



Title	Phase Equilibria in the System MgSiO <sub>3</sub> -Al <sub>2</sub> O <sub>3</sub> -Fe <sub>2</sub> O <sub>3</sub> at high Temperatures and Pressures, with Special Reference to the Solubility of Al <sub>2</sub> O <sub>3</sub> and Fe <sub>2</sub> O <sub>3</sub> in Enstatite
Author(s)	Arima, Makoto
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PHASE EQUILIBRIA IN THE SYSTEM  $\text{MgSiO}_3\text{-Al}_2\text{O}_3\text{-Fe}_2\text{O}_3$   
AT HIGH TEMPERATURES AND PRESSURES, WITH  
SPECIAL REFERENCE TO THE SOLUBILITY OF  
 $\text{Al}_2\text{O}_3$  AND  $\text{Fe}_2\text{O}_3$  IN ENSTATITE

by

Makoto Arima

(with 34 text-figures and 4 tables)

(Contribution from the Department of Geology and Mineralogy,  
Faculty of Science, Hokkaido University, No. 1550)

*Abstract*

The phase equilibria in the system  $\text{MgSiO}_3\text{-Al}_2\text{O}_3\text{-Fe}_2\text{O}_3$  were determined experimentally in the temperature and pressure range 800 – 1300°C and 8 – 16 Kb. The following phase assemblages were encountered, the single phase of enstatite solid solution(ss), enstatite<sub>ss</sub>+hematite, enstatite<sub>ss</sub>+sapphirine<sub>ss</sub>+quartz, enstatite<sub>ss</sub>+spinel<sub>ss</sub>+quartz, enstatite<sub>ss</sub>+spinel<sub>ss</sub>+hematite+quartz. The solubility of  $\text{Al}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  in enstatite was determined experimentally. The solubility of  $\text{MgFe}^{3+}\text{AlSiO}_6$  in enstatite by the substitution  $\text{MgSi} = \text{Fe}^{3+}\text{Al}$ , increases with increasing temperature and decreasing pressure. It is confirmed that  $\text{Al}_2\text{O}_3$  is incorporated in enstatite by the substitution  $\text{MgSi} = \text{AlAl}$  as well as  $\text{MgSi} = \text{Fe}^{3+}\text{Al}$ . The solubility of  $\text{Al}_2\text{O}_3$  in enstatite increases with increasing  $\text{Fe}_2\text{O}_3$  content in it at constant temperature and pressure. The solubility of  $\text{MgAl}_2\text{SiO}_6$  by the substitution  $\text{MgSi} = \text{AlAl}$ , however, is constant at constant temperature and pressure, indicating the possibility of using the  $\text{MgAl}_2\text{SiO}_6$  content of orthopyroxene as an indicator of temperature and/or pressure with taking mineral assemblage into account.

Mössbauer spectra measurements were made on some synthetic enstatites.  $\text{Fe}^{3+}$  prefers to enter in the octahedral site (MI) rather than the tetrahedral site (T). Small amount of tetrahedral  $\text{Fe}^{3+}$  was confirmed indicating the substitution  $\text{MgSi} = \text{Fe}^{3+}\text{Fe}^{3+}$  at high temperatures.

Some geological significances of  $\text{Al}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  contents of orthopyroxenes are discussed. The present experimental results indicate that total  $\text{Al}_2\text{O}_3$  contents of orthopyroxene can not be used as an indicator of temperature and/or pressure, but  $\text{Al}_2\text{O}_3$  content in  $\text{MgAl}_2\text{SiO}_6$  should be used.

Introduction

The solubility of  $\text{Al}_2\text{O}_3$  in orthopyroxene is one of the important problem in experimental mineralogy and petrology, related to the stability of high aluminous orthopyroxenes occurring in ultramafic inclusion within volcanic rocks and in high grade metamorphic rocks.

Boyd and England (1964) studied the solubility of  $\text{Al}_2\text{O}_3$  in enstatite in the pressure range 20 – 50 Kb and showed that the solubility of  $\text{Al}_2\text{O}_3$  in

enstatite coexisting with pyrope is very sensitive to pressure variation and the  $\text{Al}_2\text{O}_3$  content of orthopyroxene may be used as an indicator of pressure. This result was also confirmed by MacGregor and Ringwood (1964), Green and Ringwood (1967), and MacGregor (1974).

At 1 atmospheric pressure, the solubility of  $\text{Al}_2\text{O}_3$  in protoenstatite was studied by Biggar and Clark (1973) in the system  $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2$  and Onuma and Arima (1975) in the system  $\text{MgSiO}_3\text{-MgAl}_2\text{SiO}_6$ . From these experiments, Onuma and Arima (1975) showed that only 1.75 wt.%  $\text{Al}_2\text{O}_3$  was incorporated in protoenstatite at high temperature.

In their study on the solubility of  $\text{Al}_2\text{O}_3$  in enstatite in the pressure range 1 – 5 Kb, Anastasiou and Seifert (1972) showed that the solubility increases with increasing temperature (9 wt.%  $\text{Al}_2\text{O}_3$  at 1200°C even at 1 Kb) but does not strongly depend on the pressure.

The pressure dependence of the solubility of  $\text{Al}_2\text{O}_3$  in enstatite coexisting with spinel and forsterite was also determined by MacGregor (1974), Fujii and Takahashi (1976), and Obata (1976). The experimental results by Fujii and Takahashi (1976) and the thermodynamic study by Obata (1976), however, showed only a slight pressure dependence and they suggested that the  $\text{Al}_2\text{O}_3$  content of orthopyroxene coexisting with spinel and olivine can not be used as an indicator of pressure.

Arima and Onuma (1977) studied the phase equilibria in the system  $\text{MgSiO}_3\text{-MgAl}_2\text{SiO}_6$  in the pressure range 10 – 25 Kb with special reference to the solubility of  $\text{Al}_2\text{O}_3$  in enstatite. From these results, they suggested that the  $\text{Al}_2\text{O}_3$  content of orthopyroxene can not be used either as a pressure indicator or as a temperature indicator without taking the mineral assemblage into account.

In order to elucidate the stability of high aluminous orthopyroxene, it is important to determine the effect of other cations such as  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ , Ca, Cr, Ti, and Na on the solubility of  $\text{Al}_2\text{O}_3$  in enstatite. This problem has been studied experimentally by Wood (1973) on the system  $\text{MgSiO}_3\text{-Fe}^{2+}\text{SiO}_3\text{-Al}_2\text{O}_3$ , by Akella (1976) on the system  $\text{MgSiO}_3\text{-CaSiO}_3\text{-Al}_2\text{O}_3$  with reference to the pressure estimation on spinel lherzolites or garnet lherzolites. Holdaway (1976) also investigated the system  $\text{MgSiO}_3\text{-Fe}^{2+}\text{SiO}_3\text{-Al}_2\text{O}_3$  to determine the solubility of  $\text{Al}_2\text{O}_3$  in orthopyroxene coexisting with cordierite.

There is, however, no experimental study on the effect of  $\text{Fe}^{3+}$  on the stability of high aluminous orthopyroxene. As shown in Fig. 1, some natural high aluminous orthopyroxenes contain also high  $\text{Fe}_2\text{O}_3$ , indicating the substitution  $\text{MgSi} = \text{Fe}^{3+}\text{Al}$  in orthopyroxene. When  $\text{Al}_2\text{O}_3$  is incorporated in orthopyroxene by both the substitution  $\text{MgSi} = \text{AlAl}$  and  $\text{MgSi} = \text{Fe}^{3+}\text{Al}$ , the  $\text{Al}_2\text{O}_3$  content of orthopyroxene can not be treated in the system

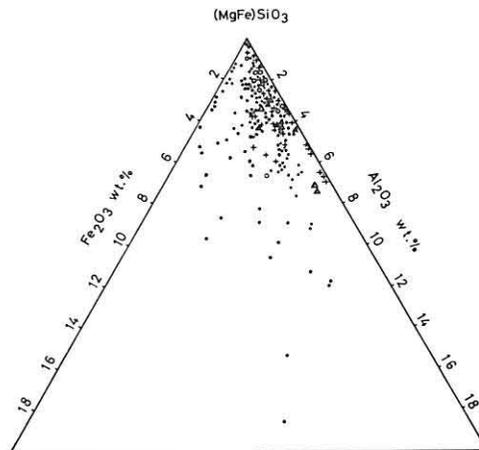
$(\text{MgFe}^{2+}\text{Ca})\text{SiO}_3\text{-Al}_2\text{O}_3$ . In order to elucidate the stability of high aluminous orthopyroxene, therefore, it is necessary to determine the pressure and temperature dependence of the substitution  $\text{MgSi} = \text{Fe}^{3+}\text{Al}$  and its influence on the substitution  $\text{MgSi} = \text{AlAl}$ .

In this paper, the stability of enstatite in the system  $\text{MgSiO}_3\text{-Al}_2\text{O}_3\text{-Fe}_2\text{O}_3$  and the solubility of  $\text{Al}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  in enstatite are determined experimentally in the pressure and temperature range 8 – 16 Kb and 800 – 1300°C. The geological significances of  $\text{Al}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  contents of orthopyroxenes are discussed.

### Previous works

#### *The join $\text{MgSiO}_3\text{-MgAl}_2\text{SiO}_6$ at 1 atm.*

The join  $\text{MgSiO}_3(\text{En})\text{-MgAl}_2\text{SiO}_6(\text{MgATs})$  was studied by Onuma and



**Fig. 1**  $\text{Al}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  contents of natural orthopyroxenes. Sources of data. *Plutonic differentiated rocks and volcanic rocks* (open circle) Hess (1952), Brown (1957), Kuno (1954, 1964), Atkins (1969). *Intrusive peridotite* (triangle) Green (1964), Onuki (1965), Challis (1965), Takeda and Onuki (1973), Niida (unpublished). *Inclusion of volcanic rock* (cross mark) Ross (1954), Banno (1964), Lovering (1964, 1969), Onuki (1965), Meyer (1976), Le Maitre (1965). *Metamorphic rock* (solid circle) Eskola (1952), Howie and Subramaniam (1957), O'hara (1960, 1961), Kranck (1961), Binns (1962, 1965), Dodd (1963), McKie (1963), Barker (1964), Engel et al. (1964), Green (1964), Howie (1963, 1964), Sen and Rege (1965), Klein (1966), Philpotts (1966), Leelanandam (1967), Chinner and Sweatman (1968), Davidson (1968), Bhattacharyya (1970), Bondarenko (1972), Lutts and Kopanava (1972), Nixon et al. (1973), Clifford (1975), Jayawardene and Carswell (1976), Murthy (1976), Wilson (1976), Woodford and Wilson (1976), Arita (unpublished).

Arima (1975) at atmospheric pressure with special reference to the solubility of  $\text{Al}_2\text{O}_3$  in protoenstatite above  $1300^\circ\text{C}$ . The phase equilibrium diagram is given in Fig. 2. MgATs is incorporated in protoenstatite as much as 3.5 wt.% (1.75 wt.%  $\text{Al}_2\text{O}_3$ ), in an agreement with the observation of Bigger and Clark (1973). At subsolidus temperature the phase assemblage protoenstatite+forsterite was confirmed in the compositional range from En(96.5)MgATs(3.5) to En(94.5)MgATs(5.5). The presence of this field indicates that the composition of protoenstatite<sub>SS</sub> extends over an area on both sides of the join En-MgATs on the ternary plane of MgO- $\text{Al}_2\text{O}_3$ - $\text{SiO}_2$  as shown in Fig. 3 (probably protoenstatite<sub>SS</sub> is nonstoichiometric). In the more aluminous region the subsolidus phase assemblages are protoenstatite<sub>SS</sub>+forsterite+cordierite<sub>SS</sub> and forsterite<sub>SS</sub>+cordierite<sub>SS</sub>+spinel. The unit cell parameters  $a$ ,  $b$  and  $V$  of protoenstatite<sub>SS</sub> decrease with increasing  $\text{Al}_2\text{O}_3$  content in it. In their discussion Onuma and Arima (1975) showed that the  $\text{Al}_2\text{O}_3$  content of protoenstatite can be used as an indicator of temperature only above  $1400^\circ\text{C}$ , and that when the  $\text{Al}_2\text{O}_3$  content is less than 2 wt.% it can not be used either as a pressure or temperature indicator.

