A hydrothermal experiment for retrograde change of gehlenite

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Abstract

Phase relations in the system gehlenite ($\text{Ak}_0\text{Ge}_{100}$ or $\text{Ak}_{20}\text{Ge}_{80}$)– SiO_2 – H_2O were investigated at 1 kbar water pressure and at temperatures from 350° to 750°C. Crystalline phases formed in the gehlenite end-member ($\text{Ak}_0\text{Ge}_{100}$)– SiO_2 – H_2O system are bicchulite, garnet, anorthite and corundum (or boehmite), and those in the gehlenite solid solution ($\text{Ak}_{20}\text{Ge}_{80}$)– SiO_2 – H_2O system are vesuvianite, xanthophyllite and diopside in addition to the phases formed in the end-member system. The results of the solid solution system are more consistent with the natural alteration reactions than the results of the end-member system.

The coexisting crystalline phases observed in the solid solution system change successively with the fall of temperature as follows: (1) gehlenite + garnet, (2) gehlenite + vesuvianite $\pm$ garnet, (3) bicchulite + xanthophyllite + vesuvianite and (4) bicchulite + vesuvianite $\pm$ garnet. The assemblage (1) is stable at temperatures above 720°C and that of (2) is stable at temperatures between 610°C and 720°C. The stability boundary between the assemblages (3) and (4) is inclined: 340°C for no silica-addition, 450°C for the added silica/gehlenite = 0.03 and 500°C for the added silica/gehlenite = 0.06. The large amounts of silica-additions result in the assemblage of garnet + anorthite $\pm$ diopside at temperatures between 350°C and 750°C.

Cell dimensions of hydrogrossular, i.e., degrees of hydration, vary depending not only on the formation temperatures but also on silica deficiencies of the starting materials. Cell dimensions of vesuvianite vary in the same manner as grossular. A linear relationship between the cell dimensions of garnet and those of vesuvianite was observed in the present experiment.

Examples consistent with the present experimental results are found in natural mineral assemblages from many localities. The alteration conditions of gehlenites at Crestmore and Kushiro, correspond to the mineral assemblage (2), whereas those at Akagane mine corresponds to the assemblage (3). The alteration conditions which were commonly observed at Fuka correspond to the assemblage (4). The experimental results may be applied to processes and conditions of natural alteration reactions of gehlenite at other localities as well. The same correlation between the cell dimensions of garnet and those of vesuvianite as in the synthetic experiments is seen in natural specimens from Fuka and Kushiro.

Introduction

Gehlenite is an important constituent of high-temperature skarns and is frequently altered to some retrograde minerals. Kusachi, Henmi and Henmi (1983) described a

representative example at Fuka, Okayama Prefecture, Japan where the gehlenite zones are divided into subzones that are characterized by retrograde mineral assemblages formed after gehlenite. These retrograde minerals include grossular, hydrogrossular, vesuvianite and bicchulite. The retrograde alteration of gehlenite is also reported at some localities (Agrell, 1965; Henmi, Kusachi, Henmi, Sabine and Young, 1973; Joesten, 1974; Sabine, 1975 and Bunno, Shimazaki and Sato, 1982).

To reveal the mechanisms of such skarnization, several investigators conducted experimental studies of the relevant synthetic systems. The akermanite end-member decomposes to monticellite + wollastonite (Harker and Tuttle, 1956) and the gehlenite end-member converts to gehlenite hydrate (Carlson, 1964) which was later found to occur as a natural mineral and was named bicchulite by Henmi et al. (1973). Experimental work on gehlenite-akermanite solid solution by Christie (1961) showed that the solid solution decomposes to vesuvianite + wollastonite + clinopyroxene or vesuvianite + hydrogrossular. However, he gave no information on the developments of monticellite and bicchulite. Henmi (1976) carried out hydrothermal experiments concerning the breakdown of gehlenite solid solution with a composition range from $\text{Ak}_0\text{Ge}_{100}$ to $\text{Ak}_{50}\text{Ge}_{50}$ and determined the conditions under which bicchulite and the associated minerals were formed. The gehlenite solid solution breaks down to a bicchulite-bearing assemblage at temperatures below about 600°C.

Bicchulite has been recorded from only three localities: Fuka, Okayama Prefecture, Japan, Carneal, Northern Ireland (C. Henmi et al., 1973) and Akagane mine, Iwate Prefecture, Japan (Nambu, Tanida, Kitamura and Oikawa, 1975; Shimazaki, Bunno and Sato, 1975 and Bunno et al., 1982). In addition to bicchulite, vesuvianite, grossular and hydrogrossular are also recognized as alteration products of gehlenite at these localities.

A petrochemical investigation of natural alteration products of gehlenite from Fuka (Kusachi et al., 1983) showed that the alteration reactions were accompanied by additions of both H_2O and SiO_2 and that the silica-addition was essential to the formation of grossular and vesuvianite. Such alteration reactions are commonly observed at other localities as well. This suggests the necessity of hydrothermal experiments with addition of silica to reveal fundamental processes of retrograde alterations.

