

## Preliminary Experimental Results on Pumpellyite Stability in Pumpellyite-actinolite Schist

TERUO WATANABE

Department of Geology, Faculty of Science, Shimane University

and

RODNEY H. GRAPES

Joint Mineral Sciences Research Laboratory, Victoria University of Wellington

(Received September 6, 1980)

### Abstract

Preliminary experimental results on pumpellyite stability are presented and discussed. The decomposition of pumpellyite occurs according to the following equation:  $18 \text{ pumpellyite} + 5 \text{ chlorite} + 57 \text{ quartz} = 38 \text{ anorthite} + 17 \text{ tschermakite} + 86 \text{ water}$ . Pumpellyite persists metastably up to  $450^{\circ}\text{C}$  at 3 kb.

### Introduction

Pumpellyite, a complex orthosilicate, is a common constituent of low-grade metamorphosed volcanic, volcanoclastic and psammitic rocks. Its ideal chemical composition can be expressed as  $\text{Ca}_4\text{Al}_5(\text{Mg}, \text{Fe})\text{Si}_6\text{O}_{21}(\text{OH})_7$ . Aluminous pumpellyite (Total FeO < 10 wt%) is typically found in relatively high pressure pumpellyite-actinolite schist facies rocks which mark the transition from zeolite and prehnite-pumpellyite metagraywacke facies assemblages to those of the greenschist facies. Therefore, the breakdown of pumpellyite with increasing temperature is a very important reaction during low-grade metamorphism.

To date there have been only a few experimental studies on the stability field of pumpellyite due to the sluggishness of reactions at low temperatures and the comparatively complex composition of pumpellyite.

LANDIS & ROGERS (1968) initially studied the decomposition of pumpellyite and demonstrated that a pumpellyite-quartz assemblage (as found in veins) decomposed to that of clinopyroxene-anorthite very near  $500^{\circ}\text{C}$  at 1 to 3 kb. They concluded that, "it is unlikely that pumpellyite persists to temperatures as high as  $500^{\circ}\text{C}$ ; in nature it is replaced by other lime-bearing minerals (e.g. epidote and Ca-amphibole) long before the appearance of metamorphic Ca-plagioclase."

Subsequently, NITSCH (1971) determined the upper stability of the assemblage of pumpellyite-chlorite-quartz at about  $350^{\circ}\text{C}$  at 4 kb. He examined the stability by

means of a starting mixture of pumpellyite-chlorite-quartz-epidote-actinolite, and the reaction point was bracketted by a change of amount of each constituent mineral in starting material. As this stability field was in harmony with natural occurrences, WINKLER (1974) adopted the reaction, e.g. pumpellyite + chlorite + quartz = epidote + actinolite, as marking the transition from pumpellyite-actinolite facies to greenschist facies metamorphism.

Recently, SCHIFFMAN & LIOU (1977) have successfully synthesized Mg-pumpellyite and found that the upper stability is very close to that of Mg-Fe pumpellyite as determined by NITSCH (1971).

Since reactions leading to pumpellyite-decomposition in natural assemblages must be complex further work utilizing natural pumpellyite-bearing starting materials is desirable. Although our experiments are still in progress, this paper reports preliminary results and problems on the breakdown of pumpellyite using a pumpellyite-actinolite schist.

### Starting Material

The starting material was a pumpellyite-actinolite schist (No. 82011) from the low grade part of Zone III,

Table 1. A bulk chemical composition of pumpellyite-actinolite schist of starting material.

SiO <sub>2</sub>	48.54
TiO <sub>2</sub>	0.07
Al <sub>2</sub> O <sub>3</sub>	15.21
Fe <sub>2</sub> O <sub>3</sub>	3.85
FeO	7.66
MnO	0.17
MgO	6.91
CaO	8.36
Na <sub>2</sub> O	3.44
K <sub>2</sub> O	0.03
P <sub>2</sub> O <sub>5</sub>	0.19
H <sub>2</sub> O <sup>(+)</sup>	4.42
H <sub>2</sub> O <sup>(-)</sup>	0.10
Total	99.58

Table 2. Chemical compositions of pumpellyite and chlorite in the starting material (EPMA analyses).

