DIFFUSION-CONTROLLED MAGNESIUM ISOTOPIC FRACTIONATION OF A SINGLE CRYSTAL FORSTERITE EVAPORATED FROM THE SOLID STATE; Jianhua Wang1, Andrew M. Davis4, Akihiko Hashimoto3 and Robert N. Clayton1,2,4; 1Department of the Geophysical Sciences, 2Department of Chemistry, 4Enrico Fermi Institute, University of Chicago, Chicago, IL 60637; 3Harvard-Smithsonian Center for Astrophysics, Cambridge, MA 02138

Though the origin of calcium- and aluminum-rich inclusions (CAIs) in carbonaceous chondrites is still a disputed issue, evaporation is no doubt one of the most important processes for the formation of CAIs in the early solar nebula. The mechanism for production of large isotopic mass fractionation effects in magnesium, silicon, oxygen and chromium in CAIs can be better understood by examining isotopic fractionation during the evaporation of minerals. We have performed new evaporation experiments on single-crystal forsterite. We measured the magnesium isotopic distribution near the evaporating surfaces of the residues using a modified AEI IM-20 ion microprobe to obtain rastered beam depth profiles. A theoretical model was used to explain the profiles and allowed determination of the diffusion coefficient of Mg\(^{++}\) in forsterite at higher temperatures than previous measurements. The gas/solid isotopic fractionation factor for magnesium for evaporation from single forsterite was also determined and found to be nearly the same as that for evaporation of liquid Mg\(_2\)SiO\(_4\).

A previous study of the evaporation of synthetic liquid Mg\(_2\)SiO\(_4\) revealed that isotopic fractionation of magnesium, silicon and oxygen follows a Rayleigh fractionation curve with close to inverse-square-root of mass fractionation factor, whereas little isotopic fractionation is detected in bulk residues from evaporation of solid forsterite [1]. Wang et al. [2] examined the isotope fractionation profiles of magnesium in residues of synthetic polycrystalline forsterite evaporated below the melting temperature and found that the distribution of magnesium isotopes near the evaporating surface was diffusion-controlled. In the Rayleigh fractionation model, instantaneous mixing (homogeneity) of the residues is assumed. This is rarely the case in the experiments and in nature because diffusion is slow enough to prevent instantaneous mixing of the residue during the evaporation process. Diffusion must be considered when modeling isotopic fractionation during the transformation process of a reservoir. Modeling of the evaporation of synthetic polycrystalline forsterite with loosely bonded single crystals is extremely complicated, as both volume and grain boundary diffusion must be considered, in addition to gas transport through a porous medium. In addition, the surface area of the synthetic polycrystalline aggregate is not well-known. For these reasons, we have performed new evaporation experiments on single-crystal forsterite.

A single crystal of synthetic forsterite (provided by Dr. Robert C. Morris of Allied Signal Corp.) was sliced perpendicular to its a-axis and polished on both surfaces. These slices were cut into small chips for evaporation experiments at 1800, 1750, 1600 and 1500°C for 1 to 96 hours. The evaporation runs were performed in a vacuum furnace [3] at a pressure of \(\leq 10^{-6}\) torr. The weight and the surface area of each chip were measured before and after the evaporation run to determine the evaporation rate. Measured evaporation rates from short duration experiments tend to have higher values than those from longer experiments, probably due to the existence of defects on the crystal surface. All measured evaporation rates for single crystal forsterite are lower than those measured by Hashimoto [3], especially at lower temperatures (Figure 1). This discrepancy is apparently the result of the underestimate of the surface area in the polycrystalline forsterite used in the earlier experiments.

Magnetism isotopic fractionation effects in the single crystal forsterite residues occur over <10 \(\mu\)m, so that our previous method of spot analyses of sections through residues [2] could not be used. Instead, magnesium isotopic profiles perpendicular to the evaporating surfaces of the residues have been measured by depth profiling using a modified AEI IM-20 ion microprobe with rastered beam. The primary beam intensities were 30-35 nA with a rastered area of \(-100 \times 100\) \(\mu\)m. In order to obtain a depth profile of only the central, flat-bottomed area of the raster pit, a digital aperture was used to collect signal from the central 52 or 25% of the total rastered area. In each measurement, signal collection was begun 2 minutes after turning on the primary beam to allow the Mg\(^{++}\) signal to stabilize. Each measurement of 500-1000 cycles through \(\text{Mg}^{2+}\), \(\text{Mg}^{25}\) and \(\text{Mg}^{24}\) took 5-7 hours and sampled the rastered area to a depth of up to 10 \(\mu\)m. Depth profiles of single-crystal forsterite starting material were measured before and after each isotope profile of a residue to standardize the results and correct for instrumental drift. A 500-scan analysis of forsterite starting material shows a constant magnesium isotopic composition with depth (or time) with a standard deviation for average of 25 scans of about \(\pm 1.5\%\) (1s) for \(\text{Mg}^{25}\). All evaporation experiments were long enough and the chips of the forsterite were thick enough that steady state isotope profiles were produced near the evaporating surface and the magnesium isotopic composition of the inner portion of the residue was not disturbed. The depth of each the raster pit was measured using a Sloan surface profiler with a precision of \(\pm 0.1\) \(\mu\)m.

A theoretical model incorporating diffusion has been developed to study the isotope fractionation effects for
transformation of a nonmixed reservoir. The present model uses a one-dimensional approach, assuming that the reservoir is shaped like a slab with phase transition at only one surface (or both surfaces) and the coordinate of length is always perpendicular to the surface. The first step in solving this problem is consideration of a semiinfinite slab. This involves solving a partial differential equation with a moving boundary and a solution was found using the Laplace transform [4]. There is also a steady state solution: \( R(x)/R_o = 1 + (\alpha-1)e^{-x} \), where \( R \) is the ratio of a minor isotope to an abundant isotope, \( \alpha \) is the fractionation factor between the solid and the gas phase and \( x \) is nondimensionalized distance from the evaporating surface relative to the diffusion coefficient and the evaporation rate.

The next step is to consider a slab with finite thickness. A set of partial differential equations was solved numerically using the Crank-Nicolson implicit method. The results of this model were used to interpret magnesium isotopic fractionation in the single-crystal forsterite residues.

By plotting \( \ln^{26}Mg \) (relative to the starting material) vs. depth from the evaporating surface, we can obtain the diffusion coefficient for \( Mg^{++} \) from the slope \( (v/D) \) and the fractionation factor of magnesium between its gas phase species and solid forsterite from the intercept \( (\ln 1000(\alpha-1)) \). Figure 2 shows the variation of the diffusion coefficient of \( Mg^{++} \) in forsterite along the \( a \)-axis with temperature. The line is a linear fit to the data. The line is a linear fit to the single crystal forsterite evaporation experiments. The line is a linear fit to the data.