Incongruent evaporation experiments on iron sulfide (Fe$_{1-e}$S) under H$_2$-rich (at 1 atm) and evacuated conditions

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Evaporation experiments using pyrrhotite single crystals (Fe$_{0.886}$S) were carried out at temperatures between 500 and 1300°C at 1 atm in an H$_2$-CO$_2$ gas flow (0.62–0.64 atm H$_2$), and at 500 and 900°C under an evacuated condition. Under the H$_2$-rich condition, spongy metallic iron layer was formed on the sulfide crystal surface at temperatures below the Fe-FeS eutectic point as a result of incongruent evaporation, and developed inward almost conserving its original shape. The thickness of the iron layer increases linearly with time at constant temperatures (linear rate law) due to transportation of evaporated gas species through pores in the spongy iron layers. If incongruent evaporation is controlled by diffusion of element(s) in an evaporation residue layer, a parabolic rate law is expected. The linear rate law shows that FeS evaporates more efficiently than expected based on a parabolic rate law. The linear rate constant obtained at various temperatures obeys the Arrhenius relation: $k_{FeS} = (1.61 \pm 0.42) \times 10^{-3} \exp(-115 \pm 2 \text{ [kJ/mol]}/RT)$ [m/sec]. A minor part of metallic iron in the surface layer diffused into the inner sulfide to form stoichiometric FeS (troilite) in the early evaporation stage. Thus, the experiments can be almost regarded as evaporation of troilite. Evaporation coefficients of FeS were obtained by comparing the experimental results with calculated rates using the Hertz-Knudsen equation. They are small (1.4 x 10$^{-4}$ – 9.4 x 10$^{-6}$) due to slow surface reaction and/or slow escape of S-bearing gas species into the gas flow. Mass-dependent isotopic fractionation of S by the evaporation was not detected within an error of ±3%o probably due to slow diffusivity of S in the sulfide crystal. In the evacuated experiments, evaporation occurred very slowly due to the absence of H$_2$ gas, which acts as a reducing agent. Iron residue layer was very thin or sometimes not detected probably because the evaporation rate of S from FeS became comparable to the evaporation rate of metallic iron, which can be neglected under the H$_2$-rich condition.

INTRODUCTION

According to the thermochemical calculations applied to the primordial solar nebula (e.g., Grossman and Larimer, 1974), the systems Mg-Si-O-H and Fe-S-H can be regarded as independent reaction systems, and are in cotectic relation with each other at high temperatures. Major elements that constitute the terrestrial planets are Mg, Si, Fe, S and O. It is expected in a general condensation scheme (e.g., Grossman and Larimer, 1974) that forsterite reacted with Si-rich gas to form enstatite, and metallic iron reacted with S-rich gas to form FeS.

In recent models for the formation of the solar nebula, the temperatures of the nebula were not so high that dust was not evaporated completely in a wide region of the nebula (e.g., Boss, 1994). If such dust had moved towards the sun in the nebula, evaporation should occur (Watanabe, personal communication). Enstatite and FeS must have evaporated incongruently to form residues of forsterite and metallic iron, respectively. In this case, the chemical compositions of solid and gas in the nebula were dependent on degrees of the incongruent evaporation reactions, and thus, elemental fractionation can be expected by separation of the solids from the gas. Accordingly, incongruent evaporation are important to understand chemical evolution of the primordial solar nebula as well as solid-gas reaction during condensation.

In the Fe-S-H system, the kinetics of Fe$_{1-e}$S (δ
formation by the reaction of metallic iron with H$_2$S gas has been determined precisely (e.g., Fryt et al., 1979). Based on those data Imae and Kitamura (1995) discussed the degree of the iron-gas reaction in the solar nebula. However, the kinetics of incongruent evaporation of solid FeS, which might be present as interstellar dust, has not been known yet. In the present study, evaporation experiments on Fe$_{0.886}$S were carried out under an H$_2$-rich condition at 1 atm and vacuum condition as a first step to understand evaporation behavior of FeS in the primordial solar nebula.

It has been known in laboratory experiments that isotopic mass fractionations occur during evaporation (e.g., Esat et al., 1986; Davis et al., 1990) and condensation (Uyeda et al., 1991). The isotopic mass fractionation reported in refractory inclusions in considered to be caused by evaporation and/or condensation in the solar nebula. It has been reported that S isotopic mass fractionation occurred in the evaporation experiments of liquid FeS (McEwing et al., 1980). In this study, isotopic mass fractionation of S was also examined for discussing possible isotopic fractionation by incongruent evaporation of solid FeS.

