta\overline{H}_{FeAlSiO_5} \\ & + RT\,[X_{Al_2SiO_5} \ln X_{Al_2SiO_5} + X_{FeAlSiO_5} \ln X_{FeAlSiO_5}] \\ & - T\,[X_{Al_2SiO_5}\Delta\overline{S}^{ex}_{Al_2SiO_5} + X_{FeAlSiO_5}\Delta\overline{S}^{ex}_{FeAlSiO_5}],\end{aligned} \quad (3)$$

where:

$\Delta\overline{S}_i^{ex}$ = change (upon mixing) in the partial molar excess entropy of component i

To derive (2) from (3), we must assume that the excess entropy terms are zero and that $\Delta\overline{H}_{Al_2SiO_5} = 0$. These simplifying assumptions are implicit in Holdaway's (1971) ΔG_m calculations. As shown in figure 1, the assumption of horizontal tangency implies that the amplitude of the minimum on the ΔG_{mix} versus composition curve for the (fictive) $FeAlSiO_5$-rich phase is identical to that of the minimum for the Al-rich phase (andalusite or sillimanite). Because the Fe-rich phase does not exist, we have no way of evaluating the minimum free energy of mixing for this fictive phase. One cannot assume (compare fig. 1 of Holdaway, 1971) that the tangent can be determined by assigning the right intercept in figure 1 to the free energy of hematite + quartz.

Therefore, we lack the requisite data with which to calculate the non-ideal contributions to the thermodynamic mixing properties of the aluminum silicates. Accordingly, we are forced into assuming ideal mixing in the present communication. Grew's (1980) analysis supports this assumption for the compositional range $0 < X_{Fe_2SiO_5} < 0.0013$ in sillimanite.

For an equilibrium assemblage of impure andalusite and sillimanite, the P-T equilibrium curve can be calculated with:

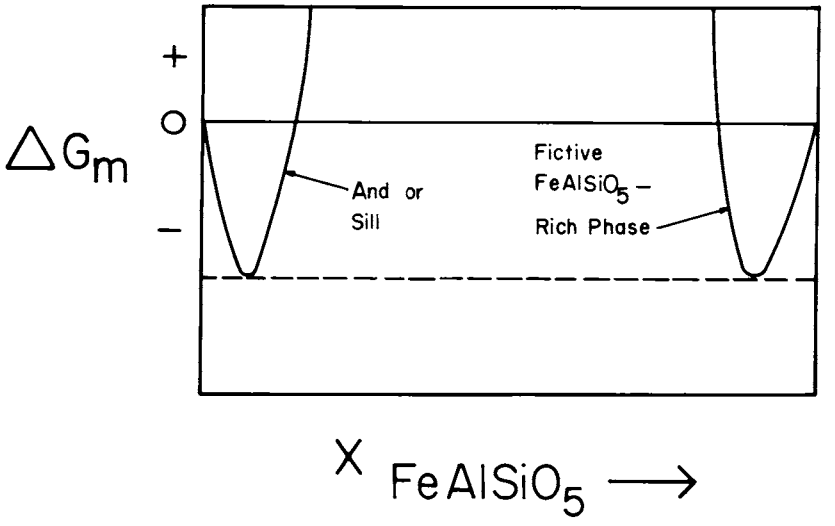

Fig. 1. Schematic illustration of free energy of mixing versus composition. The dashed line represents the mutual tangent to the two free energy curves.

$$\Delta G_r = 0 = \Delta G_r^\circ + RT \ln K_{eq}, \tag{4}$$

where:

ΔG_r = change in Gibbs free energy for the reaction,

and:

$$K_{eq} = a^{Sill}_{Al_2SiO_5}/a^{And}_{Al_2SiO_5}$$

The standard state corresponds to unit activities at P and T. Assuming ideal mixing we have:

$$K_{eq} = K_D = X^{Sill}_{Al_2SiO_5}/X^{And}_{Al_2SiO_5} \tag{5}$$

The isopleths for selected K_{eq} values in figure 2 were calculated with eq (4) using the VERTEX program of Connolly and Kerrick (1984, 1987). The standard state free energy change for the reaction (ΔG_r°) was calculated using enthalpy and heat capacity data of Robie and Hemingway (1984) and molar volume, compressibility, and thermal expansion data of Robinson and others (1982). The error in the calculated equilibrium constant arising from the ±2 percent relative error in oxide percentage (as discussed in the *Analytical Methods* section) introduces a negligible error in the P-T calibration of K_D values.

As shown in figure 2, our calculated triple point for the reference equilibrium (K = 1.0) is at 4 kb and 520°C. Although these conditions differ from the P-T values preferred by Holdaway (that is 3.76 kb and

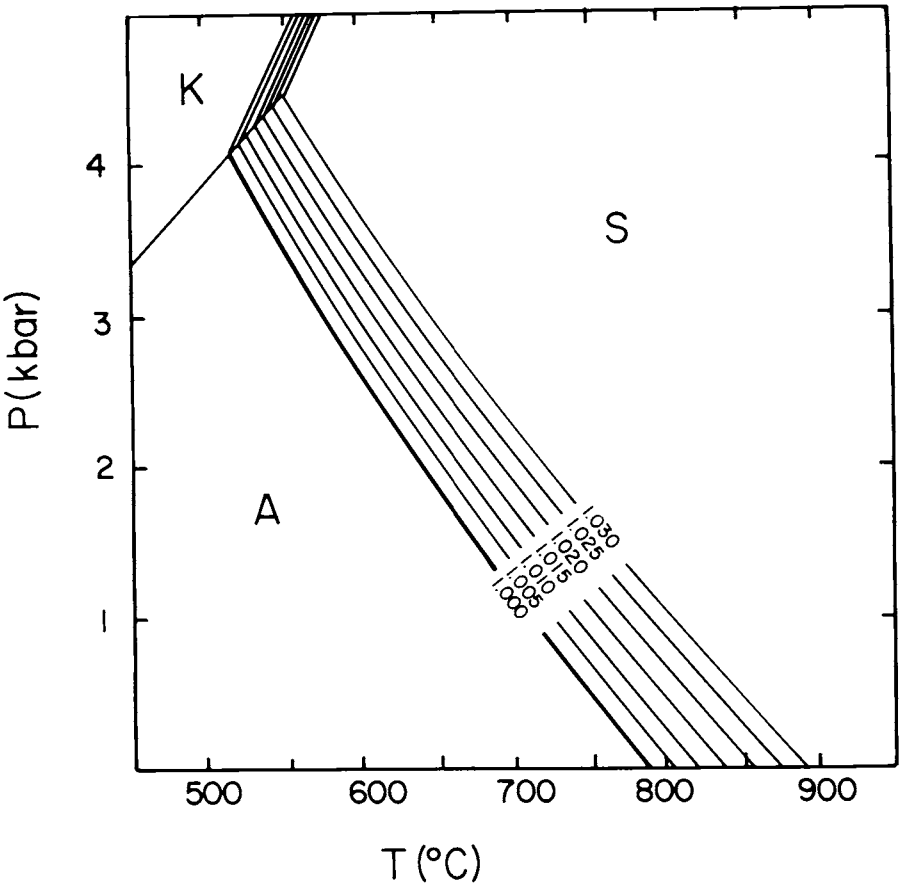

Fig. 2. Isopleths of K_{eq} (= $a^{Sill}_{Al_2SiO_5}/a^{And}_{Al_2SiO_5}$) for the andalusite-sillimanite equilibrium. The heavy line is the "reference" equilibrium involving pure andalusite and sillimanite. K = kyanite, S = sillimanite, A = andalusite.

501°C), our calculated triple point falls within the uncertainty range given by Holdaway (1971, p. 122).

Kerrick and Heninger (1984) and Nitkiewicz and Kerrick (in preparation) have confirmed Holdaway's (1971) location of the P-T boundary for the andalusite-sillimanite equilibrium. Accordingly, we strongly favor Holdaway's (1971) calibration of the andalusite-sillimanite equilibrium over that of Richardson, Gilbert, and Bell (1969).

Our analysis assumes that the impurity cations mix on one site in sillimanite and andalusite. However, there is considerable disagreement as to the site populations of minor elements in these phases (Holuj and others, 1966; Grew and Rossman, 1976; Hålenius, 1978, 1979; Le Marshall and others, 1971; Grew, 1980; Peterson and McMullan,

1986). In view of this dilemma we have opted to consider that mixing is confined to the octahedral site in andalusite and sillimanite. Accordingly, the endmember components would be $Al^{VI}Al^{V}SiO_5$-$M^{VI}Al^{V}SiO_5$ in andalusite and $Al^{VI}Al^{IV}SiO_5$-$M^{VI}Al^{IV}SiO_5$ in sillimanite (where M = "impurity" cations). As mixing is assumed to occur on one site, and there is one gram atom of octahedrally-coordinated cations per formula unit, ideal mixing would correspond to Raoult's law behavior in these phases (that is, $a_{Al_2SiO_5} = X_{Al_2SiO_5}$). However, if minor elements are partitioned onto two sites, the activity expression would have to be modified accordingly (see Grew, 1980).

Having quantified the displacement of the andalusite-sillimanite equilibrium as a function of K_D, we next consider the geologic implications of this analysis.

METAPELITES

Kerrick's (1987) analysis of metapelites suggests caution in assuming fibrolite as an equilibrium phase; thus, this section is concerned *only* with coarse, prismatic sillimanite. Throughout this paper the mineral name "sillimanite" implies the coarse, prismatic variety. Sillimanites analyzed in the present study have minimum dimensions (as measured normal to the c-axis) exceeding 10 microns. These crystal sizes are well above the size range of fibrolite.[3]

Mt. Moosilauke, New Hampshire.—The Mt. Moosilauke region of New Hampshire contains a metapelitic sequence considered to have been metamorphosed at P-T conditions near the triple point for the Al_2SiO_5 polymorphs (Rumble, 1973; Hodges and Spear, 1982). Of 11 samples described by Rumble (1973) from this area, only two contain coexisting andalusite and sillimanite. Our re-analysis of the andalusite and sillimanite in Rumble's (1973) sample no. 71-83B (table 1) yields excellent agreement with his electron probe analysis. The K_D value (1.002) is such that the andalusite-sillimanite equilibrium in this sample is virtually identical to that involving the pure Al_2SiO_5 polymorphs (fig. 2). Hence, we have reconfirmed Rumble's (1973, p. 2429) conclusion that: "The Fe_2O_3 contents . . . are not significant enough to significantly change the stability fields of the aluminum silicates."

The bivariancy introduced by crystalline solution can be analyzed with an isobaric T-X_{MAlSiO_5} diagram (fig. 3). Assuming equilibrium, partitioning of minor elements between andalusite and sillimanite is defined by a bivariant[4] "loop", analogous to those extensively used by Thompson (1976a, b) to illustrate partitioning amongst ferromagnesian phases. The compositions of andalusite-sillimanite pairs in sample 71-83B from the Mt. Moosilauke area are plotted in figure 3. Also plotted

[3] The authors consider crystals exceeding 10 microns in minimum dimensions to be coarse, prismatic sillimanite.

[4] Reference to bivariancy considers we have *assumed* that minor elements are combined into a single component.

