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Synthesis of Non-stoichiometric Clinopyroxenes in the System Diopside-Esseneite under Ambient Pressure

Masato OKUI, Yumiko KAMIMURA, Shinya HATANO, Masaya OHTA and Fumiyuki MARUMO

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Synthesis of clinopyroxenes was tried at several temperatures under the ambient pressure from powdered glasses with the compositions of $Di_{20}Es_{80}$, $Di_{30}Es_{70}$ and $Di_{40}Es_{60}$ on the join $CaMgSi_2O_6$ (Di)–$CaFe^{3+}AlSiO_6$(Es). Stoichiometric clinopyroxenes were crystallized at 1350℃ from all the compositions, while non-stoichiometric clinopyroxenes were obtained at 1325℃ and lower tempetratures from the compositions $Di_{30}Es_{70}$ and $Di_{20}Es_{80}$. Chemical formulae of all the non-stoichiometric clinopyroxenes are expressed approximately as $Ca_{0.75}(Al_{0.85}Fe^{3+}_{0.15})(Si_{1.50}Al_{0.50})O_6$, whereas those of the stoichiometric clinopyroxenes varies depending upon heating temperatures and compositions of starting materials.

Keywords: non-stoichiomeytric clinopyroxene, diopside, esseneite

1. Introduction

Non-stoichiometric aluminous clinopyroxenes have been found from several eclogites in kimberlites (Sobolev, Kuznetsova & Zyuzin, 1968; Smyth, 1980), and supposed to be products under extremely high pressures because of their occurances and pequliar textures. Actually, tchermakitic clinopyroxenes were synthesized at 1300－1450℃ and 25.0－32.3 kbar from several compositions on the joins $CaAl_2SiO_6$－SiO_2 and $[(CaAl_2SiO_6)_{0.7}$－$(CaMgSi_2O_6)_{0.3}]$－SiO_2 by Wood and Henderson (1978).

Okui, Sawada and Marumo (1998), however, recently synthesized non- stoichiometric aluminous clinopyroxenes from a composition of 23mol% $CaMgSi_2O_6$ (Di), 53mol% $CaFeAlSiO_6$ (Es) and 24mol% $CaAl_2Si_2O_6$ (An) under the ambient pressure, and elucidated structural details of the crystals and phase relations with stoichiometric clinopyroxenes. They confirmed crystallization of non-stoichiometric clinopyroxenes at relatively lower temperatures, and that of stoichiometric clinopyroxenes at higher temperatures.

Esseneite $CaFeAlSiO_6$ is known as one of important aluminous end members of clinopyroxenes, and phase equilibria of the system Di–Es were investigated at 1 atm by Hijikata and Onuma (1969). Though they did not recognized crystallization of non-stoichiometric clinopyroxenes, it should be reasonable to expect formation of non-stoichiometric clinopyroxenes at lower temperatures also in this system. In the present study, syntheses of non-stoichiometric clinopyroxenes were, therefore, tried from several compositions on the join Di-Es under the ambient pressure by changing temperature.

2. Experimental

Crystallization experiments were tried on the compositions $Di_{20}Es_{80}$, $Di_{30}Es_{70}$ and $Di_{40}Es_{60}$ at several temperatures in the air. Reagent grade chemicals of MgO, Al_2O_3, SiO_2 and Fe_2O_3, and $CaCO_3$ for alkali analysis were weighed to yield 20g of raw materials having

日本大学文理学部地球システム科学科：
〒156－8550 世田谷区桜上水3－25－40

Department of Geosystem Sciences, College of Humanities and Sciences, Nihon University: 3-25-40, Sakurajousui, Setagaya-ku Tokyo 156-8550 Japan

these compositions. The chemicals were wrapped with platinum foils after wet-mixed well utilizing ethanol, and melted at 1450℃ in an SiC electric furnace. The temperature-raising rates of 4.2℃/min, 0.5℃/min and 1.7℃/min were applied in the ranges from the room temperature to 500℃, from 500℃ to 1000℃, and from 1000℃ to 1450℃, respectively. The lower heating rate was adopted between 500℃ and 1000℃, since decomposition of $CaCO_3$ occurs in this temperature range. The melts were kept at 1450℃ for 2 h, and then, glassified by dropping into ice-water. The obtained glasses were pulverized and wet-mixted again to give chemically uniform powders, respectively. These glass powders were used for the crystallization experiments.

