ALUMINUM SUBSTITUTION IN QUARTZ,
A STUDY IN GEOTHERMOMETRY

by

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ABSTRACT

The aluminum content of a suite of quartz samples from contact metamorphosed kyanite bearing quartzites shows a regular variation with distance from the intrusive contact. The highest recorded value, 109 ppm Al, is found for a sample adjacent to the contact; concentration decreases in an approximately linear manner with distance, giving the lowest recorded value, 39 ppm Al, at a distance of 1.4 miles from the contact. A simple temperature model for the contact aureole is developed, and an attempt is made to relate aluminum concentration directly to temperature of metamorphism.

Techniques are described for the separation and phase purification of the quartz and for the spectrographic determination of aluminum and lithium in solid solution in this quartz. Final purification is accomplished by ultracentrifugation in a bromoform-ethanol mixture to which n-hexylamine hydrochloride is added as a surface agent. Lithium concentrations are all below 0.3 ppm, too low to be important in coupled Al-Li substitution.

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PART I

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I. INTRODUCTION

1.1 Review of Previous Work

The historical development of metamorphic petrology is reviewed by Fyfe, Turner and Verhoogen (1958), and by Turner and Verhoogen (1960). Although much has been learned about the conditions to which rocks are subjected during metamorphism, neither the isograds of Barrow (in general) nor the facies of Eskola provide quantitative estimates of metamorphic conditions, i.e., temperature, pressure, and chemical potential of volatile components.

Goldschmit's postulate (discussed in Fyfe, Turner, and Verhoogen, 1958) that most metamorphic rocks consist of equilibrium assemblages of minerals is fundamental to any serious study of their physical chemistry. This postulate has received recent experimental verification in the work of Kretz (1959, 1961), Krank (1961), Mueller (1960, 1961), and Clayton and Epstein (1961).

A number of techniques of geological thermometry have been proposed involving both chemical and physical variables. One of the most promising chemical approaches is that of Ramberg and DeVore (1951) who suggested the possibility of using the ratio $Mg/(Mg + Fe)$ in coexisting olivines and pyroxenes as a geologic thermometer. Kretz (op. cit.) and Mueller (op. cit.) have demonstrated that this would be feasible. Another possible way of obtaining temperature (pressure) information is suggested by the work of Carr and Turekian (1961). They studied the distribution of cobalt in rocks of the granulite, amphibolite, and epidote amphibolite facies. Their Table 23 shows a fair correlation between metamorphic facies and cobalt ratios of coexisting phases. They note that, "although the total cobalt content of a metamorphic pelitic rock is roughly a function of the Fe content, the partition of cobalt between the various minerals bears little relation to their Fe content." The disadvantage in both of these methods is that they make use of minerals which are subject to a wide range of compositional variation depending on their environment.

Keith and Tuttle (1952) and Tuttle and Keith (1954) observed wide variations in the high-low inversion temperatures of quartzes from various environments. They postulated that these differences arose because different amounts of contaminants were admitted into the quartz structure at different temperatures of formation. They were primarily interested in the variation between quartzes from high and low temperature igneous rocks.

Griffiths, Owen, and Ward (1954) and O'Brien (1954) studied quartz darkened by exposure to γ-rays. Griffiths, et al. established that both optical absorption produced by γ-rays and the paramagnetic resonance spectrum of a sample were associated with small quantities of aluminum in the crystal. O'Brien analyzed the paramagnetic resonance spectrum of aluminous quartz and concluded from it that aluminum is included in the structure in place of silicon, and that electroneutrality is preserved by monovalent cations in interstitial positions. Cohen (1956a, b, and other papers) reported this color center production in a number of quartzes. Ritter (1962) attempted a systematic study of the phenomenon in natural quartzes. His data from γ-irradiated specimens indicates that they can be fitted into broad, somewhat overlapping classes according to their absorption. From strongest to least absorbing (in white light) these are quartzes from:

rhyolite
pegmatite
granite
schist, gneiss
vein filling.

This series bears an apparent correlation with temperature of formation, particularly in the light of work by Bambauer (1961) described below which shows that color centers absorbing at 466mμ are produced by Al-Li couples. The pegmatite-granite anomaly in the above series can then be explained by the greater availability of Li in the pegmatite environment.

Bambauer (ibid.), in a comprehensive survey of vein quartzes in the Swiss Alps, found that among "ordinary" and smoky quartzes (as distinguished from low symmetry lamellar quartzes) the minor element content was: $Al < 150$ atoms/10^6Si atoms (68 ppm), $Li < 100$ atoms/10^6Si atoms (12 ppm), $H < 50$ atoms/10^6Si atoms. Also, in γ-irradiated samples, a direct correlation was observed between Al-Li content and absorption of light at 466mμ.

A further direct correlation was observed between aluminum concentration and the sum of the hydrogen and lithium concentrations.

Bambauer, Brunner, and Laves (1962) attempted to apply these relationships on a broad regional scale. Hydrogen was measured in quartz from veins throughout the Swiss Alps. Low concentrations are correlated with sedimentary rocks. High concentrations are thought to outline a "heat dome". No sampling control over the compositional environment of these veins was made. Thus, although the study has broad statistical significance, there is much variation in detail.

1.2 Objectives of this Study

The observation of Keith and Tuttle (1952) and of Tuttle and Keith (1954) that the inversion temperature of quartz depends on its geological environment, along with the work of Ritter (1962), suggested the possibility of using quartz composition as a quantitative measure of the environment of formation of a rock. The color center model of O'Brien (1954) suggested that Ritter was actually determining aluminum-alkali metal couples in the quartz. This was confirmed and amplified soon after this study was begun by the work of Bambauer (1961).

Thus the original objectives of this study were to find what elements in natural quartz could be determined simply and accurately and to see whether or not a meaningful relation between the concentration of these elements and the temperature of formation of the quartz could be established. Quartz, which is of essentially invariant composition, is useful in such a study because it may be considered a pure solvent regardless of the composition of the rock in which it occurs. However, to make a meaningful correlation one should have some measure of the amount of the chosen element that is available in the environment, i.e., some way of normalizing data. In the work of Carr and Turekian (op. cit.), for example, this could be done by studying distribution of a trace element between mineral pairs. An alternative approach is to demand that the component studied in solid solution also be present in the mineral assemblage as a separate solid phase. This procedure would be analogous to a determination of the temperature of a beaker of water saturated with salt (as shown by the presence of salt crystals) by measuring the concentration of salt in the water and comparing this with a previously determined temperature-concentration relationship.

Aluminum has been chosen as the most suitable element for study in this program of quartz geothermometry. Since virtually all common minerals contain aluminum in much greater concentration than does quartz, it is not feasible to compare the aluminum concentration in quartz with that in some coexisting phase. However, by analogy with the salt in the preceding paragraph, one can choose an assemblage saturated in a highly aluminous phase such as one of the various polymorphs of Al_2SiO_5. Quartz then acts as the solvent. To summarize, the concentration of substituted Al in quartz associated with an aluminous mineral should be temperature dependent.

The quartz studied was obtained from aluminous quartzites in the Kings Mountain area, North Carolina - South Carolina, which have been intruded by a granitic mass (the Yorkville Quartz Monzonite) producing one or more Al_2SiO_5 minerals in association with quartz over a large contact aureole. Within these quartzites it is possible to obtain samples of equivalent and restricted composition across a metamorphic temperature gradient.

There are obvious defects in this approach. First, quartz is not an ideal solvent for aluminum. Coupled substitution (Al-H), over which there is little control information, undoubtedly occurs (Katz, 1961; Bambauer, 1961). Second, although a temperature effect has been demonstrated in field occurrences, there is no correlation with any laboratory temperature-concentration relationship. Nevertheless, there is some value in demonstrating the existence of even a relatively simple temperature-composition relationship within a suite of rocks. If nothing more, this work should justify the laboratory study of aluminum solubility in quartz under controlled conditions.

II. THEORETICAL CONSIDERATIONS

2.1 Coupled Substitution

The work of Bambauer (1961) and of others on coupled substitution in quartz has already been briefly described. Bambauer has shown that quantitatively the most important type of chemical substitution in natural vein quartzes is the coupled substitution aluminum-hydrogen and aluminum-lithium. This was found to be true for a wide range of samples from the Swiss Alps (excluding low symmetry lamellar quartzes).

In the present study Al-Li substitution may be disregarded since it has been demonstrated that Li concentration is an order of magnitude too low to be of significance, p.56. Al-H substitution, although it could not be measured, is probably the dominant means by which aluminum is incorporated into the quartz structure. Unfortunately, there is no way of determining available hydrogen for this substitution in rocks of the Kings Mountain suite. Several factors, however, suggest that hydrogen was readily available for all samples:

1) Each sample is closely associated with rocks containing hydrogen-bearing minerals such as mica or chloritoid.

2) There is evidence that kyanite formed from clay by a dehydration reaction:

$$\underset{\text{kaolin}}{Al_2Si_2O_5(OH)_4} \rightarrow \underset{\text{kyanite}}{Al_2SiO_5} + \underset{\text{quartz}}{SiO_2} + 2H_2O.$$

Such a reaction would make hydrogen available during the time of metamorphism.

3) Voids in grains, or in associated rocks, were found in three of the 4 sample localities. These voids probably contained a fluid consisting at least in part of water at some time in the metamorphic history of the area.

2.2 Significance of the Al_2SiO_5 Polymorphs

Bell (1963) has experimentally determined the temperature-pressure stability fields of the three Al_2SiO_5 polymorphs. His data are reproduced here in figure 1 . This work followed the studies of Miyashiro (1949); Clark, Robertson, and Birch (1957); Clark (1961); Kennedy (1961); and others.

Prior to the work of Bell it was observed that kyanite typically occurred in tectonically disturbed areas. This led to the concept that it was a "stress mineral," i.e., that it could form stably only under intense shearing stress. The following quotation from Harker (1939, pp. 150-51) exemplified this idea:

> "It is perhaps possible to frame a more definite conception of 'stress' and 'anti-stress' minerals as they are here to be understood. Taking first only temperature and pressure as the two controlling conditions, we must suppose that for any given mineral there is a certain field of stability, to be laid down on the p-t-diagram. If now the introduction of shearing stress as an additional condition causes an extension of the field, we have to do with a stress-mineral, if contraction an anti-stress-mineral. If a sufficiently intense measure of shearing stress causes the field to contract to a point and disappear, we have an anti-stress mineral in a very special sense. On the other hand, some form may make its entry only with the coming in of the stress factor, having otherwise no field of stability: this will be a stress-mineral in a very special sense. To picture the relations more clearly we must imagine a three-dimensional diagram with temperature, pressure, and shearing-stress as co-ordinates.
>
> "One case there is which would seem to be simple; viz. that of two dimorphous forms, one a stress- and the other an anti-stress mineral. It must be remembered, however, that not a few of the common minerals of metamorphism are merely

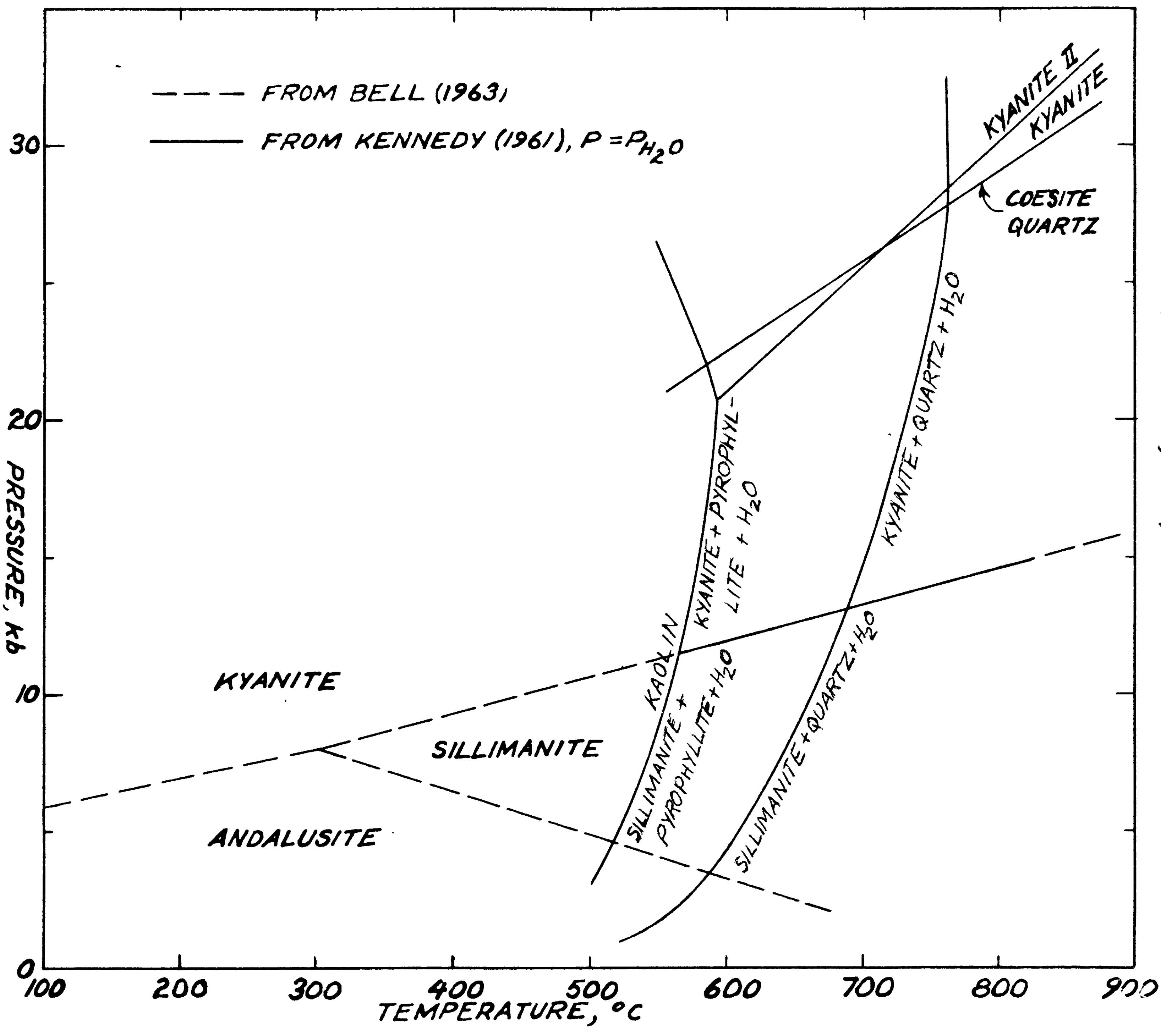

FIGURE 1. PHASE RELATIONS IN THE SYSTEMS, Al_2O_3-SiO_2 (AFTER BELL, 1963) AND Al_2O_3-SiO_2-H_2O (AFTER KENNEDY, 1961)

> metastable forms, in the sense of having no theoretical field of stability, at least under stress-free conditions, and that such metastable forms are found especially where dimorphism or polymorphism enters. Thus the anti-stress mineral andalusite and the stress-mineral cyanite are probably both metastable forms, monotropic towards the presumably stable sillimanite. We must suppose, either that under shearing stress cyanite has a field of true stability, or alternatively that the incidence of shearing stress has the effect of reversing the relative stability of the two metastable forms. It may perhaps be suggested that such rocks as cyanite-schists are formed under great hydrostatic pressure, and that we are in danger of attributing to shearing-stress effects which are really due to pressure. Since the specific gravity of cyanite (at ordinary temperature) is 3.56 and that of andalusite only 3.16, it is clear that high pressure will favour the formation of the denser cyanite wherever this form is a possible one. If this factor, however, were of foremost importance, it would still be difficult to account for the complete absence of cyanite from aureoles of thermal metamorphism even under thoroughly deepseated conditions."

In 1951 Miyashiro reported the presence of kyanite projecting into drusy cavities in kyanite quartz veins presumably filled at one time with fluid. The implication was that these crystals had formed stably under hydrostatic pressure. There seems now to be no reason to imbue kyanite with the special properties of a "stress mineral." Nevertheless extremely high pressures are required for its formation. Clark (1961) has noted that lithostatic pressure seems inadequate, in general, and introduces the concept of tectonic overpressure.

> "These great depths of burial can be escaped, or at least lessened, if pressures in the crust are sustained by the strength as well as the weight of the overlying rock. The mere existence of deformation in metamorphic terrains implies that stress differences exceeded the strength of

> the rocks, and the nature of the deformation suggests that the stresses causing it were compressive relative to $\bar{\rho}gh$ rather than tensile. [$\bar{\rho}$ = mean density between surface and depth h; g is gravitational acceleration.] This implies that the mean of the principal stresses at times exceeds $\bar{\rho}gh$. The magnitude of this 'tectonic overpressure' is set by the strength of the rocks that support it." (p. 647)
>
> "The hypothesis of tectonic overpressures represents a return to the stress mineral concept of Harker but in modified form. Harker supposed that the fields of stability of minerals were influenced by shear.... In the present view, shearing stresses make possible an increased mean principal stress and bring high-pressure minerals into their fields of stability at depths where they would normally be unstable at the prevailing temperature." (pp. 648-49)

Perhaps it is not unreasonable to extend this theory of overpressures slightly. A shallow intrusive in hydrostatic equilibrium with a deeply buried magma could exert a considerable hydraulic "overpressure" on the surrounding rocks so long as it remained confined. If the Yorkville Quartz Monzonite were such an intrusive, the apparent low temperatures and high pressures of the Kings Mountain metamorphism would be easier to explain.

The data of Kennedy (1961) is plotted as figure 1 with Bell's curves superimposed. (Note that the pressure axes are not equivalent.) These data imply that the kyanite observed in drusy cavities by Miyashiro (1951, op. cit.) could not have formed stably below ~16kb water pressure and ~700°C (rare conditions indeed). Newton and Kennedy (1963) have recently reported the decomposition of natural pyrophyllite to form kyanite + quartz + vapor at 24 kb and temperatures as low as 510°C. They postulate that pyrophyllite and other hydrated silicates persist metastably well above their dehydration temperatures and that this results in inaccurate phase diagrams of the systems involved. It would seem wise not to make too many inferences from the phase diagram for the hydrated alumina-silica system until this system has been experimentally clarified.