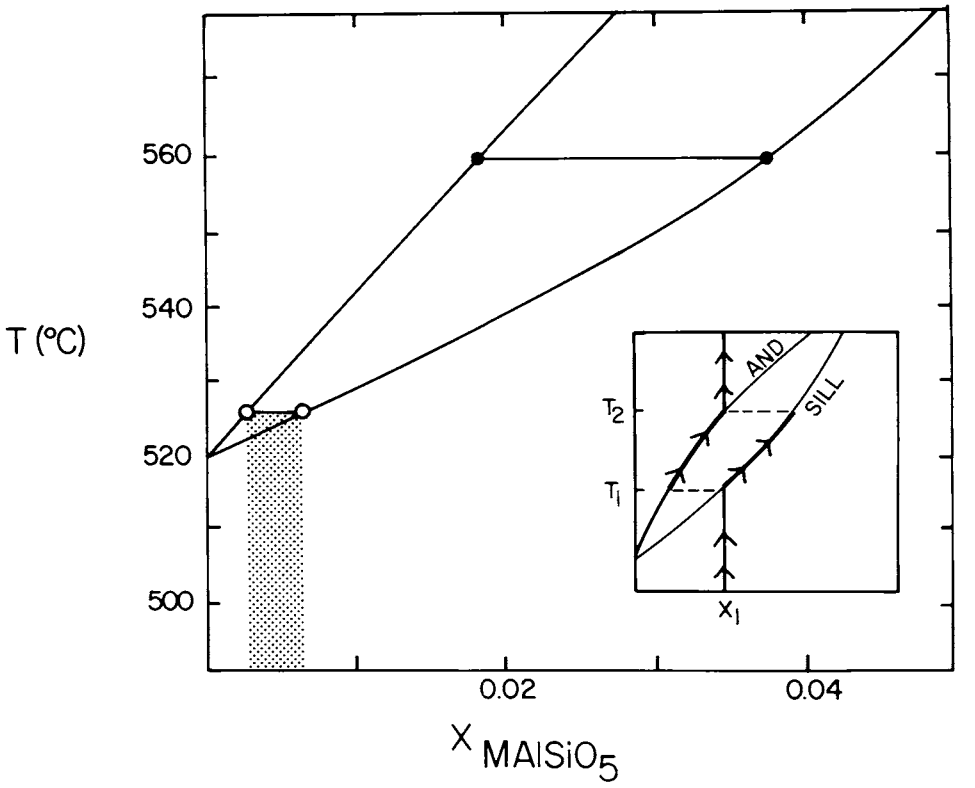

Fig. 3. T-X diagram for parageneses metamorphosed at pressures near the triple point for the Al_2SiO_5 polymorphs, showing andalusite-sillimanite pairs from Mt. Moosilauke, N.H. (open circles) and from Truchas Peaks, N.Mex. (filled circles). The shaded band encompasses the compositional range of the "reactant" andalusite for the Mt. Moosilauke assemblage (see text). The inset is a schematic illustration of the prograde compositional evolution of andalusite and sillimanite, starting with andalusite of composition X_1. Andalusite and sillimanite coexist in the interval T_1-T_2.

in this diagram is the composition of coexisting andalusite and sillimanite in Grambling and Williams' (1985) sample 78-105a from Truchas Peaks, N. Mex., a paragenesis considered to have been metamorphosed at a pressure near the triple point. Assuming our calculated triple point pressure of 4 kb for the pure phases (fig. 2), the equilibrium temperatures of the samples plotted in figure 3 were determined from the K_D values in conjunction with figure 2. Grambling and Williams (1985) did not analyze for vanadium. Thus, for comparative purposes, figure 3 presents the X_{MAlSiO_5} values for the Mt. Moosilauke sample calculated on a vanadium-free basis. The temperature interval of bivariancy can be evaluated by considering a prograde path as schematically depicted in the inset of figure 3. From this inset it is evident that, for any given analyzed andalusite-sillimanite assemblage, the composition of the

TABLE 1

Electron probe analyses of aluminum silicates in metapelites

	Mt. Moosilauke, New Hampshire		Waterville-Vassalboro Area, Maine			
Sample no.	71-83B	71-83B	917A	928B	663	666A
Al silicate*	A	S	A	A	S	S
			Wt percent oxide			
SiO_2	37.70	36.53	36.49	37.40	36.40	36.63
Al_2O_3	63.30	63.24	62.66	62.82	62.74	62.22
TiO_2	0.0	0.02	0.11	0.10	0.10	0.05
Fe_2O_3	0.32	0.14	0.40	0.31	0.22	0.23
Cr_2O_3	0.01	0.03	0.01	0.0	0.0	0.0
MnO	0.0	0.0	0.03	0.01	0.02	0.0
MgO	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
V_2O_5	0.03	0.09	0.10	0.06	0.10	0.06
Sum	101.36	100.05	99.80	100.70	99.58	99.19
			Formula basis 5 oxygens			
Si	1.004	0.986	0.988	1.003	0.987	0.997
Al	1.987	2.012	2.001	1.986	2.006	1.996
Ti	0.0	0.000	0.002	0.002	0.002	0.001
Fe^{3+}	0.006	0.003	0.008	0.006	0.004	0.005
Cr	0.000	0.001	0.000	0.0	0.0	0.0
Mn	0.0	0.0	0.001	0.000	0.000	0.0
Mg	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
V	0.001	0.002	0.002	0.001	0.002	0.001
Sum	2.998	3.004	3.002	2.998	3.002	3.000
X_{MAlSiO_5}	0.007	0.005	0.013	0.010	0.009	0.007
$X_{Al_2SiO_5}$	0.993	0.995	0.987	0.990	0.991	0.993
	$K_D = 1.002$					

*A = andalusite, S = sillimanite

Ardara aureole, Ireland

Sample no. Al silicate:	ARD-85-1A S	ARD-85-1B S	ARD-85-2A S	ARD-85-3E S	ARD-85-10 S	ARD-85-15 A	ARD-85-16 A	ARD-85-17 A	ARD-85-32A A (core)	ARD-85-32A A (rim)	ARD-85-65B A (core)	ARD-85-65B A (rim)
						Wt percent oxide						
SiO_2	37.13	36.42	36.55	37.06	36.63	36.27	36.66	36.94	36.41	36.88	37.23	37.09
Al_2O_3	62.07	62.28	62.88	62.11	62.27	62.73	62.53	62.52	61.92	61.81	62.48	62.24
TiO_2	0.02	0.01	0.02	0.0	0.0	0.05	0.05	0.0	0.09	0.03	0.05	0.02
Fe_2O_3	0.22	0.23	0.37	0.12	0.18	0.26	0.26	0.17	0.86	0.29	0.35	0.19
Cr_2O_3	0.18	0.05	0.03	0.08	0.13	0.04	0.03	0.0	0.07	0.03	0.15	0.13
MnO	0.05	0.03	0.01	0.0	0.04	0.01	0.01	0.0	0.02	0.01	0.04	0.02
MgO	0.0	0.0	0.01	0.02	0.0	0.0	0.02	0.07	n.d.	0.05	0.13	0.04
V_2O_5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Sum	99.67	99.02	99.87	99.39	99.25	99.36	99.56	99.70	99.37	99.10	100.43	99.73
						Formula basis 5 oxygens						
Si	1.006	0.993	0.989	1.006	0.997	0.986	0.994	1.000	.993	1.005	1.002	1.004
Al	1.982	2.002	2.006	1.987	1.997	2.011	2.000	1.995	1.992	1.985	1.983	1.986
Ti	0.000	0.000	0.000	0.0	0.0	0.001	0.001	0.0	0.002	0.001	0.001	0.000
Fe^{3+}	0.004	0.005	0.008	0.002	0.004	0.005	0.005	0.003	0.020	0.006	0.008	0.004
Cr	0.004	0.001	0.001	0.002	0.003	0.001	0.001	0.0	0.002	0.001	0.003	0.003
Mn	0.001	0.001	0.000	0.0	0.001	0.000	0.000	0.0	0.000	0.000	0.001	0.000
Mg	0.0	0.0	0.000	0.001	0.0	0.0	0.001	0.003	n.d.	0.002	0.005	0.002
V	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Sum	2.998	3.002	3.008	2.998	3.001	3.004	3.002	3.001	3.008	2.999	3.004	2.999
X_{MAlSiO_5}	0.010	0.007	0.009	0.005	0.007	0.007	0.008	0.006	0.023	0.009	0.018	0.009
$X_{Al_2SiO_5}$	0.990	0.993	0.991	0.995	0.993	0.993	0.992	0.994	0.977	0.991	0.982	0.991

TABLE 1 (continued)
Kiglapait aureole, Labrador

Sample no.	15	25	25	37	37	41	73	73	74	74
Al silicate:	A	A	S	A	S	A	A	S	A	S
Met. Zone:	I	II	II	II	II	I	II	II	II	II
					Wt percent oxide					
SiO_2	37.50	36.56	36.75	36.70	36.69	36.48	36.83	37.09	36.88	36.96
Al_2O_3	61.15	59.88	60.79	60.00	60.45	60.71	61.33	61.76	60.36	61.24
TiO_2	0.06	0.04	0.02	0.09	0.02	0.04	0.06	0.01	0.06	0.02
Fe_2O_3	1.97	1.38	1.07	1.86	1.42	1.14	1.81	0.99	2.01	1.26
Cr_2O_3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
MnO	0.0	0.0	0.01	0.01	0.0	0.01	0.0	0.0	0.01	0.0
MgO	0.07	0.09	0.05	0.09	0.07	0.09	0.10	0.05	0.07	0.04
V_2O_5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Sum	100.75	97.95	98.69	98.75	98.65	98.47	100.13	99.90	99.39	99.52
					Formula basis 5 oxygens					
Si	1.010	1.011	1.008	1.009	1.008	1.003	0.999	1.005	1.008	1.006
Al	1.943	1.953	1.965	1.945	1.958	1.968	1.961	1.972	1.945	1.965
Ti	0.001	0.001	0.000	0.002	0.000	0.001	0.001	0.000	0.001	0.000
Fe^{3+}	0.040	0.029	0.022	0.038	0.029	0.024	0.037	0.020	0.041	0.026
Cr	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Mn	0.0	0.0	0.000	0.000	0.0	0.000	0.0	0.0	0.000	0.0
Mg	0.003	0.004	0.002	0.004	0.003	0.004	0.004	0.002	0.003	0.002
V	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Sum	2.997	2.997	2.998	2.998	2.998	3.000	3.001	2.999	2.998	2.998
X_{MAlSiO_5}	0.044	0.033	0.025	0.044	0.033	0.028	0.042	0.022	0.046	0.028
$X_{Al_2SiO_5}$	0.956	0.967	0.975	0.956	0.967	0.972	0.958	0.978	0.954	0.972
		$K_D = 1.008$		$K_D = 1.012$			$K_D = 1.021$		$K_D = 1.019$	

Kiglapait aureole, Labrador

Sample no.	75	75	78	78	82	82	88	88	89	89
Al silicate:	A	S	A	S	A	S	A	S	A	S
Met. Zone:	II	II	II	II	II	II	II	II	II	II
					Wt percent oxide					
SiO_2	36.74	37.28	36.18	36.34	37.19	36.99	36.96	37.33	36.54	36.81
Al_2O_3	59.71	61.72	59.38	61.40	61.92	62.47	61.41	62.06	59.88	60.12
TiO_2	0.07	0.02	0.14	0.02	0.03	0.08	0.02	0.01	0.09	0.02
Fe_2O_3	1.63	0.80	1.57	0.70	0.51	0.45	1.10	0.76	1.46	0.64
Cr_2O_3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
MnO	0.0	0.0	0.0	0.02	0.0	0.0	0.0	0.0	0.0	0.0
MgO	0.09	0.03	0.13	0.08	0.08	0.09	0.06	0.06	0.08	0.04
V_2O_5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Sum	98.24	99.85	97.40	98.56	99.73	100.08	99.55	100.22	98.05	97.63
					Formula basis 5 oxygens					
Si	1.014	1.009	1.008	0.997	1.007	0.999	1.005	1.007	1.010	1.018
Al	1.943	1.970	1.950	1.986	1.977	1.988	1.969	1.973	1.951	1.961
Ti	0.001	0.000	0.003	0.000	0.001	0.002	0.000	0.000	0.002	0.000
Fe^{3+}	0.034	0.016	0.033	0.014	0.010	0.009	0.023	0.015	0.030	0.013
Cr	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Mn	0.0	0.0	0.0	0.000	0.0	0.0	0.0	0.0	0.0	0.0
Mg	0.004	0.001	0.005	0.003	0.003	0.004	0.002	0.002	0.003	0.002
V	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Sum	2.996	2.997	2.998	3.002	2.998	3.001	2.999	2.998	2.997	2.994
X_{MAlSiO_5}	0.039	0.018	0.041	0.019	0.014	0.014	0.025	0.018	0.036	0.015
$X_{Al_2SiO_5}$	0.961	0.982	0.959	0.981	0.986	0.986	0.975	0.982	0.964	0.985
	$K_D = 1.022$		$K_D = 1.023$		$K_D = 1.000$		$K_D = 1.007$		$K_D = 1.022$	