Crystallization of the glass with composition $Di_{30}Es_{70}$ was carried out at 1350, 1325, 1300 and 1250℃. The respective batches were kept at the aimed temperatures for 90 h by making use of the SiC electric furnace, then quenched by rapid cooling in ice-water. Similar crystallization experiments were performed on the glass with composition $Di_{20}Es_{80}$ by heating the raw material at 1350 and 1320℃ for 162 h, and on the glass with composition $Di_{40}Es_{60}$ by heating at 1380 and 1350℃ for 162 h, respectively.

Temperature was measured with a Pt-Pt13% Rh thermocouple. The thermocouple was calibrated by making reference to the melting points of Zn (419.6℃), Al (660.4℃), Cu (1083.4℃) and Ni (1453℃). The temperature around specimens was confirmed to be uniform and stable within 10℃.

The crystalline products were revealed to consist mainly of clinopyroxenes from X-ray powder diffraction patterns. A very small amount of unknown oxide crystals were recognized in some batches heated at the higher temperatures. In the case of composition $Di_{40}Es_{60}$, crystalline products were only the unknown metal oxide at 1380℃. The chemical compositions of clinopyroxenes were determined with an electron microprobe analyser (JOEL JSM5400S / LINK CX2000S). The obtained chemical compositions are given in Tables 1, 2 and 3. Standard deviations based on the final digits are given in parentheses for the mean values.

3. Results and discussion

Numbers of metal atoms per six oxygens were calculated from the wt% values in Tables 1, 2 and 3, and listed in Tables 4, 5 and 6, respectively.Standard deviations based on the final digits are given in parentheses for the mean values. The clinopyroxenes obtained at 1350℃ are undoubtedly stoichiometric within the experimental errors, while those obtained at the lower temperatures are non-stoichiometric in all the starting compositions.

All the non-stoichiometric clinopyroxenes have similar compositions. They contain practically no magnesium, and are quite rich in aluminium. Around a quarter of the tetrahedral sites are occupied by aluminium. The chemical formula is approximated as $Ca_{0.75}(Al_{0.85}Fe^{3+}_{0.15})(Si_{1.50}Al_{0.50})O_6$. Since the sums of metal atoms other than calcium and those at the tetrahedral sites are close to one, vacancies are supposed to lie at the M2 sites. This conclusion accords well with the results of structure analyses on non-stoichiometric clinopyroxenes reported by Smyth (1980), Oberti and Caporuscio (1991), and Okui *et al.* (1998).

Distinct differences are observed among the chemi-

Table1 Compositions of clinopyroxenes crystallized from $Di_{20}Es_{80}$ in wt%

At 1350℃

Crystal No.	SiO_2	Al_2O_3	MgO	CaO	Fe_2O_3	Total
1	28.9	14.0	3.0	24.4	28.6	98.9
2	28.3	15.3	2.9	23.6	29.2	99.3
Mean	28.6(3)	14.7(7)	3.0(1)	24.0(4)	28.9(3)	

At 1320℃

Crystal No.	SiO_2	Al_2O_3	MgO	CaO	Fe_2O_3	Total
1	42.0	31.6	0.0	21.8	4.2	99.6
2	42.1	31.7	0.0	21.2	4.7	99.7
3	42.2	31.7	0.0	21.5	4.3	99.7
4	42.0	31.8	0.4	21.2	3.8	99.2
5	42.0	32.0	0.0	21.2	4.2	99.4
6	42.4	32.0	0.0	21.4	4.0	99.8
7	42.4	31.7	0.0	21.2	4.3	99.6
8	41.9	32.1	0.0	21.1	4.4	99.5
9	42.3	31.7	0.0	21.3	4.2	99.5
10	41.4	29.8	0.3	22.9	5.5	99.9
11	41.7	30.6	0.3	22.0	5.2	99.8
Mean	42.0(3)	31.5(7)	0.1(2)	21.5(5)	4.4(5)	

cal compositions of stoichiometric clinopyroxenes crystallized from the three starting materials at 1350℃. The crystals obtained from the composition $Di_{30}Es_{70}$ have enough Al atoms to fill the tetrahedral sites together with Si, while the tetrahedral sites cannot be filled by Si and Al in crystals obtained from the compositions $Di_{40}Es_{60}$ and $Di_{20}Es_{80}$. Parts of ferric ions are expected to locate at the tetrahedral sites in the crystals derived from the latter two compositions. Partial occupation of tetrahedral sites by Fe^{3+} ions seems to be a common feature of clinopyroxenes grown at higher temperatures from Es rich compositions in the Di-Es-An system. A structure refinement of a stoichiometric clinopyroxene grown from the composition $Di_{23}Es_{53}An_{24}$ indicated that the tetrahedral sites are partly occupied by Fe^{3+} ions, though the crystal has enough amounts of Si and Al atoms to fill all the tetrahedral sites (Okui, Marumo, Sawada, Ueki & Ishizawa, 1997). Therefore, Fe^{3+} ions are also expected to locate partly at the tetra-

