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On the structure of clinohypersthene derived as a host phase from parental pigeonite by exsolution

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Structure refinement was made for a clinohypersthene $C_{.02}$ $Mg_{.51}$ $Fe_{.47}$ Si_2O_6, derived as a host phase from parental pigeonite by exsolution of augite along the metastable extension of the pigeonite solvus into the stability field of hypersthene. The particular characteristics of the structure are discussed, and compared with those of pigeonite and orthohypersthene. The clinohypersthene shows no indication of anti-phase domain structure on the reflections with (h+k) odd, and has six-fold coordination of oxygen around M2 site. Clino- and orthopyroxenes of hypersthene composition have closely similar atomic parameters. Kinetic factors are expected to be strongly responsible for the metastable extension of the pigeonite solvus.

Introduction

In general, pigeonite contains some 10% of $CaSiO_3$, an amount approximatelly three times excess of the solubility limit of this component for the structure of hypersthene (DEER *et al.*, 1978). Pigeonite has a stability field on the higher temperature side relative to the hypersthene+augite assemblage in the pyroxene quadrilateral system of $CaMgSi_2O_6-CaFeSi_2O_6-MgSiO_3-FeSiO_3$ (NAKAMURA and KUSHIRO, 1970; NAKAMURA, 1971). In studies on exsolution of pigeonite, however, monoclinic hypersthene (clinohypersthene) is found to be derived as host phase from parental pigeonite, which intercalates fine exsolved augite lamellae parallel to (001) (TAKEDA and REID, 1972; TAKEDA, 1972; YAMAGUCHI, 1973). This reveals that pigeonite can continue to deplete in Ca content on slow cooling along the metastable extension of the pigeonite solvus into the stability field of orthohypersthene. In this report we will discuss the particular characteristics of the structure of the host clinohypersthene phase based on the structure refinement, comparing them with those of pigeonite and orthohypersthene.

Specimen examined

Clinohypersthene of this study from quartz gabbro of the Koyama calc-alkaline intrusion, Susa, southwest Japan is derived as host phase from parental pigeonite by Ca depletion caused by exsolution of augite lamellae parallel to (001) on slow cooling (YAMAGUCHI, 1973; YAMAGUCHI *et al.*, 1974). The geological setting has been previously discussed by YAMAZAKI (1967) and YAMAGUCHI (1985). The host has been mainly inverted into the orthorhombic form (inverted pigeonite), but locally preserves monoclinic structure in single grains. There is no detectable chemical difference between the orhto- and clinohypersthene phases according to microprobe analyses (YAMAGUCHI *et al.*, 1974). The structure formulae of the clinohypersthene obtained by microprobe analysis was $Ca_{.02}Mg_{.51}Fe_{.47}Si_2O_6$.

Structure refinement

Crystal fragments of the clinohypersthene were examined by Weissenberg and precession photographic methods, respectively. The diffraction photographs display a diffraction pattern satisfying $P2_1/c$ symmetry, and show no diffuseness for reflections with (h+k) odd, indicating that the crystal are free from the anti-phase domain structure proposed by MORIMOTO and TOKONAMI (1969). The cell dimensions determined by the precession photographic method are: a=9.673 (10) Å, b=8.935 (10) Å c=5.226 (5) Å, b=108.60 (5)°.

Intensity measurements were made on a RIGAKU-AFC automatic four-circle diffractometer using Mo−Kα radiation with graphite monochrometer. A clinohypersthene crystal, 0.1×0.1×0.2 mm in size, elongated along the c-axis was used for the intensity data collection. Reflections with $2\theta < 70°$ were measured by $2\theta-\omega$ scan method. In all measured reflections, integrated intensities for 750 reflections are greater than 3σ (where σ is standard deviation from counting statistics). For the 750 reflections, 179 reflections were rejected after considering the effects of extra reflections by the exsolved augite. The resultant 571 reflections were used for the

Table 1. Structure parameters of host clinohypersthene of Koyama clinohypersthene.

Atom	Occupancy Ca	Occupancy Mg	Occupancy Fe	X	Y	Z	B
M1	0.00	0.85 (1)	0.15	0.2505 (3)	0.6542 (4)	0.2250 (6)	0.29 (6)
M2	0.04	0.16	0.80	0.2572 (2)	0.0161 (2)	0.2225 (4)	0.37 (4)
SiA				0.0436 (3)	0.3406 (4)	0.2873 (5)	0.28 (4)
SiB				0.5517 (3)	0.8360 (4)	0.2348 (5)	0.45 (4)
O1A				0.8671 (7)	0.3380 (10)	0.1767 (13)	0.39 (10)
O2A				0.3752 (7)	0.8352 (10)	0.1289 (14)	0.63 (11)
O3A				0.1218 (7)	0.4998 (10)	0.3306 (14)	0.63 (11)
O1B				0.6319 (7)	0.9844 (10)	0.3817 (14)	0.61 (11)
O2B				0.1043 (7)	0.2679 (9)	0.5915 (14)	0.53 (11)
O3B				0.6034 (7)	0.7014 (9)	0.4701 (14)	0.68 (12)