TABLE 1 (continued)
Kiglapait aureole, Labrador

Sample no.	96	111	127	130	131	135	136	151	160	179
Al silicate:	S	S	S	A	A	A	A	A	S	A
Met. Zone:	III	III	II	I	I	I	I	II	III	I
					Wt percent oxide					
SiO_2	37.23	36.65	36.67	37.08	36.70	36.72	37.18	37.00	36.64	36.34
Al_2O_3	61.27	61.17	60.45	61.52	59.71	60.77	60.84	60.57	63.39	59.14
TiO_2	0.03	0.04	0.01	0.05	0.08	0.06	0.05	0.06	0.03	0.09
Fe_2O_3	0.05	0.17	0.12	1.30	1.27	0.95	1.34	1.35	0.11	1.25
Cr_2O_3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
MnO	0.01	0.01	0.01	0.01	0.01	0.02	0.0	0.0	0.0	0.0
MgO	0.07	0.10	0.07	0.09	0.10	0.08	0.09	0.08	0.09	0.09
V_2O_5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Sum	98.66	98.14	97.33	100.05	97.87	98.60	99.50	99.06	100.26	96.91
					Formula basis 5 oxygens					
Si	1.017	1.008	1.016	1.004	1.015	1.008	1.012	1.012	0.987	1.015
Al	1.973	1.982	1.974	1.964	1.948	1.966	1.953	1.953	2.012	1.948
Ti	0.001	0.001	0.000	0.001	0.002	0.001	0.001	0.001	0.001	0.002
Fe^{3+}	0.001	0.004	0.003	0.026	0.026	0.020	0.027	0.028	0.002	0.026
Cr	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Mn	0.000	0.000	0.000	0.000	0.000	0.000	0.0	0.0	0.0	0.0
Mg	0.003	0.004	0.003	0.004	0.004	0.003	0.004	0.003	0.004	0.004
V	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Sum	2.995	2.999	2.996	3.000	2.996	2.998	2.997	2.997	3.005	2.995
X_{MAlSiO_5}	0.005	0.009	0.006	0.031	0.032	0.025	0.032	0.032	0.006	0.032
$X_{Al_2SiO_5}$	0.995	0.991	0.994	0.969	0.968	0.975	0.968	0.968	0.994	0.968

Kiglapait aureole, Labrador

Sample no.	195	198	198	200	202	202	212	215	215	217
Al silicate:	A	A	S	A	A	S	A	A	S	A
Met. Zone:	II	II	II	I	II	II	II	II	II	I
					Wt percent oxide					
SiO_2	37.15	36.88	36.60	36.30	37.29	36.52	35.72	36.82	36.97	37.00
Al_2O_3	62.02	60.12	60.90	59.21	61.27	61.86	58.91	60.06	61.12	59.58
TiO_2	0.05	0.06	0.02	0.08	0.13	0.01	0.03	0.10	0.02	0.05
Fe_2O_3	1.80	1.06	0.70	1.87	1.17	0.84	1.81	1.94	1.01	2.06
Cr_2O_3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
MnO	0.01	0.01	0.0	0.01	0.0	0.0	0.0	0.01	0.0	0.0
MgO	0.06	0.08	0.05	0.10	0.11	0.08	0.09	0.09	0.07	0.11
V_2O_5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Sum	101.09	98.21	98.27	97.57	99.97	99.31	96.56	99.02	99.19	98.80
					Formula basis 5 oxygens					
Si	0.998	1.016	1.007	1.010	1.010	0.995	1.004	1.010	1.008	1.017
Al	1.964	1.953	1.975	1.942	1.956	1.987	1.953	1.942	1.966	1.930
Ti	0.001	0.001	0.000	0.002	0.003	0.000	0.001	0.002	0.000	0.001
Fe^{3+}	0.036	0.022	0.014	0.039	0.024	0.017	0.038	0.040	0.021	0.043
Cr	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Mn	0.000	0.000	0.0	0.000	0.0	0.0	0.0	0.000	0.0	0.0
Mg	0.002	0.003	0.002	0.004	0.004	0.003	0.004	0.004	0.003	0.005
V	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Sum	3.001	2.995	2.998	2.998	2.997	3.003	3.000	2.997	2.998	2.996
X_{MAlSiO_5}	0.040	0.027	0.017	0.045	0.031	0.021	0.043	0.046	0.024	0.048
$X_{Al_2SiO_5}$	0.960	0.973	0.983	0.955	0.969	0.979	0.957	0.954	0.976	0.952
		$K_D = 1.010$			$K_D = 1.010$			$K_D = 1.023$		

TABLE 1 (continued)
Kiglapait aureole, Labrador

Sample no.	218	218	219	245	245	283	283	300	300	313
Al silicate:	A	S	A	A	S	A	S	A	S	S
Met. Zone:	II	II	II	II	II	II	II	II	II	II
					Wt percent oxide					
SiO_2	36.96	37.29	37.32	37.39	36.62	37.05	36.97	37.04	36.74	36.42
Al_2O_3	61.82	62.11	61.09	61.66	61.39	60.64	61.14	62.09	61.58	62.17
TiO_2	0.10	0.03	0.05	0.02	0.01	0.05	0.02	0.03	0.02	0.03
Fe_2O_3	1.43	1.16	1.42	0.67	0.61	2.61	1.66	0.25	0.27	0.84
Cr_2O_3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
MnO	0.01	0.0	0.0	0.0	0.0	0.01	0.02	0.01	0.0	0.0
MgO	0.07	0.06	0.07	0.09	0.04	0.11	0.05	0.13	0.10	0.08
V_2O_5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Sum	100.39	100.65	99.95	99.83	98.67	100.47	99.86	99.55	98.71	99.54
					Formula basis 5 oxygens					
Si	0.998	1.003	1.012	1.012	1.003	1.004	1.004	1.004	1.005	0.990
Al	1.968	1.970	1.952	1.967	1.982	1.937	1.958	1.985	1.985	1.993
Ti	0.002	0.001	0.001	0.000	0.000	0.001	0.000	0.001	0.000	0.001
Fe^{3+}	0.029	0.023	0.029	0.014	0.013	0.053	0.034	0.005	0.006	0.017
Cr	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Mn	0.000	0.0	0.0	0.0	0.0	0.000	0.000	0.000	0.0	0.0
Mg	0.003	0.002	0.003	0.004	0.002	0.004	0.002	0.005	0.004	0.003
V	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Sum	3.001	3.000	2.997	2.997	2.999	3.000	2.999	3.000	3.000	3.004
X_{MAlSiO_5}	0.034	0.026	0.033	0.018	0.014	0.059	0.037	0.011	0.010	0.021
$X_{Al_2SiO_5}$	0.966	0.974	0.967	0.982	0.986	0.941	0.963	0.989	0.990	0.979
	$K_D = 1.008$			$K_D = 1.004$		$K_D = 1.023$		$K_D = 1.001$		

Kiglapait aureole, Labrador

Sample no.	302	302	327	342	342	347	348	348	356	356	373	392
Al silicate:	A	S	A	A	S	A	A	S	A	S	S	S
Met. Zone:	II	II	I	II	II	I	II	II	II	II	I	II
						Wt percent oxide						
SiO_2	37.34	37.02	36.46	36.57	36.09	36.65	36.51	36.32	37.11	37.13	36.49	37.35
Al_2O_3	60.58	61.29	60.20	61.21	60.53	62.05	61.16	60.49	59.47	61.17	62.62	62.44
TiO_2	0.07	0.02	0.11	0.05	0.03	0.04	0.06	0.01	0.05	0.02	0.03	0.02
Fe_2O_3	1.98	1.22	1.59	0.25	0.15	0.08	0.03	0.02	1.29	0.73	0.12	0.16
Cr_2O_3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
MnO	0.0	0.0	0.01	0.01	0.01	0.0	0.0	0.01	0.01	0.01	0.0	0.0
MgO	0.08	0.07	0.08	0.09	0.04	0.09	0.10	0.08	0.07	0.06	0.06	0.06
V_2O_5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Sum	100.05	99.62	98.45	98.18	96.85	98.91	97.86	96.93	98.00	99.12	99.32	100.03
						Formula basis 5 oxygens						
Si	1.013	1.006	1.005	1.005	1.005	1.000	1.006	1.010	1.025	1.012	0.992	1.007
Al	1.938	1.964	1.956	1.984	1.988	1.995	1.987	1.983	1.936	1.966	2.006	1.985
Ti	0.001	0.000	0.002	0.001	0.001	0.001	0.001	0.000	0.001	0.000	0.001	0.000
Fe^{3+}	0.040	0.025	0.033	0.005	0.003	0.002	0.001	0.000	0.027	0.015	0.002	0.003
Cr	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Mn	0.0	0.0	0.000	0.000	0.000	0.0	0.0	0.000	0.000	0.000	0.0	0.0
Mg	0.003	0.003	0.003	0.004	0.002	0.004	0.004	0.003	0.003	0.002	0.002	0.002
V	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Sum	2.996	2.999	2.999	2.999	2.999	3.001	2.999	2.998	2.992	2.997	3.003	3.998
X_{MAlSiO_5}	0.045	0.028	0.039	0.010	0.006	0.006	0.006	0.004	0.031	0.018	0.005	0.006
$X_{Al_2SiO_5}$	0.955	0.972	0.961	0.990	0.994	0.994	0.994	0.996	0.969	0.982	0.995	0.994
	$K_D = 1.018$			$K_D = 1.004$			$K_D = 1.002$		$K_D = 1.013$			

TABLE 1 (continued)
Steinach aureole, Bavaria

Sample no. Al silicate:	OP-157 A	OP-157 S	OP-163 A	OP-164 A	OP-170 A	OP-170 S	SM-5 A	SM-6 A	SM-6 S
					Wt percent oxide**				
SiO_2	36.70	36.85	36.60	36.40	36.50	36.70	36.65	36.80	36.80
Al_2O_3	61.85	62.40	61.80	61.50	62.30	62.65	61.70	61.95	62.85
TiO_2	0.03	0.01	0.60	0.02	0.03	0.0	0.04	0.06	0.02
Fe_2O_3	1.07	0.61	1.62	1.37	1.12	0.58	1.75	1.72	0.83
Cr_2O_3	0.02	0.04	0.02	0.02	0.01	0.07	0.01	0.02	0.02
MnO	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
MgO	0.01	0.0	0.30	0.02	0.03	0.0	0.03	0.0	0.0
V_2O_5	0.01	0.03	0.03	0.0	0.01	0.06	0.01	0.0	0.01
Sum	99.69	99.94	100.97	99.33	100.00	100.06	100.19	100.55	100.53
					Formula basis 5 oxygens				
Si	0.997	0.997	0.985	0.994	0.989	0.992	0.993	0.993	0.991
Al	1.981	1.990	1.961	1.979	1.990	1.996	1.971	1.972	1.994
Ti	0.001	0.000	0.012	0.000	0.001	0.0	0.001	0.001	0.000
Fe^{3+}	0.022	0.012	0.033	0.028	0.023	0.012	0.036	0.035	0.017
Cr	0.000	0.001	0.000	0.000	0.000	0.001	0.000	0.000	0.000
Mn	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Mg	0.000	0.0	0.012	0.001	0.001	0.0	0.001	0.0	0.0
V	0.000	0.001	0.001	0.0	0.000	0.001	0.000	0.0	0.000
Sum	3.001	3.001	3.005	3.002	3.004	3.002	3.002	3.002	3.003
X_{MAlSiO_5}	0.023	0.014	0.058	0.030	0.025	0.014	0.038	0.037	0.018
$X_{Al_2SiO_5}$	0.977	0.986	0.942	0.970	0.975	0.986	0.962	0.963	0.982
	$K_D = 1.009$				$K_D = 1.011$			$K_D = 1.020$	

**Analyses from Okrusch and Evans (1970)

"reactant" andalusite[5] cannot lie outside the range of compositions defined by this pair (shaded band in fig. 3). According to figure 3, the maximum temperature interval of bivariancy for the analyzed andalusite-sillimanite pair from Mt. Moosilauke is about 10°C. Because of the uncertainty in the location of the partitioning curves in figure 3, there is corresponding uncertainty in this temperature value. For parageneses with low X_{MAlSiO_5} contents, such as the Mt. Moosilauke sample, the uncertainty in the bivariant temperature interval is unlikely to be more than ±5°C.

From this analysis we conclude that the relative rarity of the andalusite-sillimanite pair in the immediate vicinity of Mt. Moosilauke (see Rumble, 1973, fig. 1) is compatible with a narrow bivariant zone in P-T space.

As no kyanite is reported in the Mt. Moosilauke septum, we would not place the triple point isobar in this septum (as was done by Hodges and Spear, 1982). Rather, we would designate the "trace of the triple point isobar" in figure 2 of Hodges and Spear (1982) as the approximate location of the andalusite → sillimanite isograd. Accordingly, we consider that this isograd passes through the Hurricane Mountain area (the only part of this septum where andalusite coexists with sillimanite). As such, the andalusite-sillimanite equilibrium would represent an excellent thermobarometric reference for Hurricane Mountain. Therefore, our analysis supports Hodges and Spear's (1982) use of "end-member" Al_2SiO_5 equilibria in their analysis of geothermometry and geobarometry in this area, although the lack of kyanite in this septum suggests pressures below that of the triple point. This conclusion is compatible with Rumble and others' (1982) 3.5 kb estimate for metamorphism at the Beaver Brook fossil locality located about 3 km northeast of Mt. Moosilauke.

