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# THERMAL DECOMPOSITION OF PECTOLITE AND ITS HYDROTHERMAL SYNTHESIS

by

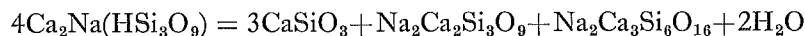
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(with 3 Tables and 5 Text-figures)

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Faculty of Science, Hokkaido University. No. 1085)

## *Abstract*

Thermal decomposition of natural pectolite from Chisaka proceeds as shown by the following equation:



Pectolite can easily be synthesized from various starting materials of anhydrous pectolite composition with water, in a test-tube bomb at 300°C, and 80–300 bars for 24–37 hrs. The synthetic pectolite has almost identical physical properties as the natural one.

D.T.A. and T.G.A. curves were determined on both natural and synthetic pectolites. The water content of synthetic pectolite is nearly double the water content of natural one. Of this one half represents “constitution water,” and the other “vagabonding water” contained in the vacant space. Genetic significance of the synthetic experiments is discussed.

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### Introduction

A new find of pectolite from Chisaka, Hidaka and Nozawa asbestos mine, Furano, Japan has been reported by YAGI, BAMBÁ and OKEYA (1968). Recently we have made thermal experiments on the Chisaka pectolite and also hydrothermal synthesis of pectolite in test-tube bomb. Comparison of natural and synthetic pectolites indicates that they are almost identical in their physical properties, and yet there are some remarkable differences between them. In the following the results of these experiments are described.

### Thermal Decomposition of Natural Pectolite

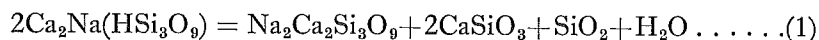
Natural pectolite from Chisaka decomposed to a mixture of anhydrous silicates after the dehydration at about 740°C. The powdered sample of Chisaka pectolite, whose chemical composition is quoted in Table 1, was heated at 1000°C for 16 hrs

Table 1. Chemical Composition of Pectolite from Chisaka

SiO <sub>2</sub>	53.72
TiO <sub>2</sub>	0.00
Al <sub>2</sub> O <sub>3</sub>	0.10
Fe <sub>2</sub> O <sub>3</sub>	0.15
FeO	n.d.
MnO	0.03
MgO	0.00
CaO	33.70
Na <sub>2</sub> O	9.20
K <sub>2</sub> O	0.00
H <sub>2</sub> O+	2.77
H <sub>2</sub> O-	0.02
Total	99.69

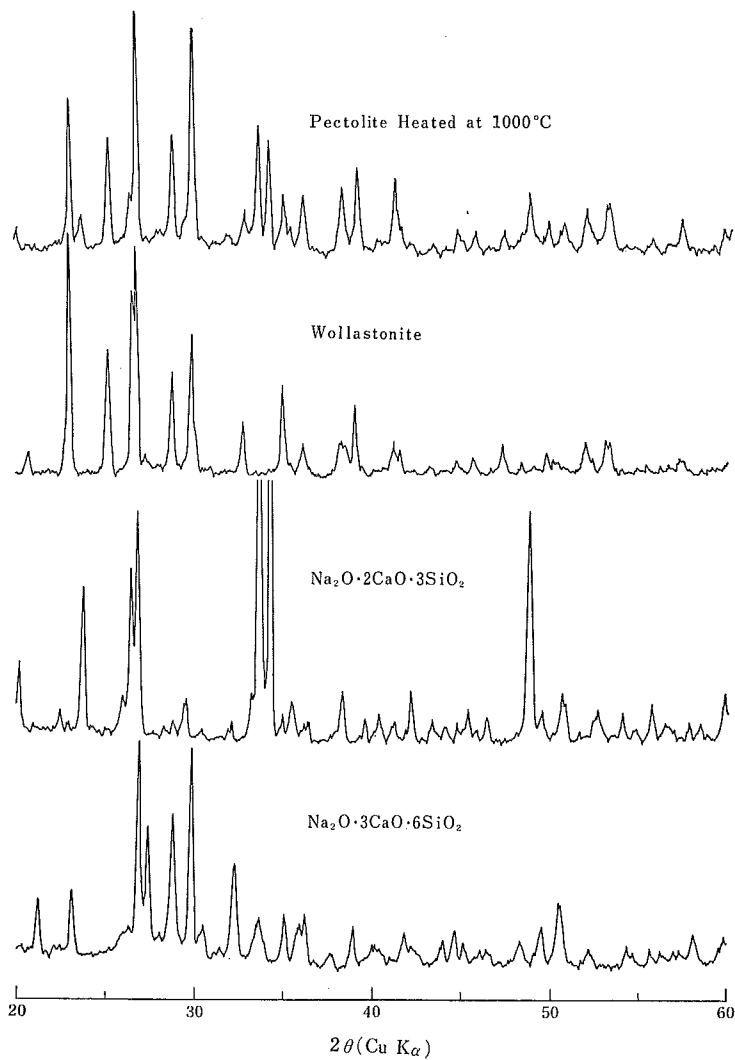
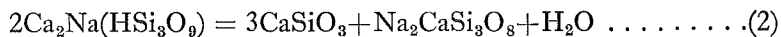
Analyst : M. Okeya

