THE BREAKDOWN OF POTASSIUM FELDSPAR, $KAlSi_3O_8$ AT HIGH TEMPERATURES AND HIGH PRESSURES[1]

YÔTÂRO SEKI[2] AND GEORGE C. KENNEDY, *Institute of Geophysics and Planetary Physics, University of California, Los Angeles, California.*

ABSTRACT

Experimental studies of synthetic pure sanidine and natural orthoclase, at high temperatures and pressures, show that potassium feldspar is transformed into a hexagonal phase $KAlSi_3O_8 \cdot H_2O$ at high water pressures by the following chemical reaction:

$$KAlSi_3O_8 + H_2O \rightleftharpoons KAlSi_3O_8 \cdot H_2O$$

Under dry conditions, however, potassium feldspar is apparently stable even at 1000° C. and 60 kilobars.

INTRODUCTION

There are four major groups of feldspar minerals in nature: potassium feldspar ($KAlSi_3O_8$), sodium feldspar ($NaAlSi_3O_8$), calcium-feldspar ($CaAl_2Si_2O_8$) and barium feldspar ($BaAl_2Si_2O_8$). Among these, sodium feldspar, calcium-feldspar and barium feldspar are easily broken down into other phases or phase assemblages either at high solid pressure or at high water pressures.

It is well known that sodium feldspar is transformed into the assemblage jadeite plus quartz at high pressure by the following chemical reaction (Birch and Le Comte 1960; Robertson *et al.*, 1957):

$$\underset{NaAlSi_3O_8}{\text{albite}} \rightarrow \underset{NaAlSi_2O_6}{\text{jadeite}} + \underset{SiO_2}{\text{quartz}}$$

At higher pressures, albite transforms into the assemblage of jadeite and coesite by the reaction (Boyd and England, 1960; MacDonald, 1956):

$$\underset{NaAlSi_3O_8}{\text{albite}} \rightarrow \underset{NaAlSi_2O_6}{\text{jadeite}} + \underset{SiO_2}{\text{coesite}}$$

Pistorius *et al.* (1962) and Newton and Kennedy (1963) showed that calcium-feldspar would be transformed into lawsonite at high water pressures by the following chemical reaction:

$$\underset{CaAl_2Si_2O_8}{\text{anorthite}} + \underset{2\ H_2O}{\text{2 water}} \rightarrow \underset{CaAl_2Si_2O_8 \cdot 2\ H_2O}{\text{lawsonite}}$$

Barium feldspar also undergoes mineralogical change into cymrite when subjected to high water pressures (Seki and Kennedy, 1964a).

[1] Publication No. 306, Institute of Geophysics and Planetary Physics, University of California, Los Angeles, California.

[2] Department of Earth Sciences, Saitama University, Urawa, Japan.

Early reconnaissance experiments showed that orthoclase undergoes a phase change at water pressures somewhat in excess of 10 kilobars. In this paper we present results of experimental work on the stability of potash feldspar at high temperatures and high confining pressure as well as at high partial pressures of water.

Experimental Techniques

Runs were made in both piston-anvil and piston-cylinder devices.

The behavior of a piston-anvil device (simple squeezer) has been discussed several times (Griggs and Kennedy, 1956; Pistorius *et al.*, 1962). In "wet" runs water is added to the starting materials in order to make confining pressures and water pressures as equal as possible. In "dry" runs, however, the starting materials were kept at least 24 hours at 110° C. in an air bath in order to eliminate all but the most tightly absorbed water from the starting materials. The samples were kept at the required temperature and pressure in the piston-anvil device for 2 hours above 500° C., 4 hours at 400°, and 8 hours or more below 400° C.

Our piston-cylinder apparatus has been described previously by Newton and Kennedy (1963). In wet runs in this apparatus, the starting material was sealed with water in platinum capsules, but in dry runs the starting material was kept at 110° C. in an air bath for 24 hours before it was sealed in the platinum capsules. The samples were kept at the required temperature and pressure in the piston-cylinder apparatus for 1 hour above 700° C., for 2 hours at 500–700° C., and, below 500° C., for 18 hours.

Recently, Newton and Kennedy (1963) have shown that results obtained by simple squeezer on the stability relations between lawsonite and anorthite plus water are much different from those obtained from the piston-cylinder apparatus. However, in the present system the results obtained from the two methods are almost identical.

Mineral phases in our experimental products were identified using both a Philips x-ray diffractometer and a petrographic microscope.

Even though identification of the new mineral phases, made at high pressures, has been by both Philips x-ray diffractometer and petrographic microscope, we relied almost wholly on the x-ray data for the positioning of the various phase boundaries shown in this paper. A few minute high index particles could always be found in the sample by careful microscopic examination even though the sample had never been to excessively high pressures or near the position of the suspected phase transition. This minute amount of high index material could either result from contamination or possibly very local high stresses on the sample. Thus, microscopic work could not be relied upon exclusively to give the lower pressure positions of the phase boundary.

