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Title	Clinopyroxenes and Spinels in the System CaMgSi2O6-CaAl2SiO6-CaCrAlSiO6 : A Preliminary Report
Author(s)	Onuma, Kosuke; Tohara, Tatsuhide
Citation	北海道大学理学部紀要, 19(4), 495-503
Issue Date	1981-02
Doc URL	https://hdl.handle.net/2115/36699
Type	departmental bulletin paper
File Information	19_4_p495-503.pdf

Hokkaido University Collection of Scholarly and Academic Papers : HUSCAP

Jour. Fac. Sci., Hokkaido Univ., Ser. IV,
vol. 19, no. 4, February, 1981, pp.495-503.

CLINOPYROXENES AND SPINELS IN THE SYSTEM $CaMgSi_2O_6$-$CaAl_2SiO_6$-$CaCrAlSiO_6$: A PRELIMINARY REPORT

by

Kosuke Onuma and Tatsuhide Tohara

(with 4 tables and 2 text-figures)

Abstract

The system $CaMgSi_2O_6$-$CaAl_2SiO_6$-$CaCrAlSiO_6$ has a wide liquidus field for spinel at 1 atm. In the $CaMgSi_2O_6$-rich portion, however, clinopyroxene appears as second phase and then spinel disappears to react with liquid and the phase assemblage at subsolidus temperatures becomes clinopyroxene single phase and clinopyroxene + spinel + anorthite, indicating incongruent melting of chromian pyroxene into spinel + liquid. Clinopyroxenes and spinels in the assemblage of clinopyroxene + spinel + liquid at 1 atm and higher pressure were analysed. The Cr_2O_3 contents of clinopyroxenes and spinels increase with increasing those of bulk compositions and attain 3.16 wt % and 48.99 wt %, respectively, at the bulk composition containing 1.86 wt % Cr_2O_3. The Cr/Al ratios of spinels are higher than those of the bulk compositions and increase with an increase of Cr/Al ratios of the bulk compositions. Spinels and clinopyroxenes crystallizing from a composition containing 1.86 wt % Cr_2O_3 at 8 kbar and 1300°C with over-saturated water contain about 70 wt % and 0.1 wt % Cr_2O_3, respectively. Spinels coexisting with clinopyroxene in the present system have higher Cr/Al ratios than the clinopyroxene.

Introduction

The present paper is a preliminary report of the experimental study on the system $CaMgSi_2O_6$(Di)-$CaAl_2SiO_6$(CaAlTs)-$CaCrAlSiO_6$(CaCrTs) which is part of a wider study of the system $CaMgSi_2O_6$-$CaCrAlSiO_6$-$CaAl_2SiO_6$-$CaFeAlSiO_6$. The distribution of Cr and Al in clinopyroxene and spinel is one of the interesting problem in petrology. To evaluate the controlling factors for the behaviors of Cr and Al in clinopyroxene and spinel, more experimental data are still needed. Therefore, we are carring out experimental studies at 1 atm and higher pressure on the system mentioned above. In this paper only the experimental results are present. The petrologic significance of the present system will be discussed elswhere (Onuma and Tohara, in preparation).

Phase Relation At 1 Atm

Starting materials were prepared in the most cases by crystallizing glasses at 1000°C which were made by melting mixtures composed of $CaCO_3$, MgO, Cr_2O_3, Al_2O_3, and SiO_2 at 1400°C, and in a few cases by sintering the mixtures. The experiments at 1 atm were performed by quenching method. The results are given in Table 1.

Clinopyroxene solid solution (Cpx), anorthite (An), melilite (probably solid solution, Mel), and spinel solid solution (Sp) are encountered in this study. Clinopyroxene forms prismatic crystals near liquidus, but forms rounded grains at lower temperatures. Spinel forming small octahedral crystals is pale green. Anorthite occurs as needles with low birefrengence. Since melilite occurs at low temperature region together with other minute

Contribution from the Department of Geology and Mineralogy, Faculty of Science, Hokkaido University, No. 1697.

Table 1 Results of quenching experiments at 1 atm.