Waterville-Vassalboro area, Maine.—Ferry (1980, 1981, 1982) has extensively studied metapelites in the Waterville-Vassalboro area of south-central Maine. This region represents a low-pressure, regionally metamorphosed terrain (Osberg, 1971; Ferry, 1981). As shown in figure 4, this area contains a well-defined sillimanite isograd marked by the abrupt disappearance of andalusite and the appearance of sillimanite. Electron probe analyses were obtained on two andalusite-bearing samples and on two sillimanite-bearing samples, located in close proximity to the sillimanite isograd (fig. 4 and table 1). Ferry (1980) found no samples with coexisting andalusite + sillimanite. Assuming that sillimanite was derived from the breakdown of andalusite, the inset of figure 3 illustrates that we expect the composition of the reactant phase (andalusite) to be identical to that of the product phase (sillimanite). The compositions of andalusite and sillimanite are indeed similar (table 1). This supports an equilibrium model for the andalusite → sillimanite

[5] The term "reactant" andalusite is used herein to refer to the precursor andalusite. With a model of progressive metamorphism, the reactant andalusite would be analogous to that just below the sillimanite isograd.

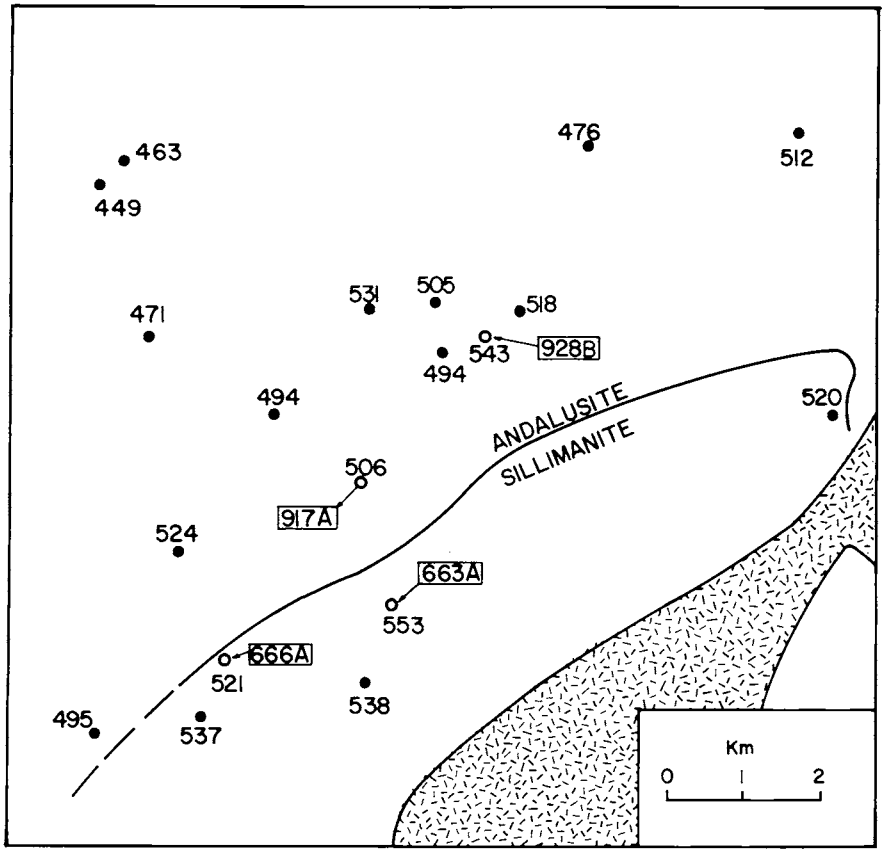

Fig. 4. Map of a portion of the Waterville-Vassalboro area, south-central Maine (from Ferry, 1980, figs. 1 and 2). The heavy line is the sillimanite isograd. The rectangles outline the sample numbers investigated in this study (table 1). The other numbers are temperature values (in °C) determined by garnet-biotite thermometry (from Ferry, 1980, fig. 2). The stippled area is a quartz monzonite intrusive.

isograd reaction. Taking the average value of X_{MAlSiO_5} as 0.010, we may depict the bivariancy with the aid of figure 3. Use of this diagram for the Waterville-Vassalboro area is supported by the fact that Ferry (1980) estimates that the pressure during metamorphism was close to that of Holdaway's (1971) triple point. Using figure 3, a prograde path starting with $X^{And}_{MAlSiO_5} = 0.010$ would constrain the bivariant temperature interval to no more than about 12°C. What is the field width of a bivariant zone of coexisting andalusite + sillimanite corresponding to a maximum temperature interval of 12°C? The answer is aided by the wealth of Ferry's (1980) garnet-biotite thermometric data. The metamorphic thermal gradient that existed at the present level of exposure in this area can be deduced from figure 5. For each sample plotted on this diagram,

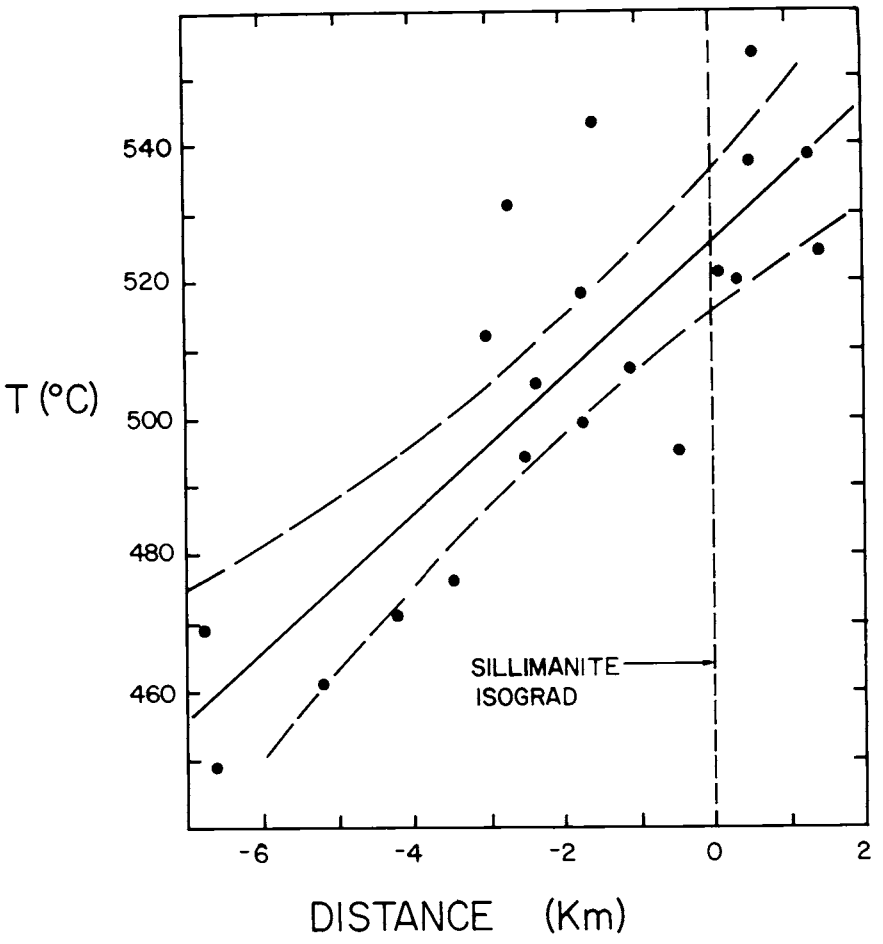

Fig. 5. Plot of Ferry's (1980) garnet-biotite thermometric data as a function of distance from the sillimanite isograd (reference line at 0 km) in the Waterville-Vassalboro area, south-central Maine. The data were derived from figure 4 (see text). The solid line is the thermal gradient deduced by least squares fitting of a straight line to the data points. The curved dash lines outline the $\pm 2\sigma$ confidence interval about the mean (solid) line.

the distance was determined from figure 4 as the shortest distance to the sillimanite isograd. The line in figure 5 obtained by least squares fitting has a gradient of 10°C/km.[6] The thermal gradient so deduced would be valid even if there were a systematic error in the calibration of the garnet-biotite geothermometer. With this thermal gradient, a maximum bivariant temperature interval of 12°C would yield a maximum

[6] Without a thermal model for this area, we have arbitrarily assumed that the thermal gradient is a linear function of distance. The distribution of the data points in figure 5 provides no cogent argument for or against this assumption.

thickness of 1.2 km for a bivariant zone of andalusite + sillimanite. The spatial distribution of Ferry's samples (Ferry, 1980; J.M. Ferry, personal commun.) constrain the bivariant zone (that is, the zone of coexisting andalusite + sillimanite) to a maximum of 700 to 800 m thick. P.H. Osberg (Ferry, 1980, p. 723) considers that the andalusite-sillimanite bivariant zone in this area is only a few meters in thickness. With a 10°C/km thermal gradient, a bivariant zone 700 to 800 m thick would correspond to a *maximum* temperature interval of 7° to 8°C. This analysis is consistent with the temperature interval deduced from figure 3.

Novak and Holdaway (1981) studied the southwestern extension of the sillimanite isograd shown in figure 4. In reexamining specimens from this area, M. J. Holdaway (personal commun.) has clarified the distribution of the aluminum silicates in the vicinity of this isograd. Fibrolite becomes considerably more abundant southwest of the area described by Ferry (1980). Sillimanite and andalusite coexist over a zone that is up to 2.6 km thick. However, most of the samples containing coarse, prismatic sillimanite coexisting with andalusite are limited to a zone within 100 m of the isograd. M. J. Holdaway (personal commun.) believes that fibrolite formed from staurolite decomposition, whereas sillimanite formed from andalusite. It is considered that the andalusite-forming event was followed by a separate sillimanite-producing event (Novak and Holdaway, 1981; Holdaway and others, 1982). M. J. Holdaway (personal commun.) contends that the zone of coexisting andalusite and sillimanite reflects sluggish kinetics. He also believes that the sillimanite isograd in this area dips gently northward; thus, the true thickness of the andalusite + sillimanite zone (as measured normal to the isograd surface) may be considerably smaller than the map width of this zone. Further interpretation of the aluminum silicates in the area described by Novak and Holdaway (1981) must await analysis of the role of minor element solid solution.

While recognizing the complications toward the southwest, we consider that the sillimanite isograd within the area shown in figure 4 may represent a close approximation to a univariant equilibrium. As such, this isograd would be an excellent thermal marker horizon. As the experimental data of Kerrick and Heninger (1984) and Nitkiewicz and Kerrick (in preparation) confirm Holdaway's (1971) P-T location of the andalusite-sillimanite equilibrium, our analysis supports Ferry's (1981) thermobarometric analysis using Holdaway's (1971) data.

Ardara aureole, Ireland.—The Ardara pluton represents one of the southernmost of the Donegal granites (Pitcher and Berger, 1972). This aureole has been described in several studies (Akaad, 1956; Pitcher and Read, 1963; Naggar and Atherton, 1970; and Kerrick, 1987). Kerrick's (1987) analysis suggests that fibrolite in this aureole formed metastably in the waning stages of the thermal event. As shown by the sampling control in figure 6, the sillimanite isograd represents the abrupt disappearance of andalusite coupled with the appearance of sillimanite.

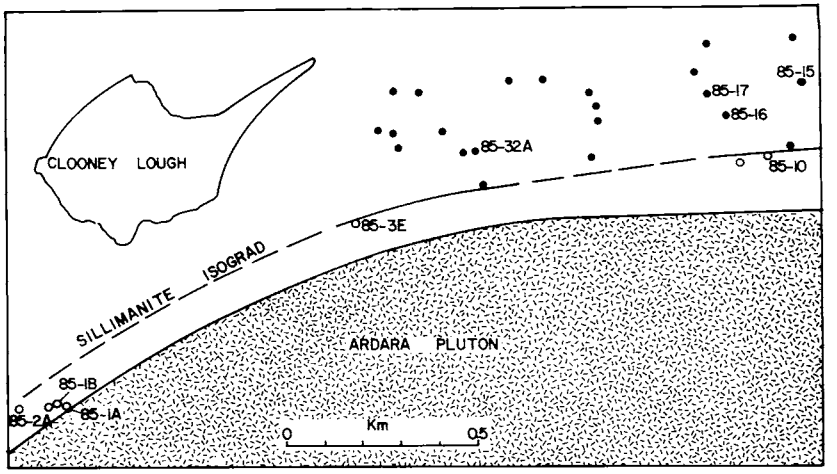

Fig. 6. Map of the northern Ardara aureole, Ireland, showing localities of samples containing andalusite (filled circles) and sillimanite (open circles) (from Kerrick, 1987). Sample numbers correspond to those in table 1.