In this paper, the author presents the results of experimental work concerning the gehlenite end-member ($\text{Ak}_0\text{Ge}_{100}$)— SiO_2 — H_2O and gehlenite solid solution ($\text{Ak}_{20}\text{Ge}_{80}$)— SiO_2 — H_2O systems. The former system is relatively simple and the results derived from this experiment can be comparable with many previous studies on CaO — Al_2O_3 — SiO_2 — H_2O system. The latter system may give more important information to better understanding of the natural modes of occurrences related to retrograde reactions of gehlenite.

Experimental

Reagent grade silica gel, active alumina, magnesium oxide and calcium carbonate were used as source materials. They were fired by gas burner except calcium carbonate. Two mixed oxides with the compositions of gehlenite end-member ($\text{Ak}_0\text{Ge}_{100}$) and gehlinite solid solution ($\text{Ak}_{20}\text{Ge}_{80}$), were prepared from the source materials. After ignition for decarbonation, the mixed oxides were hydrothermally treated at 700°C or 750°C and 1 kbar for 5 days to synthesize gehlenites. The gehlenites ($\text{Ak}_0\text{Ge}_{100}$ and $\text{Ak}_{20}\text{Ge}_{80}$) synthesized in this way and SiO_2 were used as starting materials.

The experimental works were carried out in cold seal pressure vessels (Kitahama, HW-1). The reactants were held in small silver or gold capsules (2.8 or 4.8 mm in diameter) with 15–20 wt percents of water. Experiments were carried out under the water pressure at 1 kbar and at temperatures from 350°C to 750°C. To examine the pressure dependence of the results, some experiments were carried out at 0.5 kbar water pressure. The temperatures were measured with a chromel-alumel thermocouple and controlled to $\pm 5^\circ\text{C}$. The durations of runs varied from 4 to 45 days. After each run the pressure vessel was quenched in cold water.

The products were examined with a petrographic microscope, and an X-ray diffractometer (Rigaku Geigerflex, Cu/Ni). The cell dimensions of the garnet, bicchulite, gehlenite and vesuvianite were obtained by measuring d spacings using silicon powder as an internal standard. The fractions of each mineral in the products were determined

TABLE 1. Abbreviations of products and main X-ray peaks used to determine fractions of each phase in the products.

Abbrev.	Phase	Chemical compositions	Main X-ray peaks (2θ , CuK α) used to determine fractions of each phase in the products
Ge	gehlenite		31.4°
Gee	gehlenite end-member	$\text{Ca}_2\text{Al}_2\text{SiO}_7$	
Ges	gehlenite solid solution	$\text{Ca}_2(\text{MgSi})_x(2\text{Al})_{1-x}\text{SiO}_7$	
G	garnet		33–34
Gr	grossular	$\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$	
HG	hydrogrossular	$\text{Ca}_3\text{Al}_2(\text{Si}, 4\text{H})_3\text{O}_{12}$	
B	bicchulite	$\text{Ca}_2\text{Al}_2\text{SiO}_6(\text{OH})_2$	32.0
X	xanthophyllite		35.0
V	vesuvianite		32.5
A	anorthite	$\text{CaAl}_2\text{Si}_2\text{O}_8$	27.9
D	diopside	$\text{CaMgSi}_2\text{O}_6$	35.5
C	corundum	Al_2O_3	25.6
Bo	boehmite	$\text{AlO}(\text{OH})$	14.5

by measuring the relative diffraction intensities for which the main peaks used are listed in Table 1.

The synthetic conditions of each hydrothermal run are listed in Table 2 which shows the resulting phases of each run along with the cell dimensions of main phases.

Coexisting crystalline phases

The end-member system ($Ak_0Ge_{100}-SiO_2-H_2O$)

The crystalline phases formed at 1 kbar water pressure in the end-member system are shown in Table 2 and Figure 1.

At temperatures higher than 600°C, an addition of small amounts of SiO_2 to the gehlenite end-member composition results in the association of gehlenite with garnet and an alumina mineral. As the amounts of SiO_2 increase, the garnet/gehlenite ratio in the resultant assemblages increases. Garnet is formed by the reaction of gehlenite with silica as follows:

In the experimental runs where SiO_2 is added to gehlenite in weight proportions more than $(\text{added } SiO_2)/Ge_{100} = 0.15$, gehlenite is no longer stable and an anorthite-bearing assemblage is obtained instead. Anorthite is formed according to the following reaction:

At temperatures lower than about 600°C, gehlenite is hydrated to bicchulite according to the following reaction:

The Nos. 34 and 44 runs didn't result in the hydration of gehlenite at 600°C. However, some additional runs using the materials added with small amounts of bicchulite as seeds showed a distinct increase in the amounts of bicchulite. Thus, the hydration of gehlenite in the Nos. 34 and 44 runs is considered to take place at the same temperature as that of the experimental run without added silica. As the $(\text{added } SiO_2)/Ge_{100}$ ratio in the starting material increases, the resultant assemblage changes from bicchulite alone, through bicchulite + garnet $\pm$ alumina minerals and to anorthite + garnet.

The alumina minerals observed are corundum at high temperatures and boehmite at low temperatures. At intermediate temperatures no alumina mineral was detected.

The solid solution system ($Ak_{20}Ge_{80}-SiO_2-H_2O$)

TABLE 2. Results of hydrothermal runs with the synthetic conditions. Abbreviations are as in Table 1.

