THE AMERICAN MINERALOGIST, VOL. 54, JANUARY-FEBRUARY, 1969

ELECTRON MICROPROBE STUDY OF PREHNITE AND PUMPELLYITE FROM THE KARMUTSEN GROUP, VANCOUVER ISLAND, BRITISH COLUMBIA

RONALD C. SURDAM, *Department of Geology, University of Wyoming 82070.*

ABSTRACT

Prehnite and pumpellyite are abundant low-grade metamorphic minerals in the metavolcanic rocks of the Triassic Karmutsen Group of central Vancouver Island, B. C. The prehnite and pumpellyite occur as amygdaloidal minerals and as alteration products of glass and plagioclase. An electron microprobe study of prehnite from the Karmutsen Group has shown as appreciable amount of solid solution between the two ideal end members $Ca_2Al_2Si_3O_{10}(OH)_2$ and $Ca_2Fe_2Si_3O_{10}(OH)_2$; at least 30 mole percent $Ca_2Fe_2Si_3O_{10}(OH)_2$ is present in some samples. The *average* total Fe as Fe_2O_3 content of 18 samples ranges from less than 0.1 to 8.2 percent.

Pumpellyite also shows a wide range of total iron compositions. The inverse relationship between Fe and Al indicates that much of the iron must be Fe^{3+}. The maximum determined total iron is 23.0 percent expressed as Fe_2O_3. The compositional field of pumpellyite apparently is expanded at low temperatures and pressures.

INTRODUCTION

The widespread occurrence of prehnite and pumpellyite in low-grade metamorphic terrains has been known for many years. However, it was not until Coombs (1960) proposed the prehnite-pumpellyite metagraywacke facies that general interest was aroused in prehnite and pumpellyite. Coombs proposed the prehnite-pumpellyite metagraywacke facies to include those assemblages produced under physical conditions in which the following assemblages are commonly formed: quartz-prehnite-chlorite, or quartz-albite-pumpellyite-chlorite, without zeolites and without the characteristic minerals of the glaucophane schist facies, jadeite or lawsonite. Seki (1961) also has proposed a pumpellyite-prehnite facies to fill the gap between the zeolite facies and the greenschist facies. Since the work of Coombs (1960) and Seki (1961) the reports of pumpellyite-prehnite bearing rocks have been numerous. Nevertheless, little is known about the compositional ranges or stability fields of prehnite and pumpellyite. The electron microprobe study of prehnite and pumpellyite from the Karmutsen Group in the Buttle Lake area of central Vancouver Island provides valuable information on the compositional and stability fields of these mineral phases.

The Triassic Karmutsen Group consists of approximately 18,000 stratigraphic feet of amygdaloidal flows, aquagene tuffs, pillow lavas, pillow breccias, and a few thin interlava sediments (Surdam, 1968). In the Buttle Lake area low-grade metamorphism has resulted in prehnite-pumpellyite-bearing assemblages.

ANALYTICAL TECHNIQUES

X-ray diffraction. The unit-cell parameters and unit-cell volumes designated for the minerals in this study were determined by using a Norelco X-ray diffractometer and CuKα radiation. Silicon metal ($2\theta_{CuK\alpha} = 28.468°$) was used as an internal standard. Four complete oscillations were performed on each mineral sample. Peak locations were measured to 0.005° 2θ and averaged. The unit-cell parameters and unit-cell volumes were calculated using a least-squares computer program designed by Burham (1962). The error listed for the unit-cell volume determinations is calculated by the computer program.

Electron microprobe. An EMX electron microprobe manufactured by Applied Research Laboratories and located in the UCLA Geology Department was used in this study. The operating conditions, standards, spectrometer crystals, and analyzing modes for the prehnite and pumpellyite analyses are listed in Surdam (1967, p. 276). Also the procedure for calculating the background, absorption, fluorescence, and atomic number corrections is outlined in detail by Surdam (1967, p. 275–280). The minerals were studied by means of polished thin sections.

The reproducibility of the electron microprobe data was checked by taking a number of measurements on the same spot. In general, the reproducibility of measurements for elements heavier than calcium was excellent. It was found for calcium and heavier elements that the deviation was less than one percent of the amount present. For elements lighter in weight than calcium the reproducibility ranged from 2 to 5 percent of the amount present.