**EXPERIMENTS**

A single crystal of natural pyrrhotite from Chihuahua, Mexico (non-stoichiometric; Fe$_{0.886}$S; Table 1) was used as the starting material. The crystal is chemically homogeneous and free from inclusions under a scanning electron microscope. It is important to use a single crystal as a starting material in the present experiments. If powders are used instead it is hard to evaluate the surface areas and effects of cracks in grains. However, it is difficult to obtain a large single crystal of troilite (stoichiometric FeS) although troilite is common in meteorites as an iron sulfide. Therefore, the pyrrhotite crystal was used instead of troilite.

The crystal was cut into parallelepipeds along crystallographic orientations; about 2.5, 3.5 and 4.5 mm thick nearly parallel to (001), (100) and (120) surfaces (the indices regarded as the hexagonal system are used). Thus, the surfaces of the parallelepipeds are called as (001), (100) and (120) surfaces, respectively in this paper, although the surfaces do not strictly coincide with the crystallographic orientations. Each surface was polished with diamond paste of up to 0.25 µm. The parallelepiped was put into an alumina crucible (11 mm in inner diameter and about 15 mm in height), and the crucible was hung in an alumina tube of a vertical H$_2$-CO$_2$ gas mixing furnace. The samples were heated under an H$_2$-rich condition at one-atmosphere, at temperatures ranging from 500 to 1300°C (H$_2$-rich experiments; ET-101 ~ ET-115 in Table 2). Temperature was measured by a Pt20%Rd-Pt40%Rd thermocouple. The H$_2$/CO$_2$ ratio is 3.72 to 3.87, and the total flow rate is 253 to 257 cm$^3$/min, depending on temperature to maintain constant oxygen fugacities one log unit below the iron-wüstite buffer curve. After heating for different durations from 0.5 to 90 hrs, samples were cooled in a cold part of the furnace in the H$_2$-CO$_2$ gas stream to avoid oxidation during cooling. Experiments were also done in a quartz tube of a horizontal furnace evacuated by an oil diffusion pump at 500 and 900°C (vacuum experiments; ET-1 ~ ET-6 in Table 2). In this type of experiment, the starting material was placed on an alumina plate. A Pt-Pt13%Rd thermocouple was attached to the plate, and the plate supported by a sheath of the thermocouple wires was placed in the quartz tube.

Run products were mounted in epoxy, and cut into two directions parallel to the (120) and (100) surfaces. The run products were observed under an optical microscope with reflected light and a scanning electron microscope (SEM) equipped with an electron probe microanalyzer (EPMA; JEOL JXA 733). The chemical compositions of the run products were measured by the EPMA with a focused beam, a specimen current of 12 nA, and accelerating voltage of 20 kV. Troilite in Nantan iron meteorite was used as a standard for Fe and S. X-ray intensities were corrected by the ZAF method.

Sulfur isotopic compositions ($^{34}$S/$^{32}$S) of the iron sulfide were measured by a secondary iron mass spectrometry (SIMS). A modified Hitachi
IMA-2A ion microprobe analyzer was used with Cs⁺ primary ion source. A technique specifically developed for the in-situ line analysis (Uyeda and Tsuchiyama, 1993, 1994) was applied. In isotopic analysis using a SIMS, in general, the amount of instrumental mass fractionation may change with the position of the primary ion beam at the sample surface. To evaluate the amount of discrimination due to instrumental mass fractionation, a sample was attached between two standards. Isotopic variation of the sample was measured precisely by comparing the measured data with those of the two standards. The spatial resolution was about 100 µm, and the primary beam current was 40 mA/cm². The accuracy of the measurements estimated using doped standard of BaSO₄ is about ±3‰.
Table 2. Summary of the Fe$_{1-x}$S evaporation experiments

