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SYNTHESIS AND CRYSTAL CHEMISTRY OF SODIUM-POTASSIUM RICHTERITE, $(Na,K)NaCaMg_5Si_8O_{22}(OH,F)_2$: A MODEL FOR AMPHIBOLES[1]

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Abstract

Synthesis and homogenization experiments at 775°–850°C and 1 kbar indicate a complete series of solid solutions along the amphibole join $(K,Na)NaCaMg_5Si_8O_{22}(OH)_2$. Unit cell dimensions a, β, and V do not deviate significantly from a linear relationship between end member compositions; b and c change little with composition. The molar volume decreases 3.55 cm³/mole in passing from potassic to sodic richterite compositions; other K⇌Na (A-site) amphibole series are expected to show a similar molar volume change. High pressures characteristic of the mantle will tend to stabilize potassic amphibole relative to phlogopite+pyroxene. Substitution of fluorine ion for hydroxyl causes the cell constants a and V to decrease significantly.

Introduction

Richterites are clinoamphiboles whose composition is between the compositions of calcic and sodic amphibole groups of Ernst (1968). The idealized formula, $(K,Na)NaCaMg_5Si_8O_{22}(OH,F)_2$, shows an amphibole that is rich in alkali relative to calcium and from which aluminum is absent. The formula further suggests that richterite crystallizes in an environment in which the chemical potential of alkalis is great relative to that of alumina. Sodium must be present, but a combination of sodium and potassium is permissible.

The clinoamphibole structure (Papike *et al.*, 1969, Figs. 1 and 2) consists of infinite double chains of silicon-oxygen tetrahedra linked laterally by strips of octahedral [$M(1)$,$M(2)$, and $M(3)$] sites and 6- or 8-fold coordinated [$M(4)$] sites. In synthetic richterite, the octahedral sites are filled with Mg. Equal numbers of Ca and Na are distributed over the $M(4)$ sites. To balance the 46 negative charges of O^{2-} and $(OH,F)^-$, one additional alkali atom is needed per formula unit and fills the A-site, which is located between two tetrahedral double chains. The A-site is large and irregular; the A-site alkali is coordinated by 8 to 12 oxygen neighbors. Hydroxyl or fluorine occupies the 0(3) site, which is in the octahedral strip adjacent to the A-site alkali.

Richterite is a rare mineral but forms in a wide variety of geologic environments. The paucity and diverse occurrences of this amphibole

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reflect the unique chemistry of these environments. Richterites have been reported as a product of late magmatic crystallization from potassic lavas (Prider, 1939; Carmichael, 1967; Velde, 1967); as a hydrothermal product in an alkaline complex (Larsen, 1942); as a manganiferous amphibole in metamorphosed limestones (Magnusson, 1930); as a high grade metamorphic product in a feldspathic gneiss (Bilgrami, 1955); as a potassium-bearing constituent of omphacite nodules from the Wesselton kimberlite pipe, South Africa (Erlank and Finger, 1970) and from a meteorite (Olsen, 1967). Natural richterites approximating end-member composition are reported by Prider (1939): $[K_{1.03}Na_{1.00}Ca_{1.05}(Mg_{4.49}Fe^{2+}_{0.28}Ti_{0.17}Mn_{0.01})^{VI}(Al_{0.29}Ti_{0.21}Fe^{3+}_{0.06}Si_{7.44})^{IV}O_{22.0}(OH,F)_{2.0}]$[1] and by Olsen (1967): $[K_{0.10}Na_{2.02}Ca_{0.85}Mg_{4.63}Fe_{0.05}Al_{0.07}Ti_{0.16}Cr_{0.08}Si_{8.00}O_{22}(F_{1.00}OH_{1.00})]$[2]. Many richterites do not contain two alkali atoms per 24 oxygens and can be considered to be a solid solution between richterite and tremolite (Sundius, 1945 and 1946); these amphiboles are the soda tremolites described by Larsen (1942) and Miyashiro (1957).

Many alkali-bearing amphiboles contain small amounts of potassium in addition to sodium, but potassic richterite is the only amphibole known to have an atomic site filled with potassium. Potassic amphiboles have been postulated to occur in the mantle (see, for instance, Oxburgh, 1964), and are reported from xenoliths of possible mantle origin (Erlank and Finger, 1970). Richterites offer the opportunity to study the crystal chemistry of potassic amphibole and the $Na \rightleftharpoons K$ substitution in an amphibole while the other compositional parameters are held constant. Because this substitution affects only the *A*-site geometry, it may be possible to apply to aluminous amphiboles a model for sodium-potassium substitution developed with reference to the richterites.

Previous Investigations

Although many crystal structure refinements are available for amphiboles (summarized by Ernst, 1968; Papike *et al.*, 1969), the only refinement of a richterite structure is given by Papike *et al.* (1969) for the natural potassic richterite described by Prider (1939). A satisfactory refinement was obtained by using a split- or half-atom model for potassium in the *A*-site, necessitated by disorder (probably positional, less probably thermal) in the $a \cdot c$ plane about the special position at $x=\frac{1}{2}$, $y=0$, $z=0$.

Potassic richterite has not been synthesized previously, but sodic richterite has been synthesized by several investigators; the compositions and published cell dimensions of the phases produced are sum-

[1] The analysis by Prider (1939) recalculated according to 46 negative charges (Papike *et al.*, 1969).

[2] Evidence is presented later in this paper that suggests that the richterite described by Olsen (1967) is a fluor-amphibole with little or no (OH) in the structure.

marized in Table 1. Only Phillips and Rowbotham (1968) have published cell constants for synthetic sodic calciferous richterite, $Na_2CaMg_5Si_8O_{22}(OH)_2$; their reported cell constants appear to be in error. A fixed index refinement of their *d*-spacings yields *a* 9.902±0.002, *b* 17.980±0.004, *c* 5.269±0.001 Å, β 104°12.7±1.1′, *V* 909.4±0.25 Å. Uncertainties reported here are standard errors based on a single refinement and reflect the perfection with which a single data set fits the lattice constants; the uncertainty should be doubled for comparison with other refinements. Kohn and Comeforo (1955) and Eitel (1954) successfully prepared the fluorine analogue of this amphibole.

Sodium magnesio-richterite with no calcium, $Na_2Mg_6Si_8O_{22}(OH)_2$ has been synthesized hydrothermally by Iiyama (1963), but no cell constants are given. The fluorine analogue of sodium magnesio-richterite (without calcium) was prepared by Gibbs *et al.* (1962) who analyzed their product and reported cell constants.

Experimental Procedure

Six mix-compositions in the sodium-potassium richterite series were prepared using $KHCO_3$ (Baker Lot 21551), $NaHCO_3$ (Fisher Lot 512598), $CaCO_3$ (Baker Lot 11246), MgO (Fisher Lot 787699), and SiO_2 (ignited and acid washed Corning silica glass cullet 7940; see Stewart, 1960). For fluor-richterite mixes, fluoride was added as CaF_2 (Fisher Lot 771262). A ferro-richterite mix contained iron added as Fe_2O_3 (Fisher Lot 762942). Reagents were dried, weighed, ground and heated in air or a CO_2+H_2 gas mixture to decompose the bicarbonates, carbonate, and hematite. Heating was done at 700°–900°C in platinum cruciubles for no more than three hours, and is not believed to have affected the ratio of the cations in the mix. The sintered product was crushed and stored in a desiccator.

Synthesis of hydroxyl amphibole was done hydrothermally. A gold capsule was loaded with 10 to 30 mg water and 100 to 500 mg of mix and subsequently welded shut. Most runs were loaded with only about two to four times the amount of water required to form amphibole; greater amounts of water might have caused appreciable fractionation of alkali and silica into the solution, resulting in an amphibole that contains some tremolite in solid solution with richterite. The majority of syntheses were performed at about 850°C and $P_{H2O}=1$kbar[1] (Table 3) in vertical cold-seal bombs, but a few runs were made at different temperatures and pressures. With the exception of two high temperature experiments, runs lasted ~20 to ~57 days. Pressures were measured with a Bourdon-tube gage (Heise) and are accurate to several percent. Temperatures, measured with chromel-alumel thermocouples, are accurate to an estimated ±5°C, and temperature variation of runs was generally less than ±5°C. Overall temperature uncertainty is within ±10°C.