No.	Compos. SiO ₂ /Gee (wt)	Temp. (°C)	Run dur. (d)	Phases	Cell dimensions					
					Garnet <i>a</i> (Å)	Bicch. <i>a</i> (Å)	Gehlenite <i>a</i> (Å) <i>c</i> (Å)		Vesuvianite <i>a</i> (Å) <i>c</i> (Å)	
(1) Gee (Ak ₀ Ge ₁₀₀) + SiO ₂ at 1 kbar										
2	0.000	700	3	Ge			7.687(3)	5.068(3)		
3	0.000	650	5	Ge			7.686(4)	5.067(3)		
4	0.000	630	7	B						
5	0.000	620	5	B						
7	0.000	550	7	B		8.831(3)				
9	0.000	450	7	B						
10	0.000	400	10	B						
11	0.000	350	13	B		8.831(3)				
14	0.017	600	45	BG	11.866(5)	8.823(4)				
23	0.033	650	4	GeGC						
24	0.033	600	45	BG	11.870(4)	8.823(2)				
25	0.033	550	11	BG	11.868(4)	8.823(3)				
26	0.033	500	14	BG	11.884(4)	8.823(3)				
27	0.033	450	42	BG	11.925(7)	8.823(3)				
28	0.033	400	10	BG	11.950(4)	8.825(2)				
29	0.033	350	24	BGB ₀	11.972(4)	8.829(2)				
34	0.067	600	7	GeGC	12.024(6)	8.829(3)				
35	0.067	550	21	BG	11.900(4)		7.688(3)	5.063(3)		
37	0.067	450	15	BG	11.901(4)	8.833(3)				
38	0.067	400	10	BG	11.945(4)	8.829(3)				
39	0.067	350	24	BGB ₀	11.964(5)	8.825(5)				
42	0.100	700	5	GeGC	11.990(5)					
43	0.100	650	6	GeGC	11.855(4)		7.685(4)	5.067(6)		
44	0.100	600	6	GeGC	11.865(4)					
49	0.100	350	24	BGB ₀	11.883(6)		7.695(6)	5.064(4)		
					11.993(5)	8.838(3)				

TABLE 2. (Continued) - 1.

No.	Compos. SiO ₂ /Gee (Wt)	Temp. (°C)	Run dur. (d)	Phases	Cell dimensions			
					Garnet <i>a</i> (Å)	Bicch. <i>a</i> (Å)	Gehlenite <i>a</i> (Å) <i>c</i> (Å)	Vesuvianite <i>a</i> (Å) <i>c</i> (Å)
52	0.133	700	5	GeCC	11.860(3)		7.690(5) 5.066(4)	
53	0.133	650	6	GeCC	11.862(3)			
55	0.133	550	11	BGC	11.898(3)	8.824(4)		
56	0.133	500	14	BG	11.920(4)			
57	0.133	450	42	BG	11.940(4)	8.824(4)		
58	0.133	400	13	BG	11.952(2)	8.827(2)		
59	0.133	350	33	GA	11.990(4)			
64	0.20	600	9	GA	11.885(6)			
65	0.20	550	21	GA	11.897(4)			
66	0.20	500	14	GA	11.992(4)			
67	0.20	450	42	GA	11.939(5)			
68	0.20	400	13	GA	11.951(3)			
69	0.20	350	24	GA	11.979(5)			
77	0.267	450	15	GA	11.936(2)			
83	0.33	650	6	GA	11.865(4)			
84	0.33	600	6	GA	11.877(6)			
85	0.33	550	11	GA	11.893(4)			
86	0.33	500	14	GA	11.919(4)			
87	0.33	450	42	GAW	11.941(3)			
88	0.33	400	13	GA	11.950(3)			
89	0.33	350	24	GA	11.965(5)			

TABLE 2. (Continued) - 2.

No.	Compos. SiO ₂ /Ges (wt)	Temp. (°C)	Run dur. (d)	Phases	Cell dimensions					
					Garnet <i>a</i> (Å)	Bicch. <i>a</i> (Å)	Gehlenite		Vesuvianite	
							<i>a</i> (Å)	<i>c</i> (Å)	<i>a</i> (Å)	<i>c</i> (Å)
(2) Ges (Ak ₃₀ Ges ₇₀) + SiO ₂ at 1 kbar										
101	0.003	750	3	Ge			7.704(5)	5.060(4)		
102	0.000	700	3	Ge			7.702(4)	5.061(4)		
103	0.000	650	10	Ge			7.703(4)	5.059(4)		
104	0.000	620	15	Ge						
105	0.000	600	4	BXV		8.826(2)			15.572(8)	11.845(5)
106	0.000	550	4	BXV		8.825(3)				
107	0.000	500	10	BXV		8.822(3)			15.589(8)	11.846(4)
108	0.000	450	10	BXV		8.825(3)				
109	0.000	425	38	BXV		8.828(3)				
110	0.000	400	15	BVG	12.04(2)	8.827(3)			15.64(2)	11.90(2)
111	0.000	350	40	BVG	12.100(7)	8.831(3)				
122	0.033	700	17	GeV						
123	0.033	650	10	GeV			7.697(4)	5.062(4)	15.566(8)	11.827(6)
124	0.033	600	30	BXV			7.700(4)	5.062(4)	15.570(10)	11.837(7)
125	0.033	550	7	BXV		8.825(3)			15.539(8)	11.833(6)
126	0.033	500	25	BXV		8.825(4)			15.581(9)	11.845(7)
127	0.033	450	16	BVG		8.830(4)			15.592(10)	11.845(9)
128	0.033	425	38	BVG	11.972(3)	8.825(3)			15.600(8)	11.840(6)
129	0.033	400	35	BVG	12.007(4)	8.831(3)			15.613(11)	11.870(9)
130	0.033	350	40	BG	12.018(3)	8.831(2)			15.62(2)	11.87(2)
					12.033(5)	8.830(7)				
141	0.067	750	5	GeG						
142	0.067	700	17	GeV	11.846(3)		7.706(5)	5.055(5)	15.541(9)	11.832(7)
143	0.067	650	10	GeV			7.696(7)	5.063(5)	15.546(9)	11.820(8)
144	0.067	600	7	BVG			7.700(8)	5.063(6)	15.552(9)	11.827(8)
145	0.067	550	5	BVG	11.883(3)	8.826(2)			15.555(10)	11.830(9)
146	0.067	500	25	BVG	11.899(2)	8.825(3)			15.573(16)	11.848(8)
147	0.067	450	16	BVG	11.930(3)	8.821(5)			15.585(10)	11.849(5)
148	0.067	400	35	BVG	11.958(4)	8.831(3)				
149	0.066	350	40	BG	11.999(3)	8.825(4)				
					12.085(5)					

