

SYNTHESIS AND STABILITY RELATIONS OF RICHTERITE,  
 $\text{Na}_2\text{CaMg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$

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ABSTRACT

Phase relations of the hydrothermally synthesized amphibole richterite were determined in the temperature range 400–970°C at water pressures of 75–750 bars. Richterite is refractory, decomposing at high temperatures and low vapor pressure to a diopside-forsterite-roedderite-melt-vapor assemblage. Above approximately 150 bars, richterite melts incongruently to a diopside-forsterite-enstatite-melt-vapor assemblage. Richterite's unit cell dimensions are:  $a=9.909(1)\text{\AA}$ ,  $b=17.978(5)\text{\AA}$ ,  $c=5.268(1)\text{\AA}$ ,  $\beta=104^\circ13(2)'$ ,  $v=099.9(2)\text{\AA}^3$ .

The substantially higher thermal stability limit of richterite as compared to that of tremolite suggests that the presence of sodium in the *A*-site of the amphibole structure is important in determining amphibole thermal stability limits.

INTRODUCTION

The influence of cationic substitutions on amphibole stability has been demonstrated by the experimental determination of the *P-T* ranges of several amphibole end-members. Ernst (1968) has summarized the phase equilibria studies on amphiboles and has discussed the influence of composition on the stability limits of the amphiboles. Study of the phase relations of richterite,  $\text{Na}_2\text{CaMg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$ , provides a unique opportunity to evaluate the effect of sodium on the thermal stability limit of amphibole. Richterite is related to tremolite,  $\text{Ca}_2\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$  by the substitution  $2\text{Na}\rightleftharpoons\text{Ca}$ . Using the structural formula of amphibole,  $\text{A}_{0-1}\text{X}_2\text{Y}_5\text{Z}_8\text{O}_{22}(\text{OH}, \text{O}, \text{F})_2$ , one Na replaces Ca in the *X* or *M*(4) position with the second Na ion entering the previously vacant *A*-site. By studying richterite, the effect of Na-Ca replacement on amphibole stability can be isolated. In the more chemically complex amphiboles,  $\text{Na}\rightleftharpoons\text{Ca}$  substitution is often coupled with concomitant substitution of other cations such as  $\text{Al}^{+3}$  or  $\text{Fe}^{+3}$ .

Richterite typically occurs in high temperature-low pressure environments. It has been reported from the iron-manganese skarn deposits of Långban (Magnusson, 1930) and occurs in thermally metamorphosed limestones at Iron Hill (Larsen, 1942). Nicholls and Carmichael (1969) report ferrichterite occurrences as phenocrysts and microlites in peralkaline volcanoes. Richterite has been found in two meteorites, a coarse octahedrite (Olsen, 1967a) and the enstatite chondrite, Abee (Douglas and Plant, 1968). It is probable, however, that in both cases, the amphiboles are fluor-richterites, which contain little, if any, water (Huebner and Papike, 1970; Dr. E. Olsen, pers. comm.).

## PROCEDURE

Standard hydrothermal techniques, using cold-seal pressure vessels (Tuttle, 1949) were employed. Water pressure was measured by a Heise gauge. Chromelalumel thermocouples, calibrated against the melting point of NaCl (800.5°C), were used to measure temperature. Temperature and pressure fluctuations were approximately  $\pm 5^\circ\text{C}$  and  $\pm 20$  bars respectively.

Mixtures of reagent grade  $\text{Na}_2\text{CO}_3$ ,  $\text{CaO}$ ,  $\text{MgO}$ , and  $\text{SiO}_2$  in appropriate proportions were used as starting materials in the majority of runs. Several experiments were made using carbonate-free starting material in order to evaluate the effect of  $\text{CO}_2$  on the run products. In all cases, no observable differences were found. All reagents were dried in air to reduce absorbed water. Charges consisted of approximately 30–40 milligrams of starting material plus 2–3 milligrams of water and were sealed in noble metal capsules. Water content was minimized to prevent excessive alkali leaching. Above  $650^\circ\text{C}$ , runs of 24 hour duration produced 90–95 percent richterite with small amounts of unreacted starting material, forsterite, and diopside. However in longer term runs, charges consisted wholly of richterite. Richterite was synthesized at temperatures as low as  $400^\circ\text{C}$ ; however, 3–4 week runs were required to produce 100 percent yields at this temperature. Run products were examined by optical and X-ray powder diffraction methods.

