SULFIDATION OF METALLIC IRON IN THE PRIMORDIAL SOLAR NEBULA

Naoya Imae[1] and Masao Kitamura[2]

[1]*Division of Environmental Science, Graduate School of Science and Technology,*
Kobe University, Nada-ku, Kobe 657
[2]*Department of Geology and Mineralogy, Faculty of Science, Kyoto University,*
Sakyo-ku, Kyoto 606

Abstract: The phase diagram of the Fe-S-H system was constructed based on thermochemical calculations at low total pressure (p(total)=$p(H_2)$=10^{-5} and 10^{-3} atm). Under these conditions both metallic iron and troilite, and troilite and pyrite are in reaction relation over a wide range of the phase diagram. The most important characteristic of the phase diagram is that the peritectic line is highly proximate to the H-S tie line. Based on the reaction relation 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 rate is controlled by diffusion in a FeS layer and the parabolic rate constant, k, is approximately given by k (cm^2/s)=0.3 exp(-3.5×10^4 (cal/mol)/RT) in the solar nebula condition. The reaction degree was estimated based on various conditions of the cooling solar nebula: (1) contant $p(S_2)$, (2) decreasing $p(S_2)$ and (3) a certain saturation temperature above 0 K, when the grain size of metallic iron was controlled by homogeneous nucleation theory.

1. Introduction

The Mg-Fe-Si-S-O-H system includes the most abundant elements in the solar system except N and C, and is especially important to study chemical evolutions of minerals in the solar nebula. The phase relations and the condensation sequence in such a simple system helps the understanding of the condensation and evaporation processes of various components, not only solar gas. According to thermodynamical calculations at high temperature (GROSSMAN, 1972), the condensation of Mg-Si-O-H and Fe-S-H can be treated nearly independently. The phase diagram in the Mg-Si-O-H system under hydrogen-rich conditions at low pressure has been constructed by TSUCHIYAMA (1990), and the experimental study of the solid-gas reaction in the system, which is enstatite formation between forsterite and Si-rich gas, has also been done (IMAE *et al.*, 1993).

According to LEWIS (1972), the first condensate in the Fe-S-H system is metallic iron; with further cooling, metallic iron reacts with H_2S gas to form FeS. 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 (TSUCHIYAMA, 1990). If this is the case, the degree of the reaction between metallic iron and H_2S gas affects the amount and the kind of minerals.

The problem as to whether the reaction is complete or not is important in estimating the S/Fe ratio in planets and/or asteroids as the accretionary product of solid grains. If the reaction is not completed in the solar nebula, a large amount of sulfur must remain as H_2S gas. The incomplete reaction must, therefore, result in depletion of sulfur in planets and asteroids.

For example, the S/Fe ratios of chondrites except CI are smaller than the solar ratio, and shows a large variation from 0.12–0.55 (e. g., DODD, 1981). The large S/Fe variation can be explained by a condensation process during the chondrite formation and/or an evaporation process before the chondrite formation. Reaction rims of troilite surrounding metallic iron have been found in some chondrites (IMAE, 1994). This texture suggests that sulfidation of metallic grain with S-rich gas actually occurred in some cases of chondrite formation. If the sulfidation of metallic grain with S-rich gas occurred under near equilibrium conditions, the large S/Fe variation among chondrites cannot be explained only by the condensation process. In this case, the variation can be explained by escape of sulfur due to the incongruent vaporization of pyrrhotite (TSUCHIYAMA et al., 1993) and/or by melting during chondrule formation. In contrast, if the sulfidation of metallic grain with S-rich gas occurred with different degrees among chondrites, the S/Fe variation can be explained only by the condensation process. It is therefore indispensable for explaining the S/Fe variation to determine the reaction degree of the FeS formation in the condensation process.
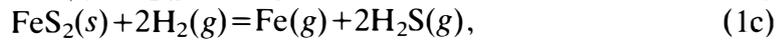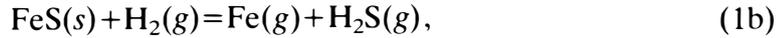
FEGLEY and PRINN (1989) first discussed the FeS formation reaction between metallic iron and H_2S gas in the primordial solar nebula, assuming that the grain size of metallic iron is 0.1 μm, that the reaction degree is determined by the collision frequency of H_2S gas on the grain surface of metallic iron, and that the reaction proceeds under constant temperature (687 K). Under these assumptions, they estimated the time scale of troilite formation, and concluded that the FeS formation reaction is kinetically favorable within the lifetime of the solar nebula. An experimental study to determine the kinetics of the troilite formation reaction near the solar nebula condition has also been in progress (LAURETTA and FEGLEY, 1994a, b).