TABLE 2. (Continued) - 3.

No.	Compos. SiO ₂ /Ges (wt)	Temp. (°C)	Run dur. (d)	Phases	Cell dimensions					
					Garnet <i>a</i> (Å)	Bicch. <i>a</i> (Å)	Gehlenite <i>a</i> (Å)	<i>c</i> (Å)	Vesuvianite <i>a</i> (Å)	<i>c</i> (Å)
151	0.100	750	5	GeG	11.848(3)				15.526(9)	11.810(7)
152	0.100	700	17	GeVG	11.855(3)		7.694(6)	5.062(7)	15.539(8)	11.820(6)
153	0.100	650	27	GeVG	11.869(5)		7.700(6)	5.064(5)	15.545(9)	11.820(7)
154	0.100	600	30	BVG	11.881(4)				15.55(2)	11.82(2)
155	0.100	550	31	BVG	11.891(7)	8.824(3)			15.56(2)	11.84(2)
156	0.100	500	13	BVG	11.924(3)	8.825(4)				
157	0.100	450	6	VG	11.958(4)					
158	0.100	400	7	VGA	11.992(4)				15.59(2)	11.86(2)
159	0.100	350	40	GA	12.035(5)					
161	0.133	750	5	GeG	11.849(3)		7.702(5)	5.058(5)		
162	0.133	700	6	GeVG	11.869(4)		7.696(4)	5.063(4)		
163	0.133	650	31	GeVG	11.858(4)					
164	0.133	600	11	BVG	11.876(5)					
165	0.133	550	5	BVG	11.894(3)					
166	0.133	500	13	VGA	11.914(6)				15.557(10)	11.830(8)
167	0.133	450	6	VGA	11.932(5)				15.566(12)	11.834(9)
168	0.133	400	28	GA	11.978(5)					
169	0.133	350	40	GA	12.005(4)					
171	0.20	750	5	GA	11.844(3)					
172	0.20	700	11	GA	11.855(4)					
173	0.20	650	22	VGA	11.861(4)					
174	0.20	600	7	VGA	11.865(5)					
175	0.20	550	5	VGA	11.883(4)					
176	0.20	500	25	GA	11.903(3)					
177	0.20	450	6	GA	11.924(5)					
178	0.20	400	35	GA	11.951(5)					
179	0.20	350	40	GA	12.000(7)					

TABLE 2. (Continued) - 4.

No.	Compos. SiO ₂ /Ges (wt)	Temp. (°C)	Run dur. (d)	Phases	Cell dimensions					
					Garnet <i>a</i> (Å)	Bicch. <i>a</i> (Å)	Gehlenite <i>a</i> (Å)	Gehlenite <i>c</i> (Å)	Vesuvianite <i>a</i> (Å)	Vesuvianite <i>c</i> (Å)
181	0.33	750	5	GAD	11.846(3)					
182	0.33	700	6	GAD	11.845(2)					
183	0.33	650	8	GAD	11.848(2)					
184	0.33	600	10	GAD	11.856(3)					
185	0.33	550	31	GAD	11.874(4)					
186	0.33	500	25	GAD	11.878(2)					
187	0.33	450	33	GAD	11.890(3)					
188	0.33	400	35	GAD	11.912(4)					
189	0.33	350	40	GAD	11.950(5)					
(3) Ges (ΔK ₂₉ G ₃₈₀) + SiO ₂ at 0.5 kbar										
204	0.000	600	7	Ge						
205	0.000	550	10	BXV			7.699(5)	5.062(3)		
207	0.000	450	18	BXV		8.824(3)				
208	0.000	400	32	BGV	12.094(5)	8.827(2)				
209	0.000	350	41	BG	12.102(6)	8.823(2)				
						8.824(3)				
218	0.033	400	32	BVG	12.001(4)	8.826(3)				
228	0.067	400	32	BVG	11.965(4)	8.824(4)			15.57(2)	11.83(1)
238	0.100	400	30	BVG	11.940(3)					
242	0.133	700	7	G ₂ G	11.855(3)					
243	0.133	650	7	G ₂ G	11.854(3)					
244	0.133	600	7	G ₂ VG	11.874(3)					
245	0.133	550	10	BVG	11.881(3)					
246	0.133	500	7	BVG	11.910(3)	8.825(4)				
247	0.133	450	42	BVG	11.901(3)	8.832(5)				
248	0.133	400	32	VG	11.941(4)					
249	0.133	350	41	GA	11.954(3)					
258	0.20	400	30	GA	11.925(3)					
262	0.33	700	28	GAD	11.855(3)					
264	0.33	600	6	GAD	11.874(3)					
268	0.33	400	30	GAD	11.925(9)

