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AN EXPERIMENTAL STUDY BEARING ON THE ABSENCE OF LEUCITE IN PLUTONIC ROCKS[1]

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ABSTRACT

An invariant point characterized by the coexistence of potash feldspar, leucite, hexagonal kalsilite, liquid and vapor has been located experimentally at 8.4±.2 Kb and 750 ±10° C. in the system $KAlSiO_4$-SiO_2-H_2O. The univariant P-T curve for the reaction leucite$\leftrightharpoons$hexagonal kalsilite+potash feldspar intersects the temperature axis at approximately 490° C. and has a slope of approximately 30° C./Kb, with leucite stable on the high temperature side of the curve. Preliminary studies in the system $NaAlSiO_4$-$KAlSiO_4$-SiO_2-H_2O indicate that the decomposition temperature of soda-bearing leucite solid solutions is somewhat greater than for "pure" leucite.

It is suggested that the reaction leucite$\leftrightharpoons$hexagonal kalsilite+potash feldspar, and compositional limitations will explain the absence of leucite in plutonic alkaline rocks.

INTRODUCTION

Goranson (1938) reported that the incongruent melting of orthoclase[5] ($KAlSi_3O_8$) was eliminated at 2.6 Kb and 950° C. in the presence of sufficient water to saturate the silicate melt. The four-phase univariant reaction in the ternary system $KAlSiO_4$-SiO_2-H_2O involving orthoclase (Or), leucite (Lc), liquid (L) and vapor (V) changes from $Or+V \leftrightharpoons Lc+L$ at pressures below 2.6 Kb, to $Or+Lc+V \leftrightharpoons L$ at pressures above 2.6 Kb, generating a singular point at this pressure. Thus at the lower pressures the univariant liquid lies in the triangle Or-SiO_2-H_2O, and at the higher pressures in the triangle Or-Lc-H_2O. At 2.6 Kb the univariant liquid lies on the Or-V join. A second univariant curve extends to pressures greater than 2.6 Kb governing the degenerate (in a ternary system) reaction $Or+V \leftrightharpoons L$, the congruent melting of orthoclase in the presence of an aqueous vapor phase. The curve shown by Goranson (1938, p. 89) extending to pressures greater than 2.6 Kb probably represents the reaction $Or+V \leftrightharpoons L$ and not the reaction $Or+Lc+V \leftrightharpoons L$. The high temperature curve shown by Goranson (1938, p. 89) at pressures below 2.6 Kb

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[5] The term orthoclase will be used in this paper for the phase having the composition $KAlSi_3O_8$; it may be high sanidine, low sanidine, orthoclase or intermediate between them.

is univariant by composition restriction in the ternary system, since Goranson limited his study to compositions on the $KAlSi_3O_8$-H_2O join.

Preliminary studies on the melting relations in the system $KAlSiO_4$-SiO_2-H_2O indicated that the reaction leucite $\overset{H_2O}{\rightleftharpoons}$ hexagonal kalsilite+orthoclase studied by Seki and Kennedy (1964) might take place at a considerably lower pressure (for a given temperature) than suggested by their results. If this is the case then the intersection of this curve ($Lc \rightleftharpoons Ks+Or$) with univariant curves involving Lc, Ks, L and V and Lc, Or, L, V in the ternary system will define an invariant point where the five phases Ks, Lc, Or, L and V coexist. It is the purpose of this paper to demonstrate experimentally the existence and nature of this invariant point.

EXPERIMENTAL METHOD

The bulk of the experiments were made in cold-seal pressure vessels (Tuttle, 1949; Luth and Tuttle, 1963). A number of runs were made in internally heated pressure vessels modified after Yoder (1950). Starting materials were gels prepared by the method described by Luth and Ingamells (1965) and crystalline materials prepared from the gels. Temperature was measured by chromel-alumel thermocouples whose e.m.f. was indicated by a Honeywell-Brown circular scale indicating potentiometer. The measuring system was calibrated at the melting point of NaCl (801° C.) and gold (1063° C.). Pressure was measured with a manganin wire coil whose resistance change was indicated on a Foxboro Dynalog indicating recorder. The temperatures and pressures are believed to be reproducible to $\pm 5°$ C. and ± 0.2 Kb. Weighed amounts of gel, or crystals, and water were sealed in gold or platinum capsules and subjected to the desired pressure and temperature. Pressure on the capsules (argon) was transmitted to the condensed phases by the vapor phase within the sealed capsule. In the case of the reaction $Lc \rightleftharpoons Ks+Or$ equilibrium was established by starting with crystalline Lc and crystalline Ks+Or in separate capsules. The definitive runs for the other univariant reactions used crystalline assemblages stable on the low temperature side of the curve.

