

EXPERIMENTAL OBSERVATION OF LARGE MASS-INDEPENDENT FRACTIONATION DUE TO MASS-DEPENDENT DIFFUSION. G. DOMINGUEZ^{1*}, E. CRISTENSEN^{1,2}, C. BOYER¹, M. PARK^{1,2}, E. BENITEZ¹
 Department of Physics, California State University San Marcos, San Marcos, California, 92096
 (gdominguez@csusm.edu)² Department of Chemistry, California State University San Marcos, San Marcos, California, 92096

Introduction: Identifying physical-chemical mechanisms that produce mass-independent fractionations is an area of high interest because of the general assumption that mass-dependent processes only produce mass-dependent isotopic fractionations [1]. The first recognition of natural compounds exhibiting deviations from the TFL were made in the analysis of Calcium Aluminum rich Inclusions (CAIs) within the Alende meteorite whose oxygen isotopic composition was found to define a line of approximately slope 1 in a $\delta^{17}\text{O}$ vs. $\delta^{18}\text{O}$ plot [4]. It is now believed, based on the recent measurements and analysis of the isotopic composition of solar wind O, that the distribution of oxygen isotopes in the solar system define a mass-independent pattern of slope ~ 1 . The origins of this distribution remains largely unexplained [2].

The exception to the rule that physical-chemical processes produce mass-dependent isotopic fractionations was discovered by Thiemens and Heidenreich, who showed that the non-equilibrium process of ozone formation in the laboratory ($\text{O}_2 + \text{O} + \text{M} \rightarrow \text{O}_3 + \text{M}$) produces mass-independent isotopic fractionations with a slope ≈ 1 [3]. Since then, only a handful of other non-equilibrium chemical processes such as the photoreduction of Hg, the formation of the peroxy radical, the photolysis of SO_2 , and photodissociation of CO have been shown to produce MIF, leading to the widespread assumption that MIF isotopic signals are strongly conserved in natural mass-dependent processes. MIF in multi-isotopic systems are now widely used to understand atmospheric photochemical reaction networks, the oxidative capacity of the atmosphere, and the history of oxygen and sulfur in terrestrial atmospheres including Mars, and the cycling of Hg in the environment [1]. Large oxygen isotopic fractionations with non-terrestrial triple-isotope trend-lines observed in the VUV photolysis of CO [4] and the gas-phase formation of SiO_2 [5] have also been reported as having potential implications for understanding the mass-independent distribution of oxygen isotopes in the solar system [5].

Here we report experimental observations of very large, seemingly mass-independent oxygen isotopic fractionations produced from the gas-phase diffusion of H_2O . We find, surprisingly, that the large MIFs observed are readily explained by the mass-dependent diffusion of water vapor.

Experimental: Our observations of large isotopic fractionations with mass-independent character were made using a stainless steel vacuum line apparatus consisting of both 1/2 inch diameter stainless steel tube connected via valves and 1/4 inch tubing to a Picarro L2120-i cavity ring-down (CRD) isotopic spectrometer capable of simultaneous quantification of the $\delta^{17}\text{O}$, $\delta^{18}\text{O}$, and δD compositions of water vapor samples [16]. The vacuum line also comes equipped with a turbomolecular pumping station and is connected to a source of ultra-high purity (UHP) N_2 that acts as a carrier gas and source of pressure (See Figure 1).

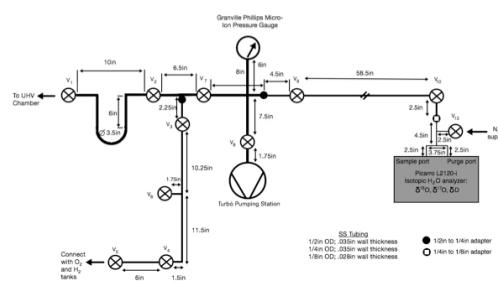


Figure 1. Stainless Steel experimental apparatus used for diffusion experiments with H_2O vapor. Figure from ref. [6].

Water vapor samples of known isotopic composition were introduced into the vacuum line apparatus using a procedure we describe in [6]. This procedure allowed us to collect H_2O vapor with reproducible and known isotopic compositions and allowed us to perform the 1-D diffusion experiments described below.

Diffusion Experiments. First, a section of our stainless steel line, between valves V1 and V2 was used to store the H_2O vapor mixed with ambient air. The volume separating this reservoir volume from the inlet of the H_2O isotopic CRD instrument was pumped out to a pressure of $< 1 \times 10^{-5}$ Torr and was then filled with UHP N_2 to pressure 760 Torr. Once this occurs, a valve (V2) separating the vacuum line section with H_2O vapor and the Picarro L2120-i CRD instrument is opened. In general we observed a time lag of about 5

minutes before the water vapor concentrations begin to increase above background and display the mass-independent “anomalous” isotopic fractionations we report here.