It should be mentioned that cavities with kyanite projecting into them occur at locality C21 (Henry Knob). These are shown in Plate 3c,d. The inferred temperature at this locality is $\leq 300^{\circ}C$ (Fig. 2). At locality C17 (a xenolith within the Yorkville Quartz Monzonite) the major assemblage is quartz, sillimanite, and kaolin (kaolinite or dickite) in which most of the sillimanite has been replaced by extremely well crystallized kaolin. These relations also seem incompatible with data in figure 1 unless μ_{H_2O} is very low in the fluid phase at C21.

Despite the uncertainty in experimental work on the system $Al_2O_3 - SiO_2 - H_2O$, the triple point determination in the system Al_2SiO_5 by Bell permits a limit to be placed on the metamorphic temperatures of the Kings Mountain area studied since, fortunately, a triple point assemblage (kyanite, sillimanite, andalusite) occurs at one place in the area. In a following section this limit is compared with an idealized theoretical model of temperature in the aureole.

In light of Bell's data, the observation of a triple point assemblage in the system Al_2SiO_5 well within the almandine amphibolite facies may require a downward revision in commonly accepted metamorphic temperature estimates, e.g., those of Turner and Verhoogen (1960, p. 553) who estimate temperature in the almandine-amphibolite facies to be 550° - $750^\circ C$ at pressures of 4000 - 8000 bars.

2.3 Temperature Model

Potter has mapped the contacts of the Yorkville Quartz Monzonite in the vicinity of the Kings Mountain aluminous quartzites (Plate 2, (Espenshade and Potter, 1960)). Various workers have, however, shown rather divergent contact relationships (King, 1954; J. L. Stuckey, 1958). Under these conditions, and in the absence of personal investigation of this intrusive, the author has assumed a simple geometrical shape for the Yorkville Quartz Monzonite based essentially on the map of King and upon the steeply dipping contacts shown by Potter.

The chosen model is of a vertical tabular plate of intrusive rock, infinite in two dimensions and 4 miles thick. This is a gross simplification and should not be expected to produce a correspondence with analytical data that is accurate in detail. Further assumptions are as follows: the diffusivity of wall rock and intrusive are the same (1.27×10^{-2} cm^2/sec), the intrusion occurred instantaneously, the intrusive and wall rock are initially at uniform temperatures, the latent heat of fusion is negligible, and the wall rock conducts heat isotropically (Lovering, 1935).

The selection of a temperature for the intrusive is based on data of Tuttle and Bowen (1954) showing that at >4kb pressure granitic rocks can exist as liquids at temperatures ranging down to $\sim 650^\circ C$ if sufficient water is available. Presence of perthitic feldspar also sets a lower limit of slightly less than $700^\circ C$ on the temperature of intrusion (ibid.). Temperatures higher than ~700°C for the intrusion at Kings Mountain are excluded by the presence of the 3 phase assemblage kyanite-sillimanite-andalusite near the contact. For the other necessary boundary condition, a wall rock temperature of 100°C was chosen somewhat arbitrarily. Standard estimates of the geothermal gradient would yield somewhat lower values.

Under these conditions one may use the equation given by Lovering (1935) (which is derived in Ingersoll, Zobel, and Ingersoll, 1954) for heat flow in an infinite medium:

$$T(x,y,z,t) = T_w + \frac{T_i - T_w}{8}[\mathrm{erf}(a)+\mathrm{erf}(b)][\mathrm{erf}(c)+\mathrm{erf}(d)][\mathrm{erf}(e)+ +\mathrm{erf}(f)] \quad (1)$$

where $T(x,y,z,t)$ = temperature of any point (x,y,z) at time t

T_w = initial wall rock temperature

T_i = initial intrusive temperature

erf(a) is the error function $\frac{2}{\pi}\int_0^a e^{-\alpha^2}\,d\alpha$

$(a = \frac{x_1 + x}{2h\sqrt{t}}$, x_1 = semidiameter of intrusive along x axis

h^2 = diffusivity)

$$\mathrm{erf}(b) = \frac{2}{\pi}\int_0^b e^{-\alpha^2}\,d\alpha$$

$(b = \frac{x_1 - x}{2h\sqrt{t}})$

etc.

For y and z infinite:

$$[\text{erf}(c) + \text{erf}(d)][\text{erf}(e) + \text{erf}(f)] = 4, \text{ and} \qquad (2)$$

equation (1) can then be simplified.

$$T(x,t) = T_W + \frac{T_1 - T_W}{2}\left[\frac{2}{\pi}\int_0^a e^{-\alpha^2}d\alpha + \frac{2}{\pi}\int_0^b e^{-\alpha^2}d\alpha\right] \qquad (3)$$

Evaluating this according to the assumptions discussed above:

$$T_W = 100^\circ C$$

$$T_1 = 700^\circ C$$

$(h^2)_{\text{granite}} \simeq (h^2)_{\substack{\text{wall}\\ \text{rock}}} \cong 1.27 \text{ x}10^{-2}\text{cm}^2\text{/sec}$, (Ingersoll, Zobel, and Ingersoll, 1954).

$$x_1 = 3.22 \text{ x } 10^5\text{cm} = 2 \text{ miles}$$

$$T(x,t) = 100 + \frac{600}{2}\left[\frac{2}{\pi}\int_0^{(3.22\text{x}10^5 + x)/\tau.226\sqrt{t}} e^{-\alpha^2}d\alpha + \right.$$

$$\left. + \frac{2}{\pi}\int_0^{(3.22\text{x}10^5 - x)/\tau.226\sqrt{t}} e^{-\alpha^2}d\alpha \right. \qquad (4)$$

The curves generated by this equation are shown in figures 2 and 3. In figure 4 the location of the three phase Al_2SiO_5 assemblage (C6) is shown along with the possible range of error in the temperature determination of the triple point as determined by Bell (1963).

Although the assumptions used in constructing figure 2 are such that only qualitative significance can be attached to it, the maximum temperature envelope developed fits

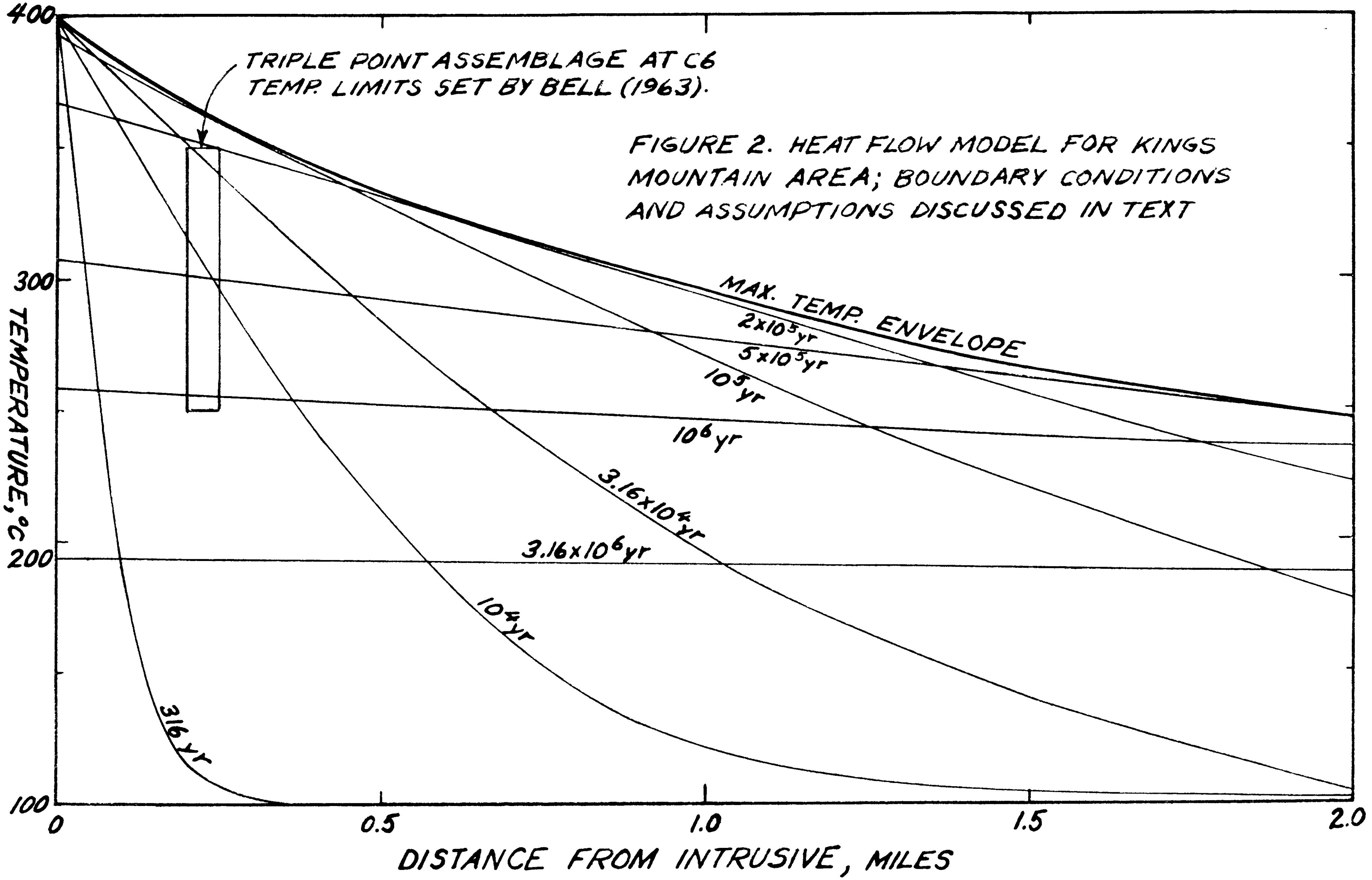

FIGURE 2. HEAT FLOW MODEL FOR KINGS MOUNTAIN AREA; BOUNDARY CONDITIONS AND ASSUMPTIONS DISCUSSED IN TEXT

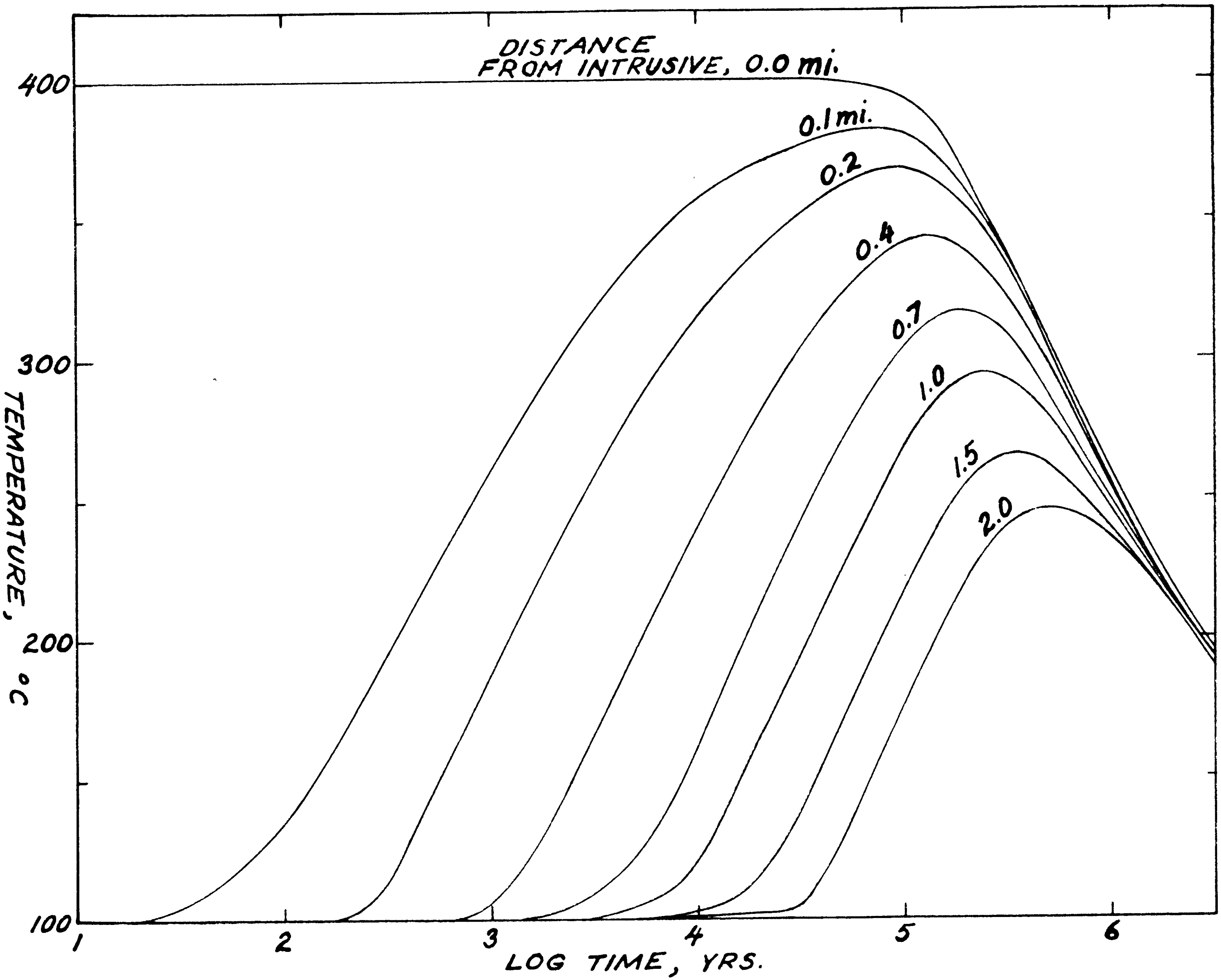

FIGURE 3. HEAT FLOW MODEL FOR KINGS MOUNTAIN AREA

reasonably well the observed triple point assemblage and the temperature gradient inferred from facies mapping (Figure 4 , taken from Espenshade and Potter, 1960). The two most likely geometrical variations from the model are that the intrusive is not infinite in two dimensions and that the heated region is truncated by the earth's surface. Neither of these effects would change the initial temperature of metamorphism at the contact, but both would cause more rapid cooling of the magma with consequent steepening of the maximum temperature envelope in figure 2.

The assumption implicit in equating the maximum temperature envelope with the temperature of metamorphism is quite general to metamorphic petrology. It is that a sample collected anywhere along the temperature gradient represents an assemblage which reached equilibrium under conditions closely corresponding to the maximum temperature achieved during metamorphism. A qualitative justification for this assumption in terms of kinetic theory is given in Fyfe, Turner, and Verhoogen, 1959, p. 96 ; and in Turner and Verhoogen, 1961, pp. 485-87.

2.4 Pressure

It is an assumption of this study that pressure over the Kings Mountain outcrop area sampled was essentially constant during the time of metamorphism and that it equalled ~8kb (a requirement set by the pressure of the triple point assemblage kyanite-sillimanite-andalusite at locality C6). A further observation may be made that kyanite occurs at locality C26 at a distance of 4.4 miles from the intrusive. At a temperature of 100°C (a minimal estimate) the pressure would have to be at least 6kb for kyanite to be stable (figure 1, from Bell, 1963). This would mean that the maximum pressure variation among the samples in this report $\leq$ 600 bars. A mechanism by which such extraordinary pressures could be achieved was suggested in the preceding section. The interesting idea of comparing natural environments to laboratory high pressure devices is developed by Jamieson (1963).

Experimental data on the effect of pressure on aluminum solubility in quartz is of limited significance because the resulting lattice changes are near the limit of detection by X-ray equipment. J. Kalnajs of the MIT Insulation Research Laboratory was unable to observe consistent variations in the lattice parameters of a suite of samples from the Kings Mountain area (samples C5, C23, C18, standard quartz from "vein 5"). This work is further described in Appendix A.

The variation of aluminum concentration in quartz (which can be expressed as Al_2SiO_5 concentration) as a function of pressure variation can be discussed by applying Eq. (9-132) of Kirkwood and Oppenheim (1961) to very dilute solid solutions. Then

$$\left(\frac{\partial \log x_{Al_2SiO_5}}{\partial P}\right)_T = -\frac{\bar{v}^{quartz}_{Al_2SiO_5} - v^{kyanite}_{Al_2SiO_5}}{g^{quartz}_{22}RT} \qquad (1)$$

Here $x_{Al_2SiO_5}$ = concentration of Al_2SiO_5 in quartz

$$g^{quartz}_{22} = \frac{\left(\frac{\partial \mu_{Al_2SiO_5}}{\partial x_{Al_2SiO_5}}\right)_{T,P} x_{Al_2SiO_5}}{RT}$$

$\mu_{Al_2SiO_5}$ = chemical potential of Al_2SiO_5
$\bar{v}^{quartz}_{Al_2SiO_5}$ = partial molar volume of Al_2SiO_5 in quartz
$v^{kyanite}_{Al_2SiO_5}$ = molar volume of kyanite

P = pressure

R = gas constant

T = absolute temperature.

The quantity $g^{quartz}_{22} > 0$, and for a ~~ideal~~ dilute solution is equal to 1.

A calculation based on the data in Table 1 is presented below. The volume of the quartz unit cell is:

$$V = \frac{\sqrt{3}\, a^2 c}{2}$$

$$\therefore\ dV = \frac{\sqrt{3}}{2}(2ac\, da + a^2 dc)$$

$$\frac{dV}{V} = \frac{2da}{a} + \frac{dc}{c} \qquad (2)$$

Table 1. Aluminum Concentration and Lattice Parameters (from Bambauer (1961)).

