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MELTING RELATIONS OF $KAlSi_3O_8$: EFFECT OF PRESSURES UP TO 40 KILOBARS

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Potassium feldspar ($KAlSi_3O_8$) has long been known to melt incongruently at 1 atmosphere to leucite ($KAlSi_2O_6$)+liquid; Schairer and Bowen (1955, pp. 718, 723) demonstrated that leucite and liquid first appear at $1150° \pm 20°$ C. and that leucite persists up to 1533° C. Goranson (1938, p. 89) found that the temperatures both of initial and of complete melting are depressed by increasing water pressure, the field of leucite +liquid becoming narrower until at 2.6 kb water pressure and 950° C., $KAlSi_3O_8$ melts congruently to a water-saturated liquid. The effect of water pressure on the melting of silicates is two-fold: higher water pressures generally increase the amount (and hence the activity) of water in the melt, thus lowering melting temperatures, whereas higher total pressures on the condensed phases (considering water as an inert medium) tend to increase melting temperatures. Observed melting temperatures in hydrothermal experiments are thus the resultants of two oppositely directed effects. Determination of melting temperature as a function of load pressure alone may help separate the two effects. This note presents data on the equilibrium melting relations of potassium feldspar at total (dry) pressures up to 40 kb. The field of leucite+liquid persists to 19 ± 1 kb dry pressure; above that pressure sanidine melts congruently. Thus where water pressure is lower than total pressure the field of leucite+liquid will be intermediate between that given by Goranson ($P_{H_2O} \cong P_{Total}$) and that presented here for $P_{H_2O} = 0$.

STARTING MATERIALS

Starting materials for the high-pressure experiments were prepared from a "gel" supplied by H. R. Shaw. The anhydrous composition of this "gel" is very close to $KAlSi_3O_8$ (Shaw, 1963). Because of its high water content and high free energy the "gel" as supplied was unsuitable as a starting material for these experiments; three anhydrous starting materials were prepared from the "gel" as follows: A portion of the "gel," dried in air at 890° C. for 39 hours and then ignited to constant weight at 1250° C. for a total of 23 hours, yielded a glass plus about 10 per cent leucite crystals. A homogeneous glass was then prepared by heating a portion of the glass+leucite in air at 1560° C. for 26 hours. Another portion of the "gel" was sealed in a gold capsule and crystallized hydro-

TABLE 1. POWDER *X*-RAY DIFFRACTION DATA FOR SYNTHETIC HIGH SANIDINE, $KAlSi_3O_8$

hkl	1		2		3	
	d, Å	*I*	*d*, Å	*I*	*d*, Å	*I*
110	6.65	6	6.65	6	6.66	7
020	6.51*	9	6.52	10	6.52	15
$\bar{1}11$	5.867	9	5.867	7	5.871	15
$\bar{2}01$	4.242	50	4.238	50	4.244	55
111	3.948	20	3.945	20	3.946	15
200	3.87*	3	—	—	—	—
130	3.789	80	3.789	70	3.790	80
$\bar{1}31$	3.623	15	3.63*	10	3.623	20
$\bar{2}21$	3.556	12	3.56*	10	3.56*	15
$\bar{1}12$	3.458	50	3.458	40	3.458	55
220	3.329	100	3.326	100	3.330	100
$\bar{2}02$	3.287	60	3.284	50	3.287	50
040	3.258	35	3.260	35	3.257	40
002	3.222	80	3.225	80	3.223	80
131	2.996	50	2.997	40	2.997	55
$\bar{2}22$	2.932	20	2.908*	20	2.909*	20
041	2.905					
022	2.890					
$\bar{1}32$	2.766	15	2.766	15	2.765	25
$\bar{3}12$	2.608	12	2.61*	10	2.61*	15
221	2.58*	30	2.58*	25	2.58*	30
$\bar{2}41$						
060	2.172	20	2.172	15	2.171	30
$\bar{2}04$	1.793	—	1.793	10	1.793	20
a, Å	8.620±0.004		8.610±0.002		8.626±0.002	
b, Å	13.028±0.002		13.034±0.002		13.031±0.002	
c, Å	7.175±0.002		7.176±0.001		7.174±0.001	
β, deg.	116.04 ±0.02		116.02 ±0.01		116.05 ±0.01	
V, Å^3	723.9 ±0.6		723.7 ±0.3		724.4 ±0.3	

Unit-cell parameters from least-squares refinement using a program developed by C. W. Burnham for the I.B.M. 7094 computer.