*The join MgSiO<sub>3</sub>-MgAl<sub>2</sub>SiO<sub>6</sub> at high pressures.*

The join MgSiO<sub>3</sub>-MgAl<sub>2</sub>SiO<sub>6</sub> was studied by Arima and Onuma (1977) in the pressure and temperature range 10 – 25 Kb and 1100 – 1500°C, with special reference to the solubility of  $\text{Al}_2\text{O}_3$  in enstatite. The T-X sections at 10, 15, 20, and 25 Kb are shown in Fig. 4. At subsolidus temperatures, the solubility of  $\text{Al}_2\text{O}_3$  increases with increasing temperature. At  $1450^\circ\text{C}$  and 15 Kb MgATs is incorporated in enstatite as much as 33 wt.% (16.5 wt.%  $\text{Al}_2\text{O}_3$ ). The P-T diagrams of the both compositions En(80)MgATs(20) and En(70)MgATs(30) are given in Fig. 5. The two univariant reactions, enstatite(En)+sillimanite(Sill) = sapphirine(Sa)+quartz(Qtz) and pyrope(Py) = En+Sill+Sa were determined experimentally. The temperature and pressure values of these univariant lines are in a good agreement with those determined by previous workers (Boyd 1959, Chatterjee and Schreyer 1972, Newton 1972). As shown in Fig. 6, these univariant lines do not intersect each other, indicating the metastable invariant point where En, Sa, Sill, Py, and Qtz coexist. The P-X sections of the join En-MgATs at various temperatures are given in Fig. 7. The pressure dependence of the solubility of  $\text{Al}_2\text{O}_3$  is variable with respect to the coexisting minerals. The solubility decreases with increasing pressure when enstatite coexists with pyrope or with sillimanite+sapphirine, but increases with increasing pressure when enstatite coexists with sapphirine+quartz. From these experimental results, the  $\text{Al}_2\text{O}_3$  content of orthopyroxene

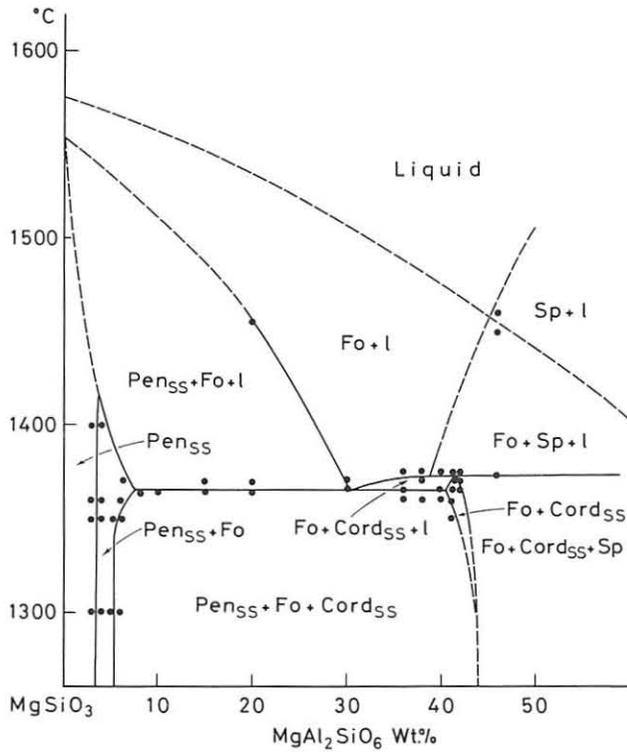


Fig. 2 Phase equilibrium diagram of the join  $\text{MgSiO}_3\text{-MgAl}_2\text{SiO}_6$  at 1 atm. Pen, protoenstatite; forsterite; Cord, cordierite; Sp, spinel; l, liquid. (after Onuma and Arima, 1975).

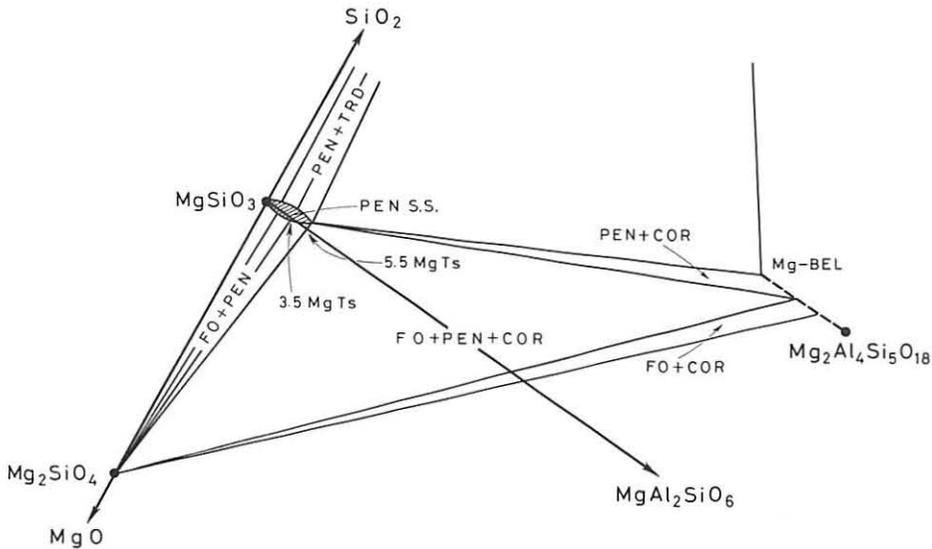


Fig. 3 A part of subsolidus diagram of the system  $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2$ . PEN, protoenstatite; FO, forsterite; TRD, tridymite; COR, cordierite. (after Onuma and Arima, 1975).

can not be used as a pressure indicator without taking the mineral assemblage into account. The unit cell parameters of the synthetic enstatites were determined as shown in Figs. 17, 18, and 19. The unit cell edges  $a$ ,  $b$  and the cell volume  $V$  decrease with increasing  $\text{Al}_2\text{O}_3$  content in it, while no significant change was observed on the cell edge  $c$ .

### Experimental methods

High pressure experiments were carried out with the piston cylinder apparatus with working volume of 1.25 cm in diameter and 5.00 cm in length. The pressure transmitting mediums were molten pyrex glass and sodium chloride as shown in Fig. 8. Pt-Pt87Rh13 thermocouples were used for

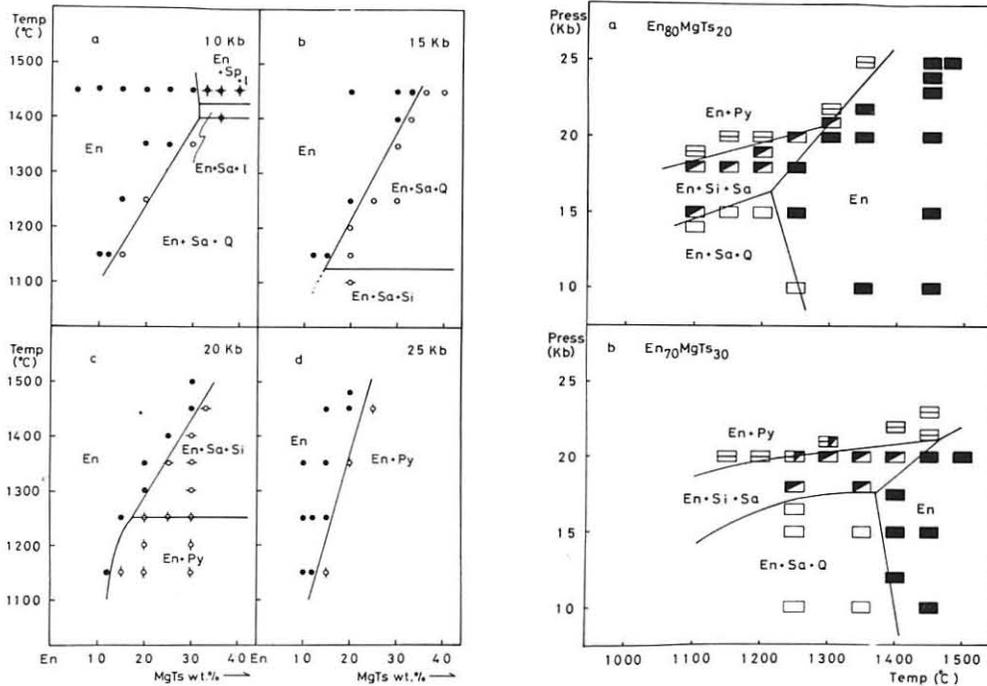


Fig. 4 (left) T-X sections in the join  $\text{MgSiO}_3$ - $\text{MgAl}_2\text{SiO}_6$  at 10, 15, 20, and 25 Kb. En, enstatite<sub>ss</sub>; Sa, sapphirine<sub>ss</sub>; Si, sillimanite; Q, quartz; sp, spinel; Py, pyrope; l, liquid. (after Arima and Onuma 1977).

Fig. 5 (right) P-T diagrams at the isocompositional planes in En(80)MgATs(20)(top) and En(70)MgATs(30)(bottom). Abbreviations are given in Fig. 4. (after Arima and Onuma 1977).

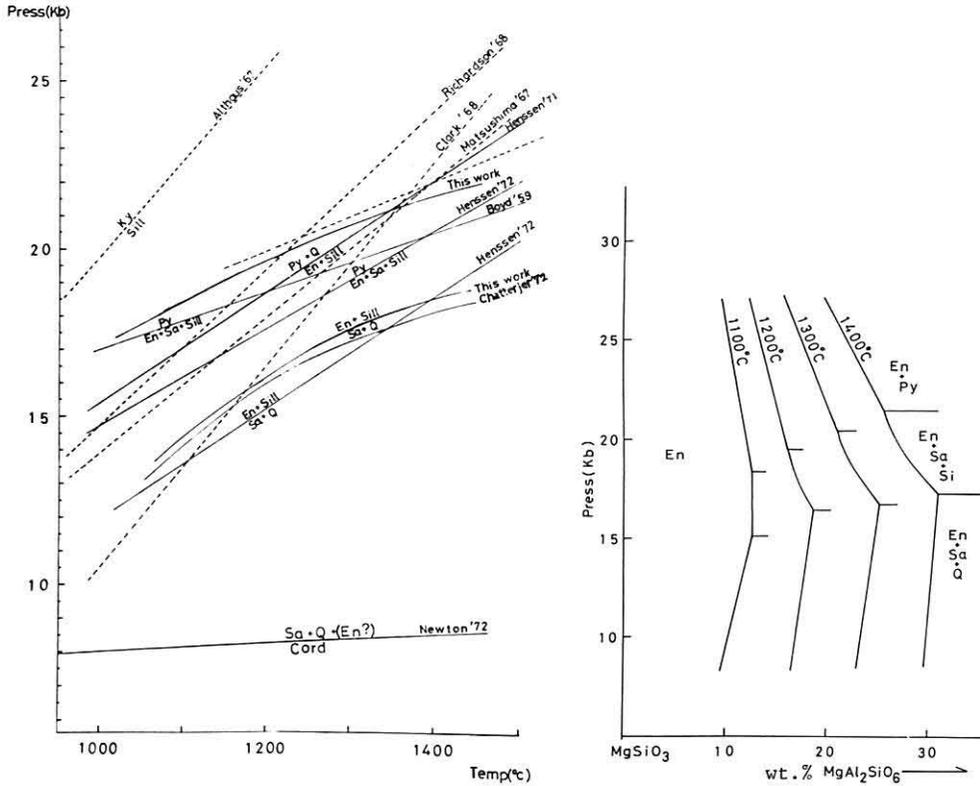
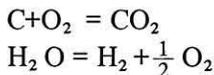


Fig. 6 (left) Comparison of the determinations of the univariant lines. (after Arima and Onuma 1977).

Fig. 7 (right) P-X sections in the join  $MgSiO_3-MgAl_2SiO_6$ . Abbreviations are given in Fig. 4. (after Arima and Onuma 1977).

temperature measurement. Temperature accuracy was estimated as  $\pm 10^\circ C$ . The correction for pressure dependence of e.m.f. of the thermocouples was ignored. The pressure calibration was made by the same method as that described by Hariya et al. (1969). To keep oxidate state of iron as trivalent, oxide starting materials were prepared from reagents of  $Fe_2O_3$ ,  $Al_2O_3$ ,  $MgO$ , and  $SiO_2$ , grounded in an agate mortar with ethylalcohole for 4 hours. In the pressure cell, graphite reacts with water from pressure transmitting talc by the following equations.