In the present paper, the phase diagram in the Fe-S-H system in hydrogen- rich conditions was first constructed to quantitatively reveal the importance of the reaction kinetics of FeS formation reaction between metallic iron and H_2S gas. The degree of the FeS formation between metallic iron and H_2S gas in the primordial solar nebula was then estimated under the following assumptions: (1) The grain size of metallic iron is given by homogeneous nucleation and growth (KOZASA and HASEGAWA, 1987), (2) the reaction rate is assumed to be controlled not by the reaction at the surface of a grain but by diffusion in a FeS layer (FRYT et al., 1979a, b), and (3) the FeS formation reaction occurred during the cooling of the primordial solar nebula.

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 in obtaining phase relations is essentially the same as applied to

the thermochemical calculations of the condensation sequence from the solar gas to the solar nebula by GROSSMAN (1972). A phase boundary between coexisting solid and gas, which is called vaporous, can be acquired from the equation $\Delta G^0 = -RT \ln K$, where ΔG^0 is the standard free energy change in the reaction, K an equilibrium constant, R gas constant and T absolute temperature. Metallic iron (Fe), troilite (FeS) and pyrite (FeS$_2$) are taken into account as the condensation species. The reactions among the species are expressed as

$$\text{Fe}(s) = \text{Fe}(g), \tag{1a}$$
$$\text{FeS}(s) + \text{H}_2(g) = \text{Fe}(g) + \text{H}_2\text{S}(g), \tag{1b}$$
$$\text{FeS}_2(s) + 2\text{H}_2(g) = \text{Fe}(g) + 2\text{H}_2\text{S}(g), \tag{1c}$$

where (s) and (g) denote solid and gas, respectively. And the reaction constants of the above reactions (eqs. 1a~1c) are

$$K_1 = p(\text{Fe}) / a(\text{Fe}), \tag{2a}$$
$$K_2 = p(\text{Fe})\, p(\text{H}_2\text{S}) / a(\text{FeS})\, p(\text{H}_2), \tag{2b}$$
$$K_3 = p(\text{Fe})\, p(\text{H}_2\text{S})^2 / a(\text{FeS}_2)\, p(\text{H}_2)^2, \tag{2c}$$

respectively, where a is activity and p partial pressure. Since metallic iron, troilite and pyrite do not form a solid solution, $a(\text{Fe})$, $a(\text{FeS})$ and $a(\text{FeS}_2)$ are equal to unity, respectively. FeS forms a solid solution due to the large 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 a 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, x and y, K_1, K_2 and K_3 are then expressed as

$$K_1 = 2\, x\, p(\text{total}), \tag{3a}$$
$$K_2 = 4\, x\, y\, p(\text{total}), \tag{3b}$$
$$K_3 = 8\, x\, y^2\, p(\text{total}). \tag{3c}$$

On the other hand, these reaction constants (eq. (3a)–(3c)) can be expressed as functions of temperature based on thermochemical data (JANAF, 1985) such as

$$K_1 = 10^{(7.6 - 21581/T)}, \tag{4a}$$
$$K_2 = 10^{(8.3 - 25191/T)}, \tag{4b}$$
$$K_3 = 10^{(13.6 - 28605/T)}. \tag{4c}$$

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

$$\log y = 0.17 \log x - 0.17 \log p(\text{total}) - 0.82, \tag{5a}$$
$$\log y = 0.16 \log x + 0.16 \log p(\text{total}) - 4.58, \tag{5b}$$

respectively.

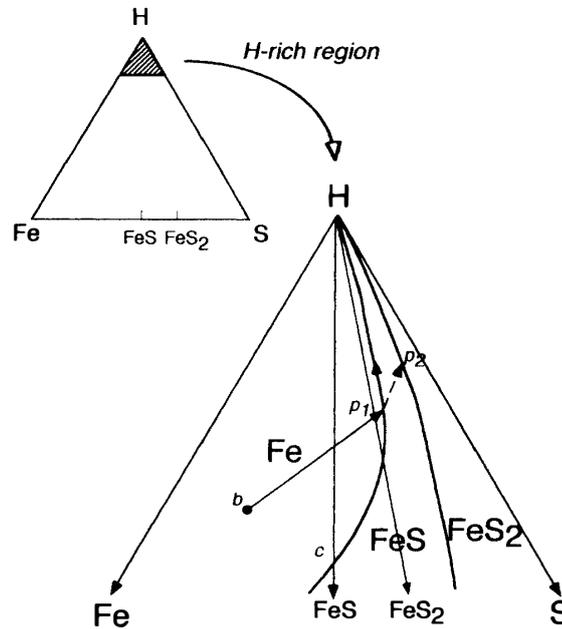Then, we can construct the phase diagram of the system from these equations