Sample No.	$Al/10^6 Si$ (atom %)	Al (ppm)	Moles Al_2SiO_5/cc	a_o(Å) ±0.0001	c_o(Å) ±0.0001
254	13	5.8	2.85×10^{-7}	4.9129	5.4049
178	115	52	25.6×10^{-7}	4.9133	5.4045

$$\Delta a = +0.0004, \quad \frac{\Delta a}{a} = \frac{0.0004}{4.9130} = 8.15\times10^{-5}(\pm4\times10^{-5})$$

$$\Delta c = -0.0004, \quad \frac{\Delta c}{c} = -\frac{0.0004}{5.4047} = -7.4\times10^{-5}(\pm4\times10^{-5})$$

$$\Delta x = 2.27\times10^{-6} \text{ moles/cc}$$

$$\frac{\Delta V}{V} = 8.9\times10^{-5}$$

$$\bar{V} = \left(\frac{\partial V}{\partial x}\right)_T = \frac{8.9 \times10^{-5}}{2.27\times10^{-6}} = 39.2 \text{ cc/mole}$$

The molar volume of kyanite is ~45cc/mole.

$$\left(\frac{\partial \log x_{Al_2SiO_5}}{\partial P}\right)_T = \frac{39.2 - 45}{2RT} = \frac{-5.8}{2RT}$$

$$R = 83 \text{ bars/}^\circ\text{mole cm}^3$$

evaluating $\Delta \log x$ for $T = 600^\circ K$ and $\Delta P = 1000$ bars:

$$\Delta \log x = \frac{-5.8(1000)}{2(83)(600)} = -0.058 .$$

This represents approximately a 6% change in x per thousand bars at an initial concentration of 10^{-6}moles Al_2SiO_5/cc. Thus, in view of the estimated maximum 600 bar pressure variation over the sample area, it can be asserted that the effect of pressure on aluminum solubility in quartz within the area studied is small and probably negligible*.

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* A slightly irrelevant point concerns a third quartz of Bambauer, the lattice parameters of which are given in the same table. It is a lamellar quartz with very high Al content. Calculation of the partial molar volume of Al in this quartz (from cell constants) shows that it is ~15 cc/mole (vs. 45 for kyanite, one of the densest of silicates). This would seem to be compelling evidence that most of the aluminum in this quartz has gone into a separate phase (perhaps submicroscopic in dimensions), a conclusion which may clarify the undefined expression "interstitial aluminum" found in the literature (Cohen, 1960).

Theoretically, a more complete way of defining metamorphic conditions would be a parallel study of $x_{Al_2SiO_5}^{quartz}$ and $x_{TiO_2}^{quartz}$ from a quartz-kyanite-rutile bearing assemblage. This could lead to a unique characterization of the temperature and pressure of metamorphism. For this it would be necessary that $(\partial x/\partial T)$ and/or $(\partial x/\partial P)$ be different for the two substances. An attempt was made to study both Al and Ti variations in the Kings Mountain quartzes. Unfortunately, $x_{TiO_2}^{quartz}$ is low (except in high quartz); and the size of rutile grains in these samples ranges from $\sim$0.5 mm to $\ll 1\mu$. It proved impossible to reduce the Ti contamination level below 30 - 50 ppm (vs. a probable solubility of $\sim$5 ppm).

III. AREA STUDIED

3.1 General Description

Kyanite (and/or sillimanite) bearing quartzites from the vicinity of Kings Mountain, North Carolina - South Carolina were selected for this study. There were three important reasons for this choice:

1) Presence of a mineralogically simple quartz-Al_2SiO_5 assemblage which is lithologically similar throughout and which contains separable phases,

2) Existence of a demonstrable thermal gradient across the area during the time of metamorphism, and

3) Availability of maps and other published material to simplify sample collection and analysis of results.

It is the second factor which distinguishes the Kings Mountain area from a number of Al_2SiO_5 bearing deposits extending from Virginia to Georgia (Plate 1). The important localities in this belt have been described by Espenshade and Potter (1960), and it is from their monograph that the location maps in this thesis are taken.

The aluminous quartzites of the Kings Mountain area (Plate 2) consist of bedded, metamorphosed, quartzose sandstones and conglomerates which probably contained, at one time, varying amounts of kaolinitic material. The conglomerate pebbles are of two kinds: single bluish quartz crystals whose color is imparted by fine inclusions, and pebbles made up of multiple quartz grains. With increasing grade of metamorphism, the conglomeratic texture of the quartzite becomes much less obvious. Other minerals present in addition to kyanite or sillimanite include pyrite, rutile (in tetragonal grains of various sizes), kaolinitic alteration products, magnetite, ilmenite, micas, and occasional topaz, zircon, tourmaline, and, in one locality, andalusite (associated with sillimanite and rare kyanite). Poikiloblastic crystals of kyanite in the area contain quartz inclusions suggesting that they were formed by the reaction:

$$\underset{\text{kaolinite}}{Al_2Si_2O_5(OH)_4} \rightarrow \underset{\text{kyanite}}{Al_2SiO_5} + \underset{\text{quartz}}{SiO_2} + 2H_2O.$$

At the lowest stages of metamorphism, rutile exists as rather spongy, reddish grains, while at higher stages of metamorphism only stubby yellowish brown tetragonal prisms and bipyramids are observed. Pyrite also seems to show a change of habit with increasing grade of metamorphism. Plate 3(a,b) shows photographs of pyrite from locality C10 (3.3 miles from the Yorkville Quartz Monzonite) and from C21 (1.2 miles from the intrusive). In the albite-epidote-amphibolite assemblage at C10, the pyrite has well developed faces which are most often cubic. In the amphibolite facies assemblage at C21, on the other hand, there is a statistical prodominance of pyritohedral faces. In addition, more grains are rounded and indented than at C10. Near the intrusive (locality C5), pyrite crystal faces are rare. Most grains here are stretched into irregular plates and indented by other minerals. This variation in habit may well represent systematic changes in composition.

The occurrence of the triple point assemblage, kyanite-sillimanite-andalusite (locality C6), is of some importance to this study. Kyanite occurs, but is not common at this locality. So far as textural evidence can be trusted, sillimanite appears to replace andalusite. Although the assumption of equilibrium is probably a good approximation, it is probable that one or more aluminous phases persisted under conditions of limited metastability. Reference to figure 1 shows that petrographic observations are most easily satisfied by constant pressure slightly below the triple point pressure of 8kb, and by a rising temperature passing from the kyanite field through the field of andalusite into the stability field of sillimanite to a maximum temperature slightly higher than the triple point temperature of $300 \pm 50^{\circ}$C.

3.2 Sample Description

C10 is a fresh outcrop of kyanite-bearing quartzite occurring near a dirt road at the south end of Sherrars Gap 3.3 miles from the nearest outcrop of the Yorkville Quartz Monzonite (this and subsequent samples are shown in Plate 2 (in pocket)). This is one of 5 kyanite-bearing samples from the entire area which contain fresh pyrite, although in all other outcrops the presence of heavy iron oxide stains, often filling cavities in the shape of pyrite grains, demonstrated that pyrite is a part of the original assemblage in all of the quartzite samples. The pyrite at this locality displays predominantly cube faces in contrast to its habit in other localities (Plate 3). The quartz here is obviously of conglomeratic origin and the quartzite contains numerous blue quartz pebbles. Kyanite is not well crystallized here and is not so easily recognized in hand specimen as it is in more highly metamorphosed rocks. Muscovite is present, and textural relations suggest that it replaces kyanite. Rutile is present in spongy, reddish brown, opaque crystals.

C23 is an excellent exposure at the south end of Crowders Mountain, 1.4 miles from the nearest outcrop of the Yorkville Quartz Monzonite. Some of the quartzite here has been exposed to relatively slight weathering and, although no pyrite was seen in hand specimen, some was observed after grinding and chemical removal of iron oxide. Kyanite occurs in well formed blades showing parallel alignment. Rutile occurs here in clear brown crystals. A heavy liquid separation of material having a density <2.65 reveals that a number of quartz grains contain voids similar to those shown in Plate 4.

C21 is the site of an active kyanite mine on Henry Knob, 1.2 miles from the nearest outcrop of Yorkville Quartz Monzonite. Mining has exposed fresh rock here, the freshest outcrops in the area. Pyrite is abundant. Pyritohedral faces are developed predominantly, although the pyrite here tends to be more rounded and indented than at C10 (Plate 3). Kyanite is abundant and occurs in well formed colorless blades. Rutile occurs in small, well formed brown crystals. Open cavities with kyanite blades projecting into them were found at one place in this mine (Plate 3). These cavities are concentrated in one portion of a hand specimen and seem to represent some sort of vein. No associated alteration of any kind was observed. These cavities may be compared with those described by Miyashiro (1951), discussed elsewhere in this report (p. 12).

C18 is an exposure of kyanite-bearing quartzite at the base of Crowders Mountain, 0.72 miles from the nearest outcrop of Yorkville Quartz Monzonite. The quartzite is somewhat weathered, and no fresh pyrite was observed. Rutile here is fine grained but well crystallized. Kyanite occurs in sub-parallel well crystallized blades. The poikiloblastic nature of kyanite from this locality is typical of all kyanite in the area and is shown in Plate 4.

Abundant voids are found in quartz from this area. Examples are shown in Plate 4. Some mica and some kaolinite alteration product were observed in the sample from here.

C5 is a sillimanite-bearing quartzite near the Yorkville Quartz Monzonite contact. Sillimanite occurs in fine needles (Plate 5), but these are considerably larger than at the place of first appearance of sillimanite (triple point locality C6). Other metamorphic minerals are rutile, pyrite, muscovite, and possibly kaolin. Kaolin is either the result of a univariant equilibrium established during metamorphism, or an alteration product, either of late metamorphism or of weathering. Pyrite is, to some extent, replaced by iron oxide, as well as by a soluble iron compound ($FeSO_4$?).

3.3 Origin

Espenshade and Potter (1960) discuss the origin of the Kings Mountain aluminous quartzites in some detail. They state (p. 24):

> "The deposits of ... kyanite quartzite and sillimanite quartzite in the Kings Mountain district, North Carolina - South Carolina, probably are metamorphosed sedimentary rocks. The principal feature ... pointing to this origin is the occurrence of the high-alumina quartzite in persistent layers that have the distribution patterns of stratigraphic units. These layers occur in rather restricted stratigraphic positions in sequences of metamorphosed sedimentary and volcanic rocks. Many layers extend for distances of more than 1 mile; the longest body ... in the Kings Mountain district [is] about 3 1/2 miles long. Two thin layers of kyanite quartzite are parallel to each other, 20 to 100 feet apart, for a distance of over 1 mile in the Kings Mountain district. In this area kyanite-bearing conglomerate, kyanite quartzite, and kyanite schist grade into one another along the strike, and kyanite quartzite is interlayered with kyanite-staurolite quartzite and with barren quartzite.... the high-alumina quartzites are strongly folded concordantly with the other metamorphic rocks.
>
> "These features are all characteristic of metamorphosed sedimentary rocks. There seem to be but two possible modes or origin for the high-alumina quartzites in the ... Kings Mountain ... [district]. They have either been formed from sandy sediments containing clay or bauxite that have been folded and metamorphosed to their present state with little bulk change in chemical composition, or they have originated by very selective replacement of certain beds, probably mainly sandstone.... it is concluded that this [the latter] process is improbable for the origin of the high-alumina quartzites in ... [this district]."

Various other origins have been suggested for the Southeastern kyanite deposits. These require such things as volcanic emanations and widespread aluminum metasomatism; and some of the earlier theories have been strongly colored by Harker's concept (1939) of kyanite as a "stress mineral." In this thesis it is necessary to assume only that:

1) The specific rocks studied arrived at their present mineralogy as the result of chemical reactions occurring under steady state conditions which approximated equilibrium for any small sample;

2) The driving force for these reactions was the intrusion of a large granitic body, the Yorkville Quartz Monzonite;

3) Certain restrictions can be placed on T, P, μ_{H_2O}.

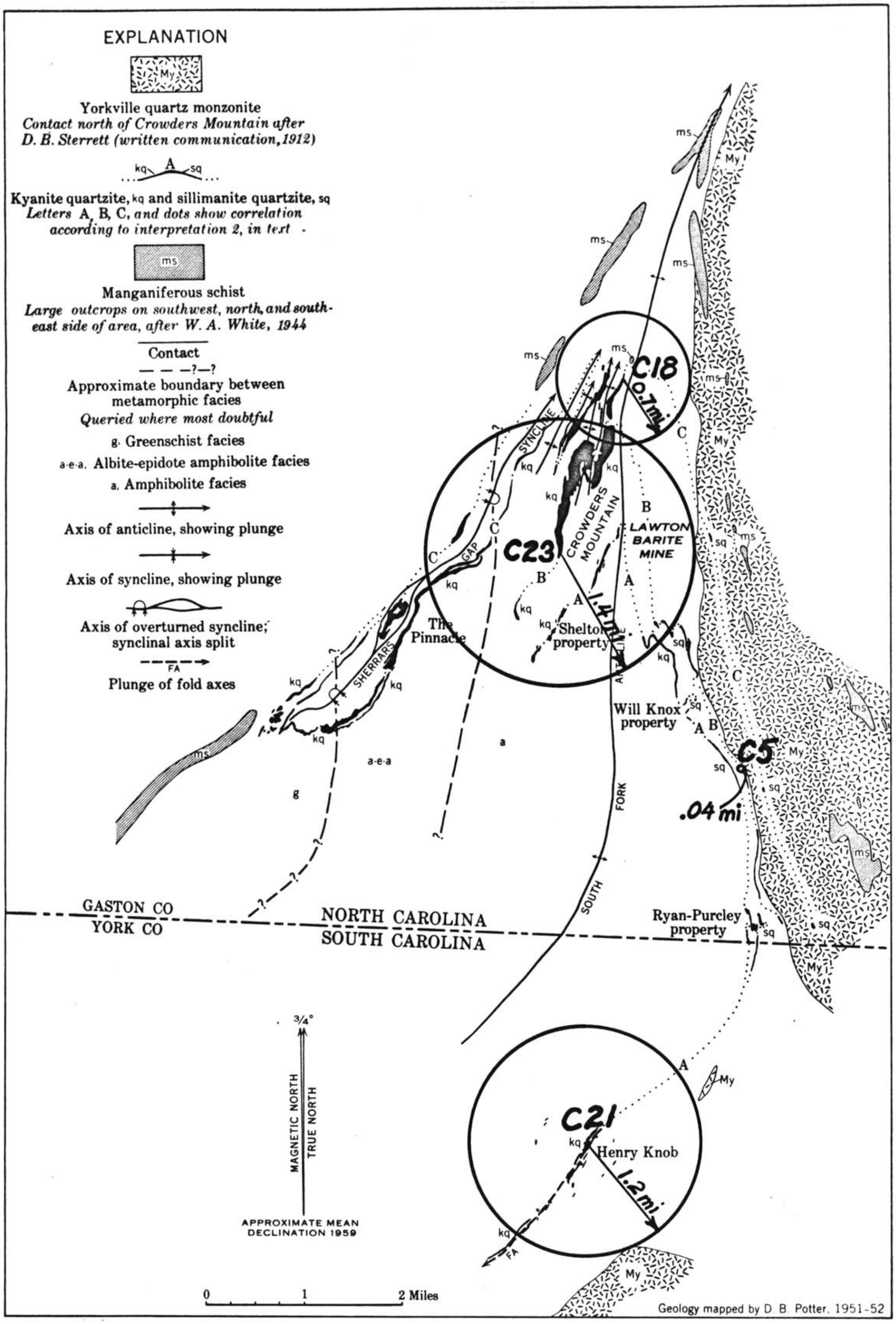

Figure 4. Sketch map of southern part of Kings Mountain area (North and South Carolinas) showing metamorphic facies boundaries. Samples are located at the centers of circles whose radii indicate distance to nearest intrusive outcrop. (From Fig. 42 of Espenshade and Potter, 1960. References in explanation refer to that publication.)

3.4 Metamorphism

The metamorphic grade of the aluminous quartzites in the area, as determined in the surrounding schists and gneisses, ranges from greenschist facies to amphibolite facies (Figure 4). Metamorphism is the result of intrusion of the Yorkville Quartz Monzonite (probably ~260 million years ago, Espenshade and Potter (1960, p. 80)). Thus, although the assemblages and textures are characteristic of regional metamorphism (Fyfe, Turner, and Verhoogen, 1958) and have been fitted into this classification (Espenshade and Potter, 1960, p. 83), they have really been produced in a large contact metamorphic aureole.

The Yorkville Quartz Monzonite is described by Espenshade and Potter (1960, p. 79) as a coarse grained quartz-monzonite (orthoclase:plagioclase ratio, 35:65). It is medium to dark grey, frequently porphyritic, with flow structure defined by parallel orientation of feldspar phenocrysts and biotite. Feldspar phenocrysts consist of perthitic microcline and of plagioclase (An_{25} - An_{38}). Hornblende occurs rarely in place of biotite. The intrusive varies from 2 to 7 miles in width and is more than 55 miles long. As is mentioned in a preceding section on the temperature gradient within the area (p. 17), there are varying interpretations of the contact relations of this intrusive.

IV. EXPERIMENTAL PROCEDURES

4.1 Separation

The research reported here has been guided by simple theoretical principles. The analytical techniques used are also quite simple and straightforward. It has, however, proved difficult to obtain pure samples for analysis. 2.3 μg of kyanite in a 15 mg quartz sample, (1.5 x 10^{-4}gm/gm), would contribute 50 ppm to the measured aluminum content of the quartz. This is greater than the measured concentration of Al in solid solution in one of the quartz samples reported on here and is about equal to that of one of the other samples. Yet one of the requirements followed in selecting samples is that at least one of the polymorphs of Al_2SiO_5 be intimately associated with quartz.

Because of the need of high purity quartz for study, and because of the difficulty in obtaining pure concentrates of quartz from typical rocks, most previous investigators have studied large, clear, atypical crystals.

A number of properties of quartz are dependent upon its composition and, therefore, indirect measurements of composition can conceivably be made. An example of this is given in the work of Tuttle and of Keith (op. cit.). Other indirect methods of possible significance are described elsewhere in this paper. These include accurate measurement of the quartz lattice constants, measurement of the infrared spectrum of quartz, and measurement of the color center activity produced by irradiation with γ-rays.

