Synthesis of a non-stoichiometric pyroxene under ambient pressure

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Crystallization experiments were carried out on powdered glasses having the composition $\text{Di}_{23}\text{Es}_{53}\text{An}_{24}$ at temperatures of 1250, 1275, 1300, 1325 and 1350°C. The resulting crystalline phases are clinopyroxenes and a trace of unknown oxide crystals. The pyroxenes grown at 1325 and 1350°C are stoichiometric clinopyroxenes rich in Al and Fe. Those grown at the lower three temperatures are non-stoichiometric clinopyroxenes which are extremely rich in Al and contain only negligibly small amounts of Mg. Non-stoichiometric clinopyroxenes are shown not to be characteristic products of high pressure conditions.

Introduction

Non-stoichiometric, aluminous clinopyroxenes have been found in eclogites from South African kimberlites (Smyth, 1977 and 1980) and those from Siberian kimberlites (Sobolev et al., 1968), and have attracted much attention from a view point of high pressure silicate mineralogy. Since these non-stoichiometric clinopyroxenes are rimmed with alteration products grown along fine fractures in respective grains of the clinopyroxenes, they are supposed to be stable only under extremely high pressures. Actually Wood and Henderson (1978) showed experimentally that non-stoichiometric clinopyroxenes crystallize from glasses with compositions lying on the joins $\text{CaAl}_2\text{SiO}_6\text{--SiO}_2$ and $[(\text{CaAl}_2\text{SiO}_6)_{0.7}(\text{CaMgSi}_2\text{O}_6)_{0.3}\text{--SiO}_2]$ at 1300–1450°C and 25.0–32.3 kbar, and that the degree of non-stoichiometry increases with increasing pressure.

On the other hand, Onuma and Ito (1988) re-examined the phase relations of the join $\text{MgSiO}_3(\text{En})\text{--CaAl}_2\text{Si}_2\text{O}_8(\text{An})$ under 1 atm, and found that aluminous protoenstatite appears in the composition

range with lower An contents than 45 mole percent at the relatively lower temperatures, confirming the results reported by Hytonen and Schairer (1961). The chemical composition given by Onuma and Ito for the protoenstatite crystallized at 1300°C from the raw material of $\text{En}_{70}\text{An}_{30}$ shows a small degree of cation deficiency from 4 for 6 oxygens, though they did not mention the possibility of non-stoichiometry of this crystal. Esseneite $\text{CaFe}^{3+}\text{AlSiO}_6(\text{Es})$ is stoichiometric and known as one of the important members of aluminium-rich clinopyroxenes stable under the ambient pressure. It forms a complete series of clinopyroxene with diopside $\text{CaMgSi}_2\text{O}_6(\text{Di})$ under 1 atm (Hijikata and Onuma, 1969).

With the intention to confirm the possibility of crystallization of non-stoichiometric clinopyroxenes under the ambient pressure, the authors conducted crystallization experiments on a glass in the system $\text{Di}\text{--Es--An}$ under 1 atm at various temperatures. The system was chosen by taking into consideration the above mentioned experimental facts and chemical compositions of natural non-stoichiometric clinopyroxenes. The present paper describes results of a trial carried out on a raw material with the composition of $\text{Di}_{23}\text{Es}_{53}\text{An}_{24}$. In this study, two types of clinopyroxenes with largely different characters were found to grow according to the heating temperature, of which the products at the lower

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temperatures were non-stoichiometric.

