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Peritectic reactions
in Mg-Si-O-H and Fe-S-H systems
in the primordial solar nebula

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Abstract

The peritectic reactions in the solar nebula have played important roles in chemical fractionations when the solar nebula cooled from high temperature. Then, the peritectic reactions in the Mg-Si-Fe-S-O-H system consisting of the most abundant refractory elements to form silicates, metal and sulfides in the primitive solar nebula were studied from the viewpoints of thermodynamics and reaction kinetics. Since Fe and S can not be included in silicates under the conditions of the primitive solar nebula, the system was divided into two independent systems: the Mg-Si-O-H and Fe-S-H systems.

In the Mg-Si-O-H system, forsterite (Mg_2SiO_4) and enstatite (MgSiO_3) are in a reaction relation (Grossman, 1972). Due to the proximity of the reaction region to the Mg-Si-O plane (Tsuchiyama, 1990), in the cooling of the solar nebula gas, the reaction between forsterite and Si-rich gas affects the amount of minerals and mineral species of final products (Imae and Kitamura, 1993). This reaction has been treated only as an equilibrium based on the equilibrium phase relation. Then, the reaction rates between forsterite and Si-rich gas were determined by the experiment, where the double capsule technique newly designed in the present study was used. The reaction is controlled by the diffusion of elements in the enstatite layer, and the parabolic rate constant is given by $k(\text{cm}^2/\text{s}) = 4.3 \times 10^3 \exp(-505(\text{kJ/mol})/RT)$. By using the reaction rate obtained in the experiment and the time dependent homogeneous nucleation theory of forsterite grains (Kozasa and Hasegawa, 1987), the reaction degrees of the reaction were calculated under the conditions of the cooling solar nebula. The calculation suggests that the enstatite formation reaction can be treated as a maximum fractional condensation over the wide range of the cooling time scale under the nebular conditions.

In the Fe-S-H system, the phase diagram was constructed under the conditions where the total pressure is controlled by H_2 gas by using the thermochemical data. The

diagram shows that a peritectic reaction exists between metallic iron and troilite, and the reaction line proximates to the H-S tie line. Therefore the reaction affects the amount of minerals and mineral species of final products. Then, the reaction rates at high $p(S_2)$ conditions obtained in corrosion science (Fryt, et al., 1979a; Fryt et al., 1979b) were extrapolated to the low $p(S_2)$ conditions of the solar nebula. The parabolic rate constant does not depend upon the total pressure of the nebula, but depends upon the S/H ratio. The parabolic rate constant in the solar nebula condition is approximately given by $k(\text{cm}^2/\text{s})=0.3\exp(-146(\text{kJ/mol})/RT)$. As in the case of the reaction of the Mg-Si-O-H system, the reaction degrees were calculated based on the homogeneous nucleation theory of metallic iron grains. The result indicates that the FeS formation reaction sufficiently occurs or can be nearly treated as an equilibrium condensation, depending upon the cooling time scale of the nebula.

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1. Introduction

It has been considered that differences of the bulk chemical composition among planets and chondrites were brought by the fractionation between solid and gas in the process of condensation and evaporation in the primordial solar nebula not by the fractionation between solid and melt (e. g., Wasson, 1985). In the 1970's, the fractionation was discussed based upon the equilibrium condensation theory (e. g., Grossman and Larimer, 1974; Lewis, 1972). Grossman and Larimer (1974) explained that the difference of the bulk composition among chondrites was brought by the difference of the accretion temperature. On the other hand, Lewis (1972) explained that the difference of the bulk composition among planets was brought by the different accretion temperature in a steady state determined by the heliocentric distance, based on the Cameron's primordial solar nebula evolutionary model (Cameron and Pine, 1973). This explanation seemed to have been successful to understand the bulk chemical composition of planets. In the Cameron's model, which was made use for the application of the formation of chondrites and planets, the temperature is relatively high since massive solar nebula, 1 solar mass, is assumed. However, at present, the equilibrium temperature determined by the Cameron's model is doubtful since the mass of the solar nebula is, theoretically and observationally, considered to be only about 0.01-0.03 solar mass (Hayashi et al., 1985; Safronov, 1972; Beckwith et al., 1991). This problem has also been pointed out by Saito (1978) and Shimizu (1978). Therefore, it is important to reconstruct the fractionation between solid and gas from a new viewpoint based upon the low mass nebula model.

According to the dynamical evolutionary model of the primordial solar nebula such as the Kyoto model (Hayashi et al., 1985) and the Safronov model (Safronov, 1972), which are called the standard model of the evolution of the primordial solar nebula at present, the equilibrium temperature in the primordial solar nebula has finally cooled down by the balance

between the radiation and the solar heat source. Therefore, though the equilibrium temperature determined by the Kyoto model or Safronov model affects the differences between bulk chemical compositions of the terrestrial planets and giant planets depending upon whether ices can condense or not, it can not be expected to bring about the difference of the chemical composition due to the condensation of the silicates and metals only by the difference of such an equilibrium temperature.

In such discussions, Grossman and Larimer (1974) and Lewis (1972) focused only on explaining the characteristic chemical composition of the available substance of chondrites or the characterized feature of planets, but did not take account of the dynamic processes. Recently, it has also been theoretically considered that the fractionation would have occurred through the dynamic process of the mechanical separation between solid and gas, which is mainly the heliocentric movement of solid grain toward the sun in the primordial solar nebula due to the force such as gravity and gas drag (Lin and Papaloizou, 1985). This type of the fractionation would have also occurred in various evolutionary stages such as a heating stage of the molecular cloud (the fractionation by the evaporation) and the cooling stage of the primordial solar nebula (the fractionation by the condensation).

Whether the chemical interaction (reaction) between solid and gas is effective or not, is determined depending on the time scale of such dynamical separation between solid and gas. Therefore, the reaction rate between solid and gas must be obtained to discuss the dynamical fractionation between solid and gas in the primordial solar nebula. If the reaction time scale between solid and gas is smaller than the mechanical separation time scale between solid and gas due to the gravity, then the reaction between the solid and gas would play an important role in the fractionation. On the other hand, if the reaction time scale is larger than the time scale of the mechanical separation the reaction but the mechanical separation would play important role in the fractionation. Therefore, it is important to determine the reaction

time scale (i. e. reaction rate) to compare with the mechanical separation time scale in order to study the fractionation in the solar nebula.

That is why, in the condensation process, the reaction between solid and gas must have an important role in the fractionation (fractional condensation), which is just the same as the concept of fractional crystallization of magma since Bowen's reaction principle (Bowen, 1922). However, the fractionation in the primordial solar nebula has been poorly focused from a point of view of the reaction principle. In the primordial solar nebula, solid solution is little formed (Grossman, 1972). Therefore a *continuous reaction series* (Bowen, 1922) is not important in the fractionation very much. On the other hand, the reaction relations such as between Mg_2SiO_4 and MgSiO_3 , which are classified into a *discontinuous reaction series* (Bowen, 1922), become important in the fractionation. Such a peritectic reaction between solid and gas in the primordial solar nebula, however, has not almost been taken into account because of the limited data on the reaction rates due to the experimental difficulties and the physical parameters of the solar nebula. Due to this, the condensation processes have been treated as an equilibrium (e. g., Grossman, 1972).

Hydrogen is considered to have played an important role in the condensation of refractory minerals, since it determined the total pressure of the solar nebula, and the partial pressures of H_2O gas and H_2S gas including hydrogen affected the condensation and solid-gas reaction processes. Mg, Fe, Si, S and O are the most abundant elements consisting of rock-forming minerals (silicates, metals and sulfides) in the solar system. Therefore, it is important to study the condensation and solid-gas reaction processes of the Mg-Fe-Si-S-O-H system which is the most simplified system of the solar nebula. Such a study using simple systems enables to consider the cooling processes of the gas with an arbitrary chemical composition under the hydrogen rich condition more precisely than the study on the cooling only from the solar gas of the multi-component system by Grossman (1972).

The Mg-Fe-Si-S-O-H system can be nearly divided into two independent systems of Mg-Si-O-H and Fe-S-H since Fe and S are not almost included into silicates, but constitutes metals and sulfides under the conditions of the solar nebula. The construction of the phase diagram between solid and gas in the simple systems intended for the solar nebula study has been insufficiently done. Only the phase diagram of Mg-Si-O-H system has been constructed by Tsuchiyama (1990).

The phase diagram of the Mg-Si-O-H system by Tsuchiyama (1990) shows that in the cooling of gas with solar composition, the first condensate is forsterite (Mg_2SiO_4), and by the cooling, forsterite reacts with Si-rich gas to form enstatite (MgSiO_3). That is to say, it is a peritectic system. This relation is just consistent with the Grossman's equilibrium condensation theory of the multi-component system (1972). In the Mg-Si-O-H system, the region of the peritectic reaction between forsterite and Si-rich gas proximates to one plane in the tetrahedron in the quaternary system of Mg-Si-O-H; the proximity to Si-O tie line in the constant H/(Mg+Si+O) cross section in the Mg-Si-O-H system (Tsuchiyama, 1990; see also chapter 2). This proximity to the tie line in the phase diagram, which is a remarkable character differing from the crystallization from magma, indicates that the degree of the reaction between enstatite and Si-rich gas greatly affects the amount and the kind of minerals (Imae and Kitamura, 1993).

In the Fe-S-H system, the first condensate is metallic iron (Fe), and by the further cooling, metallic iron reacts with H_2S gas to form FeS according to Lewis (1972). However, the detailed phase diagram in the Fe-S-H system has not been constructed. The proximity of the peritectic line to the S-H tie line can be expected in the Fe-S-H system as in the Mg-Si-O-H system. If this is the case, the reaction between metallic iron and H_2S gas also affects the amount and the kind of minerals.

The enstatite and FeS formation reactions must be a key to determine Mg/Si and S/Fe ratios of planets as indicators of the fractionations at high temperature and at low

temperature, respectively. In the present study, the reaction rate of enstatite formation between forsterite and Si-rich gas was determined by using the newly designed double capsule technique, and the reaction degree in the cooling solar nebula was quantitatively estimated (chapter 2). Next, the phase diagram in the system of Fe-S-H under the hydrogen rich condition was constructed, and the reaction rate of FeS formation between metallic iron and H₂S gas in the solar nebula condition was determined by applying the study in corrosion science (chapter 3). And the reaction degree of the reaction in the cooling solar nebula was quantitatively estimated as the same in the case of the enstatite formation reaction.

Part of this thesis has been published or submitted as follows, but modifications may be noticed in each chapter. Chapter 2 has been published in *Earth and Planetary Science Letters*, **118**, 21-30 entitled "An experimental study of enstatite formation reaction between forsterite and Si-rich gas" with authors of Imae, N., Tsuchiyama, A. and Kitamura, M. Chapter 3 has been submitted to *Earth and Planetary Science Letters* entitled "FeS formation reaction between metallic iron and H₂S gas in the primordial solar nebula" with authors of Imae, N. and Kitamura, M.

Roles of the applicant in the two papers are as follows. In the former paper, the followings have been carried out mainly by the applicant; (1) the experiments to determine the enstatite formation reaction rate, (2) the analyses of the experimental data and (3) the application of the obtained reaction rate to the primordial solar nebula. In the latter paper, the followings have been carried out mainly by the applicant; (1) the construction of the phase diagram of the Fe-S-H ternary system by log-log plot and the idea, (2) the indication of the importance of FeS formation reaction between metallic iron and H₂S gas in the primordial solar nebula due to the proximity of the reaction line to the H-S tie line, (3) the derivation of the FeS formation reaction rate on the solar nebula condition made use of the FeS formation rate from metallic iron and H₂S gas by Fryt et al. (1979a; 1979b) and (4) the application of the reaction rate to the primordial solar nebula.

2. Enstatite formation reaction between forsterite and Si-rich gas in the primordial solar nebula

Abstract

Experiments on the reaction between forsterite and Si-rich gas were carried out in a vacuum furnace by using a newly designed double-capsule technique. A thin layer of enstatite was formed on the surface of forsterite by the reaction. The thickness of the enstatite layer changes proportionally to the square root of time (parabolic rate law), indicating that the rate is controlled by diffusion in the enstatite layer. The activation energy and the logarithm of the pre-exponential term of the parabolic rate constant were obtained as 505 ± 188 kJ/mol and 3.6 ± 5.6 cm²/sec, respectively. It is difficult to definitely determine the mechanism of the reaction from these values, but consideration of strain generation due to the volume change during the reaction may suggest that the counter-diffusion of silicon and magnesium takes place along the grain boundary in the enstatite layer. The degree of the reaction of forsterite with Si-rich residual gas in the primordial solar nebula is discussed based upon the measured reaction rate, and it is suggested that very little enstatite was formed by this reaction in the cooling nebula, if the grain size of the forsterite crystals was controlled by homogeneous nucleation theory.

2.1 Introduction

In the primordial solar nebula, solid-gas reactions may have played an important role in the fractionation of elements, which establishes the distribution of elements among the planets and various chondrite groups. Magnesium and silicon are the most abundant refractory elements in the solar system (Anders et al., 1982), and the major elements of planets and chondrites. It is considered that the Mg/Si ratio is a key to understanding the evolutionary process of the solar system (Ringwood, 1989).

According to the chemical equilibrium condensation theory (Grossman, 1972), forsterite (Mg_2SiO_4) condenses at 1444 K and 10^{-3} atm, and forsterite begins to react with Si-rich residual gas to form enstatite (MgSiO_3) at 1349 K: forsterite and enstatite are in a reaction relation. This reaction determines the extent of Mg/Si fractionation since the atomic ratio of Mg/Si in the solid changes from 2 of forsterite to 1.06 (solar ratio) in the forsterite+enstatite mixture through this reaction. In spite of this cosmochemical importance of the reaction's kinetics, neither theoretical nor experimental works have been carried out, since it is generally difficult to produce a Si-rich gas atmosphere in experiments at high temperatures. In the present study, an experimental system using a newly designed double capsule technique was constructed to study the reaction between refractory solid and gas. By this technique, the steady environment of Si-rich gas was successfully produced. Using this system, the enstatite formation reaction between forsterite and Si-rich gas was experimentally investigated, and the kinetics of the reaction revealed by the experiments was applied to the condensation process in the primordial solar nebula.

2.2 Phase relation

Grossman (1972) determined the condensation sequence from the solar gas at $p(\text{total})=10^{-3}$ atm by the thermochemical calculation. By the cooling of the gas, forsterite first condenses as a major Mg-silicate mineral at 1444 K. When the cooling proceeds, the forsterite becomes unstable, and begins to react with Si-rich residual gas to form enstatite at 1349 K (Fig. 2.1a), since forsterite and enstatite are in a reaction relation. When the equilibrium condensation takes place, the cooling from $\text{Mg/Si}=1.07$ with the solar ratio makes enstatite as the main Mg-silicate (Fig. 2.1a).

According to the phase relation, the small amount of Mg component of the gas is left when the enstatite formation reaction starts. Therefore, when the maximum fractional condensation takes place, the very small amount of enstatite can be formed by the direct condensation from the gas. Thus, a large amount of forsterite must be formed as Mg-silicates (Fig. 2.1b) during the maximum fractional condensation process. Therefore, the relative amount of forsterite and enstatite as the final products due to the cooling is strongly dependent upon the degree of the enstatite formation reaction.

The reaction relation seen on the H-rich condition at low pressure is the same as the reaction relation between solid and melt at one atmosphere in the MgO-SiO_2 system. In the case of the crystallization from melt, a large amount of Mg component is left at the beginning of the enstatite formation reaction in the melt phase, because the peritectic point is close to the enstatite composition. Therefore, the relative amount of forsterite and enstatite as the final products is dependent upon the degree of the reaction, but not so much in comparing the case of the cooling of the gas. In other words, the degree of the enstatite formation reaction between forsterite and Si-rich gas has greater effects the relative amount of Mg-silicates in the condensation from high temperature gas than the reaction between forsterite and melt in the crystallization from magma.