Variation in these properties is governed by substitution in the quartz structure, but considerable refinement of the techniques is required before they are applicable to the quantitative determination of elements in the quartz of normal rocks.

Quartz grains in the suite of samples from the Kings Mountain area contain particles ranging in size to less than a micron. These are separated from one another by distances of the order of a few microns,(Plate 5). To purify material such as this it must be ground to a very fine powder. The detailed separation technique used has been developed empirically. This technique depends for its effectiveness on the fact that virtually all of the impurities in the Kings Mountain suite of samples (kyanite, sillimanite, andalusite, rutile, pyrite) are considerably denser than quartz (3.6, 3.2, 3.2, 4.2, 5.0 g/cc, respectively vs. 2.65 g/cc for quartz). Clay minerals and fluid inclusions are easily eliminated in the sequence of operations. Samples containing large quantities of mica are uncommon, and such minerals as feldspar are not encountered.

Samples chosen for analysis are coarsely ground in a large steel mortar or in a laboratory jaw crusher. The resulting coarse powder is seived through a nylon stocking. (Since exact sizing is not critical, a stocking is preferred to ordinary screens because it introduces much less contamination.) Screened fines are soaked in 6<u>N</u> HCl (Vycor distilled) at $\sim 45^{\circ}C$ for several days with 2 or more daily changes of acid until the wash acid remains clear and no oxide coatings are visible. The acid is removed by washing the sample 6 or more times with demineralized water. During this procedure only about 10 seconds are allowed for settling so that very fine material is washed out.

The next stages of purification depend somewhat upon how the sample appears under microscopic examination. Rules have been established to exclude the very fine material which contains concentrated sillimanite, rutile and kyanite, and also to eliminate large particles containing one or more inclusions of sillimanite, kyanite, or rutile. A further rough density separation (tetrabromoethane used in a column or funnel) is usually necessary to remove heavy minerals previously cemented by oxide coatings. If there is any evidence of clay alteration products, the sample is subjected to ultrasonic vibration for 5 or more hours in a polyethylene bottle partially filled with demineralized water. The water is then decanted periodically until two successive washes show no sign of suspended material. If any mica remains at this stage, the sample is placed in an evaporating dish with a dilute $\sim 1\underline{N}$ solution of HF and evaporated to dryness. Repeated HF leachings are conducted until no trace of mica remains. The quartz which remains after this treatment is washed thoroughly. Fine heavy minerals freed by the leaching are removed by centrifugation at 1000 rpm in a tetrabromoethane acetone mixture of density 2.7. At this stage the quartz tends to have a fine coating of insoluble residue on its surface. This residue has been found to contribute as much as 20% to the measured aluminum content of one test sample, To remedy this, samples are ground to a fine powder by hand in a boron carbide mortar, eluted in water and that fraction which does not settle through 10 cm. in 5 minutes (smaller than 20μ) is discarded. After the coarser material has settled and dried it is again ground and washed. This removes virtually all of the coating material.

At this stage all samples are ground to a fine powder in a boron carbide mortar. That fraction settling through 10 cm of water (the length of a 50 cc round-bottom centrifuge tube) in 5 - 15 minutes is selected for analysis. (This corresponds to ~12 - 20μ.) Repeated elutriation and grinding is carried out until 0.1 - 0.2 g of sized fines is available. The size range selected is somewhat flexible.

Standard heavy liquid separation techniques such as those described by Browning (1961) are wholly inadequate to separate the particles in this powder despite the disparity in their densities (3.36 - 2.65 g/cc). This is true because electrical surface charges on these fine particles are so great that clotting occurs in any nonpolar solvent. Among the standard heavy liquids, only a thallium formate solution would be free of this objection, and this compound was rejected because of its extreme toxicity. An alternative suggested by J. W. Irvine, Jr.

(oral communication, 1963) is to neutralize surface charges with the surface agent, n-hexylamine HCl. This chemical was prepared by adding 6N Vycor distilled HCl to n-hexylamine, evaporating to dryness, and precipitating from an acetone-water mixture. About 7 milligrams of hexylamine HCl is added to 10 ml of a bromoform-ethanol* mixture of density 2.70 g/cc (9.1 ml bromoform, .9 ml ethanol). The powder to be purified is first centrifuged in this mixture at 2000 rpm (240 g) in a closed tube for ~45 minutes after which it is washed thoroughly with acetone, dried, and examined microscopically. If large particles of heavy minerals remain, the step is repeated (two centrifugations are common). When most of the larger heavy mineral grains have been removed the sample is ready for final purification.

Final purification is done in a Beckman Instrument Company Spinco Model L ultracentrifuge equipped with an SW40 head. The main effect of this step is a more efficient removal of heavy particles than is possible with slower centrifuges and, apparently, the plucking off of grains loosely cemented to the quartz.

Runs of 180 minutes at 25,000 rpm and 65°F (~18°C) are made. With an 8 ml sample this produces an acceleration

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* The choice between bromoform and tetrabromoethane is largely a practical one. Bromoform is less viscous and therefore gives faster separations. Tetrabromoethane is considerably cheaper and can therefore be thrown away after use instead of being repurified.

at the sample surface of 39,800g (Fig.5). The heavy liquid used is ethanol-bromoform (0.91 ml:7.1 ml) plus ~7 mg of n-hexylamine HCl per tube. This mixture, together with the sample, is placed in standard polypropylene tubes with anodized aluminum tops fitted with neoprene rubber washers. At the end of a run, quartz is skimmed from the tube with a polyethylene pipette to which is attached a 25 cc syringe. None of the abrasive quartz suspension is allowed into the syringe. The sample is finally washed 4 times in acetone, once in water, once in 2N HCl and 5 times in water and is ready for analysis after drying at 110°C.

These techniques were developed on a borrowed machine which could not be modified. They are inefficient in several respects.

1) Under the pressures produced in this machine, both ethanol-bromoform and methanol-bromoform separate into 2 phase regions. Quartz appears at the interface. Therefore, the maximum density difference is not achieved with either liquid. Machine availability did not permit study of the two phase region.

2) Standard tubes supplied for this machine are poorly suited for heavy liquid work. With stainless steel tubes the sample cannot be observed. Plastic tubes supplied are polypropylene and lusterloid. The lusterloid tubes are completely soluble in heavy liquids and are therefore unusable. The polypropylene also is somewhat soluble in bromoform-ehtanol at high pressure. The tube thus becomes

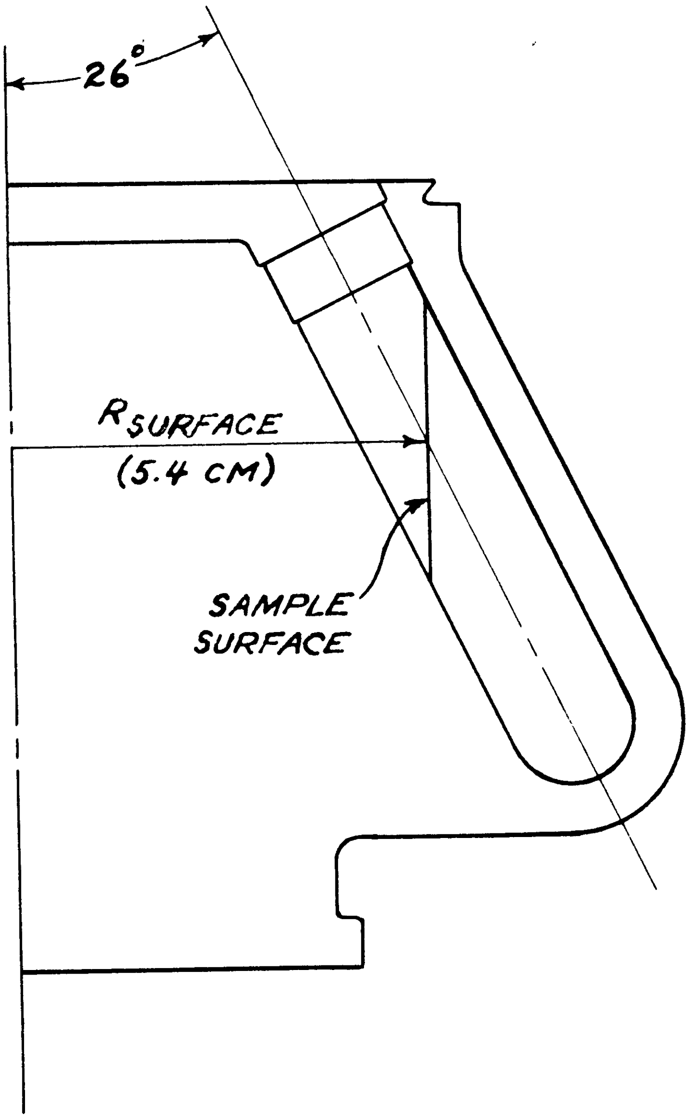


FIGURE 5. DIAGRAM OF ULTRACENTRIFUGE HEAD SW40

brittle and some of the liquid leaks through. Only stainless steel and lusterloid tubes are available for the centrifuge heads with pivoted sample holders, "swing out" type. Considerable remixing of the sample can occur during deceleration with the SW40 head (even though this is extended over ~1/2 hr.). Carefully machined and balanced teflon tubes which could be used with a swing out head would be useful.

3) The anodized aluminum caps provide a disconcerting possible source of contamination. This is paralleled by aluminum foil seals on many organic reagent bottles (methanol, isopropanol, acetone). Reaction with a centrifuge cap was observed in only one case, however; and in this case the anodized surface of the tube cap was scarred. HCl-water washings which follow are intended to remove any soluble Al that may be present.

If suitable salts could be found, it would be possible to produce density gradient cells similar to the CsCl density gradient cells of the biologist. These cells are capable of resolving molecules differing in a single isotope.

4.2 Spectrographic Analysis

4.2.1 General

Aluminum and lithium in the Kings Mountain quartz suite have been determined spectrographically in the Cabot Spectrographic Laboratory. In this work, Ahrens (1960) has served as a guide to general determinative techniques. Of more specific applicability to quartz analysis are the papers of Dennen (in preparation for publication) and of Bambauer (1961). Details of the analytical procedure used are given in Table 2. Although arrived at essentially independently, the technique for determining Al closely resembles that described by Bambauer.

The general sequence of analytical operations can be summarized as follows: Those samples requiring dilution are weighed on an analytical balance. They are then premixed on glazed weighing paper and placed in a teflon cylinder which is vibrated with a dental type homogenizer for 5 to 30 minutes depending on sample size. All samples are loaded into spectrographically pure electrodes using a teflon holder similar to that described in Holyk (1952). In the present model, a graphite rod is substituted for the brass holding screw. Tamping is accomplished with a lucite rod.

The spectrograph used is a Littröw-mounted instrument manufactured by Hilger and Watts, Ltd. and equipped with automatically interchangeable quartz and glass prisms. The image of the arc is focused on the collimating lens

Table 2. Analytical Conditions

I. General

Spectrograph	Hilger, large quartz-glass prism
Slit width	0.030 mm
Film development	4.5 minutes in Kodak D19 at 20°C (1 liter developing tank, 50 ml developer changed/plate)
Film measurement	Hilger nonrecording microphotometer

II. Aluminum Determination

Electrodes	0.18" carbon (National Carbon Company L113SP) drilled to 1/8" depth with a 1/8" diameter drill, tip honed 59° from vertical
Excitation	12 amperes, D.C., sample arced as anode (Sample arced to completion)
Diluent	1:1.2 mixture sample:specpure graphite (by weight)
Analysis lines	Al 3092.7 (Ti 3234)
Comparison standard	Si 2970.3
Sectoring	4 step, 1:4 sector
Film	Kodak Spectrum Analysis-1 plates

III. Lithium Determination

Electrodes	1/8" graphite (National Carbon Company AGKSP) drilled to 5 mm depth with a 1/16" diameter drill. These are pre-arced 15 sec. at 6 amps before use.
Excitation	5 amps, D.C., sample arced as anode for 20 sec.
Diluent	10:1 mixture sample/repurified RbCl (from Johnson-Mathey specpure No. 4418, 1 ppm Li reported)
Analysis line	Li 6707
Comparison standard	Rb 7280
Sectoring	8 step, 1:2 sector
Film	Kodak 1N plates

Table 3. Analytical Standards for Aluminum and Lithium Determination

I. Quartz (Vein 5 standard) + Al_2SiO_5 (from sample C28, contains some rutile)

Mixture designation	Al_2SiO_5 gm	Designated mixture gm	SiO_2 gm	Al added ppm
A	0.0074	-	0.2630	9.37x10^{3}
B	-	0.0266(Mix.A)	0.2204	1.01x10^{3}
C	-	0.0249(Mix.B)	0.2265	100
D	-	0.0273(Mix.C)	0.2250	10.9
E	-	0.0043(Mix.B)	0.0336	33.8

II. Quartz (Vein 5 standard) + Al_2O_3 (other oxides and halides are present in this mixture)

Mixture designation	Al_2O_3 gm	Designated mixture gm	SiO_2 gm	Al added ppm
I_B	0.0510	0.4855 (other oxides and halides)	-	5.03x10^{4}
II	-	0.0353 (I_B)	0.3176	5.04x10^{3}
III	-	0.0392 (II)	0.3512	5.05x10^{-2}
IV	-	0.0455 (III)	0.4087	50.6
V	-	0.0466 (IV)	0.4163	5.09

III. Lithium Standards (Vein 5 standard + spodumene ($LiAlSi_2O_6$))

Mixture designation	$LiAlSi_2O_6$ gm	Designated mixture gm	SiO_2 gm	Li added ppm
α	0.134	-	0.366	10^{4}
β	-	0.0333 (α)	0.3000	10^{3}
γ	-	0.0333 (β)	0.3000	10^{2}
δ	-	0.0333 (γ)	0.3000	10
ε	-	0.0333 (δ)	0.3000	1
δ.1	-	0.0450 (δ)	0.1018	3.06
γ.1	-	0.0251 (γ)	0.1046	19.3

by a long focal-length silica-glass lens placed in front of the slit. Spectra are recorded on 4"x10" glass plates and line densities are read with a Jarrell-Ash non-recording microphotometer.

4.2.2 Aluminum Determination

Samples for aluminum determination are mixed with "spectrographically pure" graphite powder in the ratio 1:1.2. These are loaded into "spec pure" 3/16" carbon electrodes and arced at 12 amps D.C. with the sample as anode. Al 3093 is used as the analysis line. Its intensity is compared with that of Si 2970. Use of a weak silicon line as an internal standard makes it unnecessary to weigh electrodes before arcing. This is true because aluminum and silicon have similar volatilization rates and ionization potentials, and because these lines have similar excitation potentials. The ratio of intensities of Al 3093 to Si 2970 thus changes smoothly with changes in aluminum concentration.

The spectrograph is set to record light of wavelength 2650Å to 4200Å. Eastman Kodak Spectrum Analysis-1 plates are used. The spectral lines are sectored with a four step 1:4 sector. Plate calibration is accomplished by plotting $(d_0/d - 1)$ vs. I using Si 2970.3 (Ahrens, 1960, p. 142). A typical calibration curve is shown in figure 6.

Standards for aluminum determination were prepared from a vein quartz with low aluminum concentration (labelled Vein 5) and from the aluminum silicate, Al_2SiO_5, of sample C28. The dilution sequence, designed to produce successive 10-fold decrements in aluminum concentration, is shown in Table 3 . Figure 7 shows the analytical curve determined from these standards. A small blank correction was needed