in Pt-envelope and then quenched by dropping into water. The products were found under the microscope to consist of wollastonite and unknown phases. According to BELJANKIN and IWANOWA (1933), decomposition proceeds as follows:



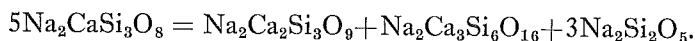
SiO<sub>2</sub>, in any form of silica minerals, however, has never been found, although the presence of wollastonite and Na<sub>2</sub>Ca<sub>2</sub>Si<sub>3</sub>O<sub>9</sub>(Na<sub>2</sub>O·2CaO·3SiO<sub>2</sub>) is confirmed by X-ray powder patterns of the decomposition products. Therefore it seems not the case in our experiments that decomposition follows the reaction (1).

During the experiments it was noticed that some of the patterns are very similar to the patterns of "Na<sub>2</sub>CaSi<sub>3</sub>O<sub>8</sub>" (Na<sub>2</sub>O·CaO·3SiO<sub>2</sub>) discussed by KRÖGER and BLÖMER (1955), and given in the A.S.T.M. identification card. Therefore it was suspected that the following equation may be the case:

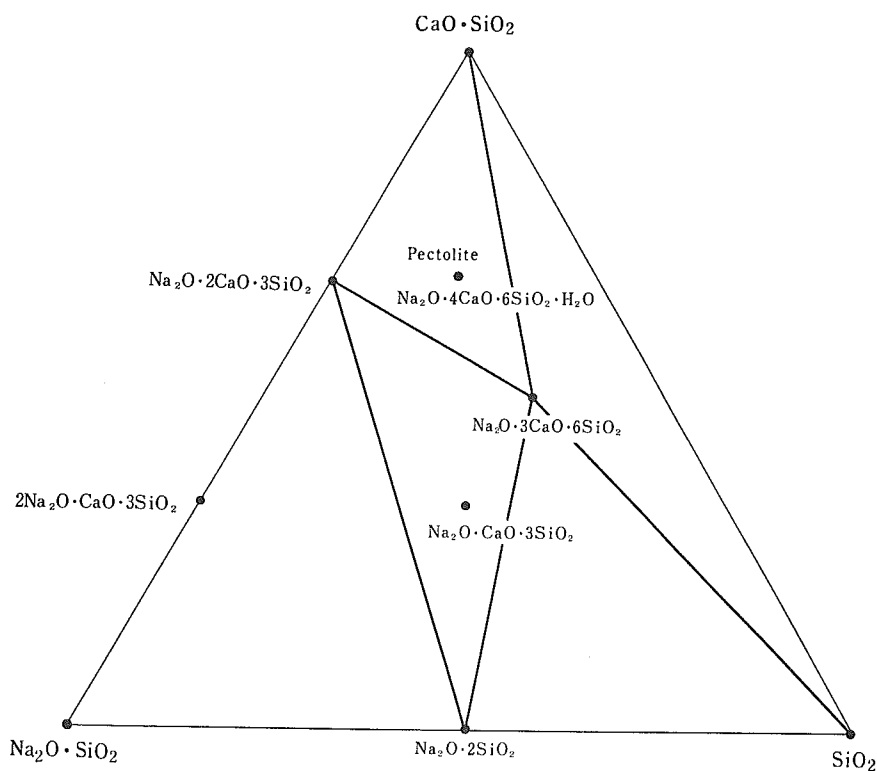


**Fig. 1**  
X-ray powder patterns of the decomposition products of pectolite heated at 1000°C (top), compared with those of wollastonite, Na<sub>2</sub>O·2CaO·3SiO<sub>2</sub> and Na<sub>2</sub>O·3CaO·6SiO<sub>2</sub> (in descending order).

However, this compound  $\text{Na}_2\text{CaSi}_3\text{O}_8$  ( $\text{Na}_2\text{O} \cdot \text{CaO} \cdot 3\text{SiO}_2$ ) was not found by MOREY and BOWEN (1925) in their study on the system  $\text{Na}_2\text{O}-\text{CaO}-\text{SiO}_2$ . Therefore, we prepared the glass of this composition and crystallized the crushed glass powder at about  $1000^\circ\text{C}$ . The crystalline products are not homogeneous, but consist of three different phases under the microscope. The X-ray powder pattern indicates the presence of the three phases of  $\text{Na}_2\text{Ca}_2\text{Si}_3\text{O}_8$  ( $\text{Na}_2\text{O} \cdot 2\text{CaO} \cdot 3\text{SiO}_2$ ),  $\text{Na}_2\text{Ca}_3\text{Si}_6\text{O}_{16}$  ( $\text{Na}_2\text{O} \cdot 3\text{CaO} \cdot 6\text{SiO}_2$ ) and  $\text{Na}_2\text{Si}_2\text{O}_5$  ( $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$ ). From this it was concluded that the hypothetical compound " $\text{Na}_2\text{CaSi}_3\text{O}_8$ " ( $\text{Na}_2\text{O} \cdot \text{CaO} \cdot 3\text{SiO}_2$ ) does not exist as stable phase, but is composed of these three compounds as follows:



Glasses of the compounds  $\text{Na}_2\text{Ca}_3\text{Si}_6\text{O}_{16}$  and  $\text{Na}_2\text{Ca}_2\text{Si}_3\text{O}_8$  were prepared and the crushed glasses were crystallized at temperatures slightly lower than  $800^\circ\text{C}$ . It was noticed that X-ray powder patterns of  $\text{Na}_2\text{Ca}_3\text{Si}_6\text{O}_{16}$  is very similar to that of

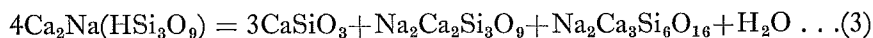


**Fig. 2**

Spatial relation between pectolite and various compounds in the system  $\text{CaO} \cdot \text{SiO}_2$ - $\text{Na}_2\text{O} \cdot \text{SiO}_2$ - $\text{SiO}_2$ .

"Na<sub>2</sub>CaSi<sub>3</sub>O<sub>8</sub>", given in A.S.T.M. card. As clearly shown in the X-ray powder patterns (Figure 1), the decomposed products of pectolite consist of wollastonite, and crystals of Na<sub>2</sub>Ca<sub>2</sub>Si<sub>3</sub>O<sub>9</sub> and Na<sub>2</sub>Ca<sub>3</sub>Si<sub>6</sub>O<sub>16</sub>. As will be described below, we could synthesize pectolite from the mixture of these three crystalline phases with water.

Therefore we conclude that the thermal decomposition of natural pectolite is expressed by the following reaction:



Mutual relation between the compounds in the system CaO·SiO<sub>2</sub>-Na<sub>2</sub>O·SiO<sub>2</sub>-SiO<sub>2</sub> and pectolite composition is graphically shown in Figure 2.