Phase Characterization

Run products were examined by optical and X-ray powder diffraction techniques. The synthetic richterites were not sufficiently coarse grained

[1] These conditions were chosen because richterite is stable, reaction proceeds at a satisfactory rate, richterites are believed to crystallize in lavas at similar temperatures, and because 850°C and 1 kbar are within the limits for continuous operation of stellite 25 cold-seal pressure vessels.

TABLE 1. COMPOSITION AND CELL CONSTANTS OF SYNTHETIC RICHTERITES

Composition	a, Å	b, Å	c, Å	β	V, Å^3	
$NaNaCaMg_5Si_8O_{22}(OH)_2$	9.902(2)	17.980(4)	5.269(1)	104°12.7(1.1)′	909.4(3)	Refinement of data of Phillips and Rowbotham (1968)
approx $Na_{0.93}Na_{0.97}Ca_{1.03}Mg_{4.93}Si_{8.04}O_{22}F_{2.0}$	9.823	17.957	5.268	104°20′		Kohn and Comeforo (1955)
$NaNaMg_6Si_8O_{22}(OH)_2$	10.012	17.911	5.279	108°23′	898.4	Witte *et al.* (1969)
$Na_{1.97}Mg_{6.01}Si_{7.97}O_{22}F_{1.96}$	9.929	17.914	5.274	108°16′		Gibbs *et al.* (1962)

to warrant a universal stage examination. Microscopic examination reveals that amphibole forms 98–100 percent of all but several charges and that other products, when present, are diopside and glass. The richterite commonly forms tiny euhedral crystals, up to 50 μm in maximum dimension, that are bounded by equant to slightly elongate, stubby pinacoids. The extinction angle ($c \wedge Z$) of potassic richterite is about 25°. Refractive indices in sodium light are similar for the sodium and potassium richterites (see Table 2).

Unit cell dimensions were determined using an X-ray powder diffraction goniometer, copper radiation, a proportional counter tube, and either a ratemeter+strip chart recorder output, or a timer+scaler interfaced to a teletype punch. A BaF_2 internal standard ($a = 6.19711 \pm 0.00011$ Å) was used for all but one unit cell determination; the BaF_2 was standardized against silicon (Johnson Matthey Lot Number S3354, $a_0 = 5.43067 \pm$ 0.00018 Å) which in turn was standardized against gem diamond ($a_0 = 3.56703$; Robie *et al.*, 1966). The BaF_2 gives eight usable reflections[1] between 24° and 68° 2θ (CuKα_1) and is free from all peak interference with the amphibole.

TABLE 2. PHYSICAL CONSTANTS FOR SODIC AND POTASSIC RICHTERITE

	Sodic Richterite $NaNaCaMg_5Si_8O_{22}(OH)_2$	Potassic Richterite $KNaCaMg_5Si_8O_{22}(OH)_2$
a, Å	9.9073(16)	10.0486(19)
b, Å	17.9794(38)	17.9880(30)
c, Å	5.2685(11)	5.2722(13)
β	104°15.06(90)′	104°48.09(55)
V, Å$_3$	909.58(39)	921.37(46)
$\overline{V}$, cm^3/mole	273.93(12)	277.48(14)
α, N_D	1.603(2)	1.604(3)
γ, N_D	1.624(3)	1.629(2)

Amphibole peak positions were determined two ways. The conventional method uses strip chart traces run at $\frac{1}{2}$ degree/minute and $\frac{1}{2}$ inch/minute. The chart paper had timing lines at every 0.1 inch which were referenced to the position of the adjacent standard reflections. Amphibole peak positions were measured to the nearest 0.01 inch in reference to the timing lines of the chart paper. The average of two patterns, each measured once, gave 2θ values which, when refined to yield cell parameters, could not be improved by measuring additional patterns or repeating the pattern measurements. Standard errors of the cell dimensions determined in this way are about 1 part in 7000 and apparently reflect the precision to which the peaks were measured, about 0.01° 2θ. Below 30°, the BaF_2 and the amphibole reflections were measured for CuKα radiation, 1.5418 Å., because the α_1 and α_2 reflections could not be distinguished; in this region, the median of the area of each peak was estimated whether or not the peak was "on scale." Above 30°, the CuKα_1 reflection was measured at the top of the peak. Only the (151) reflection went off scale, so that this pro-

[1] Calculated 2θ, CuKα_1: (111), 24.865°; (200), 28.788°; (220), 41.166°; (311), 48.692°; (222), 51.008°; (400), 59.628°; (331), 65.612°; (420), 67.542°.

TABLE 3. HYDROXY-RICHTERITE CELL CONSTANTS

X = mole fraction $KNaCaMg_5Si_8O_{22}(OH)_2$ in the series (K, Na)$NaCaMg_5Si_8O_{22}(OH)_2$

X	a, Å	b, Å	c, Å	β-104°	V, Å^3	R^a	SEUWO[b]	Method[c]	T, °C	P, bars	Time
1.000	10.0500(14)	17.9908(24)	5.2746(8)	48.59(90)′	922.01(18)	37/37	0.0171	A2	845	1000	20 days
	10.0466(10)	17.9846(18)	5.2710(6)	47.56(56)′	920.83(13)	39/40	0.0138	B	916	1000	3½ hrs
	10.0498(16)	17.9908(27)	5.2718(8)	48.15(93)′	921.52(18)	33/37	0.0182	A2	732	2000	57 days
	10.0503(12)	17.9859(23)	5.2730(7)	48.59(63)′	921.51(14)	36/40	0.0148	A2	776	2000	44 days
	10.0459(12)	17.9856(20)	5.2715(7)	48.38(62)′	920.84(14)	41/45	0.0153	A3	805	2000	43 days
	10.0493(9)	17.9905(15)	5.2718(5)	47.29(45)′	921.52(10)	42/44	0.0119	B	850	1000	42 days
	10.0468(12)	17.9898(21)	5.2714(7)	46.92(65)′	921.23(14)	38/40	0.0156	B	853	1000	42 days
0.875	10.0306(14)	17.9868(24)	5.2729(7)	44.87(62)′	919.98(15)	44/46	0.0186	A2	850	1000	47 days
	10.0288(14)	17.9853(19)	5.2714(7)	43.74(76)′	919.57(15)	33/37	0.0140	B	845	1000	41 days
0.750	10.0059(14)	17.9823(21)	5.2701(7)	37.98(68)′	917.48(15)	39/45	0.0163	A3	777	2000	47 days
	10.0101(10)	17.9856(17)	5.2705(5)	38.82(46)′	918.05(11)	44/49	0.0136	A2	850	1000	25 days
	10.0110(9)	17.9845(14)	5.2702(4)	40.04(42)′	917.94(9)	51/52	0.0119	A2	850	1000	45 days
0.50	9.9809(14)	17.9852(20)	5.2695(6)	33.18(75)′	915.58(14)	36/38	0.0137	A3	850	1000	47 days
	9.9839(13)	17.9736(22)	5.2692(6)	33.59(61)′	915.18(14)	42/46	0.0153	A2	850	1000	45 days
	9.9839(12)	17.9817(18)	5.2692(5)	33.37(58)′	915.60(12)	45/49	0.0148	A2	850	1000	45 days
0.25	9.9472(10)	17.9831(14)	5.2688(5)	24.90(44)′	912.82(10)	53/57	0.0134	A4	772±28	2000	46 days
	9.9479(12)	17.9781(16)	5.2675(6)	24.99(54)′	912.38(12)	45/47	0.0139	A2	851	1000	25 days
	9.9500(14)	17.9826(21)	5.2681(7)	25.42(71)′	912.89(15)	41/41	0.0162	A2	850	1000	45 days
0.00	9.9046(20)	17.9738(33)	5.2676(19)	15.11(45)′	908.89(31)	24/24	0.0179	A2	854	1000	8 days
	9.9093(10)	17.9778(20)	5.2701(7)	15.75(60)′	909.92(14)	43/50	0.0148	A3	849	1000	26 days
	9.9090(9)	17.9848(17)	5.2679(6)	14.28(56)′	909.96(12)	44/46	0.0132	B	916	1000	3½ hrs
	9.9065(12)	17.9824(20)	5.2695(7)	15.47(60)′	909.80(14)	45/47	0.0163	B	760	2000	56 days
	9.9075(12)	17.9776(21)	5.2682(8)	16.48(63)′	909.35(15)	48/50	0.0179	B	803	2000	41 days
	9.9071(9)	17.9791(16)	5.2670(6)	14.06(45)	909.36(11)	53/54	0.0149	B	850	1000	32 days
	9.9070(9)	17.9806(17)	5.2691(6)	14.27(49)′	909.76(12)	51.52	0.0152	B	848	1000	42 days