Other possible major sources of error include zoned standards, surface relief on polished specimens, variations in the carbon sputtering, and instrumental errors. J. V. Smith (1965, p. 830) using electron microprobe techniques similar to those utilized in this study estimates his relative accuracy as 1 to 5 percent of the amount of an element present.

PREHNITE

Occurrence. Prehnite in the Karmutsen Group, like the other hydrous calcium aluminum silicates laumontite and wairakite, occurs as an amygdaloidal mineral and as an alteration product of glass and calcic plagioclase. However, prehnite, unlike laumontite, wairakite, and pumpellyite, is ubiquitous in all the tuffaceous rocks in the Karmutsen Group (Surdam, 1967). In the tuffaceous rocks occurring in the upper half of the section, prehnite is spatially associated with laumontite. However, in the lower half of the section, prehnite occurs to the exclusion of all other hydrous calcium aluminum silicates, with the exception of epidote and pumpellyite. Amygdaloidal prehnite is present throughout the section except for the uppermost part. It is most prevalent in the thin-layered flows that occur just above the basal pillow lava and aquagene tuff unit. Amygdaloidal prehnite occurs only in flows in which the calcic plagioclase grains have been altered. Prehnite as an alteration product of calcic plagioclase occurs almost exclusively associated with prehnite amygdales.

Amygdaloidal prehnite characteristically occurs as barrel-shaped aggregates or as a shapeless mass filling the amygdale. Individual crystals are rare, but they do occur being more common in the alteration products of glass or in the decomposition products of laumontite. The physical habit of the prehnite in the Karmutsen Group is best described as extremely varied. Amygdaloidal prehnite is most often associated with pumpellyite, chlorite and quartz; however, as already reported it does occur with laumontite and wairakite. The amygdaloidal prehnite is white to gray or occasionally pink. The pink color is caused by finely disseminated native copper. The textural relationships in the amygdales usually indicate that the prehnite formed later than the pumpellyite.

Optically the prehnite differs from the other hydrous calcium aluminum silicates by higher birefringence and relief. Optical anomalies are very common in the prehnite, especially its mode of extinction. Some samples have undulatory or incomplete extinction, whereas others have perfectly normal extinction. The same is true of interference colors, for some samples have normal colors, whereas others display anomalous (blue or purple) first order interference colors.

Electron microprobe study. An electron microprobe study of prehnite from the Karmutsen Group has shown that there is an appreciable amount of solid solution between the two ideal end members $Ca_2Al_2Si_3O_{10}(OH)_2$ and $Ca_2Fe_2Si_3O_{10}(OH)_2$. Hashimoto (1964) has suggested that the $Ca_2Fe_2Si_3O_{10}(OH)_2$ molecule is mostly less than 20 mole percent and usually less than 10 mole percent in natural prehnites. However, 612 electron microprobe analyses of 18 prehnite specimens from the Karmutsen Group collected over a stratigraphic interval of 15,000 feet, suggest that at least 30 mole percent $Ca_2Fe_2Si_3O_{10}(OH)_2$ is present in three samples. The maximum determined Fe_2O_3 content (total iron expressed as Fe_2O_3) is 10.8 percent and the *average* Fe_2O_3 contents of the 18 samples range from less than 0.1 to 8.2 percent (see Fig. 1, and Table 1).

If the total iron content is assumed to be ferric iron and the remainder of the analysis is H_2O, the number of ions on the basis of 12 (O, OH) can be calculated. Making this calculation for the most iron-rich prehnite analysis suggests the following formula: $Ca_2Fe_{0.6}^{+3}Al_{1.4}Si_3O_{10}(OH)_2$. Most of the iron in prehnite probably is ferric iron. Only one of the seven prehnite analyses that Deer *et al.* (1962b) list has as much as 1 percent FeO and this analysis is of a hydrothermal prehnite sample from an amphibolite. The other six analyses show 0.3 percent or less FeO. The normally low FeO content is undoubtedly due to the absence of a R^{2+} site in prehnite for ferrous iron. It is concluded that the prehnite from the Karmutsen Group is characterized by solid solution from $Ca_2Al_2Si_3O_{10}(OH)_2$ to approximately $Ca_2Fe_{0.6}Al_{1.4}Si_3O_{10}(OH)_2$.