<table>
<thead>
<tr>
<th>Run#</th>
<th>Temp. (°C)</th>
<th>Duration (hr)</th>
<th>Initial wt. (g)</th>
<th>Residue (g)</th>
<th>log$p$(O$_2$) (atm)</th>
<th>Run product**</th>
<th>δ in Fe$_{1-x}$S</th>
<th>X(Fe) (μm)</th>
<th>S.D. (μm)</th>
<th>Porosity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ET-105</td>
<td>1300</td>
<td>0.50</td>
<td>0.1978</td>
<td>0.1697</td>
<td>-11.59</td>
<td>Melting</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ET-101</td>
<td>1000</td>
<td>1.00</td>
<td>0.1784</td>
<td>0.1629</td>
<td>-15.61</td>
<td>SM</td>
<td>0.00</td>
<td>41.9</td>
<td>14.2</td>
<td>56.4</td>
</tr>
<tr>
<td>ET-102</td>
<td>900</td>
<td>1.03</td>
<td>0.1675</td>
<td>0.1557</td>
<td>-17.41</td>
<td>SI</td>
<td>0.00</td>
<td>165</td>
<td>92.8</td>
<td>53.4</td>
</tr>
<tr>
<td>ET-104</td>
<td>900</td>
<td>4.00</td>
<td>0.1645</td>
<td>0.1366</td>
<td>-17.41</td>
<td>SI</td>
<td>0.00</td>
<td>596</td>
<td>165</td>
<td>52.7</td>
</tr>
<tr>
<td>ET-103</td>
<td>900</td>
<td>12.00</td>
<td>0.1689</td>
<td>0.1104</td>
<td>-17.41</td>
<td>SI</td>
<td>0.00</td>
<td>84.8</td>
<td>28.4</td>
<td>54.3</td>
</tr>
<tr>
<td>ET-114</td>
<td>800</td>
<td>7.00</td>
<td>0.1482</td>
<td>0.1228</td>
<td>-19.54</td>
<td>SI</td>
<td>0.00</td>
<td>221</td>
<td>105</td>
<td>50.1</td>
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<tr>
<td>ET-106</td>
<td>800</td>
<td>14.03</td>
<td>0.1626</td>
<td>0.1159</td>
<td>-19.54</td>
<td>SI</td>
<td>0.00</td>
<td>443</td>
<td>69.0</td>
<td>49.2</td>
</tr>
<tr>
<td>ET-115</td>
<td>800</td>
<td>27.00</td>
<td>0.1539</td>
<td>0.0966</td>
<td>-19.54</td>
<td>SI</td>
<td>0.00</td>
<td>68.6</td>
<td>22.2</td>
<td>53.2</td>
</tr>
<tr>
<td>ET-107</td>
<td>700</td>
<td>20.00</td>
<td>0.1687</td>
<td>0.1422</td>
<td>-22.11</td>
<td>SI</td>
<td>0.00</td>
<td>170</td>
<td>50.8</td>
<td>54.9</td>
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<tr>
<td>ET-112</td>
<td>700</td>
<td>46.00</td>
<td>0.1615</td>
<td>0.1184</td>
<td>-22.11</td>
<td>SI</td>
<td>0.00</td>
<td>457.4</td>
<td>58.8</td>
<td>52.5</td>
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<tr>
<td>ET-113</td>
<td>700</td>
<td>89.00</td>
<td>0.1583</td>
<td>0.1018</td>
<td>-22.11</td>
<td>SI</td>
<td>0.00</td>
<td>24.4</td>
<td>10.6</td>
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<td>ET-108</td>
<td>600</td>
<td>28.00</td>
<td>0.1652</td>
<td>0.1551</td>
<td>-25.27</td>
<td>SI</td>
<td>0.00</td>
<td>39.6</td>
<td>7.8</td>
<td>66.1</td>
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<td>ET-110</td>
<td>600</td>
<td>50.00</td>
<td>0.1676</td>
<td>0.1551</td>
<td>-25.27</td>
<td>SI</td>
<td>0.00</td>
<td>65.4</td>
<td>24.6</td>
<td>58.9</td>
</tr>
<tr>
<td>ET-111</td>
<td>600</td>
<td>89.00</td>
<td>0.1772</td>
<td>0.1368</td>
<td>-25.27</td>
<td>SI</td>
<td>0.00</td>
<td>9.8</td>
<td>3.8</td>
<td>55.0</td>
</tr>
<tr>
<td>ET-109</td>
<td>500</td>
<td>90.00</td>
<td>0.1739</td>
<td>0.1637</td>
<td>-29.24</td>
<td>SI</td>
<td>0.00</td>
<td></td>
<td></td>
<td></td>
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<td>ET-4</td>
<td>900</td>
<td>1.00</td>
<td>0.1728</td>
<td>0.1654</td>
<td>evacuated</td>
<td>S-X</td>
<td>0.00</td>
<td>0.00</td>
<td>0.05</td>
<td></td>
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<tr>
<td>ET-5</td>
<td>900</td>
<td>4.00</td>
<td>0.1750</td>
<td>0.1672</td>
<td>evacuated</td>
<td>S-X</td>
<td>0.00</td>
<td>0.02</td>
<td>0.00</td>
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<td>ET-6</td>
<td>900</td>
<td>12.00</td>
<td>0.1686</td>
<td>0.1616</td>
<td>evacuated</td>
<td>S-X</td>
<td>0.01</td>
<td>0.03</td>
<td>0.02</td>
<td></td>
</tr>
<tr>
<td>ET-1</td>
<td>501</td>
<td>1.00</td>
<td>0.1671</td>
<td>0.1660</td>
<td>evacuated</td>
<td>SI</td>
<td>0.09</td>
<td>0.12</td>
<td>0.08</td>
<td></td>
</tr>
<tr>
<td>ET-2</td>
<td>501</td>
<td>8.00</td>
<td>0.1753</td>
<td>0.1718</td>
<td>evacuated</td>
<td>S</td>
<td>0.07</td>
<td>0.11</td>
<td>0.06</td>
<td></td>
</tr>
<tr>
<td>ET-3</td>
<td>500</td>
<td>88.00</td>
<td>0.1645</td>
<td>0.1561</td>
<td>evacuated</td>
<td>SI</td>
<td>0.04</td>
<td>0.06</td>
<td>0.05</td>
<td></td>
</tr>
</tbody>
</table>

