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SYNTHESIS AND STABILITY RELATIONS OF PREHNITE, $Ca_2Al_2Si_3O_{10}(OH)_2$

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ABSTRACT

Prehnite, $Ca_2Al_2Si_3O_{10}(OH)_2$, was crystallized readily from mixtures of synthetic anorthite+wollastonite+excess H_2O; equilibrium synthesis of prehnite from grossular, zoisite, and quartz in the presence of H_2O was effected only on very long runs. The indices of refraction of synthetic prehnite grown from either starting material (±0.003) are $\alpha=1.615$, and $\gamma=1.642$; the average cell dimensions (±0.01 Å) are $a=4.63$, $b=5.47$, and $c=18.45$ Å.

Stability relations of prehnite were determined using conventional hydrothermal techniques employing mineral mixtures as starting materials. The dehydration reaction (1) prehnite=anorthite+wollastonite+H_2O occurs at 440°±5°C at 1 kbar, 465°±5°C at 2 kbar, 495°±5°C at 3 kbar, 520°±5°C at 4 kbar, and 550°±5°C at 5 kbar. Apparently this reaction is metastable with respect to reaction (2) 5 prehnite=2 zoisite+2 grossular+3 quartz+$4H_2O$, which takes place at 403°±5°C at 3 kbar, 399°±10°C at 4 kbar, and 393° ±5°C at 5 kbar. In the system CaO-Al_2O_3-SiO_2-H_2O, the low-pressure stability limit of prehnite probably is governed by reaction (3) prehnite+Ca-montmorillonite+quartz=2 wairakite+nH_2O which occurs at 320°±5°C at 3 kbar, 350°±5°C at 3.5 kbar, and about 378°C at 4 kbar; for appropriate compositions, the assemblage prehnite+Ca-montmorillonite+quartz is unstable below approximately 2.5 kbar under conditions where aqueous fluid pressure equals total pressure. Equilibrium has been demonstrated for the above three reactions.

The experimental information has been used to calculate the entropy of prehnite and to erect a provisional scheme of phase relations among pumpellyite, prehnite, chlorite, zoisite, and grossular in the presence of excess quartz and fluid in the system CaO-MgO-Al_2O_3-SiO_2-H_2O.

Experimental phase equilibria combined with chemographically deduced relations appear to be compatible with natural occurrences of prehnite in hydrothermal veins, cavities, and amygdules in basaltic rocks and low-grade metaclastic sediments. Stability relations among prehnite, pumpellyite, laumontite, wairakite, and related minerals delineate a petrogenetic grid for various low-grade metamorphic facies in low $\mu(CO_2)$ high $\mu(H_2O)$ environments. The prehnite-pumpellyite facies fills the gap among the zeolite facies, the pumpellyite-actinolite facies, the greenschist facies, and the lawsonite-albite facies and is estimated to be stable at pressure exceeding 2 kbar and temperature range of 250° and 380°C.

INTRODUCTION

Various calcium zeolites, prehnite, and pumpellyite are of importance in diagenesis and low-grade metamorphism. P–T stabilities of laumontite, wairakite, lawsonite, and related minerals in the system $CaAl_2Si_2O_8$-SiO_2-H_2O were experimentally determined previously and their chemographic relations with pumpellyite were discussed in some detail (Liou

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and Ernst, in press; Liou, 1970a, in press). Experimental investigation of prehnite has also been undertaken to determine the physical parameters governing the stability of this mineral and its relations with calcium zeolites. From such studies, hopefully, it will be possible to construct a petrogenetic grid more applicable to the natural occurrences. In the earlier experiments involving synthesis of prehnite, $Ca_2Al_2Si_3O_{10}(OH)_2$, Fyfe *et al.* (1958) and Coombs *et al.* (1959) considered the stability field of prehnite to be limited at high temperature by the reaction prehnite = anorthite + wollastonite + H_2O, and delineated a synthesis boundary for the reaction at about 400°C at 3 kbar and 450°C at 5 kbar. More recently, Strens (1965) suggested that the upper stability limit of prehnite is governed by the reaction 5 prehnite = 2 zoisite + 2 grossular + 3 quartz + $4H_2O$. This suggestion was verified by experimental results performed by Newton (1966): the products of prehnite dissociation reported by Coombs *et al.* (1959), anorthite + wollastonite + H_2O, are metastable phases relative to the assemblages grossular + quartz + H_2O and zoisite + quartz + H_2O. Strens (1968) also located experimentally a P–T point for the upper stability limit of prehnite at $380° \pm 25°C$ at $P_{\text{fluid}} = 2$ kbar and calculated the slope of the univariant curve to be -1000 bars/7°C. Detailed investigation of the high-temperature stability limit of prehnite was undertaken in the present work inasmuch as these previous studies were of a reconnaissance nature.

Reactions governing the transformations among calcium zeolites and prehnite have been suggested (Seki, 1965, 1966; Hawkins, 1967; Albee and Zen, 1969). However, experiments dealing with these relations had not been previously reported, although a knowledge of such equilibria would yield additional information about the maximum pressures to which the calcium zeolites can be stable. In order to approach this problem, the reaction prehnite + Ca-montmorillonite + quartz = 2 wairakite + nH_2O was also experimentally investigated in the present study.

EXPERIMENTAL METHOD

Conventional hydrothermal apparatus and procedures as described in previous reports (Liou, 1970a, b, in press) were used. The charge + excess H_2O were sealed in silver capsules and subjected to the desired conditions. The pressure inside the capsule during the runs was maintained by the excess fluid (closely approaching the composition H_2O), hence $P_{\text{fluid}} = P_{\text{total}}$. Cold seal pressure vessels were calibrated for temperature gradient against the melting point of NaCl (800.5°C). Observed temperature fluctuations in all cases were less than ±5C°. Hydrostatic run pressure was monitored continuously on a variety of gauges calibrated against a 14-inch Heise Boudon tube gauge. Fluid pressure was maintained in individual pressure vessels for periods up to 3 months with fluctuations less than ±20 bars.

Phase relations were determined for two compositions, (1) $2CaO \cdot Al_2O_3 \cdot 3SiO_2$ + excess H_2O (prehnite + fluid), and (2) $CaO \cdot Al_2O_3 \cdot 4SiO_2$ + excess H_2O (prehnite + Ca-montmorillonite + quartz = 2 wairakite + fluid). Equilibrium curves were determined by using mixtures of natural and synthetic minerals consisting of reactants and products in equal proportions or in 9:1 and 1:9 ratios. Natural minerals used in this research were wairakite, prehnite, kaolinite, zoisite, and grossular. Their localities, chemical compositions, and X-ray properties are presented in Table 1. New chemical data for prehnite, grossular, and zoisite presented in this work were obtained by analyzing polished thin sections employing an ARL electron microprobe. Synthetic quartz, anorthite, and wollastonite were prepared from hydrothermally crystallized silicic acid or oxide mixtures of compositions $CaO \cdot Al_2O_3 \cdot 2SiO_2$ and $CaO \cdot SiO_2$, all with excess H_2O in sealed gold capsules at 2000 bars and 600°C for one week. The crystalline materials were examined optically as well as by X-ray diffraction to insure homogeneity.

Nucleation difficulties were overcome by utilizing such crystalline mixtures. The charges were held at constant temperature and pressure until some of the phases had partially or completely decomposed and others had correspondingly increased. However, it was not always possible to demonstrate chemical equilibrium unequivocally because the rate of reaction in one direction, usually in the direction of decreasing temperature, was exceedingly slow at such low temperatures and pressures. Therefore, in many cases the run products had to be rerun under the same conditions before the direction of reaction could be ascertained. The reversible conversion of mixtures of minerals is one of the best and least ambiguous methods of demonstrating stable or metastable equilibrium.

Newton (1966) demonstrated that, where the extent of reaction is not large, the direction of reaction cannot positively be recognized by comparison of diffractometer charts. This difficulty has been encountered in some runs when the starting mixtures were of subequal proportions. However, in the present experiments, the run duration was extended sufficiently so that the growth and disappearance of seeds in 9:1 and 1:9 ratios conclusively demonstrate that the reaction in question has indeed taken place. Several other runs under closely similar P_{fluid}—T conditions were made and the results showed the same reaction direction. Thus, the equilibrium curve has been determined by at least 4 reaction points which are located within a 50°C and 500 bars interval.

