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Mineralogical properties of phillipsite and thomsonite from Higashi-matsuura Peninsula, Saga Prefecture, Japan

Tei-ichi UENO
Department of Earth Sciences, Fukuoka University of Education

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Abstract

Phillipsite and thomsonite were found with gonnardite and chabazite in the altered hydrothermal veins or druses in the Higashi-matsuura basaltic rocks at Hayata, Chinzei-cho and Unezaki, Hizen-cho. Phillipsite is orthorhombic with the cell parameters of a=9.93 Å, b=14.312 Å and c=14.26 Å and with the refractive indices of $\alpha=1.494$, $\beta=1.499$ and $\gamma=1.504$, and it's chemical composition is $(Na_2, K_2, Ca, Mg, Fe)_{2.93}Al_{5.29}Si_{10.57}O_{32}11.83H_2O$. Thomsonite is orthorhombic with the cell parameters of a=13.10 Å, b=13.13 Å and c=13.28 Å and with the refractive indices of $\alpha=1.505$, $\beta=1.511$ and $\gamma=1.520$, and it's chemical composition is $Na_{1.32}Ca_{1.59}Al_{4.53}Si_{5.48}O_{20}$ $7.19H_2O$.

Phillipsite exists in contact with the host rock and gonnardite crystallizes on phillipsite. Gonnardite followed by thomsonite forms spherulite and the spherulite is often covered with chabazite. From these facts it is found that the order of crystallization may be phillipsite→gonnardite→thomsonite→chabazite. This means the increasing of Ca^{2+} and the decreasing of Na^{+} in the host solution during crystallization.

Introduction

Olivine basaltic rocks developed widely in the Higashi-matsuura Peninsula have many kinds of amygdale minerals, which have been studied by Ota (1958), Ishibashi (1974), Muchi (1976) and Ueno et al. (1982). Ishibashi (1974) described five kinds of zeolites in the basalts of this area and discussed the crystallization of the amygdale minerals, and Ueno et al. (1982) described the mineralogical data of gonnardite found in this area and it's structural change by heating. The objectives of present paper are to describe the mineralogical data of phillipsite and thomsonite found in this area and to elucidate the crystallization of these zeolites including gonnardite and chabazite.

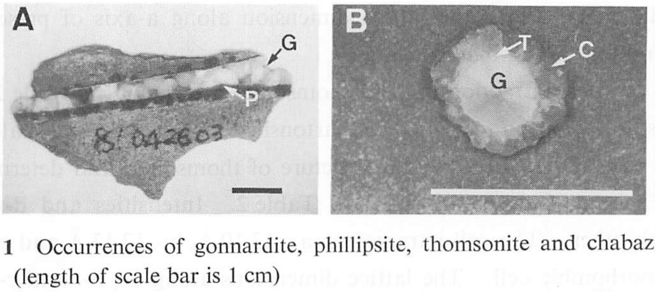

Fig. 1 Occurrences of gonnardite, phillipsite, thomsonite and chabazite. (length of scale bar is 1 cm)

A: white spherical crystals of gonnardite and light brown sheet like crystals of phillipsite in the hydrothermal vein

B: cut surface of white sphelule which is consisted of gonnardite, thomsonite, and chabazite

G: gonnardite, P: phillipsite, T: thomsonite, C: chabazite

Spacimens

Phillipsites, which coexist with white spherical gonnardites (Ueno et al., 1982), were found as dark brown sheet like minerals in the hydrothermal veins and as druse minerals in the basaltic rock, which is distributed in Hayata, Chinzei-cho, about 10 kilometers northwest of Karatsu-city. In the hydrothermal vein, phillipsites exist in contact with the host rock, and gonnardites crystallize on the sheet like phillipsites (Fig. 1A). In thin section, these phillipsites are light brown and are about 50 μm in length and 5 μm in width. The fine phillipsites strech in randum directions and form aggregates. Refractive indices measured by the immersion method are $\alpha = 1.494$, $\beta = 1.499$ and $\gamma = 1.504$ in Na light.