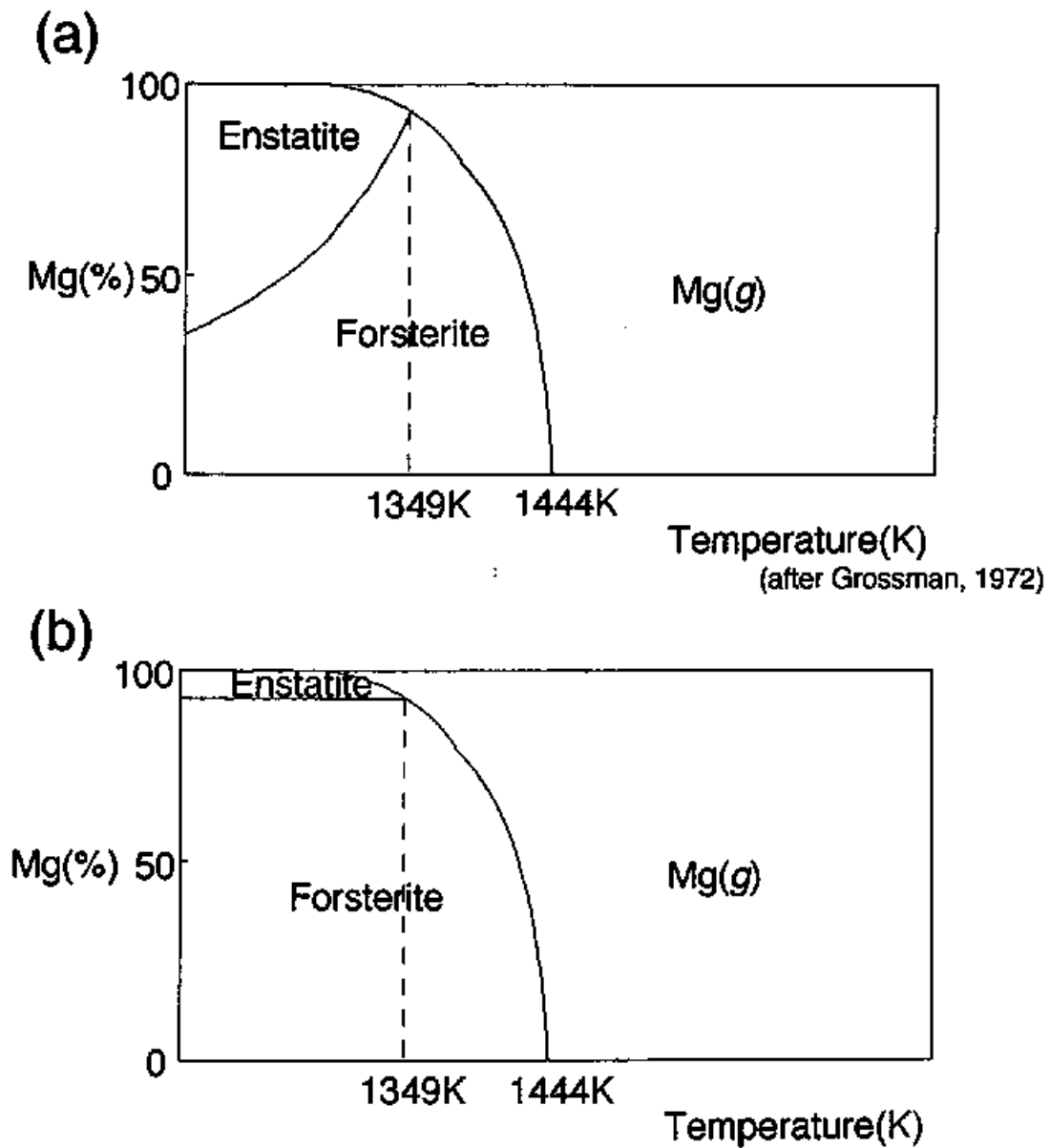


Fig. 2.1. Diagram of condensation of Mg-silicates from the solar gas at $p(\text{total})=10^{-3}$ atm. The vertical axis is the ratio of Mg element in a phase, and the horizontal axis is the absolute temperature. (a) equilibrium condensation (Grossman, 1972). (b) maximum fractional condensation.

2.3 Experiments

A new technique, called a double capsule technique in this paper, was newly designed for the present study (Fig. 2.2). The double capsule made of molybdenum is a Knudsen cell (outer capsule) with an orifice of 0.1 mm in diameter containing another small capsule (inner capsule) inside it. A cristobalite (SiO_2) powder with grain size of $<100\ \mu\text{m}$ was put into the outer capsule as a source for Si-rich gas, and a single crystal of forsterite is put into the inner capsule to avoid direct contact with the cristobalite powder. The forsterite was prepared by cutting a single crystal of synthetic forsterite (Takei and Kobayashi, 1974) in a rectangular shape bounded by (100), (010) and (001) faces with the widths of 5 mm, 1.25 mm, and 1 mm, respectively. The surfaces of these samples were polished with a diamond paste, washed with acetone, and then dried. The cristobalite powder was prepared by heating a reagent-grade SiO_2 (quartz) powder. The phase was verified by the X-ray diffraction method.

The double capsule was heated in a vacuum furnace (Fig. 2.3), which is the same furnace used in the condensation experiments of Tsuchiyama (1991). Si-rich gas in equilibrium with cristobalite (which is considered to be mainly composed of SiO and O_2 molecules after the thermochemical calculations) was formed in the Knudsen cell, in which the steady gas flow environment of Si-rich gas was produced through an orifice. This gas reacted with the forsterite crystal to form enstatite. The experiments were carried out at temperatures ranging from 1378 to 1550 °C for durations ranging from 5 to 236 hours in vacuum (6.0×10^{-5} - 2.2×10^{-6} Torr).

The temperature was measured with a W95Re5-W74Re26 thermocouple (TC-2) placed to the side of the double capsule, and was controlled by another thermocouple (TC-1) placed under the crucible, which was interfaced with a temperature controller. The temperature was calibrated against the melting point of Fe (1535 °C), Ni (1453 °C) and Au

(1064 °C). The precision is better than ± 10 °C. The maximum temperature of runs is constrained below the incongruent melting point of enstatite, 1557 °C (Kushiro, 1972). Heating was finished by shutting off the power supply to the heater. It takes about 2, 10, and 60 min. to cool down to 1000, 500 °C and room temperature, respectively from an initial furnace temperature.

After cooling to room temperature in the vacuum furnace, the double capsule was taken out from the chamber. The experimental charge in the inner capsule was mounted in epoxy, and two thin sections were prepared for each charge; one is a thin section parallel to (100) face of forsterite, and the other is parallel to either the (010) or the (001) face. The reaction products were observed using an optical microscope (OM), and a scanning electron microscope (SEM; HITACHI S-530). The chemical compositions were determined with an electron probe microanalyzer (KEVEX DELTA EDX system) with a focused beam under the SEM. The acceleration voltage was 20 kV and the beam current 1.5 nA. X-ray intensities were corrected by the ZAF method.

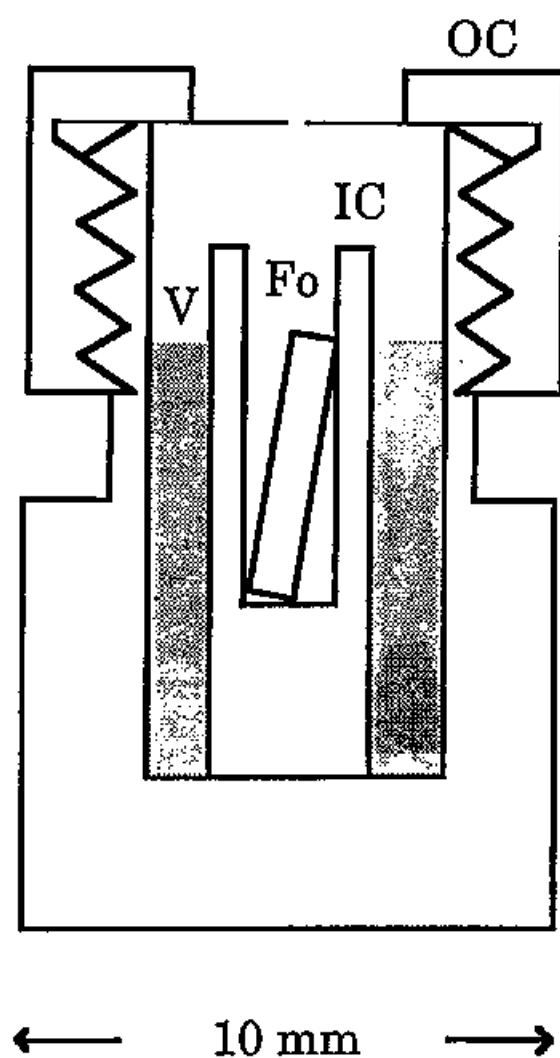


Fig. 2.2. Cross section of the double capsule. Outer capsule acts as a Knudsen cell with an orifice of 0.1 mm. OC = outer capsule (Mo); IC = inner capsule (Mo); Fo = forsterite single crystal (1x1.25x5 mm); V = cristobalite powder.

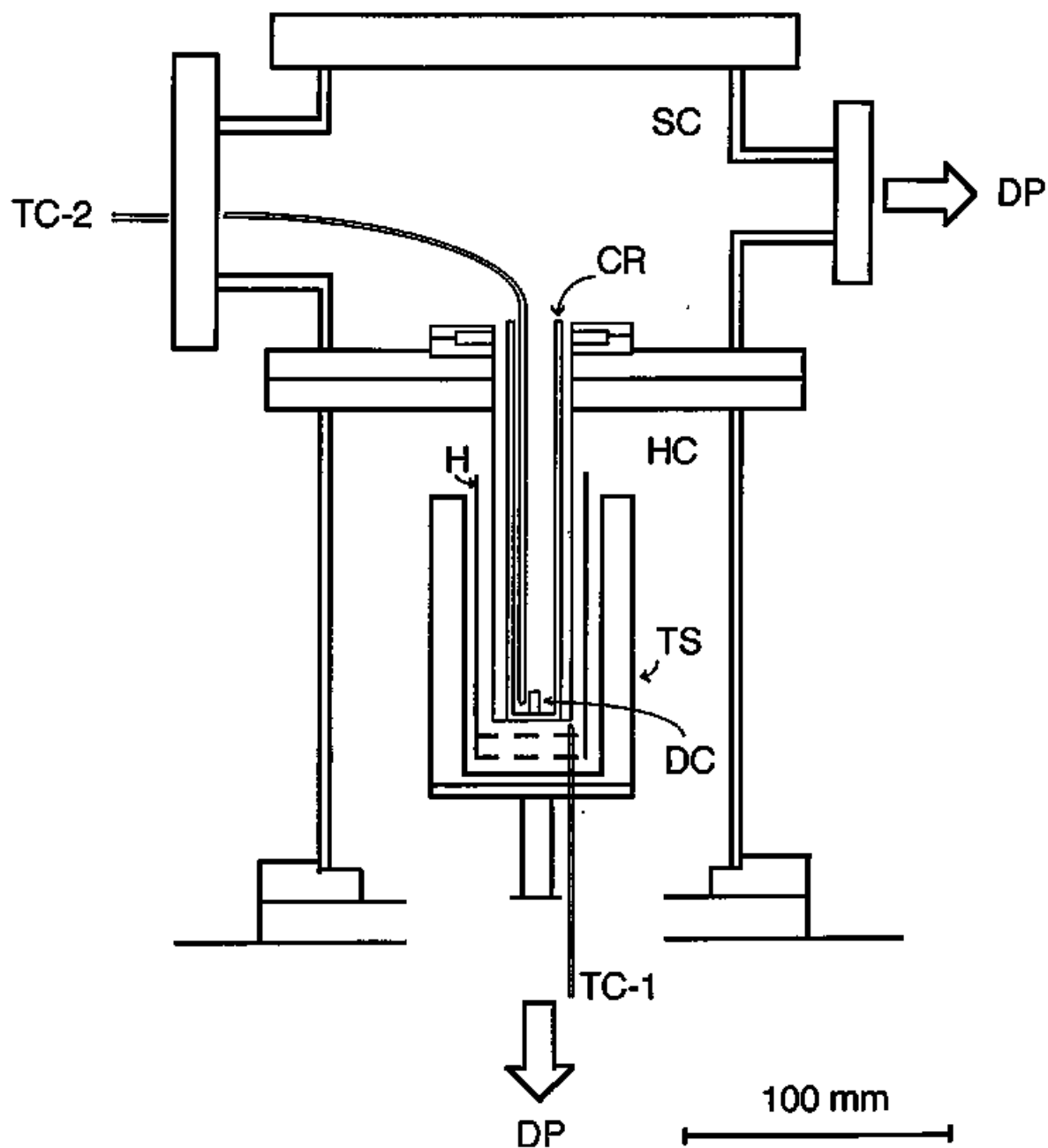


Fig. 2.3. Assembly of the vacuum furnace. *SC* = sample chamber; *HC* = heater chamber; *H* = tantalum heater; *TS* = thermal shield; *CR* = molybdenum crucible; *DP* = vacuum pump by diffusion pump; *DC* = double capsule; *TC-1* = W95Re5-W74Re26 thermocouple for temperature control; *TC-2* = W95Re5-W74Re26 thermocouple for measuring temperature.

2.4 Results

After the reaction experiments, a transparent single crystal of forsterite was surrounded by thin layers of enstatite reaction products (Fig. 2.4). The chemical analysis shows that the enstatite crystal is stoichiometric within experimental error. The thickness of the enstatite layer changes from a few to 20 μm depending upon the run duration and temperature. These reaction layers incoherently contact with the forsterite surface, and separate easily from the surface.

The enstatite is not a single crystal but polycrystalline. Each enstatite crystal tends to elongate to the [001] axis of enstatite normal to the forsterite surfaces, irrespective of the crystallographic orientation of the forsterite substrate. Thus, the epitaxial or topotaxial growth of enstatite was not observed. A large number of defects produced near the polished surfaces of forsterite may obstruct epitaxial or topotaxial growth of the enstatite. The crystals are mixtures of orthoenstatite or clinoenstatite with (100) polysynthetic twinning indicated by an arrow in Fig. 2.4. This type of texture can be formed by the transition from protoenstatite stable at high temperatures (985 – 1557 $^{\circ}\text{C}$) (Kushiro, 1972), during quenching in the experiment. Thus, the enstatite may have grown as protoenstatite during the runs. The transition may have produced the incoherent contact between the enstatite layer and the forsterite substrate.

The thickness of the enstatite layer was measured normal to the (100), (010), and (001) faces of forsterite in SEM images (TABLE 2.1). The number of measured points is from 10 to 180 per one plane of forsterite for each run. The thickness of the enstatite layer is almost constant in each run, irrespective of the crystallographic orientation of the forsterite substrates. Thus, the average thickness of the enstatite layers on the three different surfaces is used in further discussion throughout this paper.

The thickness of the enstatite layer increases with time at a constant temperature, and increases with temperature for a constant run duration. The logarithm of the average thicknesses are plotted against the logarithm of run durations in narrow temperature ranges (1458–1470 °C, Fig. 2.5a; 1484–1498 °C, Fig. 2.5b; 1514–1522 °C, Fig. 2.5c). In these figures the data are plotted nearly on linear lines with a slope of 1/2, or the reaction of forsterite and Si-rich gas to form enstatite obeys the "parabolic rate law":

$$x^2 = kt, \quad (2.1)$$

where x is the thickness of the enstatite layer, k the parabolic rate constant, and t time. If the enstatite were to have vaporized during the experiments, then the thickness would increase in the beginning but become constant with increasing time (Tedmon, 1966). However, significant deviation of the plotted points from the linear lines cannot be seen. Thus, it is considered that the evaporation of enstatite is small or negligible.

The parabolic rate constant k is expected to obey the Arrhenius relation:

$$k = k_0 \exp(-E/RT), \quad (2.2)$$

where E is activation energy, k_0 a pre-exponential term, R the gas constant, and T the absolute temperature. An Arrhenius plot of the parabolic rate constant measured over wide ranges of temperatures and run duration is required to obtain the activation energy precisely. In the present experiment, however, the number of runs at constant temperature for various durations are not enough for a satisfactory estimation. Therefore, the parabolic rate constant k was obtained by calculating x^2/t in each run, and then these values of k were plotted against the reciprocal temperature to obtain the activation energy (Fig. 2.6). The parabolic rate constant of the enstatite formation reaction obeys the Arrhenius relations of eq. (2.2)

although the data are scattered. The calculated activation energy is 505 ± 188 kJ/mol, and the logarithm of the pre-exponential term ($\log k_0$) is 3.6 ± 5.6 .