	pumpellyite	chlorite
SiO <sub>2</sub>	37.10	27.80
TiO <sub>2</sub>	0.0	0.0
Al <sub>2</sub> O <sub>3</sub>	24.62	17.75
FeO	4.20	24.98
MnO	0.0	0.19
MgO	3.08	17.36
CaO	23.07	0.0
Na <sub>2</sub> O	0.0	0.0
K <sub>2</sub> O	0.0	0.0
*H <sub>2</sub> O <sup>(+)</sup>	6.44	11.47
Total	98.51	99.55
Si	6.037	5.813
Al <sup>IV</sup>	—	2.187
	6.037	8.000
Al <sup>VI</sup>	4.723	2.188
Ti	0.0	0.0
Fe <sup>2+</sup>	0.571	4.368
Mn	0.0	0.033
Mg	0.746	5.409
	6.040	11.998
Ca	4.022	0.0
Na	0.0	0.0
K	0.0	0.0
	4.022	

\* not determined but calculated on the basis of mineral formula

Sambagawa metamorphic belt described by WATANABE (1977). The schist is laminated and pale-greenish coloured, presumably of a reworked hyaloclastic origin. The mineral assemblage is pumpellyite, actinolite, chlorite, albite and quartz with accessory sphene, calcite, etc. An important feature of the schist is that it does not contain epidote. The bulk chemical composition is given in Table 1 and EPMA analyses of pumpellyite and chlorite are listed in Table 2. Pumpellyite does not show a distinct pleochroism which is probably due to its low iron content (4.20 wt%). Chlorite is a ripidolite. The composition of actinolite was not determined because its needle-like crystal habit was too small for quantitative analysis.

### Experimental Equipment and Procedures

For our experiments conventional cold-seal vessels at Joint Mineral Sciences Research Laboratory of Victoria University of Wellington were used. Details of this equipment are described by BOETTCHER & KERRICK (1971) and the vertically orientated pressure vessel assembly is illustrated in Fig. 1. The double capsule method was employed in each experiment, with an inner capsule (about 1 cm length) of Pd and

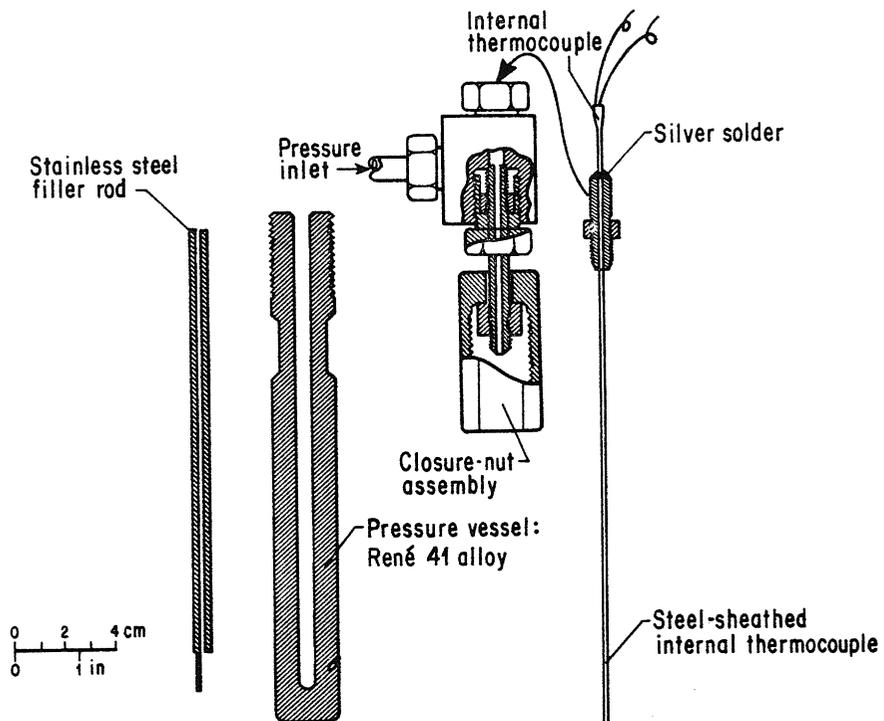


Fig. 1. Scale drawing of cold-seal pressure vessel (after BOETTCHER and KERRICK, 1971).