Thomsonites were found as white spherical minerals in the druses in the basaltic rock, which is distributed in Umezaki, Hizen-cho, about 15 kilometers west of Karatsu-city. In thin section, fibrous thomsonites and are gathered radially on gonnardites of the core. Refractive indices measured by the immersion method are $\alpha = 1.505$, $\beta = 1.511$ and $\gamma = 1.520$ in Na light. In another specimen the fine transparent chabazites crystallized on the white spherulite which consists of gonnardite (inner part) and thomsonite (middle part) (Fig. 1B). Judging from these relations, it is thought that gonnardite crystallized firstly, thomsonite secondary and chabazite finally in the druses in the basalt at Umezaki.

Experimental Results

1. X-ray powder diffraction

The X-ray powder diffraction data of phillipsite are shown in Table 1 and are compared with those of phillipsite from Mazé, Niigata Prefecture, Japan by Harada et al. (1967). Intensities and d-values well agree with each other. The cell parameters, a = 9.93 Å, b = 14.312 Å and c = 14.26 Å, were obtained as orthorhombic cell by least-square method. Steinfink (1962) studied the crystal structure of phillipsite and determined the space group, B_{2mb}, with a = 9.965 Å, b = 14.252 Å and c = 14.252 Å. Comparing with this data and the data by Harada et al. (1967), the lattice dimension along a-axis of present phillipsite is slightly small and that along b-axis is large.

The X-ray powder diffraction data of thomsonite are shown in Table 2 and are compared with those of thomsonite from Dumbartonshire by Nawaz and Malone (1981) who carried out the refinement of the crystal structure of thomsonite and determined the space group, P_{cnn}. Their hkl-indexes are used in Table 2. Intensities and d-values are well agreed with each other. The cell parameters, a = 13.10 Å, b = 13.13 Å and c = 13.28 Å, were obtained as orthorhombic cell. The lattice dimensions along a-, b-, and c-axes of present thomsonite are larger than those of Nawaz and Malone (1981).

Table 1 X-ray powder diffraction data for phillipsites

	1			2	
hkl	I/I_0	d_{obs}(Å)	d_{calc}(Å)	I/I_0	d(Å)
101	10	8.20	8.15	5	8.19
020	69	7.18	7.16	100	7.19
012	10	6.42	6.38	12	6.41
121	10	5.39	5.38	10	5.37
022	27	5.07	5.05	25	5.06
200	38	5.00	4.96	17	4.98
210	9	4.67	4.69	3	4.69
	9	4.44			
103	20	4.31	4.29	10	4.31
131	51	4.12	4.12	40	4.13
220	20	4.09	4.08	13	4.07
032	8	4.00	3.97	6	3.96
123	5	3.69	3.68	3	3.70
222	5	3.51	3.54	6	3.54
014	9	3.45	3.46	6	3.47
141	20	3.27	3.28	30	3.26
042	100	3.20	3.20	85	3.19
311	61	3.14	3.14	34	3.14
321	32	2.93	2.94	14	2.930
240	13	2.91	2.90	6	2.893
				4	2.857
143	23	2.76	2.75	21	2.754
151	49	2.695	2.700	34	2.698
				9	2.667
125	5	2.564	2.560	6	2.577
323	9	2.532	2.539	8	2.542
341	10	2.390	2.395	8	2.389
				2	2.309
026	6	2.252	2.256	4	2.259
305	6	2.160	2.160	4	2.160
				3	2.136
262	5	2.058	2.058	6	2.053
344	4	2.010	2.007	3	2.001
064 171	7	1.979	1.983 1.983	8	1.981
442	7	1.964	1.960	7	1.964
361	5	1.915	1.917	3	1.981
				7	1.834
452	4	1.817	1.813	3	1.810
080	13	1.787	1.789	17	1.787
307	4	1.735	1.735	4	1.733
317	9	1.722	1.722	7	1.721
066 280	6	1.687	1.684 1.683	4	1.680
183	6	1.650	1.651	7	1.652
	4	1.643		4	1.644
	5	1.612			
365	4	1.600	1.601	4	1.600
446	3	1.546	1.548	4	1.548
		a= 9.93 ±0.01 Å b=14.312±0.007 Å c=14.26 ±0.01 Å			a= 9.96 Å b=14.23 Å c=14.23 Å

1: from Hayata, Higashi-matsuura Peninsula, Saga Prefecture, this study

2: from Mazé, Niigata Prefecture, Harada et al. (1967)