$H_2$  is permiable through the Pt wall of the sample capsule and makes the low oxygen partial pressure in the sample capsule. Under such low oxygen pressure buffered by these reactions, the experimental products at  $1000^\circ C$  and 10 Kb in

the join En-MgFe<sup>3+</sup>AlSiO<sub>6</sub> (MgFATs) were the assemblage of orthopyroxene+olivine+magnetite and the one phase field of orthopyroxene was not encountered. These results indicate the presence of Fe<sup>2+</sup> in the run products and the composition of the run products containing olivine and magnetite are no longer on the join En-MgFATs. To keep high oxygen pressure in the sample capsule, the double capsules buffering method proposed by Ohashi and Hariya (1973) was employed. As shown in Fig. 8, starting material was contained in the sealed Pt inner capsule with 20 wt.% water, and PtO<sub>2</sub> buffer material was put into the sealed Pt outer capsule with 10 wt.% water. The length and diameter of the inner and outer capsules were 5.00 mm and 2.30 mm, and 10.0 mm and 3.5 mm respectively. After the run PtO<sub>2</sub> and Pt<sub>3</sub>O<sub>4</sub> were identified in the outer capsule by using a X-ray diffractometer. According to the experimental study by White (1971), the reaction  $3\text{PtO}_2 = \text{Pt}_3\text{O}_4 + \text{O}_2$  make the very high oxygen pressure at high temperatures. In the temperature and pressure range of the present experiment, hematite(Hem) was encountered in the run product when PtO<sub>2</sub> and Pt<sub>3</sub>O<sub>4</sub> were identified after the run. When neither PtO<sub>2</sub> nor Pt<sub>3</sub>O<sub>4</sub> was confirmed, magnetite appeared in the run product. The experimental products containing magnetite were excluded out from the present discussion.

The experimental products were examined by the aid of an optical microscope and a X-ray diffractometer.

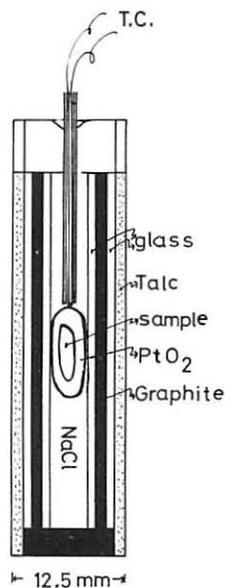


Fig. 8 Schematic diagram of high pressure cell.

Table 1. Experimental results

Composition		Temp.	Press.	Time	Results
(wt.%)		(°C)	(Kb)	(hr)	
MgSiO <sub>3</sub>	MgFe <sup>3+</sup> AlSiO <sub>6</sub>				
97.5	2.5	1100	16	49	En and rare Hem
97.5	2.5	1150	16	42	En only
97.5	2.5	970	12	45.5	En and rare Hem
97.5	2.5	1020	12	48.5	En only
97.5	2.5	920	8	48	En only
97.5	2.5	880	8	47	En only
97.5	2.5	800	8	69	En and rare Hem
95.0	5.0	1200	8	22.4	En only
95.0	5.0	950	8	46	En and rare Hem
95.0	5.0	1000	8	41	En and rare Hem
95.0	5.0	1050	8	46	En only
95.0	5.0	1100	12	29	En only
95.0	5.0	1000	12	44	En and rare Hem
95.0	5.0	1050	12	27.7	En and rare Hem
95.0	5.0	1200	16	21.4	En only
95.0	5.0	1250	16	19.8	En only
95.0	5.0	1100	16	22	En and Hem
95.0	5.0	1150	16	22.2	En only
92.5	7.5	1150	8	4.6	En only
92.5	7.5	1100	12	20	En and Hem
92.5	7.5	1200	12	26	En only
92.5	7.5	1250	8	22.5	En only
92.5	7.5	1000	5	46.5	En and rare Hem
92.5	7.5	1250	16	19.5	En and small amount Hem
92.5	7.5	1220	16	22	En only
92.5	7.5	1175	16	22.4	En, rare Hem and trace O1
92.5	7.5	1150	8	20	En only
90.0	10.0	1100	8	22	En and rare Hem
90.0	10.0	1200	8	21.5	En only
90.0	10.0	950	8	24	En and Hem
90.0	10.0	1150	8	21.4	En and Hem
90.0	10.0	1100	12	22	En and rare Hem
90.0	10.0	1200	12	19	En and rare Hem
90.0	10.0	1250	12	10.4	En and trace O1
90.0	10.0	1000	10	74	En and Hem
90.0	10.0	1200	16	22.8	En and Hem
90.0	10.0	1250	16	4	En and rare Hem
90.0	10.0	1400	12	6	En and X phase (inclusion)
85.0	15.0	1100	8	22	En and Hem
85.0	15.0	1000	8	47	En and Hem
85.0	15.0	1300	8	8	En and rare Hem
70.0	30.0	1050	8	69	En and Hem
70.0	30.0	950	8	95.	En, Hem and trace Sp
70.0	30.0	850	8	69	En, Hem and trace Sp
70.0	30.0	1000	12	29.5	En, Hem and trace Sp
70.0	30.0	1050	12	22	En and Hem
65.0	35.0	1000	8	42	En, Hem rare Sp
65.0	35.0	1100	8	26	En, Hem and rare Sp
65.0	35.0	1150	8	21.3	En, Hem and rare Sp
65.0	35.0	1200	8	21	En and Hem

Table 1. (continued)

Composition		Temp.	Press.	Time	Results	
(wt.%)		(°C)	(Kb)	(hr)		
MgSiO <sub>3</sub>	MgFeAlSiO <sub>6</sub>					
60.0	40.0	1000	8	47	En, Hem and small amount Sp	
MgSiO <sub>3</sub>	MgFe <sup>3+</sup> <sub>2/3</sub> Al <sub>4/3</sub> SiO <sub>6</sub>					
80.0	20.0	1150	12	18	En, Hem and trace Ol	
80.0	20.0	1100	12	24.4	En and rare Hem	
80.0	20.0	1150	12	22	En rare Hem and trace Sp	
85.0	15.0	1050	12	24.5	En rare Hem	
85.0	15.0	1100	12	20.4	En only	
85.0	15.0	1100	16	21	En and rare Hem	
85.0	15.0	1150	16	21.5	En only	
90.0	10.0	1000	12	33.5	En only	
90.0	10.0	950	12	42.5	En and rare Hem	
MgSiO <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>				
90.0	7.5	2.5	1100	8	20.5	En rare Sa and trace Qtz
92.0	6.0	2.0	1100	8	21.4	En only
Reversal run						
MgSiO <sub>3</sub>	MgFe <sup>3+</sup> AlSiO <sub>6</sub>					
95.5	5.0	1000	8	25.5	En → En and rare Hem	
92.5	7.5	1050	8	21.4	En → En and rare Hem	

Abbreviations, En, enstatite<sub>SS</sub>; Hem, hematite; Sp, spinel<sub>SS</sub>; Qtz, quartz; Sa, sapphirine<sub>SS</sub>; Ol, olivine.

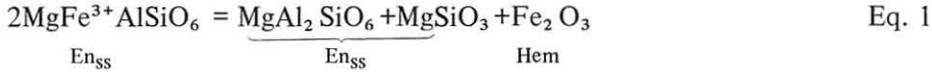
Some selected reversal run were carried out. The experimental results are given in Table 1. The crystalline mixture of enstatite single phase synthesized from oxide starting material was heated again at the temperature and pressure condition where enstatite<sub>SS</sub> and hematite were synthesized from the oxide starting materials. After the reversal run, small amount of hematite appeared. These results indicate that the concentration of Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> in enstatite determined in the present experiments was in equilibrium.

## Experimental results

### *High pressure experiments*

High pressure experiments were carried out in the pressure and temperature range 8 – 16 Kb and 800 – 1300°C. The experimental results are listed in Table 1.

The T-X sections in the join En-MaFATs at 8, 12, and 16 Kb are given in Figs. 9, 10, and 11. At 8 Kb enstatite<sub>SS</sub>, spinel(Sp)<sub>SS</sub>, and Hematite were encountered (Fig. 9). The solubility of MgFATs in enstatite increases with increasing temperature. The maximum solubility of MgFATs confirmed in this experiment was 10 wt.% at 1200°C. The solvus is presented as a straight line at higher temperature region above 1000°C and as a curved line at lower temperature below 1000°C. Only 1 wt.% MgFATs is incorporated in enstatite below 800°C. In the more MgFATs compositional region, the assemblage En<sub>SS</sub>+Hem was encountered. This results indicates the following reaction.



The assemblage En<sub>SS</sub>+Sp<sub>SS</sub>+Hem was confirmed in the experimental products in the more MgFATs compositional part. These results indicate the limit of the solubility of  $\text{Al}_2\text{O}_3$  in enstatite and the following reaction.



The boundary curve between the field of En<sub>SS</sub>+Hem and that of En<sub>SS</sub>+Sp<sub>SS</sub>+Hem was determined as shown in Fig. 9. Pale green color of this spinel phase indicates the presence of iron in it. The coexistence of hematite with spinel phase indicates the presence of magnesioferrite ( $\text{MgFe}_2^{3+}\text{O}_4$ ) rather than that of

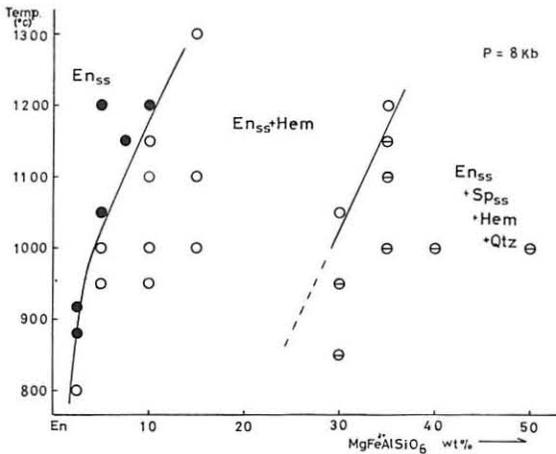


Fig. 9 T-X section at 8 Kb in the join  $\text{MgSiO}_3\text{-MgFe}^{3+}\text{AlSiO}_6$ . En<sub>SS</sub>, enstatite<sub>SS</sub>; Hem, hematite; Sp<sub>SS</sub>, spinel<sub>SS</sub>; Qtz, quartz.

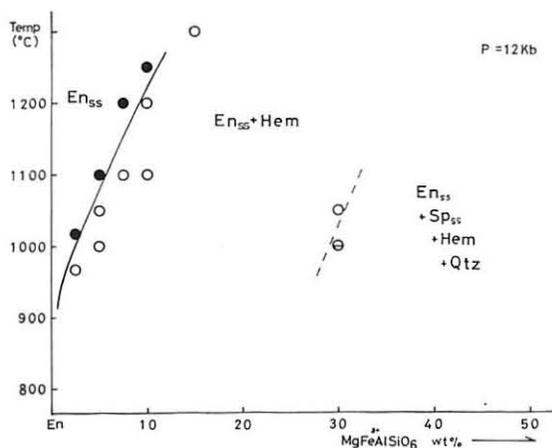


Fig. 10 T-X section at 12 Kb in the join  $\text{MgSiO}_3\text{-MgFe}^{3+}\text{AlSiO}_6$ . Abbreviations are given in Fig. 9.

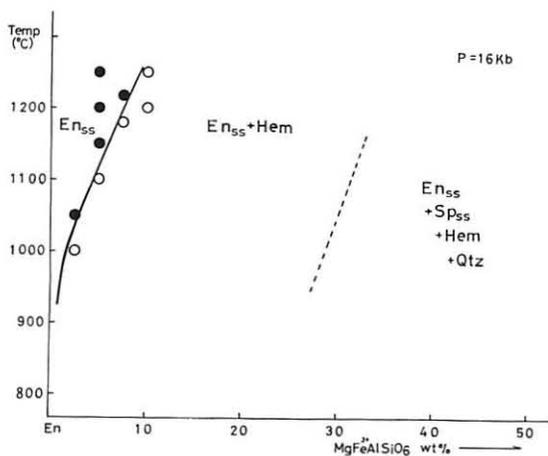
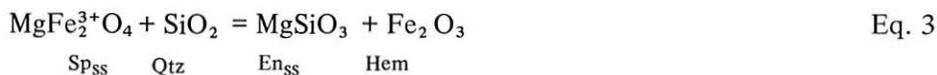


Fig. 11 T-X section at 16 Kb in the join  $\text{MgSiO}_3\text{-MgFe}^{3+}\text{AlSiO}_6$ . Abbreviations are given in Fig. 9.

magnetite ( $\text{Fe}^{2+}\text{Fe}_2^{3+}\text{O}_4$ ) or hercynite ( $\text{Fe}^{2+}\text{Al}_2\text{O}_4$ ) in its structure. Spinel<sub>SS</sub> coexisting with hematite and enstatite<sub>SS</sub> is attributed by the following reaction.