Crystallography. Hashimoto (1964) has shown that the chemical composition of prehnite can not be determined from its optical properties. In

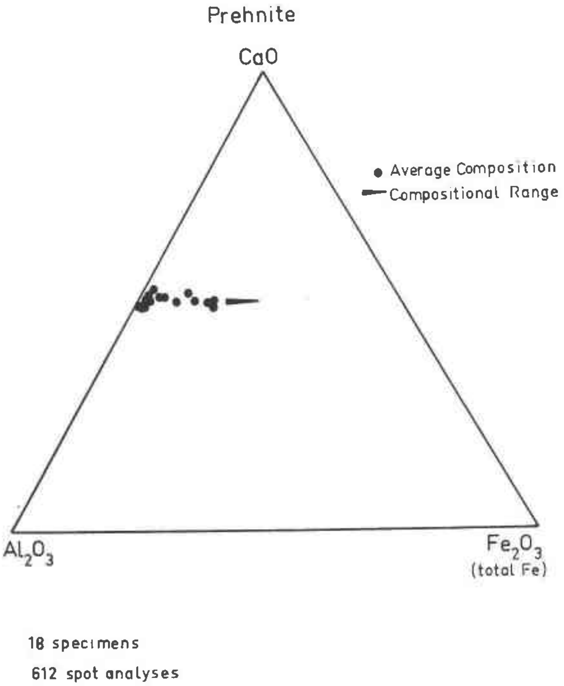

FIG. 1. $CaO:Al_2O_3:Fe_2O_3$ (total iron) variation diagram for prehnite in the Karmutsen Group.

TABLE 1. PARTIAL ELECTRON MICROPROBE ANALYSES AND CELL DATA OF PREHNITE, KARMUTSEN GROUP

A. Partial electron microprobe analyses of prehnite, Karmutsen Group

Sample no	1	2	3	4	5	6	7	8
SiO_2	43.5	43.3	43.5	44.2	44.3	43.1	44.6	43.0
CaO	26.1	26.0	25.9	25.3	25.8	26.2	25.6	26.3
Al_2O_3	22.6	23.2	24.5	24.4	24.4	25.0	17.4	17.6
Fe_2O_3 (total Fe)	2.6	2.0	0.9	1.1	0.9	0.4	8.0	7.6
Range of Fe_2O_3	0.4–6.8	0.6–10.8	0.5–1.6	0.1–1.4	0.1–5.5	0.1–1.2	4.4–10.3	0.4–9.2
Subtotal	94.8	94.5	94.8	95.0	95.4	94.7	95.6	94.5

B. Prehnite cell data, Karmutsen Group

	1	2	3	4	5	6	7	8
a Å[a]	4.63	4.63	4.63	4.62	4.62	4.63	4.64	4.64
b Å[a]	5.48	5.58	5.48	5.47	5.49	5.49	5.49	5.49
c Å[a]	18.5	18.5	18.5	18.5	18.5	18.5	18.5	18.5
V (Å^3)[b]	470	469	468	467	469	470	472	471

[a] (±0.003)
[b] (±0.2)

an effort to correlate crystallographic properties with the composition of prehnite, the unit-cell parameters for eight samples were calculated (see Table 1). The prehnite peaks were indexed using the *hkl* values suggested by Nuffield (1943). For differences of 8 wt. percent Fe_2O_3 (total iron), the unit-cell volume of prehnite changed only 5 Å^3. Each prehnite sample represents a range of compositions, and because the absolute average composition of each specimen as determined by electron microprobe analyses is difficult to ascertain, a determinative curve is not warranted by these results. However, there is a slight increase in the unit-cell volume of prehnite with an increase in iron content.

PUMPELLYITE

Occurrence. The widespread occurrence of pumpellyite is characteristic of low grade metamorphic terrains. Published examples, summarized by Seki (1961), include such terrains in California, Japan, Celebes and Borneo, New Caledonia, New Zealand, Australia, Scotland, Haiti Island, and Michigan. In addition, Jambor (1960) noted that pumpellyite occurred in the Karmutsen Group of Vancouver Island, B. C.; very recently, Vance (1966) has reported the occurrence of pumpellyite in the San Juan Islands northwest Washington. Pumpellyite has a relatively wide stability range being found in the blue schist, the greenschist, as well as in the pumpellyite prehnite metagraywacke facies.