FIG. 1. The mineral assemblages and cell dimensions of garnets formed in the gehlenite end-member system ($\text{Ak}_0\text{Ge}_{100}-\text{SiO}_2-\text{H}_2\text{O}$) at 1 kbar water pressure. Isopleths indicated by broken lines refer to cell dimensions in angstroms of garnets. Abbreviations are as in Table 1.

The crystalline phases formed at 1 kbar water pressure in the solid solution system are shown in Table 2 and Figure 2.

In addition to the minerals formed in the end-member system, vesuvianite, xanthophyllite and diopside are obtained in this system. Vesuvianite is obtained at the temperature range from 350 to 700°C and xanthophyllite from 425 to 600°C. Figure

FIG. 2. The mineral assemblages and cell dimensions of garnets formed in the gehlenite solid solutions system ($\text{Ak}_{20}\text{Ge}_{80}-\text{SiO}_2-\text{H}_2\text{O}$) at 1 kbar water pressure. Isopleths indicated by broken lines refer to cell dimensions in angstroms of garnets. Abbreviations are as in Table 1.

3 shows changes in mineral proportions among gehlenite (or bichulite), vesuvianite and garnet which are the main constituents in products. At each temperature, the mineral proportion gradually changes with the SiO_2 contents in the starting materials.

FIG. 3. The change in mineral proportions among gehlenite (or bicalcium silicate), vesuvianite, and garnet in the products of the solid solution system. The compositions of starting materials are shown by the number: 0 to 5 represent $\text{SiO}_2/\text{Ges} = 0, 0.033, 0.066, 0.100, 0.133$ and 0.200 , respectively.

Vesuvianite was formed in abundance at the temperature range from 500 to 700°C . The amounts of garnet gradually increase with increasing SiO_2 contents in the starting materials.

There is no essential difference between the results at 0.5 kbar and 1 kbar.

Cell dimensions

The cell dimensions of gehlenite change with the amounts of the Ak component in the solid solution. The gehlenite as the starting material in the end-member system has cell dimensions of $a = 7.687(3) \text{ \AA}$ and $c = 5.069(3) \text{ \AA}$. The reaction causes no change in the cell dimensions of gehlenite, indicating no change in the chemical composition of gehlenite in the end-member system. On the other hand, the gehlenite as

the starting material in the solid solution system has cell dimensions of $a = 7.704(4)$ Å and $c = 5.060(4)$ Å. Resulting gehlenite in association with vesuvianite has the cell dimensions of $a = 7.697(6)$ Å and $c = 5.062(5)$ Å. These cell dimensions correspond to gehlenite with the composition of $\text{Ak}_{15}\text{Ge}_{85}$ and suggest that about a quarter of (Mg+Si) in the starting gehlenite solid solution may be substituted by 2Al.

The cell dimensions of bicchulite formed in the present experiments are always constant ($a = 8.827 \pm 0.002$ Å), showing that there is no chemical change such as the substitution of (Mg+Si) for 2Al in gehlenite.

The cell dimensions of vesuvianite formed in the present study range between $a = 15.526(9)$ Å, $c = 11.810(9)$ Å and $a = 15.64(2)$ Å, $c = 11.90(2)$ Å. Figure 4 shows the cell dimensions a of vesuvianite as a function of temperature. The silica-poor nature of the starting material and low-temperature, generally favour the formation of vesuvianite with large cell dimensions.

FIG. 4. The cell dimensions a in angstroms of vesuvianites formed in the solid solution system are shown as a function of temperature.

The cell dimensions of garnet formed in the end-member system are in the range from 11.855(4) to 12.024(6) Å and those in the solid solution system are in the range from 11.844(3) to 12.100(7) Å. The isopleths referring cell dimensions of garnets in Figures 1 and 2 show that the cell dimensions of garnet become smaller with the rise of temperature and with the increase of added silica. These relations are more remarkable in the solid solution system than in the end-member system.

Discussion

Cell dimensions of garnet

Isomorphic substitution of 4H for Si in grossular garnet is sometimes observed in natural and synthetic materials. Flint, McMurdie and Wells (1941) insists that this substitution is accompanied by an increase in cell dimensions.

Hydrothermal syntheses of the grossular-hydrogrossular series have been made by several investigators (Carlson, 1956; Pistorius and Kennedy, 1960; Shoji, 1974; Hsu, 1980; Schiffman and Liou, 1980 and others). They obtained hydrogrossulars at temperatures lower than 600°C. Lower temperatures favour more substitutions which are inferred from larger cell dimensions. Experiments using starting materials with silica contents less than that of grossular were performed by Carlson (1956) and Shoji (1974). Their results show that the cell dimensions of the hydrogrossulars are distinctly larger than those formed at the same conditions except for the less silica-contents.