TABLE 1. *X*-RAY POWDER DATA, UNIT-CELL DIMENSIONS AND UNIT-CELL VOLUME OF SANIDINES

hkl	A: Sanidine synthesized from $KAlSi_3O_8$ glass (20 kb, 600° C.) (this paper)			B: Sanidine formed by breakdown of leucite (L.97, 29 kb, 700° C.) (this paper)		C: Sanidine associated with jadeite and quartz in breakdown product of natural orthoclase under dry condition (#12, 25 kb, 730° C.) (this paper)		D: Sanidine associated with jadeite and coesite in breakdown product of natural orthoclase (#4, 24 kb, 600° C. (this paper)		E: Synthesized sanidine from $KAlSi_3O_8$ glass (Donnay and Donnay, 1952)	
	Measured		Calculated								
	d(Å)	I	d(Å)	d(Å)	I	d(Å)	I	d(Å)	I	d(Å)	I
110 1$\bar{1}$0	6.68	7	6.68	6.63	9	—	—	—	—	6.65	6
020	6.51	4	6.50	6.51	9	—	—	6.52	5	6.51	9
1$\bar{1}$1	5.87	6	5.87	5.87	9	—	—	5.87	6	5.869	9
20$\bar{1}$	4.25	48	4.25	4.23	63	4.22	45	4.23	50	4.241	50
111	3.94	8	3.95	3.94	11	—	—	3.94	18	3.947	20
200 2$\bar{0}$0	3.88	3	3.89	—	—	—	—	—	—	3.87	3
130 1$\bar{3}$0	3.782	80	3.782	3.784	82	3.780	80	3.776	70	3.789	80
1$\bar{3}$1	3.620	8	3.619	3.620	21	3.619	21	3.620	18	3.623	15
221	3.552	6	3.554	3.551	18	3.550	15	3.542	18	3.557	12
1$\bar{1}$2	3.458	71	3.460	3.461	60	3.455	58	3.455	40	3.459	50
220 2$\bar{2}$0	3.339	100	3.339	3.337	100	3.319	100	3.324	100	3.328	100
202	3.293	88	3.293	3.289	89	3.283	75	3.285	60	3.287	60
040	3.249	70	3.249	3.250	71	Jadeite*		Jadeite*		3.258	35
002	3.228	85	3.228	3.228	91	3.228	90	3.229	80	3.223	80
131	2.993	65	2.995	2.995	60	2.991	60	2.998	60	2.995	50
2$\bar{2}$2	2.934	7	2.937	—	—	—	—	—	—	2.932	—
041	2.902	34	2.902	2.904	40	Jadeite*		Jadeite*		2.905	20
022	2.891	15	2.891	Kalsilite	(003)*	2.891	17	2.890	14	2.889	—
1$\bar{3}$2	2.765	13	2.764	2.766	25	2.766	20	Coesite		2.766	15
3$\bar{1}$2	2.608	8	2.606	2.606	24	—	—	2.611	15	2.608	12
241	2.588	32	2.586	2.589	60	2.579	40	2.583	21	2.582	30
112	2.555	10	2.554	—	—	—	—	—	—	plus many ill-defined peaks	
310 3$\bar{1}$0	2.548	13	2.545	—	—	—	—	2.546	15		

TABLE 1—*continued*

hkl	A: Sanidine synthesized from $KAlSi_3O_8$ glass (20 kb, 600° C.) (this paper)			B: Sanidine formed by breakdown of leucite (L. 97, 29 kb, 700° C.) (this paper)		C: Sanidine associated with jadeite and quartz in breakdown product of natural orthoclase under dry condition (#12, 25 kb, 730° C.) (this paper)		D: Sanidine associated with jadeite and coesite in breakdown product of natural orthoclase (#4, 24 kb, 600° C.) (this paper)		E: Synthesized sanidine from $KAlSi_3O_8$ glass (Donnay and Donnay, 1952)	
	Measured		Calculated								
	d(Å)	I	d(Å)	d(Å)	I	d(Å)	I	d(Å)	I	d(Å)	I
150 1$\bar{5}$0	2.465	4	2.465	Kalsilite (111)*		—	—	2.465	6		
1$\bar{5}$1	2.418	6	2.418	Kalsilite (103, 013)*		Jadeite*		Jadeite*			
2$\bar{4}$2	2.316	8	2.314	2.315	12	2.313	10	2.314	10		
042	2.290	8	2.290	2.290	10	2.296	7	—	—		
3$\bar{3}$2	2.276	15	2.276	2.275	16	2.275	17	2.271	19		
223 132	2.231	14	2.231 2.233	2.231	12	2.231	14	2.231	11		
151	2.204	4	2.204	2.204	12	2.199	10	2.204	19		
060 3$\bar{1}$3	2.167	27	2.166 2.165	Kalsilite (201)*		Jadeite*		Jadeite*			
311	2.083	6	2.082	2.079	10	2.076	8	2.084	4		
1$\bar{3}$3	2.071	6	2.070	2.069	6	Jadeite*		Jadeite*			
222	1.975	25	1.978	1.976	20	Jadeite*		Jadeite*			
2$\bar{6}$1 3$\bar{5}$1	1.930	13	1.931	1.929	13	1.929	15	1.929	14		
2$\bar{4}$3	1.917	6	1.917	1.918	14	—	—	—	—		
113	1.855	6	1.855	1.853	10	—	—	—	—		
350	1.835	6	1.836	—	—	—	—	—	—		
043	1.794	24	1.794	1.796	30	1.793	25	1.794	24		
1$\bar{5}$3	1.747	6	1.746	1.746	7	—	—	—	—		
3$\bar{3}$4	1.632	11	1.631	—	—	—	—	—	—		
	a= 8.66 (2) Å b=13.00 (0) Å c= 7.18 (3) Å β=116° *C* 2/*m* unit-cell volume=181.7 Å									a= 8.617 Å b=13.030 Å c= 7.176 Å β=116.077° *C* 2/*m* unit-cell volume =181.1 Å^3	

Results from x-ray examination were much more unequivocal. Runs spaced no more than $\frac{1}{2}$ kb apart near the transition boundary normally showed either very little new phase or a very large amount of the new high index phase. For this reason we have relied almost exclusively on the x-ray data in the selection of our phase boundary.

Starting Materials

Two kinds of starting materials were used:

(1) Pure sanidine crystallized from $KAlSi_3O_8$ glass in the simple squeezer.

Table 2. X-ray Powder Data of Natural Orthoclase Used as a Starting Material

hkl	d(Å)	I	hkl	d(Å)	I
020	6.51	4	$\bar{1}51$	2.416	4
$\bar{1}11$	5.83	4	$\bar{2}42$	2.320	3
$\bar{2}01$	4.17	15	060	2.274	13
111	3.92	8	$\bar{1}52$	2.114	4
$\bar{1}30$, 130	3.75	30	061	2.050	5
$\bar{1}31$	3.627	6	$\bar{3}33$	1.958	3
$\bar{2}21$	3.517	4	043	1.794	34
$\bar{1}12$	3.461	10	$\bar{3}34$	1.624	3
$\bar{2}02$	3.269	53			
002	3.221	100			
131	2.982	18			
041	2.903	17			
$\bar{1}32$	2.751	9			
$\bar{2}41$	2.568	18			
$\bar{3}10$, 310	2.540	6			

The $KAlSi_3O_8$ glass was prepared by Dr. Schairer of the Geophysical Laboratory and supplied to us through the courtesy of Dr. F. R. Boyd. X-ray powder data for the sanidine are shown under Column A of Table 1.