*Values of log$p$(O$_2$) are shown only for experiments in the H$_2$-CO$_2$ flow (H$_2$-rich experiments).

**Run product**
- SM: Iron sulfide crystal (troilite or pyrrhotite) surrounded by eutectic melt.
- SI: Iron sulfide crystal (troilite or pyrrhotite) surrounded by iron layer.
- S: Iron sulfide crystal (troilite or pyrrhotite).
- X: Crystal became X-shaped (see Fig. 1(e)).

n.d.: Not determined.
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RESULTS

In the H$_2$-rich gas flow experiments, the pyrrhotite crystal evaporated incongruently at temperatures below the Fe-FeS eutectic point (988°C; Kullerud, 1967). A metallic iron layer was formed on the surface of the crystal as the evaporation residue (Figs. 1(a) and (c)). The iron layer was also formed along cracks which were present in the starting material mainly due to parting parallel to the (100) surface (Fig. 1(a)). The iron layer was spongy and highly porous. It looks like randomly packed iron foils of about a few μm thick (Figs. 1(b) and (c)). X-ray diffraction patterns of run products by the back Laue method showed that the iron layer was polycrystalline. The spongy layer and the inner sulfide crystal altogether kept the original shape of the crystal, indicating that the spongy layer obviously developed from the pyrrhotite crystal inward. The original size might have changed slightly, but it was too small to be measured. At 1000°C, the temperature between the eutectic and melting point (1195°C; Robie et al., 1978), an Fe-S melt surrounded the sulfide crystal due to the Fe-FeS eutectic melting (Fig. 1(d)). The chemical composition of the melt was not determined because the melt part became a mixture of troilite and iron as a result of recrystallization during quenching (Table 1, Fig. 1(e)). At 1300°C, the temperature above the melting point, the whole sulfide crystal melted. It is now a mixture of troilite and iron. This indicates that the melt became rich in Fe by incongruent evaporation of the melt, in which S evaporated more rapidly than Fe.

In the vacuum experiments, evaporation took place more slowly than in the H$_2$-rich experiments (Table 2). At 500°C, a comb-like structure developed along the (100) and (120) surfaces, while the (001) surfaces were kept flat (Fig. 1(f)). Small amounts of metallic iron were formed on the tips of the comb except for run ET-2 (8 hrs). The metallic iron was partly oxidized due to residual air in vacuum as pointed out by Tsuchiyama and Fujimoto (1995). At 900°C, the crystal became X-shaped by evaporation (Fig. 1(g)). No metallic iron was detected by SEM observation although the (100) and (120) surfaces became zigzag. Ef-
Fig. 1. SEM microphotographs of run products of the incongruent evaporation experiments on Fe$_{0.886}$S. (a) A back scattered image (BEI) of run ET-103 of the H$_2$-rich experiment (900°C, 12 hrs). An iron layer covers the sulfide crystal. The iron layer formation is promoted along cracks. (b) A secondary electron image (SEI) of an enlarged part of the iron layer of (a). Spongy texture is seen. (c) A SEI image of run ET-104 of the H$_2$-rich experiment (900°C, 4 hrs). A spongy iron layer uniformly covers the sulfide crystal. (d) A BEI image of run ET-101 of the H$_2$-rich experiment (1000°C, 12 hrs). Mixture of Fe and FeS (quench product of an Fe-S melt at 1000°C) covers sulfide crystal. (e) A BEI image of an enlarged part of the eutectic melt of (d). A mixture of metallic iron (white droplets) and FeS (gray matrix) was formed by recrystallization during cooling the run product. Black spots are cavities. (f) A SEI image of run ET-3 of the vacuum experiment (500°C, 88 hrs). A comb-like structure developed on the shorter surfaces nearly parallel to (100), while the longer surfaces nearly parallel to (001) were kept flat by evaporation. (g) A SEI image of run ET-6 of the vacuum experiment (900°C, 12 hrs). The crystal became X-shaped by evaporation. No metallic iron was detected under the SEM although the shorter surfaces nearly parallel to (100) became zigzag.
Fig. 1. (continued).
Fig. 2. The thickness of spongy iron layer formed by the incongruent evaporation of Fe$_{0.885}$S, X(Fe), plotted against time in the H$_2$-rich experiments. Linear rate constants, $k_{FeS}$, are obtained from the slopes of the regression lines. Error bars were obtained from 8–20 measurements of each run product.