Coexisting andalusite and sillimanite are rare (the only reported occurrence of this mineral pair is by Akaad, 1956). According to figure 6, the bivariant zone (assuming it exists) would be constrained to a maximum thickness of 50 m. From figure 7, the temperature interval correlated with a 50 m-wide zone would be about 25°C. As the bivariant zone may be less than 50 m in thickness, this temperature interval is a *maximum* value. As shown in figure 2, the K isopleths are virtually parallel to the reference curve (K = 1.0). Thus, we may use figure 3 to evaluate the temperature interval of bivariancy for areas metamorphosed at pressures other than that of the triple point. Because the average compositions of andalusite and sillimanite in this aureole are virtually identical (table 1), we may envision a prograde path in figure 3 with an initial andalusite composition of $X_{MAlSiO_5} = 0.008$ (that is, the average andalusite composition for the Ardara samples); the temperature interval of bivariancy would be about 10°C. This interval is compatible with the maximum temperature interval (25°C) deduced from figure 7. As with the sillimanite isograd in the Waterville-Vassalboro area, we conclude that the sillimanite isograd in the northern Ardara aureole is a close analogue to the univariant reaction involving endmember compositions. As shown in figure 6, this isograd forms a smooth curve paralleling the intrusive contact. This supports Kerrick's (1987) contention that this isograd corresponded to an isothermal surface during metamorphism.

Central Ryoke Belt, Japan.—Yokoi (1983) described a sequence of amphibolite facies pelitic gneisses in the Hiraoka-Kadoya area in the central part of the Ryoke metamorphic belt of Japan. To the northwest, this area is bounded by a biotite-hornblende quartz diorite, whereas the

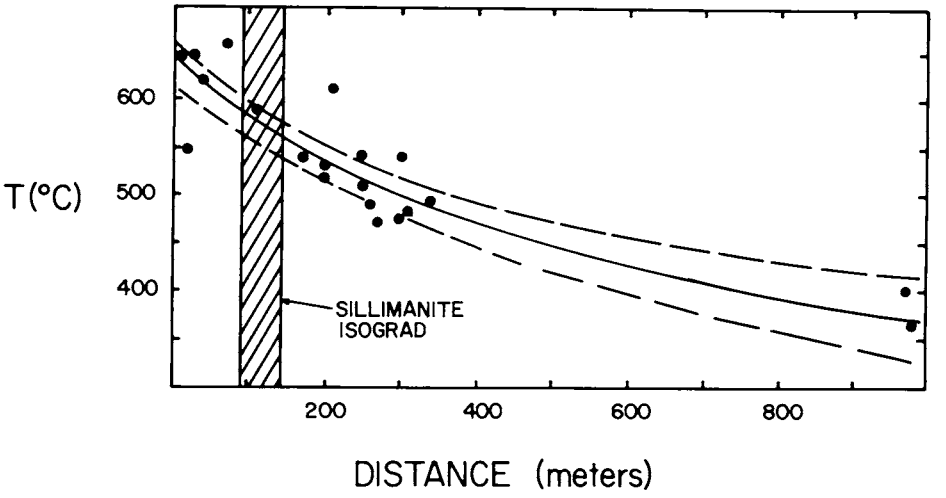

Fig. 7. Garnet-biotite thermometric data for the Ardara aureole as a function of distance from the intrusive contact (from Kerrick, 1987). The solid curve was obtained by least squares fitting to the data points. The dashed lines encompass the $\pm 2\sigma$ confidence interval about the line fit by least squares. The hachured area gives the maximum width of a zone containing andalusite + sillimanite.

intrusive forming the southeast boundary is a biotite granodiorite. Based on the distribution of fibrolite and on the variation in K_D for Mg-Fe partitioning between biotite and cordierite, Yokoi (1983) concluded that metamorphic grade increases from southeast toward the northwest.

As shown in figure 8, andalusite-sillimanite pairs display a consistent prograde increase of Fe_2O_3 content.[7] Considering that the vertical axis of figure 8 is correlative with temperature, the prograde variation in Fe content of coexisting andalusite and sillimanite appears to outline a bivariant partitioning loop. In the Ryoke area, however, we cannot rationalize the prograde evolution along the partitioning loop by assuming that the reactant andalusite[8] had the same composition in all samples. As discussed in the section on the Mt. Moosilauke area, the composition of the reactant andalusite is constrained by the compositional range of the andalusite-sillimanite pairs. Consider the prograde T-X loop that would be constrained by the composition of reactant andalusite in the lowest grade samples. Of particular note are the compositional ranges of reactant andalusite in samples AS9 ($X_{FeAlSiO_5}$ = 0.0034 – 0.0039) and AS8 ($X_{FeAlSiO_5}$ = 0.0037 – 0.0042). As these compositional ranges are below those of the higher grade samples (AS1–AS6), one cannot derive the entire

[7] Yokoi's (1983) analysis was restricted to Fe as the only minor element.
[8] As there is no distinct andalusite-only zone in the Ryoke area, the reactant andalusite is unobservable in this case.

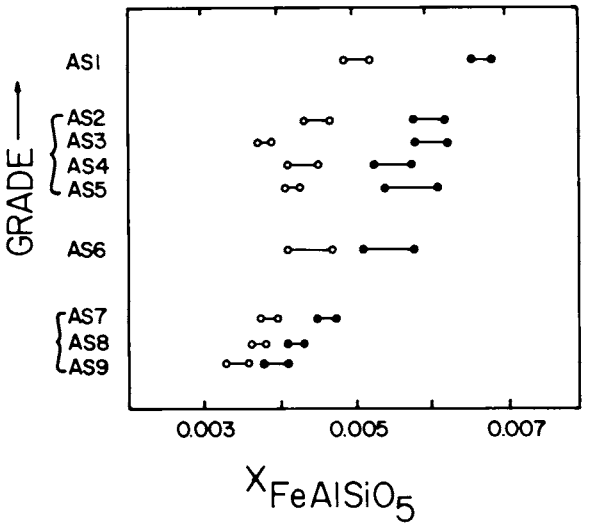

Fig. 8. Compositional data of rims for andalusite-sillimanite pairs in the central Ryoke Belt of Japan (from Yokoi, 1983, fig. 9). The sample numbers are given on the ordinate; the brackets enclose samples that are essentially at the same metamorphic grade. The open circles refer to sillimanite, whereas the filled circles correspond to andalusite; the bars give compositional ranges.

T-X loop from the same reactant andalusite. Accordingly, there must have been an increase in Fe content of the reactant andalusite in progressing upgrade from sample AS9 to AS1. This is compatible with Grew's (1980) analytical and theoretical treatment showing that the Fe_2O_3 content of sillimanite in metapelites increases with metamorphic grade. Grew (1980) considered that the equilibrium:

$$Fe_2O_3 + SiO_2 = Fe_2SiO_5$$

$$\begin{pmatrix}\text{ilmenite}\\ \text{component}\end{pmatrix} \quad (\text{quartz}) \quad \begin{pmatrix}\text{sillimanite}\\ \text{component}\end{pmatrix}$$

was responsible for the prograde increase in Fe_2O_3 of sillimanite. Although Yokoi (1983) did not list ilmenite as an accessory, it is very common in metapelites. Thus, an analogous equilibrium *could* be responsible for the apparent increase in Fe content of reactant andalusite with increasing metamorphic grade in the central Ryoke area. If ilmenite is not present, it is nevertheless possible that the prograde changes in the Fe content of sillimanite could be rationalized by reaction with coexisting ferromagnesian minerals (that is, biotite and cordierite).

The values of K_D for andalusite-sillimanite pairs in samples from this area are between 1.000 and 1.002. Assuming ideal mixing, these K_D

values, coupled with figure 2, suggest negligible temperature variation across the area. If true, the lack of significant temperature variation across this belt could be explained by a gentle dip of the isothermal surfaces during metamorphism or by thermal buffering due to partial melting. The widespread abundance of migmatitic gneisses would be compatible with the hypothesis of thermal buffering due to anatexis. These conclusions follow from K_D values calculated from ideal mixing; however, non-ideal mixing could strongly influence the prograde variation in K_{eq}. For example, let us assume arbitrarily that for sillimanite the activity coefficient (γ) of the Al_2SiO_5 component changes linearly from 1.0 to 1.5 in the compositional range $X_{Al_2SiO_5} = 1.0$ to 0.993. Furthermore, we assume Raoult's Law behavior in andalusite over the compositional range shown in figure 8. In this case $K_{eq} = (\gamma^{Sill}_{Al_2SiO_5} X^{Sill}_{Al_2SiO_5}/X^{And}_{Al_2SiO_5})$ would increase from 1.243 in sample AS9 to 1.359 in sample AS1. At a pressure of 3 kb, for example, this K_{eq} variation would correspond to a temperature variation of 40°C (fig. 2). In this case, the prograde changes in Fe contents of andalusite and sillimanite would correspond to a progressive increase in temperature from southeast to northwest (as implied by Yokoi, 1983). This argument would also hold with the more reasonable assumption of non-ideal mixing in andalusite (as well as in sillimanite), but, as $X_{Al_2SiO_5}$ is decreased, the activity coefficient of the Al_2SiO_5 component in sillimanite increases at a greater rate than the change in the activity coefficient of this component in andalusite. This argument is not unreasonable if we compare the crystal chemistry of andalusite and sillimanite assuming that transition metals dominantly substitute into the Al octahedron. This site is larger and more distorted in andalusite compared to sillimanite (Ribbe, 1980). As the mean Al^{VI}-O bond distances in andalusite are greater than sillimanite, we might expect that the activity coefficient of Fe^{3+} in the octahedral site of sillimanite would exceed that in andalusite.[9] Because Yokoi (1983) shows a significant upgrade change in the distribution coefficient for Mg/Fe of cordierite-biotite pairs, we consider that non-ideal mixing is a more likely explanation for the constancy of K_D compared to the argument of constant temperature due to thermal buffering by anatexis or to the gentle dip of isothermal surfaces during metamorphism.

Kiglapait aureole, Labrador.—The northern aureole of the Kiglapait gabbroic intrusion includes metasediments of the Proterozoic Snyder group (Speer, 1982; Berg and Docka, 1983). Contact metamorphism in this area has been discussed by Speer (1982), Berg and Docka (1983), and Docka, Berg, and Klewin (1986). As in Kerrick's (1987) study of contact aureoles in Donegal, Ireland, Speer (1982) suggests that fibrolite may be metastable in this aureole. On the basis of the distribution of andalusite and sillimanite, the aureole is divided into three zones

[9] Because activity coefficients are correlative with enthalpy, and enthalpy of a cation is a function of cation-oxygen bond distances, we expect the activity coefficient of a cation on a particular lattice site to be inversely proportional to mean cation-oxygen bond distances.