(2) Natural orthoclase[1] was obtained from the mineral collection of the Geology Department of UCLA. X-ray powder data of the orthoclase are shown in Table 2. Na_2O and K_2O contents of the orthoclase are as follows: $Na_2O = 4.40\%$, $K_2O = 11.17\%$

[1] "Orthoclase," as defined by Laves (1951), is a mineral that deviates from a truly monoclinic sanidine but that appears to be monoclinic because of triclinic domains too small to be resolved by the microscope or even by x-ray diffraction.

Experimental Results

(1) Results obtained by the simple squeezer using sanidine as a starting material under high water pressures are summarized in Fig. 1.

Sanidine+H_2O changed into a hexagonal phase at very high water pressures. *X*-ray diffraction patterns, unit-cell dimensions, unit-cell volume, optical properties and density of this new phase are represented

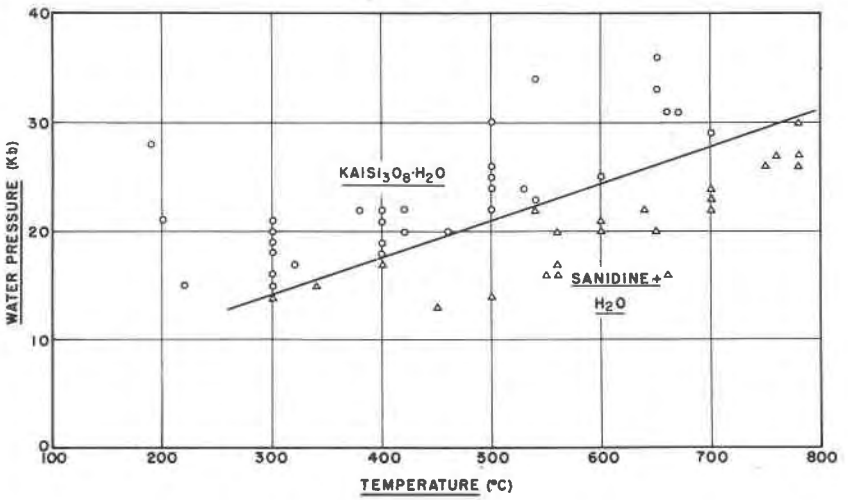

Fig. 1. Diagram showing the synthesis fields of sanidine and $KAlSi_3O_8 \cdot H_2O$ determined by the simple squeezer

○ sanidine + water ⇀ $KAlSi_3O_8 \cdot H_2O$

△ sanidine + water ⇀ sanidine + water

X-ray powder data often show the presence of small amount of sanidine associated with $KAlSi_3O_8 \cdot H_2O$ crystals. The presence of the sanidine must be due to either deficiency of water in these runs or to incomplete chemical reaction.

under Column A in Table 3. Refractive indices were measured by the immersion method. Density was measured by means of suspension method using methylene iodide liquid. The measured value of density agrees well with the value calculated from unit-cell dimensions and the assumed chemical composition of $KAlSi_3O_8 \cdot H_2O$. The *x*-ray powder data and other physical properties corresponded closely with those of cymrite ($BaAlSi_3O_8(OH)$, (Col. B, Table 3), a naturally occurring barium analog of our mineral.

Thus the new phase; the assumed chemical composition of which is

TABLE 3. *X*-RAY POWDER DATA, UNIT-CELL DIMENSIONS AND OTHER PHYSICAL PROPERTIES OF $KAlSi_3O_8 \cdot H_2O$ SYNTHESIZED FROM $KAlSi_3O_8$ GLASS PLUS WATER, AND OF CYMRITE, $BaAlSi_3O_8(OH)$

hkl	A $KAlSi_3O_8 \cdot H_2O$ (35 kb,640° C.)			B Cymrite (Smith *et al.*, 1949)	
	Measured		Calculated		
	d(Å)	I	d(Å)	d(Å)	I
001	7.67	5	7.69	7.7	S
010 100	4.61	30	4.61	4.6	VVW
101 011	3.96	30	3.96	3.95	VS
002	3.85	33	3.84	—	
102 012	2.957	100	3.956	2.95	VS
110	2.667	89	2.667	2.67	S
003	—	—	—	2.57	VW
111	2.518	10	2.518	2.53	VW
200 020	2.308	15	2.308	2.32	W
103	2.241	4	2.241	2.24	M
201 021	2.211	17	2.212	2.21	M
	—	—	—	2.11	VW
202	—	—	—	1.990	W
004	1.924	13	1.925	1.920	MW
113	1.848	13	1.849	1.849	M
211	—	—	—	1.783	VW
120 210	1.746	3	1.746	—	—
023 203	1.715	4	1.716	—	—
211 121	1.703	5	1.703	1.705	MW
122 212	1.591	13	1.591	1.594	MW
114	1.560	7	1.560	1.565	W
005 300 030	1.541	10	1.541	1.544	W
105	—	—	—	1.468	W
213	—	—	—	1.452	VW
220 115	1.334	10	1.334	1.341	VW
033 303	1.321	3	1.320	1.324	VW

TABLE 3—(*continued*)

hkl	A $KAlSi_3O_8 \cdot H_2O$ (35 kb,640° C.)			B Cymrite (Smith *et al.*, 1949)	
	Measured		Calculated		
	d (Å)	I	d(Å)	d(Å)	I
006	1.283	8	1.283	1.283	W
222	1.260	3	1.260		
132, 312	1.216	3	1.216		
304, 034	1.203	3	1.203		
223	1.184	3	1.184		
	$a=5.33$ (5) Å $c=7.70$ (O) Å Hexagonal Unit-cell volume = 189.8 Å^3 $\omega=1.545$, $\epsilon=1.535$ ± 0.003 Uniaxial negative Elongation positive Calculated density = 2.60 Measured density = 2.58 $\pm$ 0.02			$a=5.32$ Å $c=7.67$ Å Hexagonal Unit-cell volume = 188.0 Å^3 $\omega=1.6225$, $\epsilon=1.6125$ ± 0.001 Uniaxial negative Measured density = 3.413 $\pm$ 0.005	

$KAlSi_3O_8 \cdot H_2O$; is believed to have been formed by the following chemical reaction:

	potash feldspar + water		hexagonal new phase
	$KAlSi_3O_8$	H_2O ⟶	$KAlSi_3O_8 \cdot H_2O$
molecular volume	182Å^3	30Å^3	190Å^3
total volume	212Å^3		190Å^3

The volume relation shows that a high partial pressure of water should promote the formation of the new phase.