Ag(Pd<sub>30</sub>Ag<sub>70</sub>) contained the starting material and distilled water (usually less than 10% of the starting material), enclosed within an outer capsule of Ag or Au containing a solid oxygen buffer (mainly QFM) and distilled water.

Conditions of the experimental runs are given in Table 3. Pressures ( $P_{\text{fluid}}$ ) were 2 and 3 kb and temperatures ranged from 250°C to 500°C. Run times of the experiments were usually 2 to 3 months and those of a few experiments exceeded 4 months. The grain size of the experimental products are usually so fine that it is difficult to determine phase changes under the microscope. Accordingly, XRD methods were employed to check the phase changes but because of very limited amounts of the run charges a quartz plate without the refracted crystal plane in XRD was used to attach and analyze the small amounts of experimental products.

Table 3. A list of experimental runs for a pumpellyite-actinolite schist.

	Temperature	Pressure ( $P_{\text{H}_2\text{O}}$ )	Duration	Buffer
Run 1	400°C	3 kb	144 hours	QFM
Run 2	450	3	528 h	QFM
Run 3	350	3	83 days	QFM
Run 4	400	3	596 h	QFM
Run 5	500	3	62 days	QFM
Run 6	250	3	126 days	QFM
Run 7	300	3	83 days	QFM
Run 8	325	3	108 days	QFM
Run 9	312	3	113 days	QFM
Run 11	400	3	105 days	QFM
Run 12	300	2	124 days	QFM
Run 17	325	3	106 days	HM
Run 18	300	3	120 days	HM

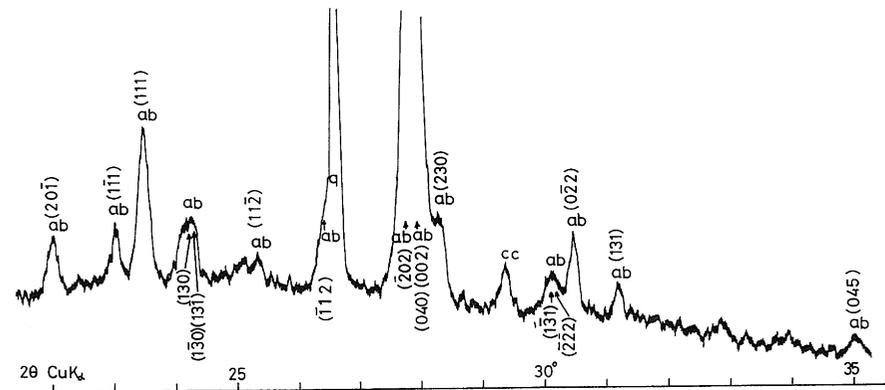
Since natural pumpellyite-actinolite schist was used as the starting material, complex polyphases reactions occurred and determinations of phase changes are difficult because of the many duplicated intensity peaks. To overcome this problem the run charges were separated by an isodynamic separator into a quartz-feldspathic part (non-magnetic) and pumpellyite-actinolite-chlorite part (relatively magnetic). This enabled each refracted peak in the starting material to be compared with a peak obtained from the experimental products.

### Experimental Results and Discussion

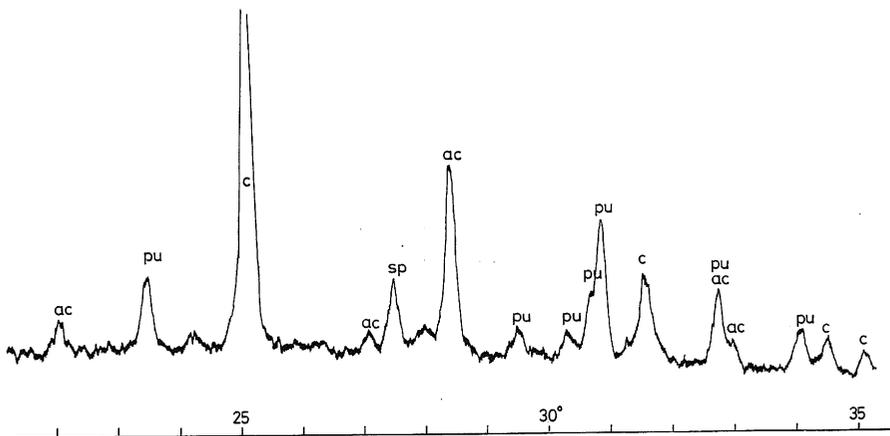
XRD patterns of the starting material are given in Fig. 2 and those from representative experimental runs are given in Figs. 3, 4, 5 and 6, which cover the temperature range from 350°C to 500°C. All peaks shown in the starting material trace are es-