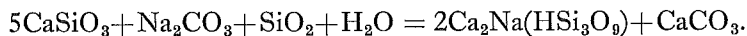
### *Hydrothermal Synthesis of Pectolite*

Synthesis of pectolite was done by means of a test-tube bomb, from various starting materials as follows:

1. Glass of pectolite composition.
2. Natural pectolite heated at 1000°C.
3. Mixture of wollastonite, Na<sub>2</sub>CO<sub>3</sub> and SiO<sub>2</sub>.
4. Mixture of wollastonite, crystalline Na<sub>2</sub>Ca<sub>3</sub>Si<sub>6</sub>O<sub>16</sub> and Na<sub>2</sub>Ca<sub>2</sub>Si<sub>3</sub>O<sub>9</sub>.

In all of them the total composition of the starting materials was the same as the anhydrous pectolite composition except No. 3. These materials were placed in the Ag-tubes together with small amount of distilled water and the tightly sealed Ag-tubes were heated in a test-tube bomb at 300°C and 80 bars for 37 hrs. Wollastonite crystals collected from the limestone-granodiorite contact at Tonoura, Moji, Kita-Kyushu City (TAKESHITA and YAGI, 1968) were used in these experiments.

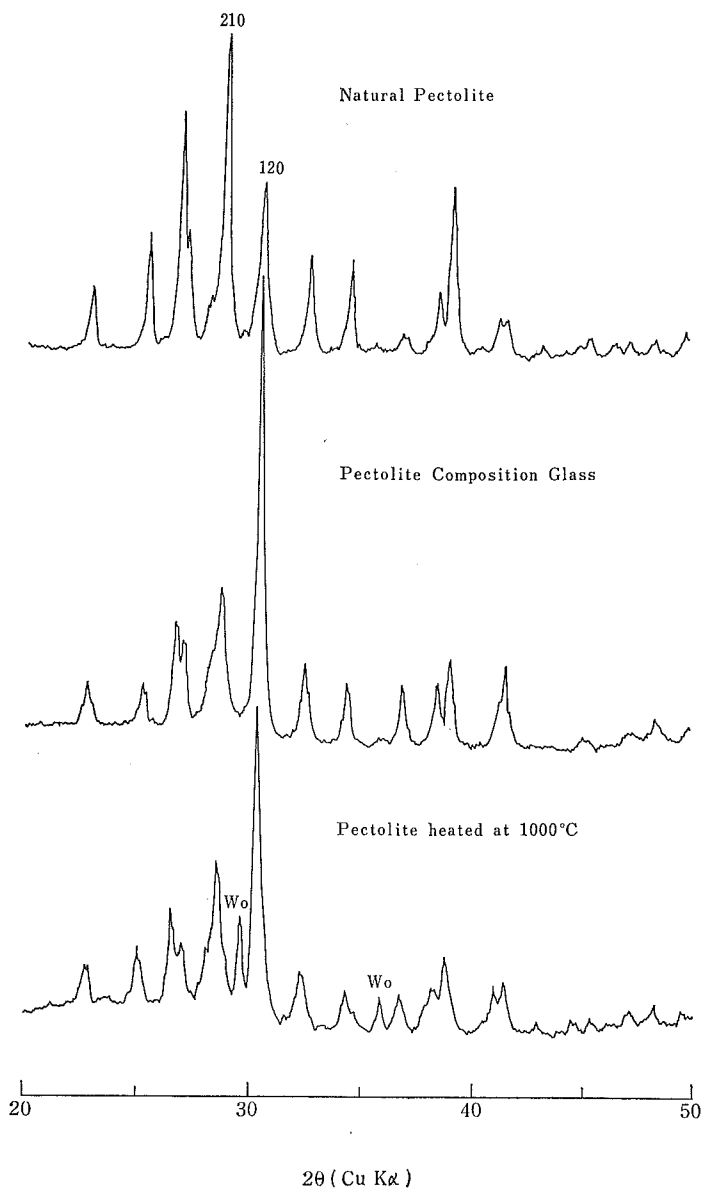
The product obtained from No. 1 was pectolite only, whereas small amounts of wollastonite were present in the products from Nos. 2 and 4. In the case of No. 3, the result was more complex. Small amounts of quartz and wollastonite were present in addition to pectolite and calcite even in runs as long as 90 hrs at 300°C and 300 bars. The reaction may be expressed as follows:



X-ray powder patterns of the synthetic pectolites derived from Nos. 1 and 2 are shown graphically in Figure 3, compared with that of the natural pectolite from Chisaka.

Synthesis was also done at 300°C and 300 bars for 24 to 90 hrs. There was no difference between the results obtained at different pressures.

Under the microscope the synthetic pectolite always form narrow tabular crystals, elongated in subparallel positions and shows undulatory extinction, indicat-

**Fig. 3**

X-ray powder pattern of the natural pectolite from Chisaka, compared with those of the synthetic pectolites derived from pectolite composition glass and decomposition products of pectolite heated at 1000°C. Note the reversal of intensities of (210) and (120) peaks in the natural and synthetic pectolites.

ing the aggregates of crystals slightly different in their optic orientation.

When wollastonite was used as starting material fine needles of wollastonite were replaced by pectolite crystals with different optic orientation. This is in contrast to the natural pectolite which always show acicular crystals, nearly parallel to z-axis with positive elongation, with well-developed cleavages. The refractive indices of synthetic pectolite are compared with those of natural one in Table 2.

Table 2. Refractive indices of pectolites

	Synthetic pectolite	Chisaka pectolite
$\alpha$	1.600	1.598
$\beta$	n.d.	1.604
$\gamma$	1.630	1.631

### Comparison of Natural and Synthetic Pectolites

#### 1. X-ray Powder Patterns

X-ray powder data on the synthetic pectolite are given as compared with those

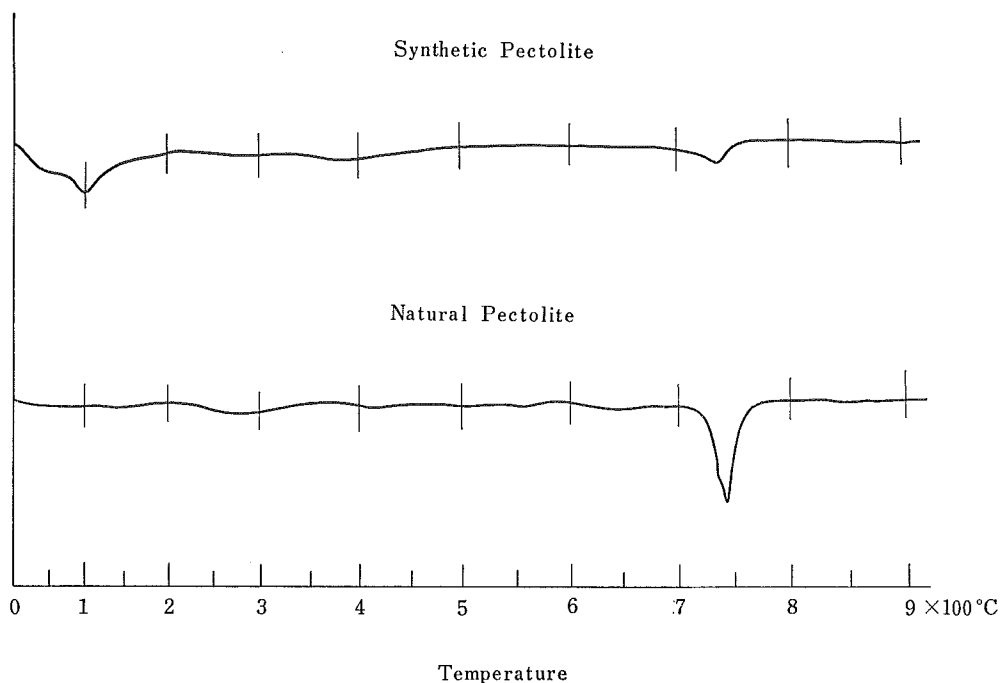


Fig. 4  
D.T.A. curves of natural and synthetic pectolites.