Unfortunately we did not establish by direct analysis that our new phase was of the assumed composition, potash feldspar + water. However, anhydrous runs at 1300° C. and 60 kilobars failed to make this phase directly from orthoclase, presumptuous evidence that the phase cannot be made from pure orthoclase. The exact structural identity of our phase

and the barium analogue is further striking evidence that it is indeed a hydrate. Perhaps the strongest evidence, however, is the close agreement of our measured density, 2.58 ± 0.02 and the calculated density of 2.60. This agreement of the two densities, within 1%, is compelling. If our new phase had either none or two waters of hydration, disagreement should be approximately 8% between the measured and calculated density.

The boundary shown in Fig. 1, for the formation of the dense hydrate of orthoclase, corresponds closely to the boundary reported by Kennedy (1961) for the transition of orthoclase to orthoclase II. In the earlier work Kennedy (1961) added small amounts of water to orthoclase to flux the reaction. He did not suspect that the new formed dense phase was a hydrate and consequently labeled this phase Orthoclase II.

The relation between the new phase and cymrite will be discussed later in some detail.

(2) Figure 2 shows the stability of sanidine and its hydrate determined in the piston-cylinder apparatus, using pure sanidine as a starting material with added water.

The boundary between sanidine and hexagonal phase $KAlSi_3O_8 \cdot H_2O$ previously determined by means of the simple squeezer (Fig. 1) shows close agreement with that determined by the piston-cylinder method (Fig. 2). We could not find any evidence showing the formation of microcline from sanidine in any of our experiments.

Petrographic studies of potash-feldspars in metamorphic and igneous rocks show that order-disorder transition in monoclinic and triclinic potash-feldspar takes place very close to the granulite-amphibolite facies transition (Heier, 1957). Laves (1952) and Tuttle and Bowen (1958) estimated the transition temperature between monoclinic and triclinic potassium feldspar to be 650–700° C. and 650° C. respectively.

Attempts to synthesize microcline or to convert sanidine to microcline have been unsuccessful (Goldsmith and Laves, 1954).

Recently Tomisaka (1962), placed natural monoclinic potash feldspar and water in the simple squeezer for 5 to 1000 hours (400 hours in average) and found some evidence showing the transformation of the orthoclase into microcline. The transition temperatures at various water pressures as estimated from his data, are as follows:

470° C. at 4 kilobars
460° C. at 2.4 kilobars
450° C. at 1.5 kilobars
400° C. at 1 kilobar

Any appreciable transformation from monoclinic form into triclinic form

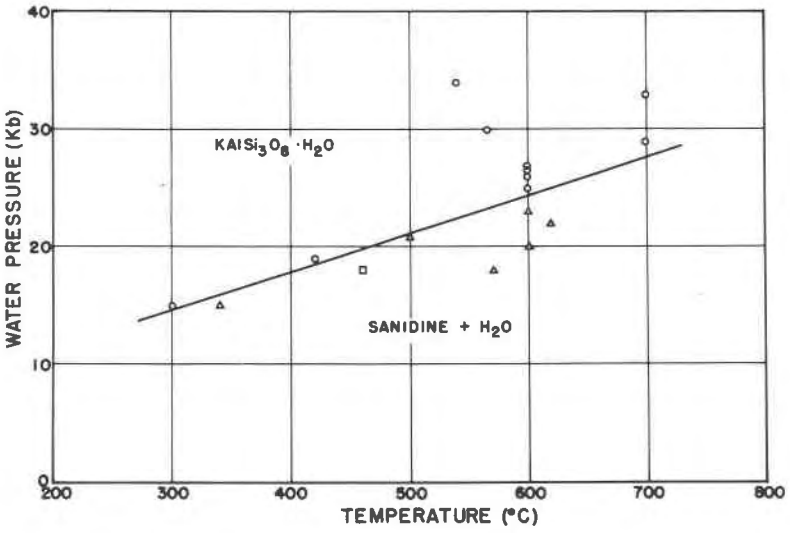

FIG. 2. Diagram showing stability fields of sanidine and $KAlSi_3O_8 \cdot H_2O$ determined by piston-cylinder high pressure apparatus.

○ Sanidine + $H_2O \rightarrow KAli_3O_8 \cdot H_2O$
△ Sanidine + $H_2O \rightarrow$ Sanidine + H_2O
□ $KAlSi_3O_8 \cdot H_2O \rightarrow$ Sanidine + H_2O

did not take place when the starting material was dry. This implies that the solution-recrystallization action of water or aqueous solution is very important in the order-disorder transition in potash-feldspar.

(3) Completely dry sanidine was held at 60 kb and 1300° C. for two hours in the piston-cylinder apparatus and showed no change. This contrasts sharply with the fact that dry albite is easily transformed into the assemblage jadeite+quartz or coesite at the same physical conditions. Potassium feldspar must be stable under the range of temperatures up to 1300° C. and pressures up to 60 kilobars when it is kept in the absence of water.

(4) Figure 3 shows the phase relations of natural orthoclase deduced from the experimental work with wet samples in the simple squeezer. Natural orthoclase was transformed into the assemblages sanidine +jadeite+quartz, sanidine+jadeite+coesite, and $KAlSi_3O_8 \cdot H_2O$+jadeite+coesite with increasing water pressure.