The change of  $\Delta 2\theta$  of enstatite<sub>SS</sub> in the variable compositions of the run materials at 1000°C were determined as shown in Fig. 13. In the single phase field of En<sub>SS</sub> and the two phase field of En<sub>SS</sub>+Hem, the  $\Delta 2\theta$  increases with increasing MgFATs in the run materials indicating that  $\text{Al}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$

contents of enstatite<sub>SS</sub> increase. In four phase field of  $\text{En}_{\text{SS}}+\text{Sp}_{\text{SS}}+\text{Hem}+\text{Qtz}$ , however, it is a constant value indicating the fixed composition of enstatite<sub>SS</sub>, which is determined by the invariant reactions of Eqs. 2 and 3. Though quartz was not confirmed in the run materials, its presence was theoretically assumed. Rare amount of spinel in these run products implied that quartz is probably present in trace amount and it is difficult to identify the presence of quartz.

At 12 Kb (Fig. 10), the single phase field of  $\text{En}_{\text{SS}}$ , the two phase field of  $\text{En}_{\text{SS}}+\text{Hem}$ , and the assemblage of  $\text{En}_{\text{SS}}+\text{Sp}_{\text{SS}}+\text{Hem}(\text{+Qtz})$  were encountered. The solvus was determined as a straight line in the temperature range 1000 – 1250°C. The boundary curve between the field of  $\text{En}_{\text{SS}}+\text{Hem}$  and that of  $\text{En}_{\text{SS}}+\text{Sp}_{\text{SS}}+\text{Hem}+\text{Qtz}$  was determined in the composition of  $\text{En}(70)\text{-MgFATs}(30)$  at 1025°C, and its slope was presented on the analogy of that determined at 8 Kb.

At 16 Kb (Fig. 11), the single phase field of  $\text{En}_{\text{SS}}$  and the two phase field of  $\text{En}_{\text{SS}}+\text{Hem}$  were encountered. Though no experiment was made in the part with high MgFATs content of this join, the boundary between the field of  $\text{En}_{\text{SS}}+\text{Hem}$  and that of  $\text{En}_{\text{SS}}+\text{Sp}_{\text{SS}}+\text{Hem}+\text{Qtz}$  is provisionally given by the

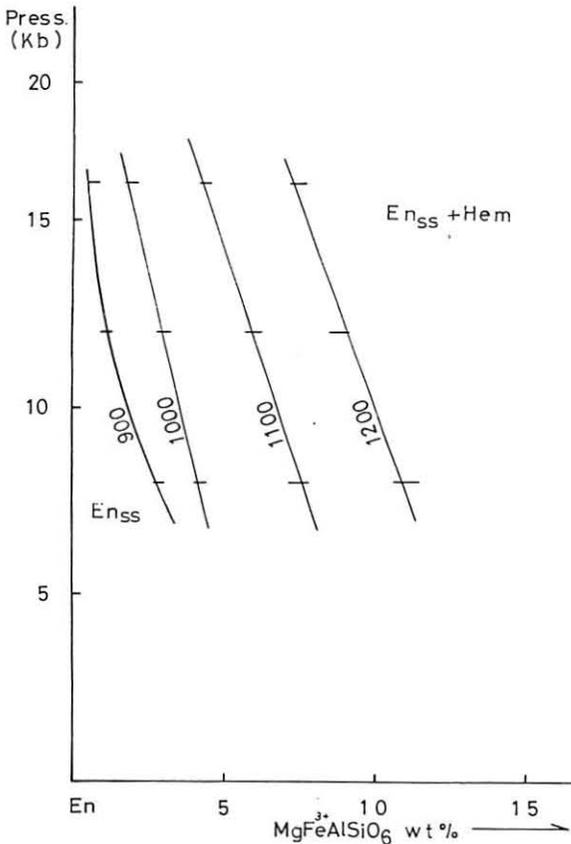


Fig. 12 P-X sections in the join  $\text{MgSiO}_3\text{-MgFe}^{3+}\text{AlSiO}_6$ . Abbreviations are given in Fig. 9.

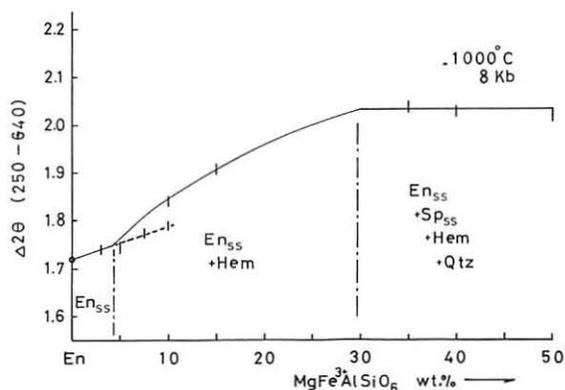


Fig. 13 The relationship between  $\Delta 2\theta$  of the enstatite<sub>SS</sub> and bulk composition at 1000°C and 8 Kb. Broken line indicates  $\Delta 2\theta$  of enstatite<sub>SS</sub> in the enstatite single phase field at higher temperature than 1000°C.

consideration of the pressure and temperature dependence of this curve determined at 8 and 12 Kb.

The phase equilibria in the more aluminous join  $\text{MgSiO}_3\text{-MgFe}_{2/3}^{3+}\text{Al}_{4/3}\text{SiO}_6$  ( $\text{MgFA}_2$  Ts) were studied experimentally in the pressure and temperature range 12 – 16 Kb and 950 – 1150°C, for the purpose to determine the single phase field of enstatite<sub>SS</sub>. The T-X section in the part with lower  $\text{MgFA}_2$  Ts content of this join at 12 Kb is given in Fig. 14. The single phase field of  $\text{En}_{SS}$  and the two phase field of  $\text{En}_{SS}+\text{Hem}$  were encountered. The boundary curve between these field was determined as a straight line between 950 – 1150°C. The single phase field of  $\text{En}_{SS}$  expands with increasing temperature. The solvus at 16 Kb was determined experimentally to pass through a point of  $\text{En}(85)\text{MgFA}_2$  Ts(15) at 1125°C as shown in Fig. 15. In this join a reaction of Eq. 1 also takes place and the temperature and pressure dependences of Eq. 1 determined in this join are in a good agreement with that determined in the join  $\text{En-MgFATs}$ . In Fig. 15 the boundary between the field of  $\text{En}_{SS}$  and that of  $\text{En}_{SS}+\text{Hem}$  at 8, 12, and 16 Kb are given. The single phase field of  $\text{En}_{SS}$  decreases with increasing pressure and decreasing temperature.

Some high pressure experiments were carried out at 1100°C and 8 Kb in the two compositions of  $\text{En}(90)\text{Al}_2\text{O}_3(7.5)\text{Fe}_2\text{O}_3(2.5)$  and  $\text{En}(92)\text{Al}_2\text{O}_3(6.0)\text{Fe}_2\text{O}_3(2.0)$ . The experimental results are given in Table 1. In the later composition only enstatite<sub>SS</sub> was encountered and in the former the assemblage of  $\text{En}_{SS}+\text{Sa}_{SS}+\text{Qtz}$  was encountered. These results indicate that the following reactions are present between these two compositions at 1100°C and 8 Kb.

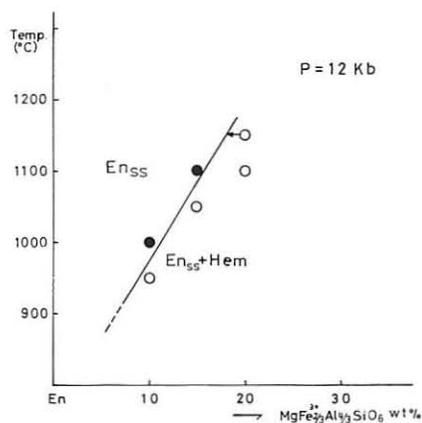


Fig. 14 T-X section at 12 Kb in the join En-MgFA<sub>2</sub> Ts.

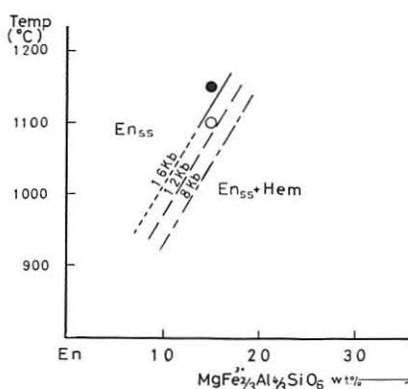
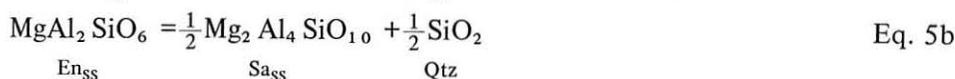
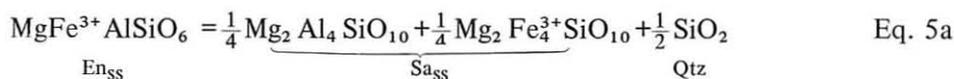


Fig. 15 T-X sections at 8, 12, and 16 Kb in the join En-MgFA<sub>2</sub> Ts.



The solubility of  $\text{Al}_2\text{O}_3$  in enstatite determined by Eq. 5b in the ternary system  $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2$  has been determined by Arima and Onuma (1977). The subsolidus phase equilibria diagram in the  $\text{MgO-Al}_2\text{O}_3\text{-Fe}_2\text{O}_3\text{-SiO}_2$  at  $1100^\circ\text{C}$  and 8 Kb is given in Fig. 16. The solubility of  $\text{Al}_2\text{O}_3$  in enstatite coexists with sapphirine and quartz in the  $\text{Fe}^{3+}$  bearing system is much more than that of enstatite in the ternary system  $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2$ . This result indicates that  $\text{Al}_2\text{O}_3$  is incorporated in enstatite by the substitution  $\text{MgSi} = \text{AlAl}$  as well as  $\text{MgSi} = \text{Fe}^{3+}\text{Al}$  in the  $\text{Fe}^{3+}$  bearing system. At  $1100^\circ\text{C}$  and 8 Kb, the solubility of  $\text{Al}_2\text{O}_3$  is about 5 wt.% in the ternary system  $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2$  and maximum value is 6.5 wt.% in the quaternary system  $\text{MgO-Al}_2\text{O}_3\text{-Fe}_2\text{O}_3\text{-SiO}_2$ .

### Crystalline phases

Enstatite<sub>SS</sub>, spinel<sub>SS</sub>, sapphirine<sub>SS</sub> hematite, and quartz were identified by the aid of a X-ray diffractometer and an optical microscope.

Enstatite<sub>SS</sub> forms euhedral crystal, up to  $30\mu$  in size, pale yellow in color, needle like shaped at lower temperature around  $900^\circ\text{C}$  and elongated recutangular or rounded shaped at higher temperature around  $1100^\circ\text{C}$ . The

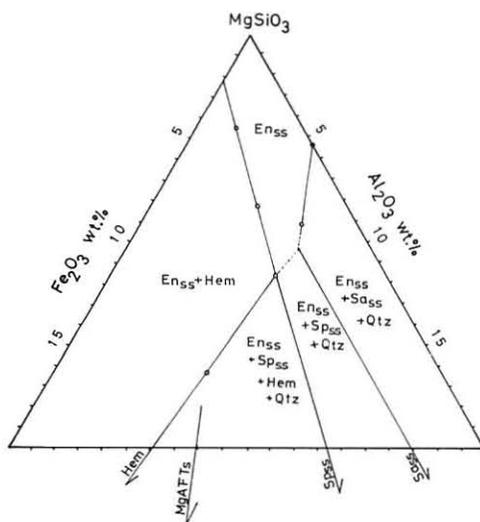


Fig. 16 The subsolidus phase diagram in the system  $\text{MgSiO}_3\text{-Al}_2\text{O}_3\text{-Fe}_2\text{O}_3$  at  $1100^\circ\text{C}$  and 8 Kb. Abbreviations are given in Fig. 9.

unit cell parameters of enstatites were determined by using the following diffraction lines, (060), (10,31), (250), (541), (640), (621), (631), (241), (820), (721), (531), and (630). Silicon was used as an external standard. The cell parameters given in Table 2 were calculated by using the UNICS computer program by Sakurai (1968). In Figs. 17, 18, and 19 the cell edges  $a$ ,  $b$ , and  $c$  and the cell volume  $V$  of enstatites synthesized in the system  $\text{MgSiO}_3\text{-Al}_2\text{O}_3\text{-Fe}_2\text{O}_3$  are given with those of enstatites synthesized in the system  $\text{MgSiO}_3\text{-Al}_2\text{O}_3$  by Skinner and Boyd (1964) and Arima and Onuma (1977). The cell edges  $a$  and  $c$  show no significant change in the narrow compositional range of the join, En-MgFATs and En-MgFA<sub>2</sub>Ts as shown in Fig. 18. The cell edge  $b$  and the cell volume  $V$  decrease with increasing MgFATs or MgFA<sub>2</sub>Ts content of enstatite. Figs. 17, 18, and 19 show that  $\text{Fe}^{3+}$  bearing enstatite has the larger cell edges  $b$  and  $a$  and the larger cell volume  $V$  than those of  $\text{Fe}^{3+}$  free enstatite, as supported by the larger ionic radius of  $\text{Fe}^{3+}$  than that of Al. These results indicate that the substitution  $\text{MgSi} = \text{Fe}^{3+}\text{Al}$  makes a weak decrease of cell volume compared with that made by the substitution  $\text{MgSi} = \text{AlAl}$ .