The cell dimensions of garnet obtained in the gehlenite end-member system, $\text{Gee}(\text{Ak}_0\text{Ge}_{100})\text{—SiO}_2\text{—H}_2\text{O}$, vary depending on temperature and the amounts of silica added to gehlenite as shown in Figure 1. At each temperature, garnet with smallest cell dimension is formed from the starting materials in which large amounts of silica were added to the gehlenite, whereas garnet with the largest cell dimension is formed from those in which only very small amount of silica was added to the gehlenite. It is concluded that cell dimensions of hydrogrossular, i.e., amounts of 4H substituting Si, vary depending not only on the formation temperatures but also on silica deficiencies of the starting materials.

There is an uncertainty about stability of the hydrogrossulars. Hsu (1980) indicated that hydrogrossular is metastable at temperatures above 420°C and becomes anhydrous grossular under equilibrium conditions. Schiffman and Liou (1980) treated starting materials oversaturated with silica at 400°C and concluded that hydrogrossular is unstable when it is associated with quartz. To examine the stability of hydrogrossulars obtained in the present experiments, the author made some experiments following the method used by Hsu (1980). A product at 400°C was mixed with a small amount of a product at 650°C as seeds and was treated hydrothermally once again for

75 days at 400°C. The results revealed that the cell dimension of hydrogrossular did not change. The same result was obtained using a product at 350°C. It is concluded that hydrogrossular is not stable under the silica-sufficient conditions as studied by Hsu (1980) and Schiffman and Liou (1980) and is stable under the silica-insufficient conditions as the present experiment.

Garnets from the gehlenite solid solution system, $\text{Ges}(\text{Ak}_{20}\text{Ge}_{80})\text{--SiO}_2\text{--H}_2\text{O}$, have wider ranges of cell dimensions than those from the end-member system. Figure 5 shows differences in the range of cell dimensions of garnets between the two systems. The cell dimensions of garnets from the solid solution system vary with the amount of added silica from smaller to larger than those from the end-member system. The ranges of the cell dimensions become wider with decreasing temperature. In the solid solution system, the magnesium ion substituting calcium contracts the dodecahedron by its smaller ionic radius. On the other hand, the higher water affinity of magnesium ion expands the tetrahedron whose volume depends on the content of $(\text{OH})_4$ substituting SiO_4 . It is likely that the difference of the ionic radii of cations is effective at high temperatures and the difference of the water affinities is effective at low temperatures.

FIG. 5. Comparison of cell dimensions of garnets formed in the end-member system (solid symbols) and in the solid solution system (open symbols).

Cell dimensions of vesuvianite

Christie (1961) assumed that vesuvianite, like garnet, can form hydrovesuvianite, in which some of the Si-positions in the vesuvianite structure are replaced by 4H. Shoji (1971) obtained some synthetic vesuvianite with relatively large cell dimensions. Figure 4 shows that cell dimensions of vesuvianite obtained in the present work vary depending on the formation temperature and also on silica contents of the starting materials. The variation trend is similar to that for the grossular-hydrogrossular series.

Numano, Kusachi, Henmi and Henmi (1978) described occurrences of a variety of vesuvianite with cell dimensions larger than those of usual vesuvianite. It was found in association with hydrogrossular at Kushiro, Hiroshima Prefecture and at Fuka, Okayama Prefecture. The present author (in preparation) found a close relation between the cell dimensions of the two minerals. The results are shown in Figure 6, in which the cell dimensions of grossular and vesuvianite formed in the present syntheses are also given. Large vesuvianites coexist with large garnets and small vesuvianites coexist with small garnets, except for some natural specimens which are plotted at the right and lower part in Figure 6. The cell dimensions of vesuvianites bear a linear relation to those of garnets: $a(V) = 0.740 a(G) + 6.742$ in angstroms. Because the axial ratios

FIG. 6. Cell dimensions of garnet and vesuvianite. Circles are natural materials and others are synthesized materials in the present experiment. The symbols of a cross, open squares, solid squares, open triangles and solid triangles represent the (added SiO_2)/Ges ratios in the starting materials = 0.000, 0.033, 0.067, 0.100 and 0.133, respectively. The numbers beside the symbols show the formation temperatures in $^{\circ}\text{C}$.

(a/c) of these vesuvianites are approximately constant (about 1.314), the choice of the c dimension gives an equivalent figure. This relation suggests that the mechanism for expansions of cell dimensions of vesuvianite is common to those of hydrogrossular, i.e., the mechanism is the substitution of 4H for Si.

Natural assemblages

Natural gehlenite has been often altered to some retrograde minerals. The results of the present experiment would give better understanding the alterations of natural gehlenite. Here the author uses the term of “retrograde” changes for alterations which take place during the cooling stage following after the primary decarbonation. Natural gehlenites and their retrograde minerals are sometimes remetamorphosed by later igneous activities and are sometimes replaced along fractures. The experimental results can be applied not only to retrograde change but also to remetamorphism and replacement along fractures.