Fig. 3. An Arrhenius plot of the linear rate constant, $k_{FeS}$, in Eq. (1) in the H$_2$-rich experiments. The corrected rates of the Fe$_{0.885}$S evaporation without and with the effect of cracks are also shown. The errors for the corrected data should be large due to simplicities of the models and errors of the porosity measurements.

Effects of the alumina plate were not detected in the vacuum experiments. The chemical compositions of the pyrrhotite crystal changed towards the stoichiometric one, but some of them did not reach the stoichiometric composition (Tables 1 and 2). Large heterogeneity was not detected in the non-stoichiometric crystals.

Figure 4 shows S isotopic compositions of the
Table 3. Linear rate constant, $k_{FeS}$, incongruent evaporation rate of sulfur from FeS, $J(S/FeS)$, and apparent evaporation coefficients with $p(H_2S) = 0$, $\alpha_{FeS}$, in the experiments

<table>
<thead>
<tr>
<th>Temperature ($^\circ$C)</th>
<th>$k_{FeS}$ $(10^{11} \text{ m sec}^{-1})$</th>
<th>$\log J(S/FeS)_{\text{measured}}$ (m$^{-2}$sec$^{-1}$)</th>
<th>$\log J(S/FeS)_{\text{calc.}}$ (m$^{-2}$sec$^{-1}$)</th>
<th>$\alpha_{FeS}$ apparent</th>
</tr>
</thead>
<tbody>
<tr>
<td>900</td>
<td>1236 (87)</td>
<td>20.61 (0.03)</td>
<td>24.49</td>
<td>$1.32 \times 10^{-4}$</td>
</tr>
<tr>
<td>800</td>
<td>423.1 (36.7)</td>
<td>20.15 (0.04)</td>
<td>24.23</td>
<td>$8.21 \times 10^{-5}$</td>
</tr>
<tr>
<td>700</td>
<td>124.5 (15.3)</td>
<td>19.62 (0.05)</td>
<td>23.91</td>
<td>$5.00 \times 10^{-5}$</td>
</tr>
<tr>
<td>600</td>
<td>21.91 (0.74)</td>
<td>18.86 (0.01)</td>
<td>23.52</td>
<td>$2.17 \times 10^{-5}$</td>
</tr>
<tr>
<td>500</td>
<td>3.025 (1.173)</td>
<td>18.00 (0.17)</td>
<td>23.03</td>
<td>$9.37 \times 10^{-6}$</td>
</tr>
</tbody>
</table>

Fig. 4. $^{34}S/^{32}S$ fractionations, $\Delta^{34}S$, of run ET-113 (700°C, 46 hrs). Error bars indicate $2\sigma_m$. Analyzed points (R1 to R10 on the sample and St1 to St7 on the starting pyrrhotite as a standard) are shown in the top diagram.
run product (Run ET-113). The mass fractionation of the samples with respect to the average of the starting material, $\Delta^{34}S$, was calculated as follows:

$$\Delta^{34}S = \left[ \frac{^{34}S/^{32}S_{\text{sample}}}{^{34}S/^{32}S_{\text{starting}}} - 1 \right] \times 1000 / \%o. \quad (3)$$

Change in the isotopic compositions of the run product by evaporation was not detected within an error of $\pm 3\%o$. Although S was not detected in the spongy layer by an EPMA, S was detected by a SIMS as a minor component. This S was probably due to recondensation during cooling the run product.