Compositiosn (wt.%) Di	CaAlTs	CaCrTs	Temp. (°C)	Time	Results
90	8	2	1250	14 days	Cpx+rare gl
			1360	48 hr	Cpx+gl
			1370	24 hr	gl
90	6	4	1200	14 days	Cpx
			1250	14 days	Cpx+Sp+gl
			1360	48 hr	Cpx+rare Sp+gl
			1370	24 hr	Sp+gl
			1400	24 hr	very rare Sp+gl
80	18	2	1250	14 days	Cpx+rare gl
			1320	24 hr	Cpx+gl
			1330	24 hr	Cpx+very rare Sp+gl
			1350	48 hr	Sp+gl
			1380	24 hr	very rare Sp+gl
			1400	24 hr	gl
80	16	4	1250	14 days	Cpx+Sp+gl
			1330	24 hr	Cpx+Sp+gl
			1350	48 hr	Sp+gl
			1400	24 hr	very rare Sp+gl
72	26	2	1230	14 days	Cpx+An?+Mel?
			1250	14 days	Cpx+gl
			1290	48 hr	Cpx+gl
			1295	48 hr	Cpx+Sp+gl
			1300	18 hr	Sp+gl
			1400	24 hr	very rare Sp+gl
71	28	1	1230	14 days	Cpx+An+Mel?
			1260	48 days	Cpx+An+gl
			1270	24 hr	Cpx+gl
			1295	48 hr	Cpx+gl
			1300	18 hr	Sp+gl
			1320	24 hr	Sp+gl
			1330	48 hr	gl
70	28	2	1230	14 days	Cpx+An?+Mel?
			1250	14 days	Cpx+gl
			1285	48 hr	Cpx+gl
			1290	48 hr	Cpx+Sp+gl
			1295	48 hr	Cpx+Sp+gl
			1300	18 hr	Sp+gl
			1400	24 hr	very rare Sp+gl
70	26	4	1230	14 days	Cpx+An?+Mel?
			1250	14 days	Cpx+gl
			1270	24 hr	Cpx+gl
			1275	72 hr	Cpx+Sp+gl
			1295	48 hr	Cpx+Sp+gl
			1300	18 hr	Sp+gl
			1400	24 hr	Sp+gl
70	24	6	1240	14 days	Cpx+An+Mel
			1250	14 days	Cpx+Sp?+gl
			1270	24 hr	Cpx+Sp+gl
			1290	24 hr	Cpx+Sp+gl
			1295	48 hr	Cpx+Sp+gl
			1300	18 hr	Sp+gl
			1400	24 hr	Sp+gl

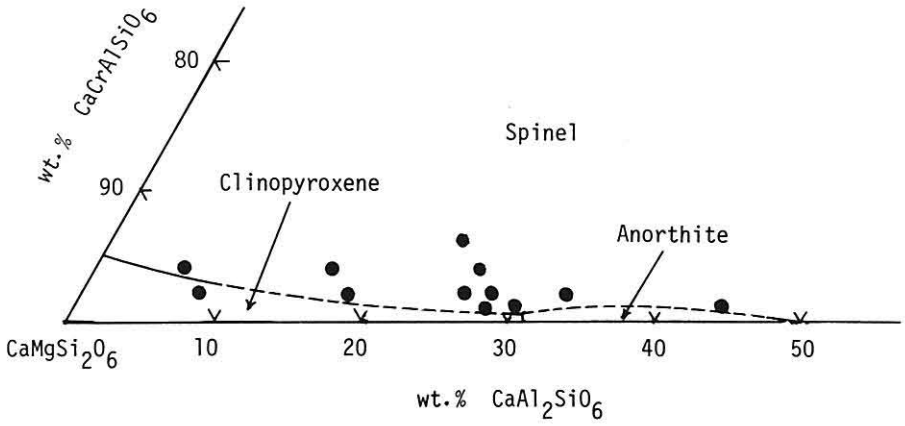
(continued)