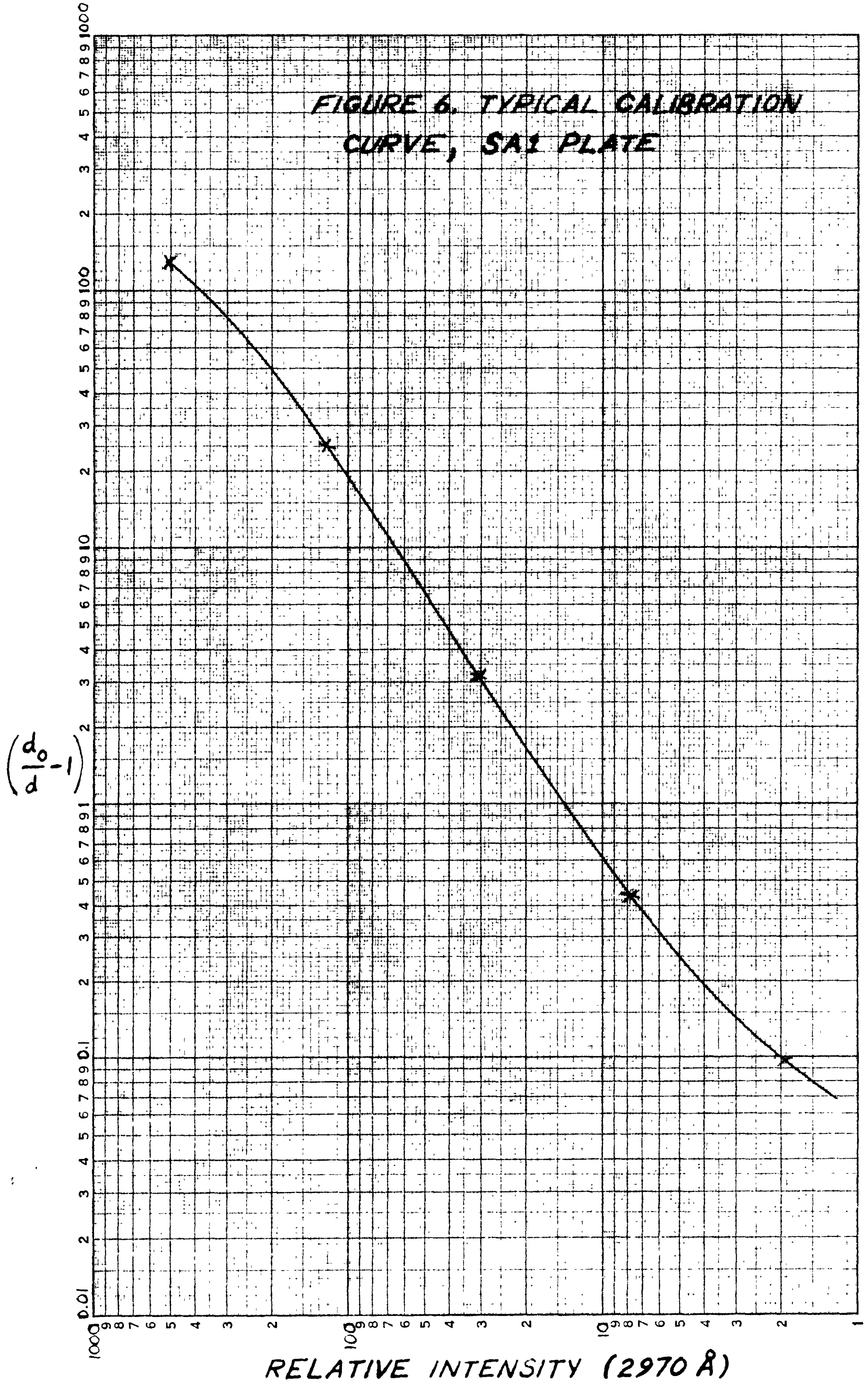


FIGURE 6. TYPICAL CALIBRATION CURVE, SA1 PLATE

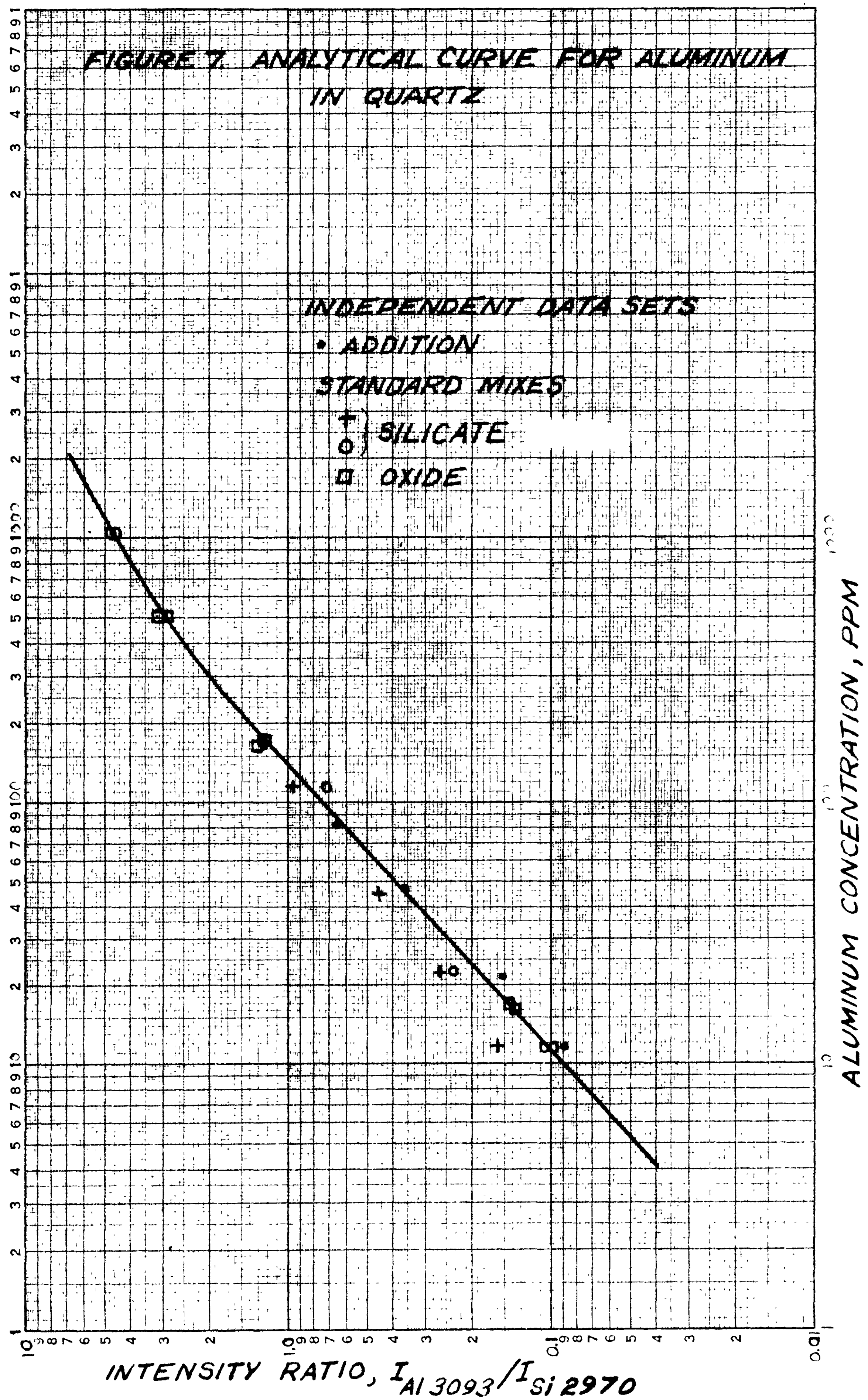


FIGURE 7. ANALYTICAL CURVE FOR ALUMINUM IN QUARTZ

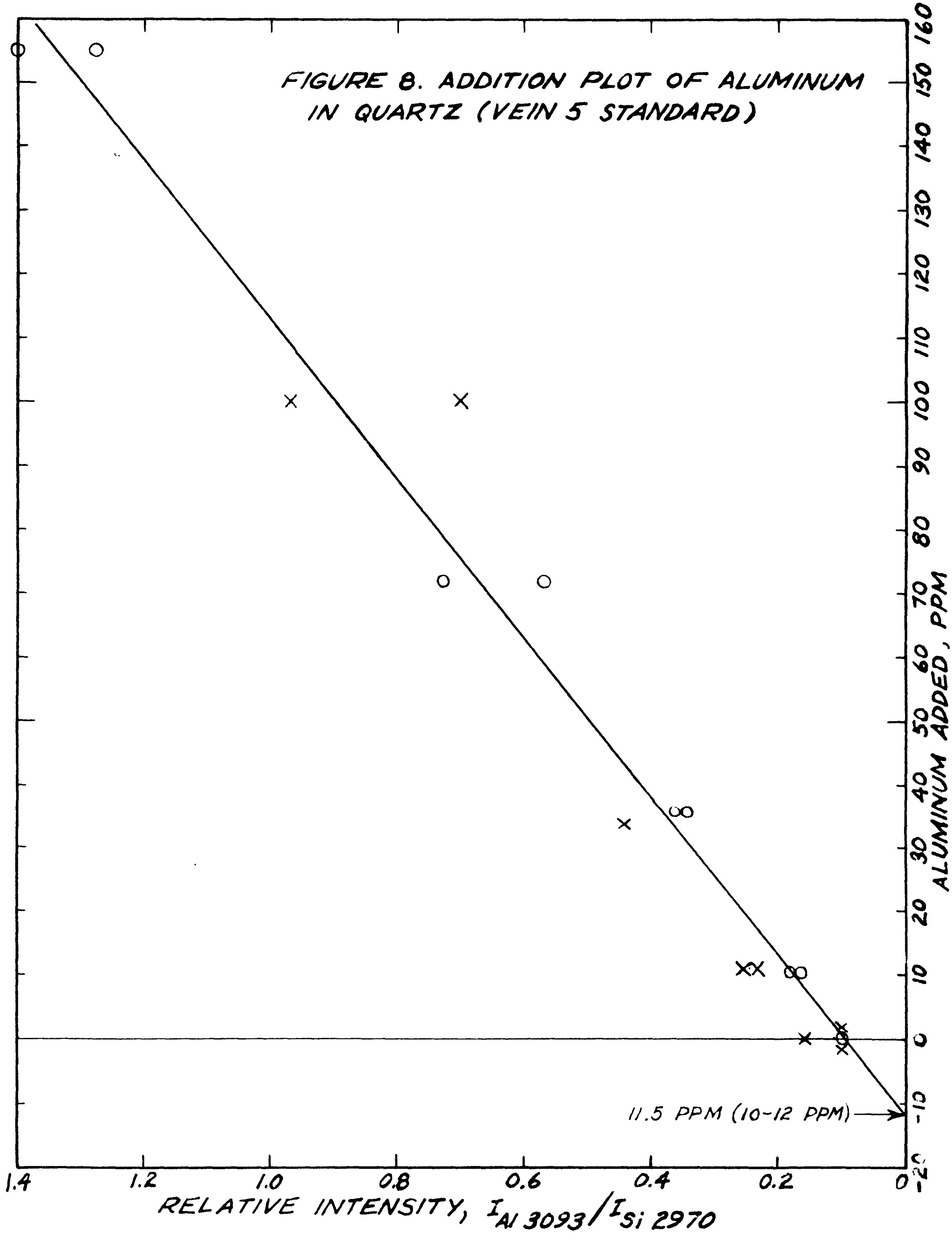


FIGURE 8. ADDITION PLOT OF ALUMINUM IN QUARTZ (VEIN 5 STANDARD)

for the initial aluminum content in Vein 5. This was determined by mixing Vein 5, in various proportions, with a quartz having 155 ppm Al. The addition plot derived from this mixing sequence is shown in figure 8.

Low-level interference with Al 3093 occurs from a weak line identified by Dennen (personal communication, 1963) as one of the components of the double subhead in the OH molecular spectrum. The other component of this subhead was found to have the same intensity within the precision of measurement. A correction for this interference was applied by subtracting the intensity of the non-interfering subhead from the aluminum intensity.

4.2.3 Lithium Determination

The spectrum of an alkali metal present in trace amounts is enhanced by the presence of large amounts of another alkali metal in the sample (Ahrens, 1960; Bambauer, 1961). This keeps the arc at a relatively low temperature and permits the element sought to volatilize slowly. To utilize this phenomenon, however, requires that one find a compound which contains the desired added element but which is free of the element sought in the sample.

Rubidium chloride was chosen as an enhancing substance for lithium. Johnson-Mathey spectrographically pure RbCl, Serial No. 4418 (manufacturers analysis, 1 ppm Li), was used as a starting material. This was passed through a Vycor column containing Dowex-50 ion exchange resin. Elution was performed with 2N Vycor distilled HCl, and the progress of rubidium in the column was monitored by flame testing. The discharged RbCl solution was collected in a Vycor evaporating dish and evaporated to dryness. In the resulting RbCl, lithium was below the spectrographic limit of detection (<<0.2 ppm).

Samples for analysis are diluted in the ratio 10 parts sample:1 part RbCl. The Li 6707Å line is measured, and this is normalized by taking the ratio of Li 6707/Rb 7280. The spectrum from 4650Å to 10,000Å is resolved with the glass prism and is recorded on Eastman Kodak 1-N plates. An 8 step 1:2 sector is used for plate calibration. The calibration curve is shown in figure 9 and analytical con-

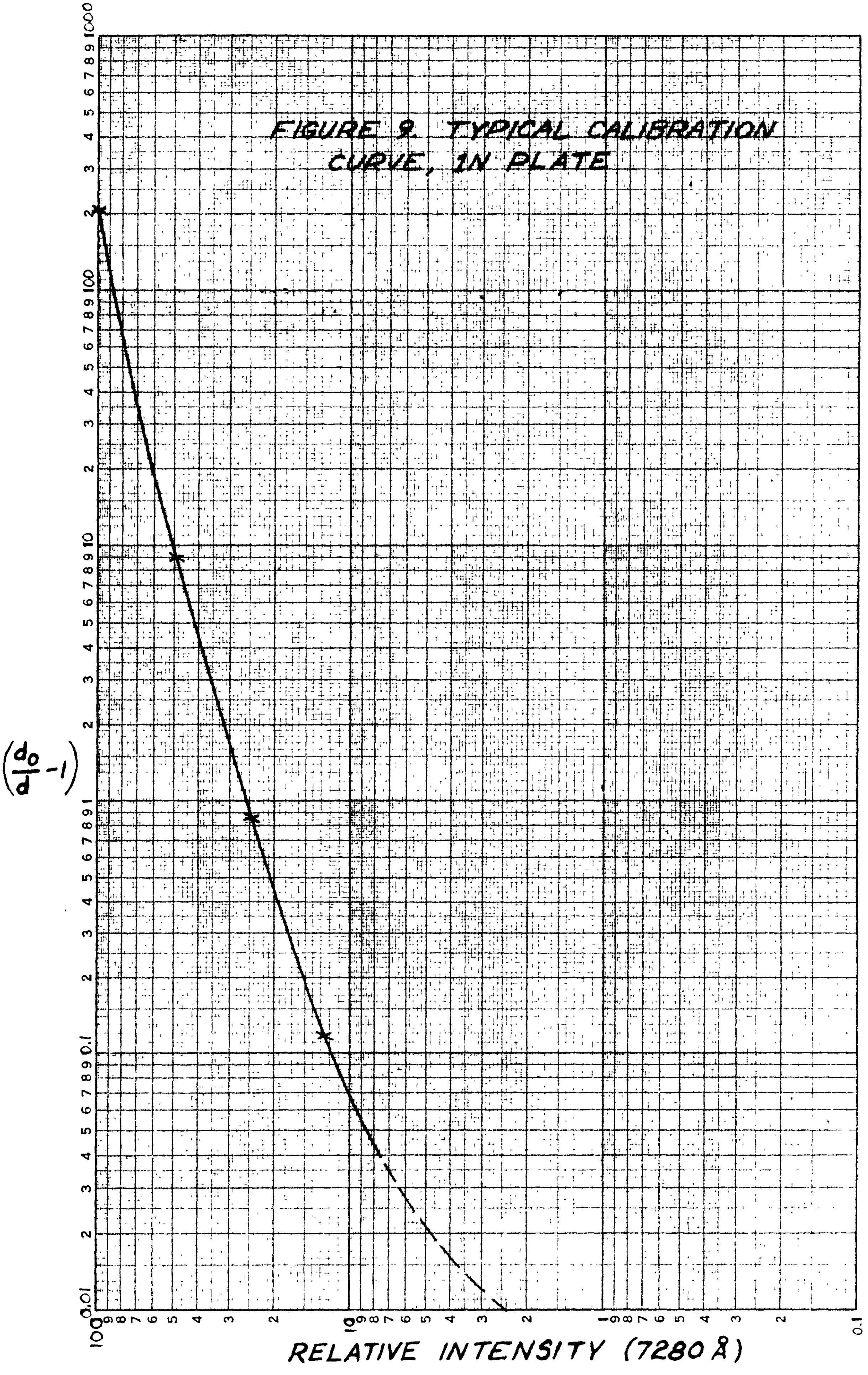


FIGURE 9. TYPICAL CALIBRATION CURVE, 1N PLATE

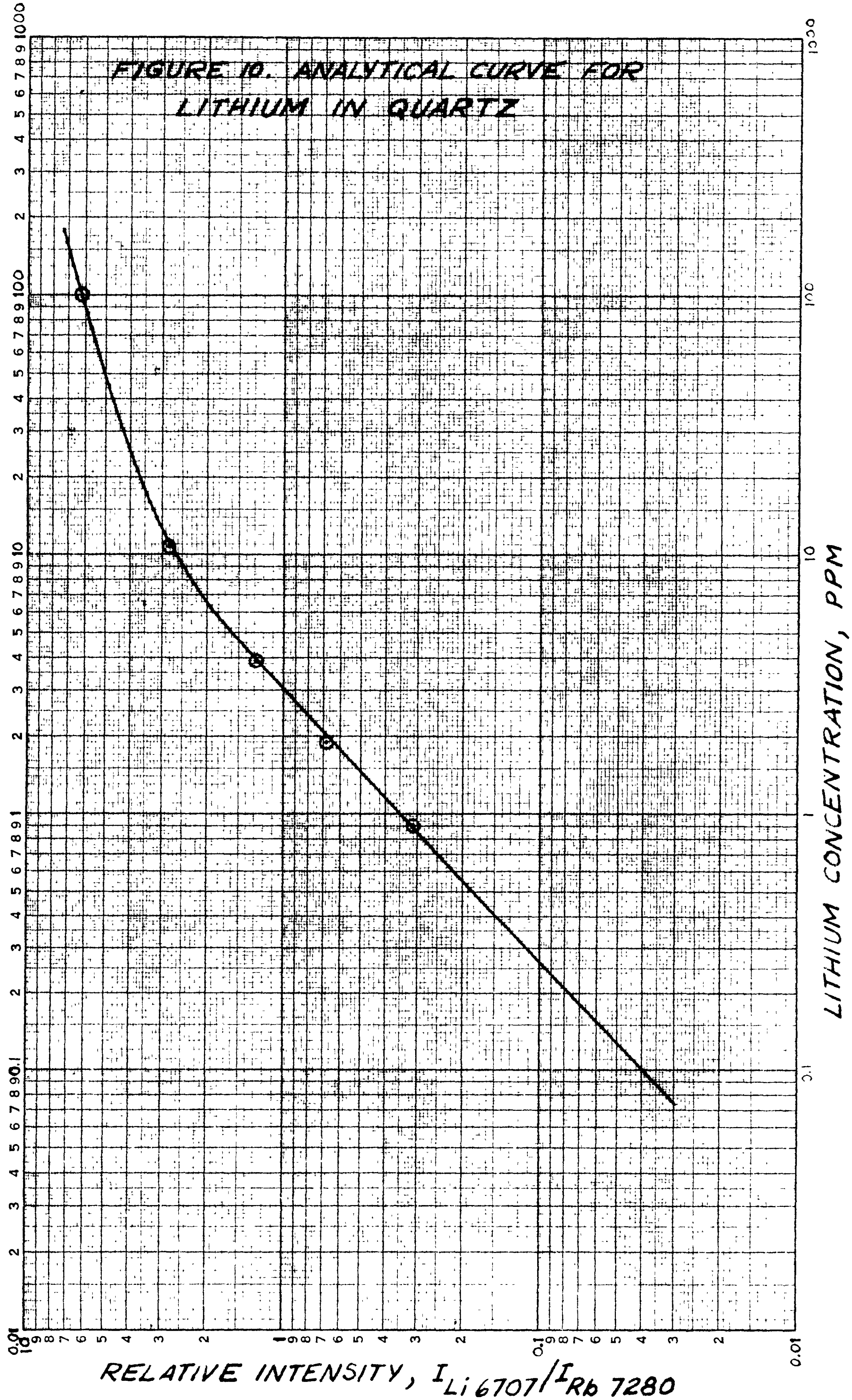


FIGURE 10. ANALYTICAL CURVE FOR LITHIUM IN QUARTZ

ditions are outlined in Table 2.