[a] Reflections accepted in refinement/reflections submitted; the criterion is $2\theta(\text{calc}) - 2\theta(\text{obs}) < 0.04°$.
[b] Standard error unit weight observation which is the standard error of an observation, in $°2\theta$.
[c] AX indicates patterns measured by hand; X is the number of patterns averaged. B signifies that the data were collected on punched paper tape and reduced by computer, as described in text.

cedure is applicable generally. Several refinements were run for data based on CuKα_1 radiation ($\lambda = 1.540562$; Bearden, 1967) throughout and gave results that were, for all practical purposes, identical to the results using a mixture of Kα_1 and Kα wavelengths.

In an effort to improve the precision of the peak position measurements, eliminate systematic error (bias), determine peak heights and areas, and speed the measurement process, the information that normally goes into the production of a strip chart was punched on paper tape and subjected to computer reduction. A scaler was gated every 1.2 seconds by a timer with a tuning fork time base. At the end of a 1.2 second counting interval, the accumulated number of counts was stored in a memory buffer for readout (through an interface) to a teletype paper tape punch. Immediately after the scaler accumulation was read into the buffer, the scaler was automatically reset and counting resumed for another time inteval. The goniometer ran continuously at 0.25° 2θ/minute; thus, there are 200 counting intervals per degree. The data on paper tape were transferred to cards for input to a data reduction program (U.S. Geological Survey Program 9208, "CURVE" and "PEAKS" for the IBM 360/65 system by M. Hellman) that calculates peak positions from supplied positions of the internal standard reflections, and provides intensity information. Precision with this method is slightly improved over the hand measurement method and in some cases resultant cell dimensions have standard errors that are less than 1 part in 10,000.

When using the paper tape output and computerized data reduction, all peaks were assumed to be measured for CuKα_1 radiation. This procedure is valid at angles less than 30° because the data reduction program fits a curve to the data and takes as peak positions the curve maxima, and because the peaks cannot go "off scale" (maximum permissible intensity is 99999 counts per time interval with the paper tape format selected). Experimentation with different assignments of Kα and Kα_1 radiation for both the BaF_2 standard and the least squares unit cell refinement demonstrates that the use of the Kα_1 wavelength yields the most internally consistent data (smallest standard error of observed 2θ) and best agreement with patterns measured by hand. Comparison of the two methods indicates that they do indeed yield similar 2θ values and cell dimensions that do not differ significantly (one standard deviation or less).

The least squares refinement of the cell constants was performed with a computer program written by Evans, Applemen, and Handwerker (1963) and subsequently modified by Appleman and Handwerker. Miller indices were assigned to the 24 to 57 amphibole reflections that could be uniquely and unambiguously indexed with the single-crystal intensity data collected for a refinement of the potassic richterite crystal structure (Papike *et al.*, 1969). Powder diffraction intensity values presented in this investigation (Table 4) indicate that the intensities of equivalent *hkl* reflections of potassic and sodic richterites are similar. This fact, plus the continuous change in peak 2θ with composition, validates the use of the potassic richterite single-crystal data in indexing all of the synthetic richterite powder reflections.

Results of Hydroxy-Richterite Syntheses

X-ray diffraction data for the richterite series $(K,Na)NaCaMg_5Si_8O_{22}(OH)_2$ are summarized in Tables 1–4 and in Figure 1. The data indicate that a complete solid-solution series between sodic and potassic richterite can be synthesized, and that the cell constants of intermediate members of the series do not show great deviations from a linear relationship between end member compositions.

TABLE 4. POTASSIC AND SODIC RICHERITE: CALCULATED 2θ VALUES FOR CuKα_1 RADIATION, d SPACINGS, AND CALCULATED AND OBSERVED POWER PATTERN INTENSITIES

POTASSIC RICHERITE

2θ,Calc	h	k	l	d,Å(Calc)	I(Calc)	I(Obs)	Mea
9.82608	0	2	0	8.994003	2.8		
10.33998	1	1	0	8.548124	27.5	21	1
17.36542	1	3	0	5.102457	.01		
17.38330	0	0	1	5.097249	.1		
18.13400	-1	1	1	4.887893	12.8	5	1
18.24805	2	0	0	4.857600	5.0	8	5
19.72537	0	4	0	4.496999	22.5	20	4
20.00583	0	2	1	4.434584	.3		
20.76537	2	2	0	4.274063	.1		
21.79309	-2	0	1	4.074605	.4		
22.20406	1	1	1	4.000273	21.2	9	4
22.92848	-1	3	1	3.875498	19.9	13	3
23.95636	-2	2	1	3.711492	2.6		
26.29767	1	3	1	3.386122	100.0	100.0	4
26.39612	1	5	0	3.373716	1.7		
26.40811	0	4	1	3.372211	3.0		
26.99690	2	4	0	3.299985	77.1	108	4
27.97166	3	1	0	3.187162	65.4	109	4
28.41190	2	0	1	3.138771	.2		
29.04503	-3	1	1	3.071774	13.6	11	3
29.55925	-2	4	1	3.019697	1.3		
29.77611	0	6	0	2.997999	.3		
30.13098	2	2	1	2.963493	64.4	85	4
30.42271	-1	5	1	2.935737	20.5	21	3
31.36815	3	3	0	2.849376	23.2	35	4
32.33890	-3	3	1	2.766025	49.5	55	4
33.08878	1	5	1	2.705032	106.6	126	4
34.35495	-1	1	2	2.608177	1.6		
34.68427	0	6	1	2.584164	53.5	54	4
34.82791	2	4	1	2.573834	.5		
35.14651	2	6	0	2.551229	1.1		
35.18362	0	0	2	2.548624	8.3		
35.31418	-2	0	2	2.539499	85.0	73	4
36.12589	1	7	0	2.484280	1.2		
36.61703	0	2	2	2.452077	.02		
36.66492	-4	0	1	2.448985	.5		
36.74319	-2	2	2	2.443946	.8		
36.79575	3	1	1	2.440578	.2		
36.98059	4	0	0	2.428800	2.7		
37.20306	-2	6	1	2.414785	3.0	4	1
37.22955	-1	3	2	2.413129	.2		
37.32950	3	5	0	2.406898	13.8	24	4
38.05011	-4	2	1	2.362954	25.6	69	4
38.16635	-3	5	1	2.356026	30.8		
38.35608	4	2	0	2.344807	.1		
39.05127	1	1	2	2.304649	.01		
39.25888	-1	7	1	2.292940	30.5	51	4
39.28989	-3	1	2	2.291200	20.3		
39.51694	3	3	1	2.278558	2.8		
40.06769	0	8	0	2.248699	1.3	2	1
40.65634	0	4	2	2.217292	2.3		
40.77188	-2	4	2	2.211274	15.3	9	3
41.42630	1	7	1	2.177861	3.9		
41.62375	2	6	1	2.167965	43.9	74	4
41.64789	1	3	2	2.166765	.2		
41.67421	-3	3	2	2.155577	10.5	5	1
41.97278	-4	4	1	2.150742	.2		
42.25491	4	4	0	2.137031	.5		
42.47778	-1	5	2	2.126333	7.2	3	1
43.97754	0	8	1	2.057235	.03		
44.10672	2	0	2	2.051509	22.8	19	4
44.35724	2	8	0	2.040502	1.8		
44.43063	-4	0	2	2.037302	12.8	15	2
44.54025	3	5	1	2.032541	9.5	17	3
44.99707	3	7	0	2.012963	3.7		
45.23575	4	0	1	2.002895	.01		
45.30161	2	2	2	2.000136	.1		
45.61877	-4	2	2	1.986964	.1		
45.71710	-3	7	1	1.982920	.5		
45.76804	-5	1	1	1.980830	.1		
46.06760	-2	8	1	1.968645	.3		
46.34091	1	9	0	1.957668	9.9	7	4
46.40775	4	2	1	1.955006	1.7		
46.48343	1	5	2	1.951998	.4		
46.69095	-3	5	2	1.943805	7.9	3	2
46.74219	0	6	2	1.941793	.2		
46.84655	-2	6	2	1.937749	.2		
46.99841	5	1	0	1.931802	16.3	29	4
47.92413	-4	6	1	1.896826	6.8	4	4
48.06976	-5	3	1	1.891219	.8		
48.17856	4	6	0	1.887203	.1		
48.74847	2	4	2	1.866454	3.4		
48.93332	-1	9	1	1.859844	9.8		
49.04852	-4	4	2	1.855745	5.2	7	2
49.25607	5	3	0	1.848410	3.5	3	1
49.49451	-1	7	2	1.840062	2.0		
49.79587	4	4	1	1.829630	.7		
49.86674	2	8	1	1.827882	.3		
50.70917	0	10	0	1.798800	5.7	8	3
50.76895	1	9	1	1.796822	3.0	7	2
51.16888	3	1	2	1.783712	1.8	8	1
51.33698	3	7	1	1.778267	.1		
51.55481	-5	1	2	1.771263	3.2		
52.25714	-2	0	3	1.749099	.00		
52.44327	-5	5	1	1.743327	.03		
52.45114	-1	1	3	1.743085	1.1		
53.09100	1	7	2	1.723575	1.5		
53.27927	-3	7	2	1.717927	.1		
53.29556	3	3	2	1.717441	.5		
53.31256	-2	2	3	1.716932	.02		
53.55859	5	5	0	1.709624	.7		
53.67062	-5	3	2	1.706320	.05		
53.85822	3	9	0	1.700818	.2		
53.91769	0	0	3	1.699082	.1		
54.01419	0	10	1	1.696275	1.0		
54.12509	2	6	2	1.693061	.00		
54.34048	2	10	0	1.686857	1.7		
54.36679	0	8	2	1.686104	2.7		
54.38611	-3	1	3	1.685550	.6		
54.40366	-4	6	2	1.685048	.1		