sentially recognized in each XRD chart of the experimental runs except in the 500°C run. The peak shift of some critical peaks such as (131) of plagioclase is not so clear, although some changes are apparent within the region between 30° and 31°2θ and between 24° and 25°2θ in Figs. 3, 4 and 5.

Changes in peak intensity indicate a decrease in the amount of pumpellyite and a change in plagioclase composition. Since changes of peak intensity are influenced by many factors such as preferred orientation of powdered sample, etc., conclusive proof of reactions must await electron microprobe analysis.



a: quartz-feldspathic part, ab; albite, q: quartz, cc; calcite



b: mafic part, pu; pumpellyite, c; chlorite, ac; actinolite, sp; sphene

Fig. 2. Charts of XRD pattern of the starting material. Target: Cu, Time Constant: 2 (These are same for all XRD charts), Range: 1000 cps 35 kv, 20 mA

Abbreviations for minerals are same in Figs. 3-5. Peak positions of each mineral are indicated by these abbreviations.



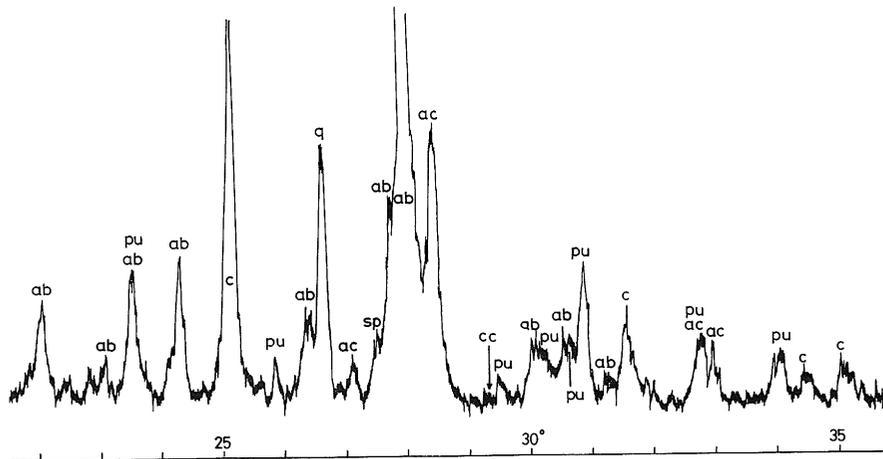


Fig. 5. Chart of XRD pattern of Run 2(450°C, 3 kb). Range: 200 cps 35 kv, 30 mA

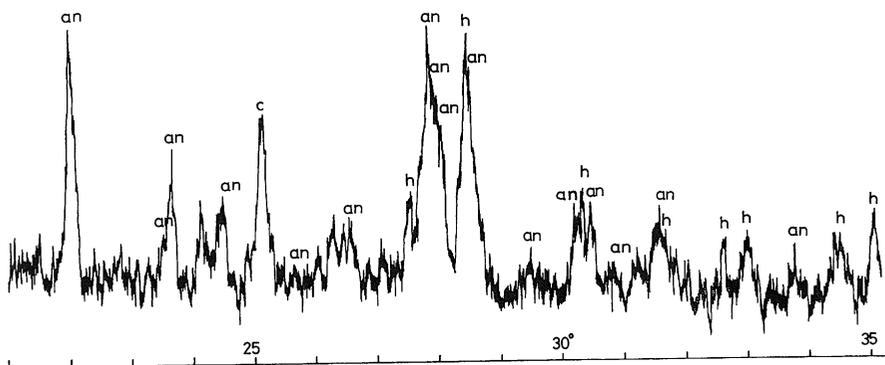
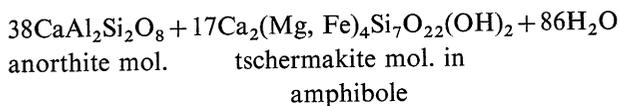