Columns C and D in Table 4 represent *x*-ray powder diffraction patterns of jadeites associated with sanidine+coesite and $KAlSi_3O_8 \cdot H_2O$ +coesite in the breakdown products of natural orthoclase under high water pressure. The *x*-ray data of these jadeites are similar to those of

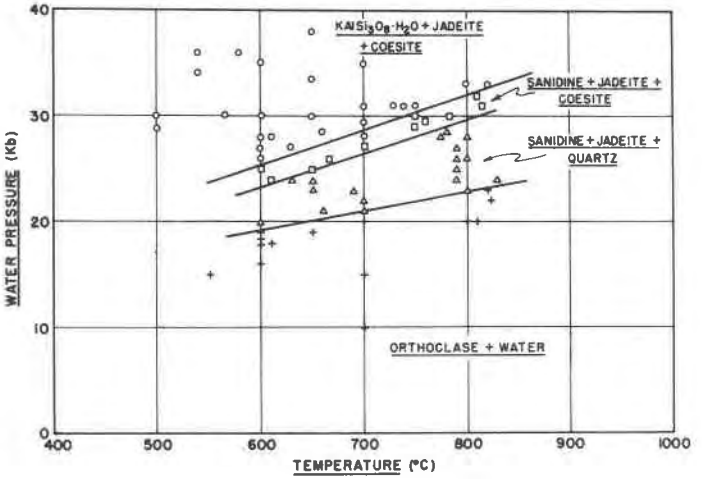

FIG. 3. Diagram showing the stability field of natural orthoclase, sanidine+jadeite +quartz, sanidine+jadeite+coesite and $KAlSi_3O_8 \cdot H_2O$+jadeite+coesite determined by the simple squeezer using natural orthoclase plus water as starting material.

+ orthoclase + water ⇀ orthoclase + water

△ orthoclase + water ⇀ sanidine + jadeite + quartz + water

□ orthoclase + water ⇀ sanidine + jadeite + coesite

○ orthoclase + water ⇀ $KAlSi_3O_8 \cdot H_2O$ + jadeite + coesite

X-ray powder data of some of these runs show the presence of sanidine crystals as well as $KAlSi_3O_8 \cdot H_2O$. This is believed to be either due to deficiency of water or to incomplete chemical reaction.

natural jadeite (Col. E, Table 4) except d-value of the former are generally a little smaller than those of the latter.

(5) Natural orthoclase was transformed into the assemblages sanidine +jadeite+quartz, and sanidine+jadeite+coesite without water in the piston-cylinder apparatus (Fig. 4).

X-ray powder data of sanidines associated with jadeite and quartz or coesite synthesized from natural orthoclase are shown under Columns C and D in Table 1.

Jadeites, synthesized without water, appearing in the breakdown products of natural orthoclase show almost exactly the same *x*-ray diffraction patterns as those of jadeites formed by the transformation of the orthoclase under high water pressures. (Cols. A, B, Table 4).

The stable association of sanidine with jadeite and quartz or coesite is believed to show that sanidine is stable even under very high pressures, providing no water is present.

TABLE 4. *X*-RAY POWDER DATA OF JADEITES

	A Jadeite associated with quartz and sanidine in breakdown product of natural orthoclase under dry condition (#12, 95 kb, 730° C.)		B Jadeite associated with coesite and sanidine in breakdown product of natural orthoclase under dry condition (#3 30 kb, 1000° C.)		C Jadeite associated with coesite and sanidine in breakdown product of natural orthoclase under wet condition (#4 21 kb, 600° C.)		D Jadeite associated with coesite and $KAlSi_3O_8 \cdot H_2O$ in breakdown product of natural orthoclase under wet condition (RCN 1 35 kb, 800° C.)		E Jadeite forming veins in altered gabbroic rocks associated with serpentinite[2] (Seki *et al.*, 1960)	
	d(Å)	I	d(Å)	I	d(Å)	I	d(Å)	I	d(Å)	I
110	—	—	6.20	12	6.19	10	6.19	7	6.19	10
020	4.28	31	4.27	16	4.27	14	4.28	11	4.28	20
021	Sanidine[1]		Sanidine[1]		Sanidine[1]		3.24	6	3.25	5
220	3.09	40	Coesite[1]		Coesite[1]		Coesite[1]		3.10	20
221	2.919	100	2.913	100	2.915	100	2.919	78	2.919	70
310, 311	2.824	80	2.825	70	2.825	82	2.824	100	2.835	100
202	2.530	40	2.530	30	2.529	17	2.530	10	2.533	40
002	4.487	30	2.489	34	2.489	37	2.489	32	2.495	30
22$\bar{1}$	Sanidine[1]		Sanidine[1]		Sanidine[1]		2.411	24	2.416	30
312	—	—	—	—	—	—	2.210	16	2.211	20
022	Sanidine[1]		Sanidine[1]		Sanidine[1]		2.156	6	2.160	5
330, 331	Sanidine[1]		Sanidine[1]		Sanidine[1]		2.058	28	2.068	20
421	2.053	6	2.052	12	—	—	2.052	8	2.052	5
420	1.994	3	—	—	—	—	1.989	13	1.997	5
041	Sanidine[1]		Sanidine[1]		Sanidine[1]		1.962	13	1.966	30
241	—	—	—	—	—	—	—	—	1.888	5
13$\bar{2}$, 510	—	—	1.761	7	—	—	1.764	8	1.764	10
150	—	—	1.680	5	—	—	$KAlSi_3O_8 \cdot H_2O$[1]		1.683	5
531	—	—	—	—	1.571	7	1.571	6	1.574	10
440	1.551	18	1.550	7	1.550	18	1.550	6	1.552	20

[1] Hidden by *x*-ray diffraction of sanidine, coesite and $KAlSi_3O_8 \cdot H_2O$.