**DISCUSSION**

*Effects of non-stoichiometry*

It is expected from the phase diagram of the system Fe-S (Kullerud, 1967) that the stoichiometric FeS (troilite) is in equilibrium with metallic iron. Therefore, the pyrrhotite crystal changed its composition to the stoichiometric one during the incongruent evaporation process with the metallic iron residue. We can estimate the time scale required for changing the chemical compositions from the non-stoichiometric to stoichiometric FeS by diffusion of Fe into the sulfide crystal, $\tau_D$;

$$\tau_D \sim \frac{x^2}{D_{\text{Fe}}}. \quad (4)$$

where $x$ is the diffusion distance in the sulfide crystal, and $D_{\text{Fe}}$ the self-diffusion coefficient of Fe in pyrrhotite, which is a function of the degree of non-stoichiometry. Because the residual iron was formed along the cracks as well as on the surfaces, $x$ is smaller than the half of the smallest thickness of the sulfide parallelepiped, $a/2$ ($a = 0.25$ cm). When $x \sim (a/2)/10$ is assumed, and the values of $D_{\text{Fe}}$ with $\delta = 0.05-0.13$ (Fryt et al., 1979) are adopted, the values of $\tau_D$ are approximately 30, 6, 2, 0.6 and 0.3 hrs at 500, 600, 700, 800 and 900°C, respectively. These time scales are much shorter than those for evaporation of S from the sulfide crystal estimated from the present H$_2$-rich experiments, $\tau_E$ ($\tau_E \sim a/(2D_{\text{FeS}})$; 12000, 1600, 300, 79 and 26 hrs at 500, 600, 700, 800 and 900°C, respectively), and shorter than the run durations of the experiments. Thus, it is presumed that the pyrrhotite became troilite in an early stage of evaporation, and the present experiments can be regarded essentially as the evaporation of troilite.

Condit et al. (1974) carried out self-diffusion experiments of Fe and S in Fe$_{1-x}$S crystal, and found that S atoms diffuse at the rate several orders of magnitude more slowly than Fe atoms. Therefore, it is expected that the compositional change took place by Fe diffusion in the crystal, and the Fe atoms were supplied from the iron layer. In this case, the linear rate constants for the evaporation, $k_{\text{FeS}}$, obtained from the thickness of the iron layer should be underestimated. Amounts of Fe incorporated into the sulfide crystal were roughly estimated from the width of the iron layer, the porosity, and the amounts of S evaporated by assuming that only S was evaporated, and that the total weight of Fe was not changed. An alternative model considering the effect of evaporation along cracks was also made. The corrected evaporation rates are also shown in Fig. 3 together with the non-corrected rates. It is seen from the diagram that the corrected rates are similar to the non-corrected rates. If we take the errors of $X(\text{Fe})$ (e.g., Fig. 2) and errors of porosity into consideration, we cannot distinguish corrected and non-corrected evaporation rates exactly. Therefore, we use simply the non-corrected rate ($k_{\text{FeS}}$ in Eq. (2)) for further discussion.

*Mode of evaporation*

An evaporation residue layer is formed by incongruent evaporation. If the evaporation rate is controlled by diffusion of element(s) in the evaporation residue layer, the thickness of the layer increases proportionally to the square root of time ("parabolic rate law"). The diffusion-controlled evaporation with a parabolic rate law occurs in incongruent evaporation of many oxides, such as enstatite (Sata et al., 1978a). In the present H$_2$-rich
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experiments, however, the reaction obeyed the linear rate law. This result suggests that the evaporated gas species in the present experiments can move through pores in the spongy iron layers. It has been also known that LaCrO₃ evaporates incongruently by similar mechanism with a linear rate law (Sata et al., 1978b).

Based on equilibrium calculation, the reaction for the evaporation among dominant species is as follows:

$$\text{FeS(s)} + \text{H}_2(g) \rightarrow \text{Fe(s)} + \text{H}_2\text{S(g)}.$$  (5)

where s and g denotes solid and gas, respectively. In this reaction, it is assumed that gas species in equilibrium with FeS(s) and Fe(s) are formed in the H₂-rich experiments. Thermochemical calculation which considers all the H-O-C-S species listed in the thermochemical data of JANAF (Chase et al., 1986) (H(g), H₂(g), O(g), O₂(g), H₂O(g), OH(g), C(g), CO(g), CO₂(g), CH₄(g), CH₃(g), C₂H(g), C₂(g), C₃(g), C₄(g), C₅(g), C₃O(g), CH(g), CH₂(g), C₂H₂(g), C₂H₄(g), CHO(g), CH₂O(g), C₂H₄O(g), HS(g), H₂S(g), S(g), S₂(g), S₃(g), S₄(g), S₅(g), S₆(g), S₇(g), S₈(g), COS(g), CS(g), CS₂(g), SO(g), SO₂(g), S₂O(g), SO₃(g), and H₂SO₄(g)) showed that H₂S(g) was the only major gas species for S under conditions in the experiments. The partial pressure of H₂, p(H₂), was calculated to be 0.62–0.64 atm at 500–900°C in the experiments.