Experimental

Ten grams of the starting mixture was prepared by weighing reagent grade chemicals of MgO , Al_2O_3 , Fe_2O_3 and SiO_2 , and CaCO_3 for alkali analysis in the ratios to give the average composition of $\text{Di}_{23}\text{Es}_{53}\text{An}_{24}$ (i.e. Al_2O_3 20.80, CaO 22.66, Fe_2O_3 17.10, MgO 3.75, SiO_2 35.69 wt%). The chemicals were wet-mixed with ethanol and put in a platinum envelope. Then, the mixture was heated to 1400°C in an SiC electric furnace and kept at this temperature for 2 hours. The melt was dropped into ice-water together with the platinum envelope to get a glass. The obtained glass was pulverized and wet-mixed again with ethanol. The glass powder was melted at 1400°C , and the vitrifying procedure was repeated. Then, the product was pulverized, well mixed and used for the starting materials in the subsequent crystallization experiment. The chemical composition of the starting material was checked by analyzing a part of the glass with electron probe microanalyzer (JEOL JSM5400S/LINK CX2000S), and found it to have the

aimed composition within the experimental errors of the present study.

The pulverized starting material was separated into five parts and put in platinum capsules. They were heated at 1350, 1325, 1300, 1275 and 1250°C for 90 hours in air, respectively, and then dropped into ice-water to be quenched. The temperature in the furnace was measured with a Pt-Rh13Pt thermocouple. The stability of temperature was better than $\pm 10^\circ\text{C}$ in the furnace around the specimens.

The obtained materials were observed under a polarized optical microscope by making thin sections, and examined with powder X-ray diffractometry and electron probe microanalysis. Single-crystal X-ray diffraction experiments were carried out on some crystalline products to reveal detailed characters of the crystals.

Results

All the X-ray powder diffraction patterns of the products showed only the peaks of clinopyroxenes and broad haloes from glasses. However, unknown oxide crystals were found sometimes in the products with

Figure 1. X-ray powder diffraction pattern of the product obtained at 1325°C recorded with synchrotron radiations of $0.749817(3) \text{ \AA}$.

Figure 2. X-ray powder diffraction pattern of the product obtained at 1275°C recorded with synchrotron radiations of 0.749817(3) Å.

electron microscopic observations. These crystals were so small that they could not be recognized under the optical microscope. Figures 1 and 2 show the diffraction patterns of the products at 1325 and 1275°C recorded on a Rigaku SOR-PD1 diffractometer at SPring-8 BL15XU WEBRAM with radiations of 0.749817(3) Å in wavelength. Indices are given for the stronger reflections.

Crystal sizes of clinopyroxenes depend on the heating temperature: higher the temperature, larger the maximum size of grown crystals. The maximum sizes of the obtained crystals are about $40 \times 40 \times 100 \mu\text{m}$ and $10 \times 10 \times 40 \mu\text{m}$ in the heating temperatures of 1350°C and 1250°C, respectively. The pyroxenes obtained at 1350°C and 1325°C are brownish green, while those obtained at the lower temperatures are pale green. Since apparent colours are dependent upon sizes of crystals, it is not clear if the tint difference is intrinsic or not. The crystals show distinct cleavages parallel to the elongated direction as usually observed in pyroxenes, and have higher refractive indices than the surrounding glasses.

Chemical analyses were performed on crystals in

the thin sections used for microscopic observations with the electron probe microanalyzer. The results are shown in Table 1. The values are means of analyses carried out on several crystals in the respective products at different temperatures. As to the product at 1275°C, only one crystal was available for the analysis in the thin section. The numerals in parentheses are the standard deviations expressed in the final digit. No compositional differences were observed between the center and rim of the analyzed crystals. Numbers of atoms for 6 oxygens were derived from the obtained compositions, and given in Table 2. The obtained pyroxenes were confirmed to be C2/c clinopyroxenes by taking Weissenberg photographs on several single-crystals.

Discussion

Distinct differences are observed between clinopyroxenes synthesized at the higher two temperatures (1350 and 1325°C) and those synthesized at the lower three temperatures in chemical compositions. The clinopyroxenes grown at the higher two temperatures are stoichiometric

Table 1. Chemical compositions of clinopyroxenes obtained from $\text{Di}_{23}\text{Es}_{53}\text{An}_{24}$ glass at various temperatures

	1250°C	1275°C	1300°C	1325°C	1350°C
SiO_2	43.4(0)	44.2	43.5(7)	36.3(4)	45.4(3)
Al_2O_3	30.2(10)	29.9	31.5(13)	9.3(2)	11.3(3)
Fe_2O_3	7.1(11)	6.4	5.4(16)	26.4(10)	16.3(6)
MgO	0.6(3)	0.4	0.4(3)	6.8(4)	3.3(1)
CaO	19.4(3)	19.5	19.6(3)	23.7(1)	23.7(3)
Total	100.7	100.4	100.4	102.5	100.0

The values for 1250, 1300, 1325 and 1350°C are the averages of measurements on 2, 12, 3 and 6 crystals, respectively. The standard deviations based on the final digit are given in parentheses.