Phases were identified by means of the petrographic microscope and x-ray powder diffraction techniques. Phases encountered in this study include glass, hexagonal kalsilite, leucite, potash feldspar and vapor. Least squares refinement of powder diffraction data (Luth and Tuttle, 1966) gave the following values for potash feldspar produced by the decomposition of leucite: $a=8.578\pm.006$; $b=13.042\pm.003$; $c=7.184\pm.002$ Å; $\alpha=90.00°$; $\beta=115.91\pm.02°$; $\gamma=90.00°$; unit cell volume 722.97 $Å^3$.

RESULTS

The univariant curve for the reaction Lc⇆Or+Ks was found to be located at lower pressures than given by Seki and Kennedy (1964), both curves are presented in Fig. 1. We believe the disagreement is due to the non-uniform distribution of pressure in the "simple squeezer" type of apparatus used by Seki and Kennedy. In locating the position of the curve for this study starting materials consisted of crystalline leucite and kalsilite+orthoclase in leucite proportions sealed in separate capsules and run simultaneously. Thus the curve was "reversed" in the conventional fashion.

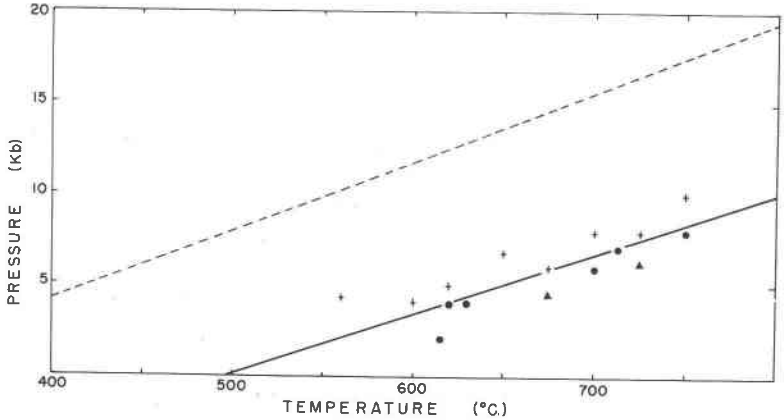

FIG. 1. The univariant curve leucite⇆orthoclase+hexagonal kalsilite (— — — — Seki and Kennedy (1964), ——— present study, i.e., +Or+Ks, ●Lc, ▲ reversal).

The invariant point involving Ks, Lc, Or, L and V is at 750±10° C. and 8.4±0.2 Kb. If the invariant liquid lies within the triangle Ks-Lc-V then the five univariant curves radiating from the invariant point are governed by the reactions:

(Lc)[1] Or + Ks + V = L (V) Lc = Or + Ks (Ks) Lc + V = Or + L
(Or) Lc+Ks+V=L (L)Lc=Or+Ks

as in Fig. 2a. If the invariant liquid lies within the triangle Lc-Or-V then the five univariant curves radiating from the invariant point are governed by the reactions:

(Lc) Or + Ks + V = L (V) Lc = Ks + Or (Or) Lc + V = Ks + L
(Ks) Or + Lc + V = L (L) Lc = Ks + Or

as in Fig. 2b.

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[1] Parentheses indicate the phase that is absent from the reaction.

