N70-11823
NASA CR-106967

Final Report

on

Stability of Silicate Minerals

February, 1969

Sponsored by:

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

NASA Grant No. NGR 44-007-006
SMU Grant No. 83-11

Prepared by:

Michael J. Holdaway
Department of Geological Sciences

SOUTHERN METHODIST UNIVERSITY

DALLAS, TEXAS 75222

Final Report

on

Stability of Silicate Minerals

February, 1969

Period: February 1, 1966
to June 1, 1968

Prepared by: Michael J. Holdaway

Sponsored by:

NATIONAL AERONAUTICS AND
SPACE ADMINISTRATION

Grant No. NGR 44-007-006

Approved by:

Michael J. Holdaway

Michael J. Holdaway
Principal Investigator

Department of Geological Sciences
Southern Methodist University
Dallas, Texas 75222

Two projects concerning silicate mineral stability have been undertaken with the aid of NASA support: (1) Stability of epidote, a calcium iron aluminum silicate as a function of pressure, temperature, and oxygen fugacity; and, (2) stability of aluminum silicates. Each of these projects has been the subject of a paper by the principal investigator at a national meeting. Copies are attached in the Appendices. The major findings of each project are summarized below.

EPIDOTE STABILITY. Epidote breaks down under oxidizing conditions along a pressure-temperature curve which has the formula

$$T = 528 + 60P - 1.5P^2 \ (T\ ^{o}C,\ Pkb).$$

The effect of progressively more reducing conditions on epidote stability may be summarized as follows: (1) epidote decomposition proceeds at a lower temperature for a given pressure; (2) equilibrium epidote becomes more aluminous; (3) garnet in the reaction products becomes more aluminous and contains more ferrous iron; and, (4) the iron oxide mineral in the reaction products changes from hematite to magnetite to hercinite, and eventually corundum occurs instead of an iron-bearing mineral. Anorthite is always a reaction product, and quartz is a reaction product under oxidizing conditions.

Coexisting epidote and grossularite-andradite garnet compositions have been worked out experimentally. $Fe^{+3}/Fe^{+3}+Al$ in garnet is approximately twice as high as the comparable ratio in epidote, but as the composition becomes more aluminous garnets are relatively less enriched in iron relative to epidote.

ALUMINUM SILICATE STABILITY. Significant success on this system was achieved only with seeding techniques on natural andalusite, sillimanite, and kyanite. All studies were below 5 kb. The kyanite-andalusite stability curve is a nearly straight line through the points 185°C, 0 kb and 635°C, 5.5 kb, while the andalusite-sillimantie stability curve is a nearly straight line passing through 635°C, 5.5 kb and 890°C, 0 kb. This indicates a slightly larger stability field for andalusite than previously suspected.

No affect has been observed from small variations of Fe_2O_3 content or grain size of minerals.

APPENDIX I

M. J. Holdaway
Department of Geological Sciences
Southern Methodist University
Dallas, Texas

American Geophysical Union
Volcanology, Geochemistry,
and Petrology, 1967

Stability of Epidote

The decomposition of epidote has been investigated as a function of oxygen fugacity. The reaction products include grandite, anorthite, and one of the following: Hematite-quartz, magnetite-quartz, magnetite or magnetite-hercynite. Two methods of study gave identical results. (1) A mixture of equal parts of epidote and experimentally produced breakdown products was used as starting material. Comparison of relative X-ray peak heights before and after each run demonstrated the direction of reaction. (2) Materials were prepared as above, except that minerals of one side of the reaction were seeded with 3 to 5% of minerals of the other side, and the reaction direction was detected from microscopic study of the seeds. In a magnetite-hematite buffer epidote breaks down according to the reaction:

4 Epidote ($Cz_{65}Ps_{35}$) = 1.56 Grandite ($Gr_{35}And_{64.5}Alm_{0.5}$) +

3.35 Anorthite - .98 Hematite (or .65 Magnetite) + .62 Quartz +

.01 Oxygen + 2 Water

Between 1 and 4 kb the equilibrium curve is given by the relation $T = 528 + 60P - 1.5P^2 \pm 10$ (T ^{o}C, P kb). Experiments with progressively more reducing buffers produce the following changes in the reaction: (1) epidote decomposition proceeds at lower temperatures for a given pressure; (2) equilibrium epidote becomes more aluminous; (3) grandite becomes more aluminous and its almandine content increases; (4) the iron-bearing minerals change from hematite to magnetite to magnetite-hercynite. In the presence of excess quartz and reducing buffers the iron oxide phase is completely converted to hedenbergite which further reduces the equilibrium temperature. In nature epidote may become unstable either through increase in temperature or presence of reducing conditions. The specific process involved may be deduced from the composition of epidote and/or its breakdown products, especially garnet.

Geological Society of America
Meetings in Mexico City, 1968

Stability of Andalusite

There have been few studies to date involving the stability relations of aluminum silicates at pressures below five Kb. For the past two years I have been working on this system with cold-seal pressure vessels and water as the pressure medium. The project is nearly complete.

Starting materials (slide 1) were andalusite from Brazil, kyanite from North Carolina, sillimanite from Williamstown, Australia (I) and from Jefferson County, Colorado (II). Sillimanite I has a high fibrolite content. Note that the maximum ferric iron content is .40%. The sillimanites probably contained a little water, and the Colorado sillimanite contained a few per cent of quartz in the sample.

The unit cell parameters agree well with those given by Skinner, Clark, and Appleman (slide 2) except that the c dimension of the andalusite is a bit lower than their values (5.557).

Four hydrothermal techniques (slide 3) have been attempted. In the x-ray approach 95% of one mineral and 5% of the other were mixed and reaction direction was attempted by measurement of relative changes of peak heights. It was not possible to be sure of reaction direction in runs of 60 days duration.

In the crystal growth method a ground crystal of andalusite was immersed in kyanite for 30 day experiments. Reaction was detected from weight change in the crystal. The only conditions for which this method gave a progressive series from weight loss to weight gain were at 2.4Kb on the kyanite-andalusite reaction. Until the method is better understood these results cannot be considered reliable.

The most satisfactory results were gained from runs containing quartz and one aluminum silicate and 1% seeds of the other. After each run of 30 or 60 days the seeds were examined with the petrographic microscope for signs of growth or corrosion. Andalusite growth or corrosion is relatively easily detected because of the irregular shape of grains. On the other hand kyanite and sillimanite changes are considerably harder to detect. Recrystallization never occurred; that is, in the andalusite field a run with mostly andalusite and seeds of kyanite showed no andalusite recrystallization whereas a run with andalusite seeds at the same conditions showed thin rims and crystal faces.

A few runs on the andalusite-sillimanite boundary were attempted with equal amounts of the two in a muscovite granite melt. It was hoped that the melt would increase reaction rates. It was very difficult, after 30 days, to detect the reaction direction.

Let us now look at the crystal results (slide 4). At 2.4Kb the temperature of no weight change is 394°. These data and the data of seeded runs are plotted in slide 5. The data of Newton and Richardson and others on the extension of the kyanite-andalusite boundary are shown as a field of reversal, a line drawn to enclose the points of reversibility closest to the equilibrium. The curve shown is consistent with slope calculations made at 100° intervals, the previous data on the extension, and the present data from seeded runs. The equilibrium at 2.4Kb from the crystal runs is a minimum of 10° above the curve. The fact that the calculated slope is consistent with experimental data for the reaction suggests that the measured entropies of kyanite and andalusite are accurate.

The curves have been drawn in such a way as to be as consistent as possible with all recent data (slide 6). The procedure is as follows: plot all data which demonstrates reversal and involves accurate pressure measurements. Next the slopes of all curves are calculated. The entropy of sillimanite is inconsistent with all experimental work on sillimanite stability and would produce slopes too flat. I suggest that Al-Si disorder is contributing to sillimanite entropy. If we assume a model of .6 entropy units disorder in sillimanite at 600° and an additional .15 entropy units per hundred degrees, slope calculations fit the available data. This corresponds to 20% disorder at 600° and 70% disorder at 1300°. Slide 7 shows the results of such an analysis. The sillimanite-kyanite curve is essentially that of Richardson, Bell and Gilbert.