EPMA chemical analyses were carried out on some synthetic enstatites. The results are listed in Table 3. Enstatite crystals analyzed were present as a single phase in the run products except the run product of En(80)MgFA<sub>2</sub>Ts(20) consisting of En<sub>55</sub>+Hem. Fine grain of enstatite crystals (up to  $30\mu$ , average  $10\mu$ ) made it difficult to analyze by EPMA. The chemical compositions determined show a variation in the range of  $\pm 1.0$  wt.%. These variations could

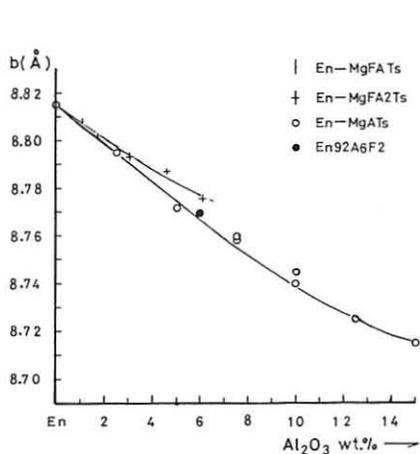


Fig. 17 The relationship between the unit cell edge  $b$  and the  $\text{Al}_2\text{O}_3$  content of synthetic enstatite<sub>SS</sub>.

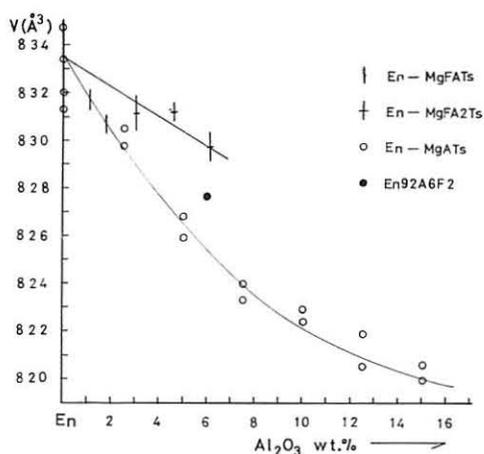


Fig. 19 The relationship between the unit cell volume  $V$  and the  $\text{Al}_2\text{O}_3$  content of synthetic enstatite<sub>SS</sub>.

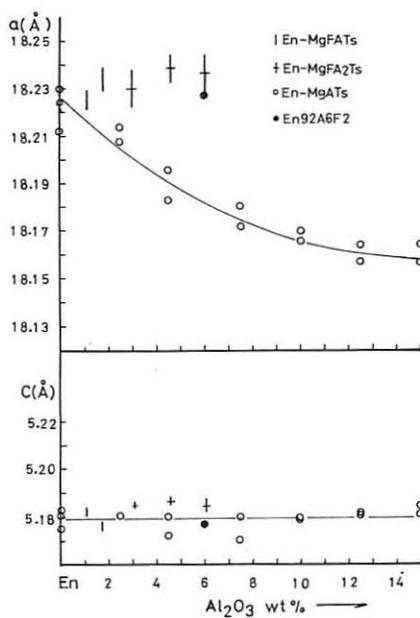


Fig. 18 The relationship between the unit cell edges  $a$  and  $c$  and the  $\text{Al}_2\text{O}_3$  content of synthetic enstatite<sub>SS</sub>.

be attributed to the analytical error caused by a fine grain of enstatite crystals. The composition of enstatite in the run product in En(92.5)MgFA<sub>2</sub>Ts(7.5) at 1220°C and 16 Kb, and that at 1200°C and 12 Kb show more SiO<sub>2</sub> and less MgO than these of planned composition. The chemical formulas of these enstatites imply the presence of Fe<sup>2+</sup>SiO<sub>3</sub> in them. On the other hand the chemical composition and the formula of the enstatite synthesized at 1150°C and 12 Kb show a good agreement with those of planned composition. This agreement was also confirmed in the analytical result in En(85)MgFA<sub>2</sub>Ts(15) at 1100°C and 8 Kb. Mössbauer spectra on the enstatite synthesized at 1400°C and 12 Kb indicate that high temperature around 1400°C is not favourable to the presence of Fe<sup>3+</sup> in enstatite. There is a probability of the presence of some amount of Fe<sup>2+</sup>SiO<sub>3</sub> in enstatite synthesized above 1200°C. The composition of the enstatite coexisting with hematite in the run product of En(80)MgFA<sub>2</sub>Ts(20) was determined by EPMA. The composition of this enstatite is plotted in the more aluminous region than that of the starting material. This result is explained by the reaction of Eq. 1. The composition of enstatite coexisting with hematite is plotted on the tie line of hematite-starting material in the system MgSiO<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub>-Fe<sub>2</sub>O<sub>3</sub>. The single phase field of enstatite<sub>SS</sub> in the join En-MgFA<sub>2</sub>Ts at 1150°C and 12 Kb was determined as shown in Fig. 14 by using this EPMA analytical result and the compositional relation among En<sub>SS</sub>, Hem, and starting material.

Spinel<sub>SS</sub> forms octahedral crystal, 1μ in size. Pale green color indicates the presence of iron in it. It is easily distinguished from other phases by its high refractive index and isotropic property under the optical microscope. Because of the lower intensity of the diffraction lines and the presence of the other phases, it was impossible to determine the unit cell parameter hence its compositional change.

Hematite appeared as euhedral crystals. No shift of its X-ray diffraction line was observed suggesting the fixed composition close to Fe<sub>2</sub>O<sub>3</sub>.

Sapphirine<sub>SS</sub> was observed only optically in the run product of En(90)Al<sub>2</sub>O<sub>3</sub>(7.5)Fe<sub>2</sub>O<sub>3</sub>(2.5) at 1100° and 8 Kb. Fine grained euhedral crystals, brown in color were identified. Quartz was identified by the aid of a X-ray diffractometer in the same run product. In the assemblage of En<sub>SS</sub>+Sp<sub>SS</sub>+Hem, it was unsuccessful to find out the presence of quartz optically.

#### *The Mössbauer spectra of the synthetic enstatites*

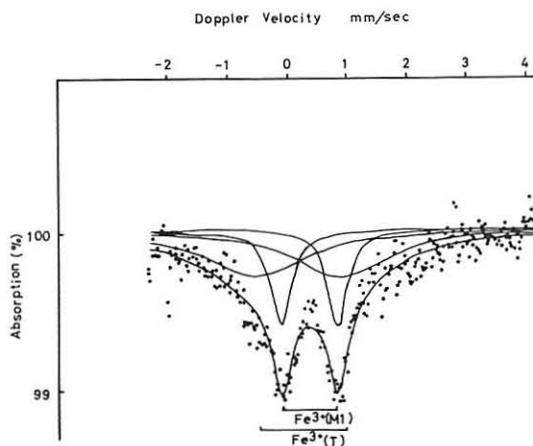
The Mössbauer spectra measurements were made on the two synthetic enstatites containing 3.5 wt.% Fe<sub>2</sub>O<sub>3</sub> synthesized at 1150°C 8 Kb, and

**Table 2** Cell parameters of synthetic enstatites

Composition (wt.%)		a(Å)	b(Å)	c(Å)	V(Å <sup>3</sup> )	
En	MgFATs					
95.0	5.0	18.225±0.004	8.808±0.001	5.182±0.002	831.8±0.4	
92.5	7.5	18.234±0.005	8.802±0.001	5.176±0.002	830.7±0.5	
90.0	10.0	18.233±0.009	8.800±0.005	5.183±0.003	831.7±0.8	
En	MgFA2Ts					
90.0	10.0	18.230±0.008	8.793±0.002	5.185±0.005 <sup>a</sup>	831.3±0.9	
85.0	15.0	18.238±0.006	8.787±0.001	5.186±0.002	831.2±0.3	
80.0	20.0	18.236±0.007	8.776±0.002	5.185±0.003	829.81±0.7	
En	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>				
92.0	6.0	2.0	18.229±0.008	8.769±0.002	5.177±0.004	827.6±0.8

1400°C 12 Kb.

In Fig. 20, the computer plot of the Mössbauer spectra of the enstatite synthesized at 1150°C and 8 Kb is given. The spectra consist of two doublets which have chemical shift(Cs) 0.17 mm/sec and 0.36 mm/sec, quadropole splitting(QS) 1.42 mm/sec and 0.94 mm/sec, respectively. According to the crystallographic study by Takeda (1972) on the Takashima bronzite (2.67 wt.% Fe<sub>2</sub>O<sub>3</sub> and 4.35 wt.% Al<sub>2</sub>O<sub>3</sub>), Fe<sup>3+</sup> and Al are present in smaller octahedral site(M1) rather than larger octahedral site(M2) in orthopyroxene structure, and Al is also present in tetrahedral site(T). From this crystallographical data, the inner doublet is assigned for Fe<sup>3+</sup> in (M1) site. The QS and CS values of this doublet resemble to those of other silicate minerals such as clinopyroxene and sapphirine (Table 4).



**Fig. 20** The Mössbauer spectra of enstatite synthesized at 1150°C and 8 Kb.

Table 3 Chemical compositions of synthetic enstatites

Starting Material Temp. Press. Analytical No.	En (85) MgFA <sub>2</sub> Ts (15) 1150°C, 16 Kb				
	1	2	3	4	5
SiO <sub>2</sub>	53.66	55.59	54.63	55.37	54.88
Al <sub>2</sub> O <sub>3</sub>	5.20	3.75	5.03	3.83	4.60
Fe <sub>2</sub> O <sub>3</sub> *	3.77	2.53	3.72	2.53	3.77
MgO	35.51	37.06	36.06	36.64	36.48
Total	98.14	98.93	99.44	98.37	99.73
Si	1.853	1.895	1.861	1.899	1.865
Al	0.212	0.152	0.203	0.154	0.184
Fe <sup>3+</sup>	0.098	0.066	0.096	0.066	0.096
Mg	1.828	1.885	1.832	1.872	1.848
Starting Material Temp. Press. Analytical No.	En (85) MgFA <sub>2</sub> Ts (15) 1100°C, 12 Kb		En (80) MgFA <sub>2</sub> Ts (20) 1150°C, 12 Kb		
	1	2	1	2	3
SiO <sub>2</sub>	54.51	54.30	53.91	53.39	54.66
Al <sub>2</sub> O <sub>3</sub>	5.44	4.55	5.17	5.61	5.71
Fe <sub>2</sub> O <sub>3</sub> *	3.90	3.53	3.97	4.02	3.53
MgO	35.99	35.73	35.52	34.27	35.72
Total	99.74	98.11	98.57	97.29	99.62
Si	1.853	1.870	1.855	1.860	1.857
Al	0.219	0.184	0.209	0.230	0.229
Fe <sup>3+</sup>	0.100	0.101	0.103	0.105	0.090
Mg	1.826	1.832	1.822	1.778	1.808
Starting Material Temp. Press. Analytical No.	En (92.5) MgFATs (7.5) 1220°C, 16 Kb				
	1	2	3	4	5
SiO <sub>2</sub>	58.21	58.59	57.53	59.01	57.60
Al <sub>2</sub> O <sub>3</sub>	1.21	1.56	1.60	1.20	1.58
Fe <sub>2</sub> O <sub>3</sub> *	1.79	1.97	2.19	1.54	2.38
MgO	37.94	37.90	37.11	37.61	37.34
Total	99.15	99.99	98.43	99.36	98.90
Si	1.972	1.969	1.967	1.990	1.961
Al	0.048	0.061	0.064	0.048	0.061
Fe <sup>3+</sup>	0.045	0.049	0.055	0.039	0.061
Mg	1.916	1.898	1.891	1.890	1.894
Starting Material Temp. Press. Analytical No.	En (92.5) MgFATs (7.5) 1200°C, 12 Kb				
	1	2	3		
SiO <sub>2</sub>	60.25	58.15	58.61		
Al <sub>2</sub> O <sub>3</sub>	1.17	2.24	2.11		
Fe <sub>2</sub> O <sub>3</sub> *	2.20	2.34	2.97		
MgO	37.19	36.45	36.83		
Total	100.81	99.18	100.52		
Si	2.002	1.970	1.974		
Al	0.045	0.088	0.083		
Fe <sup>3+</sup>	0.055	0.060	0.074		
Mg	1.845	1.827	1.817		

\* Total iron as Fe<sub>2</sub>O<sub>3</sub>

In some synthetic  $\text{Fe}^{3+}$ -bearing clinopyroxenes, the presence of  $\text{Fe}^{3+}$  in tetrahedral site has been reported (Shinno 1972, Ohashi and Hariya 1973). The Qs and Cs values of the outer doublet of synthetic enstatite resemble to those assigned for  $\text{Fe}^{3+}$  in (T) site of clinopyroxene as shown in Table 4. In Fig. 22, the single phase field of enstatite<sub>SS</sub> in the system  $\text{MgSiO}_3\text{-Fe}_2\text{O}_3$  could be assumed as a narrow area at  $1150^\circ\text{C}$  (2 wt.%  $\text{Fe}_2\text{O}_3$  could be incorporated in enstatite). This single phase field decreases with decreasing temperature. These experimental results indicate that  $\text{MgFe}_2^{3+}\text{SiO}_6$  ( $\text{Fe}^{3+}$  in M1 and T sites) could be present at higher temperature. From these reasons the outer doublet may be assigned for  $\text{Fe}^{3+}$  in tetrahedral site of orthopyroxene structure. The lower absorption of the outer doublet than that of inner doublet indicates that  $\text{Fe}^{3+}$  strongly prefers (M1) site than (T) site. This assumption is supported by the unit cell parameters of this enstatite. The cell edge *c* does not show significant change expected by the replacement of smaller Si by larger  $\text{Fe}^{3+}$ . From the spectra of this enstatite, the presence of  $\text{Fe}^{2+}$  could not be confirmed.

