

HIGH-PRESSURE DECOMPOSITION OF THE SYSTEM FeSiO_3 – MgSiO_3

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Stability relations of $(\text{Mg, Fe})\text{SiO}_3$ solid solutions ranging in composition from pure FeSiO_3 to $(\text{Mg}_{0.3}\text{Fe}_{0.7})\text{SiO}_3$ have been studied at high temperatures in the pressure range to 96 kb. High-pressure decomposition of $(\text{Mg, Fe})\text{SiO}_3$ clinopyroxene

into $(\text{Mg, Fe})_2\text{SiO}_4$ spinel solid solution and stishovite was established. The decomposition curve for FeSiO_3 , clinoferrosilite, was found to coincide with the coesite–stishovite transformation curve.

The pyroxenes are accepted to be the most abundant class of minerals next to the olivines in the upper mantle. Reconnaissance study of the high-pressure transformation of $\text{A}^{2+}\text{B}^{4+}\text{O}_3$ type silicates and germanates with pyroxene structure has already been reported by Ringwood *et al.* (RINGWOOD, 1967; RINGWOOD and MAJOR, 1966a, b, c, 1967, 1968; RINGWOOD and SEABROOK, 1963). They successfully discovered various types of transformations such as the transformation to ilmenite, to garnet and to perovskite, and the decomposition into spinel and rutile-type structure. Construction of the reliable transformation diagram of the MgSiO_3 – FeSiO_3 system over the wide range of pressure and temperature is, however, indispensable for the quantitative analysis of the high-gradient zone of seismic wave velocities in the mantle. In the present study, some preliminary experimental results upon phase equilibria at high pressures in the iron-rich side of the pyroxene system MgSiO_3 – FeSiO_3 are reported.

High-pressure and high-temperature experiments were carried out by means of a tetrahedral press using pyrophyllite as pressure transmitting material. Two different sizes of cemented tungsten carbide anvils with 9 mm and 7 mm edge length were used. Pressure values were calibrated at room temperature on the basis of the pressure standard proposed by JEFFERY *et al.* (1966).

Powder samples were directly embedded in the graphite tube which was used as a heating element as well. Temperatures were measured with a Pt/Pt–13% Rh

thermocouple without any corrections for the effect of pressure on the emf of the thermocouple.

Starting materials used in the present study are in general orthopyroxenes of known composition which were synthesized at 40 kb and at 1200 °C. Equimolar mixtures of fayalite and amorphous silica were also used as starting materials for the study of high-pressure transformation in ferrosilite. The experimental method used in determining the stability diagram of $(\text{Mg, Fe})\text{SiO}_3$ at high-pressures and high-temperatures was the usual quenching method. Samples were subjected to desired pressures at desired temperatures for a pre-determined interval of time and quenched isobarically by turning off the heating power. After relaxation of the pressure and recovery of the samples, the phases present were examined by optical and X-ray diffraction technique.

Equilibrium data of ferrosilite at various pressure–temperature–time conditions are summarized in table 1 and illustrated in fig. 1. A previous report by RINGWOOD and MAJOR (1966a) that clinoferrosilite decomposes into Fe_2SiO_4 spinel plus stishovite was confirmed over a wide temperature range. The present data also indicate that the boundary curve for this decomposition of clinoferrosilite is well represented by the boundary curve for the coesite–stishovite transition which was determined as $P \text{ (kb)} = 69 + 0.024 T \text{ (}^\circ\text{C)}$ in our recent study (AKIMOTO and SYONO, 1969) and reproduced by the solid straight line in fig. 1. The olivine–spinel transformation in Fe_2SiO_4 is known to take

TABLE 1

Results of runs on the high-pressure and high-temperature phase transformations in FeSiO_3

Run no.	Pressure (kb)	Temperature (°C)	Time (min)	Phases present
2*	83	790 ± 5	30	clinoferrosilite
3	89	790 ± 5	30	spinel + stishovite + clinoferrosilite (small amount)
1*	94	790 ± 5	30	spinel + stishovite
5	88	1000 ± 5	20	clinoferrosilite
4	94	1000 ± 5	20	spinel + stishovite
7	98	1150 ± 10	15	spinel + stishovite
6	94	1210 ± 10	10	clinoferrosilite

* Starting materials used in the runs with asterisk mark are equimolar mixtures of fayalite and amorphous silica. Unless otherwise designated, starting materials are orthoferrosilite.

place at pressures of about 45 kb to 55 kb in the temperature range of 800 °C to 1200 °C (AKIMOTO *et al.*, 1967). These pressure values are much lower than the transition pressure of coesite to stishovite at the corresponding temperatures. Consequently, the formation of the stishovite plays a decisive role in realizing the reaction, $\text{FeSiO}_3 \rightarrow \text{Fe}_2\text{SiO}_4$ (spinel) + SiO_2 (stishovite). Substantial agreement of the boundary curve for the decomposition of clinoferrosilite with the coesite–stishovite transition curve may be caused by these reasons. It is similarly suggested from the present study that the decomposition curve of CoSiO_3 clinopyroxene to Co_2SiO_4 spinel plus stishovite coincides with the coesite–stishovite transition curve.