Compositions of some phases reported in this paper are projected on the H_2O-free surface as shown in Figure 1 and listed together with their abbreviations in Table 2. The composition of prehnite here considered is restricted to $Ca_2Al_2Si_3O_{10}(OH)_2$, although ferric iron substitution for octahedral Al is important in natural samples (Hashimoto, 1964; Papike and Zoltai, 1967; Surdam, 1969). Phase relations previously discussed in the system $CaAl_2Si_2O_8$-SiO_2-H_2O are restricted to the pseudobinary join quartz-anorthite of Figure 1 (Liou, in press).

EXPERIMENTAL RESULTS[1]

Synthesis of Prehnite. Synthesis of prehnite was achieved from crystalline mixtures of synthetic anorthite and synthetic wollastonite in the presence of seeds of natural prehnite. It crystallized readily in the temperature range 350° to 530°C at pressures above 2 kbar. Below this pressure, anorthite and wollastonite persisted indefinitely. The effect of pressure on the growth of prehnite has long been recognized (Fyfe *et al.*, 1958, p. 169–171). In most runs of 3 days duration, 80 percent of the charge crystal-

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[1] To obtain a copy of Tables 1, 2, and 3, containing tabulated run data, order NAPS Document # 01316 from National Auxiliary Publications Service of the A.S.I.S., c/o CCM Information Corporation, 909 Third Avenue, New York, New York 10022; remitting $.200 for microfiche or $5.00 for photocopies, in advance payable to CCMIC-NAPS.

TABLE 1. CHEMICAL COMPOSITIONS, REFRACTIVE INDICES AND CELL PARAMETERS OF WAIRAKITE, PREHNITE, KAOLINITE, GROSSULAR, AND ZOISITE USED AS STARTING MATERIALS

	Wairakite[1]	Prehnite[2]		Kaolinite[3]	Grossular[4]		Zoisite[5]
		(a)	(b)		(a)	(b)	
SiO_2	54.91	43.70	43.22	45.48	39.79	39.75±0.16	39.54
Al_2O_3	22.75	24.05	24.42	38.84	20.65	21.37±0.36	32.59
Fe_2O_3	0.64	0.93	0.81	0.19	2.09	1.89±0.38	1.87
FeO	0.44	0.03		—			
MnO	0.01	—	—	—	0.13	0.10±0.08	0.14
MgO	0.23	0.11		0.17	0.64	0.43±0.15	0.03
CaO	11.69	26.85	27.55	0.24	37.50	37.26±0.22	24.46
Na_2O	0.60	0.04		0.24			
K_2O	0.31	tr		0.42			
H_2O^+	8.23	4.54	3.88	13.66	—	—	1.34
Total	100.01	100.28	99.88	100.81	100.80	100.80	99.79
α	1.498±0.002	1.61	1.614±0.002	1.561±0.002	1.742±0.002		1.698±0.003
β		1.62	1.623±0.002	1.565±0.002			
γ	1.502±0.002	1.64	1.643±0.002	1.567±0.002			1.708±0.003
a_0	13.65Å		4.64±0.01Å	5.147±0.004Å	11.869±0.001Å		16.212±0.008Å
b_0	13.66Å		5.48±0.01Å	8.939±0.004Å			5.559±0.006Å
c_0	13.56Å		18.46±0.02Å	7.403±0.004Å			10.036±0.004Å
α				91.88±0.06°			
β	90°20′			104.80±0.06°			
γ				89.99±0.06°			

[1] Wairakite from a drill-hole core GO-7 (397.64–398.64m), Onikobe, Japan (Seki, 1966).

[2] Natural prehnite from Prospect, New South Wales: (a) data from Coombs *et al.*, 1959; (b) data from the present work.

[3] Natural kaolinite from Murfreesboro, Arkansas: Chemical composition from Kerr *et al.*, 1950; refractive indices from Main, 1950; and cell parameters from the present work.

[4] Natural grossular from Lake Jaco, Chihuahua, Mexico: (a) data from the present work; (b) data from Murray (C.I.T. Microprobe standard File).

[5] Natural zoisite from Shelburne Falls, Massachusetts: Chemical composition and refractive indices from the present work; Cell parameters from Dollase (1968).

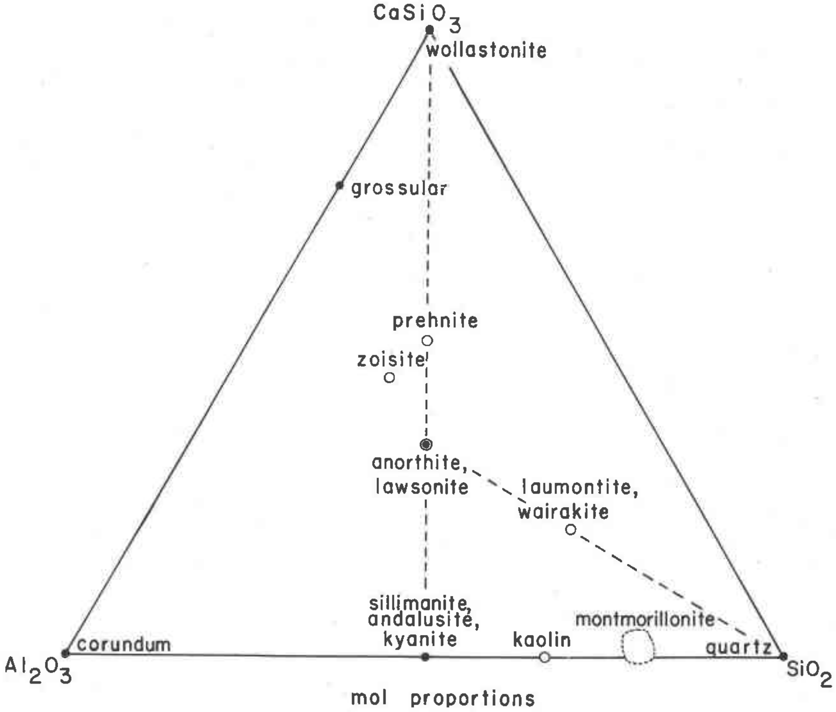

FIG. 1. Crystalline phases in the system $CaSiO_3$-Al_2O_3-SiO_2-H_2O projected onto the water-free face. Solid circles: anhydrous phases; open circles: hydrous phases. Note that the composition of montmorillonite is not well-defined.

lized to prehnite overgrowths. In longer experiments 100 percent prehnite grew readily. Experimental details will be discussed in a later section.

The synthetic prehnite obtained in the present study appears as distinct euhedral crystals with stubby barrel-shaped orthorhombic prisms about 10×15 microns in size. Prismatic crystals show parallel extinction with positive elongation and rather high birefringence. The refractive indices were measured to be $\alpha = 1.615$ and $\gamma = 1.641 \pm 0.002$. Within the error of measurement, the indices of refraction were found to be constant over the range of conditions investigated.

The unit cell dimensions were measured based on 7 peaks; 108, 118, 0.0.10, 119, 130, 217, and 133, using the synthetic quartz 112 line as an internal standard. The results together with data for some natural prehnites are listed in Table 3. It is evident that no systematic correlation exists between the cell edge or volume and the experimental conditions. The average values of $a = 4.63$ Å, $b = 5.47$ Å, $c = 18.45 \pm 0.02$ E, and $V = 468 \pm 0.5$ Å^3 (141.1±0.2 cc/gram formula) are quite close to those of

TABLE 2. COMPOSITIONS AND ABBREVIATIONS FOR SYNTHETIC PHASES AND ASSEMBLAGES

Wr = Wairakite, $CaAl_2Si_4O_{12} \cdot 2H_2O$
Lm = Laumontite, $CaAl_2Si_4O_{12} \cdot 4H_2O$
Lw = Lawsonite, $CaAl_2Si_2O_7(OH)_2 \cdot H_2O$
Zo = Zoisite, $Ca_2Al_3Si_3O_{12}(OH)$
Ka = Kaolinite, $Al_2Si_2O_5(OH)_4$
Am = Amesite, $Mg_4Al_4Si_2O_{10}(OH)_8$
Mt = Montmorillonite, $Al_2Si_4O_{11}(OH)_2 \cdot nH_2O$
Pm = Pumpellyite, $Ca_4MgAl_5O(OH)_3(Si_2O_7)_2(SiO_4)_2 \cdot 2H_2O$
Pr = Prehnite, $Ca_2Al_2Si_3O_{10}(OH)_2$
Gr = Grossular, $Ca_3Al_2Si_3O_{12}$
Wo = Wollastonite, $CaSiO_3$
An = Anorthite, $CaAl_2Si_2O_8$
Qz = Quartz, SiO_2
F = Fluid

( ) = Phase or phases interpreted as metastable

the natural prehnite used for starting material. However, it should be noted that the volume of synthetic prehnite is significantly smaller than that of some natural iron-rich prehnites. Increase in iron content in prehnite tends to increase the cell size and the refractive indices (Deer *et al.*, 1962; Surdam, 1969).