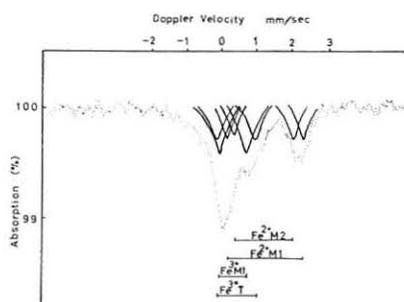


Fig. 21 The Mössbauer spectra of enstatite synthesized at  $1400^\circ\text{C}$  and 12 Kb.

The Mössbauer spectra of the enstatite synthesized at  $1400^\circ\text{C}$  and 12 Kb is shown in Fig. 21. On the basis of the data of  $\text{Fe}^{2+}$ -bearing orthopyroxenes by Bancroft and Maddock (1967), Virgo and Hafner (1969) and those of the  $\text{Fe}^{3+}$ -bearing enstatite mentioned above, it is estimated that there are four doublets assigned for  $\text{Fe}^{3+}$ (M1),  $\text{Fe}^{3+}$ (T),  $\text{Fe}^{2+}$ (M1), and  $\text{Fe}^{2+}$ (M2) in these spectra. The computed QS and CS values are listed in Table 4. The presence of  $\text{Fe}^{2+}$  in this enstatite makes it difficult to study the phase equilibria in the system  $\text{MgSiO}_3\text{-Al}_2\text{O}_3\text{-Fe}_2\text{O}_3$  around  $1400^\circ\text{C}$ . From this result, the present experimental study was carried out only below  $1300^\circ\text{C}$ .

Table 4 Mössbauer spectra parameters of iron silicates

Mineral	Type of iron	Position in crystal structure	Apporoximate configuration of co-ordination site	Chemical shift (mm/sec.)	Quadrupole splitting (mm/sec.)
Fe-Mg olivine*	Fe <sup>2+</sup>	M1, M2	Octa	1.25–1.27	2.89–3.02
Opx*	Fe <sup>2+</sup>	M1	Octa	1.24–1.27	2.35–2.65
	Fe <sup>2+</sup>	M2	Distorded Octa	1.22–1.27	1.91–2.13
Andradite*	Fe <sup>3+</sup>		Octa	0.50	0.58
Epidote*	Fe <sup>3+</sup>		Irregular Octa	0.43	2.01
Sapphirine*	Fe <sup>3+</sup>		Tetra	0.04	0.78
	Fe <sup>3+</sup>		Tetra	0.37	1.37
	Fe <sup>3+</sup>		Tetra	0.40	0.87
	Fe <sup>2+</sup>		Octa	1.25	2.57
Cpx*	Fe <sup>3+</sup>	M1	Octa	0.63–0.74	1.12–0.91
	Fe <sup>3+</sup>	T	Tetra	0.36–0.48	1.49–1.74
Opx 1150°C 8 Kb	Fe <sup>3+</sup>	M1	Octa	0.36	0.94
	Fe <sup>3+</sup>	T	Tetra	0.17	1.42
Opx 1400°C 12 Kb	Fe <sup>3+</sup>	M1	Octa	0.45	0.50
	Fe <sup>3+</sup>	T	Tetra	0.43	1.26
	Fe <sup>2+</sup>	M1	Octa	1.19	2.37
	Fe <sup>2+</sup>	M2	Distorded Octa	1.17	1.98

\* from Bancroft and Maddock (1967, 1968)

\* from Shinno (1972)

## Discussions

### *Phase relations in the system MgSiO<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub>-Fe<sub>2</sub>O<sub>3</sub>*

From the experimental results mentioned above, the diagram showing the single phase field of enstatite<sub>SS</sub> in the system MgSiO<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub>-Fe<sub>2</sub>O<sub>3</sub> at 8 Kb and various temperatures is given in Fig. 22. At lower temperature than 900°C, only less than 1 wt.% Fe<sub>2</sub>O<sub>3</sub> is expected to be incorporated in enstatite by the substitution MgSi = Fe<sup>3+</sup>Fe<sup>3+</sup>. Mössbauer spectra of the synthetic enstatite indicate the strong preference of Fe<sup>3+</sup> to octahedral site than tetrahedral site. In Fig. 16, the solubility of Fe<sub>2</sub>O<sub>3</sub> in enstatite at constant pressure and temperature increases with increasing Al<sub>2</sub>O<sub>3</sub> content in it, indicating that Fe<sub>2</sub>O<sub>3</sub> is mainly incorporated in enstatite by the substitution MgSi = Fe<sup>3+</sup>Al. In natural orthopyroxenes, moreover, the presence of Fe<sup>3+</sup> in tetrahedral site has not been reported. Therefore, in the present discussion MgFe<sub>2</sub><sup>3+</sup>SiO<sub>6</sub> is ignored and MgFe<sup>3+</sup>AlSiO<sub>6</sub> is considered as a reliable orthopyroxene molecule.

The present system is actually a join in the expanded quaternary system

MgO-Al<sub>2</sub>O<sub>3</sub>-Fe<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>. The phase relations in the join MgSiO<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub>-Fe<sub>2</sub>O<sub>3</sub> of the system MgO-Al<sub>2</sub>O<sub>3</sub>-Fe<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> at 1100°C and 8 Kb are given schematically in Fig. 23. At 1100°C and 8 Kb, following reactions were confirmed.

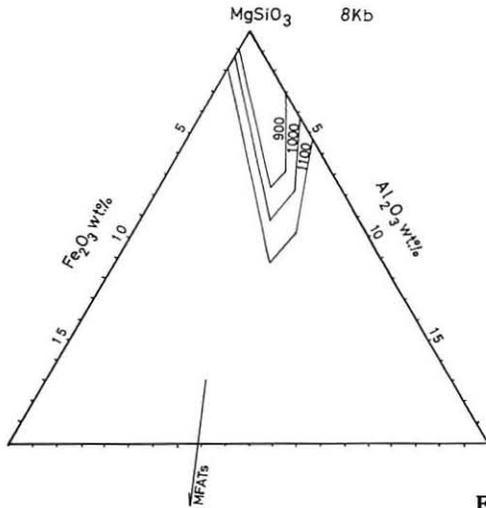
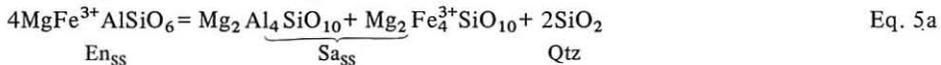
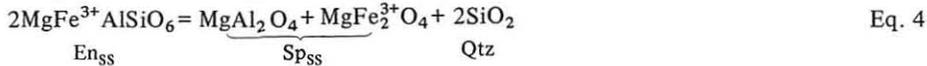
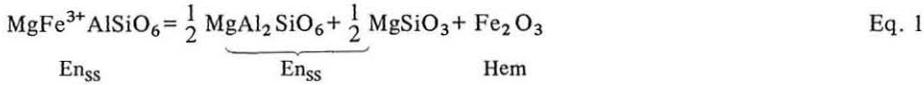


Fig. 22 The single phase field of enstatite<sub>SS</sub> at 8 Kb and various temperatures in the system MgSiO<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub>-Fe<sub>2</sub>O<sub>3</sub>.

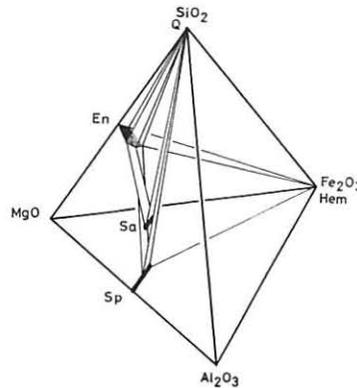


Fig. 23 The schematic diagram showing the phase relations in the system MgO-Al<sub>2</sub>O<sub>3</sub>-Fe<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> at 1100°C and 8 Kb. Abbreviations are given in Fig. 9.

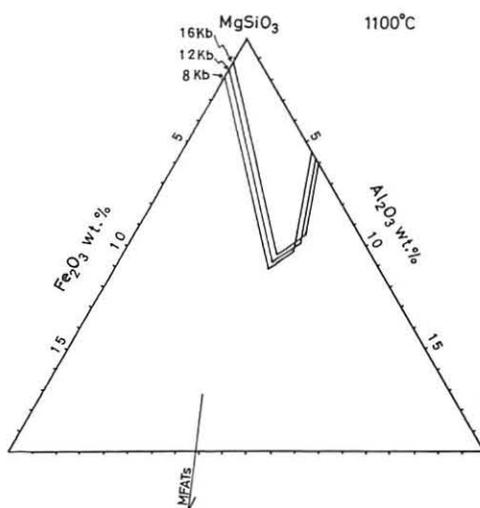


Fig. 24 The single phase field of enstatite<sub>SS</sub> at 1100°C and various pressures in the system MgSiO<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub>-Fe<sub>2</sub>O<sub>3</sub>.

Eq. 1 is an univariant reaction in the pseudoternary system MgSiO<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub>-Fe<sub>2</sub>O<sub>3</sub> and the composition of enstatite<sub>SS</sub> coexisting with hematite is variable with respect to the bulk composition at constant temperature and pressure. The variable compositions of enstatites coexisting with hematite are indicated by the increase of  $\Delta 2\theta$  of enstatite with increasing MgFATs and MgATs contents of ruh materials as shown in Fig. 13. The solubility of Fe<sub>2</sub>O<sub>3</sub> in enstatite coexisting with hematite increases with increasing Al<sub>2</sub>O<sub>3</sub> content in it, indicating that Fe<sub>2</sub>O<sub>3</sub> is incorporated in enstatite by the substitution MgSi = Fe<sup>3+</sup>Al. In four phase field of En<sub>SS</sub>+Sp<sub>SS</sub>+Hem+Qtz, there are two reactions of Eqs. 2 and 3. Eq. 2 is an invariant reaction in the ternary system MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> and Eq. 3 is an invariant reaction in the quaternary system MgO-Al<sub>2</sub>O<sub>3</sub>-Fe<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>. By both reactions of Eqs. 2 and 3, the composition of enstatite<sub>SS</sub> and that of spinel<sub>SS</sub> are fixed. The  $\Delta 2\theta$  of enstatite<sub>SS</sub> in the four phase field shows the constant value indicating its fixed composition as shown in Fig. 13.

Sharma et al. (1973) synthesized the spinel solid solution series between MgAl<sub>2</sub>O<sub>4</sub> and MgFe<sub>2</sub><sup>3+</sup>O<sub>4</sub> at 1300°C in air and stated the possibility of existence of solvus between them below 950°C at 7 Kb. However, since there is no experimental study on the relation between them at higher pressure than 7 Kb, the tie line between enstatite<sub>SS</sub> and spinel<sub>SS</sub> are presented provisionally as shown in Fig. 16.

Though no experiment was made in the compositional region where three phase field of En<sub>SS</sub>+Sp<sub>SS</sub>+Qtz is expected, this three phase field is presented as

shown in Fig. 16 on the basis of the experimental results in the other compositional region. In this field Eqs. 2 and 4 should be taking place.