## RESULTS

The high-temperature phase relationships of richterite at fluid pressures between 75 and 750 bars are shown in Figure 1. Experimental data pertinent to Figure 1 are given in Table 1. The experiments were confined to this pressure range because of equipment limitations. At high temperatures and low vapor pressures, richterite melts incongruently to produce a roedderite-diopside-forsterite-melt-assemblage. At relatively greater vapor pressures, richterite decomposes to a diopside-forsterite-enstatite-melt assemblage. The two high temperature anhydrous phase assemblages are separated by the melting curve for roedderite. The intersection of the three univariant melting curves, AC, AD, and AB defines an invariant point, A, at approximately  $145 \pm 10$  bars  $P_{\text{H}_2\text{O}}$  and  $900 \pm 10^\circ\text{C}$ . The positions of the melting curves were first indicated by the presence of anhydrous phases in direct synthesis runs. Curve AD was determined on the basis of reversal runs at 200, 300 and 500 bars. The position of curve AB was based on a set of reversal runs at 85 and 100 bars. The position of the melting curve AC is less accurately known. Very slow reaction rates at low vapor pressures and temperatures less than  $880^\circ\text{C}$  inhibited decay of metastable phases. Therefore the curve is based on the results of the direct synthesis runs. The reversal runs used previously synthesized high and low temperature assemblages and they are indicated by arrows in Figure 1. Decomposition of the anhydrous phases outside their stability field occurred fairly readily; however richterite was a persistent metastable product.

The richterite bulk composition contains five components. Thus the

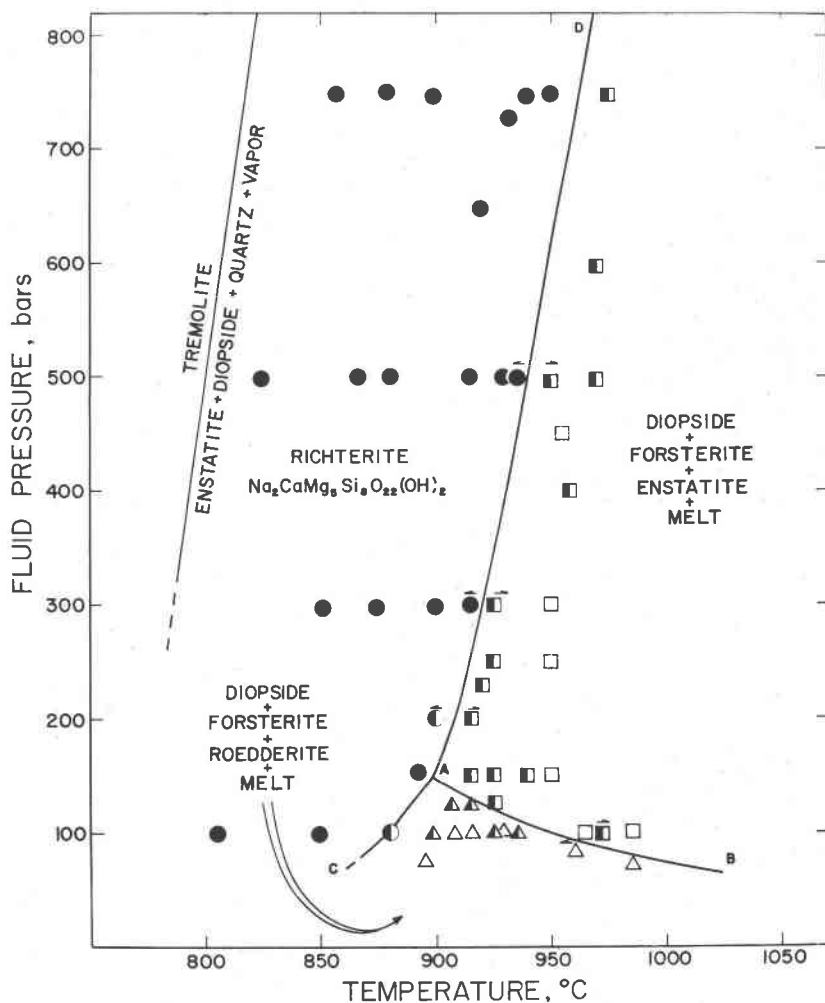


FIG. 1. Phase relations for the bulk composition  $\text{Na}_2\text{CaMg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$  plus excess water. Assemblage symbols: circles = richterite; triangles = diopside + forsterite + an osumilite-type phase + melt; squares = diopside + forsterite + enstatite + melt. All assemblages coexist with vapor. Partial shading indicates the presence of metastable phases. The stability limit of tremolite (Boyd, 1959) is shown for comparison.

phase rule requires that seven univariant curves emanate from the invariant point A. Three of these curves have been defined by the experimental work. The four other reactions were not observed because of the compositional restrictions imposed by using only the richterite bulk composition.