The next slide (slide 8) gives equations for the stability curves. These are given in such a way that the initial slope and the intercept on the temperature axis may be read directly from the equation. The derivative of the equation gives the slope consistent with the above model.

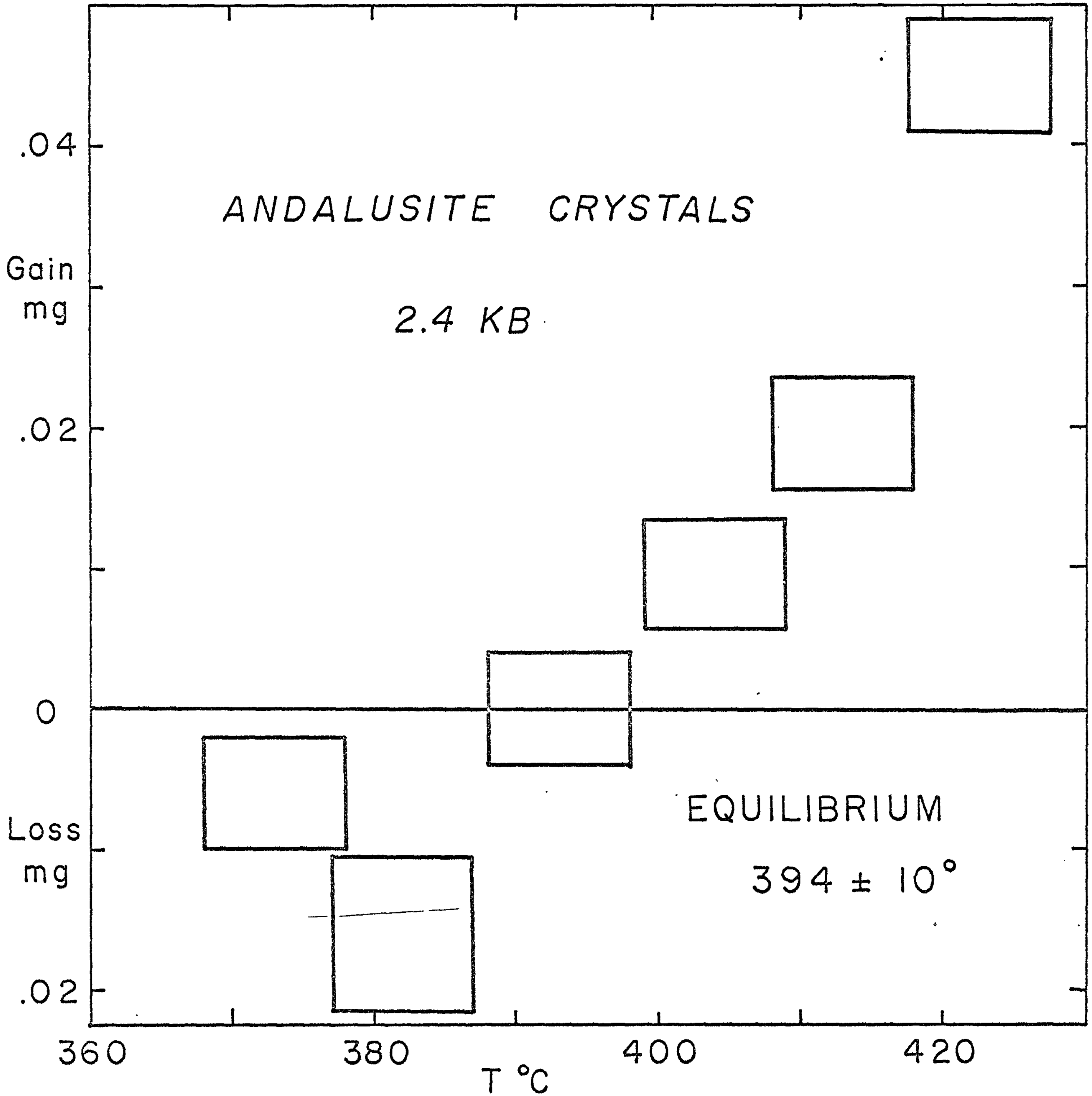
I now want to consider some of the geological implications of these results (slide 9). Note the positions of Kerrick's pyrophyllite curve and the granite minimum melting curve relative to the andalusite field. To emphasize some of the important implications (slide 10), (1) the minimum temperature for sillimanite stability is about 635° $\pm$ 20°, (2) the maximum pressure of andalusite stability is 5.5Kb indicating that Barrovian metamorphism occurs above this pressure, (3) kyanite may form from pyrophyllite at 3 Kb or from pyrophyllite-corundum at about 2.5Kb, (4) andalusite granites are consistent with the experimental results; sillimanite granites would generally be drier granites or result from the earliest stages of granite crystallization, (5) sillimanite should be absent from contact aureoles which were produced by wet true granites.