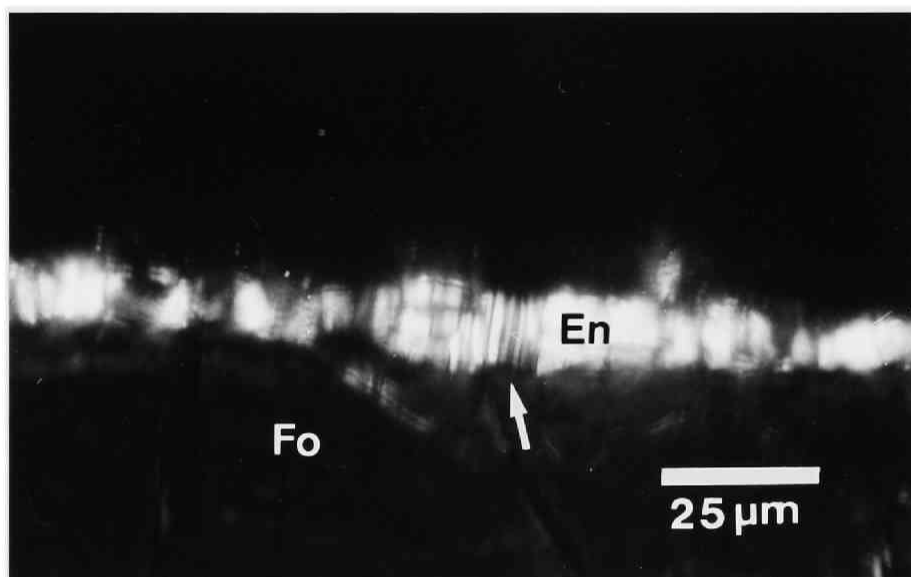


Fig. 2.4. A micrograph of enstatite (En) under an optical microscope on (010) face of the forsterite (Fo). Cross nicol. 1470 °C, 91.3hr (Run 20). Indicated polysynthetic twinning by an arrow.

TABLE 2.1
Thickness of enstatite on surfaces of forsterite and the standard deviations

Run	T[°C]	Time[hr]	* x_a [μ m]	* x_b [μ m]	* x_c [μ m]	** x_{ave} [μ m]
1	1378	21.0	0	0	0	0
18	1418	89.4	6.68 (0.88)	6.15 (0.57)	4.21 (0.41)	5.24 (1.25)
15	1438	46.8	5.14 (0.64)	5.52 (1.00)	4.72 (0.65)	5.08 (0.81)
17	1438	89.1	-	4.79 (0.45)	4.51 (1.47)	4.62 (1.18)
10	1451	16.1	4.12 (0.30)	4.42 (0.19)	3.65 (0.46)	3.96 (0.50)
3	1456	20.0	-	2.73 (0.44)	3.04 (0.81)	2.97 (0.75)
31	1458	44.5	5.47 (0.72)	5.50 (0.58)	7.42 (0.61)	6.02 (1.08)
16	1462	86.3	9.92 (0.73)	10.40 (0.72)	9.80 (0.90)	10.00 (0.83)
14	1470	21.5	6.13 (0.43)	4.31 (0.37)	5.12 (0.42)	4.97 (0.90)
20	1470	91.3	11.21 (1.57)	11.50 (0.76)	13.59 (2.43)	12.18 (2.12)
26	1472	117.4	16.67 (1.31)	14.20 (1.22)	14.11 (1.15)	14.88 (1.65)
28	1484	192.0	16.90 (1.28)	22.22 (0.97)	18.23 (3.09)	18.83 (3.15)
32	1490	45.7	-	8.46 (0.54)	7.11 (1.35)	7.28 (1.36)
37	1490	70.8	8.30 (0.72)	7.67 (1.04)	8.55 (0.85)	8.15 (0.92)
7	1492	13.5	4.38 (0.62)	4.44 (0.49)	3.87 (0.54)	4.22 (0.61)
9	1492	100.3	10.88 (1.47)	10.65 (1.95)	10.45 (1.20)	10.64 (1.48)
8	1498	44.2	5.87 (0.95)	6.69 (1.31)	6.19 (0.82)	6.28 (1.10)
4	1514	5.0	3.19 (0.18)	-	2.31 (0.36)	2.44 (0.46)
2	1520	21.0	5.90 (0.75)	6.27 (1.06)	6.56 (0.60)	6.35 (0.87)
35	1522	67.8	23.18 (1.20)	17.21 (0.63)	14.07 (1.85)	16.75 (3.90)
36	1522	90.3	11.25 (1.31)	9.96 (1.65)	9.67 (1.59)	10.21 (1.67)
5	1544	5.0	-	5.62 (0.71)	5.62 (1.98)	5.62 (1.75)
6	1550	5.0	-	5.46 (0.15)	4.77 (0.68)	5.00 (0.65)

*thickness of enstatite on (100), (010) and (001) of the forsterite, respectively.

**average thickness of enstatite on three surfaces of the forsterite with the weight.

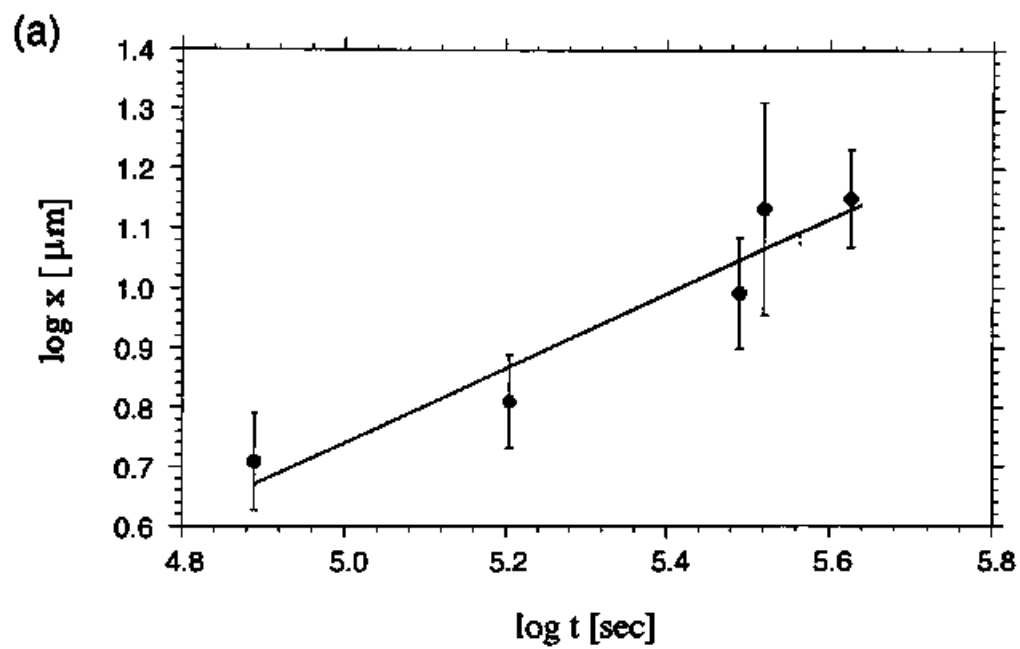


Fig. 2.5a. The logarithm of the enstatite thickness plotted against the logarithm of time under nearly constant temperature ranges. 1458–1472 °C.

(b)

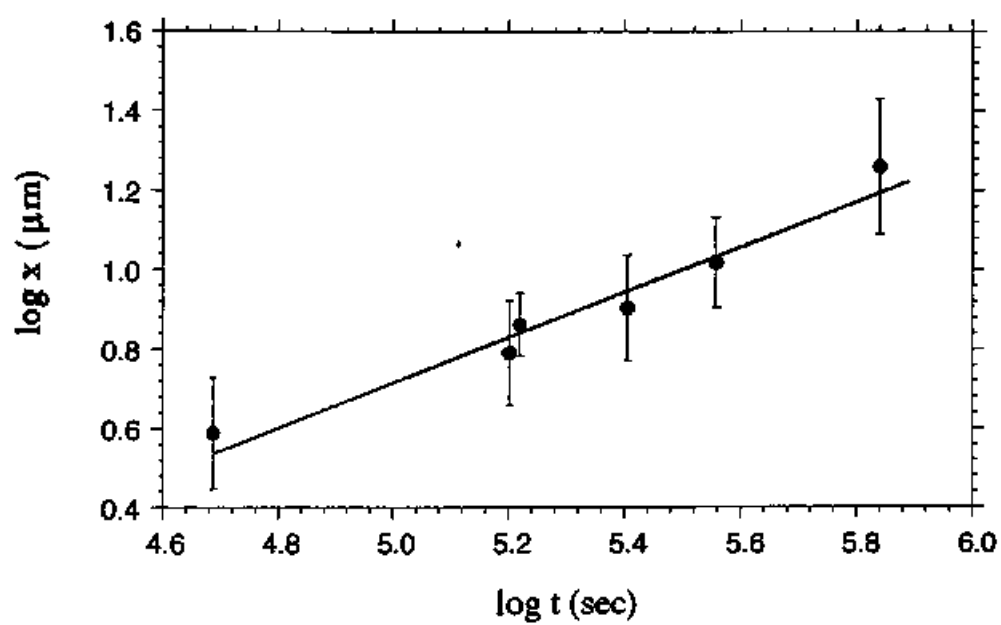


Fig. 2.5b. See the caption of Fig. 2.5a. 1484 - 1498 °C.

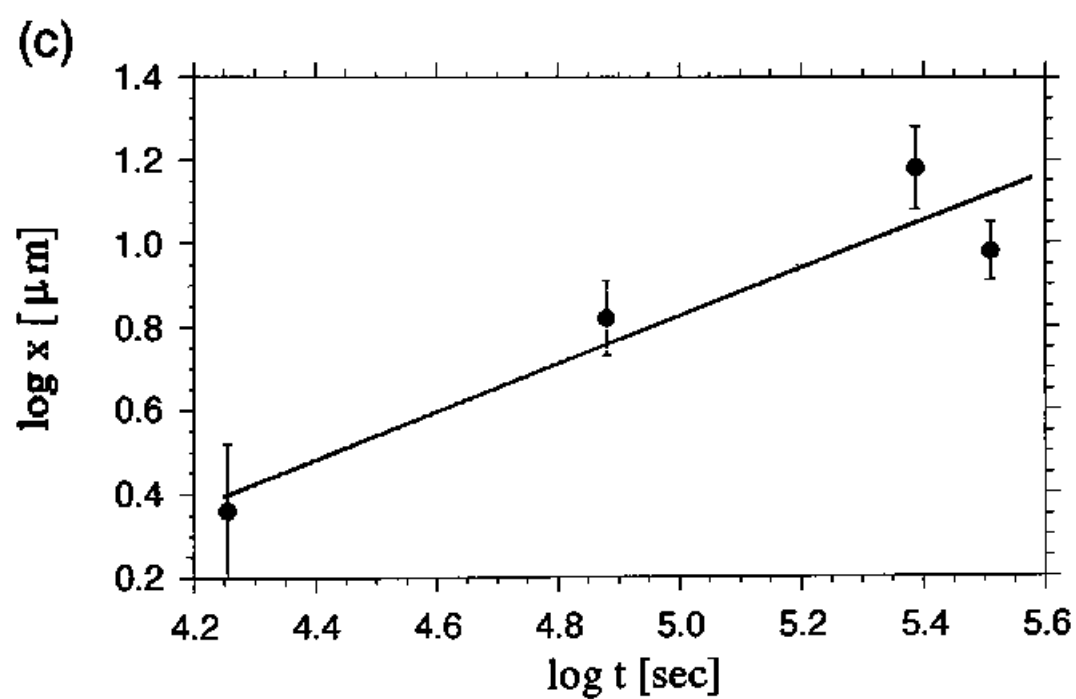


Fig. 2.5c. See the caption of Fig. 2.5a. 1514 - 1522 °C.

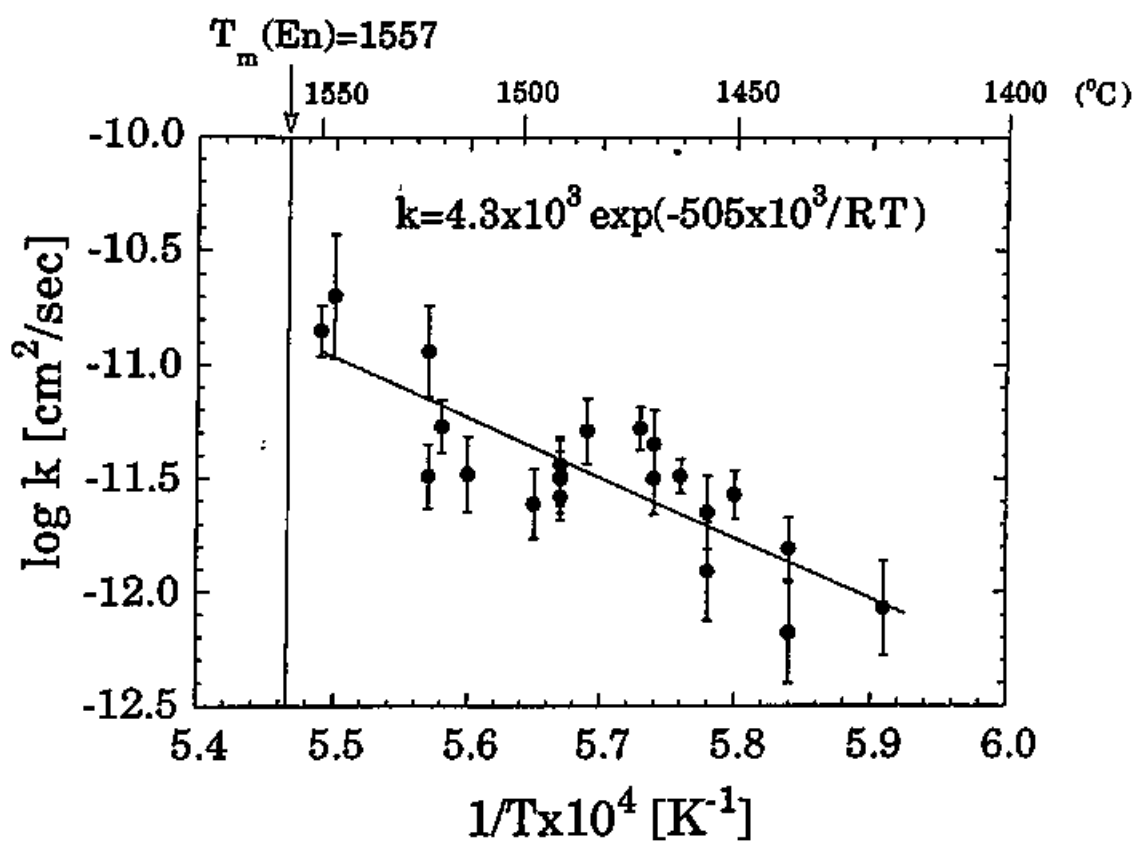


Fig. 2.6. Arrhenius plot of the parabolic rate constant k . The high temperature limit of the run is the melting temperature of enstatite (1557 °C).

2.5 Discussion

2.5.1 Molecular species in the capsule

During the runs, there exist three kinds of solids in the double capsule, cristobalite and forsterite as starting materials, and enstatite as a reaction product. The fact that the kinetics obeys the parabolic rate law not the linear rate law shows that forsterite did not have direct contact with the gas in spite of the incoherency between forsterite and enstatite. It is therefore considered that only cristobalite and enstatite have direct contact with the gas. When the gas in the Knudsen cell is assumed to be in equilibrium with cristobalite and enstatite, the molecular species of the gas can be calculated by thermochemical calculations. If we assume that the main gas species are SiO, O₂ and Mg molecules, the following reactions take place:



where (s) and (g) denote solid and gas, respectively. The equilibrium constants of the above reactions (2.3) and (2.4), K_{SiO_2} and K_{En} , respectively, are as follows:

$$K_{\text{SiO}_2} = p(\text{SiO})^2 p(\text{O}_2) \quad (2.5)$$

$$K_{\text{En}} = p(\text{Mg}) p(\text{SiO}) p(\text{O}_2), \quad (2.6)$$

where $p(\text{SiO})$, $p(\text{O}_2)$ and $p(\text{Mg})$ are the partial pressures of SiO, O_2 and Mg, respectively. $p(\text{SiO})$ and $p(\text{O}_2)$ are assumed to be buffered by $\text{SiO}_2(s)$ based on eq. (2.5) because the surface area for evaporation of cristobalite ($\text{SiO}_2(s)$) is much larger than that of enstatite (MgSiO_3). According to the kinetic theory of gases, the effusion rate of SiO or O_2 molecules from an orifice of the Knudsen cell, $J(\text{SiO})$ or $J(\text{O}_2)$, is related to $p(\text{SiO})$ or $p(\text{O}_2)$, respectively, as follows:

$$J(\text{SiO}) = p(\text{SiO}) / [2\pi M_{\text{SiO}} RT]^{1/2} \quad (2.7)$$

$$J(\text{O}_2) = p(\text{O}_2) / [2\pi M_{\text{O}_2} RT]^{1/2}, \quad (2.8)$$

where M_{SiO} and M_{O_2} are the molecular weights of $\text{SiO}(g)$ and $\text{O}_2(g)$, respectively. Since cristobalite evaporates congruently (eq. (2.3)), the ratio of the effusion rates of SiO and O_2 , $J(\text{SiO}) / J(\text{O}_2)$, must be two. Accordingly, in the interior of the Knudsen cell at steady state, $p(\text{SiO}) / p(\text{O}_2)$ must be equal to $2(M_{\text{O}_2}/M_{\text{SiO}})^{1/2}$. From this $p(\text{SiO}) / p(\text{O}_2)$ value and eq. (2.5), we can calculate the values of $p(\text{SiO})$ and $p(\text{O}_2)$, then $p(\text{Mg})$ can be calculated from eq. (2.6) with the JANAF thermochemical tables (1985). K_{SiO_2} and K_{En} are given by $\log K_{\text{SiO}_2} = 26.38 - 83308.23/T$ and $\log K_{\text{En}} = 24.41 - 82330.40/T$, respectively, as a function of temperature (Fig. 2.7). The thermochemical calculation shows that the abundances of the other molecular species, such as O, Mg, MgO or SiO_2 are smaller or much smaller than those of SiO and O_2 . This is also shown in Fig. 2.7. Thus, it can be suggested that the system is mostly filled with SiO and O_2 molecules.