Table 3. X-ray Powder Data of Pectolites

(1)			(2)	
d (Å)	I	hkl	d (Å)	I
7.83	50	100	7.76	2
7.03	50	001		
5.50	50	$\bar{1}01$	5.47	2
4.98	10	101		
4.55	10	$\bar{1}\bar{1}1$		
4.00	20	$\bar{1}\bar{1}\bar{1}$		
3.90	60	200	3.88	8
3.77	20	111, $2\bar{1}0$		
3.52	50	$2\bar{0}1$	3.51	5
3.43	40	020		
3.33}		$\bar{1}02$	3.31	20
3.28}	60 B	201	3.27	15
3.16	50	$2\bar{1}1$		
3.10	80	210, $\bar{1}21$	3.08	57
2.921	100	120, $220+$	2.91	100
2.739	60		2.73	18
2.600	60		2.59	11
2.430	50		2.426	12
2.338	50		2.330	12
2.298	60		2.293	16
2.227	20			
2.191}				
2.166}	60 B		2.163	21
2.090	20			
2.053}				
2.002}	30 B		2.000	4 B
1.945	20			
1.926	40		1.914	2
1.877	40		1.873	5 B
1.831	40		1.824	1
1.781	30			
1.752	60		1.760	31
1.716	60		1.710	18
1.675	20			
1.661	40		1.653	4
1.603	40		1.599	7 B
1.570	20			
1.554	50		1.549	10
1.521	20		1.526	5 B
1.490	50		1.482	7
1.475}				
1.465}	50 B		1.463	13

(1) Pectolite from Bergen Hill, New Jersey (Hildebrand, 1953).

(2) Synthetic pectolite:  $\text{CuK}\alpha$ , 35 KV, 20 mA,  $1/2^\circ/\text{min}$ . Intensity was determined by relative area of each peak.

of natural pectolite by Hildebrand (1953) (Table 3). As shown in Figure 3, natural and synthetic pectolites are very similar in their powder patterns. Nevertheless it is remarkable that the two peaks (120, $\bar{2}$ 20) and (210, $\bar{1}$ 21) are reversed in their intensities: i.e. in the natural one (210) peak is the highest, while in the synthetic one (120) peak is the highest. As pointed out by Hildebrand (1953), the apparent highest peak of (210) is due to the effect of preferred orientation, and it is difficult to eliminate this effects in the X-ray powder patterns of natural pectolite. In the case of synthetic pectolite such effects are easily removed, and the (120) peak becomes the highest. However, it is not clear why (210) peak is so low in the synthetic one.

## 2. Differential Thermal Analysis

Differential thermal analysis curves determined for both natural and synthetic pectolites are compared in Figure 4. Because of very small amount of the sample the curve of the synthetic pectolite is not so accurate as in the natural pectolite. In the case of natural pectolite there is a distinguished endothermic peak, beginning at 710°C and ending at 770°C, with a maximum at about 740°C, whereas two endothermic peaks are noticed in the synthetic one: i.e., at about 100° and 740°C. The first is noticeable and is probably due to the hygroscopic water absorbed in synthetic crystals, whereas the second one at about 740°C is not so distinct, but lies in exactly the same position as the natural one.