We have previously observed that Goranson (1938) indicated that the univariant reaction involving Lc, Or, L, and V at pressures above 2.6 Kb was $Or+Lc+V \leftrightarrows L$. If the case illustrated by Fig. 2a is correct this univariant reaction changes from $Or+Lc+V \leftrightarrows L$ to $Lc+V \leftrightarrows Or+L$ at some pressure between 2.6 and 8.4 Kb, thereby generating a second singular point,[1] as shown schematically in Fig. 2c. Thus the univariant curve where the four phases Lc, Or, L, and V coexist would have two singular points. If, on the other hand, the case illustrated by Fig. 2b is correct the univariant reaction $Or+Lc+V \leftrightarrows L$ persists to the invariant point. In this case, however, a singular point on the univariant curve where Ks, Lc, L and V coexist is generated where the reaction changes from $Ks+Lc+V \leftrightarrows L$ at lower pressures to $Lc+V \leftrightarrows Ks+L$ at higher pressures, as in Fig. 2d. These effects can be visualized most simply by polybaric-polythermal diagrams illustrating the change in composition of the univariant liquids along the various postulated P-T curves. Schematic diagrams of this type are given in Fig. 2e for the case when the invariant liquid is within the triangle Ks-Lc-V (2a) and in Fig. 2f for the case when the invariant liquid is within the Lc-Or-V triangle (2b). The singular points are generated where the univariant liquids cross the pertinent joins, Lc-V and Or-V.

Experimental studies (Table 1) indicate that the composition of the liquid lies in the triangle Ks-Lc-V, hence the sequence of curves given in Figs. 2a, c and e are applicable. The data are also presented in Fig. 3, which suggests that the second singular point on the Or-Lc-V-L curve is at approximately 5.0±0.5 Kb and 840°±10° C. At pressures above this singular point and below the invariant point at 8.4 Kb leucite melts incongruently to orthoclase and liquid in the presence of an aqueous vapor phase; in the same sense that orthoclase melts incongruently to leucite and liquid in the presence of a vapor phase at pressures below 2.6 Kb.

Spengler (1965) has also studied the melting relations of orthoclase and leucite in the presence of an aqueous vapor phase. He gives the following values for the respective melting curves:

High—leucite		High—sanidine	
4.0 Kb	895± 5° C.	3.0 Kb	905±15° C.
5.0 Kb	850±10° C.	4.0 Kb	880±10° C.
6.5 Kb	785±20° C.	5.0 Kb	855± 5° C.
		6.5 Kb	845±10° C.

The curve where Or-L-V coexist as determined by Spengler does not agree well with an extrapolation of Goranson's (1938) data, or Goranson's

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[1] A point in P and T where a univariant curve for a ternary reaction $A+B+C \rightleftharpoons L$ crosses a binary join and changes to $A+B \rightleftharpoons C+L$, generating a binary univariant curve $A+B \rightleftharpoons L$.