The evaporation rate of metallic iron (Tsuchiyama and Fujimoto, 1995) indicates that the evaporation of Fe can be neglected in the experiments. Therefore, the evaporation rate of S from solid FeS, J(S/FeS), can be obtained from the experimental results:

$$J(\text{S/FeS}) = \frac{N_A}{\Omega_{\text{FeS}}} k_{\text{FeS}},$$  (6)

where Ω_{FeS} is the molar volume of FeS, and N_A, the Avogadro number. On the other hand, if the evaporation reaction (5) at the sulfide surface is considered, we can calculate the evaporation rate, J(S/FeS)_calc., using the Hertz-Knudsen equation (e.g., Hirth and Pound, 1963);

$$J(\text{S/FeS})_{\text{calc.}} = \frac{\alpha_{\text{FeS}} K_{\text{FeS}} p(\text{H}_2) - p(\text{H}_2\text{S})}{\sqrt{2\pi n_{\text{H}_2\text{S}} kT}}.$$  (7)

where α_{FeS} is the evaporation coefficient for FeS, p(H₂S) the partial pressure of H₂S(g) in the pore of the iron residue layer, m_{H₂S} the mass of H₂S molecule, and k, the Boltzmann constant. K_{FeS} is the equilibrium constant of the reaction (5):

$$K_{\text{FeS}} = \frac{p(\text{H}_2\text{S})}{p(\text{H}_2)}.$$  (8)

The value of K_{FeS} was obtained from the thermochemical data of JANAF (Chase et al., 1986). J(S/FeS)_calc. with α_{FeS} = 1 and p(H₂S) = 0 gives the maximum rate, where kinetic constraints, such as mass transportation in a surrounding gas, interface kinetics due to reaction at the interface, and so forth, are absent. However, the value of α_{FeS} is generally less than unity (α_{FeS} ≤ 1), and depend on kinetic processes of the evaporation (Hirth and Pound, 1963). Moreover, p(H₂S) is not zero if H₂S molecules stagnated in the pore of the iron residue layer due to slow escape of the molecules from the pore to the gas flow. By comparing the measured J(S/FeS) values to the calculated maximum values with p(H₂) = 0.63 atm (Fig. 5), we obtained apparent values of α_{FeS} with p(H₂S) = 0, and 1.3 × 10⁻⁴ at 900°C to 9.4 × 10⁻⁵ at 500°C (Table 3). The small apparent values of α_{FeS} may be due to the interface kinetics, involved in decomposition of the solid FeS, formation of H₂S(g), and transportation of Fe and/or S in the solid FeS near the surface, or slow escape of H₂S molecules to the gas flow. There is a possibility that the value of p(H₂) in the crucible was smaller than 0.63 atm, and this may cause partly a decrease of α_{FeS} too. Although a rate-determining process was not determined definitely from the resent experiments, at least the escape process should be important because the width of the iron layer was
Fig. 5. An Arrhenius plot of the evaporation rate of S from FeS, J(S/FeS). The values of J(S/FeS) obtained from the H2-rich experiments using Eq. (6) are shown as solid circles. The calculated rate, J(S/FeS)calc., with $\alpha_{FeS} = 1$, $p(H_2S) = 0$ and $p(H_2) = 0.63$ (Eq. (7)) is shown as a solid line. The apparent evaporation coefficient with $p(H_2S) = 0$, $\alpha_{FeS}$, can be obtained from this diagram (also see Table 3). The calculated evaporation rate of S from FeS in vacuum with $\alpha_{FeS} = 1$ and that of metallic iron with $\alpha_{Fe} = 1$ are also shown. Note that $p(S_2) = 0$ and $p(Fe) = 0$ in vacuum, and that the evaporation rate of Fe is not changed by the presence or absence of $H_2(g)$ because the evaporation reaction is $Fe(s) \rightarrow Fe(g)$.