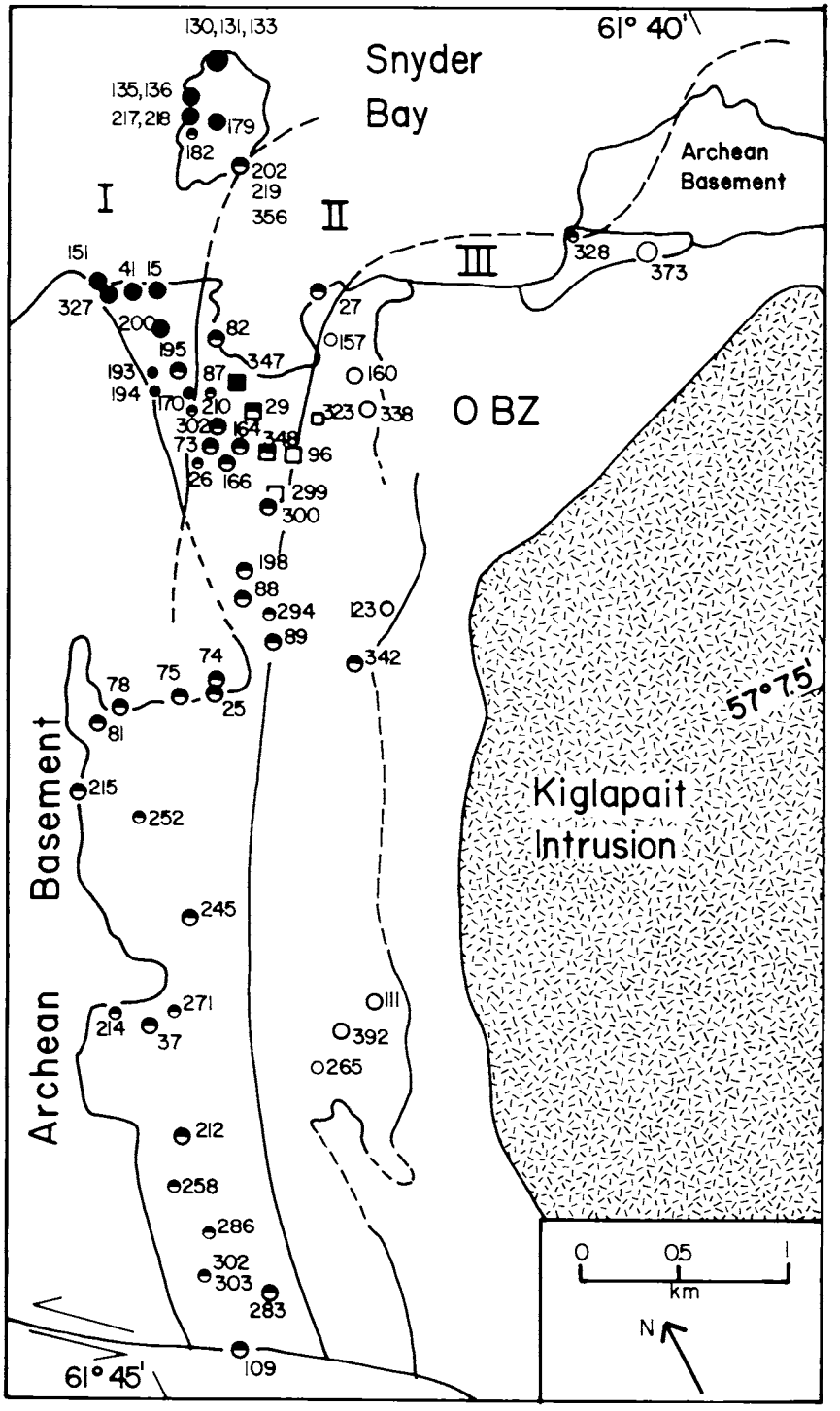

Fig. 9. Sample locality map for the Snyder Group, Labrador. The squares represent graphite-sulfide metasiltstones, whereas the circles are lower and upper metaquartzites. The aluminum silicates are denoted by: filled = andalusite only; half-filled = andalusite + sillimanite; open = sillimanite only. Sample numbers are given for those specimens for which modal and/or compositional data were obtained.

(fig. 9): zone I (andalusite), zone II (andalusite + sillimanite), and zone III (sillimanite). At the present level of exposure, zone II has a map thickness of about 700 m (Speer, 1982).

The distribution of the metapelite aluminum silicate assemblages in samples from the Kiglapait aureole is shown in figure 9. The zone boundaries are from Speer (1982). The 30° to 40° southeast dip of the lithologic layering in the aureole conforms to that of the igneous layering of the intrusion, and the isograds are assumed to conform to this geometry. Accordingly, the 700 m map width of zone II corresponds to a "true" thickness (as measured normal to the isograd surfaces) of about 300 m. In figure 9, the few samples with aluminum silicate assemblages outside their respective zone result from the irregular surface topology intersecting shallow, southeasterly dipping isograd surfaces or from rock compositional differences. Because of the shallowly dipping isograds, it is possible to find misplaced aluminum silicate assemblages in topographic lows and highs (the relief is up to 400 m).

Two distinct lithologies are indicated in figure 9; that is, lower and upper metaquartzites versus graphite-sulfide metasiltstone (Speer, 1978, 1982). Coexisting silicates in the metasiltstone contain much less iron than the silicates in the metaquartzite units. The effect of this compositional difference on the andalusite → sillimanite transition is discussed below.

To monitor the progress of the andalusite → sillimanite reaction in zone II, samples from the metaquartzites and aluminous metapelites of the lower metaquartzite unit were chosen. The modal amounts of andalusite and sillimanite were determined by counting a square 0.33 × 0.33 mm grid consisting of 1200 to 2000 points per thin section. The modal data, plotted against distance from the intrusive contact (fig. 10), suggest that, as zone II is traversed upgrade, there is an increase in the amount of sillimanite with a corresponding decrease in the amount of andalusite. Using the modal sillimanite/(sillimanite + andalusite) ratio as a monitor of metamorphic grade, coupled with the iron content of the coexisting aluminum silicates in samples containing the assemblage: aluminum silicate + biotite + cordierite + muscovite + quartz + K-feldspar + plagioclase + magnetite + ilmenite ± pyrite ± pyrrhotite, figure 11 shows that the prograde changes in minor element contents of andalusite and sillimanite apparently define a partitioning loop (as in the Ryoke area). The data in figure 11 suggest that the $T\text{-}X_{MAlSiO_5}$ loop narrows toward higher T and X_{MAlSiO_5} values. As shown in figure 12, this phenomenon is compatible with a model assuming that, with increasing Fe content, the increase in activity coefficient of the Al_2SiO_5 component in sillimanite significantly exceeds that of andalusite.

As shown in figure 2, the variation in K_{eq} with temperature is relatively insensitive to pressure. Thus, we may compare the $T\text{-}X_{MAlSiO_5}$ loops of metapelites metamorphosed at different pressures. The reference temperature (T_o) of each loop illustrated in figure 13 would correspond to that of the equilibrium involving pure endmember

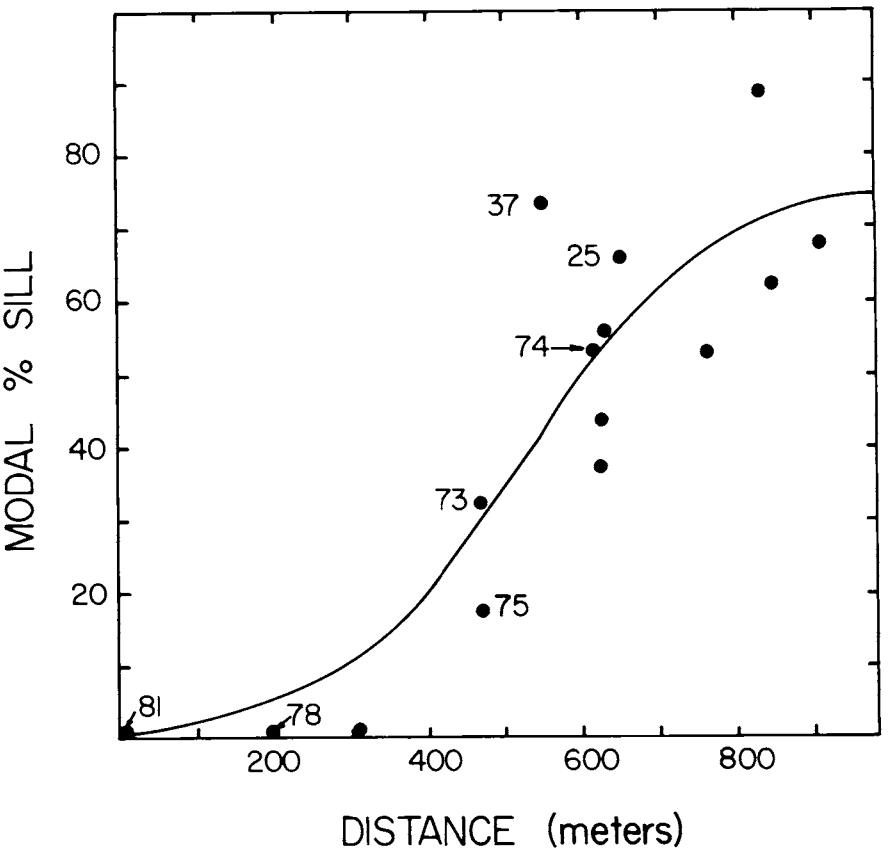

Fig. 10. Modal percentage of sillimanite (Sill/And + Sill) as a function of map distance in metamorphic zone II of the Kiglapait aureole, Labrador. On the abscissa, the zero value corresponds to the boundary between metamorphic zones I and II, whereas the boundary between zones II and III is at 1 km. The sigmoidal curve was obtained by least squares fitting to the data points using the function: $y = 1/a + be^{-x}$, where a and b are constants, y = ordinate values, x = abscissa values.

andalusite and sillimanite at the prevailing pressure during metamorphism of that area. As the regionally metamorphosed metapelites of the Ryoke belt *may* have been metamorphosed at higher pressures than those of the Kiglapait aureole, figure 13 depicts the T_o value of the Ryoke Belt to be lower than that of the Kiglapait aureole. The X_{MAlSiO_5} values of andalusite-sillimanite pairs in the Ryoke metamorphic belt are lower than those of the Kiglapait aureole. Thus, with increasing metamorphic grade (and, thus, increasing T), we propose that the Ryoke area corresponds to the *divergent* portion of the T-X loop whereas the Kiglapait aureole corresponds to the *convergent* portion of the T-X loop (fig. 13).

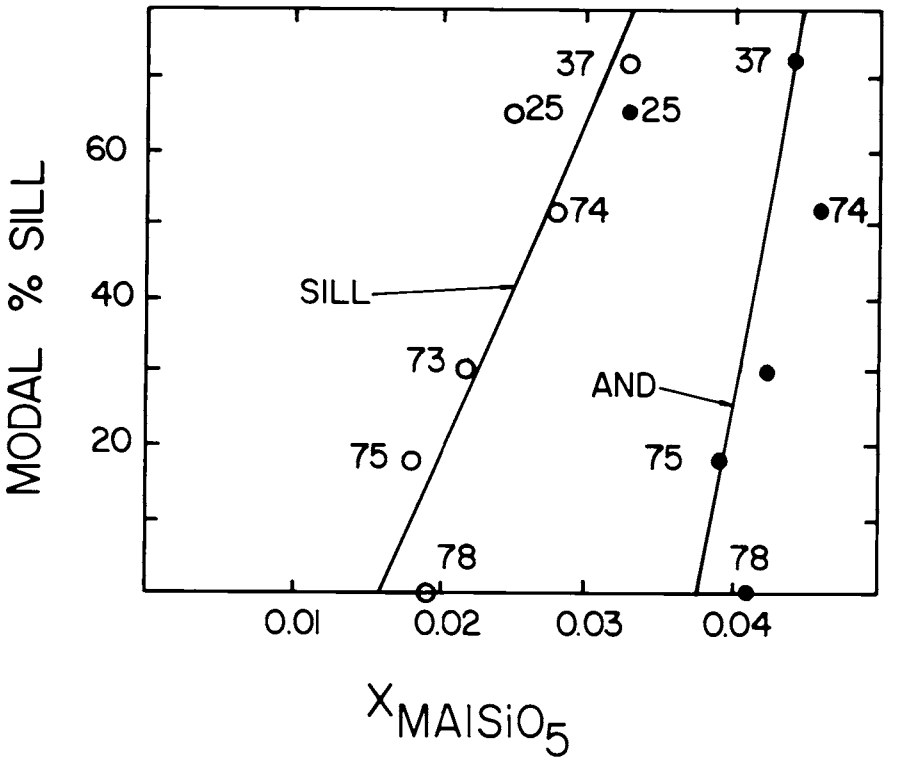

Fig. 11. Plot of modal percent sillimanite (in relation to modal amounts of andalusite + sillimanite) as a function of composition of andalusite-sillimanite pairs from zone II of the Kiglapait aureole, Labrador. The open circles represent sillimanite, whereas the filled circles correspond to andalusite. The sample numbers are indicated next to each data point.

In figure 11, the data points for sample 25 appear to be anomalous in relation to the general trend of the partitioning loop suggested by the other data points. If we exclude sample 25, the entire prograde T-X loop of figure 11 *could* be generated by the same initial value of X_{MAlSiO_5} of the "reactant" andalusite. However, the compositional range of this andalusite would be restricted (X_{MAlSiO_5} = 0.032–0.038). Because most analyzed andalusites in zone I samples have compositions that span a wider range (fig. 14), we consider it unlikely that the samples plotted in figure 11 had the same composition of reactant andalusite.