Pumpellyite in the Karmutsen Group occurs as needles and radiating clusters in amygdales, as an alteration product of calcic plagioclase, and as amoeboid patches in the matrix of flows and tuffs. Typical pumpellyite from the Karmutsen Group is various shades of green, blue and brown, and it is always pleochroic. Under crossed nichols, the pumpellyite characteristically displays anomalous interference colors, especially greens and blues. A strong color zoning in some of the pumpellyite when studied with the electron microprobe was found to reflect differences in iron contents.

Amygdaloidal pumpellyite has been found only in flows in which the calcic plagioclase has been altered and is usually in one of the following assemblages: *pumpellyite*, *pumpellyite-quartz*, *pumpellyite-prehnite-quartz*, *pumpellyite-epidote-Ca carbonate-quartz*, *pumpellyite-epidote-quartz*, and *all assemblages* ± *chlorite*. Also it should be noted that laumontite commonly occurs in the same amygdale, but it is always surrounded by quartz, and it is never in direct contact with pumpellyite. Members of the analcime-wairakite series are never found in the same amygdale with pumpellyite.

Electron microprobe study. The study of pumpellyite from the Karmutsen Group sheds light on the inferred stability relations of pumpellyite in regional metamorphism. Unlike the Japanese occurrence studied by Seki (1961) which is characterized by low temperatures and relatively high solid pressures, the low grade metamorphism of the Karmutsen Group is characterized by low temperatures and relatively low solid pressures (Surdam, 1967). As noted in Table 2, there are important chemical differences in the pumpellyite from the two districts. Pumpellyite from the Karmutsen Group is much more iron-rich and magnesium-poor than pumpellyite from California and Michigan (Coombs, 1953) and Japan (Seki, 1958; 1961), the only other low grade metamorphic terrains for which reliable analyses are published (see Fig. 2). Coombs (1953, p. 129) noted that in pumpellyite from North Range, Taringatura

TABLE 2. PARTIAL ELECTRON MICROPROBE ANALYSES AND CELL DATA OF PUMPELLYITE

A. Partial electron microprobe analyses of pumpellyite

Sample no.	1	2	3	4	5	6	7	8[a]	9[b]	10[c]
SiO_2	38.5	37.2	37.3	38.4	38.7	38.4	37.4	37.18	38.09	37.99
CaO	21.9	21.2	22.4	20.9	21.4	21.4	21.3	23.08	22.96	21.72
Al_2O_3	19.6	19.1	19.2	20.9	21.1	21.3	18.2	23.50	23.53	24.89
Fe_2O_3 (total Fe)	13.8	15.2	15.7	10.4	10.2	10.5	16.1	7.6[d]	4.6[d]	6.3[d]
Range of Fe_2O_3	12.8–16.4	13.5–23.0	13.0–17.0	8.3–11.8	7.7–12.6	8.5–12.3	13.2–19.3	nd	nd	nd
MgO	1.0	0.9	1.3	1.2	1.4	1.3	0.6	3.18	3.58	1.54
MnO	nd	0.2	0.3	0.4	0.4	0.3	nd	nd	0.50	0.42

Number of ions on the Basis of 28(O,OH,H_2O)

	1	2	3	4	5	6	7
Si	6.35	6.40	6.16	6.01	6.16	6.15	6.42
Al	3.84	3.86	3.76	3.94	4.05	4.09	3.68
Fe^{3+}	1.16	1.14	1.24	1.06	0.95	0.91	1.32
Mg	0.25	0.22	0.33	0.28	0.33	0.31	0.17
Fe^{2+}	0.52	0.76	0.61	0.16	0.27	0.34	0.79
Mn	nd	0.02	0.04	0.06	0.06	0.04	nd
Ca	3.90	3.90	4.00	3.52	3.74	3.76	3.90

B. Pumpellyite cell data

Sample no.	1	5	8	9	10	11[e]
a, Å[f]	8.84	8.82	8.82	8.81	8.81	8.81
b, Å[f]	5.92	5.92	5.92	5.89	5.89	5.90
c, Å[f]	19.21	19.20	19.18	19.12	19.12	19.11
β[g] in°	97.5	97.4	97.4	97.4	97.4	97.4
V (Å³)	1000 ± 1	994 ± 1	992 ± 1	984 ± 1	986 ± 1	985 ± 1
Total Fe as Fe_2O_3	13.8	10.2	7.6	4.6	6.3	3.0