SODIC RICHERITE

2θ,Calc	h	k	l	d,Å(Calc)	I(Calc)	I(Obs)	Mea
9.83079	0	2	0	8.989649	14.4		
10.43550	1	1	0	8.470040	66.9	37	2
17.35205	0	0	1	5.106358	2.2		
17.42841	1	3	0	5.084157			
18.21957	-1	1	1	4.865129	26.7	14	5
18.44426	2	0	0	4.801201	10.8	11	5
19.73491	0	4	0	4.494867	33.1	37	5
19.98091	0	2	1	4.440059	5.0		
20.95885	2	2	0	4.235044	.7		
22.05208	-2	0	1	4.027497	.03		
22.17522	1	1	1	4.005413	15.8	11	3
23.00102	-1	3	1	3.863440	33.3	37	3
24.19453	-2	2	1	3.679491	.6		
26.27669	1	3	1	3.388777	100.00	100	5
26.39438	0	4	1	3.373934	1.2		
26.44586	1	5	0	3.367506	.4		
27.15358	2	4	0	3.281300	74.0	92	5
28.29700	3	1	0	3.151254	65.4	140	5
28.45636	2	0	1	3.133967	.9		
29.45532	-3	1	1	3.029915	10.2	5	5
29.78048	-2	4	1	2.999537	.3		
29.79070	0	6	0	2.996565	.01	10	3
30.17473	2	2	1	2.959295	64.4	89	5
30.46449	-1	5	1	2.929889	17.6	24	5
31.44470	3	3	0	2.843462	20.5	33	5
32.71472	-3	3	1	2.735102	47.0	50	5
33.07767	1	5	1	2.705915	135.5	157	5
34.38596	-1	1	2	2.605897	.1		
34.68050	0	6	1	2.583629	54.1	60	5
34.87057	2	4	1	2.570782	.1		
35.11880	0	0	2	2.553179	11.8	11	5
35.27714	2	6	0	2.542078	.4		
35.49734	-2	0	2	2.526833	90.2	87	5
36.17145	1	7	0	2.481254	.5		
36.35576	0	2	2	2.456045	.3	13	1
36.92130	-2	2	2	2.432565	2.0		
36.94169	3	1	1	2.431256	.7		
37.22763	-4	0	1	2.413249	1.2		
37.26111	-1	3	2	2.411157	.01		
37.37408	-2	6	1	2.404128	5.3	5.2	3
37.43106	4	0	0	2.400599	2.2		
37.58969	3	5	0	2.390834	12.4	17	5
38.49734	-3	5	1	2.336526	40.2	45	3
38.59486	-4	2	1	2.330730	23.9	45	3
38.79819	4	2	0	2.318329	.01		
38.95963	1	1	2	2.309859	.1		
39.31625	-1	7	1	2.289724	30.3	29	5
39.64998	-3	1	2	2.271220	26.8	29	4
39.65707	3	3	1	2.270828	2.1		
40.08768	0	8	0	2.247423	.9	10	2
40.60397	0	4	2	2.220030	1.6		
40.93878	-2	4	2	2.202643	14.4		
41.42644	1	7	1	2.177936	6.1		
41.56345	1	3	2	2.170973	.5		
41.66653	2	6	1	2.165838	46.0	69	5
42.21832	-3	3	2	2.138799	9.4	5	5
42.48083	-4	4	1	2.126147	.01		
42.51083	-1	5	2	2.124756	6.5		
42.66318	4	4	0	2.117521	.2		
43.98267	0	8	1	2.057008	.02		
44.04291	2	0	2	2.054334	24.8	24	5
44.47296	2	8	0	2.035211	1.3		
44.67203	3	5	1	2.026852	12.7	14	5
44.97852	-4	0	2	2.013749	12.4	10	5
45.22723	3	7	0	2.003252	5.5	4	4
45.24020	2	2	2	2.002707	.3		
45.49473	4	0	1	1.991886	.1		
46.00992	-3	7	1	1.970980	.7		
46.15674	-4	2	2	1.965051	.3		
46.21509	-2	8	1	1.962645	.1		
46.38696	1	9	0	1.955832	9.4	5	5
46.41052	1	5	2	1.954895	.8		
46.47620	-5	1	1	1.952285	.4		
46.69766	4	2	1	1.944720	2.6	1	1
46.70087	0	6	2	1.943415	.05		
47.00055	-2	6	2	1.931720	.02		
47.01126	-3	5	2	1.931304	7.2	2	4
47.57791	5	1	0	1.909616	16.0	19	5
48.38788	-4	6	1	1.879526	6.2	5	2
48.55267	4	6	0	1.873532	.01		
48.69366	2	4	2	1.868436	4.8		
48.75439	-5	3	1	1.866251	.4		
48.99005	-1	9	1	1.857823	13.3	12	4
49.53024	-1	7	2	1.838819	3.2		
49.56113	-4	4	2	1.837746	4.6	7	1
49.81781	5	3	0	1.828875	4.9	3	2
49.89127	2	8	1	1.826355	.1		
50.04559	4	4	1	1.821084	.5		
50.73517	0	10	0	1.797938	5.7	3	3
50.77563	1	9	1	1.796600	3.6		
51.17319	3	1	2	1.783573	1.7		
51.46152	3	7	1	1.774255	.03		
52.28711	-5	1	2	1.748166	4.5	7	4
52.37961	-2	0	3	1.745264	.05		
52.43808	-1	1	3	1.743487	.9	6	1
53.03091	1	7	2	1.725386	1.3		
53.09048	-5	5	1	1.723590	.1		
53.30170	3	3	2	1.717257	.8	4	1
53.43436	-2	2	3	1.713306	.1		
53.57629	-3	7	2	1.709102	.3		
53.61375	0	0	3	1.702119	.2		
54.04783	0	10	1	1.689888	1.7		
54.06781	3	9	0	1.694718	.1		
54.07922	2	6	2	1.694388	.02		
54.09204	5	5	0	1.694017	.4		
54.33670	0	8	2	1.686966	2.5		
54.38486	-5	3	2	1.685586	.2		
54.44901	2	10	0	1.683752	1.4		
54.53177	-1	3	3	1.681392	10.8	9	3
54.60532	-2	8	2	1.679300	8.5	12	1