Table 2. The number of atom per six oxygens in pyroxenes obtained at various temperatures

	1250°C	1275°C	1300°C	1325°C	1350°C
Si	1.53(0)	1.56	1.55(2)	1.41(1)	1.78(1)
Al	1.26(4)	1.24	1.32(5)	0.43(1)	0.52(2)
Fe^{3+}	0.19(3)	0.17	0.15(4)	0.77(3)	0.48(2)
Mg	0.03(2)	0.02	0.02(1)	0.39(2)	0.19(1)
Ca	0.73(1)	0.74	0.75(1)	0.99(1)	0.99(1)
Total	3.74	3.73	3.79	3.99	3.96

Standard deviations based on the final digit are given the parentheses for the values obtained from measurements on plural specimens.

within the experimental errors, whereas those grown at the lower three temperatures are evidently non-stoichiometric as seen in Table 2. In addition, there are marked differences in the atomic ratios of constituent elements between the stoichiometric clinopyroxenes (henceforth abbreviated as Sto-CPx) and the non-stoichiometric clinopyroxenes (abbreviated as Non-Sto-Cx). The Sto-CPx contains practically one Ca atom for six oxygens, while the Non-Sto-Cpx has much lower Ca contents: around 0.75 for six oxygens. The lower Ca contents in the Non-Sto-CPx are supposed to have a close relation with the non-stoichiometry, since the vacancies reside mainly at the M2 sites according to previous studies (Wood and Henderson, 1978; Smyth, 1980; Oberti and Caporuscio, 1991; Okui et al., 1998).

A significant feature of Non-Sto-CPx exists in its negligibly small content of Mg. In contrast, the Sto-CPx contains 0.2 to 0.4 Mg atoms for 6 oxygens. The Non-Sto-Cpx is extremely aluminium rich. Similar features are recognized in natural Non-Sto-CPx and those synthesized under high pressures. On the other hand, the Sto-CPx obtained in the present experiments are richer in Fe than the Non-Sto-CPx. The chemical

composition of Sto-CPx obtained at 1325°C indicates occupation of ferric ions at the T sites. The authors carried out structure refinement of Sto-CPx synthesized from a raw material with the same chemical composition as those used in the present study, but with somewhat different heat treatment from the present ones, namely with a slow cooling from 1400 to 1000°C (Okui et al., 1997). The refinement indicates that a part of ferric ions occupy the T sites, though the crystal contains enough amounts of Si and Al atoms to fill the T sites. The result of chemical analysis on Sto-CPx synthesized at 1325°C should be reasonable in view of this fact, though the total of Si and Al is insufficient to fill the T sites. Similarly, a part of ferric ions are also expected to occupy T sites in Sto-CPx obtained at 1350°C, though the crystals contain enough Al to fill the T sites with Si. The differences are negligibly small between chemical compositions of Non-Sto-CPx crystals synthesized at different temperatures, whereas a distinct difference is observed between the chemical compositions of the Sto-CPx crystals synthesized at 1350 and 1325°C.

With the present study, Non-Sto-CPx is shown not to be a unique product of high pressure conditions as

previously supposed. The mineral can be grown even under the ambient pressure according to the chemical composition of raw material and the thermal condition. It is also very interesting that two types of CPx with largely different characters are crystallized from the identical raw material depending upon the growing temperature. In the present case, the temperature boundary lies between 1325°C and 1300°C.

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