Fig. 6. Chart of XRD pattern of Run 5(500°C, 3 kb). Range: 100 cps 35 kb, 30 mA  
an: anorthite, h: hornblende



Although SCHIFFMAN & LIU (1977) found that grossular formed by the decomposition of Mg-pumpellyite in their experiments, grossular, hydrogrossular peaks were not detected in our XRD analyses. Also peaks of epidote and/or clinozoisite were not detected. Calcite appeared to decompose at temperatures between 400°C and 450°C judging from the disappearance of the strongest peak in Fig. 4.

Based on the results of NITSCH (1971) and SCHIFFMAN & LIU (1977), and natural occurrences, pumpellyite should break down long before the temperature of decomposition apparent in our experiments is reached. It is therefore concluded that pum-

pellyite persisted metastably above about 325°C. Metastable pumpellyite was also observed by LANDIS & ROGERS (1968). On the basis of natural occurrences the disappearance of pumpellyite is marked by a shift in epidote composition to an iron-poor variety (ERNST *et al.*, 1970; KAWACHI, 1974). Therefore, the appearance of grossular accompanying the decomposition of pumpellyite observed by SCHIFFMAN & LIOU (1977) also suggests a metastable reaction.

Thus, metastable assemblages are probably the rule rather than the exception in pumpellyite stability experiments at pressures less than 3 kb and may be governed by the very small free energy difference amongst epidote, grossular and anorthite-bearing assemblages.

Other factors such as activation energy or the conditions of epidote nucleation are also important.

Comparison with experiments using starting material containing epidote, the effect of mole fraction of CO<sub>2</sub> in the fluid phase, and studies utilizing reaction catalyzers are needed for solving the problem of the persistence of metastable assemblages in pumpellyite stability reactions in future experiments.

### Acknowledgements

The authors wish to express their thanks to Mr. C. SNELL of Joint Mineral Sciences Research Laboratory, Victoria University of Wellington, for his valuable assistance with our experiments. T. W. would also like to acknowledge the helpful support of Dr. E. ITO, Institute for Thermal Spring Research of Okayama University, with XRD analysis.

The present study was aided by funds from the Internal Research Grant of Victoria University of Wellington (Research Grant Number 171/78).

Professor H. KOBAYASHI, Shimane University, kindly read the paper in manuscript and gave valuable comments.

### References

- BOETTCHER, A. L. and KERRICK, D. M. (1971) Temperature Calibration in Cold-Seal Pressure Vessel: In *Research Techniques for High Pressure and High Temperature* (Edited by G. C. ULMER) Springer Verlag, Berlin 367 p.
- ERNST, W. G., SEKI, Y., ONUKI, H. & GILBERT, M. C. (1970) Comparative study of low-grade metamorphism in the California Coast Ranges and the outer metamorphic belt of Japan. *Geol. Soc. Am. Mem.* **124**, 246p.
- KAWACHI, Y. (1975) Pumpellyite-actinolite and contiguous facies metamorphism of the upper Wakatipu district, South Island, New Zealand. *N. Z. J. Geol. Geophys.* **18**, 401-441.
- LANDIS, C.A. and ROGERS, J. (1968) Some experimental data on the stability of pumpellyite. *American Mineralogist* **53**, 1038-1041.
- NITSCH, K.H. (1971) Stabilitätsbeziehungen von Prehnit- und Pumpellyit-haltigen Paragenesen. *Contr. Mineral. Petrol.* **30**, 240-260.
- SCHIFFMAN, P. and LIOU, J. G. (1977) Synthesis and stability relation of Mg-pumpellyite. *Proc.*

*2nd Internat. Symp. on Water-Rock Interaction*, strasbourg, France, 157-164.

WATANABE, T. (1977) Metamorphism of the Sambagawa and Chichibu Belts in the Oshika District, Nagano Prefecture, central Japan. *Jour. Fac. Sci., Hokkaido Univ., Ser. IV*, 17, No. 4, 629-694.

WINKLER, F.G. (1974) *Petrogenesis of Metamorphic Rocks* (third edition) Springer Verlag, Berlin 320p.