Introduction: The chemical compositions of planetary bodies are extremely diverse. In contrast, the isotopic compositions of most elements are uniform at large scales, indicating that the protosolar nebula was homogenized at some stage. The diversity of chemical compositions among undifferentiated meteorites must therefore reflect processes within the nebula such as gas-dust decoupling, partial condensation and evaporation, and metal-silicate differentiation. The abundance and oxidation of iron in chondrites has long been recognized as a valuable tool for classifying meteorites [1]. Iron isotopes add a third dimension to the already useful Urey-Craig diagram [2]. Among the processes that left their imprints on the chemical composition of solar system materials, evaporation is a major one. A simple system amenable to experimental investigation is evaporation of molten droplets, such as chondrules [3-6] and deep-sea spherules [7-9]. Application of the Hertz-Knudsen equation governing the evaporation of a liquid leads to the following fractionation factor between the residue and the gas for the isotopes with atomic masses m₁ and m₂ [10],

\[ \alpha = \frac{\gamma_2}{\gamma_1} \frac{m_1}{m_2}, \]

where \( \gamma_1 \) and \( \gamma_2 \) are evaporation coefficients. These coefficients are often assumed to be identical (\( \gamma_1 = \gamma_2 \)). During prolonged evaporation of FeO [11], the isotopic composition of the residue follows a Rayleigh distillation, with a fractionation factor equal to (\( m_1/m_2 \))\(^{0.5} \), in complete agreement with theory. Such behavior is not the general rule. Various elements do follow a Rayleigh distillation when evaporated but with fractionation factors that are closer to unity than expected [10,12,13]. The reason for this is not known but it does not result from back reactions at the surface or slow diffusion in the residue [14]. It is therefore important to document experimentally these fractionation factors in order to (i) understand the physical mechanism responsible for this non-ideal behavior and (ii) have a set of parameters applicable to natural systems when evaporative processes are involved. Here, we report the isotopic mass fractionation of iron during vacuum evaporation of molten wüstite and solar compositions.

Experimental and Analytical Methods: Evaporation experiments were performed at the Department of the Geophysical Sciences (The University of Chicago) following protocols described elsewhere [15,16]. Samples of wüstite (FeO) and solar (24.3 wt% MgO, 2.8 % Al₂O₃, 34.1 % SiO₂, 1.9 % CaO, and 36.8 % FeO) compositions were suspended by an Ir wire in a resistance-heated chamber. The pressure in the vacuum furnace was 1-5x10⁻⁴ atm. The run temperature was set at 1823 K. The duration of the experiments ranged from 0 to 25200 s. For wüstite experiments, the fraction of iron lost was determined by measuring the mass loss. For solar experiments, it was determined by calculating the Fe/(Al+Ca) ratio of the starting material and the residues from 2000–3000 SEM-EDS spot analyses of each sample. During evaporation of solar composition, poikilitic olivine crystallized and segregated.

After digestion in a few ml of HF 18 M-HNO₃ 5 M, iron was separated from the matrix and potential interfering elements using anion exchange chemistry (HCl with AG1-X8 200-400 mesh). The procedural blank is 50 ng, of which 20 ng derive from column chemistry. The isotopic composition was then analyzed at the Isotope Geochemistry Laboratory (IGL) at the Field Museum, equipped with a GV Instruments Isoprobe MC-ICPMS. A Cetac Aridus desolvating nebulizer was used in order to increase the sensitivity and minimize hydride formation. Argon and hydrogen were introduced in the hexapole collision cell, which reduced argide isobaric interferences. The samples were run at ppm levels with concentration-matched standards analyzed in-between. All iron isotopes were measured on Faraday collectors (54, 56, 57, and 58). The ⁵⁶Fe⁵⁴Fe isotope pair was used to calculate mass fractionation in the evaporation residues. The external reproducibility (digestion, separation, and analysis) is 0.1 % amu⁻¹ at 2σ. Isotope determinations can potentially be affected by isobaric interferences, matrix elements that could modify the instrumental mass bias, and isotopic fractionation during chemistry. These problems can be addressed by analyzing the isotopic composition before and after separation. As illustrated in Fig. 1, the isotope determinations are accurate.
\[ y = 0.9991x \]
\[ R^2 = 0.9999 \]

**Results:** If the isotopic composition of the residue follows a Rayleigh distillation then,
\[
\ln \left( \frac{R}{R_0} \right) = (1 - 1/\alpha)(-\ln f),
\]
where \( f \) is the fraction remaining of the denominator isotope (\(^{54}\text{Fe}\)). For the wüstite experiment (Fig. 2), the residue follows a Rayleigh distillation evolution with a fractionation coefficient very close to that expected (1.0185±0.0026 versus 1.0184). This result agrees with prior observations [11]. For the solar experiment, the residue also follows a Rayleigh distillation evolution but with more scatter and a fractionation factor that is apparently somewhat lower than the square root of the masses. This observation is reminiscent of the non-ideal behavior observed for other elements [10,12,13]. However, a complication arises with these experiments due to the crystallization and segregation of poikilitic olivine. This could potentially bias our estimate of the fraction of iron remaining if the area covered by SEM-EDS is not representative of the whole sample. In a MgO-FeO-SiO\(_2\) ternary diagram [17], the starting composition lies very close to the forsterite-fayalite binary join (Fo\(_{45}\)). The liquidus is 100 K above the run temperature for this composition. As the evaporation proceeds, iron is lost and the melt is even more prone to crystallize. Some of the poikilitic olivines are reversely zoned, thus iron loss from olivine was diffusion limited. More work is required to test whether the hint of non-ideal behavior is a real effect that has significance for early solar system materials or not.