The Reaction: Prehnite + Montmorillonite + Quartz = 2 Wairakite + nH_2O. The most probable reaction relating the transformation of wairakite to prehnite in the system $CaAl_2Si_2O_8$-SiO_2-H_2O has been suggested to be 2 wairakite = prehnite + kaolinite + 3 quartz + H_2O (Seki, 1966). Recent experiments on the stability of Kaolinite + quartz indicate that at 2kbar P_{fluid}, kaolinite + quartz is stable at temperatures less than 320°C (Kornprobls & Velde, 1969) or 380°C (Althaus, 1969). However, in the presence of Ca-bearing phases, such as calcite or calcium zeolites, the recrystallization of kaolinite + quartz to Ca-montmorillonite probably takes place at temperatures lower than 250°C and within the laumonite field, *i.e.*, at temperatures below the wairakite + fluid stability field. This has been verified by previous investigations (*i.e.*, Coombs, 1960a) and in the present study. Therefore, a possible reaction governing the stability relations between wairakite and prehnite is prehnite + Ca-montmorillonite + 3 quartz = 2 wairakite + nH_2O (the value of n depends on the interlayer nature of the montmorillonite).

The condensed charge for the experimental study of the above reaction was made from a mixture of natural prehnite + natural kaolinite + synthetic quartz and natural wairakite in 9:1 and 1:9 ratios. The resultant mixture was relatively unstable and readily converted to prehnite + Ca-montmorillonite + quartz + wairakite. However, these results do not give a conclusive indication as to the position of the reaction. Therefore, the equilibrium data for this reaction are based on rerun synthetic assemblages consisting of prehnite + Ca-montmorillonite + quartz and wairakite in about 9:1 and 1:9 ratios.

The composition of the synthetic montmorillonite produced in these

TABLE 3. UNIT CELL PARAMETERS OF SYNTHETIC AND NATURAL PREHNITES

Run # (Ap)	Experimental Conditions			Unit Cell Parameters			
	Temp (°C)	P_{fluid} (bars)	Duration (hours)	a_0 (Å) ±0.01	b_0 (Å) ±0.008	c_0 (Å) ±0.02	V_0 (Å^3) ±0.8
42	440	3000	746	4.63_1	5.48_1	18.45_6	468.4
29	427	3000	574	4.63_0	5.47_3	18.45_7	468.2
8	400	3000	136	4.63_2	5.47_8	18.45_5	468.3
3	382	3000	161	4.62_7	5.47_6	18.45_8	467.7
44	362	3000	161	4.63_2	5.47_7	18.45_8	468.3
33	516	4000	62	4.62_9	5.47_7	18.45_9	467.9
23	497	4000	75	4.63_3	5.47_7	18.45_2	468.3
24	477	4000	75	4.63_4	5.47_6	18.45_3	468.3
11	443	4000	106	4.63_7	5.46_9	18.45_7	467.9
2	378	4000	237	4.63_2	5.47_6	18.45_3	468.0
37	540	5000	68	4.63_2	5.47_7	18.45_2	468.1
Natural prehnite from Prospect, New South Wales				4.64_1	5.48_2	18.46_3	469.4
Natural prehnite from Africa (Peng *et al.*, 1959)				4.64 ±0.02	5.50 ±0.02	18.40 ±0.06	469.6
Natural prehnite from Radautal, Harzburg (Preisinger, 1965)				4.627 ±0.005	5.490 ±0.005	18.48 ±0.01	469.4
Natural prehnite from Tyrol, Austria (Papike & Zoltai, 1967)				4.646 ±0.002	5.483 ±0.002	18.486 ±0.005	470.9
Natural iron-rich prehnite (4.4–10.3%) from the Karmutsan, B. C. (Surdam, 1969)				4.64	5.49	18.50	470.9

experiments was not determined. Judging from the basal spacing (the 001 spacing is normally 15 Å, about 12 Å after heating treatment at 250°C for 15 hours, or 17 Å on glycolization), small amounts of interlayer Ca are probably present in this phase. The synthetic montmorillonite is evidently not a pure Al-hydrate silicate (*i.e.*, beidellite). The pure Al-type montmorillonite has been synthesized; for this material, the 001 spacing of 11 Å swells to 14 Å with ethylene glycol treatment and collapses to 9.9 Å resulting from air drying at 110°C (Roy and Osborn, 1954, Table 3).

Results of the critical runs are illustrated in Figure 2. It should be noted that the results are based on examination of two sets of paired condensed run products. The squares in the figure represent the results from the unstable starting mixture of kaolinite+prehnite+quartz+wairakite whereas the circles symbolize results from the rerun synthetic assemblages.

Wairakite grew with certainty in all 2kbar experiments where prehnite +montmorillonite seeds disappeared in one of the run charges. In runs at 3kbar and above the equilibrium temperature, most prehnite+montmorillonite+quartz seeds showed a tendency to decrease in amount.

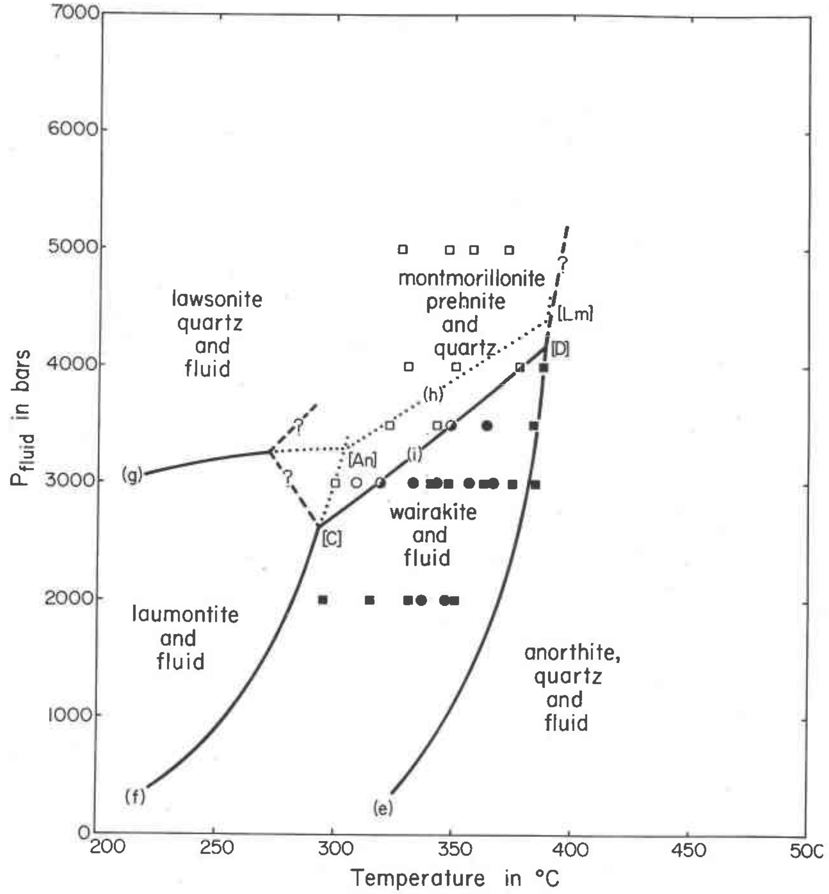

FIG. 2. $P_{fluid}T$ diagram for the equilibrium reaction (i) prehnite+montmorillonite+quartz=2 wairakite+fluid. The reactions (e) wairakite=anorthite+2 quartz+fluid (Liou, 1970b); (f) laumontite=wairakite+fluid, (g) laumontite=lawsonite+2 quartz+fluid, and (h) lawsonite+2 quartz=wairakite (Liou, in press) are also shown. [Lm], [An], [C], and [D] are invariant points. Squares: results from the mixtures of kaolinite+prehnite+quartz+wairakite+excess H_2O; circles: results from the rerun synthetic assemblages.