In most aluminous region, the three phase field of  $\text{En}_{\text{SS}}+\text{Sa}_{\text{SS}}+\text{Qtz}$  is present as shown in Fig. 16. In this field there are two reaction of Eqs. 5a and 5b. Eq. 5b is an invariant reaction in the system  $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2$  and Eq. 5a is an univariant reaction in the system  $\text{MgO-Al}_2\text{O}_3\text{-Fe}_2\text{O}_3\text{-SiO}_2$ . The composition of enstatite<sub>SS</sub> is determined by these two reactions in this field. With increasing  $\text{Fe}_2\text{O}_3$  content of enstatite<sub>SS</sub> coexisting with  $\text{Sa}_{\text{SS}}+\text{Qtz}$ , the solubility of  $\text{Al}_2\text{O}_3$  in it strongly increases at constant pressure and temperature as shown in Fig. 16. This result indicates that the solubility of  $\text{Al}_2\text{O}_3$  in enstatite depends on the  $\text{Fe}_2\text{O}_3$  content of it as well as temperature and pressure variations. Therefore, the  $\text{Al}_2\text{O}_3$  content of orthopyroxene can not be used as an indicator of temperature and/or pressure without taking the  $\text{Fe}_2\text{O}_3$  content of it into account. On the other hand, the solubility of  $\text{MgAl}_2\text{SiO}_6$  in enstatite is constant at constant temperature and pressure when it coexists with  $\text{Sa}_{\text{SS}}+\text{Qtz}$  as shown in Fig. 16. The increase of  $\text{Al}_2\text{O}_3$  content of enstatite<sub>SS</sub> with increasing  $\text{Fe}_2\text{O}_3$  content of it is attributed to the solubility of  $\text{MgFe}^{3+}\text{AlSiO}_6$  in it. This results makes it possible to use the  $\text{MgAl}_2\text{SiO}_6$  content as an indicator of temperature and/or pressure.

Present experimental results indicate that sapphirine breaks down to the assemblage of  $\text{Sp}_{\text{SS}}+\text{Qtz}$  in the part of high  $\text{Fe}_2\text{O}_3$  content in the system

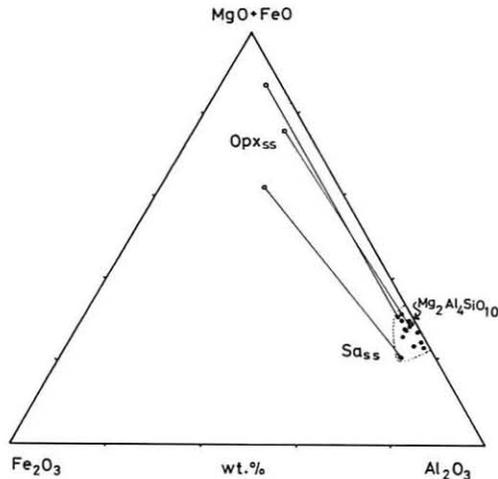


Fig. 25 The compositional relationships between natural orthopyroxenes and sapphirines in the system  $\text{MgO-Al}_2\text{O}_3\text{-Fe}_2\text{O}_3$ . A tie line indicates a coexisting relation. Sources of data, Segnit (1957), McKie (1963), Barker (1964), Lutts and Kopaneva (1967), Moore (1969), Haapala et al. (1971), Monchoux (1972), Merlino (1973), Woodford and Wilson (1976).

$\text{MgO-Al}_2\text{O}_3\text{-Fe}_2\text{O}_3\text{-SiO}_2$ . This breaking down reaction is expressed by the Eqs. 6a and 6b. In fig. 25,  $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$  ratio of several natural sapphirines are plotted, implying the narrow field of sapphirine<sub>SS</sub> between  $\text{Mg}_2\text{Al}_4\text{SiO}_{10}$  and  $\text{Mg}_2\text{Fe}_4^{3+}\text{SiO}_{10}$ . Though there is no experimental study on the relation between them, the presence of solvus is assumed and a tie line between  $\text{Sa}_{\text{SS}}$  and  $\text{En}_{\text{SS}}$  is presented as shown in Fig. 16.

*The temperature and pressure dependence of the solubility of  $\text{Al}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  in enstatite*

In Fig. 22, the single phase field of enstatite<sub>SS</sub> at various temperatures and 8 Kb are given. Independently of coexisting phases, the solubility of  $\text{Al}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  in enstatite increases with increasing temperature. Fig. 24 shows the single phase field of enstatite<sub>SS</sub> at  $1100^\circ\text{C}$  in the pressure range 8 – 16 Kb. The solubility of MgFATs slightly decreases with increasing pressure when enstatite coexists with hematite (Fig. 12). The pressure dependence of the solubility of MgATs in enstatite coexists with spinel<sub>SS</sub>+quartz is estimated to be slight. From these data, the pressure dependence of the solubility of MgFATs in enstatite (maximum solubility) coexisting with sapphirine<sub>SS</sub>+quartz is determined as shown in Fig. 24.

Geological applications

$\text{Al}_2\text{O}_3$  content of orthopyroxene has been given an attention by many investigators as a geobarometer and a geothermometer. The experimental studies have been made on the incorporation of  $\text{Al}_2\text{O}_3$  in enstatite by the substitution  $\text{MgSi} = \text{AlAl}$ , and these experimental results have been used to estimate the pressure and/or temperature conditions of natural rocks (Boyd 1973, Hermans et al. 1976).

In general, natural orthopyroxenes show small amount of silica deficiency in these chemical formulas. These silica deficiencies are explained by the replacement of Si by Al in tetrahedral site and the corresponding replacement of Mg by Al in octahedral site(M1). This substitution of  $\text{MgSi} = \text{AlAl}$  leads to the hypothetical pyroxene molecule  $\text{MgAl}_2\text{SiO}_6$  (MgATs). In chemical formulas of natural orthopyroxenes, Al in M1 site is generally less than Al in T site, and Cr, Ti, and  $\text{Fe}^{3+}$  are regarded to enter in M1 site, filling up the vacancy. These assumption lead to the hypothetical pyroxene molecules such as  $\text{MgCrAlSiO}_6$ ,  $\text{MgTiAl}_2\text{O}_6$ . As shown in Fig. 1, some natural orthopyroxenes show both high contents of  $\text{Al}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  (exceed 2 – 3 wt.%), indicating the substitution  $\text{MgSi} = \text{Fe}^{3+}\text{Al}$  as well as  $\text{MgSi} = \text{AlAl}$ . While  $\text{Cr}_2\text{O}_3$  and  $\text{TiO}_2$  contents are

generally very low and scarcely exceed 1 wt.%. Therefore  $\text{MgCrAlSiO}_6$  and  $\text{MgTiAl}_2\text{O}_6$  molecules in natural orthopyroxenes are not so important with respect to the solubility of  $\text{Al}_2\text{O}_3$  in orthopyroxenes.

Orthopyroxenes from volcanic rocks and plutonic differentiated rocks have both low  $\text{Al}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  contents as shown in Figs. 26 and 27, while from intrusive peridotites have high  $\text{Al}_2\text{O}_3$  content. Figs. 26 and 27 show the low  $\text{Fe}_2\text{O}_3$  and high  $\text{Al}_2\text{O}_3$  contents of these orthopyroxenes.  $\text{Fe}_2\text{O}_3$  content scarcely exceed 2 wt.% and amount of  $\text{Fe}^{3+}$  in M1 site is low as shown in Figs. 28 and 29. Low  $\text{Fe}_2\text{O}_3$  content of these orthopyroxenes indicate that  $\text{Al}_2\text{O}_3$  is incorporated in orthopyroxene mainly by the substitution  $\text{MgSi} = \text{AlAl}$ , whereas the substitution  $\text{MgSi} = \text{Fe}^{3+}\text{Al}$  is not so significant.

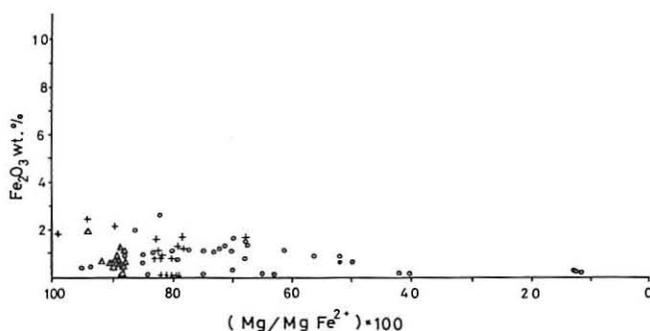


Fig. 26 The relationship between  $\text{Mg}/\text{Mg} + \text{Fe}^{2+}$  and  $\text{Fe}_2\text{O}_3$  contents of igneous orthopyroxenes. Symbols and data sources are given in Fig. 1.

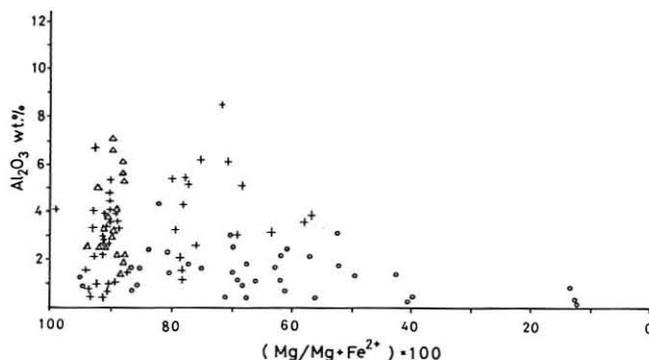


Fig. 27 The relationship between  $\text{Mg}/\text{Mg} + \text{Fe}^{2+}$  and  $\text{Al}_2\text{O}_3$  contents of igneous orthopyroxenes. Symbols and data sources are given in Fig. 1.

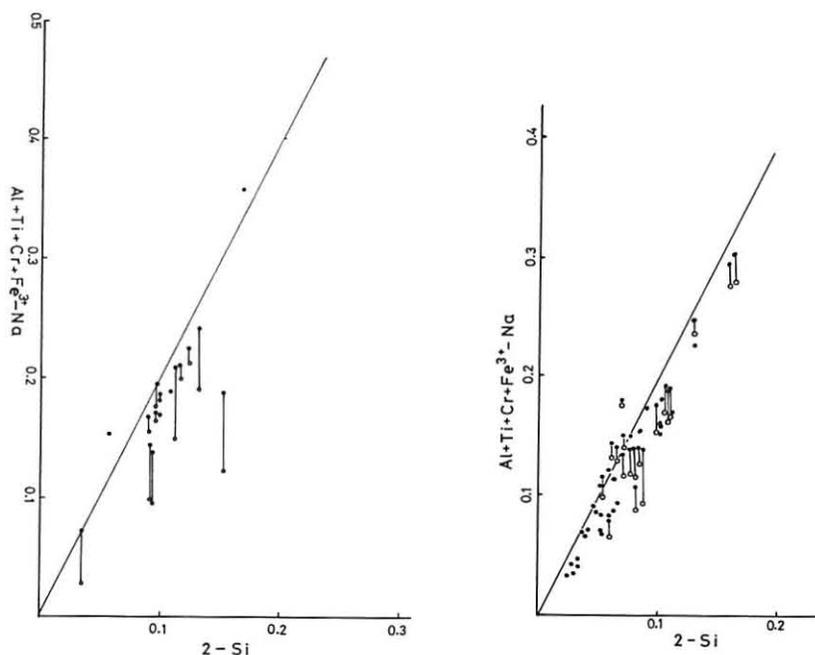


Fig. 28 (left) The relationship between (2-Si) in the tetrahedral site and (Al+Cr+Ti+Fe<sup>3+</sup>-Na) in the octahedral site of orthopyroxenes from inclusions within volcanic rocks. Calculation is based on 6 oxygens. Of the two circles connected by a line, the composition of the open circle is calculated without considering Fe<sup>3+</sup>. Sources of data are given in Fig. 1.

Fig. 29 (right) The relationship between (2-Si) in the tetrahedral site and (Al+Cr+Ti+Fe<sup>3+</sup>-Na) in the octahedral site of orthopyroxenes from intrusive peridotites. Calculation is based on 6 oxygens. Of the two circles connected by a line, the composition of the open circle is calculated without considering Fe<sup>3+</sup>. Sources of data are given in Fig. 1.