Table 2 X-ray powder diffraction data for thomsonites

		1		2	
hkl	I/I_0	d_{obs}(Å)	d_{calc}(Å)	I	d(Å)
110	10	9.35	9.27	20	9.205
020	77	6.60	6.57	70	6.566
012	17	5.95	5.93	60	5.901
112				15	5.391
220	100	4.66	4.64	100	4.625
212	25	4.40	4.39	30	4.377
130	62	4.16	4.15	30	4.133
131				5	3.960
222	5	3.81	3.80	10	3.792
312	40	3.52	3.51	70	3.504
040	15	3.29	3.28	5	3.273
232	29	3.20	3.19	70	3.194
042 240	44	2.940	2.943 2.935	100	2.944
412	73	2.871	2.866	100	2.857
332	10	2.805	2.802	15	2.793
242	50	2.687	2.684	100	2.674
150?	12	2.585	2.575	30	2.579
432	13	2.439	2.439	25	2.430
334 530	12	2.256	2.262 2.248	30	2.252
060	44	2.183	2.188	70	2.182
532	5	2.128	2.129	15	2.122
620	12	2.065	2.071	15	2.062
542	4	1.961	1.957	15	1.952
326				10	1.882
064				5	1.824
640	19	1.817	1.818	30	1.811
552	3	1.782	1.786	5	1.777
624	3	1.759	1.757	10	1.755
		a=13.10±0.01 Å b=13.13±0.01 Å c=13.28±0.04 Å			a=13.051 Å b=13.092 Å c=13.263 Å

1: from Umezaki, Higashi-matsuura Peninsula, Saga Prefecture, Japan, this study

2: from Dumbartonshire (I 1543), Nawaz & Malone (1981)

2. Thermal analyses

The differential thermal analyses for phillipsite and thomsonite were carried out for about 25 milligrams in the range from room temperature to 1000°C at the heating rate of 20°C per minute. The DTA and TG curves for phillipsite are shown in Fig. 2. Endothermic phenomena are observed from about 30°C, which may be produced by the

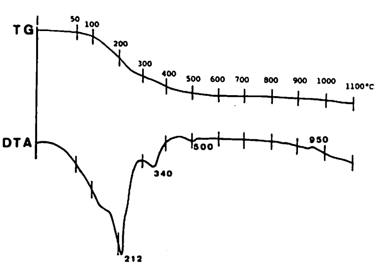

Fig. 2 Differential thermal analysis curve for phillipsite.

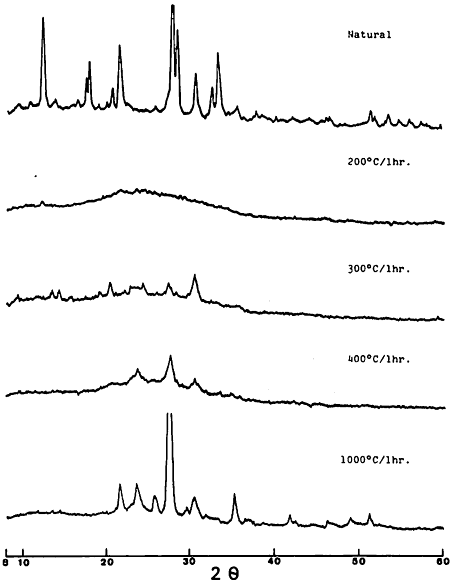

Fig. 3 Changes of X-ray powder pattern for phillipsite by heating. diffraction condition: CuKα, 30 Kv, 20 mA, with Ni-filter.