The reverse is true for those reruns at 5 kbar where prehnite+montmorillonite+quartz grew at the expense of the wairakite seeds. The equilibrium curve passes through 320°±5°C at 3 kbar, about 350°C at 3.5 kbar, and about 378°C at 4 kbar.

Several equilibrium curves discussed elsewhere (Liou, in press) are also presented in Figure 2. Apparently the reaction lawsonite+2 quartz=

wairakite (the dotted line (h)) is metastable with respect to the reaction prehnite+Ca-montmorillonite+quartz=2 wairakite+nH_2O; this latter reaction provides a further restriction on the stability of wairakite at high pressure. The two invariant points, [An], and [Lm], previously reported (see Liou, in press) are therefore metastable where an aqueous fluid phase subjected to the total pressure is present. The presently determined curve together with the upper and lower thermal stability limits of wairakite define two uew invariant points in the system CaO-Al_2O_3-SiO_2-H_2O: invariant point [C] in which laumontite, wairakite, prehnite, and Ca-montmorillonite coexist with quartz and fluid is located at 290°C and 2.7kbar; and invariant point [D] where wairakite, anorthite, prehnite, and Ca-montmorillonite coexist with quartz and fluid is located at about 390°C, 4.2 kbar.

It is interesting to note that the relative stability of a univariant reaction or invariant point appears to be dependent on the starting materials employed in the investigations. In the experiments on the reaction wairakite=lawsonite+2 quartz (Liou, in press), the assemblage prehnite+Ca-montmorillonite was not encountered even though this assemblage is thermodynamically more stable than wairakite+H_2O or lawsonite+2 quartz+H_2O at pressures above those of the equilibrium curve defined by the reaction prehnite+Ca-montmorillonite+quartz=2 wairakite+nH_2O. These and earlier results show that determination of stable equilibrium is difficult to achieve unequivocally within a reasonable length of time, especially in relatively low temperature experiments on mineral mixtures. The metastable equilibrium lawsonite+2 quartz= wairakite was recorded as a stable univariant reaction by Liou (in press). It has been shown that another assemblage is more stable in this P–T range. Further work may show that still other assemblages are more stable. Provided the lowest free energy phases are recognized and their compositions are known, chemographic analysis using Schreinemaker's principle is necessary to depict the relative stabilities of the phases in a system. The detail of such treatment has been discussed in the previous report (Liou, in press).

The Reaction: Prehnite=Anorthite+Wollastonite+H_2O. Experimental investigation of the metastable equilibrium curve for this reaction was carried out using natural phrenite and synthetic anorthite and wollastonite. The condensed starting materials consisted of reactant and product in 1:1 ratios. The growth of prehnite from this mixture to 100 percent was achieved in runs of less than 50 hours at relatively high pressures. For such rapid reactions the possible effect of crystallization during quenching must be considered. In order to test this effect, runs at exactly the same conditions (5–10°C above the equilibrium temperature–near 500°C) were cooled in two different ways: air-quenching, attaining room temperature in about one hour; and water-quenching, achieving room temperature within one minute. There was no observable difference in run products, either in phase proportions or in textures.

The results of the experiments are shown in Figure 3. The reaction was readily reversed over a range of temperatures at several fluid pressures. The best fit of the data yields a nearly straight equilibrium line with a slope of about 1000 bars/30°C.

The influence of pressure in accelerating the reaction is very pronounced. At a fluid pressure of 1000 bars, the change in run products did not exceed 20 percent over a 10 day run duration even at temperatures above 400°C. In contrast, over the same temperature range, almost 100 percent prehnite was obtained in 120 hours from condensed crystalline starting mixes under $P_{\text{fluid}}=3$ kbar (Ap No. 7 and 8). At 3 kbar P_{fluid} experiments of 10 days yielded pure prehnite at temperatures around 360°C (Ap No. 4). As shown in the table the rate of growth or decay of prehnite is exponentially increased as the P_{fluid} is increased. The same pressure effect was also noted by Fyfe *et al.*, (1958) and by Coombs *et al.*, (1959) in synthesizing prehnite from glass mixtures.

It should be noted that the reaction considered, as mentioned previously, is not a stable reaction and therefore the univariant curve presented in Figure 3 can only be considered as a metastable equilibrium boundary. The minimum temperature for the stable co-existence of anorthite+wollastonite is 600°C at 2 kbar P_{fluid} (Newton, 1966). At lower temperatures, grossular and anorthite (low P) or zoisite (high P), are stable in the presence of quartz and fluid (see Figure 4). The failure to synthesize stable assemblages such as grossular+quartz or zoisite+quartz at temperatures above the metastable breakdown of prehnite presumably is due to a nucleation problem for such short experiments. According to Newton (1966), the recrystallization of zoisite or grossular from higher-temperature assemblages (*i.e.*, anorthite+wollastonite+fluid) requires more than one month from a mixture of equal proportions at $P_{\text{fluid}}=2$ kbar.

The experimental demonstration of this metastable reaction is interesting in that the condensed products of prehnite dehydration are anorthite+wollastonite and the metastable dissociation temperature is high above the true equilibrium curve. The reverse reaction was easily obtained. Such experiments reinforce the point that simply the fact of reversibility—especially on short runs—is inadequate to demonstrate true stability (see also Zen, 1967).

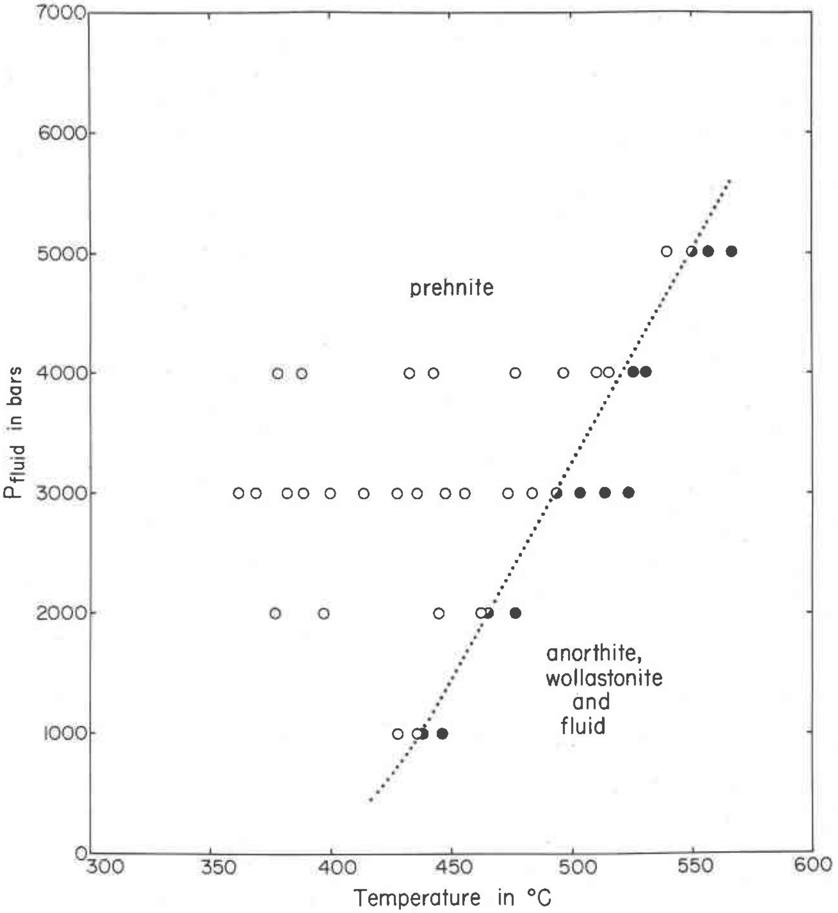

FIG. 3. P_{fluid}-T diagram for the metastable equilibrium prehnite=anorthite+wollastonite+fluid.

Open circles: growth of prehnite from anorthite+wollastonite+fluid; solid circles: growth of anorthite+wollastonite at the expense of prehnite.

The Reaction: 5 Prehnite=2 Zoisite+2 Grossular+3 Quartz+4H_2O. The investigation of this reaction was carried out employing mineral mixtures consisting of reactants and products in 9:1 and 1:9 ratios. The charges containing the two different proportions of reactants and products+excess H_2O were set side-by-side in the pressure vessels. The proportion of the phases in the two charges, although different, yield the same bulk composition $2CaO \cdot Al_2O_3 \cdot 3SiO_2$+excess H_2O (prehnite+H_2O).