Fig. 1. Schematic drawing of the phase diagram in the ternary Fe-S-H system.
Three vaporous are shown as Fe = metallic iron, FeS = troilite and FeS₂
= pyrite. Two thick lines between vaporous represent cotectic lines. The
path of the gases due to condensation is indicated by arrows. log x =
−1.99 at p(total) = 10⁻⁵ atm and log x = −1.59 at p(total) = 10⁻³ atm are
satisfied at point c where the boundary between the eutectic and peritectic
relations 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; p₁ = peritectic point
where troilite formation starts (700 K); p₂ = peritectic point where pyrite
formation starts (347 K).

(eqs. (3a)∼(4c)). The H-rich part of the phase diagram of the ternary system
(Fe-S-H) is shown only schematically in Fig. 1, because the cotectic lines between
metallic iron and troilite, and troilite and pyrite, are very close to the H-S tie line
(eqs. (5a) and (5b)) and could not be drawn in their proper positions.

The phase boundaries between metallic iron and troilite, and between troilite
and pyrite, are peritectic, except for the region $\log x > -1.99$ at p(total)$=10^{-5}$ atm
and $\log x > -1.59$ at p(total)$=10^{-3}$ atm where they change to eutectic. 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 in H-free
conditions. In addition, note that in such an H-rich region, sulfur does not condense
due to the thermodynamical instability.

As a quantitative diagram instead of the schematic drawing in Fig. 1, the phase
diagram is represented by introducing the logarithmic scales of S/H and Fe/H ratios
(Figs. 2a and b). Since the phase diagram calculated in the present study is correct
only in the region where both $x \ll 1$ and $y \ll 1$, the phase diagram was shown only in
that region by taking log (Fe/H) and log (S/H) as the axes in Fig. 2. In Fig. 2, the
cotectic lines are expressed by straight lines different from Fig. 1. Only the phase
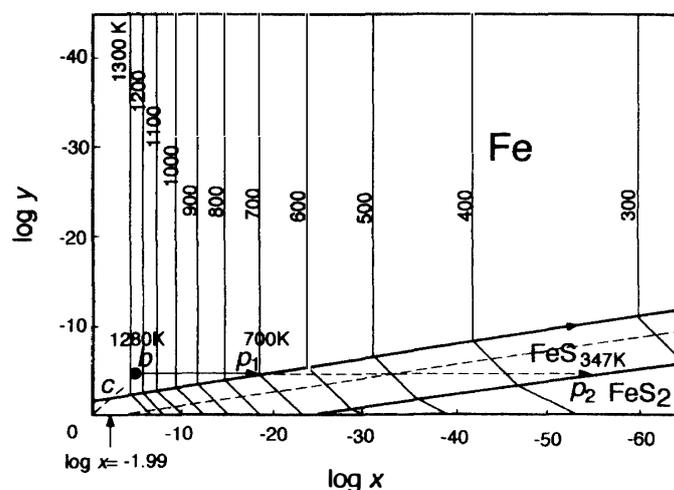
Fig. 2a. Fe-S-H phase diagram. The graph is shown as a logarithmic plot. The dotted line is the peritectic line where metallic iron and pyrite coexist metastably. Condensation paths are comparable to those in Fig. 1. b = bulk component; p_1 = peritectic point where troilite formation starts (700 K); p_2 = peritectic point where pyrite formation starts (347 K); c = the boundary between eutectic and peritectic relations; Fe = metallic iron; FeS = troilite; FeS_2 = pyrite. p(total) = 10^{-5} atm.
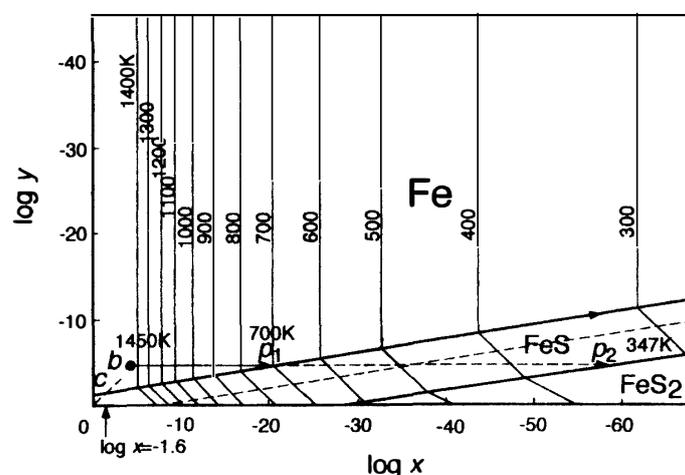

