EVAPORATION AND ACCOMPANYING ISOTOPIC FRACTIONATION OF SULFUR FROM FE-S MELT DURING SHOCK WAVE HEATING.
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Introduction: Chondrules probably formed by melting and subsequent cooling of solid precursors. Evaporation during chondrule melting may have resulted in depletion of volatile elements in chondrules. It is known that kinetic evaporation, especially evaporation from a melt, often leads to enrichment of heavy isotopes in an evaporation residue. However, no evidence for a large degree of heavy-isotope enrichment has been reported in chondrules for K, Mg, Si, and Fe (as FeO) [e.g., 1, 2].

The lack of isotopic fractionation has also been found for sulfur in troilites (FeS) within Bishunpur (LL3.1) and Semarkona (LL3.0) chondrules by an ion microprobe study [3, 4]. The largest fractionation, found in only one grain, was 2.7 ± 1.4 ‰/amu, while all other troilite grains showed isotopic fractionations of <1 ‰/amu. The suppressed isotopic fractionation has been interpreted as results of (i) rapid heating of precursors at temperatures below the silicate solidus and (ii) diffusion-controlled evaporation through a surrounding silicate melt at temperatures above the silicate solidus [3, 4]. The kinetic evaporation model suggests that a rapid heating rate of $>10^4$-10^6 K/h for a temperature range of 1000-1300°C is required to explain observed isotopic fractionations [4].

Such a rapid heating rate seems to be difficult to be achieved in the X-wind model [5], but can be achieved in shock wave heating models [e.g., 6-8]. In this study, we have applied the sulfur evaporation model [4] to the shock wave heating conditions of [8] to evaluate evaporation of sulfur and accompanying isotopic fractionation during shock wave heating at temperatures below the silicate solidus.

Shock wave heating: When we consider a moving coordinate system referenced to a shock front, the incoming nebula gas is decelerated at the shock front. Dust particles, having relative velocities to the decelerated gas, are heated by gas-drag. Gas-drag heating can be strong enough to melt solid grains and form chondrules [6-9]. The heating/cooling rate of dust particles is determined by energy transfer between gas and dust, radiative cooling of dust, and latent-heat cooling due to evaporation of dust or melt.

Sulfur evaporation model: Evaporation of sulfur from troilite and Fe-S melt and the accompanying isotopic fractionation are modeled in an Fe-S-H system, which is open for gas-solid and gas-liquid reactions but is closed for elemental abundances.

Evaporation of sulfur from troilite and Fe-S melt is controlled by a surface reaction [e.g., 10], and the evaporation flux of sulfur can be expressed by the Hertz-Knudsen equation:

$$J = \alpha \, (P^{eq}_i - P_i)/(2\pi m_i kT)^{1/2},$$

where P^{eq}_i is the equilibrium vapor pressure of gas species i (i = H_2S, HS, and S_2), P_i is the vapor pressure of i, m_i is the molecular weight of i, k is the Boltzmann constant, T is the absolute temperature, and α is the evaporation coefficient ($0 \leq \alpha \leq 1$). The α expresses kinetic barriers for evaporation and condensation. The values of α for H_2S, HS, and S_2 are taken from [10]. The P^{eq}_i for each S-bearing gas species for troilite and Fe-S melt are calculated from [11, 12]. Evaporation of iron was not considered because its evaporation rate is <1 % of that of sulfur.

Isotopic fractionation of sulfur is assumed to occur only for evaporation from Fe-S melt for simplicity. Instantaneous isotopic homogenization within Fe-S melt is also assumed. The square root of mass ratio is used for an isotopic fractionation factor for each gas species.

Kinetics of melting and crystallization are not taken into account in the model, so that the proportions of solid phases (FeS or Fe metal) and melt in a bulk condensed phase and the composition of the melt at a certain temperature are determined uniquely based on the bulk composition of the condensed phase with the Fe-S phase relation.

Evaporation of sulfur during shock wave heating was simulated by heating the Fe-S-H system at heating rates predicted in a shock wave heating model for various parameters such as an initial number density of gas ($n_0 = 10^{13}$-10^{14} cm^{-3}), a shock velocity (v = 6-10 km/s), and an initial dust radius (r = 10-1000 μm). The dust/gas mass ratio for the pre-shock region was set to 0.01 (the solar dust/gas ratio). We used temperature profiles that forsterite particles experience. Evaporation behavior was simulated up to 1300°C (1573 K), above which no activity data for sulfur in Fe-S melt is available.