dehydations of adsorped water. A large sharp endothermic peak is seen at 212°C with a great decreasing of weight in the TG curve, which is caused by the dehydration of structural water. At 340°C and 500°C, endothermic peaks are seen and at 950°C a small exsothermic peak is observed. In order to elucidate these peaks, phillipstie specimens were heated every 100 degrees from 100°C to 1000°C for one hour using an electric furnace, and after cooling in a desicator the X-ray powder diffraction patterns of the heated specimens were obtained (Fig. 3). Although no changes were observed at 100°C, almost all the peaks disappeared at 200°C. However some new peaks began to appear at 300°C and some of them disappeared at 400°C. The peak of d=2.9 Å disappeared at 800°C and furthermore some new peaks appeared, and at 1000°C many weak peaks were observed with the strongest peak of d=3.23 Å, whose diffraction pattern is similar to that of high-form anorthoclase. It is considered that the diffraction pattern at 400°C corresponds to one phase, and the diffraction pattern at 300°C corresponds to two phases, which are named phase 1 and 2 here. The all X-ray diffraction lines are indexed as orthorhombic cells, whose cell dimensions are a=6.17 Å, b=6.11 Å and c=6.58 Å for phase 1 and a=6.51 Å, b=6.66 Å and c=6.35 Å for phase 2. The endothermic peak at 340°C in the DTA curve is explained by this structural change.

Fig. 4 shows a large endothemic peak at 350°C, small endothermic peaks at 421, 508 and 940°C, and a small exsothermic peak at 962°C in the DTA curve of thomsonite. There are some differences in the positions and intensities of endothermic and exsothermic peaks of thomsonites among this study, Koisumi (1953) and Muchi (1976). They are thought to be derived from the differences in compositions. Thomsonite specimens were heated at every 100 degrees from 100°C to 1000°C for one hour in order to examine the

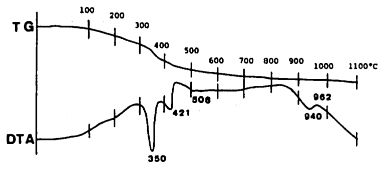

Fig. 4 Differential thermal analysis curve for thomsonite.

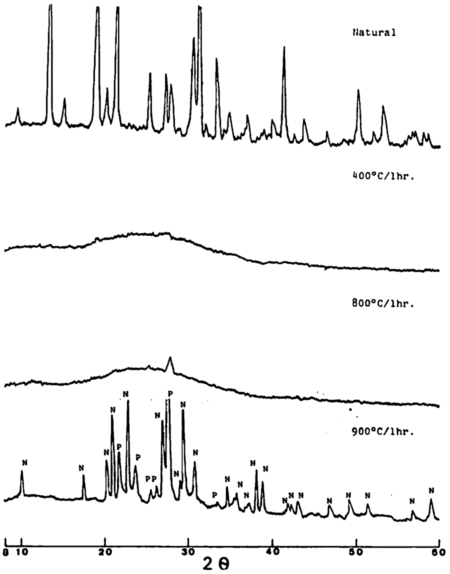

Fig. 5 Changes of X-ray powder pattern for thomsonite by heating diffraction condition: CuKα, 30 Kv, 20 mA, with Ni-filter N: nepheline, P: plagioclase.

Table 3 Chemical compositions of phillipsites

	1	2	3
SiO_2	48.25	46.11	46.03
Al_2O_3	20.49	21.96	21.43
$FeO+Fe_2O_3$	0.78*	—	0.99
MgO	0.11	0.03	—
CaO	2.24	3.84	5.73
Na_2O	7.62	7.59	3.13
K_2O	4.33	3.65	5.59
H_2O	16.18	16.96	17.22
Total	100.00	100.14	100.12
	Numbers of ions O=32		
Si	10.57	10.18	10.24
Al	5.29	5.72	5.62
Fe	0.14	—	0.16
Mg	0.04	0.01	—
Ca	0.53	0.91	1.36
Na	3.23	3.25	1.36
K	1.21	1.03	1.58
H_2O	11.83	12.49	12.78

* total iron as FeO

1: $(Na_2, K_2, Ca, Mg, Fe)_{2.93}Al_{5.29}Si_{10.57}O_{32}11.83H_2O$ from Higashi-matsuura Peninsula, Saga Prefecture, Japan, Electron probe micro-analysis, this study

2: $(Na_2, K_2, Ca, Mg)_{3.06}Al_{5.72}Si_{10.18}O_{32}12.49H_2O$ from Agnone, Syracuse, Sicily, wet chemical analysis, Tosto (1948)