As evident from figure 9, the andalusite-sillimanite transition in the graphite sulfide metasiltstones behaves differently from that in the metaquartzites. Lying within zone II, the metasiltstones have assemblages that contain either andalusite or sillimanite. Only two samples have coexisting andalusite + sillimanite: sample 29 with subequal amounts and sample 348 with only traces of sillimanite. The lithologic

Fig. 12

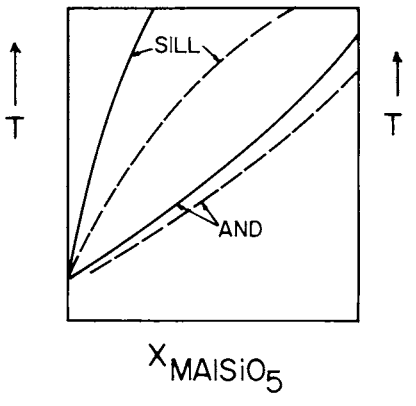

Fig. 13

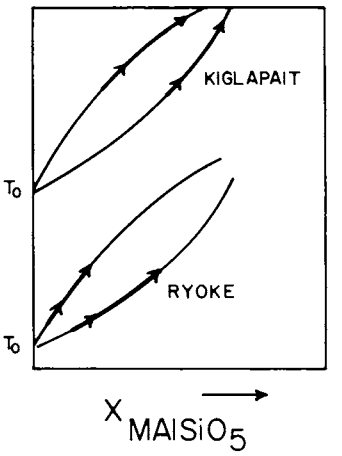

Fig. 12. Schematic illustration of partitioning loops between andalusite (And) and sillimanite (Sill). The solid lines correspond to ideal mixing whereas the dashed lines are for non-ideal mixing. For the non-ideal solid solutions, it is assumed that, with increasing X_{MAlSiO_5}, the increase in the activity coefficient of the Al_2SiO_5 component in sillimanite significantly exceeds that in andalusite.

Fig. 13. Schematic comparison of the andalusite-sillimanite partitioning "loops" in the Kiglapait aureole (Labrador) versus the central Ryoke Belt (Japan). The heavy lines with arrows correspond to the prograde paths in each area.

control is illustrated by comparing sample 300, a metaquartzite containing andalusite + sillimanite, with sample 299, a graphite-sulfide metasiltstone containing only sillimanite—these samples were collected within a few meters of one another. Considering a T-X partitioning loop (fig. 3), these differences can be explained by the lower minor element content of the aluminum silicates in graphite-sulfide metasiltstones ($X_{MAlSiO_5} \leq 0.01$) as compared to that in the metaquartzites ($X_{MAlSiO_5} \geq 0.01$). The differences in minor element concentrations of aluminum silicates in these contrasting lithologies, coupled with the presence of graphite only in the metasiltstones, illustrates the inverse correlation between f_{O_2} and impurity concentrations of andalusite and sillimanite (see also Grambling and Williams, 1985).

In the vicinity of Snyder Bay, Berg and Docka (1983) claim that the zone of coexisting andalusite + sillimanite has a much broader map width than that described in this study and by Speer (1982). However, the relatively gentle dip of the isograds, coupled with topographic relief variations, complicates correlation of distance with metamorphic grade (as was done by Berg and Docka, 1983). Because Berg and Docka (1983) do not give mineral assemblages for the sample locations given in figure 2 of their paper, we are unable to evaluate further the relationship of their mineral assemblage localities with topography.

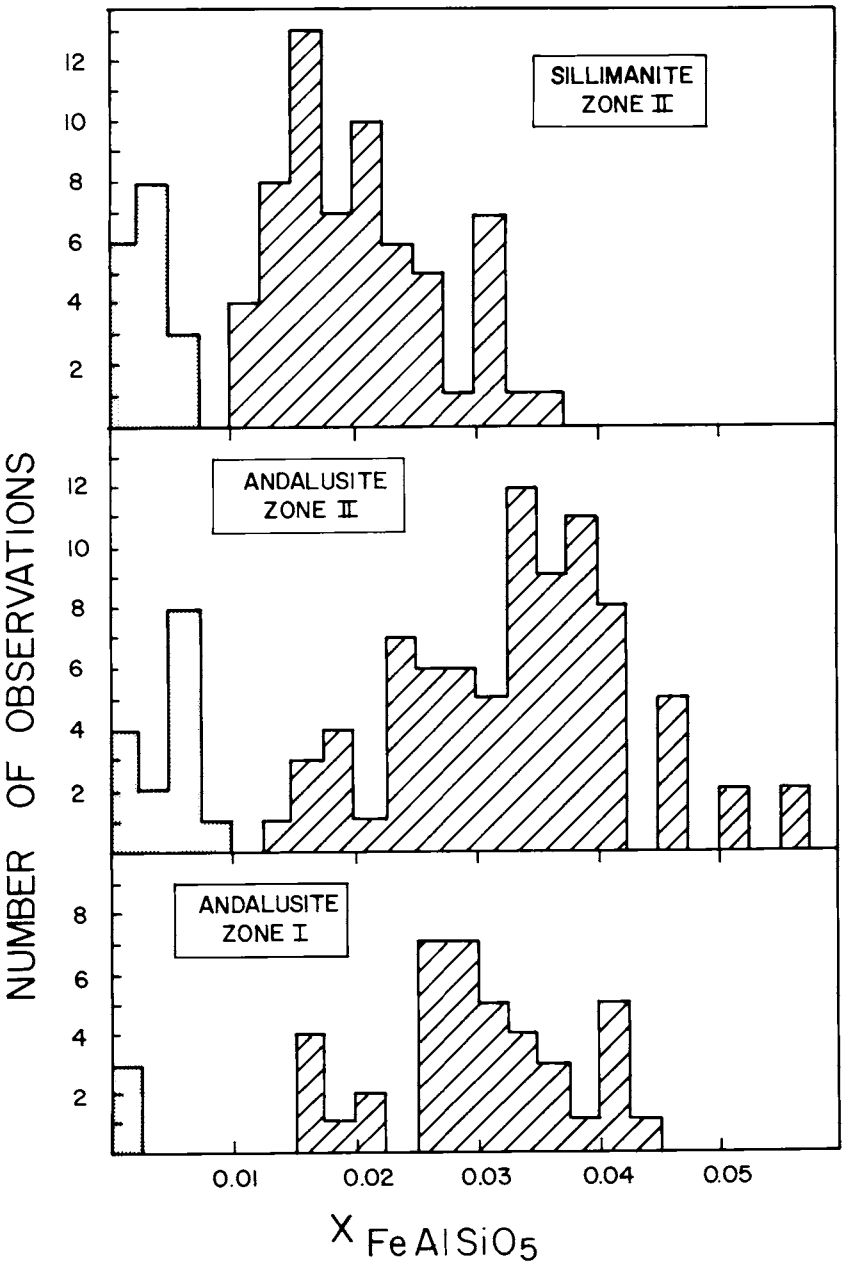

Fig. 14. Compositional data for aluminum silicates in metamorphic zones I and II of the Kiglapait aureole, Labrador.

Steinach aureole, Bavaria.—In metapelites of the Steinach aureole of Bavaria, andalusite and sillimanite coexist in a zone several hundred meters in thickness (Okrusch, 1969, 1971). The andalusite and sillimanite contain appreciable Fe contents. As the iron concentrations and K_D values (table 1) are comparable to those of the Kiglapait aureole, we expect (by analogy) that minor element partitioning results in a significant bivariant zone. The three samples analyzed by Okrusch and Evans (1970) are float with no outcrops in the immediate vicinity of the sample localities (M. Okrusch, personal commun.). Because the *in situ* distances from the intrusive contacts cannot be determined, we are unable to evaluate the relationship between metamorphic grade and minor element content of the aluminum silicates in this aureole.

PERALUMINOUS GRANITOIDS

Andalusite and sillimanite are moderately common constituents of peraluminous granitoids (Clarke and others, 1976; Lorenzoni and others, 1979; Abbott and Clarke, 1979; Currie and Pajari, 1981; Price, 1983; Brandstätter and Zemann, 1984). In many cases it is considered that these aluminium silicates formed at the magmatic stage and not as products of sub-solidus reactions (Clarke, 1981). If we consider the water-saturated granodiorite solidus, the Al_2SiO_5 phase equilibria of Holdaway (1971) precludes a stability field of andalusite + melt (fig. 15). This *presumably* explains why Clarke and others (1976) used the Al_2SiO_5 phase relations determined by Richardson, Gilbert, and Bell (1969), as this allows a stability field for andalusite + melt. In addressing this dilemma, Holdaway (1971, p. 128) appealed to expansion of the P-T field of melt ". . . by volatiles such as fluorine".

If Holdaway's (1971) phase diagram is accepted, as suggested in the section on *Thermodynamic Analysis and Phase Equilibria,* we need to rationalize his phase diagram with the fact that textural evidence supports the equilibrium coexistence of andalusite + melt (Clarke and others, 1976). One possibility is that the minor element contents of magmatic andalusites are large enough to expand the andalusite P-T field into that of melt. This possibility was alluded to by Clarke and others (1976) in their analysis of phase equilibria of peraluminous granitoids.

We have obtained electron probe analyses of aluminum silicates in selected samples of peraluminous granitoids (table 2). As shown in figure 16, the andalusite in a sample of peraluminous aplite dike forms individual subhedral crystals; thus, we find no cogent evidence against textural equilibrium. Clarke and others (1976) provide similar arguments for textural equilibrium of andalusite in granitoids from the South Mountain batholith.

Fibrolite and coarse, prismatic sillimanite occur in sample 1-SL-1, whereas fibrolite is the only form of sillimanite in sample 5-1#1. In sample 1-SL-1 (table 2) fibrolite occurs as elongated bundles concentrated along grain boundaries of quartz and feldspar. Thus, fibrolite

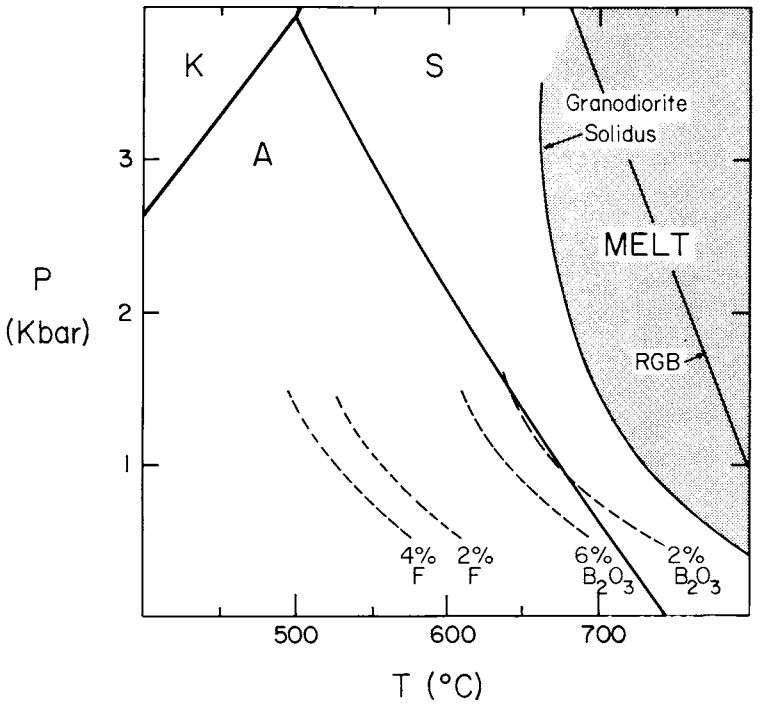

Fig. 15. Phase diagram relating to the occurrence of aluminum silicates in peraluminous granitoids. The heavy lines are the Al_2SiO_5 stability relations from Holdaway (1971). RGB is the andalusite-sillimanite equilibrium determined by Richardson, Gilbert, and Bell (1969). The granodiorite solidus and the position of the solidus for selected weight percentages of F and B_2O_3 in granodiorite melts (dashed lines) are from Manning and Pichavant (1983).

probably crystallized after quartz and feldspar. Fibrolite in sample 5-1#1 (table 2) is spatially associated with micas (biotite and muscovite). Following Kerrick's (1987) interpretation of fibrolite in metapelites, this association *may* imply that fibrolite formed by the relatively late-stage replacement of micas. Accordingly, there is doubt about assuming that fibrolite was in equilibrium with melt. Nevertheless, we have obtained electron probe analyses to compare minor element chemistry of coexisting andalusite + fibrolite. If we make the assumption of equilibrium, the K_D values of andalusite-sillimanite and andalusite-fibrolite pairs (table 2), coupled with figure 2, suggest that the P-T location of the andalusite-sillimanite equilibrium in these samples would differ little from that of the reference curve ($K_D = 1.0$). This analysis is strengthened by the fact that the minor element contents of the andalusite and sillimanite are low enough that the assumption of Raoultian behavior may be reasonable. These arguments are valid even if we disregard fibrolite as a phase in equilibrium with peraluminous melts. As shown in the inset of figure 3, the composition of andalusite alone (for example, X_1) would yield a