The effect of pressure in accelerating the reaction is pronounced. The total disappearance of prehnite seeds took place in some 2 month experiments at $P_{\mathrm{fluid}}=5$ kbar. However, in the runs of similar temperatures and durations at 3 kbar P_{fluid}, the change in run products proceeded to only about 3 to 7 percent. It is clear that the reaction takes place at an exceedingly slow rate at low pressures. It should be noted that none of the charges has shown total disappearance of grossular, zoisite, and quartz seeds. Moreover, in some run products, the diminished peak heights of grossular, zoisite, and quartz are not in the stoichiometric proportions for the reaction: 2 grossular+2 zoisite+3 quartz+$4H_2O \rightarrow$5 prehnite. Thus, special care had to be taken in detecting the reversal reaction, and charges under P–T conditions in the vicinity of the equilibrium curve were run long enough to ensure that reaction had indeed taken place. Microscopic examination of the paired run products demonstrated that no other phase than those here considered had formed.

The equilibrium temperature was located at $P_{\mathrm{fluid}}=3$ kbar first. Knowing the approximate $P_{\mathrm{fluid}}-T$ location, the equilibrium curve at $P_{\mathrm{fluid}}=5$, 4, and 2 kbars was then determined. The preliminary results on the basis of new runs at 5 kbar has been shown as curve K in Figure 8 of Liou (1970b). Further extensive and longer duration experiments have revised that curve and the results are plotted as circles in Figure 4. The triangles are results from Strens (1968), who used natural iron-rich (5 percent Fe_2O_3) prehnite seeded with zoisite as starting material. The stable univariant equilibrium curve in the iron-poor system has a $P_{\mathrm{fluid}}-T$ slope about -1000 bars/4°C and is located at these $P_{\mathrm{fluid}}-T$ points: $403° \pm 5°$C and 3000 bars, $399° \pm 10°$C and 4000 bars, and $393° \pm 5°$C and 5000 bars. The large negative volume change for solid ($\Delta V_s = -112$ cc/mole) with respect to the volume of fluid at 400°C, 3000 bars ($4 \cdot V_{\mathrm{fluid}} = 84.7$cc) for this reaction may account for the steep negative slope of the equilibrium curve. Apparently the upper stability limit of prehnite is about 100°C lower than that defined by the metastable equilibrium prehnite = anorthite + wollastonite + H_2O which is also shown in Figure 4.

The identification of the energetically possible reactions and distinction between stable and metastable reactions are important. The assemblage relationships shown in Figure 4 obtained from the present and Newton's results (1966) can be illustrated in an isobaric G–T plot to explain the observed phase equilibria. The Gibbs free energies of 4 possible assemblages, (a) 10 prehnite, (b) 4 zoisite+4 grossular+6 quartz+fluid, (c) 5 (anorthite+grossular+quartz+$2H_2O$), and 10 (anorthite+wollastonite +H_2O), are plotted schematically against temperature at $P_{\mathrm{fluid}}=3$ kbar in Figure 5. Prehnite has been shown to be stable at temperature below T_{e1} (400°C); anorthite+grossular has been experimentally determined to

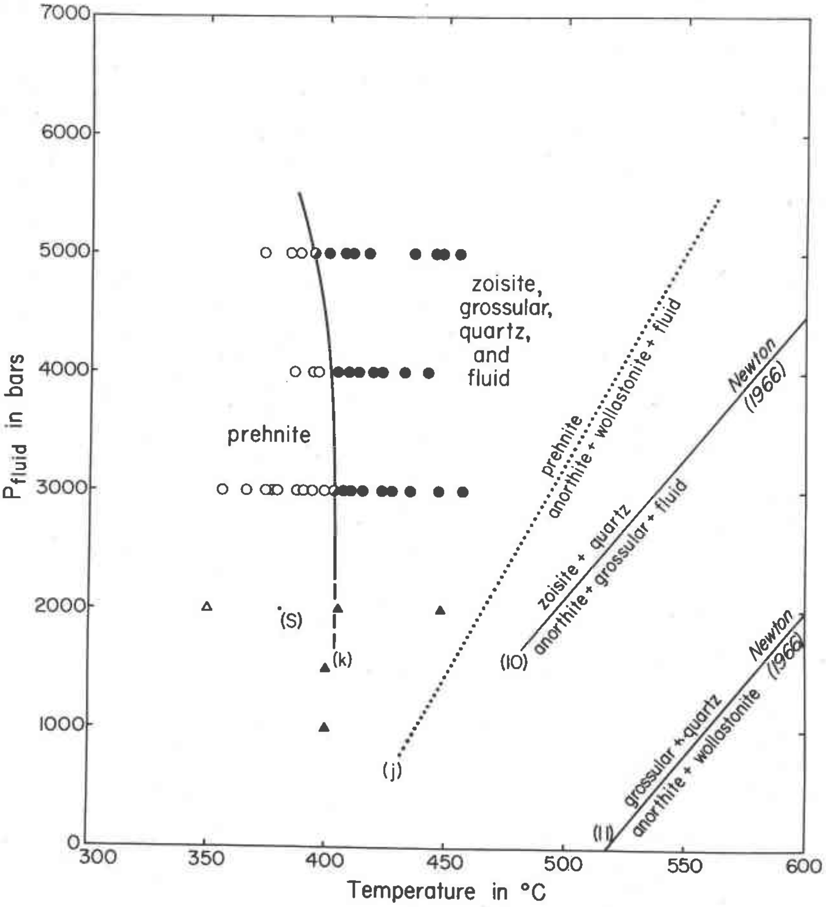

FIG. 4. P_{fluid}-T diagram for equilibrium (k) 5 prehnite=2 zoisite+2 grossular+3 quartz+fluid.

The metastable equilibrium (j) prehnite=anorthite+wollastonite+fluid (from Figure 3), the stable equilibria (10) zoisite+quartz=anorthite+grossular+fluid and (11) grossular +quartz=anorthite+wollastonite (from Newton, 1966) are also shown. Circles: results from the present study; triangles: results from Strens (1968). The point (S) is the equilibrium point located by Strens.

be a stable assemblage in between Te_2 (535°C) and Te_3 (660°C); and anorthite+wollastonite above Te_3 (660°C) (Newton, 1966). The assemblage grossular+zoisite+3 quartz+fluid is stable inbetween Te_1 and Te_2. From combinations of these four assemblages, 3 metastable and 3 stable equilibria are immediately obvious, as shown in Figure 5. Prehnite may persist metastably at temperatures above T_{e1} and at and above T_{m1}

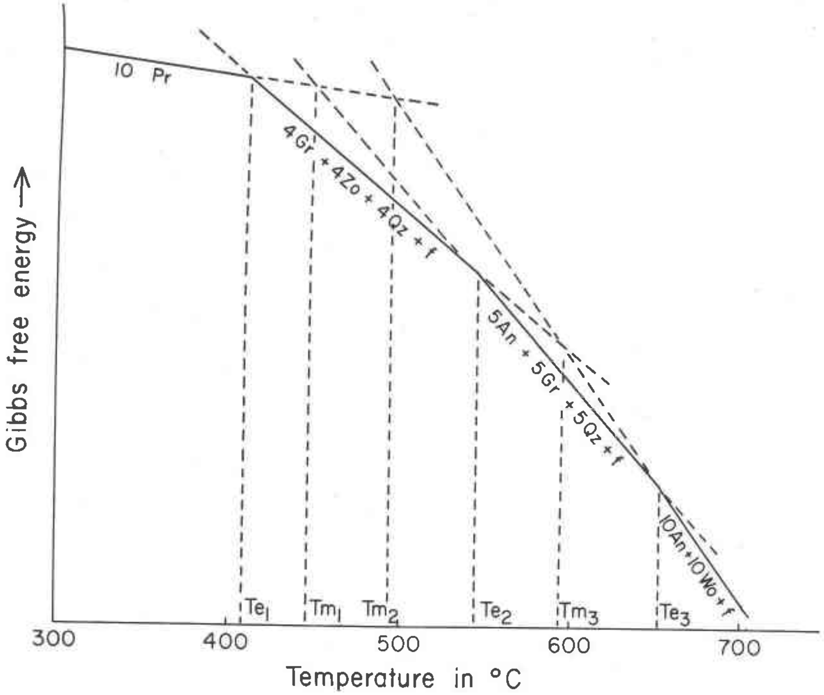

FIG. 5. Schematic isobaric *G-T* diagram illustrating stable and metastable equilibria for the prehnite bulk composition. Te_1, Te_2, and Te_3 are stable equilibria and Tm_1, Tm_2, and Tm_3 are metastable equilibria (temperatures are partly taken from the data plotted in Figure 3 and 4 at 3 kbar P_{fluid}).

prehnite may break down according to the reaction 2 prehnite = grossular + anorthite + quartz + $2H_2O$. Similarly, anorthite + wollastonite + fluid could develop metastably from prehnite at temperatures above Tm_2 and from grossular + zoisite + quartz above Tm_3. The equilibrium prehnite = anorthite + wollastonite + H_2O, taking place at Tm_2 (495°C) is clearly metastable. Given a sufficiently long time—which may be beyond reasonable experimental possibility—both assemblages may first transform to anorthite + grossular + quartz and eventually to grossular + zoisite + quartz + fluid. Therefore, the upper thermal stability limit of prehnite can only be defined by the equilibrium Te_1, which occurs at 403°C and 3000 bars.