TABLE 4. (*Continued*)

POTASSIC RICHTERITE								SODIC RICHTERITE							
2θ,Calc	h	k	l	d,Å(Calc)	I(Calc)	I(Obs)	Meas	2θ,Calc	h	k	l	d,Å(Calc)	I(Calc)	I(Obs)	Meas
54.49005	-3	9	1	1.682580	4.1										
54.56251	-1	3	3	1.681087	10.5	10	4	54.84933	0	2	3	1.672485	11.9	6	2
54.88788	-6	0	1	1.671322	.00			54.88510	-4	6	2	1.671400	.00		
54.89148	5	1	1	1.671222	.04			55.28473	5	1	1	1.660261	.00		
54.95096	0	2	3	1.669553	11.2			55.33624	4	6	1	1.658838	41.3	36	5
55.09872	4	6	1	1.665424	38.0	42	4	55.75691	-6	0	1	1.647260	.02		
55.42908	-4	8	1	1.656278	.1			55.85440	-4	8	1	1.644670	.01		
55.65857	4	8	0	1.649992	8.3	4	3	55.96158	-2	10	1	1.641773	.00		
55.82089	-2	10	1	1.645577	.1			56.00330	4	8	0	1.640649	10.5	7	5
55.90906	-6	2	1	1.643191	.3			56.51692	-2	4	3	1.626955	.3		
56.39667	-2	4	3	1.630136	.4			56.71513	-3	3	3	1.621710	.6		
56.42825	-3	3	3	1.629297	.3			56.77060	-6	2	1	1.620282	.6		
56.81201	6	0	0	1.619200	4.6	2	3	57.11554	1	11	0	1.611314	13.7	11	3
56.92148	5	3	1	1.616345	.3			57.30737	5	3	1	1.606375	.2		
57.06625	1	11	0	1.612598	10.6	9	4	57.39349	3	5	2	1.604169	.7		
57.38382	3	5	2	1.604417	.8			57.44394	1	1	3	1.602880	.3		
57.58987	1	1	3	1.599165	.1			57.54179	6	0	0	1.600400	4.6	5	4
57.67575	-4	0	3	1.596989	.1			57.88120	0	4	3	1.591808	.01		
57.74100	-5	5	2	1.595339	.6			57.88707	-1	9	2	1.591638	.1		
57.81044	6	2	0	1.593582	.6			58.16431	-4	0	3	1.584732	.04		
57.84830	-1	9	2	1.592635	.02			58.42581	-5	5	2	1.578260	1.1		
57.97644	0	4	3	1.589419	.05			58.53290	4	2	0	1.575627	.9		
58.36522	-5	7	1	1.579836	.4			58.56601	-1	8	3	1.574816	27.8	17	5
58.57245	-1	5	3	1.574658	22.7	14	4	58.88748	4	8	2	1.566983	6.8	3	3
58.66501	-4	2	3	1.572394	.1			59.14941	-4	2	3	1.560668	.05		
58.78851	4	0	2	1.569386	6.3	5	1	59.17282	-5	7	1	1.560106	3.2		
58.90228	-6	4	1	1.566625	.01			59.19714	2	10	1	1.559524	2.7		
59.14802	2	10	1	1.560677	2.8			59.37930	-1	11	1	1.555173	.05		
59.22803	-6	0	2	1.558784	18.8	12	4	59.41895	1	3	3	1.554230	.06		
59.32019	-1	11	1	1.556581	.2			59.63080	3	9	1	1.549213	.2		
59.51041	3	9	1	1.552056	.1			59.73869	-6	4	1	1.546668	.00		
59.55997	1	3	3	1.550886	.1			59.86514	4	2	2	1.543708	.9		
59.60342	5	7	0	1.549859	.1			60.10696	5	7	0	1.538074	.3		
59.76627	4	2	2	1.546025	.7			60.15594	-6	0	2	1.536939	19.5	10	5
60.20139	-6	2	2	1.535887	.2			60.65596	-3	5	3	1.525460	.6		
60.37625	-3	5	3	1.531856	.3			60.95340	1	11	1	1.518727	.6		
60.74420	6	4	0	1.523456	.6			61.05865	1	9	2	1.516360	6.7	1	1
60.84927	5	5	1	1.521076	6.9	2	4	61.06096	2	8	2	1.516310	.1		
60.93820	1	11	1	1.519069	.7			61.12125	-6	2	2	1.514967	.1		
61.09698	2	8	2	1.515502	.02			61.22336	5	5	1	1.512675	8.5	6	5
61.10617	1	9	2	1.515295	6.4	5	2	61.42731	-2	6	3	1.508142	35.7	20	5
61.27620	-3	9	2	1.511154	1.8			61.44794	6	4	0	1.507685	.5		
61.30859	-2	6	3	1.510477	32.7	19	4	61.48516	-3	9	2	1.505271	1.6		
61.35492	-4	8	2	1.509448	5.3			61.80774	-4	8	2	1.499768	5.3		
61.57349	-4	4	3	1.504911	.3			61.87585	0	12	0	1.498281	16.9	14	5
61.84299	0	12	0	1.498999	15.6	9	4	62.04681	-4	6	3	1.494563	.2		
61.99969	4	8	1	1.495585	.1			62.13104	2	0	3	1.492722	.1		
62.27719	2	0	3	1.489586	.03			62.22681	4	8	1	1.490671	.3		
62.64389	4	4	2	1.481746	6.3	3	1	62.72522	0	6	3	1.480020	1.4		
62.81149	0	6	3	1.478194	1.4			62.74280	4	4	2	1.479648	6.8	3	3
62.95938	-5	1	3	1.475077	.6			63.07938	2	2	3	1.472560	2.6		
63.06729	-6	4	2	1.472813	3.8			63.20068	0	10	2	1.470025	.6		
63.19281	3	7	2	1.470190	.7			63.20734	3	7	2	1.469887	1.0		
63.21994	0	10	2	1.469624	.7			63.25494	1	5	3	1.468695	.6		
63.22266	2	2	3	1.469567	2.0			63.44537	-2	10	2	1.464944	3.2		
63.30432	-2	10	2	1.467868	3.3			63.49762	-5	1	3	1.460570	.5		
63.38730	1	5	3	1.466146	.4			63.89682	3	11	0	1.455678	5.3	5	3
63.53003	-5	7	2	1.463196	.1			63.96591	-6	6	2	1.454272	4.9	5	1
63.69492	-6	6	1	1.459805	37.5	33	4	64.18292	-5	7	2	1.449878	.05		
63.69891	3	11	0	1.459723	4.0			64.31558	-1	7	3	1.447206	3.8		
64.18936	-4	10	1	1.449748	1.8			64.49930	-6	8	1	1.443528	39.6	44	5
67.85876	5	1	2	1.380008	15.5	8	3	68.07507	5	1	2	1.376149	18.2	10	5

X-ray powder diffraction intensity data for end-member sodic and potassic richterite are presented in Table 4 where they are compared with calculated powder pattern intensities for respective compositions (using a modification of D. Smith's program and the potassic richterite atomic parameters given by Papike *et al.* (1969)).

Individual least squares unit cell refinements of end-member richterite were averaged (7 each for sodic and potassic richterite) and the standard deviation was calculated for the averages (Table 2). Comparison with the standard deviation of the individual refinements (Table 3), which represents the internal consistency of a data set, suggests that the standard error associated with random scatter of data within a set is half the standard deviation produced by replicate determinations.