TABLE 1. CRITICAL HYDROTHERMAL RUN DATA FOR THE COMPOSITION  $\text{Na}_2\text{O} \cdot \text{CaO} \cdot 5\text{MgO} \cdot 8\text{SiO}_2$  PLUS EXCESS  $\text{H}_2\text{O}$ . ABBREVIATIONS: R=RICHTERITE, Di=DIOPSIDE, Fo=FORSTERITE, Ro=ROEDDERITE, E=ENSTATITE, M=MELT. PARENTHESES INDICATE PHASES CONSIDERED TO BE METASTABLE. CROSSES INDICATE REVERSAL RUNS.

Starting Material	Temp. (°C)	PH <sub>2</sub> O Bars	Duration (hours)	Phases Present
Mix	940	750	87	R
Mix	950	750	3	R
Mix	975	750	2½	(R)+Di+Fo+E+M?
Di+Fo+E+M	920	650	75	R
Mix	970	600	15	Fo+Di+E+(R)+M
Mix	935	500	49	R+Di?
Di+Fo+E+M	+932	500	38	R(+Di+Fo+M?)
R	+951	500	167	Di+Fo+E+M(+R)
Mix	970	500	27	(R)+Di+Fo+E+M
Mix	955	450	144	Di+Fo+E+M
Mix	957	400	172	Di+Fo+E+M+(R)
Mix	900	300	240	R
Di+Fo+E+M	+915	300	173	R+(Di)
Mix	923	300	43	(R)+Di+Fo+M
R	+925	300	121	Di+Fo+E+M(+R)
Mix	950	300	169	Fo+Di+E+M
Mix	925	250	46	(R)+Di+Fo+E+M
Mix	920	230	44	(R)+Di+Fo+E?
Di+Fo+E+M	+900	200	52	R(+Di+Fo?+M)
R	+917	200	96	Di+Fo(+R)+M+E?
R	895	150	123	R
R	915	150	48	(R)+Di+Fo+M
Mix	925	150	122	Fo(+R)+Di+M
Mix	907	125	17	(R)+Fo+Di+Ro+M?
Mix	915	125	45	Di+Ro+M+Fo?(+R)
Mix	925	125	92	Di+Fo+E+M(+R)
Mix	850	100	140	R
Mix	880	100	192	R+Fo+M+Ro?
R	898	100	157	(R)+Di+Fo+Ro+M
Mix	925	100	25	(R+)Di+Ro
Mix	929	100	126	Di+Ro+Fo+M
Mix	935	100	70	Di+Fo+Ro+M(+R)
Mix	965	100	64	Di+Fo+E+M
Di+Ro+Fo+M	+972	100	73	Di+Fo+E+M
Mix	985	100	360	Di+Fo+M+E?
Di+Fo+E+M	+960	85	97	Di+Fo+Ro+M+E?

## DESCRIPTION OF PHASES

Unit cell dimensions of synthetic richterite are:  $a=9.909(1) \text{ \AA}$ ,  $b=17.978(5) \text{ \AA}$ ,  $c=5.268(1) \text{ \AA}$ ,  $\beta=104^\circ 13(2)'$ ,  $V=909.8(2) \text{ \AA}^3$ . These parameters are in good agreement with the data for synthetic sodic richterites presented by Phillips and Rowbotham (1968) and Huebner and Papike (1970). The unit cell parameters were computed using the program of Evans, Appleman, and Handwerker (1963). At least 15 uniquely indexed reflections, calibrated against the (104) reflection of calcite ( $29.418^\circ 2\theta$ ,  $\text{CuK}\alpha$ ) were used in the computation. No variation in cell dimensions could be detected in richterites synthesized at various  $P$ - $T$  conditions. Therefore, it is assumed that richterite has a constant composition throughout its stability range. The refractive indices are:  $\alpha=1.602(2)$ ,  $\gamma=1.620(3)$ ; the extinction angle,  $Z \wedge c$  is  $16 \pm 2^\circ$ .

The unit cell dimensions of tremolite are:  $a=9.818(5) \text{ \AA}$ ,  $b=18.047(8) \text{ \AA}$ ,  $c=5.275(3) \text{ \AA}$ ,  $\beta=104^\circ 39(3)'$ ,  $V=904.2(6) \text{ \AA}^3$  (Papike, Ross, and Clark, 1969). Comparing these dimensions to those of richterite, it is evident that substitution of Na for Ca in  $M(4)$  and entry of Na into the  $A$ -site produces an increase in  $a$  and  $V$  and a decrease in the  $b$  and  $\beta$  parameters. The small increase  $a$ ,  $0.091 \text{ \AA}$ , relative to the ionic radius of Na, indicates that the  $A$ -site can easily accommodate the Na ion with minimal displacement of the tetrahedral chains in the  $a$  direction. Colville *et al.*, (1966) and Ernst (1968) have shown that the  $b$  dimension is strongly controlled by the radii of the  $X$  and  $Y$  cations which cross-link the tetrahedral chains. However, the closeness of the ionic radii of sodium and calcium in 8-fold coordination,  $1.16 \text{ \AA}$  and  $1.12 \text{ \AA}$  respectively (Shannon and Prewitt, 1968), indicates that the Na-Ca substitution is not responsible for the  $0.069 \text{ \AA}$  decrease in  $b$ . It is possible that the Na in the  $A$ -site deforms the tetrahedral chains in the  $b$ - $c$  plane, producing a decrease in  $b$ .