THERMODYNAMIC CONSIDERATIONS

Entropy of Prehnite. The entropy of prehnite has not yet been measured calorimetrically. A value at 465°C, 2 kbar, can be computed from the slope

1000 bars/30°C of the metastable reaction prehnite = anorthite + wollastonite + H_2O, using known entrophy values of anorthite, wollastonite, and H_2O (Kelley, 1960; Sharp, 1962; Robie, 1968; Burnham, *et al.*, 1969) and assuming that the volume change for the solids is independent of temperature. Applying the Clapeyron equation, $dP/dT = \Delta S/\Delta V$, the calculated entropy at this temperature and pressure is about 164 ± 2 entrophy units (e.u.). This figure is quite comparable to the value of 160.3 e.u. estimated by adding together the entropies of the constituent oxides and applying a volume correction of 0.6 e.u./cc. (Fyfe *et al.*, 1958, p. 34). The close agreement between these two estimations lends confidence to the accuracy of the present experimentally determined curve.

Stability of Mg-Pumpellyite. In order to consider the possible paragenetic relationships involving prehnite- and pumpellyite-bearing assemblages, a graphical analysis using Schreinemaker's principle was discussed and the reaction 2[prehnite+kaolinite] [2 pumpellyite+kaolinite]+2 quartz $+H_2O$[1] was suggested in a previous report (Liou, 1970a, in press). This treatment was made assuming that (1) pumpellyite possesses the ideal composition of $Ca_2Al_3\ (SiO_4)\ (Si_2O_7)\ (OH)_3$, and (2) the composition of [2 pumpellyite+kaolinite] and [prehnite+kaolinite] lie in the plane anorthite-quartz-H_2O. However, in view of the fact that Mg, Fe_3^+, and Fe_7^+ are ubiquitous in natural pumpellyites (Gottardi, 1965; Galli and Alberti, 1959), these assumptions cannot be strictly correct.

The probable reaction relating the transformation of iron-free pumpellyite to prehnite has been suggested by Seki (1965) as

$$\begin{aligned}&\underset{\text{pumpellyite}}{4Ca_4MgAl_5(Si_2O_7)_2(SiO_4)_2O(OH)_3\cdot 2H_2O} + \underset{\text{quartz}}{2SiO_2}\\ &\quad = \underset{\text{prehnite}}{8Ca_2Al_2Si_3O_{10}(OH)_2} + \underset{\text{chlorite (amesite)}}{Mg_4Al_4Si_2O_{10}(OH)_8} + 2H_2O \qquad \text{(a)}\end{aligned}$$

Recently, Hinrichsen and Schürmann (1969) have experimentally located this equilibrium at 265° ± 10°C at 5.5 kbar and 250° ± 10°C at 7 kbar with a steep negative d*P*/d*T* slope. Furthermore, the equilibrium dehydration of magnesian pumpellyite

$$\begin{aligned}&\underset{\text{pumpellyite}}{20Ca_4MgAl_5O(OH)_3(Si_2O_7)_2(S_iO_4)_2\cdot 2H_2O}\\ &\quad = \underset{\text{zoisite}}{16Ca_2Al_3Si_3O_{12}(OH)} + \underset{\text{grossular}}{16Ca_3Al_2Si_3O_{12}} \qquad \text{(b)}\\ &\qquad + \underset{\text{chlorite(amesite)}}{5Mg_4Al_4Si_2O_{10}(OH)_8} + \underset{\text{quartz}}{14SiO_2} + \underset{\text{fluid}}{42H_2O}\end{aligned}$$

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[1] The net reaction should be 2 Pr+Ka = 2 Pm+2 Qz+H_2O.

was also experimentally determined at 310° ± 10°C at 5.5 kbar and 325° ± 10°C at 7 kbar (Hinrichsen and Schürmann, 1969). Their results, shown as thick solid lines in Figure 6A, indicate that prehnite should be stable at temperatures less than 300°C and an invariant point was tentatively located at about 290°C and 4.3 kbar P_{fluid}.

The compositions of prehnite, grossular, zoisite, Mg-pumpellyite, and Mg-chlorite (amesite) are listed in Table 2 and plotted in the pseudoternary diagram Al_2O_3-CaO-MgO with excess H_2O and SiO_2 (Figure 6A). The association of these five phases (in the presence of quartz and fluid) in this system defines as invariant point where reactions (a), (b) and

$$\underset{\text{prehnite}}{5Ca_2Al_2Si_3O_{10}(OH)_2} = \underset{\text{zoisite}}{2Ca_2Al_3Si_3O_{12}(OH)} + \underset{\text{grossular}}{2Ca_3Al_2Si_3O_{12}} + \underset{\text{quartz}}{3SiO_2} + \underset{\text{fluid}}{4H_2O} \qquad \text{(k)}$$

intersect. The reaction (k) was experimentally located and discussed in detail in the present paper.

However, the $P_{\mathrm{fluid}} - T$ loci of these three reactions from Hinrichsen and Schürmann (1966) and the present studies are apparently in disagreement. The upper stability limits of laumontite and wairakite have been determined (Liou, 1970a, b, in press; Liou & Ernst, in press) and shown in Figure 6. If one accepts these results, wairakite would have a much higher thermal stability field and such sequences as laumontite+chlorite→prehnite+chlorite (without pumpellyite)→lawsonite+chlorite should be common in an area of very low geothermal gradient. However, such a paragenesis has been recorded *only* in the Upper Permian rocks of South Island, New Zealand (Landis, 1969). In contrast, laumontite +chlorite→pumpellyite+chlorite (or pumpellyite+prehnite)→lawsonite+chlorite and luamontite→wairakite→prehnite zonations are common. Lawsonite is restricted to lithologic sections of relatively low geothermal gradient and wairakite is restricted to those of relatively high geothermal gradient. Thus, the phase relations shown in Figure 6A from Hinrichsen and Schürmann (1969) do not seem to be any more compatible with the field observations than with the present experimental results.

An alternative arrangement of these three reactions deduced from the present study and the calculated dP/dT slope for the reaction (a) (about 30 bars/C°) is plotted in Figure 6B. The invariant point, which has not been located experimentally, should lie on the presently determined curve (k). From Figure 6B, it is apparent that the formation of Mg-pumpellyite requires higher pressure over considerable range of temperature than for many other hydrous Ca-Al silicates, thus explaining the stable associa-