Experimental results for the decomposition of the $\text{FeSiO}_3\text{--MgSiO}_3$ system over the pressure range to 96 kb at 800 °C are shown in table 2 and fig. 2. It is seen that at this temperature the starting orthopyroxene solid solutions transform to clinopyroxene solid solu-

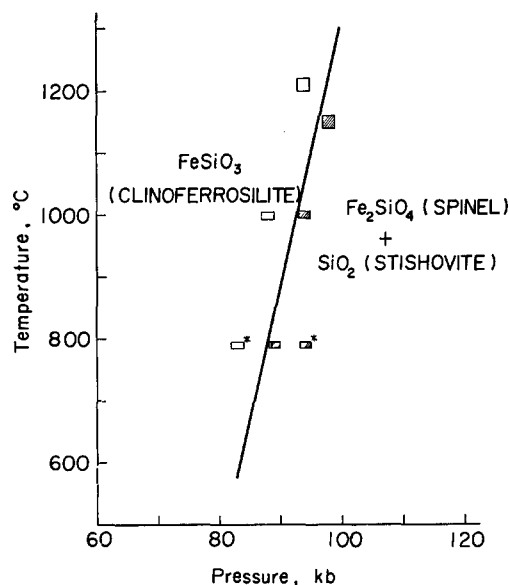


Fig. 1. Stability diagram for the high-pressure and high-temperature decomposition of FeSiO_3 . * indicates the runs using equimolar mixtures of fayalite and amorphous silica as the starting materials. Unless otherwise designated, the starting material is orthoferrosilite.

tions at high pressures and further decomposes to stishovite plus spinel solid solutions of the $\text{Fe}_2\text{SiO}_4\text{--Mg}_2\text{SiO}_4$ system at higher pressures. This agrees well with the previous report by RINGWOOD and MAJOR (1966c, 1968).

The compositions of spinel s.s. (solid solutions) in the three phase region (spinel s.s. + stishovite + clinopyroxene s.s.) were determined from their lattice parameters based on the lattice parameter–composition relationship for $(\text{Fe, Mg})_2\text{SiO}_4$ spinel s.s. previously published by us (AKIMOTO and FUJISAWA, 1968). This information made it possible to estimate the boundary curve in fig. 2 separating the two phase region (spinel

TABLE 2

Results of runs on the high-pressure and high-temperature phase transformations in the system $\text{FeSiO}_3\text{--MgSiO}_3$

Run no.	Composition*	Pressure (kb)	Temperature (°C)	Time (min)	Phases present**	Lattice parameter of spinel s.s. (Å)
1004	10M90F	86	805 ± 5	30	cpx	
1001	idem	90	800 ± 5	30	sp + st + cpx	8.227 ± 0.001
1003	idem	96	800 ± 5	30	sp + st + cpx	8.222 ± 0.002
2001	20M80F	90	800 ± 5	30	cpx	
2002	idem	93	810 ± 5	30	sp + st + cpx	8.222 ± 0.001
3002	30M70F	96	810 ± 5	30	cpx + sp + st	8.220 ± 0.002

* M = MgSiO_3 ; F = FeSiO_3 .

** cpx = clinopyroxene solid solutions; sp = spinel solid solutions; st = stishovite.

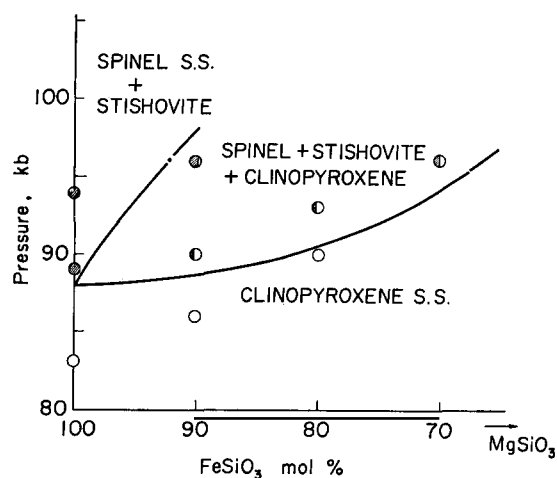


Fig. 2. Phase diagram for the high-pressure and high-temperature decomposition of the system FeSiO_3 – MgSiO_3 at $800 \pm 10^\circ\text{C}$. The dot indicates the boundary estimated from the spinel composition obtained from the lattice parameter.

s.s. + stishovite) from the three phase region (spinel s.s. + stishovite + clinopyroxene s.s.). Since the boundary curves determined in this study are only limited to the narrow composition range of the iron-rich side of the FeSiO_3 – MgSiO_3 system, it is still difficult to elucidate the general transformation behavior of the whole composition range of the system. It is clear, however, that the three phase region ranges over some

twenty or thirty kilobars in the intermediate composition of the FeSiO_3 – MgSiO_3 system. Thus, the decomposition of the $(\text{Mg}, \text{Fe})\text{SiO}_3$ clinopyroxene may probably contribute to the formation of the transition zone in the mantle. The present results also support the previous conclusion by RINGWOOD and MAJOR (1966c) that $(\text{Mg}, \text{Fe})\text{SiO}_3$ clinopyroxenes remain stable at pressures which are substantially higher than required to cause olivines with similar Mg/Fe ratios to transform to spinels.

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