structure refinement. Least-squares refinement of atomic coordinates, isotropic temperature factors and site occupancy factors for Mg and Fe atoms in the pyroxene M1 and M2 sites were carried out on a FACOM M-200 computer at Kyoto University, using RFINE (FINGER, 1969). The weights used are $1/\sigma^2$ (F_0) and no absorption correction was made. In the refinement of site occupancy factors Ca atoms are assumed to be in the M2 site. The final R value is 0.049 for the 571 reflections. The final parameters for the clinohypersthene are given in Table 1.

Discussion

Since structure refinement of pigeonite from the Isle of Mull by MORIMOTO and GÜVEN (1970), many structural studies of pigeonite from terrestrial and extraterrestrial rock have been made (CLARK *et al.*, 1971; SMYTH and BURNHAM, 1972; BROWN *et al.*, 1972, 1973; TAKEDA, 1972; TAKEDA *et al.*, 1974). In Table 2, atomic parameters from the refinement data for the Koyama clinohypersthene $Ca_{.02}Mg_{.51}Fe_{.47}$ and Mull pigeonite $Ca_{.09}Mg_{.39}Fe_{.52}$ are shown, together with those of synthetic Ca-free clinohypersthene $Mg_{.30}Fe_{.70}$ determined by SMYTH and BURNHAM (1972).

The effects of Ca substitution in M2 site for $P2_1/c$ pyroxene structure are discussed here based on the above refinement data. MORIMOTO and GÜVEN (1970) postulated that pigeonite has irregular seven-fold coordination of oxygen around M2 site, including the coordination of the bridging oxygen O3B′ of SiB chain in addition to octahedral six M2–O bondings. The M2–O3B′ distance is responsible for the degree of kink of Si–O tetrahedra of SiB chain on (100) (0-rotation, PAPIKE *et al.*, 1973). The SiB chain in the Koyama clinohypersthene is more kinked than that of pigeonite (Table 2). This relates to the large M2–O3B′ distance (3.094 Å), relative to that of pigeonite (2.968 Å), but similar to that of the synthetic Ca-free clinohypersthene.

The structure obtained for pigeonite was interpreted by MORIMOTO and GÜVEN as an average structure of Ca-rich clinopyroxene and Ca-free clinopyroxene due to anti-phase domain structure. The large temperature factor for the M2 site (1.26) was attributed to positional disorder. The seven-fold coordination of the M2 site can be interpreted as an average of eitht-fold coordination of Ca and six-fold coordination of Mg and Fe atoms (MORIMOTO and GÜVEN, 1970; CLARK *et al.*, 1971). Pigeonite $Ca_{.09}Mg_{.63}Fe_{.28}$ from Lunar rock 12052 has similarly large temperature factor for M2 (1.24) (TAKEDA, 1972). TAKEDA *et al.* (1974) studied pigeonite containing exsolved augite from Lunar rock 14310. The host pigeonite $Ca_{.05}Mg_{.39}Fe_{.56}$ is not so much depleted in Ca content as the Koyama clinohypersthene, and has relatively large temperature factor (0.86) for M2 site. The Koyama clinohypersthene and the synthetic Ca-free clinohypersthene have, however, smaller values of temperature factors for M2 site (0.37 and 0.54, respectively) relative to pigeonites. Thus the temperature factors for M2 site generally decrease with a decrease in the Ca content of $P2_1/c$ pyroxene.

Table 2. Interatomic distances and angles.