Composition (wt.%) Di	CaAlTs	CaCrTs	Temp. (°C)	Time	Results
69	30	1	1240	14 days	Cpx+An+Mel
			1250	14 days	Cpx+An+gl
			1260	48 hr	Cpx+An+gl
			1265	72 hr	Cpx+gl
			1285	48 hr	Cpx+Sp+gl
			1290	14 hr	Sp+gl
			1340	24 hr	Sp+gl
			1350	48 hr	gl
65	33	2	1240	14 days	Cpx+An+Mel
			1250	14 days	Cpx+gl
			1270	24 hr	Cpx+gl
			1275	24 hr	Sp+gl
			1400	24 hr	rare Sp+gl
65	33	2	1240	14 days	Cpx+An+Mel
			1250	14 days	Cpx+gl
			1270	24 hr	Cpx+gl
			1275	24 hr	Sp+gl
			1400	24 hr	rare Sp+gl
55	44	1	1240	14 days	Cpx+An+Mel+Sp
			1250	14 days	An+Sp+gl
			1295	48 hr	An+Sp+gl
			1300	18 hr	Sp+gl
			1400	24 hr	Sp+gl

Cpx, clinopyroxene; Sp, spinel; An, anorthite; Mel, melilite; gl, glass.

crystals, sometimes it was difficult to identify this mineral under the microscope. The strongest peak of melilite in X-ray diffraction varies between 31.1° and 31.3° in 2θ, suggesting that the melilite consists of akermanite and gehlenite components.

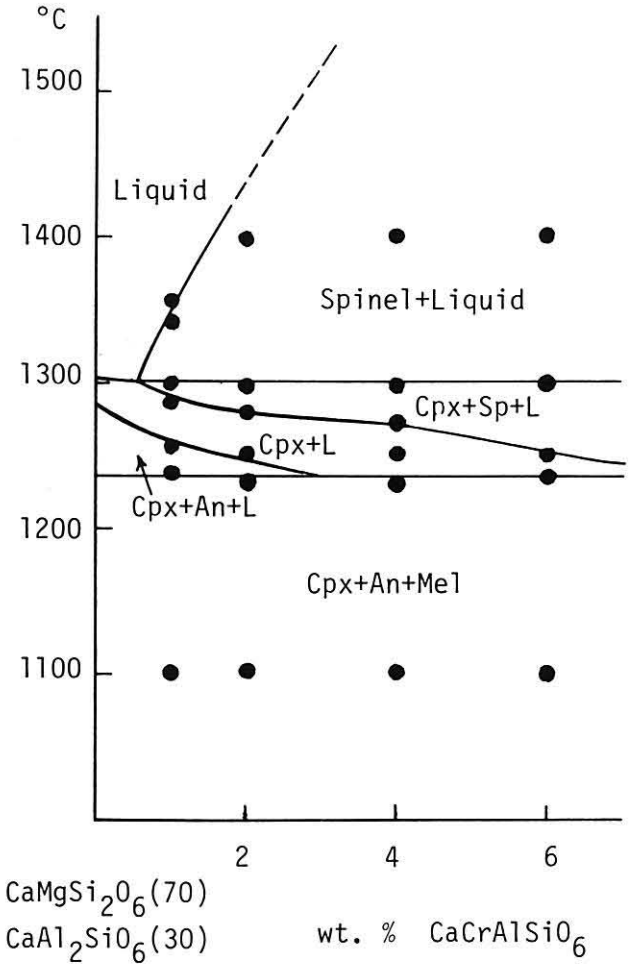
A tentative liquidus diagram is shown in Text-fig.1. A large primary field for spinel is present, and judging from the quenching data (Table 1) there are narrow liquidus fields for



Text-fig. 1 Liquidus diagram of the system $CaMgSi_2O_6$-$CaAl_2SiO_6$-$CaCrAlSiO_6$

clinopyroxene and spinel along the Di-CaAlTs join. There is a point where clinopyroxene, spinel, anorthite and liquid coexist, but this point is not a piercing point because of the quinary nature of the system.

In the Di-rich portion of the area studied spinel is absent at subsolidus temperatures even at the compositions in spinel primary field, indicating that the spinel reacts with liquid. In the compositions richer in Di component than 80 wt %, the subsolidus phase consists only of clinopyroxene, while in those poorer than 72 wt % anorthite and then melilite join the phase assemblage after the spinel disappears. This indicates that the clinopyroxene single phase field extents to the composition at least between 80 wt % and 72 wt % Di component. In the Di-poor portion spinel persists at subsolidus temperatures to have the phase assemblage of Cpx + Sp + An + Mel. Dickey et al. (1971) demonstrated that clinopyroxenes containing more than 3 wt % CaCrTs component melt incongruently to spinel + liquid, and