Fig. 2b. See the caption of Fig. 2a. p(total) = 10^{-3} atm.

diagram for the case p(total)$=10^{-5}$ atm (Figs. 1 and 2a) will be explained in detail in the following discussion, because the character of the diagram of p(total)$=10^{-3}$ atm in Fig. 2b is essentially the same as Fig. 2a.

When we consider the cooling of the solar composition gas, b ($x = 3 \times 10^{-5}$, $y = 2 \times 10^{-5}$), in Fig. 1 and Fig. 2a, the first condensate (the condensation temperature is 1280 K) is metallic iron, which has an extremely wide vaporous region. As the cooling continues, the gas changes its composition by condensing metallic iron toward p_1 ($x=10^{-18}$, $y=2\times10^{-5}$) at 700 K on the peritectic line between metallic iron and troilite. In Fig. 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, since almost all Fe in the gases has already been consumed as metallic iron, a little amount of troilite can condense and the S content in the gas phase does not change significantly. Then, in the maximum fractionation, the gas composition changes almost parallel to the horizontal axis from p_1 to p_2 in Fig. 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 iron changes depending upon the total pressure (Figs. 2a and b). On the other hand, the temperature where the FeS formation reaction starts is the same in spite of the change of total pressure since condensation of metallic iron does not change the S/H ratio in the gas. Furthermore, the essential characteristics of the reaction relation such as the proximity of reaction lines to the H-S tie line are unchanged between Figs. 2a and 2b. A large amount of troilite is therefore formed by the reaction in equilibrium condensation in the range of the total pressure of 10^{-5} and 10^{-3} atm. On the other hand, only an extremely small amount of troilite is formed in maximum fractional condensation. Thus the degree of the troilite formation reaction between metallic iron and H_2S gas greatly influences the amount of minerals and the mineral species as final products.

3. FeS Formation Reaction Rate Between Metallic Iron and H_2S Gas in the Solar Nebula Condition

Experiments on the FeS formation reaction between metallic iron and H_2S gas have been carried out under H_2S and H_2 gas flow by FRYT *et al.* (1979a, b). According to these experiments, polycrystalline FeS layers grow around metallic iron. This reaction is controlled by outer diffusion of Fe in the FeS layer from an Fe-FeS interface toward an FeS-gas interface. Iron sulfides formed in this experiment are nonstoichiometric ($Fe_{1-\delta}S$, pyrrhotite). When sufficient equilibration occurs between pyrrhotite and metallic iron, the pyrrhotite changes to troilite. In the following discussion, pyrrhotite and troilite are described as FeS for simplicity.

The reaction rates obtained in the experiments (FRYT *et al.*, 1979a, b) 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 $p(S_2)$ pressure region than in the primordial solar nebula condition. Then we extrapolated the data to the solar nebula condition at extremely low $p(S_2)$ as follows.

The reaction rate k (cm^2/s) is expressed (FRYT *et al.*, 1979b) as the product of the chemical diffusion coefficient, $D=6.7\times10^{-2}\exp(-2.09\times10^4/RT)$, and the deviation from the stoichiometry of FeS, $\delta=p(S_2)^{1/2}\exp-((-3.12\times10^4+19.98T+4\delta(2-\delta)$

$(7.9 \times 10^3 + 4T))/RT$), where R is the gas constant (1.987 cal mol^{-1} K^{-1}). Thus, $k = D\delta$ is a function of T, $p(S_2)$ and δ. An approximation to cancel δ can be made by using the relation:

$$\left[\frac{d \ln \delta}{d \ln p(S_2)} \right]_{T, \delta \approx 0} = \frac{1}{2}, \tag{6}$$

which is valid in the low sulfur partial pressure region ($p(S_2) < 10^{-8}$ atm, $\delta < 0.009$) (FRYT et al., 1979b). When eq. (6) is integrated by taking the initial condition $\delta = 0$ at the Fe-FeS interface and making use of the experimental data (FRYT et al., 1979b), δ can be expressed as a function of $p(S_2)$ and T:

$$\delta = p(S_2)^{1/2} \exp(20.1 - 1.5 \times 10^{-2}/T). \tag{7}$$

Substituting eq. (7) into the relation $k = D\delta$, k is expressed as a function of only $p(S_2)$ and T as

$$k = 6.7 \times 10^{-2} p(S_2)^{1/2} \exp\left(\frac{-1.5 \times 10^{-2} RT^2 + 20.1 RT - 2.09 \times 10^4}{RT} \right). \tag{8}$$