According to the present result (Figure 2), the alteration conditions of natural gehlenites are divided as follows:

1: Alteration reactions at temperatures above the stability limit of vesuvianite (ca. 700°C). At these temperatures, the assemblage of gehlenite and grossular is stable.

2: Alteration reactions at temperatures where vesuvianite is stable and above the upper stability limit of bicchulite (ca. 600–700°C). At these temperatures, the stable minerals are gehlenite, vesuvianite and garnet with small cell dimensions.

3: Alteration reactions at temperatures where bicchulite is stable and above the lower stability limit of xanthophyllite (ca. 400–600°C) with a small amount of silica addition. The stable phases are bicchulite, xanthophyllite and vesuvianite.

4: Alteration reactions at temperatures below the stability field of xanthophyllite. This condition is characterized by the absence of xanthophyllite. The boundary of the condition 3 and 4 is inclined: 400°C for no silica-addition and 500°C for silica-addition of (added SiO₂)/Ges = 0.05. Therefore, when SiO₂-addition was not small, the temperature would be higher than 400°C. The stable phases are bicchulite, vesuvianite and hydrogrossular.

Natural occurrences of type 1

The assemblage of gehlenite and grossular (without vesuvianite) is rare in natural skarns. The stage at condition 1 may be included in the progressive stage of the skarn formation. The silica added to gehlenite does not react with gehlenite to form garnet but reacts with limestone to form spurrite or wollastonite which is usually found between the gehlenite zone and limestone.

Kusachi et al. (1978) reported that at an outcrop in Fuka the skarns in the vicinity of an andesite dike consist of mixtures of gehlenite and garnet, whereas those far

from the dike are mixtures consisting vesuvianite and hydrogrossular. The gehlenite can be understood as to be rejuvenated by a later intrusion of the dike. The rejuvenation can be regarded as a result of remetamorphism, which took place under the condition 1. The association of gehlenite with garnet indicates that the primary gehlenite zone had been altered, prior to the remetamorphism, by a retrograde reaction accompanied by silica addition.

Natural occurrences of type 2

The mineral assemblage formed under this condition may be represented by that found at Kushiro (Numano, 1979). There are garnet subzones and vesuvianite subzones in gehlenite zones at the contact part with igneous rocks. The vesuvianite subzone represents small addition of silica and water to gehlenite, and the garnet subzone represents larger addition of silica.

Garnet and vesuvianite related with melilite occur at Crestmore, California (Burnham, 1959). It is probable that they have been formed by mechanisms similar to those at Kushiro.

Natural occurrences of type 3

The assemblage of bicchulite and xanthophyllite was found at Akagane mine, Iwate Prefecture (Nambu et al., 1975; Shimazaki et al., 1975 and Bunno et al., 1982). Bunno et al. reported that the assemblage containing bicchulite was formed as an alteration product of gehlenite at a temperature between 400 and 630°C. Not only the mineral assemblage but also the assumed temperature are compatible with the condition 3.

Natural occurrences of type 4

The assemblage of bicchulite, vesuvianite and hydrogrossular is widely distributed at Fuka (C. Henmi et al., 1973). At Fuka the primary gehlenite zones are divided into some subzones according to their degrees of retrograde alterations. Garnet, vesuvianite and bicchulite subzones and unaltered gehlenite are successively arranged from the contact with igneous rocks toward the spurrite zone (Kusachi et al., 1983). The arrangement can be understood as a result of the difference in the amounts of silica-addition, which decreases with the increase in distance from the contact with igneous rocks. At many outcrops, unaltered gehlenite scarcely remains and most of the primary gehlenite zones actually consist of secondary subzones. The bicchulite subzone consists of bicchulite, hydrogrossular, vesuvianite and sometimes diaspore. Bicchulite subzones contain various amounts of bicchulite from place to place, and some of them lack in bicchulite and form vesuvianite-hydrogrossular subzones, which suggest a formation condition of the similar temperature and somewhat large amount of silica-addition. The cell dimensions of garnet in the garnet subzones are usually as small as those

of anhydrous grossular, whereas those of garnet in the bicchulite and vesuvianite-hydrogrossular subzones are distinctly large. This difference seems to be a result of the difference in the silica contents of the subzones: in the garnet subzones the high silica contents prevent the hydration of garnets at low temperatures.

Agrell (1965) reported vesuvianite and grossular as retrograde minerals associated with melilite at Kilchoan, Ardnamurchan. It is inferred that the alteration reactions were taken place under the conditions 2 and 4. His "polythermal" metamorphism may be regarded as a general term including not only primary and retrograde changes like at Fuka but also remetamorphism.

At Kushiro and Fuka, gehlenite is sometimes replaced by a mixture of vesuvianite and hydrogrossular along fractures. Common replacing veins consist of the mixture of vesuvianite with the usual cell dimensions and hydrogrossular with cell dimension of around 12.2 Å, plotted at the right and lower part of the Figure 6. This assemblage may indicate that natural process is favorable to form vesuvianite with no replacement of Si by 4H and hydrogrossular with replacement of one third of Si by 4H. In rare cases, however, hydrous vesuvianite closely associated with hydrogrossular is found at Kushiro and Fuka. They are characterized by the positive correlation between the cell dimensions of the two minerals, as shown in Figure 6. It may be assumed that these states are products of the transitional stages in the course of the stable assemblage consisting of water-poor vesuvianite and 12.2 Å hydrogrossular. Figure 6 shows that the correlation of cell dimensions between garnet and vesuvianite in the natural materials coincides with those in the synthetic materials.