[2] Unit-cell dimensions are as follows: $a=9.46$ Å, $b=8.56$ Å, $c=5.25$ Å, $\beta=72°34'$.
The chemical composition of this jadeite is represented below:
SiO_2 59.67, Al_2O_3 23.61, Fe_2O_3 0.33, FeO 0.16, MnO 0.16, MgO 0.47, CaO 0.82, Na_2O 14.24, K_2O 0.71, H_2O+ 0.13, Total 100.30

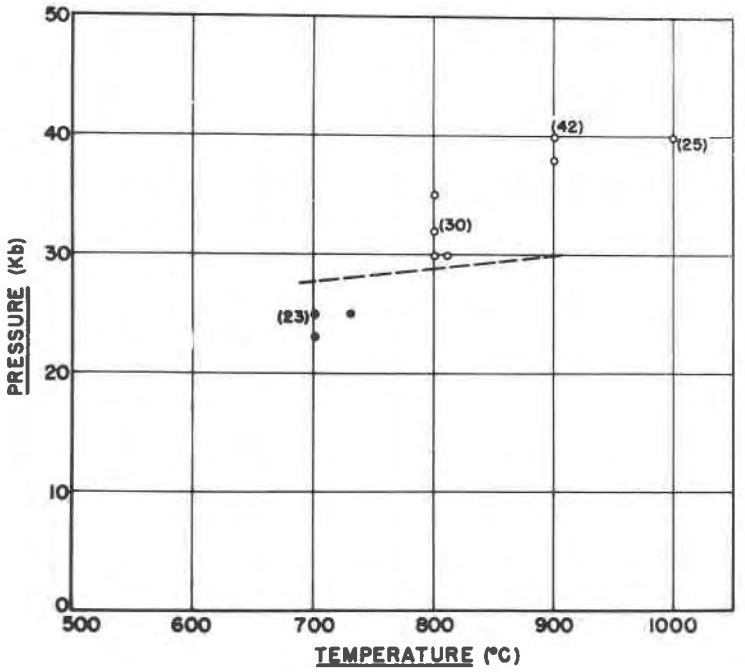

FIG. 4. Diagram representing the stability fields of sanidine+jadeite+quartz- and sanidine+jadeite+coesite- assemblages derived from natural orthoclase under completely dry conditions. The piston-cylinder high pressure apparatus was used.

○ Natural orthoclase ⇀ sanidine + jadeite + coesite
○ Natural orthoclase ⇀ sanidine + jadeite + quartz

Numbers show the ratio of

$$\frac{\text{I (310) jadeite}}{\text{I (310) jadeite} + \text{I (002) sanidine}} \times 100$$

DISCUSSION

Solid solution with the phase $KAlSi_3O_8 \cdot H_2O$. We have already noted the hexagonal phase of $KAlSi_3O_8 \cdot H_2O$ shows very similar x-ray diffraction patterns to those of hexagonal cymrite ($BaAlSi_3O_8$ (OH)). This indicates the phase $KAlSi_3O_8 \cdot H_2O$ and cymrite have almost the same internal framework, and have an isostructural relationship.

It is to be expected that the phase $KAlSi_3O_8 \cdot H_2O$ and cymrite form a complete or partial solid solution because these two phases are isostructural and the ionic radii of Ba (1.43 Å) and K (1.33 Å) are not greatly different.

Further, although we have written the formula for the new phase as $KAlSi_3O_8 \cdot H_2O$, we might perhaps have better written it as $KHAlSi_3O_8(OH)$, a structural analog of cymrite $BaAlSi_3O_8(OH)$, the substitution is $K^+ + H^+$ for Ba^{2+}.

We have succeeded in synthesizing a hexagonal phase which is believed to have an intermediate chemical composition between $KAlSi_3O_8 \cdot H_2O$ and $BaAlSi_3O_8(OH)$ at 620 °C. and 30 kilobars water pressure by the simple squeezer. The starting material was a 1:1 molecular mixture of sanidine and cymrite which had been synthesized from $KAlSi_3O_8$ glass and $BaAlSi_3O_8$ oxide mixture respectively (Seki and Kennedy 1964a). Resulting grain size was approximately .05 mm. As far as could be determined by *x*-ray powder data and by microscopic examination, the product was homogeneous and sanidine did not appear. *X*-ray powder data, unit-cell dimensions and optical properties of this hexagonal phase are shown in Table 6 and are intermediate between the phase $KAlSi_3O_8 \cdot H_2O$ and cymrite. Thus the following ionic substitution is presumed to have occurred to form a solid solution between the phase $KAlSi_3O_8 \cdot H_2O$ and cymrite:

$$(Ba)^{2+} \leftrightharpoons (K^+) + (H^+)$$

TABLE 5. *X*-RAY POWDER DATA OF COESITES.

Coesite formed by breakdown of natural orthoclase[1] (28 kb, 810° C.) (this paper)		Synthetic coesite (Boyd and England, 1960)	
d(Å)	I	d(Å)	I
6.19	4	6.19	3
4.36	3	4.37	2
3.43	26	3.436	52
Jadeite[2]		3.099	100
2.761	2	2.765	18
2.696	3	2.698	11
2.333	3	2.337	3
2.293	6	2.295	6
2.182	3	2.186	4
2.026	5	2.033	6
$KAlSi_3O_8 \cdot H_2O$[2]		1.849	5
1.833	3	1.839	3
1.795	4	1.794	4
1.788	3	1.787	4
$KAlSi_3O_8 \cdot H_2O$[2]		1.698	10
1.654	4	1.655	6

[1] Associated with jadeite and $KAlSi_3O_8 \cdot H_2O$.

[2] Hidden by *x*-ray diffractions of jadeite and $KAlSi_3O_8 \cdot H_2O$.

TABLE 6. *X*-RAY POWDER DATA, UNIT-CELL DIMENSIONS AND OPTICAL PROPERTIES OF A HEXAGONAL PHASE MADE FROM A 1:1 MIXTURE OF SANIDINE AND CYMRITE AT 620° AND 30 KILOBARS WATER PRESSURE

hkl	d(Å)	I
001	7.67	12
010, 100	4.62	27
101, 011	3.96	50
002	3.84	40
102, 012	2.955	100
110	2.670	100
111	2.520	27
020, 200	2.310	35
103, 013	2.240	8
201, 021	2.215	27
112	2.190	18
202, 022	2.980	10
004	1.923	25
113	1.847	23
120, 210	1.745	7
121, 211	1.704	12

$a = 5.34$ Å
$c = 7.68$ Å
$n = 1.570 \pm 0.003$

The formation of a hexagonal crystal of the chemical composition of $KAlSi_3O_8 \cdot H_2O$ from sanidine requires very high water pressures (Figs. 1, 2). However, far less water pressure is necessary to form cymrite from monoclinic barium feldspar (celsian) (Seki and Kennedy, 1964a).

Monoclinic potash-feldspar and barium-feldspar form a partial solid solution through the intermediate hyalophane series.