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

$$2H_2S(g) = 2H_2(g) + S_2(g), \tag{9}$$
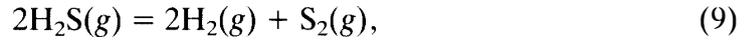
and the equilibrium constant of the reaction, K, is expressed by using the data of JANAF (1985) as

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

Thus, $p(S_2)$ under the hydrogen-rich condition can be expressed by using eq. (10) and the elemental abundances of sulfur $A(S)$ and hydrogen $A(H)$ as

$$p(S_2) = \left[2\frac{A(S)}{A(H)} \right]^2 10^{(4.97 - 9.2 \times 10^3/T)}. \tag{11}$$

Now since $A(H)/A(S) = 5.3 \times 10^4$ in the solar gas composition, then $p(S_2)$ is obtained from eq. (11):

$$p(S_2) = 1.43 \times 10^{(-4.03 - 9.2 \times 10^3/T)}. \tag{12}$$

Hence, substituting eq. (12) into eq. (8), k is expressed as

$$k = 4.3 \times 10^5 \exp\left(- \frac{4.2 \times 10^4}{RT} - 1.5 \times 10^{-2} T \right). \tag{13}$$

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

The experimental study of troilite formation kinetics under the solar nebula condition has been carried out directly to determine the rate (LAURETTA and FEGLEY, 1994a, b). The FeS formation rate obtained in the present study is a few times larger
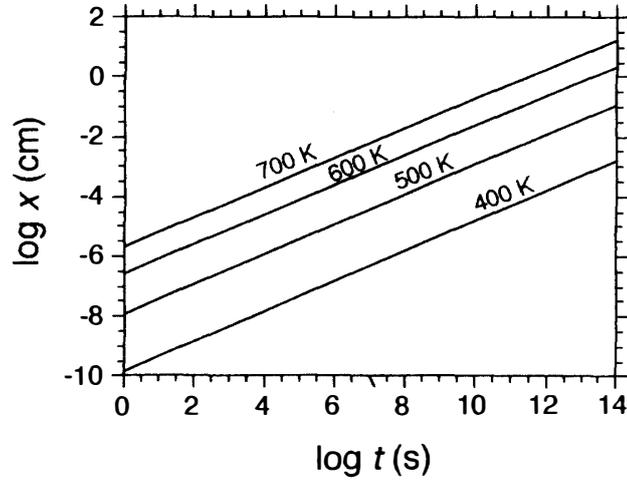
Fig. 3.   Relationship between the thickness of the FeS reaction layer x and time t at different temperatures (400–700 K) calculated from the rate constant under the solar nebula condition.

than the rate found by Lauretta and Fegley (1994a, b), while the order of the reaction rate is about the same.

Since the reaction is controlled by diffusion through the FeS layer, the layer thickness can be obtained from the relation $x^2 = kt$ (parabolic rate law) at a constant temperature using this rate of k under the solar nebula condition, where x is the thickness of FeS and t is the time (Fig. 3).

4.   FeS Formation Reaction in the Cooling Primordial Solar Nebula

In the cooling of the solar gas in the Fe-S-H system, metallic iron condenses first. 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, of metallic iron is approximately expressed as

$$r = 5 \times 10^{-3} \, p\,(\text{total}) \, \tau \,(\mu\text{m}),\qquad(14)$$

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

$$\tau = \left| \frac{d \ln T}{d t} \right|^{-1}\qquad(15)$$

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 H_2S gas to form FeS from this equilibrium temperature because of the 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 for three cases. The first (Section 4.1) is the case of constant $p(S_2)$, which is approximately maintained due to the contraction of the primordial solar nebula. The second (Section 4.2) is the case of decreasing $p(S_2)$, which is caused by the FeS formation reaction in

the primordial solar nebula with constant volume. And the third (Section 4.3) is that the nebula cools a certain temperature. This takes into account that the nebula might have approached various temperatures depending upon the heliocentric distance.