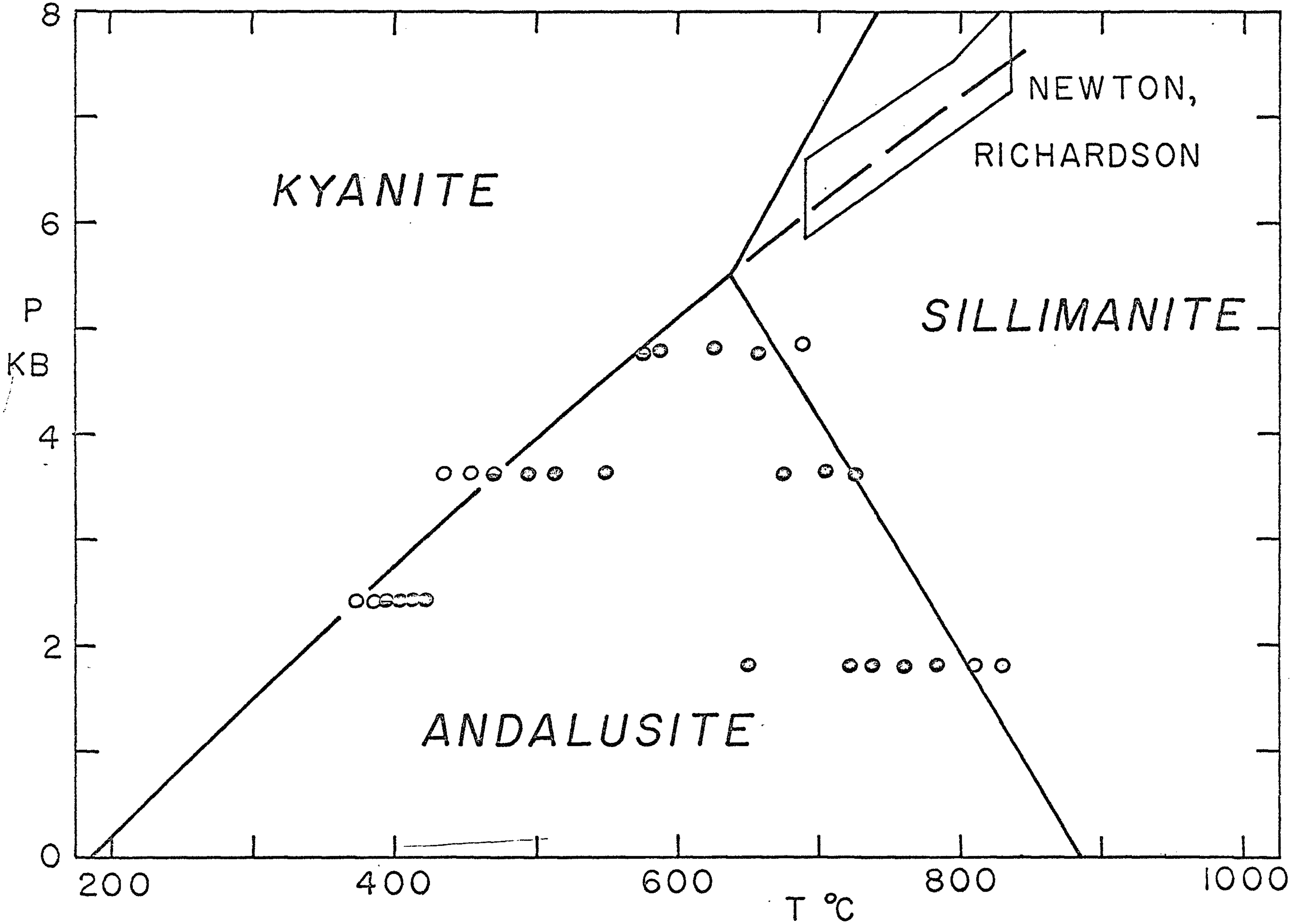
M. J. Holdaway

	ANDALUSITE	KYANITE	SILL. I	SILL. II
SiO_2	37.1	36.7	38.3	43.0
Al_2O_3	62.1	62.0	58.9	54.5
Fe_2O_3	0.38	0.40	0.39	0.15
MnO	-	-	-	0.01
MgO	0.04	0.02	0.01	0.06
TOTAL	99.6	99.1	97.6	97.7

	ANDALUSITE	KYANITE	SILL. I	SILL. II
a	7.795	7.121	7.483	7.484
b	7.901	7.851	7.671	7.672
c	5.551	5.588	5.771	5.769
V	341.9	294.2	331.1	331.3
α		90.13		
β		101.10		
γ		105.99		

METHOD	SUCCESS
1. X-RAY	NONE
2. CRYSTAL GROWTH	AT LOW P, T
3. SEEDED EXPERIMENTS	GOOD
4. MUSCOVITE GRANITE MELT	NOT PROMISING


ANDALUSITE CRYSTALS
2.4 KB
Gain mg
Loss mg
.04
.02
0
.02
EQUILIBRIUM
394 ± 10°
360
380
400
420
T °C