The set of 24 cell constants for 6 richterite compositions was subjected to a least-squares curve fitting routine (Table 5). The standard error of the curve for a, β, and V dropped noticeably between degree (of fit) two and three; there was little change between degrees one and two or

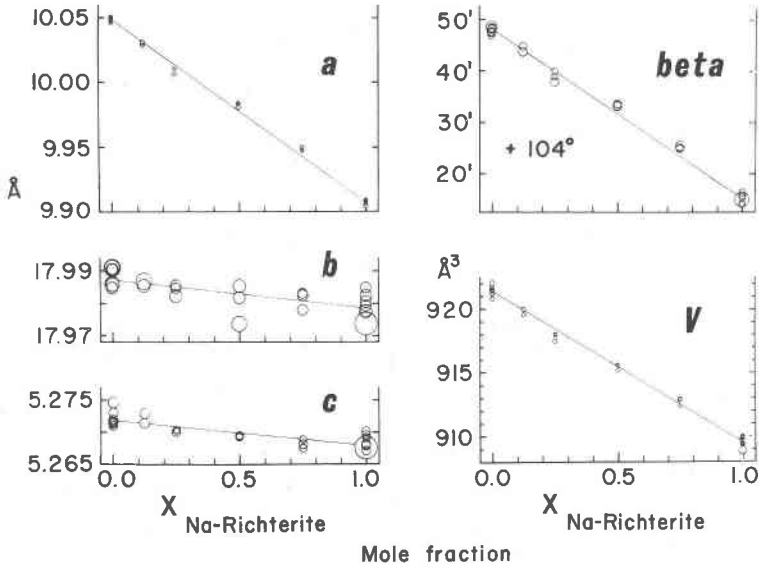

FIG. 1. Cell constants a, b, c, β, and V of richterite as a function of the mole fraction of sodic richterite, $NaNaCaMg_5Si_8O_{22}(OH)_2$, in the potassium-sodium richterite series $(K,Na)NaCaMg_5Si_8O_{22}(OH)_2$. The compositions shown are the intended compositions of the mixes. The radius of each circle is equal to one standard error of the corresponding refined cell parameter. Straight lines are drawn between cell constants of end members to show that the data do not deviate significantly from this linear relationship.

between degrees three and four. A cubic equation was selected as giving the most significant fit of the data. Cell constants b and c show little change with composition and hence greater relative scatter; the standard deviation was similar for all polynomials attempted. Linear equations are presented for b and c.

In addition to the random error associated with the set of cell dimensions (Table 3, Fig. 1) used to determine the regression equations for cell constants (Table 5), systematic errors may be present in the measurements. Uncertainties associated with the preparation of the

TABLE 5. REGRESSION EQUATIONS FOR RICHTERITE CELL CONSTANTS

X = mole fraction K-Richterite, $KNaCaMg_5Si_8O_{22}(OH)_2$; σ = one standard deviation

a, Å $= 9.9072 + 0.2028X - 0.1586X^2 + 0.0971X^3$; $\sigma = 0.0021$

b, Å $= 17.9788 + 0.0085X$; $\sigma = 0.0033$

c, Å $= 5.2680 + 0.0039X$; $\sigma = 0.0012$

β-104°, minutes $= 15.03 + 49.89X - 39.97X^2 + 23.01X^3$; $\sigma = 0.84$

V, Å$^3 = 909.57 + 14.73X - 9.80X^2 + 6.86X^3$; $\sigma = 0.37$

$\overline{V}_{excess}$, cm^3/mole $= -3.10X + 9.80X^2 - 6.86X^3$

mix, which are probably the most important systematic uncertainties, arise from impurities in the reagents, weighing errors, differential loss of constituents during grinding and heating of the mix, and inhomogeneity of the mix. We estimate that the constituents in the prepared mixes are present to within 0.5 weight percent of the amount reported. During amphibole synthesis, there is the possibility that solids are dissolved by the fluid phase. For this reason the amount of H_2O added to the capsule was kept small, commonly 5–10 percent by weight (magnesiorichterite contains 2.2 percent H_2O). The solubility of silicates in water vapor is small. Incongruent dissolution of amphibole in the small amounts of H_2O present will not appreciably effect the composition of the richterite. Finally, if phases other than richterite are present and in total do not have the richterite composition, the richterite must be off composition. Runs used to construct Figure 1 and Table 4 have yields of $\geq 98\%$ richterite. Diopside is the most common accessory phase. Glass is less commonly observed to be present as a thin coating about the richterite grains in dried charges, but is difficult to see in small quantities. It is assumed that the composition of glass+diopside equals that of richterite.

Results of Fluor-Richterite Syntheses

The substitution of fluorine for hydroxyl produces changes in richterite unit cell constants that are similar to the changes due to the substitution of sodium for potassium. Although the hydroxyl-fluorine position 0(3) is not within the *A*-site, both lie in the $a \cdot c$ plane (Fig. 1 of Papike *et al.*, 1969). It was suspected that a fluor-richterite would have a smaller a cell dimension than the corresponding hydroxyl-bearing species. Previous investigations gave conflicting results. Although fluor-magnesiotremolite has a smaller a cell dimension (9.78 Å; Comeforo and Kohn, 1954) than hydroxy-magnesiotremolite (9.833 Å; Colville *et al.*, 1966), and sodic fluor-richterite (Kohn and Comeforo, 1955) has $a = 9.823$ compared with our hydroxy-richterite value of 9.907 Å, both fluor- and hydroxy-edenite have the same value for a, 9.85 Å (Colville *et al.*, 1966; Kohn and Comeforo, 1955). Variation in b and c in these cases is not systematic. In an attempt to clarify these relationships, potassic fluor-richterite and sodic fluor-richterite were were synthesized dry in sealed platinum capsules at 1 atm. These charges were heated above the melting point to about 1200°C, then cooled to 800°C in steps that took several days. Another charge was sealed, dry, in a gold capsule and run at 2 kbar and 818°C. Run products were predominantly fluor-richterite with lesser amounts of glass and traces of diopside. The crystalline products were coarse grained and showed euhedral outlines where in contact with glass (melt).

Fluor-richterite cell constants are tabulated in Table 6. The major results of substituting fluorine ion (radius 1.33 Å,[1] Shannon and Prewitt, 1969) for hydroxyl ion (O^{2-} has radius 1.40 Å,[1] ibid) are a decrease in a (or $a \cdot \sin \beta$) of 0.08–0.10 Å and a concomitant decrease in the unit cell volume. Although the effects are much smaller, b and c also decrease slightly. The angle β does not change significantly. These results show that the substitution of F for OH in the O(3) site has the same effect as substitution of sodium for potassium.[2] We suspect that the unit cell constants a and V for chlor-amphiboles, if such species exist or can be made, will be larger than a and V for hydroxy-amphiboles. Substitution of chlorine for hydroxyl ion has the same effect as substituion of potassium for sodium ions in the A-site.

Present knowledge indicates that if an iron-deficient clino-amphibole has an a dimension in excess of 10.05 Å, it is probably chlorine-rich.

"Iron Richterite"

An iron-rich amphibole, presumably richteritic in composition, was synthesized from a potassic iron richterite mix of bulk composition $KNaCaFe_5Si_8O_{22}(OH)_2$ at 601°C, 1000 bars total pressure, in an aqueous fluid whose hydrogen fugacity was defined by the methane-graphite buffer (Eugster and Skippen, 1967). Pleochroic green and brown clinopyroxene was also present. Amphibole cell constants were refined from the 13 reflections that could be indexed: a 10.172 ± 0.003, b 18.201 ± 0.007, c 5.290 ± 0.002 Å, β 104°32 ± 2′, V 948.2 ± 0.4 Å^3. Of the lattice constants, a, b, c, and V have increased; a and V are the largest known for any clinoamphibole. The substitution of iron for magnesium causes the entire amphibole structure to expand. The large value of a compared with other iron-rich amphiboles suggests that the A-site is at least partially occupied and that this synthetic amphibole is richteritic in composition.

Results of Homogenization Experiments

Mixtures of end-member sodic hydroxy-richterite and potassic hydroxy-richterite were homogenized to demonstrate the absence of a

[1] Effective ionic radii; coordination number = 6.

[2] Hydroxyl—fluorine substitution cannot be confused with potassium-sodium substitution in the case of the analyzed sodic richterite from a meteorite (Olsen, 1967). Olsen's X-ray powder diffraction interplanar spacings were indexed and refined, yielding the unit cell: a 9.832 ± 0.006, b 17.954 ± 0.007, c 5.269 ± 0.004 Å, β 104°21 ± 3′, V 901.2 ± 0.7 Å^3. The a dimension of this sodic richterite is smaller than the a of synthetic sodic hydroxy-richterite. Comparison of the value for a with those for synthetic sodic richterite listed in Table 6 strongly suggests that the O(3) site of this meteorite richterite is fully occupied by fluorine ion ($F_{2.0}$), not ($F_{1.00}OH_{1.00}$) as given by Olsen (who determined the fluorine content by microprobe analysis and assumed the hydroxyl to be present).