Table2 Compositions of clinopyroxenes crystallized from $Di_{30}Es_{70}$ in wt%

At 1350℃

Crystal No.	SiO_2	Al_2O_3	MgO	CaO	Fe_2O_3	Total
1	36.4	19.1	8.6	23.4	11.0	98.5
2	37.8	18.9	8.4	23.3	10.5	98.9
3	37.4	18.3	8.0	24.8	10.5	99.0
4	37.7	19.9	8.0	24.7	9.3	99.6
5	38.7	19.6	7.9	24.8	8.9	99.9
6	39.7	15.9	9.1	24.3	10.7	99.7
Mean	38.0(10)	18.6(13)	8.3(4)	24.2(6)	10.2(8)	

At 1325℃

Crystal No.	SiO_2	Al_2O_3	MgO	CaO	Fe_2O_3	Total
1	42.7	31.0	0.4	19.6	5.6	99.3
2	42.8	26.1	1.2	20.6	8.8	99.5
3	42.6	32.3	0.4	19.0	5.3	99.6
4	43.0	31.7	0.0	19.4	5.4	99.5
5	43.1	31.9	0.3	19.2	5.1	99.6
6	42.4	31.6	0.5	19.2	5.7	99.4
7	42.3	32.3	0.4	19.7	5.3	100.0
8	42.9	31.9	0.4	19.5	4.6	99.3
9	42.1	27.7	1.2	20.2	8.8	100.0
10	42.7	31.8	0.3	19.7	5.4	99.9
Mean	42.7(3)	30.8(20)	0.5(4)	19.6(5)	6.0(14)	

At 1300℃

Crystal No.	SiO_2	Al_2O_3	MgO	CaO	Fe_2O_3	Total
1	42.2	33.3	0.4	19.6	4.3	99.8
2	42.7	31.4	0.5	18.9	5.7	99.2
3	43.2	30.7	0.0	19.4	6.2	99.5
4	42.9	32.5	0.2	19.3	4.7	99.6
5	42.1	30.2	0.9	19.6	7.1	99.9
6	43.3	31.6	0.2	19.1	5.4	99.6
7	44.1	27.5	0.6	19.8	7.5	99.5
8	42.8	32.3	0.3	19.3	5.1	99.8
9	42.5	31.4	0.5	19.2	6.0	99.6
10	43.2	31.1	0.4	19.3	5.6	99.6
Mean	42.9(6)	31.2(15)	0.4(2)	19.4(2)	5.8(10)	

At 1250℃

Crystal No.	SiO_2	Al_2O_3	MgO	CaO	Fe_2O_3	Total
1	43.4	31.2	0.3	19.7	5.3	99.9
2	43.4	29.2	0.9	19.0	7.4	99.9
Mean	43.4(0)	30.2(10)	0.6(3)	19.4(4)	6.4(11)	

Table3 Compositions of clinopyroxenes crystallized from $Di_{40}Es_{60}$ in wt%

At 1350℃

Crystal No.	SiO_2	Al_2O_3	MgO	CaO	Fe_2O_3	Total
1	33.8	11.5	6.3	23.7	23.9	99.2
2	33.8	11.8	5.7	24.0	23.9	99.2
3	34.2	11.5	5.8	24.1	23.8	99.4
4	33.9	12.5	6.0	24.2	23.3	99.9
5	33.6	12.4	6.0	24.4	22.2	98.6
Mean	33.9(2)	11.9(4)	6.0(2)	24.1(2)	23.4(5)	

Table4 Number of cations per six oxygens in clinopyroxenes crystallized from $Di_{20}Es_{80}$

At 1350℃

Crystal No.	Si	Al	Mg	Ca	Fe	Total
1	1.18	0.68	0.19	1.07	0.89	4.01
2	1.15	0.74	0.18	1.03	0.89	3.99
Mean	1.17(2)	0.71(3)	0.19(1)	1.05(2)	0.89(0)	

At 1320℃

Crystal No.	Si	Al	Mg	Ca	Fe	Total
1	1.50	1.33	0.00	0.83	0.11	3.77
2	1.50	1.33	0.00	0.81	0.13	3.77
3	1.50	1.33	0.00	0.82	0.10	3.75
4	1.49	1.34	0.02	0.81	0.10	3.76
5	1.49	1.34	0.00	0.81	0.11	3.75
6	1.51	1.34	0.00	0.81	0.11	3.77
7	1.51	1.33	0.00	0.81	0.11	3.76
8	1.49	1.35	0.00	0.80	0.12	3.76
9	1.50	1.33	0.00	0.81	0.11	3.75
10	1.49	1.26	0.02	0.88	0.15	3.80
11	1.49	1.29	0.01	0.84	0.14	3.77
Mean	1.50(1)	1.32(3)	0.00(1)	0.82(2)	0.12(2)	