[a] From Coombs, 1953, p. 123
[b] From Seki, 1953, p. 242, no. 6
[c] From Seki, 1953, p. 242, no. 7
[d] Total iron recalculated as Fe_2O_3
[e] Sample from Hicks Ranch, California (see Coombs, 1953)
[f] (±0.001)
[g] (±0.1)

survey district, Southland, New Zealand, the β index of refraction was in the range of 1.70 to 1.72. When $\beta = 1.72$ is placed on a plot of β versus total iron (Coombs, 1953, p. 131) it indicates an iron value near those obtained for pumpellyite from the Karmutsen Group. The iron-rich pumpellyite from the Karmutsen Group suggests appreciable replacement of (Al, Mg) by Fe^{3+}, Fe^{2+}; the replacement of Ca by (Na, K) is negligible.

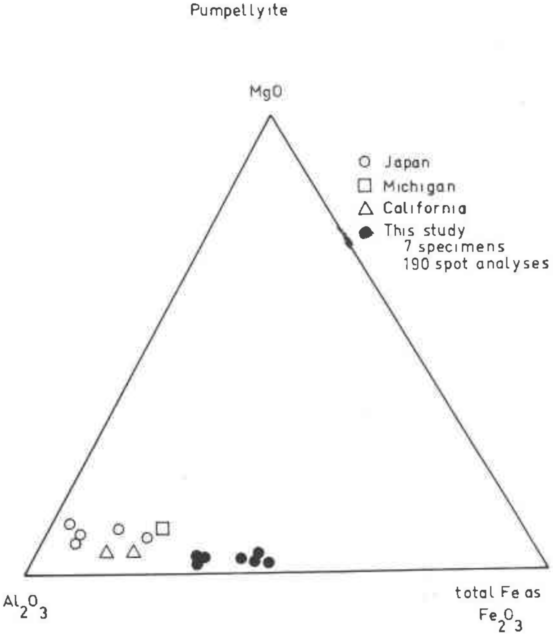

FIG. 2. $MgO:Al_2O_3:Fe_2O_3$ (total iron) variation diagram for pumpellyite from Japan (Seki, 1958, 1961), Michigan (Coombs, 1953), California (Coombs, 1953), and this study.

Seki (1961, p. 417) has stressed the significance of the Fe^{3+}/R^{3+} ratio, observing that pumpellyite in glaucophanitic regional metamorphic has a low Fe^{3+}/R^{3+} ratio. Only the total iron has been determined in the partial electron microprobe analyses reported in Table 2, and this has been reported at Fe_2O_3. Judging by the inverse relationship between Fe and Al in the Karmutsen Group pumpellyite, much of the iron must be Fe^{3+} (see Figs. 3 and 4). In an effort to determine approximate Fe^{2+}/Fe^{3+} ratios, the number of ions on the basis of 28(O,OH, H_2O) were calculated from the partial analyses. The calculations were made assuming that the remainder of the partial analyses was H_2O; only very rough estimates

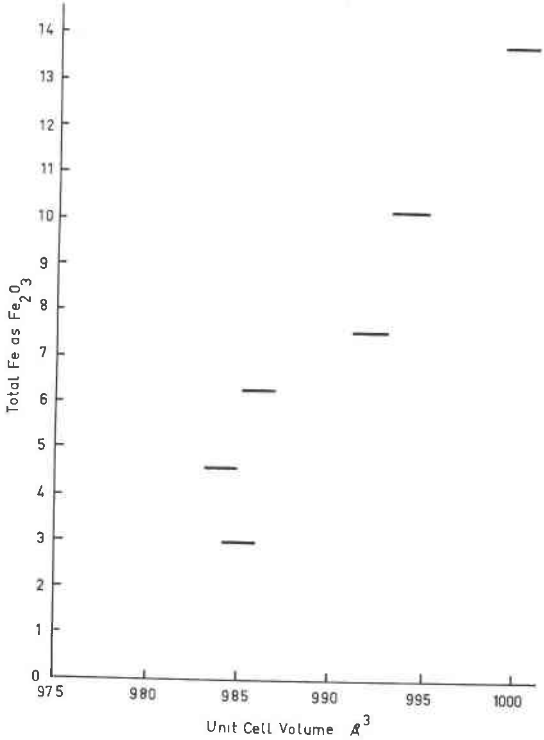

FIG. 3. Plot of the wt. % of Fe_2O_3 (total iron) versus the unit-cell volume for pumpellyite, from the Karmutsen Group.

can be obtained in this manner. Iron was allotted to the R^{3+} site until it was filled, and the remaining iron was allotted to the R^{2+} site.