TABLE 6. FLUOR-RICHTERITE UNIT CELL CONSTANTS

	a, Å	b, Å	c, Å	β-104°	V, Å^3	R[a]	SEUWO[b]	Method[c]	T, °C	P, bars	Time
Sodic	9.8336(12)	17.9630(20)	5.2621(8)	12.34(79)′	901.09(15)	32/37	0.0140	A3	818	2000	39 days
	9.8255(10)	17.9628(18)	5.2626(9)	13.51(62)′	900.33(15)	46/52	0.0155	A3	1244–791	1	9 days
	9.8280(10)	17.9625(28)	5.2616(10)	14.55(68)′	900.32(18)	38/41	0.0166	A2	1132–843	1	9 days
From data of Kohn and Comeforo (1955)	9.8231(8)	17.9571(12)	5.2671(9)	19.69(54)′	900.18(14)	44/46	0.0110				
Potassic	9.9478(21)	17.9774(37)	5.2666(14)	48.14(1.40)′	910.60(28)	32/36	0.0242	A2	1244–791	1	9 days
	9.9532(13)	17.9812(21)	5.2640(9)	48.87(73)′	910.78(16)	28/30	0.0126	A3	1132–843	1	9 days

[a,b,c] Footnotes are explained in Table 3.

TABLE 7. HOMOGENIZATION EXPERIMENTS

Intended mix Composition	Composition by X-ray	a, Å	b, Å	c, Å	β-104°	V, Å^3	R[a]	SEUWO[b]	Method[c]	T°C	P,10^3 bars	Time
$K_{0.28}Na_{1.72}$	$Na_{1.72}$	9.9533 (14)	17.9791 (20)	5.2691 (7)	25.44 (63)′	913.20 (14)	44/46	0.0164	B	845	1	123 days
$K_{0.26}Na_{1.74}$	$Na_{1.70}$	9.9557 (14)	17.9829 (18)	5.2686 (6)	26.32 (63)′	913.47 (13)	47/49	0.0151	A2	829	1	67
$K_{0.25}Na_{1.75}$	$Na_{1.69}$	9.9566 (21)	17.9847 (25)	5.2695 (9)	25.36 (1.07)′	913.85 (21)	31/32	0.0186	A2	800	1	94
$K_{0.25}Na_{1.75}$	$Na_{1.70}$	9.9573 (16)	17.9782 (19)	5.2683 (7)	26.68 (76)′	913.29 (15)	38/41	0.0154	A2	775	1	90
$K_{0.50}Na_{1.50}$	$Na_{1.51}$	9.9831 (14)	17.9836 (18)	5.2697 (6)	32.36 (80)′	915.79 (15)	31/35	0.0131	A4	819	1	51
$K_{0.58}Na_{1.42}$	$Na_{1.34}$	9.9929 (20)	17.9831 (26)	5.2696 (9)	34.84 (95)′	916.46 (20)	38/40	0.0194	B	829	1	90
$K_{0.70}Na_{1.30}$	$Na_{1.28}$	10.0071 (15)	17.9828 (24)	5.2735 (8)	37.35 (69)′	918.27 (17)	36/39	0.0174	B	829	1	90
$K_{0.72}Na_{1.28}$	$Di_{\frac{1}{2}}Na_{1.24}+Na_{1.00}$	10.0117 (12)	17.9954 (20)	5.2724 (6)	38.08 (65)′	919.08 (14)	35/38	0.0135	B	845	1	123
$K_{0.74}Na_{1.26}$	$Na_{1.17}$	10.0251 (16)	17.9797 (25)	5.2701 (9)	42.67 (1.04)′	918.78 (19)	38/40	0.0192	A2	829	1	67
$K_{0.74}Na_{1.26}$	$Na_{1.13}$	10.0286 (9)	17.9868 (14)	5.2713 (5)	43.26 (39)′	919.63 (9)	41/44	0.0109	A2	775	1	90
$K_{0.74}Na_{1.26}$	$Na_{1.11}$	10.0311 (12)	17.9888 (17)	5.2724 (6)	44.00 (58)′	920.10 (13)	40/42	0.0139	A2	800	1	94

[a,b,c] Footnotes are explained in Table 3.

solvus at selected bulk compositions within the range 775°–845°C. Synthetic sodic and potassic richterites were ground together in the desired proportions. Because it is difficult to remove the water that adheres to the matted richterite grain intergrowth, the synthetic richterites were ground and dried repeatedly until the pasty consistency disappeared and the amphibole could be brushed as a dry powder. 7–50 mg of the mix of two amphiboles were sealed in small gold capsules with, commonly, 10–20 weight percent water.

Results of the homogenization runs are tabulated in Table 7. Two bulk compositions are listed for each run: the bulk composition of the mix calculated from the weighed amounts of amphibole; and the composition of the richterite product determined by using Table 5 and Fig. 1 and measured values of a, β, and V. In view of the difficulty in completely drying matted synthetic richterite, especially sodic richterite, the composition based on weighed amounts of starting material may be erroneous. Compositions based on cell constants are preferred, and are generally slightly more potassic than compositions based on the weighed amounts.

For any homogenized richterite, the three cell constants, a, β, and V used to determine composition from Table 5 and Figure 1 each give similar results. The b and c dimensions are appropriate for stoichiometric richterites. There is no evidence for a deviation from the general compositional formula $(K,Na)NaCaMg_5Si_8O_{22}(OH)_2$.

Homogenization of two richterites to a single richterite phase was successful in most cases. The experiments indicate compositions at which a two-phase region is absent at 1000 bars and the temperature of individual experiments (775°–845°C). If a two-phase region is present at this P and T, it must be restricted to a small range of compositions between the compositions of the runs. A two-phase richterite region could appear at lower temperatures.

Discussion

Sodium substitution for potassium in the A-site of richterite causes a monotonic decrease in a, β, and volume. The effective ionic radius of potassium in 8-fold coordination is 1.51 Å; of sodium, 1.16 Å (Shannon and Prewitt, 1968), a decrease of 0.35 Å or 23%. The substitution causes a to decrease from 10.049 to 9.907 Å, a decrease of 0.142 Å or 1.41 percent. The entire decrease in alkali ion diameter, 0.70 Å, is much greater than the decrease in unit cell edge, and suggests that sodium in the A-site occupies a hole that is relatively large compared to the ionic diameter; sodium does not fit as tightly in the A-site as does potassium.

The change in β as sodium substitutes for potassium is regular; how-

ever, the change is slight, and it is not possible at this time to assign to this change a significance other than stating that the chains slide slightly along their length relative to one another. It is possible that changes in both a and β reflect the split-atom behavior of the A-site alkali; structural refinements of sodic and potassic fluor-richterite are planned to elucidate this behavior.

The b and c cell parameters change very little as sodium substitutes for potassium in the A-position. These cell parameters are sensitive indicators of changes in the tetrahedral and octahedral network occupancy (see Ernst, 1968) and geometry. It is apparent that in richterite, changes in the Na/K of the A-site do not significantly affect the geometry of the tetrahedral chains or the octahedral sheets. The significant change that occurs is that the chains move apart along the a direction.

The unit cell volume changes regularly as Na substitutes for K in the A-site, and the molar volume of mixing is insignificantly small. By analogy with the micas, a significantly large positive excess molar volume, asymmetrically positioned in the series and with the maximum located in potassic compositions, might have been expected (see Burhnam and Radoslovich, 1964, especially Figure 101). In the case of muscovite, the substitution of a small amount of sodium does not change the average six-coordinated alkali-oxygen distance as much as does the substitution of an equivalent mole fraction of potassium in paragonite. The large potassium ions still maintain the separation between the sheets; sodium occupies a site that is similar to but larger than the site it occupies in paragonite. (Similarly, alkali feldspars show a positive molar volume of mixing; Wright and Stewart, 1968; Waldbaum and Thompson, 1968.) In richterite the gradual decrease in $a \cdot \sin \beta$ as the Na/K increases suggests that the A-site collapses gradually as the proportion of Na is increased, and that the mean alkali ion to neighbor oxygen distance varies linearly as a function of composition. One possible explanation of the contrasting mica and amphibole behavior is that the one-dimensional tetrahedral chains of amphibole are weaker and collapsible, whereas the two-dimensional tetrahedral sheet structure of mica does not permit collapse around randomly distributed Na atoms.