Results and Discussion: The shock model predicts that the heating rate of dust particles ranges

from $\sim 10^4$ K/h to $\sim 10^7$ K/h at temperatures of 1000-1300°C, depending on shock parameters.

An example of the evaporation behavior of sulfur is shown in Fig. 1, where changes of troilite and melt proportions, the sulfur content relative to its initial abundance (S/S_0), and isotopic fractionation of sulfur in a bulk condensed phase are plotted against time after the shock front passes. Note that little evaporation of sulfur occurs from troilite due to rapid heating and sulfur evaporates mainly from Fe-S melt after temperature rises above the troilite liquidus. The isotopic composition of sulfur becomes heavier as evaporation proceeds. However, rapid heating (~ 5 x 10^4 K/h) prevents a large degree of sulfur evaporation, resulting in the fractionation of <2 ‰/amu at 1300°C. In all sets of shock parameters, isotopic fractionations in evaporation residues are at most 2.4 ‰/amu at temperatures below 1300°C, which is consistent with the observation by [3]. The kinetics of melting, which was ignored in our modeling, would somewhat suppress both evaporation and isotopic fractionation compared to our model.

Figure 2 shows changes of isotopic compositions of sulfur in condensed phases with different initial radii. It is seen that the heating rate for a smaller grain is larger than that for a larger grain because smaller grains with larger surface/volume ratios are decelerated (i.e., heated) more efficiently by gas drag than larger grains. Although the heating rates for grains with different sizes are different, the degrees of their isotopic fractionations are almost the same. This is explained as follows. Rapid heating suppresses evaporation from smaller grains. On the other hand, evaporation occurs efficiently from smaller grains due to their larger surface/volume ratios. The effects of heating rate and evaporation, both of which are approximately proportional to the grain size, are thus canceled out [7], resulting in the similar degrees of evaporation and accompanying isotopic fractionations for grains with different sizes and different heating histories seen in Fig. 2.

The evaporation model in this study suggests that, if the shock wave heating is abrupt enough, the isotopic fractionation of sulfur can be suppressed irrespective of grain sizes at temperatures below the silicate solidus (~ 1200-1300°C). At higher temperatures, the isotopic fractionation would be suppressed by evaporation through the silicate melt [3, 4]. It should also be noted that the dust/gas ratio should be close to or less than the solar ratio for suppressed isotopic fractionation. Under dust-rich conditions, dust particles in the pre-shock region are

heated for hours up to ~ 1500°C by radiation from heated dust in the post-shock region [9].

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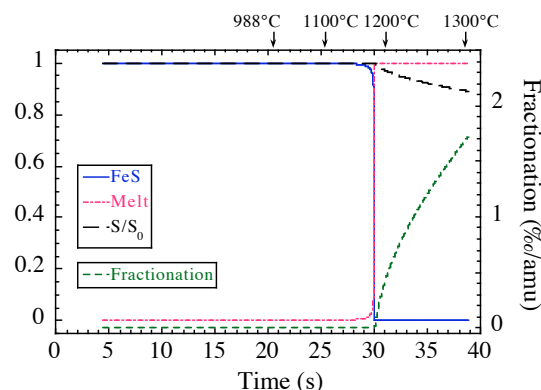

Fig. 1. An example of the result for our model calculation for the evaporation of sulfur. Shock parameters: $n_0 = 10^{13.5}$ cm^{-3}, $v = 9$ km/s, and $r = 1000$ μm.
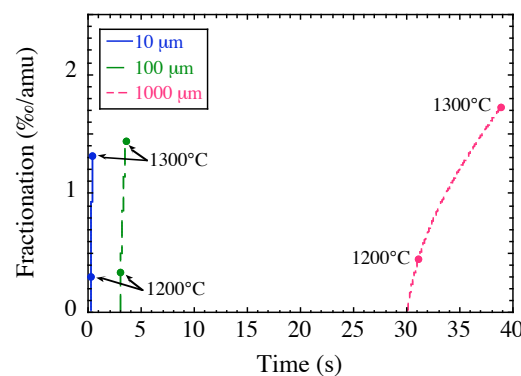

Fig. 2. Sulfur isotopic fractionations for the bulk condensed phases with different initial grain radii (10, 100, and 1000 μm) plotted against time after the shock front passes. $n_0 = 10^{13.5}$ cm^{-3} and $v = 9$ km/s.