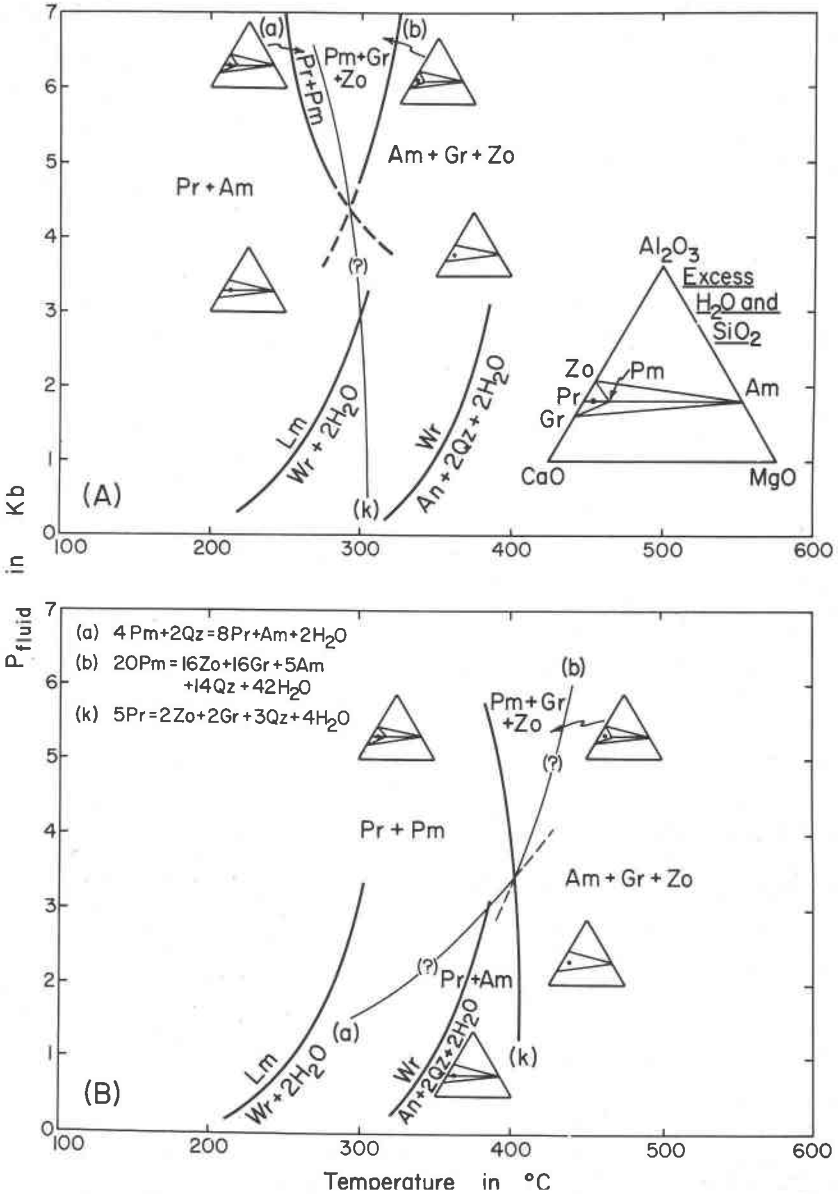

FIG. 6. Schematic phase relations of pnumpelyite, prehnite, chlorite (amesite), zoisite, and grossular in the presence of quartz and fluid in system CaO-MgO-Al_2O_3-SiO_2-H_2O from the results of Hinrichsen and Schürmann (A) and the present study (B). The compositions of these phases are shown in Table 2 and are plotted in pseudoternary diagram Al_2O_3-CaO-MgO (with excess SiO_2 and H_2O). The reactions (a) 4 pumpellyite+2 quartz=8 prehnite+amesite+$2H_2O$, and (b) 20 pumpellyite=16 zoisite+16 grossular+5 amesite +14 quartz+fluid are experimentally determined by Hinrichsen and Schürmann (1969); the reaction (k) 5 prehnite=2 zoisite+2 grossular+3 quartz+fluid is from the present study. The upper stability limits of laumontite and wairakite (Liou, 1970b, in press; Liou & Ernst, in press) and the stable assemblages for the composition are also shown. (see Table 2 for abbreviations used).

tion lawsonite-pumpellyite (+chlorite). (Iron-rich pumpellyite may be stable at much lower pressures as indicated by pumpellyites of deuteric origin (Raam *et al.*, 1969; Mason, 1969) and the pumpellyite+wairakite association (Surdam, 1969). The broad *P-T* field for the coexistence of pumpellyite-prehnite in Figure 6B may account for the common association of these two phases. This diagram also illustrates the observed direct passage from lawsonite- to prehnite+pumpellyite- assemblages in Southern New Zealand (Coombs, 1960b). Moreover, the metamorphic sequence of laumontite$<$wairakite→prehnite resulting both from deep burial and igneous intrusion has been increasingly recognized (Wise, 1959; Fiske *et al.*, 1963; Seki *et al.*, 1969). In metamorphic terrains with normal geothermal gradients, the mineral zonations are characterized by laumontite+chlorite→prehnite+chlorite→prehnite+pumpellyite (or pumpellyite+chlorite)→pumpellyite+epidote (±actinolite) with increasing depth of burial (*e.g.*, Seki, 1969). Therefore, the proposed prehnite-pumpellyite relationship shown in Figure 6B appears to be consistent with field observations.

GEOLOGIC APPLICATION

Petrogenesis. Prehnite occurs as a hydrothermal mineral in veins, cavities, and amygdules of mafic volcanic rocks, as a secondary mineral after plagioclase, as a serpentinization product in rodingite, and as a low-grade contact metamorphic mineral in mafic and calcareous sediments (for detailed references see Deer *et al.*, 1962; Seki, 1965). It has also been reported as a common product of burial metamorphism of pyroclastics, graywackes, and spilites and has been used as an index mineral for delineating the prehnite-pumpellyite metamorphic facies intermediate between the zeolite and the greenschist facies (Coombs *et al.*, 1959; Brown and Thayer 1963; Hawkins, 1967; Smith, 1969; Coombs *et al.*, 1970; Coombs, in preparation).

One distinctive feature in low-grade metamorphic sequences is the common association of prehnite (±quartz) with calcium zeolites or with pumpellyite. The difference in CaO/Al_2O_3 ratios among these phases may account for these contrasting assemblages. Moreover, prehnite is known to carry an appreciable amount of Fe^{3+} in octahedral sites occupied chiefly by aluminum (Papike and Zoltai, 1967; Surdam, 1969). The maximum substitution of Fe^{3+} may be up to 10 weight percent Fe_2O_3, the phase approaching the composition $Ca_2Fe^{3+}AlSi_3O_{10}(OH)_2$. Therefore, the stability field of $Fe_3{}^{+}$-prehnite may overlap those of laumontite and wairakite in rocks of appropriate bulk composition (*i.e.*, $CaO/Al_2O_3>1$). Oxygen fugacity must significantly influence the Fe-prehnite stability field. The coexistence of wairakite and Fe-prehnite or laumontite and

Fe-prehnite in $P_{\text{fluid}}-f_{O_2}$ space therefore might cover a considerable range of physical conditions.

The occurrence of prehnite in hydrothermally altered gabbroic rocks has been described extensively (Watson, 1942, 1953; Bloxam, 1954; Bilgrami and Howie, 1960; Bilgrami, 1963). The plagioclase is replaced by grossular or hydrogrossular and subordinate zoisite whereas pyroxene has decomposed chiefly to chlorite. Prehnite occurs as discrete patches or as veins of variable thickness. In some cases, zoisite is intimately penetrated by a network of prehnite veinlets in zoisite-prehnite rocks (*e.g.*, 83% zoisite, 15% prehnite and 2% actinolite), as described by Watson (1942). From these field and petrographic observations, prehnite evidently is stable at lower temperatures than zoisite-grossular. The reaction 5 prehnite-2 zoisite+2 grossular+3 quartz+fluid, determined as part of this study, defines the maximum temperature for crystallization of prehnite at 403°C at 3 kbar and 393°C at 5 kbar. However, it should be borne in mind that lime-rich hydrothermal solutions probably contain a considerable amount of CO_2 (Watson, 1953; Bloxam, 1954; Bilgrami, 1963). The presence of CO_2 decreases the activity of H_2O by dilution and also tends to fix calcium in a carbonate phase. Thus, the dehydration curve would be deplaced toward lower temperatures and the prehnite-calcite (-chlorite) assemblage of the rodingite forms probably at temperatures much less than 400°C at $P_{\text{fluid}}=3$ kbar. Moreover, the most probable reaction governing the formation of prehnite in alterated gabbroic rock would be 2 zoisite+3 quartz+2 calcite+$2H_2O=3$ prehnite $+2CO_2$.

Occurrences of prehnite in well-studied geothermal areas are relatively uncommon. In bore hole No. 11 of Wairakei, New Zealand, prehnite is accompanied by adularia and sphene through a short vertical range (Coombs *et al.*, 1959). Prehnite has also been described in detail in the Pauzhetka geothermal wells, Kamchatka Peninsula (Rusinov, 1965). In altered clastic tuffs, prehnite with laumontite is extensively developed at depths of 300–750 m and at temperatures of 150°–200°C. In these rocks, the association of prehnite with quartz was not found. On this basis, Rusinov (1965) concluded that the transition of laumontite to prehnite should occur at temperatures above 200°C. Prehnite developed in a geothermal aureole surrounding Ata volcano, Japan (at depth 200–600 m) was also reported by Seki (1965).