* Peak not used in least-squares refinement.

1. High sanidine, crystallized from glass at 1000 kg/cm^2 water pressure, 700° C., for 1 day (Donnay and Donnay, 1952, p. 124). *d* values calculated by Lindsley; Donnay and Donnay (1952, p. 129) give the following unit-cell parameters: *a*, 8.617 Å; *b*, 13.030 Å; *c*, 7.176 Å; *β*, 116.07°; *V*, 723.7 Å^3. Intensities from Powder Data File card 10-353, based on the Donnays' data.

2. High sanidine, crystallized from "gel" at 700° C., 2 kb water pressure, for 20 hours; dried for 28 hours in air at 950° C. Used as a starting material for high-pressure experiments, this report.

3. High sanidine, coexisting with 25 per cent liquid. Crystallized from $KAlSi_3O_8$ glass at 20 kb, 1415° C., for 75 minutes (experiment No. 10, this report).

Data for 2 and 3 obtained using Ni-filtered $CuK\alpha$ and $K\alpha_1$ radiation, scanned at $\frac{1}{4}$° per minute. Intensities measured from potentiometer chart.

thermally at 740° C. and 2 kb for 20 hours. The crystallized material, dried for 28 hours in air at 950° C., was a homogeneous single phase on optical examination and showed only the peaks of high sanidine (Donnay and Donnay, 1952) in a powder *x*-ray diffraction pattern (Table 1). All starting materials were cooled and stored in a desiccator over activated alumina.

EXPERIMENTAL TECHNIQUES

All experiments reported in this note were performed in a solid-media piston-and-cylinder pressure apparatus essentially similar to that described by Boyd (1962) and Boyd and England (1963). Prior to insertion into the high-pressure apparatus, the boron nitride sleeve, furnace assembly, ceramic inserts, and sample (enclosed in a platinum capsule) were dried for 45 minutes in nitrogen at 1080° C. Spot checking of the dried samples revealed that the starting materials were unaffected by this drying process—not a surprising result in view of the celebrated reluctance of $KAlSi_3O_8$ compositions to react at 1 atmosphere (Schairer and Bowen, 1955).

All experiments below 30 kb and one at that pressure utilized pressure vessels with unflawed tungsten carbide cores; pressure was generated by "piston-in" displacement.[1] The effect of friction between the piston and vessel wall on the actual sample pressure is probably small for such experiments. All other experiments at and above 30 kb utilized a vessel in which the carbide core was lined with a hardened steel shell. "Piston-in" friction effects in such vessels may be considerable at high pressures. However, from a careful study of the apparent pressure of the quartz-coesite transition at 1400° C. in a variety of pressure vessels, F. R. Boyd (pers. comm., 1965) has demonstrated that there is only minor friction between the steel liner and carbide piston for "piston-out" displacement at 35–40 kb. Determinations of the apparent pressure of the quartz-coesite transition at 1400° C. in the steel-lined vessel used in the present study confirm that the "piston-out" friction is 1 kb or less. Experiments on $KAlSi_3O_8$ at 40 kb were therefore first overpumped by 5 kb and then lowered to 40 kb to ensure "piston-out" displacement. All pressures are reported as the product of oil pressure on the ram (measured with a bourdon gauge) and the areal ratio of the ram to the carbide piston (64:1).

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[1] "Piston-in" displacement is achieved simply by moving the piston into the pressure vessel until the desired nominal pressure is shown on the oil-line gauge. "Piston-out" displacement is achieved by pumping the piston inward until the pressure on the sample exceeds the desired pressure and then withdrawing the piston until the nominal pressure appears on the gauge. Any difference in sample pressure for the same nominal pressure developed by these two methods is a measure of the internal friction of the apparatus.