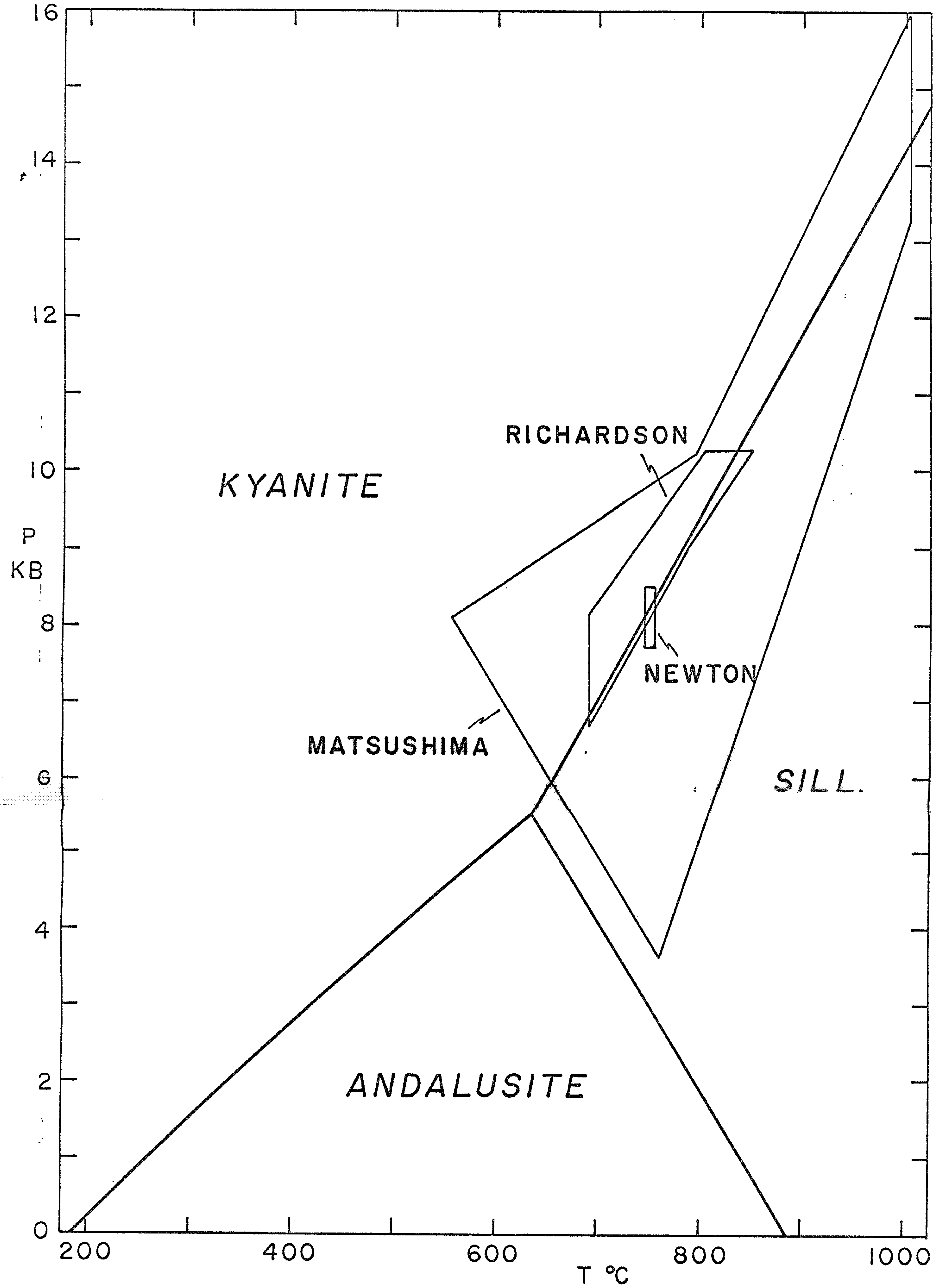
NEWTON,
RICHARDSON
KYANITE
SILLIMANITE
ANDALUSITE
P
KB
T °C
8
6
4
2
0
200
400
600
800
1000