2.5.2 Kinetics of the reaction

The parabolic rate law in the present experiments (Fig. 2.5) shows that the reaction is controlled by the diffusion of elements through the enstatite layer. Four models are possible for diffusion of elements in the enstatite layer according to the mass valance of the reaction (model 1-4, in Fig. 8). In model-1, MgO is released from forsterite when enstatite is formed at the forsterite-enstatite interface. Mg^{2+} and O^{2-} ions diffuse from the forsterite-enstatite interface across the enstatite layer, and these ions react with the Si-rich gas to form enstatite at the enstatite-gas interface. In this case, Si is fixed in the frame of the enstatite crystal. In model-2, Si^{4+} and O^{2-} ions diffuse from the enstatite-gas interface, and enstatite is formed by a reaction with forsterite at the forsterite-enstatite interface. In this case, Mg is fixed in the crystal frame. In model-3, Si^{4+} diffuses into the enstatite layer and reacts with forsterite to form enstatite at the forsterite-enstatite interface, while Mg^{2+} diffuses to the enstatite-gas interface and reacts with the gas to form enstatite. In this mechanism, O is fixed in the crystal frame. In model-4, Si^{4+} and O^{2-} ions diffuse into enstatite and react with forsterite to form enstatite at the forsterite-enstatite interface, while Mg^{2+} diffuses to the enstatite-gas interface and reacts with the gas to form enstatite. In this model Si^{4+} , Mg^{2+} and O^{2-} diffuse across the enstatite layer.

The values of parabolic rate constant obtained in this study and the diffusion coefficients of elements in enstatite must have the same order if the reaction is controlled by diffusion in enstatite. The parabolic rate constant and the available diffusion coefficients in pyroxenes are summarized in Fig. 2.9. Diffusion data on pyroxenes are limited due to experimental difficulties, such as the preparation of diffusion couples. Therefore the diffusion coefficients of ions in olivine (Morioka, 1981; Reddy et al., 1980; Jaoul et al., 1981) are also shown in Fig. 2.9 as a reference.

As shown in Fig. 2.8, the data of the parabolic rate constant in the present study is nearly on the extrapolated line of the data of the Ca-(Mg, Fe) interdiffusion coefficient in pigeonite (Fujino et al., 1990), the Fe-Mg interdiffusion coefficient in clinopyroxene

(Wilson, 1982) and the Ca-(Mg, Fe) interdiffusion coefficient in clinopyroxene (Rietmeijer, 1983). In the diffusion models shown in Fig. 2.8, the reaction cannot proceed by diffusion of Mg, but the coupled diffusion of Si and/or is also required. The O self-diffusion coefficient in clinopyroxene (McKeegan and Ryerson, 1990) has a smaller value than the cation diffusion coefficients (Fujino et al, 1990; Wilson, 1982; Rietmeijer, 1983). The data of Si self-diffusion coefficient in pyroxene can't be found. In the case of olivine, the relation of $D_{\text{Mg, Fe}} \gg D_{\text{O}}$ and $D_{\text{Mg, Fe}} \gg D_{\text{Si}}$ can be seen in Fig. 2.9. It is expected that this relationship among the diffusion coefficients in olivine is also maintained in pyroxenes. Therefore, since the slower diffusion of Si or O in enstatite would control the reaction rate, the reaction would proceed faster than expected by the volume diffusion in the enstatite layer. Then grain boundary diffusion or dislocation diffusion must control the reaction rate. In this case, it may be possible that all the diffusing species along the grain boundaries are not necessarily ions but gas.

As discussed above, the possible model among the reaction mechanisms suggested in Fig. 2.8 is not decided by the comparison with the available diffusion coefficients. However, the diffusion mechanism can be constrained if the volume change of the reaction is taken into consideration. Enstatite can be formed without strain at the enstatite-gas interface, but not at the forsterite-enstatite interface due to the volume change, ΔV . ΔV is defined as $(V_{\text{En}} - V_{\text{Fo}}) / V_{\text{Fo}}$, where V_{En} and V_{Fo} are molar volume of enstatite and forsterite, respectively. Thus, the reaction with the smaller strain, or smaller ΔV , should take place. The volume change by the enstatite formation reaction at forsterite-enstatite interface, ΔV , is shown for each reaction mechanism in Fig. 2.8. The volume change (-0.01 in model-3) is smaller than the others (-0.3 in model-1, 0.5 in model-2 and 0.1 in model-4) (Fig. 2.8). Therefore, the counter diffusion mechanism of Si^{4+} and 2Mg^{2+} (model-3) would seem to be the most probable diffusion mechanism. Such counter

diffusion is considered to occur by a high-speed mechanism such as grain boundary diffusion as suggested above.

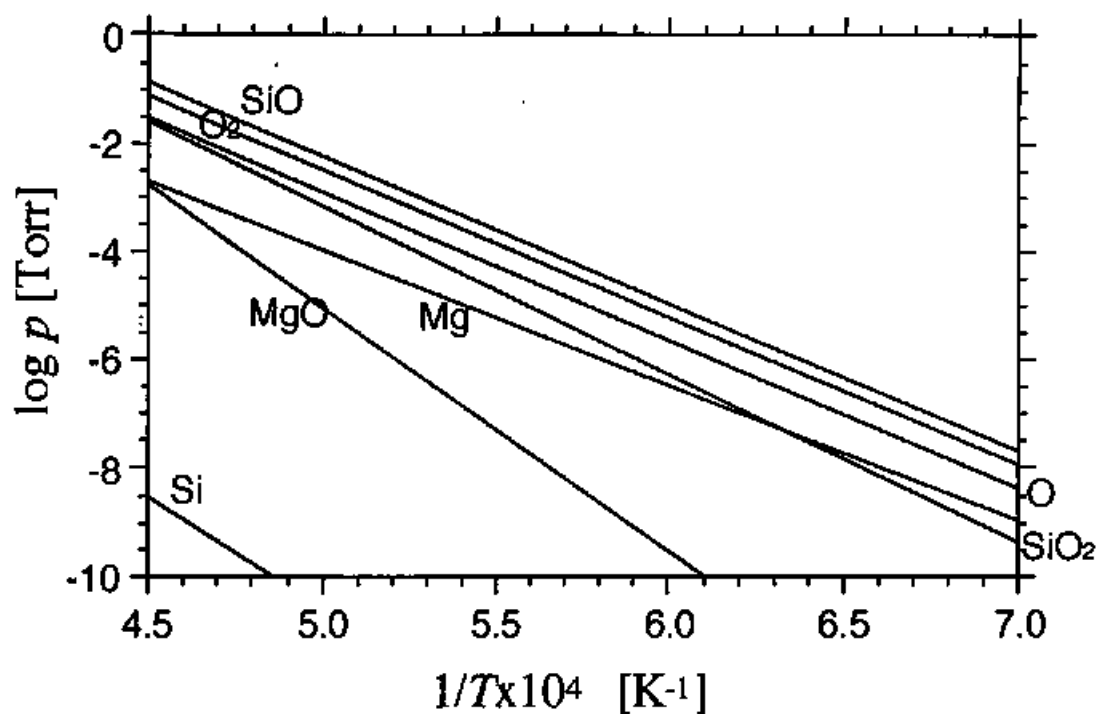


Fig. 2.7. Calculated partial pressures of SiO, SiO₂, O₂, Mg and MgO molecules equilibrated with cristobalite and enstatite in the Knudsen cell as a function of the reciprocal of temperature [$1/T \times 10^4 \text{ (K}^{-1}\text{)}$].

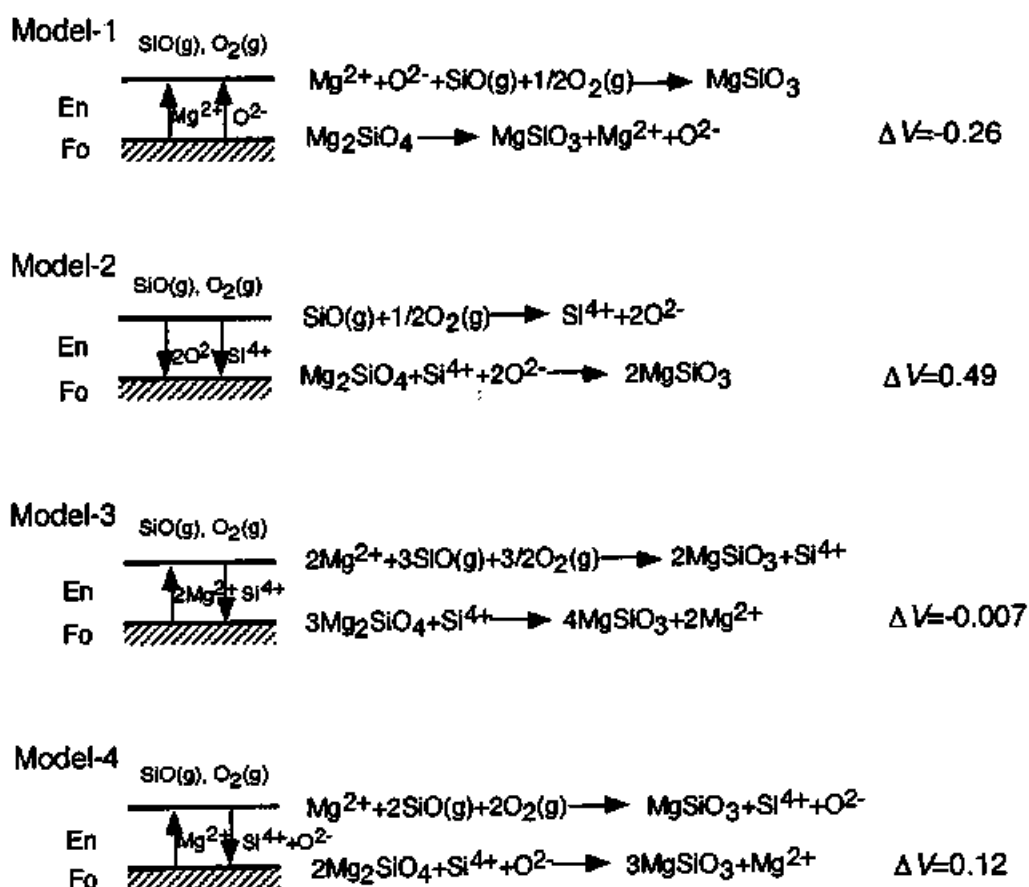


Fig. 2.8. A schematic representation of four reaction mechanisms which may control the reaction rate of enstatite formation. The diffusion species of ion might be replaced to the gas species in the case of grain boundary diffusion. The volume change (ΔV) due to the enstatite formation at the forsterite-enstatite interface is also shown. See text for more details.

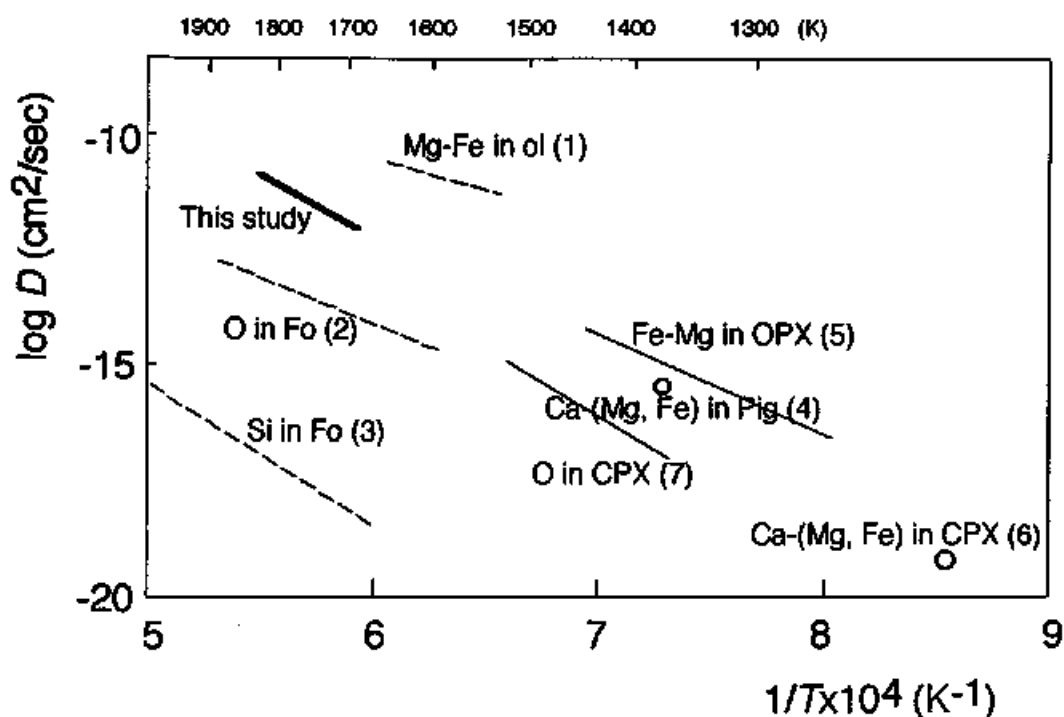


Fig. 2.9. Comparison of the parabolic rate constant k with the available diffusion coefficients in pyroxene and olivine. (1) Mg-Fe interdiffusion coefficient in olivine (Morioka, 1981). (2) O diffusion coefficient in forsterite (Reddy et al., 1980). (3) Si diffusion coefficient in forsterite (Jaoul et al., 1981). (4) Ca-(Mg, Fe) interdiffusion coefficient in pigeonite (Fujino et al., 1990). (5) Fe-Mg interdiffusion coefficient in orthopyroxene (Wilson, 1982). (6) Ca-(Mg, Fe) interdiffusion coefficient in clinopyroxene (Rietmeijer, 1983). (7) O self-diffusion coefficient in clinopyroxene (McKeegan and Ryerson, 1990).

2.6. Application to the condensation in the primordial solar nebula

2.6.1 Estimation of the reaction degree

It has been suggested that enstatite can be formed by the reaction between forsterite and Si-rich gas in the primordial solar nebula (Grossman, 1972). The reaction rates in the solar nebula can be estimated from the parabolic rate constants k obtained in the present experiments.

The reaction expected in the solar nebula, where H_2 is the most abundant gas molecules,



is different from the reaction in the experiments,



If the reaction in the solar nebula was controlled by a surface reaction, such as decomposition of H_2O to H_2 and O_2 molecules of the enstatite-gas interface, then the reaction rate may not be discussed from the present results. However, the rate of a surface controlled reaction is linear with time, while the rate of the diffusion controlled reaction is linear with the square root of time. Therefore, even if the reaction is considered to be controlled by a surface reaction at an initial stage, it will be a diffusion controlled reaction as the reaction proceeds.

If the reaction in the nebula was controlled by the diffusion of reactants through enstatite, the rates would be similar to those in the experiments even though the gas species

in the reactions eq.(2.9) and eq.(2.10) are different. In the experiments, the reaction takes place under conditions where Si-rich gas is in equilibrium with cristobalite. Accordingly, the rate of the enstatite formation in the present experiments should give a maximum rate compared to that expected in the nebula. As already mentioned, no difference in enstatite formation rate among the different crystallographic orientations of forsterite substrates was not observed in the experiments. However, different growth behavior of enstatite might be possible in the solar nebula if the forsterite surface is free from crystal defects. If this were the case, then the reaction rates would be different on different crystallographic surfaces. Therefore, it should be noted that the application of the present data to the solar nebula will be discussed without considering crystallographic orientation of the substrate.