Unfortunately, data are not at hand to investigate the possible effects of long or short range order of the Na/K A-site occupancy. It is possible that richterites with intermediate Na/K in the A-site may have regions of high Na/K and regions of low Na/K, and yet appear homogeneous to X-ray powder diffraction methods. In this case there would not be a random distribution of Na and K; there would be regions with the mean alkali-oxygen distance greater than in other regions. It should be noted that the powder pattern reflections (which give information about the

average or mean of the many unit cells sampled) of richterites with both K and Na in the *A*-site are as sharp as the reflections of richterites with the *A*-site occupied entirely by either K or Na. A planned detailed single crystal X-ray diffraction investigation and structural refinement may elucidate this matter, as may transmission electron microscopy.

Substitution of fluoride ion for hydroxyl ion causes a to decrease by 0.08–0.10 Å in richterite. The parameters b and c decrease by a small amount, about 0.01 Å. The fluoride ion is incorporated in the octahedral strip (O(3) position), resulting in a shrinking of the strip. The decrease in a is much larger than the decrease in b and c and is probably caused largely by the absence of hydrogen ion which is located between O(3) and the *A*-site alkali.[1] Without the hydrogen ion the *A*-site alkali can settle more deeply into the ring formed by the SiO_4 tetrahedra of the double chain, permitting the chains to approach one another more closely along the $a \cdot \sin \beta$ direction. Indeed, the fact that a decreases by a large amount suggests that the positioning of the hydrogen is correct.

Geologic Application

Oxburgh (1964) recognized that the potassium in mantle-derived rocks must be accommodated by the mantle in some manner and suggested that the potassium is contained in amphibole. In discussing mantle mineral assemblages, Green and Ringwood (1967) postulate an amphibole-bearing assemblage in the upper mantle. To date the only descriptions of potassium-bearing amphiboles have come from studies of appropriate natural amphiboles. This investigation demonstrates that it is possible to crystallize a synthetic potash-amphibole, richterite. Perhaps the application of suitable experimental techniques will result in the crystallization of other potassic amphiboles, notably edenite, pargasite, and hastingsite. The second planned paper in this series on richterite will describe alkali halide exchange experiments in which sodic richterite was partially or completely exchanged to potassic richterite (see Huebner and Papike, 1970, abstract).

It is of interest to compare the coordination of potassium in richterite with the coordination of potassium in mica. In clino-amphibole, specifically richterite, potassium is surrounded by 8 oxygen neighbors within 3.0 Å (Papike *et al.*, 1969), whereas in mica the coordination is six oxygens within 3.0 Å. (Burnham and Radoslovich, 1964; Güven, 1968). Expressed differently, the mean of the 8 shortest alkali-oxygen distances in potassic richterite is 2.868 Å; for 12 alkali-oxygen distances,

[1] Papike *et al.* (1969) determined the O(3)–H distance to be 0.85 ± 0.07 Å with the O(3)′–H vector lying within the (010) mirror plane and directed nearly perpendicular to the (100) plane of the octahedral strip with angle O(3)–O(3)′-H of 94°.

3.071 Å. In muscovite the mean of the six shortest alkali-oxygen distances is 2.855 Å; for 12 distances, 3.108 Å. This fact indicates that potassium in richterite is more tightly packed into the structure than is potassium in mica. In other words, the molar volume of potassium and its coordination polyhedron is greater in mica than in richterite.

By analogy with the potassium-sodium richterite series, it is possible to predict the molar volumes of potassic pargasite and edenite from the known values for the sodic end members (*A*-site occupied by Na^+). The most important assumption involved is that the geometry of the octahedral and tetrahedral sheets does not change; it has been shown for richterite that this is a good assumption, for only a and β change. Table 8 presents estimated molar volumes for potassic amphiboles; each is 3.55 cm³/mole greater than the molar volume of the sodium analogue calculated from cell volumes reported in Ernst (1968) and this paper.

TABLE 8. ESTIMATED MOLAR VOLUMES OF K-AMPHIBOLES IN CM³/MOLE

K-Richterite	$KNaCaMg_5Si_8O_{22}(OH)_2$	277.5
K-Pargasite	$KCa_2Mg_4AlSi_6Al_2O_{22}(OH)_2$	276.0
K-Ferropargasite	$KCa_2Fe^{+2}{}_4AlSi_6Al_2O_{22}(OH)_2$	283.0
K-Magnesiohastingsite	$KCa_2Mg_4Fe^{+3}Si_6Al_2O_{22}(OH)_2$	277.3
K-Hastingsite	$KCa_2Fe^{+2}{}_4Fe^{+3}Si_6Al_2O_{22}(OH)_2$	283.9
K-Edenite	$KCa_2Mg_5Si_7AlO_{22}(OH)_2$	274.5
K-Ferroedenite	$KCa_2Fe^{+2}{}_5Si_7AlO_{22}(OH)_2$	284.5
K-Eckermannite	$KNa_2Mg_4AlSi_8O_{22}(OH)_2$	274.2

(It must be emphasized that errors in the cell volume of sodic amphiboles will result in erroneous values for the molar volume of potassic amphiboles.)

Using the molar volume data for potassic amphiboles, it is possible to examine the effect of pressure on some reactions between possible mantle phases. The simplest cases involve the equilibrium between amphibole and phlogopite+pyroxene:

$$KCa_2Mg_4AlSi_6Al_2O_{22}(OH)_2 = KMg_3AlSi_3O_{10}(OH)_2 + CaMgSi_2O_6 \cdot CaAlSiAlO_6 \quad (1)$$

K-pargasite	Phlogopite	Pyroxene solid solution[1]
276.0 cm³/mole	149.9	129.2

$$KCa_2Mg_5Si_7AlO_{22}(OH)_2 = KMg_3AlSi_3O_{10}(OH)_2 + 2CaMgSi_2O_6 \quad (2)$$

K-edenite	Phlogopite	Diopside
274.5 cm³/mole	149.9	132.2

Molar volume data for amphiboles are taken from Table 8, for phlogopite from Wones (1963), for diopside from Robie *et al.* (1966), and for pyroxene solid solution from Clark *et al.* (1962). The molar volume of

[1] Diopside and calcium Tschermak's molecule.

reaction indicates that the estimated molar volume of the reactant, K-pargasite, is 3.1 cm^3 per mole smaller than that of the reaction products phlogopite+pyroxene solid solution. Similarly, the estimated molar volume of the reactant K-edenite is 7.6 cm^3 smaller than that of a compositionally equivalent amount of phlogopite+diopside product. Although K-pargasite and K-edenite have not been synthesized and may not be stable, these calculations suggest that high pressures will tend to stabilize potassic amphibole relative to phlogopite+pyroxene, and thus will favor entry of potassium into the amphibole structure.[1] Synthesis of potassic amphiboles might best be attempted at very high pressures. But it must be remembered that the appearance of even denser phases such as garnet and spinel may obliterate the amphibole field entirely at very high pressures.

Note Added in Proof

Two short publications which pertain to the problem of amphiboles in the mantle appeared after we submitted our manuscript. In the summary of a talk entitled "Amphibole-biotite relations," Wones [*Amer. Mineral.* **55,** 295–296 (1970)] discusses criteria for the presence of biotite-pyroxenite and amphibolite as mantle assemblages. Kushiro, in a short paper entitled Stability of amphibole and phlogopite in the upper mantle [*Carnegie Inst. Wash. Year Book,* **68,** 245–247 (1970)] found that the assemblage diopside+phlogopite persisted at 32 kbar.

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[1] Lovering and White (1969) report that a potassic pargasitic amphibole occurs as fragments in the matrix of a basic breccia pipe.

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