Standards were prepared by mixing spodumene, ($LiAlSi_2O_6$), and quartz (from Vein 5) in the ratio of .366:1.00. This mixture was then diluted with quartz from Vein 5 by successive factors of 10 as shown in Table 3. The analytical curve is shown in figure 10. Above 10 ppm lithium, strong self-absorption of Li 6707 occurs and Li 6104 should be used. This method has an estimated detection limit for lithium of <0.2 ppm. No lithium was found in samples C23, C21 or C5; sample C18 gave a lithium value of < 0.3 ppm.

The aim of these lithium determinations was to demonstrate whether or not a stoichiometric relation existed between lithium and aluminum in these samples. Because the extremely low lithium concentration in all samples precludes any such relationship, this method of lithium determination was not developed to its full potential. It is felt that further experimentation with electrode size, excitation conditions, and the ratio of weight RbCl to weight sample could result in an excellent quantitative method. An increase in amperage of excitation, for example, results in a considerable increase in sensitivity but also causes the sample to volatilize erratically in the arc when it is held in 1/8" electrodes. The optimum ratio of RbCl:sample was not investigated systematically; for maximum sensitivity it should probably be increased.

The purification technique used here to remove lithium from RbCl resulted in a demonstrable lowering of sodium content. Perhaps repeated ion exchange column separations would make this technique applicable to the determination of low concentrations of sodium as well as to lithium.

4.3 Evaluation of Data

4.3.1 Precision of Spectrographic Analyses

Analytical results of the spectrographic determination of aluminum in various quartz samples together with standard deviations and class intervals in percent are presented in Table 4. It should be emphasized that these are multiple analyses of the same prepared sample, and thus reflect analytical error but not the effectiveness of sample preparation. Within the concentration range covered, the percent deviation of the class interval varies from 6.1% to 22%, with an average value of 10.9%. The low concentration sample (39 ppm Al) has a high percent deviation, probably because of the increasing importance of background effects at low concentration. Average percent deviation for all other samples is 8.1%.

The reality of the analytical data is demonstrated by the fact that c for the analytical technique is ~11% whereas the aluminum content varies by a factor greater than 3.

Table 4

Analytical Results of the Spectrographic Determination of Aluminum in Quartz

Sample No.	Al, ppm		d	d^2	σ	c%
	x	$\bar{x}$				
C5	115 115 104 103	109	6 6 5 6	36 36 25 36	6.7	6.1
C18	82 72	77	5 5	25 25	7.1	9.2
C21	55 49	52	3 3	9 9	4.2	8.1
C23	45 33	39 ~~80~~	6 6	36 36	8.5	22.0
C28	85 75	80	5 5	25 25	7.1	8.9

$\bar{c} = 10.9\%$

4.3.2 Effectiveness of Separations

All interpretations of these data hinge on whether the aluminum determinations really reflect aluminum in solid solution in quartz or whether they merely measure aluminous phases accidentally included in the samples. Several observations bear on this problem. Accidental impurities should not show systematic variation (the suite of samples in this study varies in a regular manner). Accidental impurities, when present in significant quantity, can be detected by lines other than aluminum; the magnesium spectrum is a particularly sensitive indicator of mica or kyanite inclusions, and any sample containing more than a trace of magnesium is arbitrarily excluded.

A rather subjective test of the maximum amount of accidentally included aluminous phases consists of comparing, under a microscope, the volume percent of Al_2SiO_5 and of rutile. One can then measure the concentration of titanium spectrographically (from Ti 3234, analytical curve in Fig. 11); and, assuming that there is no titanium in the quartz, one can calculate the rutile present in the sample. From this and the kyanite/rutile volume ratio (R) one can estimate the aluminum contributed to the sample by Al_2SiO_5. The equation is:

Aluminum contamination (ppm Al) = 0.474 R x (ppm Ti).

For sample C18, John Philpotts kindly measured the kyanite/rutile ratio as between 1/3 and 1/5. The measured titanium concentration for this sample was 50 ppm. Using the con-

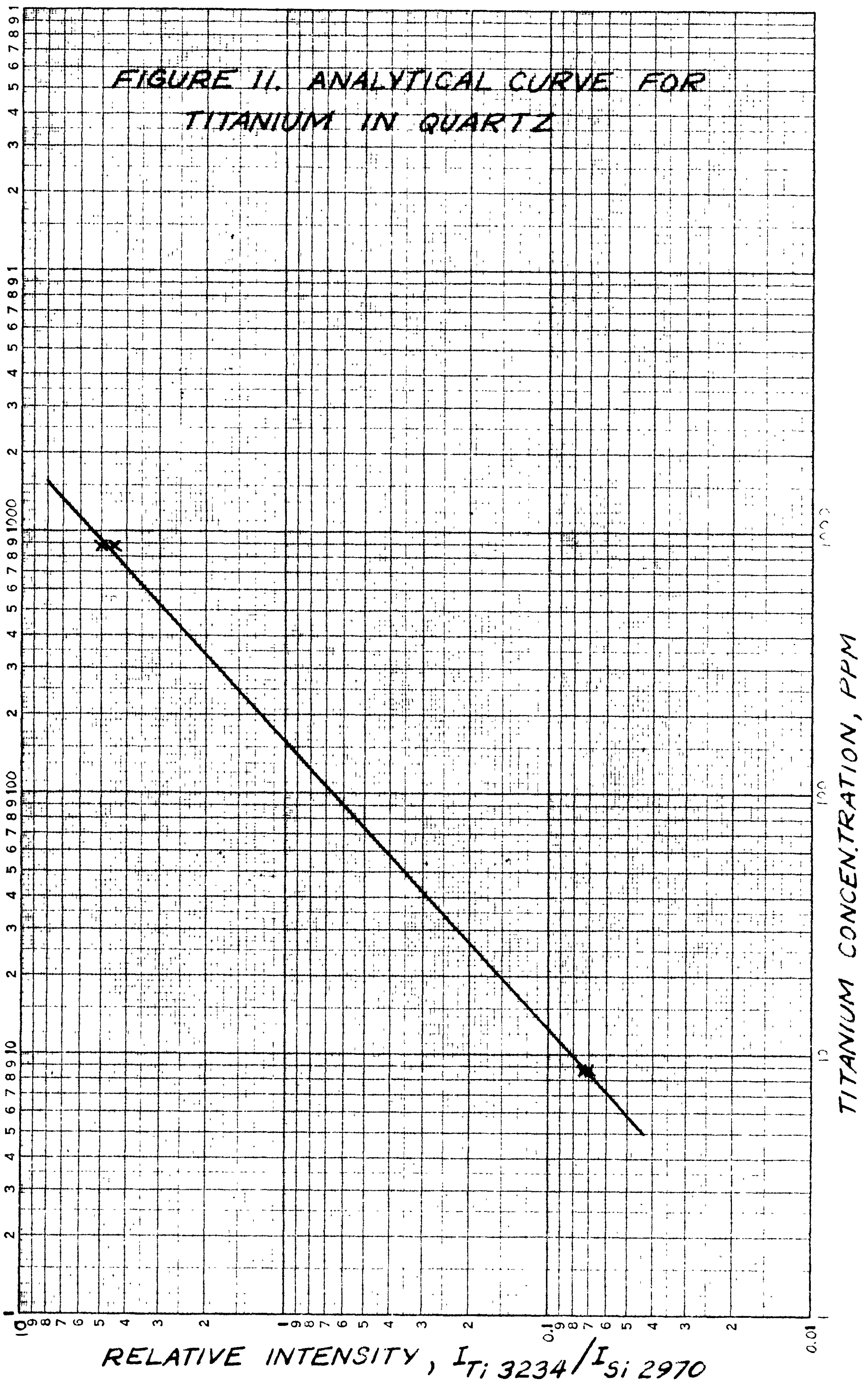


FIGURE 11. ANALYTICAL CURVE FOR TITANIUM IN QUARTZ

servative ratio $R = 1/3$, aluminum contamination from Al_2SiO_5 is seen to equal a maximum of 7.6 ppm or ~10%.

V. RESULTS AND CONCLUSIONS

5.1 Aluminum as a Geothermometer

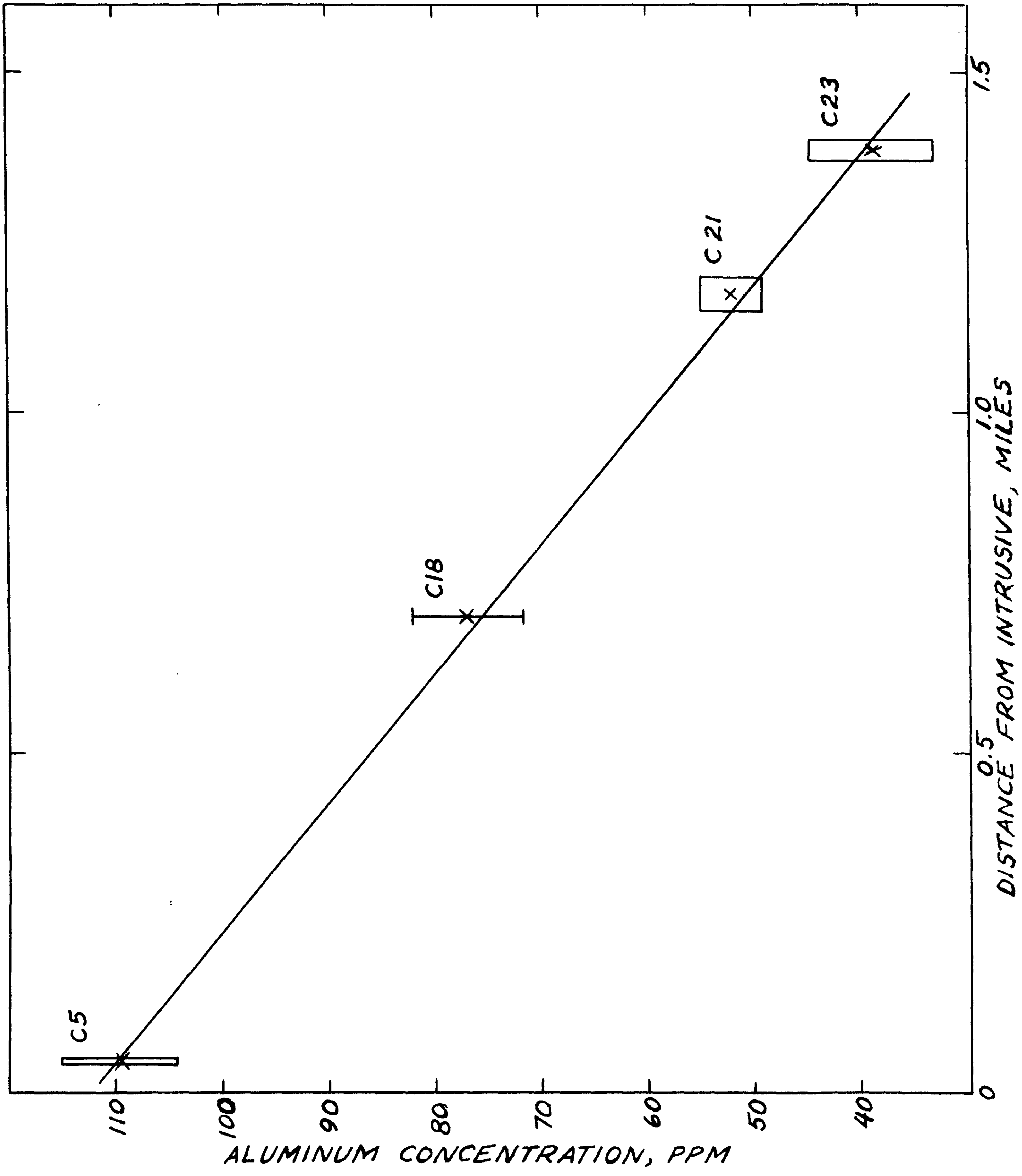
The aluminum and lithium content of 4 selected samples of quartz have been measured. These samples came from a highly aluminous environment in which the chemical potential of aluminum is controlled by the presence of one or more of the Al_2SiO_5 polymorphs. So far as can be determined, all are from equivalent environments except that each was metamorphosed at a different temperature. Since all samples occur in an area of contact metamorphism, the temperature at any point is a function of the distance from the intrusive Yorkville Quartz Monzonite.

It has been established that lithium has not participated significantly in coupled Al-Li substitution in these quartz samples. Further, it is postulated that hydrogen is readily available and that the measured aluminum concentration in each sample represents the amount of aluminum substituted for silicon in the quartz structure, with hydrogen filling channelways in the structure for charge balance. It is also postulated that temperature variation across the contact is relatively small.

A plot of aluminum concentration versus distance of the sample from the nearest outcrop of intrusive reveals a progressive and approximately linear decrease in concentration with distance from the intrusive body (Fig. 12). The range of concentration is from ~~76~~ 109 ppm Al near the contact to ~~19~~ 39 ppm at a distance of 1.4 miles (in good

FIGURE 12. RELATIONSHIP BETWEEN ALUMINUM DISSOLVED IN QUARTZ AND DISTANCE OF SAMPLE FROM NEAREST INTRUSIVE OUTCROP

ALL QUARTZ IS FROM Al_2SiO_5 BEARING ASSEMBLAGES

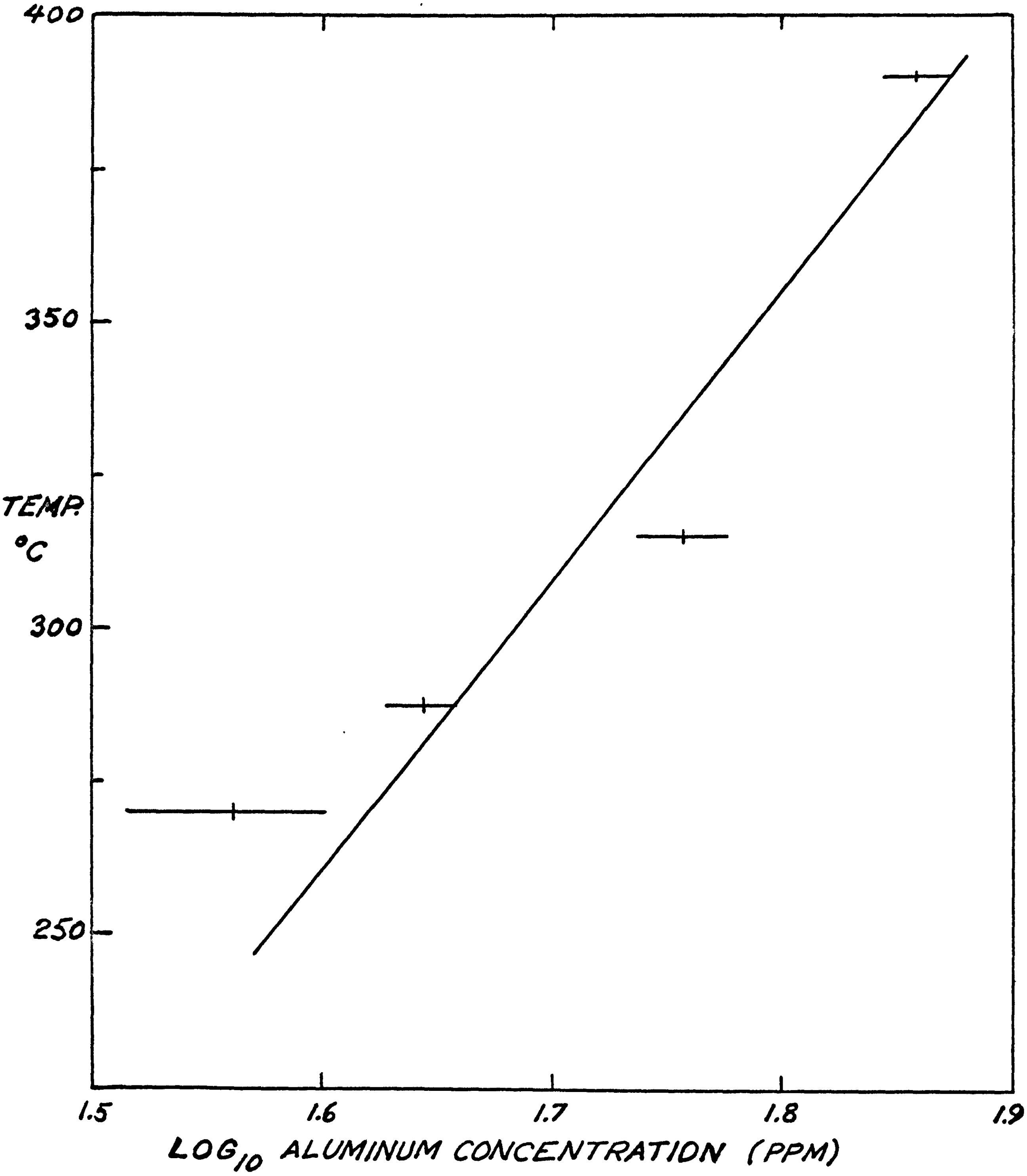


agreement with absolute values published by Bambauer (1961)). This is the chief finding of this thesis; that under controlled conditions, the aluminum concentration of quartz can act as a sensitive geothermometer. If such a device were to be properly calibrated by laboratory measurements it could provide an inexpensive way of determining the temperature of formation of rocks containing Al_2SiO_5 as a phase.

Perhaps more important is the possibility of extending the concept of minor element geothermometry to other systems. The simplest system for analysis would be that of a trace element distributed between coexisting phases. Studying an element which is not common in any phase would tremendously simplify sample preparation.