Table 5 Numbers of cations per six oxygens in clinopyroxenes crystallized from $Di_{30}Es_{70}$

At 1350℃

Crystal No.	Si	Al	Mg	Ca	Fe	Total
1	1.39	0.86	0.49	0.96	0.32	4.02
2	1.43	0.84	0.47	0.95	0.30	3.99
3	1.42	0.82	0.45	1.01	0.30	4.00
4	1.42	0.88	0.45	1.00	0.26	4.01
5	1.44	0.86	0.48	0.99	0.25	4.02
6	1.50	0.70	0.51	0.98	0.30	3.99
Mean	1.43(3)	0.83(4)	0.48(2)	0.98(2)	0.29(2)	

At 1325℃

Crystal No.	Si	Al	Mg	Ca	Fe	Total
1	1.52	1.30	0.02	0.75	0.15	3.74
2	1.55	1.11	0.07	0.80	0.24	3.77
3	1.51	1.35	0.02	0.72	0.14	3.74
4	1.52	1.32	0.00	0.74	0.14	3.72
5	1.52	1.33	0.02	0.73	0.14	3.74
6	1.51	1.32	0.02	0.73	0.15	3.73
7	1.50	1.35	0.02	0.75	0.14	3.76
8	1.52	1.33	0.02	0.74	0.12	3.73
9	1.52	1.18	0.06	0.78	0.24	3.78
10	1.51	1.33	0.02	0.75	0.14	3.75
Mean	1.52(1)	1.29(8)	0.03(2)	0.75(2)	0.16(4)	

At 1300℃

Crystal No.	Si	Al	Mg	Ca	Fe	Total
1	1.49	1.39	0.02	0.74	0.12	3.76
2	1.51	1.31	0.03	0.72	0.15	3.72
3	1.53	1.28	0.00	0.74	0.17	3.72
4	1.51	1.35	0.01	0.73	0.12	3.72
5	1.50	1.27	0.05	0.75	0.19	3.76
6	1.53	1.32	0.01	0.72	0.14	3.72
7	1.58	1.16	0.03	0.76	0.20	3.73
8	1.51	1.35	0.02	0.73	0.13	3.74
9	1.51	1.31	0.03	0.73	0.16	3.74
10	1.53	1.30	0.02	0.73	0.15	3.73
Mean	1.52(2)	1.30(6)	0.02(1)	0.74(1)	0.15(3)	

At 1250℃

Crystal No.	Si	Al	Mg	Ca	Fe	Total
1	1.55	1.31	0.02	0.75	0.16	3.79
2	1.56	1.24	0.05	0.73	0.22	3.80
Mean	1.56(1)	1.28(4)	0.04(2)	0.74(1)	0.19(3)	

Table 6 Numbers of cations per six oxygens in clinopyroxenes crystallized from $Di_{40}Es_{60}$

At 1350℃

Crystal No.	Si	Al	Mg	Ca	Fe	Total
1	1.34	0.54	0.38	1.01	0.72	3.99
2	1.34	0.56	0.34	1.03	0.72	3.99
3	1.36	0.54	0.34	1.03	0.72	3.99
4	1.35	0.58	0.36	1.03	0.70	4.02
5	1.34	0.58	0.36	1.04	0.67	3.99
Mean	1.35(1)	0.56(2)	0.36(2)	1.03(1)	0.71(2)	

hedral sites in stoichiometric clinopyroxenes grown from $Di_{30}Es_{70}$.

In all the clinopyroxenes grown at 1350℃, numbers of Ca atoms per six oxygens are 1 within the experimental errors. The fact indicates that M2 sites are completely occupied by Ca atoms. All the crystals contain Mg as one of the main constituent elements, though the amount depends on compositions of the starting materials. These features observed on alkaline earth contents clearly differ from those in the non- stoichiometric clinopyroxenes.

Non-stoichiometric clinopyroxenes have been shown not to be distinctive minerals of high pressure conditions. They can crystallize even under the ambient pressure depending upon the compositions of starting materials and heating temperatures. It is of interest that two different types of clinopyroxenes crystallize from the identical starting material depending upon the heating temperature. Since these two clinopyroxenes have similar cell dimensions and the same symmetry, it requires careful examination to discriminate them with powder X-ray diffractometry.

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