The phase $KAlSi_3O_8 \cdot H_2O$ cannot be expected to be found in nature because of the very high water pressure required for its formation even at low temperatures (Fig. 5). However, cymrite has been found in nature (Smith *et al.*, 1949a, b). We believe it is not improbable to find, though perhaps rarely, an intermediate member between cymrite and $KAlSi_3O_8 \cdot H_2O$.

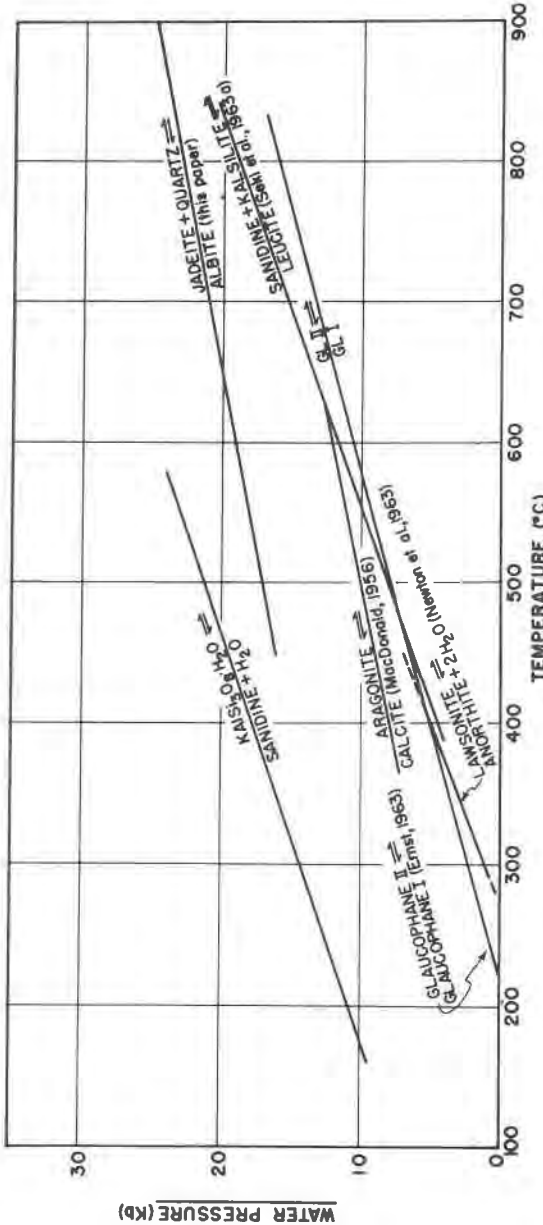

FIG. 5. Comparative representation of phase boundaries of $KAlSi_2O_8 \cdot H_2O$=sanidine+H_2O, coesite=quartz, jadeite+quartz=albite, sanidine+hexagonal kalsilite=leucite, aragonite=calcite, lawsonite=anorthite+2 H_2O, and glaucophane II=glaucophane I.

We unsuccessfully attempted to synthesize a hexagonal phase from albite glass plus water and albite crystal plus water by the simple squeezer and by the piston-cylinder apparatus. Only the assemblages of jadeite +quartz or jadeite+coesite have been obtained at temperatures of 500° C. and water pressures to 40 kilobars.

As was noted, natural orthoclase with some sodium usually decomposed into the assemblage $KAlSi_3O_8 \cdot H_2O$, jadeite, and quartz or coesite at very high water pressures. Thus there is no hexagonal phase of $NaAlSi_3O_8 \cdot H_2O$ which forms a solid solution series with the hexagonal phase of $KAlSi_3O_8 \cdot H_2O$. Further study on the stability relations between nepheline, analcite, albite and jadeite however are necessary.

The substitution of K for Na in jadeite structure. Sanidine alone is stable even at very high pressures and temperatures. At high water pressures, however, it can be easily transformed into the hexagonal phase of $KAlSi_3O_8 \cdot H_2O$. The phase $KAlSi_2O_6$, with a pyroxene structure that is pure potassium jadeite was not found even at 62 kb and 1000° C.

We have studied the high pressure breakdown products of the natural orthoclase (Fig. 3). Figures 4 and 6 show the intensity of x-ray peaks of jadeite increase with increasing distance into the jadeite P-T field. However, the d-spacing of the jadeite shows no shift with change of pressure or temperature. There is an equilibrium partition coefficient of sodium between the jadeite molecule and between orthoclase. At successively higher pressures the sodium is squeezed out of the orthoclase molecule and into the jadeite with coesite or quartz appearing as an additional product. We thus interpret the increased amounts of jadeite with increasing pressure as the result of this equilibrium partition changing with pressure. We do not see any evidence to suggest that appreciable amounts of the potassium molecule are going into the jadeite structure inasmuch as our 2θ values of all x-ray peaks remain independent of pressures and temperatures.

Figure 6 shows x-ray diffraction charts of some high pressure breakdown products of natural orthoclase. These charts were taken by a Philips x-ray diffractometer carefully controlled to keep all conditions the same.

However, it is not impossible that at high pressure some Na (ionic radius=0.98 Å) in jadeite structure may have been partly substituted for by the larger ion of K (ionic radius=1.33 Å) which came from associated potash feldspar.

ACKNOWLEDGMENTS

We are greatly indebted to Dr. R. C. Newton and Dr. J. R. Goldsmith of The University of Chicago for their valuable advice, help and criticism

