THE ROLE OF DIFFUSION IN THE ISOTOPIC FRACTIONATION OF MAGNESIUM DURING THE EVAPORATION OF FORSTERITE;

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Calcium- and aluminum-rich refractory inclusions (CAIs) in carbonaceous chondrites show up to a few percent per a.m.u. mass fractionation of Mg, Si, O and Cr isotopes relative to normal (terrestrial) values [1]. This large mass fractionation has been interpreted as a kinetic isotopic effect between vapor and liquids or solids resulting from nonequilibrium evaporation and/or condensation processes that occurred in the primordial solar nebula [2]. The study of isotopic fractionation in mineral evaporation experiments can help us to better understand the origin of CAIs (evaporation or condensation). If their origin is by evaporation, we can obtain information about the state (solid or liquid), time duration and temperature range of their formation.

Evaporating synthetic liquid Mg_2SiO_4 shows that isotopic fractionation follows a Rayleigh fractionation curve with close to inverse-square-root of mass fractionation factor ($\alpha = \sqrt{M_1/M_2}$, where M_1 is the mass of the evaporating gas species with lighter isotopes and M_2 is the mass of the gas with heavier isotopes). Little isotopic fractionation is detected in bulk residues from evaporation of solid forsterite [3]. Hashimoto [4] studied the evaporation kinetics of Mg_2SiO_4 and found that Mg, SiO_2 and O (or O_2) are predominant gas molecules during forsterite evaporation and that Mg_2SiO_4 evaporates stoichiometrically. The small difference between the experimental results and those predicted from evaporation of Mg, SiO_2 and O_2 is the result of either evaporation of heavier gas species or heterogeneity of isotopic composition in the residue. 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 a rate process and prevents instantaneous mixing of the residue during the evaporation process. Diffusion must be considered when modeling isotopic fractionation during the evaporation of minerals.

Traverses perpendicular to the evaporating surfaces of four forsterite residues evaporated from the solid state at 1750 °C with 15.6, 35.6, 62.4 and 77.7% mass loss have been analyzed for their Mg isotope distribution using a modified AEI IM-20 ion microprobe. The primary beam has a diameter of about 10 μm with current of 2 nA. In each measurement, signal collection was begun 2 minutes after turning on the primary beam to allow the Mg signal to stablilize; ^{26}Mg, ^{25}Mg peaks were counted for 5 seconds and ^{24}Mg for one second. Forty counting cycles were completed for each measurement. The average standard deviation for each measurement is about ±0.68‰ (1σ) for $\delta^{25}Mg$ and ±0.72‰ for $\delta^{26}Mg$. The core of each solid residue remained unfractionated during the evaporation and $\delta^{25}Mg$ and $\delta^{26}Mg$ were calculated relative to the center of each residue. The sequence of measurement positions on each traverse was randomly chosen to avoid systematic instrumental effects. All these traverses show a significant enrichment of ^{26}Mg and ^{25}Mg relative to the center of the solid residue within a few tens of microns from the surface (Figure). The patterns within 100 μm of the evaporating surface are similar for all four samples. The interior (more than 100 μm from the surface) of each sample is uniformly unfractionated. The similarity of the patterns in the first 100 μm implies that a steady state was reached quickly during evaporation of solid forsterite.

A numerical model has been used to study the isotope fractionation during the evaporation process. For each time increment Δt, the thickness of effective total mixing (>98%) of isotopes due to diffusion is set to be one half of $\sqrt{D\Delta t}$, where D is the diffusion coefficient of the element studied. This layer is considered as an evaporation-fractionation layer, beneath which diffusion occurs. The evaporation rate used (3.5×10^{-3} %/sec) is the average of the four solid evaporation experiment runs at 1750 °C. The diffusion coefficient of Mg in forsterite of 5.2×10^{-9} cm^2/sec is extrapolated

from Morioka's experimental data [5] at temperature range over 1300-1400 °C. Using a diffusion coefficient of 5.2×10^{-10} cm^2/sec gives a much better fit to the experimental data than using 5.2×10^{-9} cm^2/sec. This suggests that precise measurement of diffusion coefficients of elements at higher temperatures than are normally employed for diffusion experiments may be obtained from the evaporation experiments. The evaporation experiments and the results of this model are similar in both the shape of the profile near the surface and in the magnitude of the isotopic fractionation (Figure). For the limited spatial resolution (~10 μm) of ion microprobe analysis, the details of the outermost 5 μm, most isotopically fractionated, layer of the residue is probably not well-revealed. The result of using a diffusion coefficient of 1.0×10^{-9} cm^2/sec shows the effect of the change of diffusion coefficient on the calculated isotopic fractionation pattern of evaporated residue (Figure).

The detailed measurement of evaporated forsterite residues and theoretical modeling of this process suggests:

1. Diffusion plays a key role in isotopic fractionation during evaporation of solid forsterite.

2. Undetected isotope fractionation of the bulk (or part of) of a mineral (or CAI) does not imply that it is not isotopically fractionated. Fractionation gradients due to diffusion may exist in the outer few μm of a sample.

3. Isotopically unfractionated (bulk) minerals including CAIs do not necessarily indicate that they had not experienced evaporation during their formation. Careful isotope measurements are needed to confirm this.

References: [1] R.N. Clayton *et al.* (1988) Phil. Trans. Roy. Soc. A325, 483-501. [2] R.N. Clayton & T.K. Mayeda (1977) Geophys. Res. Lett. 4, 295-298. [3] A.M. Davis *et al.* (1990) Nature 347, 655-658. [4] A. Hashimoto (1990) Nature 347, 53-55. [5] N. Morioka (1981) GCA 45, 1573-1580.