Text-fig. 2 Phase diagram of the 70 wt % $CaMgSi_2O_6$ section.

that the temperature intervals, in which clinopyroxenes and spinels coexist, increase with increasing CaCrTs component in bulk compositions. The same phenomena are observed in addition of CaAlTs component. The temperature intervals between the appearence of spinel and disappearence of clinopyroxene in the join at constant Di component increase with increasing CaCrTs component as also indicated by Dickey et al. (1971) (Text-fig.2). Clinopyroxene single phase field, however, is not observed in this join. The clinopyroxene primary field deminishes from 3 wt % in the Di-CaCrTs join with increasing CaAlTs and is terminated at the composition containing about 30 wt % CaAlTs component.

Clinopyroxenes And Spinels At 1 Atm

Clinopyroxenes obtained show green to pale green color in the temperature ranges of quenching experiments, although unusual blue diopside was reported in the Cr-poor portion of the systems Di-CaCrTs (Dickey et al. 1971) and Di-$NaCrSi_2O_6$ and Di-$CaCr_2SiO_6$ (Ikeda and Yagi, 1972, 1977). On the other hand, clinopyroxenes in the starting materials crystallized at 1000°C from glass through the area studied are pale blue. This seems to indicate that the color of chromian pyroxene depends on the temperature at which the clinopyroxene crystallizes. Dickey et al. (1971) considered that the blue color is mainly due to Cr^{2+} ions in the clinopyroxene structure, whereas Ikeda and Yagi (1977) claimed that this color is probably attributed to the tetrahedrally coordinated Cr^{3+} ions. The problem on the color of chromian pyroxene is beyond this study. Further studies on this problem are needed.

Table 2 Chemical compositions of clinopyroxenes and spinels coexisting with liquid at 1 atm, 1290°C

	$Di_{70}CaAlTs_{28}CaCrTs_2$			$Di_{70}CaAlTs_{26}CACrTs_4$			$Di_{70}CaAlTs_{24}CaCrTs_6$		
	Bulk Comp.	Cpx	Sp	Bulk Comp.	Cpx	Sp	Bulk Comp.	Cpx	Sp
SiO_2	47.05	50.57	–	46.99	50.23	–	46.94	49.89	–
Al_2O_3	13.51	5.90	30.17	12.99	6.19	28.89	12.48	6.64	26.94
Cr_2O_3	0.63	2.51	45.00	1.25	3.02	46.85	1.86	3.16	48.99
MgO	13.03	15.55	24.64	13.03	15.21	24.28	13.03	15.14	24.11
CaO	25.78	24.62	–	25.74	24.75	–	25.69	24.87	–
total	100.00	99.15	99.81	100.00	99.40	100.02	100.00	99.70	100.04
	Numbers of ions on the basis of 6(0) for Cpx and 4(0) for Sp								
Si		1.85	–		1.84	–		1.83	–
Al		0.25	0.99		0.27	0.95		0.29	0.90
Cr		0.07	0.99		0.09	1.04		0.09	1.09
Mg		0.85	1.02		0.83	1.01		0.83	1.01
Ca		0.96	–		0.97	–		0.98	–
total		3.98	3.00		4.00	3.00		4.02	3.00
Cr/Al	0.03	0.28	1.00	0.06	0.33	1.09	0.10	0.31	1.21

Cpx: clinopyroxene; Sp: spinel

The clinopyroxenes and spinels in the assemblage of Cpx + Sp + liquid at 1290°C along the Di 70 wt % join were analysed with the electron microprobe at the Institute of Petrology, Mineralogy and Economic Geology, Tohoku University (Table 2).

The Cr_2O_3 contents of clinopyroxenes increase from 2.51 wt % to 3.16 wt % with increasing those of bulk compositions from 0.63 wt % to 1.86 wt %, and the Al_2O_3 contents of clinopyroxenes also increase from 5.90 wt % to 6.64 wt % although those of bulk compositions decrease from 13.5 wt % to 12.48 wt %. The Cr/Al ratios of the clinopyroxenes therefore increase with increasing those of bulk compositions. It is noticed that the clinopyroxenes are higher in the Cr_2O_3 content and lower in the Al_2O_3 content than the bulk compositions, and therefore that the Cr/Al ratios of clinopyroxenes are considerably higher than bulk Cr/Al ratios. $(Cr/Al)_{cpx}/(Cr/Al)_{bulk}$ decreases with increasing CaCrTs component in the system.