The evaporation rate of S from FeS in vacuum can also be estimated similarly using the Hertz-Knudsen equation together with the following reaction for the evaporation among dominant gas species based on the equilibrium calculation:

$$FeS(s) \rightarrow Fe(g) + 1/2S_2(g).$$

The maximum evaporation rate with $\alpha_{FeS} = 1$ ($p(S_2) = 0$ in vacuum) is also shown in Fig. 5. The evaporation rate is lower than that under the H2-rich condition ($p(H_2) = 0.63$ atm) because $H_2$ gas acts as a reducing agent for the evaporation reaction of Eq. (5), and thus enhances the evaporation rate. The present result that the evaporation rate in the vacuum experiments is lower than that in the H2-rich experiments is consistent with this $H_2$ effect.

Incongruent evaporation of FeS is also expected in vacuum because the maximum evaporation rate of metallic iron with $\alpha_{Fe} = 1$ is lower than
the S evaporation rate from FeS in vacuum (Fig. 5). However, if the value of $\alpha_{FeS}$ is small as in the case of the H$_2$-rich experiments, the S evaporation rate from FeS becomes comparable to that of metallic iron because the evaporation coefficient of metallic iron is unity (Tsuchiyama and Fujimoto, 1995). If this is the case, residual iron formed by incongruent evaporation of FeS evaporates instantaneously, and thus apparently congruent evaporation of FeS occurs. Although the exact evaporation rate in vacuum was not measured in the present experiments, the experimental result that iron was not detected in some runs may be explained by the above kinetic effect ($\alpha_{FeS} \ll 1$). Some of iron may be incorporated into the sulfide crystal.

**Sulfur isotopic fractionation during evaporation**

If sulfur is evaporated as H$_2$S molecules, the $^{34}$S/$^{32}$S fractionation factor between solid and gas should be $\sqrt{m(H_2^{34}S)/m(H_2^{32}S)} = 1.0290$. In this case, large isotopic mass fractionation is expected by evaporation. In fact, large isotopic fractionation of S of $>10\%$ was detected in the evaporation experiments on liquid FeS (McEwing et al., 1980). In the present experiments, however, fractionation was not observed within the error of $\pm 3\%$ (Fig. 4). Similar situation has been reported for the evaporation of forsterite; large isotopic mass fractionation was associated with evaporation of liquid forsterite, while not with evaporation of solid forsterite (Davis et al., 1990). The different behavior in the fractionation between the solid and liquid phases has been explained by the slow diffusivity of elements in the solid; isotopic composition of the crystal very close to the surface is changed by evaporation, but the isotopic composition of the crystal interior cannot be changed as long as the diffusion rate of the isotope species in the crustal is smaller than the evaporation rate (Davis et al., 1990). The present result can also be explained by the small diffusivity of S in the sulfide crystal, and suggests that mass dependent isotopic fractionation of S may not have occurred with incongruent evaporation of FeS in the primary solar nebula.

**Cosmochemical implications**

Evaporation behavior in the primordial solar nebula at $10^{-3}$–$10^{-6}$ atm H$_2$ would be between those in the H$_2$-rich experiments at 1 atm and the vacuum experiments. The reaction relation between metallic iron and troilite under the nebula conditions (e.g., Grossman and Larimer, 1974) suggests that FeS evaporates incongruently with metallic iron residue in the nebula. The thermochemical calculation shows that H$_2$S(g) is the major gas species in the nebula at low temperatures ($\leq 900^\circ$C at $10^{-3}$ atm H$_2$ and $\leq 600^\circ$C at $10^{-5}$ atm H$_2$), and thus the reaction of Eq. (5) is expected.

If the temperatures of the nebula were not so high as proposed by the recent nebula models (e.g., Boss, 1994), evaporation rates of primitive materials, such as FeS, should be important parameters for studying time scales of the nebula evolution. The evaporation rate is constant in a linear rate law, while it decreases with time in a parabolic rate law. Thus, models on the nebula evolution including the time scale should be different depending on the evaporation mechanism. If FeS incongruent evaporation obeys a linear rate law in the solar nebula, FeS evaporates more efficiently than expected from a parabolic rate law. It has been found for the first time from the present experiments that FeS incongruent evaporation obeys a linear rate law at least under H$_2$-rich conditions at 1 atm, and the evaporation residue has a porous structure which had not been expected before. We cannot predict definitely from the present experiments whether the FeS incongruent evaporation obeyed a linear rate law by forming a porous metallic iron layer or it obeyed a parabolic rate law by forming dense layer in the solar nebula. However, the present results are important as a first step to understand the evaporation behavior under the nebula conditions. In future, it is important to make evaporation experiments near the nebula conditions and discuss the evaporation process in the nebula.

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