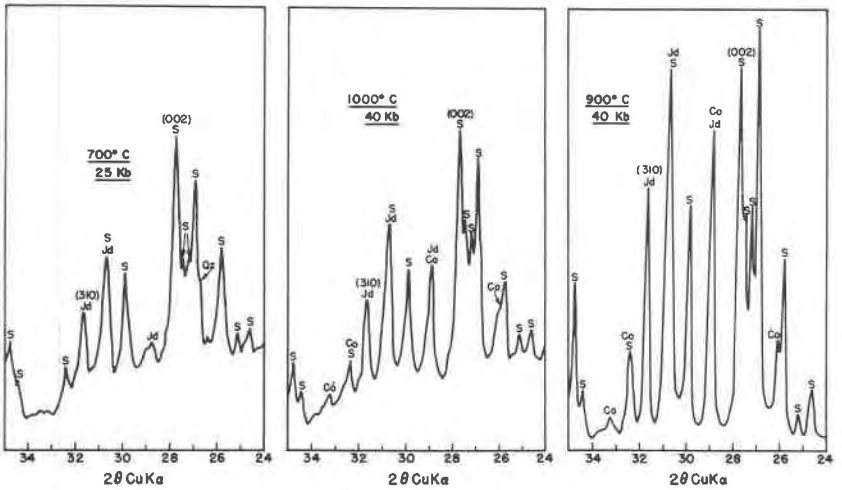

FIG. 6. *X*-ray powder data of high pressure breakdown products of natural orthoclase. S: Sanidine; Jd: Jadeite; Qz: Quartz; Co: Coesite. All of these three runs were done under completely dry conditions by the piston-cylinder apparatus. These *x*-ray data were taken under the same conditions of *x*-ray diffractometer (Fig. 5).

in carrying out this research and to Dr. L. H. Adams of the Institute of Geophysics and Planetary Physics, University of California, Los Angeles for his many helpful suggestions in taking the *x*-ray data.

Dr. F. R. Boyd of the Geophysical Laboratory kindly supplied us with $KAlSi_3O_8$ glass. Dr. A. Miyashiro and Dr. H. Hagiwara of the University of Tokyo helped us to get the chemical data of natural orthoclase. Mr. Terrence J. Thomas and Mrs. E. Szentvari assisted us greatly in the progress of this work. To these people our sincere thanks are due.

Partial financial support is from our contract for Mineral Synthesis from the Geophysics Branch of the Office of Naval Research, Nonr 233(28).

REFERENCES

BIRCH, F. AND P. LE COMTE (1960) Temperature-pressure plane for albite composition. *Am. Jour. Sci.* **258,** 209–217.

BOWEN, N. L. AND O. F. TUTTLE (1950) The system $NaAlSi_3O_8$-$KAlSi_3O_8$-H_2O. *Jour. Geol.* **58,** 489–517.

BOYD, F. R. AND J. L. ENGLAND (1960) The quartz-coesite transition. *Jour. Geophys. Res.* **65,** 749–756.

DONNAY, G. AND J. D. H. DONNAY (1952) The symmetry change in the high-temperature alkali-feldspar series. *Am. Jour. Sci. Bowen Vol.* 115–132.

ERNST, W. G. (1963) Polymorphism in alkali amphiboles. *Am. Mineral.* **48,** 241–260.

GOLDSMITH, J. R. AND F. LAVES (1954) The microcline-sanidine stability relations. *Geochim. Cosmochim. Acta,* **5,** 1–19.

GRIGGS, D. T. AND G. C. KENNEDY (1956) A simple apparatus for high pressures and temperatures. *Am. Jour. Sci.* **254,** 722–735.

HEIER, K. S. (1957) Phase relations of potash feldspar in metamorphism. *Jour. Geol.* **65,** 468–479.

KENNEDY, G. C. (1961) Phase relations of some rocks and minerals at high temperatures and high pressures. *Advances in Geophysics* **7,** 303–322, Academic Press.

——— AND R. C. NEWTON (1963) Solid-liquid and solid-solid phase transitions in some pure metals at high temperatures and pressures. *Solids Under Pressure.* Paul & Warschauer ed. McGraw-Hill, 163–178.

LAVES, F. (1951) Artificial preparation of microcline. *Jour. Geol.* **59,** 511–512.

——— (1952) Phase relations of the alkali feldspars I, Introductory remarks. *Jour. Geol.* **60,** 436–450.

——— AND J. R. GOLDSMITH (1961) Polymorphism, order, disorder, diffusion and confusion in the feldspars. *Cursillos y Conferencias Fasc.* **7,** 71–80.

MACDONALD, G. J. F. (1956a) Experimental determination of calcite-aragonite equilibrium relations at elevated temperatures and pressures. *Am. Mineral.* **41,** 744–756.

——— (1956b) Quartz-coesite stability relations at high temperatures and pressures. *Am. Jour. Sci.* **254,** 713–721.

NEWTON, R. C. AND G. C. KENNEDY (1963) Some equilibrium reactions in the join $CaAl_2Si_2O_8$-H_2O. *Jour. Geophys. Res.* **68,** 2967–2983.

PISTORIUS, C. W. F. T., G. C. KENNEDY AND S. SOURIRAJAN (1962) Some relations between the phases anorthite, zoisite and lawsonite at high temperatures and pressures. *Am. Jour. Sci.* **260,** 44–56.

ROBERTSON, E. C., F. BIRCH AND G. J. F. MACDONALD (1957) Experimental determination of jadeite stability relations to 25,000 bars. *Am. Jour. Sci.* **255,** 115–137.

SEKI, Y., M. AIBA AND C. KATO (1960) Jadeite and associate minerals of metagabbroic rocks in the Sibukawa district, Central Japan, *Am. Mineral.* **45,** 668–679.

——— AND G. C. KENNEDY (1964a) Phase relations between cymrite, $BaAlSi_3O_8(OH)$, and celsian, $BaAl_2Si_2O_8$. *Am. Mineral.* **49,** 1407–1426.

——— AND G. C. KENNEDY (1964b) An experimental study on leucite-pseudoleucite problem. *Am. Mineral.* **49,** 1267–1280.

SMITH, W. C., F. A. BANNISTER AND M. H. HEY (1949a) Cymrite, a new barium mineral from the Benallt manganese mine, Rhiw, Carnarvonshire, *Mineral. Mag.* **28,** 676–681.

———, F. A. BANNISTER AND M. H. HEY (1949b) A new barium mineral from the Benallt manganese mine, Rhiw, Carnarvonshire. *Am. Mineral.* **34,** 614.

TOMISAKA, T. (1962) On order-disorder transformation and stability range of microcline under high water vapor pressure. *Min. Jour.* **3,** 261–281.

TUTTLE, O. F. AND N. L. BOWEN (1958) The origin of granite in the light of experimental studies in the system $NaAlSi_3O_8$-$KAlSi_2O_8$-SiO_2-H_2O. *Geol. Soc. Am. Mem.* **74.**

Manuscript received, February 7, 1964; accepted for publication, June 17, 1964.