4.1. The case of constant $p(S_2)$

Since $p(S_2)$ is assumed to be constant throughout the reaction, k is only a function of temperature. Under the isobaric cooling to zero K at p(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:

$$d = \left[\int_0^\infty k(T)\, dt \right]^{1/2},$$
(16)

where $T=T_e$ at $t=0$ and $T=0$ at infinite. The cooling is assumed to obey eq. (15). In order to obtain the analytical result of the integration, the reaction constant k given by eq. (13), was approximated as a function that $\ln K$ changes linearly with $1/T$ below or around 700 K as:

$$k = 0.3 \exp(-3.5 \times 10^4 \text{ (cal/mol)}/RT).$$
(17)

Hence, by the integration of eq. (16) by using eq. (17), d (μm) is derived only as a function of τ:

$$d = 3.2 \times 10^{-3}\ \tau^{1/2}.$$
(18)

Then we can estimate the reaction degree d/r as a function of the cooling time scale from eqs. (14) and (18) as:

$$d/r = 0.64\, p\,(\text{total})^{-1}\tau^{-1/2}.$$
(19)

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

$$\frac{\rho_{FeS}\, \Delta V\, N_A\, N}{M_{FeS}} = A(\text{S})^{SA},$$
(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 is completed, N_A Avogadro's number, N grain density normalized to solar abundance, M_{FeS} atomic weight of troilite and $A(\text{S})^{SA}$ 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 reaction experiments where the layer overgrew around the metallic iron with 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 the iron is included in the solid grain before the FeS formation reaction, the relation:

$$\frac{4\ \pi r^3\ \rho_{Fe}\, N_A\, N}{3\ M_{Fe}} = A(\text{Fe})^{SA},$$
(21)

holds, where ρ_{Fe} is the density of metallic iron (7.87 g/cm^3), M_{Fe} the atomic weight of iron and $A(Fe)_{SA}$ the abundance of iron, 9×10^5 (Anders and Ebihara, 1982). Thus N can be obtained as a function of r from eq. (21):

$$N = 2.53\times10^{-18} / r^3. \qquad (22)$$

By substituting eq. (22) into eq. (20), the reaction degree in the maximum thickness becomes

$$d^* / r = 0.36. \qquad (23)$$

Two lines representing the relations (reformed as $r = 4.88\times10^2 \, p(total) \, d^2$) between r and d in eq. (19) and between r and d^* in eq. (23) are plotted as a function of the cooling time scale at $p(total)=10^{-5}$ and 10^{-3} atm in Figs. 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 maximum thickness is placed lower than that of eq. (19), the reaction is completed. On the other hand, the reaction is not completed on the right side 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 $p(total)=10^{-5}$ atm and $10^{7.5}$ s at $p(total)=10^{-3}$ atm. On the other hand, the larger cooling time scale brings larger deviation from equilibrium. For example, in the case of $\tau=10^8$ s at $p(total)=10^{-3}$ atm and $\tau=10^{12}$ s at $p(total)=10^{-5}$ atm, both nearly have the same value, S/Fe$=0.08$. This can be obtained from the relation $A(S)/A(Fe)=0.38[\{1+3.2/(5\,p(total)\,\tau^{1/2})\}^3-1]$. That is to say, the paradoxical result can be obtained that slower cooling (large τ) deviates more from equilibrium because the grain size of metallic iron is approximately a linear function in τ, while the FeS formation reaction rate is linear to $\tau^{1/2}$.

4.2. The case of decreasing $p(S_2)$

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

$$A(S)=5.15\times10^5 - \left[\frac{4\pi r^3 \rho_{FeS} N_A N}{3M_{FeS}}\left\{\left(1+\frac{\Delta d}{r}\right)^3 -1\right\}\right], \qquad (24)$$