Spinels in this study are green. The color may be ascribed to Cr^{3+} ions in the structure. The Cr/Al ratios in the spinels so far as analysed are higher than 1, and therefore these spinels are chrome spinel. The Cr_2O_3 contents of spinels increase from 45.00 wt % to 48.99 wt % with increasing those of bulk compositions, whereas the Al_2O_3 contents decrease from 30.17 wt % to 26.94 wt %, indicating that the chemistry of spinel is controlled by bulk composition of host liquid. This supports the suggestions of Sigurdsson (1977) and Nagao et al. (1980) that the Al_2O_3 content of spinel is influenced by the chemistry of host magma. The Cr/Al ratios of spinels increase with increasing bulk Cr/Al ratios and are considerably higher than those of coexisting clinopyroxenes.

Preliminary Experiments Under Water Vapor Pressure

High pressure experiments were carried out on the compotions of $Di_{70}CaAlTs_{26}CaCrTs_4$ and $Di_{70}CaAlTs_{24}CaCrTs_6$ using piston-cylinder type apparatus under high water vapor pressure. The compositions of $Di_{70}CaAlTs_{26}CaCrTs_4$ and $Di_{70}CaAlTs_{24}CaCrTs_6$ are consists of Cpx + Sp + liquid at 8 kbar P_{H_2O}, 1200°C and 8 kbar P_{H_2O}, 1300°C, respectively. In the latter composition clinopyroxene disappears and spinel remains at 12 kbar P_{H_2O}, 1300°C. This probably indicates that the incongruent melting of clinopyroxene into Sp + liquid also takes place at high P_{H_2O} and the incongruent melting temperature decreases with increasing P_{H_2O}.

Clinopyroxenes and spinels obtained in the high pressure experiments were analysed using electron microprobe at the Faculty of Engineering, Hokkaido University (Table 3). It is noticed that spinels crystallized at high P_{H_2O} have considerably higher Cr/Al ratios than those crystallized at 1 atm from the same bulk composition; 6.58 at 8 kbar and 1.21 at 1 atm at the composition of $Di_{70}CaAlTs_{24}CaCrTs_6$. On the other hand, the Cr/Al ratios of clinopyroxenes crystallized at high P_{H_2O} are lower than those of clinopyroxenes at 1 atm; 0.07 at 8 kbar and 0.31 at 1 atm. Although more experiments are needed to establish the distribution of Cr and Al between clinopyroxene, spinel and liquid which are coexisting in equilibrium, this is a very interesting phenomenon, because this suggests that when spinel coexist with liquid, high P_{H_2O} is favorable to the entrance of Cr into spinel structure.

Table 3 Chemical compositions of clinopyroxenes and spinels at high pressure

	$Di_{70}CaAlTs_{26}CaCrTs_4$	$Di_{70}CaAlTs_{24}CACrTs_6$		$Di_{70}CaAlTs_{24}CaCrTs_6$
Phases Ass.	Cpx+Sp+L	Cpx+Sp+L		Sp+L
Condition	8kb, 1200°C	8kb, 1300°C		12kb, 1300°C
	Sp	Sp	Cpx	Sp
SiO_2	0.10	0.30	50.38	0.23
Al_2O_3	8.37	7.14	6.53	7.48
Cr_2O_3	67.53	69.85	0.49	68.72
MgO	22.38	21.84	16.66	21.93
CaO	0.03	0.17	25.47	0.18
total	98.41	99.03	99.53	98.54
Numbers of ions on the basis of 6(0) for Cpx and 4(0) for Sp				
Si	0.00	0.01	1.83	0.01
Al	0.31	0.26	0.28	0.28
Cr	1.66	1.71	0.02	1.69
Mg	1.04	1.01	0.90	1.02
Ca	0.00	0.00	0.99	0.01
total	3.01	2.99	4.02	3.01
Cr/Al	5.35	6.58	0.07	6.04