3: $(Na_2, K_2, Ca, Fe)_{2.99}Al_{5.62}Si_{10.24}O_{32}12.78H_2O$ from Maze, Niigata Prefecture, Japan, wet chemical analysis, Harada et al. (1976)

structural changes by heating as in the case of phillipsite. The changes of X-ray powder diffraction patterns are shown in Fig. 5. Although no changes were observed till 200°C, the intensities of reflections were observed to decrease at 300°C, and almost all the peaks disappeared at 400°C. This amorphous state continued to 700°C, but some new peaks began to appear at 800°C and showed strong intensities at 900°C. The reflection pattern at 900°C may correspond to the mixture of nepheline type phase and plagioclase type phase. Hexagonal cell parameters of the nepheline type phase are a = 9.976 Å and c = 8.362 A, while triclinic cell parameters of the plagioclase type phase are a = 8.16 Å, b = 12.79 Å, c = 7.10 Å, $\alpha = 93°$ $\beta = 117°$ and $\gamma = 89°$. Judging from these X-ray data, it is thought that the large endothermic peak at 350°C was attributed to the decompsition of crystal structure, whereas the small endothermic peak at 940°C and the exothermic peak at 962°C were attributed to the formation of the nepheline type phase and the plagioclase type phase.

3. Electron probe micro-analyses

In order to obtain the chemical compositions of phillipsite and thomsonite, electron probe micro-analyses were performed using a JXA 50 A type instrument at the same operating condition and by the same correction method as described before (Ueno et al., 1982). In Table 3 the analytical value of phillipsite from Hayata, Higashi-matsuura Peninsula, is shown with the data of phillipsites from Agnone, Sicily (Tosto, 1948) and from Mazé, Niigata Prefecture, Japan (Harada et al., 1967). The composition of the phillipsite in this study is richer in Si and Na and poorer in Al and Ca than other two data, meaning the

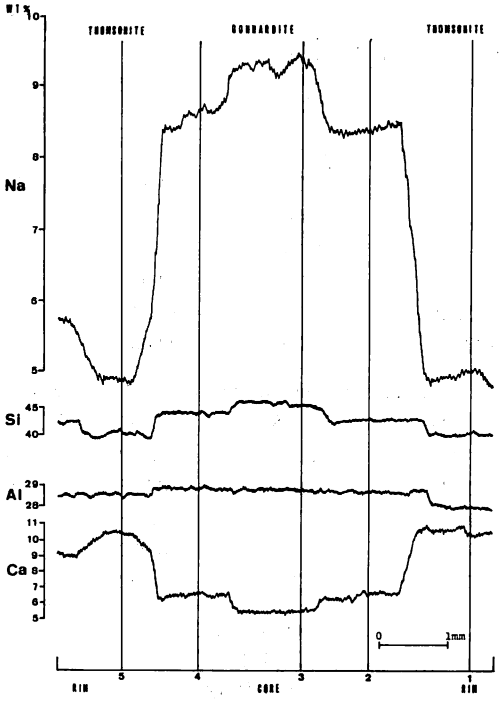

Fig. 6 Profiles of the zoned spherical zeolite traversed across the diameter.

substitution of $CaAl \rightleftharpoons NaSi$.

Cutting the white spherulite from Umezaki, about 6 mm in the diameter, line scanning was carried out in the diameter direction, and the profile is shown in Fig. 6. Na, Si, Al and Ca varied 5~10 wt%, 40~45 wt%, 28~29 wt% and 5~11 wt%, respectively. In the core (about 1 mm in the diameter), Na and Si are rich and Ca is poor, around the core Na and Si decrease and Ca increases slightly and in the outer part (about 1 mm in the width), Na and Si decrease and Ca increases abruptly. The point analyses were performed on the five points numbered in Fig. 6 and the results are summarized in Table 4. In the analytical value at point 3, Na is more than Ca, and considering the numbers of ions, it is found that this composition corresponds to gonnardite. Comparing with the ideal composition of gonnardite, $Na_2CaAl_5Si_5O_{20}6H_2O$, Na and Si are rich and Al and Ca are poor, meaning substitution of $CaAl \rightleftharpoons NaSi$. In the analytical values at points 2 and 4, Na is decreased and Ca is increased, but considering the numbers of ions, Na is contained two times as much as Ca, which means that these analytical values correspond to gonnardite. In the analytical values at points 1 and 5, Ca is more than Na, and considering the numbers of ions, it is found that these compositions correspond to thomsonite. Comparing with the ideal composition of thomsonite, $NaCa_2Al_5Si_5O_{20}6H_2O$, Na and Si are rich and Ca and Al are poor, meaning substitution of $CaAl \rightleftharpoons NaSi$ as in the cases of gonnardite and phillipsite. Examining by X-ray powder diffraction, the core part and the edge part of this spherulite showed the patterns of gonnardite and thomsonite, respectively.