Table 2. Critical Experiments Defining the Melting Relations of $KAlSi_3O_8$

Experiment No.	*P*, kb	*T*, °C.	Duration, minutes	Reactants	Products
1	10	1615	15	Gl+10% Lc	Liq
26	10	1475	75	Hi-San	Liq+Lc (+ minor Hi-San)
20	10	1290	165	Gl	Liq+Lc+Hi-San
22	15	1475	90	Hi-San	Liq (+ minor Hi-San)
14	15	1440	50	Gl	Liq+Lc
13	15	1390	75	Gl	Liq+Lc
17	15	1350	120	Gl	Hi-San (+Liq)
36	16	1415	150	Hi-San	Liq+Lc
24	17.5	1435	90	Gl	Liq+Lc
25	19	1460	75	Hi-San	Liq (+minor Hi-San)
7	20	1465	45	Gl+10% Lc	Liq
12	20	1440	61	Gl	Hi-San (+80% Liq)
37	20	1440	180	Gl	Hi-San (+40% Liq)
11	20	1415	30	Gl	Hi-San (+80% Liq)
10	20	1415	75	Gl	Hi-San (+25% Liq)
23*	30	1565	30	Hi-San	Liq
30	30	1525	45	Hi-San	Liq (+Hi-San)
21*	30	1515	60	Gl	Hi-San (+Liq)
19*	30	1490	60	Gl	Hi-San (+Liq)
28*	35	1575	30	Hi-San	Liq
29*	40	1585	20	Hi-San	Liq
34*	40	1550	45	Hi-San	Liq (+Hi-San)
35*	40	1530	60	Gl	Hi-San (+minor Liq)

Abbreviations: Gl, glass; Liq, liquid (quenched to glass); Lc, leucite; Hi-San, high sanidine.

Product phases in parentheses are interpreted on textural evidence to be relic starting material (see text).

* Experiment in steel-lined pressure vessel.

Temperatures are nominal for $Pt\text{-}Pt_{90}Rd_{10}$ thermocouples in contact with the platinum sample capsules and are uncorrected for the effect of pressure. 40 kb experiments were overpumped by 5 kb and then lowered to nominal pressure to ensure "piston-out" displacement. All other experiments are at nominal pressures for "piston-in" displacement.

Experimental Results

Experimental data critical to the determination of the *P-T* melting relations of $KAlSi_3O_8$ composition are listed in Table 2 and plotted in Fig. 1. The congruent melting curve high sanidine = liquid and the triple point in Fig. 1 have been closely bracketed by reversed reactions; the boundaries of the leucite+liquid field are less closely bracketed and are given as straight lines connecting the triple point with the 1 atmosphere data. In many experiments the reactions did not go to completion; this might result either from insufficient duration of the experiments or from

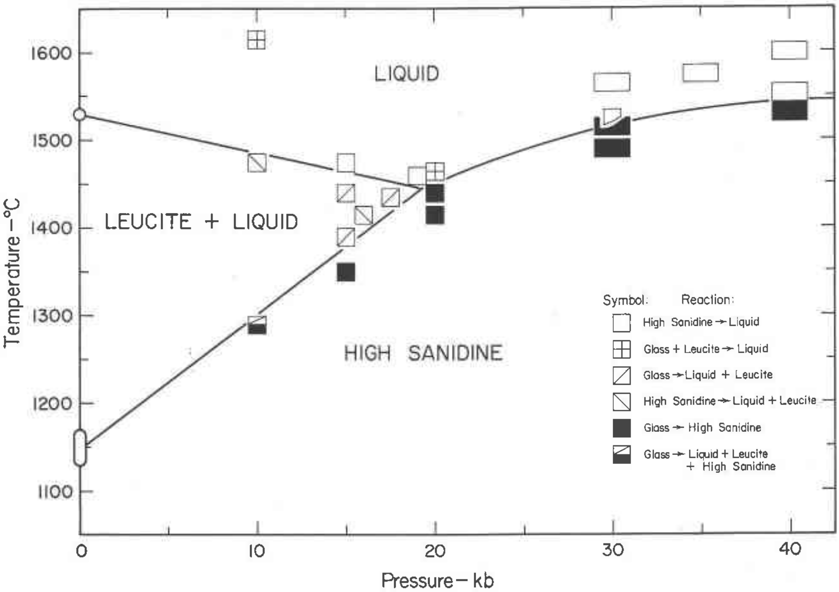

FIG. 1. Melting diagram for the composition $KAlSi_3O_8$ as a function of temperature and pressure. Size of symbol indicates uncertainty in temperature and pressure of each experiment. Wider symbols at 30–40 kb show greater pressure uncertainty of experiments in steel-lined bombs (see text). Symbols indicate *direction* of reaction but do not necessarily show complete reaction (see text). The 1 atmosphere data are from Schairer and Bowen (1955). The curve leucite+liquid=liquid is univariant only for the composition $KAlSi_3O_8$; the other two curves are truly univariant in the binary system leucite-silica.