The rarity of prehnite, in contrast to extensive development of wairakite in geothermal areas probably reflects its limited stability under these conditions. Hydrothermal study of the prehnite bulk composition indicates that high pressures favor the formation of prehnite simply by increasing the rate of growth. However, high pressures are not required for its stability in a rock approaching its own bulk composition. So far prehnite has been synthesized at $P_{fluid} = 1000$ bars and its stability field may extend to lower pressures. Thus, in low $\mu(CO_2)$ environments where CaO is present in excess ($CaO/Al_2O_3 > 1$) relative to the wairakite composition, prehnite may be stable in geothermal areas and associated with calcium zeolites. However, in environments where bulk compositions have $CaO/Al_2O_3 \leq 1$ (*e.g.*, wairakite composition), prehnite is probably limited to moderate pressures (say above P_{fluid}) by reaction wairakite+fluid = prehnite+Ca-montmorillonite+quartz or laumontite = prehnite+kaolinite+quartz+fluid.

Prehnite-Pumpellyite Facies. Coombs *et al.*, (1959) recognized a broad non-zeolitic transition zone characterized by prehnite and pumpellyite between the zeolite and the greenschist facies. This paragenetic stage was named the prehnite-pumpellyite metagraywacke facies by Coombs (1960a, p. 342) or the prehnite-pumpellyite facies by Seki (1961). Since the works of Coombs and Seki, reports of prehnite-, and pumpellyite bearing rocks have been numerous (Brown, 1961; Dickinson, 1962; Hashimoto, 1966; Hawkins, 1967; Vance, 1968; Smith, 1969; Coombs *et al.*, 1970; Coombs, in preparation). Coombs *et al.* (1970, Figure 2) delineated the prehnite-pumpellyite facies boundaries in a schematic $\mu(CO_2) - \mu(H_2O)$ diagram at arbitrary P and T. The reaction 5 prehnite = 2 zoisite + 2 grossular + 3 quartz + $4H_2O$ was taken as approximating the upper temperature limit of the prehnite-pumpellyite facies whereas the reaction 2laumontite = prehnite + kaolinite + 3 quartz + $5H_2O$ was used to limit the boundary between the zeolite and the prehnite-pumpellyite facies.

On the basis of the present experimental results, the high temperature stability limit of prehnite is 403°C at 3 kbar and 393°C at 5 kbar where fluid pressure equals total pressure. In natural environments where P_{H_2O} is less than P_{total}, the upper thermal stability limit of prehnite should be lower. Moreover, in more complex reactions such as chlorite + prehnite + quartz = actinolite + epidote + H_2O, prehnite should disappear at still lower temperatures. The transition of laumontite to prehnite is suggested to occur at temperatures above 200°C (Rusinov, 1965). Therefore, a range of conditions from about 250°C to 380°C at 3 kbar might be a reasonable estimate for the stability field of the prehnite-pumpellyite facies. At increasing values of $\mu(CO_2)$ these boundaries would be progressively displaced toward lower temperatures. At sufficiently high values of $\mu(CO_2)$ a clay carbonate assemblage would be stable under physical conditions between those appropriate to the greenschist facies and those of unmetamorphosed sediments (Zen, 1961; Albee and Zen, 1969; Coombs *et al.*, 1970).

The association prehnite-pumpellyite has been reported in clastic rocks which have been buried to a minimum depth of about 3km (Otalora, 1964) and the assemblages quartz-prehnite-chlorite and/or quartz-albite-pumpellyite-chlorite appear to be stable down to a depth of about 16km (Brown, 1961; Hay, 1966). The depth range would be equivalent to pressure of about 1 to 4 kbar. The prehnite-pumpellyite bearing graywacke-shale series in Mount Olympus, Washington, is estimated to have crystallized over a temperature range of 300° to 380°C and 2 to 3.8 kbar P_{fluid} (Hawkins, 1967). These field observations are compatible with the present laboratory determinations.

Facies Series. The petrogeneses for zonations of Ca-zeolites, prehnite, pumpellyite, lawsonite, and related minerals in the system $CaAl_2Si_2O_8$-SiO_2-H_2O in certain sections of geosynclinal sediments and volcanic rocks have been discussed in detail previously (Liou, in press). The similar zonations consistently found in a variety of environments have been determined to be dependent on the geothermal gradient, burial depth, and mineralogical and chemical compositions of the parental rocks. The modified petrogenetic grid for the low-grade metamorphic facies now to be presented is proposed in light of the stability of prehnite (Figure 4) and the chemographic relations in the system MgO-CaO-Al_2O_3-SiO_2-H_2O (Fig. 6B).

Experimental studies have indicated that the stability fields of the index minerals change with the composition and with the chemical potential of H_2O, O_2, and CO_2 (Coombs *et al.*, 1959, 1970; Liou, 1970a,b). The maximum *P–T* fields for various low-grade metamorphic facies and the four facies series (Seki, 1969; Coombs, in press) are shown in Figure 7. The *high* pressure type of low-grade metamorphism (curve 1) (the Franciscan terrain of California and the Kanto Mountains of the Sanbagawa terrain, Japan) is characterized by the sequence laumontite→pumpellyite→lawsonite→jadeite. The sequence for the *intermediate* pressure type such as the alpine belt of New Zealand and Central Kii Peninsula, Japan (curve 2) is heulandite+alalcime→laumontite+albite→prehnite+pumpellyite→pumpellyite+actinolite. The *lower* pressure type (curve 3) (Tanzawa Mountains, Japan, and Mount Rainier, Washington), is characterized by the sequence heulandite→laumontite→wairakite→prehnite→actinolite. The zonation for the *lowest* pressure type in active geothermal areas (curve 4) is mordenite→laumontite→wairakite. Most of these paragenetic sequences may be found as characteristic of contrasting *P–T* trajectories in Figure 7.

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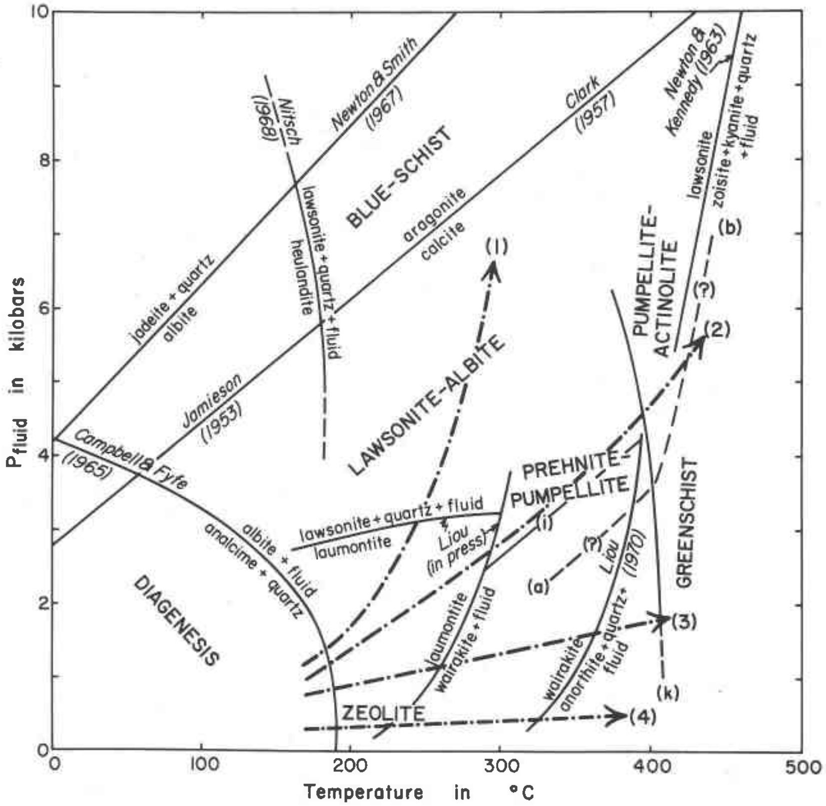

FIG. 7. P_{fluid}-T diagram showing possible fields of low-grade metamorphic facies and P-T trajectories in various types of metamorphism: (1) the high pressure type, (2) the intermediate pressure type, (3) the low pressure type, and (4) the lowest pressure type. The reactions (i) prehnite+Ca-montmorillonite+quartz=2 wairakite+fluid, and (k) 5 prehnite =2 zoisite+2 grossular+3 quartz+fluid are from Figures 3 and 5. The reactions (a) and (b) are from Figure 6 (B).

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