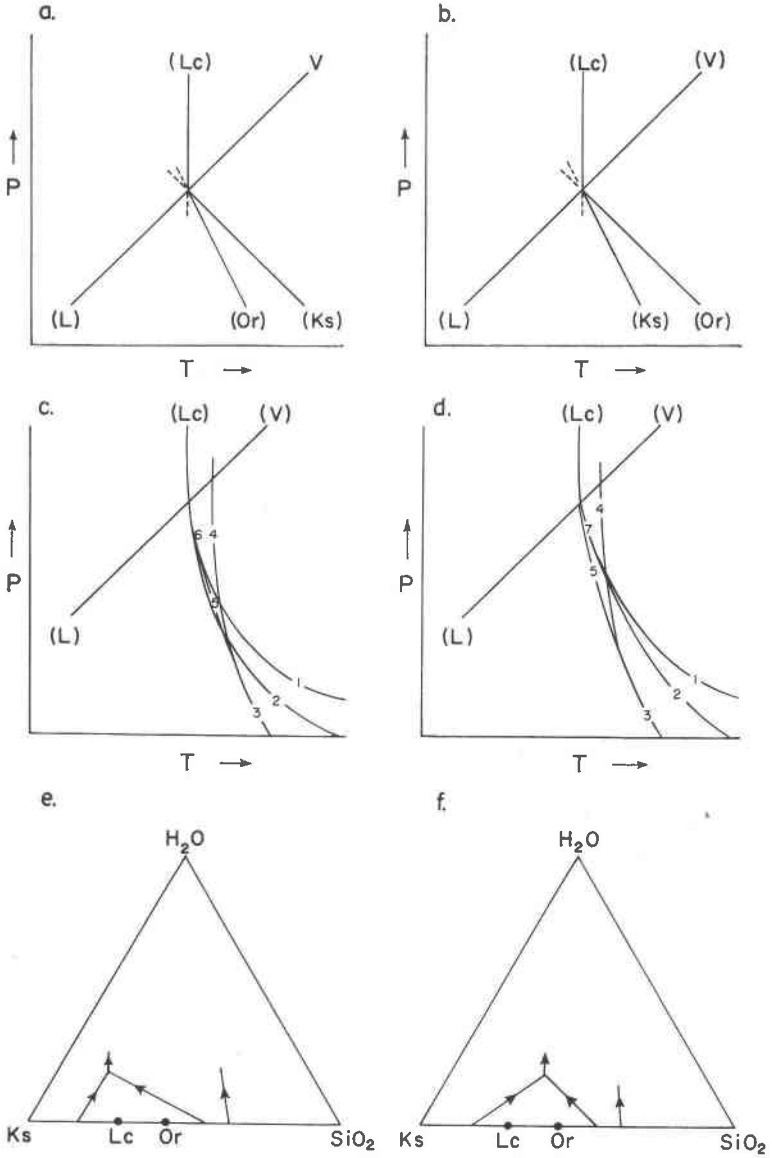

FIG. 2. a. The invariant point where orthoclase, leucite, hexagonal kalsilite, liquid and vapor coexist if the invariant liquid is in the triangle kalsilite-leucite-H_2O. See text for the univariant reactions.

b. The invariant point if the invariant liquid is in the triangle leucite-orthoclase-H_2O. See text for the univariant reactions.

(Continued on next page)

determination at 3.0 Kb (945 ± 10° C.). This disagreement may be due to differences in the experimental technique. Spenglers' data points are also given in Fig. 3 together with Goranson's. The curves given in Fig. 3 represent an attempt to fit the curves to the data of Spengler and Goranson at low pressures. A series of isobaric diagrams at 2, 4, 6, 8 and 10 Kb are given in Fig. 4 illustrating in schematic fashion the probable phase relations as a function of pressure.

EFFECT OF Na_2O ON THE STABILITY OF LEUCITE

Several runs were made using two compositions (90% Lc+10% analcite and 80% Lc+20% analcite) obtained from R. F. Fudali. The purpose was to establish whether the Lc=Or+Ks breakdown curve would be displaced up or down at the same temperature by the introduction of soda. Runs below the curve showed Or+Ks in the products, whereas runs above the curve continued to show leucite to be unstable, indicating that with solid solution of the analcite molecule in leucite the decomposition takes place at a lower pressure for a given temperature.

DISCUSSION

Leucite is common in volcanic rocks and virutally unknown in plutonic rocks. Why the difference? First of all the composition of plutonic alka-

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c. The invariant point and the two singular points for the case where the invariant liquid is in the triangle kalsilite-leucite-H_2O. The univariant reactions are

(Ks) 1. Lc + V = L (Or) 2. Lc + Ks + V = L
3. Or + V = Lc + L
4. Or + V = L
5. Lc + Or + V = L
6. Lc + V = Or + L

d. The invariant point and the two singular points for the case where the invariant liquid is in the triangle leucite-orthoclase-H_2O. The univariant reactions are:

(Ks) 3. Or + V = Lc + L (Or) 1. Lc + V = L
4. Or + V = L 2. Lc + Ks + V = L
5. Or + Lc + V = L 7. Lc + V = Ks + L

e. Polythermal-polybaric composition diagram illustrating, in schematic fashion, the change in composition of the univariant liquids along the univariant P-T curves (Or), (Ks), and (Lc) where the invariant liquid is in the triangle Ks-Lc-H_2O.

f. Polythermal-polybaric composition diagram illustrating, in schematic fashion, the change in composition of the univariant P-T curves (Or), (Ks), and (Lc) where the invariant liquid is in the triangle Lc-Or-H_2O.

Table I. Results of Quenching Experiments in the System $KAlSiO_4$-SiO_2-H_2O. 10% H_2O Added to All Anhydrous Compositions

(Ks = Hex. kalsilite, Lc = leucite, Or = orthoclase, Gl = glass, V = vapor, Tr = trace amounts. All Starting material completely crystalline except ** = gel starting material, * = Or + Ks starting material)