PROCEDURE FOR DRAWING CURVES

1. USE DATA WITH GOOD P CALIBRATION AND REACTION REVERSALS

2. SLOPE CALCULATED AT 100° INTERVALS

3. SILLIMANITE ENTROPY ADJUSTED TO FIT Al-Si DISORDER MODEL



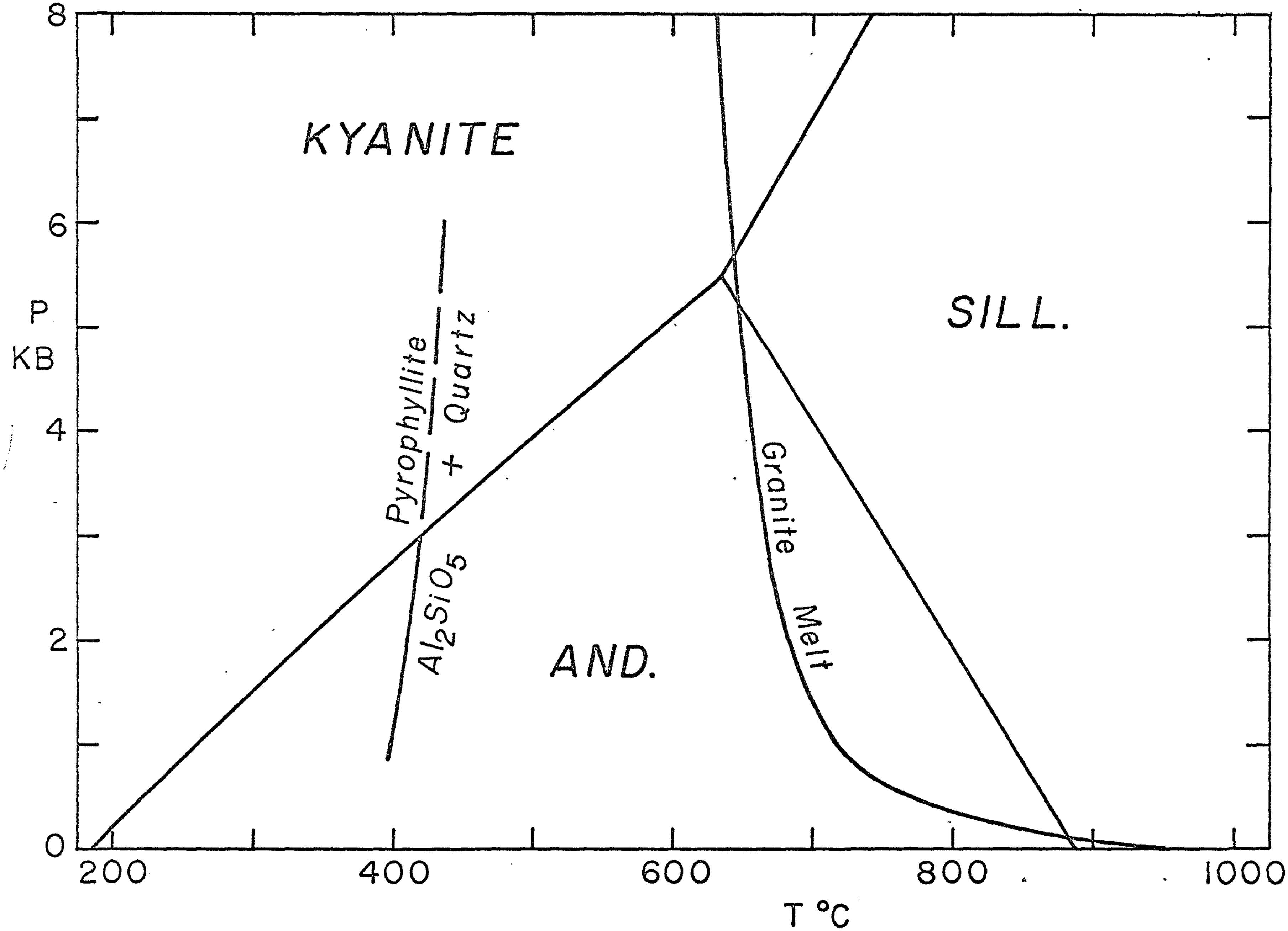
16
14
12
10
8
6
4
2
0
P
KB
KYANITE
RICHARDSON
NEWTON
MATSUSHIMA
SILL.
ANDALUSITE
200
400
600
800
1000
T °C

EQUATIONS FOR CURVES

K - A $P = 13.37\,(T-185) - .0027\,(T-185)^2$

A - S $P = -22.25\,(T-887) - .002\,(T-887)^2$

K - S $P = 22.55\,(T-400) + .0026\,(T-400)^2$


KYANITE
SILL.
AND.
Pyrophyllite + Quartz
Al2SiO5
Granite Melt
P KB
T °C
0
2
4
6
8
200
400
600
800
1000

GEOLOGICAL IMPLICATIONS

1. MINUMUM TEMPERATURE FOR SILLIMANITE = 635°

2. MAXIMUM PRESSURE FOR ANDALUSITE = 5.5 KB

3. KYANITE MAY FORM AT PRESSURE AS LOW AS 2.5 KB

4. ANDALUSITE GRANITES ARE EXPLAINED

5. CONTACT AUREOLES WITH NO SILLIMANITE ARE POSSIBLE