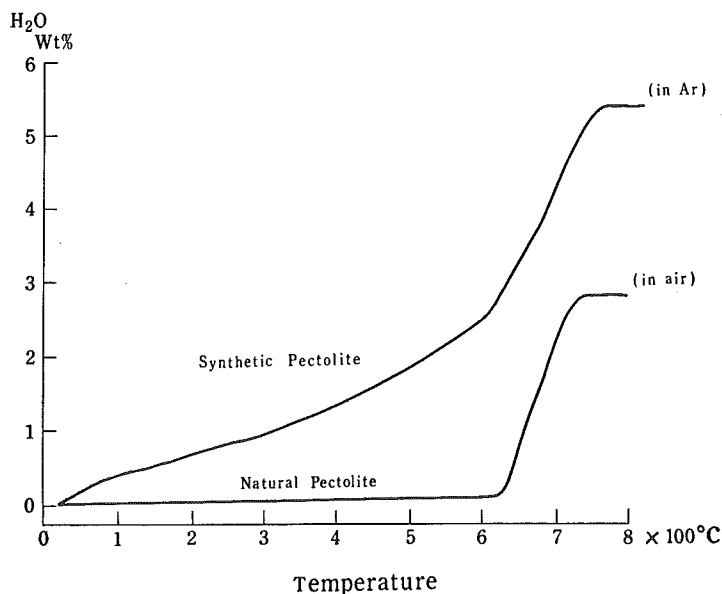


Fig. 5  
T.G.A. curves of natural and synthetic pectolites.

### 3. *Thermogravimetric Analysis*

The result of the thermogravimetric analysis of the natural and synthetic pectolites is graphically shown in Figure 5. The amount of the sample of natural pectolite was 1.8813 gr and the weight loss amounted to 0.0487 gr or 2.59 weight per cent. The loss began at about 630° and was completed at about 730°C, the rate of rise of temperature being 2.5°C/min in the room air. This loss is nearly the same as the water content of Chisaka pectolite in which H<sub>2</sub>O+ is 2.77 per cent (see Table 1). This corresponds to the theoretical H<sub>2</sub>O content of 2.7 per cent or 0.5 mole H<sub>2</sub>O per mole Ca<sub>2</sub>Na(HSi<sub>3</sub>O<sub>9</sub>).

The thermogravimetric analysis of the synthetic pectolite was made on the sample, only 0.2022 gr in weight. In this case, because of very small amount of the sample used, the experiment was made by a silica-glass balance in dried Ar gas stream at the flow rate of 340 cc/min in order to minimize the effect of the contamination of moisture in the room air. The temperature was raised manually at the rate of 2.5°/min. It is noticed that the curve can be divided into two parts, with discontinuity at about 620°C. The total weight loss attained to 0.0108 gr or 5.34 per cent, of which 0.0053 gr or 2.62 per cent was lost gradually below 620°C and 0.0055 gr or 2.72 per cent slightly more abruptly above 620°C. Therefore the total water content 5.34 per cent of the synthetic pectolite is almost double that of the natural one. Of this water content, the water lost above 620°C corresponds to the water content of natural pectolite, i.e., so-called "constitutional water", whereas water content below 620°C is the so-called "vagabonding water" (Eitel, 1966), which behaves in a way similar to "zeolite water".

The behavior of dehydration of these pectolites are different from those described by THILO and FUNK (1950), though the total water contents are the same. This difference may be due to the different way of the heating conditions in the experiments. THILO and FUNK showed that both natural and synthetic pectolites have the same dehydration curves in the stream of dried air, and nearly the same water contents.

Probably the "vagabonding water" is contained in the vacant space of the synthetic pectolite, but is absent from the natural pectolites.

### *Genetic Significance*

In Chisaka district, pectolite is associated with diopside and nephrite at the contact of rodingite and the surrounding serpentine. Sometimes albitite veins are also found in this vicinity (YAGI, BAMBA and OKEYA, 1968). Rodingite is rich in CaO and forms skarn-like aggregates of diopside, nephrite, and grossularite garnet, cutting through the serpentine. It is quite common that sodium is enriched in the later stage of serpentine crystallization, sometimes forming associated albitite

veins.

The synthesis of pectolite from mixtures of wollastonite,  $\text{SiO}_2$  and  $\text{Na}_2\text{CO}_3$  with water is suggestive for such occurrence. Probably the hydrothermal solutions of such serpentine are enriched both in sodium and silica, and their reaction with the pre-existing diopside or nephrite resulted in the formation of pectolite crystals along the boundary between the serpentine and rodingite.

#### *Acknowledgements*

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