

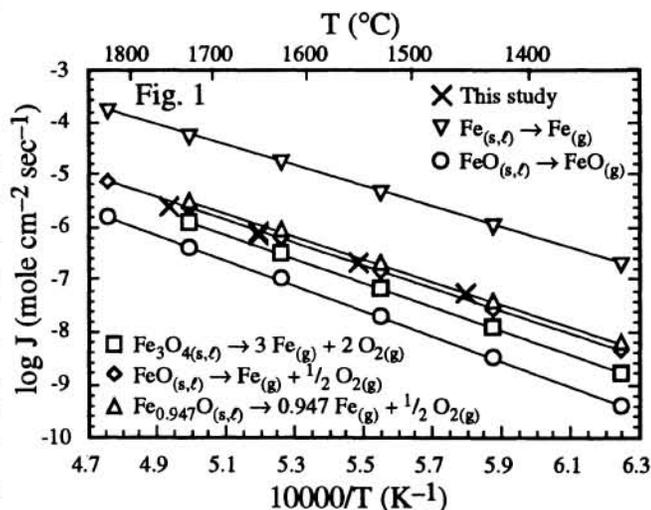
KINETIC ISOTOPIC FRACTIONATION DURING THE EVAPORATION OF THE IRON OXIDE FROM LIQUID STATE; Jianhua Wang¹, Andrew M. Davis², Robert N. Clayton^{1,2,3} and Toshiko K. Mayeda², ¹Department of the Geophysical Sciences, ²Enrico Fermi Institute, ³Department of Chemistry, University of Chicago, Chicago, IL 60637

Large enrichments in the heavy isotopes of oxygen, iron and nickel have been reported in magnetite-wüstite deep-sea spherules of cosmic origin [1,2,3,4]. These cosmic spherules are thought to have been Fe-Ni metal particles that were oxidized, melted and evaporated during atmospheric entry. The heavy isotope enrichments have been attributed to Rayleigh fractionation during evaporation [2,3,4]. Davis *et al.* [2] inferred that iron and oxygen evaporated as FeO, because of the agreement between the average amount of isotopic mass fractionation of iron and oxygen for all spherules. Assuming that FeO and NiO are the phases involved in the evaporation reaction, Davis and Brownlee [4] obtained a range of 76 to 94% mass loss for iron and 52 to 99.2% mass loss for nickel.

The sample preparation and the evaporation procedures are similar to those described by Wang *et al.* [5]. We evaporated reagent-grade wüstite (Alfa Products) at 1450, 1550, 1650 and 1750 °C for durations of 30 to 420 minutes. Ten evaporation runs produced a weight loss range of 3.5% to 87.2% of the original mass. We calculated evaporation rates of iron oxide by assuming that the density of the liquid residue is the same as that of the final solid residue. We also assumed that the liquid residue was spherical during evaporation. Fig. 1 shows the experimental data compared with evaporation rates (J) calculated from the kinetic theory of gases using ther-

modynamic data [6]: $J = p/\sqrt{2\pi MRT}$, where p is the equilibrium vapor pressure, M the molecular weight, R the gas constant and T the temperature (K). This equation only applies in cases involving a single solid phase going to a single gas-phase species, whereas many of the possible reactions for evaporation of iron oxide involve two gas-phase species. The evaporation rate (J) can be calculated from each of the gas phase species involved in a reaction. Rates calculated from $\text{Fe}_{(g)}$ are generally slower than those calculated from $\text{O}_{2(g)}$, so we have calculated rates from $\text{Fe}_{(g)}$ for all reactions involving two gas-phase species. The experimental data exhibit a remarkable fit to the evaporation rate calculated for the reaction: $\text{FeO}_{(l)} \rightarrow \text{Fe}_{(g)} + 1/2 \text{O}_{2(g)}$. As this is the fastest of the possible evaporation reactions, evaporation of FeO must not be kinetically hindered.

SEM examination of polished FeO residues using backscattered electron imaging indicates that there are two phases in most residues. We dissolved starting iron oxide and residues with 6N HCl and determined their Fe content by atomic absorption spectrophotometry. The starting iron oxide is of wüstite composition ($\text{Fe}_{0.947}\text{O}$) rather than stoichiometric FeO. The residues usually contain less iron than wüstite, suggesting that the minor phase in the SEM images is magnetite (Fe_3O_4). No systematic relationship was found between the magnetite content and the degree of



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evaporation loss. Since most residues have a bubble in their center, we suspect that oxygen is not efficiently evacuated from the residue. This hypothesis is supported by the oxygen isotope fractionation results which will be discussed later. We should point out that the kinetic theory that we used is a crude approximation to this complicated system.

We measured the iron isotopic composition of the residues with a modified AEI IM-20 ion microprobe, using melted starting material as a standard (Fig. 2). The linear relationship shows that the isotopic fractionation obeys the Rayleigh equation ($R/R_0 = f^{1/\alpha-1}$, where R is the isotope ratio in the residue, R_0 is the isotope ratio in the starting material, f is the fraction evaporated and α is the fractionation factor between liquid and gas). The fractionation factors can be obtained from the slopes of linear fits to the data (slope = $1-1/\alpha$). They are 1.0183 for $^{56}\text{Fe}/^{54}\text{Fe}$, 1.0274 for $^{57}\text{Fe}/^{54}\text{Fe}$ and 1.0345 for $^{58}\text{Fe}/^{54}\text{Fe}$. These α 's are almost identical to the theoretical values of 1.0184, 1.0274 and 1.0364 (inverse-square-root of mass ratio) assuming iron leaving the liquid as $\text{Fe}_{(g)}$. Because the theoretical value of α is the upper limit for the fractionation factor of iron, any species heavier than monatomic $\text{Fe}_{(g)}$ would lower the fractionation factor. This confirms our conclusion that $\text{Fe}_{(g)}$ rather than $\text{FeO}_{(g)}$ is the species evaporated. Using our results, we only need a range of 67 to 89% of Fe loss to account for the iron isotope fractionation found in the deep-sea spherules [2, 4].

Oxygen isotopic compositions of the residues and starting material were obtained using conventional oxygen extraction by fluorination and mass spectrometry. The results are shown in Fig. 3. The oxygen isotopic data also obey the Rayleigh equation, with α 's of 1.0217 for $^{18}\text{O}/^{16}\text{O}$ and 1.0110 for $^{17}\text{O}/^{16}\text{O}$. These values are smaller than the theoretical values of 1.0308 and 1.0155 calculated for O_2 as the gas-phase species. Since we have verified that $\text{FeO}_{(l)} \rightarrow \text{Fe}_{(g)} + 1/2 \text{O}_{2(g)}$ from both iron isotopes and kinetic experiments, we think that the kinetically hindered oxygen evaporation rate which makes it inefficient to fractionate isotopes can explain the observed fractionation factors for oxygen. The retention of O_2 gas in the central vesicle of most residues maintains an interaction between oxygen in the gas phase and the liquid residue. This will also reduce the efficiency of fractionating oxygen isotopes as O_2 will not be isolated from the liquid after its formation.

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