Under isothermal conditions, we can estimate the maximum thickness or the minimum duration to form a certain thickness of enstatite by the reaction in the solar nebula by extrapolating the average parabolic rate constants k obtained in the present experiments to lower temperatures (Fig. 2.10). If the forsterite grains were similar in size to the olivine grains in matrices in chondrites (less than a few μm), then it is expected from Fig. 2.10 that the reaction would be completed within a few years at the calculated temperature of enstatite appearance (1349 K at 10^{-3} atm, Grossman (1972)) and 10^5 years even at 1000 K.

On the other hand, in the cooling nebula, more complicated processes than those under isothermal conditions should be taken into consideration. Hasegawa (1984) theoretically discussed the diffusion controlled reaction between solid and gas in the cooling nebula. According to his discussion, the final thickness d of enstatite formed by the reaction is approximately given by the following equation:

$$d = \sqrt{\frac{k(T_e)RT_e\tau}{E}}, \quad (2.11)$$

where T_e is the absolute temperature for the appearance of enstatite, and τ the cooling time scale of the nebula:

$$\tau = \left| \frac{d \ln T}{dt} \right|^{-1}_{T=T_e} \quad (2.12)$$

Using the eqs. (2.2) and (2.11), the final thickness of the enstatite was calculated from the values of E and k_0 obtained in the present experiments as a function of temperature and cooling time scale of the nebula (Fig. 2.11).

If forsterite condensed in the cooling nebula, the size of the forsterite grain is also dependent on the cooling time scale of the nebula. Kozasa and Hasegawa (1987) theoretically estimated the final grain size for a Mg-silicate in cooling nebula by applying homogeneous nucleation theory as a function of both total pressure $p(\text{total})$ and the cooling time scale τ . According to their theory, the grain size r (μm) can be approximately estimated to be

$$r = 1.9 \times 10^{-2} p(\text{total}) \tau. \quad (2.13)$$

In their calculation, enstatite is assumed to condense directly from the gas. If the final grain size of forsterite is of the same order as that of enstatite in these calculations (Kozasa and Hasegawa, 1987), we can compare the grain size of forsterite with the thickness of the enstatite reaction layer to estimate the degree of the reaction. According to the thermochemical calculation (Grossman, 1972), more than 90 percent of the forsterite had already condensed before the reaction of enstatite formation began. Thus, when the reaction started, the size of the forsterite grains should be almost the same as the calculated final size of forsterite. The size r of such forsterite is also given in Fig. 2.11 as a function of τ for

two different $p(\text{total})$. The thickness of the enstatite layer is estimated from eq. (2.11). The ratio of the forsterite grain size and the final enstatite layer thickness d/r can be regarded as a degree of the reaction.

At $p(\text{total})=10^{-3}$ atm, enstatite starts to form by the reaction between forsterite and Si-rich gas from 1349 K based on the thermochemical calculation (Grossman, 1972). In this case the d/r ratio is always much less than unity over a wide range of τ (Fig. 2.11a). Especially for large τ , that is, in a slowly cooling nebula, the size of the forsterite grains is large but d/r is small. This is because d is proportional to $\tau^{0.5}$ (eq. 2.11), while r is proportional to $\tau^{0.8}$ (Kozasa and Hasegawa, 1987). Watanabe and Nakagawa (1988) estimated that τ of the primordial solar nebula is approximately 10^8 - 10^{10} s. If we adopt this value, the d/r ratio is only 5×10^{-4} - 10^{-4} . Even if the error of the reaction rate is taken into account, the degree of the reaction remains in the same order of magnitude and very little reaction is expected. At $p(\text{total}) = 10^{-5}$ atm, enstatite starts to form by the reaction between forsterite and Si-rich gas from about 1200 to 1250 K. In this case, the d/r ratio is also less than unity over a wide range of τ (Fig. 2.11b). In order for the enstatite formation reaction between forsterite and Si-rich gas to take place, it is required that the grain size of the forsterite should be very small. That is to say, very rapid cooling of the primordial solar nebula is necessary to bring about the increase of the degree of the reaction.

As discussed above, if the extrapolated values of the parabolic rate constant are adopted in the condensation theory of Kozasa and Hasegawa (1987), the reaction would not be expected to occur to any measurable degree over the probable cooling time scale of the solar nebula. Thus maximum fractionation between Mg and Si would have taken place in the cooling nebula. In the case of the maximum fractionation, a small amount of enstatite and a large amount of silica rich minerals, such as feldspar or silica minerals, would directly condense from the residual gas by further cooling.

2.6.2 Mg/Si fractionation in the primordial solar nebula

The Mg/Si values in the bulk compositions of chondrites and planets are approximately unity (Dodd, 1981; Ringwood, 1989) (the vertical axis in Fig. 2.12), and is very close to the solar value (1.075). That is to say, a large fractionation of Mg and Si from the solar ratio has not been taken place during the formation of chondrites and planets. On the other hand, the present study of the enstatite formation reaction between forsterite and Si-rich gas clarified that the reaction has not almost occurred and that the condensation has occurred under the condition near a maximum fractional condensation. Therefore, the nearly complete separation between forsterite ($\text{Mg/Si}=2$) and Si-rich gas ($\text{Mg/Si}=0$) must have occurred. If the forsterite and Si-rich component accrete separately, the similar Mg/Si ratio of chondrite and planets to the solar ratio cannot be explained. Therefore, it is necessary to consider the different process other than the reaction process as discussed above to explain the bulk composition of chondrites and planets. Then, the following three processes can be possible; (1) *reaction between heterogeneously nucleated forsterite and Si-rich gas* (2) *metastable direct condensation of pyroxene from the solar gas*, or (3) *accretion of mixtures of forsterite and felsic minerals*.

(1) *reaction between heterogeneously nucleated forsterite and Si-rich gas:*

The reaction discussed in section 2.6.1 was based on the Kozasa and Hasegawa's time dependent homogeneous nucleation theory. If minerals more refractory than forsterite, such as the minerals in Ca-Al minerals and presolar grains (e. g., Amari et al., 1993) act as nuclei for the heterogeneous nucleation of forsterite, then the behavior might be different. When the number density of primary condensates or presolar grains is smaller than (or nearly equal to) the nucleation density of Mg-silicate in the Kozasa and Hasegawa's model, the forsterite grain size becomes larger, and the conclusion of the above discussion that the reaction does not take place, is not changed. On the other hand, when the nucleation density

of primary condensates and/or presolar grains is much larger than the number density of the Mg-silicate, the grain size of the resultant heterogeneously nucleated forsterite becomes smaller. In this case, the calculated reaction degree becomes larger, and the enstatite formation reaction becomes more effective. As a result, the reaction approaches to an equilibrium, and large Mg/Si fractionation becomes difficult to occur.

(2) metastable direct condensation of enstatite:

The existence of enstatite which is considered to be a direct condensation product in the primordial solar nebula, has been reported in interplanetary dust particles (Bradley et al., 1983). In the result of the present study, the amount of enstatite formed by the condensation process is significantly small. That is why, we consider the possibility of the metastable condensation of enstatite from the solar gas in order to make sufficient enstatite. The difference of the equilibrium condensation temperature between forsterite and enstatite in the solar nebula condition is quite small (forsterite is about 5-12 K larger than enstatite depending upon the total pressure at 10^{-5} - 10^{-3} atm, Grossman, 1972), and the larger the heliocentric distance is, the smaller the difference is. And also, the Mg/Si ratio (=1) of enstatite is closer to the solar value (1.075) rather than the ratio (=2) of forsterite. Therefore, the collision ratio between Mg and SiO molecules would be closer 1:1 rather than 2:1. Thus, enstatite instead of forsterite would condense metastably and directly from the nebula when the cooling is rapid. In the case of the direct metastable condensation of enstatite, the solid materials have Mg/Si=1, which is near the solar ratio of Mg/Si=1.075. The metastable condensation is considered to depend strongly upon the cooling time scale. For, instance, when the cooling is very slow, forsterite will nucleate as a stable phase. Since the nucleation rates of stable and metastable phases has not been evaluated in the cooling process, the possibility of the metastable crystallization of enstatite in the Mg-Si-O-H system is only pointed out in the present study.

(3) accretion of mixtures of forsterite and felsic minerals:

Si-rich component can condense at the temperature, which is lower only by one hundred K than the temperature of forsterite condensation as felsic minerals (Tsuchiyama, unpublished). The accretion temperature would have been lower than the condensation temperature of felsic minerals. When both forsterite and felsic solid grains accreted without large Mg/Si fractionation into the same body, the bulk composition of the body must have Mg/Si~1. After the accretion, pyroxene might have formed by the solid-solid reaction between forsterite and felsic minerals in the body.

Three possibilities mentioned above ((1)-(3)) for bringing about the bulk composition of planets close to the solar Mg/Si value were suggested based on the present result of maximum fractionation. While, these seem to be highly probable. However, it is difficult to choose the most probable possibility among them at present.

In addition, the Mg/Si ratio is slightly different among chondrites and/or planets (Dodd, 1981; Ringwood, 1989) (Fig. 2.12). Only by the considerations ((1)-(3)) might not be enough, but the dynamic separation processes of between solid and gas should be also taken into account. In the present study, it was found that the reaction rate of enstatite formation has been late in the probable cooling time scale, and the nearly complete separation between forsterite and Si-rich gas have occurred. In order to make clear the variations in the bulk compositions among chondrites and planets, the effect of the fractionation between forsterite and Si-rich gas due to the heliocentric movement of solids toward the sun (Lin and Papaloizou, 1985) should be also quantitatively estimated during the condensation process of Si-rich gas process in the cooling solar nebula (see section 1.1).

2.6.3. Significance of the reaction in the primordial solar nebula

We have postulated that forsterite condensation and the following enstatite formation is the result of the cooling from the high temperature gas in the present discussion.

According to the recent solar nebula dynamical evolutionary model (Watanabe, 1992) and the recent observation of the classical T-Tauri stars (Shu et al., 1987), the overall disk of the solar nebula might not necessarily become high temperature enough to vaporize silicates or metal. Nevertheless, it would be possible that at least in the inner region in the nebula such a high temperature was attained within the asteroidal orbit. Therefore, in such a region the present discussion would be applied properly.

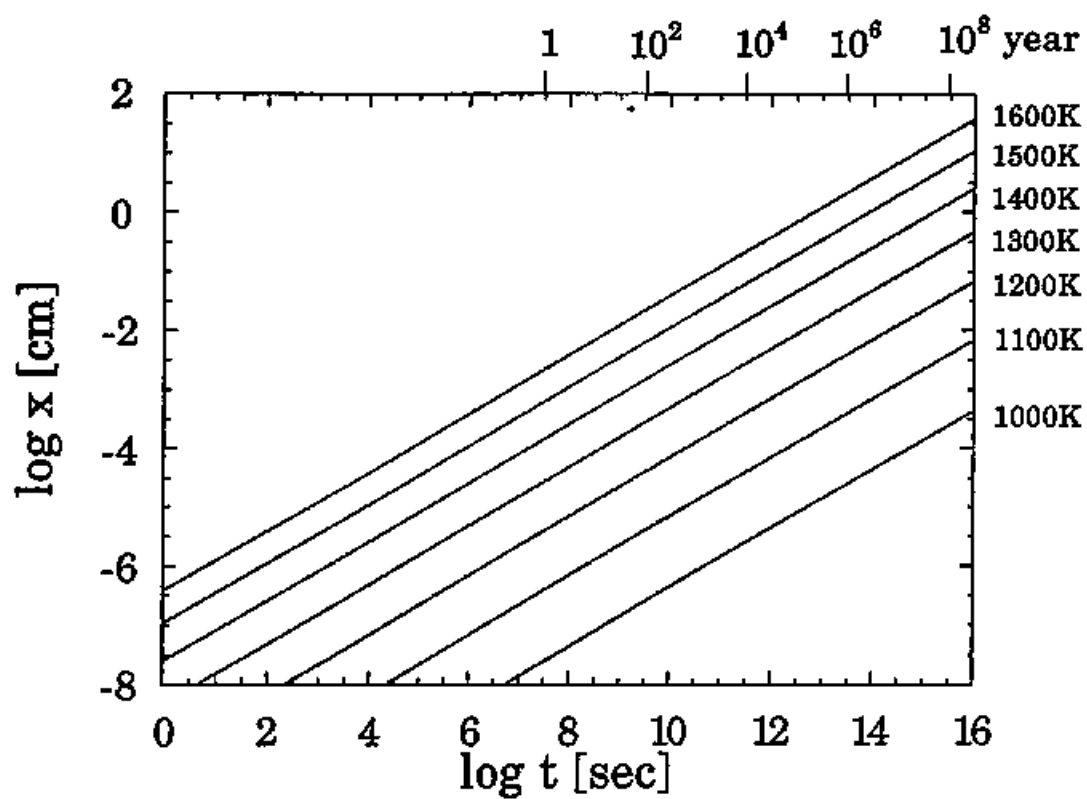


Fig. 2.10. Relation between the width of enstatite reaction layer x and time t at different temperatures (1000 K - 1600 K) calculated from the parabolic rate constant obtained in the experiments.

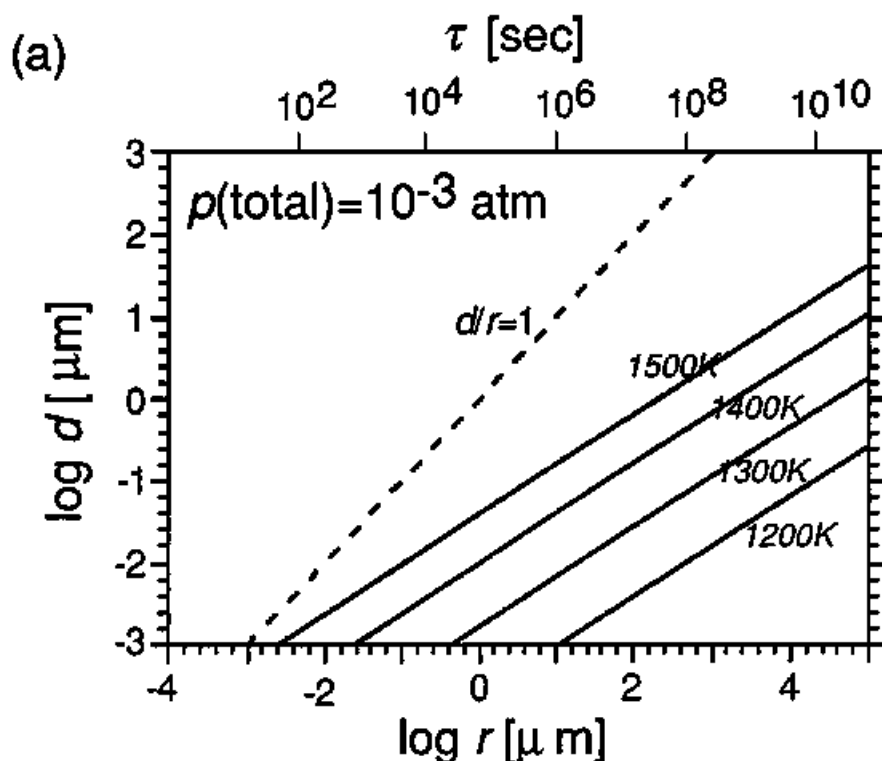


Fig. 2.11a. A degree of the forsterite-gas reaction to form enstatite in the cooling nebula calculated from the parabolic rate constant in the experiments and nucleation and growth theory of Kozasa and Hasegawa (1987). Final thickness of enstatite d and the grain size of forsterite r are shown as a function of the cooling time scale of the solar nebula τ . Solid lines show the appearance temperature of enstatite under the chemical equilibrium, and broken line shows the completion of the reaction $d/r = 1$. $p(\text{total})=10^{-3} \text{ atm}$.