Run	Anhydrous Composition $KAlSiO_4$-SiO_2	P. (Kb)	T. (°C.)	Time (hrs)	Results
101**	72.5—27.5	10.0	750	2	Or+Ks+V (Tr. Gl)
110	72.5—27.5	8.0	750	1	Lc+V
116	75.0—25.0	10.0	750	24	Or+Ks+V
128	72.5—27.5	8.0	700	26	Or+Ks+V
130	72.5—27.5	8.0	725	8	Or+Ks+V
132	72.5—27.5	6.0	700	10	Lc+V
134	72.5—27.5	6.0	675	6	Or+Ks+V
136	72.5—27.5	2.1	615	41	Lc+V
138	72.5—27.5	4.0	630	4	Lc+V
144	72.5—27.5	4.0	628	11	Lc+V
146	72.5—27.5	4.1	600	18	Ks+Or+V
148	72.5—27.5	4.25	563	18	Ks+Or+V
150	72.5—27.5	7.15	713	6	Lc+V
110	72.5—27.5	8.0	750	1	Lc+V
181	72.5—27.5	6.15	750	8	Lc+V
140	72.5—27.5	7.65	765	49	Gl+V
173	72.5—27.5	5.4	775	8	Lc+V
185	72.5—27.5	8.6	775	7	Gl+V
178	72.5—27.5	5.8	800	7	Lc+V (Tr. Gl)
120	72.5—27.5	5.0	800	40.5	Lc+V
168	72.5—27.5	4.8	825	8	Lc+V (Tr. Gl)
163	72.5—27.5	4.9	850	8	Lc+Gl+V
125	72.5—27.5	5.0	1000	50	Gl+V
143	75.0—25.0	7.65	765	49	Or+Gl+V
182	75.0—25.0	6.15	750	8	Ks+Lc+V
172	75.0—25.0	5.4	775	8	Ks+Lc+V (Tr. Gl)
121	75.0—25.0	5.0	800	40.5	Ks+Lc+V (Tr. Or)
179	75.0—25.0	5.8	800	7	Lc+Gl+V
169	75.0—25.0	4.8	825	8	Lc+Gl+V
160	75.0—25.0	4.9	850	8	Lc+Gl+V
126	75.0—25.0	5.0	1000	50	Gl+V
174	57.0—43.0	5.4	775	8	Or+V
118	57.0—43.0	5.0	800	40.5	Or+V
167	57.0—43.0	4.8	825	8	Or+V
162	57.0—43.0	4.9	850	8	Or+V (Tr. Gl)
123	57.0—43.0	5.0	1000	50	Gl+V
183	68.0—32.0	6.15	750	8	Or+Lc+V
142	68.0—32.0	7.65	765	49	Or+Lc+V
171	68.0—32.0	5.4	775	8	Or+Lc+V
119	68.0—32.0	5.0	800	40.5	Or+Lc+V
180	68.0—32.0	5.8	800	7	Lc+V (Tr. Or+Gl)
161	68.0—32.0	4.9	850	8	Lc+Gl+V (Tr. Or)
124	68.0—32.0	5.0	1000	50	Gl+V
101**	72.5—27.5	10.0	750	2	Or+Ks+V (Tr. Gl)
175*	72.5—27.5	9.7	750	2	Or+Ks+V (Tr. Gl)
176*	75.0—25.0	9.7	750	2	Or+Ks+V (Tr. Gl)
177*	68.0—32.0	9.7	750	2	Or+Ks+V (Tr. Gl)