one or more phases being off composition. The known composition of the gel and the careful drying procedures employed preclude appreciable deviation from $KAlSi_3O_8$ bulk composition. Incongruent melting (other than to leucite+liquid) seems ruled out because (a) high sanidine coexisting with liquid yields *x*-ray patterns that correspond with those from pure high sanidine (Table 1) and (b) a glass quenched from a liquid coexisting with high sanidine has an index of refraction identical with that quenched from 100 per cent liquid *at the same pressure*. Extremely sluggish reaction rates at 1 atmosphere suggest that the problem may be one of duration of the experiments. Experiments at the same pressure and temperature but of different duration show significantly more reaction in those of longer duration (Table 2, experiments 10 and 11; 12 and 37). Limitations of the high-pressure apparatus prevented experiments of greater duration. It seems clear, however, that these experiments with incomplete reaction accurately show the *direction* of reaction and may be used to bracket equilibrium curves.

DISCUSSION

Two noteworthy features of Fig. 1 are the persistence of the leucite +liquid field to a triple point involving leucite+liquid, high sanidine, and liquid at 19±1 kb, 1445°±10° C.; and the negative slope of the leucite+liquid=liquid boundary. The negative value of dT/dP for this boundary indicates that the ratio $\Delta V/\Delta S$ for the reaction leucite+ liquid =liquid must also be negative. As the entropy change for a reaction with crystals+liquid going to liquid is almost certainly positive, it is the volume change which must be negative. This result might be expected in view of the low density of leucite relative to potassium feldspar (Deer *et al.* 1963).

The triple point in Fig. 1 is invariant only by restriction to $KAlSi_3O_8$ bulk composition. In the binary system leucite-silica the curve leucite +liquid=liquid is dependent on bulk composition and hence is not univariant. The triple point is actually a singular point (analogous to point S_1, Fig. 44, Bell and Roseboom, 1965) in the binary system, being the intersection of the univariant curves high sanidine=leucite+liquid and high sanidine=liquid, and the high sanidine+leucite=liquid eutectic, which would lie below the high sanidine=liquid curve in Fig. 1. Thus Fig. 1 does not delineate the ultimate stability of leucite for bulk compositions close to $KAlSi_2O_6$.

The curve for congruent melting of high sanidine above 19±1 kb is concave toward the pressure axis, as is the melting curve for albite (Boyd and England, 1963), but the slope for albite is much greater.

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This study was undertaken at the suggestion of D. B. Stewart in connection with the "Short Course in Feldspars" presented prior to the 1965 Annual Meeting of the Geological Society of America. Constructive criticisms of the manuscript by Dr. Stewart and Dr. P. M. Bell improved both the content and the presentation of this note. H. R. Shaw generously provided the analyzed $KAlSi_3O_8$ "gel," without which the investigation would not have been made.

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PHENOCRYSTIC SPINELIFEROUS TITANOMAGNETITES FROM TRACHYANDESITES, IKI ISLAND, JAPAN

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Introduction

Titanomagnetite is one of the most important rock forming minerals in basic igneous rocks; extensive studies of natural and synthetic iron ores have been made by many investigators over the past decade. These studies have furnished much data on the mineralogical character and petrological significance of titanomagnetites of igneous and metamorphic rocks.

Although theoretical and experimental relation indicates that magnetite (Fe_3O_4)-ulvöspinel (Fe_2TiO_4) form a complete solid solution series with the spinel ($MgAl_2O_4$)-hercynite ($FeAl_2O_4$) solid solution series at high temperatures, natural titanomagnetites that have crystallized as primary phases from basaltic magma have compositions on or near the join Fe_3O_4-Fe_2TiO_4 in the system TiO_2-FeO-Fe_2O_3, and other components such as spinel-hercynite solid solutions and magnesiochromite-chromite solid solutions are generally negligible in titanomagnetites.

The present investigation deals with the titanomagnetite phenocrysts from trachyandesites of Iki Island, Japan and shows the extent to which a spinel-hercynite solid solution is included in titanomagnetites crystallized from an alkali basalt magma.

Occurrence and Microscopic Observation

The mineralogy and petrology of the alkaline volcanic rocks of the Iki Island region of southwestern Japan have been described elsewhere (Aoki, 1959, 1963a, 1963b, 1964).