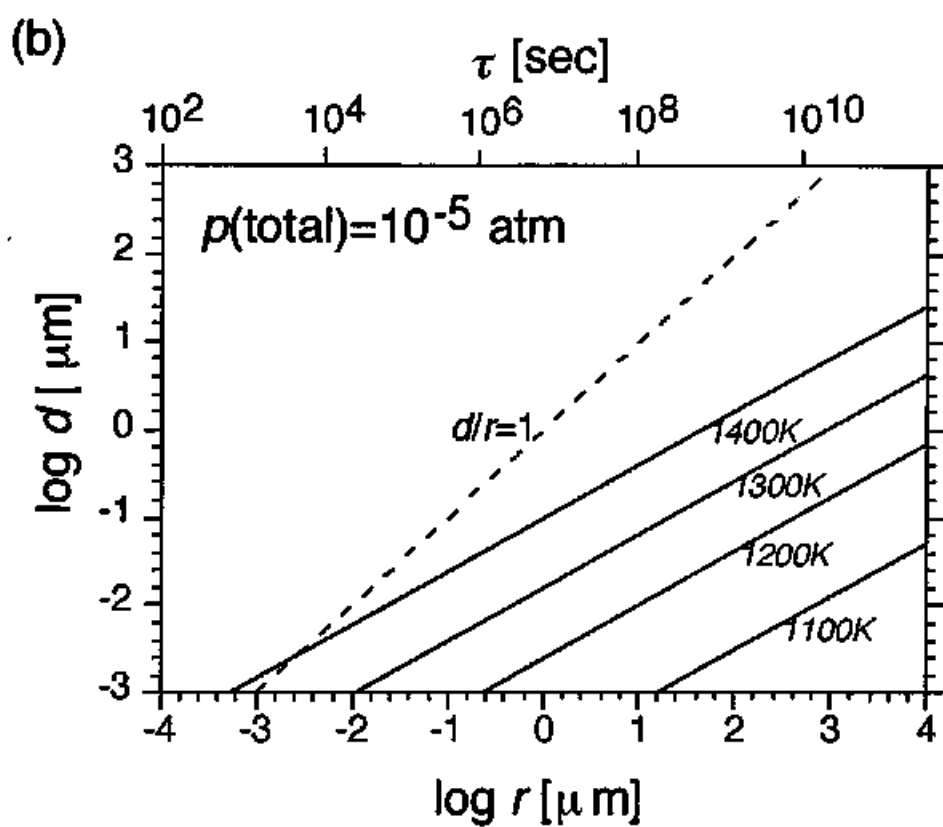


Fig. 2.11b. See the caption of Fig. 2.11a. $p(\text{total})=10^{-5} \text{ atm}$.

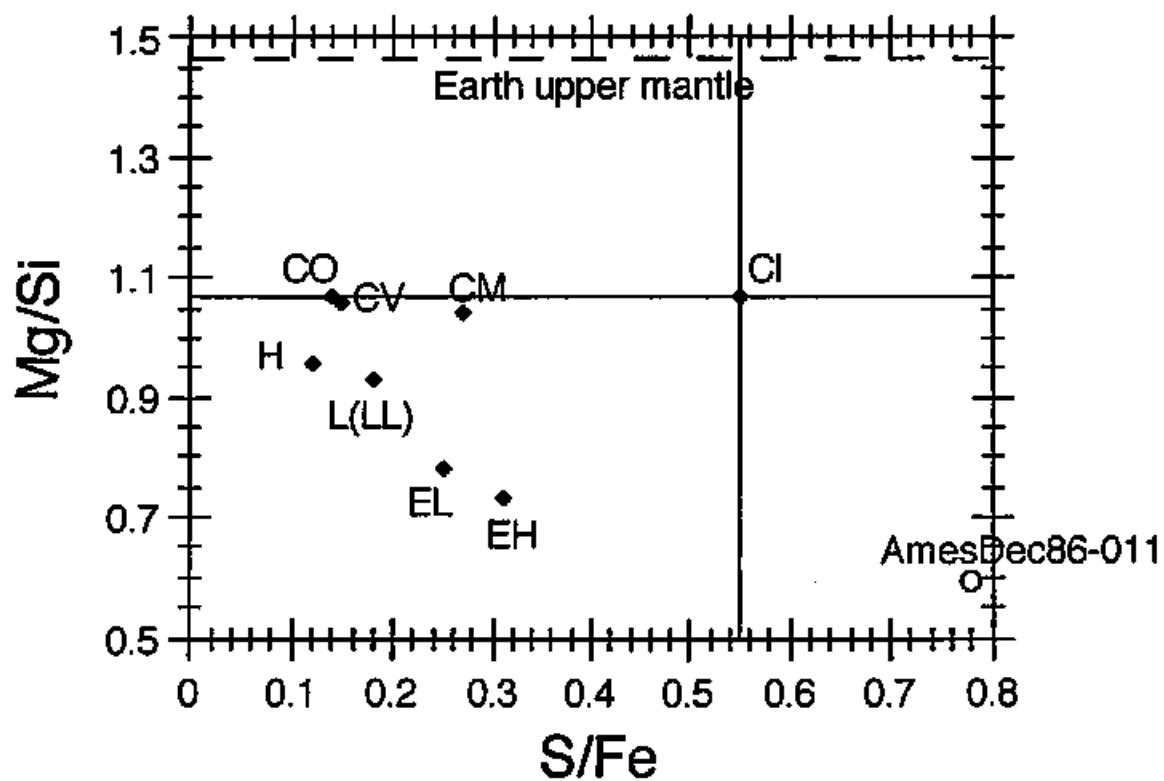


Fig. 2.12. Variation of Mg/Si and S/Fe atomic ratios in chondrites (EH, EL, H, L(LL), CI, CO, CV and CM) (Dodd, 1981) and IDP (AmesDec86-011) (Blake et al., 1988). Mg/Si value in earth upper mantle (Ringwood, 1989) is also drawn in the figure.

2.7 Conclusion

The experiments on the enstatite formation reaction between forsterite and Si-rich gas were successfully carried out using the double-capsule technique, and it was found that this reaction obeys a parabolic rate law. In the primordial solar nebula, the importance of this reaction mechanism for the formation of enstatite depends upon the initial forsterite grain size. If the present results can be extrapolated using the condensation theory of Kozasa and Hasegawa (1987) in the cooling nebula, the degree of the reaction would be very small, and the maximum fractionation between Mg and Si would have occurred.

3. FeS formation reaction between metallic iron and H₂S gas in the primordial solar nebula

Abstract

The phase diagram of the Fe-S-H system was constructed to understand the condensation processes of metallic iron and iron sulfides (troilite and pyrite) from hydrogen-rich gas. It was found that both metallic iron and troilite, and troilite and pyrite are in a reaction relation over the wide range of the phase diagram under the low pressure condition that the total pressure is determined by hydrogen gas. Thus the reaction between metallic iron and H₂S gas plays an important role in the fractionation of the primordial solar nebula because the peritectic curve is highly proximate to the H-S tie line. Then the rate of the reaction in the solar gas was studied by applying the experimental data of the FeS formation reaction in the field of corrosion science of metals. The reaction degree was estimated on various cooling conditions of the nebula when the grain size of metallic iron was controlled by the homogeneous nucleation theory.

3.1 Introduction

The Mg-Fe-Si-S-O-H system consists of the most abundant elements except N and C of volatile elements in the solar system, and is especially important to the study of the chemical evolutions of the solar nebula. According to the thermodynamical consideration at high temperature (Grossman, 1972), the condensation in the systems of Mg-Si-O-H and Fe-S-H can be nearly treated independently (see chapter 1). In the present study, as a sequence of our study on the reaction in the nebula (chapter 2; Imae et al., 1993), we focus on the FeS formation reaction between metallic iron and H_2S gas.

FeS formation reaction has not been quantitatively considered, and has been treated to have occurred very rapidly as the equilibrium condensation (Lewis, 1972). A problem on whether the reaction is completed or not, is extremely important in establishing the S/Fe ratio in planets and/or chondrites as the accretion products of solid grains. Especially, in the inner region of the solar system, if the reaction should not be completed, sulfur is expected to be left as H_2S gas in the solar nebula, and not to be included in the solid body, planets and/or chondrites. This will bring about the depletions of sulfur in cores of planets, bulk planets and chondrites from the solar value. In the present paper, the phase diagram in the Fe-S-H system will be first constructed. Then, the reaction degree of FeS formation in the primordial solar nebula will be discussed.

3.2 Fe-S-H phase diagram

The phase diagram of the Fe-S-H system was constructed by assuming an ideal gas under the condition that the total pressure is determined by hydrogen gas. The calculation method is essentially the same as applied to the solar nebula by Grossman (1972). A phase boundary coexisting of solid and gas, which is called vaporous, can be acquired from the equation of $\Delta G^\circ = -RT \ln K$, where ΔG° is a standard free energy change of a reaction, K an equilibrium constant, R gas constant and T absolute temperature. Metallic iron (Fe), troilite (FeS) and pyrite (FeS₂) are taken into account as the condensation species. The reactions among the species are expressed as



where (s) and (g) denote solid and gas, respectively. And the equilibrium constants of the above reactions (eqs. (3.1a)-(3.1c)) are

$$K_1 = p(\text{Fe}) / a(\text{Fe}) \quad (3.2a)$$

$$K_2 = p(\text{Fe}) p(\text{H}_2\text{S}) / a(\text{FeS}) p(\text{H}_2) \quad (3.2b)$$

$$K_3 = p(\text{Fe}) p(\text{H}_2\text{S})^2 / a(\text{FeS}_2) p(\text{H}_2)^2, \quad (3.2c)$$

respectively, where a is activity and p pressure. Since metallic iron, troilite and pyrite do not form solid solution, $a(\text{Fe})$, $a(\text{FeS})$ and $a(\text{FeS}_2)$ equal to unity, respectively. Exactly speaking, FeS forms solid solution due to the nonstoichiometry expressed as $\text{Fe}_{1-\delta}\text{S}$. However, in the study, only the stoichiometric FeS or troilite is considered as a first approximation because δ is very small number.

The atomic fractions of Fe, S and H are expressed as x , y and $(1-x-y)$, respectively. Because $p(\text{total})=p(\text{H}_2)$ is also assumed as already mentioned, $x \ll 1$, $y \ll 1$ and $(1-x-y)$ can be approximated to be 1. Using two variables of x and y , K_1 , K_2 and K_3 are then expressed as

$$K_1 = 2 x p(\text{total}) \quad (3.3a)$$

$$K_2 = 4 x y p(\text{total}) \quad (3.3b)$$

$$K_3 = 8 x y^2 p(\text{total}). \quad (3.3c)$$

On the other hand, these equilibrium constants (eqs. (3.3a)-(3.3c)) can be expressed from the thermochemical data of JANAF (1985) as a function of temperature such as

$$K_1=10(7.6-21581/T) \quad (3.4a)$$

$$K_2=10(8.3-25191/T) \quad (3.4b)$$

$$K_3=10(13.6-28605/T). \quad (3.4c)$$

Then the equations giving the boundaries (cotectic lines) between vaporouses of metallic iron and troilite, and between vaporouses of troilite and pyrite are expressed as

$$\log y = 0.17 \log x + 0.17 \log p(\text{total}) - 0.82 \quad (3.5a)$$

$$\log y = 0.16 \log x + 0.16 \log p(\text{total}) - 4.58, \quad (3.5b)$$

respectively.

Then, we can construct the phase diagram of the system from the equations (eqs. (3.3a)-(3.4c)). The phase diagram of the ternary system (Fe-S-H) is schematically shown as a triangle in Fig. 3.1. Since the composition is assumed to be hydrogen-rich, the diagram of the region close to the H-end is shown in this figure.

The cotectic curves between metallic iron and troilite, and between troilite and pyrite are peritectic curves, except for the region of $\log x > -1.99$ at $p(\text{total})=10^{-5}$ atm and $\log x > 1.59$ at $p(\text{total})=10^{-3}$ atm where they change to an eutectic relation. This figure is schematically drawn, because the cotectic curves between metallic iron and troilite, and troilite and pyrite are very close to the H-S tie line (eqs. (3.5a) and (3.5b)) and could not be drawn in their proper positions. Such reaction relations of metallic iron and troilite, and troilite and pyrite in the H-rich region are different from the eutectic relations of the Fe-S binary system at 1 atm on H-free conditions. In addition, note that in such a H-rich region, sulfur does not condense due to the thermodynamical instability.

As a quantitative diagram instead of the schematic drawing in Fig. 3.1, the peritectic curves are plotted by introducing the logarithmic scales of S/H and Fe/H ratios (Figs. 3.2a and b). The diagrams under the pressures of $p(\text{total}) = 10^{-5}$ and 10^{-3} atm are given in Figs. 3.2a and b, respectively. Since the phase diagram calculated in the present study is correct only in the region of both $x \ll 1$ and $y \ll 1$, it was shown only in the region by taking

two axes of $\log (\text{Fe}/\text{H})$ and $\log (\text{S}/\text{H})$ in Fig. 3.2. In Fig. 3.2, the cotectic curves are expressed by straight lines different from Fig. 3.1. Only the phase diagram for the case of $p(\text{total})=10^{-5}$ atm (Figs. 12 and 13a) will be explained in detail in the following discussion, because the character of the diagram of $p(\text{total})=10^{-3}$ atm in Fig. 3.2b is essentially the same as Fig. 3.2a.

When we consider the cooling of the solar gas with the composition, b ($x = 3 \times 10^{-5}$, $y = 2 \times 10^{-5}$), in Fig. 3.1 and Fig. 3.2a, the first condensate (the condensation temperature is 1280 K) is metallic iron, which has an extremely wide vaporous region. Proceeding the cooling, the vapor composition changes by condensing metallic iron toward p_1 ($x=10^{-18}$, $y=2 \times 10^{-5}$) at 700 K on the peritectic line between metallic iron and troilite. In Fig. 3.2a, the gas composition changes parallel to the horizontal axis. When the gas composition reaches p_1 , the metallic iron becomes unstable, and the reaction between metallic iron and H_2S gas starts to form troilite. In the case of the equilibrium condensation, the gas composition changes along the peritectic line, forming troilite by the reaction between metallic iron and H_2S gas.

On the other hand, in the case of maximum fractional condensation where the reaction between metallic iron and H_2S gas does not occur, the gas composition changes from p_1 to p_2 by condensing troilite. In this case, a little amount of troilite can condense and the S content in the gas phase does not change significantly, because almost all Fe in the gases is already consumed as a metallic iron. Then, in the maximum fractionation, the gas composition changes almost parallel to the horizontal axis from p_1 to p_2 in Fig. 3.2a, as similar with the metallic iron condensation. When the gas composition reaches p_2 at 347 K on the peritectic line between troilite and pyrite, the formation of pyrite starts.

The condensation temperature of metallic iron changes depending upon the total pressure (Figs. 3.2a and b). On the other hand, the temperature where the reaction starts is the same in spite of the change of total pressure since the condensation of metallic iron does

not change S/H ratio in the gas. Furthermore, the essential characters of the reaction relation such as the proximity of the reaction lines to the H-S tie line are unchanged between Figs. 3.2a and b. Therefore a large amount of troilite is formed by the reaction in equilibrium condensation in the range of the total pressure of 10^{-5} to 10^{-3} atm. On the other hand, only the extremely small amount of troilite are formed in the maximum fractional condensation. Thus it is found that the troilite formation reaction between metallic iron and H_2S gas greatly influences the amount of minerals and the mineral species as final products.