The average analyses of the amygdaloidal pumpellyite samples fall into two groups. The first group requires the addition of approximately one ion of Fe^{3+} to the Al to fill the R^{3+} site (see table 2, nos. 1, 2, 4–6). The second group requires approximately 1.3 ions of Fe^{3+} to fill the R^{3+} site (see table 2, nos. 3 and 7). The pumpellyite samples in this latter group have relatively low MgO contents, suggesting that they contain more ferrous iron than the first group. Differences in the Fe^{2+}/Fe^{3+} ratios between the two groups are to be expected since pumpellyite in the first group was intimately associated with native copper-bearing prehnite, whereas pumpellyite in the second group was intimately associated with chalcopyrite or magnetite. If the opaque minerals reflect the oxidation conditions in the amygdale at the time of pumpellyite

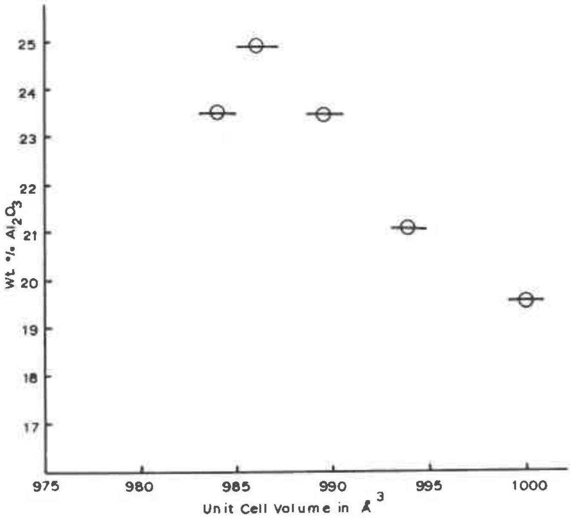

FIG. 4. Plot of the wt. % of Al_2O_3 versus the unit-cell volume for pumpellyite, from the Karmutsen Group.

formation, then presumably the Fe^{2+}/Fe^{3+} ratios would have been higher in amygdales in which chalcopyrite or magnetite, rather than native copper, was forming. Seki (1961), on the basis of chemical and optical data, has suggested the highest Fe^{3+}/R^{3+} ratio of pumpellyite is about 0.200, i.e., one Fe^{3+} per unit cell.

Some of the pumpellyite samples from the Karmutsen Group have compositions that agree with the findings of Seki (1961), but some of the pumpellyite samples have more than one ion of ferric iron per unit cell. It is apparent when examining the range of iron contents of the pumpellyite analyses that ferric iron can exceed one ion per unit cell. In fact, in

TABLE 3. CALCULATION OF THE NUMBER OF IONS ON THE BASIS OF 28 (O, OH, H_2O) FOR THE MOST IRON-RICH ELECTRON MICROPROBE SPOT ANALYSES OF SAMPLES 2 AND 7 FROM TABLE 2

	2	7
Si	5.94	6.15
Al	2.89	3.41
Fe^{3+}	2.11	1.59
Mg	0.20	0.17
Fe^{2+}	0.66	0.80
Mn	0.02	nd
Ca	3.62	3.75

two specimens (Table 2, nos. 2 and 7) the iron content ranges as high as 23.0 and 19.3 percent Fe_2O_3 (total iron) and this is roughly equivalent to 2.0 and 1.5 ions of ferric iron per unit cell (Table 3). The lowest iron content measured in pumpellyite from the Karmutsen Group is 7.7 percent Fe_2O_3. Therefore, in the low grade metavolcanic rocks in the Buttle Lake area, pumpellyite, with respect to iron, has a wide compositional field.

Seki (1961) has noted that pumpellyite relatively rich in Fe^{3+} may be stable only when solid pressure is low. When rocks in which the Fe^{3+}/R^{3+} ratio is high are metamorphosed under high solid pressure conditions, stilpnomelane, epidote, chlorite, or other minerals in which Fe^{3+} can easily replace R^{3+}, would be formed instead of pumpellyite (Seki, 1961).