where Δd is a fraction of FeS thickness given by d^*/l, where l is number of steps in the calculation and was taken to be 1000. Substituting eq. (24) into eq. (11), $p(S_2)$ can be calculated as a function of Δd. By giving initial and step values of Δd, FeS layer formation due to the reaction can be calculated, by repeating this procedure. The representative values by calculation are given in Table 1. The FeS layers in the present case are thinner than those in the case of 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 10^6–10^{12} s (Table 1). Therefore, the plot of r vs. d as a function of the cooling time scale on a logarithmic scale appears almost as the same as Fig. 4 for the case of constant $p(S_2)$.
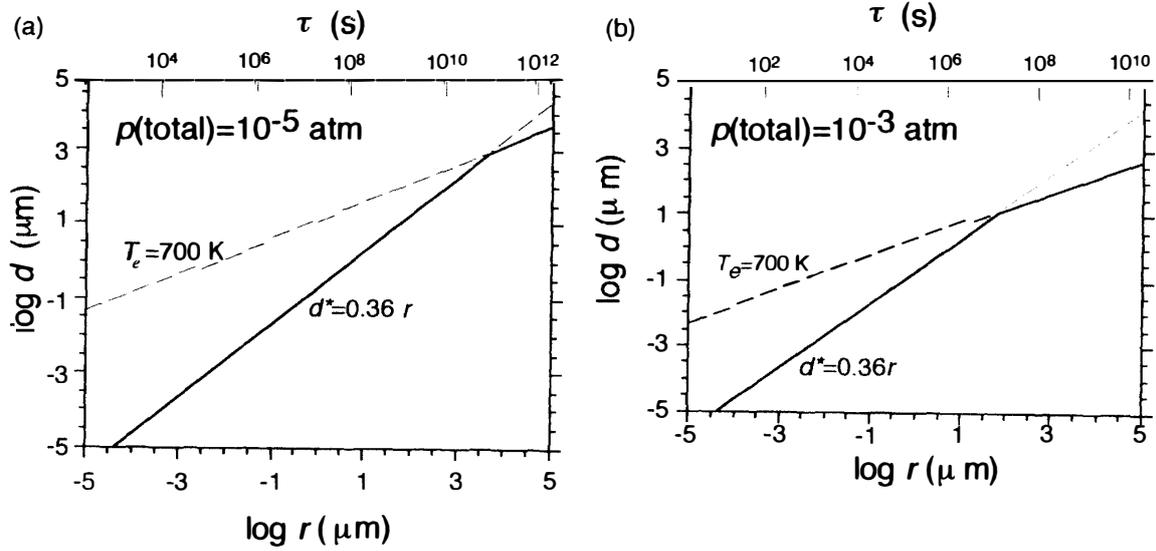
Fig. 4a. Reaction degree of the FeS formation between metallic iron and H_2S gas in the case of a constant $p(S_2)$ condition. The thickness of FeS d obtained by the present calculation and the grain size of metallic iron r obtained from the nucleation and growth theory by KOZASA and HASEGAWA (1987) 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 reaction completion (maximum thickness) under the solar composition (0.36 r). $p(total) = 10^{-5}$ atm. In cooling below about $\tau = 10^{11}$ s, the reaction is completed.

Fig. 4b. See the caption of Fig. 4a. $p(total) = 10^{-3}$ atm. In cooling below about $\tau = 10^{7.5}$ s, the reaction is completed.

Table 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: $\tau(s)$	10^6	10^8	10^{10}	10^{12}
$p(total)=10^{-5}$ atm	$d(\mu m)$	1.8×10^{-2}	1.8	1.4×10^2	2.0×10^3
	(d in constant $p(S_2)$)	(1.8×10^{-2})	(1.8)	(1.8×10^2)	(3.2×10^3)
$p(total)=10^{-3}$ atm	$d(\mu m)$	1.4	20.2	2.3×10^2	3.6×10^3
	(d in constant $p(S_2)$)	(1.8)	(32)	(3.2×10^2)	(3.2×10^3)

4.3. The case of a certain saturation temperature in the cooling nebula

In the above discussion, it is postulated that the cooling obeys eq. (15), and temperature approaches zero K with time. In the present section, the case in which temperature approaches a certain temperature T_s is treated.

The cooling time scale, τ', is defined by

$$\tau' = \left| \frac{d \ln (T - T_s)}{d t} \right|^{-1}_{T=T_e},$$ (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 4.1. The cooling path defined here is naturally different from the cooling path defined in eq. (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 to each other in the following discussion. Integration of eq. (16) under the condition of eq. (25) yields

$$d' \cong \left[\frac{T_e}{T_e-T_s} \frac{k(T_e) RT_e \tau'}{E} \right]^{1/2},\qquad(26)$$

where d' 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 reaction completion becomes wider when the distance from the sun is smaller. However, according to a 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 less than ten at most. The magnitude of the value is not therefore so large, and the results are almost unchanged from those in Sections 4.1 and 4.2.

4.4. Concluding remarks

In calculations described in Sections 4.1–4.3, we concluded that significant FeS formation by reaction between metallic iron and H_2S gas in the primordial solar nebula occurs and the reaction is nearly in equilibrium. This conclusion is essentially the same as those obtained by Fegley and Prinn (1989), while the treatments are different from each other.