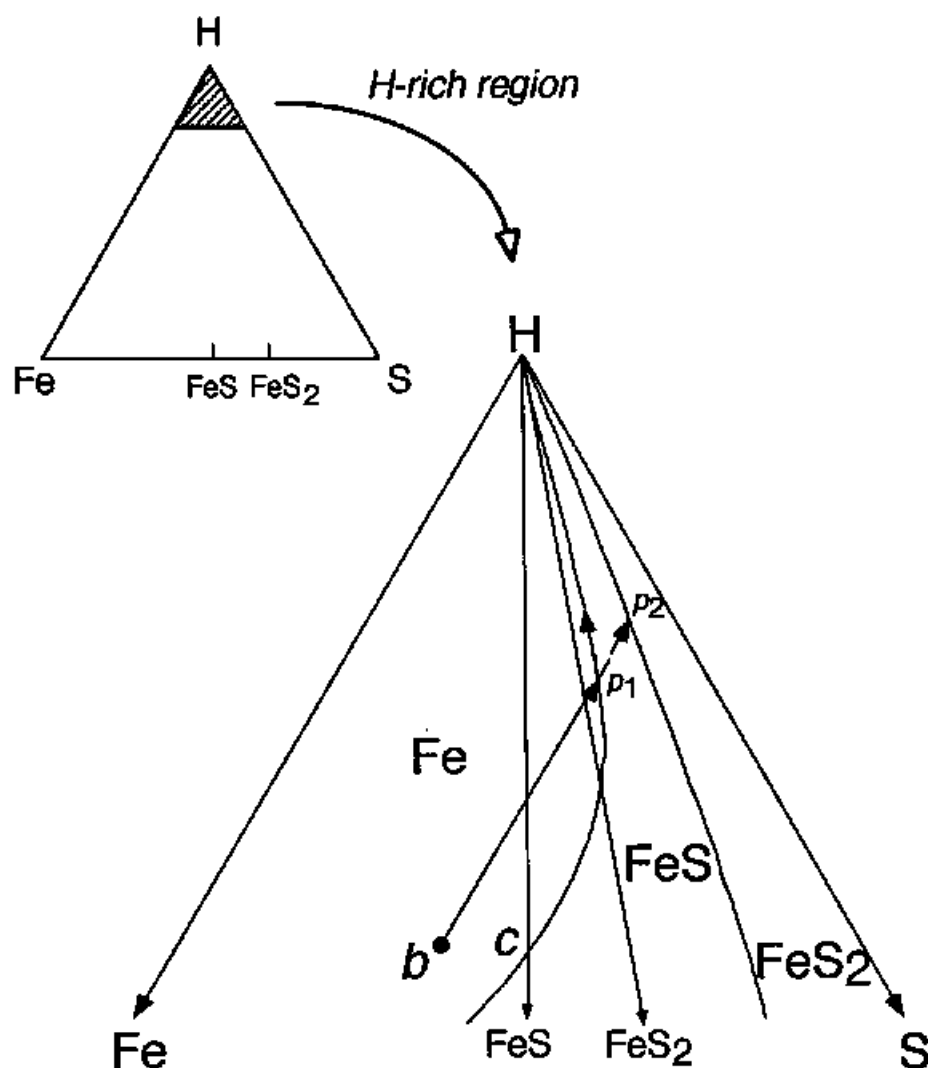


Fig. 3.1. Schematic drawing of the phase diagram in the ternary Fe-S-H system. Three vapours are shown as Fe = metallic iron, FeS = troilite and FeS₂ = pyrite. Two thick curves between vaporises represent cotectic curves. The path of the gases due to the condensation is indicated by arrows. $\log x = -1.99$ at $p(\text{total}) = 10^{-5}$ atm and $\log x = -1.59$ at $p(\text{total}) = 10^{-3}$ atm are satisfied at the point c where the boundary between eutectic and peritectic relation is defined. The plain arrow shows the case of the equilibrium condensation path, while the dotted arrow shows the case of the maximum fractional condensation path. b = bulk component; p_1 = peritectic point where troilite formation starts (700 K); p_2 = peritectic point where pyrite formation starts (347 K).

(a)

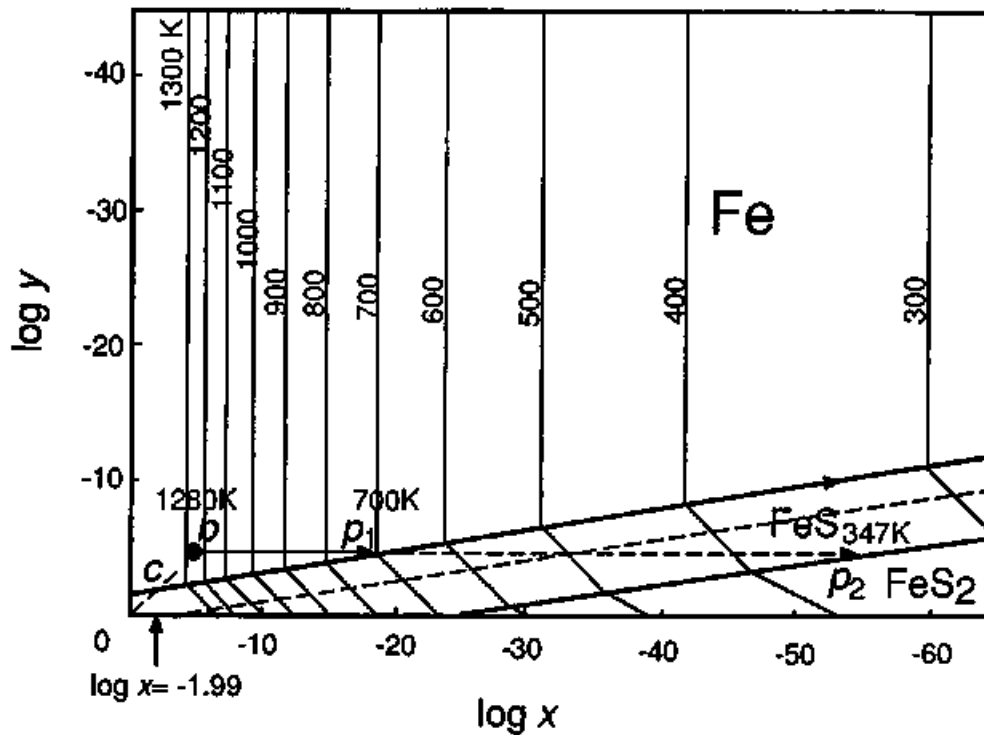


Fig. 3.2a. Fe-S-H phase diagram. The graph is shown as a logarithmic plot. The dotted line nearly parallel to the peritectic lines coexisting of metallic iron and troilite, and troilite and pyrite is the peritectic line metastably coexisting of metallic iron and pyrite. Condensation paths are comparable to in Fig. 1. b = bulk component; p_1 = peritectic point where troilite formation starts (700 K); p_2 = peritectic point where pyrite formation starts (347 K); c = the boundary between eutectic and peritectic relation; Fe = metallic iron; FeS = troilite; FeS₂ = pyrite. $p(\text{total}) = 10^{-5}$ atm.

(b)

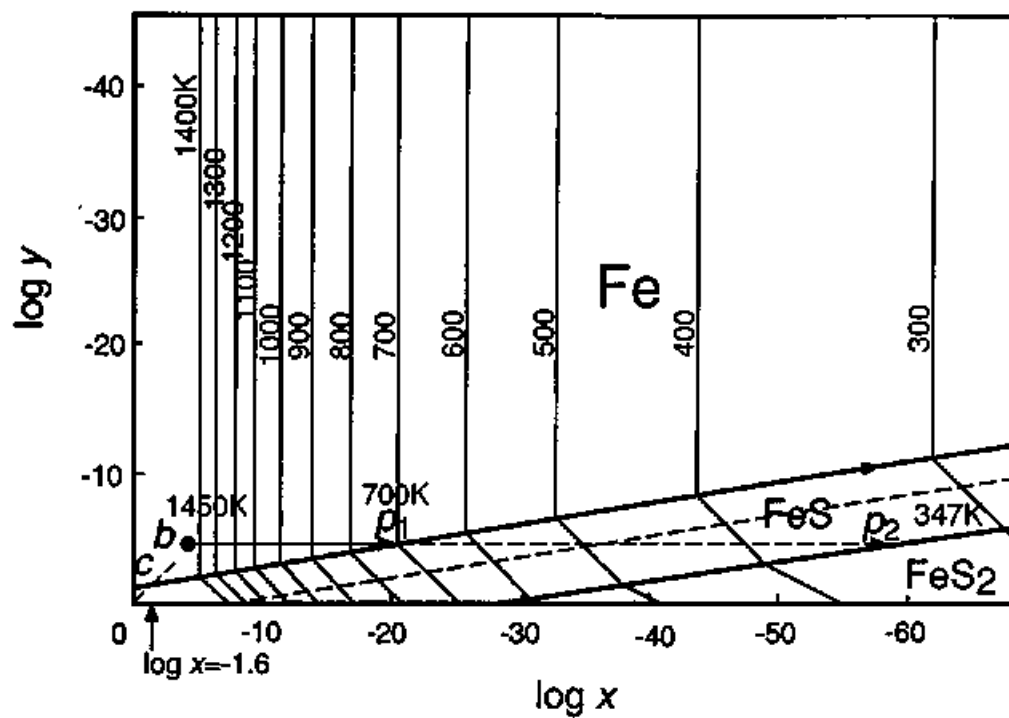


Fig. 3.2b. See the caption of Fig. 3.2a. $p(\text{total}) = 10^{-3}$ atm.

3.3. Reaction rate between metallic iron and H₂S gas in the solar nebula condition

Experiments on FeS formation reaction between metallic iron and H₂S gas have been carried out under the condition of the H₂S and H₂ gas flow by Fryt et al. (1979a and 1979b). By the reaction, polycrystalline FeS layers overgrew surrounding the metallic iron. The reaction is controlled by outer diffusion of Fe in the FeS layer from a Fe-FeS interface toward a FeS-gas interface. Iron sulfides formed in this experiments are nonstoichiometric (Fe_{1-δ}S, pyrrhotite). When the sufficient equilibration occurs between pyrrhotite and metallic iron, the pyrrhotite changes to troilite. In the following discussion, pyrrhotite and troilite are expressed for simplicity as FeS.

The reaction rates obtained in the experiments (Fryt et al., 1979a; Fryt et al., 1979b) can be used in the discussions about the reaction in the primordial solar nebula. However, we cannot directly use the experimental data in the following discussions because they were obtained in a higher $p(\text{S}_2)$ pressure region than in the primordial solar nebula condition. Then we extrapolated the data to the solar nebula condition at extremely low $p(\text{S}_2)$ as follows.

The parabolic rate constant k (cm²/sec) is expressed (Fryt et al., 1979b) as the product of the chemical diffusion coefficient, $D = 6.7 \times 10^{-2} \exp(-2.09 \times 10^4/RT)$, and the deviation from the stoichiometry of FeS, $\delta = p(\text{S}_2)^{1/2} \exp(-(-3.12 \times 10^4 + 19.98T + 4\delta(2 - \delta)(7.9 \times 10^3 + 4T))/RT)$, where R (1.987 cal mol⁻¹ K⁻¹) is gas constant. Thus, $k = D\delta$ is a function of T , $p(\text{S}_2)$ and δ . Approximation to cancel δ can be made by using the relation:

$$\left[\frac{d \ln \delta}{d \ln p(\text{S}_2)} \right]_{T, \delta=0} = \frac{1}{2}, \quad (3.6)$$

which is valid under the low sulfur partial pressure region (about $p(S_2) < 10^{-8}$ atm, $\delta < 0.009$) (Fryt et al., 1979b). When integration of eq. (3.6) is carried out by taking the initial condition of $\delta=0$ at the Fe-FeS interface and making use of the experimental data (Fryt et al., 1979a), δ can be expressed as a function of $p(S_2)$ and T :

$$\delta = p(S_2)^{1/2} \exp(20.1 - 1.5 \times 10^{-2} T), \quad (3.7)$$

Substituting eq.(3.7) into the relation of $k = D\delta$, k is expressed as only $p(S_2)$ and T as

$$k = 6.7 \times 10^{-2} p(S_2)^{1/2} \exp\left(\frac{-1.5 \times 10^{-2} RT^2 + 20.1 RT - 2.09 \times 10^4}{RT}\right), \quad (3.8)$$

On the other hand, $p(S_2)$ in the solar nebula is determined by the following reaction,



and the equilibrium constant K is expressed by using the data of JANAF (1985) as

$$K = \frac{p(H_2)^2 p(S_2)}{p(H_2S)^2} = 10^{(4.97 - 9.2 \times 10^3/T)} \quad (3.10)$$

Thus, $p(S_2)$ on the hydrogen-rich condition can be expressed by using eq.(3.10) and the elemental abundances of sulfur $A(S)$ and hydrogen $A(H)$ as

$$p(S_2) = \left[2 \frac{A(S)}{A(H)} \right]^2 10^{(4.97 - 9.2 \times 10^3/T)} \quad (3.11)$$

Now since $A(H)/A(S) = 5.3 \times 10^4$ in the solar gas composition, then $p(S_2)$ is obtained from eq.(3.11);

$$p(S_2) = 1.43 \times 10^{(-4.03-9.2 \times 10^3/T)} \quad (3.12)$$

Hence, substituting eq. (3.12) into eq. (3.8), k is expressed as

$$k = 4.3 \times 10^5 \exp \left(-\frac{4.2 \times 10^4}{RT} - 1.5 \times 10^{-2} T \right) \quad (3.13)$$

Then, k is not dependent upon $p(\text{total})$, but upon the $A(S)/A(H)$ ratio.

3.4. Application to the condensation in the primordial solar nebula

In this section, the FeS formation reaction between metallic iron and H₂S gas in the cooling primordial solar nebula is discussed. In the cooling of the solar gas in the Fe-S-H system metallic iron can first condense. According to the time dependent-homogeneous nucleation theory applied to the condensation in the cooling solar nebula (Kozasa and Hasegawa, 1987), the grain size r (μm) of metallic iron is approximately expressed as

$$r = 5 \times 10^{-3} p(\text{total}) \tau, \quad (3.14)$$

where τ (sec) is a cooling time scale of the solar nebula, and defined as

$$\tau = \left| \frac{d \ln T}{d t} \right|^{-1}. \quad (3.15)$$

When the cooling proceeds, it can be considered that metallic iron becomes unstable at the equilibrium reaction temperature (T_e), 700 K, and immediately starts to react with H₂S gas to form FeS from this temperature because of a small kinetic barrier of the reaction.

Calculations of the reaction degree which is defined as the ratio d/r of the grain size of metallic iron r and the thickness of FeS d were carried out on three cases. The first (section 3.4.1) is a case of constant $p(\text{S}_2)$, which is approximately kept due to the contraction of the primordial solar nebula. The second (section 3.4.2) is a case of decreasing $p(\text{S}_2)$, which is caused by proceeding of the FeS formation reaction in the primordial solar nebula with constant volume. And the third (section 3.4.3) is that the nebula cools towards not zero K but a certain temperature. This takes into account that the nebula might have approached to various temperatures depending upon the heliocentric distance.

3.4.1 A case of constant $p(S_2)$

Since $p(S_2)$ is assumed to be constant throughout the reaction, k is a function of only temperature. Under the isobaric cooling to zero K at $p(\text{total})=10^{-5}$ or 10^{-3} atm, the final thickness d of the FeS layer around the pre-existing metallic iron grain by the reaction obeys,

$$d = \left[\int_0^\infty k(T) dt \right]^{1/2}, \quad (3.16)$$

where $T = T_e$ at $t = 0$ and $T = 0$ at $t = \text{the infinite}$. The cooling is assumed to obey eq.(3.16). In order to obtain the analytical result of the integration, the parabolic rate constant k given by eq.(3.13), was approximated as a function that $\ln K$ changes linearly with $1/T$ below or around 700 K as

$$k = 0.3 \exp(-3.5 \times 10^4 (\text{cal/mol})/RT). \quad (3.17)$$

Hence, by the integration of eq.(3.16) by using eq.(3.17), d (μm) is derived only as a function of τ ,

$$d = 3.2 \times 10^{-3} \tau^{1/2}, \quad (3.18)$$

Then we can estimate the reaction degree d/r as a function of the cooling time scale from eqs. (3.14) and (3.18) as

$$d/r = 3.2 \times 10^{-3} p(\text{total}) \tau^{1/2} \quad (3.19)$$

On the other hand, the reaction is restricted from relative abundances of iron and sulfur. If the reaction completes, the amount of sulfur consumed by the reaction almost equals to the sulfur abundance with the solar composition:

$$\frac{\rho_{\text{FeS}} \Delta V N_A N}{M_{\text{FeS}}} \approx A(\text{S})_{\text{SA}}, \quad (3.20)$$

where ρ_{FeS} is the density of troilite (4.72 g/cm^3), ΔV the maximum FeS volume produced around one iron grain when the reaction completes, N_A Avogadro number, N grain density normalized to solar abundance, M_{FeS} atomic weight of troilite and $A(\text{S})_{\text{SA}}$ the solar abundance of sulfur, 5.15×10^5 (Anders and Ebihara, 1982). Since the FeS layer is assumed to form in the same manner as in the reaction experiments where the layer overgrew around the metallic iron with the constant size r by the outer diffusion of Fe in the layer (Fryt et al., 1979a), ΔV is given by $(4/3)\pi r^3\{(1+d^*/r)^3-1\}$, by using the maximum thickness of the FeS layer d^* . In addition, since most of iron is included in the solid grain before the FeS formation reaction, the relation:

$$A(\text{Fe})_{\text{SA}} \approx \frac{4 \pi r^3 \rho_{\text{Fe}} N_A N}{3 M_{\text{Fe}}} \quad (3.21)$$

can be made, where ρ_{Fe} is the density of metallic iron (7.87 g/cm^3), M_{Fe} the atomic weight of iron and $A(\text{Fe})_{\text{SA}}$ abundance of iron, 9×10^5 (Fryt et al., 1979a). Thus N can be obtained as a function of r from eq.(3.21),

$$N = 2.53 \times 10^{-18} / r^3, \quad (3.22)$$

By substituting eq.(3.22) into eq.(3.20), the reaction degree in the maximum thickness becomes

$$d^*/r = 0.36. \quad (3.23)$$

Two lines representing the relations (which is reformed as $r = 4.88 \times 10^2 p(\text{total}) d^2$) between r and d in eq. (3.19) and between r and d^* in eq. (3.23) are plotted as a function of the cooling time scale at $p(\text{total})=10^{-5}$ and 10^{-3} atm in Figs. 3.3a and b, respectively. There can be seen a crossover between two lines in both figures. On the left hand side of the crossover point where the line of the maximum thickness is placed lower than that of eq.(3.19), the reaction is completed. On the other hand, the reaction is not completed on the right hand of the crossover point. As a result, the FeS formation reaction can be treated as a near-equilibrium process when the cooling time scale τ is less than 10^{11} s at $p(\text{total})=10^{-5}$ atm and $10^{7.5}$ s at $p(\text{total})=10^{-3}$ atm. On the other hand, the larger cooling time scale brings the larger deviation from the equilibrium. For example, in the case of $\tau=10^8$ s at $p(\text{total})=10^{-3}$ atm and $\tau=10^{12}$ s at $p(\text{total})=10^{-5}$ atm, both nearly have the same value, $S/\text{Fe}=0.08$. This can be obtained from the relation of $A(\text{S})/A(\text{Fe})=0.38[\{1+3.2/(5 p(\text{total}) \tau^{1/2})\}^3-1]$. That is to say, the paradoxically result can be obtained that the slower cooling (large τ) becomes larger from the deviation from equilibrium because the grain size of metallic iron is approximately linear function of τ , while the FeS formation reaction rate is linear to $\tau^{1/2}$.