The unit cell dimensions and refractive indices of the roedderite produced by decomposition of richterite ( $a=10.15(2)$ ,  $c=14.28(2) \text{ \AA}$ ;  $\omega=1.537(2)$ ;  $\epsilon=1.542(2)$ ) are in good agreement with the data for this phase reported by Fuchs *et al.*, (1966) and Seifert and Schreyer (1969). The cell parameters were calculated using only the (0002), (10 $\bar{1}$ 2), (2020), and (0004) reflections. Other reflections of this phase are coincident with reflections of the coexisting diopside and forsterite and were excluded from the calculations. The cell dimensions quoted, therefore, may be of low accuracy. Fuchs *et al.*, (1966), Olsen (1967b), Dodd, *et al.*, (1965), and Bunch and Fuchs (1969) have shown that extensive solid solution within natural members of the osumilite group has little effect on the physical parameters of the minerals. Thus it is possible that the phase produced here may contain substantial amounts of Ca and may have an alkali stoichiometry other than that defined by the 1:5:12 ratio.

## DISCUSSION

The experimental results show that the upper thermal stability limit of richterite substantially exceeds that of tremolite and is slightly less than that of pargasite. The increase in the stability limit of richterite as compared to tremolite is solely attributable to the substitution of two 2Na atoms for one Ca. The resultant structure is generally assumed to have equal Na-Ca distribution in  $M(4)$  and only Na in the previously empty  $A$ -site.

The effects of various cation substitutions on amphibole high temperature stability limits have been considered in detail by Ernst (1968). Comparison of the stability limits of tremolite and glaucophane shows that substitution of Na in  $M(4)$  and Al for Mg in  $M(2)$  results in a slight increase in the decomposition temperature. The stability limit data of pargasite, (Boyd, 1959) demonstrate that introduction of Na into the  $A$ -site plus Al for Si substitution substantially raises the thermal stability limit of the amphibole. Therefore, the comparable thermal stability limits of richterite and pargasite indicate that the presence of Na in the  $A$ -site may greatly influence the amphibole stability field. This had been previously suggested by Ernst (1968, p. 103). The enhanced upper thermal stability limits of amphiboles with fully occupied  $A$ -sites probably results from the cross-bonding of the amphibole chains by the  $A$ -site cation.

The close similarity of the pressure-temperature ranges of richterite and magnesio-richterite [ $\text{Na}_2\text{Mg}_4\text{Si}_8\text{O}_{22}(\text{OH})_2$ ] (Schreyer and Seifert, 1968) suggest that  $\text{Ca} \rightleftharpoons \text{Mg}$  substitution in  $M(4)$  has relatively little effect on the stability ranges of richterites.

The Mg-Fe and calcic amphibole groups as well as the sodic and Mg-Fe groups are apparently separated by miscibility gaps as intermediate compositions between these end-member groups are extremely rare. The suggestion of a solvus condition between calcic and sodic amphiboles, however, is complicated by richterite which is compositionally intermediate. Ernst (1968) has suggested that because richterite typically forms in high temperature-low pressure environments, richterites may represent hypersolvus Ca-Na amphiboles. However, a solvus condition does not exist, at least in the  $P$ - $T$  conditions of this study; there may be extensive  $\text{Na} \rightleftharpoons \text{Ca}$  solid solution between calcic and sodic amphiboles. Thus, the infrequent occurrence of richterite in nature is probably attributable to the scarcity of Ca, Na-rich, Al-poor rocks in nature. The low pressure stability of roedderite is similar to the synthesis conditions of an iron bearing roedderite reported by Ernst (1968). This phase formed as a decomposition product of magnesioriebeckite at vapor pressures less than 500 bars. Occurrences of the isostructural osumilite minerals in

nature are limited to high temperature-low pressure environments. Therefore the presence of minerals with the milarite structure in meteorites suggests that the assemblages containing these phases crystallized under low vapor pressure conditions.

## ACKNOWLEDGMENTS

The advice and criticisms of E. Olsen and W. H. Baur are gratefully acknowledged.

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*Manuscript received, August 30, 1970; accepted for publication, December 23, 1970.*