occurrence		Mull pigeonite	Koyama clinohypersthene	Synthetic clinohypersthene
composition		$Ca_{.09}Mg_{.39}Fe_{.52}$	$Ca_{.02}Mg_{.51}Fe_{.47}$	$Mg_{.30}Fe_{.70}$
M(1) octahedron Distance, Å(σ)	occupancy Ca	0.00	0.00	0.00
	Mg	0.73	0.85 (1)	0.49 (4)
	Fe	0.27	0.15	0.51 (4)
	M1–O1A	2,158 (11)	2.152 (9)	2.155 (3)
	M1–O1A′	2.062 (10)	2.044 (7)	2.074 (3)
	M1–O1B	2.162 (9)	2.170 (10)	2.187 (3)
	M1–O1B′	2.068 (10)	2.074 (7)	2.089 (3)
	M1–O2A	2.057 (10)	2.049 (9)	2.065 (3)
	M1–O2B	2.086 (9)	2.074 (9)	2.094 (3)
	Mean M1–O	2.099	2.094	2.111
	B	0.67	0.29 (6)	0.24 (3)
M(2) octahedron Distance, Å(σ)	occupancy Ca	0.18	0.04	0.00
	Mg	0.05	0.16 (1)	0.11 (4)
	Fe	0.77	0.80	0.89 (4)
	M2–O1A	2.143 (10)	2.160 (8)	2.156 (3)
	M2–O1B	2.156 (10)	2.125 (9)	2.121 (3)
	M2–O2A	2.093 (10)	2.053 (7)	2.029 (3)
	M2–O2B	2.006 (10)	2.004 (7)	2.002 (3)
	M2–O3A	2.430 (6)	2.395 (8)	2.393 (4)
	M2–O3B	2.614 (7)	2.537 (8)	2.543 (4)
	(M2–O3B′)	(2.968 (6))	(3.065 (8))	(3.079 (4))
	Mean M2–O	2.240	2.212	2.207
	B	1.26	0.37 (4)	0.54 (2)
Si tetrahedra Angle, degrees (σ)	O3A–O3A′ –O3A″	169.6 (5)°	166.0°	164.1°
	O3B–O3B′ –O3B″	148.5 (5)°	143.2°	142.5°

It is concluded that the Koyama clinohypersthene has six-fold coordination for the M2 site similar to that of the synthetic Ca-free clinohypersthene. No indication of anti-phase domain structure on the reflections with (h + k) odd is additional evidence in support of this.

MORIMOTO and KOTO (1969) examined the structural relationship between orthoenstatite and clinoenstatite, and explained that the atomic parameters of orthoenstatite derived by twinning of the unit cell of clinoenstatite by b-glide plane on (100) are closely similar to those of real orthoenstatite. In Table 3, atomic parameters of the Koyama clinohypersthene are compared with those of orthohypersthene $Ca_{.03}Mg_{.45}Fe_{.52}$ from

Table 3. Interatomic distances and angles of granulite hypersthene and Koyama clinohypersthene.

occurrence	granulite hypersthene	Koyama clinohypersthene
composition	$Ca_{.03}Mg_{.45}Fe_{.52}$a	$Ca_{.02}Mg_{.51}Fe_{.47}$
SiA–O1A	1.597	1.619 (7)
O2A	1.601	1.593 (9)
[Å] O3A	1.648	1.641 (7)
O3A′	1.647	1.648 (9)
Mean	1.623	1.625
SiB–O1B	1.615	1.616 (7)
O2B	1.578	1.603 (9)
[Å] O3B	1.682	1.678 (8)
O3B′	1.660	1.649 (9)
Mean	1.634	1.637
Ca		0.00
occupancy Mg	0.85	0.85 (1)
Fe	0.15	0.15
M(1)–O1A	2.152	2.152 (9)
O1A′	2.036	2.044 (7)
O1B	2.166	2.170 (10)
[Å] O1B′	2.087	2.074 (7)
O2A	2.038	2.049 (9)
O2B	2.075	2.074 (9)
Mean	2.092	2.094
Ca		0.04
occupancy Mg	0.10	0.16
Fe	0.90	0.80
M(2)–O1A	2.175	2.160 (8)
O1B	2.119	2.125 (9)
O2A	2.066	2.053 (7)
[Å] O2B	2.037	2.004 (7)
O3A	2.405	2.395 (8)
O3B	2.519	2.537 (8)
Mean	2.220	2.212
SiA–O3A–SiA	139.5°	138.3°
SiB–O3B–SiB	132.2°	132.6°
[Å] SiA–SiA	3.074	3.074 (5)
SiB–SiB	3.035	3.032 (5)
O3A–O3A′–O3A″	167.8°	166.0°
O3B–O3B′–O3B″	143.9°	143.2°

granulite from Greenland, determined by Ghose (1965). The granulite orthohypersthene is similar to the Koyama clinohypersthene both in composition and in Fe–Mg occupancy for M1 and M2 sites. The clino- and orthohypersthene have similar M–0 distances and angles for M1 site, M2 site, SiA chain and SiB chain. The slightly larger M2–O distances in the orthohypersthene may be due to slightly larger Fe occupancy. Clino- and orthopyroxene of hyperthene composition are concluded to have closely similar atomic parameters. Kinetic factors are, therefore, expected to be strongly responsible for the metastable extension of the pigeonite solvus into the stability filed of orthohypersthene. The clinohypersthene could have monoclinic form if structural control was exerted by the intercalation of fine monoclinic exsolution lamellae of augite. The exsolution of augite must be considered to have mainly taken place well above the $C2/c \rightarrow P2_1/c$ transition of pigeonite, but may also have continued below the transition (Robinson *et al.*, 1977; Nakazawa and Hafner, 1977). A further extended approach to solve the exsolution mechanism will lead to an exact explanation of the kinetic factors operative to the metastable extension of the pigeonite solvus.

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