Conclusion

1. In the gehlenite end-member ($\text{Ak}_0\text{Ge}_{100}-\text{SiO}_2-\text{H}_2\text{O}$) system, the synthesized phases are bicchulite, garnet, anorthite and corundum (or boehmite). Additions of small amounts of SiO_2 to gehlenite result in the mineral association of gehlenite + garnet + corundum at high temperatures and of bicchulite + garnet + boehmite at low temperatures. Additions of large amounts of SiO_2 result in the mineral association of garnet + anorthite.

2. In the gehlenite solid solution ($\text{Ak}_{20}\text{Ge}_{80}-\text{SiO}_2-\text{H}_2\text{O}$) system, vesuvianite, xanthophyllite and diopside were formed in addition to the phases formed in the end-member system, suggesting that small MgO contents in the starting materials significantly affect the mineral associations of the products. The mineral associations formed from the gehlenite solid solution with small amounts of SiO_2 are gehlenite + garnet, gehlenite + vesuvianite → garnet, bicchulite + vesuvianite + xanthophyllite and bicchulite + vesuvianite + garnet at high to low temperatures. And the gehlenite solid solution reacts with large amounts of SiO_2 to produce the association of garnet +

anorthite $\pm$ diopside.

3. Cell dimensions of garnet formed from gehlenite range from those of nearly anhydrous grossular to hydrogrossular with distinct amounts of water. They depend not only on temperatures but also on silica contents of the starting materials. The ranges of cell dimensions are wider for the solid solution system than for the end-member system. The cause of the differences are interpreted by the differences of the ionic radii and of water affinities between Ca and Mg.

4. Cell dimensions of vesuvianite have also some ranges. The correlation between cell dimensions of garnet and vesuvianite is clear, suggesting the cause of enlargements of cell dimensions of the two minerals are common to each other and are substitution of 4H for Si. The same correlations as this results are seen between the two minerals in some Japanese specimens.

5. The formation conditions of natural retrograde minerals of gehlenite can be well estimated based on the present results. The results for the solid solution system are more profitable to the natural applications than those for the end-member system.

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References

- AGRELL, S. O. (1965) *Miner. Mag.*, **34**, 1-15.
 BUNNO, M., SHIMAZAKI, H. and SATO, K. (1982) *Mining Geol.*, **32**, 141-150.
 BURNHAM, C. W. (1959) *Bull. Geol. Soc. Amer.*, **70**, 879-920.
 CARLSON, E. T. (1956) *Natl. Bur. Standards Journ. Res.*, **56**, 327-335.
 CARLSON, E. T. (1964) *Natl. Bur. Standards Journ. Res.*, **68A**, 449-452.
 CHRISTIE, O. H. J. (1961) *Norsk. Geol. Tidsskr.*, **41**, 255-269.
 FLINT, E. F., MCMURDIE, H. F. and WELLS, L. S. (1941) *Natl. Bur. Stand. Jour. Res.*, **26**, 13-33.
 HARKER, R. I. and TUTTLE, O. F. (1956) *Amer. Journ. Sci.*, **254**, 468-478.
 HENMI, C., KUSACHI, I., HENMI, K., SABINE, P. A. and YOUNG, B. R. (1973) *Miner. Journ.*, **7**, 243-251.
 HENMI, C. (1976) *Miner. Journ.*, **8**, 171-183.
 HSU, L. C. (1980) *Contr. Miner. Petrol.*, **71**, 407-415.
 JOESTEN, R. (1974) *Amer. Miner.*, **59**, 694-699.
 KUSACHI, I., HENMI, C. and HENMI, K. (1978) *Bull. Sch. Educ. Okayama Univ.*, **48**, 25-39.
 KUSACHI, I., HENMI, C. and HENMI, K. (1983) *Bull. Sch. Educ. Okayama Univ.*, **64**, 171-182.
 NAMBU, M., TANIDA, K., KITAMURA, T. and OIKAWA, S. (1975) *Abstr. Annual Meeting of Miner. Soc. Japan*, **22**.
 NUMANO, T., KUSACHI, I., HENMI, K. and HENMI, C. (1978) *Bull. Sch. Educ. Okayama Univ.*, **49**, 49-60.

- NUMANO, T. (1979) *Bull. Sch. Educ. Okayama Univ.*, **50**, 257-282.
PISTORIUS, C. W. F. T. and KENNEDY, G. C. (1960) *Amer. Journ. Sci.*, **258**, 247-257.
SABINE, P. A. (1975) *Philos. Trans. R. Soc. L.*, **280**, 225-269.
SCHIFFMAN, P. and LIOU, J. G. (1980) *Journ. Petrol.*, **21**, 441-474.
SHIMAZAKI, H., BUNNO, M. and SATO, K. (1975) *Abstr. Annual Meeting of Geol. Soc. Japan*.
SHOJI, T. (1971) *Mining Geol.*, **21**, 457-460.
SHOJI, T. (1974) *Journ. Miner. Soc. Japan*, **11**, 359-372.

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