We have postulated that Fe condensation and subsequent FeS formation are results of cooling from high temperature gas. According to a recent solar nebula dynamical evolutionary model (Morfill et al., 1985) and recent observation of classical T-Tauri stars (Shu et al., 1987), the overall disk of the solar nebula might not necessarily become hot enough to vaporize silicates or metal. Nevertheless, it is possible that at least in the inner region of the solar nebula (within 3 AU) such a high temperature was reached. In such a region the present discussion would apply, and the FeS formation reaction between metallic iron and H_2S gas is considered to have occurred as discussed for three cases in Sections 4.1–4.3.

for helpful suggestions.

References

ANDERS, E. and EBIHARA, M. (1982): Solar-system abundance of the elements. Geochim. Cosmochim. Acta, **46**, 2363–2380.

DODD, R. T. (1981): Meteorites. Cambridge, Cambridge Univ. Press, 368p.

FEGLEY, B., Jr. and PRINN, R. G. (1989): Solar nebula chemistry: Implications for volatiles in the solar system. The Formation and Evolution of Planetary Systems, ed. by WEAVER *et al.* Cambridge, Cambridge Univ. Press, 171–211.

FRYT, E. M., SMELTZER, W. W. and KIRKALDY, J. S. (1979a): Chemical diffusion and point defect properties of iron sulfide ($Fe_{1-\delta}S$) at temperatures 600°–1000°C. J. Electrochem. Soc., **126**, 673–683.

FRYT, E. M., BHIDE, V. S., SMELTZER, W. W. and KIRKALDY, J. S. (1979b): Growth of the iron sulfide ($Fe_{1-\delta}S$) scale on iron at temperatures 600°–1000°C. J. Electrochem. Soc., **126**, 683–688.

GROSSMAN, L. (1972): Condensation in the primitive solar nebula. Geochim. Cosmochim. Acta, **36**, 597–619.

HAYASHI, C., NAKAZAWA, K. and NAKAGAWA, Y. (1985): Formation of the solar system. Protostars and Planets II, ed. by D. C. BLACK and M. S. MATTHEWS. Tucson, Univ. Arizona Press, 1100–1153.

IMAE, N., TSUCHIYAMA, A. and KITAMURA, M. (1993): An experimental study of enstatite formation reaction between forsterite and Si-rich gas. Earth Planet. Sci. Lett., **118**, 21–30.

IMAE, N. (1994): Direct evidence of sulfidation of metallic grain in chondrites. Proc. Jpn. Acad., **70**, Ser. B, No. 9, 133–137.

JANAF Thermochemical Tables, 3rd ed. (1985): J. Phys. Chem. Ref. Data, **14**.

KOZASA, T. and HASEGAWA, H. (1987): Grain formation through nucleation process in astrophysical environments II. Prog. Theor. Phys., **77**, 1402–1410.

LAURETTA, D. S. and FEGLEY, B., Jr. (1994a): Troilite formation kinetics and growth mechanism in the solar nebula. Meteoritics, **29**, 490.

LAURETTA, D. S. and FEGLEY, B., Jr. (1994b): Kinetics and grain growth mechanism for troilite formation on iron metal in H_2-H_2S gas mixtures. Papers Presented to the 19th Symposium on Antarctic Meteorites, May 30–June 1, 1994. Tokyo, Natl Inst. Polar Res., 62–65.

LEWIS, J. S. (1972): Metal/silicate fractionation in the solar system. Earth Planet. Sci. Lett., **15**, 286–290.

MORFILL, G. E., TSCHARNUTER, W. and VÖLK, H. J. (1985): Dynamical and chemical evolution of the protoplanetary nebula. Protostars and Planets II, ed. by D. C. BLACK and M. S. MATTHEWS. Tucson, Univ. Arizona Press, 493–533.

SHU, F. H., ADAMS, F. C. and LIZANO, S. (1987): Star formation in molecular clouds: Observation and theory. Ann. Rev. Astron. Astrophys., **25**, 23–81.

TSUCHIYAMA, A. (1990): Condensation in the primordial solar nebula. Dynamic Process of Material Transport and Transformation in the Earth's Interior, ed. by F. MARUMO, 499–518.

TSUCHIYAMA, A., UEDA, C. and MAKOSHI, Y. (1993): An experimental study of evaporation kinetics of FeS, and its cosmochemical significance. Papers Presented to the 18th Symposium on Antarctic Meteorites, May 31–June 2, 1993. Tokyo, Natl Inst. Polar Res., 121–124.