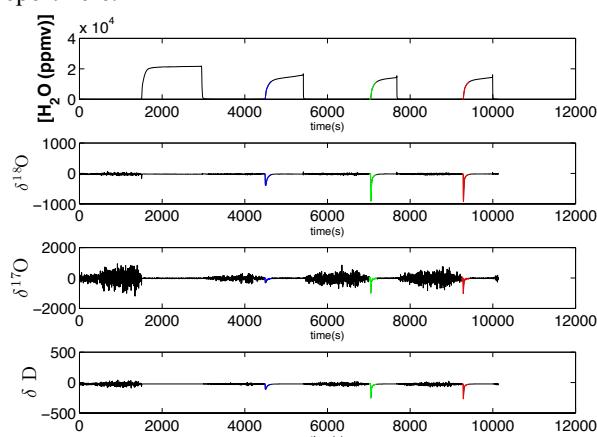


Figure 2. Isotopic composition of water vapor pulses vs. time. Note the large fractionations associated with the front end of the pulses. The leading edge of the pulses are color coded (blue,green, red).

We used a Picarro L2120-i CRD spectrometer to quantify the concentrations of H_2^{16}O , H_2^{17}O , and H_2^{18}O vs. time [7]. We quantified the multi-isotopic content ($\delta^{17}\text{O}$, $\delta^{18}\text{O}$, δD) of water vapor using the standard δ notation.

Results: We observed significant isotopic fractionations in $\delta^{17}\text{O}$, $\delta^{18}\text{O}$, δD associated with the leading edge of water vapor plumes arriving at the CRD water vapor isotopic spectrometer. When we first observed these plumes and associated isotopic fractionations as part of our work measuring the isotopic composition of astrophysical water samples, we were quite surprised at the magnitude of the isotopic fractionations (See Figure 2). This pattern appears to be consistent across several different experimental conditions. What was even more surprising was our observation that, when plotted on a triple-oxygen isotope plot, the isotopic composition of the leading edge of these plumes was distinctly mass-independent.

Diffusion Modeling: We developed 1,2, and 3-D diffusion models of the diffusion of water vapor within the experimental apparatus. We considered possible mass-independent wall-water molecule interactions but found the potential well-depths to be insufficient to account for the magnitudes of the mass-independent fractionations. Instead, we modeled the diffusion of water vapor as a random walk with effective mass-dependent diffusion constants for each of the isotopomers. The relationship between the diffusion constant of one isotopomer (D_1) to another (D_2) was given by: $D_1/D_2 = (m_2/m_1)^\beta$. This basic relationship, together

with solutions to the diffusion equation was sufficient to account for the major features of our isotopic data. The model data plotted in Figure 3 is for a 1-D diffusion model, but we emphasize that 2-D and 3-D solutions give similar results. More details on this modeling are given in ref[6].

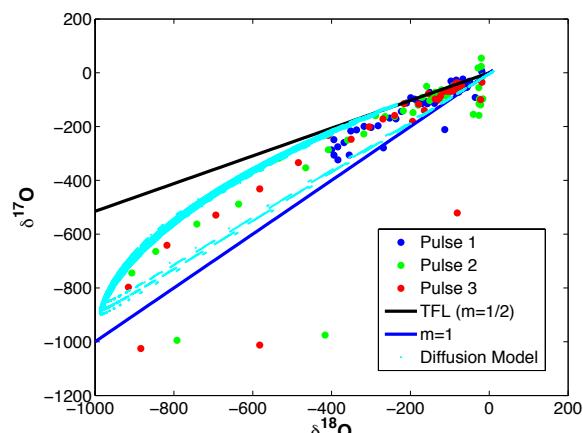


Figure 3 Triple-isotope plot of the isotopic composition of water pulses shown in Figure 2. In addition, the results of a mass-dependent plume diffusion model (cyan)of the experiments is also shown.

Discussion: Much effort has been placed on understanding the origins of mass-independently fractionated reservoirs in the early-solar system in a variety of elements (O, S, Hg, etc.). To our knowledge, this is the first experimental and theoretical evidence that mass-dependent diffusive processes can produce substantial mass independent fractionations. While it is not clear whether plume diffusion processes like the one we describe here could have produced the CCAM line that characterizes the distribution of oxygen isotopes in the solar system, our results and explanation do suggest that the photochemical origins for modest and small MIF signatures in sulfur, for example, need to be carefully re-examined and assessed for the potential influence of plume induced MIF [8]. Careful attention needs to be placed to overall mass-balance to rule out the influence of plume diffusion induced MIF.

References: [1] M. H. Thiemens et. al, *Ann. Rev. of P. Chem.*, 63, 155 [2] McKeegan et al. *Science*, 332, 1528 (2012) [3] Thiemens and Heidenreich, *Science*, 219, 1073 (1983) [4] Chakraborty et al., *Science*, 321, 1338 (2008). [5] Chakraborty et al., *Science*, 342, 463 (2013). [6] Dominguez et al., submitted. [7] Salvo et al., *Anal.Chim.Acta*, 804, 176 [8] Rai et al., *Science*, 309, 1062 (2005).