Crystallography. Coombs (1953, p. 122) observed slight changes in lattice spacings of pumpellyite as Fe^{3+} replaces Al. In order to evaluate this change in lattice spacings, the writer measured the unit-cell parameters and unit-cell volume for two Karmutsen Group pumpellyite samples, and for two Japanese samples kindly provided by Dr. Seki. From the litterature (Coombs, 1953), the indexed spacings for the Calumet specimen from Michigan and the Hicks Ranch specimen from California were obtained. Chemical data were available for all samples used (Table 2). Utilizing the (*hkl*) values suggested by Coombs (1953) the unit-cell parameters and unit-cell volumes were determined for the six pumpellyite samples (see Table 2). There is strong correlation between an increase in unit-cell volume and an increase in total iron (Fig. 3). A corresponding correlation was found between an increase in unit-cell volumes and a decrease in Al (Fig. 4); the correlation between unit-cell volume and Mg content is very poor. This indicates that the amount of Fe^{3+} in the pumpellyite is the major determinant of unit-cell volume. The same correlation has been made between iron content and optical properties (Coombs, 1953 and Seiki, 1961).

ACKNOWLEDGMENTS

I would like to thank the Geology Faculty of the Uuiversity of California, Los Angeles, for their helpful criticism when this work was presented to them as part of a dissertation (Surdam, 1967). In particular I would like to thank Dr. Donald Carlisle for his helpful comments. The instruction that Dr. Paul Ribbe and Mr. Monte Hall gave me in operating the UCLA electron microprobe is gratefully acknowledged. Mr. Gene Gonzalez provided excellent polished thin sections.

REFERENCES

BURNHAM, C. W. (1962) Lattice constant refinement. *Carnegie Insti. Wash., Year Book* **61**, 132–134.

COOMBS, D. S. (1953) The pumpellyite mineral series. *Mineral. Mag.*, **30**, 113–135.

——— (1960) Lower grade mineral facies in New Zealand. *Int. Geol. Cong., 21st, Copenhagen, 1960. Sec. 13,* 339–351.

DEER, W. A., HOWIE, R. A., and ZUSSMAN, J. (1962a) *Rock Forming Minerals. Vol. 1, Ortho- and Ring Silicates.* John Wiley and Sons, New York.

——— (1962b) *Rock Forming Minerals. Vol. 3, Sheet Silicates.* John Wiley and Sons, New York.

HASHIMOTO, M. (1964) The chemistry and optics of prehnite. *J. Geol. Soc. Jap.,* **70,** 180–183.

JAMBOR, J. L. (1960) Volborthite from British Columbia. *Amer. Mineral.,* **45,** 1307–1309.

MIYASHIRO, A., AND SEKI, Y. (1958) Enlargement of the compositional field of epidote and piemontite with rising temperature. *Amer. J. Sci.,* **256,** 423–428.

NUFFIELD, E. W. (1953) Prehnite from Ashcroft, British Columbia. *Univ. Toronto Stud., Geol. Ser.,* **48,** 49–64.

SEKI, Y. (1958) Glaucophanitic regional metamorphism in the Kanto Mountains, central Japan. *Jap. J. Geol. Geog.,* **20,** 233–258.

——— (1961) Pumpellyite in low-grade metamorphism. *J. Petrology,* **2,** 407–423

SMITH, J. V. (1965) X-ray-emission microanalysis of rock-forming minerals I. experimental techniques. *J. Geol.,* **73,** 830–864

SURDAM, R. C. (1967) *Low-grade metamorphism of the Karmutsen Group, Buttle Lake area, Vancouver Island, B.C.* Ph.D. Diss. Univ. Calif., Los Angeles

——— (1968) The stratigraphy and volcanic history of the Karmutsen Group, Vancouver Island, B.C. *Contrib. Geology,* **7,** 15–26

VANCE, J. A. (1968) Prehnite-pumpellyite facies metamorphism on Orcas Island, San Juan Islands, northwest Washington. (abstr.) *Geol. Soc. Amer, Spec. Pap.* **101,** 342.

Manuscript received, May 3,1968; accepted for publication, July 2, 1968.