In an attempt to relate observed aluminum concentration in quartz to the actual temperature of formation of the Kings Mountain samples, a series of temperature-distance curves and their upper temperature envelope have been plotted (Fig. 2). Inferred maximum temperatures range from 400°C at the intrusive contact to 270°C at a distance of 1.4 miles. The nature of the assumptions involved is such that undue significance should not be attached to the result. Nevertheless, for whatever value it may have, figures 2 and 11 have been combined with the distance parameter removed as figure 13.

FIG. 13. INFERRED TEMPERATURE-COMPOSITION DIAGRAM FOR ALUMINUM SOLUBILITY IN QUARTZ



5.2 Heat of Solution of Al_2SiO_5 in Quartz

The heat of solution of a solid in a dilute solution can be written

$$\left(\frac{\partial \ell n\ x}{\partial T}\right)_P = \frac{L}{g_{22}^{quartz} R T^2}$$

where L is the heat of solution of the solid component and is equal to the latent heat of melting of the solid at the temperature of the solution. g_{22}^{quartz} is defined on page 24. From figure 13,

at $575^\circ K$, $x = 49.6$ ppm Al $= 49.6$ M moles Al_2SiO_5/cc

$625^\circ K$, $x = 71.6$ ppm Al $= 71.6$ M moles Al_2SiO_5/cc

$$(M = \frac{\text{moles } Al_2SiO_5}{(\text{ppm Al})(\text{cc})})$$

$$\Delta T = 50,\ \Delta \ell n\ x = \ell n\left(\frac{71.6}{49.6}\right) = 0.368$$

$$R = 2 \text{ cal/}^\circ\text{mole}$$

$$T^2 = 3.6\text{x}10^5, \text{ (for } T = 600^\circ K)$$

and L, the heat of solution of Al_2SiO_5 in SiO_2,

$$L = \frac{0.368(2)(3.6\text{x}10^5)}{2(50)} = 2.6\text{x}10^3 \text{ cal/mole.}$$

5.3 A Successful Test

An interesting and not entirely planned test of the assumptions in this thesis came about in the investigation of the sample from locality C28. This locality is in the general Kings Mountain region but lies in the Reese Mountain-Clubb Mountain area, North Carolina, which is several miles to the northeast of the area from which previously described samples were obtained (Fig. 14, Plates 1, 7 in pocket). The Reese Mountain-Clubb Mountain area is characterized by considerable hydrothermal activity. The assemblage at Clubb Mountain includes the minerals pyrophyllite, lazulite, rutile, and clay; as well as kyanite and quartz. Espenshade and Potter (1960, p. 90) report the following additional accessory minerals: pyrite, tourmaline, andalusite(?), diaspore, goyazite, and zonyite. This is clearly an unusual assemblage that might merit detailed study of coexisting phases.

Locality C28 is near Machpelah Church at the north edge of plate 7. As mapped by Potter, it lies in sillimanite quartzite ~0.06 miles from the nearest contact (inferred) with the Yorkville Quartz Monzonite. The sample obtained from here is a fine grained rock in which sillimanite, quartz, magnetite, rutile, as well as iron stains from pyrite, and clay were identified megascopically. Sillimanite was observed to occur in relatively coarse needles. Voids were found in the separated quartz fraction.

Analysis of the separated and purified quartz from

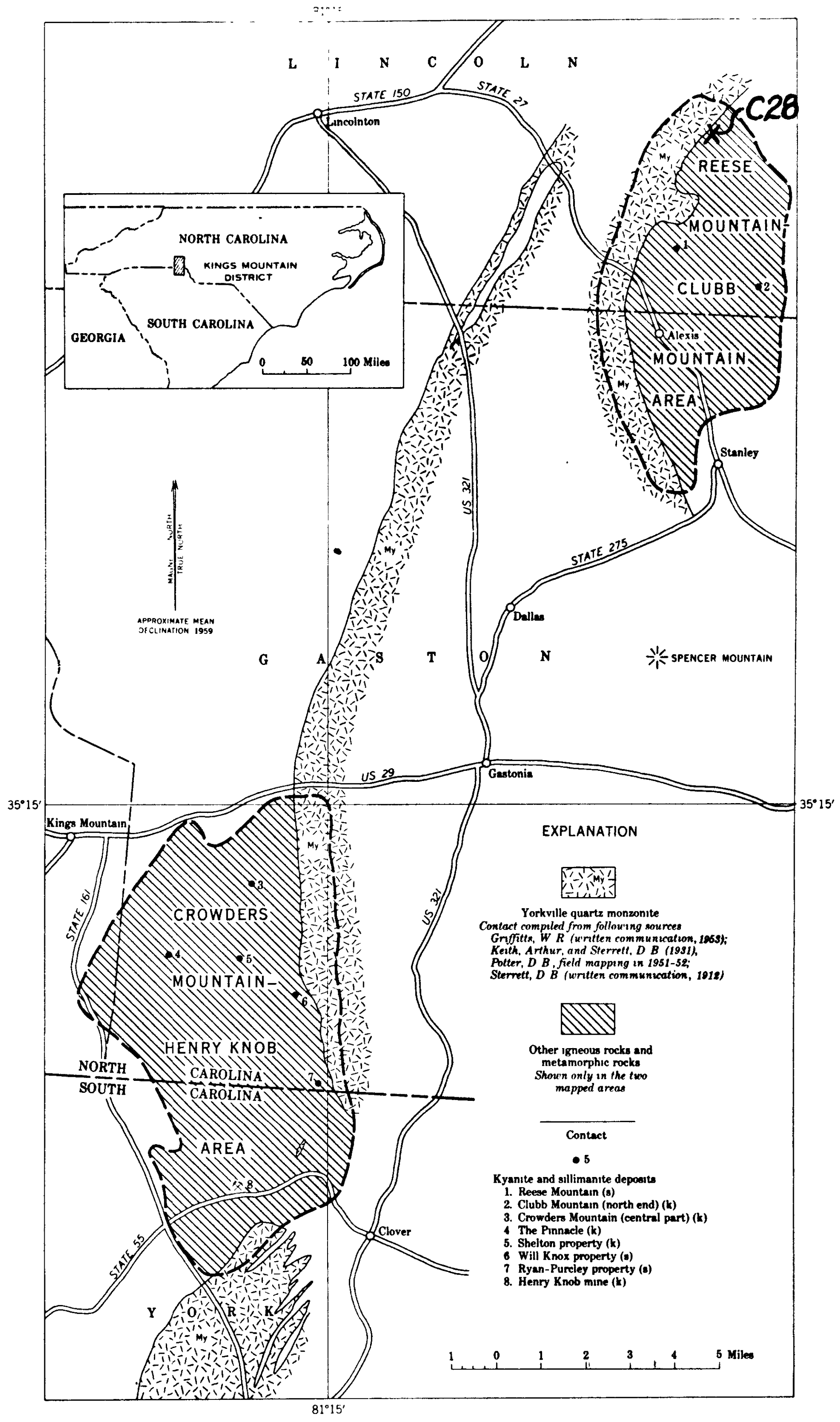


Figure 14. Sketch map of entire Kings Mountain area (North Carolina - South Carolina) showing location of C28 in relation to main sample area. Geology by D. B. Potter (Appears as Fig. 41 of Espenshade and Potter, 1960. References are to that publication.).

C28 gave a duplicate analysis of 75 ppm and 85 ppm, average 80 ppm. There is obviously no way in which this value for a sillimanite bearing assemblage could be rationalized with the data presented in figures 1 and 12. Thus an evaluation of possible errors in procedure was made. One such error was a rather cursory verification of Potter's identification of the Al_2SiO_5 polymorph at C28. More careful optical petrography established that the mineral is actually very fine kyanite, probably pseudomorphous after sillimanite, suggesting retrograde metamorphism. The value of 80 ppm dissolved aluminum in quartz associated with kyanite is entirely consistent with data in the main body of this thesis. Thus information obtained from C28 tends to support the usefulness of aluminum solubility measurements in geothermometry.

APPENDIX A

Investigation of Lattice Expansion of Quartz as a Function of Aluminum Substitution

Because of the dearth of analyses of quartz which are accompanied by accurate measurements of physical properties, it was thought useful to attempt an X-ray investigation of the lattice constants in the Kings Mountain quartz suite. Equipment of sufficient accuracy for such a study is not readily available, but J. Kalnajs of the Massachusetts Institute of Technology Insulation Research Laboratory kindly undertook to see whether the accurately aligned North American Phillips Company goniometer and accompanying temperature controlled stage in his laboratory were sufficiently sensitive for such an investigation.

He was supplied with the following samples:

Standard, vein 5	~11 ppm Al
C23	39 ppm Al
C18	77 ppm Al
C5	109 ppm Al.

Each sample had been finely ground and then annealed for 8 - 12 hrs. at ~350°C. Each contained 1% or less of material other than quartz. Peak positions of several lines in the back reflection region were measured for each of these samples. During recording, temperature of the sample was maintained at 25.0 ±0.1°C to exclude line shifting. Peak position of each diffraction line was found by counting the intensity over the line in steps of 0.02°

with the aid of a step scanning device. Data was not subjected to statistical analysis, but no obvious trend in peak displacement was found.

APPENDIX B

A Note on Infrared Absorption Spectroscopy and its Application to Quartz Analysis

The applicability of infrared absorption spectroscopy to quartz analysis has been demonstrated by Kats and Haven (1960); Bambauer (1961); Brunner, Wondratschek, and Laves (1961); Kats (1961); Bambauer, Brunner, and Laves (1962); Haven and Kats (1962); Kats, Haven, and Stevels (1962). No attempt will be made here to describe their work in detail. They have demonstrated the sensitivity of the method and have used it to study geologic problems. Nevertheless all published work of which this author is aware has been done on large clear quartz crystals. So long as the method is limited to such crystals it will be difficult to apply to geologic studies.

In response to a request by the author, Brunner has discussed the possibility of doing infrared measurements on powdered samples (written correspondence, April 4, 1963).

> "As the OH-absorption of the bulk material usually is relatively weak, one would have to use cells with a thickness in the order of millimeters. For a first try, I would suggest to heat the quartz powder during 1 hr at 500°C and to use the mull technique with Nujol or Perfluorcarbone. As the adsorbed H_2O causes a very broad OH-absorption, whereas the structural OH causes several relatively sharp peaks, it will be easy to see whether the procedure for the removal of the adsorbed H_2O is successful or not."

Plate 3

a Pyrite crystals from locality C10. Note predominance of cube faces.

b Pyrite crystals from C21. Pyritohedral faces predominate. Many faces are rounded.

c Cavities in kyanite-bearing quartzite specimen from locality C21. Note kyanite blades projecting into cavities. Dark shiny mineral is pyrite; matrix is quartz.

d A kyanite crystal extending through a cavity at C21. Striae are saw marks.

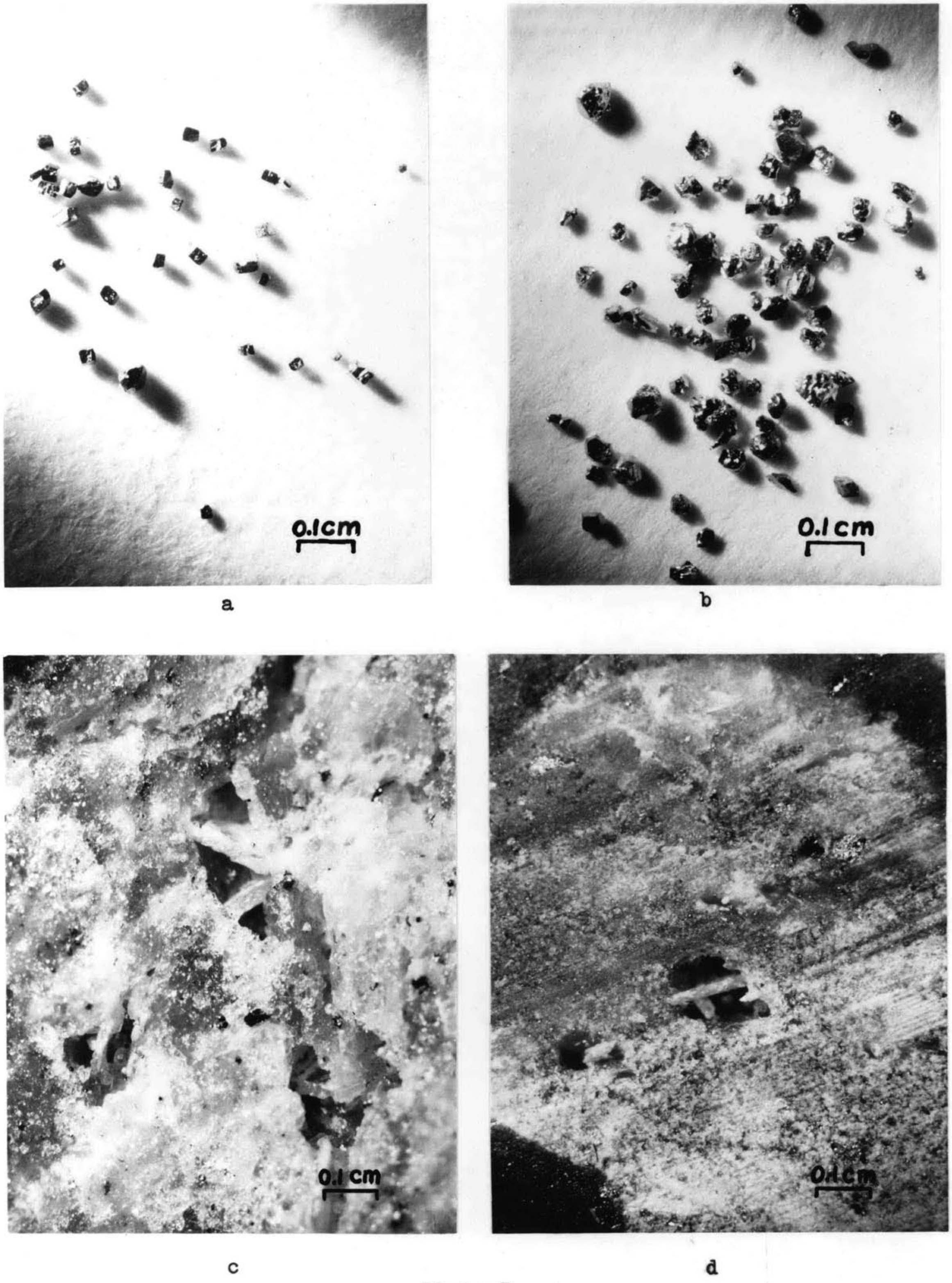


Plate 3

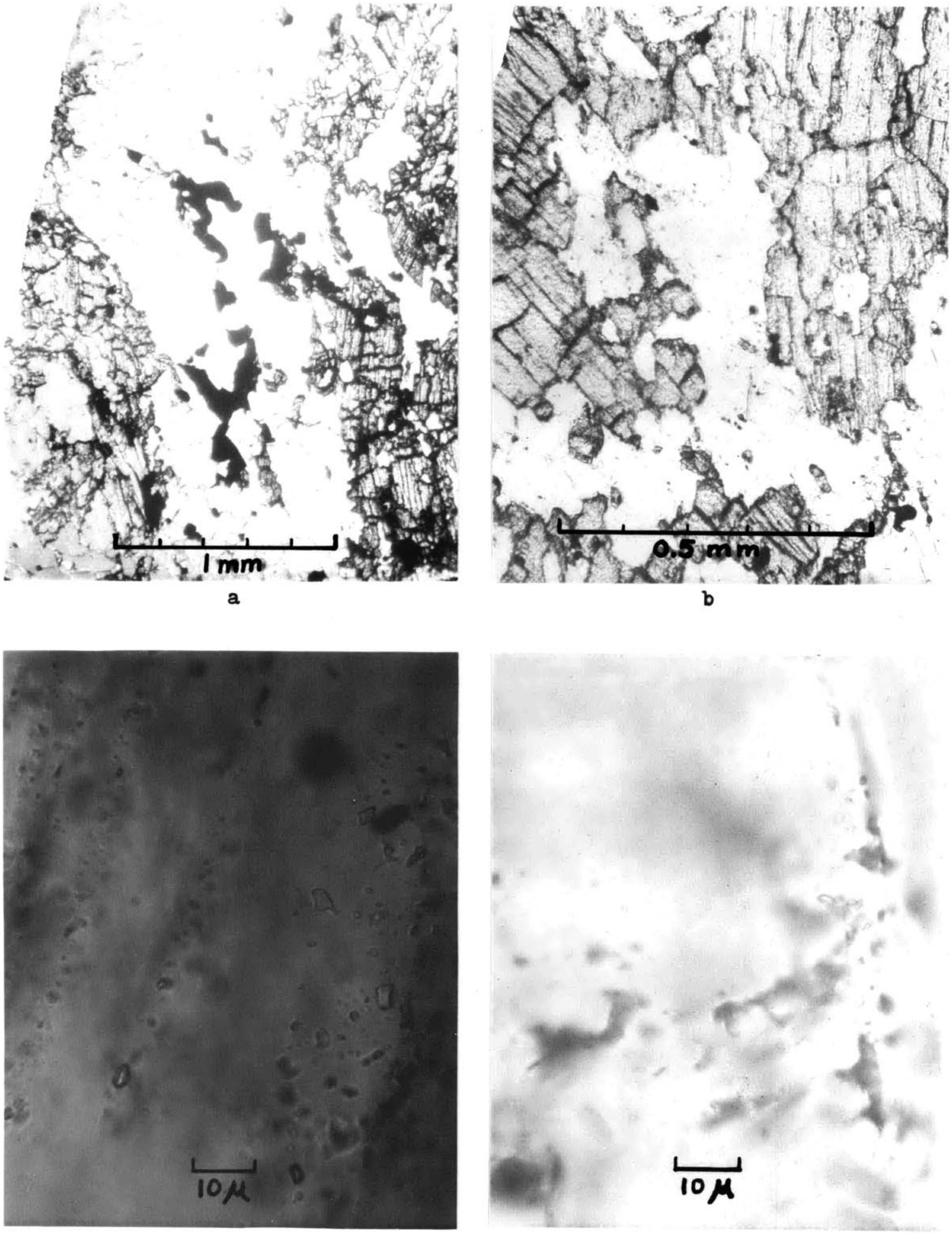
Plate 4

a Thin section of specimen from C18 showing the relationship of the fine quartz grains (low relief) to poikiloblastic kyanite (high relief). Opaque material is iron oxide and rutile. Maximum distance from any quartz grain to a kyanite grain is ~0.5 mm.

b Detail of quartz-kyanite intergrowth at C18. Dark grains are rutile.

c Voids in C18; these frequently display strong lineation.

d Voids in C18. The nature of the filling is not known.



a

b

c

d

Plate 4

Plate 5

a Sample of raw quartz from locality C23. Inclusions are kyanite, rutile, and voids.

b Quartz sample from locality C18. Inclusions are kyanite, rutile, and voids.

c Quartz grains from locality C5 showing long slender sillimanite crystals. Opaque crystals are rutile.

d Grains from same fraction as (c) which have been ground but not otherwise treated. Although these crystals are still not clean, a notable purification has been achieved. (Crossed polars.)