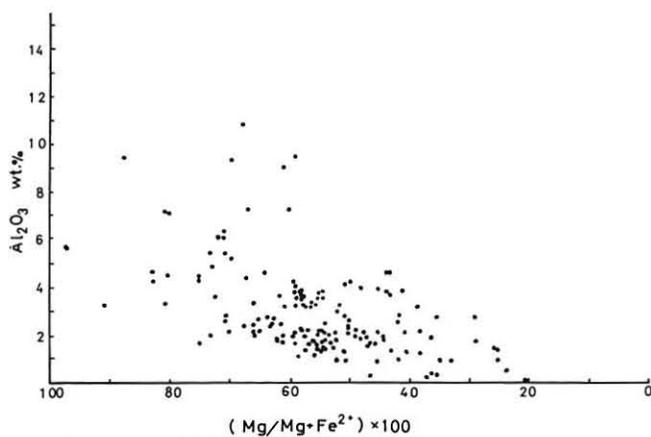
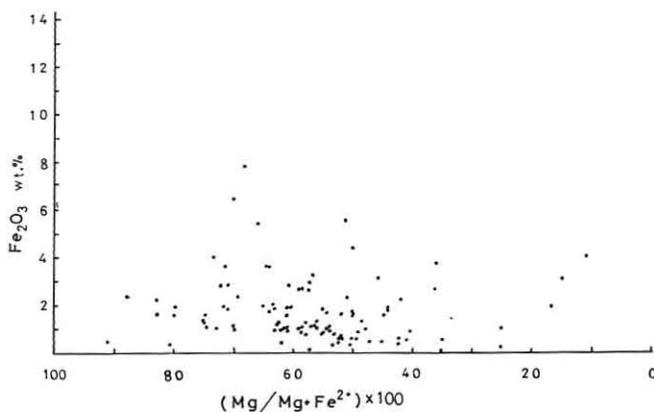
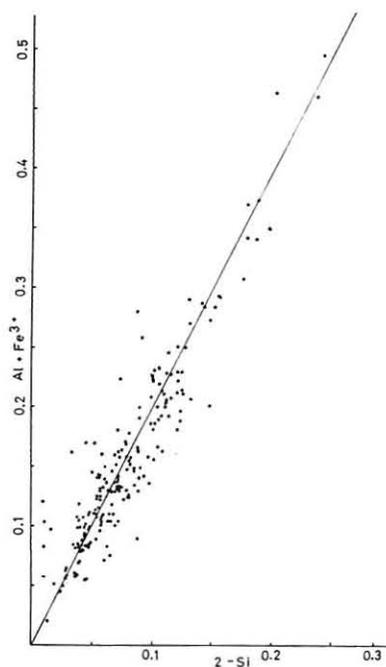


Fig. 30 The relationship between Mg/Mg+Fe<sup>2+</sup> and Al<sub>2</sub>O<sub>3</sub> contents of orthopyroxenes from metamorphic rocks. Sources of data are given in Fig. 1.

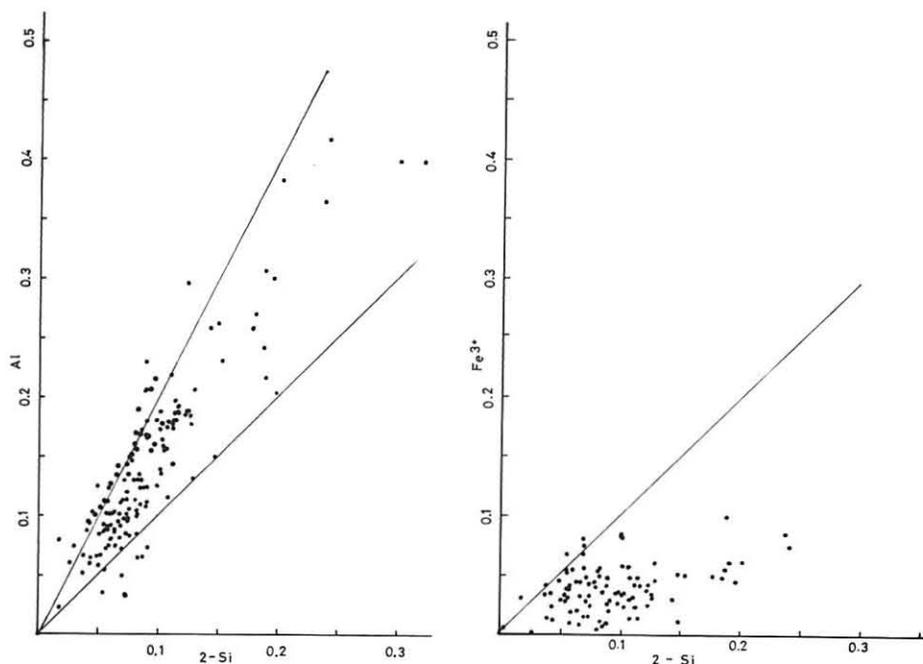
Some orthopyroxenes from metamorphic rocks, however, show high  $\text{Al}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  contents as shown in Figs. 30 and 31. As shown in Figs. 32 and 33, the  $\text{Al}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  contents are attributed to the solubility of  $\text{MgFe}^{3+}$ - $\text{AlSiO}_6$  and  $\text{MgAl}_2\text{SiO}_6$  in orthopyroxene. The  $\text{Fe}^{3+}$  occupies a large part of



**Fig. 31** The relationship between  $\text{Mg}/\text{Mg}+\text{Fe}^{2+}$  and  $\text{Fe}_2\text{O}_3$  contents of orthopyroxenes from metamorphic rocks. Sources of data are given in Fig. 1.



**Fig. 32** The relationship between (2-Si) in the tetrahedral site and  $(\text{Al}+\text{Fe}^{3+})$  in the octahedral site of orthopyroxenes from metamorphic rocks. Calculation is based on 6 oxygens. Sources of data are given in Fig. 1.



**Fig. 33** (left) The relationship between (2-Si) in the tetrahedral site and (Al) in the octahedral site of orthopyroxenes from metamorphic rocks. Calculation is based on 6 oxygens. Sources of data are given in Fig. 1.

**Fig. 34** (right) The relationship between (2-Si) in the tetrahedral site and ( $\text{Fe}^{3+}$ ) in the octahedral site of orthopyroxenes from metamorphic rocks. Calculation is based on 6 oxygens. Sources of data are given in Fig. 1.

M1 site and there is distinct trend of increase of  $\text{Fe}^{3+}$  in M1 site with increasing silica deficiency as shown in Fig. 34. From these facts,  $\text{MgFe}^{3+}\text{AlSiO}_6$  molecule is important with respect to the solubility of  $\text{Al}_2\text{O}_3$  in orthopyroxene of some metamorphic rocks.

Present experimental results indicate that the solubility of  $\text{Al}_2\text{O}_3$  increases with increasing  $\text{Fe}_2\text{O}_3$  content in it at constant temperature and pressure, indicating that total  $\text{Al}_2\text{O}_3$  content can not be used as an indicator of pressure and/or temperature. The solubility of  $\text{MgAl}_2\text{SiO}_6$  in enstatite is, however, constant at constant pressure and temperature. When  $\text{Al}_2\text{O}_3$  content is used as an indicator, it is necessary to examine the  $\text{Fe}_2\text{O}_3$  content and only the  $\text{Al}_2\text{O}_3$  in the  $\text{MgAl}_2\text{SiO}_6$  molecule can be used.

The assemblage of high aluminous orthopyroxene+sapphirine+quartz or high aluminous orthopyroxene+sapphirine+sillimanite have been reported in several localities (Hermans et al. 1976, Morse and Talley 1971, Bondarenko 1972, Dallwitz 1968). Hermans et al. (1976) described the high aluminous orthopyroxene (9.2 wt.%  $\text{Al}_2\text{O}_3$ ) coexisting with sapphirine and quartz from the migmatite near Vikeså and estimated the crystallization temperature and pressure as  $900^\circ\text{C}$  and 3 – 6 Kb. Though  $\text{Fe}_2\text{O}_3$  content of this orthopyroxene was not determined, the chemical formula suggests that about 6 wt.%  $\text{Al}_2\text{O}_3$  is incorporated in orthopyroxene by the substitution  $\text{MgSi} = \text{AlAl}$ . On the basis of the experimental results by Arima and Onuma (1977), the estimated temperature from 9.2 wt.%  $\text{Al}_2\text{O}_3$  is about  $1200 - 1250^\circ\text{C}$ , while taking  $\text{MgAl}_2\text{SiO}_6$  into account an estimation from 6 wt.%  $\text{Al}_2\text{O}_3$  by the substitution  $\text{MgSi} = \text{AlAl}$  gives temperature  $1000 - 1050^\circ\text{C}$ .

An aluminous and high  $\text{Fe}_2\text{O}_3$  orthopyroxene (6.29 wt.%  $\text{Al}_2\text{O}_3$  and 3.63 wt.%  $\text{Fe}_2\text{O}_3$ ) coexisting with sapphirine and sillimanite was described by Bondarenko (1972) from Anabar Massif. This orthopyroxene shows following chemical formula,  $(\text{Mg}_{1.27}\text{Fe}_{0.50}^{2+}\text{Mn}_{0.01}\text{Ca}_{0.02}\text{Fe}_{0.10}^{3+}\text{Al}_{0.09}) (\text{Al}_{0.18}\text{Si}_{1.82})\text{O}_6$ . This formula indicates that 2.1 wt.%  $\text{Al}_2\text{O}_3$  is incorporated in orthopyroxene as a molecule  $\text{MgFe}^{3+}\text{AlSiO}_6$  and 4.2 wt.%  $\text{Al}_2\text{O}_3$  as  $\text{MgAl}_2\text{SiO}_6$ . On the basis of the data by Arima and Onuma (1977), the solubility of 4.2 wt.%  $\text{Al}_2\text{O}_3$  gives the estimation of temperature and pressure about  $900^\circ\text{C}$  and 12 – 16 Kb.

$\text{Mg}/\text{Mg}+\text{Fe}^{2+}$  of orthopyroxene is generally lower than that of coexisting sapphirine (Bondarenko 1972, Lutts 1968, Hermans 1976). When there is small amount of FeO in orthopyroxene and sapphirine, the molar fraction of  $\text{MgFe}^{3+}\text{AlSiO}_6$  and that of  $\text{MgAl}_2\text{SiO}_6$  of orthopyroxene in Eqs. 5a and 5b should decrease more than that of  $\text{Mg}_2\text{Al}_4\text{SiO}_{10}$  and that of  $\text{Mg}_2\text{Fe}_3^+\text{SiO}_{10}$  in sapphirine<sub>SS</sub>. With increasing  $\text{Fe}^{2+}\text{SiO}_3$  content in orthopyroxene<sub>SS</sub> coexisting with sapphirine<sub>SS</sub>, Eqs. 5a and 5b go toward left hand side, making the increase of  $\text{Al}_2\text{O}_3$  content of orthopyroxene. Therefore the estimation of temperature and pressure on the basis of the experimental results in the system  $\text{MgO-Al}_2\text{O}_3\text{-Fe}_2\text{O}_3\text{-SiO}_2$  gives the maximum values, and the actual temperature and pressure of the crystallization of such high aluminous orthopyroxenes coexisting with sapphirine and quartz, or sapphirine and sillimanite would be lower than the estimated temperature and pressure.

## Conclusions

From the present experimental study, the following conclusions are obtained.

1. The phase equilibria in the system  $\text{MgSiO}_3\text{-Al}_2\text{O}_3\text{-Fe}_2\text{O}_3$  are determined experimentally in the temperature and pressure range 800 – 1300°C and 8 – 16 Kb. The following phase assemblages were encountered, the single phase field of enstatite<sub>SS</sub>, enstatite<sub>SS</sub>+hematite, enstatite<sub>SS</sub>+spinel<sub>SS</sub>+quartz, enstatite<sub>SS</sub>+sapphirine<sub>SS</sub>+quartz, enstatite<sub>SS</sub>+spinel<sub>SS</sub>+hematite+quartz.
2.  $\text{Al}_2\text{O}_3$  is incorporated in enstatite by the substitution  $\text{MgSi} = \text{AlAl}$  as well as  $\text{MgSi} = \text{Fe}^{3+}\text{Al}$ . The solubility of  $\text{Al}_2\text{O}_3$  increases with increasing  $\text{Fe}_2\text{O}_3$  in enstatite at constant emperature and pressure.
3. The solubility of  $\text{MgAl}_2\text{SiO}_6$  in enstatite is constant at constant temperature and pressure when enstatite<sub>SS</sub> coexists with sapphirine and quartz.
4. The solubility of  $\text{MgFe}^{3+}\text{AlSiO}_6$  in ensatite coexisting with hematite increases with increasing temperature and decreasing pressure.
5. The  $\text{Al}_2\text{O}_3$  content of orthopyroxene can not be used as an indicator of temperature and/or pressure without taking the  $\text{Fe}_2\text{O}_3$  content into account.

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