TABLE 2

Electron probe analyses of aluminum silicates in peraluminous granitoids

	Cooma granodiorite, Australia*		Sebec Lake, Maine**		
Sample no.	5-1#1	5-1#1	1-SL-1	1-SL-1	1-SL-1
Al silicate:***	A	F	A	F	S
			Wt Percent Oxide		
SiO_2	36.21	37.14	37.60	37.17	36.60
Al_2O_3	62.74	62.96	62.65	61.37	63.80
TiO_2	0.11	0.15	0.09	0.14	0.09
Fe_2O_3	0.56	0.26	0.31	0.57	0.19
Cr_2O_3	0.04	0.04	0.02	0.03	0.01
MnO	0.03	0.0	0.0	0.0	0.0
MgO	n.d.	n.d.	n.d.	n.d.	n.d.
V_2O_5	0.0	0.0	0.0	0.0	0.0
Sum	99.69	100.55	100.67	99.28	100.69
			Formula basis 5 oxygens		
Si	0.983	0.997	1.008	1.011	0.982
Al	2.007	1.993	1.980	1.969	2.018
Ti	0.002	0.003	0.002	0.003	0.002
Fe^{3+}	0.011	0.005	0.006	0.012	0.004
Cr	0.001	0.001	0.000	0.001	0.000
Mn	0.001	0.0	0.0	0.0	0.0
Mg	n.d.	n.d.	n.d.	n.d.	n.d.
V	0.0	0.0	0.0	0.0	0.0
Sum	3.005	3.000	2.997	2.995	3.005
X_{MAlSiO_5}	0.015	0.009	0.008	0.015	0.006
$X_{Al_2SiO_5}$	0.985	0.991	0.992	0.985	0.994
	$K_D = 1.006$		$K_D^{A-F} = 0.993$		
			$K_D^{A-S} = 1.002$		

*The Cooma granodiorite is described by Chappell and White (1976).
**Sample locality: 12 km northwest of the town of Dover-Foxcroft, central Maine. This intrusive is part of the Katahdin magma series described by Chacko (1983).
***A = andalusite, S = sillimanite, F = fibrolite

maximum temperature (T_1) at the pressure of crystallization. Our electron probe analyses of andalusite in samples of peraluminous granitoids (table 2) yield minor element contents which suggest (by analogy with fig. 3) that the andalusite P-T stability field for these compositions is similar to that of the pure endmember. Accordingly, minor element concentrations of the aluminum silicates in these samples suggest that impurities are insufficient to expand the andalusite P-T field into that of melt (fig. 15). We arrive at the same conclusion if we consider the analytical data of other workers on andalusite and sillimanite in peraluminous intrusives (Clarke and others, 1976; Brandstätter and Zemann, 1984).

Barring significant expansion of the andalusite P-T stability field due to minor element solid solution, we require an alternative explanation for the textural evidence supporting andalusite in equilibrium with

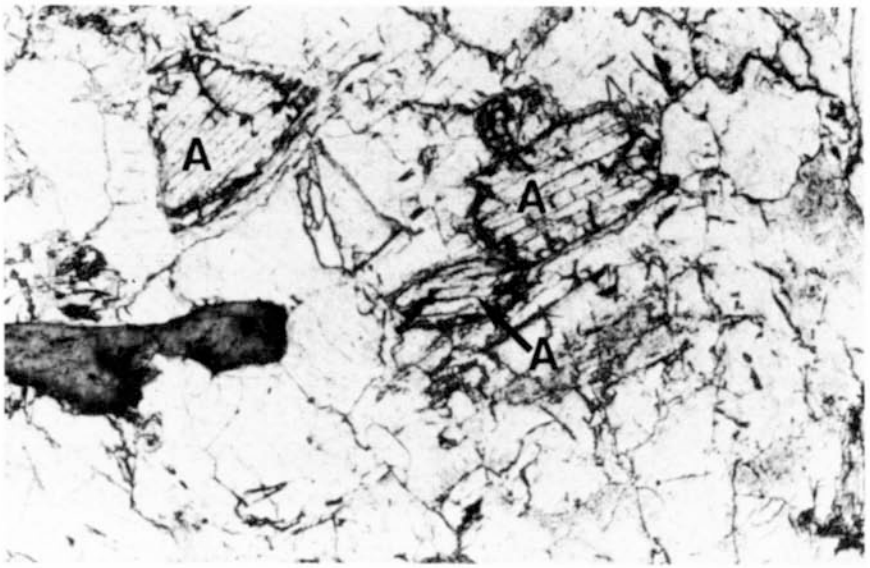

Fig. 16. Andalusite (A) in a sample of aplite dike from the South Mountain Batholith, southern Nova Scotia. Width of photo corresponds to 1.37 mm.

melt, coupled with the phase equilibria for melts. Recent work (Manning and Pichavant, 1983; Pichavant, 1983; Pichavant and Manning, 1984) has shown that relatively small amounts of B and (especially) F yield a significant temperature depression of the solidus for the granite minimum composition as compared to the minimum for the pure (F- and B-free) system. For example, these studies suggest that, in the pressure range 1 to 2 kb, addition of 2 wt percent B_2O_3 to this system lowers the solidus 50° to 60°C, whereas 2 wt percent F depresses the solidus 170° to 180°C (fig. 15). That small amounts of F and B could exist in peraluminous melts is supported by the fact that tourmaline and topaz are moderately common constituents of peraluminous granitoids (Clarke, 1981). Furthermore, experimental data (Burnham and Nekvasil, 1986) show that the liquidi of peraluminous compositions are at lower temperatures than those of metaluminous compositions that lack excess Al. Because we expect the addition of excess Al to have the same effect on solidi as it does liquidi, we conclude that the P-T stability field of peraluminous melts is significantly larger than that of metaluminous melts.

We propose that excess Al, along with the presence of F and/or B, results in a P-T stability field for andalusite + melt. Accordingly, we consider that the presence of andalusite in peraluminous granitoids does not provide an argument favoring the Al_2SiO_5 phase equilibria of Richardson, Gilbert, and Bell (1969) over that of Holdaway (1971).

DISCUSSION AND CONCLUSIONS

This study shows that minor element contents are an important factor to consider in evaluating the andalusite → sillimanite isograd reaction. Comparison of several different field examples of andalusite-sillimanite parageneses confirms the conclusion (based on T-X_{MAlSiO_5} loops) that the temperature interval of bivariancy is a function of the minor element concentration. If we assume a model of progressive metamorphism, bivariancy should be reflected in the concentration of minor elements in andalusite immediately below the sillimanite isograd. With low minor element contents of this reactant andalusite, the bivariant interval should be narrow, and the isograd should closely approximate the andalusite-sillimanite univariant reaction. Such behavior is confirmed in metapelites of the Ardara aureole and in the regionally metamorphosed pelites of the Waterville-Vassalboro and Mt. Moosilauke areas. We believe that the sillimanite isograd in these areas forms an excellent thermobarometric reference. Larger minor element contents of reactant andalusite should produce more widespread bivariancy, as is suggested by the relatively broad zone of coexisting andalusite + sillimanite in the Kiglapait aureole.

The lack of knowledge of activity coefficients of impure andalusite and sillimanite introduces error in the P-T calibration of the K_D values as determined by compositional data on andalusite-sillimanite pairs. Our confidence in using the ideal mixing approximation to quantify the P-T conditions of the equilibrium as a function of K_D (as in fig. 2) diminishes with increasing minor element concentrations of andalusite and sillimanite. In this regard, we consider that the accuracy of Grambling and Williams' (1985) calculated perturbations of the Al_2SiO_5 phase equilibria to be best for the Picuris Range, less for the Truchas Range, and least for the Rio Mora Uplift (see Grambling and Williams, 1985, fig. 12). However, in our analysis of the Ryoke metamorphic belt, we suggested that non-ideal mixing could significantly affect the equilibrium constant for andalusite-sillimanite pairs. In the light of the fact that the impurity levels of andalusite and sillimanite in the Ryoke area are relatively low, we might therefore question the use of figure 2 in calibrating the P-T displacement of the andalusite-sillimanite equilibrium in other parageneses with such low impurity levels (for example, the Ardara aureole, and the Waterville-Vassalboro and Mt. Moosilauke areas). However, compared to the Ryoke Belt, the Ardara aureole and the Waterville-Vassalboro area have the advantage of garnet-biotite thermometric data which provide information on the thermal gradient during metamorphism. Because the map widths of the bivariant zones in these areas are compatible with the temperature range of bivariancy as deduced from equilibrium constants calculated from ideal mixing, we conclude that the approximation of ideal mixing is reasonable for andalusite and sillimanite with relatively low impurity levels (that is, $X_{MAlSiO_5} \leq 0.01$). This conclusion is in agreement with Grew's (1980) thermodynamic analysis of the mixing of Fe in sillimanite.

The sillimanite isograds in the Ardara aureole and in the Waterville-Vassalboro area are notable for the abrupt appearance of sillimanite coupled with the disappearance of andalusite. This suggests that the andalusite → sillimanite isograd reaction is kinetically rapid in the temperature-time path of prograde metamorphism in rocks at the isograd. This implies that there are no significant barriers in the nucleation and growth of sillimanite at P-T conditions close to the andalusite-sillimanite equilibrium curve. The apparent rapidity of the transformation lends credence to the assumed close correspondence of these isograds to the andalusite-sillimanite univariant reaction and to application of an equilibrium model for minor element partitioning between andalusite-sillimanite pairs. In the light of the rapidity of the andalusite → sillimanite isograd reaction, we consider minor element partitioning as a very likely reason for regimes where andalusite-sillimanite pairs form a zone of significant thickness. An excellent candidate for such a regime is the Mt. Raleigh pendant in British Columbia (Woodsworth, 1979). In this area, andalusite and sillimanite coexist in a zone that is 1.5 to 2 km in thickness. As is well illustrated in figure 2 of Woodsworth (1979), the intersection of the isograds with the topography suggests they are essentially vertical (this analysis is aided by the high relief in this area). Thus, the width of the andalusite + sillimanite zone in this area represents a true measure of the zone thickness (measured normal to isograd surfaces).

The correlation between aluminum silicate minor element concentrations and redox state is exemplified by metapelites of the Kiglapait aureole. Accordingly, univariant behavior is expected to be most closely attained in reduced systems. The low minor element concentrations of aluminum silicates of the Mt. Moosilauke area are compatible with the fact that Hodges and Spear (1982) reported graphite + ilmenite in all their samples. Yokoi (1983) implied that graphite is a common accessory in metapelites of the Central Ryoke Belt, which contain relatively pure andalusite and sillimanite (fig. 8). However, in the Ardara aureole, no graphite was found in the specimens described in this study and in those of Kerrick (1987). In the Waterville-Vassalboro area, Ferry (1980) reported graphite as an accessory. However, of the four samples from this area that were analyzed in the present study (table 1), J. M. Ferry (personal commun.) found graphite in only one sample (663). Thus, low concentrations of minor elements in the aluminum silicates and the nearly univariant behavior of the andalusite → sillimanite isograd reaction apparently do not require the presence of graphite. This conclusion must be qualified by the fact that fine-grained graphite could be overlooked in our petrographic and qualitative E.D.S. examinations of the opaque assemblages.

Earlier studies on the shift of the andalusite-sillimanite equilibrium as a function of minor element partitioning (for example, Okrusch and Evans, 1970) used the entropy data of Robie and Waldbaum (1968). However, recent Cp measurements by Robie and Hemingway (1984) yield ΔS_r values that are approximately one-half the values computed

using the data of Robie and Waldbaum (1968). Accordingly, the P-T displacement of the andalusite-sillimanite equilibrium as a function of K_D is approximately twice that computed in earlier studies.

Our analysis has lumped minor elements into a single component ($M^{VI}Al^{V}SiO_5$ in andalusite and $M^{VI}Al^{IV}SiO_5$ in sillimanite). For thermodynamic analysis this is *only* valid for an ideal mixture or for a non-ideal solution with all minor elements having the same activity-composition relations for substitution in the octahedral site. Because Fe^{3+} is the dominant "impurity" cation in andalusite and sillimanite of most Mn-poor assemblages, this supports considering andalusite and sillimanite as "pseudobinary" mixtures of $AlAlSiO_5$ and $FeAlSiO_5$ endmembers. Accordingly, this conclusion supports comparison of $T\text{-}X_{MAlSiO_5}$ loops in Mn-poor assemblages (as in fig. 13).

Because of poor counting statistics due to low peak/background ratios, we did not carry out analyses of boron contents of the aluminum silicates. Grew and Hawthorne (1983) concluded that B has little effect on the sillimanite stability field. However, Grew (1986) suggested that B partitioning into sillimanite could produce a 600 bar displacement of the andalusite-sillimanite equilibrium at 800°C. Consequently, the role of B should be addressed by obtaining analyses of B in coexisting andalusite and sillimanite. The senior author is carrying out such an investigation using secondary ion mass spectroscopy.

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