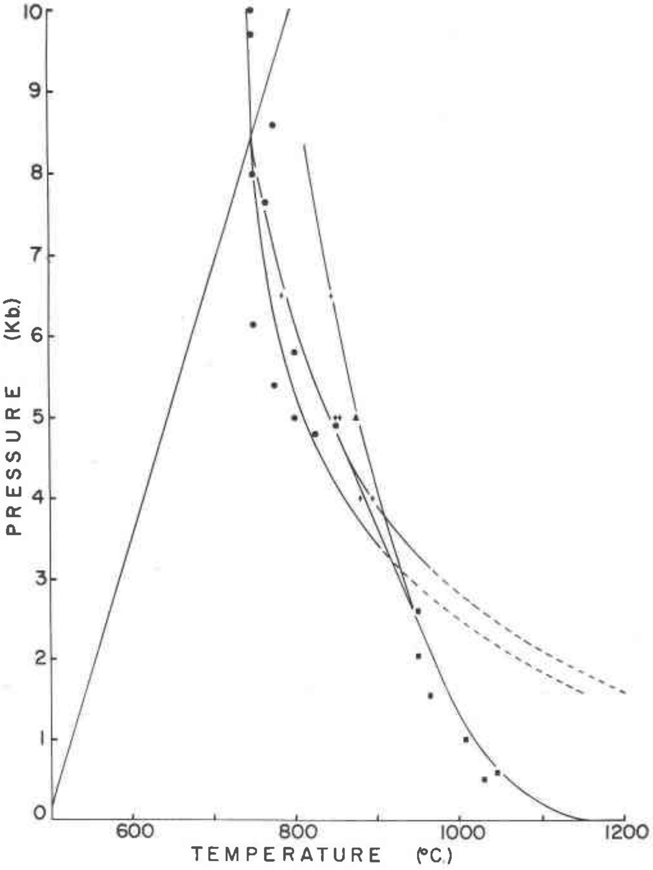

FIG. 3. Experimental data on the pressure-temperature melting relations in the system $KAlSiO_4$-SiO_2-H_2O. (● present study, +Spengler (1965), ■ Goranson (1938), ▲ Yoder, Stewart and Smith (1957).)

line rocks does not often fall in the appropriate range to permit leucite to be in a stable assemblage and second, the breakdown of leucite to orthoclase and kalsilite at elevated pressure as reported by Seki and Kennedy (1964) restricts the PT stability field of leucite to the area under the curve for the reaction Lc⇆Or+Ks. Addition of water to the system further restricts the stability to the area under the melting curve *and* the breakdown curve. Also, the addition of soda to the system raises the temperature of the breakdown reaction and lowers the temperature, at a given pressure, at which melting will take place; thereby restricting the P-T stability field of leucite still further. In plutonic rocks the reaction Lc⇆Or+Ks will eliminate leucite as a stable mineral.

A study of assemblages in the leucocratic plutonic alkaline rocks indicates that the join from orthoclase to nepheline cuts off leucite from albite (plagioclase) so that the bulk of the rocks have compositions which preclude leucite as a stable phase. On the other hand at low pressures the primary field of leucite at the liquidus overlaps the region orthoclase-nepheline-albite and because of this leucite is common in the alkaline volcanic rocks. The bulk of these rocks will lose their leucite during cooling by the reaction described by Fudali (1963) before they cool enough to reach the leucite breakdown curve described above.

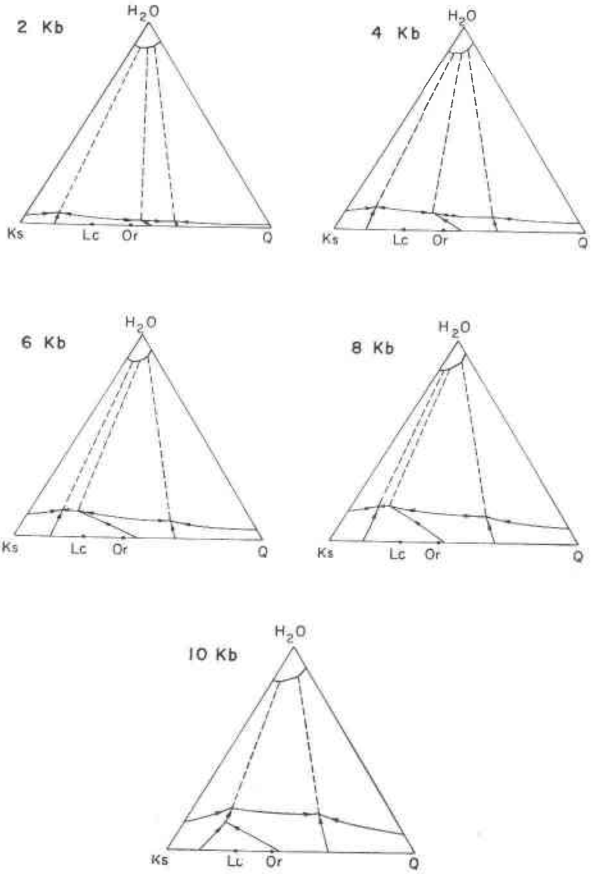

FIG. 4. Isobaric-polythermal diagrams illustrating, in schematic fashion, the phase relations in the system $KAlSiO_4$-SiO_2-H_2O at various pressures.

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