Plate 5

a Sample of raw quartz from locality C23. Inclusions are kyanite, rutile, and voids.

b Quartz sample from locality C18. Inclusions are kyanite, rutile, and voids.

c Quartz grains from locality C5 showing long slender sillimanite crystals. Opaque crystals are rutile.

d Grains from same fraction as (c) which have been ground but not otherwise treated. Although these crystals are still not clean, a notable purification has been achieved. (Crossed polars.)

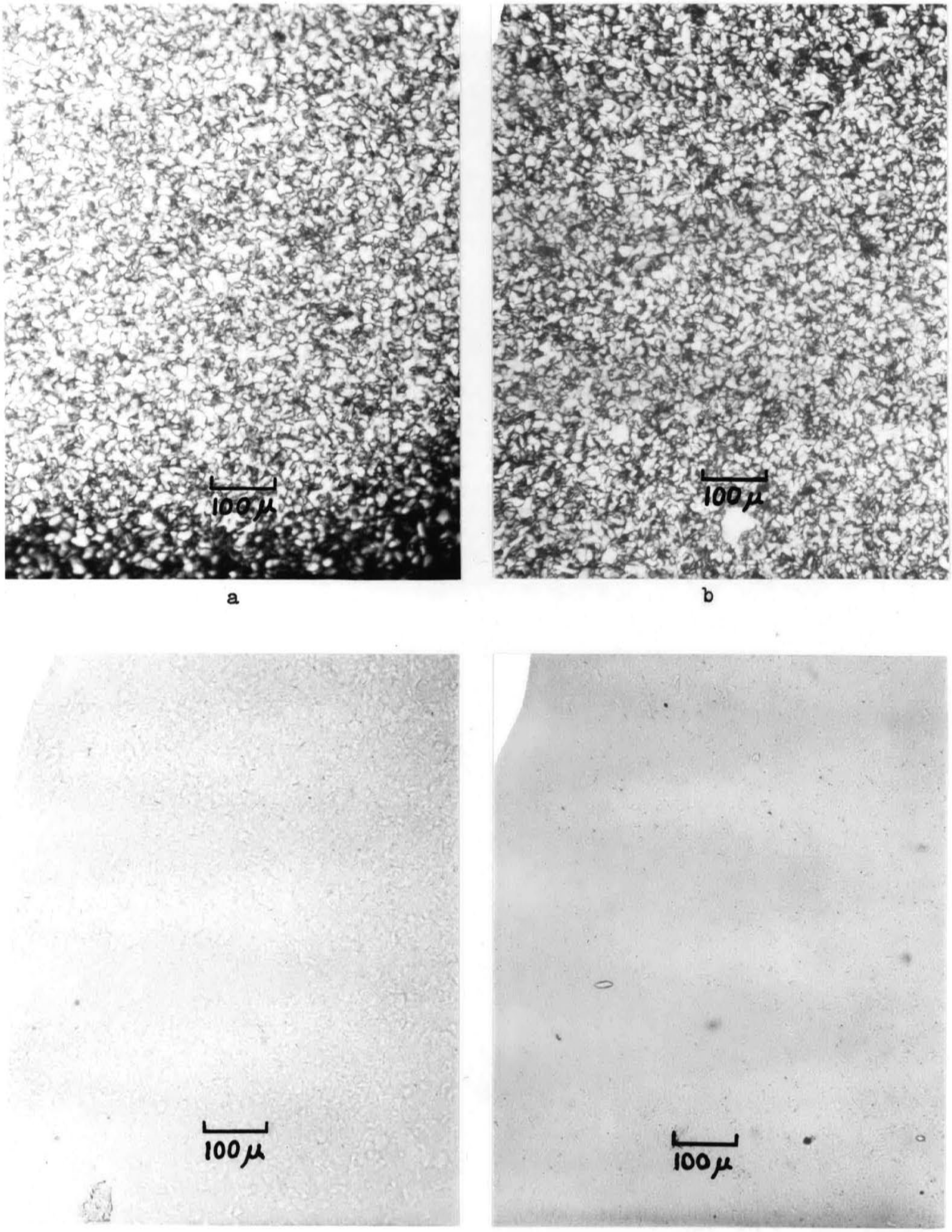
Plate 6

a C5, purified fraction shown under crossed polarizers.

b C21.4, purified fraction shown under crossed polarizers.

c C5, purified fraction. Same area as above (a) showing residual impurities. Blob at lower left is an imperfection in the film. The small sillimanite needles weight an estimated $5x10^{-5}$μg each.

d C21.4, impurities remaining in the purified fraction above (b). Prominent grain in left center contributes an estimated 10^{-3}μg kyanite to the sample.



a b

c d

Plate 6

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Addendum

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AUTOBIOGRAPHY

The author, the son of Eugene Carleton Perry and Ruth Elizabeth (Walker) Perry, was born in Worcester, Massachusetts 23 March 1933. He observed, firsthand, the variability and general mediocrity of U. S. education in some 12 primary and secondary schools. He graduated in 1950 from Newnan High School, Newnan, Georgia.

The author attended the Georgia Institute of Technology from 1950 to 1954, graduating with a Bachelor of Science degree in Chemistry. The following three years he spent in the U. S. Navy, aboard the U.S.S. Putnam (DD757). From 1957 to 1959 the author studied geology at Emory University. He has been at the Massachusetts Institute of Technology since 1959.

Eugene Carleton Perry, Jr. was married to Joan Elizabeth Fisher on 12 February 1963.

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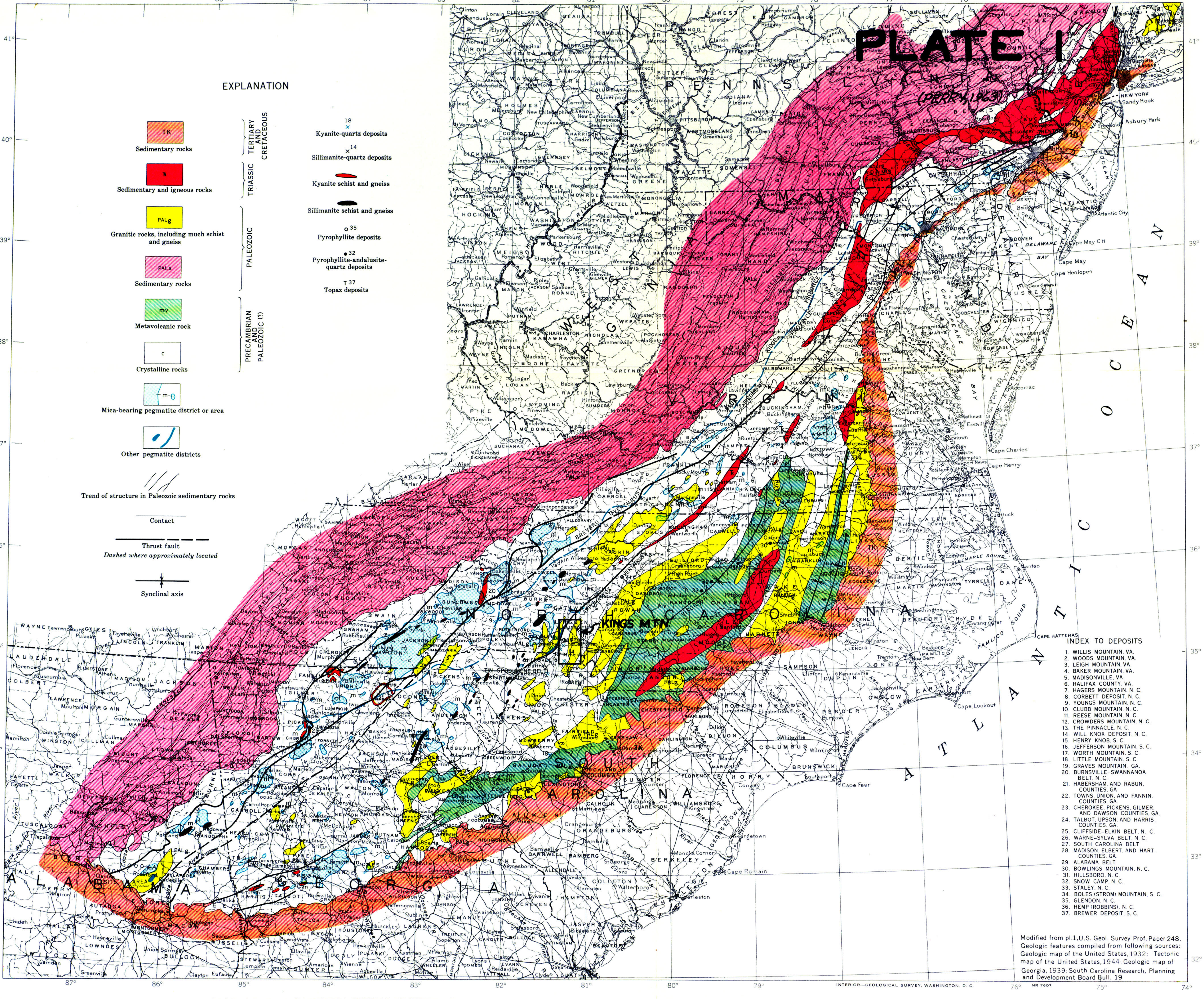
FROM PROFESSIONAL PAPER 336 PLATE 1

PLATE I

(PERRY, 1963)



INDEX TO DEPOSITS

1. WILLIS MOUNTAIN, VA.
2. WOODS MOUNTAIN, VA.
3. LEIGH MOUNTAIN, VA.
4. BAKER MOUNTAIN, VA.
5. MADISONVILLE, VA.
6. HALIFAX COUNTY, VA.
7. HAGERS MOUNTAIN, N. C.
8. CORBETT DEPOSIT, N. C.
9. YOUNGS MOUNTAIN, N. C.
10. CLUBB MOUNTAIN, N. C.
11. REESE MOUNTAIN, N. C.
12. CROWDERS MOUNTAIN, N. C.
13. THE PINNACLE, N. C.
14. WILL KNOX DEPOSIT, N. C.
15. HENRY KNOB, S. C.
16. JEFFERSON MOUNTAIN, S. C.
17. WORTH MOUNTAIN, S. C.
18. LITTLE MOUNTAIN, S. C.
19. GRAVES MOUNTAIN, GA.
20. BURNSVILLE–SWANNANOA BELT, N. C.
21. HABERSHAM, AND RABUN, COUNTIES, GA
22. TOWNS, UNION, AND FANNIN, COUNTIES, GA.
23. CHEROKEE, PICKENS, GILMER, AND DAWSON COUNTIES, GA.
24. TALBOT, UPSON, AND HARRIS, COUNTIES, GA.
25. CLIFFSIDE–ELKIN BELT, N. C.
26. WARNE–SYLVA BELT, N. C.
27. SOUTH CAROLINA BELT
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30. BOWLINGS MOUNTAIN, N. C.
31. HILLSBORO, N. C.
32. SNOW CAMP, N. C.
33. STALEY, N. C.
34. BOLES (STROM) MOUNTAIN, S. C.
35. GLENDON, N. C.
36. HEMP (ROBBINS), N. C.
37. BREWER DEPOSIT, S. C.

Modified from pl.1, U.S. Geol. Survey Prof. Paper 248. Geologic features compiled from following sources: Geologic map of the United States, 1932; Tectonic map of the United States, 1944; Geologic map of Georgia, 1939; South Carolina Research, Planning and Development Board Bull. 19

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MAP OF THE SOUTHEASTERN UNITED STATES SHOWING GENERAL GEOLOGIC FEATURES, DISTRIBUTION OF PRINCIPAL KYANITE SILLIMANITE, AND ANDALUSITE DEPOSITS, AND PRINCIPAL PEGMATITE OCCURRENCES

Scale 1:2 500 000

50 0 50 100 150 200 Miles

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FROM PROFESSIONAL PAPER 336 PLATE 7

PLATE 2
(PERRY, 1963)

Map compiled by U. S. Geological Survey from aerial photographs

INTERIOR—GEOLOGICAL SURVEY, WASHINGTON, D. C.
MR 7607

Geology mapped by D. B. Potter, 1951–52

GEOLOGIC MAP OF THE CROWDERS MOUNTAIN-HENRY KNOB AREA, CLEVELAND AND GASTON COUNTIES NORTH CAROLINA, AND YORK COUNTY, SOUTH CAROLINA

Scale 1:24 000

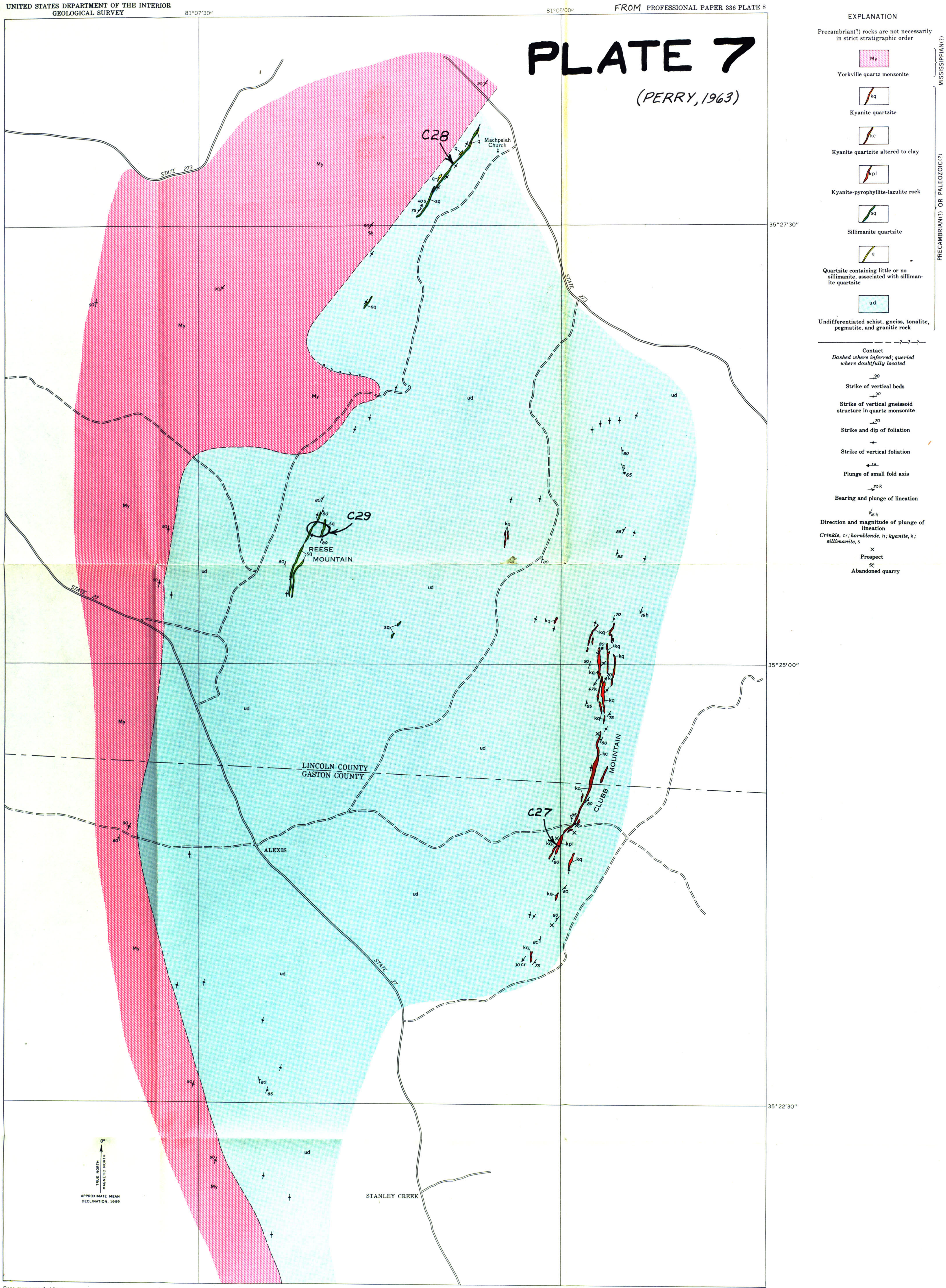
1 0 1 2 Miles

UNITED STATES DEPARTMENT OF THE INTERIOR
GEOLOGICAL SURVEY

FROM PROFESSIONAL PAPER 336 PLATE 8

PLATE 7

(PERRY, 1963)



Base map compiled from aerial photographs

M R-7607 INTERIOR—GEOLOGICAL SURVEY, WASHINGTON, D. C.

Geology by D. B. Potter, April 1952

GEOLOGIC MAP OF THE REESE MOUNTAIN-CLUBB MOUNTAIN AREA, LINCOLN AND GASTON COUNTIES, NORTH CAROLINA

Scale 1:24,000

0 ½ 1 Mile