Cpx: clinopyroxene; Sp: spinel; L: liquid

Crystallization And Fusion In The System

In the most part of the present system crystallization begins with separation of chrome spinel with Cr/Al≥1 and the chemistries of spinels and bulk compositions show that the liquid containing only small amount of Cr_2O_3 has a potential to crystallize spinel with Cr/Al≥1; for example, spinel containing 45.00 wt % Cr_2O_3 (Cr/Al=1.00) crystallizes from the bulk composition with 0.63 wt % Cr_2O_3 content. At the temperature between 1270°C and 1300°C through the area studied chrome spinel begins to react with liquid and chromian pyroxene appears. The liquid may become poor in Cr_2O_3 and rich in Al_2O_3 abruptly as crystallization of spinel and clinopyroxene proceeds, because the Cr/Al ratios of these minerals are higher than those of the liquid. At certain temperatures spinel disappears to react with aluminous liquid and to form new clinopyroxene which is higher in the Al_2O_3 content and lower in the Cr_2O_3 content than the clinopyroxene coexisting with chrome spinel (Table 4). This newly formed clinopyroxene still keep higher Cr/Al ratio than the bulk composition and the distribution coefficient of Cr in Clinopyroxene is significantly high (about 10). The liquid, therefore, continues to become rich in Al_2O_3 and poor in Cr_2O_3. The clinopyroxene itself also becomes rich in Al_2O_3 and poor in Cr_2O_3 by continueing to react with and crystallize from this liquid. Finally anorthite and melilite crystallize from more aluminous liquid. The crystallization process stated here probably a useful model for the formation of natural chromian spinel and chromian clinopyroxene from magma at lower pressure. In natural rocks, especially in tholeiite and calc-alkalic rocks,

	Bulk comp.	1250°C	1290°C
SiO_2	47.05	49.84	50.57
Al_2O_3	13.51	9.00	5.90
Cr_2O_3	0.63	1.08	2.51
MgO	13.03	14.52	15.55
CaO	25.78	25.08	24.62
total	100.00	99.52	99.15
Phase Ass.		Cpx+L	Cpx+Sp+L
Cr/Al	0.03	0.08	0.28

Cpx: clinopyroxene; Sp: spinel; L: liquid

Table 4 Clinopyroxenes in the composition of $Di_{70}CaAlTs_{78}CaCrTs_2$

melilite component may combine with SiO_2 to form anorthite or CaAlTs component. It is unlikely that Cr ions enter into anorthite or melilite structure. Cr ions, therefore, is fixed in clinopyroxene, indicating that the Cr_2O_3 contents of bulk compositions represent those of clinopyroxene at subsolidus temperatures. This suggests that the partial fusion of the compositions in the present system produces a liquid that is more aluminous than the starting compositions, leaving the clinopyroxene richer in the Cr_2O_3 content. The liquid produced at this stage does not have potential to crystallize spinel. Then the fusion more proceeds, the clinopyroxene begins to decompose to chrome spinel and liquid, and the clinopyroxene disappears by further fusion. From the liquid thus formed, chrome spinel crystallizes. The experiments under water vapor pressure also show incongruent melting of clinopyroxene, and therefore similar fusion process as at 1 atm would be expected at high P_{H_2O}. However, spinels formed at high P_{H_2O} have higher Cr_2O_3 content than those formed at 1 atm. This is contradictry with the experimental results of Jaques and Green (1980) who demonstrated that spinels produced under anhydrous high pressure condition are lower in the Cr_2O_3 content than those produced at lower pressure. Therefore, it seems that spinel chemistry is significantly governed by the water content in liquid from which the spinel crystallizes. Although to lead the conclution, further studies are necessary, the fusion process of the present system provide a model to understand the mechanism of formation of a liquid from which chromian spinel and chromian clinopyroxene are formed by partial fusion of plagioclase-bearing peridotite.

Acknowledgement

The analyses of pyroxenes and spinels were carried out by the courtesy of Prof. Aoki and Dr. Fujimaki of Tohoku University and also Mr. Kuwahata of Hokkaido University. Prof. Katsui of Hokkaido University encouraged us during the study. Mrs. Yokoyama typed the manuscript. We wish to express our thanks to all of these persons. Part of the cost for the present experiments was defrayed by the grant for Scientific Researches from the Ministry of Education, Science and Culture of Japan.

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(Manuscript received on Octover 31, 1980)