3.4.2 A case of decreasing $p(\text{S}_2)$

In this section, the FeS formation reaction accompanying the depletion of sulfur from the gas by the reaction phase is discussed. Now, $A(S)$ changes by the depletion of the sulfur from the gas phase due to the proceeding of the FeS formation reaction, and is given by

$$A(S) = 5.15 \times 10^5 \cdot \left[\frac{4\pi r^3 \rho_{\text{FeS}} N_A N}{3M_{\text{FeS}}} \left(\left(1 + \frac{\Delta d}{r} \right)^3 - 1 \right) \right] \quad (3.24)$$

Δd is the FeS thickness determined by one step in a certain duration. Substituting eq. (3.24) into eq. (3.11), the $p(S_2)$ can be calculated as a function of Δd . By giving initial and step values of Δd , the calculation of FeS layer formation due to proceeding of the reaction can be made, by repeating this procedure. The representative values by the calculation with the step number of one thousand are given in TABLE 3.1. The FeS layers in the present case are thinner than those in the case of the constant $p(S_2)$ in section 4.1. However, the change is less than fifty percent in the range of the cooling time scale of $10^6 \sim 10^{12}$ s (TABLE 3.1). Therefore, the plot of r vs. d as a function of the cooling time scale in a logarithmic scale appears almost as the same as Fig. 3.3 for the case of the constant $p(S_2)$.

3.4.3 A case of a certain saturation temperature in the cooling nebula

In the above discussion, it is postulated that the cooling obeys eq.(3.15), and temperature approaches to zero K when the time passes. In the present section, the case that temperature approaches to a certain temperature T_s is treated.

Then the cooling time scale τ is defined by

$$\tau = \left| \frac{d \ln(T - T_s)}{dt} \right|_{T=T_s}^{-1}, \quad (3.25)$$

where T_e and T_s are the reaction starting temperature and the saturation temperature, respectively. It is obvious that $T_s = 0$ is equivalent to the case in section 3.4.1. The cooling path defined here is naturally different from the cooling path defined in eq.(3.15) even when both τ' and τ are the same value. Therefore, the grain size of metallic iron given by τ (Kozasa and Hasegawa, 1987) is different from the size determined by τ' when $\tau = \tau'$. However, since the difference in the grain size can be considered to be small, we assume that both the grain sizes of the metallic iron determined by τ and τ' are similar with each other in the following discussion. The integration of eq.(3.16) under the condition of eq.(3.25) yields

$$d^n \approx \left[\frac{T_e}{T_e - T_s} \frac{k(T_e) R T_e \tau'}{E} \right]^{1/2}, \quad (3.26)$$

where d^n is the FeS thickness in the present case. As can be understood from this equation, $[T_e/(T_e - T_s)]^{1/2}$ is an increasing factor of the reaction degree. The values (e.g., 1.9 at $T_s = 500$ K, 1.5 at 400 K and 1.3 at 300 K) are dependent upon the saturation temperature, and must be higher in the inner region in the solar nebula near to the sun. Therefore, the reaction degree is expected to become higher, and the condition for the reaction completion becomes wider when the heliocentric distance is smaller from the sun. However, according to the recent dynamical evolution model in the primordial solar nebula (Hayashi et al., 1985), the equilibrium temperature in the nebula has been mainly determined by the radiation, and is a few hundred K. From this relationship, the value of $[T_e/(T_e - T_s)]^{1/2}$ is roughly estimated to be only a few at most. Therefore, the degree of increasing the value is not so large, and the results are not almost changed as in the former section 3.4.1 and 3.4.2.

3.4.4 S/Fe fractionation in the primordial solar nebula

It was clarified that the FeS formation reaction between metallic iron and FeS gas has sufficiently occurred or can be nearly treated as an equilibrium in the preceding discussions. Contrastively, the S/Fe variation in chondrites is large (0.12-0.55, Dodd, 1981) (the horizontal axis in Fig. 2.12), and S/Fe ratios in chondrites except CI are all depleted from the solar ratio.

Two possibilities to bring about the variation of S/Fe depleted from the solar value can be also inferred from this; (1) *difference of the reaction degree*, (2) *vaporization of sulfur*.

(1) *difference of the reaction degree*:

Though the reaction completed region where the reaction occurs as an equilibrium is large as seen in Fig. 3.3, the region where the reaction does not complete still exists in the probable cooling time scale. Therefore, such a difference in the cooling time scale can be explained only by the difference of the reaction degree.

(2) *vaporization of sulfur*:

If we assume the reaction as an equilibrium by taking the probable cooling time scale of $10^8 - 10^{10}$ s (Watanabe and Nakagawa, 1988) and the probable total pressure of the solar nebula of $10^{-5} - 10^{-7}$ atm at 3 AU (Wood and Morfill, 1988), the reaction is completed. Therefore, the behavior in S/Fe variation seen in chondrites can not be obtained only by such a equilibrium condensation process. In this case, the evaporation process of sulfur might play an important role in the fractionation since sulfur is a volatile element. The incongruent evaporation of sulfur from iron-sulfide crystal by Tsuchiyama (1993) supports the evaporation of sulfur. If this is the case, S/Fe variation seen in chondrites can be explained.

In the considerations bringing about S/Fe variation, the three possibilities discussed in 2.6.2 in (1) *reaction between heterogeneous nucleated forsterite and Si-rich gas* and (2) *metastable direct condensation of enstatite*, are not described in the above

discussions. The surface energy difference between metallic iron and silicates can be considered to be large, therefore the heterogeneous nucleation is difficult to occur. That is why, the possibility ((1) in 2.6.2) was excluded. The metastable condensation of FeS has been considered to be difficult to occur (Kozasa and Hasegawa, 1988), therefore, this ((2) in 2.6.2) was not taken into account. As already described, sulfur left behind in the gas phase without forming FeS can be expected not to condense at least in the inner region in the solar nebula due to the thermochemical instability. Therefore, the condensation of sulfur component after fractional condensation was not also taken into account ((3) *accretion of mixtures of forsterite and felsic minerals* in 2.6.2).

On the other hand, in 2.6.2, the degree of reaction ((1) in 3.4.4) was not taken into account. This is of course due to the maximum fractional condensation over the wide range of the probable cooling time scale. The reason why the evaporation of sulfur is only taken into account and the evaporation of silicon has not taken into account (in 2.6.2) are due to the highly volatility of sulfur rather than silicon.

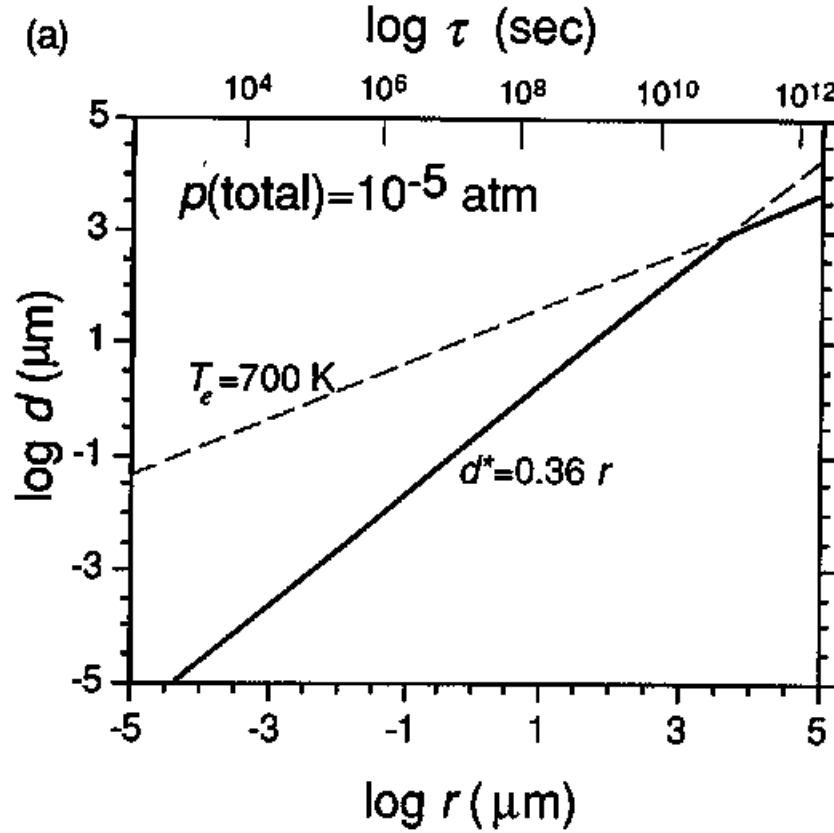


Fig. 3.3a. Reaction degree of the FeS formation between metallic iron and H_2S gas in the case of constant $p(\text{S}_2)$ condition. The thickness of FeS d obtained by the present calculation and the grain size of metallic iron r obtained from the nucleation and growth theory by Kozasa and Hasegawa (1987) are shown as a function of the cooling time scale of the solar nebula τ . T_e = equilibrium temperature where the FeS formation reaction starts, 700 K; d^* = thickness due to the reaction completion (maximum thickness) under the solar composition ($0.36 r$). $p(\text{total}) = 10^{-5}$ atm. In the cooling below about $\tau = 10^{11}$ sec, the reaction is completed.

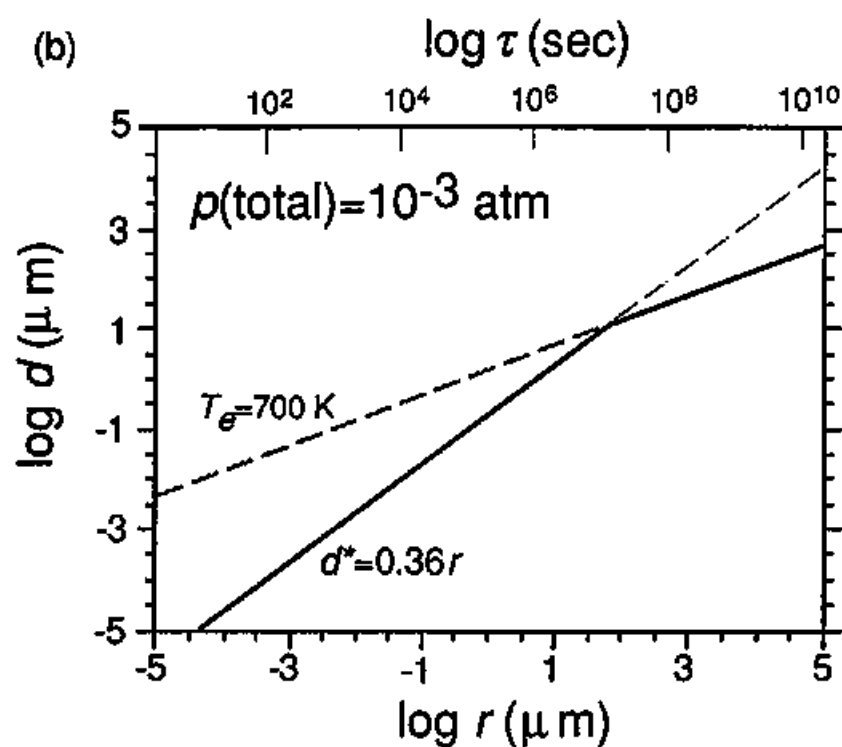


Fig. 3.3b. See the caption of Fig. 3.3a. $p(\text{total}) = 10^{-3} \text{ atm}$. In the cooling below about $\tau = 10^{7.5} \text{ sec}$, the reaction is completed.

TABLE 3.1

FeS thickness due to the reaction between metallic iron and H_2S gas in the cooling solar nebula condition in the case of the decreasing $p(S_2)$ condition

	cooling time scale:			
	τ (sec)	10^6	10^8	10^{10}
$p(\text{total})=10^{-5}$ atm	d (μm) (d in constant $p(S_2)$)	1.8×10^{-2} (1.8×10^{-2})	1.8 (1.8)	1.4×10^2 (1.8×10^2)
				2.0×10^3 (3.2×10^3)
$p(\text{total})=10^{-3}$ atm	d (μm) (d in constant $p(S_2)$)	1.4 (1.8)	20.2 (32)	2.3×10^2 (3.2×10^2)
				3.6×10^3 (3.2×10^3)

3.5. Conclusion

The Fe-S-H phase diagram was constructed by the thermochemical calculation. It was shown that the proximity to the H-S tie line of the peritectic line between metallic iron vaporous and troilite vaporous brings about the extremely small FeS formation through direct condensation from the gas in the case of the maximum fractional condensation. Therefore the FeS formation reaction between metallic iron and H₂S gas plays extremely important role in the following processes such as accretion of planets and chondrite formation. The application to the condensation of FeS formation reaction between metallic iron and H₂S gas in the solar nebula condition showed that the reaction sufficiently happens in the probable cooling time scale.

4. Summary

(1) Mg-Si-O-H system

(1-1) It was pointed out that the peritectic enstatite formation reaction between forsterite and Si-rich gas greatly affects the amount of minerals and mineral species from the phase diagram by the Grossman's equilibrium condensation theory (1972).

(1-2) The rate of the peritectic reaction by the reaction between forsterite and Si-rich gas to form enstatite was determined by the new technique called the double capsule technique. The reaction is controlled by diffusion of elements in the enstatite layer, and the parabolic rate constant is given by $k(\text{cm}^2/\text{s}) = 4.3 \times 10^3 \exp(-505(\text{kJ/mol})/RT)$.

(1-3) It was concluded that the enstatite formation reaction between forsterite and Si-rich gas have not almost happened but the maximum fractional condensation have occurred in the cooling solar nebula by combining the rate of the enstatite formation obtained by the experiments with the nucleation growth theory (Kozasa and Hasegawa, 1987).

(2) Fe-S-H system

(2-1) The phase diagram of the Fe-S-H system under the H-rich condition at low pressure was constructed by the thermochemical calculations. It was shown that the peritectic reaction of FeS formation between metallic iron and H_2S gas in the system of Fe-S-H plays an important role in the fractionation due to the proximity of the peritectic line to the one side (H-S tie line) of the phase diagram.

(2-2) The reaction rate in the solar nebula condition was determined by extrapolating the corrosion rate of metallic iron by Fryt et al. (1979a; 1979b) to the low $p(\text{S}_2)$ condition. The

parabolic rate constant in the solar nebula condition is given by $k(\text{cm}^2/\text{s})=0.3\exp(-146(\text{kJ/mol})/RT)$.

(2-3) As the same manner in the Mg-Si-O-H system, the degree of the FeS formation in the cooling solar nebula was estimated by using the grain size of metallic iron by the Kozasa and Hasegawa's nucleation theory. And it was concluded that the reaction sufficiently occurs or can be nearly treated as an equilibrium depending upon the cooling time scale of the nebula.

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