Table 4 Chemical compositions determined by scanning analyses of the spherical zeolite from Higashi-matsuura Peninsula.

	1	2	3	4	5
SiO_2	40.17	44.48	45.20	44.20	40.87
Al_2O_3	28.16	28.73	28.85	29.12	28.04
CaO	10.89	7.08	5.57	6.45	11.06
Na_2O	4.99	8.53	9.23	8.76	4.76
K_2O	—	—	0.01	—	—
H_2O	15.79	11.18	11.14	11.47	15.06
Total	100.00	100.00	100.00	100.00	100.00
	Numbers of ions on the basis of 20 oxygens				
Si	5.480	5.718	5.783	5.693	5.532
Al	4.527	4.352	4.350	4.420	4.472
Ca	1.591	0.972	0.763	0.890	1.603
Na	1.319	2.125	2.288	2.187	1.248
K	—	—	0.002	—	0.002
H_2O	7.187	4.792	4.752	4.930	6.801

1: thomsonite, $Na_{1.32}Ca_{1.59}Al_{4.53}Si_{5.48}O_{20}7.19H_2O$
2: gonnardite, $Na_{2.13}Ca_{0.97}Al_{4.35}Si_{5.72}O_{20}4.79H_2O$
3: gonnardite, $Na_{2.29}Ca_{0.76}Al_{4.35}Si_{5.78}O_{20}4.75H_2O$
4: gonnardite, $Na_{2.19}Ca_{0.89}Al_{4.42}Si_{5.69}O_{20}4.93H_2O$
5: thomsonite, $Na_{1.25}Ca_{1.60}Al_{4.47}Si_{5.53}O_{20}6.80H_2O$

Table 5 Order of crystallization of zeolites found at Hayata and Umezaki, Higashi-matsuura Peninsula.

phillipsite	↓	$Na > K > Ca$
gonnardite		$Na > Ca$
thomsonite		$Ca \geq Na$
chabazite		$Ca > K \geq Na$

Discussions

The order of crystallization and the change of compositions of the zeolites found at Hayata and Umezaki, Higashi-matsuura Peninsula, are summarized in Table 5. Harada et al. (1967) examined the amygdale minerals of the altered basalt from Maze, Niigata Prefecture, Japan, and showed some types of order of crystallization. Many of those sequences were explained by decreasing of Ca^{2+} and increasing of Na^{+} in the host solution during crystallization. Ishibashi (1974) also showed the sequence of amygdale minerals of basaltic rock from Iwano, Higashi-matsuura Peninsula, which sequence is as following; calcite→chabazite→herscherite→natrolite→analcime. This means the decreasing of Ca^{2+} and the increasing of Na^{+}. But the reverse zoning of crystallization was found in this study. It is thought that the order of crystallization of amygdale minerals depends on the change of the compositions of the hydrothermal solution, the mineral assemblages and their chemical compositions of the wall rock, and the physical conditions (temperature, pressure). Consequently there are differences of order of crystallization by places.

By heating phillipsite changed to the high-form anorthoclase type phase at 1000°C and thomsonite changed to the nepheline type phase and the plagioclase type phase at 900°C. Aumento (1966) found that stilbite changed to β-cristobalite and anorthite at 920°C. Kim & Burley (1980) showed in their $NaAlSi_3O_8$-$NaAlSiO_4$-H_2O system study that analcime solid solution changed to albite and nepheline in high temperature. Ueno et al. (1982) showed that gonnardite changed to nepheline by heating at 900°C for one hour. Generally, zeolite minerals are thought to be changed to feldspars, feldspathoids or SiO_2-minerals by heating. Goldsmith (1952) synthesized thomsonite from anorthite in the low temperature hydrothermal condition. These facts suggest the possibility that the natural zeolites formed secondary are crystallized by the reaction between hydrothermal solution and wall rock including feldspars, feldspathoids or SiO_2-minerals.

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